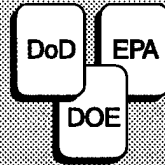


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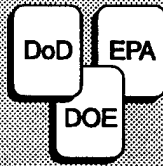
Strategic Environmental Research  
and Development Program

Improving Mission Readiness through  
Environmental Research



# 1995 ANNUAL REPORT AND FIVE-YEAR (1995-1999) STRATEGIC INVESTMENT PLAN

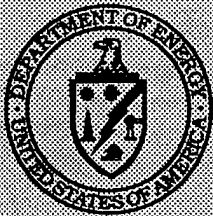
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# SERDP

Strategic Environmental Research  
and Development Program

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# 1995 ANNUAL REPORT AND FIVE-YEAR (1995-1999) STRATEGIC INVESTMENT PLAN

August 1995

This document was prepared for the Executive Director, Strategic Environmental Research and Development Program (SERDP) by

LABAT-ANDERSON Incorporated

under contract Number DAAA21-90-D-1015. Questions regarding the SERDP should be directed to the SERDP Program Office located at 901 North Stuart Street, Suite 303, Arlington VA, 22203

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## FOREWORD

The Strategic Environmental Research And Development Program (SERDP) is mandated in 10 U.S.C. §§2901-2904. SERDP addresses environmental matters of concern to the Department of Defense (DoD) and the Department of Energy (DOE). It is conducted as a tri-agency program jointly managed by the DoD, DOE and Environmental Protection Agency (EPA) with participation by other Federal agencies.

This report includes information required by 10 U.S.C. §2902 for the annual report to Congress. It provides the details of funds appropriated in Fiscal Years 1994 and 1995. The individual research projects were reviewed and selected by the SERDP Council in response to specific requirements for research and development. Prior to funding, all projects valued greater than or equal to \$900,000 were reviewed and recommended by the SERDP Scientific Advisory Board (SAB). Their comments on each project can be found in the *SERDP Scientific Advisory Board FY 1994 Annual Report* which has been forwarded to Congress from the Chairman of the SAB via the Chair of the SERDP Council, and the combined *SERDP Scientific Advisory Board FY 1995/1996 Annual Report* which will be published by March 1996.

The *SERDP Five-Year (1995-1999) Strategic Investment Plan* is based on a FY 1995 appropriation of \$61.9 million. It is submitted on behalf of the SERDP Council whose membership consists of: the Director of Defense Research and Engineering; the Deputy Under Secretary of Defense (Environmental Security); the Vice Chairman of the Joint Chiefs of Staff and representatives from each of the uniformed Services and Coast Guard; the Assistant Secretary of the Air Force, Space; the Director of the DOE Office of Energy Research; the Assistant Secretary of Energy for Environmental Management; the Assistant Secretary of Energy for Defense Programs; and the Administrator of the EPA.

## ACRONYMS

Each acronym used in the text is defined in its first use. This section provides a summary list of acronyms.

A	U.S. Army
AAP	Army Ammunition Plant
AEC	Army Environmental Center
AEERL	Air and Energy Engineering Research Laboratory
AERL	Athens Environmental Laboratory
AF	U.S. Air Force
AFCEE	Air Force Center for Environmental Excellence
AFCESA	Air Force Civil Engineering Support Activity
AFM	Atomic Force Microscopy
AFOSR	Air Force Office of Scientific Research
AICUZ	Air-Installation Compatible Use Zone
Al-Mn	Aluminum-Manganese
AL	Armstrong Laboratory
ALCs	Air Logistics Centers
ANL	Argonne National Laboratory
ANSI	American National Standards Institute
AOP	Advanced Oxidation Process
AQMD	Air Quality Management Districts
ARA	Applied Research Associates
ARDEC	Army Armaments Research, Engineering & Development Center
AREP	Alternative Refrigerant Evaluation Program
ARM	Atmospheric Radiation Measurement
ARPA	Advanced Research Projects Agency
ARSAP	Atmospheric Remote Sensing and Assessment Program
ASTE	Advanced Strategic and Tactical Expendables
ATEDS	Advanced Technology Expendables and Dispenser System
ATLAS	Advanced Testing Line for Actinide Separations
ATMOS	Atmospheric Observing Satellite
ATRP	Automatic Target Recognition Processor
BAA	Broad Agency Announcement
BDC	Background Data Center



Ben	Benzene
BLM	Bureau of Land Management
BTEX	Benzene, Toluene, Ethylbenzene, and Xylene
CAA	Chromic Acid Anodizing
CAAA	Clean Air Act Amendments
CAME	Clean Agile Manufacturing of Energetics
CARB	California Air Resources Board
CATS	Controlled Archeological Test Site
CCAC	Close Combat Armament Center
CCDs	Charge Coupled Devices
Cd	Cadmium
CER	Center for Environmental Research
CERCLA	Comprehensive Environmental Response, Compensation, and Liability Act of 1980 (called Superfund)
CERL	U.S. Army Construction Engineering Research Laboratory
CFC	Chloroflourocarbons
CIA	Central Intelligence Agency
CP	Compliance Thrust Area
cPahs	Carcinogenic (heavy) Polycyclicaromatic Hydrocarbons
CPATS	Corrosion Prevention Advisory Teams
CPT	Cone Penetrometer
Cr	Chromium
Cr	Chromates
CRADA	Cooperative Research and Development Agreement
CRREL	U.S. Army Cold Region Research and Engineering Laboratory
CS	Conservation Thrust Area
CSS	Coastal Systems Station
CU	Clean Up Thrust Area
Cu	Copper
CUSP	Commander, Undersea Surveillance Pacific
D/NETDP	DoD/National Environmental Technology Demonstration Program
DCA	Dynamic Contact Angle Analyzer
DECIM	Defense Environmental Corporate Information Management Program
DFSS	Dedicated Feedstock Supply Systems
DMMF	Developmental Manufacturing and Modification Facility
DNA	Defense Nuclear Agency

DNAPL	Dense Non-Aqueous Phase Liquid Pools
DNL	Dry Low NO <sub>x</sub>
DoD	Department of Defense
DOE	Department of Energy
DOI	Department of the Interior
DPG	Dugway Proving Ground
DSPO	Defense Support Program Office
DUECC	Defense Utility Energy Coordinating Council
EAs	Environmental Assessments
ECIP	Energy Conservation Investment Program
ECPs	Engineering Change Proposals
ECUs	Environmental Control Units
EDA	End-use Disaggregation Algorithm
EISs	Environmental Impact Statements
EMAA	Encapsulated Micron Aerosol Agents
EMP	Environmental Monitoring and Assessment Program
EN	Energy Conservation/Renwable Resources Thrust Area
EO	Electro-optic
EOS	Earth Observing System
EPA	Environmental Protection Agency
EPCRA	Emergency Planning and Community Right to Know Act
ERDEC	US Army Edgewood Research, Development and Engineering Center
ESA	Endangered Species Act
EQ Strat Plan	Environmental Quality Technology Research and Development Strategic Plan
EQT	Environmental Quality and Technology Program
EXCEL	Experimental Chloride Extraction Line
FAA	Federal Aviation Administration
FEDS	Federal Energy Decision Screening Model
FEMP	Federal Energy Management Program
FID	Free-Induction Decay
FORS	Fiber Optic Raman Sensor
FOX	Fluoroalkoxymehyl-3methyl-Oxetane
FS	Feasibility Study
FTS	Fourier Transform Spectrometer
FWPPCA	Federal Water Pollution Prevention a Control Act 1987
GAC	Granular Activated Carbon

GAMOT	Global Acoustic Mapping of Ocean Temperature
GBERL	Gulf Breeze Environmental Research Laboratory
GC	Gas Chromatography
GCDIS	Global Change Distributed Information System
GC/MS	Gas Chromatography/Mass Spectrometry
GCM	Global Climate Monitoring
GCW	Groudwater Circulation Well
GEC	Global Environmental Change Thrust Area
GIMI	Global Imagery Monitor of the Ionosphere
GHPs	Geothermal Heat Pumps
GIS	Geographic Information System
GISS	Goddard Institute for Space Studies
GOCO	Government-Owned/Contractor-Operated
GOMAP	Global Ocean Monitoring and Prediction
GPS	Global Positioning System
GRASS-PRISM	Geographic Resource Analysis Support System - Planning and Resource Integration Stewardship Model
GSE	Ground Support Equipment
GV	Grassland Value Function
H <sub>2</sub> O <sub>2</sub>	Hydrogen Peroxide
HAZMATS	Hazardous Material
HAZMIN	Hazardous Waste Minimization
HCFC	Hydrochlorofluorocarbon
HFC	Hydrofluorocarbon
HMX	Octahydro-1,3,5,7-Tetranitro 1,3,5,7-Tetrazocine
HOPS	Heuristic Optimized Processing Systems
HPLC	High Performance Liquid Chromatography
HUD	Department of Housing and Urban Development
HWs	Hazardous Wastes
HWRC	Hazardous Waste Research Center
IBEAM	Installation Baseline Energy Analysis Model
ICUZ	Installation Compatible Use Zone
IDLAMS	Integrated Dynamic Landscape Analysis and Modeling System
IHDIVNAVSURF- WARCEN	Indian Head Division, Naval Surface Warfare Center
INEL	Idaho National Engineering Laboratory
IPD	Integrated Product Development

IPPD	Integrated Product/Process Development
IRP	Installation Restoration Program
ISB	In situ bioremediation
IUSS	U.S. Navy Integrated Undersea Surveillance System
IVD	Ion Vapor Deposited
JATO	Jet Assisted Take Off
JETCs	Jet Engine Test Cells
JHUAPL	John Hopkins University Applied Physics Laboratory
JPL	Jet Propulsion Laboratory
LAAP	Louisiana Army Ammunition Plant
LAMS	Laser Ablation Mass Spectroscopy
LANL	Los Alamos National Laboratory
LARPS	Large Aircraft Robotic Paint Stripping
LCA	Life Cycle Assessment
LCAAP	Lake City Army Ammunition Plant
LIBS	Laser-Induced Breakdown Spectroscopy
LIF	Improved Laser-Induced Fluorescence
LIN	Liquid Nitrogen
LLNL	Lawrence Livermore National Laboratory
LMS	Lead Hazard Mitigation Management System
LNAPL	Light Non-Aqueous Phase Liquid Pools
LOVA	Low Vulnerability Ammunition
LRS&T	Long Range Science and Technology Program
MADOM	Magnetic and Acoustic Detection of Mines
MAHRSI	Middle Atmospheric High Resolution Spectrograph
MARPOL	International Maritime Organizations Marine Pollution Convention
MAS	Millimeter-Wave Atmospheric Sounder
MB/MS	Molecular Beam/Mass Spectrometric
MCFC	Molten Carbonate
MECL	Methylene Chloride
MEK	Methyl Ethyl Ketone
MMPA	Marine Mammals Protection Act
MM's	Modifier Molecules
MPC	Mobile Power Center
MR/H	Mine Reconnaissance/Hunter
MRTFB	Major Range and Test Facility Base
MSDEM	Mass Spectrometer Performance Prediction Model

MTR	Military Training Routes
MTR, Inc.	Membrane Technology and Research
MTV	Magnesium-Teflon-Viton
MUDSS	Mobile Underwater Debris Survey System
MWCO	Molecular Weight Cutoff
MWOs	Modification Work Orders
N	U.S. Navy
NADEP	Naval Depots
NAPL	Non-Aqueous Phase Liquid
NASA	National Aeronautics and Space Administration
NAVFAC	U.S. Navy Engineering Facilities Command
NBS	National Biological Survey
NCAR	National Center for Atmospheric Research
NCBC	Naval Construction Battalion Center
NDFT <sup>2</sup>	Nonlocal Density Functional Theory
NDSC	Network for Detection of Stratospheric Change
NEETC	National Environmental Education and Training Center
NEPA	National Environmental Policy Act
NESHAP	National Emission Standard for Hazardous Air Pollution
NFESC	Naval Facilities Engineering Science Center
NFESC	Naval Facilities Engineering Service Center
NGB	National Guard Bureau
Ni	Nickel
NMERI	New Mexico Engineering Research Institute
NMR	Nuclear Magnetic Resonance
NOAA	National Oceanic and Atmospheric Administration
NOVs	Notices of Violation
NO <sub>x</sub>	Nitrogen Oxide
NPS	National Park Service
NRaD	Naval Research and Development Center
NRL	Naval Research Laboratory
NSPS	New Source Performance Standards
NTIS	National Technical Information Service
O <sub>3</sub>	Ozone
O&M	Operating and Maintenance
OB/OD	Open Burning/Open Detonation
OC-ALC	Oklahoma City Air Logistics Center

ODC	Ozone Depleting Chemicals
ODS	Ozone Depleting Substances
OEM's	Original Equipment Manufacturers
OH	Hydroxyl Radical
OOAM	Orbiting Ozone and Aerosol Monitor
OPC	Organophilic Clays
OTD	Office of Technology Development
PAFC	Phosphoric Acid Fuel Cells
PAH	Polycyclic Aromatic Hydrocarbons
Pb	Lead
PCA	Tetrachloroethane
PCB	Polychlorinated Biphenyls
PEO/FAS	Program Executive Officer for Field Artillery Systems
PEP	Propellants, Explosives, Pyrotechnics
PI	Principal Investigator
PNL	Pacific Northwest Laboratory
POL	Petroleum, Oil, Lubricants
POPS	Peroxone Oxidation Pilot System
PP	Pollution Prevention Thrust Area
ppb	Parts Per Billion
PTT	Platform Transmitting Terminals
PVD	Physical Vapor Deposition
PVRC	Photovoltaic Review Committee
QA/QC	Quality Assurance/Quality Control
QMP	Quality Management Plan
R&D	Research and Development
RAIDS	Remote Atmospheric and Ionospheric Detection System
RCRA	Resource Conservation and Recovery Act
RDT&E	Research, Development Test & Evaluation
RDX	hexahydro-1,3,5-trinitro-1,3,5-triazine
REEP	Renewable and Energy Efficiency Planning
REMPI	Resonance-Enhanced Multiple Photon Ionization
RMA	Rocky Mountain Arsenal
ROI	Return on Investment
RREL-EPA	Risk Reduction Engineering Laboratory - Environmental Protection Agency
RSKERL	Robert S. Kerr Environmental Research Laboratory
RTG	Room Temperature Gradiometer

S-O&CS	Smokes, Obscurants & CS agents
SAB	Scientific Advisory Board
SAPT <sup>3,4</sup>	Symmetry Adapted Perturbation Theory
SAR	Structural Activity Relationships
SBAA	Sulfuric-Borie Acid Anodize
SBIR	Small Business Innovative Research
SBP	SBP Technologies, Inc.
SCAMP	Subsurface Cleanup and Mobilization Processes
SCAPS	Site Characterization and Analysis Penetrometer System
SCWO	Supercritical Water Oxidation
SDI	Strategic Defense Intiative
SEDAAR	Strategic Environmental Distributed Active Archive Resources
SEM	Scanning Electron Microscope
SERDP	Strategic Environmental Research and Development Program
SF	Supercritical Fluid
SIFDT	Selected Ion Flow-Drift Tube
SMCA	Single Manager for Conventional Ammunition
SNL	Sandia National Laboratory
SNRM	Strategic Natural Resources Management
SOF	Solid Oxide
SRTC	Savannah River Technology Center
STR	Synthetic Tandem Repeat
STRAT	Strategic
SW	Shallow Water
TAMU	Texas A&M University
TAP	Technical Advisory Panel
TAP's	Toxic Air Pollutants
TCE	Trichloroethylene
TDL	Tunable Diode Laser
TES	Threatened and Endangered Species
TIPPP	Tidewater Interagency Pollution Prevention Program
TIWET	The Institute for Wildlife and Environmental Toxicology
TNT	Trinitrotoluene
Tol	Toluene
TPE	Thermal Plastic Elastomer
TTAWG	Technology Thrust Area Working Group
TV	Training Value Function

UARS	Unmanned Air Reconnaissance System
UAVs	Unmanned Aerospace Vehicles
UFA	Unsaturated Flow Apparatus
UM	University of Minnesota
USACERL	U.S. Army Corps of Engineers, Construction Engineering Research Laboratories
U.S.A.E.	United States Army Corps of Engineers
USATHAMA	U.S. Army Toxic and Hazardous Materials Agency
USDA	United States Department of Agriculture
USFWS	US Fish and Wildlife Service
USGCRP	U.S. Global Change Research Program
USGS	U.S. Geological Survey
UST	Underground Storage Tanks
UV	Ultraviolet
UVRs	Ultraviolet Remote Sensing
UXO	Unexploded Ordnance
VAAP	Volunteer Army Ammunition Plant
VLA	Vertical Line Arrays
VOC	Volatile Organic Compound
VPI	Virginia Polytechnic Institute and State University
VSW	Very Shallow Water
WES	Waterways Experiment Station
WIC	Water-Injected Combustor
WHV	Wildlife Habitat Value Function
WS	Weapon Systems
XCRIS	X-windows-based Cultural Resource Information System
XPS	X-ray Photo-Electron Spectroscopy
XRD	X-ray Diffraction
XRS	X-ray Spectrometry
Zn	Zinc



## INTRODUCTION

The Strategic Environmental Research and Development Program (SERDP) is mandated in Title 10 U.S.C. §§2901-2904. SERDP addresses environmental matters of concern to the Department of Defense (DoD) and the Department of Energy (DOE). According to this law, the purposes of the Program are to:

- (1) Address environmental matters of concern to DoD and the DOE through support for basic and applied research and development of technologies that can enhance the capabilities of the departments to meet their environmental obligations.
- (2) Identify research, technologies, and other information developed by the DoD and the DOE for national defense purposes that would be useful to governmental and private organizations involved in the development of energy technologies and of technologies to address environmental restoration, waste minimization, hazardous waste substitution, and other environmental concerns, and to share such research, technologies, and other information with such governmental and private organizations.
- (3) Furnish other governmental organizations and private organizations with data, enhanced data collection capabilities, and enhanced analytical capabilities for use by such organizations in the conduct of environmental research, including research concerning global environmental change.
- (4) Identify technologies developed by the private sector that are useful for DoD and DOE defense activities concerning environmental restoration, hazardous and solid waste minimization, and prevention, hazardous material substitution, and provide for the use of such technologies in the conduct of such activities.

SERDP identifies and develops technology to enhance capabilities to meet the environmental commitments of the Department of Defense and those environmental requirements of the Department of Energy that are of common interest to the DoD. It also serves to foster the exchange of scientific information and technologies among the participants, other governmental agencies, and the private sector. The SERDP leverages and interacts with other environmental programs to identify and solve defense specific needs, extends applications of defense information to others, and builds on existing science and technology to derive more useable and cost-effective approaches for achieving reductions in environmental risks.

## PROGRAM SUMMARY

The Strategic Environmental Research and Development Program is the DoD's Corporate environmental technology development program and transfer mechanism. It fully leverages the complementary programs found within the uniformed Services, and those of DOE and EPA. The SERDP Council has collectively implemented policies that take full advantage of the inherent capabilities of the participating organizations and has directed the development of the Program which is fully compliant with the desires of the SERDP authorizing language.

### SERDP Goals

The Departments' matters of concern may be stated in terms of operational and other cost impacts of meeting environmental obligations, and identifying those obligations that cause the greatest impact. Under policy guidance existing at the commencement of the FY 1995 Program build, SERDP shall be implemented to minimize all negative impacts on the Departments' primary missions in fully meeting their environmental objectives. However, SERDP only supports activities relevant to the DoD mission and those mission related activities that address problems which are common to both DoD and DOE.

The goals of SERDP in FY 1995 were to support environmental quality programs that research and develop new knowledge, technology, systems, and applications to:

- Address matters of concern to unencumber military operations, enhance military systems' effectiveness, and improve the safety of personnel in meeting the Departments' environmental obligations.
- Address defense concerns for reducing the future life-cycle costs, including those associated with environmental cleanup and costs of full compliance with environmental regulations.
- Help solve significant national and international environmental problems through the application of the Departments' technical capabilities, analytical systems and information.

The purposes of SERDP were achieved through:

- Promoting the maximum exchange of information, and to minimizing duplication regarding environmentally related research and development activities.
- Ensuring that research and development (R&D) activities under the SERDP complement, but do not duplicate, other ongoing activities.
- Providing for appropriate access to data under the control of, or otherwise available to, the Departments of Defense and Energy that is relevant to environmental matters.

- Providing governmental and nongovernmental entities with analytical assistance to address significant national and international environmental problems, including global environmental change research.
- Providing for the identification of energy technologies developed for national defense, or other Federal purposes, that might have environmentally sound, energy efficient applications.
- Providing for the identification of, and planning for the demonstration and use of, existing environmentally sound, energy-efficient technologies developed by the private sector.
- Providing for the identification and support of programs of basic and applied research and development in technologies useful -
  - to facilitate environmental compliance, remediation, and restoration activities;
  - to minimize waste generation, including reduction at the source; and
  - to substitute use of non-hazardous, non-toxic, non-polluting, and other environmentally sound materials and substances.
- Providing for the identification and support of research, development and application of other technologies developed for national defense purposes.
- Conducting joint research and development projects relating to innovative technologies, management practices and other approaches.

#### SERDP Technical Strategy

SERDP has pursued four lines of approach in formulating and executing its support for environmental quality R&D. SERDP:

1. Identified and funded break-through or major-impact joint R&D programs that address mutual priority concerns of the Departments, and are within the goals of SERDP.
2. Assumed the lead to identify and support R&D programs to help solve major national and international environmental problems using the Departments' technical and research capabilities, as well as their unique data collection and analysis capabilities.
3. Identified opportunities to accelerate existing defense environmental quality R&D programs, and fund those that address the priority concerns of the Departments.
4. Identified and leveraged existing technologies to address environmental concerns of DoD and DOE.

## Technical Thrust Areas

In executing this strategy, SERDP has used the existing four pillars as stated within the Services' Environmental Quality Technology Strategic Plan - Cleanup, Compliance, Conservation, and Pollution Prevention - and continued to include two additional areas, Global Environmental Change and Energy Conservation/Renewable Resources. Individual requirements, goals and R&D objectives have been developed for each of the six SERDP technology thrust areas.

### Cleanup

Cleanup focuses on conducting research and development to achieve more efficient and effective environmental cleanup of soil, sediment, groundwater, surface water and structures already contaminated by past practices with hazardous materials (including unexploded ordnance), radioactive (low-level or mixed wastes) and toxic substances. The principal focus of this area is: cleanup/remediation techniques and technologies, monitoring and characterization methods and technologies, and assessment methods.

The Departments of Defense and Energy own and operate thousands of installations, ranging from training bases to industrial production facilities. Many of the defense facilities have been operating for over a century. During this time, the agencies, like much of American society, operated them without full respect for the environment. As a result, the defense agencies now have more than 17,000 sites that require environmental cleanup. Using today's technology, the cost to remediate DoD sites alone is estimated at \$35 billion, and the total cost of cleanup at current and former defense sites (including DOE sites) is projected to exceed \$200 billion.

DoD and DOE need technology to reduce remediation costs, quicken the pace of cleanup, and protect human health and the environment. Experience with past environmental technology development has demonstrated a return on investment from a factor of 10 to 1000. The government must take advantage of these high returns on R&D investment and implement new innovative technologies.

The Departments' cleanup goals are: (1) to attend to imminent threats to public health and safety, and (2) to remediate all defense sites as quickly as feasible within the constraints of available resources. In support of this goal, the site remediation objective is to provide project managers with products that will enable the initiation and/or completion of cost effective, timely remediation requirements from the user that focus on assessment, characterization, and treatment in coordination with Research and Development activities that support those requirements.

Within the Cleanup technology thrust area, the primary environmental concerns are the need to:

- Comply with various Federal and State regulations.
- Implement timely, effective, and affordable methods for site characterization.
- Ensure the use of effective, affordable remediation technologies.

- Continue development of knowledge about health and environmental effects from environmental impacts.

To facilitate transfer of cleanup technologies to field use, SERDP has developed the DoD National Environmental Technology Demonstration Program to conduct side-by-side demonstrations and compare the efficacies of two or more technologies that have the same objective. SERDP Cleanup demonstrations are expected to plan on conducting their efforts at one of these sites, as applicable.

#### Research and Development Objectives:

1. Develop site investigation methods and technologies that are capable of locating and characterizing wastes in a timely, cost effective, and quality manner.
2. Develop innovative, compliant remediation technologies that reduce costs for sites containing explosives, propellants, fuels, solvents, heavy metals, organic contaminants, radioactive (low-level or mixed wastes), and other inorganic contaminants.
3. Develop reliable and cost effective means to identify, assess, and remediate lands and underwater areas (inland, estuarian and marine) contaminated with unexploded ordnance.
4. Develop cost-effective, risk-based assessment tools, methods and protocols to determine fate and transport effects and determine ecological impacts of significant defense-related contaminants.
5. Develop a risk-based assessment methodology to establish cleanup levels for planned land use.

#### Compliance

This technology thrust area includes research and development to support environmental monitoring, waste treatment and disposal, marine risk assessment, and environmental management not directly related to site restoration, but related to meeting current and future environmental compliance requirements. It also includes end-of-pipe recycling, that being waste that is recycled for other than its original purpose. Further, it addresses understanding the fate and transport of defense-related air and waste water discharges.

Both domestic and international environmental regulations are becoming more demanding. These regulations affect issues ranging from control of hazardous materials and effluents, and air and water quality, to remediation methodologies. The affected defense activities and assets include training and operating installations; ordnance and weapons manufacturing; repair and rebuilding installations; and ships and aircraft.

At the international level, the International Maritime Organization's Marine Pollution Convention (MARPOL) Annexes (to which the United States subscribes) are restricting or prohibiting DoD operations in international waters and MARPOL Special Areas unless vessels meet international environmental statutes. In addition, countries that host DoD

facilities are implementing and enforcing compliance with regulations and standards that restrict or prohibit DoD operations in foreign ports and bases. DoD is projected to spend between \$2-3 billion annually for compliance through the year 2000. New technology must be developed to reduce this cost and enable compliance with the increasingly stringent requirements of evolving national and international regulations to fulfill its mission unencumbered by regulatory fines, restricted access, and negative public reactions.

The Departments' compliance goal is two fold: (1) to ensure that all applicable environmental rules and regulations are met; and (2) to eliminate or reduce the chances for Notices of Violation (NOVs).

The primary concerns of this thrust area have a direct relationship to losses of operational capability, costs of compliance, and significant legal requirements. These concerns are embodied within pertinent domestic legislation, and include the need to:

- Control and monitor air and wastewater discharges.
- Control and monitor solid waste, including plastics processing and biodegradation for maritime and land-based uses.
- Conduct effective treatment and disposal of hazardous waste.
- Monitor and control noise generation and transport.
- Characterize pollutants and waste behavior.
- Implement compliance, monitoring, and assessment tools.
- Understand and control electromagnetic emissions.

#### Research and Development Objectives:

1. Develop control, treatment and disposal technologies for ship operations (bilge, grey/black waste water, solid waste management and air pollution).
2. Perform research on environmentally and economically acceptable alternatives to open burning or open detonation of propellants, munitions and energetic materials.
3. Develop new control, treatment and disposal technologies for hazardous wastes resulting from manufacturing, maintenance and industrial operations.
4. Develop control, treatment and disposal technologies for installation support operations (waste, waste water, solid waste management and air pollution).
5. Develop control and monitoring techniques for non-energy related air toxic emissions to include development and testing of models to predict emissions of, and exposures to, pollutants from defense facilities and to design effective, multimedia environmental management strategies.

6. Develop management and mitigation technologies for noise pollution.
7. Develop control technologies to mitigate the impacts of inadvertent spills or discharges and facilitate expediency of cleanup efforts.
8. Develop improved monitoring, characterization and assessment tools related to environmental compliance and management.
9. Develop standardized risk assessment methods, protocols, models and data for air and waste water discharges from defense activities.

### Conservation

There is a growing need to effectively use and maintain training and testing facilities to support newly defined requirements. An important consideration in maintaining the use of these facilities is the management of natural resources, which often provide the realistic training environment in which to exercise and test the capabilities of the military forces. Various national laws (such as the National Environmental Policy Act (NEPA), the Endangered Species Act (ESA), the National Historic Preservation Act (NHPA), and local laws, regulations, and requirements provide specific stewardship direction for these training and testing areas. When use of a facility is limited due to environmental noncompliance or public concern, management solutions which provide compliance and enable the Commander to maintain readiness must be available.

The Departments' goals are to conserve, protect, enhance, and manage the natural and cultural resources under its control as consistent with the mission, thus fully complying with all laws and regulations, and providing optimal use of those resources. These goals include assessing, conserving, preserving, and restoring ecological resources and being responsive to cultural and natural resource concerns. By better understanding the environment in which they operate, the Departments' can improve their land-use decisions to promote conservation, while continuing to fulfill their military mission.

In attempting to attain these goals, several concerns must be addressed, specifically our ability to: a) adequately protect our natural and cultural resources, including conservation of wetlands, forests, threatened and endangered species, historic and archeological sites, rivers and waterways, and coastal barrier islands; b) provide access to training and testing areas for benefits such as recreation, agriculture, forestry, and multiple uses; and c) comply with NEPA.

These concerns result in the following requirements for Conservation, which are the need to:

- Protect the biological health and diversity of defense installation natural ecosystems.
- Reduce the cost of ecosystem rehabilitation.
- Improve assessment tools for monitoring long- and short-term effects.

- Recapture valuable testing/training lands lost due to conservation and stewardship issues, such as soil erosion.
- Improve protection of threatened and endangered species, including marine animals.
- Obtain natural and cultural resources baseline data.

#### Research and Development Objectives:

1. Develop standardized, cost effective methods to inventory, characterize, and monitor natural and cultural resources.
2. Develop and demonstrate methods and techniques to maximize availability of military lands with minimal impact to natural and cultural resources in a manner consistent with the Services' mission and Federal environmental regulations.
3. Develop and demonstrate efficient and effective techniques to proactively conserve and restore natural and cultural resources, particularly threatened and endangered species and the ecosystems on which they depend.
4. Develop and demonstrate computer-based models to determine the incremental and cumulative impact of military activities on natural and cultural resources, and assess effectiveness of conservation and restoration techniques.
5. Develop techniques to assess and predict the impact of military use of areas on the critical elements of the ecosystem impacting biodiversity.
6. Develop and demonstrate methods and techniques for human resource management, including recreation, economic evaluation and environmental education.

#### Energy Conservation/Renewable Resources

The DoD, is the single largest user of energy in the world, with an annual energy consumption of over 190 million barrels of oil equivalent at a yearly cost of over \$6.9 billion. This equates to 2.1 percent of all of the energy used in the United States and accounts for 85 percent of all the energy used by the Federal Government. Electricity accounts for \$2 billion of the annual energy bill.

In 1988, DoD set a goal of reducing its FY95 energy consumption by 10 percent over its FY85 consumption. This goal was extended to all Federal agencies by the Federal Energy Management Act of 1988. In 1991, Executive Order 12759 increased the amount of energy reduction to 20 percent for all Federal agencies by FY2000 compared to the FY85 base year. Executive Order 12902 has further revised DoD's energy reduction goal by calling for a 30% reduction in energy usage throughout the DoD by the year 2005. This equates to saving 45 million barrels of oil equivalent and saving \$975 million annually.



The Energy Conservation/Renewable Resources thrust area focuses on the generation, transmission, use and conservation of energy. It includes research, technology development, and demonstration of environmentally sound alternative energy sources to focus on the major concerns, which are to reduce (1) dependence on fossil fuel sources; (2) overall energy consumption; (3) energy costs; and (4) "greenhouse effects." It also focuses on processes that control fossil-fuel air emissions of fixed and mobile energy sources.

The mission of the Department of Energy is to develop innovative energy technologies to achieve the target objectives listed above. The Department of Defense is relying upon the technology development efforts of DOE, in that SERDP will act as a means to transfer this technology to the defense establishment and other federal agencies, as intended by the original SERDP authorizing language.

The principal needs of this thrust area are to provide technology to help:

- Reduce DoD facility energy consumption by 30 percent.
- Maintain energy security (conserve strategic petroleum reserve).
- Reduce emissions to comply with regulations.
- Use alternative energy sources.
- Reduce carbon dioxide emissions to 1990 levels by the year 2000.

Research and Development Objectives:

1. Demonstrate, test, and evaluate innovative technologies, techniques, and energy generating systems, components and processes that contribute to reduced emissions and energy consumption.
2. Demonstrate additional uses of alternative/renewable energy resources, such as geothermal, solar photovoltaic, wind and hydropower.

#### Global Environmental Change

The SERDP authorizing language directs that the DoD/DOE technical advantage and infrastructure be employed toward understanding major environmental issues, recognizing the potential dual use application of this research. While this Thrust Area focuses on elements of Global Environmental Change (GEC) defined by the U.S. Global Change Research Program (USGCRP), it also serves to enhance our understanding of the weapons system environment.

The scientific community is responding to questions recently posed by national and international policy makers. The central goal of the USGCRP is to establish the scientific basis for national and international policy-making related to changes in the global Earth system. Responding to that charge, DoD, DOE, and EPA SERDP research objectives will

focus on the need to distinguish natural changes from anthropogenic impacts over a range of scales commensurate with those questions.

A primary interest of the Global Environmental Change Thrust is identification of national assets and capabilities that concurrently address environmental concerns of DoD/DOE and stated goals of the USGCRP. Research opportunities invited to address these concerns include:

- Integration of new and existing programs in data collection and analysis methodologies.
- Conduct fundamental studies of essential environmental processes addressing identified GEC issues.
- Environmental modeling of atmospheric, oceanographic and terrestrial phenomena at local and regional scales.

Research and Development Objectives:

1. Develop innovative technologies to measure the global distribution of greenhouse gases, aerosols and ozone and to develop adaptive analysis technologies to understand the effects on the climate system.
2. Develop innovative technologies to measure, analyze and determine the impact of global climate change on ocean variability and the air-ocean interface.
3. Develop an understanding of hydrologic system response to energy and weather system changes, including how the energy regime affects the hydrologic regime (terrestrial) including water supply, navigation, water quality, flood control and ecosystem viability issues.
4. Develop an understanding of surface and marine processes and ecosystems and their relationship to GEC.
5. Develop, demonstrate and apply DoD, DOE and EPA remote sensing capabilities and technologies to support environmental change research and establish enhanced observation strategies and systems.
6. Determine and demonstrate the applicability of existing archives of classified data products and related database capabilities to understand and mitigate climate change.
7. Develop methods for analyzing and merging remote sensing and in-situ data measurements from various sources and times.
8. Develop enhanced ocean/atmospheric circulation models with the capability to forecast significant global environmental events at local and regional scales.

9. Develop numerical methods to establish efficient environmental monitoring systems at regional and global scales.

### Pollution Prevention

Pollution Prevention focuses on reducing or eliminating the creation of pollution. The application of pollution prevention will positively influence the other SERDP Thrust Areas by encouraging the use of innovative technologies and practices, reducing pollutants to be managed at the source, and promoting the sustainable use of natural resources.

As defined under the Pollution Prevention Act of 1990, pollution prevention means "source reduction" and other practices that reduce or eliminate the creation of pollutants through increased efficiency in the use of raw materials including energy, water and other resources, or materials substitution. Source reduction is defined as any practice that reduces the amount of any hazardous substance, pollutant, or contaminant entering any waste stream or otherwise released into the environment (including fugitive emissions) prior to recycling, treatment or disposal. Source reduction includes: equipment or technology modifications, process or procedure modifications, reformulation or redesign of products, substitution of materials and improvements in housekeeping, maintenance, training, or inventory control. Source reduction does not include energy recovery, treatment, disposal, or end-of-pipe recycling if the waste is used for other than its original purpose. However, SERDP Pollution Prevention does address end-of-pipe recycling of wastes, if used for the same purpose. For example, munitions and their materials may be recycled for production of new munitions. Practices commonly described as "in-process recycling" also qualify as source reduction.

Executive Order 12856 "Federal Compliance with Right-to-Know Laws and Pollution Prevention Requirements" states that the Federal Government should become the leader in the field of pollution prevention through the management of its facilities, its acquisition practices, and in supporting the development of innovative pollution prevention programs and technologies. The Executive Order challenges the heads of the Departments of Defense and Energy to voluntarily set goals to reduce their agency's total releases of toxic chemicals to the environment and off-site transfers of such toxic chemicals by 50 percent by December 31, 1999, to the maximum extent practicable through source reduction. Toxic chemicals are those listed in section 313(c) of the Emergency Planning and Community Right-to-Know Act (EPCRA).

The DoD and DOE have many unique functions, such as the development and operation of sophisticated weapons systems, that demand specialized, high-performance materials. Many of these materials are the same toxic chemicals that are targeted for voluntary reduction. The challenge to DoD and DOE is to find new high performance materials that are not toxic under EPCRA, or to determine innovative ways to use toxic chemicals in order to reduce releases and off-site transfers.

Waste minimization programs in the commercial sector have demonstrated that pollution prevention saves money. Clearly, pollution prevention will be a key approach for users to cost-effectively meet their environmental obligations, and improved technology is the catalyst for better pollution prevention. Material substitutions, manufacturing process changes, inventory and stockpile controls, and adjustments to routine, daily processes will be

required. Also, significant behavior and attitude changes by field commanders will be required before the Services can effectively conduct their missions in a manner that minimizes waste.

The Pollution Prevention Thrust Area is concerned with DoD and DOE's need to:

- Identify alternatives for hazardous and toxic chemicals/materials.
- Reduce the use of hazardous and toxic chemicals/materials.
- Reduce the volume and toxicity of wastes and pollutants through source reduction.
- Improve the efficiencies of mechanical and chemical systems.
- Design and acquire major systems with environmental ramifications as key evaluation components.
- Consider the life-cycle effect of materials and systems.

Research and Development Objectives:

1. Develop alternative materials and processes to replace hazardous heavy metals and metallic compounds (e.g. chromium, cadmium, lead, nickel) used in plating, surface finishing, adhesives, and sealants.
2. Develop alternatives to hazardous and toxic chemicals used for surface cleaning, degreasing and stripping.
3. Develop alternatives to volatile organic compound (VOC) coatings, adhesives, sealants and lubricants.
4. Develop alternatives to hazardous and toxic chemicals, especially ozone depleting substances (ODS) used in climate control, refrigeration, as solvents, and as fire-fighting agents. SERDP will focus on "second generation" ODS substitutes for refrigeration and fire-fighting agents. Current substitutes shall be funded under the DoD's ODS Technology Development Plan.
5. Develop on-line sensors and monitoring systems to prolong usefulness of toxic chemicals in operations such as plating, stripping, and mechanical maintenance.
6. Develop techniques to regenerate, recycle, re-use, and stockpile toxic chemicals and materials, such as acids, metals, solvents, ODS, propellants, explosives and heavy metals within the operational process (in-process recycling).

7. Develop techniques to reduce secondary waste generation during environmental cleanup, and methods to most efficiently handle cleanup wastes through proper waste characterization and recycling.
8. Develop predictive models to aid in the development of environmentally sound weapon systems and platforms during concept development, design, test and evaluation, maintenance (logistics support documentation), and decommissioning.
9. Develop cost effective, environmentally preferable packaging and recycling approaches to reduce generation of solid waste from defense related operations.

### Investment Strategy

A significant reduction in appropriated funds from \$160 million in FY 1994 to \$61.9 million in FY 1995 has caused the SERDP Council to revise its investment strategy. The Council recognized that this Department of Defense Program must focus on defense mission-relevant environmental issues; other programs and industry should address environmental and other concerns that are not defense mission related.

Accordingly, the SERDP Council voted to complete the major efforts in Global Environmental Change and Energy Conservation/Renewable Resources in FY 95 and 96. Beginning in FY 97 these two Technology Thrust Areas will not be funded. However, relevant technologies/capabilities that contribute to the defense mission may be competed in the other four remaining mission-relevant environmental Technology Thrust Areas.

### Actions to Preclude Duplication of Effort

SERDP initiated several actions to improve Program quality and responsiveness. In addition to continuing to leverage the existing management structure created by the Services' Reliance coordinating mechanism to assist in managing SERDP, the Council appointed a full-time Senior Executive Service government employee as the SERDP Executive Director. Dr. John Harrison, formerly the Director of the Environmental Laboratory at U.S. Army Engineers Waterways Experiment Station, selected a small full-time staff with which to manage the Program. This staff is organized to incorporate technical program area managers that provide direct oversight of each of the six Technical Thrust Areas.

One of Dr. Harrison's first actions was to conduct a full-scale Program review of all ongoing and completed projects. This review resulted in several programmatic adjustments and set the precedent for future annual reviews.

The Executive Director has placed increased emphasis on communicating program development actions with members of the Executive Working Group (a coordinating body representing members of the SERDP Council) and the SERDP Scientific Advisory Board (SAB). Additionally, he increased the level of input for the SAB by asking the Board to review all new starts, regardless of requested value, as well as continuing efforts valued in excess of \$900 million. As part of this increased involvement, he arranged a series of informational briefings to review the R&D efforts in related areas within the DOE, EPA and the DoD. Briefings included the efforts of the DOE Office of Technology Development (EM-50), EPA Office of Research and Development, Deputy Under Secretary of Defense (Environmental Security) focusing on the Environmental Security Technology Certification Program, and the Interagency Environmental Technology Office. These briefings, in addition to Thrust Area overviews and project/proposal briefings provided significant internal technology transfer opportunities as well as providing the SAB and attendees with a full understanding of the interrelationships of the various related R&D programs. In a similar initiative, the SERDP hosted its first annual SERDP Symposium - a significant technology transfer event that assembled nearly 500 participants involved in all aspects of environmental science and technology R&D from academia, industry and the federal government.

Dr. Harrison cochaired, with the DOE Director, Office of Technology Development (EM-50), a workshop on promoting the development and use of innovative remediation technologies as one segment of an Environmental Technology Strategy for President Clinton to highlight on Earth Day 1995 (22 April 95). This overall effort is a follow up to the Vice President's report, *Technology for Sustainable Future*.

Changes in Military Specifications

TABLE I

NUMBER	PROJECT	SPEC #	CHANGE
PP-67	Solvent Substitution and Low VOC Cleaners	MIL-C-85704	Revised to include a low VOC type turbine engine cleaner to replace the high solvent type. 2 products were qualified.
PP-65	Organic Protective Coatings and Application Technology  High Solids Epoxy Primer	MIL-P-2337	Addition of Non-Chromate Primer Class (N) to meet proposed Clean Air Act rule. Demonstration of this technology is in progress and will continue in FY96. Spec was also revised to eliminate all non-VOC compliant classes and all ODS chemicals.
PP-65	Organic Protective Coatings and Application Technology  Water-borne Epoxy Primer	MIL-P-85582	Addition of Non-Chromate Primer Class (N) to meet proposed Clean Air Act rule. Tech Demo on-going. 1 material qualified to non-chromate class. Spec also revised to eliminate all non-VOC compliant classes and all ODS chemicals.
PP-65	Organic Protective Coatings and Application Technology  Touch-up Lacquer Coating	MIL-C-81352	Addition of a Water-borne Polyurethane Class (II) to provide a low VOC one-component touch-up coating to meet proposed Clean Air Act CTG limits. Service demo of 2 materials in progress.
PP-65	Organic Protective Coatings and Application Technology  Elastomeric Primer	TT-P-2760	Addition of Non-Chromate Primer Class (N) to meet proposed Clean Air Act rule.
PP-66	Aircraft Maintenance Chromium Replacement  Anodize Process	MIL-A-8625	Revised to include both Sulfuric/Boric Acid (IC) and Thin Film Sulfuric Acid (IIB) types as alternatives to Chromic Acid Anodizing to meet proposed Clean Air rule. Technology has been implemented at NADEP North Island, and is in progress at the other Depots. Transition to entire Aerospace industry via the spec revision.

## Contracts, Agreements, or Other Documents for Cooperative Research and Development Activities

In FY 1995, over 65% of all funds were distributed to industry, not-for-profit organizations, or universities via contracts, interagency agreements, cooperative R&D agreements and grants. This figure has remained relatively consistent over the life of the SERDP and is planned to continue at a similar level.

## Transferring Technology and Information

Transferring technology into field use is a principle goal of SERDP. Accordingly, SERDP management has taken significant steps to facilitate and enhance technology transfer and transition.

SERDP hosted its first annual symposium - a technical exposition that assembled nearly 500 attendees in the Washington DC area to hear keynote policy addresses, 63 technical presentations and to view 94 technical exhibits - which provided a forum to exchange defense-relevant, environmental technology information and ideas.

A SERDP Quarterly Information Bulletin was developed and distributed to over 2,600 people at all levels of developers and managers, both in the private and governmental sectors. This document featured SERDP accomplishments, articles on management initiatives, and highlights of Program development issues. A complete listing of SERDP products' is included annually in the Bulletin to insure all readers/researchers are completely aware of the documents, briefings and other publications that are available.

A SERDP Home Page was created and placed on the Internet World Wide Web. The Home Page allows users of the Internet to become familiar with SERDP goals and objectives, technical areas of interest, planning calendars, performers, management structure, and program results. Plans for the future include providing project summary data and SERDP performers with associated hypertext information to describe the work being performed at various locations.

Several SERDP projects have technology information transfer as their primary goal. In Pollution Prevention, the EPA leads a project entitled, "Integrated Solvent Substitution Data Base", having a common name of "EnviroSense". EnviroSense links and shares information from the data bases of several Federal Agencies and Associations that focus on substitutes for hazardous solvents. Users of this data base can easily conduct a search for acceptable substitutes that are requirement specific. Another project, the "DoD/National Environmental Technology Demonstration Program", cooperates with the regulators, stakeholders, and industry to conduct standardized, controlled remediation technology demonstrations. Results are standardized and well-documented. Validation of these technologies may also be conducted on these sites with contributing funds from other R&D programs, such as the Environmental Security Technology Certification Program.

## Additional Recommendations or Proposals to Congress

There are no additional recommendations or proposals to Congress.



## FY 1994 PROGRAM

In FY 1994, 128 projects out of 1,300 proposals were funded from the \$160 million appropriation.

A summary of the FY 1994 Program funding distribution by Technology Thrust Area is shown in Table II. Tables III through VIII show titles, executing organizations and actual FY 1994 funding received by the projects and described in the SERDP 1994 *Annual Report and Five-Year (1994-1998) Strategic Investment Plan*, which was distributed in September 1994.

TABLE II FY 1994 FUNDING SUMMARY	Congressional Interest \$(K)	Project Amount \$(K)	FY94 Total Amount \$(K)
Cleanup	4,000	34,494	36,539
Compliance	3,950	13,013	16,963
Conservation	---	9,215	9,215
Energy Conservation/Renewable Resources	---	10,900	11,000
Global Environmental Change	1,250	48,645	49,895
Pollution Prevention	---	26,883	26,753
FY 1994 Scientific Advisory Board and Council Support			1,686
Undistributed Reductions			6,074
Unfunded Congressional Interest Item			1,875
<b>FY 1994 APPROPRIATION TOTAL</b>			<b>160,000</b>

<b>TABLE III FY 1994 CLEANUP PROJECTS</b>		<b>Actual Funding FY94 \$(K)</b>
<b>Characterization, Monitoring, Modeling, Measurement, Methods - Field</b>		
Accelerated Tri-Services SCAPS Sensor Development (A)		3,375
The Sensitive Detection of Unexploded Ordnance and other Hazardous Materials (A)		290
Field Portable FTS Fiber Optic VOC Sensor (AF)		55
Real Time Neural Network Raman Signal Enhancement (DOE)		180
Integrated Characterization Program Combining DOE, EPA and DoD Sensor Technologies (DOE)		300
Silica Fiberoptic Probe for Site Characterization (DOE)		435
Subsurface Gas Flowmeter (DOE)		125
Removal of VOCs from Contaminated Groundwater and Soils by Pervaporation (EPA)		280
Subsurface Bioremediation Process Monitoring Indicators (EPA)		550
In Situ "Inside-Out" NMR Sensor for Contaminant ID (N)		450
Mobile Underwater Debris Survey System (N)		1,595
Rapid Detection of Explosives and Other Pollutants (N)		112
<b>Hazard Risk Assessment, Modeling, Methodologies - Fate/Transport Models</b>		
Toxicology and Human Health Risks (AF)		1,400
<b>Hazard Risk Assessment, Modeling, Methodologies - Methodology and Protocol</b>		
Hazard Assessment Techniques and Biomonitoring Technology (A)		1,745
<b>Treatment Technologies - Groundwater/Surface Water</b>		
Biosorption Treatment of Plasticizers and Solvents (A)		750
Enhancing Bioremediation Processes in Cold Regions (A)		700
Peroxene Treatment of Contaminated Groundwaters (A)		950
Aerobic Bioremediation of a Contaminated Aquifer (AF)		430
Air Waste Stream Treatment Technologies (AF)		700

<b>TABLE III FY 1994 CLEANUP PROJECTS</b>		<b>Actual Funding FY94 \$(K)</b>
Bioremediation of Hydrazine/Energetic Materials (AF)		420
Catalytic In Situ Treatment of Chlorinated Solvents (AF)		720
Joint US/Germany In-Situ Bioremediation Demonstration (AF)		250
Aquifer Restoration by Enhanced Source Removal (EPA)		2,200
Removal and Encapsulation of Heavy Metals from Ground Water (EPA)		350
Encapsulated Bacteria for In Situ PAH Bioremediation (N)		350
In Situ Bioremediation of Fuel and Efficacy Monitoring (N)		2,450
<b>Treatment Technologies - Soils/Sludges</b>		
Air Sparging and In-Situ Bioremediation Research (A)		557
Explosives Conjugation Products in Remediation Matrices (A)		500
Integrated Biotreatment Research Program: From Flask to Field (A)		2,450
Surfactant-Enhanced Biodegradation of Contaminants (A)		700
Cleanup of TRU Contaminated Soils with CO <sub>2</sub> Soluble Ligands (DOE)		0
Fuel Hydrocarbon Remediation (N)		550
<b>Other</b>		
National Environmental Technology Test Sites Program (A)		6,620
Northeast Institute for Environmental Remediation (A) *		4,000
	<b>Cleanup Total</b>	<b>36,539</b>

\* Congressional Interest

<b>TABLE IV FY 1994 COMPLIANCE PROJECTS</b>		<b>Actual Funding FY94 \$(K)</b>
<b>Boiler/Engine Emissions</b>		
Metal Perovskite Catalysts for NOx Reduction (AF)		175
Steady-State/Nonsteady-State Nox Emission Control (AF)		850
e-SCRUB - The Application of DNA Pulsed Power to Electron Scrubbing of Flue Gas to Remove Unwanted By-Products (DNA)		1,000
Compact, Closed-Loop Controlled Waste Incineration (N)		700
Reduction of NOx Emissions from Marine Power Plants (N)		750
<b>General Hazardous Waste Management</b>		
Lead-Based Paint Hazard Mitigation (A)		700
Emission Reduction Planning Model (AF)		200
Laser Ablation/Ionization Characterization of Solids (DOE)		380
Vapor Permeation VOC Recovery from Refueling and Storage (EPA)		250
Solid Waste Encapsulation (DOE) *		100
<b>Monitoring</b>		
Advanced Mass Spectrometry for Atmospheric Monitoring (AF)		500
Leak Location in Underground Pipelines (EPA)		1,921
Air Quality Monitor (AF) *		350
<b>Noise Impacts</b>		
Controlling, Assessing, Managing, and Monitoring the Noise Impact from Weapons, Helicopters, and Aircraft on Training and Readiness (A)		550
<b>Open Burning/Open Detonation</b>		
Characterization Open Burning/Open Detonation Emissions (A)		1,128
Measuring and Modeling for OB/OD Permitting (EPA)		350
<b>Physical Treatment Processes</b>		
Hydrothermal Reduction of Energetic Wastes (AF)		375

<b>TABLE IV FY 1994 COMPLIANCE PROJECTS</b>		<b>Actual Funding FY94 \$(K)</b>
Encapsulation of Hazardous Ions in Smectite Clays (DOE)		380
Kinetics of Supercritical Water Oxidation (DOE)		740
Waste Forms Based on Separations Media (DOE)		200
Supercritical Water Oxidation of Organic Wastes (N)		364
<b>Shipboard Emissions</b>		
Shipboard Non-Oily Wastewater Treatment System (N)		700
<b>Waste Minimization/Recycling</b>		
Evaluation of the Use of Waste Energetics as Supplemental Fuels (A)		800
<b>Other</b>		
National Environmental Education and Training Center (NEETC) (A) *		3,500
<b>Compliance Total</b>		<b>16,963</b>

\* Congressional Interest

<b>TABLE V FY 1994 CONSERVATION PROJECTS</b>		<b>Actual Funding FY94 \$(K)</b>
<b>Community Ecosystem - Management</b>		
Landscape Watershed/Ecosystem Management (A)		1,161
Strategic Natural Resource Management Methodology (DOE)		863
<b>Multiple - Risk/Impact Assessment</b>		
Assessment and Management of Risks to Biodiversity and Habitat (EPA)		1,325
<b>Species/Genetic - Management</b>		
Threatened, Endangered and Sensitive Resources (A)		805
<b>Species/Genetic - Resource Characterization</b>		
Fishing Enforcement/Whale Monitoring Using IUSS (N)		3,000
<b>Species/Genetic - Risk/Impact Assessment</b>		
The Effects of Aircraft Overflights on Birds of Prey (AF)		311
Ecological Biomarkers: Monitoring Wild Fauna at DoD Installations (EPA)		800
Genetic Diversity Monitoring in Plants and Wildlife (EPA)		200
Marine Mammal Health Monitoring (N)		250
<b>Watershed/Landscape - Management</b>		
Strategy for Resource Management on DoD/DOE Lands Combined with Decision Support for Disturbed Ecosystem Renewal (DOE)		500
<b>Conservation Total</b>		<b>9,215</b>

<b>TABLE VI FY 1994 ENERGY CONSERVATION/RENEWABLE RESOURCES PROJECTS</b>		<b>Actual Funding FY94 \$(K)</b>
<b>Energy Conservation</b>		
Low Energy Model Installation Program (A)		1,650
Natural Gas Based Air Conditioning Demonstration (A)		230
Advanced Cogeneration and Absorption Chilling (DOE)		300
Optimize Energy Efficiency of AC Induction Motors (EPA)		250
<b>Renewable Energy</b>		
Fuel Cells for Military Applications (A)		350
Advanced Cycle Mobile Heat Pump (AF)		1,150
Thermal Acoustic Piezoelectric Power Generator (DNA)		0
Geothermal Space Conditioning for Large DoD Buildings (DOE)		1,050
Clean Liquid Fuel from Biomass and Carbonaceous Wastes (EPA)		500
Utilization of Biomass Technologies on Military Installations (EPA)		920
Low Emissions Shipboard Fuel Cell Power Plants (N)		600
Photovoltaics for Military Applications (N)		4,000
<b>Energy Conservation/Renewable Resources Total</b>		<b>11,000</b>

<b>TABLE VII FY 1994 GLOBAL ENVIRONMENTAL CHANGE PROJECTS</b>		<b>Actual Funding FY94 \$(K)</b>
<b>Air/Ocean Interface Research</b>		
Global Ocean Monitoring and Prediction (GOMAP) (N)		900
<b>Atmospheric Research</b>		
Comparison of CIRRIS 1A and UARS/ATMOS Databases (AF)		395
Environmental Requirements for Cloud Analysis (DSPO)		800
Atmospheric Remote Sensing and Assessment Program (ARSAP) (DOE) *		25,650
<b>Ocean Research</b>		
Acoustic Monitoring of Global Ocean Climate (includes GAMOT) (ARPA) *		20,300
<b>Terrestrial Research</b>		
Global Inventory of Biomass Burning (EPA)		600
<b>Other</b>		
Strategic Environmental Distributed Active Archive Resources (SEDAAR) (N) *		1,250
<b>Global Environmental Change Total</b>		<b>49,895</b>

\* Congressional Interest



<b>TABLE VIII FY 1994 POLLUTION PREVENTION PROJECTS</b>		<b>Actual Funding FY94 \$(K)</b>
<b>Coatings</b>		
PVD Coatings and Ion Beam Processing as Alternatives to Electroplating (A)		550
Electro Magnetic Powder Spray (AF)		630
Large Area Powder Coating (AF)		315
Alternative Coatings for Cadmium Plating of Small Parts (N)		800
Fluorinated Ship-Hull Coatings for Non-Polluting Control (N)		895
Organic Protective Coatings and Application Technology (N)		400
<b>Data Base</b>		
Integrated Expert Solvent Substitution Data Base (EPA)		3,000
<b>Diagnostic</b>		
Rapid Testing for Acceptable Materials and Processes (AF)		263
Life Cycle Engineering and Design Program (EPA)		750
Model for Facilities Life Cycle Decisions (EPA)		400
<b>Hazardous Materials Substitutes</b>		
Advanced Zinc Phosphate Metal Pre-Treatment (A)		175
Non-Chromate Conversion Coatings and Sealers for Aluminum Alloys (A)		300
High-Performance, Lead-Free Electrical Sealants (DOE)		110
Reduce VOCs and HAPs from Painting and Cleaning Operations (EPA)		600
Nonchromatic/Noncarcinogenic Etching for Bonded Structures (A)		30
Aircraft Maintenance Chromium Replacement (N)		180
Dry Nitrogen for Ship Boiler Layup (N)		55
Solvent Substitution and Low VOC Cleaners (N)		150
<b>Hazardous Materials Processing</b>		
Non-Chemical Surface Preparation (AF)		998

<b>TABLE VIII FY 1994 POLLUTION PREVENTION PROJECTS</b>		<b>Actual Funding FY94 \$(K)</b>
Solid State Metal Cleaning (AF)		900
<b>Hazardous Waste Reduction</b>		
Large Aircraft Robotic Paint Stripping (LARPS) (AF)		1,717
Laser Cleaning and Coatings Removal (AF)		1,552
Aircraft Depainting Technology (N)		445
Recycle Boiler Nitrite Solution (N)		475
<b>Mixed Waste</b>		
Acid Recycle (DOE)		258
Capacitive Deionization for Elimination of Wastes (DOE)		700
<b>Metal Working Process</b>		
Alternate Electroplating Technology (N)		360
Recycling/Purification of Plating/Cleaning Baths (N)		800
<b>Ordnance Processing</b>		
Extraction and Recycling of LOVA Propellants Using Supercritical Fluids (A)		450
Laser Ignition to Replace Chemical Ordnance Igniters for Propulsion (A)		200
Recycling Propellants in Nonpolluting Supercritical Fluids: Novel Computational Chemistry Models for Predicting Effective Solvents (A)		350
DoD/DOE Clean Agile Manufacturing of Energetic Materials (N)		3,700
Alternate Solvents for Propellant Manufacture (A)		50
Solventless Pyrotechnic Manufacturing (N)		500
<b>Ozone Depleting Substances</b>		
Chemical and Physical Processes Responsible for Flame Inhibition Using Halon Agents and Their Alternatives (A)		400
Chemistry of Halon Substitutes (A)		155
Continuous Aqueous Cleaning to Eliminate ODC (A)		110
Non Ozone Depleting Sealants for Ammunition Applications (A)		250

<p style="text-align: center;"><b>TABLE VIII</b> <b>FY 1994 POLLUTION PREVENTION PROJECTS</b></p>	<p style="text-align: center;"><b>Actual Funding FY94 \$(K)</b></p>
<p>Replacements of Hydrochlorfluorocarbon (HCFC-22) with Non-Ozone Depleting Substitutes in Military Environmental Control Units (ECUs) (A)</p>	<p style="text-align: center;">250</p>
<p>Advanced Streaming Agent (AF)</p>	<p style="text-align: center;">850</p>
<p>Encapsulated Micron Aerosol Fire Suppression Technology (AF)</p>	<p style="text-align: center;">630</p>
<p>Electrically Charged Water Mist for Fire Suppression (N)</p>	<p style="text-align: center;">50</p>
<p>Non-Ozone Depleting Refrigerants for Navy Chillers (EPA)</p>	<p style="text-align: center;">1,000</p>
<p style="text-align: right;"><b>Pollution Prevention Total</b></p>	<p style="text-align: center;"><b>26,753</b></p>

## FY 1995 PROGRAM

As the FY 1994 SERDP represented the first year of a multi-year program plan, the FY 1995 Program is by-and-large a continuation of the previous year efforts. Due to the reduction in resources, many projects that were not responding to the highest priority defense environmental requirements, or were not of the highest technical quality were eliminated from the Program.

A summary of the FY 1995 Program funding distribution by Technology Thrust Area is shown in **Table IX**. **Tables X through XV** show titles, executing organizations and actual FY 1995 funding received by the projects. Amounts made available to each Federal laboratory for the FY 1994 appropriations are shown in **Table XVI**. The FY 1995 projects approved by the SERDP Council are described in the SERDP *Five-Year (1995-1999) Strategic Investment Plan* and include project duration, actual costs in past years and requested amounts for future years.

<b>TABLE IX FY 1995 FUNDING SUMMARY</b>	<b>FY 95 Funding \$(K)</b>
Cleanup	14,586
Compliance	6,500
Conservation	3,050
Energy Conservation/Renewable Resources	3,200
Global Environmental Change	16,700
Pollution Prevention	7,846
FY 1995 Scientific Advisory Board and Council Support	458
Undistributed Reductions	9,567
<b>FY 1995 APPROPRIATION TOTAL</b>	<b>61,907</b>

<b>TABLE X FY 1995 CLEANUP PROJECTS</b>		<b>Actual Funding FY95 \$(K)</b>
<b>Characterization, Monitoring, Modeling, Measurement, Methods - Field</b>		
Accelerated Tri-Services SCAPS Sensor Development (A/AF/N)		1,060
The Sensitive Detection of Unexploded Ordnance and other Hazardous Materials (A)		94
Field Portable FTS Fiber Optic VOC Sensor (AF)		150
In-Situ "Inside-Out" Nuclear Magnetic Resonance Sensor for Contaminant Identification (N)		200
Integrated Characterization Program Combining DOE UFA and DoD Sensor Technologies (DOE/N)		100
Subsurface Gas Flowmeter (DOE)		250
Removal of VOCs from Contaminated Groundwater and Soils by Pervaporation (EPA/N)		250
Subsurface Bioremediation Process Monitoring Indicators (EPA)		200
UXO Detection Feasibility Study (A/N/AF/DOE)		100
Mobile Underwater Debris Survey System (N)		575
Rapid Detection of Explosives and Other Pollutants (N)		125
<b>Hazard Risk Assessment, Modeling, Methodologies</b>		
Trichloroethylene Risk Assessment (AF/EPA)		0
<b>Treatment Technologies - Groundwater/Surface Water</b>		
Biosorption Treatment of Plasticizers and Solvents (A)		681
Enhancing Bioremediation Processes in Cold Regions (A)		220
Peroxene Treatment of Contaminated Groundwaters (A)		180
Aerobic Bioremediation of a Contaminated Aquifer (AF)		600
Bioremediation of Hydrazine/Energetic Materials (AF/A)		0
Catalytic In Situ Treatment of Chlorinated Solvents (AF/EPA)		300
Joint US/Germany In-Situ Bioremediation Demonstration (AF)		200
Aquifer Restoration by Enhanced Source Removal (EPA/AF)		860

<p style="text-align: center;">TABLE X FY 1995 CLEANUP PROJECTS</p>	<p style="text-align: center;">Actual Funding FY95 \$(K)</p>
Removal and Encapsulation of Heavy Metals from Ground Water (EPA/DOE/A)	100
Encapsulated Bacteria for In Situ PAH Bioremediation (N)	0
In Situ Bioremediation of Fuel and Efficacy Monitoring (N/EPA)	850
<b>Treatment Technologies - Soils/Sludges</b>	
Air Sparging and In-Situ Bioremediation Research (A/USGS)	271
Explosives Conjugation Products in Remediation Matrices (A)	146
Integrated Biotreatment Research Program: From Flask to Field (A)	1,101
Surfactant-Enhanced Biodegradation of Contaminants (A)	234
Fuel Hydrocarbon Remediation (N)	280
<b>DoD National Environmental Technology Demonstration Program</b>	
Volunteer Army Ammunition Plant (VAAP) - Chattanooga, TN (A)	350
Naval Construction Battalion Center (NCBC) - Port Hueneme, CA (N)	900
Dover AFB Groundwater Remediation Field Lab - Dover, DE (AF)	1,279
McClellan AFB - Sacramento, CA (AF)	0
National Center for Integrated Bioremediation R&D Wurtsmith AFB - Oscoda, MI (EPA)	2,580
Site Characterization Consortium (EPA)	350
<b>Cleanup Total</b>	<b>14,586</b>

<b>TABLE XI FY 1995 COMPLIANCE PROJECTS</b>		<b>Actual Funding FY95 \$(K)</b>
<b>Boiler/Engine Emissions</b>		
Evaluation of Metal Perovskite Catalysts for NOx Reduction (AF)		25
Compact, Closed-Loop Controlled Waste Incineration (N)		300
Reduction of NOx Emissions from Marine Power Plants (N/EPA)		300
<b>General Hazardous Waste Management</b>		
Lead-Based Paint Hazard Mitigation (A)		400
Emission Reduction Planning Model (AF)		100
Laser Ablation/Ionization Characterization of Solids (DOE)		100
Vapor Permeation VOC Recovery from Refueling and Storage (EPA/N)		100
<b>Monitoring</b>		
Advanced Mass Spectrometry for Atmospheric Monitoring (AF)		150
Leak Location in Underground Pipelines (EPA/A/N/NSF)		0
<b>Noise Impacts</b>		
Controlling, Assessing, Managing, and Monitoring the Noise Impact from Weapons, Helicopters, and Aircraft on Training and Readiness (A)		325
<b>Open Burning/Open Detonation</b>		
Characterization Open Burning/Open Detonation Emissions (A)		3,000
Measuring and Modeling for OB/OD Permitting (EPA)		550
<b>Physical Treatment Processes</b>		
Encapsulation of Hazardous Ions in Smectite Clays (DOE)		200
Kinetics of Supercritical Water Oxidation (DOE)		300
Waste Forms Based on Separations Media (DOE)		100

<b>TABLE XI FY 1995 COMPLIANCE PROJECTS</b>		<b>Actual Funding FY95 \$(K)</b>
<b>Shipboard Emissions</b>		
Shipboard Non-Oily Wastewater Treatment System (N)		250
<b>Waste Minimization/Recycling</b>		
Evaluation of the Use of Waste Energetics as Supplemental Fuels (A/N/DOE)		300
<b>Compliance Total</b>		<b>6,500</b>



<b>TABLE XII FY 1995 CONSERVATION PROJECTS</b>		<b>Actual Funding FY95 \$(K)</b>
<b>Community Ecosystem - Management</b>		
Terrain Modeling and Soil Erosion Simulation (A)		195
Phased Array Ultrasonic Detection of Cultural Artifacts (A)		120
Advanced Biotelemetry for Resource Management (A)		270
Strategic Natural Resource Management Methodology (DOE/A)		50
<b>Multiple - Risk/Impact Assessment</b>		
Assessment and Management of Risks to Biodiversity and Habitat (EPA)		100
<b>Species/Genetic - Management</b>		
Threatened, Endangered and Sensitive Resources (A)		300
<b>Species/Genetic - Resource Characterization</b>		
Integration of Radiotelemetry, Remote Sensing and GIS (DOE)		50
Fishing Enforcement/Whale Monitoring Using IUSS (N/NOAA)		1,625
<b>Species/Genetic - Risk/Impact Assessment</b>		
The Effects of Aircraft Overflights on Birds of Prey (AF)		80
Genetic Diversity Monitoring in Plants and Wildlife (EPA)		0
Ecological Biomarkers: Monitoring Wild Fauna at DoD Installations (EPA)		0
<b>Watershed/Landscape - Management</b>		
Ecological Modeling for Military Land Use Decision Support (DOE/A)		260
<b>Conservation Total</b>		<b>3,050</b>

<b>TABLE XIII FY 1995 ENERGY CONSERVATION/RENEWABLE RESOURCES PROJECTS</b>		<b>Actual Funding FY95 \$(K)</b>
<b>Energy Conservation</b>		
Low Energy Model Installation Program (A/DOE)		500
Natural Gas Based Air Conditioning Demonstration (A/N)		270
<b>Renewable Energy</b>		
Fuel Cells for Military Applications (A)		150
Geothermal Space Conditioning for Large DoD Buildings (DOE)		100
Utilization of Biomass Technologies on Military Installations (EPA)		580
Photovoltaics for Military Applications (N/DOE/EPA)		1,600
<b>Energy Conservation/Renewable Resources Total</b>		<b>3,200</b>

<b>TABLE XIV FY 1995 GLOBAL ENVIRONMENTAL CHANGE PROJECTS</b>		<b>Actual Funding FY95 \$(K)</b>
<b>Atmospheric Research</b>		
Atmospheric Remote Sensing and Assessment Program (ARSAP) (DOE)		13,000
<b>Ocean Research</b>		
Acoustic Monitoring of Global Ocean Climate (ARPA)		3,700
<b>Global Environmental Change Total</b>		<b>16,700</b>

<b>TABLE XV FY 1995 POLLUTION PREVENTION PROJECTS</b>		<b>Actual Funding FY95 \$(K)</b>
<b>Paint Stripping/Coatings</b>		
Life Cycle Engineering and Design Program (EPA)		180
Organic Protective Coatings and Application Technology (N)		248
Fluorinated Ship-Hull Coatings for Non-Polluting Control (N)		414
Aircraft Depainting Technology (N)		428
High-Performance, Lead-Free Electrical Sealants (DOE/AF/N)		126
Solvent Substitution and Low VOC Cleaners (N)		99
Laser Cleaning and Coatings Removal (AF)		273
Large Area Powder Coating (AF)		0
Large Aircraft Robotic Paint Stripping (LARPS) (AF)		223
<b>Advanced Material/Processes</b>		
Rapid Testing for Acceptable Materials and Processes (AF)		118
Model for Facilities Life Cycle Decisions (EPA/A)		135
<b>Other Hazardous Wastes</b>		
Capacitive Deionization for Elimination of Wastes (DOE)		300
Acid Recycle (DOE)		169
Recycle Boiler Nitrite Solution (N)		68
Integrated Expert Solvent Substitution Data Base (EPA)		0

<b>TABLE XV FY 1995 POLLUTION PREVENTION PROJECTS</b>		<b>Actual Funding FY95 \$(K)</b>
<b>Metal Working Process</b>		
Alternate Electroplating Technology (N)		248
Solid State Metal Cleaning (AF)		100
Non-Chromate Conversion Coatings and Sealers for Aluminum Alloys (A)		68
Aircraft Maintenance Chromium Replacement (N)		158
Non-Chemical Surface Preparation (AF)		274
Recycling/Purification of Plating/Cleaning Baths (N/AF/EPA)		360
PVD Coatings and Ion Beam Processing as Alternatives to Electroplating (A)		218
<b>Ordnance Materials and Processing</b>		
Laser Ignition to Replace Chemical Ordnance Igniters for Propulsion (A)		313
Extraction and Recycling of LOVA Propellants Using Supercritical Fluids (A)		248
Recycling Propellants in Nonpolluting Supercritical Fluids: Novel Computational Chemistry Models for Predicting Effective Solvents (A)		158
Non Ozone Depleting Sealants for Ammunition Applications (A)		113
Solventless Manufacture of Propellants using Thermoplastic Elastomer Binder (N)		0
Minimization of Uranium Alloy Waste by Electron Beam Melter (A)		0
DoD/DOE Clean Agile Manufacturing of Energetic Materials (N/DOE)		600
Solventless Pyrotechnic Manufacturing (N)		113
<b>Fire/Explosion Suppression</b>		
Encapsulated Micron Aerosol Fire Suppression Technology (AF)		284
Chemical and Physical Processes Responsible for Flame Inhibition Using Halon Agents and Their Alternatives (A/NIST)		203
Chemistry of Halon Substitutes (A)		200
Advanced Streaming Agent (AF)		383

<b>TABLE XV FY 1995 POLLUTION PREVENTION PROJECTS</b>		<b>Actual Funding FY95 \$(K)</b>
<b>Refrigerants</b>		
Non-Ozone Depleting Refrigerants for Navy Chillers (EPA)		788
Replacements of Hydrochlorfluorocarbon (HCFC-22) with Non-Ozone Depleting Substitutes in Military Environmental Control Units (ECUs) (A)		236
<b>Pollution Prevention Total</b>		<b>7,846</b>

TABLE XVI FY 1995 LABORATORY FUNDING		Actual Funding FY95 \$(K)
<b>ARMY</b>		
Construction Engineering Research Laboratories		1,945
Armament Research, Development, and Engineering Center		397
Army Research Laboratory-Aberdeen Proving Ground		1,410
Cold Regions Research & Engineering Laboratory		157
Waterways Experiment Station		3,105
Dugway Proving Ground		3,000
Communications and Electronics Command RD&E Center		236
Army Environmental Center		550
<b>ARMY LABORATORY TOTAL</b>		<b>10,800</b>
<b>AIR FORCE</b>		
Armstrong Laboratory - Tyndall AFB		2,772
Armstrong Laboratory - Brooks AFB		80
Wright Laboratory		1,571
Phillips Laboratory		150
<b>AIR FORCE LABORATORY TOTAL</b>		<b>4,573</b>

TABLE XVI FY 1995 LABORATORY FUNDING		Actual Funding FY95 \$(K)
<b>NAVY</b>		
Naval Command Control & Ocean Surveillance Center		1,342
Naval Surface Warfare Center-Carderock		250
Naval Surface Warfare Center-Crane		113
Naval Surface Warfare Center-Indian Head		270
Naval Surface Warfare Center-Panama City		575
Naval Surface Warfare Center-Philadelphia		237
Naval Air Warfare Center - China Lake		1,450
Naval Air Warfare Center-Warminster		1,206
Naval Research Laboratory		5,420
Naval Facilities Engineering Service Center		1,632
<b>NAVY LABORATORY TOTAL</b>		<b>12,495</b>
<b>DEPARTMENT OF DEFENSE LABORATORY TOTAL</b>		<b>27,868</b>
<b>DOE</b>		
Argonne National Laboratory		238
Brookhaven National Laboratory		30
Lawrence Livermore National Laboratory		619
Oak Ridge National Laboratory		203
Pacific Northwest Laboratory		291
Sandia National Laboratory-CA		8,830
Sandia National Laboratory-NM		376
<b>DOE LABORATORY TOTAL</b>		<b>10,587</b>

<b>TABLE XVI FY 1995 LABORATORY FUNDING</b>		<b>Actual Funding FY95 \$(K)</b>
<b>EPA</b>		
Air and Energy Engineering Research Laboratory		1,045
Atmospheric Research and Exposure Assessment Laboratory		550
Environmental Research Laboratory - Athens		137
Environmental Research Laboratory - Corvallis		100
Environmental Research Laboratory - Gulf Breeze		2,730
Environmental Monitoring Systems Laboratory-Las Vegas		350
R.S. Kerr Laboratory		785
Risk Reduction Engineering Laboratory		566
<b>EPA LABORATORY TOTAL</b>		<b>6,263</b>
<b>NOAA</b>		
Marine Mammal Laboratory		437
<b>NOAA LABORATORY TOTAL</b>		<b>437</b>
<b>OTHER RECIPIENTS</b>		
Army Test and Evaluation Command		78
Ft. Lewis		3
Ft. Knox		3
Advanced Research Projects Agency		3,700
Office of Naval Research		970
National Institute of Standards and Technology		20
Space and Naval Warfare Systems Command		675
Headquarters, Department of Energy (EE)		100
U.S. Geological Survey		251
<b>OTHER RECIPIENTS FUNDING TOTAL</b>		<b>5,800</b>
<b>TOTAL FY95 LABORATORY FUNDING</b>		<b>50,955</b>



**TABLE XVI  
FY 1995 LABORATORY FUNDING**

<b>TOTALS</b>		
<b>LABORATORIES</b>		45,155
	DoD	27,868
	DOE	10,587
	EPA	6,263
	NOAA	437
<b>OTHER FEDERAL RECIPIENTS</b>		5,800
<b>UNDISTRIBUTED REDUCTIONS</b>		9,567
<b>FY 1995 SCIENTIFIC ADVISORY BOARD AND COUNCIL SUPPORT</b>		1,385
<b>TOTAL FY 1995 SERDP FUNDING</b>		<b>61,907</b>

### FY 1996 PROGRAM PLANS

The Department has requested \$58.4 million in the FY 1996 President's budget request. SERDP plans to continue most projects funded in FY 1995 and complete the major efforts within Global Environmental Change and Energy Conservation/Renewable Energy Resources. Actual FY 1996 funding amounts requested by Federal laboratories will be determined after a review of ongoing and proposed efforts is conducted by the Executive Director. A draft FY 1996 Program will be reviewed by the Scientific Advisory Board and final approval provided by the SERDP Council in late August 1995.

**FIVE YEAR (1995-1999)**  
**STRATEGIC INVESTMENT PLAN**

TABLE XVII FY 1995 CLEANUP PROJECTS		FUNDING \$(K) FY95	ID Number	Page Number
Characterization, Monitoring, Modeling, Measurement, Methods - Field				
Accelerated Tri-Services SCAPS Sensor Development (A/AF/N)	1,060	729	CU-4	
The Sensitive Detection of Unexploded Ordnance and other Hazardous Materials (A)	94	713	CU-10	
Field Portable FTS Fiber Optic VOC Sensor (AF)	150	103	CU-14	
In-Situ "Inside-Out" NMR Sensor for Contaminant ID (N)	200	38	CU-17	
Integrated Characterization Program Combining DOE, UFA and DoD Sensor Technologies (DOE/N)	100	592	CU-22	
Subsurface Gas Flowmeter (DOE)	250	404	CU-26	
Removal of VOCs from Contaminated Groundwater and Soils by Pervaporation (EPA/N)	250	371	CU-31	
Subsurface Bioremediation Process Monitoring Indicators (EPA)	200	383	CU-35	
UXO Detection Feasibility Study (A/N/AF/DOE)	100	860	CU-40	
Mobile Underwater Debris Survey System (MUDSS) (N)	575	52	CU-43	
Rapid Detection of Explosives and Other Pollutants (N)	125	28	CU-49	
Hazard Risk Assessment, Modeling, Methodologies				
Trichloroethylene Risk Assessment (AF/EPA)	0	115	CU-53	
Treatment Technologies - Groundwater/Surface Water				
Biosorption Treatment of Plasticizers and Solvents (A)	681	711	CU-57	
Enhancing Bioremediation Processes in Cold Regions (A)	220	712	CU-62	
Peroxone Treatment of Contaminated Groundwaters (A)	180	726	CU-67	

TABLE XVII FY 1995 CLEANUP PROJECTS		FUNDING \$(K) FY95	ID Number	Page Number
Aerobic Bioremediation of a Contaminated Aquifer (AF)		600	95	CU-74
Bioremediation of Hydrazine/Energetic Materials (AF/A)		0	118	CU-76
Catalytic In Situ Treatment of Chlorinated Solvents (AF/EPA)		300	107	CU-79
Joint US/Germany In-Situ Bioremediation Demonstration (AF)		200	99	CU-83
The Engineering Design of In-Situ Bioremediation (DOE)		0	514	CU-86
Aquifer Restoration by Enhanced Source Removal (EPA/AF)		860	368	CU-91
Removal and Encapsulation of Heavy Metals from Ground Water (EPA/DOE/A)		100	387	CU-96
Encapsulated Bacteria for In-Situ PAH Bioremediation (N)		0	23	CU-100
In Situ Bioremediation of Fuel and Efficacy Monitoring (N/EPA)		850	30	CU-104
Treatment Technologies - Soils/Sludges				
Air Sparging and In-Situ Bioremediation Research (A/USGS)		271	744	CU-109
Explosives Conjugation Products in Remediation Matrices (A)		146	715	CU-113
Integrated Biotreatment Research Program: From Flask to Field (A)		1,101	720	CU-117
Surfactant-Enhanced Biodegradation of Contaminants (A)		234	731	CU-124
Fuel Hydrocarbon Remediation (N)		280	20	CU-130
DoD National Environmental Technology Demonstration Program				
Volunteer Army Ammunition Plant (VAAP) - Chattanooga, TN (A)		350	723	CU-135
Naval Construction Battalion Center (NCBC) - Port Hueneme, CA (N)		900	863	CU-140
Dover AFB Groundwater Remediation Field Lab - Dover, DE (AF)		1,279	866	CU-144

TABLE XVII FY 1995 CLEANUP PROJECTS				
	FUNDING \$(K) FY95	ID Number	Page Number	
McClellan AFB - Sacramento, CA (AF)	0	861	CU-150	
National Center for Integrated Bioremediation R&D Wurtsmith, AFB - Oscoda, MI (EPA)	2,580	864	CU-154	
Site Characterization Consortium (EPA)	350	374	CU-160	
<b>Cleanup Total</b>	<b>14,586</b>			

## SERDP FY95 PROJECT

1. **SERDP Thrust Area:** Cleanup
2. **Title:** Accelerated Tri-Services SCAPS Sensor Development
3. **Agency:** Army
4. **Laboratory:** United States Army Corps of Engineers (U.S.A.E.) Waterways Experiment Station (WES)
5. **Project ID:** #729

### 6. **Problem Statement:**

Currently, site characterization represents a significant portion of remediation efforts, accounting for approximately one-third of the total costs. Environmental site characterization has been traditionally based on drilling, sampling, and laboratory analysis. Complete delineation of subsurface contaminants usually requires trial-and-error placement of a significant number of monitoring wells and extensive sample collection efforts. Laboratory analysis of samples taken in the field is time consuming, costly, and often imprecise due to site history, contaminant profiles, and biogeochemical interactions. This traditional approach to site characterization hampers remediation efforts because of its uncertainty, time requirements, and cost.

The Site Characterization and Analysis Penetrometer System (SCAPS) was developed to address many of these deficiencies. SCAPS combines traditional cone penetrometer technology with contaminant and geophysical sensors to rapidly provide a profile of contaminants and geophysical properties in a cost effective manner. The SCAPS has progressed under sponsorship of the Tri-Services and DOE, and is an ideal platform for advanced sensor systems.

There exists a critical need to develop advanced sensor technologies to characterize sites containing metals, petroleum oil lubricants (POL's), solvents, explosives, and radioactive contaminants. In order to maximize their payoff in future remediation efforts, it is critical that environmental sensors be developed and transitioned as rapidly as possible. This proposal addresses the need to accelerate the research, development, and demonstration of sensor, sampling, and associated data processing technologies for SCAPS.

### 7. **Project Description:**

The goal of the accelerated sensor program is to develop technologies for detecting and delineating contaminants and for characterizing geophysical properties in situ. This Tri-Service program is leveraged with supporting research sponsored by DOE and EPA. It includes a comprehensive and jointly executed set of tasks to significantly accelerate the development of sensors for the SCAPS system. The proposed work partially fulfills SCAPS thrust milestones as identified in the FY93 Tri-Service Environmental R&D Strategic Plan.

Under the proposed scope of work, the Tri-Services will accelerate the development of new sensor systems that will expand the capability of the SCAPS for in situ detection of chemical contamination. Additionally, the proposed work includes development of improved sampling, analysis, and processing technologies to support the enhanced sensor technologies. The following are the primary thrusts for this project:

(1) Laser-Induced Breakdown Spectroscopy (LIBS). A fiber optic based LIBS system using pulsed laser energy to generate plasma from solid and liquid samples is being developed jointly by the DoD. Emission spectra from the plasma provides simultaneous multi-element analysis of metals including Zn, Cr, Pb, Cu, Ni and Cd. However, several technical challenges remain to be overcome before LIBS technology is viable for SCAPS implementation. The research effort proposed includes: (a) evaluate potential approaches for in situ generation of the plasma in the soil with the penetrometer probe, (b) characterize and optimize the fiber optic delivery system for the laser pulse, (c) develop software techniques for detecting atomic line spectra of heavy metals and, (d) develop neural network pattern recognition schemes for processing spectral emission data.

(2) Fiber Optic Raman Sensor (FORS). A prototype Raman sensor system is currently being evaluated for measurement of selected volatile aromatic hydrocarbons and solvents in soils. Technical issues include sensitivity and interferences from fluorescence components in the sample. Sensitivity enhancements will be accomplished by improvements in sensor and probe design. Wavelength shifting of the Raman excitation source will be evaluated for minimizing interferences from background fluorescence. Multiple wavelength and tunable laser sources will be developed and tested as a means of minimizing fluorescence background signals and for performing resonance enhanced Raman spectroscopy.

(3) Improved Laser-Induced Fluorescence (LIF) Sensor. The Tri-Services are currently evaluating new laser sources and detectors for improving the existing LIF sensors for POL contaminant detection. In order to enhance both the sensitivity and range of POL contaminants detected, the following research efforts will be conducted: (a) evaluate multiple wavelength UV sources including Raman shifters and Optical Parametric Oscillators as alternatives to the current dye lasers, and (b) increase the amount of information collected by LIF SCAPS probes including the capability to acquire complete time resolved excitation-emission matrices. Additionally, the feasibility of laser based sensors for detection of explosives in soils by photofragmentation/LIF methods will be investigated.

(4) Electrochemical Sensors. Electrochemical sensors for detecting volatile organic compounds (VOC) and low concentrations of explosives contaminants are currently being developed. These sensors presently require probes that provide thermal energy necessary to vaporize or desorb volatile and semi-volatile contaminants in situ for detection. Development of these probes and interfacing with electrochemical sensors will require extensive laboratory testing to fully characterize operation and robustly compare electrochemical sensor results to conventional methods. The laboratory testing will encompass a number of soil matrices to identify and mitigate possible interference sources, and to quantify their detection limits. Subsequent development efforts may be required to improve sensor performance and overcome soil matrix effects.

(5) Spectral Gamma Probe. A SCAPS spectral gamma probe for detection of radioactive wastes is currently under development by DoD for DOE. Enhancements to the detector

hardware, signal conditioning, and data processing will be made to increase sensitivity and selectivity, and to better characterize the collected emission spectra. Laboratory tests will be conducted to define and document system performance.

(6) Sampling Technology. Improved and innovative sampling technology to enhance the capability to collect soil, groundwater, and vapor samples using SCAPS will be developed. A critical issue common to all sampling technology is analyte behavior in the region of the sampler. An extensive laboratory testing program based on the multiport sampler technology previously developed will be used as a base to describe analyte behavior. Multiport sampling technology will be developed to increase sampler range to an umbilical length of 45 meters. Analyte behavior will be related to contaminant pressure and concentration consistent with site characterization objectives, and sampler performance will be fully characterized for diverse geophysical environments. Coupling sampler technology to surface analytical instrumentation will be investigated including such methods as extraction into an inert carrier gas with an infrared heated flexible fused quartz transporter column.

(7) Data Processing Methodologies. Data acquisition, analysis, and visualization software for SCAPS will be developed to fully exploit the capabilities of the emerging sensor and sampler technologies. Developed software will include a data base management system, graphic display capability, geostatistical decision analysis, and an interface to groundwater and contaminant transport decision analysis models. The approach will be to develop a basic set of software tools which can be used to evaluate the contaminant distribution and site stratigraphy, locate subsequent sounding and sampling locations, provide a data base of all pertinent site data, and graphically display all site data in three dimensions.

(8) Technology Demonstration and Implementation. This accelerated program of sensors development will aggressively move to demonstrate the sensors on the SCAPS platform. Tri-service demonstrations, coordinated by the U.S. Army Environmental Center will be performed on VOC and improved laser-based fiber optic sensors in FY94/95. Field tests will be conducted on the Fiber Optic Raman sensor (FORS) in FY95.

## **8. Expected Payoff:**

Proposed work will provide the DoD and DOE an expanded scope of sensor and sampling technologies coupled with data processing and analysis software tools for SCAPS. Immediate payoff will be technology for VOC, explosives, and heavy metal contaminant detection, and improved POL detection. Improved SCAPS sampling technology will provide alternative cost effective methods to obtain site characterization and verification data. Hybrid sampling technologies coupled to sensors and in situ methods for contaminant extraction will greatly expand the utility of SCAPS technology. The Tri-Service SCAPS will serve as a test platform for all technology development and will accelerate the evaluation of effectiveness and feasibility for subsequent demonstration activities. Rapid development of sensor technologies for SCAPS will significantly increase its return on investment (ROI).



## 9. Milestones:

### Research Area I - LIBS Sensor

- |    |   |       |
|----|---|-------|
| 1. | Complete characterization of optical fiber        | 09/94 |
| 2. | Complete laboratory prototype F.O. LIBS system    | 10/94 |
| 3. | Complete design of prototype LIBS probe           | 09/95 |
| 4. | Complete LIBS software development                | 11/95 |
| 5. | Complete fabrication of LIBS prototype probe      | 03/96 |
| 6. | Complete field tests/demonstration of LIBS system | 12/96 |

### Research Area II - LIF Sensors

#### A. LIF POL Sensor

- |    |  |       |
|----|--|-------|
| 1. | Complete development of improved POL sensor          | 03/95 |
| 2. | Complete field demonstrations of improved POL sensor | 03/96 |

#### B. Photofragmentation/LIF Explosives Sensor

- |    |   |       |
|----|---|-------|
| 1. | Demonstrate feasibility of PF/LIF for in situ explosives sensor | 11/95 |
| 2. | Complete prototype sensor                                       | 09/26 |
| 3. | Complete field tests of explosives sensor                       | 06/97 |

### Research Area III - FOR Sensor

- |    |   |       |
|----|---|-------|
| 1. | Complete development of laboratory FORS system                | 08/94 |
| 2. | Complete characterization of detection capabilities           | 09/94 |
| 3. | Complete fabrication of prototype FORS probe                  | 03/95 |
| 4. | Complete design of resonance enhanced FORS probe              | 09/95 |
| 5. | Complete fabrication of resonance enhanced FORS probe         | 12/95 |
| 6. | Complete FORS software development                            | 03/96 |
| 7. | Complete field demonstration of resonance enhanced FORS probe | 01/97 |

### Research Area IV - Electrochemical Sensors

- |    |   |       |
|----|---|-------|
| 1. | Complete fabrication of prototype VOC and explosives sensors      | 09/94 |
| 2. | Complete initial field test of first generation TNT sensors       | 09/94 |
| 3. | Complete demonstration of improved electrochemical sensor systems | 01/96 |

### Research Area V - Spectral Gamma Probe

- |    |  |       |
|----|--|-------|
| 1. | Complete improved SCAPS spectral gamma probe                 | 05/95 |
| 2. | Complete field testing/demonstration of improved gamma probe | 02/96 |

### Research Area VI - Sampling Technology

- |    |  |       |
|----|--|-------|
| 1. | Complete initial testing of thermal desorption VOC sampler | 05/95 |
| 2. | Complete field evaluations of multipoint VOC sampler       | 10/95 |

- |    |  |       |
|----|--|-------|
| 3. | Complete laboratory testing of analyte behavior in soils                                   | 08/96 |
| 4. | Complete field tests of thermal desorption VOC sampler interfaced to analytical instrument | 10/96 |
| 5. | Complete description of analyte behavior in soils  | 12/96 |
| 6. | Complete evaluation of quantitative aspects of SCAPS samplers                              | 12/96 |

#### Research Area VII - Data Processing Methodologies

- |    |   |       |
|----|---|-------|
| 1. | Complete development of data processing methodology                                     | 11/94 |
| 2. | Complete development of enhanced data acquisition, analysis, and visualization software | 03/96 |
| 3. | Complete testing and user review of enhanced software                                   | 06/96 |

#### Research Area VIII - Demonstration and Implementation

- |     |  |       |
|-----|--|-------|
| 1.  | Complete EPA SITE demonstration of LIF POL Sensor                              | 09/94 |
| 2.  | Complete initial field demonstration of electrochemical TNT sensor             | 10/94 |
| 3.  | Conduct Wurtsmith AFB, MI demonstration  | 07/95 |
| 4.  | Conduct Columbus AFB demonstration of POL sensor                               | 03/95 |
| 5.  | Conduct Dover AFB demonstration  | 04/95 |
| 6.  | Complete initial field evaluation of thermal desorption VOC sampler            | 05/95 |
| 7.  | Conduct Port Hueneme CA demonstration  | 06/95 |
| 8.  | Conduct field demonstrations of improved multiport sampler                     | 10/95 |
| 9.  | Conduct demonstration of SCAPS electrochemical probes with associated software | 01/96 |
| 10. | Complete validated and demonstrated enhanced SCAPS LIF POL sensor and software | 01/96 |
| 11. | Initiate field testing/demonstration of FORS system                            | 04/96 |
| 12. | Complete demonstrations of improved sampler technologies                       | 10/96 |
| 13. | Conduct demonstrations of LIBS sensor system                                   | 12/96 |
| 14. | Complete demonstrations of FORS system   | 01/97 |
| 15. | Conduct demonstrations of PF/LIF explosives sensor system                      | 06/97 |

#### Research Area IX - Program Management

- |    |  |       |
|----|--|-------|
| 1. | Conduct coordination meeting with peer review panel researchers, developers, and users | 08/94 |
| 2. | Progress reports detailing first year progress   | 10/95 |
| 3. | Conduct second coordination meeting  | 10/95 |
| 4. | Progress report detailing second year progress   | 10/96 |
| 5. | Conduct third coordination meeting   | 10/96 |
| 6. | Final program report   | 10/97 |

### 10. Transition Plan:

Technology developed under this proposed effort will be transitioned to the Army's Environmental Center (AEC) which is the agency responsible for demonstrating and transitioning SCAPS technologies to the U.S. Army Corps of Engineers District Offices, the Naval Facilities Engineering Command, the Air Force System Program Office (HSC/YAQ),

and DOE. This provides a conduit for all developed technology to DoD and DOE through a comprehensive plan that includes demonstration, documentation, training, and technical support. Transition of SCAPS technology to private industry will be pursued by licensing agreements for patented technology and through Cooperative Research and Development Agreements (CRADA).

**11. Funding: \$(K)**

	FY94	FY95	FY96	FY97	TOTAL
AF	825	220	380	400	1825
ARMY	1700	520	880	1250	4350
NAVY	850	320	530	700	2400
TOTAL SERDP	3375	1060	1089	2350	7874

**12. Performers:**

SCAPS development is primarily a Tri-Service activity including the Army (U.S.A.E. Waterways Experiment Station, Army Environmental Center), AF (Armstrong Laboratory, AF Center for Environmental Excellence), and the Navy (Naval Command Control & Ocean Surveillance Center). Additional performers include DOE, EPA, and private industry and Universities.

**13. Principal Investigators:**

ARMY:  
 Dr. Ernesto Cespedes  
 USAE Waterways Experiment Station  
 CEWES-EE-S  
 3909 Halls Ferry Road  
 Vicksburg, MS 39180-6199  
 PHONE: (601) 634-2655  
 FAX: (601) 634-2732  
 E-MAIL: cespedes@mudbug.wes.army.mil

ARMY:  
 Mr. George Robitaille  
 Army Environmental Center  
 SFIM-AEC-TSC, Bldg E4435  
 Aberdeen Proving Ground, MD  
 21010-5401  
 PHONE: (410) 671-6865  
 FAX: (410) 671-6836

NAVY:  
 Dr. Stephen H. Lieberman  
 NCCOSC RDT&E Division 521  
 53475 Strothe Road  
 San Diego, CA 92152-6325  
 PHONE: (619) 553-2778  
 FAX: (619) 553-6305

AIR FORCE:  
 Mr. Bruce Nielsen (AL/EQW)  
 139 Barnes Drive, Suite 2  
 Tyndall AFB, FL 32403-5323  
 PHONE: (904) 283-6011  
 FAX: (904) 283-6090

**14. Keywords:**

SCAPS, Sensor, Environmental Sensors, Samplers, Site Characterization, Contaminant, Remediation.

## SERDP FY95 PROJECT

1. **SERDP Thrust Area:** Cleanup
2. **Title:** The Sensitive Detection of Unexploded Ordnance and Other Hazardous Materials
3. **Agency:** Army
4. **Laboratory:** Army Research Laboratory, Aberdeen Proving Ground, MD
5. **Project ID:** #713
6. **Problem Statement:**

The development of laser-based, analytical sensors for the rapid detection and monitoring of trace atmospheric vapors in real-time has been of great interest in recent years. Environmental issues pertaining to pollution prevention, compliance, and cleanup have been an important driving force behind this development. Another related issue deals with the detection of trace atmospheric vapors of energetic materials such as explosives and propellants. This is not to surprising given the potential civilian and military applications for these developing technologies in aviation security, demilitarization, and cleanup activities. The overall objective of this proposal is to develop and deploy a reliable and cost-effective apparatus for the sensitive detection of energetic materials as well as toxic halogenated compounds and heavy metals as identified by the Major Range and Test Facility Bases (MRTFB) Environmental Coordinating Committee.

### 7. Project Description:

At the 1992 Army Science Conference, we presented a paper which received first prize and was awarded the Paul A. Siple Memorial Award. In this paper, we described a novel technique for sensing trace atmospheric vapors of energetic materials and chemical agent simulants. This technique (patent pending) is based on the use of one laser operating to both photofragment, the target molecule and detect the characteristic fragments by resonance-enhanced multiphoton ionization (REMPI) and/or laser-induced fluorescence (LIF). The analytical utility was demonstrated on a number of compounds, including TNT and RDX, employing molecular beam mass spectrometry. A detection limit of 8 and 24 parts-per-billion (ppb) was obtained for RDX and TNT, respectively, using only 100  $\mu$ J/pulse of laser energy.

A literature review of the electronic transitions of NO reveals that they are also resonant with 193 nm or 222 nm radiation, the output from an excimer laser. The advantages of using this laser over that used previously is that it is more rugged, more compact, and readily fieldable. In addition, the output is approximately a few thousand times more than the 226 nm radiation used for the detection of TNT and RDX. As a result, we expect to improve substantially on our limits of detection of these and other energetic materials. For this proposal we plan the following:

- Replace 226 nm laser system with a compact excimer laser.

- Replace our molecular beam time-of-flight apparatus (approximately 64 ft<sup>3</sup>) with a hand held optogalvanic detector. In addition to reducing the size of the apparatus, a ten to one hundred fold increase in sensitivity is projected due to direct atmospheric sampling.
- Add a cryogenic stage for enhanced selectivity and modify sample delivery for enhanced sensitivity.
- Extend this technique for the detection of volatile organic compounds (VOC's).
- Fabricate and deploy prototype.
- Identify source of pollutants for cleanup/remediation actions.

Complementary conventional monitoring techniques such as x-ray fluorescence and atomic absorption will also be used if needed.

This project is presently being supported by an Army Research Lab Independent Laboratory Innovative Research Award and leveraged by Small Business Innovative Research funds.

### 8. Expected Payoff:

Potential Users: DoD, DOE, EPA, Federal Aviation Administration (FAA), Custom and Postal Services, and other agencies involved with the ultra-sensitive detection of energetic materials or pollutants.

Benefits:

- A rapid and ultra-sensitive, real-time, laser-based detector which will have both military and civilian applications. Excellent potential for opening up new commercial and military markets.
- Reduction of costs of cleanup/remediation for sites containing energetic materials, heavy metals, and halogen-containing compounds.
- Increased safety to personnel working at site or involved with cleanup activities.

### 9. Milestones:

1.	Program start	10/94
2.	Coordinate research with performers from universities, industry and government labs	10/94
3.	Initiate CRADA and international agreements	10/94
4.	Initiate procurement requests and STAS's	10/94
5.	Contract award to University of Iowa and Tel Aviv University for complementary EM detection research, and Lambda Physik for engineering of miniature laser	04/95
6.	Update literature search for detection of EM. Review and analyze data needed for spectral simulations	12/94
7.	Perform literature search on detection of halogenated species and heavy metals in various media	12/94
8.	Update, debug, and test computer program for spectral simulations	12/94
9.	Replace 226 nm laser system with compact excimer laser. Fabricate and replace our molecular beam time-of-flight apparatus (approx 64 ft <sup>3</sup> ) with hand held optogalvanic detector	02/95

- |     |  |       |
|-----|--|-------|
| 10. | Test system performance. Record spectra and compare to spectral simulations. Measure limits of detection for various EM's and compare results to existing technologies | 08/95 |
| 11. | Measure limits of detection for various nitro compounds using 452 nm radiation and compare with previous results using 226 nm or 193 nm radiation                      | 12/95 |
| 12. | Record spectra and compare to spectral simulations obtained using a computer program developed in-house  | 03/96 |
| 13. | Measure limits of detection of various target molecules, and determine dependence of signal intensity on laser energy and pressure                                     | 05/96 |
| 14. | Measure internal energy distributions of the NO photofragment and compare to ambient NO for possible discrimination  | 08/96 |
| 15. | Determine best excitation scheme for discrimination and measure various mixtures of nitrogen compounds doped with NO   | 12/96 |
| 16. | Determine best photolysis/excitation wavelength for optimal system performance, cost effectiveness, and fieldability   | 03/97 |
| 17. | Design prototypical system for field use   | 04/97 |
| 18. | Prepare appropriate patent disclosures, reports, and manuscripts for open literature publications  | 05/97 |
| 19. | Prepare appropriate patent disclosures, reports and manuscripts for presentation and open literature publications  | 09/97 |

**10. Transition Plan:**

Technology transfer would take place via the Army Safety, Health, and Environmental Directorate. Cooperative Research and Development Agreements with Navy, DOE, EPA, FAA, and various industries would be established. Financial support for transitions would result from ARL and DSHE, leveraged by Stablase, Inc., Polymicro, Inc., and General Fiber Optics, Inc. via SBIR Phase II Projects. Funds from other agencies requesting sensor technology are also projected.

**11. Funding: \$(K)**

FY94	FY95	FY96	FY97	Total
290	94	0	500	884

Leveraged Funds Supplied by other Sources:

\$145,000, FY94, ARL Independent Laboratory Innovative Research Award  
 \$585,000, from currently funded SBIR Program Stablase, Inc. Phase II SBIR: Small, Compact Field-Worthy Excimer and Solid State Laser Systems. Contract DAAA15-93-C-0074.

\$590,000, from Polymicro, Inc. Phase II SBIR: High Performance Ultraviolet Infrared Optical Fibers, Contract DAAA15-93-C-0122.

\$744,000, from currently funded SBIR Program, General Fiber Optics, Inc. Phase II SBIR: Optical Fiber Feed through/Connectors. Contract DAAA15-93-C-0068.

## **12. Performers:**

Drs. R.C. Sausa, B.E Forch, and H. Rogers, ARL Senior Staff; Drs. G. Lemire and J. Simeonsson, NRC/NAS Postdoctoral Research Associates; Dr. James Baily, Safety, Health, and Environment Directorate (DSHE), Aberdeen Proving Ground, MD; Professor Kenneth Ledingham, Department of Physics, University of Glasgow, Scotland, UK; Professor A. Amirav, Dept. of Chemistry, Tel Aviv University, Israel; Stablelase, Inc., SBIR Phase II: General Fiber Optics, Inc., Polymicro, Inc.

## **13. Principal Investigators:**

Dr. Rosario C. Sausa  
Co-Investigator: Dr. J. Simeonsson  
US Army Research Laboratory  
AMSRL-WT-PC  
Aberdeen Proving Ground, MD 21005  
PHONE: (410) 278-7070  
FAX: (410) 278-9734  
E-MAIL: Sausa@ARL.MIL

## **14. Keywords:**

Laser Photofragmentation/Ionization Spectroscopy

## SERDP FY95 PROJECT

1. **SERDP Thrust Area:** Cleanup
2. **Title:** Field Portable FTS Fiber Optic VOC Sensor
3. **Agency:** Air Force
4. **Laboratory:** Wright Laboratory
5. **Project ID:** #103
6. **Problem Statement:**

The goal of this project is to develop a prototype field portable Fourier Transform Spectrometer (FTS) that will detect and measure the presence of volatile organic compounds (VOCs) in soil at hazardous waste sites and long term compliance monitoring stations. Rapid on site screening of soils for VOCs can be accomplished by analyzing Raman or laser-induced fluorescent signatures. This project builds a new type of FTS that marries a fiber-optic light delivery and collection system with a compact optical design that requires no mechanical scanning. The spectrometer is based on a miniature common-path interferometer and a unique solid-state light sensor that provides light detection and spectral processing on a single integrated circuit. The prototype's monolithic FTS chip will also be tested for dual-use applications in laser warning receivers, IFF, and laser communications configurations.

VOC sorption in soil depends on the availability of bonding sites, and the amount of mineral surfaces, organic matter, and moisture in the soil. This creates problems when trying to determine the actual VOC concentration in a particular sample. Current analysis protocols mitigate this problem by calling for bulk soil collection taken from the hazardous waste sites to be shipped to laboratories. At the laboratory, sub samples are drawn from the bulk sample and analyzed by purge-and-trap gas chromatography/mass spectrometry (EPA SW-846, method 8240). To overcome the soil property variances and rapidly characterize a hazardous waste site, the ideal instrumentation for in situ VOCs determination would allow multiple VOCs of interest to be identified and measured simultaneously in real time. Additionally, such an instrument should be hand-held and should not use water as an extractant or dispersion medium (to avoid displacing the VOCs). Direct spectral measurement of VOC analytes using remote spectroscopy techniques should avoid sample preparation involving water.

### 7. Project Description:

This project investigates feasibility of producing a ruggedized instrument package that includes a set of fiber optic sensors with coupling to a proprietary FTS configuration comprised of a miniature common path interferometer and proprietary imager/signal processing chip. The objective is to develop an instrument that will have sufficient performance to support VOC detection in a field environment.



The technical approach to this effort will include the use of a proven method of obtaining the spectral signatures of target contaminants including a fiber optically coupled FTS. Spectrochemical analysis will be used to characterize the optical signatures of the contaminants and develop appropriate and effective detection algorithms. The Proof-of-Concept investigation will focus on trichloroethylene (TCE), Benzene (Ben), and Toluene (Tol) because they are frequently encountered due to use in industrial solvents and petroleum products and are on the EPA 17 Target Chemicals Lists.

This program's effort will be a synergistic combination of integrated research spectrochemical analysis, detection and identification algorithms, optical design, and novel detector design and fabrication.

This project directly contributes to the objectives identified in the Tri-Service Environmental R&D Strategic Plan, Pillar 1: CLEANUP: Requirement Thrust; 1C Characterization and Monitoring.

### **8. Expected Payoff:**

This device will have dual-use application, with potential government and commercial users. Potential users would have a need to detect, categorize, and measure VOCs and HAZMATS. The impact of this device would be a device capable of mapping VOC concentration contours at hazardous waste sites or EPA soil pollution limit compliance monitoring at DoD and DOE facilities and throughout the industrial base. The FTS chip/interferometer design will be of important and immediate use for priority laser warning receiver research on single aperture laser warning receivers and combined missile warning/laser warning receivers.

### **9. Milestones:**

1.	Breadboard FTS fabrication	10/93
2.	Complete review of detection methods	04/94
2.	Estimated Contract Commencement date	07/94
3.	Detection and recognition algorithms definition	09/94
4.	Laser subsystem/interferometer designs	02/95
5.	Interferometer fabrication and FTS chip design	06/95
6.	FTS chip/electronics fabrication	03/95
7.	Prototype hardware integration and validation	09/95
8.	Final report and prototype hardware delivered	03/96

### **10. Transition Plan:**

WL/AAWP-3 LWR EO Laboratory will be the Government agency managing the program. The development contractor and Cooperative Research and Development Agreement (CRADA) partner will be Remote Spectral Capture. Validation testing in the interested instrument-manufacturing firms will lead to cooperative opportunities for technology transfer to the commercial market. Potential users will be involved in all aspects of the test execution and post test analysis.

**11. Funding: \$(K)**

	FY94	FY95	FY96	TOTAL
SERDP	55	150	0	205

**12. Performers:**

This project will be a CRADA effort between RSC and WL/AAWP-3. RSC will perform the FTS chip design and oversee foundry fabrications of the chip. RSC and WL/AAWP-3 will share interferometer design, prototyping, testing and calibration tasks as well as detection and algorithm development. Final integration, laboratory and field testing will be accomplished at the WL/AAWP-3 nationally recognized Electro-Optics, Laser Test Facilities.

**13. Principal Investigator:**

Matthew P. Dierking  
WL/AAWP-3  
Hangar 4B, 3050 C Street  
Wright-Patterson AFB, Ohio 45433-7300  
PHONE: 513-255-2471  
DSN: 785-2471  
E-MAIL: matt@wplm2a.aa.wpafb.af.mil

**14. Keywords:**

Stationary Interferometer, Fourier-Transform Spectrometer, Fiber Optic, Interferometry, Surface Enhanced Raman Scattering, Spectrochemical Analysis

## SERDP FY95 PROJECT

1. **SERDP Thrust Area:** Cleanup
2. **Title:** In-Situ "INSIDE-OUT" NMR Sensor for Contaminant ID
3. **Agency:** Navy
4. **Laboratory:** Naval Command, Control and Ocean Surveillance Center  
RDT&E Division - San Diego, CA
5. **Project ID:** #38
6. **Problem Statement:**

Determination of the feasibility for the adaptation of the emerging "INSIDE-OUT" Nuclear Magnetic Resonance (NMR) technique of compound identification to rapid site screening of hazardous waste sites. Recent developments in the area of high energy density magnets (rare earth and high temperature superconducting magnets) will allow for a significant reduction in the physical size of this type of sensor. This technique allows a well defined volume of soil surrounding the sensor to be analyzed without collection of samples.

### 7. Project Description:

The concept of reversing the locations of the sample and the source of the magnetic fields required to Nuclear Magnetic Resonance Spectroscopy was proposed and verified by Jackson, Burnett and Harmon<sup>1</sup> for the Department of Energy, Los Alamos Scientific Laboratory in 1980. The technique developed produces a region of homogeneous magnetic field external to the apparatus. A coaxial nuclear magnetic resonance coil is periodically pulsed at radio frequencies to briefly produce a toroidal magnetic field at 90° to the steady homogeneous field. If the frequency of the rf magnetic field is adjusted to synchronize or "resonate" with the Larmor frequency of precession of the nuclei present in steady magnetic field and realign the direction of their nuclear magnetization vector accordingly. The intersection of the steady homogeneous magnetic field and the toroidal rf magnetic field define the "sensitive sample volume". With the cessation of the rf magnetic pulse, the realigned or "flipped" nuclei will start to precess due to the Earth's magnetic field. The coupling between the precessing magnetization vector and the NMR coil allows the NMR free-induction decay (FID) signal to be detected. The amplitude of the signal is related to the number of nuclei present, and the rate of signal decay is related to the local environment of the nuclei, i.e., the chemical bonds to other near by atoms.

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J.A. Jackson, L.J. Burnett, and J.F. Harmon, "Remote (Inside-Out) NMR. III. Detection of Nuclear Magnetic Resonance in a Remotely Produce Region of Homogeneous Magnetic Field", *Journal of Magnetic Resonance*, 41, 411-421, (1980).

Jackson<sup>2</sup> has demonstrated the variation of the radial magnetic field ( $H_r$ ) vs. radial distance  $r$ , as a fraction of the axial magnetic field ( $H_0$ ) at the center of an isolated magnet. With a  $h/a$  value of 3, where  $h$  is the axial distance from the pole face to the midplane and  $a$  is the radius of the pole face respectively, the radial magnetic field is very uniform for the region defined by the ratio  $r/a$  between the values of 1.9 - 2.8.

The Larmor frequency of the precessing magnetization is given by:  $B = B_p \cos(\omega_0 t)$  where:  $B_p$  is the value of the radial magnetic field in the region discussed above,  $\omega_0$  is the Larmor frequency, and  $t$  is time. If the quantity  $g$  is referred to as the relative signal per unit volume of toroidal sample, referenced to a known coaxial sample of volume  $V_r$ , then  $g$  can be expressed as

$$g \equiv (I_s/V_s) / (I_r/V_r) \quad [1]$$

where  $I$  is signal amplitude and  $V$  is the volume of material involved, and the subscripts  $s$ ,  $r$  and  $c$  denote the toroidal and reference samples, and the NMR resonance coil respectively.

For brevity, the following simplifications will be made:  $R$  is taken to be the average of the inner and outer radii of the toroid in the mid-plane, and  $R \gg$  than the radius of the cross section of the toroid. That Faraday's law for the sample coil, with a quality factor of  $Q$  and  $N$  number of turns, can be expressed as  $I = -NQA(d\phi/dt)$  with  $\phi = B \cdot A$  and  $B = B_p \cos \omega_0 t$ . Then, the peak value  $B_p$  for the reference sample can be expressed as  $B_p = 4\pi\mu_p n f$  &  $\mu_p n f = M$  where  $M$ , the magnetization, is based on the proton magnetic moment, the number density of protons, and the Boltzmann factor for the fraction of protons contributing to the net magnetization.

For the sample, only a portion of the flux is link and  $A = A_c = \pi a^2$ , then  $B_p = MV_s/R^3$  and  $I_s = NQA_c \omega_0 B_p \sin \omega_0 t = NQA_c \omega_0 [MV_s/R^3] \sin \omega_0 t$  so that,

$$(I_s/V_s) = NQA_c \omega_0 [M/R^3] \sin \omega_0 t \quad [2]$$

Similar manipulation for the reference sample's value results in

$$(I_r/V_r) = 4\pi NQ\omega_0 M/l \sin \omega_0 t \quad [3]$$

where  $l$  is the length of the reference sample and  $V_r = A_r l$ .

Combining Eqs. [1], [2], and [3] results in the relative signal per unit volume  $g = a^2 l / 4R^3$

involving only geometric parameters of, or define by, the apparatus and the maximally coupled reference sample (the best instrumental signal that can be obtained).

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J.A. Jackson, "Nuclear Magnetic Resonance Well Logging", *THE LOG ANALYST*, 16 - 30, SEPTEMBER-OCTOBER, 1984.

Substitution of practical values for these parameters, as reported by Jackson<sup>3</sup>, for the radial magnetic field in an acceptable operating configuration ( $r/a = 2$ ,  $a = 5$  cm, reference sample length  $\approx 5$  cm) yields a value for  $gP_g^9C^A^S^DX19P\#^Af$  reversing the locations of the sample and the source of the magnetic fields required to Nuclear Magnetic Resonance Spectroscopy was proposed and verified by Jackson, Burnett and Harmon<sup>4</sup> for the Depart for its envisioned use, particularly for high explosive compounds and petroleum based products. He has also proposed to cooperatively develop this project, manufacture and market any viable product which may evolve as part of the technology transfer effort.

## 8. Expected Payoff:

This detector, when fully developed, will allow for rapid and cost effective screening of proven and/or suspected sites contaminated with chemical compounds for which it has been calibrated. The ability to identify and quantify contaminants in subterranean strata behind well casings will allow the placement of a single test well, drilled and cased to the maximum investigative depth, rather than many wells which vary in depth in order to collect the necessary strata effluent. The reduction in the number of unnecessary test wells and their attendant costs in time and money, for installation, sample collection, laboratory analysis, and sample transportation, is considerable. If the number of test wells can be reduced by a factor of five (80% reduction in the number of wells), it is estimated to reduce the overall cost of this phase of site remediation approximately 40 - 50%, by accurate determination of the boundaries and depth of the contaminant plume before and after site remediation efforts.

If we conservatively estimate the cost of drilling and casing a well at \$20/ft, for a 50 ft well, and disposal of the tailings, at \$4,000.00; the associated required test well lifetime of analytical laboratory analysis (X samples per year for Z years as required by EPA) at \$5,000.00; then the cost per well is \$10,000.00. Further, assume that the time required to install a well and receive the initial laboratory analysis report (approximately 4 weeks) would not be lost. If the number of well installed per year is reduced by 500, then the monetary savings will be \$5,000,000.00. Also, the environmental and personnel health risks are reduced since the amount of hazardous tailings wastes generated during the drilling operations will be reduced in proportion to the number of wells drilled.

## 9. Milestones:

1.	Start project	12/94
2.	Complete review of applicable technologies	10/94
3.	Complete assessment of high strength permanent magnets	06/95
4.	Complete functional specifications for equipment	10/95
5.	Complete procurement & assembly of system	10/95
6.	Complete measurements of target compounds	01/96
7.	Complete assessment of feasibility	03/96

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J.A. Jackson, *ibid.*

J.A. Jackson, L.J. Burnett, and J.F. Harmon, "Remote (Inside-Out) NMR. III. Detection of Nuclear Magnetic Resonance in a Remotely Produce Region of Homogeneous Magnetic Field", *Journal of Magnetic Resonance*, 41, 411-421, (1980).

- |     |   |       |
|-----|---|-------|
| 8.  | Complete design & fabrication of prototype        | 07/96 |
| 9.  | Start field trials                                | 11/96 |
| 10. | Complete field trials & assess results            | 09/97 |
| 11. | Complete documentation for transition to industry | 11/97 |

**10. Transition Plan:**

Under the guidance of the Technical Program Officer and Technical Program Manager, the operable system will be subject to field trials at selected DoD/DOE sites. The results of those field trials shall be reported and distributed as requested. At the conclusion of this effort the operable hardware, procured as part of this effort, shall be turned over to the identified program office within the SERDP defined lead agency. This will be handled through the DoD/National Environmental Technology Demonstration Program. In addition to providing well characterized sites, this program will provide or simplify: testing protocol requirements; data format requirements for information fusion; data quality assurance/quality control (QA/QC) guidance and objectives necessary for acceptance; oversight for cost/performance data collected; and additional avenue for transfer of this technology. The basic technology will be transferred through the development of U.S. government patents, and through the cooperative development with the responsible industry partner, Quantum Magnetics in the United States, along with the transfer of technology previously developed from the Department of Defense as part of this effort.

**11. Funding: \$(K)**

	FY94	FY95	FY96	FY97	FY98	FY99	TOTAL
SERDP	450	200	100	380	520	315	1760

**12. Performers:**

1. NCCOSC, Research, Development Test & Evaluation (RDT&E) DIV, San Diego, CA (Codes 524, 754)
2. DOE : Los Alamos National Laboratory (LANL)
3. Quantum Magnetic; San Diego, CA
4. San Diego State University Foundation, San Diego, CA (Contractor support and consultation with faculty)

**13. Principal Investigators:**

Gary Mastny & Dr. Mark North  
 NCCOSC RDT&E DIV 524 & 754  
 SAN DIEGO, CA 92152-6320  
 PHONE: (619) 553-2802, 553-6761  
 FAX: (619) 553-6305  
 E-MAIL: mastny@nosc.mil

Dr. Lowell Burnett, President  
Quantum Magnetix  
11578 Serrento Valley Rd.  
San Diego, CA 92121  
PHONE: (619) 481-4015

**14. Keywords:**

Nuclear Magnetic Resonance, Inside-Out NMR, Nuclear Magnetic Logging

## SERDP FY95 PROJECT

1. **SERDP Thrust Area:** Cleanup
2. **Title:** Integrated Characterization Program Combining DOE (PNL) UFA and DoD (NRAD) Sensor Technologies
3. **Agency:** Department of Energy
4. **Laboratory:** Pacific Northwest Laboratory (PNL)
5. **Project ID:** #592
6. **Problem Statement:**

Defining the nature and extent of subsurface chemical contamination is a costly and time-consuming process at sites requiring remediation. Detailed site investigations require installation of many monitoring wells and subsequent analysis of discrete soil and groundwater samples. Effective site characterization is often limited by the ability to select optimal locations for monitoring wells. Furthermore, the ability to resolve horizontal and vertical features in the distribution of chemical contaminants and to determine the transport rates of these contaminants in various stratigraphic layers is a function of limitations imposed by the spacing between wells and the vertical spacing between samples. At present, locations for monitoring wells are usually based on information gleaned from site historical data, ground water hydrology, and/or indirect chemical screening such as soil gas measurements. Because of the limitations of these methods, many wells are not properly positioned and, therefore, yield information of marginal utility. By utilizing cone penetrometer (CPT) mounted sensor technology it is possible to obtain continuous coverage over the investigated depth intervals and more precisely delineate the boundaries of contaminant plumes, thus it is less likely that "clean" material will be unnecessarily removed or subjected to costly remediation procedures.

Although determining the current position of contaminant plumes is important, obtaining the information necessary for predicting future contaminant movement may be of even greater long term importance. Knowledge of the transport characteristics of soils (including hydraulic conductivity) under unsaturated and saturated conditions is required for modeling the transport of contaminants in subsurface materials surrounding hazardous and mixed waste sites. Once the nature and extent of the contamination are determined, it is also necessary to understand the transport properties of the soil to determine the potential risk to public health and environment that will ultimately control the degree and time frame of remediation. If stratigraphic horizons where future contaminant transport will likely occur can be identified, remediation efforts can be more efficiently directed. The hydraulic conductivity of soil depends strongly on the characteristics of the fluid and substrate, and on the volumetric water content of the soil. Traditionally, it has been difficult to obtain transport data on unsaturated and multicomponent systems because of the long experimental durations (weeks to years) necessary for achieving hydraulic steady state. By using the Unsaturated Flow Apparatus (UFA), it is possible to experimentally measure transport characteristics in a very short time frame (hours to days) under the wide range of conditions that exist in the field.



This project is an applied research program that couples two relatively new characterization techniques to provide a more powerful characterization procedure. Both techniques stress innovative technologies that allow rapid completion of the installation characterization procedure so that planning future remediation programs may be done in a more cost effective manner. The first technology is the CPT mounted sensors that rapidly delineate contaminant plume boundaries in the subsurface. Developed through a Tri-service DoD collaboration, the Site Characterization and Analysis Penetrometer System has been successfully employed for characterization at several DoD installations. The second technology is the UFA, a system that allows rapid determination of subsurface transport parameters in porous media. It was developed at DOE's Pacific Northwest Laboratories (PNL) for use at many DOE sites, including characterization studies at the Hanford Site.

## **7. Project Description:**

This project is structured to develop and demonstrate the synergistic integration of two characterization techniques. The project scope is divided into two phases. This phased approach will allow continual refinement and streamlining of the interactions between the two government laboratories. The initial phase will include a pilot-scale demonstration of the current capabilities of both systems to aid in the planned development of sensor technology that will better evaluate the soil matrix. This development includes work at NRAD on new optical based imaging systems to evaluate grain size distribution that will improve the textural determinations (sand, silt, clay) currently made by CPT point and sleeve resistances. This matrix sensor will optically image the soil matrix at depth, providing a digitized image from which grain size distribution (and pore geometry) can be derived. Additional sensor development will focus on determinations of soil moisture content. The work at PNL will focus on determining the sensitivity of hydraulic conductivities to the variations in soil textural data properties that the CPT with new sensors can detect. This will determine how many representative soil types will be required for UFA measurement to sufficiently characterize the hydraulic properties at a selected field site. The digitized soil matrix images can then be used to develop image analysis programs as input to models for deriving hydraulic transport properties over the full range of soil types observed at a site. The second phase of the project will involve the field scale demonstration of the capabilities of the combined techniques. An installation will be selected based on the type of contaminant (compatibility with developed sensors) and soil textures (initially a limited range in soil texture variations) present at the site. The CPT will be deployed with a combination of sensors and will recover soil samples from representative stratigraphic horizons for UFA studies. Continuous matrix image analysis and moisture content data over the investigated depths will allow continuous determinations of fluid transport properties across the site. As the field demonstration progresses, evaluation of the data will indicate where additional CPT deployments are required to obtain detailed information from specific stratigraphic horizons.

During both phases of the program industrial partners will be working with the laboratories so technology transfer opportunities to promote commercialization will be possible.

## **8. Expected Payoff:**

The potential benefit of this project is the development of a superior, rapid characterization program that will allow a more cost effective remediation plan to be developed. The CPT sensor technology is a more rapid, cost effective method to delineate contaminant boundaries

than traditional well drilling. The UFA technology is a more rapid, cost effective method to directly determine transport parameters (required for estimating or modeling contaminant movements) than other traditional techniques. Direct determinations are preferable to any estimation techniques because estimations are often overly conservative and lead to extremely expensive remediation programs. By developing the process in conjunction with an industrial partner, commercially available applications could be possible in the near term.

**9. Milestones:**

- |    |   |       |
|----|---|-------|
| 1. | Complete pilot-scale sensor and UFA studies             | 08/94 |
| 2. | Demo CPT sensor and UFA method at field-scale           | 10/94 |
| 3. | Complete bench-scale work on CPT optical imaging system | 07/95 |
| 4. | Field-scale demo of combined CPT and UFA method         | 07/96 |
| 5. | Assess and evaluate results of demo                     | 04/97 |
| 6. | Final report  | 09/97 |

**10. Transition Plan:**

PNL will be the lead laboratory for this project. During the initial phase, a contaminated site will be identified for demonstration and participation in the development of the coupling process between these techniques so that the site will be available for later phase field operations. Both laboratories are involved with industrial partners in attempts to transfer these technologies to the private sector.

**11. Funding: \$(K)**

	FY94	FY95	FY96	FY97	TOTAL
SERDP	300	100	0	550	950

**12. Performers:**

The proposed project will be managed by PNL. Battelle operates PNL for the Department of Energy.

An industrial partner that provides field CPT support is currently working with NRAD. It is anticipated that they will participate in the development and field demonstration of the process to facilitate technology transfer. An industrial partner has already agreed to work with PNL on commercialization of the UFA through the CRADA process. Demonstration of the coupled technologies will assist in commercialization of the UFA and CPT sensor technologies by demonstrating the additional utility of the combined techniques. This should help to provide the means for near-term industrial applications.

### **13. Principal Investigator:**

JM Leather, PhD  
Mail Stop B1-34  
Battelle-PNL  
Richland, WA 99252  
PHONE: (509) 375-3268  
E-MAIL: JCONCA@BETA.TRIICITY.WSU.EDU

JV Wright, PhD.  
Mail Stop B1-34  
Battelle-PNL  
Richland, WA 99252  
PHONE: (509) 375-3268  
FAX: (509) 375-4838

SH Lieberman, PhD.  
NRAD  
Code 522  
San Diego, CA 92152  
PHONE: (619) 533-2778  
FAX: (619) 533-6305

### **14. Keywords:**

Characterization, Contaminant, Transport, Sensors, UFA, CPT

## SERDP FY95 PROJECT

1. **SERDP Thrust Area:** Cleanup
2. **Title:** Subsurface Gas Flowmeter
3. **Agency:** Department of Energy
4. **Laboratory:** Sandia National Laboratories
5. **Project ID:** #404
6. **Problem Statement:**

In situ air stripping is a process for removing volatile organic compounds (VOC's) from the subsurface which is currently enjoying widespread use in the environmental restoration industry. Air stripping involves injecting and/or extracting air from the subsurface through vertical or horizontal wells penetrating the contaminated horizons. The flow of air through the subsurface results in the VOC's being volatilized and removed from the ground by the flowing air. In assessing the effectiveness, efficiency and zone of influence of this technology it is important to understand the dynamics of the gas flow in the subsurface. In a perfectly isotropic, homogeneous medium the gas would travel uniformly through the ground. In the real world, however, the transport properties of the subsurface are decidedly inhomogeneous, with the result that the gas travels along preferred, high permeability pathways. To properly evaluate the remediation process, one needs to delineate these pathways and define how broad and diffuse or narrow and constricted they are. Another important consideration when gas is being injected and/or extracted from the subsurface is the amount of interaction between the gas in the pore spaces in the vadose zone and atmospheric air. These effects have not been adequately investigated because of the difficulties involved in directly measuring air flux in soil. In this technology demonstration proposal it is proposed to develop a gas flowmeter which will address these needs by providing the capability to directly measure gas flow velocities in the subsurface.

The gas flowmeter being proposed is a new project that represents an extension of a technology called the In Situ Permeable Flow Sensor which has been developed by the PI with funding from DOE's Office of Technology Development. The In Situ Permeable Flow Sensor, which measures the full 3 dimensional groundwater flow velocity at a point in a saturated permeable material, was field demonstrated during the VOC Non-Arid Integrated Demonstration at the Savannah River Site and has recently been licensed to a private company which plans to commercialize the technology. The new gas flowmeter, while similar in many respects to the previously developed In Situ Permeable Flow Sensor, differs in several important aspects.

### 7. Project Description:

Both the existing groundwater flow sensor and the proposed gas flowmeter are based on the principle that the temperature distribution on the surface of a finite length, heated cylinder buried in a permeable flow field is related to the flow velocity of fluid past the cylinder. When there is no flow past the cylinder, the temperature distribution on the surface of the

cylinder is independent of azimuth and symmetric about the vertical midpoint of the cylinder. In a flow field with a significant vertical component, the vertical temperature distribution will become skewed in the direction of the flow as some of the heat emanating from the cylinder is advected along the length of the cylinder by the moving fluid. In a flow field with a significant horizontal component, the azimuthal temperature distribution will no longer be independent of azimuth. The downstream side of the cylinder will be relatively warm compared to the upstream side.

The key to implementing this basic operating principle is to ensure that the heat flux from the surface of the probe is outwardly directed with as little heat transfer occurring through the interior of the rod as possible. To accomplish this, the proposed gas flowmeter, like the groundwater flow sensor, will consist of a cylinder of low thermal conductivity polyurethane foam 75 cm long and 5 cm in diameter on the surface of which is mounted a thin film flex circuit style heater and an array of 30 temperature sensors. This assembly is then encased in a waterproof seal.

The most significant difference between measuring groundwater and gas flow with this technology will be the method used to deploy the instrument. The groundwater flow sensor is emplaced by drilling down to the desired depth using a hollow stem auger, lowering the probe down the center of the auger and then retracting the auger, leaving the probe at the bottom of the hole. In unconsolidated, saturated soils, the formation quickly collapses around the probe, leaving it permanently buried in the ground. This technique will not be appropriate for measuring gas flow, in part because unsaturated sediments do not collapse as readily as saturated sediments, but primarily because the technique introduces too large a disturbance in the formation gas permeability. Instead, the gas flowmeter will be deployed directly in a borehole where it will be capable of measuring either the vertical gas flow within the hole or the horizontal component of the formation gas flow velocity, depending on how the borehole is completed.

To measure the horizontal component of the formation gas flow, the probe will be deployed along the axis of the hole within a screened interval of the borehole and the borehole will be packed off above and below the screened interval. The diameter of the probe will be smaller than the inner diameter of the borehole so that there will be an annulus of open space between the outer surface of the probe and the inner wall of the borehole. If there is any gas flow in the formation then air will enter the borehole on one side of the screened hole, impinge upon the surface of the probe, flow around the probe and exit the hole on the opposite side from where it entered. Relatively cool temperatures would be observed on the upstream side of the probe and warm temperatures on the downstream side as some of the heat emanating from the probe is advected around the probe by the flowing air.

The same probe could also be used to measure vertical gas flow within screened or uncased holes. This type of measurement would be very useful for determining the relative permeability of different layers intersected by a borehole. If the borehole were logged as air was being pumped into or out of the hole, either artificially with a pump or naturally by a change in barometric pressure, layers of the formation with relatively high permeability would be characterized by high gradients in the vertical gas flow. Characterization of the gas flow field in the subsurface would be very useful to environmental engineers and regulators trying to understand the dynamics of natural and induced air stripping waste remediation processes and the fate and transport of contaminants in the unsaturated zone.

For both the groundwater flow sensor and the proposed gas flowmeter the direction of the fluid velocity vector can be determined very easily by analyzing the pattern of the temperature distribution on the surface of the probe. Determining the magnitude of the fluid velocity vector is more difficult. The mathematical expression which relates the magnitude of the temperature distribution on the probe to the magnitude of the fluid velocity past the probe assumes that the probe is deployed in intimate contact with an infinite, homogeneous medium. This expression cannot be used when the probe is deployed in a borehole because this assumption is grossly violated in the borehole environment. As a result, the gas flowmeter will be calibrated in a simulated borehole under conditions of known gas flow velocity. The most significant technical hurdle to be overcome is to determine the degree to which the casing material, screen size, thermal and pneumatic properties of the formation, and other factors, influence the response of the instrument. Preliminary estimates suggest that the probes should be quite sensitive to gas flow velocities as low as on the order of 0.1 ft/min. This represents a significant improvement over current technology.

The method by which formation gas flow velocity is currently measured is to deploy an array of pressure transducers at different points in the formation to determine the pressure gradient at the point of interest. The product of the pressure gradient and gas permeability of the soil yields the gas flow velocity. The problem is that the gas permeability of soils is very difficult to determine with any degree of accuracy. The PI is unaware of any other techniques for direct measurement of gas flow velocity in the subsurface. The current technique for measuring gas flow into or out of a borehole involves attaching a mass flow meter to the top of the hole and measuring the integrated flux across the entire screened interval of the hole. The gas flow meter being proposed has the advantage that it can also indicate which horizons penetrated by the hole are yielding or absorbing the most gas. These types of measurements are currently made with impeller type flow meters which are not nearly as sensitive as the proposed flow meter.

The first task will be to conduct laboratory studies in simulated boreholes to develop calibration procedures and to determine the sensitivity of the proposed technology to both vertical and horizontal gas flows. The second task will be to test the probes in a real borehole and finally to deploy them at an actual waste site where in situ air stripping is being used to remediate the contaminant. Personnel from the Hanford Environmental Restoration Department have expressed a strong interest in this technology and have offered their site as a potential field test location.

## **8. Expected Payoff:**

The technology has the potential to dramatically improve our understanding of the dynamics of air stripping waste remediation activities, an extremely important technology currently being used extensively, both by government and private industry, to remediate hazardous waste sites. The availability of the gas flowmeter technology will improve the cost effectiveness of air stripping projects by providing information about the zone of influence of the process at a given site, thereby alleviating the necessity of conducting overly conservative cleanup sweeps. At sites where nutrients intended to enhance bioremediation of the contaminant are being delivered into the subsurface by gas injection, this technology can yield information migration paths of the injected nutrients in the subsurface.

## 9. Milestones:

- |    |   |       |
|----|---|-------|
| 1. | Complete lab studies and sensitivity analysis | 09/95 |
| 2. | Complete and document calibration procedures  | 03/96 |
| 3. | Deploy instruments at a hazardous waste site  | 06/96 |
| 4. | Complete data collection                      | 12/96 |
| 5. | Complete final report on technology           | 03/97 |

## 10. Transition Plan:

By the completion of the work described in this proposal, the technology will have been developed to the point of commercial viability and have been tested and demonstrated at an actual waste site. As the technology is being developed, industrial partners interested in commercializing the technology will be actively sought. S. I. E., Inc. of Fort Worth, Texas, the company which is currently commercializing the In Situ Permeable Flow Sensor, has expressed an interest in participating in the development of this technology and in commercializing it, if it proves marketable.

The ultimate users of this technology will be Environmental Restoration Departments at the various DoD and DOE facilities around the country as well as private industries. Discussions with ER representatives at the DOE Hanford Site have been very encouraging. They expressed a strong interest in using the technology once developed and offered their site as a possible field test location.

## 11. Funding: \$(K)

	FY94	FY95	FY96	TOTAL
SERDP	125	250	125	500

## 12. Performers:

The work described in this proposal will be carried out by the Principal Investigator, a Senior Member of Technical Staff at Sandia National Laboratories. As mentioned above, S. I. E., Inc., has expressed an interest in participating in the development of this technology. If this project goes forward, the option of concluding a CRADA with them will be vigorously pursued very early in the project.

## 13. Principal Investigator:

Sanford Ballard  
Geophysics Department, 6116 (Mail Stop 0750)  
Sandia National Laboratories  
Albuquerque, NM 87185-0750  
PHONE: (505) 844-6293  
FAX: (505) 844-7354  
E-MAIL: sballar@ca.sandia.gov

**14. Keywords:**

Gas, Flow, Flowmeter, Air-Stripping, Bioremediation, Vadose.



## SERDP FY95 PROJECT

1. **SERDP Thrust Area:** Cleanup
2. **Title:** Removal of VOCs from Contaminated Groundwater and Soils by Pervaporation
3. **Agency:** Environmental Protection Agency
4. **Laboratory:** Risk Reduction Engineering Laboratory (RREL)
5. **Project ID:** #371
6. **Problem Statement:**

Petroleum hydrocarbons, and other volatile organic compounds (VOCs), which are found to contaminate groundwater and soils, are usually treated by pump-and-treat methods, which are very time-consuming, expensive, and not very effective. We are proposing the use of pervaporation for effectively removing these hydrocarbons and VOCs from contaminated soil and groundwater (with or without using surfactants) and concentrating them by at least a thousand-fold, for economical disposal or recycle/reuse using specially designed hydrophobic membranes.

### 7. Project Description:

Petroleum hydrocarbons and other volatile organic compounds (together described hereafter as VOCs) form various industrial activities in both civilian and military sectors are frequently found to contaminate groundwater and soils. These VOCs typically are transportation fuels, and solvents including chlorinated organic compounds such as trichloroethylene (TCE), carbon tetrachloride, tetrachloroethane (PCA). Many of these VOCs are potential carcinogens. In groundwater the VOCs exist as non-aqueous phase liquid pools (NAPLs), which are of two types, light NAPL (LNAPL) which floats on water, and dense NAPL (DNAPL) which sinks under water. The NAPL pools are a long-term source of contamination, as the organics slowly leaks into the aquifer water, which then is unusable for human use, and if the water discharges into a river or a lake, it poses danger to aquatic life. Soil contamination by VOC is a source for continuous air pollution and is also a source for groundwater pollution.

The technology of choice for remediating these environmental problems is the so-called pump-and-treat method, one variation of which is circulating water through the contamination area and pumping it out to a treatment stage, typically carbon adsorption, which needs to be subsequently regenerated, and the VOCs disposed of chemically. We propose to develop a simpler and more effective technology which will use the membrane pervaporation method. This method removes the VOCs from the water and concentrates it by at least a thousand-fold, which permits much more economical recovery for recycle/reuse.

In the "pump" part of the pump-and-treat process, the use of surfactants has been proposed for enhancing the removal of VOCs from the groundwater or soil matrix (surfactant flushing). While the VOCs will indeed be removed more efficiently by emulsification, the oil-water emulsion is harder to dispose of by ordinary means of bioremediation or carbon

adsorption. We are proposing pervaporation as a means of breaking the emulsion while removing the VOCs from the contaminated water. The efficiency of pervaporation for VOC removal from water has already been demonstrated in several studies to be better than 99%. The use of pervaporation for breaking oil-water emulsions is protected by an invention disclosure at RREL-EPA.

Pervaporation works on the principle of solution diffusion, i.e. the organic compounds dissolves in the non-porous membrane, diffuses out to the permeation side, and evaporates. The energy for this evaporation is conveniently provided with the feed stream itself. In contrast to conventional membrane processes, which use porous membranes, pervaporation membranes are not akin to filtration, and are therefore less prone to mechanical fouling. For VOCs, which are hydrophobic, a hydrophobic membrane is appropriate. Either a vacuum or an inert sweep gas is employed on the permeate side of the membrane. Usually the VOCs permeate through a hydrophobic membrane, such as one made of polydimethylsiloxane or silicone, orders of magnitude faster than water, as a result of which the VOCs are highly concentrated. For instance, it is possible to concentrate a 100 ppm VOC-solution to over 10% VOC solution (or suspension).

The composition and morphology of the membranes are a key to effective use of pervaporation technology. It is best to use a thin film of the discriminating layer deposited on a highly porous support structure. In addition, RREL-EPA has invented specially doped membranes that enhance the selectivity by 40% or more. An invention disclosure has also been made on the use of these membranes for pervaporation.

The proposed research has four parts:

1. Use of special membranes: These membranes will be designed, fabricated and tested for their superior VOC-selectivity and transport rates.
2. Bench-scale test: Laboratory research will be conducted to investigate the removal of VOCs from simulated ground water and surfactant-flushed VOC-solutions. Transport rates, selectivity, and separation factors will be measured.
3. Mathematical modeling will be conducted to predict the design features of a prototype for a designated removal efficiency. This is a mere extension of modeling currently being done at RREL in cooperation with the University of Cincinnati.
4. We will collaborate with a membrane company, such as Membrane Technology and Research (MTR, Inc.), Palo Alto, California, for a pilot demonstration of VOC-removal from contaminated water (with or without surfactant in it). MTR, Inc. specializes in pervaporation research and has tested several pilot modules for removing VOCs and CFCs from air and water streams. We propose to demonstrate the technology at a defense facility.

All work from proof-of-concept of the removal of VOCs from VOC-emulsion in water to pilot demonstration can be completed in two years from the inception of the study.

## 8. Expected Payoff:

The proposed technology will make two specific advances: (1) provide a cost-effective way of dealing with surfactant-VOC solutions, and (2) provide a boost to the use of surfactants for groundwater and soil remediation. Large savings will accrue from this practical and efficient technology.

## 9. Milestones:

- |    |  |       |
|----|--|-------|
| 1. | Complete preliminary technical plan for FY95 work and overall 2 year outline   | 02/95 |
| 2. | Visit Naval Facilities Engineering Science Center (NFESC) at Port Hueneme for detailed discussion of technical plan and outline - determine solute, contaminants of interest   | 02/95 |
| 3. | Complete detailed in-house experimental plan based on simulated groundwater, surfactant flushed VOC solution, and emulsions. Tests are to determine transport rates, selectivity and separation factors for individual and mixed solutions | 07/95 |
| 4. | Complete detailed extramural experimental plan   | 07/95 |
| 5. | Procure hollow fiber membrane module and complete assembly of experimental approaches  | 08/95 |
| 6. | Complete laboratory experiments  | 01/96 |
| 7. | Complete data analysis   | 03/96 |
| 8. | Complete model development to predict performance of the hollow fiber module   | 05/96 |
| 9. | Complete Phase I interim progress report   | 05/96 |

## 10. Transition Plan:

The pilot demonstration at a defense site will constitute technology transfer to DoD.

## 11. Funding: \$(K)

	FY94	FY95	FY96	TOTAL
SERDP	280	250	250	780

~~Risk Reduction Engineering Laboratory (RREL)~~ will complement the proposed program with \$60K already earmarked in FY94 for the in-house study. The in-house study, which is currently focused on fundamentals, will be redirected to this high priority research.

## 12. Performers:

The first three parts of the delineated research will be conducted in-house at RREL-EPA. The demonstration will be conducted under contract by a membrane company based on the model prediction and laboratory results.

The Naval Facilities Engineering Science Center (NFESC), will collaborate with us in all phases of this work. Point of contact: Ms. Leslie Karr, Code 411, NFESC, Port Hueneme, CA 93043, Tel: 805-982-1618. The Air Force's Armstrong Laboratory Environics Directorate was contacted (Capt. Mark Smith, Tel: 904-283-6126). They will be interested in demonstrating the technology at an appropriate Air Force facility, if it is shown to be cost-effective.

**13. Principal Investigator:**

Dr. Subhas K. Sikdar, Director  
Water and Hazardous Waste Treatment Research Division  
Risk Reduction Engineering Laboratory  
Cincinnati, OH  
PHONE: 513-569-7528  
FAX: 513-569-7787  
E-MAIL: sikdar.subhas@epamail.epa.gov

**14. Keywords:**

Emulsion, surfactant, pump-and-treat, pervaporation, membrane.

## SERDP FY95 PROJECT

1. **SERDP Thrust Area:** Cleanup
2. **Title:** Subsurface Bioremediation Process Monitoring Indicators
3. **Agency:** Environmental Protection Agency
4. **Laboratory:** Robert S. Kerr Environmental Research Laboratory (RSKERL)
5. **Project ID:** #383
6. **Problem Statement:**

The application of in-situ, active or passive bioremediation of fossil fuel contamination holds promise of achieving both detoxification and source removal of regulated compounds such as benzene, toluene, ethylbenzene and xylene (BTEX). BTEX as well as other mobile constituents of fuels and solvents are a major category of subsurface contaminant mixtures present at DoD installations. These contaminant mixtures entered the subsurface as a result of spills or releases from fuel tanks, pipelines, maintenance areas, and fire-training installations. The scope of known problems, in a variety of hydrogeologic settings, requires a systematic, cost-effective approach to monitoring the progress of bioremediation processes and plume transport. In most cases, methods applied to the detection or assessment of specific subsurface contaminant distributions in aqueous or solid matrices have been applied to long-term monitoring during remedial action operations. However, disappearance of source-related compounds from ground water alone is insufficient evidence for removal. Reliable indicators of the progress of bioremediation actions, including the monitoring of metabolic intermediates in aquifer solids and water are needed in order to evaluate the performance of remediation schemes and to complement source contaminant monitoring efforts. (National Research Council, *In-Situ Bioremediation When Does It Work?*, National Academy Press, 1993.)

The major problem we intend to address is the need to identify biochemical pathway metabolites and critical substrates so that engineered mass-balances can be approached. In this way it may be possible to link net contaminant destruction or transformation to both hydrogeochemical conditions and specific biodegradation pathways. With this process level understanding, we should be able to more easily apply bioremediation to other sites. Acceptance of passive or "low-technology" bioremediation schemes can be achieved when mass-balances and definable endpoints for contaminant removal are achieved.

The needs for these monitoring improvements are recognized in several SERDP Thrust Areas: 1.B: Site Characterization and Analysis Penetrometer System, 1.III.1.e. Improved Standards and Analytical Techniques for Defining "Clean"; 1.C: Characterization/Monitoring, 1.III.3.a. Improved Subsurface Condition Description and Simulation; 1.D: Chemical Analytical Systems, 1.III.1.o. Improved Chemical Analysis Technology for Finger-Printing Organic Contaminants; 1.J: Treatment of Fuels in Groundwater, 1.I.1.e. Process to remediate Groundwater Contaminated with Hydrocarbon Fuels; and 1.T: Bioassay/Biomonitoring Methods; 1.III.1.j. Long-term, In-place Monitoring of Remediation Effectiveness and 2.II.2.e. Improved Biomonitoring Capability.

The specific applied research needs addressed by this project are: (1) the correspondence between apparent oxidation-reduction and hydrogeochemical conditions with major organic metabolite concentration distributions in source, transitional and downgradient zones, (2) the identification of mass distributions (i.e. including solid-associated and aqueous) of the principal electron acceptors, metabolites of regulated compounds and potential organic substrates present in the media (e.g. microbially derived: such as, acetate, formate, etc., and background organics, fatty acids, hydrocarbons and fire-fighting foam constituents), and (3) the temporal and spatial variability in: critical geochemical indicators (e.g.  $O_2$ ,  $NO_3^-$ ,  $NO_2^-$ ,  $NH_3$ ,  $Fe_{Total}$ ,  $Fe^{2+}$ ,  $Mn_{Total}$ ,  $Mn_{Diss}$ ,  $CO_2$ ,  $CH_2$  and  $CH_4$ ) and major metabolites (e.g. formate, acetate, propionate, as well as, benzoic, toluic, salicylic acids and isomers).

This applied research project builds on the basic work begun with USEPA-RSKERL support (Barcelona, Tomczak, Lu & Virkhaus, Petroleum Hydrocarbons in the Subsurface Conf, In-Press, 1993) which had the general goal of redox-specific characterization of organic matter in both contaminated and uncontaminated aquifers. In this work, major fractions of soluble organic matter and acidic metabolites from the microbial decomposition of hydrocarbon fuels were determined. It showed the importance of hydrogeologic and oxidation-reduction (i.e. redox) potential control over major transformation pathways and that significant degradation of fuel constituents occurs even under anoxic or reducing conditions. The methods developed in this work and that of Cozzarelli et al. (Geochimica Cosmochimica Acta, In-Press, 1993; Environ. Geol. Wat. Sci., 16, 293-297, 1990) are directly applicable to monitoring the progress of microbial processes which occur under a variety of subsurface remediation measures (e.g. air sparging, bioventing, solvent or surfactant flushing). The project's emphasis on both inorganic and organic indicators of bioremediation will aid in the definition of cleanup benchmarks and endpoints. It directly addresses the approach to answering the question of "how clean is clean"?

## **7. Project Description:**

The overall goal of the project is to determine those hydrogeochemical conditions under which hydrocarbon fuels can be degraded in the subsurface with an emphasis on: major transformation conditions and pathways, mass distributions of both source-related compounds and metabolic products, and the spatial and temporal variability in these distributions which bear on the extent of bioremediation efficiency. It directly relates to the Cleanup Thrust Area's R & D objectives which aim at both verifiable and cost-effective site investigation, characterization and remediation technologies.

The objectives of the work include: (1) Hydrogeochemical Zonation; determination of the correspondence between redox and hydrogeochemical zones of the subsurface with loci of microbial transformation, (2) Contaminant Distributions; determination of the fractionation of critical inorganic and organic transformation indicators in water and aquifer solids, and (3) Spatial and Temporal Variability; determinations of the variability in the mass distributions to evaluate techniques for volumetric averaging and performance criteria for bioremediation operations. The project has been designed to be conducted in parallel with either operational or experimental remediation efforts at sites where hydrocarbon fuels constitute a contamination problem. As such, the project can be conducted at any number of DoD or DOE installations where access can be assured. The Wurtsmith AFB, Oscoda, MI, would be an excellent candidate site given our familiarity with the hydrologic setting, hydrogeochemistry and the focus on bioremediation at the site. It represents a "fast" site

characterized by potentially high fluxes of both nutrients and water, as well as high hydraulic conductivity which facilitate high biodegradation rates and potential options for engineered enhancements (Hickman et al. J.W.P.C.F. 61, 9, 1564-1575, 1989).

The three main objectives of the project will be approached in a phased manner building on the existing array of monitoring points and initial site data review. Overall scheduling is flexible based on a FY94 or FY95 start.

Phase 1. Initial Reconnaissance and Delineation of Hydrogeochemical Zones. The existing array of monitoring wells will be sampled and preliminary borings will be made taking water and solid samples at alternate depths for the initial delineation of redox-zones. Field analyses will include: O<sub>2</sub>, temperature, pH, conductance, Fe<sup>2+</sup>, NO<sub>3</sub><sup>-</sup>, NH<sub>4</sub><sup>+</sup>, alkalinity, CH<sub>4</sub>, CO<sub>2</sub>, and volatile organic compounds (VOC's). Solid and H<sub>2</sub>O samples will be returned to the lab for determination of: total VOC's, inorganic and organic carbon, extractable acid metabolites and intermediates, non-volatile organic compounds (e.g. hydrocarbons, fatty acids, surfactants, fire-fighting foam agent), total Fe and Mn. Appropriate microcosm experiments will be run to evaluate biological activity in selected redox zones. On the basis of these results the initial hydrogeochemical zones and loci of bioactivity will be located and geostatistical estimations of sources and downgradient plume composition will be done. Selected areas for supplemental borings will be determined to expand the biomonitoring array in Phase 2.

Phase 2. Development of Optimized Biomonitoring Network and Long-Term Microcosm Experiments. The geostatistically (kriging) based distributions of redox/hydrogeochemical zones and loci of bioactivity include levels of confidence in estimating concentrations between known points. Supplemental borings and water sampling points will be located to reduce uncertainty within regions of the subsurface and the field and lab work in Phase 1 will be repeated with improved resolution. Refined estimates of background conditions and total contaminant mass per unit volume of aquifer will be developed and the network will be optimized (i.e. minimizing uncertainty) for the evaluation of spatial and temporal variability in critical indicators of contaminant removal. The approximate rates of biotransformation of the principal contaminants from microcosm experiments will be evaluated with respect to increases in metabolic products and correlated with the distributions found in the field.

Phase 3. Evaluation of Variability and Net Bioremediation Over Time. The network will be sampled at intervals (e.g. quarterly) to evaluate temporal and spatial variability in redox/hydrogeochemical zonation and progress of contaminant removal/metabolite production. It is anticipated that the methods we have used in past work (Barcelona et al., Environmental Science and Technology 25, 5, 991-1003, 1989) will serve to control sampling and analytical error so that actual subsurface variability can be determined at known levels of confidence. Seasonal effects on nutrient supply, dispersion and transport will be evaluated at selected intervals simulating the field results with stepwise applications of two-dimensional flow and transport models. It is likely that at least eight quarters of data collection will be needed to evaluate these effects. Borings will be taken and characterized as before to benchmark the progress of bioremediation and estimate time frames for net contaminant removal.

## 8. Expected Payoff:

The results of the work will provide a conceptual model for the design and operation of cost-effective remediation efforts. Minimizing the number of wells/borings at such sites and uncertainties in contaminant distributions while providing known levels of confidence in net contaminant removal will reduce the life-cycle costs of remediation efforts. Also, definable benchmarks for evaluating the performance of remediation efforts will serve to better allocate fiscal and human resources at DoD and DOE installations.

## 9. Milestones:

### Phase 1

- |    |  |       |
|----|--|-------|
| a. | Initiate Reconnaissance (borings, water sampling/microcosm setup)  | 07/95 |
| b. | Initiate microcosm setup   | 07/95 |
| c. | Initial well water sampling  | 08/95 |
| d. | Delineation of Hydrogeochemical Zones  | 12/95 |
| e. | Initiate quarterly sampling  | 12/95 |
| f. | Correspondence between loci of bioactivity and hydrogeochemical zones based on results of first six months of sampling | 05/96 |

### Phase 2

- |    |  |       |
|----|--|-------|
| a. | Initiate Quarterly Sampling                    | 10/96 |
| b. | Supplemental Borings/Water Sampling/Microcosms | 01/97 |
| c. | Estimation of Bioremediation Rates             | 04/97 |
| d. | Geostatistical Refinement of Network           | 02/98 |

### Phase 3

- |    |  |       |
|----|--|-------|
| a. | Continued Quarterly Sampling               | 03/99 |
| b. | Complete refined estimates of mass removal | 03/99 |
| c. | Complete conceptual Model Development      | 03/99 |

## 10. Transition Plan:

In addition to peer-reviewed papers and reports which will issue from the project it is clear that technology transfer must occur within DoD, DOE and the environmental restoration community. Public presentation at conferences, short-courses, and workshops which we support will be enriched in the future by the results of the project. We would welcome the opportunity to offer focused short-courses for DoD and DOE personnel as well as contractors to broaden the communication of results. It is likely that a pilot course could be offered at the experimental site(s) during the project period if logistics can be arranged. A two-day monitoring short-course with field exercises has been budgeted for Year 2 of the work (FY96). The pilot course could be made part of the project review process involving DoD or DOE project officers, AFIT staff and others as participants.



**11. Funding: \$(K)**

	FY94	FY95	FY96	FY97	FY98	FY99	TOTAL
SERDP	550	200	0	730	400	450	2330

**12. Performers:**

Dr. Candida West of the USEPA-RSKERL will be the project manager and provide overall direction of the laboratory work on non-volatile organic compounds and microcosm studies. Dr. West's current research activities include identification of dissolved and solid-associated organic carbon compounds associated with sorption and biodegradative processes. The participation of faculty and graduate students from the host institution of Dr. Michael Barcelona will be key to the project. Dr. Barcelona has worked with both the USEPA-RSKERL and EMSL-Las Vegas laboratories for the past thirteen years, bringing considerable benefit to the field of groundwater contaminant monitoring and subsurface geochemistry during this period.

**13. Principal Investigator:**

Dr. Candida C. West  
USEPA-RSKERL  
P.O. Box 1198  
Ada, OK, 74820  
PHONE: 405-436-8551  
FAX: 405-436-8529

**14. Keywords:**

Subsurface remediation, bioremediation, monitoring network design, geostatistics, cleanup endpoints, contaminant transformation.

## SERDP FY95 PROJECT

1. **SERDP Thrust Area:** Cleanup
2. **Title:** Unexploded Ordnance (UXO) Detection Feasibility Study
3. **Agency:** Army
4. **Laboratory:** U.S. Army Engineer Waterways Experiment Station
5. **Project ID:** #860
6. **Problem Statement:**

The identification of UXO represents a substantial challenge to the effective cleanup of many DoD sites. The UXO problem is found on all categories of DoD sites: Installation Restoration Program, Base Realignment and Closure, and Formerly Used Defense Sites.

### 7. Project Description:

The objective of this study is to evaluate the necessity for research and development in the field of unexploded ordnance (UXO) detection, if necessary, to develop a joint integrated research and development (6.1 through 6.3) strategy to meet identified DoD requirements. The scientific and technical state of the art for UXO identification will be reviewed and appropriate interfaces with technology demonstration and transfer organizations will be established.

The study will initially examine and evaluate currently available and developmental UXO technology. Particular attention will be given to technological limitations and associated science and knowledge gaps. At a minimum, input will be solicited from organizations with substantial commitments to UXO detection systems development.

A four phase investigation will be undertaken:

- a. A Technical Advisory Panel will be formed to provide technical advise on the current state of the art for UXO identification development requirements. The committee will include representation from key DoD laboratories conducting research applicable to the UXO problem. A key input is expected from the Explosives Safety Board.
- b. The American and international literature will be reviewed to ascertain the current status of UXO identification as documented through the open literature. The grey literature will also be reviewed as appropriate. It will include non-DoD agencies such as DOE, EPA, and industry.
- c. Given the information ascertained in the efforts above paragraphs, assess the need for 6.1 through 6.3 research and development.

d. Develop an integrated technology development program (6.1-6.3) to fill the knowledge, science and technology gaps identified above and recommend SERDP investment strategy.

**8. Expected Payoff:**

This work will provide DoD with an integrated research and development plan, potentially culminating in the fielding of advanced systems for identification of UXO. If deemed appropriate, the successful development and fielding of advanced UXO detection technologies offer the potential to generate vast savings to the DoD and accelerate site cleanup efforts. This work will significantly improve DoD's understanding of the policy, science, knowledge, and technology gaps affecting the development and fielding of efficient and reliable systems for UXO detection.

**9. Milestones:**

1.	Form technical advisory panel	04/05
2.	Review literature	06/95
3.	Assess technology gaps	07/95
4.	Draft report	08/95
5.	Final report	09/95

**10. Transition Plan:**

The scientific and technical state of the art for unexploded ordnance (UXO) identification will be reviewed and appropriate interfaces with technology demonstration and transfer organizations will be established.

**11. Funding: \$(K)**

	FY94	FY95	TOTAL
SERDP	0	100	100

**12. Performers:**

The U.S. Army Engineer Waterways Experiment Station (WES) will be responsible for overall management and coordination of the study. A panel of experts will be assembled to provide basic input and analysis.

**13. Principal Investigator:**

John Cullinane  
U.S. Army Waterways Experiment Station  
ATTN: CEWES-EP-P  
3909 Halls Ferry Rd.  
Vicksburg, MS 39180-6199  
PHONE: (601)634-3723  
FAX: (601)634-3833  
E-MAIL: cullinm@ex1.wes.army.mil

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**14. Keywords:**

UXO, unexploded ordnance, feasibility, technology

## SERDP FY95 PROJECT

1. **SERDP Thrust Area:** Cleanup
2. **Title:** Mobile Underwater Debris Survey System (MUDSS)
3. **Agency:** Navy
4. **Laboratory:** Naval Surface Warfare Center, Dahlgren Division, Coastal Systems Station (CSS)
5. **Project ID:** #52

### 6. Problem Statement:

The goal of the MUDSS project is to demonstrate the technologies necessary for underwater surveys of shallow water inland and coastal sites littered with ordnance. A successful demonstration will prove the concept of a trailerable, low-maintenance, catamaran-based system capable of finding and mapping the locations of ordnance ranging from small shells to large bombs in water depths of from four to forty feet. MUDSS will supply the object detection and classification technology necessary for the environmental cleanup of ordnance at scores of underwater ordnance litter sites.

To solve the underwater ordnance search and mapping problem it addresses, MUDSS will marry technologies CSS has been developing over the past twenty years for similar minehunting problems with data fusion and visualization technologies developed at Jet Propulsion Laboratory (JPL) for NASA.

### 7. Project Description:

The technical objective of MUDSS is to demonstrate sensor and processing capabilities which enable (1) the detection and classification at underwater sites of ordnance that may be partially or fully buried in sediment, and (2) the discrimination between ordnance and false targets in the area such as rocks and sea shells.

To accomplish this objective, existing acoustic, magnetic, electro-optic (EO), and chemical sensors and associated signal processing hardware and software developed for other Navy and JPL projects will be leveraged for the MUDSS application. To minimize risk, the project will proceed in two phases:

- Phase I (12 months duration) assembles a prototype MUDSS and executes a feasibility demonstration (FD) against an ordnance target field in very shallow water (VSW) at CSS.
- Phase II (24 months duration) refines the MUDSS prototype and executes a technology demonstration (TD) at multiple shallow and very shallow water (SW/VSW) sites.

CSS successfully addressed the similar problem of proud and buried bottom mine minehunting for deeper water (depths greater than thirty feet) in the late 1980's through the development of superconducting magnetic field gradiometer and active synthetic aperture sonar technologies in the MADOM (Magnetic and Acoustic Detection of Mines) developmental program. This program culminated in a successful ATD in 1990. A large follow-on technology development effort (the Mine Reconnaissance/Hunter, or MR/H, program) is now underway at CSS to further improve the Navy's minehunting capability in very shallow water. MUDSS is very similar to MADOM and MR/H, and will leverage \$8.6M of the Navy's FY 93-95 investment in MR/H.

The integration of a sophisticated field-deployable sensor suite of the kind proposed for MUDSS is a difficult technological undertaking. Cost and risk are minimized by using state-of-the-art magnetic, acoustic, and EO sensors that have already been developed by MADOM or are being developed by MR/H; by using a chemical sensor already developed at JPL; and by employing a joint CSS/JPL team experienced with these sensors.

The cost and risk of the MUDSS processing development is minimized by using a COTS (commercial off-the-shelf) hardware design for the required 2 Gflop processor similar to a design used for the MR/H processor; by taking advantage of automated classification algorithms for sonars and gradiometers developed at CSS for other programs; and by leveraging \$7.0M of JPL's FY 93-95 processor hardware, automatic target recognition, sensor fusion, and 3-D visualization development programs for NASA.

The MUDSS project will have four tasks:

- Sensor suite adaptation and integration
- Automatic target recognition processor (ATRP) development
- Data fusion and visualization tools development
- Platform system development, systems engineering, and MUDSS demonstration

The task objectives and approaches are described below.

#### Sensor suite adaptation and integration task

The task objectives are to modify sensors that have been or are being developed by other programs and to integrate them into a sensor suite capable of:

- high resolution, multi-aspect acoustic imaging of proud or shallowly buried ordnance in SW/VSW at ranges up to 50 m
- high resolution optical imaging of proud ordnance in SW/VSW at ranges up to seven optical attenuation lengths
- multi-target magnetic localization of buried and proud ordnance at ranges up to 50 m
- short-range chemical detection of explosives

The task approach in Phase I is to:

- Assemble a prototype MUDSS sensor suite of modified and/or refurbished off-the-shelf sensors: the MADOM gradiometer (SGMS), CSS's High Performance Sidescan

Sonar, the MADOM synthetic aperture sonar, the MR/H EO sensor, and the JPL mass spectrometer explosives detector (MSED).

- Collect ordnance test articles for the FD and measure their magnetic moments, acoustic target strengths, EO reflectivities, and underwater chemical signatures.
- Expand the CSS magnetics performance prediction model (MAPPS), the CSS acoustics performance prediction model (SWAT), the CSS electro-optic performance prediction model (IMPERSonator), and JPL mass spectrometer performance prediction model (MSEDM) to include the target and environmental parameters of the FD, and predict the prototype sensor suite performance.
- Validate these expanded models, or improve them as necessary, using the FD data.

The task approach in Phase II is to:

- Use the validated performance prediction models to determine modifications to the proposed MUDSS TD sensor suite. Use SWAT to design changes to the MR/H sonars to optimize SW/VSW performance against the selected ordnance target types; IMPERSonator to determine modifications to the MR/H EO sensor; MAPPS to select between SGMS and a room temperature gradiometer (RTG) being developed by a Navy Special Warfare program; and MSEDM to determine modifications to MSED.
- Modify the MR/H sonar and EO systems as necessary; refurbish the SGMS gradiometer probe, data link, and dewar if RTG is not selected; and modify MSED as necessary.

#### ATRP development task

The task objective is to develop a high-speed (approximately 200 Mbit/sec) ATRP for MUDSS sensor suite operation, automatic target detection and classification, and 3-D visualization of fused sensor data in a noisy and cluttered background.

The task approach in Phase I is to:

- Modify and improve existing CSS automated acoustic and magnetic target classification routines.
- Develop initial EO morphological classification routines.
- Exercise the classification routines off line against the FD data.

The task approach in Phase II is to:

- Design and build a COTS-based sensor operation system and processor.
- Develop improved classification routines and implement them on the processor for real-time operation during the TD.

#### Data fusion and visualization tools development task

The task objective is to develop a near real-time, dynamic, 3-D visualization capability to maximize operator understanding of the multi-sensor data.

The task approach in Phase I is to:

- Develop prototype visualization and fusion tools for the MUDSS sensor suite.
- Exercise these tools off line against the FD data.

The task approach in Phase II is to:

- Refine and expand the MUDSS visualization and fusion tools.
- Implement these tools on the ATRP for near real-time operation during the TD.

#### Platform system development, systems engineering, and MUDSS demonstration task

The task objectives are to:

- Develop a trailerable, low-draft, low-maintenance, single unit catamaran platform for MUDSS.
- Perform the prototype and TD system integrations.
- Execute the MUDSS feasibility and advanced technology demonstrations.

The task approach in Phase I is to:

- Procure a low-cost, commercially available, non-magnetic vessel to deploy the MUDSS prototype sensors and to house the data acquisition system.
- Plan and execute the FD.

The task approach in Phase II is to:

- Develop a specially made non-magnetic catamaran for the TD.
- Perform system integration and execute system configuration control for the TD system.
- Plan and execute the TD.

The MUDSS project is under the Clean-Up part of the Tri-Service Environmental R&D Strategic Plan with specific application to requirement number 1.III.2.f for improved site characterization and monitoring/sensing. No military platform is required.

### **8. Expected Payoff:**

With its capacity to map the locations of ordnance from small shells to large bombs in all coastal or inland waters with depths between four and forty feet, MUDSS will be a capable clutter surveying system for scores of underwater ordnance litter sites. Each MUDSS sensor will out-perform any COTS sensor, and the integrated MUDSS system will provide performance against ordnance (including buried ordnance) far exceeding any COTS system. As a self-contained, easily transportable, low maintenance, and low operating cost system whose development costs have been heavily born by parallel Navy and NASA programs, MUDSS will be efficiently amortized.



## 9. Milestones:

### Phase I - Task I Sensor Suite Adaptation and Integration

1.	Refurbish/integrate madom gradiometer	12/94
2.	Refurbish/integrate madom synthetic aperture sonar*	01/95
3.	Refurbish/integrate high performance sidescan sonar*	02/95
4.	Lease COTS EO sensor	03/95
5.	Lease ALS*	05/95
6.	Develop data acquisition system*	02/95
7.	Characterize OEW test articles	05/95
8.	Expand sensor models to include FD targets	01/95
9.	FD test support	08/95
10.	Validate sensor models using FD data	09/95
11.	Chemical analyzer concept study	09/95

\* Effort expanded over original plan using newly leveraged projects

### Task II Aided Target Recognition Processor

1.	Modify acoustic and magnetic classification routines	08/95
2.	Analyze FD data	09/95
3.	Test report	09/95

### Task III Data Fusion and Visualization Tools

1.	Develop functional requirements	02/95
2.	Prepare madom test database	02/94
3.	Develop graphic sensor icons	03/95
4.	Build target recognition info database	05/95
5.	Develop ATRP data interface	06/95
6.	Write target data fusion program	06/95
7.	Write 3D target area view tool	05/95
8.	Develop graphical user interface	07/95
9.	Data gathering mission - fused data relay	08/95
10.	Install prototype at CSS	09/95

### Task IV Platform Development and System Testing

1.	Identify platform/enclosure requirements*	12/94
2.	Procure commercially available platform*	04/95
3.	Design/fabricate winch system*	05/95
4.	Develop navigation system	12/94
5.	Develop sensor deployment system*	06/95
6.	System integration/checkout	07/95
7.	Install FD test field	06/95
8.	Feasibility demonstration	08/95
9.	Recover FD test field	09/95

\* Effort expanded over original plan using newly leveraged projects

## Phase II Technology Demonstration (TD)

- |     |  |       |
|-----|--|-------|
| 1.  | Develop TD requirements  | 01/96 |
| 2.  | Develop aided target recognition processor (ATRP)                                | 01/96 |
| 3.  | Develop real-time survey map system, real-time ATRP displays                     | 09/96 |
| 4.  | Modify/integrate TD acoustic, magnetic, EO sensors                               | 12/96 |
| 5.  | Design and build chemical analyzer   | 05/97 |
| 6.  | Integrate to sensor package and navigation system with ATRP                      | 05/97 |
| 7.  | Refine post-processing visualization tools and ATR algorithms, implement on ATRP | 05/97 |
| 8.  | Develop/integrate non-magnetic TD platform, sensor deployment system             | 09/97 |
| 9.  | Integrate complete TD system   | 10/97 |
| 10. | Execute TD   |       |
|     | - Target classification test   | 12/97 |
|     | - FUDS test  | 02/98 |
| 11. | Analyze TD data, write TD report   | 05/98 |

### 10. Transition Plan:

A viable transition to a commercial capability is ensured by the early insertion of industry into the MUDSS program. CRADA's and/or procurement will be used to provide industry sensor, sensor fusion, data processing, visualization, and system integration expertise.

### 11. Funding: \$(K)

	FY93	FY94	FY95	FY96	FY97	FY98	TOTAL
SERDP	0	1595	575	500	1120	180	3970

### 12. Performers:

CSS and JPL are the lead performers. The magnetic sensors for MUDSS will be supplied by International Business Machines and/or Quantum Design; the sonars will be supplied by Westinghouse; additional major contractors will supply the EO sensor and system integration support.

### 13. Principal Investigator:

John D. Lathrop  
Code 10T2, Coastal Systems Station  
NSWC, Panama City Detachment  
Panama City, FL 32407-7001  
PHONE: (904) 234-4667  
FAX: (904) 235-5462

### 14. Keywords:

Gradiometry, acoustics, electro-optics, mass spectrometry, fusion

## SERDP FY95 PROJECT

1. **SERDP Thrust Area:** Cleanup
2. **Title:** Rapid Detection of Explosives and Other Pollutants
3. **Agency:** Navy
4. **Laboratory:** Naval Research Laboratory
5. **Project ID:** #28
6. **Problem Statement:**

This 6.2/6.3 project addresses Requirement 1.III.1.i. "Improved sensor technologies for measurement of environmental pollutants." The DoD has over 1200 sites contaminated with explosives and 87% of these exhibit contamination in the groundwater. Remediation of munition sites contaminated with explosives and monitoring of the surrounding area requires accurate analyses of field samples. Tests should be conducted rapidly and on site for the most effective remediation to proceed. Recent advances in antibody technology have allowed the introduction of immunoassay techniques to environmental monitoring. Unlike the sophisticated detection systems used in laboratory analysis, including atomic absorption spectrometers or gas chromatographs, immunoassays are specific for each target molecule. Existing immunoassay methods are also sensitive enough to detect molecules at the ppm and ppb level. Immunoassays now being marketed for environmental analysis, such as products from Ensys and Editek, while extremely selective, have several disadvantages for field use. First, the tests require multiple, timed steps, or user manipulation. Also, these techniques measure single samples rather than flow streams. Finally, costly reagents are used for each test, whether positive or negative.

NRL has developed a biosensor which can be configured to measure either discrete samples containing explosives in under one minute or to monitor process streams at timed intervals. Using a displacement immunoassay, multiple samples can be injected into a microcolumn containing a fluorescent explosive molecule bound to immobilized antibody. If explosives are present in a sample, the fluorescent molecule is displaced and detected. If the sample contains no explosive molecules, reagents are not expended.

The objective of the present work will be to use the existing biosensor for TNT and DNT to test soil and water samples from known sites of contamination. Operating parameters for selected molecules, including detection limits, possible interferences in samples, and useful system lifetime will be investigated. If the laboratory studies are successful, we will perform on site analyses for explosives.

This effort will be a demonstration of technology already developed at NRL to detect explosives. The proposed work will be a new project for the SERDP. Previous work on the explosive biosensor was performed under the sponsorship of the Federal Aviation Administration Technical Center.

## **7. Project Description:**

An assay for the explosive trinitrotoluene (TNT) using the flow immunosensor and fluoresceinated TNT as the signal molecule is already well-developed and thoroughly tested on aqueous laboratory samples. An assay for the plastic explosive PETN is also being optimized. To adapt this technology for site characterization, the primary tasks in the first year of funding will be to look at field samples on the laboratory device and minimize problems due to background noise from interferents. Since environmental samples often contain multiple species which could interfere with fluorescence detection, particularly at emission wavelengths less than 550 nm, it is necessary to examine field samples for intrinsic fluorescence and select a signal molecule that fluoresces outside the range of background noise. Fluorescein, the principal label used to date for the signal molecule, emits at 520 nm-- a region for which some background signal would be expected. Several new fluorescent dyes have become available recently that have the potential to greatly reduce the problems. Two of these dyes, Cy5 and Cy3, are excited in the red region (630-650 nm excitation), where there is little natural fluorescence from the environment. There are also good, low cost diode lasers which can be used for the flow sensor instrument at these wavelengths. These dyes, as well as others that emit in the upper wavelengths, will be linked to TNT and tested as signal molecules in the flow immunosensor. Samples of TNT will be spiked into buffer and into environmental samples to confirm the sensitivity of the assay.

Field tests will be conducted on soil and groundwater samples using our current lab prototype at the selected test site. For confirmation of results, an independent test for the presence of the compounds in the sample will be done. This will involve performing a separate analysis such as gas chromatography/mass spectrometry (GC/MS) on the sample.

If the proof-of-principle tests for environmental monitoring with the flow immunosensor are successful, work will proceed on engineering a portable device. The flow immunosensor developed at NRL is currently a laboratory prototype. Though transportable enough for field tests, the system still requires two heavy carrying cases, and is dependent upon an outside source of electricity. We have discussed the possibility of constructing a shoebox-size device with several small businesses, including Universal Sensors, Micro Fluid Systems and Physical Optics Corporation. Each claims that there should be no problem engineering an effective, user friendly, and inexpensive device.

## **8. Expected Payoff:**

The flow immunosensor has many advantages over existing technologies. Operation of the sensor is straightforward and fast, and does not require a skilled operator or extensive training. The prototype now in use requires only two computer keystrokes. In its simplest version, the user introduces the sample at the beginning of the system and records the results within 1 minute of sample introduction. Again, this is in contrast to the user intensive and time consuming operation of currently available detection devices. The widely used methods often require addition of different reagents throughout the assay and lengthy incubation times, or demand the use of large, sophisticated instruments. Even if an initial sample extraction procedure is required, the solvents required are less noxious than the solvents used to prepare samples for GC or high performance liquid chromatography (HPLC) analysis. In the NRL sensor, all the components required to recognize the target in an aqueous solution and release a signal are contained within a small column.

The flow immunosensor is also well-characterized. Experimental parameters, including column size, antibody density, and flow rate, have been studied extensively. Using a mathematical framework recently developed, we are able to predict the behavior of the sensor for a given antibody-analyte pair. In addition, because the immunosensor is antibody-based, detection is extremely specific for the target molecule.

System manufacturing costs and portability are also important considerations. The components of the current system are inexpensive and off-the-shelf. Cost for the laboratory prototype is under \$10,000, and the sensor can be engineered to fit into a single briefcase with microprocessor control.

An additional strength of the NRL flow immunosensor is its adaptability for use in a variety of environments. It can be readily used with individual samples injected by hand, air samplers that extract vapors into water, or super sipper systems that rapidly inject samples from hundreds of vials. If initial field tests results are positive, the instrument could be easily reconfigured to allow for monitoring contaminants in process or waste streams. Alternatively, it could be configured to analyze samples individually introduced as the device is moved from place to place. If the samples are not in aqueous medium, they will need to be prepared by the extraction procedures developed specifically for the explosives.

Finally, the detection limit of the flow immunosensor is already comparable to established, more complicated systems. Using the NRL sensor, TNT in water has been detected at levels below 5 parts per billion (equivalent to 5 ng/ml). This level of sensitivity is well beyond that obtained using precipitation, dip stick, most enzyme immunoassays, and fluorescence polarization methods, and is comparable to radioimmunoassays.

The flow immunosensor has already been shown to have extreme specificity, sensitivity, and the versatility required to detect a wide range of molecules. This technology will be particularly relevant for testing groundwater, streams and lakes for wastes from explosive manufacture, for monitoring chemical & fuel storage, and for checking the progress of bioremediation-compliance efforts. If married to air samplers and aqueous extracts of soil samples, the device can also be used for monitoring ground contamination.

## 9. Milestones:

- |    |   |       |
|----|---|-------|
| 1. | Adapt sensor for TNT detection in field samples   | 12/94 |
| 2. | Determine limits of sensitivity and column lifetime for analysis of samples               | 02/95 |
| 3. | Conduct tests on environmental samples in the lab and in the field. Build portable device | 06/95 |
| 5. | Lab test portable device  | 09/95 |
| 6. | Field test portable device  | 09/96 |

## 10. Transition Plan:

This technology has already been successfully transferred to private industry on an exclusive license for drug detection applications only. Development work for this effort was conducted under a CRADA. In addition, the USDA is actively pursuing the development of a flow

immunosensor for pesticide detection. Finally, the EPA has requested that NRL work with them to develop a device for polychlorinated biphenyls (PCB) and polycyclic aromatic hydrocarbons (PAH) detection and process control.

**11. Funding: \$(K)**

	FY94	FY95	FY96	FY97	Total
SERDP	112	125	200	200	637

**12. Performers:**

The primary performers for this project will be personnel from NRL's Center for Bio/Molecular Science and Engineering. The portable device will be fabricated by a small business.

**13. Principal Investigator:**

Anne W. Kusterbeck  
Code 6900  
Naval Research Laboratory  
Washington, D.C. 20375-5348  
PHONE: (202) 404-6042  
FAX: (202) 767-9594

**14. Keywords:**

Biosensor, immunoassay, environmental monitoring, antibody/antigen, fluorescence detection

## SERDP FY95 PROJECT

1. **SERDP Thrust Area:** Cleanup
2. **Title:** Trichloroethylene Risk Assessment
3. **Agency:** U.S. Air Force
4. **Laboratory:** Armstrong Laboratory
5. **Project ID:** #115
6. **Problem Statement:**

Chemical contamination of groundwater and soil is a national problem which consumes extensive technological and financial resources. Cleanup levels are determined on the basis of risk calculations, usually requiring extrapolation from laboratory animal studies. Determining acceptable levels for humans from animal studies is a conservative, policy driven process that involves extrapolation and interpretation of scientific findings. Scientific uncertainties in this process are often compensated for by conservative assumptions that result in lower cleanup levels with inherent increased costs.

Current costs to clean up to the low parts per billion (ppb) range in water and soil are in the hundred of millions of dollars. Operating costs of a groundwater treatment system for a single plume at Wright-Patterson AFB, contaminated with high levels of trichloroethylene (TCE), are \$1.3 million/year. TCE remediation at 31 DoD installations has cost \$670 million to date, while work for all solvents has cost \$2 billion. It has been estimated that for 125 Air Force sites with TCE contamination, raising the drinking water standard from 5 to 50 ppb would save \$620 million.

TCE, tetrachloroethylene, and other volatile organics are priority groundwater contaminants for DoD and the US EPA. These chemicals often greatly exceed current risk-based cleanup levels at Superfund landfill sites. This project is designed to further the development of newer risk assessment methodologies for developing reasonable health protective criteria for important groundwater contaminants for use in establishing cleanup requirements.

### 7. Project Description:

The goal of this project is to develop innovative risk assessment methods that are applicable to common volatile organic water and air contaminants for use in development of scientifically defensible cleanup criteria. Objectives have been defined in each of the areas of the four step risk assessment process: hazard identification, exposure assessment, dose-response assessment, and risk characterization. The objectives focus particularly on the critical dose-response assessment step in light of the efforts by US EPA to adopt revised guidelines for Cancer Risk Assessment. TCE will be used as the case study chemical for development of these approaches concluding with development of Provisional Remediation Goals.

This project is a joint venture for Air Force, Army, Navy, and US EPA that has had national and international input and cooperation from academic and industrial sectors. Many elements of this program were reviewed and supported at an international TCE Workshop which included nearly 40 leading researchers and policy analysts from academia, industry, US EPA, and DoD in areas of epidemiology, metabolism, pharmacokinetics modeling, tumor promotion, peroxisomal proliferation, biological effects modeling, and risk assessment.

This project is an enhancement of a previously funded SERDP applied (6.2) project. It contributes directly to the objectives identified in the Tri-Service Environmental R&D Strategic Plan, Pillar 1: CLEANUP: 1.V Risk/Hazard Assessment and 1.X: Hazard Assessment. Methods developed in this project are generally applicable to the development of risk based criteria.

Objective 1: Evaluate new EXPOSURE ASSESSMENT approaches to address the future use scenarios used to derive cleanup criteria.

1.1 Evaluate utilization of probability (Monte Carlo) analysis for future use exposure scenarios for volatile organics in water such as drinking (oral) or showering (inhalation).

Objective 2: Improve DOSE estimation across species (mouse, rat, human) using physiologically based pharmacokinetics modeling and supporting research.

2.1 Expand PBPK modeling beyond its current strength with volatile organics, to better address toxicologically relevant water soluble compounds such as metabolites of TCE.

2.2 Improve quantitative descriptions of the metabolic pathways and uptake mechanisms for TCE and its metabolites in mice, rats, and humans using appropriate *in vivo* and *in vitro* laboratory studies.

2.3 Evaluate the pharmacokinetics competency of carcinogenic metabolites of TCE to account for the cancer induced by the parent compound.

Objective 3: Improve RESPONSE comparisons across species using alternative modeling approaches and supporting research.

3.1 Evaluate the correlation of biomarkers of the cancer process with production of radicals during TCE metabolism.

3.2 Develop conceptual frameworks for biological based dose-response (BBDR) modeling to integrate pharmacokinetics (exposure, dose, tissue-dose) with markers of early and late biological responses.

Objective 4: Propose new RISK CHARACTERIZATION strategies for utilization in development of cleanup criteria.

4.1 Evaluate the implications of alternate dose-response modeling methods for acceptable risk levels.



4.2 Recommend Provisional Remediation Goals for TCE to DoD and draft suggestions to US EPA for TCE risk assessment under new EPA guidelines.

## 8. Expected Payoff:

One result of this effort will be to persuade the US EPA to revisit the cancer potency calculations for TCE under the new proposed guidelines for cancer. Within the next year or so, dioxin will go through this process. Central to the dioxin issues is the use of a biologically-based response model. Our goal is to have TCE be the second chemical that goes through the new cancer guideline evaluation process. The result could be savings of millions of dollars.

Two critical elements are required in working with US EPA. One is to build up the supporting peer reviewed scientific literature to support their decision making. The other is to provide alternatives to the default methodologies that they normally employ. These methods generally incorporate greater scientific information to minimize the use of conservative default assumptions.

This project is designed to provide both of these elements. Alternative risk assessment methods will have great applicability to other volatile organic chemicals whether for developing cleanup criteria, evaluating pollution prevention alternatives, or establishing operating limits on environmental emissions.

## 9. Milestones:

1.	Interagency agreement with EPA	10/93
2.	Literature reviews for TCE and biological determinants of cancer	10/93
3.	Initiate in vitro metabolism studies	11/93
4.	MIPR \$300K to EPA	12/93
5.	Hire analytical chemist	01/94
6.	Prepare animal use protocols and research proposals	02/94
7.	Complete TCE/vinyl chloride mixture metabolism study	02/94
8.	Start biologically-based modeling	04/94
9.	EPA agreement to WA State Univ to conduct human studies	06/94
10.	EPA agreement to Wayne State Univ to conduct kidney studies	06/94
11.	Complete literature reviews for pharmaco-kinetics of TCE metabolites	06/94
12.	Complete development of analytical methods for TCE and metabolites	08/94
13.	Complete in vitro metabolism kinetics studies for dichloroacetate	09/94
14.	Complete field exposure assessment for TCE	09/94
15.	Issue request for proposals (EPA)	08/94
16.	Initiate research on metabolic pathway from chloral hydrate to subsequent metabolites	10/94
17.	Establish EPA agreements for research	06/95
18.	Complete studies of early biological effects related to cancer	06/95
19.	Initiate bioeffects inhalation study	06/95
20.	TCE Project Coordination Meeting	05/95
21.	Evaluation of benchmark dose for low dose extrapolation of tumor promoters	05/95
22.	Initiate development of biologically-based dose response modeling	03/95
23.	Working mouse PBPK models (TCE+metab)	06/95

- |     |  |       |
|-----|--|-------|
| 24. | Report on CH split in TCE metabolic pathway      | 08/95 |
| 25. | Working human PBPK models for TCE+metab          | 09/95 |
| 26. | Report on probability analysis exposure in water | 09/95 |

**10. Transition Plan:**

The first step was to have an expert group (TCE workshop), which includes the US EPA, endorse the research issues that need to be addressed in order for the US EPA to revisit the US EPA's TCE potency calculation for cancer. This involved industry, government and academia. Air Force Office of Scientific Research (AFOSR) (6.1) monies are being used to leverage the research costs in house. American Waterworks Association is funding a few university grants and Dow Chemical is conducting environmental fate and neurotoxicity studies. The Air Force is leading the effort to bring together the regulatory and research scientists to address this pressing national environmental problem.

**11. Funding: \$(K)**

	FY92	FY93	FY94	FY95	FY96	FY97	TOTAL
SERDP	1000	1700	1400	0	900	1600	6500

**12. Performers:**

This research is being conducted by the US EPA/OHEA, Army (SGRD-UBG-O), Navy (NMRI/TD), and USAF (OL AL HSC/OET). Dow Chemical Company in Midland, Michigan; Colorado State University; Washington State University; Indiana University, Chem-Risk, Kaiser-ICF Clement and US Army Basic R&D Lab, Ft. Detrick, MD., are involved in related research activities.

**13. Principal Investigator:**

Jeffrey W. Fisher, Ph.D.  
 OL AL HSC/OET Bldg 79  
 2856 G Street  
 Wright-Patterson AFB, OH 45433-7400  
 PHONE: (513) 255-3423  
 FAX: (513) 255-1474  
 E-MAIL: jfisher%raven@eagle.aamrl.wpafb.af.mil

**14. Keywords:**

Risk Assessment, Trichloroethylene, Cleanup, Cancer, Dosimetry

## SERDP FY95 PROJECT

1. **SERDP Thrust Area:** Cleanup
2. **Title:** Biosorption Treatment of Plasticizers and Solvents
3. **Agency:** US Army
4. **Laboratory:** USAE Waterways Experiment Station (WES)
5. **Project ID:** #711
6. **Problem Statement:**

The Department of Defense (DoD) and Department of Energy (DOE) have many sites that contain groundwaters contaminated with low levels of plasticizers (acetone) and chlorinated solvents (trichloroethylene [TCE]). Current or traditional treatment technologies available for use in TCE treatment are granular activated carbon (GAC) and air stripping; however, neither technology results in the direct destruction of the organic contaminant. An innovative technology, ultraviolet (UV) chemical oxidation, will be available for use in the near future for chlorinated solvent oxidation. Remediation costs for all of these technologies generally falls within the \$1.00 to \$5.00 per 1,000 gallons range. In the case of GAC, treatment of groundwaters containing low levels of chlorinated solvents is not economically feasible.

Acetone poses a very unique challenge to both traditional and innovative technologies. Acetone does not adsorb onto GAC due to its high water solubility, it does not strip in air strippers due to its low Henry's Law constant, and it does not oxidize in chemical oxidation systems due to its stable chemical structure. Acetone is degraded biologically, but biotreatment is unsuitable for treatment of low level contaminated groundwaters because an active biomass cannot be sustained due to low substrate loadings. Unfortunately, most groundwaters contain acetone at relatively low levels; therefore, expensive cometabolite addition is almost always required.

TCE can also be treated using biological degradation. TCE is somewhat more difficult to biodegrade than acetone, but recent advances in cometabolic pathways (methanotrophic) indicate that biotreatment of TCE is feasible. One problem associated with TCE degradation is the tapering off of microbial activity, over time, in continuous and semi-continuous biological systems. Biosorption is almost always associated with GAC. Primarily, GAC is used as a means of extending the service life of a GAC bed by regeneration of the spent carbon within the bed. Recent work on phenolic compounds has resulted in the development of an innovative technology known as biofilters. This technology utilizes GAC as a means of structurally supporting an active biomass.

Organophilic clays (OPCs), have been successfully used to remove low levels of wood preserving waste from contaminated groundwater. Results of this evaluation are encouraging, but disposal of the spent OPC is a problem. OPCs are innovative adsorbents

that have received limited evaluation and application for the removal of low levels of acetone and TCE.

The USAE Waterways Experiment Station (WES) has conceptualized a treatment system for low level contaminated groundwaters based on biosorption and bioslurry systems. In this treatment scheme, the contaminants are adsorbed onto the OPC until all adsorption sites of the OPC are spent. The spent OPCs are removed from the reactors, ground into small particles, and then an on-site bioslurry reactor is used to biologically degrade the adsorbed contaminants. This converts OPC adsorption from a simple phase-change technology into an on-site destruction technology.

This proposed treatment approach is an applied research and technology field pilot application (6.2). This research is an enhancement to an existing FY 93 SERDP proposal.

Specific identified user requirements to be addressed through performance of this work unit include:

- 1.I.1.b. Technology for removal of energetics/other organics contamination.
- 1.I.1.f. Treatment system for water contaminated with organic contaminants.
- 1.I.1.g. Treatment system for water contaminated with chlorinated and defense hydrocarbons.
- 1.I.1.j. Treatment of Navy repellent contaminants in salt/brackish/groundwater matrices.
- 1.I.6.c. Isolation and treatment technology for contaminated surface water impoundments.
- 1.I.1.h. Treatment system for water contaminated with mixtures of chlorinated solvents.
- 1.I.2.i. Contamination under buildings and roads.
- 1.I.4.n. Remedial treatment technology for soils contaminated with chlorinated and non-chlorinated organics.
- 1.I.2.e. Improved marine sediment remediation technologies for metals, organics, and PCBs.
- 2.III.1.d. Enzyme and bacterial treatment technology.

## **7. Project Description:**

The USAE Waterways Experiment Station (WES) under the Environmental Quality and Technology Program (EQT) is developing a means of biologically regenerating spent GAC. WES also plans to evaluate the use of OPCs for treatment of explosives contaminated groundwater. It is believed that OPC biosorption can be utilized for the treatment of low level explosive contaminated groundwater.

The USAF Tyndall AFB has been active in development of microbial consortia capable of effectively degrading TCE from contaminated groundwaters. This technology can be tailored to interact with the conceptualized OPC biosorption schemes. Tyndall AFB is currently developing a bioreactor for treatment of contaminated groundwater with higher levels of TCE. The consortia developed in these efforts will be useful in the development of the OPC biosorption concept. Tyndall has also developed a surfactant which may further enhance the sorptive capacity of the OPCs. An increase in sorptive capacity will result in improved costs benefits. There has been little or no direct development of OPC biosorption. Past efforts on bioregeneration of spent GAC containing phenolic compounds indicates promise for the use of microorganisms to degrade adsorbed compounds.

A recent evaluation of OPCs for wood preserving waste treatment indicates the utility of OPCs for groundwater remediation. Unfortunately, there are few options for disposal of spent OPCs (and GAC). Under US Environmental Protection Agency funding, WES has demonstrated the feasibility of using bioslurry systems for treatment of soils contaminated with plasticizers and wood preserving wastes. The contaminated soils used in these studies did contain significant clay fractions.

Tyndall AFB has demonstrated the feasibility of biologically treating TCE using aerobic microorganisms. Much of this work has resulted in the development of a microbial consortia that demonstrates excellent activity toward chlorinated solvents.

The overall objective of this study is to develop an OPC based biosorption process. Development of this technology will, in the case of acetone, provide environmental engineers with a practical means of treating acetone. With respect to TCE, this technology may eliminate the problem of TCE activity loss over time.

The development of OCP biosorption into a fieldable technology for site remediation will be approached through a series of tasks detailed below:

- a. Task I. The adsorption capacity of various OPCs and other sorbents will be preliminarily evaluated by contacting the sorbent with spiked solutions containing acetone and TCE. Three to four sorbents will be selected for further testing in adsorption isotherms. Activated carbon performance will be compared to the performance of the sorbents. Cosolvency effects will be evaluated through the addition of solvents to the spiked solutions. One or two of the most effective sorbents will be selected for small column studies.
- b. Task II. Evaluation of microbial activity toward adsorbed acetone and TCE. Toxicity effects of TCE concentrations on microbial consortia will be evaluated using the Microtox procedure. The ability of a microbial consortia to desorb and subsequently biodegrade the adsorbed acetone and TCE from the OPC will be evaluated using laboratory batch systems. Much of this effort will be directed toward TCE biodegradation since acetone biodegradation is much more refined.
- c. Task III. Bench Scale Bioslurry Studies. Bench scale bioslurry studies will be performed to determine process feasibility, verify reaction kinetics and pathways, and set pilot studies test matrices. The bench studies will be performed using five liter all glass reactors operated in batch mode. Two oxygenase pathways, aromatic and aliphatic, will be described.
- d. Task IV. Pilot Scale Studies. Pilot scale studies will be performed using pilot OPC absorbers and bioslurry reactors. The complete pilot system will be designed for complete mobility to other candidate sites. If required, a process gas management system may be used if off-gassing of TCE and the selected cometabolite is deemed problematic. These pilot scale studies will be performed in the field at two DoD sites. Once completed, the pilot system will be available for field pilot application at other installations.

e. Task V. Draft Report. A report detailing the following will be drafted:

1. Describe techniques on how to perform bench scale treatability studies used for process evaluation during Feasibility Studies (FS).
2. Discuss process feasibility and potential limitations.
3. Present the results from the bench and field pilot studies.
4. Summarize available full scale equipment availability.

The report will be design and applications orientated. The report will serve as a handbook for implementation of OPC biosorption at other field sites.

The information obtained from the performance of this study will assist in meeting several DoD/DOE environmental remediation objectives. This work effort will result in the development of a contaminant-destruction technology applicable toward both chlorinated solvent and plasticizer compounds.

Technical issues to overcome as identified to date are to determine if OPCs have appreciable adsorption capacities for acetone and TCE; if bioslurry treated OPCs can be treated to levels that render them environmentally safe and regulatory acceptable; and if process gas recirculation will be required for TCE biodegradation of the ground OPCs. This project falls under the 1.H and 1.I requirement thrust areas under the Tri-Service Environmental R&D Strategy Plan.

### **8. Expected Payoffs:**

Potential users include all groups, both private and governmental, that are involved in remediation of groundwaters contaminated with organic and explosives compounds. OPC biosorption treatment will fill a gap that currently exist in terms of treatment of low level acetone contaminated groundwaters. OPC biosorption may eliminate problems associated with reduce TCE bioactivity over time. The actual economic benefit is difficult to ascertain due to the innovative nature of the concept. A conservative estimate is that the technology could be implemented at a cost range of \$1.00 - \$3.00 per 1,000 gallons treated.

### **9. Milestones:**

Major milestones under this work effort are listed below along with the respective fiscal year they will be completed.

- |    |   |       |
|----|---|-------|
| 1. | Initiate the evaluation of adsorbents       | 03/94 |
| 2. | Initiate microbial processes investigations | 06/94 |
| 3. | Initiate bench bioslurry systems            | 09/94 |
| 4. | Complete bench scale evaluations            | 10/95 |
| 5. | Design and construct pilot systems          | 12/95 |
| 6. | Initiate pilot studies                      | 04/96 |
| 7. | Final report                                | 09/96 |

## 10. Transition Plan:

This technology development will generally follow the typical transitional path detailed under DoD's EQT Program. Within three years, the technology will be transitioned from a bench concept to an implementable technology. Technical assistance will be available to technology users during design and implementation of OPC biosorption. Collaboration with private organizations for improving process development through CRADAs will be proposed. The technology will be transitioned to the user community through technical papers, presentations, briefings by the performers of this proposal.

## 11. Funding: \$(K)

	FY93	FY94	FY95	TOTAL
SERDP	500	750	681	1931
WES	250	250	200	700
USAF	500	500	300	1300

## 12. Performers:

The performers for this work unit are USAE Waterways Experiment Station and Tyndall AFB. Advice from OPC manufacturers will be incorporated into the final technical approach for this study.

Ms. Beth Fleming  
Mr. Mark Zappi  
Dr. Doug Gunnison  
USAE Waterways Experiment Station  
ATTN: CEWES-EL  
3909 Halls Ferry Road  
Vicksburg, MS 39180

Ms. Catherine M. Vogel  
Dr. Jim Spain  
USAF Armstrong Laboratory  
AL/EQW/OL  
139 Barnes Drive, Suite 2  
Tyndall AFB, FL 32403-5323

## 13. Principal Investigator:

Ms. Cynthia L. Teeter  
Environmental Engineering Division  
USAE Waterways Experiment Station  
ATTN: CEWES-EE-R  
3909 Halls Ferry Road  
Vicksburg, MS 39180  
PHONE: 601-634-4260  
FAX: 601-634-3833

## 14. Keywords:

Biosorption, bioslurry, biotreatment, adsorption, trichloroethylene, acetone.

## SERDP FY95 PROJECT

1. **SERDP Thrust Area:** Cleanup
2. **Title:** Enhancing Bioremediation Processes in Cold Regions
3. **Agency:** U.S. Army
4. **Laboratory:** Cold Regions Research and Engineering Laboratory (CRREL)
5. **Project ID:** #712
6. **Problem Statement:**

This project is basic, 6.1 research and has received FY94 SERDP funds. This proposal is for continued funding of the FY93 funded research and expands the scope to include rhizosphere effects. The objectives are to improve remediation ability in areas subject to low temperatures and to facilitate treating large volumes of soil at contaminated sites where low temperatures are inhibitory. Many of these sites are also subjected to extended freezing or freeze-thaw cycling, have short operating seasons, frequently have insufficient soil nutrient levels, and are often in remote locations where cost-effective alternatives do not exist. Easily implemented on-site and in-situ technologies such as biotreatment are needed for soil cleanup at these sites.

The primary strategy in bioremediation is to remove the limitations to microbial activity, but the extensive amounts of soil that are typically involved require using large-volume techniques that necessarily expose soil to seasonal temperature cycles. The net influence of freezing temperatures on the overall rate and extent of soil biotreatment is a complex interaction of microbial and chemical rates, substrate-nutrient solubility and availability, and physical-chemical phenomena. It is not sufficiently understood to exploit or manage biotreatment systems in advantageous ways.

Enhanced microbial activity in rhizosphere zones is documented for some pesticides and may offer a significant mechanism for low-cost soil treatment. Coupled with low-temperature effects, we propose to quantify low-temperature soil-rhizosphere activity and identify relationships with associated plant species. Because bioremediation is often constrained by nitrogen, phosphorus, and carbon co-substrate limitations, we hypothesize that nutrient and co-substrate limitations to bioremediation at remote sites can be overcome by stimulating soil-rhizosphere effects.

### 7. Project Description:

This effort applies to DoD Pillar 1-Cleanup, Thrusts 1K, 1L, 1M, 1N, Biological Treatment of Explosives, Organics, Solvents, and Fuels in Contaminated Soils. The technical objectives are:  
i.) to describe, for different classes of compounds, the kinetics and endpoints of biotransformations as functions of soil moisture, available carbon, and low temperatures and  
ii.) to elucidate the impact of rhizospheric zones on soil bioremediation potential.



Successful application of bioremediation at low temperatures requires knowledge of how freezing induced processes influence the pathways and rates of biologically mediated processes. Recent research indicates that at lower temperatures the interacting influences of moisture, soluble carbon, and temperature on microbial activity are unpredictable from data obtained at higher temperatures. Rate adjustments based on traditional approaches, such as scaling from laboratory studies or  $Q_{10}$  values obtained from higher temperatures, do not account for interacting phenomena encountered in field situations, and may not realistically describe processes governing bioremediation in soils exposed to severe or repeated freezing.

We have developed a system for measuring microbial activity at low temperatures and constant moisture potentials. A preliminary conceptual model is being developed from a series of laboratory experiments designed to integrate freezing and freeze-thaw influences on biological activity with chemical and physical processes. Field projects are in place to provide both authentic soil samples and field data. Freezing and freeze-thaw influences on biological, chemical, and physical processes will be integrated. Our approach will couple laboratory and field studies. Chemical structural activity relationships (SAR) will be used to select and group chemical classes of contaminants. Results will, therefore, be transferable based on structural activity relations rather than individual compounds.

Using rhizosphere effects to degrade organics is a promising, innovative technique which would be advantageous at many sites, particularly at remote locations where no feasible alternatives exist. The impact of low temperatures and extended or frequent freezing on the remediation abilities of these biological systems is unknown. Laboratory, growth chamber, and cold room studies will transition into our ongoing field projects. Plants tolerant to seasonally frozen soil and having fibrous root systems will be selected to provide improved root distribution and root-soil contact. Enhanced root exudates may provide additional carbon that is frequently needed as a co-substrate for contaminant degradation. Root mycorrhizal associations will be promoted for their positive impact on phosphorus nutrition. Legumes will be exploited for their potential for mid-depth root penetration, nitrogen fixation capabilities, and resulting microbial stimulation in poor quality soils.

In accompanying field studies, larger native plant species, acclimated to specific geographic areas and climates, will be investigated for their ability to reach deeper depths, and to recycle soil moisture and associated mobile, solution-phase contaminants through the rhizosphere and towards the soil surface, zones of enhanced microbial activity.

This research differs from previous work in cold regions bioremediation because:

- a. Private industry efforts have used biopiles, treatment cells, and similar technologies. These efforts are minimally monitored with limited on-site or laboratory analysis. Documentation is sparse and restricted. Freezing effects are not addressed although treatment systems are subject to freezing.
- b. EPA effort in EXXON Valdez cleanup was a coastal environment and subject to wave and storm action.
- c. In-situ bioventing of lighter petroleum compounds (JP-4) in cold regions (Air Force) has focused on sub-surface, unfrozen soil systems. Improving our knowledge base may extend bioventing to environmentally acceptable use in the active zone of permafrost soils.

## 8. Expected Payoff:

Soil cleanup is required at military, federal, and civilian sites. Many sites are in cold, remote locations. The few alternatives that are available either use more costly, methods or incur liability due to non-compliance. Low input, scientifically defensible biotreatment alternatives would treat such sites at minimal cost, reduce or remove liability, and minimize cleanup-associated damage to the site. The regulatory community is open to innovative biotreatment.

The results from this research are dual use and would readily transition to the public sector through field research and demonstration sites that are part of CRREL's ongoing related projects. Increased knowledge would extend the operating season and potentially provide guidance for using natural freeze-thaw cycles advantageously.

Envisioned benefits include:

- a. Application to the northern tier of the continental US to extend the biotreatment operating season.
- b. In-situ treatment of contamination in the active zone of permafrost soils with minimal disturbance to fragile surface ecosystems, as well as application to the northern tier of the US.
- c. Transition to Arctic and Sub Arctic sites, including Northern European and Former Soviet Union sites, where conditions, location, available infrastructure, and cost preclude more intensive technologies, is highly feasible.
- d. Acquired knowledge would support a dual-use technology applicable to joint DOE-DoD soil-freezing containment technology by adding a cold-adapted bioremediation capability to soils contained by cryogenic barriers.

## 9. Milestones:

1. Develop lab system for measuring soil microbial activity at low temperatures and constant moisture potential. 06/93
2. Based on preliminary observations, define components of conceptual model. 12/93
3. Evaluate importance of component processes, including rhizosphere effects. 06/94
4. Evaluate interactions of processes with SAR-grouped chemical classes. 06/95
5. Compare field observations to laboratory based predictions (field data collected from ongoing projects). 06/96
6. Manipulate field systems based on gained knowledge (field systems from ongoing projects) 06/97
7. Evaluate altered field systems (ongoing projects will be leveraged to serve as field experimental sites) 06/98

## 10. Transition Plan:

Knowledge gained from this research will transition into related 6.2 projects, Low Temperature Biotreatment, Natural Remediation, and Biotreatment of Explosives in Cold Regions. Cold Regions Research and Engineering Laboratory (CRREL) is cooperating with WES on these work units.

The high cost of conducting research at actual field sites essentially precludes using research funding alone to support field testing, but the field experimental component is fundamental to realistic bioremediation research. CRREL's strategy has been to leverage research funds by partnering with State, Federal, and private sector cooperators who are involved in cleanup operations. CRREL is currently involved in field projects through partnering programs with Alaska Science and Technology Foundation, Alaska DOT&PF (CPAR), University of Alaska (CPAR), FAA, Air Force (Shemya and Elmendorf AFB), and private industry (Weston and Sampson Engineering, Inc., CPAR and RZA-AGRA, Inc.). These projects are primarily applied research and demonstrations; they provide authentic soil samples and field experimental sites, and facilitate laboratory-field communication. This approach also provides a real and highly visible avenue for transitioning and technology transfer, as demonstrated by our CPAR projects and cooperative projects with the Districts and Air Force. CRREL is also in the preliminary stages of developing additional cooperative field projects with private industry through CRADAs.

CRREL has coordinated transitioning with the a) Air Force, through the Engineering and Services Laboratory at Tyndall AFB and briefing the Center for Environmental Excellence at Brooks AFB on our projects. Additionally, CRREL has a cooperative project on Shemya Island through Elmendorf AFB; b) Navy, for future transitioning at the proposed Navy National Test Site and c) EPA, through the Risk Reduction Engineering Lab., Cincinnati, OH, and Environmental Research Laboratory, Gulf Breeze, FL.

**11. Funding: \$(K)**

	FY93	FY94	FY95	FY96	FY97	FY98	FY99	TOTAL
SERDP	500	700	220	200	950	750	700	4020

**12. Performers:**

CRREL is uniquely well equipped for low-temperature research and the basic research will be conducted primarily at CRREL.

This research has been coordinated with Dr. D. Gunnison at WES, the lead laboratory for cleanup. CRREL will work with Dr. Gunnison at WES to maintain coordination with related research at WES.

A limited number of Universities have recently begun research in rhizosphere-based soil bioremediation. CRREL has discussed with the EPA the potential of involving Universities and intends to do so as appropriate. We have coordinated with the Air Force, Navy, and EPA to prevent duplication and facilitate cooperation.

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**13. Principal Investigator:**

Dr. C. M. Reynolds  
US Army Corps of Engineers  
CRREL  
72 Lyme Road  
Hanover, NH 03755-1290  
PHONE: 603-646-4394  
FAX: 603-646-4561  
E-MAIL: REYNOLDS@HANOVER-CRREL.ARMY.MIL

**14. Keywords:**

Bioremediation, Sub Arctic, Freeze, Cold, SAR, Rhizosphere

## SERDP FY95 PROJECT

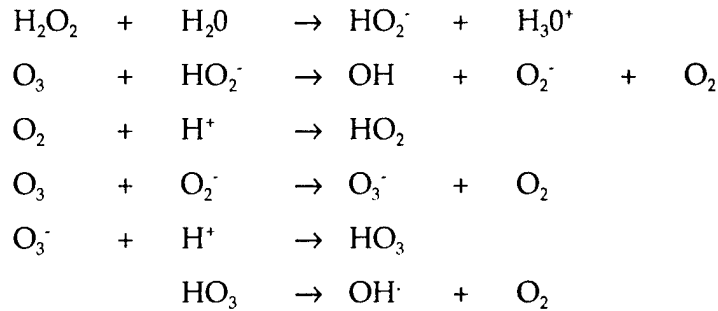
1. **SERDP Thrust Area:** Cleanup
2. **Title:** Peroxone Treatment of Contaminated Groundwaters
3. **Lead Agency:** US Army
4. **Laboratory:** US Army Engineer Waterways Experiment Station (WES)
5. **Project ID:** #726
6. **Problem Statement:**

The Department of Defense (DoD) and Department of Energy (DOE) have many sites that contain groundwaters contaminated with explosives compounds. The current or traditional treatment technology available for use in explosives contaminated groundwater remediation is granular activated carbon (GAC). An innovative technology, ultraviolet (UV) chemical oxidation, will be available for use in the very near future under the DoD's Environmental Quality and Technology Program (EQT). Remediation costs for both of these technologies fall within the \$1.00 to \$5.00/1,000 gallons range. UV/chemical oxidation is advantageous to GAC because it is a destruction technology and it does not produce a waste stream (i.e. spent GAC) requiring disposal. Also, unlike GAC, UV/chemical oxidation processes are still economically viable at relatively low groundwater concentrations. UV/chemical oxidation systems are often referred to as advanced oxidation processes because they result in the formation of powerful oxidizer species such as the hydroxyl radical (OH $\cdot$ ).

DoD installations requiring remediation of explosives contaminated groundwaters will require that GAC or UV based chemical oxidation systems treat literally millions to billions of gallons of groundwater. The cost to the DoD alone will be extremely high. Many environmental engineers and scientists are hopeful that *in situ* technologies will one day completely replace pump-and-treat systems that use above-ground treatment systems. Unfortunately, the technical truth of the matter is that above-ground treatment systems will always have a place in groundwater remediation activities. *In situ* treatment technologies are not a panacea. Not all sites or site situations are capable of supporting an *in situ* treatment system. More cost effective, contaminant destruction, above-ground based treatment systems are required by the DoD.

Peroxone oxidation is a groundwater treatment technology that has great potential for treating contaminated groundwaters at reduced treatment costs. The main driving force in the development and presentation of this proposal is the potential cost savings that may be incurred with the fielding of this technology. Peroxone is a chemical oxidation process that has been used primarily for treatment of drinking water in both the United States and Europe. The process involves the addition of ozone (O $_3$ ) and hydrogen peroxide (H $_2$ O $_2$ ) into a reactor system containing the contaminated groundwater. Peroxone generates hydroxyl radicals (OH $\cdot$ ) through the reaction of ozone with hydrogen peroxide. Peroxone does not require the addition of ultraviolet light to form radicals or destroy organic compounds. The hydroxyl radical is a powerful oxidizer that can destroy organic compounds into

environmentally safe compounds. The stoichiometric reactions that result in the generation of the radical during peroxone treatment are listed below,



Since the process does result in the formation of radicals, it is considered an advanced oxidation process (AOP). Actual cost information obtained from French engineers indicate treatment costs as low as \$0.02 to \$0.10 per 1,000 gallons treated (for dilute concentrations) have been reported. This represents an order of magnitude reduction in remediation costs as compared to traditional technologies such as activated carbon and traditional UV based AOPs. Since peroxone does not require UV addition, operational problems associated with fouling of the quartz sleeves housing UV lamps or poor groundwater UV transmissivity are not of concern; thereby, eliminating a big operational concern and expense associated with UV based oxidation processes.

This work unit will support unfunded components of the DoD STRAT Plan and will meet or partially meet several DoD user requirements. These requirements are:

- 1.I.1.b. Technology for removal of energetics/other organics contamination.
- 1.I.1.f. Treatment system for water contaminated with organic contaminants.
- 1.I.1.j. Treatment of Navy revalent contaminants in salt/brackish/groundwater matrices.
- 1.I.6.c. Isolation and treatment technology for contaminated surface water impoundments.
- 1.I.4.c. Decontamination of soils containing energetics materials.
- 1.I.2.i. Contamination under buildings and roads.
- 1.I.4.n. Remedial treatment technology for soils contaminated with chlorinated and non-chlorinated organics.
- 1.I.4.c. Decontamination of soils containing energetic materials.

## 7. Project Description:

The WES has evaluated the use of peroxone processes for treatment of explosives contaminated groundwaters using bench scale peroxone reactors. Experiments using laboratory prepared solutions of TNT-distilled water have indicated that peroxone has similar removal kinetics to traditional UV based AOPs. WES, working with Mr. Randy Cerar, Army's Environmental Center (AEC), has evaluated peroxone for treatment of two explosives contaminated groundwaters from Milan Army Ammunition Plant (AAP) with the results being very encouraging. WES and Rocky Mountain Arsenal (RMA) have determined that peroxone has a high potential for treating groundwaters contaminated with a variety of other contaminants. Estimated costs fall within the \$0.35 to \$0.60/1,000 gallons treated range. WES has also performed studies using sonolytic catalyzation indicating that the addition of ultrasound may dramatically enhance oxidation reaction rate. In summary, bench efforts

performed by WES indicate that peroxone processes are ready for evaluation at DoD installations using pilot scale equipment.

The overall objective of this project is to accelerate development of peroxone oxidation processes for treatment of explosives contaminated groundwaters. Process feasibility will be evaluated at both the bench and field pilot scale, with particular emphasis placed on-site pilot studies. The objectives of this project will be approached through performance of a series of research tasks. These tasks are listed and discussed below:

Task I. Determination of Reaction Pathways and Kinetics. Other funding sources will be used by WES to determine reaction pathways of explosives parent compounds. This effort will investigate oxidation pathways of environmental explosives by-products, such as amino-toluenes, which are typically found in explosives contaminated groundwaters. Since peroxone is a destruction technology, determination of the predominant oxidation pathway of selected explosives environmental by-products will be determined using laboratory solutions of buffered distilled water and reagent grade target chemicals. Only single solute solutions will be used so additional carbon sources do not interfere with pathway determination. Kinetic parameters (at minimum, pseudo-first order rate constants) will also be determined. Analytical methods to be employed in determination of treatment pathways and kinetics will include high performance liquid chromatography (HPLC), stopped-flow spectrophotometry, and gas chromatography (GC).

Task II. Selection and Shipment of Groundwater Samples. Actual groundwater samples from contaminated DoD sites will be used in both the bench and pilot scale studies. This will ensure that the study remains focused on rapid field implementation. Candidate sites include Milan Ammunition Plant, Cornhusker Ammunition Plant, Sub-Base Bangor, and Hastings East Industrial Plant. Samples will be collected and shipped to WES for the bench scale studies. NOTE: All pilot studies will be performed on-site. Results from the bench testing will be used to design comprehensive pilot studies at a minimum of at least two DoD sites (one Army and one Navy). Obviously, site groundwater samples used in the bench study will be carried through to the pilot level of effort.

Task III. Bench Scale Studies. Bench scale studies will be performed to determine process feasibility, verify reaction kinetics and oxidation pathways, estimate initial treatment cost estimates, and set pilot studies test matrices. The bench studies will be performed using one liter all glass reactors operated in semi-batch mode with respect to ozone application. Groundwater samples from various candidate pilot study sites will be evaluated in this study task. These studies will be performed at chemical oxidation laboratory of the Hazardous Waste Research Center (HWRC) located at the USAE Waterways Experiment Station (WES). These studies will also investigate the feasibility of integrating ultrasonic catalyzation as a means of enhancing contaminant oxidation rate and improving mass transfer limitations. If feasible, a CRADA with a reputable ultrasound process equipment manufacturer will be initiated for collaboration in terms of adding sonolytic catalysis to the pilot system.

Task IV. Pilot Scale Studies. Pilot scale studies will be performed using a mobile pilot peroxone system with 2.5 to 15 gallon per minute operating range referred to herein as the WES Peroxone Oxidation Pilot System (POPS). Four all-glass columns plumbed in series will serve as multiple contact chambers. The system will include several automated process operations and data collection systems that will be used to fully evaluate process feasibility

in the field. At least two sites containing groundwater contaminated with explosives will be treated using the pilot system. This task will verify the results derived from the bench studies, evaluate process equipment, and refine cost estimates. The WES will perform these activities with AEC and NFESC providing site management and technical support.

Task V. Draft Applications and Design Manual. An applications manual in the form of a WES report will be drafted by WES, US Army Corps of Engineers (COE)-Omaha District, and COE-Missouri River Division (MRD) for use by the user community in designing and fielding the technology. It is believed that inclusion of the design user community (COE) early in process development will ensure development of a useful and easily transferable product. Key issues to be included in the design manual are:

1. Techniques for performance of bench scale peroxone treatability studies - This information will ensure that engineering firms under contract to the installations and COE district offices will be able to properly evaluate peroxone during the FS stage of site remediation. The research team for this proposal will be available for consultation at any time during full field implementation to ensure a smooth transition of the technology from the research and development community to the user community.
2. Process feasibility and potential limitations - One important factor in development of any technology is a firm understanding of the limitations of the technology. The manual will detail all limitations and short-comings associated with implementation of peroxone that are identified. Close coordination with the full user community will be maintained during the full-field application stage to further identify any additional limitations and problems as they occur. It is believed that the manual should be a "living" document that is periodically updated to ensure that corporate memory (DoD) is not lost during implementation at various sites. Lessons learned, whether good or bad, must be recorded so that other installations attempting implementation are keep fully abreast of new technical developments in order to ensure a higher potential for successful implementation at reduced costs compared to existing technology. Particular emphasis will placed on ensuring that this information is added to various prominent technology bulletin boards.
3. Results from the bench and pilot studies - The results of both the bench and pilot studies will be presented in a concise and applications oriented manner. These results will be further transmitted to the user and regulatory communities. It is important that the regulatory community is completely confident that peroxone can be safely applied at DoD sites.
4. Summarize cost estimates and full scale equipment availability - The manual will also include full cost estimates based on the results of both the Rocky Mountain Arsenal (RMA) and EQT/SERDP demonstrations. An assessment of available equipment will be included to assist the design engineer in equipment selection. Basically, all equipment required for peroxone implementation are already available due to its operational history within the drinking water industry and relative simplicity in terms of equipment requirements. The assessment of equipment will be oriented toward hazardous waste site remediation and the particularities associated with this unique technical and regulatory arena.

As stated above, the implementation manual will be very design and applications orientated. The manual will serve as a handbook for implementation of peroxone at other field sites. Peer review from other agencies such as the USEPA laboratories and other COE design



centers will be coordinated. Potential collaboration with the USEPA's SITE Program will be pursued by WES.

Task VI. Verification of Toxicity Reduction. Toxicity assessment of both test influents and effluents will be performed to ensure significant reductions in toxicity has occurred during peroxone treatment. Detail of the toxicology methods used will be published in the manual for use by engineering firms during evaluation of technology feasibility (i.e. FS efforts).

Key technical issues to overcome as identified to date are listed below:

- a. Ensure that the parent explosives and amino based environmental byproducts are oxidized into environmentally safe, non-regulated (benign) compounds.
- b. Determine if peroxone can effectively treat contamination levels typically found at DoD/Doe installations as opposed to organics levels that have traditionally associated with drinking water (which is what peroxone was originally developed for).
- c. Determine the impacts of complex contamination matrices on treatment predicted from kinetic models.
- d. Determining the economics and scale-up potential of ultrasound systems.

## **8. Expected Payoff:**

The DoD has numerous sites that contain groundwaters contaminated with explosives. The existing technology, activated carbon adsorption, is costly, does not destroy the explosives, and results in the production of spent carbon which may pose a disposal problem. The WES has recently completed evaluation of traditional ultraviolet (UV) based chemical oxidation processes for treating explosives contaminated groundwaters. AEC plans to demonstrate these processes in FY94. The cost of traditional UV based oxidation processes is expected to range from \$1.00 to \$5.00/1,000 gallons of water treated. This is the same cost range experienced with activated carbon adsorption systems; however, chemical oxidation is much more flexible, is a destruction process, and produces no residuals requiring disposal. Peroxone processes are expected to costs in the \$0.10 to \$1.00 range, which represents potentially a full order of magnitude in cost savings over both activated carbon and traditional UV based chemical oxidation processes. The expected ease of system design and operational flexibility over the other chemical oxidation processes make this process appear extremely promising.

Potential users include all groups, both private and governmental, that are involved in remediation of groundwaters contaminated with organic and explosives compounds. Peroxone treatment will economically fill a gap that currently exist in terms of treatment of low level contaminated groundwaters. Although no funding is requested for the RMA pilot studies evaluating DIMP, pesticides, and aromatics removal, performance of this work unit will improve the overall quality of the RMA study by allowing RMA/WES to use an improved pilot system then could be developed on the RMA budget alone. In return, the RMA pilot studies (FY94) will allow for evaluation of the POPS unit in terms of mechanical performance prior to performing the explosives pilot studies in FY94-96. Potential research agreements with the private section (CRADAs) will also be investigated to ensure rapid transition to the user community.

## 9. Milestones:

1.	Complete first bench scale evaluation	07/94
2.	Complete construction of pilot unit	05/94
3.	Perform RMA pilot study	08/94
4.	Perform first pilot study	05/95
5.	Perform second pilot study	07/95
6.	First draft of design package	09/95
7.	Perform third pilot study	05/96
8.	Final design package	06/96

## 10. Transition Plan:

After pilot scale evaluation of the technology is complete, transition to the user community will be accomplished through various technical reports, publications, briefings, and conference presentations. Interfacing with COE-MRD through this project partnership should accelerate transition of the technology into COE activities, while the USEPA, DOE, and USAF will be briefed periodically on the progress of this effort to ensure smooth transition into their programs. It is fully anticipated that the technology developed under this effort will be directly applicable toward other organic contaminants that are a major concern of these agencies. Once the pilot studies at the explosives contaminated sites have been completed, additional partnering with these agencies can be initiated for evaluation of peroxone for treatment of groundwaters contaminated with other organic compounds such as chlorinated solvents, fuels, and wood preserving wastes using the WES POPS unit.

## 11. Funding: \$(K)

	FY93	FY94	FY95	TOTAL
SERDP	570	950	180	1700
WES	400	350	100	850
CRREL	200	200	50	450
AEC	0	150	0	150

## 12. Performers:

The WES will have the technical lead on this project. The US Army Engineer Cold Regions Research and Engineering Laboratory (CRREL), Dr. Tom Jenkins, will provide chemistry expertise toward identification of potential intermediates of incomplete oxidation. Mr. Ted Streckfuss, US Army Corps of Engineers-Omaha District and Mr. Lindsey Lien, COE-Missouri River Division, will develop a process design package and provide design concern input to ensure that the products of this effort can be easily utilized by and are of benefit to the user community. Messrs. Randy Cerar and Richard O'Donnell, US Army Environmental Center (AEC), will assist WES with the Army facility pilot study(s). Ms. Carmen Lebron, US Naval Facilities Engineering Services Center (NFESC), will also participate in this study by assisting WES in performing a pilot study at a Navy Site.

**13. Principal Investigator:**

Mr. Mark E. Zappi, P.E.  
Environmental Engineering Division (EE-R)  
USAE Waterways Experiment Station  
3909 Halls Ferry Road  
Vicksburg, MS 39180  
PHONE: (601) 634-2856  
FAX: (601) 634-3833

**14. Keywords:**

Peroxone, explosives, groundwater, advanced oxidation processes, pilot study, oxidizers

## SERDP FY95 PROJECT

1. **SERDP Thrust Area:** Cleanup
2. **Title:** Aerobic Bioremediation of a Contaminated Aquifer
3. **Agency:** U.S. Air Force
4. **Laboratory:** Armstrong Lab
5. **Project ID:** #95

### 6. **Problem Statement:**

In situ bioremediation of fuels requires adequate nutrient and electron acceptor addition to enhance natural biodegradation. Current methods of in situ biological treatment often fail to provide adequate electron acceptor to metabolize fuel contaminants in groundwater. Problems with the rapid decomposition of hydrogen peroxide, nutrient-induced plugging, and poor oxygen distribution have all been documented in previous field studies. This is a continuation of a FY93 SERDP funded project.

### 7. **Project Description:**

This project will demonstrate novel methods of introducing nutrients and oxygen (or another suitable electron acceptor) into an aquifer contaminated with jet fuels. The approach will be to use lab testing (if recommended by review panel) to develop improvements to nutrient formulations and new methods of providing an electron acceptor in situ. Field studies will be performed utilizing in situ monitoring systems to provide real-time measurement of CO<sub>2</sub> production by microbes, in situ oxygen levels, and contaminant removal. The project will be composed of 3 tasks: task 1 will be an expert panel meeting to review the state-of-the-art and define promising ideas yet to be field tested; task 2 will be the development of a nutrient/electron acceptor delivery system controlled by in situ monitors; task 3 will be the successful pilot-scale test, the integrated system which can monitor and feed back information on subsurface environmental conditions so an in situ bioremediation technology can be run in the most effective manner. This project directly contributes to the objectives identified in the Tri-Service Environmental R&D Strategic Plan, Pillar 1: CLEANUP: Requirement Thrust 1.J: Treatment of Fuels in Groundwater.

### 8. **Expected Payoff:**

These improvements to in situ biodegradation will provide Air Force and DoD engineers with a more reliable and less expensive alternative for removing fuels from groundwaters.

## 9. Milestones:

- |     |   |       |
|-----|---|-------|
| 1.  | Expert panel meeting                        | 02/94 |
| 2.  | Selection of iron quantification techniques | 02/95 |
| 3.  | Background sampling and analysis            | 02/95 |
| 4.  | Establish quarterly monitoring program      | 07/95 |
| 5.  | USGS data analysis and final report         | 09/95 |
| 6.  | Air sparging research contract              | 05/95 |
| 7.  | Site #1 Selection/characterization          | 06/95 |
| 8.  | Site #1 Installation of experimental cell   | 09/95 |
| 9.  | Site #2 Selection/characterization          | 12/95 |
| 10. | Site #2 Installation of experimental cell   | 03/96 |

## 10. Transition Plan:

This project will transition to the Air Force Environmental Systems Program Office (HSC/YAQ) and the Air Force Center for Environmental Excellence (AFCEE/ES) for full scale remediations and finalization of the technical data package. A preliminary Principles of Practice Manual, Technical Reports and professional publications will be produced for distribution to all DoD IRP offices and the appropriate Army, Navy, AF, DOE, and EPA technology transition offices.

## 11. Funding: \$(K)

	FY93	FY94	FY95	TOTAL
PE63723F	82			82
SERDP	400	430	600	1430
TOTAL	482	630	420	1512

## 12. Performers:

The Environics Directorate of Armstrong Laboratory will coordinate this research with the EPA's Robert S. Kerr Environmental Research Laboratory and the Risk Reduction Engineering Laboratory.

## 13. Principal Investigator:

Catherine Vogel  
AL/EQW  
7139 Barnes Dr., Suite 2  
Tyndall AFB, FL 32403-5323  
PHONE: (904) 283-6035  
FAX: (904) 283-6090  
E-MAIL: CATHERINE\_VOGEL@CCMAIL.ALEQ.TYNDALL.AF.MIL

## 14. Keywords:

Aerobic, Bioremediation, In Situ, Fuels, Hydrocarbons, Biodegradation

## SERDP FY95 PROJECT

1. **SERDP Thrust Area:** Cleanup
2. **Title:** Bioremediation of Hydrazine/Energetic Materials
3. **Agency:** U.S. Air Force
4. **Laboratory:** Armstrong Lab
5. **Project ID:** #118
6. **Problem Statement:**

Current methods for disposal of highly energetic materials are open burn/open detonation, static firing, and incineration. These disposal processes produce significant quantities of air pollution and residual wastes. Recent restrictive regulations make these disposal options unacceptable. Also, impacts from past activities at energetic disposal sites must now be addressed. The current method for hydrazine spill decontamination is the addition of oxidizers which, in turn, produce hazardous conditions or more toxic contaminants in the environment. Treatment techniques need to be developed to replace existing disposal options and address environmental contamination from past disposal activities of these materials. Biological treatment techniques offer the most cost-effective alternative to meet these needs.

### 7. Project Description:

Advances in biotechnology and enzymology will allow for the exploitation of biological treatment for the degradation of hydrazine and other energetic materials. More specifically, recent successes in discovering the pathways involved in the metabolism of nitroaromatic compounds and ammonium perchlorate suggest similar techniques may be applied to hydrazine. The approach for the successful implementation of this biotechnology will involve process discovery, determination of limiting factors, process development, and scale-up of the biological system. This will include bench-scale testing to optimize the required biological systems to be followed by field testing of an appropriate bioreactor system at a contamination site. In accordance with DoD's Project Reliance, the Armstrong Lab's in-house 6.2 research will be transitioned to the Army Environmental Center (AEC) in FY95. The AF 6.2 research will generate biochemical and genetic information for pure microbial strains capable of completely biodegrading energetic materials. Ongoing work includes enzyme purification and pathway identification. Regulation mechanisms of pathways are also being studied. The final product of this research will be a thorough understanding of the molecular basis of the biodegradation which will allow us to extend the substrate range, alter the kinetics or regulation of the system, or otherwise improve upon the effectiveness of the process. This knowledge base will be transitioned to AEC to allow for scale-up of these biological systems. This knowledge base is crucial to fielding an efficient, optimized bioreactor system versus a 'black box' whose operation is not completely understood. The AF would collaborate during AEC's scale-up work in terms of providing scientific guidance in the areas of microbiology, biochemistry and genetics of the

cultures/microorganisms. This will allow for the development of a properly designed reactor that will provide the microorganisms all necessary physiological requirements. This project directly contributes to the objectives identified in the Tri-Service Environmental R&D Strategic Plan, Pillar 1: CLEANUP: Requirement Thrust 1.G: Treatment Technology for Explosives in Groundwater, also Requirement Thrust 1.K: Treatment Technology for Explosives in Soils.

**8. Expected Payoff:**

Development of alternative disposal procedures, and understanding the fate of material already released into the environment is critical to maintaining compliance with the 1990 Clean Air Act Amendments (CAAA), the Federal Water Pollution Prevention and Control Act 1987 (FWPPCA), the Federal Facility Compliance Act 1992 (P. L. 102-386), and Executive Order 12865 (Aug 1993)/Federal Compliance with Right-To-Know Laws and Pollution Prevention Requirements. This project will produce a cost-effective, more efficient, destructive process to remediate sites contaminated with hydrazine and other energetic compounds within the regulatory requirements.

**9. Milestones:**

- |    |   |       |
|----|---|-------|
| 1. | In-house literature evaluation and review         | 02/95 |
| 2. | Transition of nitroaromatic prototype to AEC      | 01/95 |
| 3. | Identify microorganisms for hydrazine degradation | 02/95 |
| 4. | Perform bench-scale testing                       | 04/95 |
| 5. | Develop pilot-scale bioreactor system             | 04/97 |
| 6. | Field testing complete                            | 02/99 |
| 7. | Report results                                    | 04/99 |

**10. Transition Plan:**

This project will transition to the Air Force Environmental Systems Program Office (HSC/YAQ), the Air Force Center for Environmental Excellence (AFCEE/ES) and the Army Environmental Center for fielding of a remediation unit and finalization of the technical data package. A preliminary Principles of Practice manual, technical reports and professional publications will be produced for distribution to all DoD IRP offices and the appropriate Army, Navy, AF, DOE, and EPA technology transition offices.

**11. Funding: \$(K)**

	FY94	FY95	FY96	FY97	FY98	TOTAL
SERDP	420	0	655	1,830	1000	3905

**12. Performers:**

This effort will be performed by the Environics Directorate of Armstrong Laboratory (AL/EQ), the Occupational and Environmental Health Directorate of Armstrong Laboratory (AL/OE), and the Army Environmental Center (AEC).

**13. Principal Investigator:**

LT David Kuch  
AL/EQW  
139 Barnes Dr.  
Tyndall AFB, FL 32403-5323  
PHONE: (904) 283-6170  
FAX: (904) 283-6286  
E-MAIL: david kuch@ccmail.aleq.tyndall.af.mil

**14. Keywords:**

Bioremediation, Bioreactor, Energetics, Hydrazine, Nitroaromatic, Biodegradation.



## SERDP FY95 PROJECT

1. **SERDP Thrust Area:** Cleanup
2. **Title:** Catalytic In Situ Treatment of Chlorinated Solvents
3. **Agency:** U.S. Air Force
4. **Laboratory:** Armstrong Laboratory
5. **Project ID:** #107
6. **Problem Statement:**

Organic liquids, such as chlorinated solvents, nonchlorinated solvents, and fuels, have been used in massive quantities over the last four decades. Release of these liquids to the environment accounts for a significant portion of environmental contamination requiring cleanup. These contaminants have migrated through the subsurface and entered ground water at over 2000 DoD sites. There is a comparable degree of contamination at DOE and private Superfund sites.

The limiting factor to satisfactory remediation at over 75 percent of the hazardous waste sites in the United States is restoration of ground water quality. The technology chosen at over 90 percent of the sites with contaminated ground water is extraction followed by surface treatment. This technology, commonly known as pump-and-treat, contains contaminant plumes and removes dissolved-phase contamination in relatively homogeneous geologic formations. As a result of the slight solubility of the contaminant into the surrounding groundwater, and sorption to aquifer materials during transport, pump-and-treat processes require the treatment of massive amounts of water to remove relatively little contamination. Estimates of the duration of pump-and-treat necessary to fully remediate contaminated sites range from decades to centuries.

The high cost of pump-and-treat technologies are due to operations and maintenance costs, including energy for pumping and water decontamination, materials for treatment, and labor for constant operation of the process. A newly-developed process, called funnel-and-gate, is an in situ technique which directs contaminated groundwater under passive flow through an engineered subsurface region for decontamination. While this process may not reduce the duration of treatment, once installed, it will operate with little or no operating and maintenance (O&M) investment, resulting in considerable savings over the life of the project.

The best test of this technology will be in a well-characterized aquifer, treating a well-characterized plume. An accurate mass balance can be obtained only when the plume results from a controlled release of pollutant. The Air Force was recently awarded a SERDP grant to construct just such a controlled release site, which will be used for this demonstration. The groundwater can be decontaminated by a number of chemical, physical, biological, or a combination of methods. Existing research projects at both Armstrong and Athens (EPA) Laboratories have identified treatment methods which are well suited to funnel-and-gate deployment.

## 7. Project Description:

The funnel-and-gate consists of low hydraulic conductivity cutoff walls with gaps that contain in situ reactors (such as reactive porous media), which remove contaminants by abiotic or biological processes. The cutoff walls (the funnel) modify flow patterns so that ground water flows primarily through high conductivity gaps (the gates). Ground water plumes are thus directed through the in situ reactors in the gates where physical, chemical or biological processes remove contaminants from ground water. Remediated ground water exits the downgradient side of the reactor.

This applied research program will develop guidance on the use of funnel and gate systems containing various reactive media to treat chlorinated solvents in groundwaters. Studies will address two critical unknowns: 1) hydrogeologic uncertainties that have led to at least one failure of the technology, and 2) chemical reactions between reactive media and contaminants that lead to better designs. These studies will lead to a rigorous pilot-scale field demonstration to prove the technology.

An understanding of site-specific hydrogeology is critical to the design of funnel and gate systems. Groundwater flow rates and pathways must be known to position gates and to design the amount of reactive media required. New or improved groundwater flow and transport models will be developed to ensure that designers understand the system they will treat.

The proposed research will apply hydrogeological principles and aquifer modeling techniques to develop the most efficient designs and methods for construction of the walls. An increased understanding of groundwater flow through the engineered systems will allow for the most frugal emplacement while ensuring complete capture of the contaminant plume. The proposed work will develop new (or modify existing) three-dimensional groundwater flow models to simulate the flow of groundwater and contaminant plumes through aquifers modified with a funnel and gates. Of particular interest will be the influence of aquifer heterogeneities and site characterization. Variables to be examined will include size and shape of the funnels, requirements for wall integrity, number and placement of gates, and groundwater velocity through the gates. New modeling techniques will be developed to account for effects like aquifer clogging by iron bacteria. The models will be verified in field demonstrations using non-hazardous tracers to monitor groundwater movement through the system.

Concurrently, gate technologies will be designed and scaled for use with funnel-and-gate configurations. Environics Laboratory has for several years been investigating abiotic dechlorination in order to develop in situ treatment processes. Other research has been directed at contaminant mobility reduction using surfactants, a process which may enhance biological treatment in gates. The Environmental Research Laboratory at Athens has been studying abiotic dechlorination using elemental iron, enhanced with sulfur compounds, as an in situ process. All of these processes can potentially be used as gates to treat groundwater contaminated with chlorinated solvents. The elemental iron/sulfur catalytic dechlorination system developed by the Athens Laboratory is proposed as the first demonstration gate. Regardless of the nature of the gate, pathway analyses must be conducted in the field and laboratory, not only to predict residual toxicity, but also to aid in deriving the optimum design configuration. Mass accounting must be fully balanced to ensure complete

destruction of the contaminant. Where necessary, labeled compounds and tracers will be used. By coordinating the hydrogeologic modeling project with further development of the gates, a fully integrated system can be installed and tested in the field.

Failure of innovative technologies at a regulated site would result in wasted cleanup dollars and may actually complicate subsequent cleanup. Proving technologies in a well-controlled, isolated site will limit the risk and possible damage resulting from failure.

This project directly contributes to the objectives identified in the Tri-Service Environmental R&D Strategic Plan, Pillar 1: CLEANUP: Requirement Thrust 1.I: Treatment Technology for Solvents in Groundwater.

### 8. Expected Payoff:

Most contaminated sites currently undergoing pump-and-treat remediation are expected to be tractable to funnel and gate configurations. Installation of passive treatment zones will save on O&M costs for what will likely be decades of continued treatment. With no active pumping involved in the process, these systems may be installed at sites for which power utility installation is a formidable obstacle to installation of pump-and-treat systems.

### 9. Milestones:

1.	Report on the mass balance of iron/iron sulfide reaction	09/95
2.	Develop computer model(s)	10/95
3.	Apply computer models to predicting modified hydrology	02/96
4.	Guidance documents on designing funnel and gate systems	05/96
5.	Report on the dehalogenase enzyme reaction and plant sources	08/96
6.	Design funnel-and-gate hydrology demonstration(s)	11/96
7.	Construct field demonstration	04/97
8.	Collect and analyze operational and monitoring data	08/98

### 10. Transition Plan:

The reports and guidance documents resulting from this work will be written so that they will be suitable for planning implementation at scales larger than the field studies of this project. The Air Force Environmental Systems Program Office (HSC/YAQ) and the Air force Center for Environmental Excellence (AFCEE/ES) will further develop the technical information obtained from this research and apply it to full scale remediations and finalization of the technical data package. A preliminary Principles of Practice Manual, Technical reports and professional publications will be produced for distribution to the appropriate technology transfer offices of the Air Force, Army, Navy, DOE, and EPA.

### 11. Funding: \$(K)

	FY94	FY95	FY96	FY97	FY98	TOTAL
SERDP	720	300	550	990	850	3410

**12. Performers:**

The performers for the proposed work are US Air Force Armstrong Laboratory, Environics Directorate (AL/EQW), the EPA Environmental Research Laboratory at Athens, and the University of Waterloo, Waterloo, Ont, Can.

**13. Principle Investigator:**

Major Mark H. Smith, PhD  
AL/EQW-OL  
139 Barnes Drive, Suite 2  
Tyndall AFB, FL 32403-5323  
PHONE: (904) 283-6126  
FAX: (904) 283-6286  
E-MAIL:MARK\_SMITH@CCMAIL.ALEQ.TYNDALL.AF.MIL

**14. Keywords:**

Funnel and Gate, Remediation, Cleanup, Aquifer, TCE, Chlorinated Solvents

## SERDP FY95 PROJECT

1. **SERDP Thrust Area:** Cleanup
2. **Title:** Joint US/Germany In-Situ Bioremediation Demonstration
3. **Agency:** U.S. Air Force
4. **Laboratory:** Armstrong Laboratory
5. **Project ID:** #99
6. **Problem Statement:**

The goal of this effort is to conduct a field demonstration of bioventing concurrent with two groundwater treatment strategies at a JP-4 jet fuel contamination site at Rhein Main AB, Germany. The results generated from this field project will assist in successfully transferring these technologies to the German regulatory authorities and the German environmental consulting firms working on U.S. military base cleanup activities in Germany.

There are approximately 2,000 fuel/hydrocarbon contamination sites the US Air Force must address in it's Installation Restoration Program. There are also numerous such sites at military facilities throughout Germany and other NATO countries. Any in-situ method for soil or groundwater cleanup will offer huge cost savings over the currently used ex-situ disposal or treatment methods.

This effort represents an enhancement to several existing programs: "Bioventing for In-Situ Cleanup of JP-4 Contaminated Soils," "Anaerobic Degradation of Fuel-Contaminated Groundwater," and "Natural Attenuation."

### 7. Project Description:

The technical objective of this effort is to demonstrate bioventing for the cleanup of JP-4 contaminated soil located beneath the taxiway at Rhein Main AB Germany. To improve the effectiveness of bioventing, the "bioslurper system" will also be demonstrated to remove free product from the site prior to bioventing. Specific tasks are outlined below. The rationale for using natural or enhanced attenuation to address the contaminated groundwater will also be tested at a separate JP-4 contamination site at Rhein-Main AB.

The technical approach will include a field demonstration site to allow for the testing outlined above has been selected at Rhein Main AB. Construction of the experimental plots/areas and outfitting with the necessary hardware and monitoring equipment will be accomplished jointly by the University of Karlsruhe and an AL/EQ contractor. The mechanism which facilitates this collaboration is the DoD's US-German Data Exchange Agreement. Both the University of Karlsruhe and AL/EQ's technical objectives will be accomplished at this field site. This will be a three-year demonstration.

The tasks to be accomplished are as follows. The primary party responsible for accomplishing the tasks is noted in parentheses:

- Construction of treatment cell (GE)
- Perform experiments to better define mass balance and monitoring methods (primarily US with some GE involvement)
- Testing methods to improve biodegradation rates (GE)
- Testing methods to improve application of bioventing such as bioslurper (US) and surfactants (GE)
- Nitrate enhancement for groundwater treatment (GE)
- Natural attenuation (US)
- Sampling/Monitoring/Analysis (US + GE)

This work will assist the DoD in achieving its Year 2000 cleanup goals and also be applicable to similar fuel contamination sites on DOE facilities. The proposed effort relates closely to AF, Navy, and EPA's previous and ongoing work in bioventing. AL/EQ and the US Environmental Protection Agency's Robert S. Kerr Environmental Research Laboratory are also currently involved in development of nitrate enhancement for groundwater decontamination as are a few select researchers in Germany. Lastly, the AF is involved in a collaborative effort with TVA on a natural attenuation demonstration.

The technical risk is medium. This judgment is based not on the feasibility of bioventing or the other technologies to be tested, but on the fact that they are to be tested on contaminated soil lying beneath an active taxiway.

This project directly contributes to the objectives identified in the Tri-Service Environmental R&D Strategic Plan, Pillar 1: CLEANUP: Requirement Thrust 1N: Treatment of Fuels in Soils.

## **8. Expected Payoff:**

The bottom-line payoff is that these very low-cost technologies will save the US and German governments millions of dollars per contaminated site over conventional cleanup technology. The key outcome of this joint demo will be performance and cost information to convince the German regulatory authorities that bioventing/bioslurper/natural attenuation are viable treatment options for hydrocarbon contaminated aquifer material. We will also identify the operating difficulties associated with attempting these technologies beneath an active taxi way (8-10 inches concrete). Lastly, the two bioremediation technologies, independently developed by the US and Germany, could be enhanced as a result of this joint effort.

## **9. Milestones:**

- |    |  |       |
|----|--|-------|
| 1. | Draft Treatment Study Test Plan          | 11/94 |
| 2. | Final Treatment Study Test Plan          | 12/94 |
| 3. | Draft Quality Assurance Project Plan     | 12/94 |
| 4. | Final Quality Assurance Project Plan     | 01/95 |
| 5. | Construction of Experimental Field Plots | 03/95 |
| 6. | Completion of Bioslurper Experiments     | 07/95 |
| 7. | Completion of All Field Experiments      | 10/97 |

- |    |                        |       |
|----|------------------------|-------|
| 8. | Draft Technical Report | 10/97 |
| 9. | Final Technical Report | 12/97 |

**10. Transition Plan:**

Technical results from this demonstration will be transferred via interim reports throughout the life of the project, final technical report, and design guidance. Design packages, technical data, and operator manuals will be available and will be transitioned to the Air Force Environmental Systems Program Office (HSC/YA), the Air Force Center for Environmental Excellence (AFCEE) for development and fielding, and will be distributed to all DoD Installation Restoration Program (IRP) offices and the appropriate Army, Navy, AF, DOE, and EPA technology transition offices.

The users (contracting and consulting firms such as Battelle) will be the performers. The main coordination needed will be with the German regulators to keep them informed of the project's progress. The industries ability to assume production is high.

**11. Funding: \$(K)**

	FY94	FY95	FY96	TOTAL
SERDP	250	200	300	750

**12. Performers:**

The project will be jointly managed by the Environics Directorate of Armstrong Laboratory (AL/EQ) and the German BWB through our existing Data Exchange Agreement. It will be performed by a qualified AL/EQ contractor and the University of Karlsruhe, Germany. No CRADAs are anticipated.

**13. Principal Investigator:**

Catherine Vogel, Project Manager  
 AL/EQ-OL  
 139 Barnes Drive, Suite 2  
 Tyndall AFB FL 32403-5323  
 PHONE: (904) 283-6035  
 FAX: (904) 283-6090  
 E-MAIL: CATHERINE\_VOGEL@CCMAIL.ALEQ.TYNDALL.AF.MIL

**14. Keywords:**

Bioremediation, Natural Attenuation, Bioventing, Remediation, Cleanup, Nitrate Enhancement

## SERDP FY95 PROPOSAL

1. **SERDP Thrust Area:** Cleanup
2. **Title:** The Engineering Design of In Situ Bioremediation
3. **Agency:** Department of Energy
4. **Laboratory:** Idaho National Engineering Laboratory
5. **Proposal ID:** #514
6. **Problem Statement:**

In situ bioremediation (ISB) has been used successfully for two decades for the restoration of soils and groundwater contaminated with hydrocarbons. ISB is more environmentally sensitive and less expensive than more invasive alternatives (e.g., excavation, incineration). In addition, it acts as a useful complement to other in situ technologies such as air-stripping (vapor vacuum extraction and groundwater sparging), hydraulic containment and pump and treat. Recently attempts have been made to apply ISB to situations that are more microbiologically complex, including; contaminants present at elevated concentrations that inhibit microbial growth, contaminants (like explosives) that can only be completely mineralized by a consortia of microorganisms and contaminants like the chlorinated solvents that are not a carbon/energy source for bacteria but can be degraded through cometabolic pathways. Results from these projects have often been disappointing.

The basic hypothesis of this proposal is that the variable record of ISB is due to the lack of a consistent engineering design process. The input to this process would be all the site-specific geochemical, hydrological and microbiological data that can be gathered with reasonable expenditure of time and money. It's output would consist of:

- A statement of whether ISB can achieve compliance with the applicable regulations (i.e., drinking water standards, etc.).
- A decision about how ISB can best be combined with other contaminant-removal technologies.
- A design and control scheme specifying close-to-optimum values for process variables (i.e., well types, flow rates, composition of the injected nutrient stream, etc.) and how they should be varied over the life of the project.

The objective is field-scale ISB projects that can be turned on and left to run with confidence. Once the design and control strategy have been established, major changes should be unnecessary. It may be argued that treating ISB as a "Field-Scale Experiment" is an opportunity to learn something new. To the engineer, any such need to manipulate process variables once the process has begun is an expensive admission of the failure of the design process.



The author's experience suggests several reasons for the lack of a clear-cut design procedure. First is the shortage of process variables. The designer of a surface bioreactor is free to pick the type and size of reactor, to control the pH and to include agitation and/or cell recycle to mix the bacteria, nutrients and contaminants together. The ISB designer tries to achieve the same ends by varying only the flow rate and composition of the injected nutrient stream. Second, some of the tools of engineering design are difficult to apply to ISB. What, for example, does "scale-up" mean at an ISB site with no natural boundaries? Similarly, experience is a valuable tool for designing traditional processes such as sewage treatment because municipal sewage varies little from town to town. However, the performance of ISB is so site-specific that experience gained at one site may not be transferable to the next. The third reason is the sheer complexity of the underlying phenomena of ISB. These include, the details of the hydrology, geochemistry and microbial metabolism as well as questions regarding the adsorption of contaminants and microorganisms to soil particles. In order to integrate the available information into a workable design, the details of all of these phenomena must necessarily be simplified. Unfortunately, such simplifications often lead to interdisciplinary disputes. For example, mathematical models are potentially valuable design tools but are often written by hydrologists with little knowledge of microbiology. Meanwhile, microbiologists conduct biodegradation experiments in such a way that critical modelling parameters can not be extracted from the results. Development of a standardized procedure would eliminate such confusion and keep all the relevant scientific and engineering disciplines working efficiently towards the good of successful ISB.

## **7. Project Description:**

The ISB designer actually has two tools available; the mathematical model and experiments. The objective of this project is to show that best results are obtained only if these tools are properly integrated. The obvious, but often overlooked, requirement that no parameter be allowed into a model unless an experimental procedure exists to measure its value, automatically limits the complexity of the model. For example, there is little point in employing complex dispersion models if only simple tracer data will be available from the site. Similarly, designing the experiments so that their results can be translated into site-specific parameter values, maximizes their utility. This project involves three tasks; a) developing design models with appropriate levels of complexity, b) designing treatability experiments so that they provide data in a useful form, and c) transferring these procedures to the ISB industry.

### **a) Model Development**

No one person will ever be sufficiently expert in all of the underlying phenomena of ISB to say whether it will achieve compliance at a particular site and how it should be designed and controlled. A mathematical model is an essential repository for the combined quantitative knowledge of many specialists. Such a model can be used to test different combinations of the process variables (well location, nutrient concentration, etc.) and to select the best combination. It can also provide the best prediction of the outcome of the process and suggest a rational control strategy based on differences between model predictions and field measurements.

The difficulty with existing models is that by attempting scientifically-exact descriptions of all facets of the problem, they become too complex for use in process design. The overall problem is so complex that methods for separating what is truly important from the mass of

detail must be employed. One such method is dimensional analysis, a valuable design tool that has yet to be applied to ISB. Another is the concept of the biologically-active zone (BAZ). As injected nutrients spread out from an injection well, they reach a point where their flow velocity is small compared to the growth rate of the microorganisms. The BAZ is the region around the expanding nutrient front where the contaminant, the nutrient and the microbes are mixed together by the effects of dispersion and adsorption. If this zone is thin, considerable simplification of the mathematics (and thus of our quantitative understanding) is possible.

These methods will be explored by solving a series of well-posed model problems. For example, in a plume of a biodegradable contaminant at inhibitory concentrations in a two-dimensional confined aquifer where should nutrient injection wells be located in order to provide the fastest clean-up with minimum displacement of the contaminant off the site? Can this optimum positioning be related to other variables (dispersion coefficients, inhibition constants, etc.) by correlations of dimensionless numbers? Are solutions based on the BAZ concept adequate approximations to the complete solution?

#### b) Design of Treatability Experiments

Many workers seek to simulate ISB by constructing laboratory columns of aquifer material and flowing groundwater through them. While this approach provides some insight into the process it is impossible to determine the inherent kinetics for growth and degradation by the indigenous bacteria from such data (the reasons involve the form of the mass conservation equations for a column; 2-dimensional partial differential equations). Batch microcosm experiments have a different drawback. Fluid flow (even if only that caused by nutrient injection) is an essential part of ISB. Since there is no flow in a batch experiment, it is unlikely that phenomena like adsorption/desorption of microbes will be well-simulated in the experiment.

In previous work under the DOE Subsurface Science Program and the Non-Arid Lands Integrated Demonstration at the Savannah River site, the authors have developed a system called the Differential Soil Bioreactor (DSBR) which overcomes these difficulties. It consists of a disc-shaped element of soil through which groundwater is recirculated so that all of the microorganisms are exposed to the same physicochemical conditions. Further refinement of the experimental and data analysis procedures are needed to extend the range of sites to which this device is applicable. Also, a modified version of the DSBR will be designed and built to extend the concept to bioremediation in the vadose zone.

#### c) ISB Technology Transfer

Several companies have installed ISB operations. The type of treatability studies and design procedures they employ (at least those that have been published) show little consideration for the complex interactions between flow, dispersion, microbial attachment, contaminant adsorption, biodegradation, etc. that influence the outcome of ISB. During the first year of the project discussions of this problem will be conducted with these companies and EPA personnel responsible for treatability study procedures. Any company wishing to collaborate on the project will be included through the establishment of a CRADA.

## 8. Expected Payoff:

ISB has many potential advantages. It can treat many contaminants of interest to DoD including fuels, chlorinated solvents and explosives. It can treat large volumes of contaminated soils down to compliance levels at a much lower cost and less environmental impact than competing technologies. There are several variants of ISB including injection of liquid-phase nutrients into a contaminated aquifer, bioventing (passive ventilation of the subsurface to minimize volatilization and maximize biodegradation), and horizontal wells for sparging gas-phase nutrients into contaminated groundwater. What they have in common is that they will only function properly if they are designed correctly, which means that the details of the process must be related to the geological, hydrological and microbiological characteristics of the particular site. Successful development of the procedure proposed here will remove many of the uncertainties presently associated with the application of this technology. Its benefits can then be employed with confidence at many DoD, DOE and private industrial sites.

## 9. Milestones:

- |    |   |       |
|----|---|-------|
| 1. | Complete ISB site selection, preliminary characterization and establish industrial partnerships | 03/96 |
| 2. | Complete DSBR studies   | 12/96 |
| 3. | Complete model for implementation of ISB  | 03/97 |
| 4. | Complete status report of ISB industry  | 09/97 |
| 5. | Complete ISB field study  | 09/98 |

## 10. Transition Plan:

The proposed combined modelling/experimental procedure will be tested and evaluated at a appropriate site during FY97 and FY98. Present candidate sites are severe solvent contamination problem at Hill Air Force Base Ogden, Utah and a Trichloroethylene problem in the groundwater in Pocatello, Idaho. The former would be performed in cooperation with the USAF and Montgomery Watson (currently contracted to provide restoration support). The latter is currently under study by CH2M Hill Co. with ISB as a possible remediation technology. Other sites will be selected in accordance with CRADA guidelines.

## 11. Funding: \$(K)

	FY95	FY96	FY97	FY98	TOTAL
SERDP	0	350	350	290	990

## 12. Performers:

The Office of Industrial Biotechnology and Process Engineering at the Idaho National Engineering Laboratory (INEL) is an interdisciplinary group of geneticists, microbiologists and bioprocess/environmental engineers, with considerable experience in environmental microbiology and bioremediation. It also maintains strong links with the geochemists and hydrologists at the INEL. The Principal Investigator and members of the proposal team have been involved in ISB research through the DOE/OHER Subsurface Science Program and the DOE/OTD Non-arid Lands Integrated Demonstration. Dr. Andrews also has served as Co-

Chairman of a session on "Bioremediation of Soil" at the AIChE Annual Meeting in Los Angeles, November 1991; and a panel member for a workshop on "Bioremediation Research" at the AIChE Annual Meeting in Minneapolis, August 1992.

**13. Principal Investigator:**

Graham F. Andrews, PhD  
Office of Industrial Biotechnology and Bioprocess Engineering  
Idaho National Engineering Laboratory  
P.O. Box 1625  
Idaho Falls, ID 83415-2203  
PHONE: (208) 526-0174  
FAX: (208) 526-0828

**14. Keywords:**

soil, groundwater, in situ, bioremediation, bioreactor, solvents

## SERDP FY95 PROJECT

1. SERDP Thrust Area: Cleanup
2. **Title:** Aquifer Restoration by Enhanced Source Removal
3. **Agency:** Environmental Protection Agency
4. **Laboratory:** Robert S. Kerr Environmental Research Laboratory
5. **Project ID:** #368
6. **Problem Statement:**

The goal of this project is to provide field demonstrations of innovative processes to remediate aquifers contaminated by non-aqueous phase liquids (NAPLs) including fuels, solvents, and other organic contaminants in a timely and cost-effective manner. These demonstrations are targeted at DoD, DOE, EPA, their contractors, and other public and private organizations responsible for remediation of contaminated ground water. Low-solubility organics such as chlorinated solvents were used and released to the environment in massive quantities during the 1950's, 60's and 70's. These contaminants have migrated through the subsurface and entered ground water at over 2000 DoD sites. At these sites the organic contaminants are found in one of three phases: (1) dissolved in the ground water (dissolved phase), (2) sorbed to the aquifer solids (sorbed phase), or (3) as a separate non-aqueous phase liquid (NAPL phase), all of which need to be removed if the ground water is to be restored to a usable quality.

The limiting factor to satisfactory remediation at over 75 percent of the hazardous waste sites in the United States is restoration of ground-water quality. For those contaminants that have found their way into ground water in the deeper subsurface, remediation technology options are extremely limited. The technology chosen at over 90 percent of ground-water contaminated sites is extraction followed by surface treatment. This technology, commonly known as *pump-and-treat*, has had some success in containing contaminant plumes and removing dissolved-phase contamination in relatively homogeneous geologic formations, but, as currently implemented, has not proved to be effective at restoring contaminated ground water to desired levels of cleanliness. The major limitations to the successful use of pump-and-treat are related to difficulties in extracting contaminants from the subsurface. Aquifer characteristics important in limiting the success of pump-and-treat include: (a) aquifer heterogeneity, (b) sorption of the contaminant to aquifer solids, and (c) the presence of a separate immiscible non-aqueous phase liquid (NAPL).

There is a particular need for enhancements to pump-and-treat technology that can overcome the limitations imposed by aquifer heterogeneity, sorption, and the presence of NAPLs. A number of enhanced pump-and-treat technologies have been proposed and demonstrated in the laboratory, but none have been subject to an objective field evaluation, nor is engineering design guidance available for routine application to contaminated ground-water remediation.

The EPA's Robert S. Kerr Environmental Research Laboratory (RSKERL), through its subsurface cleanup and mobilization processes (SCAMP) program, and the Armstrong Laboratory, Environics Directorate (AL/EQ) at Tyndall AFB, FL, and both agencies through the SERDP program, have been working on innovative methods to increase the removal rates of toxic organic compounds from the subsurface. This proposal is an enhancement to the programs of both institutions.

## **7. Project Description:**

The objective of this research is to demonstrate processes for enhancing contaminant removal (enhanced pump-and-treat technologies) in a variety of geologic settings and to produce engineering design guidance documents for applying these processes to remediate contaminated ground water. The guidance will address the entire remediation effort, including site characterization and supporting laboratory work, required to achieve the maximum benefit from the remediation technologies included in the study.

The proposed work will be a series of field demonstrations at two or more sites of enhanced pump-and-treat technologies supported by site characterization and laboratory research required to produce a credible field demonstration and a credible evaluation. The work will focus on remediation of sites believed to be contaminated by non-aqueous phase liquids (NAPLs), such as chlorinated solvents. The proposal is to conduct these demonstrations at contaminated DoD sites to increase the likelihood that the results will be directly applicable to actual remediation projects.

The tests will be conducted as small-scale field projects. Each technology will be compared, at the same site, with several alternative remedial technologies including pump-and-treat. The results of these comparisons will show the differential improvement achieved by one process relative to another.

The proposed work will demonstrate and evaluate processes to enhance subsurface contaminant removal that are presently at a stage of development where they can be seriously considered for use in installation/restoration programs at DoD facilities. Such processes include innovative methods, such as: pulsed pumping, to optimize system design and operation for conventional as well as enhanced pump-and-treat; solvent flushing with water-miscible solvents such as ethanol; surfactant flushing; hot water flushing; and methods for forcing fluids through regions of low hydraulic conductivity.

Each evaluation will involve a set of similar tasks: site selection and characterization, design and construction of test facility, operation and monitoring, and evaluation and reporting. Each site will be characterized using state-of-the-art non-invasive and invasive techniques to provide the data necessary to select, design, operate and evaluate the remedial technology under study. Existing research design models will be utilized to develop the actual test facilities. The last part of each demonstration will be an evaluation of the test data and the preparation of a report. The report will describe site characterization, system design and operation, performance evaluation, degree of remediation achieved, cost analysis, factors limiting the success of the technology, and additional research, if any, required to overcome these limitations. These reports will form the basis for an engineering design guidance manual scheduled for completion 06/97.

The proposed work is a continuation of work performed under SERDP Phase I and Phase III and addresses Thrust 1I: Treatment of Solvents in Groundwater, and Thrust 1J: Treatment of Fuels in Groundwater under Pillar 1: Cleanup of the Tri-Service Strategic Environmental Quality Strategic Plan. The proposed work extends RSKERL's SCAMP research program, which is an effort to improve the efficacy of pump-and-treat remedial actions for ground water contaminated by chlorinated solvents. The proposed work complements the (AL/EQ) Small Business Innovative Research (SBIR) and SERDP (Phase I) funding to encourage businesses to work on DoD environmental problems. A fully contained hazardous waste unit at Hill AFB has tentatively been selected as the first demonstration site. The selected site has a mixture of LNAPLs including: POLs, pesticides, PCBs and Dioxin. A small amount of the LNAPL is still mobile but the majority is now at residual saturation. Hydraulically, the site appears to be sufficiently permeable to permit delivery of the remedial fluid to the point of contamination. The contamination is sufficiently close to the surface to minimize construction cost. State and Federal regulators have been approached to obtain permission to make Hill a demonstration facility for extraction technologies. Site characterization is underway at Hill by the University of Florida to collect data needed to design the first co-solvent field study. EPA/RSKERL and AL/EQ both have strong laboratory and field programs directed toward in-situ remediation of contaminated ground water. The subsurface remediation expertise from these programs is available to provide support to the proposed work.

Each of the proposed processes has been shown to overcome some limitations that prevent remediation of contaminated aquifers. However, there are a number of factors that have not been field evaluated. Three of these factors are: the high degree of spatial variability in the subsurface environment, the difficulty of obtaining in-situ mixing of a remedial additive with a subsurface contaminant, and changes in the hydraulic properties of the system as the NAPL is removed.

## 8. Expected Payoff:

Pump-and-treat systems are the primary technology in use at sites with contaminated ground water. Because of their inability to effectively clean up source regions of contaminated waste sites, many of them are being used primarily to provide hydraulic containment; and the forecasts are that they will need to be operated "in perpetuity." The proposed work will allow developing technologies to be implemented faster and with more confidence in their performance. The demonstrations will provide guidance in the application based on carefully documented field experience, which should, in turn, improve acceptance within the regulatory community. Estimated costs for ground-water remediation by DoD and other federal agencies range upwards of hundreds of billions of dollars, and even incremental improvements in efficiency will justify the costs of the proposed research.

## 9. Milestones:

- |    |  |       |
|----|--|-------|
| 1. | Select site and technologies for first tests                                 | 08/94 |
| 2. | Initiate site characterization and project design for the first set of tests | 08/94 |
| 3. | Construct and install treatment systems for first set of tests               | 12/94 |

- |     |   |       |
|-----|---|-------|
| 4.  | Initiate first set of tests; collect and analyze operational and monitoring data  | 12/95 |
| 4a. | Install remaining test cells at first site  | 07/95 |
| 4b. | Initiate within cell characterization in remaining cells at site 1                | 12/95 |
| 4c. | Initiate remediation in remaining cells at site 1                                 | 03/96 |
| 5.  | Select test sites and technologies for second test                                | 04/96 |
| 6.  | Conduct site characterization and project design for the second set of tests      | 05/96 |
| 6a. | Write test report for first tests   | 05/96 |
| 7.  | Construct and install treatment systems for second test                           | 09/96 |
| 8.  | Initiate second set of tests; collect and analyze operational and monitoring data | 03/97 |
| 9.  | Complete data collection for first set of tests and write test reports            | 05/97 |
| 10. | Complete data collection for second set of tests and write reports                | 03/98 |
| 11. | Produce summary report/engineering design guidance report                         | 03/99 |

**10. Transition Plan:**

The proposed work will consist of small-scale controlled field demonstrations. The reports and guidance documents resulting from this work will be written such that they will be suitable for full-scale planning and implementation.

The EPA/RSKERL Technology Support Center (TSC) has provided technical assistance on over 300 Superfund sites since 1987. RSKERL has an on-site professional staff with a primary responsibility for technical assistance. RSKERL has conducted numerous technology transfer seminars. The TSC will provide a very effective means for transferring the results of this research to the user community. The Air Force Environmental Systems Program Office (HSC/YAO) and the Air Force Center for Engineering Excellence (AFCEE/ES) will further develop the technical information and finalization of the technical data package. Preliminary principals of practice manuals, technical reports and professional publications will be produced for distribution to appropriate technology transfer offices of the Air Force, Army, Navy, and DOE.

**11. Funding: \$(K)**

	FY93	FY94	FY95	FY96	FY97	FY98	FY99	TOTAL
SERDP	500	2200	860	1100	1300	1300	2200	9460
EPA	530	678	700	750	400	0	0	3058
DoD*	629	462	138	0	0	0	0	1229
Total	1659	3340	1698	1850	1700	1300	2200	13747

\* Armstrong Laboratory, Environics Directorate



## **12. Performers:**

The performers for the proposed work are: EPA - Robert S. Kerr Environmental Research Laboratory, Ada, OK; University of Florida, Gainesville, FL; DoD (Air Force) - Armstrong Laboratory, Environics Directorate, Tyndall Air Force Base, FL; DoD (Air Force) - Environmental Management Directorate, Hill AFB, UT. Cooperative agreements with academic and research organizations already involved in development of aquifer remediation technology will be used to conduct part of the proposed research. CRADAs will be developed as the project progresses.

## **13. Principal Investigator:**

Carl G. Enfield, Senior Research Environmental Scientist  
US EPA, Robert S. Kerr Environmental Research Laboratory  
P. O. Box 1198, Ada, Oklahoma 74820  
PHONE: (405) 436-8530  
FAX: (405) 436-8582  
E-MAIL: ENFIELD@3100.ADA.EPA.GOV

## **14. Keywords:**

extraction, NAPL, ground-water, surfactant, co-solvent, sparging

## SERDP FY95 PROJECT

1. **SERDP Thrust Area:** Cleanup
2. **Title:** Removal and Encapsulation of Heavy Metals from Ground Water
3. **Agency:** Environmental Protection Agency
4. **Laboratory:** Risk Reduction Engineering Laboratory (RREL)
5. **Project ID:** #387
6. **Problem Statement:**

The goals of this proposed applied research (6.2) program are to develop a unique, innovative technological approach for many of the difficult problems, found on both DoD and DOE facilities: 1) that of removing metal contamination from dilute matrix (i.e. water); 2) managing metal residuals that can not be destroyed; 3) protecting surplus equipment from environmental exposure. This effort will (1) develop high-capacity low-cost adsorbents, based on cellulose or starch, natural polymer or synthetic polymers (with functional groups) for selectively adsorbing toxic metals such as uranium, plutonium, mercury, and then (2) demonstrate permanent encapsulation of the solid adsorbent matrix by extrusion in recycled plastics such as high density polyethylene for long-term disposal, or (3) allow for temporary storage of these metals for future resource recovery or protection of surplus equipment from environmental exposure. The metal contaminants (i.e. mercury, lead, uranium) can be directly adsorbed from ground water or wastewater. If present in a solid matrix, the metals can first be leached selectively into a concentrated aqueous medium, which then will be subjected to the low-cost adsorption technique and encapsulation. Likewise, this encapsulation concept has application to solid material such as depleted uranium or plutonium found at the Y12 plant, Rocky Flats, or Aberdeen Proving Ground. The proposed research will result in a highly efficient, yet affordable technology for remediating metal contaminated water as well as protect surplus equipment from environmental exposure.

Restoration of metal-contaminated water or solids is a generic problem, with many sites belonging to both DOE and DoD. Indeed the problem is so extensive that affordable technologies are critically needed now. For ground water the dominant methods used today are of the pump-and-treat type. The treatment part usually uses activated carbon or a resin, which on saturation is regenerated by acid leaching. The metals in aqueous stream are then isolated by precipitation. The precipitate sludge is further treated, then disposed of in a hazardous waste landfill. The problem may continue over the years as the metals will gradually form leachates. It has been estimated by industry that for every one dollar of operating cost in the adsorption part of this technology, about 3 to 6 dollars are spent in regeneration. Thus developing low-cost adsorbents that do not need regeneration provides a very attractive technical approach. This is a new idea, no prior art exists.

One dominant method of metals disposal is the cement-based solidification/stabilization process. The long-term effectiveness of this technique, however, has not been determined. Alternatively vitrification has been tried, and proposed especially for radioactive wastes but does not allow for resource recovery of the encapsulated material. Encapsulating radioactive

wastes in thermoplastics has been demonstrated in the U.S., U.K., France, and Israel, and no leaching has been observed for a long time (years). Metals and their compounds have no detectable diffusive transport through polymer films. In landfills thermoplastics do not begin to biodegrade in less than 400 years; in low moisture environment and in absence of microbial action, therefore, these encapsulants will last much longer. The thermoplastics are also stable to high levels of irradiation, which is important for storing radioactive compounds. The longevity of these encapsulants of course can be increased by multiple encapsulation. The Brookhaven National laboratory and the University of Cincinnati have done some preliminary work in this area. Furthermore, temporary encapsulation of surplus DoD material will alleviate many of the concerns expressed in the Office of Technology Assessment's critical report of DoD's equipment storage systems that are wasting millions of dollars due to corrosion from unprotected environmental exposure.

## **7. Project Description:**

The project has several distinct parts, requiring different technical skills for their solution. First, low-cost adsorbents need to be designed and developed and produced. In the environmental restoration area, adsorbents such as carbon, zeolites, or ion exchange resins have been used. Each technology is based on the concept of regenerating the adsorbents for reuse. As has been mentioned before, even with regeneration, these adsorption processes tend to be very expensive for large dilute matrices. Moreover these adsorbents do not possess high adsorption capacity (mostly fraction of a percent), which imparts two undesirable effects on process economics, namely adsorbent cost and eventual dilution of the metals on regeneration. Highly selective adsorbents with specific ligands have made chromatography a mainstay in protein separation from very dilute solutions. In that spirit, this effort will develop low-cost adsorbents which have inexpensive but highly efficient ligands attached to them. These adsorbents will have higher capacity and high specificity for chosen metals. The resulting adsorbents will not need to be regenerated.

The technical approach consists of attaching specific amine or imine-based (or other promising) ligands on chosen adsorbents, which can be selected from cellulose, starch, saw dust, peat moss, chitin/chitosan etc., and tested for their efficacy. EPA has discussed the prospect of this approach with Prof. Jerker Porath, the famous inventor of sepharose and sephadex, the two universally used chromatography column material. Prof. Porath, who spends six months at Upsala University in Sweden and the rest at the University of Arizona, is interested in collaboration with EPA. Prof. Porath will take the prime responsibility of synthesizing the low-cost adsorbents. The engineered material most likely will be in pellets or beads form. EPA will build laboratory apparatus to demonstrate the idea of metals adsorption from contaminated water. For uranium, or plutonium, a toxic metal surrogate will be used.

In another section of the project, the separation (volume reduction) data from the laboratory will be used to design experiments for encapsulating the adsorbents or for encapsulating surplus equipment in recyclable plastics, to reduce life cycle cost. Prof. Don White, a plastics conversion specialist, and Prof. David Wolf (working at the University of Arizona) would be responsible for this effort. EPA will have access to the University extruders for demonstrating the technology. Lastly, EPA will propose demonstrating this concept at a DoD or DOE site.

Important technical issues to overcome: (i) attaching inexpensive ligands to low-cost substrate to impart high capacity, (ii) preparing appropriate engineered (thermoplastic) materials which are easily handled, (iii) demonstrating the stability of the polymers to internal or environmental effects such as radiation and (iv) demonstrating ability of resource recovery of both the encapsulated heavy metals and thermoplastic material.

**8. Expected Payoff:**

This technological approach can be tailor-made to many civilian or military site-related problems. This approach will establish a new paradigm in adsorption technology -- i.e. disposal with adsorption without regeneration.

Impact: This technology will have far-reaching impact on particularly dilute contaminated matrices for which no inexpensive alternatives exist. In addition, this technology will allow resource recovery, when needed, from solid material such as uranium. Also, millions of dollars of DoD equipment can be protected from environment exposure. Life cycle cost can be reduced if the encapsulating material is recyclable.

**9. Milestones:**

1.	Develop QAPP (DoD)	05/95
2.	Develop QAPP (DOE)	08/95
3.	Screen sorbents (DoD)	08/95
4.	Evaluate polymer limitations	09/95
5.	Select sorbent (DoD)	05/96
6.	Produce copolymer (EPA)	06/96
7.	Compatibility Evaluation (DoD)	09/96
8.	Durability evaluation (DoE)	09/96
9.	Demonstration site selection	09/96
10.	Develop Demo, H&S, S&A plan	12/96
11.	Conduct demo	07/97
12.	Demo Report completion at DoD/DOE site	12/97

**10. Transition Plan:**

After 24 months technical support will be provided to build prototype for demonstration of technology at a DoD or DOE site.

**11. Funding: \$(K)**

EPA has already allocated \$100K towards basic research into low-cost adsorbents research. WES has spent this much on starch xanthates.

	FY94	FY95	FY96	TOTAL
SERDP	350	100	650	1100

## 12. Performers:

EPA Risk Reduction Engineering Laboratory (Sikdar, Barth); Cooperative research agreement with University of Arizona; and University of Cincinnati; Waterways Experimental Station

Mark Bricka, Ph.D., Waterways Experimental Station, 601-634-3700, Fax 601-634-3833

Brookhaven National Laboratory (Colombo, Kalb)

Peter Colombo, Head, Environmental and Waste Technology Center, BNL

516-282-7644, Fax 516-282-5305;

Paul Kalb, Group Leader, Waste Treatment and Disposal, BNL,

516-282-7644, Fax 516-282-5305

## 13. Principal Investigators:

Subhas K. Sikdar, Ph.D., Director

Water & Hazardous Waste Treatment Research Division, RREL

Edwin Barth, P.E.

Environmental Engineer

Center for Environmental Research Information

Risk Reduction Engineering Laboratory

Cincinnati, OH

PHONE: (513) 569-7528 FAX: (513) 569-7787 (Sikdar)

PHONE: (513) 569-7669 FAX: (513) 569 7585 (Barth)

E-MAIL: sikdar.subhas@epamail.epa.gov

### Sponsoring Organizations:

Jeffrey S. Walker

Program Manager

Office of Technology Demonstration

U.S. DOE

EM 542 Trevion II

1000 Independence Ave, SW

Washington, DC 20585

PHONE: (301) 903-7966

FAX: (301) 903-7457

Robert Scola

Director, Environmental R&D

Army Production Base

Modernization Activity

Bldg. 172 AMSMC-PB

Picatinny Arsenal

Dover, NJ 07806

PHONE: (201) 724-2044

FAX: (201) 724-4407

## 14. Keywords:

Adsorbents, Encapsulation, Recycled Plastics, Ligands, Metal-binding

## SERDP FY95 PROJECT

1. **SERDP Thrust Area:** Cleanup
2. **Title:** Encapsulated Bacteria for In Situ PAH Bioremediation
3. **Agency:** U.S. Navy
4. **Laboratory:** Naval Research Laboratory
5. **Proposal ID:** #23
6. **Problem Statement:**

This project addresses Requirement 1.I.4.m, and is for the continuation of an existing SERDP-funded project entitled "Encapsulated or Immobilized Enzymes, Bacteria and Nutrients for Remediation of Fuel Spills" and is applied research (6.2/6.3).

The soils and sediments at Naval refueling facilities are often contaminated with petroleum products that are classified as hazardous wastes. The petroleum products that remain as long term contaminants, include polycyclic aromatic hydrocarbons (PAHs; hazardous waste CFR# K001). Removal and cleanup of these materials is expensive and disruptive to Naval operations. Current methods for treatment of contaminated harbor sediments involve dredging with subsequent off-site detoxification. Development of remediation technologies that treat contaminated soils and sediments in situ, would save the Navy considerable expense and eliminate procedures disruptive to Naval operations.

This project addresses the SERDP goals of lowering environmental cleanup costs, compliance with environmental regulations, and unencumbrance of military operations. It focuses on the Thrust Area of cleanup of soil, sediment, groundwater, and subsurface water. The overall goal of this project is to develop an in situ treatment strategy using microencapsulated bacteria for low-cost bioremediation of petroleum products that are poorly degraded by naturally-occurring bacteria. In situ treatment strategies lower the cost over ex situ treatments by eliminating the need for expensive excavation, transportation, and storage of the hazardous waste prior to detoxification.

If successful, this treatment strategy may be useful for remediation of some toxic hot spots (PAH contamination) in San Diego Bay sediments. The magnitude of the problem, in terms of PAH contamination, is considerable as the sediment of nearly every harbor is contaminated from ship oil and creosote treatment of docks. In San Diego Harbor alone, nearly 4.5 million cubic yards of sediment is being dredged for Naval harbor deepening projects (e.g. carrier turnaround basin, Pier Bravo), with an expected 0.5 million cubic yards being too contaminated for oceanic dumping or beach replenishment projects. According to the San Diego Regional Quality Control Board, once sites in the Bay are declared 'toxic hot spots', dredging and off-site disposal will not be a legal means of detoxification as a precursor to harbor deepening. In lieu of effective in situ remediation technologies, such as this microencapsulated bacteria strategy, the Navy will either have to receive an exemption from the law (which may lead to public relations difficulties) or will have to limit access of Naval vessels to the base. These harbor and pier deepening projects should be considered

crucial for continued Naval vessel access to the base. Even if this proposed strategy is not successful at complete removal of the toxicant, treatment may lower PAH levels to the threshold that would allow for the dredging and further off-site cleanup of the sediment.

## 7. Project Description:

With previous SERDP funding, strains of petroleum-degrading bacteria were microencapsulated in an alginate matrix cross-linked with divalent cation bridges (calcium). The published system has been adapted using an internal set with solid calcium particles. As the calcium slowly solubilizes in the alginate matrix, the cross-links form which encapsulate the bacteria. This adaptation is expected to reduce ionic stress to the bacteria, resulting in increased encapsulation efficiencies and higher cell viability with long term storage. Higher encapsulation efficiencies and cell viability lowers the cost of the bioremediation treatment strategy.

For the bacterial microencapsulation strategy to be successful and low-cost, the conditions for encapsulation have been optimized to enhance cell viability and petroleum-degrading activity. By developing such a system, fewer microcapsules are needed per volume of treated material, thus lowering the overall treatment cost. Bacterial growth conditions prior to encapsulation have been examined for their effect on cell viability. In addition, the effect of various storage conditions (lyophilization, refrigeration, freezing) on cell viability of encapsulated bacteria was determined to enhance treatment effectiveness. These tasks address the primary environmental concern of ensuring the use of effective and affordable remediation technology.

Microencapsulation of petroleum-degrading bacteria allows for the storage and delivery of strains that are normally found in nature, but may be present in reduced abundance at the spill site. These strains were originally isolated from Superfund sites that were contaminated over decades with creosote. Over time, similar strains will increase in abundance at the spill sites resulting in eventual degradation of the petroleum, but this process may take fifty years or more. The goal is to use microencapsulated bacteria to reduce the contamination level over time scales of months instead of decades. This would reduce exposure of Naval personnel to toxic and carcinogenic waste, and enable the site to be used by either the Navy or the public sector within a reasonable time frame and at an acceptable cost.

Poor performance of in situ treatments involving the addition of bacteria have been due to the unknown effects of site conditions on the ability of bacteria to degrade contaminants. Naval Research Laboratory (NRL) is currently developing specialized indicator strains of bacteria that produce light in response to the presence of bioavailable polycyclic aromatic hydrocarbons (PAH). The indicator strains would enable us to predetermine, whether or not the appropriate nutrient and environmental conditions exist at a site making it amenable to the in situ treatment using microencapsulated bacteria. This system would allow us to alter the site conditions, with nutrients or buffers, prior to adding the bacteria. Though this project involves the construction of genetically engineered strains for assays, it does not involve the release of genetically engineered bacteria into the environment.

Previously, it has been demonstrated that disturbing contaminated soils has resulted in abiotic removal of the toxin from the site. These treatments have often erroneously been characterized as 'bioremediation'. To determine whether or not the microencapsulation

treatment is resulting in actual bacterial degradation of PAH at the site, newly developed molecular probing techniques (16S rRNA hybridization) will be used to identify the added PAH-degrading bacteria in the soils and sediments. These tasks address the primary environmental concern to implement affordable methods for site characterization, namely the field location and abundance of PAH-degrading bacteria.

The microencapsulated bacteria will be tested as a bioremediation strategy in model microcosm systems (5 liter) and subsequently in pilot-plant scale systems (100 liter). These series of tests will be designed to demonstrate the potential of employing microencapsulated PAH-degrading bacteria, along with essential inorganic nutrients and electron acceptors, as part of an in situ bioremediation strategy. Finally, the system will be field tested in coordination with an EPA project examining the use of stable isotopic methods for determining efficacy of bioremediation treatments. This important collaboration will help determine the effectiveness of microencapsulated bacteria at degrading PAH under field conditions.

## 8. Expected Payoff:

Using microencapsulated bacteria to detoxify a site of hazardous waste compounds would be a low-cost alternative to excavation and off-site treatment of contaminated soils. Aside from the lower cost of removal of PAH from Naval soils and sediments, an important aspect of the strategy is that Naval operations in the treated area are less disrupted when compared with treatment requiring excavation and off-site cleanup. It is exceedingly difficult to estimate the dollar value of this savings to the Navy. Also, because of the potential of causing collateral damage to areas adjacent to the treated area, there is sometimes no alternate ex situ treatment that can be used for cost comparison. In situations where soils and sediments are co-contaminated with heavy metals and PAH, removal of PAH allows for the immobilization of the metals with subsequent landfilling of the treated materials.

## 9. Milestones:

1.	Complete review of technologies	09/92
2.	Define and optimize microencapsulation procedures	05/93
3.	Coencapsulate nutrients	07/93
4.	Encapsulate densifying agents	08/93
5.	Optimize encapsulation for enhanced bacterial viability	11/93
6.	Completed development of microcapsule system	11/93
7.	Construct microcosm model testing system	11/93
8.	Perform bench top assays of petroleum degradation	03/94
9.	Scale up of 8 (microcosm model system)	06/94
10.	Complete development of indicator strain assay	06/94
11.	Evaluate molecular probe techniques for treatment efficacy in microcosm model	07/94
12.	Test treatment in second microcosm evaluation	10/94
13.	Treatment efficacy in model system	03/95
14.	Optimize treatment for test site field conditions	05/95
15.	Physical characterization of test site	07/95
16.	Field demonstration of treatment system	08/95
17.	Final report	09/96



**10. Transition Plan:**

The technology will be transitioned to the industrial collaborator, SBP Technologies, Inc. SBP and its parent company, Eicon, have the technology base and expertise and equipment necessary to use this treatment strategy for eventual cleanup of Naval sites. Their research facilities are on-site at the EPA's Gulf Breeze Environmental Research Lab in Pensacola, FL where they work on encapsulated and immobilized cell technologies for creosote degradation in bioreactors.

**11. Funding: \$(K)**

	FY92	FY93	FY94	FY95	FY96	TOTAL
SERDP	180	250	350	0	500	1480

**12. Performers:**

The lead organization is NRL Code 6900 (Center for Biomolecular Science and Engineering). The principal contractor is SBP Technologies, Inc. (POC: Dr. James Mueller). Development of methods for determining treatment efficacy is being coordinated with management of a SERDP funded project at EPA (POC: Dr. Raymond Wilhour, Gulf Breeze Environmental Research Lab, Pensacola, FL).

NRL: Dr. Bruce Gaber, Program Manager, Dr. Michael Montgomery, Environmental Microbiology, Mr. David Flaherty, Molecular Genetics

Collaboration with Industry: SBP, Technologies, Inc., Dr. James Mueller, PAH Bioremediation Ms. Susanne Lantz, Bioremediation.

Collaboration with EPA's Gulf Breeze Environmental Research Lab: Dr. Hap Pritchard, Branch Chief, Bioremediation and Risk Assessment, Dr. Richard Coffin, Microbial Ecology Group Head

**13. Principal Investigator:**

Dr. Bruce Gaber  
NRL Code 6900  
4555 Overlook Avenue  
Washington, DC 20375  
PHONE: (202) 767-3344  
FAX: (202) 767-1295

**14. Keywords:**

Bioremediation; Petroleum; PAH; Bacteria; In Situ.

## SERDP FY95 PROJECT

1. **SERDP Thrust Area:** Cleanup
2. **Title:** In Situ Bioremediation of Fuel and Efficacy Monitoring.
3. **Agency:** U.S. Navy
4. **Laboratory:** Naval Research Laboratory
5. **Project ID:** #30
6. **Problem Statement:**

This project (6.2/6.3) addresses Requirement 1.III.1.g & j. Contamination of soil, sediment and waters by fossil fuel-based contaminants represents the world's largest environmental problem. In the U.S., the frequency of occurrence of fossil fuel contamination is greater in magnitude than that reported for chlorinated solvent pollution. Given the scope and magnitude of these environmental contamination problems, bioremediation often represents the only practical and economically feasible solution. When depth of contamination or nature of contaminated material precludes all other remedial actions short of the no-response alternative, in situ treatments are frequently recommended. However, cost-efficient and effective implementation strategies need to be specifically developed and/or refined to address these needs. At the same time, unequivocal approaches for demonstrating in situ bioremediation of target contaminants need to be established.

With past support of the SERDP program we have developed and refined innovative in situ bioremediation strategies including approaches using stable carbon and nitrogen isotope geochemistry to monitor progress during in situ bioremediation of polycyclic aromatic hydrocarbons (PAHs) and other priority pollutants (e.g., BTEX). Approaches in stable isotope geochemistry may allow one to monitor progress of the bioremediation effort by tracing the fate of individual compounds of interest: including bacterial assimilation and respiration, formation of toxic intermediates, and transport of the compound from the site. With this information, a mass balance for a contaminant may be conducted and efficacy of various bioremediation approaches may be tested.

To establish tests using stable isotopes as a monitoring protocol for bioremediation, SERDP has funded researchers at Gulf Breeze Environmental Research Laboratory (GBERL), Texas A&M University (TAMU), Naval Research Laboratory (NRL) and SBP Technologies, Inc. (SBP) to setup stable isotope laboratories and to conduct preliminary experiments. The objective of the current proposal is to transition this 6.2/6.3 research, through a series of field demonstration programs, yielding valid, cost-efficient technologies for in situ bioremediation and on-line performance monitoring. A coordination plan, not included herein, with CU-720 (Integrated Biotreatment Research Program-Army), CU-428 (Ground Water Cleanup) and CU-723 (National Environmental Test Site Program). Sites included in CU-723 will be included in the project.

## 7. Project Description:

Collaborating researchers at the GBERL, NRL, SBP, and TAMU received SERDP funds in June of 1993. The progress of these collaborations to date is as follows. Two laboratories have been equipped with elemental analyzer/ gas chromatograph/ isotope ratio mass spectrometers (EA/GC/IRMS). One system at TAMU is dedicated to measuring natural abundance stable isotope ratios. The other system at GBERL is set up for experiments with tracer additions of stable isotopes. Each is equipped so that carbon, nitrogen and sulfur isotope ratios may be measured as gases, gross organic matter or as individual compounds. One is also equipped with an ion trap mass spectrometer (ITMS) to assist with compound identification. This addition will make it possible to follow intermediate compounds during the degradation process.

The development of methods to measure bioremediation effectiveness involved the in situ degradation of PAH mixtures in lab systems. Drs. Cifuentes and Coffin have been measuring the natural abundance carbon isotope ratio of CO<sub>2</sub> that is evolved upon degradation of various mixtures of compounds. Results indicate a direct correspondence of the stable carbon isotope ratio of CO<sub>2</sub> and the carbon source that is respired by bacteria. This information suggests that on-line monitoring of CO<sub>2</sub> carbon isotope ratios will be appropriate for examining, monitoring and evaluating the bioremediation of contaminant mixtures.

Along with the development of stable isotope monitoring tools, SBP has integrated innovative technologies and support from various other industrial collaborators (i.e., Beazer East, Inc., Chevron, IEG Technologies, Inc.) to yield full-scale and practical applications for in situ bioremediation strategies. Various modifications of in situ soil flushing, aeration, and groundwater circulation technologies have proven effective for simultaneous treatment of vadose/phreatic zone soil, capillary fringe, groundwater and saturated soil contaminated with refined petroleum products at over 100 sites world-wide. However, successful application to environments contaminated with more biologically persistent compounds, such as jet fuel constituents and certain PAHs, has been somewhat limited. Presently, there are few examples of successful in situ bioremediation projects in the technological database. Moreover, trial demonstrations of more conventional bioremediation approaches, such as hydrogen peroxide injection and pump-and-treat technologies, have met with limited success in their applications to PAH contaminated environments. Two key factors responsible for this poor performance are bioavailability and presence of PAH-degrading microorganisms.

The program objective is to demonstrate the usefulness of innovative in situ bioremediation technologies by introducing inoculants and maintaining their activity in the field. The project approach is to develop the treatment strategy, identify the contaminated site, employ the biotreatment in small-scale laboratory tests, and finally in a large-scale field demonstration. This project has three unique thrust areas: development of techniques for measuring effectiveness of bioremediation treatments; integration of multiple technologies for treatment strategy; and, use of bacterial encapsulation and inoculation for enhancement of PAH degradation in the field. Laboratory studies will model the biodegradation of individual chemicals by axenic bacterial cultures available in our culture collections. The studies will be used to measure biodegradation rates, identify catabolic intermediates, assess the formation of toxic end-products, and perform mass balances of the contaminant under controlled and defined conditions. Similar studies will be conducted with field samples to define the fate and effect of parent compounds and biotransformation products for mass balances.

Activity and survival of microencapsulated PAH-degrading bacteria will be characterized. For example, new, more efficient strains may be encapsulated and applications for different environments will be considered. Researchers at NRL will examine a series of microbially produced biosurfactants for use in the enhancement of degradation of PAHs bound to soil and sediment surfaces. The optimal conditions for production of biosurfactants in field systems will also be determined. Successful completion of this task would expand the use of the well treatment system to include PAH remediation in soils. Under a separate task, NRL will continue to lead the development of indicator strains of bacteria that will enable us to better monitor successful bioremediation attributable to the introduction of encapsulated microorganisms.

Samples of contaminated soil will be thoroughly characterized according to standard methods. Contaminants will be extracted, fractionated and chemically analyzed: the natural abundance isotope ratios of these materials will be determined. These values will be compared with those for indigenous carbon sources (i.e., humic materials, humin, fulvic acid, et cetera). Knowing these values, mineralization of contaminants will be assessed by the  $^{12}\text{C}/^{13}\text{C}$  ratio of liberated  $\text{CO}_2$ . These values will be compared with those generated using more conventional chemical and biological analyses. The effect of various amendments on contaminant degradation by naturally-occurring bacteria will be determined.

Mesocosms will be constructed to conduct studies examining the ability of in situ soil flushing and groundwater circulation well (GCW) technology, combined with subsurface bioreactors employing co-immobilized biodegradation agents to biodegrade PAHs. The mesocosms will be loaded with aquifer material artificially contaminated with a known amount of pollutant. The system will be monitored using on-line measurements of microbial respiration, water movement, etc. Stable isotope analyses will help monitor environmental fate of transformed chemicals. This test system will allow for mass balance chemical analyses to document biodegradation of target compounds using these stable isotope techniques. As recommended by the SERDP Science Advisory Board (SAB), field-scale demonstrations will be conducted at five or more contaminated sites to test the efficacy of the monitoring technology across five different remediation strategies. Sites will be offered through collaboration with Chevron (refined petroleum products), Beazer East, Inc. (creosote), and the Navy (jet fuel). Sites will be characterized and the bioremediation process will be monitored for 2 years. Field work will be conducted to use natural abundance stable carbon isotope ratios of  $\text{CO}_2$  to measure the degradation of PAH mixtures. This work will involve surveys of natural abundance isotope ratios of pollutant compounds, extracted mixtures of pollutants, indigenous/natural organic matter, PAHs and  $\text{CO}_2$  evolving from field sites. "CO<sub>2</sub> collection chambers" will collect gases from soil or groundwater wells thus providing on-line, real-time analysis of bioremediation performance.

## **8. Expected Payoff:**

Techniques for assessing efficacy of remedial technologies are critically needed. Such tools are essential to help ensure that the efforts undertaken are effective and that the remedial technologies are implemented in a cost-efficient manner. Using conventional chemical and biological assays in combination with the proposed on-line stable isotope analyses developed here, offers an ability to follow assimilation, respiration, immobilization, transport and biotransformation of pollutants in situ. The payoff is development of the first unequivocal assessment of treatment efficacy for in situ bioremediation strategies.

## 9. Milestones:

1.	Program start	10/94
2.	Initiate Port Hueneme site	12/94
3.	Port Hueneme sampling	01/95
4.	Start-up mesocosm	05/95
5.	Gainsville sampling	05/95
6.	Complete stable isotope efficacy studies	06/95
7.	Port Hueneme sampling	07/95
8.	Initiate Tyndall site	08/95
9.	Gainsville sampling	09/95
10.	Initiate S. Cavalcade site	10/95
11.	Port Hueneme sampling	10/95
12.	Complete biometer GC-IRMS interface	01/96
13.	Complete mesocosm experiments	02/96
14.	Complete biosurfactant work	03/96

## 10. Transition Plan:

Rapid and successful transition of developed technology from demonstration stage to full-scale implementation is enhanced through the active participation of SBP Technologies, Inc. (an EICON Company) and other industrial affiliates (IEG Technologies, Inc.). EICON is a holding company for 85+ professionals employed by: 1) SBP (remedial services, technology development), 2) Environmental Laboratories, Inc. (site characterization, engineering, analytical testing and services), 3) FGA Services, Inc. (civil and public works engineering), 4) FGA Surveys, Inc. (land surveying capabilities, engineering), 5) Ver-Val Environmental Enterprises, Inc. (mechanical engineering, fabrication, and general environmental services); and 6) Westcott & Mapes, Inc. (architectural and engineering services). EICON has over 20 years of experience in environmental services and engineering. With a number of dedicated end-users (i.e., Beazer East, Inc., Chevron) active in this and previous stages of technology development, we are convinced that we have integrated expertise in all aspects of technology development, commercialization and full-scale implementation of systems.

## 11. Funding: \$(K)

	FY94	FY95	FY96	TOTAL
SERDP	2455	850	700	4017

## 12. Performers:

NRL, EPA GBERL, TAMU, SBP

**13. Principal Investigator:**

Capt. Warren Schultz  
Naval Research Laboratory  
Code 6106  
4555 Overlook Avenue  
Washington, DC, 20375-5348  
PHONE: (202) 767-0192  
FAX: (202) 404-7139  
E-MAIL: WSCHULTZ@CBMSE.NRL.MIL

**14. Keywords:**

Cleanup, bioremediation, fuels, bacteria, in situ.

## SERDP FY95 PROJECT

- 1. SERDP Thrust Area:** Cleanup
- 2. Title:** Air Sparging and In-Situ Bioremediation Research and Demonstration
- 3. Agency:** U.S. Army
- 4. Laboratory:** Picatinny Arsenal, New Jersey
- 5. Project ID:** #744
- 6. Problem Statement:**

**Goal:** Bioremediation enhancement to air sparging technology may provide a cost effective strategy for removing trichlorethylene (TCE) and related chlorinated solvents from ground water. However, unresolved technical issues focus on quantifying the incremental benefit and designing efforts to stimulate microbial degradation. The overall goal of Phase I of this project is to develop laboratory and field methods for determining the effect of sparge gas-composition on the partition of mass removal due to volatilization and microbial processes. The methods will be demonstrated at Picatinny Arsenal, New Jersey, a site with a well-characterized plume of TCE contamination. Phase II of the project will involve the design and operation of a full-scale sparging/bioremediation demonstration at Picatinny Arsenal based on the findings of Phase I. The overall project will resolve technical and institutional issues that inhibit operational use of the technology.

**Background:** Air-sparging and coupled in-situ bioremediation has been implemented at the Savannah River site. The Savannah River Project was designed as a scientific demonstration. In addition, the site is characterized by specific geochemical conditions, most notably, the plume was aerobic. An anaerobic contaminant plume, like the one at Picatinny Arsenal, is perhaps more typical of TCE plumes, and introduces questions related to the rate of adaption of the microbial consortium and engineering considerations related to induced precipitates.

TCE is the dominant contaminant in a plume within an unconfined glacial aquifer at Picatinny Arsenal. The unconfined aquifer is about 50 feet thick in the vicinity of the contaminant plume. In 1991, the highest measured concentration of TCE was 21,000 micrograms per liter. In 1986, the site was selected by the USGS Toxic Substances Hydrology Program as its research site chlorinated solvents. Research includes characterization of TCE, related contaminants, and contaminant geochemistry in the aquifer and the unsaturated zone, and fate and transport evaluation. The Army has initiated an interim action under CERCLA to contain and treat the plume by pumping before it enters a continuing source of contamination may necessitate that the pump and treat operation continue indefinitely. The enhanced sparging technology could mitigate this condition.

## 7. Project Description:

Technical Objective: The objective is to develop methods to quantify the total rate of removal of TCE contaminant for an air sparging remediation system adapted to enhance contaminant removal with aerobic cometabolism. The total rate of removal is the sum of a component due to physical stripping (volatilization) and a component due to aerobic cometabolism. Both components will be quantified to allow for an evaluation of the cost effectiveness of the microbial enhancement. The methods are to be demonstrated at an existing site of TCE contamination and in the laboratory with porous media collected from the site.

Technical Approach: The workplan has three major components: (1) development of methods to conduct sparging/cometabolism laboratory experiments with contaminated sediment, (2) application of overall method to pilot scale experiments at Picatinny Arsenal, and (3) development of a mathematical model to analyze the transport of sparged vapor phase constituents from the water table to extraction wells for the purpose of determining the distribution of mass flux across the water table.

Site geochemistry will be monitored to assess initial conditions with respect to a wide range of inorganic and organic solutes. Initial site assessment will also include analysis of sediment cores to define lithology, total contaminant mass, physical characteristics, and selected microbial guild characterizations.

Laboratory experiments will be conducted with sediment collected during the site assessment described above. Two types of experiments will be conducted: closed systems microcosm experiments and open system column experiments. The microcosm experiments will determine the feasibility of aerobic cometabolism over the range of anticipated geochemical conditions and methane concentration. The open column experiments will allow for emulation of the field experiments under controlled conditions. Cores of sediment taken from the Picatinny site will be instrumented for the columns. Control experiments conducted with pure nitrogen as the sparge gas will provide physical removal rate information to be compared with experiments conducted with sparge gases with various methane and oxygen concentration. These experiments will allow for quantification of the effect of varying design parameters on system performance. The information obtained for the Picatinny sediment will allow for the rational design of pilot-scale experiments.

Pilot scale sparging experiments will be conducted at Picatinny Arsenal within the well-characterized site. The purpose of these experiments is to apply the overall method in-situ and to demonstrate the scaling up of laboratory information and application of the mathematical model (discussed below). The experiments will be conducted with a single sparge well. Mass removal rates will be calculated by collecting vapors with a vapor extraction well and analyzing the exhaust stream for a wide suite of vapors, including TCE and related contaminants, methane as well as signature gases like carbon dioxide, oxygen, and hydrogen sulfide. The monitoring will allow for separation of removal into a physical volatilization component and into a microbial component inferred by stoichiometric relationship to signature gases. It is anticipated that the experiment can be repeated at the same location to study variable injection rates and methane loading after a time interval passes which allows for the recontamination of the sparged column from surrounding ground water. It is anticipated that pilot scale experiments can be by-passed in subsequent operational applications of the technology.



A mathematical model of the vapor extraction process will be constructed to determine the spatial effect of the sparge well by allowing for the calculation of constituent-specific mass flux across the water table to the extraction well. Reactions that occur in the unsaturated zone while TCE, methane and oxygen are in transit to the extraction well(s) will also be simulated. This model is currently under development at USGS. It will be completed, applied, and published as a public domain code during this project.

### 8. Expected Payoffs:

- (1) Development of methods for performance evaluation and development of design criteria for air sparging with bioremediation enhancement.
- (2) Demonstration of methods at a site with geochemical conditions different than previously investigated at Savannah River.

### 9. Milestones:

1.	Project start	02/94
2.	Finalize work plan, finish literature search	05/94
3.	Begin instrumenting site. Site assessment	05/94
4.	Begin laboratory microcosm experiments	07/94
5.	Begin air-permeability tests	09/94
6.	Complete air-permeability tests	12/94
7.	Finish site assessment/instrumentation	02/95
8.	Begin field air sparging experiments	04/95
9.	Begin field cometabolism experiments	10/95
10.	Start laboratory column experiments	03/95
11.	Complete laboratory column experiments	03/95
12.	Finish laboratory column experiments	03/96
13.	Complete field cometabolism experiments	03/96
14.	Final report	12/96

### 10. Transition Plan:

The subject technology, which was developed under a DOE program, will be implemented at a DoD site under regulatory auspices of the U.S. Environmental Protection Agency and the New Jersey Department of Environmental Protection and Energy. Appropriate aspects of the project will be published in peer review journals.

### 11. Funding: \$(K)

	FY94	FY95	FY96	TOTAL
SERDP	557	271	321	1149

## **12. Performers:**

U.S. Army - Coordinate contractor procurement and regulatory compliance

U.S. Geological Survey - responsible for conducting Phase I research

Private Contractor - assist in the design of vapor extraction system and development of unsaturated zone transport model in cooperation with U.S.G.S.

Hazardous Substance Management Research Center (HSMRC) - coordinate and chair expert advisory panel which will provide technical oversight

Expert Advisory Panel:

Dr. Richard Brown - Groundwater Technologies Inc., Princeton, N.J.

Dr. Peter Jaffe - Dept. of Civil Engineering, Princeton University

Dr. Peter Lederman - Director, Center for Environmental Engineering and Science, N.J. Institute of Technology

Dr. Brian Looney - Westinghouse Savannah River, Aiken, S.C.

Dr. John Wilson - USEPA, Kerr Research Lab, Ada, Oklahoma

## **13. Principal Investigators:**

Mr. Jeffery M. Fisher

U.S. Geological Survey

810 Bear Tavern Road

West Trenton, N.J. 08628

PHONE: (609) 771-3953

FAX: (609) 771-3915

E-MAIL: fischer@usgs.gov

Mr Thomas Solecki

ARDEC, ATTN: SMCAR-SEA, Bldg. 1

Picatinny Arsenal, N.J. 07806-6582

PHONE: (201) 724-5818

FAX: (201) 724-6582

## **14. Keywords:**

Air Sparging, TCE, Chlorinated Solvents, Bioremediation Enhancement, Ground Water Remediation

## SERDP FY95 PROJECT

1. **SERDP Thrust Area:** Cleanup
2. **Title:** Explosives Conjugation Products in Remediation Matrices
3. **Agency:** U.S. Army Corps of Engineers
4. **Laboratory:** USAE Waterways Experiment Station (WES)
5. **Project ID:** #715

### 6. Problem Statement:

During investigations of potential treatment technologies for explosives contaminated soils, specifically during bioslurry treatability studies and composting, TNT has been observed to interact with some component of the treatment matrix in such a way as to preclude extraction with organic solvents. Similar interactions have been observed in explosives amended soils. Mass balance determinations using radiolabelled TNT reveal that the radioactivity is still present in the matrix in some unknown form. As much as 80 percent of the radioactivity added to tests is accounted for in the unextractable matrix. Therefore, the parent compound has not been completely destroyed, but has changed to a more complex form. The long-term stability and environmental safety of these uncharacterized conjugates are unknown. Objectives of this basic research include characterization of these explosives conjugates, development of an analytical methods for identifying them in treatment systems and in soils, and determining the long-term stability and environmental safety of the conjugates. Accomplishment of these objectives will ensure the development of effective remediation technologies that ameliorate environmental health effects and lead to a more complete characterization of the end products of new treatment technologies. Research was initiated to determine the basic mechanisms of interactions between TNT and humus, soil enzymes and clays under SERDP in FY 93. This proposed research would expand upon that effort.

### 7. Project Description:

The project will consist of five tasks as follow:

- Task 1: Characterization of interactions of explosives with humus and other organic components of soils and remediation matrices.
- Task 2: Characterization of interactions of explosives with clays and other mineral components of soils and remediation matrices.
- Task 3: Development of an analytical method for identifying conjugates in various matrices.
- Task 4: Determination of the role of microbiological processes in formation and stability of conjugates.
- Task 5: Assessment of the ecotoxicology of conjugates.

The ability of explosives to form conjugates with soil organic fractions (i.e., humin, humic acids, fulvic acids, and enzymes such as peroxidase, laccase, and tyrosinase), clays (i.e., montmorillonites and kaolinites), and other mineral components of remediation matrices (i.e., oxy/hydroxy compounds of iron and other minerals) will be evaluated. The influence of environmental factors such as temperature, Ph and moisture regimes on development and characteristics of conjugates will also be determined. Classical extraction and analytical techniques have been ineffective in removing and describing these unextractable conjugates. Therefore, innovative analytical techniques such as surface plasmon resonance, microcalorimetric titration, and new application of high performance liquid chromatography, X-ray diffraction and nuclear magnetic resonance will be applied. The role of microbial processes in the formation of the conjugates through precursor compounds or conjugation of explosive to microbial cell walls will be investigated. Factors affecting stability of the conjugates to leaching and microbial degradation will be determined.

Characterization of the ecotoxicology of conjugates answer the question of whether conjugates in soils and remediation matrices are environmentally compatible. An appropriate bioassay/biomarker suite will be selected based on the chemical nature of the parent compounds, the conjugates, and the potential functional groups present in metabolites. The potential for reappearance of toxicity from hydrolysis and re-release of parent compound or from the formation of toxic metabolites will be investigated. Microbial mutagenic and cultured cell line *in vitro* assays, and whole organism adult and early life-stage bioassays will be used. The influence of environmental factors on bioavailability and on the time course of toxic potency will be determined.

Specific user requirements that will benefit from performance of this work include:

- (1.I.1.b) Technology for removal of energetics/other organics contamination (A,N)
- (1.I.4.c) Decontamination of soils containing energetic materials (A,N,AF)

## 8. Expected Payoff:

This study will improve existing and future remediation technologies by identifying the composition and potential environmental impacts of explosives conjugates. The credibility of several existing technologies will be enhanced with regulatory agencies and with other users who are concerned with the ultimate safety and environmental effects of explosives. An understanding of the nature and properties of conjugation products formed during remediation and their fate and effects may also lead to new approaches to remediation.

## 9. Milestones:

- |    |   |       |
|----|---|-------|
| 1. | Evaluate dialysis methods for assessing interaction with soil organic components (Natick)         | 03/95 |
| 2. | Evaluate extraction and/or derivitization techniques for analytical methods development (CRREL)   | 07/95 |
| 3. | Determine degradation rates for soil fractions containing explosives conjugates (WES)             | 09/95 |
| 4. | Evaluate nuclear magnetic resonance techniques for determining interactions with clays (WES)      | 09/95 |
| 5. | Select bioassay/biomarker toxicity tests for determining environmental safety of conjugates (WES) | 03/95 |

- |     |  |       |
|-----|--|-------|
| 6.  | Evaluate surface plasmon resonance for measuring binding kinetics of organic conjugates (Natick) | 03/96 |
| 7.  | Develop extraction and analysis procedures (CRREL)   | 09/96 |
| 8.  | Characterize products of microbial degradation (WES)   | 09/96 |
| 9.  | Evaluate effects of clay type on interactions with explosives (WES)                              | 09/96 |
| 10. | Determine microbial mutagenicity and conduct <i>in vitro</i> assays (WES)                        | 09/96 |
| 11. | Determine conjugation kinetics (Natick)  | 09/97 |
| 12. | Determine precision and accuracy of analytical method in various matrices (CRREL)                | 06/97 |
| 13. | Identify factors controlling biodegradation of conjugates (WES)                                  | 09/97 |
| 14. | Determine bioavailability of explosives after interaction with clays                             | 09/97 |
| 15. | Conduct whole organism and early life stages bioassays (WES)                                     | 09/97 |
| 16. | Characterize organic conjugates from natural soils (Natick)                                      | 09/98 |
| 17. | Determine ruggedness of analytical method (CRREL)  | 09/98 |
| 18. | Determine environmental factors affecting interactions with clays (WES)                          | 09/98 |
| 19. | Determine effects of environmental factors on toxicity (WES)                                     | 09/98 |

### 10. Transition Plan:

Those who are developing remediation technologies will have access to results and their implications for 6.2 and 6.3a levels as they are developed through conference presentations and published reports. Direct interactions between principal investigators of this project and other relevant projects under Environmental Quality and Technology Program 6.2 remediation technology work units and SERDP work units will be initiated in the form of briefings and informal discussions.

### 11. Funding: \$(K)

	FY94	FY95	FY96	FY97	FY98	TOTAL
SERDP	500	146	0	500	500	1646

### 12. Performers:

The lead laboratory for the proposed research is the U. S. Army Engineer Waterways Experiment Station who will be responsible for completion of Tasks II, IV and V. The U. S. Army Natick Research, Development, and Engineering Center will conduct Task I and contribute to Task II. The U. S. Army Cold Regions Research and Engineering Laboratory will conduct Task III. At least one cooperative agreement with a university is anticipated.

### **13. Principal Investigators:**

Judy Pennington (Sr Principal Investigator)  
Douglas Gunnison, and Vic McFarland  
U. S. Army Engineer Waterways  
Experiment Station  
3909 Halls Ferry Road  
Vicksburg, MS 39180-6199  
PHONE: (601) 634-2802, -3873, and -3721  
FAX: (601) 634-3120  
E-MAIL: pennij@exl.wes.army.mil

Thomas Jenkins  
U. S. Army Cold Regions Research and  
Engineering Laboratory  
72 Lyme Road  
Hanover, NH 03755  
PHONE: (603) 646-4385  
FAX: 603-646-4644

David Kaplan  
U. S. Army Natick Research  
Development, and Engineering Center  
Natick, MA 01760-5020  
PHONE: (508) 651-5525  
FAX: (508) 651-5521

### **14. Keywords:**

explosives, conjugates, remediation, analytical methods, toxicology, microbiology

## SERDP FY95 PROJECT

1. **SERDP Thrust Area:** Cleanup Thrust Area
2. **Title:** Integrated Biotreatment Research Program: From Flask to Field
3. **Agency:** US Army
4. **Laboratory:** USAE Waterways Experiment Station (WES)
5. **Project ID:** #720
6. **Problem Statement:**

The DoD has literally thousands of sites that are contaminated with organic compounds that pose a serious threat to the environment on land entrusted by the public to be properly maintained by the DoD. As part of the realization by DoD of its responsibility toward cleanup of the numerous sites contaminated from past military activities, the majority of these sites are slated for cleanup (remediation). Unfortunately, the remediation of these sites using existing technologies is problematic from an economic, technical, and political point of view. Current technologies for soil and groundwater are incineration and phase change technologies (activated carbon and air stripping), respectively. The projected costs associated with site restoration using these current technologies are astronomical. All too often because of these high costs, landfilling is selected instead of true on-site remediation. From a technical point of view, phase change technologies do not result in the on-site destruction of the contaminants posing serious disposal and transportation problems. Politically, siting of an incinerator is a publicity nightmare. Also, the US Environmental Protection Agency (USEPA) and DoD is encouraging strong investment and application of innovative technologies. Of all the innovative technologies under development and in some cases, application, biotechnologies are considered by most remediation experts to be the most promising.

Biotreatment processes have been successfully demonstrated for treatment of a variety of contaminants. Research, regulatory, and user communities collectively agree that biotreatment of easy-to-degrade compounds, such as fuels and simple phenols, are established processes. Based on the success of these biotreatment applications, a strong potential exists for development of biotreatment processes with expanded application toward more difficult to degrade contaminant groups such as explosives, chlorinated solvents, polychlorinated biphenyls (PCBs), and carcinogenic (heavy) polycyclic aromatic hydrocarbons (cPAHs). Several governmental and academic research groups are currently investigating biotreatment techniques for treatment of these traditionally difficult to degrade contaminants. Although a high potential exists for development of vastly improved remediation techniques using biological processes for remediation of media contaminated with these compounds; unfortunately, sporadic and often sparse funding and inaccessibility to actual sites have severely hindered process development. Other factors contributing to the delay of process development include poor intercommunication between research groups, the lack of design and application engineering input into research plans, and poor technology transfer to applied research and technology user groups.

This program is proposed as a 6.2 program that will enhance, but not duplicate, existing funded efforts in the DoD STRAT Plan. This program also fits nicely into USEPA's long-term research plans. The following DoD user requirements will be met or partially met by performance of this R&D program:

- 1.I.1.f. Treatment system for water contaminated with organic contaminants.
- 1.II.1.a. Improved fate, effects, and transport models for groundwaters.
- 1.I.1.g. Treatment system for water contaminated with chlorinated and defense hydrocarbons.
- 1.I.1.j. Treatment of Navy relevant contaminants in salt/brackish/groundwater matrices.
- 1.I.6.c. Isolation and treatment technology for contaminated surface water impoundments.
- 1.I.1.h. Treatment system for water contaminated with mixtures of chlorinated solvents.
- 1.I.1.e. Process to remediate groundwater contaminated with hydrocarbon fuels.
- 1.I.4.c. Decontamination of soils containing energetics materials.
- 1.I.2.i. Contamination under buildings and roads.
- 1.I.4.n. Remedial treatment technology for soils contaminated with chlorinated and non-chlorinated organics.
- 1.I.3.a. Technologies for isolation and decontamination of sludges.
- 1.I.2.b. Dredged soil area decontamination and reclamation.
- 1.I.2.e. Improved marine sediment remediation technologies for metals, organics, and PCBs.
- 1.I.6.d. Improved shore and open Ocean hazardous materials cleanup/restoration.
- 2.III.1.d. Enzyme and bacterial treatment technology.
- 1.I.4.c. Decontamination of soils containing energetic materials.
- 2.III.2.d. Improved cleanup procedures at locations where UST leaked.

## **7. Project Description:**

This project represents a collective research initiative by several key governmental and academic organizations with a long history of developing treatment technologies. All of the partnering organizations are bringing into the initiative not only experience, but additional funding and experimental resources that will be "dovetailed" into this comprehensive program. The partnering approach proposed will ensure that appropriate scientific and engineering disciplines interact to form a formidable research team of a magnitude never attempted within the DoD environmental biotreatment research program. The project will be approached through investigation of several primary technical issues. The level of research effort expended on each issue will vary depending on state of the art for that issue. The ultimate goal of this program is to perform research efforts that will result in the fielding of several biotreatment processes for remediation of predominant DoD contaminants.

The proposed experimental approach will be to first investigate a variety of promising biotreatment techniques at the bench scale. During performance of bench activities, engineers with design and implementation experience (the Baltimore COE District) will assess the overall implementation potential and projected costs associated with these techniques. This effort will ensure that the research groups are developing processes that are realistic and on firm technical ground. Upon completion of the bench efforts several small scale pilot studies (referred herein as intermediate scale) will be performed using those techniques considered most promising. After performance of the intermediate scale studies, at least four of the most economically and technically sound processes will be evaluated on the field pilot scale at actual DoD sites.



The primary technical issues to be addressed in this research initiative are listed and briefly discussed below:

Issue I. Biotreatment of Explosives Contaminated Soils and Groundwaters. A variety of promising biotreatment techniques will be investigated for remediation of soil and groundwater contaminated with explosives compounds. Explosives contamination represents one of the most prevalent organic contamination within the DoD. Although research into the feasibility of biotreatment of explosives has been undertaken by both DoD and USEPA over the last few years, funding limitations and the lack of a comprehensive research approach have hindered significant advances toward the field scale. The following biotreatment mechanisms will be investigated for explosives:

- a. Enzymatic degradation performed under a variety of controlled systems. Controlled enzyme manufacturing methods will also be investigated.
- b. The use of specialty surfactants, both manufactured and natural, will be evaluated for their ability to enhance the bioavailability of the explosives compounds to the microbial populations during treatment.
- c. The metabolic pathways and biodegradation of key intermediates.
- d. Alternating redox conditions and techniques for establishment of either condition within an active bioreactor system.
- e. The use of genetically altered microorganisms as reactor seeds.

Issue II. Soils and Groundwaters Contaminated with Chlorinated Solvents. Chlorinated solvents represent a class of contaminants that is detected at more DoD sites (and CERCLA and RCRA sites for that matter) than any other contaminant group. Several significant breakthroughs in the biological degradation of these compounds have been made over the last several years; however, limited funding and access to contaminated sites has hindered further development. Issues under investigation for chlorinated solvents within this program include:

- a. Bioventing of chlorinated solvents using aliphatic oxygenase pathways via addition of simple aliphatic gases (i.e. propane, methane, etc.).
- b. Evaluation and modeling of enzyme production and substrate interactions.
- c. Anaerobic biodegradation in aqueous and soil phase systems.
- d. The impact of co-distributed solvents on biodegradation rate.
- e. Bioslurry treatment using process air recirculation.

Issue III. Soils and Sediments Contaminated with PCBs. Soils and sediments contaminated with PCBs represent one of the most challenging compound groups under investigation in this project; yet, development of a viable biotreatment process could result in significant savings to the DoD. PCBs are found at many DoD installations due to improper disposal of hydraulic fluids and waste lubricating oils. Primary issues under investigation are:

- a. Degradation and production kinetics of enzyme based degradation.
- b. Cycling of redox conditions from anaerobic to aerobic as a means of dechlorinating higher substituted Aroclors into lower substituted, easier to degrade Aroclors.
- c. Use of surfactants both natural and manufactured as a means of enhancing bioavailability during biological treatment.

- d. An evaluation of candidate cometabolites for enhanced degradation of selected PCB Aroclors.
- e. Use of genetically altered microorganisms as potential seed sources.
- f. The impact of other co-distributed contaminants, such as petroleum hydrocarbons, on PCB biodegradation.
- g. Evaluation of various natural isolates and consortia toward PCB biodegradation using a variety of biotreatment systems.

Issue IV. Soils Contaminated with cPAHs. This group of contaminants represent the most regulated of PAH compounds due to their carcinogenic properties. Also, because of their large and complex molecular structure, they also represent the most difficult of all the PAHs to biologically degrade. Key research issues are:

- a. Surfactant, both natural and manufactured, for enhancing biodegradation rate in a variety of biotreatment systems.
- b. Evaluation of candidate cometabolites for initiating and economically maintaining effective cPAH biodegradation rate.
- c. Use of genetically altered organisms for enhancing biodegradation.
- d. Cascading aerobic bioslurry treatment.
- e. Composting techniques for degradation of highly complex cPAH contaminated matrices.
- f. Evaluation of various natural isolates and consortia activity toward cPAHs under a variety of implementation scenarios.

Issue V. Development and Design of Specialty Reactors. Many of the biological systems required for implementation of concepts under development in this project require specialty reactors. Periodically, the results of the various contaminant specific activities will be reviewed for determination and selection of appropriate implementational strategy and respective reactor type. As expected, the actual reactor designs will be governed by the breakthroughs and conditions dictated by the results of the above listed study issues. Expected reactor designs that are to be developed are:

- a. Zero-head aerobic bioreactors which utilize hydrogen peroxide as an alternative oxygen source.
- b. Evaluation of solid and semi-solid oxygen sources for both *in situ* and *ex situ* strategies.
- c. Cascading bioslurry systems (as mentioned above in the cPAHs section).
- d. Improved process gas recirculation systems for treatment of contaminated media containing volatile compounds such as chlorinated solvents.
- e. Side-stream dual aerobic reactor systems for treatment of refractory compounds and low level contaminated groundwaters.
- f. Evaluation of low carbon loaded attached growth systems for treatment of low level contaminated groundwaters.
- g. Development of biocells as an economically attractive reactor option.

Issue VI. Applications Potential of Genetically Engineered Microorganisms. Although science is rapidly approaching the time when genetically altered organisms may play an important part in future bioremediation processes; unfortunately, the political and social implications surrounding these organisms may hinder implementation of these organisms

into reactors. This project will assess and identify problems associated with implementation of engineered organisms. A logical plan of action in terms what actions may be taken to accelerate and enhance the use of these microorganisms will be drafted.

Issue VII. Toxicity Reduction. The success of treatment will be assessed on processes selected for intermediate scale evaluation using a variety of toxicological assays used to properly quantify toxicity reductions.

### **8. Expected Payoff:**

The primary benefit of this study is reduced remediation costs associated with development of "realistic" biotreatment processes for cleanup of contaminated DoD sites. Projected treatment costs are expected to fall at or below the \$150 per cubic yard of soil treated (incineration costs are usually above \$350/cy) or \$1.00 per thousand gallons of groundwater treated (carbon costs are usually greater than \$1.00/Kgal). Secondary benefits include; expanded implementation potential of existing and developing biotreatment processes, biotreatment technologies that result in the on-site destruction of contaminants, increased regulatory and political acceptance of DoD cleanup activities will be realized as these technologies are used, and increased user acceptance of the technologies will be realized because of the involvement of the user community (COE-Baltimore District) within the project structure.

### **9. Milestones:**

Major milestones for this program are listed below. For each milestone listed at least a WES report will be drafted by the performing research group; however, each partner involved in the milestone will be encouraged to publish the report under their agency framework to accelerate transfer of information to the user community. The primary, completion based milestones (assuming a two year FY funding life) are:

1.	Biocell field pilot scale study	9/95
2.	Low level organic loaded bioreactor field pilot study	9/95
3.	Field pilot scale evaluation of zero-head bioreactor	9/95
4.	PAH bench scale studies	9/95
5.	Report on fielding potential of engineered microbes	9/96
6.	Chlorinated solvent bench studies	9/96
7.	PAH intermediate scale study	9/96
8.	Explosives bench studies	9/96
9.	Chlorinated solvents intermediate scale studies	9/96
10.	PAH field pilot study	9/97
11.	PCB bench scale studies	9/97
12.	Explosives intermediate scale studies	9/97
13.	PCB intermediate scale studies	9/98
14.	Explosives field pilot scale studies	9/99
15.	PCB field scale study	9/00

## 10. Transition Plan:

The results of this study will be presented in a form that will easily be utilizable by AEC, COE, USEPA, and the private sector for demonstration and implementation. Efforts will be made to collaborate with private organizations for enhanced process development through CRADAs. Additional collaboration with the USEPA via the SITE program will also be investigated. Also, partnering efforts with AEC, DoD installations, and USEPA/COE will be encouraged as an additional means of technology transition.

In addition to official project reports, partners within this program will be encouraged to publish in peer reviewed journals, present information at national and international symposia, and informal briefings at DoD, COE, and USEPA offices. Additional tech transfer will be encouraged through an annual open symposia at WES where the results from this program and related partnering activities will presented by the various program partners. One final note, the efforts proposed in this program directly fit in the DoD Tri-Services STRAT plan.

## 11. Funding: \$(K)

The funding requirements for this program and collective partnering 6.2 research funds and reimbursable funds:

	FY94	FY95	FY96	FY97	FY98	FY99	FY00	TOTAL
SERDP (6.2)	2450	1101	1962	2250	2500	2250	3000	15513
USA	1500	1250	800	1000	500	0	0	5050
USAF	500	500	100	0	0	0	0	1100
USN	500	300	300	0	0	0	0	1100
USEPA	1500	1500	500	100	100	0	0	3700
DOE	500	500	500	500	500	0	0	2500
GLRC	300	300	200	200	0	0	0	1000
TOTAL	6250	5451	4362	4050	3600	2250	3000	29963

## 12. Performers:

The partners for this research initiative are listed below. Under each partnering agency, at least one point of contact is presented.

Mr. Mark Zappi  
Dr. Doug Gunnison  
Dr. Judy Pennington  
USAE Waterways Exp. Sta.  
Vicksburg, MS

Dr. Jim Spain  
Ms. Cathy Vogel  
Armstrong Lab  
Tyndall Air Force Base  
Panama City, FL

Dr. Joanne Jones-Meehan  
Naval Surface Warfare Center  
Dahlgren, VA

Dr. Steve McCutcheon  
USEPA-Env. Res. Lab  
Athens, GA

Dr. Hap Pritchard  
USEPA-Env. Res. Lab  
Gulf Breeze, FL

Ms. Chris Correale  
USAE Baltimore District  
Baltimore, MD

Dr. Sabine Apitz  
USN-Navy/NRAD  
San Diego, CA

Dr. John Wilson  
USEPA-R. S. Kerr Lab  
Ada, OK

Dr. Jim Johnson (Howard University)  
Dr. Walter Weber (U. of Mich.)  
Great Lakes and Mid-Atlantic Hazardous  
Substance R&D Center  
Ann Arbor, MI

Dr. David Kaplan  
US Army-Natick R,D, and E Center  
Natick, MA

### **13. Principal Investigator:**

Mr. Mark E. Zappi, P.E.  
CEWES-EE-R  
USAE Waterways Experiment Station  
3909 Halls Ferry Rd.  
Vicksburg, MS 39180  
PNone: 601-634-2856  
FAX: 601-634-3833  
E-MAIL: ZAPPIM@EX1.WES.ARMY.MIL

### **14. Keywords:**

Biotreatment, explosives, polychlorinated biphenyls, chlorinated solvents, polycyclicaromatic hydrocarbons, bioreactors

## SERDP FY95 PROJECT

1. **SERDP Thrust Area:** Cleanup
2. **Title:** Surfactant-Enhanced Biodegradation of Contaminants
3. **Agency:** U.S. Army
4. **Laboratory:** USAE Waterways Experiment Station
5. **Project ID:** #731

### 6. **Problem Statement:**

Overall Goal: This research will investigate the basic processes limiting the bioavailability of contaminants sorbed to soils and evaluate the applicability of biologically-mediated, desorption-enhancing processes to increase microbial destruction of these contaminants.

Problem Statement: The DoD has over 12,000 sites contaminated with a variety of energetic and organic compounds. Long-term persistence of these materials in soils is directly related to poor mobility of the contaminants and to resistance of the contaminant to microbial degradation. Many of these organic contaminants are sorbed onto clays or organic matter in soils. Through a combination of sorption processes, the contaminant may move deep into soil pores and/or clay mineral lattice structures, effectively immobilizing the contaminant. Inability of sorbed contaminants to partition back into the aqueous phase severely limits microbial degradation of contaminants in soil treatment systems. Correspondingly, effective biotreatment for those compounds is impaired because the bacteria are unable to contact the sorbed compound. As a result of these processes, immobilization is a significant problem to overcome in site restoration.

Current remediation technologies are deficient. Incineration is expensive and bioremediation often fails. Mobilization of contaminants is highly desirable for the development of new remediation technologies and improvement of existing technologies. For example, initial research at the U.S. Army Engineer Waterways Experiment Station (WES), the U.S. Environmental Protection Agency Athens Environmental Laboratory (AERL), and the U.S. Naval Surface Weapons Center (NSWC) indicates that certain surfactants can accelerate microbial degradation of TNT and chlorinated aromatic hydrocarbons and that microorganisms produce bioemulsifiers that may promote removal of contaminants previously bound to the soil. Other investigations indicate that enzymes modify certain contaminants that strongly sorb to soil, altering their affinity for soil by modifying the structure of substituents on the contaminant molecule. As a result, an intermediate transformation product having increased solubility may be produced, thus enhancing complete microbial degradation of the contaminant.

Enhancing the effectiveness of bioremediation will require an integrated investigation of the physical, chemical, and biological factors affecting sorption of organic contaminants as they relate to bioavailability. The information gained from this 6.1 level basic research can be directly applied to 6.2 level investigations to promote bioremediation technologies.

**Project Objectives:** Determine the role of sorption on availability of contaminants to microbial degradation. Reduce costs for microbial treatment of soils in sites contaminated with explosives and other organics by identifying ability of microbially-supported, desorption-enhancing processes to overcome sorption limitations.

**Status of Project:** Research was initiated to identify basic sorption processes and determine their possible relationship to microbial degradation of contaminants under SERDP in FY 93. This proposed basic research will further develop that effort in conjunction with preliminary work supported under the Environmental Quality and Technology Program. This research is jointly submitted by the US Army (WES) and the US Navy (Naval Surface Warfare Center) and US EPA (ERL-Athens) for SERDP funding.

## **7. Project Description:**

**Technical Objectives:** Determine the significance of soil sorption on biological availability of representative explosives, chlorinated pesticides, polychlorinated biphenyls (PCBs), and polycyclic aromatic hydrocarbons (PAHs). Provide procedures to determine the most effective means by which microorganisms overcome sorption limitations. Develop methods to determine applicability of microbiologically-mediated, desorption-enhancing processes to improve microbial destruction of contaminants. Provide this information in a form suitable for use at the 6.2 level.

**Technical Approach:** Determine the importance of sorption in controlling bioavailability of several organic contaminants of military importance and identify the means microorganisms utilize to overcome these limitations. This will be accomplished in a series of tasks listed below. Critical portions of Tasks II, III, and IV require application of several microbiological and biochemical technologies that are at the cutting edge of present-day research. For this reason, the proposed research could not have been undertaken 2-3 years ago.

- a. Task I. Compare diffusion of organic contaminants within soil particles with microbial degradation to determine limiting rates and focus research on the more significant knowledge gaps. Identify suitable systems in which to study processes. Determine presence or absence of biosurfactant and/or bioemulsifier production by key microbial species active in contaminant degradation. Identify the potential for alteration of sorption properties and bioavailability through reductive modification of contaminant structures.
- b. Task II. Develop techniques for investigating sorption sites on and diffusion within soil particles. Develop techniques for investigating movement of microorganisms producing biosurfactants and/or bioemulsifiers and reductive processes having sorption-modifying capabilities.

- c. Task III. Develop predictive sorption kinetics models to evaluate importance of sorption to bioavailability and select the most appropriate procedures for determining sorption limitations. Develop a data base for verification of general predictive techniques with soils having a wide range of properties.
- (1) Procedures for determining impacts of sorption on microbial availability, including equipment, chemicals, and methods.
  - (2) Guidance on how to interpret results.
  - (3) Guidance for application of predictive techniques. Descriptions of procedures to evaluate ability of microbial processes to overcome sorption limitations.
  - (4) Develop technology transfer documents, seminars, and laboratory demonstrations to transition the technology to 6.2 level. Where appropriate, supply technology in a form suitable for direct application to 6.3 level.

Relationship to DoD/EPA Environmental Objectives: Information obtained from the performance of this study will contribute to several DoD/EPA environmental remediation objectives. This work will improve contaminant destruction technology by enhancing bioavailability of contaminants sorbed to soil. Specific user requirements that will benefit from performance of this work include:

- (1.I.4.c) Decontamination of soils containing energetic materials (A,N,AF)
- (1.I.2.i) Contamination under buildings and roads (A,N,AF)
- (1.I.4.n) Remedial treatment technology for soils contaminated with chlorinated and nonchlorinated organics (A,N,AF)
- (1.I.1.g.) Treatment systems for water contaminated with Chlorinated and dense hydrocarbons.
- (1.I.3.a.) Technologies for the isolation and decontamination of sludge.
- (1.I.2.e.) Improved marine sediment remediation technologies for metals, organics and PCBs.
- (1.I.4.c.) Decontamination of soils contaminated with energetic materials.
- (1.I.1.j.) Treatment of Navy relevant contaminants in salt/brackish/groundwater matrices.
- (1.I.1.e.) Processes to remediate groundwater contaminated with hydrocarbon fuels.
- (1.I.1.n.) Remedial treatment technology for soils contaminated with chlorinated and non-chlorinated organics.
- (1.I.2.b.) Dredged sediments area decontamination and reclamation.
- (1.I.6.c.) Isolation and treatment technology for contaminated surface water impoundments.
- (1.I.2.i.) Contamination under building and roads.



(1.I.6.d.) Improved shore and open ocean hazardous materials cleanup/restoration.

(2.III.1.d.) Enzyme and bacterial treatment technology.

(2.III.2.d.) Improved cleanup procedures at locations where UST have leaked.

## 8. Expected Payoff:

Potential Users: DoD, DOE, private Superfund, and Resource Conservation and Recovery Act (RCRA) site managers will benefit from procedures to enhance bioremediation. Development of this technology will allow cost-effective in-situ and landfarming biotreatment of soils and sediments contaminated with explosives and other organic compounds. Current soil incineration techniques destroy local ecosystems. The technology will also benefit ex-situ techniques, such as bioslurry reactor treatment. This will be especially important at those sites where microbial destruction of crystalline TNT is required.

Positive Impacts: This study will integrate technology development and basic research to provide better means to develop the most cost-effective treatment options. Rapid determination of factors affecting microbial accessibility to contaminants has the potential to decrease the overall costs of in-situ, landfarming, and bioslurry treatment of contaminated soils.

## 9. Milestones:

Major milestones under this work effort are listed below, along with the respective month and year they will be completed.

### FY94 Milestones:

1.	Organizational meeting of biosurfactant team	08/94
2.	Distribution of FY 94 funds	01/95
3.	Identify systems in which to study processes (Task I)	12/94
4.	Select and document the microorganisms producing biosurfactants and bioemulsifiers (Task I)	01/95
5.	Research Meeting in Bozeman, MT	06/95
6.	Initial comparison of desorption and biodegradation rates for standard sorbents and soils (Task I)	03/95
7.	Determine effects of contaminant structural modification on desorption (Task I)	06/95
8.	Evaluate the effects of contaminants and surfacants on microbial community structure and function	07/95
9.	Derive basic concepts of biosurfactant-contaminant sorbent model	09/95
10.	Research Progress Meeting	09/95

FY95 Milestones:

- |     |  |       |
|-----|--|-------|
| 11. | Rate the most promising biosurfactants/microorganisms  | 05/95 |
| 12. | Produce biosurfactant in sufficient quantities to be evaluated ex situ   | 11/95 |
| 13. | Investigate structure-function relationships of ex situ-added biosurfactants and bioemulsifiers with contaminated soil | 12/95 |
| 14. | Evaluate in situ survival and performance of best surfactant-producing microorganism in sorbents and soils (Task II)   | 12/95 |

FY96 Milestones:

- |     |  |       |
|-----|--|-------|
| 15. | Select the best performing biosurfactant - contaminant system for bench-scale study (Task II)        | 10/95 |
| 16. | Optimize performance of the selected biosurfactant-contaminant biotreatability system at bench scale | 02/96 |
| 17. | Develop and verify predictive desorption and microbial degradation models (Task III)                 | 04/96 |
| 18. | Research Progress Meeting  | 06/96 |
| 19. | Derive treatment cost data for biosurfactant enhanced degradation                                    | 08/96 |
| 20. | Develop protocol to enhance microbial accessibility (Task IV)  | 09/96 |

**10. Transition Plan:**

This 6.1 level research will directly support bench-scale assessments at the 6.2 level. As work progresses, briefings and direct input by principal investigators will be provided to relevant Environmental Quality and Technology Program 6.2 level biotreatment work units and corresponding work units in the environmental programs of other agencies. In addition, the proposed work will directly support the work developed in the Integrated Biotreatment Research Program SERDP proposal developed by WES. Technical assistance for these purposes will be available during and after the course of the research. The technology will also be transferred through technical papers, presentations, and work unit reports. Professors, post-doctorals and graduate students will be involved in helping to develop the studies and conduct the work, which will indirectly aid education. We will also consider application of this technology to suitable field scale technologies through use of cooperative research and development agreements (CRADAs).

**11. Funding: \$(K)**

	FY94	FY95	FY96	TOTAL
SERDP	700	234	397	4900

**12. Performers:**

The lead laboratory for the proposed research will be the U.S. Army Engineer Waterways Experiment Station (WES). WES will make contributions to all the tasks and have responsibility for Tasks II, IV, and V. The NSWC Biotechnology Laboratory, Silver Springs, MD will have responsibility for Task I and will make major contributions to Tasks II and III, plus some contribution to Task V. AERL will make some contributions to Task I, major contributions to Tasks II-V and have primary responsibility for Task III. The NSWC will

continue cooperative work with the University of Maryland; AERL will conduct some research on desorption kinetics and biodegradation with competitive cooperative agreements. WES and AERL will work with either the Hazardous Substance Research Center/South and Southwest or the Hazardous Substances Research Center/West. WES may also work with Texas A&M in its University Research Initiative with the Army Research Office. WES personnel will interact directly with university personnel through the Visiting Professor Program, with the National Research Council Post Doctoral Program, and by direct contacts between WES and graduate students.

### **13. Principal Investigators:**

Dr. Douglas Gunnison (Senior Principal Investigator)  
Dr. Judith C. Pennington  
US Army Engineer Waterways Experiment Station  
3909 Halls Ferry Road  
Vicksburg, MS 39180-6199  
PHONE: (601) 634-3873 and -2802 respectively  
FAX: (601) 634-3120

Dr. John Rogers (POC for AERL)  
960 College Station Road  
Athens, GA  
PHONE: (706) 546-3592  
FAX: (706) 546-3252

Dr. Joanne Jones-Meehan (POC for NSWC)  
10901 New Hampshire Avenue  
Silver Spring, MD 30903-5000  
PHONE: (301) 394-4839  
FAX: (301) 394-4841

### **14. Keywords:**

Mineralization, Sorptive Processes, Bioavailability, Surfactant, Reduction

## SERDP FY95 PROJECT

1. **SERDP Thrust Area:** Cleanup
2. **Title:** Fuel Hydrocarbon Remediation
3. **Agency:** U.S. Navy
4. **Laboratory:** Naval Facilities Engineering Service Center (NFESC)
5. **Project ID:** #20

### 6. **Problem Statement:**

Fuel-contaminated water and soil remediation technologies evaluation is one of several thrusts managed under the umbrella of the National DoD Environmental Technology Demonstration Program initiative started in FY93. This demonstration program supports SERDP program efforts to meet DoD environmental obligations, and reduce the future life-cycle costs associated with cleanup and compliance with environmental regulations. Success will be measured by the ability to meet cleanup levels, acceptance by regulators, and by transferring technologies with performance data and design guides to industry.

The goal is to achieve regulatory and institutional acceptance of, and transfer to industry, innovative remediation technologies for fuel contaminated water and soils. The most common fuel contaminated sites within DoD are those with jet fuels (JP-5), marine diesel, gasoline and bunker fuel. These sites are located near underground storage tanks (UST), fuel farms and other locations where spills have occurred, resulting in extensive fresh and brackish surface and groundwater contamination, and soil contamination.

Remedial action at these sites are often complicated. This is due to numerous UST excavation sites being in areas of shallow water tables overlying brackish water, and others with fresh water containing high dissolved solids. Some of these sites are located in extreme geologic and climatic conditions. This effort applies to the DoD Cleanup Pillar, Requirement Thrusts 1.N: Treatment of Fuels in Soil and 1.J: Treatment of Fuels in Groundwater, as identified in the Tri-Service Environmental R&D Strategic Plan.

### 7. **Project Description:**

The objective of the National DoD Environmental Technology Demonstration Program for fuel contaminated water and soil is to conduct side-by-side field demonstrations comparing advanced technologies under similar conditions. The DoD requirements being addressed are (1.I.1.e) Process to Remediate Groundwater Contaminated with Hydrocarbon Fuels and (1.I.4.m) Process to Remediate Soils Contaminated with Hydrocarbon Fuels.

Demonstration projects will test innovative remediation treatment train technologies at ex-situ soil treatment site(s), ex-situ surface and groundwater treatment facilities, and in-situ soil and groundwater treatment site(s) in a wide range of climatic conditions. Candidate

technologies selected within specific treatment method areas will be technologies emerging from DoD laboratories as identified in the Tri-Service Environmental Quality Research and Development Strategic Plan, and Broad Agency Announcement (BAA) solicitations. Projects from the EPA SITE Technology and Demonstration program may also be candidates for demonstration. Emerging technologies such as the following proposed projects will be demonstrated:

Bioremediation technology (Phase I) will be demonstrated using soil contaminated with different types of fuel. This will include gasoline, diesel, JP-5 and possible combinations of these hydrocarbons. The technical objective is to determine biocell and nutrient feed design parameters. In this innovative biocell demonstration, highly mobile nutrient mixtures will be evaluated with respect to optimizing native soil hydrocarbon degrading microorganisms to quicken the pace of cleanup. Because of uncertainties with regard to dynamic living organisms, and environmental factors which influence these systems, low-to-moderate risk is associated with the bioremediation effort.

Bioremediation has been field studied for a number of years. Biological treatment processes investigated have used indigenous or selectively cultured bacteria and/or fungi. Some biological processes studied used existing soil conditions while other studies, including this effort, altered/enhanced environmental factors influencing microorganism transformation of hazardous waste with changes in pH, temperature, oxygen concentration, and availability of essential nutrients.

The enhanced bioremediation project demonstration for ex-situ treatment of fuel-contaminated soil is being conducted at the Naval Construction Battalion Center (NCBC), Port Hueneme, California. This site is one of the National DoD Environmental Technology Demonstration Program fuel and solvent remediation demonstration sites.

In Phase II and onward, other technologies, or treatment trains, will be evaluated at fuel and solvent remediation demonstration sites including in-situ decontamination treatment of soil and groundwater with brackish and high dissolved solids content. Demonstrations will be prioritized and scheduled in five phases. Each demonstration project will last approximately two years. These technologies will be identified and selected by a multi-disciplinary peer review panel. Candidate projects may come from emerging modifications to treatment trains such as the following areas: (1) thermal or chemical enhanced soil vapor extraction, (2) soil flushing and washing amendments, (3) chemical catalytic reduction/oxidation mixed product recovery, (4) emission controls for low temperature thermal desorption, and (5) free product recovery.

Because of uncertainties with regard to potential responding organizations and companies, low-to-moderate risk is associated with these remediation projects.

## **8. Expected Payoff:**

Field and laboratory data collected will be incorporated into a Tri-Service Data Package to develop life-cycle cost information and design engineering guidelines. Those technologies transferred would reduce remediation costs, accelerate the pace of cleanup, and facilitate

compliance with various Federal and State regulations in order to protect human health and the environment. The transfer of critical technologies into full scale implementation is an integral and strategic part of the DoD environmental objective.

The data presented in technology transfer media will be comparable with data from other DoD, EPA and DoE SERDP projects. Technology transfer involves dissemination of information within the DoD engineering and environmental organizations which are making remedial action decisions and external transfers to industry and other Federal, State and Municipal organizations evaluating those decisions or implementing the technologies. Major benefits resulting from these technology demonstration projects are applicable and transferable to a large number of DoD sites reducing the cost associated with site demonstrations and the time needed to remediate sites.

**9. Milestones:**

Phase I: Ex-situ treatment of contaminated soil (bioremediation)

- |     |  |       |
|-----|--|-------|
| 1.  | Establish peer review panel  | 12/93 |
| 2.  | Complete contract award  | 02/94 |
| 3.  | Complete site plans (QA/QC, safety, demo)                            | 05/94 |
| 4.  | Complete peer review of plans  | 06/94 |
| 5.  | Obtain permits   | 07/94 |
| 6.  | Complete excavated soil characterization                             | 07/94 |
| 7.  | Complete final design  | 07/94 |
| 8.  | Construct bioremediation cells                                       | 08/94 |
| 9.  | Initiate field demo (gasoline & diesel soils)                        | 08/94 |
| 10. | Complete first monthly sampling                                      | 09/94 |
| 11. | Complete soil bioremediation field demo                              | 06/95 |
| 12. | Complete technical evaluation report and tech transfer documentation | 09/95 |

Phase I: Ex-situ treatment of contaminated soil (thermal)

- |     |  |       |
|-----|--|-------|
| 1.  | Complete Broad Agency Announcement                                   | 03/94 |
| 2.  | AC review and technology selection                                   | 06/94 |
| 3.  | Complete contract award  | 08/94 |
| 4.  | Complete site plans (QA/QC, safety, demo)                            | 11/94 |
| 5.  | Complete peer review of plans  | 12/94 |
| 6.  | Obtain permits   | 12/94 |
| 7.  | Complete soil characterization                                       | 12/94 |
| 8.  | Complete final design  | 01/95 |
| 9.  | Complete setup & startup   | 02/95 |
| 10. | Complete 2nd technology demonstration                                | 02/95 |
| 11. | Complete technical evaluation report and tech transfer documentation | 9/95  |
| 12. | Complete Phase I tech transfer package                               | 02/96 |

## Phase II: Ex-situ treatment of contaminated groundwater

- |     |   |       |
|-----|---|-------|
| 1.  | Complete Broad Agency Announcement  | 05/95 |
| 2.  | AC review and technologies selection  | 09/95 |
| 3.  | Complete contract(s) award  | 11/95 |
| 4.  | Complete site plans   | 02/96 |
| 5.  | Complete peer review of plans   | 04/96 |
| 6.  | Obtain permits  | 05/96 |
| 7.  | Complete groundwater characterization                                       | 05/96 |
| 8.  | Complete final design   | 06/96 |
| 9.  | Complete setup & startup  | 07/96 |
| 10. | Complete field demo (2 technologies)  | 01/97 |
| 11. | Complete Phase II technical evaluation report & tech transfer documentation | 04/97 |

## Phase III: In-situ remediation of soil and groundwater

- |    |   |       |
|----|---|-------|
| 1. | Complete BAA/peer review selection        | 10/95 |
| 2. | Complete contract for Phase III           | 04/97 |
| 3. | Complete start up Phase II demonstrations | 09/97 |
| 4. | Complete Phase III demonstrations         | 06/98 |
| 5. | Complete Phase III tech transfer report   | 09/98 |
| 6. | Complete NTS program evaluation report    | 02/99 |

## Phase IV: Emerging Technologies

- |    |  |       |
|----|--|-------|
| 1. | Complete BAA/peer review selection       | 10/97 |
| 2. | Complete contracts for Phase IV          | 02/98 |
| 3. | Complete start up Phase IV demonstration | 05/98 |
| 4. | Complete Phase IV demonstrations         | 04/99 |
| 5. | Complete Phase IV tech transfer package  | 08/99 |

### 10. Transition Plan:

At the completion of each field demonstration, a technology transfer package which includes an Implementation Guidance Document will be prepared and disseminated with organizations (DoD, EPA, DOE) which are making remedial action decisions. These technologies will be transferred to industry and other Federal, State and Municipal organizations for implementation at multiple DoD sites national and world-wide. The National DoD Environmental Technology Demonstration Program Test Organization is responsible for a multi-media technology transfer package that will include: (1) technical short courses/seminars, (2) on-site visitor's workshops, (3) field assistance, (4) conference exhibits, and (5) demonstration videotapes and brochures. The principal investigator/project officer will develop professional journal articles.

**11. Funding: \$(K)**

	FY94	FY95	FY96	FY97	TOTAL
SERDP	550	280	0	800	1630

**12. Performers:**

The field bioremediation demonstration will be conducted by Mr. William Major and Ms. Leslie Karr for the Naval Facilities Engineering Service Center (NFESC). Mr. Dharam Pal, NFESC, will be the principal investigator/coordinator for Phase II Emerging Technologies projects. DoD laboratories as identified in the Tri-Service Environmental Quality Research and Development Strategic Plan, and Broad Agency Announcement (BAA) solicitations will be used to solicit proposals for demonstration projects. A peer review panel will review proposals and recommend contract award for a specific method.

**13. Principal Investigator:**

Mr. Ernst Lory  
Project Officer  
Naval Facilities Engineering Service Center  
ESC411, 560 Center Dr., Port Hueneme, CA 93043-4328  
PHONE: 805-982-1299  
FAX: 805-982-1409  
E-MAIL: ELORY@NFESC.NAVY.MIL

**14. Keywords**

Remediation, Fuels, Demonstrations (remediation technology), Treatment, Soil (decontamination), Groundwater (decontamination)



## SERDP FY95 PROJECT

1. **SERDP Thrust Area:** Cleanup
2. **Title:** National Test Location, Volunteer Army Ammunition Plant, Chattanooga, TN  
[component of DoD/National Environmental Technology Demonstration Program (D/NETDP)]
3. **Agency:** Army
4. **Laboratory:** Army Environmental Center
5. **Project ID:** #723
6. **Problem Statement:**

The current process for gaining acceptance of cost-effective, innovative technologies for the cleanup of federal installations is laborious and costly. The problem stems from several causes: the lack of certification for new technologies as presumptive remedies, the lack of formally established technology demonstration programs ensuring protocols and quality assurance/quality control procedures sufficient to meet requirements of regulators and users, and the lack of information dissemination in formats suitable for all interested parties. The first problem cause listed above can only be addressed by legislative change through the political process. The latter causes can be addressed by a comprehensive technology demonstration/evaluation/transfer program. The DoD/National Environmental Technology Demonstration Program (D/NETDP) provides such a comprehensive technology demonstration/evaluation/transfer program. The goal is to provide test locations for comparative demonstration and evaluation of cost-effective and innovative technologies to enable transfers from research to full-scale use. The Air Force, Army, Navy, and EPA are partners in D/NETDP, and there are five test locations.

Achieving this goal requires the accomplishment of the following objectives: (1) query regulators, users, and the public to ascertain what information is needed from a demonstration, and what presentation format is preferred in order for their acceptance of new technology; (2) standardize the data collection and analysis to the extent possible across the partnering Services and EPA; (3) provide characterized test locations together with the infrastructure required for the demonstration and evaluation of innovative technologies under comparable and well-characterized hydrogeologic and climatic conditions; (4) involve regulators, users, and the public throughout the course of technology demonstrations; (5) provide test beds for supporting environmental research; (6) support the widespread dissemination of technical evaluations, performance or guidance specifications, and economic data.

Each D/NETDP test location provides well-characterized test sites and the infrastructure required for technology demonstration. Dedicated sites allow better use of resources compared to one-off, developer-staged demonstrations because site selection, permitting,

characterization, and provision of infrastructure are not required for each new technology demonstration.

In addition to infrastructure, demonstration oversight, and support services at each D/NETDP test location, there is also a joint programmatic effort undertaken by the partnering Services and EPA to support technology demonstrations. With FY 94 funding, the D/NETDP (Army Environmental Center lead) is developing a Quality Management Plan (QMP) which will include guidance for writing test plans, cost and performance data collection criteria, QA/QC plans, success criteria, regulatory and user interface, and technology transfer strategy. The QMP is a common link among the Services and EPA to expedite the development of better, more efficient cleanup technologies. A cost-and-performance database, which will serve as a repository for results of demonstrations to facilitate technology transfer, is also being developed with FY 94 funding (McClellan AFB lead). EPA provides additional guidance and support to each D/NETDP test location through its Site Characterization and Monitoring Technology Demonstration Program at NERL, CRD-LV.

## **7. Project Description:**

The contamination of soil, sediments and groundwater by explosives and heavy metals has become a problem at many industrial facilities due to past disposal practices. The U.S. Army established a National Test Location for explosives and heavy metals contamination at Volunteer Army Ammunition Plant (VAAP) with FY 93 funding. With FY 94 funding, the Army selected Louisiana Army Ammunition Plant (LAAP) as a satellite location with different hydrogeologic conditions and broader spectrum of explosives and heavy metals contamination.

At VAAP, FY 95 funding will support technology demonstrations by providing project oversight and technology transfer assistance.

At LAAP, FY 95 funding will provide site preparation including NEPA documentation, installation of utilities, preparation of site safety plans, and detailed site characterization. LAAP will be ready to support demonstrations in January 1996.

There will be a technology selection committee of explosives or heavy metal experts (depending upon the contamination) to identify the technologies for demonstration. The criteria will include the maturity of the technology applicability to DoD needs, potential to meet established clean up levels, and potential cost savings over currently used technologies. Selected technologies can come from U.S. Army Corps of Engineer laboratories, or from private firms under Broad Agency Announcement solicitations or Cooperative Research and Development Agreements.

The technical risks associated with the development and management of the test location are low.

## 8. Expected Payoff:

By including private technology demonstrators, regulators, users, and the public in the demonstration planning process, each D/NETDP test location provide opportunities for identifying and developing acceptable cost effective technologies for transfer to other Government agencies and the private sector. By achieving the goals and objectives of this program, the ultimate, long-term payoff will be lower remediation costs for the federal government.

However, the more immediate benefits that can be derived from an integrated demonstration and evaluation program include: (1) identification of practically achievable and cost effective goals for cleanup; (2) establishment of a research and development platform for advancement of remediation technologies; (3) accelerated acceptance of innovative technologies as presumptive remedies for the reduction in the time and cost of cleanup; (4) well documented engineering packages (where appropriate) for the broader application of effective technologies; (5) cost savings for SERDP sponsored (and other) demonstrations; and (6) advanced understanding of the fate and transport of contaminants.

## 9. Milestones:

### A. VAAP

A.1	Conduct SCAPS demonstration (729-A)	5/95
A.2	Begin demonstration #2	9/95
A.3	Begin demonstration #3	11/95
A.4	Complete demonstration #2	12/95
A.5	Complete demonstration #3	2/96
A.6	Begin demonstration #4	3/96
A.7	Complete demonstration #4	7/96

### B. LAAP

B.1.	Completes LAAP site characterization	11/95
B.2.	Provide on-site laboratory (canceled)	11/95
B.3.	Complete site preparation	2/96
B.4.	Begin demonstration #5	2/96
B.5.	Begin demonstration #6	4/96
B.6.	Complete demonstration #5	5/96
B.7.	Complete demonstration #6	7/96

## 10. Transition Plan:

Cost and performance data will be collected by the standardized methodology and entered into the D/NETDP cost-and-performance database (when available, McClellan AFB lead). At the conclusion of each demonstration, the PI for the demonstration project will write a technology evaluation report and produce a technical data package. From these, the Test Location Manager will write a demonstration summary sheet and technology brief. Where appropriate, engineering design, fabrication and procurement guidance will also be provided

by the Test Location Manager, which will provide regulators, users, and the public with the information, presented in a useable fashion, necessary to implement technology acceptance and transfer to commercial use. Other technology transfer efforts will include technical short courses/seminars, on-site visitor's workshops, field assistance, conference exhibits, and demonstration videotapes and brochures.

**11. Funding: \$(K)**

	FY 93	FY 94	FY 95	FY 96	FY 97	FY 98	FY 99	TOTAL
Test Location Management/ Infrastructure SERDP	2,180	1,030	350	740	740	740	740	6,520
QMP Development SERDP	830	210	0	0	0	0	0	1,040
TOTAL SERDP	3,010	1,320	350	740	740	740	740	7,640

**12. Performers:**

Demonstrations at VAAP and LAAP are managed by a Test Location Manager. On site execution and day-to-day oversight will be performed by a private firm contractor (ICI Americas) and/or government agencies (TVA). Background Site Characterization is performed by a private contractor (TRW). The SERDP Program Office provides D/NETDP management and program oversight.

Development of the Quality Management Program (QMP) for D/NETDP is managed by the Test Location Manager. The work is performed by a private contractor (TRW).

For purposes of coordination within the D/NETDP, each National Test Location Manager is a member of a Test Location Managers' committee, which comprises SERDP representatives as well as Test Location Managers. This committee represents a Tri-Services and EPA coordinated effort to work with other organizations on uniform reporting formats and test protocols guidance.

### **13. Principal Investigator:**

Principal Investigator

Mr. Erik B. Hangeland  
SFIM-AEC-TSD  
Technical Support Division  
U.S. Army Environmental Center  
Beal Road, Building E4435  
Aberdeen Proving Ground, MD 21010-5401  
PHONE: (410) 612 6858  
FAX: (410) 612 6836

Test Location Manager

Mr. Albert. J. Walker  
SFIM-AEC-TSD  
Technical Support Division  
U.S. Army Environmental Center  
Beal Road, Building E4435  
Aberdeen Proving Ground, MD 21010-5401  
PHONE: (410) 612 6863  
FAX: (410) 612 6836

### **14. Keywords:**

Energetics, explosives, heavy metals, National Test Location, technology demonstration, demonstration site

## SERDP FY95 PROJECT

1. **SERDP Thrust Area:** Cleanup
2. **Title:** National Test Location, Naval Construction Battalion Center (NCBC), Port Hueneme, CA [component of DoD/National Environmental Technology Demonstration Program (D/NETDP)]
3. **Agency:** U.S. Navy
4. **Laboratory:** Naval Facilities Engineering Service Center (NFESC)
5. **Project ID:** #863
6. **Problem Statement:**

The current process for gaining acceptance of cost-effective, innovative technologies for the cleanup of federal installations is laborious and costly. The problem stems from several causes: the lack of certification for new technologies as presumptive remedies, the lack of formally established technology demonstration programs ensuring protocols and quality assurance/quality control procedures sufficient to meet requirements of regulators and users, and the lack of information dissemination in formats suitable for all interested parties. The first problem cause listed above can only be addressed by legislative change through the political process. The latter causes can be addressed by a comprehensive technology demonstration/evaluation/transfer program. The DoD/National Environmental Technology Demonstration Program (D/NETDP) provides such a comprehensive technology demonstration/evaluation/transfer program. The goal is to provide test locations for comparative demonstration and evaluation of cost-effective and innovative technologies to enable transfers from research to full-scale use. The Air Force, Army, Navy, and EPA are partners in D/NETDP.

Achieving this goal requires the accomplishment of the following objectives: (1) query regulators, users, and the public to ascertain what information is needed from a demonstration, and what presentation format is preferred in order for their acceptance of new technology; (2) standardize the data collection and analysis to the extent possible across the partnering Services and EPA; (3) provide characterized test locations together with the infrastructure required for the demonstration and evaluation of innovative technologies under comparable and well-characterized hydrogeologic and climatic conditions; (4) involve regulators, users, and the public throughout the course of technology demonstrations; (5) provide test beds for supporting environmental research; (6) support the widespread dissemination of technical evaluations, performance or guidance specifications, and economic data.

Each D/NETDP test location provides well-characterized test sites and the infrastructure required for technology demonstration. Dedicated sites allow better use of resources compared to one-off, developer-staged demonstrations because site selection, permitting, characterization, and provision of infrastructure are not required for each new technology demonstration.

In addition to infrastructure, demonstration oversight, and support services at each D/NETDP test location, there is also a joint programmatic effort undertaken by the partnering Services and EPA to support technology demonstrations. With FY 94 funding (Army Environmental Center lead), the D/NETDP is developing a Quality Management Plan (QMP) which will include guidance for writing test plans, cost and performance data collection criteria, QA/QC plans, success criteria, regulatory and user interface, and technology transfer strategy. The QMP is a common link among the Services and EPA to expedite the development of better, more efficient cleanup technologies. A cost-and-performance database, which will serve as a repository for results of demonstrations to facilitate technology transfer, is also being developed with FY 94 funding (McClellan AFB lead). EPA provides additional guidance and support to each D/NETDP test location through its Site Characterization and Monitoring Technology Demonstration Program at NERL, CRD-LV.

## **7. Project Description:**

The objective is to support D/NETDP and to demonstrate systems for characterizing and remediating soil, sediments, and ground water contaminated with fuel hydrocarbons and/or waste oil.

The NCBC Port Hueneme National Test Location management will provide D/NETDP programmatic, infrastructure and technical support for fuel hydrocarbon and waste oil characterization and remediation demonstrations. D/NETDP support will include development and integration of the following: (1) QA/QC procedures, (2) test protocol guidance, (3) demonstration reporting format, and (4) cost and performance data retrieval guidance.

Infrastructure at NCBC Port Hueneme and its management (operation and maintenance) will include: (1) monitoring wells, (2) in-line sensor network, (3) ex situ treatment facility with hazardous material handling capability, (4) utilities, and (5) contaminated soil, sediments and ground water resources. Technical support to demonstration project PIs will include: (1) characterizing and monitoring contaminants, (2) processing permits, (3) supporting stakeholder involvement, and (4) transferring technologies.

## **8. Expected Payoff:**

By including private technology demonstrators, regulators, users, and the public in the demonstration planning process, each D/NETDP test location provide opportunities for identifying and developing acceptable cost effective technologies for transfer to other

Government agencies and the private sector. By achieving the goals and objectives of this program, the ultimate, long-term payoff will be lower remediation costs for the federal government.

However, the more immediate benefits that can be derived from an integrated demonstration and evaluation program include: (1) identification of practically achievable and cost effective goals for cleanup; (2) establishment of a research and development platform for advancement of remediation technologies; (3) accelerated acceptance of innovative technologies as presumptive remedies for the reduction in the time and cost of cleanup; (4) well documented engineering packages (where appropriate) for the broader application of effective technologies; (5) cost savings for SERDP sponsored (and other) demonstrations; and (6) advanced understanding of the fate and transport of contaminants.

The NCBC Port Hueneme National Test Location for fuel hydrocarbon and waste oil provides the following: (1) well characterized test sites, (2) controlled field conditions for comparative evaluations of technologies, (3) uniform evaluation criteria for demonstrations, reporting of results and technology transfer, and (4) cost savings through amortization of infrastructure and management.

## 9. Milestones:

### Test Location Management

1.	Contracts awards to GSA for infrastructure O&M	07/95
2.	Contract award to MCA Engineering for sensor network O&M	07/95
3.	Contract award to Geo-Insight contaminant historical database	07/95
4.	Forward 2nd quarter monitoring reports	07/95
5.	Forward 3rd quarter monitoring reports	10/95
6.	Operate and maintain NTL Infrastructure (on-going)	12/95
7.	Support D/NETDP (on-going)	12/95
8.	Conduct quarterly Fuel Hydrocarbon Advisory Committee meetings (on-going)	12/95
9.	Participate in community relation forums (on-going)	12/95
10.	Support technology transfer (on-going)	12/95

### Demonstration Oversight

1.	Conduct SCAPS LIF demonstration (729-A)	4/95
2.	Complete Biopile (phase I) demonstration (020-N)	7/95
3.	Start HAVE demonstration (020-N)	8/95
4.	Start Biopile (phase II) demonstration (020-N)	9/95
5.	Start new demonstration (720-A)	11/95
6.	Start new demonstration (731-A)	12/95

## 10. Transition Plan:

Cost and performance data will be collected by the standardized methodology and entered into the D/NETDP cost-and-performance database (when available, McClellan AFB lead). At the conclusion of each demonstration, the PI for the demonstration project will write a technology evaluation report and produce a technical data package. From these, the Test



Location Manager will write a demonstration summary sheet and technology brief. Where appropriate, engineering design, fabrication and procurement guidance will also be provided by the Test Location Manager, which will provide regulators, users, and the public with the information, presented in a useable fashion, necessary to implement technology acceptance and transfer to commercial use. Other technology transfer efforts will include technical short courses/seminars, on-site visitor's workshops, field assistance, conference exhibits, and demonstration videotapes and brochures.

**11. Funding: \$(K)**

	FY93	FY94	FY95	FY96	FY97	FY98	FY99	TOTAL
SERDP	800	550	900	725	725	725	725	5,750

**12. Performers:**

The NCBC Port Hueneme National Test Location for fuel hydrocarbon and waste oil characterization and remediation demonstrations is managed from within the Installation Restoration Division of the Naval Facilities Engineering Service Center (NFESC). The commanding officer of the Naval Construction Battalion Center, Port Hueneme is the steward of the base and is ultimately responsible for the results of remedial actions which takes place on the base where the NTL is located. The CBC environmental officer represents the CBC command concerning oversight of the NTL and his staff supports the obtaining and retaining of permits. Contractor support is used to operate and maintain (O&M) the NTL infrastructure at Port Hueneme.

For purposes of coordination within the D/NETDP, each National Test Location Manager is a member of a Test Location Managers' committee, which comprises SERDP representatives as well as Test Location Managers. This committee represents a Tri-Services and EPA coordinated effort to work with other organizations on uniform reporting formats and test protocols guidance.

**13. Principal Investigator:**

Ernest Lory  
Naval Facilities Engineering Service Center, ESC 411  
560 Center Drive  
Port Hueneme, CA 93043  
PHONE: (805)-982-1299  
FAX: (805) 982-5226  
E-MAIL: elory@nfesc.navy.mil

**14. Keywords:**

National Test Location, fuel, solvent, fuel hydrocarbon, waste oil, remediation, technology demonstration, demonstration site

## SERDP FY95 PROJECT

**1. SERDP Thrust Area:** Cleanup

**2. Title:** National Test Location, Dover AFB, DE - Groundwater Remediation Field Laboratory [component of the DoD/National Environmental Technology Demonstration Program (D/NETDP)]

**3. Agency:** U.S. Air Force

**4. Laboratory:** Armstrong Laboratory, Environics Directorate, (AL/EQ)

**5. Project ID:** #866

### **6. Problem Statement:**

The current process for gaining acceptance of cost-effective, innovative technologies for the cleanup of federal installations is laborious and costly. The problem stems from several causes: the lack of certification for new technologies as presumptive remedies, the lack of formally established technology demonstration programs ensuring protocols and quality assurance/quality control procedures sufficient to meet requirements of regulators and users, and the lack of information dissemination in formats suitable for all interested parties. The first problem cause listed above can only be addressed by legislative change through the political process. The latter causes can be addressed by a comprehensive technology demonstration/evaluation/transfer program. The DoD/National Environmental Technology Demonstration Program (D/NETDP) provides such a comprehensive technology demonstration/evaluation/transfer program. The goal is to provide test locations for comparative demonstration and evaluation of cost-effective and innovative technologies to enable transfers from research to full-scale use. The Air Force, Army, Navy, and EPA are partners in D/NETDP, and there are five test locations.

Achieving this goal requires the accomplishment of the following objectives: (1) query regulators, users, and the public to ascertain what information is needed from a demonstration, and what presentation format is preferred in order for their acceptance of new technology; (2) standardize the data collection and analysis to the extent possible across the partnering Services and EPA; (3) provide characterized test locations together with the infrastructure required for the demonstration and evaluation of innovative technologies under comparable and well-characterized hydrogeologic and climatic conditions; (4) involve regulators, users, and the public throughout the course of technology demonstrations; (5) provide test beds for supporting environmental research; (6) support the widespread dissemination of technical evaluations, performance or guidance specifications, and economic data.

Each D/NETDP test location provides well-characterized test sites and the infrastructure required for technology demonstration. Dedicated sites allow better use of resources compared to one-off, developer-staged demonstrations because site selection, permitting, characterization, and provision of infrastructure are not required for each new technology demonstration.

In addition to infrastructure, demonstration oversight, and support services at each D/NETDP test location, there is also a joint programmatic effort undertaken by the partnering Services and EPA to support technology demonstrations. With FY 94 funding, the D/NETDP (Army Environmental Center lead) is developing a Quality Management Plan (QMP) which will include guidance for writing test plans, cost and performance data collection criteria, QA/QC plans, success criteria, regulatory and user interface, and technology transfer strategy. The QMP is a common link among the Services and EPA to expedite the development of better, more efficient cleanup technologies. A cost-and-performance database, which will serve as a repository for results of demonstrations to facilitate technology transfer, is also being developed with FY 94 funding (McClellan AFB lead). EPA provides additional guidance and support to each D/NETDP test location through its Site Characterization and Monitoring Technology Demonstration Program at NERL, CRD-LV.

The goal of the SERDP D/NETDP is to enable efficient demonstration of candidate innovative technologies for detection, monitoring and cleanup either on an individual basis or in parallel with similar technologies, under representative hydrogeological and climate regimes as found at many contaminated sites in the DoD. The D/NETDP will provide test beds for research to fully understand the mechanisms in proposed treatment processes. Test beds will be fully characterized and monitored areas where new technologies can be quickly and effectively demonstrated. This will save time and money for technology demonstrators and SERDP by providing on-site management, precharacterization, and more timely permitting.

## **7. Project Description:**

The Groundwater Remediation Field Laboratory (GRFL) is the Armstrong Laboratory, Environics Directorate (AL/EQ), contribution to the D/NETDP. Its primary focus is the provision of a Contained Release facility to research and demonstrate technologies for detection, monitoring, and cleanup of dense, nonaqueous phase liquids (DNAPLs). On-site D/NETDP management and regulatory interface established for the GRFL make it appropriate that other SERDP-sponsored DNAPL technology development efforts could also be demonstrated elsewhere at Dover AFB at other existing, well-characterized contamination sites, when no additional cost would be incurred by the D/NETDP.

The proposed action is to construct and operate the GRFL at Dover, AFB, DE. Construction and operation activities will consist of detailed characterization, installation of test cells and monitoring wells, and provision of a temporary building and fencing. Operations will consist of emplacement of the constituent (primarily TCE), demonstration of innovative technologies, and disposal of associated wastes.

Test cells will be spaced approximately 50 feet apart and constructed and operated in a way to minimize the potential for environmental contamination. Basic design consists of interconnected, steel barrier piling sections (2 feet width) forming a rectangular cell. Test cells will range from 36 to 1800 square feet. The sheet piling is manufactured to allow for joining of one sheet pile to another. The joints will be tremie-sealed with bentonite grout to ensure a tight seal. By driving the sheet piling 305 feet into the clay aquitard (approximately 30-40 feet below the surface), a coffer is formed which prevents vertical and lateral migration outside the confines of the box. Additionally, a secondary containment coffer will be constructed surrounding the primary coffer, and will be similarly sealed at the bottom and at each joint. The annulus between the cell will be filled with water to produce an inward hydraulic gradient. The annulus and inner cell will be continuously monitored for leakage. Both upgradient and downgradient monitoring wells, which will be designed to also function as an emergency pump and treat system if required, will be installed outside the secondary coffer. A vapor barrier will be installed to retain solvent within the experimental universe, both to achieve mass balance and to prevent air emissions.

Risks for the project as designed are minimal and can be controlled. The primary risk is that material introduced into a cell might escape and contaminate an aquifer. Vertical migration is retarded very well by a twenty foot thick clay layer with a hydraulic conductivity four orders of magnitude less than the overlaying strata. Double sheet piling, grouting, monitoring, the emergency pump-and-treat system, and distance to the nearest potential receptors virtually eliminate any risk from lateral migration. A worst-case risk analysis has shown that risk of significant aquifer and surface water contamination and human health impact is negligible — even in the unlikely event that one barrier is eliminated, the remaining one is seriously ruptured, no emergency treatment is attempted, and the TCE source area is left in place indefinitely. Potential risk of not being able to obtain a permit is considered minimal by the regulators from the State of Delaware and EPA Region III.

## **8. Expected Payoff:**

By including private technology demonstrators, regulators, users, and the public in the demonstration planning process, each D/NETDP test location provide opportunities for identifying and developing acceptable cost effective technologies for transfer to other Government agencies and the private sector. By achieving the goals and objectives of this program, the ultimate, long-term payoff will be lower remediation costs for the federal government.

However, the more immediate benefits that can be derived from an integrated demonstration and evaluation program include: (1) identification of practically achievable and cost effective goals for cleanup; (2) establishment of a research and development platform for advancement of remediation technologies; (3) accelerated acceptance of innovative technologies as presumptive remedies for the reduction in the time and cost of cleanup; (4) well documented engineering packages (where appropriate) for the broader application of effective technologies; (5) cost savings for SERDP sponsored (and other) demonstrations; and (6) advanced understanding of the fate and transport of contaminants.

One of the most formidable problems facing the Air Force Installation Restoration Program (IRP) is that of removing DNAPLs from the subsurface. The term DNAPL describes a number of materials which are immiscible with, and denser than, water. As a result of these properties, they migrate downward when spilled on the ground, and can migrate below the water table. Once below the water table, they are difficult to locate and remove. For the Air Force, the term DNAPL is virtually synonymous with chlorinated solvents, which were used for years as industrial cleaners and degreasers and are responsible for contamination at approximately one third of all Air Force contaminated sites. Currently there are no acceptable methods for removing or treating the bulk solvent material that sinks into aquifers or is trapped within the soil interstices. Technologies must be developed to protect the public from the potential health risks associated with DNAPLs in drinking water.

There are many contaminated sites where field experiments, which provide excellent opportunities to verify some of the conclusions drawn from laboratory experiments, are being performed. However, a number of gross assumptions must be made since these experiments are being conducted in previously contaminated aquifers. These assumptions include, but are not limited to: the amount and composition of the contamination originally introduced into the soil/water matrix, the exact location where the contamination was introduced, and the initial condition of the soil/water matrix prior to contamination. To eliminate the need to make these assumptions, it will be necessary to monitor the development of contaminant plumes from their inception, while maintaining a strict mass balance of the contaminants. This information can be obtained only from well-planned, carefully-controlled experiments involving contained releases of DNAPL materials into naturally deposited soil.

For this purpose, AL/EQ, Tyndall AFB, FL is establishing the GRFL. It will be a unique resource for the Cleanup community by providing opportunities for development of technologies for cleanup of DNAPL materials. The primary purpose of the GRFL will be to provide contained release cells for DNAPL contamination research and development.

## 9. Milestones:

### A. Test Location Management

- |    |   |       |
|----|---|-------|
| 1. | Contained Release Site Preparation (including site characterization) begins | 08/95 |
| 2. | Site Preparation complete   | 10/95 |
| 3. | Laboratory Emplacement completed  | 12/95 |
| 4. | First Contained Release cell constructed                                    | 12/95 |
| 5. | Waste management plan completed   | 12/95 |
| 6. | Safety plan completed   | 12/95 |

### B. Demonstration Oversight

- |    |   |       |
|----|---|-------|
| 1. | Complete SCAPS tunable laser demonstration (729-A)                            | 10/95 |
| 2. | Start demonstration #2<br>(AATDF: Co-oxidation of TCE/JP-4 during Bioventing) | 12/95 |

## 10. Transition Plan:

Cost and performance data will be collected by the standardized methodology and entered into the D/NETDP cost-and-performance database (when available, McClellan AFB lead). At the conclusion of each demonstration, the PI for the demonstration project will write a technology evaluation report and produce a technical data package. From these, the Test Location Manager will write a demonstration summary sheet and technology brief. Where appropriate, engineering design, fabrication and procurement guidance will also be provided by the Test Location Manager, which will provide regulators, users, and the public with the information, presented in a useable fashion, necessary to implement technology acceptance and transfer to commercial use. Other technology transfer efforts will include technical short courses/seminars, on-site visitor's workshops, field assistance, conference exhibits, and demonstration videotapes and brochures.

## 11. Funding: \$(K)

	FY93	FY94	FY95	FY96	FY97	FY98	FY99	TOTAL
SERDP	1100	1000	1279	921	700	700	700	6400

## 12. Performers:

An on-site Test Location Manager (TLM) will be responsible to the Government Program Officer. The TLM will disseminate GRFL publicity material to potential demonstrators. A peer review group is being formed to review the scientific merit of potential efforts coming to the GRFL. Arrangements have been made for utilizing the Installation Advisory Group (IAG) at Dover AFB as the vehicle for public involvement, regulatory input, and general local program review.

For purposes of coordination within the D/NETDP, each National Test Location Manager is a member of a Test Location Managers' committee, which comprises SERDP representatives as well as Test Location Managers. This committee represents a Tri-Services and EPA coordinated effort to work with other organizations on uniform reporting formats and test protocols guidance.

## 13. Principal Investigator:

Government Program Officer

Mark Smith, Maj USAF, BSC  
AL/EQW  
139 Barnes Drive, Suite 2  
Tyndall AFB, FL 32403-5323 (Stop 37)  
PHONE: (904) 283-6126  
FAX: (904) 283-6286  
E-MAIL:  
Mark\_Smith@ccmail.aleq.tyndall.af.mil

Test Location Manager

Mr. Paul Kerch  
AL/EQ-OL, Armstrong Laboratory  
139 Barnes Drive, Building 1120, Suite #2  
Tyndall AFB, FL 32403-5323  
PHONE: 904-283-6296  
FAX: 904-283-6286  
E-MAIL:  
Paul\_Kerch@ccmail.aleq.tyndall.af.mil

**14. Keywords:**

GRFL, DNAPL, chlorinated solvent, Contained Release, fate and transport, National Test Location, technology demonstration, demonstration site

## SERDP FY95 PROJECT

- 1. SERDP Thrust Area:** Cleanup
- 2. Title:** National Test Location, McClellan AFB, Sacramento, CA  
[component of DoD/National Environmental Technology Demonstration Program (D/NETDP)]
- 3. Agency:** U.S. Air Force
- 4. Laboratory:** Armstrong Laboratory, Environics Directorate, (AL/EQ)
- 5. Project ID:** #861
- 6. Problem Statement:**

The current process for gaining acceptance of cost-effective, innovative technologies for the cleanup of federal installations is laborious and costly. The problem stems from several causes: the lack of certification for new technologies as presumptive remedies, the lack of formally established technology demonstration programs ensuring protocols and quality assurance/quality control procedures sufficient to meet requirements of regulators and users, and the lack of information dissemination in formats suitable for all interested parties. The first problem cause listed above can only be addressed by legislative change through the political process. The latter causes can be addressed by a comprehensive technology demonstration/evaluation/transfer program. The DoD/National Environmental Technology Demonstration Program (D/NETDP) provides such a comprehensive technology demonstration/evaluation/transfer program. The goal is to provide test locations for comparative demonstration and evaluation of cost effective and innovative technologies to enable transfers from research to full-scale use. The Air Force, Army, Navy, and EPA are partners in D/NETDP, and there are five test locations.

Achieving this goal requires the accomplishment of the following objectives: (1) query regulators, users, and the public to ascertain what information is needed from a demonstration, and what presentation format is preferred in order for their acceptance of new technology; (2) standardize the data collection and analysis to the extent possible across the partnering Services and EPA; (3) provide characterized test locations together with the infrastructure required for the demonstration and evaluation of innovative technologies under comparable and well-characterized hydrogeologic and climatic conditions; (4) involve regulators, users, and the public throughout the course of technology demonstrations; (5) provide test beds for supporting environmental research; (6) support the widespread dissemination of technical evaluations, performance or guidance specifications, and economic data.



Each D/NETDP test location provides well-characterized test sites and the infrastructure required for technology demonstration. Dedicated sites allow better use of resources compared to one-off, developer-staged demonstrations because site selection, permitting, characterization, and provision of infrastructure are not required for each new technology demonstration.

In addition to infrastructure, demonstration oversight, and support services at each D/NETDP test location, there is also a joint programmatic effort undertaken by the partnering Services and EPA to support technology demonstrations. With FY 94 funding (Army Environmental Center lead), the D/NETDP is developing a Quality Management Plan (QMP) which will include guidance for writing test plans, cost and performance data collection criteria, QA/QC plans, success criteria, regulatory and user interface, and technology transfer strategy. The QMP is a common link among the Services and EPA to expedite the development of better, more efficient cleanup technologies. A cost-and-performance database, which will serve as a repository for results of demonstrations to facilitate technology transfer, is also being developed with FY 94 funding (McClellan AFB lead). EPA provides additional guidance and support to each D/NETDP test location through its Site Characterization and Monitoring Technology Demonstration Program at NERL, CRD-LV.

## **7. Project Description:**

This project involves the preparation and management of demonstration sites at McClellan AFB, CA for innovative monitoring and remediation technologies for chlorinated hydrocarbons in soil and groundwater. The focus will be technologies for the treatment of soil gases and remediation process offgases. Ex situ processes for the treatment of groundwater will also be conducted.

The work will also include the development of a computerized data management system which will act as a repository for the cost and performance data from all D/NETDP demonstrations. The data management system will also inform other agency remediation managers of the status of the technology development. Decision matrices will be used to encourage other potential users of the technology.

## **8. Expected Payoff:**

By including private technology demonstrators, regulators, users, and the public in the demonstration planning process, each D/NETDP test location provide opportunities for identifying and developing acceptable cost effective technologies for transfer to other Government agencies and the private sector. By achieving the goals and objectives of this program, the ultimate, long-term payoff will be lower remediation costs for the federal government.

However, the more immediate benefits that can be derived from an integrated demonstration and evaluation program include: (1) identification of practically achievable and cost effective goals for cleanup; (2) establishment of a research and development platform for advancement of remediation technologies; (3) accelerated acceptance of innovative technologies as

presumptive remedies for the reduction in the time and cost of cleanup; (4) well documented engineering packages (where appropriate) for the broader application of effective technologies; (5) cost savings for SERDP sponsored (and other) demonstrations; and (6) advanced understanding of the fate and transport of contaminants.

Furthermore, the data management system will greatly assist in the transfer of technology from the research/demonstration sites to potential customers anywhere in the US or the world.

**9. Milestones:**

A. Test Location Management/Infrastructure

A.1. Publicize and coordinate test site	complete	09/94
A.2. Update site characterization data	complete	10/94
A.3. Complete action plan for site development	complete	12/94
A.4. Site development for Offgas demonstrations	complete	12/94

B. Demonstration Oversight

B.1. Start demonstration #1		9/95
B.2. Complete demonstration #1		12/95
B.3. Start demonstration #2		1/96

C. Database Development

C.1. Develop data model		9/95
C.2. Develop first prototype		10/95
C.3. Develop full prototype		12/95
C.4. Install and operate data network		03/96

**10. Transition Plan:**

Cost and performance data will be collected by the standardized methodology and entered into the D/NETDP cost-and-performance database (when available). At the conclusion of each demonstration, the PI for the demonstration project will write a technology evaluation report and produce a technical data package. From these, the Test Location Manager will write a demonstration summary sheet and technology brief. Where appropriate, engineering design, fabrication and procurement guidance will also be provided by the Test Location Manager, which will provide regulators, users, and the public with the information, presented in a useable fashion, necessary to implement technology acceptance and transfer to commercial use. Other technology transfer efforts will include technical short courses/seminars, on-site visitor's workshops, field assistance, conference exhibits, and demonstration videotapes and brochures.

## 11. Funding: \$(K)

	FY94	FY95	FY96	FY97	FY98	FY99	TOTAL
Test Location Management/ Infrastructure SERDP	0	0	375	250	250	250	1125
Database Development SERDP	500	0	625	250	250	250	2575
TOTAL SERDP	500	0	1000	500	500	500	3700

## 12. Performers:

12.1 Test Location Management. Demonstrations at McClellan AFB are managed by a Test Location Manager. On site execution and day-to-day oversight will be performed by a private firm contractor (Clean Sites). The SERDP Program Office provides D/NETDP management and program oversight.

For purposes of coordination within the D/NETDP, each National Test Location Manager is a member of a Test Location Managers' committee, which comprises SERDP representatives as well as Test Location Managers. This committee represents a Tri-Services and EPA coordinated effort to work with other organizations on uniform reporting formats and test protocols guidance.

12.2 Database Development. Database development is managed by a McClellan AFB staff manager. The work is performed by private firm contractors (Mitre Corporation) and government agencies (Sandia National Lab, EPA RREL)

## 13. Principal Investigator:

Mr. Bud Hoda  
SM-ALC/EMR  
5050 Dudley Blvd, Suite 3  
McClellan AFB, CA 95652  
PHONE: (910)-643-1742  
FAX: (910)-643-0827

## 14. Keywords:

National Test Location, Chlorinated Hydrocarbons, Cost-and-Performance Database, Data Management

## SERDP FY95 PROJECT

**1. SERDP Thrust Area:** Cleanup

**2. Title:** National Test Location, National Center for Integrated Bioremediation Research and Development (NCIBRD), Wurtsmith AFB, Oscoda, MI

**3. Agency:** Environmental Protection Agency

**4. Laboratory:** Gulf Breeze Laboratory

**5. Project ID:** #864

**6. Problem Statement:**

The current process for gaining acceptance of cost-effective, innovative technologies for the cleanup of federal installations is laborious and costly. The problem stems from several causes: the lack of certification for new technologies as presumptive remedies, the lack of formally established technology demonstration programs ensuring protocols and quality assurance/quality control procedures sufficient to meet requirements of regulators and users, and the lack of information dissemination in formats suitable for all interested parties. The first problem cause listed above can only be addressed by legislative change through the political process. The latter causes can be addressed by a comprehensive technology demonstration/evaluation/transfer program. The DoD/National Environmental Technology Demonstration Program (D/NETDP) provides such a comprehensive technology demonstration/evaluation/transfer program. The goal is to provide test locations for comparative demonstration and evaluation of cost-effective and innovative technologies to enable transfers from research to full-scale use. The Air Force, Army, Navy, and EPA are partners in D/NETDP, and there are five test locations.

Achieving this goal requires the accomplishment of the following objectives: (1) query regulators, users, and the public to ascertain what information is needed from a demonstration, and what presentation format is preferred in order for their acceptance of new technology; (2) standardize the data collection and analysis to the extent possible across the partnering Services and EPA; (3) provide characterized test locations together with the infrastructure required for the demonstration and evaluation of innovative technologies under comparable and well-characterized hydrogeologic and climatic conditions; (4) involve regulators, users, and the public throughout the course of technology demonstrations; (5) provide test beds for supporting environmental research; (6) support the widespread dissemination of technical evaluations, performance or guidance specifications, and economic data.

Each D/NETDP test location provides well-characterized test sites and the infrastructure required for technology demonstration. Dedicated sites allow better use of resources compared to one-off, developer-staged demonstrations because site selection, permitting, characterization, and provision of infrastructure are not required for each new technology demonstration.

In addition to infrastructure, demonstration oversight, and support services at each D/NETDP test location, there is also a joint programmatic effort undertaken by the partnering Services and EPA to support technology demonstrations. With FY 94 funding (Army Environmental Center lead), the D/NETDP is developing a Quality Management Plan (QMP) which will include guidance for writing test plans, cost and performance data collection criteria, QA/QC plans, success criteria, regulatory and user interface, and technology transfer strategy. The QMP is a common link among the Services and EPA to expedite the development of better, more efficient cleanup technologies. A cost-and-performance database, which will serve as a repository for results of demonstrations to facilitate technology transfer, is also being developed with FY 94 funding (McClellan AFB lead). EPA provides additional guidance and support to each D/NETDP test location through its Site Characterization and Monitoring Technology Demonstration Program at NERL, CRD-LV.

## **7. Project Description:**

The project objective is to support the establishment and operation of the National Center for Integrated Bioremediation Research and Development (NCIBRD) which is a national field research and demonstration facility for advanced technologies for decontamination of hazardous wastes and remediation of spills and disposal sites. The facility is being established at the recently decommissioned Wurtsmith AFB in Oscoda, MI, and will serve as the EPA National Test Location in the D/NETDP program addressing fuels and solvents problems, which are USAF-lead contaminants.

NCIBRD is addressing a broad array of research and development need pertaining to the transfer and conversion of laboratory findings into successful remediation practice. The program focuses on several specific problems relating to the development of core biotechnologies such as the enhanced understanding of microbiology and biochemistry, improved means for implementing biotechnology in engineering applications, and remediation of contaminated soils. The facility is focusing on technologies having evident promise for complete and cost effective remediation with minimal environmental disruption. These technologies involve on-site and in-situ processes which integrate biological and physicochemical methods.

Controlled on-site research and demonstration programs dealing with the advanced integrated technologies or decontamination of hazardous substances in wastes, soils, and groundwater are to be conducted at the facility. The majority of the contaminated sites at Wurtsmith AFB are already characterized. Site characterization will continue as required to establish well-characterized background conditions at selected demonstration sites. Several of the sites are under remediation by way of pump and treat systems. The facility provides a focal point for coordination and cooperation within the broad community of institutions, agencies, and corporations currently attempting to develop these technologies.

## 8. Expected Payoff:

By including private technology demonstrators, regulators, users, and the public in the demonstration planning process, each D/NETDP test location provide opportunities for identifying and developing acceptable cost effective technologies for transfer to other Government agencies and the private sector. By achieving the goals and objectives of this program, the ultimate, long-term payoff will be lower remediation costs for the federal government.

However the more immediate benefits that can be derived from an integrated demonstration and evaluation program include: (1) identification of practically achievable and cost effective goals for cleanup; (2) establishment of a research and development platform for advancement of remediation technologies; (3) accelerated acceptance of innovative technologies as presumptive remedies for the reduction in the time and cost of cleanup; (4) well documented engineering packages (where appropriate) for the broader application of effective technologies; (5) cost savings for SERDP sponsored (and other) demonstrations; and (6) advanced understanding of the fate and transport of contaminants.

NCIBRD will provide significant direct and indirect benefit to the Department of Defense, Department of Energy, and the US Environmental Protection Agency environmental research and development program. Research and demonstration programs on advanced remediation technologies can be evaluated on a common baseline. This will ensure that the most cost effective technologies can be implemented for the remediation of thousands of contaminated military, public, and industrial sites throughout the country. It will also provide a standard test bed that environmental regulators can evaluate and accept. This will result in a simplified approval process for new technologies and the transfer of those technologies from the laboratory to the user. Field site testing at a location which is extensively characterized and controlled with monitoring well systems will save considerable amounts of money in developing individual research projects. The Michigan Department of Natural Resources provides matching funds to support NCIBRD and strongly supports the goals of the effort.

## 9. Milestones:

### A. Infrastructure Development

- |    |   |       |
|----|---|-------|
| 1. | Test-location-wide site characterization database construction  | 4/95  |
| 2. | Integrate database with GIS system and USAF BCA   | 7/95  |
| 3. | Conduct site surveys for 5 prospective sites<br>for in situ bioremediation                                | 7/95  |
| 4. | Conduct comprehensive survey/analysis of candidate Controlled<br>Subsurface Injection sites               | 7/95  |
| 5. | Design and obtain bids for construction<br>of decontamination facility                                    | 4/95  |
| 6. | Construct decontamination facility  | 6/95  |
| 7. | Design system of parallel test cells for controlled<br>subsurface injection of aqueous phase contaminants | 12/95 |

8. Construction of first Test Cell for controlled subsurface injection (including monitoring and control systems) 4/96

**B. Demonstration Oversight**

- 1. Conduct demonstration of SCAPS tunable laser (729-A) 7/95
- 2. Conduct demonstration of Field GC-MS system (private vendor, assistance from NERL) 8/95
- 3. Start demonstration Ecological Biomarkers (244-EPA) 10/95
- 4. Complete second year of sampling and analysis program for intrinsic bioremediation demonstration at site FT-2 (405-EPA) 12/95
- 5. Complete initial sampling and analysis program for intrinsic bioremediation demonstration at site KC-135 (383-EPA) 3/96

**10. Transition Plan:**

Cost and performance data will be collected by the standardized methodology and entered into the D/NETDP cost-and-performance database (when available, McClellan AFB lead). At the conclusion of each demonstration, the PI for the demonstration project will write a technology evaluation report and produce a technical data package. From these, the Test Location Manager will write a demonstration summary sheet and technology brief. Where appropriate, engineering design, fabrication and procurement guidance will also be provided by the Test Location Manager, which will provide regulators, users, and the public with the information, presented in a useable fashion, necessary to implement technology acceptance and transfer to commercial use. Other technology transfer efforts will include technical short courses/seminars, on-site visitor's workshops, field assistance, conference exhibits, and demonstration videotapes and brochures.

**11. Funding: \$(K)**

	FY93	FY94	FY95	FY96	FY97	FY98	FY99	TOTAL
Test Location Management/ Infrastructure SERDP	2300	1900	2580	1600	1600	1600	1600	13180

**12. Performers:**

EPA Gulf Breeze Laboratory has a Cooperative Agreement with the University of Michigan Department of Civil and Environmental Engineering, which is the lead institution in the NCIBRD Consortium, for technical management and execution of this project. The Consortium comprises EPA, DoD, University of Michigan, and the Michigan Department for Natural Resources. It coordinates with representatives of academic research institutes, industrial corporations and associations (for example, through the Remediation Technologies Development Forum), and government agencies (through the Great Lakes and Mid-Atlantic Center for Hazardous Substance Research). Dr. Walter J. Weber, Jr., of the University of

Michigan College of Engineering is the Executive Director of the Consortium. Dr. Michael Barcelona of the same institution will serve as the Operating Director of the Consortium. The Consortium maintains offices and staff in Ann Arbor, MI, and on the NCIBRD Test Location at Wurtsmith AFB. Demonstration activities are coordinated with the USAF Base Closure Agency (BCA).

For purposes of coordination within the D/NETDP, each National Test Location Manager is a member of a Test Location Managers' committee, which comprises SERDP representatives as well as Test Location Managers. This committee represents a Tri-Services and EPA coordinated effort to work with other organizations on uniform reporting formats and test protocols guidance.

### **13. Principal Investigator:**

Dr. Robert Menzer  
Director, Gulf Breeze Environmental Research Laboratory  
Office of Research and Development  
U.S. Environmental Protection Agency  
Sabine Island  
Gulf Breeze, FL 32561

NCIBRD Executive Director

Walter J. Weber, Jr., Ph.D., P.E., D.E.E.  
Suite 181 EWRE Building  
1351 Beal Avenue, North Campus  
University of Michigan  
Ann Arbor, MI 48109-2125  
PHONE: (313)-747-2904  
FAX: (313)-736-2275  
E-MAIL: walter.j.weber@um.cc.umich.edu

NCIBRD Operating Director/Test Location Manager

Dr. Michael J. Barcelona  
Director, Field Operations and Research — NCIBRD  
Department of Civil and Environmental Engineering  
IST Building — 1221  
University of Michigan, North Campus  
2200 Bonisteel Boulevard  
Ann Arbor, MI 48109-2099  
PHONE: (313)-763-9666  
FAX: (313)-763 6513  
E-MAIL: mikebar@engin.umich.edu



**14. Keywords:**

NCIBRD, National Test Location, fuels, solvents, organic mixtures, in situ, bioremediation, technology demonstration, demonstration site

## SERDP FY95 PROJECT

### 1. SERDP Thrust Area: Cleanup

**2. Title:** DoD/National Environmental Technology Demonstration: Site Characterization and Monitoring Technology Demonstration Program, [component of DoD/National Environmental Technology Demonstration Program (D/NETDP)]

**3. Agency:** Environmental Protection Agency

**4. Laboratory:** National Exposure Research Laboratory (NERL, CRD-LV)

**5. Project ID:** #374

### 6. Problem Statement:

The current process for gaining acceptance of cost-effective, innovative technologies for the cleanup of federal installations is laborious and costly. The problem stems from several causes: the lack of certification for new technologies as presumptive remedies, the lack of formally established technology demonstration programs ensuring protocols and quality assurance/quality control procedures sufficient to meet requirements of regulators and users, and the lack of information dissemination in formats suitable for all interested parties. The first problem cause listed above can only be addressed by legislative change through the political process. The latter causes can be addressed by a comprehensive technology demonstration/evaluation/transfer program. The DoD/National Environmental Technology Demonstration Program (D/NETDP) provides such a comprehensive technology demonstration/evaluation/transfer program. The goal is to provide test locations for comparative demonstration and evaluation of cost-effective and innovative technologies to enable transfers from research to full-scale use. The Air Force, Army, Navy, and EPA are partners in D/NETDP.

Achieving this goal requires the accomplishment of the following objectives: (1) query regulators, users, and the public to ascertain what information is needed from a demonstration, and what presentation format is preferred in order for their acceptance of new technology; (2) standardize the data collection and analysis to the extent possible across the partnering Services and EPA; (3) provide characterized test locations together with the infrastructure required for the demonstration and evaluation of innovative technologies under comparable and well-characterized hydrogeologic and climatic conditions; (4) involve regulators, users, and the public throughout the course of technology demonstrations; (5) provide test beds for supporting environmental research; (6) support the widespread dissemination of technical evaluations, performance or guidance specifications, and economic data.

Each D/NETDP test location provides well-characterized test sites and the infrastructure required for technology demonstration. Dedicated sites allow better use of resources compared to one-off, developer-staged demonstrations because site selection, permitting, characterization, and provision of infrastructure are not required for each new technology demonstration.

In addition to infrastructure, demonstration oversight, and support services at each D/NETDP test location, there is also a joint programmatic effort undertaken by the partnering Services and EPA to support technology demonstrations. With FY 94 funding (Army Environmental Center lead), the D/NETDP is developing a Quality Management Plan (QMP) which will include guidance for writing test plans, cost and performance data collection criteria, QA/QC plans, success criteria, regulatory and user interface, and technology transfer strategy. The QMP is a common link among the Services and EPA to expedite the development of better, more efficient cleanup technologies. A cost-and-performance database, which will serve as a repository for results of demonstrations to facilitate technology transfer, is also being developed with FY 94 funding (McClellan AFB lead). EPA provides additional guidance and support to each D/NETDP test location through its Site Characterization and Monitoring Technology Demonstration Program at NERL, CRD-LV.

There is a clear need to ensure that better, faster, and less expensive technologies are available to those responsible for cleaning up contaminated sites. Achieving cost-effective site cleanup is in everyone's best interest. Currently there is a long lag time between the successful field demonstration of a new technology and its routine use. This will likely continue unless someone takes the lead in advancing innovative and emerging technologies. It is also apparent that without active involvement by EPA, the emergence and use of new technologies will continue only slowly. This project is considered a technology transfer and diffusion activity.

## **7. Project Description:**

The purpose of this project is to sustain the EPA-led portion of the DoD's National Environmental Technology Demonstration Program (D/NETDP) for facilitating the development, commercialization, and use of innovative monitoring, measurement and site characterization technologies. NERL, CRD-LV is responsible for planning and administering demonstrations of SERDP-developed technologies for site characterization and monitoring technology, as well as technologies funded by other sources (where the technology can be used to support a DoD requirement). NERL, CRD-LV is also responsible for producing guidance on how to conduct and evaluate these types of technologies, and for managing and disseminating information on demonstrated technologies. NERL, CRD-LV also provides general advice and support to the other D/NETDP National Test Location Managers for conducting demonstrations.

The FY95 resources will be used for supporting site characterization technology demonstrations and EPA's role in supporting the other National Test Location Managers. With regard to demonstrations, these resources will be used in FY96 to complete the demonstrations that were started in FY95 and to start additional demonstrations of SERDP-

supported technologies. We are in the process of contacting the project officers identified in the FY94 SERDP Strategic Investment Plan to determine which technologies will require our support in FY96. We will identify those SERDP technologies that will be demonstrated in the subsequent quarterly reports. We are also in the process of identifying technologies from other sources that may be suitable candidates for demonstration at the National Test Locations. These too will be identified in subsequent quarterly reports. However, we will seek the approval of the Thrust Area Working Group and SERDP Program Office before committing to a demonstration of non-SERDP derived technologies.

## **8. Expected Payoff:**

By including private technology demonstrators, regulators, users, and the public in the demonstration planning process, each D/NETDP test location provide opportunities for identifying and developing acceptable cost effective technologies for transfer to other Government agencies and the private sector. By achieving the goals and objectives of this program, the ultimate, long-term payoff will be lower remediation costs for the federal government.

However, the more immediate benefits that can be derived from an integrated demonstration and evaluation program include: (1) identification of practically achievable and cost effective goals for cleanup; (2) establishment of a research and development platform for advancement of remediation technologies; (3) accelerated acceptance of innovative technologies as presumptive remedies for the reduction in the time and cost of cleanup; (4) well documented engineering packages (where appropriate) for the broader application of effective technologies; (5) cost savings for SERDP sponsored (and other) demonstrations; and (6) advanced understanding of the fate and transport of contaminants.

Savings in site cleanup will reduce the need for new or additional federal taxes to support federally funded cleanups. Lower costs for cleanups funded by private parties should reduce inflationary pressures. The demonstration program will provide a central conduit to channel new technologies to the marketplace more expediently than current methods. Investment capital should be easier to obtain because the developer will have a technology acceptance road map to show to investors. The verification of technology should help in reducing the amount of uncertainty that users often have regarding new technology to an "acceptable" level. We will support the use and implementation of new technologies by rapidly introducing them to the user community through training, field trials, and direct application to current sites. This demonstration activity satisfies many of the SERDP objectives. It is designed to maximize information transfer and reduce duplication; provide assistance to public and private sector users and developers; support the diffusion of technologies derived from basic R&D programs; be a collaborative effort; and support demonstrations of private sector technology demonstrations.

**9. Milestones:**

- 1. Final guidance for conducting demonstrations of site characterization and monitoring technologies 07/95
- 2. Final data validation criteria 12/95
- 3. Demonstration report technology #1 01/96
- 4. Demonstration report technology #2 03/96
- 5. Demonstration report technology #3 04/96

**10. Transition Plan:**

Cost and performance data will be collected by the standardized methodology and entered into the D/NETDP cost-and-performance database (when available, McClellan AFB lead). At the conclusion of each demonstration, the PI for the demonstration project will write a technology evaluation report and produce a technical data package. From these, the Test Location Manager will write a demonstration summary sheet and technology brief. Where appropriate, engineering design, fabrication and procurement guidance will also be provided by the Test Location Manager, which will provide regulators, users, and the public with the information, presented in a useable fashion, necessary to implement technology acceptance and transfer to commercial use. Other technology transfer efforts will include technical short courses/seminars, on-site visitor's workshops, field assistance, conference exhibits, and demonstration videotapes and brochures.

It is expected that the NERL, CRD-LV technology demonstration activity will be necessary through at least FY 03. This effort, in and of itself, will not be transitioned to others. Its function is to assist developers in transitioning their technologies into routine use.

**11. Funding: \$(K)**

SERDP	FY93	FY94	FY95	FY96	FY97	FY98	FY99	TOTAL
	500	200	350	259	250	250	250	2059

**12. Performers:**

The lead organization for this project is EPA. It will be administered by the Office of Research and Development's National Exposure Research Laboratory, Characterization Research Division in Las Vegas, NV. DOE's Sandia National Lab (SNL) is a partner in this activity. SNL is administering DOE's Mixed Waste Landfill Integrated Demonstration (MWLID). We are also working with Lockheed Environmental Systems & Technology Company (LESAT). LESAT is the NERL, CRD-LV mission support contractor. In DoD, the Navy's Naval Research Laboratory has become a member of the team. Their support is being provided by EPA through the Environmental Technology Initiative.

For purposes of coordination within the D/NETDP, each National Test Location Manager is a member of a Test Location Managers' committee, which comprises SERDP representatives as well as Test Location Managers. This committee represents a Tri-Services and EPA coordinated effort to work with other organizations on uniform reporting formats and test protocols guidance.

**13. Principal Investigator:**

Eric N. Koglin  
U.S. EPA NERL, CRD-LV  
PO Box 93478  
Las Vegas, NV 89193-3478  
PHONE: (702) 798-2432  
FAX: (702) 798-2261  
E-MAIL: KOGLIN.ERIC@EPAMAIL.EPA.GOV

**14. Keywords:**

Site characterization, monitoring, National Test Location, technology demonstration, and demonstration site

TABLE XVIII FY 1995 COMPLIANCE PROJECTS		Funding \$(K) FY95	ID Number	Page Number
Boiler/Engine Emissions				
Evaluation of Metal Perovskite Catalysts for NOx Reduction (AF)	25	177	CP-3	
Compact, Closed-Loop Controlled Waste Incineration (N)	300	34	CP-7	
Reduction of NOx Emissions from Marine Power Plants (N/EPA)	300	42	CP-12	
General Hazardous Waste Management				
Lead-Based Paint Hazard Mitigation (A)	400	521	CP-18	
Emission Reduction Planning Model (AF)	100	175	CP-23	
Laser Ablation/Ionization Characterization of Solids (DOE)	100	362	CP-28	
Vapor Permeation VOC Recovery from Refueling and Storage (EPA/N)	100	252	CP-33	
Monitoring				
Advanced Mass Spectrometry for Atmospheric Monitoring (AF)	150	192	CP-36	
Leak Location in Underground Pipelines (EPA/A/N/NSF)	0	249	CP-41	
Noise Impacts				
Controlling, Assessing, Managing, and Monitoring the Noise Impact from Weapons, Helicopters, and Aircraft on Training and Readiness (A)	325	523	CP-46	
Open Burning/Open Detonation				
Characterization Open Burning/Open Detonation Emissions (A)	3,000	247	CP-51	
Measuring and Modeling for OB/OD Permitting (EPA)	550	251	CP-56	

TABLE XVIII FY 1995 COMPLIANCE PROJECTS		Funding \$(K) FY95	ID Number	Page Number
<b>Physical Treatment Processes</b>				
Encapsulation of Hazardous Ions in Smectite Clays (DOE)		200	315	CP-60
Kinetics of Supercritical Water Oxidation (DOE)		300	364	CP-65
Waste Forms Based on Separations Media (DOE)		100	360	CP-70
<b>Shipboard Emissions</b>				
Shipboard Non-Oily Wastewater Treatment System (N)		250	29	CP-75
<b>Waste Minimization/Recycling</b>				
Evaluation of the Use of Waste Energetics as Supplemental Fuels (A/N/DOE)		300	524	CP-79
<b>Compliance Total</b>		<b>6,500</b>		



## SERDP FY95 PROJECT

1. **SERDP Thrust Area:** Compliance
2. **Title:** Evaluation of Metal Perovskite Catalysts for NO<sub>x</sub> Reduction
3. **Agency:** U.S. Air Force
4. **Laboratory:** Armstrong Lab (AL)
5. **Project ID:** #177
6. **Problem Statement:**

**Goal:** The goal of this research is to investigate whether oxygen deficient strontium-lanthanum cobaltate ( $\text{Sr}_x\text{La}_{1-x}\text{CoO}_3$ ) can be stabilized for long-term use as a catalyst for reduction of oxides of nitrogen (NO<sub>x</sub>).

**Background:** The control of NO<sub>x</sub> emissions is mandated by federal, state, and local regulations. These sources are generally characterized by high-temperature combustion of fossil fuels, where organically bound nitrogen in the fuel oxidizes to form NO and small amounts of NO<sub>2</sub> and N<sub>2</sub>. (In most cases, NO<sub>2</sub> emissions will be as low as 5-10 percent by volume of total NO<sub>x</sub> emissions.) While fuel combustion to produce commercial power and motor vehicle emissions are the two largest contributors in the United States to NO<sub>x</sub> production, other sources have been targeted as well, including jet engine test cells (JETCs). Existing methods to remove NO<sub>x</sub> from combustion exhausts do so only under a narrow range of conditions.

Previous investigations have shown that NO can be reduced by levels greater than 90 percent by LaCoO<sub>3</sub> catalysts. Conversion of NO increases from less than 10 percent at temperatures below about 450°C to over 90 percent at about 525°C for internal combustion engine exhausts with air-to-fuel ratio of 12.85. At 660°C, an air-to-fuel ratio of 14.35 resulted in 90 percent conversion of NO (excess air requires higher conversion temperatures). Stability can be expected at relatively higher temperatures, as LaCoO<sub>3</sub> has a melting point of 1607°C, and the La--Co--O system has a low temperature eutectic in air at 1482°C. The presence of CO in exhaust air enhances the conversion of NO while O<sub>2</sub> reduces NO conversion. CO reacts with H<sub>2</sub>O and produces H<sub>2</sub>, which at sufficiently high temperatures, acts to reduce the LaCoO<sub>3</sub> catalyst, resulting in an oxygen deficient structure. This oxygen vacancy allows for chemisorption of CO or NO, and likewise acceleration of the conversion reaction of NO and CO to N<sub>2</sub> and CO<sub>2</sub>. As the conversion process continues, the LaCoO<sub>3</sub> is reduced through a complex series of reactions, which are accelerated in the presence of O<sub>2</sub>. At weight losses above 3.5 percent, phase changes begin to occur and Co metal is formed, resulting in loss of catalytic activity. The addition of an Sr ion by replacing one La ion (yielding  $\text{Sr}_x\text{La}_{1-x}\text{CoO}_3$ ) may result in a faster and lower temperature conversion of NO, while withstanding higher levels of reduction before losing effectiveness as a catalyst. Previous investigations suggest that the  $\text{Sr}_x\text{La}_{1-x}\text{CoO}_3$  catalyst can withstand weight losses of between 8-9 percent before reverting to Co metal. Concentrations of selected species (such as oxygen) during reactions

can be monitored using electrochemical cells. By controlling the oxygen concentrations, the reduction of the catalyst can be controlled.

## 7. Project Description:

**Technical Objective:** The technical objective of this project is to investigate the thermodynamics and kinetics of reduction of  $\text{Sr}_x\text{La}_{1-x}\text{CoO}_3$  in NO and determine the limits of stability of the active oxygen deficient phase to establish the effectiveness of  $\text{Sr}_x\text{La}_{1-x}\text{CoO}_3$  for use as a long-term  $\text{NO}_x$  catalyst. Representative NO environments containing gases which can be expected in exhaust streams of interest (e.g., JETCs) will be used.

**Technical Approach:** All basic research for this project will be on the laboratory scale, including modeling of representative exhaust streams. (1) The thermodynamics and kinetics of reduction of  $\text{Sr}_x\text{La}_{1-x}\text{CoO}_3$  will be analyzed using techniques involving thermogravimetric analysis (TGA), differential scanning calorimetry (DSC), and the use of high-temperature electrochemical cells to measure oxygen activity. X-ray diffraction techniques will be used for crystallographic examinations. Models for thermodynamic and kinetics of phase equilibria of the oxygen deficient phase will be developed. (2) Developing techniques for stabilizing the oxygen deficient phase will involve investigating effects of varying stoichiometry on stability of the ceramic material and examining the feasibility of using solid state electrolytes (YSZ) to control the extent of reduction of the catalyst. Once a technique to stabilize the active phase has been developed, the kinetics of conversion of NO will be investigated to determine efficiency and speed of catalysis of NO. (3) Models of the catalysis of NO by  $\text{Sr}_x\text{La}_{1-x}\text{CoO}_3$  will be developed and reported.

Technology demonstration will be performed at an Air Force facility; Tyndall AFB FL and McClellan AFB CA are potential candidates. (1) Technical data required for installation of the slipstream and full-scale emission control systems will be gathered. Prior experience and information gained from related projects will be beneficial in completing this task. (2) A sub-scale system will be designed and installed to evaluate performance of the catalyst under near-full scale operating conditions. A multigas analyzer in conjunction with a computer data acquisition system will be utilized to provide continuous emissions monitoring during testing. (3) Results from the sub-scale prototype system will be evaluated and reported. These results will be used in the design of a full-scale prototype control system for a JETC. (4) The control system will remain in use for a sufficient time to determine the long-term stability and life cycle of the catalysts. The same data acquisition system will be utilized. (5) Test results will be evaluated and reported.

**Relationship to DoD Environmental Objectives:** This research, as applied to DoD JETCs, directly contributes to the requirement to control maintenance process emissions as identified in the Tri-Service Environmental R&D Strategic Plan, DoD Pillar 2: COMPLIANCE; Requirement Thrust 2.B.2: Maintenance Process Emissions (Test Stands and Cells).

**Relationship to Other Work:** This is an alternative approach applicable to  $\text{NO}_x$  removal from JETCs. A Small Business Innovative Research (SBIR) program initiated seven independent approaches to  $\text{NO}_x$  control for JETCs and identified one, a vermiculite--MgO sorbent process, as the most practical and cost-effective at present state of development. Promising technologies such as the  $\text{Sr}_x\text{La}_{1-x}\text{CoO}_3$  catalyst should be pursued as a potential marketable

NO<sub>x</sub> reducer and replacement NO<sub>x</sub> control for JETCs in the event the vermiculite--MgO sorbent fails as a practical control device.

Technical Risks: There are some limited risks in this research. It may be difficult to control the degree of reduction of the catalyst, precluding long-term use. In addition, the catalytic activity of strontium-doped lanthanum cobaltate may be too slow to act as a fast catalyst needed for current applications.

## 8. Expected Payoff:

Potential Users: Air Force major command operations and maintenance activities that emit combustion exhausts, other DoD operations and maintenance activities, and private operations could benefit from this research.

Impact: If successful, this work can lead to effective and inexpensive catalysts for NO and CO conversion. The catalyst has the potential to benefit many applications with high-temperature NO<sub>x</sub> reduction, including JETC emission controls, and possibly direct emissions from jet engines and combustion sources. Sr<sub>x</sub>La<sub>1-x</sub>CoO<sub>3</sub> has a relatively low concentration of strategic materials and applications where Sr<sub>x</sub>La<sub>1-x</sub>CoO<sub>3</sub> could replace platinum may be identified.

## 9. Milestones:

1.	Materials Preparation	09/94
2.	Design and Construction of Testing Apparatuses	12/94
3.	Investigate Thermodynamics and Kinetics of Reduction of Oxygen Deficient Phase	09/95
4.	Phase I Final Report	10/95
5.	Identify Techniques to Stabilize the Oxygen Deficient Structure	03/96
6.	Investigate the Kinetics of NO Reduction by Stabilized Sr <sub>x</sub> La <sub>1-x</sub> CoO <sub>3</sub>	09/96
7.	Phase II Final Report	10/96
8.	Complete Investigations and Development of Models	09/97
9.	Final Report	10/97

## 10. Transition Plan:

The results of the 6.2 basic research will be used in a follow-on 6.3 technology demonstration effort where catalyst performance in controlling emissions from an operational JETC will be demonstrated at an Air Force facility. Favorable results would allow technology transfer to the Environmental Systems Program Office (HSC/YA) for EMD and fielding. Technical reports and articles will also be produced for the R&D community, other agencies, and industry.

## 11. Funding: \$(K)

	FY94	FY95	FY96	FY97	Total
SERDP	175	25	75	90	365

## **12. Performers:**

This is a joint research effort between: Air Force Armstrong Laboratory Environics Directorate, Environmental Compliance Division (AL/EQS); and Army Construction Engineering Research Laboratories (USACERL). Research will be conducted in-house by USACERL and field-demonstrated at an Air Force facility.

## **13. Principal Investigators:**

AIR FORCE

Dr. Joseph D. Wander

AL/EQS

139 Barnes Dr., Suite 2

Tyndall AFB, FL 32402-5323

PHONE: (904) 283-6240

FAX: (904) 283-6286

E-MAIL: JOSEPH\_WANDER@CCMAIL.ALEQ.TYNDALL.AF.MIL

ARMY

Dr. Ellen G. Segan

US Army CERL

PO Box 9005

Champaign IL 61826-9005

PHONE: (217) 373-6768

FAX: (217) 373-7222

## **14. Keywords:**

Perovskite, NO<sub>x</sub>, Air pollution, Catalyst, Doping, Cintering.

## SERDP FY95 PROJECT

1. **SERDP Thrust Area:** Compliance
2. **Title:** Compact, Closed-Loop Controlled Waste Incinerator
3. **Agency:** U.S. Navy
4. **Laboratory:** Naval Air Warfare Center Weapons Division China Lake (NAWC)
5. **Project ID:** #34
6. **Problem Statement:**

A new generation of incinerators based on recently developed active ramjet-combustion control is required for ship-board waste disposal to enable Navy ship access to ports and bodies of water around the world without operational constraints from environmental laws and regulations. The present practice of over-board discharge and storage/off-loading becomes unacceptable. Thermal destruction is considered the ultimate solution beyond 2000 for all types of waste, including trash, garbage, plastics, medical and hazardous wastes. The need for improved waste disposal is clearly identified in the Tri-Service Environmental Quality R&D Strategic Plan as shown later. Present commercial incinerators are typically unsuitable for Navy shipboard installation and operation because they are oversized and often do not meet incineration standards, in particular at off-design operation. Oversizing in the present system, in terms of air and auxiliary fuel mass flows, reactor size, and air pollution control system is necessary because physical understanding of interrelated processes in mixing and combustion is limited and control authority over the various steps which make-up the incineration process does not exist.

For ship-board use, compact (small size) incinerators with assured (pollution-free) waste destruction during design and off-design operation are essential. Potential development of these advanced incinerators is made possible through recent accomplishments in combustion control which is based on the detailed understanding of acoustic/fluid dynamic/combustion interactions. This new understanding was in part developed under ONR sponsorship to improve ramjet performance. When applied to waste incineration, improved waste destruction efficiency was demonstrated in preliminary tests with controlled pressure oscillations for improved heat transfer using solid waste and for establishing organized vortical structures for controlled incineration using gaseous and potentially liquid waste. In particular, the use of active control to maintain optimum conditions between pressure oscillations, vortical structures and waste/fuel injection was effective and emerged as a promising feature for advanced incinerators. For active combustion control, novel sensors are continuously monitoring in real-time the combustion process and the exhaust, and are actively manipulating the important steps of the incineration process via a controller and actuators. Further improvements can be expected from closed-loop active control.

Based on the above results, the ONR research program "Combustion Control in Compact Waste Incinerators" within the Environmentally Sound Ship Program was started in late FY93. This collaborative research program between NAWCWPNS and three universities is aimed to provide scientific insight for the demonstration of a compact incinerator with Dr.

Klaus Schadow, NAWCWPNS, on detail to ONR as program coordinator. Future funding originally planned for this research program has been absorbed into the SERDP program. This present SERDP proposal will (1) provide continued funding of the basic research program started at ONR, (2) expand current basic research efforts to include novel sensor research, (3) start applied research in actuator and sensor technology, and (4) initiate transition of the research to demonstrate assured (pollution-free) incineration in a compact prototype device for ship-board use. Technology transfer will be an important part of the proposal. Several companies including APV Chemical Machinery, Hypertat Corporation, Energy and Environmental Research Corporation, and SonoTech Inc., have expressed interest in applying the new technology of compact incinerators to the civilian sector. Compact incinerators will allow disposal of the waste on the same site where it is generated, without need for waste transportation. This is of particular importance for medical waste.

## **7. Project Description:**

The overall goal of the proposal is the demonstration of a compact prototype incinerator with closed-loop active combustion control. This new approach for achieving assured (pollution-free) waste destruction in a compact system requires the physical understanding of the various steps in the incineration process, and the use of appropriate sensors and actuators. The project consists of four concurrent tasks of basic and applied research, and incinerator prototype demonstration:

(1) The physical understanding for active combustion control is presently extended to waste incineration in the above mentioned ONR program. It is proposed to continue this basic research under SERDP funding to control the mechanisms of pyrolysis, gasification, combustion and pollution in the core of acoustically driven vortical structures and define mechanisms of the recently observed increases in solid waste incineration efficiencies in the presence of resonant acoustics. In particular, closed-loop active control will be studied.

(2) With the new physical understanding, control authority on the incineration process will be established. To implement active, closed-loop control, sensors for real-time, continuous exhaust monitoring are required which provide the input to the actuators to maintain desired pressure oscillations and modulate auxiliary air/fuel and waste injection. It is proposed to expand the basic research to explore new laser-based diagnostics. Surrogate species will be used as a performance indicator as also proposed for compliance with the Clean Air Act. There are a number of potential optical techniques for real-time sensing of target species, which include Broadband Infrared Absorption/Emission, Laser-Induced Fluorescence, Fourier Transform Infrared Spectroscopy, and Tunable Diode-Laser Spectroscopy.

(3) Concurrent with the basic research, an applied research program will be initiated to develop sensors and actuators for combustion control. Research and development work is required for sensors to monitor critical combustion steps, for acoustic actuators to maintain desired resonant pressure oscillations, and for mass-flow actuators to modulate gaseous and liquid flows at high frequencies.

(4) The basic and applied research provides the foundation for the demonstration of a closed-loop controlled compact incinerator. One concept of a solid waste incinerator consist of a combination of a primary and secondary chamber. In the primary chamber (for example rotary kiln), controlled pressure oscillations will be used for improved heat transfer and

waste decomposition/combustion; in the secondary chamber, complete waste combustion (afterburning) is obtained with synchronized air/fuel injection into acoustically driven vortices. Output from emission sensors will be used as control input. In another concept for hazardous gaseous and liquid wastes, waste combustion in the core of vortices with synchronized waste/fuel injection using closed-loop active control will be demonstrated.

The proposed advanced incinerator solution addresses many requirements of the Tri-Service Environmental Quality R&D Strategic Plan (for example 2.L.1.-2.III.1.b.; 2.L.7.-2.III.3.b.; and 2.I-2.III.1.f.) listed under Pillar II (Compliance), which involves waste treatment and disposal. The proposed demonstration of a compact incinerator with assured destruction is of immediate need to the Navy for ship-board use, but also for off-shore use by the Navy, Army, Air Force, and DOE for on-site waste destruction.

## 8. Expected Payoff:

Successful demonstration of a compact incinerator with real-time exhaust monitoring for active combustion control represent a significant step towards assured waste incineration. The type of system proposed here has the potential for ship-board applications, and will be essential to the development of environmentally sound ships beyond 2000. Compact incinerators are also desirable for on-shore use in the government and private sector. Small, compact incinerators will allow on-site waste destruction and avoid waste transportation to large incineration sites. In particular, medical waste incineration is a prime candidate in the private sector for a compact system. The closed-loop active control of the incineration process will for the first time assure proper operation during design and off-design operation. Successful demonstration of the assured waste incineration on-board ships will result in significant cost savings by avoiding cost, for waste off-loading and on-shore destruction, in particular in foreign countries.

## 9. Milestones:

The following milestone schedule for the four tasks assume funding will be on board 6/94.

### Combustion control research (6.1)

- |    |  |      |
|----|--|------|
| 1. | Determine critical incineration processes for active control   | 9/94 |
| 2. | Provide concept/design input for all other tasks   | 3/95 |
| 3. | Provide specifications for sensor research and actuator R&D work   | 6/94 |
| 4. | Complete basic active control research and provide input for incinerator demonstration                       | 9/95 |
| 5. | Complete active control with different waste surrogate types and provide input for incinerator demonstration | 9/96 |

### Sensor Research (6.1)

- |    |  |      |
|----|--|------|
| 1. | Complete review of possible scientific approaches  | 9/94 |
| 2. | Provide concept/design input for sensor R&D program  | 3/95 |
| 3. | Complete laboratory evaluation of a prototype sensor and provide input to sensor R&D program | 9/95 |
| 4. | Complete evaluation of additional sensors in a lab and hostile environment                   | 9/96 |

### Sensor and Actuator R&D Program (6.2)

1. Complete review of possible actuator technologies 9/94
2. Provide concept/design input of actuator for compact-incinerator demonstration 3/95
3. Complete design and fabrication of actuator/input to demo program 9/95
4. Complete laboratory evaluation of sensor and provide input for incinerator demonstration 3/96
5. Complete system evaluation of various sensors and actuators and provide input for incinerator demonstration 3/97

### Incinerator demonstration

1. Select industrial partner 9/94
2. Complete design of incinerator concept 6/95
3. Complete exploratory incinerator tests 6/96
4. Complete preliminary incinerator evaluation against incineration standards and regulations 3/99
5. Complete evaluation of optimized incinerator 9/97

## 10. Transition Plan:

At the beginning of the incinerator demonstration program, negotiations of technology transfer agreements (CRADA) will be initiated. Potential partners are Inerson, Simonds, and Consumat. These companies are prime candidates with manufacturing experience in small medical and municipal waste incinerators. In addition, a Small Business Innovation Research (SBIR) request for the demonstration of a compact, closed-loop controlled waste incineration has been submitted in September 1993. Also, additional funding sources for the incineration demonstration program will be explored, including the Gas Research Institute, the American Plastics Council and the Medical Industry Council.

## 11. Funding: \$(K)

	FY94	FY95	FY96	FY97	FY98	Total
SERDP	700	300	1400	1500	1200	5100

## 12. Performers:

The active control research described earlier is a collaboration between Georgia Institute of Technology, University of Colorado, Boulder, University of California, Los Angeles, and the Naval Air Warfare Center Weapons Division, China Lake, CA, with Dr. Klaus Schadow, NAWCWPNS/ONR (on detail), as program coordinator. The sensor research will be performed at Sandia National Laboratory, Livermore, CA, in collaboration with a yet to be determined university with Dr. Jay Keller, SNL, as program coordinator. The sensor and actuator R&D program and the integrated prototype incinerator demonstrator will be done by NAWCWPNS and SNL in collaboration with industrial partners. Prime candidate is Environmental Research Corporation (Dr. Seeker). This company is presently evaluating a different integrated prototype waste demonstrator for DOE. They have expressed strong interest in the compact, actively controlled waste incinerator. Dr. Klaus Schadow will be program coordinator of the sensor and actuator program, as well as the incinerator demonstration program.



### **13. Principal Investigator:**

Dr. Klaus C. Schadow  
Head, Propulsion Research Branch  
Naval Air Warfare Center Weapons Division, Code C02392  
China Lake, CA 93555  
PHONE: (619) 939-6532  
FAX: (619) 939-6569  
E-MAIL: klaus\_schadow@cl\_63mtp\_gw.chinalake.navy.mil

### **14. Keywords:**

Incineration, compact design, active combustion control, real-time monitoring, closed-loop control, acoustic/fluid dynamic/combustion interactions

## SERDP FY95 PROJECT

1. **SERDP Thrust Area:** Compliance
2. **Title:** Reduction of NO<sub>x</sub> Emissions from Marine Power Plants
3. **Agency:** U.S. Navy
4. **Laboratory:** Naval Surface Warfare Center (NSWC)
5. **Project ID:** #42
6. **Problem Statement:**

The California Air Resources Board (CARB) and the Environmental Protection Agency (EPA) are expected to mandate limitations on the emissions of NO<sub>x</sub> from ships passing through or operating within 100 nautical miles of the United States littoral by CY1995. Consequently, the Navy has been directed by OPNAVINST 5090.1A to make a good-faith attempt to comply with these limits on emissions in order to avoid costly fines and litigation.

At least 131 destroyer and frigate class ships employ gas-turbines plants, the LM2500, for propulsion, and many more also use the 501K gas turbine for power generation, representing an all-ship inventory of about 700 turbine units. These ships, returning periodically from remote tactical duty stations to replenish resources at home ports, pass through coastal waters within the 100-mile limit. The emissions from their power plants are presently in severe violation of the proposed NO<sub>x</sub> limits for gas turbines.

Current state-of-the-art developments in low-emissions gas turbines are based on a dry low NO<sub>x</sub> (DLN) combustor, and a water-injected low-NO<sub>x</sub> combustor (which is similar in some aspects to the steam-injected combustor of General Electric's steam-injected gas turbine). Both are capable of reducing NO<sub>x</sub> emissions below the anticipated CARB-mandated 42 volume ppm limit for gas turbines. Both combustors rely on a decrease in the average temperature of the flame zone to reduce the production of NO<sub>x</sub>. (High temperature catalyzes the cleavage of the nitrogen molecule.) However, to cool the flame zone by air dilution, the size of the DLN combustor must increase substantially. To cool the flame zone with water, purified water normally available from the ship distillation plant, is required.

It is anticipated that for new construction, of the two technologies, the DLN combustor will have the least ship impact and cost. Nevertheless, the DLN spatial requirements reflect some uncertainty over whether the DLN system is subject to immediate retrofit without some rearrangement within the existing unmodified LM2500 enclosure. Modification of the component configuration within the enclosure. Modification to the component configuration within the enclosure to provide compatibility with the geometry and spatial requirements of the DLN combustor appears necessary. Based upon the fact that the General Electric Company already markets, for NO<sub>x</sub> suppression in the existing engine, a water-free manifold, the water-injected combustor (WIC) represents an inexpensive, low-risk, alternative system, which is immediately amenable to retrofit in the LM2500 enclosure. Even if no problems are encountered in the DLN modifications, demonstration of a WIC system for NO<sub>x</sub> reduction

represents a prudent fallback development of a proven (in land-based plants), simpler, retrofit system.

Guiding principles expounded above for gas turbines are not universally applicable to diesel engines. For example, the DLN combustor approach would not be employed. Of the combustion-flame-cooling methods, water injection has been examined by many researchers in the academic and/or diesel contractor community with positive expectations that WIC methods may satisfy Navy needs for abatement of emissions in diesel plants. However, there will be a different retrofit response for ocean-going (such as the LST41 and some LCD-class ships) as opposed to harbor craft. Although the emission levels of diesels are much greater than the emissions of gas turbines (as high as 2300 ppm compared with 400 ppm for gas turbines), the new CARB limits for diesels will be 600 ppm, versus the more stringent 42 ppm for gas turbines.

The task of assessing the ship impact of a WIC retrofit has been superficially examined with respect to water needs, which appear manageable. It is expected that a typical speed profile for a DDG-Class ship traversing the 100-mile coastal zone will operate about 70% of the time at 20 knots (cruise), 20% of the time at about 12 knots and 10% of the time at 5 knots. The total time will be under 5.92 hrs and the total fuel consumption will be 26.4 long tons (lt). The ships service generator is assumed to operate at 2500 kW with overall fuel consumption of 4.5 lt, or a total of 30.8 lt. Water requirements for the WIC system will approximate the fuel requirements at 31 lt. Slower speed profiles will require less fuel, and therefore, less water.

A typical DDG is outfitted with two 12000-gal/day distillation plants. Each can produce 45 lt/day of water containing less than 1 ppm of total dissolved solids. Although General Electric has specified 0.1 ppm of total dissolved solids for continuous STIG engine operation (many thousands of hours per year), the total salt accumulation per gas turbine unit would be under 0.035 lbm during the few hours of traverse. Since salt is normally ingested via the input air and fuel streams, the LM2500 is washed down after 24 hrs of operation during regular service (this corresponds to washing down a unit every six days). Since a DDG will pass through a coastal zone once every six to twelve weeks, there will be about twelve additional washdowns per year.

Since the water purity level required for WIC-equipped diesel engines, is less exacting than the water purity level of gas turbines, potable water may be employed. Nevertheless, the diesel plants for seafaring ships will tap into the distilled water system in the same manner as proposed (vide infra) for the gas turbines. It is expected that prot-bound boats will utilize a separate water storage tank, equal in capacity to that of the fuel tank, replenished along with fuel, from at-dock, potable-water resources.

The water storage capabilities of a DDG are 60 lt in four tanks. The anticipated operational procedure would dedicate the water of two of the four distilled water tanks (about 30 lt) for water injection of two LM2500 units (only two units are required to maintain cruise speed) during the time of traverse of the coastal zone.

Engineering aspects of the fuel-injection system, the water system, the water feed manifold, monitoring systems for the NO<sub>x</sub>, WIC system control, and shipboard testing need to be rigorously evaluated through analysis and operational investigation. Indeed, the

aforementioned naval, at-sea, operating scenario for the reduction of NO<sub>x</sub> has not been confirmed, either in simulation or test. The credibility of the water-injected combustor system, within the Navy community, as a viable alternative for acceptable NO<sub>x</sub> reduction in the emissions of Navy gas turbines may be achieved only through a realistic shipboard evaluation.

## **7. Project Description:**

The water-injected combustor approach to NO<sub>x</sub> reduction in gas turbines will be evaluated in a shipboard configuration aboard a designated Navy destroyer or frigate on a routine mission.

The WIC-modified LM2500 (the 501K is not included in this project) gas turbine plant, and its components, the water-injected combustor, distillation plant, potable water storage tanks, an electronic feed control system, NO<sub>x</sub>-monitoring equipment, and the impact of the WIC system on the ambient ship systems will be closely examined. The emission of NO<sub>x</sub> from the gas turbine will be measured before entry into the coastal zone to establish a baseline reference condition. Measurements of the NO<sub>x</sub> emissions will be automated to obtain a continuous record of emissions performance, which may ultimately be demanded by CARB. Real speed profiles will replicate the most likely naval experience.

The existing LM2500 combustors require orderly investigation of system hardware choices, system specification, and some fabrication of new components. Water feed will enter through the secondary row of fuel nozzles. Mixing and homogenization of water and fuel will be effected in a "tee" connection to the fuel manifold, which is adequate according to the manufacturer's (General Electric) experience.

Modification of water, and fuel feed pumps, and the electronic feed-control system (contractor supplied) will ensure conformity with the constraints of the gas turbine container and the ambient ship environment.

Modification of shipboard diesel engines for water injection will be explored at land-based facilities, in conjunction with contractors, who have already faced the problems of fuel-injector erosion and corrosion. The method of mixing the fuel will be investigated to avoid the unpredictable effects of slug flow, flame quenching, with consequent "missing" of cylinders, and loss of power. Fuel-water emulsion may be essential for predictable performance. Methods of facilitating the emulsification process with detergents must be examined. The corrosive effects of detergents on the structural metals must be closely observed. Testing of diesel fuel injector configurations will take place largely in shoreside facilities pending successful resolution of fuel injector studies and tests.

Distilled water from the distillation plant will be manifolded to the potable water tanks with new valve controls dedicated to priority delivery of the distillate to new water-feed pumps during passage through the coastal zone. However, tests of the WIC system will be undertaken during regular cruise conditions with the permission of NAVSURFLANT and the ship commander.

Following each traverse of the coastal zone (and any other test), a washdown, examination, and a close analysis of the combustor for corrosion damage will occur. Corrosion could

develop in the combustors of gas turbines, should the combustor be exposed to continuous, long-time, high levels of sodium exceeding 0.3 ppm of water, reduce the life of the engine, and invalidate the manufacturer's guarantees. Corrosion could limit the efficiency of fuel injectors in diesel engines with similar negative effects on guaranties.

The ship impact and influence factor of each element of the WIC system will be measured, in order to permit design of a fix should any problems arise.

The project will provide data on the performance of the WIC system with respect to reduction of emissions and efficiency during anticipated realistic operations. It will provide assessment of the corrosion resistance of the gas turbine exposed to marginally critical salt levels, and estimates of overall life cycle costs of the water-injected gas turbine, and estimates of the corrosion damage from water-fuel mixtures in the fuel injectors of diesels. The alternative NO<sub>x</sub>-reduction methods will be assessed, because the scrubbing approach to diesel emissions will be proceeding simultaneously. The delivered products will include a credible statement of WIC characteristics, and a relative cost assessment of the alternative NO<sub>x</sub> reduction systems. Based upon these experimental test data, and the relative cost estimates, a set of management recommendations will be offered to the Navy.

This project is in support of the Compliance Pillar in the Tri-Service Environmental R&D Strategic Plan.

## **8. Expected Payoff:**

This project provides the Navy with a less risky, competitive, alternative retrofit of existing engines complying with EPA and CARB-mandated operational limits on the emission of NO<sub>x</sub> from ship gas turbine power plants during traverse of the coastal zone. It will deliver data on the operational characteristics and relative merits of the water-injected combustor system for gas turbines, and fuel-plus-water injectors for diesels, providing reasonable bases for critical decisions necessary for complying with the CARB mandates.

## **9. Milestones:**

1.	Develop Joint Navy-Contractor Strategy	10/94
2.	Commit the Navy to a Test Ship and Test Engine	10/94
3.	Identify Long Lead-Time Components and Systems	12/94
4.	Design Test Components and Test Monitoring Systems	03/95
5.	Modify Diesel Engine Fuel-Injectors	03/95
6.	LM2500 water-injection with manual water control	05/95
7.	Water manifold and controller procurements	08/95
8.	Engineering assessment of alternative NO <sub>x</sub> reduction methods for diesels	05/95
9.	Complete component Procurement Process	07/95
10.	Assemble Land-Based Systems (Turbine & Diesel)	09/96
11.	Test the Land-Based Systems	03/96
12.	Management Review and Go/No-Go Decision	05/97
13.	Modify the Test Ship Turbines for Water Injection	07/97
14.	Start Shipboard Tests	10/97
15.	Complete Shipboard Tests	01/98

**10. Transition Plan:**

Discussions with Contractor (General Electric Co., Allison Gas Turbine Co. and Detroit Diesel Co.) principals have been underway to determine whether the milestone schedule is not too compact. There is a verbal agreement over the participation of the Contractor and the forms of cooperation needed to facilitate the project.

The project will ultimately go forward to retrofit-system specification and fleet procurement of retrofit hardware for the water-injected gas turbines, and to recommendation of diesel modifications and a set of system layouts for Navy harbor craft.

**11. Funding: \$(K)**

	FY94	FY95	FY96	FY97	FY98	Total
SERDP	750	300	900	850	500	3300
EPA	250	250	50	50	0	600
DON	0	0	150	250	0	400
Total	1000	550	1100	1150	500	4300

**12. Performers:**

Participants in the study include CDNSWC, U.S. EPA, MEERL, MD-4, the Norfolk Naval Shipyard, and contractors. Program management, development facilities, land-based LM2500 and 501K test engines, a Navy diesel test engine, distilled water system components, and NO<sub>x</sub>-monitoring systems will be supplied by the CDNSWC. Water feed manifold(s), manifold interconnections, and the electronic water and fuel control system will be provided by the Contractor(s). Installation of shipboard gas turbine manifolds, and water manifolds will be performed by the Norfolk Naval Shipyard. NAVSURFLANT will designate a test ship for evaluation.

**13. Principal Investigators:**

Dr. Herman B. Urbach  
 Naval Surface Warfare Center  
 Carderock Division  
 Annapolis Detachment, Code 82T  
 3A Leggett Circle  
 Annapolis, MD 21402-5067  
 PHONE: (410) 267-2864  
 FAX: (410) 267-3553  
 E-MAIL: URBACH@OASIS.DT.NAVY.MIL

Mr. John H. Wasser  
U.S. EPA  
AEERL, MD-65  
Research Triangle Park, NC 27711  
PHONE: (919) 541-2476

**14. Keywords:**

Gas turbine, Diesels, NO<sub>x</sub> emissions, Water injection

## SERDP FY95 PROJECT

1. **SERDP Thrust Area:** Compliance
2. **Title:** Lead-Based Paint Hazard Mitigation
3. **Agency:** U.S. Army Corps of Engineers
4. **Laboratory:** Construction Engineering Research Laboratories (USACERL)
5. **Project ID:** #521
6. **Problem Statement:**

The DoD wide lead-based paint (LBP) hazard mitigation cost has been estimated to be more than \$1 billion over the next 10 years. The increased cost for LBP abatement is due to the additional requirements for containment of dust/waste, environmental monitoring, worker protection, and record keeping. Human exposure to lead is associated with adverse health effects, including permanent damage to the central nervous system. About 75% of all homes constructed in the United States before 1980 have some LBP. While many sources of lead exposure exist, lead from lead-based paint is the most significant source of exposure at DoD installations. Although lead is no longer used in house paints and the application of lead primers on steel structures is declining, old paints with hazardous levels of lead remain on many surfaces today. Traditional methods of paint removal, such as abrasive blasting, or chemical stripping, can be used to remove LBP. However, the costs of containment, worker protection, and waste disposal make many of these traditional methods cost prohibitive where the paint contains lead. The overall goal of this project is to develop improved methods for LBP hazard mitigation to reduce costs and enable compliance. The majority of the work in this proposal falls under Applied Research/Technology Demonstration/Technology Transfer (6.2/6.3).

This is an enhancement of a funded SERDP FY93 project titled "Glassy Materials Modeling for Hazardous Waste Immobilization".

### 7. Project Description:

This SERDP project is in support of Tri-Service Environmental Quality Strategic Plan (Green Book) Requirement Thrust 2.L.5a: Satisfy RCRA (Treatment/disposal of Operations Waste). Furthermore, this work addresses Army-wide Prioritized Requirement Statements, Compliance 2.3.k Lead-Based Paint Testing/Disposal, Compliance 2.5.a Lead-Based Paint Removal, Compliance 2.6.a Find Abrasive Substitutes for Removing Paint; and Pollution Prevention 3.2.c. Cost Effective Lead-Based Paint Abatement.

This is an integrated multi-disciplinary, multi-agency project. The technical objectives of this project are (a) to develop novel vitrification technology for lead-based paint removal that can be used effectively for immobilization of heavy metal hazardous waste (b) to evaluate the use of new abrasive sponge blasting media for lead-based paint removal (c) to develop a robotics system for removal of lead-based paint and (d) to develop and demonstrate an integrated "Lead Hazard Mitigation and Management System (LMS)". Objective (a) will minimize the



amount of hazardous waste produced during LBP removal. Objectives (b) and (c) focus on improving worker and public safety. Finally, objective (d) will assist installations in developing the most cost effective LBP hazard mitigation strategy. The technical approach for this project will be phased to include the following:

a. Glassy Materials Modeling for Hazardous Waste Immobilization.

Heavy metal hazardous waste residues have been effectively vitrified in situ in the matrix of glassy materials. The actual mechanisms by which these materials are immobilized have not yet been determined. Laboratory experiments have determined that bonds within the glass network break, providing bonding sites within this network for the heavy metal cations. Similarly, the cations may become part of the lattice structure by randomly occupying interstitial and/or defect sites. The Resource Conservation and Recovery Act (RCRA) mandated Land Ban requires that hazardous waste be treated to below the characteristic level prior to disposal. The long term durability of the vitrified and stabilized wastefoms needs to be evaluated so that the leaching behavior of materials under actual field conditions can be modeled and predicted.

The technical approach will involve the preparation of vitrified materials containing heavy metal hazardous waste and determining through characterization techniques such as X-ray diffraction (XRD), X-ray Spectrometry (XRS), Scanning Electron Microscope (SEM), how the hazardous waste is incorporated within the glass structure and immobilized. The mechanisms of the vitrification and ion leaching processes will be modeled to optimize hazardous waste immobilization. The tetrahedral structure, bond angles, and ionic field strengths of the glass forming and glass modifying oxides will be investigated. One application process, is to thermally spray a molten glass compound directly onto a lead containing substrate. This has shown the potential to effectively contain the hazardous waste residues. The mechanism by which heavy metals become immobilized will be investigated. Existing and recently developed laboratory tests will be used to predict the long term durability of the vitrified wasteform.

A paper titled "Vitrification of Lead Contained in Lead Based Organic Coatings Using Thermal Spray Technology" was presented at the ASTM sponsored Third International Symposium on Stabilization/Solidification of Hazardous, Radioactive, and Mixed Waste, held in Williamsburg, VA, 1 November 1993. A patent application titled "Removal of Lead Based Coatings by Vitrification Using Thermal Spray" has been filed.

b. Sponge Blasting.

USACERL is evaluating emerging technologies for the removal of lead-based paint from DoD buildings and structures. The technologies being evaluated include cryogenic blasting, laser paint removal, chemical stabilizers, alternate chemical strippers, and confined hydraulic blasting. The sponge media blasting technique appears to be particularly promising for LBP removal from surfaces of buildings. Soft (sponge) media abrasive products have been developed to address issues of worker and public safety, hazardous waste minimization, and pollution prevention. The sponge media consists of a matrix of water-based urethane foam within which the abrasive particles are dispersed. The media can be wet with water or chemical solutions to increase productivity. The aggressiveness of the sponge media can be tailored for the specific application by changing the characteristics of the abrasive particles

inside the urethane foam. For the field demonstration of emerging LBP technologies, sites will be selected from typical building surfaces. Pre-abatement testing of the structures will be done to characterize the painted surface, including paint thickness, type, and uniformity. Post-abatement tests will be done to determine how efficiently the paint removal is performed from the viewpoint of completeness of the lead removal. Hazardous wastes will be carefully contained, collected, tested, and disposed. Cost data will be recorded for all work phases and the performance envelope will be validated.

c. Robotics Paint Removal System.

USACERL is developing an automated platform which will use plastic media blasting for removal of lead-based paint from interior of buildings. Another automated technology being developed is a portable thermal spray system which could be used for vitrification. Robotics technology is particularly well suited for simple, repetitive tasks such as paint removal. Additionally, a complete collection of blast wastes and dust is possible with a simple recovery apparatus. These systems will be integrated with sensors. A practical robotics paint removal system will be assembled, resulting in a low cost, environmentally safe LBP removal. The mobile robotics platform will be equipped with necessary sensors, controllers, blasting nozzle, abrasive media feeder and a vacuum waste collector to complete a functional robotics system. The robotics paint removal system will be evaluated using the sponge media and more traditional abrasives such as coal slag and steel shot. After laboratory evaluation, the robotics paint removal system will be field tested at DoD installations to establish the technical validity and cost-effectiveness.

d. Lead Hazard Mitigation Management System (LMS).

A Lead Hazard Mitigation Management System (LMS) will be developed to assist engineers in developing the best LBP abatement strategy for their specific installation. The system will provide assistance with (1) installation-wide prioritization of abatement projects, and (2) selection of the best abatement method for a given situation. User inputs to LMS will include (1) a structure inventory which catalogs background information such as substrate type, building use, and age, and (2) field test information such as identification of potential lead-based paint hazards, lead testing results, and coating condition index. LMS will utilize the user-provided data in conjunction with knowledge bases containing information on regulations, abatement technologies, risk assessment, waste management, and cost to generate the best abatement strategy. LMS will be highly interactive and will allow the user to "test" various alternatives. The knowledge base will be able to be updated as new hazard assessment and abatement technologies emerge or as regulations change. LMS will also assist in providing information to occupants and workers to reduce the panic that is often associated with LBP abatement projects. The technical approach will include development of the inventory and field test databases to include all information that is required for decision making; development of the knowledge bases; development of methodologies and decision trees for prioritization and alternative selection; development of occupant & worker support packages; LMS software development; demonstration of LMS at a DoD installation; and publication and documentation of results.

Key technology barriers which need to be overcome are: prediction of the long term durability of the vitrified glass, mechanisms of leaching of stabilized wasteform, urethane foam abrasives, and robotics and sensor systems integration. The proposed research has

many innovative and novel aspects and therefore, the probability of overcoming these barriers is high. This project has a low risk and high payoff.

## 8. Expected Payoff:

The urgency of the lead-based paint problem has increased due to the Base Realignment and Closure Act, where the installations are required to abate their residential buildings of lead-based paint. The DoD wide cost of lead-based paint hazard mitigation is estimated to be more than \$1 billion, therefore it is imperative that effective decision making tools be utilized to ensure that the most cost effective, environmentally safe project plans are developed using emerging technologies. The proposed lead paint removal technologies combine the advantages of robotics with sponge media blasting and with in situ vitrification. If we assume 10% reduction in this cost then the return on investment is approximately 25:1.

Use of the LMS integrated hazard abatement strategy will allow full consideration of appropriate abatement technologies, installation budget, scheduling constraints, occupant management, and master maintenance plan. The ultimate payoff is that this project would provide valuable assistance to insure that a DoD installation is not in violation of regulatory requirements for lead-based paint hazard mitigation, as well provide healthier homes to military service members and their families.

## 9. Milestones:

1.	Prepare vitrified materials	06/94
2.	Lab Study of Varied Processing Parameters	09/94
3.	Investigate Microstructure through Characterization	09/95
4.	Complete evaluation of Sponge Media	06/96
5.	Complete Glassy Materials	07/96
6.	Develop the alpha version of LMS	09/96
7.	Complete Robotics system prototype tests	03/97
8.	Complete Field Tests and Demonstrations	06/97
9.	Complete Reports and Technology Transfer Documents	09/98

## 10. Transition Plan:

Demonstrations of vitrification and sponge blasting in conjunction with robotics will be conducted at DoD installations. LMS will be implemented, from assessment to the production of the hazard mitigation strategy, at a DoD installation. In order to transfer the methods and technologies developed in this program an intense documentation effort will be required and full coordination will be achieved through the "DoD Interagency Lead-Based Paint Task Force". Tri-service guidance documents including Engineering Technical Letters, Guide Specifications, User Guides, and Technical Manuals will be prepared for the use of DoD installations.

The technologies developed and demonstrated under this SERDP project have dual use application in the Department of Housing and Urban Development (HUD).

**11. Funding: \$(K)**

	FY94	FY95	FY96	FY97	FY98	Total
SERDP	700	400	700	600	750	3150
DA	310	0	0	0	0	740
TOTAL	1010	400	700	600	750	3890

**12. Performers:**

U.S. Army Construction Engineering Research Laboratories, Champaign, Illinois, will be the lead laboratory. Other performers in this project are the U.S. Environmental Protection Agency, Risk Reduction Research Laboratory (POC: Ms. Diana Kirk); and DOE Lawrence Livermore National Laboratory (POC: Mr. Tehmau Kan). Academic involvement includes but is not limited to University of Illinois. Industry involvement includes but is not limited to TDJ Group, Strip It, and APS Materials. The work in this project has a high potential for a CRADA with the industry.

**13. Principal Investigator:**

Dr. Ashok Kumar  
U.S. Army CERL  
P.O. BOX 9005  
Champaign, IL 61826-9005  
PHONE: (217) 373-7235  
FAX: (217) 373-7222  
E-MAIL: ASHOK-KUMAR@CECER.ARMY.MIL

**14. Keywords:**

Vitrification, Leaching, Modeling, Hazardous, Robotics, Lead Abatement

## SERDP FY95 PROJECT

1. **SERDP Thrust Area:** Compliance
2. **Title:** Emission Reduction Planning Model
3. **Agency:** U.S. Air Force
4. **Laboratory:** Armstrong Laboratory (AL)
5. **Project ID:** #175
6. **Problem Statement:**

The 1990 Clean Air Act Amendments (CAAA-90), the first major revisions to federal air legislation since 1977, mandate a substantially more complex air pollution compliance program. Title III (Air Toxics Provisions) and Title V (Permit Provisions) of the CAAA-90 present especially difficult, long-term compliance challenges for Department of Defense (DoD) installations. Although air pollution programs at DoD facilities are similar in that they consider similar sources, the program at any site must consider specific local conditions. These conditions include the number and type of air pollution sources, operation and maintenance activities, the facility's mission, and the regulatory environment to include both regional and local concerns. Prevention, minimization, and control of pollution, as well as administrative management, are all components of an optimal, cost-effective compliance strategy. Development of a compliance strategy can become overwhelming for DoD environmental personnel at the base level due to the complexity of the problem and possible solution approaches. Poorly planned compliance strategies can lead to (i) non-compliance with air pollution regulations, (ii) mission impairment from regulatory action (notice of violation, fine, activity limitation, shutdown), or (iii) excessively expensive or inappropriate solutions. Conversely, well-planned, cost-effective compliance strategies will avoid compliance problems, leading to enhanced relationships with regulatory agencies and surrounding communities, as well as reducing air pollution.

Previous funding for the Emission Reduction Planning Model (ERPM) has led to the development of a prototype decision support system. A full-scale decision support system for establishing and maintaining optimal, cost-effective compliance strategies would greatly aid environmental personnel in developing appropriate compliance strategies. Funds are requested to expand an existing joint Air Force/Army/EPA applied research initiative and to support the demonstration of the ERPM at several federal facilities.

### 7. Project Description:

a. **Technical Objective:** The objective of this project is to develop a state-of-the-art decision support system to aid environmental personnel in reducing air pollution compliance problems. The availability of such a system will allow for consistent, optimal, and cost-effective application of control technologies, prevention measures, and mitigation techniques. The proposed decision support system is intended to support, not replace, experienced environmental personnel.

b. Technical Approach: To date, the ERPM research program has resulted in the development of a prototype decision support system. The prototype system tested assumptions on how to encode facts, relationships, and inference methods required to develop air pollution compliance strategies. The prototype system, while small in scale, has demonstrated that a decision support system of this type is feasible and potentially very useful for developing compliance strategies.

The full-scale decision support system will follow design and function of the prototype system. Algorithms based upon EPA, DOE, and DoD expertise will be constructed to assess current base emissions, applicable regulations, available control devices, and compliance alternatives (i.e., pollution prevention, pollution minimization, and administrative techniques) in order to recommend prioritized actions that optimize regulatory, economic, and environmental benefits. Draft software packages will be user tested at selected Air Force and Army installations to gain insight for improving system utility and ease of operation.

c. Technical Challenges: The primary technical challenge will be integrating expert system algorithms with external databases and pre-existing models. Secondary challenges include obtaining acceptable execution times on a user-friendly software platform.

d. Tasks: Phase I of the project will include the incorporation of control technologies and federal regulations into the decision support system as well as the development of an interface with existing emission inventory databases and dispersion screening models. Phase I will be completed with an in-house review of work to that point and a field demonstration of the phase I decision support system.

Incorporating control technologies into the decision support system involves a survey of the state-of-the-art control devices. Both criteria pollutants and air toxics will be considered for each source category as control devices often affect more than one pollutant. A broad spectrum of alternatives will be considered so that the most cost-effective and environmentally acceptable approaches are identified. As each of the various control devices for each source category are specified, the corresponding expert-system rules will be written and implemented in the decision support system.

Incorporating applicable federal regulations into the decision support system involves a survey of the regulations that apply to various sources present at federal facilities. As regulations are identified, the expert-system rules associated with these regulations will be developed and implemented into the decision support system.

Development of an interface with existing emission inventory database systems (e.g., AQUIS, APES, etc.) will allow the decision support system to take advantage of the vast number of source and emissions data that are available in emission inventory databases. The interfaces will prevent the duplication of functions already performed by emission inventory database systems such as estimating emissions.

Developing an interface with dispersion screening models will provide a link between source emissions and regulations based on ambient air quality standards. The screening technique will provide a conservative estimate as to whether a source is out of compliance with ambient air quality standards, as well as to determine if a proposed control technology's efficiency will be sufficient to meet an applicable ambient standard.

Phase II of the project will include the incorporation of compliance strategies beyond control technologies into the decision support system, and the development of an interface with advanced EPA-approved dispersion models.

Phase II will be completed with a field demonstration of the entire decision support system. Once the phase II field demonstration is complete, modifications to the decision support system will be affected and the final software package, documentation and report will be prepared.

Incorporating compliance strategies beyond control technologies involves a survey of pollution prevention, pollution minimization, and administrative management techniques that are applicable to DoD facilities. Optimal, cost-effective and environmentally acceptable compliance strategies can only be developed when considering this complete range of compliance methods. As each of the various compliance strategies for each source category is specified, the corresponding expert-system rules will be written and implemented in the decision support system.

Developing an interface with advanced EPA-approved dispersion models will provide a link between source emissions and regulations based on ambient air quality standards. The incorporation of dispersion modeling capability will provide a more accurate estimate as to whether a source is out of compliance with ambient air quality standards, as well as to determine if a proposed compliance strategy will be sufficient to meet an applicable ambient standard.

e. Relationship to DoD Environmental Objectives: This project directly supports Tri-Service Environmental Quality Strategic Plan requirements 2.I.2.e, DoD-Wide Emission Management System and Database, and 2.I.2.k, Assess Atmospheric Impact of Air Base and Aircraft Operations for Compliance with CAA and for EIAP.

## **8. Expected Payoff:**

This project will ultimately provide a state-of-the-art decision support system to aid environmental personnel in determining areas of potential violations and compliance options, thus leading to installation-specific, cost-effective air pollution compliance strategies. Moreover, DoD-wide use of the decision support system will provide consistency in the treatment of air pollution problems. The decision support system will be designed to easily adapt to other industries as well as to the needs of local, state, and federal regulatory agencies. Further, incorporating EPA-approved methodologies in the decision support system will help to expedite the regulatory acceptance of a facility's compliance strategy. Finally, the design of the decision support system allows for its application many years into the future, and easy integration of new compliance strategies and regulations.

## **9. Milestones:**

1.	Incorporate Control Technologies	05/95
1a.	Federal regulations (emission based standards)	07/95
1b.	Federal regulations (non-emission based standards)	12/95
2.	Interface with emission inventory databases	11/95
2a.	Dispersion screening model	02/96

- |     |   |       |
|-----|---|-------|
| 3.  | Complete phase I internal review              | 09/95 |
| 4.  | Complete phase I field demonstration          | 09/95 |
| 5.  | Modify per phase I feedback                   | 04/96 |
| 6.  | Incorporate alternative compliance strategies | 10/96 |
| 7.  | Complete advanced dispersion model interface  | 12/96 |
| 8.  | Complete phase II field demonstration         | 02/97 |
| 9.  | Modify per phase II feedback                  | 05/97 |
| 10. | Completed software/documentation/final report | 09/97 |

### 10. Transition Plan:

The resultant decision support system will be implemented at Air Force and Army installations throughout the United States via the Air Force Center for Environmental Excellence (AFCEE) and Army Environmental Center (AEC), respectively, as well as potential application by DOE and other federal agencies. Further, there exists significant potential for EPA adoption as an accepted and encouraged means of compliance evaluation and planning.

### 11. Funding: \$(K)

	FY94	FY95	FY96	FY97	TOTAL
SERDP	200	100	200	400	900
Air Force S&T	201	0	0	0	373
Army S&T	190	205	0	0	470
EPA	0	0	0	0	15
Total Project	591	505	400	400	1758

### 12. Performers:

The Environics Directorate of Armstrong Laboratory (AL/EQ) will coordinate this development effort with the Army's Construction Engineering Research Laboratories, Department of Energy's Argonne National Laboratory, and the Environmental Protection Agency's Air and Energy Engineering Research Laboratory.

### 13. Principal Investigators:

Capt Carolyn Vadnais  
 AL/EQS  
 139 Barnes Drive, Suite 2  
 Tyndall AFB, FL 32403-5323  
 PHONE: (904) 283-6249  
 FAX: (904) 283-6286

Secondary POC:

Mr. Mike Kemme  
 USACERL  
 PHONE: (217) 373-4554



**14. Keywords:**

Air Pollution, Compliance, Planning, Emissions, Controls, Model.

## SERDP FY95 PROJECT

1. **SERDP Thrust Area:** Compliance
2. **Title:** Laser Ablation/Ionization Characterization of Solids
3. **Agency:** Department of Energy
4. **Laboratory:** Pacific Northwest Laboratory (PNL)
5. **Project ID:** #362
6. **Problem Statement:**

The Department of Energy (DOE) is currently undertaking the enormous task of remediating defense wastes and environmental insults which have occurred over 50 years of weapons production. It is abundantly clear that significant technology advances are needed to characterize, process, and store highly radioactive waste and to remediate contaminated zones. Aside from the processing and waste form issues, analytical technologies needed for the characterization of solids, and for monitoring storage tanks and contaminated sites do not exist or are currently labor-intensive tasks. The purpose of this research is to develop widely applicable mass spectrometry techniques for analysis of mixed chemical wastes. The sensitive and rapid analysis of organics, inorganics, and TRU's in contaminated soils, groundwater, and in tank wastes is a key Hanford-site need. The urgent need for this work has been highlighted by recent findings of the DNFSB, and by the agreement between the DOE, EPA, and Washington State.

The remediation of Hanford-site defense waste and long-term disposal of high-level mixed wastes requires chemical analysis of the waste streams. The projected costs of these tasks, with current methods, is in excess of \$500M. Analysis of mixed waste is needed to characterize the chemical classes and concentrations of a wide variety of waste materials. Tank and crib waste sites contain broad distributions of both organic compounds; aromatics, nitrates, chelating agents, and halogenated hydrocarbons, and inorganic compounds; chromates, ferrocyanides, metals, and TRU's. The chemical speciation and concentration of these materials must be determined in order to design effective clean-up strategies. Additionally, the high concentrations of radioactive waste materials, in tanks and cribs, provide an energetic driving force that continuously transforms mixed waste in complex kinetic pathways. Hence, analyses need to be made in a timely fashion. Current methods require as much as six months for a single waste tank core sample analysis and report. Initial research will develop rapid laser-based analysis techniques, the principles of which may be extended to on-line field measurements.

This research impacts needs in both basic and applied research categories and will help determine the design parameters and evolution of field analytical platforms. The hot cell and field instruments being developed under the DOE/Hanford Mobile Analytical Reconnaissance System (MARS) program constitutes a major effort in meeting Hanford-site remote analytical and characterization needs. The proposed research is part of an existing SERDP program designed to conduct fundamental studies in support of the MARS program. It is currently operating under SERDP FY94 funds. Significant progress has occurred in the

previous FY. This includes the assembly and testing of the ultra-high-vacuum laser ablation chamber, the design and construction of the time-of-flight mass spectrometer, and initial experiments on laser ablation of simulated tank waste forms.

For certain critical trace elements, it will also be important to focus on the method of ionization of the ablated material. Technetium-99 has been identified as a significant ground water contaminant at a number of locations on the Hanford Site. Because of its long half-life (214,000 years), high fission yield, and high rate of mobility in the subsurface, Technetium-99 is considered a hazardous radioisotope waste. Furthermore, Technetium-99 can be used as a critical path isotope for performance assessment of nuclear waste isolation barriers. Because Tc-99 is a long-lived pure beta-emitter, routinely available radiochemical counting methods do not provide adequate sensitivity for use of Tc-99 as a performance assessment tool. However, the long half-life of Tc-99 does make it an ideal case for high-sensitivity detection by laser resonance ionization methods, which are responsive to the quantity of atoms present rather than the radioactive decay rate. Pioneering work conducted at Johannes Gutenberg Universitat Mainz in Germany has demonstrated that multiple-resonance laser induced ionization techniques can be successfully applied to the measurement of Tc-99 in environmental samples. In the previous fiscal year, our capabilities for detection of technetium have advanced in that a large number of possible excitation schemes have been investigated to optimize the overall efficiency and to suppress unwanted non-resonant ionization of other species. To date, the best excitation scheme involves a three step (3 laser) excitation into an autoionizing state using wavelengths of 313.2, 821.1, and 670.7 nm. Current investigations are designed to determine optimal excitation schemes, using resonances that overlap the emission wavelengths of reliable diode and titanium-sapphire laser sources. Improvements on this methodology, are expected to ultimately result in a field-portable, routine analytical technology capable of rapid, accurate and sensitive measurements.

The major objectives of this research are:

- 1) To develop general and sensitive techniques for determining the molecular speciation of organics and inorganics in tank wastes and those chemisorbed on mineral soil substrates. These methods must be sensitive to a broad spectrum of compounds to detect the many species present in mixed waste environments.
- 2) To develop new methods for the detection of technetium. Development of multiphoton-ionization techniques is required to satisfy the critical need for sensitive and rapid detection of Tc-99. Current methods require weeks, laser analysis can be completed in hours.
- 3) To transfer this new knowledge to other applied DOE analytical programs such as MARS.

## **7. Project Description:**

Laser-based analysis techniques are proposed to achieve these goals, primarily laser ablation mass spectroscopy (LAMS) and resonance enhanced multiple photon ionization (REMPI). Laser ablation can vaporize nearly any solid material in pulsed plumes of sufficient concentration for detailed analysis by mass spectrometry, laser-induced fluorescence, and other techniques. The LAMS approach couples laser vaporization with ultra-sensitive mass spectrometry. Analysis of even complex, multicomponent mixtures can be performed rapidly and requires very little sample. This is highly desirable for the analysis of many

environmental samples and hazardous wastes. When the concentrated laser ablation pulses are combined with multiphoton ionization time-of-flight mass spectroscopy, the result is a versatile and sensitive analysis techniques of very high mass resolution. The excellent mass resolution provides superb differentiation between compounds of similar masses and between isotopes. In addition, the resonant ionization process can provide excellent spectral resolution which extends and compliments the mass resolution. These features are crucial for the successful chemical speciation of complex waste samples.

The advantages of the LAMS approach include: Small sample requirements, minimum sample preprocessing, minimum waste generation, and reliable technology. However, several uncertainties are introduced by the ablation process. For instance, it is not clear how well the composition of the ablated (gaseous) products reflects the sample composition; some sample components can be preferentially ablated. Changes in the chemical state (e.g., changes in the oxidation state of metals) in the solid and gas phase are also potential problems. We propose to use several concurrent approaches to determine in more detail the mechanisms and consequences of laser ablation on model samples of simulated waste, and on relevant wide band gap inorganic materials, with and without chemisorbed species. Of particular importance are the effects of the ablation process, the defect-mediated coupling of light into the solid, the mechanism of particle emission, and particle interactions after emission but prior to the actual analysis.

The analysis of organic species chemisorbed on mineral substrates is an extremely important application of laser analysis techniques due to the need to detect toxic wastes contained in soils for waste characterization and environmental compliance. Many organic waste compounds absorb strongly in the UV (e.g., trimethylamine, benzene, naphthalene, toluene, phenol, and chlorinated aromatics) and may prove especially amenable to laser techniques. The mechanisms of desorption and ionization of such molecules on macroscopic single crystals of MgO, quartz, NaNO<sub>3</sub>, and CaCO<sub>3</sub> would also aid analysis. Developing quantitative analytical methods requires the study of both neutral and ionic species desorbed from the surface, their kinetic energies, and possible electronic excitations (gas phase luminescence studies) as a function of laser fluence and wavelength.

Technetium-99 measurement systems to be addressed by this project will expand upon existing expertise and technology that has been developed at Pacific Northwest Laboratory (PNL). Resonance enhanced multiphoton ionization, coupled with mass spectrometry, has been shown to be an extremely sensitive and selective approach to the analysis of rare isotopes. This work at PNL has emphasized the use of high-resolution continuous-wave lasers to simultaneously maximize isotopic selectivity and absolute sensitivity, and has demonstrated detection limits in the attogram (10<sup>-18</sup>g) range and the ability to detect a target isotope in the presence of a 10<sup>10</sup> or greater excess of other isotopes of the same element. Applying these methods to the measurement of Tc-99 will initially involve offsite assignment of B.A. Bushaw at Universitat-Mainz to understand the spectroscopy, thermal atomization dynamics, and handling and preparation of environmental technetium samples. Working in collaboration with the researchers at Mainz (and taking advantage of their existing experience) will facilitate the rapid development of specific excitation schemes and measurement procedures that can be addressed with compact solid state laser systems. Solid state laser technology has the advantage that it is reliable and easily incorporated into field analytical instrumentation.

## 8. Expected Payoff:

These programs will increase our capabilities to analyze mixed waste and detect Technetium. The results will be useful in performing the analysis of tank and crib wastes and contaminated soils and groundwater. The near real-time analysis capabilities of these methods will also be important for monitoring waste retrieval, facilities decontamination, and other site restoration actions. It will contribute to the success of the MARS program which is predicted to result in a savings of \$30-75M during the first three years following its implementation. Similar percentage savings can be expected at other DoD and DOE sites.

## 9. Milestones:

1.	Modify time-of-flight apparatus for rapid sample exchange.	10/95
2.	Develop a cw diode laser scheme for excitation of Strontium and Calcium	12/95
3.	Determine matrix effects on ablation of waste compound EDTA and HEDTA	2/96
4.	Determine ablation/iodization efficiency using picosecond laser source	4/96
5.	Report results to MARS Program	9/96
6.	Calibrate ablation yield of waste compounds oxalic and citric acids, TBP and sulfate	2/97
7.	Evaluate laser ablation for contaminated soil analysis.	5/97
8.	Final report.	9/97

## 10. Transition Plan:

Key to the impact of this project is the teaming of the end user (WHC and PNL staff from the MARS and related programs), and the SERDP scientific staff. The MARS team provides the engineering staff who have extensive experience in the development and delivery of highly technical, on-line, field and mobile instrumentation for the DOE and DoD. They are also in direct contact with potential industrial partners for the eventual production of instrumentation at Hanford and other federal facilities. Through this approach the findings of the SERDP program will be readily available to the end users.

## 11. Funding: \$(K)

	FY94	FY95	FY96	FY97	TOTAL
SERDP	380	100	310	340	1130
DOE*	425	425	425	0	1700
TOTAL	825	525	735	340	5877

\*MARS related technology development program.

**12. Performers:**

The organizations performing the work are: The Department of Energy, Division of Basic Energy Research, and Pacific Northwest Laboratory operated by Battelle Memorial Institute. A major beneficiary is the DOE MARS Program managed by PNL for the DOE.

**13. Principal Investigator:**

Dr. Steven D. Colson  
Pacific Northwest Laboratory, Molecular Science Research Center  
PO Box 999, MS K2-14  
Richland, WA 99352  
PHONE: (509) 375-6882  
FAX: (509) 375-6916  
E-MAIL: SD\_COLSON@PNL.GOV

**14. Keywords:**

Mixed-waste, Analysis, Laser-ablation, Ionization, Characterization, Technetium.

## SERDP FY95 PROJECT

1. **SERDP Thrust Area:** Compliance
2. **Title:** Vapor Permeation VOC Recovery from Refueling and Storage (VOC Control Fueling/Fuel Storage Operations)
3. **Agency:** U.S. Environmental Protection Agency
4. **Laboratory:** Risk Reduction Engineering Laboratory (RREL)
5. **Project ID:** #252

### 6. Problem Statement:

Ocean tankers and storage tanks for petroleum products such as gasoline, diesel fuel, or aviation fuel, emit a large amount of the lighter fraction of the fuel through evaporation during filling and storage process. While the evaporative losses can be a health-hazard to workers and the neighborhood, the economic loss is large and unnecessary. Thin-film non-porous membranes specially made of a hydrophobic resin are capable of recovering the volatile organic compounds (VOCs) from petroleum for direct recycle/reuse. In the vapor permeation process, the VOCs are removed from the VOC-air mixture and condensed back to a liquid phase with very high selectivity.

This is an applied research [i.e., 6.2] project. It is an effort recommended for inclusion in the EQ Strat Plan by the Naval Civil Engineering laboratory (NCEL, now the NFESC). It addresses SERDP Thrust 2.D; Other Hazardous Wastes and supports the SERDP goal to develop affordable and effective control technology for priority pollutants emitted from operations and training activities. Because of its importance to the DoD, it is scheduled using the accelerated program description chart of the EQ Strat Plan (p.II.98).

### 7. Project Description:

VOCs from air can be recovered by simple condensation. When the VOC in the air is dilute, which would be the case when VOCs are lost to air during filling a tanker or a storage tank, direct condensation is not practical because of the large air volume involved. It would however be economical if the VOCs can be concentrated by a factor of 1000 or more before condensing. Such is the purpose of the use of vapor permeation membranes.

The process of vapor permeation is very similar to pervaporation, which is usually reserved for VOC-recovery from a liquid stream. In both processes, the membrane is hydrophobic and non-porous. The hydrophobic VOCs must first dissolve in the membrane itself. This phenomenon of absorption is characterized by Henry's Law, and a constant, Henry's Law constant, represents the efficiency of adsorption. The VOC then diffuses through the thickness of the membranes and finally desorbs at the permeating side of the membrane. A vacuum is usually applied and a condenser condenses the VOCs. An inert gas sweep can also be used to achieve similar, and in some cases, superior results. The energy for evaporation generally needs to be provided, although in the case of vapor permeation, the energy demand is much lower than pervaporation, since the VOCs are already in vapor phase.

Some amount of research has been done on the recovery of VOCs, chiefly chlorofluorocarbons (CFCs), from air by vapor permeation process. The present research involves:

1. Characterizing the chemical composition of VOC emissions from petroleum, and determining the kind of membranes needed to apply vapor permeation. The latter will involve screening adsorption studies (Henry's Law constants measurements);
2. Constructing a laboratory apparatus to conduct vapor permeation experiments on simulated VOC emissions, and modeling the permeation process for predicting performance of a scaled-up prototype;
3. Constructing membrane modules for the purpose;
4. Preparing an economic analysis to determine capital requirement and payback period; and
5. Demonstrating the technology with a prototype.

Part 1 of this research will be conducted in EPA-RREL. The expertise exists for conducting bench-scale research on vapor permeation (and pervaporation), and for casting specialty membranes. A bench-scale adsorption study will be done using a microbalance to measure minute mass differences of membrane fragments. The modeling that is involved is only an extension of work previously performed in the RREL on a pervaporation project in cooperation with the University of Cincinnati. Part 2 will also be done in-house in RREL. Parts 3, 4 and 5 will be contracted out. Research-based membrane companies, such as Membrane Technology and Research (MTR, Inc.), Palo Alto, CA, are particularly equipped to conduct these parts most efficiently and cost-effectively. MTR, Inc., for instance, is collaborating with Hoechst-Celanese for large-scale demonstration of pervaporation processes.

The technical risk of this proposed approach is low. The project addresses the Tri-service Environmental R&D Environmental Plan Requirement (2.I.1.o); Control Emissions from Energetics manufacturing and stationary sources.

**8. Expected Payoff:**

The VOC removal is needed to reduce the formation of photochemical smog and ozone non-abatement.

**9. Milestones:**

1.	Test site selection continued	12/95
2.	Set objectives for prototype	12/95
3.	Membrane screening continued	02/96
4.	High surface area condenser	02/96
5.	Develop test plan for demo	04/96
6.	Begin system design model based on lab studies	12/96
7.	Acquire contractor for demo	04/96
8.	Acquire prototype for demo	07/96
9.	Conduct field tests	09/96
10.	Complete field tests	12/96
11.	Complete system design model	03/97
12.	Final report	06/97
13.	Technology transfer reports	09/97



## 10. Transition Plan:

Design data and results of demonstrations will be provide to DoD during the third year. The project will be coordinated with the NFESC for the development of User Data Packages and technology transfer needed to communicate the technology development results in a form that will enhance DoD-wide exploitation. Although newly formed, the NFESC has excellent capabilities to assist in the RD&E efforts and will become the primary technology transfer vehicle as the technology moves from the research through the field study phase.

## 11. Funding: \$(K)

	FY94	FY95	FY96	FY97	Total
SERDP	250	100	400	200	950

## 12. Performers:

Parts 1 and 2 will be done in-house in RREL-EPA. Parts 3-5 will be contracted out for demonstrating the technology. NFESC will collaborate with RREL in parts 1 and 2, and will closely monitor the pilot and demonstration work that follows.

Ms. Jennie Koff, NFESC  
Code ESC 421jk, 560 Center Drive  
The Naval Facilities Engineering Service Center  
Port Hueneme, CA 93043-4328  
PHONE: (805) 982-1674  
FAX: (805) 982-1409

## 13. Principal Investigator:

Dr. Subhas K. Sikdar  
USEPA; Office of Research and Development  
Water and Hazardous Waste Treatment Research Division  
Risk Reduction Engineering Laboratory  
Cincinnati, OH 45268  
PHONE: (513) 569-7528  
FAX: (513) 569-7787  
E-MAIL: sikdar.subhas@epamail.epa.gov

## 14. Keywords:

Pervaporation, Vapor Permeation, Hydrophobic Membrane, Hydrocarbon Recovery.

## SERDP FY95 PROJECT

1. **SERDP Thrust Area:** Compliance
2. **Title:** Advanced Mass Spectrometry for Atmospheric Monitoring
3. **Agency:** US Air Force
4. **Laboratory:** Armstrong Laboratory, AL/XP
5. **Project ID:** #192
6. **Problem Statement:**

The need for accurate measurements of the identity, concentration, and spatial distribution of atmospheric pollutant species is fundamental to many areas of environmental research and development and crosses the boundaries of several of the SERDP pillars:

- Compliance with standards for emission of pollutants into the air from waste sites, rocket and jet engine operations, power plants, manufacturing and weapons destruction facilities, etc., can only be demonstrated by the use of reliable measurements of the emissions.
- Air pollution reduction efforts must be founded on accurate assessments of current emission levels and must be monitored for effectiveness.
- Cleanup of underground hazardous waste sites requires first that the sites be found and characterized. Detection of airborne emissions from such sites is an efficient and cost-effective alternative to traditional bore hole drilling methods.

The goal of the research proposed here is to develop and demonstrate technology to measure the concentrations of essentially all neutral species in the atmosphere at ground level, in the troposphere, and in the stratosphere. Traditional mass spectrometry for detection of major pollutant species such as CO<sub>2</sub> and NO<sub>x</sub> will be combined in a single instrument with a novel chemical ionization technique for ultra-high sensitivity detection of trace neutrals. The technique is broadly applicable to the many requirements listed above, is adaptable to field measurements on the ground and on research aircraft, is low risk, and provides greater than 10<sup>12</sup> dynamic range with part-per-trillion sensitivity.

### 7. Project Description:

**Approach:** In recent years the range of techniques available for analysis of natural and pollutant species in the troposphere and stratosphere has expanded. In particular, ion mass spectrometry techniques have become much more sensitive and, in combination with laboratory kinetics measurements, have led to the quantitative analysis of trace neutral species present in concentrations much too small for direct measurement by traditional mass spectrometry.

Chemical reactions between neutral pollutant gas molecules and the ions that are naturally present in the atmosphere frequently produce new ion species that are unique signatures of the original trace neutral. Detection of the product ion species unambiguously shows the presence of the original neutral. The concentration of the neutral species can be calculated from the intensities of the reactant and product ions measured in the atmospheric environment of interest and from measurements of the rate coefficients of the relevant ion-molecule reactions. This technique has been used to determine the concentrations of such species as sulfuric acid, nitric acid, pyridine, and picoline in the unperturbed atmosphere and to measure the concentration of the important hydroxyl radical (OH), which cannot be detected easily by other methods. Because of the very small background signal level for ions, the technique routinely gives sensitivities in the part-per-trillion range and can sometimes be optimized to detect neutrals in parts-per-quadrillion.

Several novel techniques for making very high sensitivity measurements of ions in the atmosphere have been pioneered by F. Eisele. In the simplest of these, a flow of gas at atmospheric pressure is brought into a high voltage drift tube in which the drift direction for the ions of interest opposes the neutral flow direction. The ions are slowed down, extracted from the primary neutral flow, and directed toward a sampling orifice. The ions then enter a high vacuum region of the apparatus and are detected with a pulse counting quadrupole mass spectrometer. The concentrations of the neutrals of interest are calculated from the signals of their product ions generated in reactions with ambient charged species. In a variation of the method, ambient ions are excluded from the flow tube, and specific test ions are injected into the neutral flow to create unique product ions that are detected the same way. Eisele (Georgia Tech and NCAR) is currently under contract to us using FY92 SERDP funds to make initial measurements of ion composition in rocket and jet plumes and will make the first measurements in the spring of 1994. In a collaborative effort closely related to this SERDP proposal, one of the members of our in-house research team is currently investigating the ion chemistry of jet engine plumes at the Max Planck Institute for Atomic Physics in Heidelberg, Germany, under the AFOSR Window-on-Europe program.

Our in-house mass spectrometer development effort will focus on incorporating Eisele's novel chemical ionization techniques into a quadrupole mass spectrometer used for standard measurements of neutral composition at atmospheric pressure. In addition to the ultra-high sensitivity techniques described above, the instrument will also provide variable energy electron impact ionization with differential pumping for detection of the major pollutant species. The portable instrument package will be easily adaptable to field and flight experiments. We have used basic research funding to construct the high vacuum portion of the instrument, containing the mass spectrometer, detectors, differential pumping stages, and electronics and data handling equipment. The sampling flow-drift tube system is currently being designed. SERDP funding will be used primarily to complete the design and assembly of the sampling system, to integrate and test the sampling system, and to make the initial field measurements.

Laboratory measurements of ion chemical rate constants will be made in an existing variable temperature selected ion flow-drift tube (SIFDT), which is the only such instrument available in any DoD laboratory, and in a new high temperature flowing afterglow apparatus, which is the only such instrument anywhere in the world. These types of apparatus have provided most of the previous measurements of the chemical kinetics important in atmospheric ion chemistry. The specific species and reactions to be studied will be chosen after

measurements of ion composition in the field are started. We expect that the ion chemistry of trace pollutant species will pose new challenges to the laboratory measurement program. Although the bulk of funding for the laboratory effort is provided by the Air Force Office of Scientific Research, some SERDP funding may be used in future years to develop new laboratory techniques required to make measurements of specific pollutant species under the extremes of temperature and pressure represented in the actual atmospheric environments.

SERDP funding in FY93 has been used in the laboratory program to develop an ion chemical technique for detection of chlorine nitrate,  $\text{ClONO}_2$ , and to determine the atmospheric lifetimes of perfluorocarbons, which have been proposed as substitutes for ozone depleting chlorofluorocarbons. In a related SBIR Phase II research effort, the heterogeneous decomposition of halocarbons on  $\text{Al}_2\text{O}_3$  particles from solid fuel rocket engines is being investigated.

The effort proposed here directly supports many of the requirements listed in the Tri-Service Environmental Quality R & D Strategic Plan, including:

Pillar 1, Clean-up:	Thrust 1.C: "Characterization/ Monitoring," Thrust 1.D: "Chemical Analytical Systems,"
Pillar X:	Thrust X.1: "Hazard Assessment,"
Pillar 2, Compliance:	Thrust 2.A.2: "Routine Emissions," Thrust 2.A.3: "Detection and Monitoring," Thrust 2.C: "Manufacturing and Disposal," Thrust 2.0: "Compliance Evaluation,"
Pillar 3: Pollution Prevention:	Thrust 3.N: "Reduce Greenhouse Gas Emissions."

Our research group has been studying atmospheric ion composition and charged particle chemistry as its core research effort for several years. Applying this experience to specific environmental problems using SERDP funding will therefore be highly leveraged with other funding sources. Specific tasks that will be accomplished with the SERDP funds are:

- 1) Use existing high sensitivity atmospheric ion detection equipment (Eisele, Georgia Tech, NCAR) to measure ion composition in jet engine exhaust plumes.
- 2) Develop in-house mass spectrometric capability based on Eisele's techniques; test and calibrate instrumentation in concert with complementary techniques; demonstrate usefulness of technology in field tests using jet engine exhausts, rocket exhausts, and other measurements of opportunity.
- 3) Perform laboratory measurements of the kinetics of the ion chemistry of trace neutral pollutant species as required to calculate the concentrations of the pollutants measured in the field programs.

## 8. Expected Payoff:

The Geophysics Directorate of the Phillips Laboratory is an acknowledged world leader in measuring the chemical kinetic properties of ion-molecule, ion-ion, electron-molecule and electron-ion reactions relevant to atmospheric, ionospheric and high temperature plasma processes, and in measuring the ion composition of these environments with mass spectrometers. For this work, our research group was selected to be one of the 1991-1993 Air Force Office of Scientific Research (AFOSR) Star Teams recognizing excellence in basic

research relevant to Air Force requirements. The Geophysics Directorate is the only DoD laboratory facility where the in-house expertise in ion chemistry and mass spectrometry can be brought together to develop the high sensitivity trace neutral detection method that we propose.

We plan to focus our efforts initially on the effluents from jet and rocket engine operations in the troposphere and stratosphere. In order to assess the environmental impact of the pollutant species generated by the combustion process in such engines, the concentrations and lifetimes of the foreign species and the chemistry which they undergo in the atmosphere must be understood. Our proposed research program will lead to high sensitivity measurements of the concentrations of many species in the atmosphere. Models of the chemistry of polluted environments can then be improved by adjusting the model to match the measurements. The validated models can then be applied with confidence to environmental scenarios where direct measurements have not been made and will also lead the way to future research needs. The immediate benefit of the research will be to ensure compliance of jet or rocket engine emissions with mandated standards, to point the way to problems that might cause high emissions, and in general to support DoD efforts to reduce pollution from jet and rocket operations.

In addition, we expect that our ion chemistry technique will be broadly applicable to other requirements for environmental monitoring in the areas of compliance, cleanup, and pollution prevention. We will actively seek opportunities to bring the techniques developed in this research effort to collaborative field campaigns where other complementary trace gas detection techniques are deployed. Comparison and cross-calibration of many techniques will ultimately lead to a battery of instruments which between them can detect pollutant species under more varied environmental conditions than any one technique could alone.

#### **9. Milestones:**

1.	Complete first measurements of jet plume composition	07/94
2.	Complete core in-house mass spectrometer	02/95
3.	Develop ion chemical detection scheme for ClONO <sub>2</sub>	05/95
4.	Integrate flow sampling system into mass spectrometer	07/95
5.	Perform first field-scale demonstration	01/96
6.	Perform second field-scale demonstration	12/96
7.	Complete commercialization prototype	09/97
8.	Perform validation comparison measurements	04/98

#### **10. Transition Plan:**

The end product of this proposed research will be a portable, highly sensitive, calibrated and tested instrument for determining trace neutral composition in polluted regions of the atmosphere. This product should be suitable for commercialization and sale to the environmental monitoring community, and we will actively seek industry partners interested in developing this technology with us via CRADA agreements or other appropriate vehicles.

**11. Funding: \$(K)**

	FY93	FY94	FY95	FY96	FY97	FY98	TOTAL
SERDP	320	500	150	400	600	600	2250
AFOSR	400	400	400	400	400		2000
TOTAL	720	900	550	800	1000	600	4250

**12. Performers:**

Development of the portable mass spectrometer equipment, measurement of relevant ion chemical kinetics, and analysis of all data will be performed at the Ionospheric Interactions Branch, Geophysics Directorate, Phillips Laboratory, Hanscom AFB, Massachusetts. Georgia Tech and the National Center for Atmospheric Research (NCAR) are under contract to us to make initial measurements of ion composition in jet engine exhaust plumes. The Max Planck Institut für Kernphysik, Heidelberg, Germany, will be an unfunded collaborator. This effort will be closely coordinated with an associated SERDP proposal, "Rocket Plume Mass Spectroscopic Stratospheric Sampling," in which mass spectroscopic instrumentation will be used on research aircraft to measure rocket plume pollutant species.

**13. Principal Investigators:**

Dr. John O. Ballenthin and Dr. Albert A. Viggiano  
Geophysics Directorate  
Phillips Laboratory  
PL/GPID, 29 Randolph Road  
Hanscom AFB, MA 01731-3010  
PHONE: (617) 377-4028  
FAX: (617) 377-7091  
E-MAIL: ballenthin@plh.af.mil

**14. Keywords:**

ion chemistry, mass spectrometry, airborne pollutants, detection, atmosphere/troposphere/stratosphere, high sensitivity.

## SERDP FY95 PROJECT

1. **SERDP Thrust Area:** Compliance
2. **Title:** Leak Location in Underground Pipelines
3. **Agency:** U.S. Environmental Protection Agency
4. **Laboratory:** Risk Reduction Engineering Laboratory (RREL)
5. **Project ID:** #249
6. **Problem Statement:**

The goal of this applied research and technology development effort is to develop and demonstrate a portable and on-line acoustic leak detection/leak location system to accurately and reliably test single and double walled pipelines of various sizes and content (i.e., gasoline, diesel, jet fuel, potable water, low level radioactive wastes, etc.) Such a system would not only assist the regulated community in complying with existing state and Federal regulations but would also reduce the spread of contamination and loss of drinking water through early and more accurate leak detection/location.

Existing Federal regulations (40 CFR Parts 280 and 281, September 1988) require that underground tanks and pressurized pipelines containing petroleum and other hazardous substances be tested for leaks on a regular basis and that once a leak is detected it must be mitigated. This is an onerous task when one considers the enormous number of miles of pipeline associated with retail gasoline service stations nationwide, airport hydrant systems, Army and Navy fueling depots, DOE low level radioactive waste systems, etc. Over 250,000 releases from underground storage systems have been confirmed to date and the EPA estimates that as many as 15 to 20% of the approximately 1.8 million regulated underground systems nationwide either are leaking or are expected to leak in the near future. The environmental threat from these leaking systems has a direct impact on public health because approximately half of the Nation's drinking water supply comes from ground water. Small quantities of gasoline released underground can contaminate millions of gallons of potable ground water with suspected carcinogens such as benzene, etc. The threat is not limited to ground water; leaking petroleum and chemicals can also contaminate surface waters and contribute to air pollution. In addition, these products release vapors that can seep into the sewerage systems of homes and businesses and accumulate to explosive levels. Besides the environmental threats and astronomical costs associated with addressing these threats (over \$30.0 billion for site remediation alone) we are also wasting valuable drinking water and energy resources.

Rapid and cost-efficient remediation can occur if the source of an underground leak can be pinpointed quickly and accurately. Current technologies utilizing volumetric- and pressure-based methods are unable to effectively accomplish this objective. Since 1990, EPA's Risk Reduction Engineering Laboratory has been conducting applied research on acoustic technology for rapid, near-real-time leak detection/location in pressurized pipelines typical of those found at retail service stations. Results of this work indicate that acoustic measurements combined with advanced signal processing methods can provide a means by

which to detect and locate small leaks over long distances in pressurized pipelines. Additional applied research and technology development work is required to optimize system performance and application on larger and longer lines and on lines of different configuration. A Science Advisory Board Review (June 1992) of this earlier work (which was funded solely with EPA/ORD funds) recommended continued research in this area.

## **7. Project Description:**

In 1990, EPA's Risk Reduction Engineering Laboratory initiated a program to develop a non-invasive, non-destructive method for detecting and locating small leaks in pressurized pipelines containing petroleum products. Experiments were conducted at the UST/Pipeline Test Facility in Edison, New Jersey in which three acoustic sensors separated by a maximum distance of 125 ft were used to monitor signals produced by 3.0, 1.5, and 1.0 gal/hr leaks in the wall of a 2 inch diameter petroleum pipeline. Line pressures ranged from 10 to 30 psi. Application of a leak location algorithm based upon the technique of coherence function analysis resulted in mean differences between predicted and actual leak locations of approximately 4 inches. This is a significant improvement over current techniques and provides results in a matter of minutes; however, additional experiments with higher pressures and over longer and larger pipelines are required to optimize system performance and expand system application.

The objective of this proposal is to develop, design, fabricate, and demonstrate both a portable and an on-line passive acoustic leak detection/location system that can be used on: (1) existing pipelines, (2) pipeline systems that cannot be breached, (3) newly installed systems, and (4) double-walled pipelines. To meet this objective, a three-phased development and demonstration program will be conducted over a three year period.

### **Phase I: Modifications to UST/Pipeline Test Facility and Preliminary Experiments**

This phase will involve (a) modification of the existing UST pipeline system to make it more representative of systems found at retail service stations, (b) design and installation of a double-walled steel pipeline system typical of DOE systems used to transport low level radioactive wastes, and (c) design and installation of a large diameter (10-12 inches) and longer (300-500 ft.) high pressure pipeline system typical of Army and Navy facilities.

Detailed experiments will be conducted on the representative pipeline systems to determine the accuracy and performance of acoustic technology for locating leaks of differing sizes over variable distances and to identify and evaluate potential differences in performance due to pipeline configuration. Experiments will be designed and conducted to optimize and validate the previously developed "breadboard" system which is based on a coherence function analysis approach; and to evaluate other approaches such as signal attenuation, time of flight, and cross-correlation analysis. The performance of the location system as a function of leak flow rate, line pressure, pipeline diameter, and pipeline length will be determined and validated. Based upon these experiments, recommendations will be made to modify/redesign the existing "breadboard" system.

A protocol appropriate for each pipeline configuration will also be developed for field application of the modified system. The protocol(s) will be based on the current test method



which will be refined through selective studies to address questions such as: (a) when testing on longer and wider pipelines, are additional sensors necessary to characterize the signal created by the leak and at what intervals must the sensors be spaced; (b) how will the signal be affected by leaking valves, changes in pipeline connection hardware, multiple bends and elbows, corrosion anomalies, etc.; and (c) what are the affects of multiple leaks?

#### Phase II: Prototype Development and Demonstration

Based upon the recommendations of Phase I, a portable acoustic leak detection/location prototype system will be designed and fabricated. The system will enable field testing of pipelines with minimal interruption to commercial operations; most tests will take less than one hour to perform. Using the protocol(s) developed in Phase I, additional "shakedown" testing of the prototype system will be conducted at the UST/Pipeline Test Facility and field validation will be accomplished at actual retail service stations, and Army, Navy, and DOE sites of opportunity.

Phase II will also include initiation of the development of an on-line automatic acoustic system that can be attached to existing pipeline systems or integrated into new systems (single or double-walled) during installation. This would provide constant monitoring with an immediate release detection/location information alarm. System hardware will be developed and preliminary experiments will be conducted on the respective test pipeline systems to identify and evaluate performance characteristics associated with an on-line monitoring system. Recommendations will be provided for prototype design and fabrication, and a protocol will be developed for field application.

#### Phase III: Final Prototypes and Users Manual

During this phase, final modifications and refinements will be made to the portable acoustic leak detection/location system hardware and software. The system may be further field tested if significant modifications are made and further optimization is required. This effort will result in a user friendly, field applications manual and a final prototype and hardware system (including software) ready for commercial application.

Phase III will also involve fabrication of the on-line prototype leak location/detection system. The system will be evaluated for performance and accuracy on the respective test pipeline configurations. Studies will include signal characterization and algorithm verification. Based on these results, the on-line system software program will be modified and refined. Final field validation of the on-line system will be conducted at new installations or recently upgraded installations (as per the regulations) at DOE, Army, and Navy facilities. The final prototype will then be developed for commercial application.

### **8. Expected Payoff:**

Underground pipelines are used by numerous industries worldwide to transfer liquid products. Presently, only two methods are used to locate leaks in pipelines. The first involves uncovering the line and performing a visual inspection. This is very disruptive to operations, destructive to facility hardware, time consuming and costly. The second method uses a helium or halogen tracer. This technique has serious operational and performance problems, and is also time consuming and costly. Passive acoustic leak detection/location

provides an accurate and cost effective workable solution to this problem. Pipelines can be tested in minutes rather than days. Leaks can be located in any line without having to use invasive techniques which are especially costly in low-level radioactive wastelines typically found at DOE facilities. Furthermore, the cost of remediations will diminish significantly as releases are detected earlier and the amount of excavation associated with a repair is reduced. Most importantly, with more accurate on-line monitoring capabilities, there is better control over product transfer systems, resulting in the prevention of millions of gallons of fuel being released to the environment (and subsequently resulting in the reduction of irreparable damage to our natural resources) and the conservation of a limited energy resource.

## 9. Milestones:

- |     |  |          |
|-----|--|----------|
| 1.  | Complete SOTA review on leak detection for underground storage tank systems  | Pre FY94 |
| 2.  | Design and construct UST/Pipeline Test Facility  | Pre FY94 |
| 3.  | Complete studies of pressure and temperature affects on the performance of leak detection in pipelines   | Pre FY94 |
| 4.  | Complete feasibility study of acoustic leak detection/location technology for pressurized pipelines and develop "breadboard" system  | Pre FY94 |
| 5.  | Modify existing UST/Pipeline Test Facility to represent "typical" (a) retail service stations (b) large diameter/high pressure systems at Army and Navy facilities (c) double-walled systems at DOE facilities | 12/94    |
| 6.  | Complete experimental program on portable acoustic system and develop protocol for field application   | 03/95    |
| 7.  | Design and fabricate portable acoustic system and conduct field demonstrations at Army, Navy and DOE facilities  | 09/95    |
| 8.  | Final "portable" system prototype and users manual(s)  | 12/95    |
| 9.  | Complete experimental program on-line system and develop protocol for field application  | 09/95    |
| 10. | Design and fabricate on-line acoustic system and conduct field demonstrations at Army, Navy and DOE facilities   | 06/96    |
| 11. | Final "on-line" system prototype and users manual(s)   | 09/96    |

## 10. Transition Plan:

Once the technology has been developed, the National Leak Prevention Association, National Leak Detection Association, American Petroleum Institute, National Association of Corrosion Engineers, and the participating agencies in this project will actively market this technology to their constituents. In addition, the EPA will pursue commercialization through the Federal Technology Transfer Act mechanism. There is a great deal of interest in using this technology by the commercial sector due to the tremendous cost savings that may be realized from immediate location of releases, more timely remediations, and conservation of fuel (energy). In addition, the technology has cross-application to pipeline systems involving other contents such as gas, water, sewage, etc.

**11. Funding: \$(K)**

	FY94	FY95	FY96	FY97	FY98	Total
SERDP	1921	0	79	800	200	3000
EPA	250	250	250	0	0	950
DOE	200	200	200	0	0	600
NAVY	150	0	0	0	0	150
TOTAL	2521	450	529	800	200	4700

**12. Performers:**

This project will be conducted by EPA's Risk Reduction Engineering Laboratory in conjunction with DOE's Oak Ridge National Laboratory, the Naval Facilities Engineering Service Center, Port Hueneme, CA, and the Army Civil Engineering Research Laboratory, Champaign, IL. The project will be coordinated through an Interagency Agreement, whose performers and sponsors will include: U.S. Environmental Protection Agency: David Ziegler, Director, Office of Underground Storage Tanks, Washington, DC; Anthony N. Tafuri, Robert W. Hillger, Underground Storage, Tank Program, Risk Reduction Engineering Lab, Edison, NJ; U.S. Navy: Elsie L. Munsell, Deputy Assistant Secretary of the Navy, Washington, DC; Ted Zagrobelney, Division Director, Naval Facilities Engineering, Command, Washington, DC; William Powers, Program Manager, Naval Facilities, Engineering Service Center, Port Hueneme, CA; Leslie Karr, Environmental Engineer, Naval Facilities, Engineering Service Center, Port Hueneme, CA; U.S. Army: Dr. Charles Marsh, Materials Engineer, U.S. Army Civil, Engineering Research Laboratory, Champaign, IL; Vincent Hock, Metallurgist, U.S. Army Civil Engineering, Research Laboratory, Champaign, IL; Major Mike McDevitt, Program Manager, U.S. Army Civil Engineering, Research Laboratory, Champaign, IL; U.S. Department of Energy: Sherry Gibson, Program Director, Department of Energy, Washington, DC; Richard Korynta, Program Manager, Oak Ridge National Laboratory, Oak Ridge, TN.

**13. Principal Investigators:**

Anthony N. Tafuri / Robert W. Hillger  
U.S. EPA RREL/RCB  
2890 Woodbridge Avenue  
Edison, New Jersey 08837  
PHONE: (908) 321-6604 / (908) 321-6639  
FAX: (908) 321-6640

**14. Keywords:**

Acoustics; Leak Detection; Underground Storage Tanks; Pipelines; Petroleum; Remediation

## SERDP FY95 PROJECT

1. **SERDP Thrust Area:** Compliance
2. **Title:** Controlling, Assessing, Managing, and Monitoring the Noise Impact from Weapons, Helicopters, and Aircraft on Training and Readiness
3. **Agency:** U.S. Army
4. **Laboratory:** Construction Engineering Research Laboratories (CERL)
5. **Project ID:** #523
6. **Problem Statement:**

Preservation of the Department of Defense (DoD) training, testing and readiness mission requires that DoD be capable of controlling, assessing, managing and monitoring noise problems in the vicinity of its bases and installations. They cannot now consistently do this. The DoD faces continual challenges to planned operations and changes to operations because of negative community responses to the noise created by weapons, helicopters, and aircraft. The direct impact is an insidious loss of training and readiness capability through the closure of ranges and firing points, altered flying, and nighttime curfews. Because of noise, the DoD has lost significant mission capability at over 50 installations. Equally important are delays due to procedural or litigational challenges (as provided for in the National Environmental Policy Act) to environmental impact analysis documents, such as Environmental Assessments (EAs) and Environmental Impact Statements (EISs) that propose changes in DoD operations. Such changes include, for example, introduction of a larger battle tank main gun, introduction of supersonic flying in an area not previously exposed to these operations, changing from an older aircraft or helicopter to a newer one, and increases in nighttime military training. Such challenges are difficult to refute when substantiating information is not available. It is expected that the impacts of environmental noise from military operations will continue to be a significant problem, and with enhanced emphasis on nighttime training, will worsen for the foreseeable future.

DoD needs the ability to predict physical sound levels in the community surrounding an installation due to training activity on post. With such a prediction, training could be conducted at times that are less favorable for sound propagation and thus reduce the community noise exposure. Basic Research is needed to advance our understanding of wave propagation in a turbulent atmospheric (meteorological) medium to augment existing sound prediction tools which currently fail when applied under these conditions.

No present physical models are adequate for predictions in the presence of wind driven turbulence or thermal plumes from solar heating. In these situations, a wave that propagates through atmospheric eddies or thermal drafts experiences refraction and diffraction from its normal path. Predicted focus locations on the ground are moved or diminished and acoustic shadows are insonified via scattering. No theoretical or computational method exists that

can simultaneously account for acoustic wave propagation through anisotropic, inhomogeneous, turbulent media (the outdoor air) in proximity with an irregular surface of complex acoustic impedance (the ground). In terms of human response, the DoD continues to have difficulty meeting NEPA compliance requirements and executing the Air-Installation Compatible Use Zone (AICUZ) and Installation Compatible Use Zone (ICUZ) Programs because there is a lack of adequate scientific data on the effects of environmental noise from DoD operations on the health and welfare of people. The National Environmental Policy Act (NEPA) of 1970 requires federal agencies to predict the expected environmental impacts of their activities.

The DoD requires the ability to assess the combined/cumulative human impacts of joint and/or co-located installations and operations. For example, the DoD has been receiving major challenges to environment impact analysis documents because we do not currently address the combined and cumulative effects of Army and Air Force operations there. Most current community (annoyance) impact assessment methodologies for predicting the effects of aircraft noise on humans rely on annualized average exposure descriptions. These annualized procedures are the day-night A-weighted sound level for fixed-wing aircraft, motor vehicles and most continuous industrial noises, etc. A separate annualized procedure, C-weighted day night average level is applied to blast noise and sonic booms. No method exists to combine these two procedures into one overall assessment. Further, there are serious questions about the efficacy of the current C-weighted procedure for blast and sonic-boom noise. Current methodology combines two categories of noise, blast noise, and sonic boom, together, equally into one assessment. However, the technical basis for this methodology exhibits distinct differences between these categories of sound. Sound character and background ambient present two additional challenges to present assessment methodology.

## **7. Project Description:**

The major purpose of this proposed research and development program is to address the issues described above in a coordinated program involving several major federal agencies including the U.S. Army (USA) and the U.S. Air Force (USAF), the Department of Transportation (DOT), the Federal Aviation Administration (FAA) and the NASA Langley Research Center. This effort supplements and complements current and planned USA and USAF programs, which only together will provide the funding required to adequately address a series of challenging technical issues. The major focus of this effort is assessing and mitigating military noise. The combined human effects model is a dose response empirical model that provide the means for DoD to assess and mitigate noise. The propagation research will lead to better analytical physical sound propagation models which will be used to improve the underlying physical predictions of sound for the human effects model. The improved physical prediction model also will be used for direct prediction and warning of high level for noise mitigation purposes. The proposed program is part of the DoD Environmental Quality R&D Plan and is highly rated by the user community. It relates directly to Project Reliance DoD Pillar 2: Compliance (Reliance Sub-area: Noise) and covers several requirements. It addresses several of the Research and Development Objectives of the Compliance Pillar, as listed in the SERDP Strategic Guidance which was provided to

prospective proposers to the SERDP program. This program will build on previous research by USA, USAF, FAA, and NASA.

Central to control and management of noise are a set of demonstrated methods to reduce noise. This SERDP program continues the 1993 effort to develop a system to forecast high noise levels and thereby provide for inexpensive noise control at training ranges. Central to assessment and monitoring are the technical capabilities to predict the physical noise environment and the expected effects of these environments on human populations. In this project, we will attempt to answer basic questions about acoustic wave propagation through turbulent media:

- 1) Under what circumstances is multiple scattering theory necessary for accurate predictions?
- 2) How can the statistical moments of the propagated signal be themselves propagated over a ground surface?
- 3) What is the effect of propagation through a medium where the turbulence distributions are layered?
- 4) What is the correlation between atmospheric fluctuations and changes in acoustic propagation?

Results from these approaches will be used to seek a valid approximate model for the influence of turbulence on the average propagation, and for statistics of the fluctuating signal, which will incorporate measured values of wind and temperature versus height.

The combined noise model will be developed in three phases. During Phase 1, an initial combined effects model will be developed based on the current state-of-the-art. This initial model development will be accomplished through working group consensus building using a contract with NAS and ANSI. By 1997, the initial combined noise effects model, developed by consensus by appropriate cognizant bodies, will be completed. During phase 2, the results of other, related RDT&E by the Army, Air Force and NASA and international partners will be used to revise the Phase 1 preliminary combined noise effects model. During Phase 2, new laboratory and field research will focus on specific issues developed by the NAS and ANSI deliberations and the results from other RDT&E. During Phase 3, the combined noise effects model resulting from Phase 2 will be validated in a series of field tests. Traditional community attitudinal survey techniques will be used at a set of sites where combined noise is received. These might include sites near Army installations which include Air Force air-to-ground gunnery ranges such as Ft. Sill or Ft. Drum. Data collection near Navy or Air Force bombing ranges also will be considered. NAS and ANSI will then be asked to review and approve the final, validated combined noise effects mode.

Research on a high-energy impulsive sound effects model (annoyance) will center on two factors (sub-thrusts) which must be better understood in order to reach the overall goal of a combined noise effects model. For the first sub-thrust, there will be studies to compare and contrast community response to blast noise and sonic boom. Current methodology combines these two categories of noise into one assessment. Laboratory-field studies of these two sounds in the same test will quantify these differences, if any. For the second sub-thrust, there will be studies to better quantify the role of vibration and rattle in response to these

sounds. The technical data strongly indicate that vibration and rattle play a major role in large-energy impulsive noise annoyance. However, it is not currently possible to quantify and predict the annoyance generated by these factors in combination with the audible sound.

## **8. Expected Payoff:**

Ultimately, results of this program will be used to decrease loss of military mission operational capability through defending against encroachment and decreasing costs associated with compliance with NEPA requirements. The latter will be accompanied by reducing costs associated with defending planned changes in DoD operations. The payoff will be improved training efficiency and operational force readiness.

The benefit/cost associated with encroachment and compatible land use can be estimated as follows. The Navy has spent over \$500M in land purchases through the AICUZ program because of encroachment. A conservative estimate of off-post noise sensitive encroachment growth is 3 acres per day, DoD wide in Zone II and .03 acres per day in Zone III. Conservative estimates of noise-related property devaluation because of noise is 10% in Zone II and 50% in Zone III. This translates to the present value of about \$750M at a 7.5% interest rate. Proven noise mitigation techniques are needed to avoid these costs.

Results from the physical model study will be used in computer program for predicting noise levels and in constructing noise contours. These programs, NOISEMAP and BNOISE, are used by the Army Environmental Hygiene Agency to map noise contours for Army installations as apart of the ICUZ and NEPA processes.

The combined human response model will develop improved impact assessment and control methodologies which will be able to deal with the multiple issues and questions raised concerning the current "universal" assessment methodology. This more robust and improved understanding of the issues will manifest itself as increased public acceptance of AICUZ/ICUZ studies and the noise portions of environmental impact analysis documents (EA's, EIS's) for future DoD operations. The results of the proposed program will provide more technically and legally defensible analyses of the effects of noise from DoD operations, less controversy surrounding the issues to be addressed, and less time required to implement changes in DoD operations.

## **9. Milestones:**

Turbulent Boundary Layer Effects on Sound Propagation.

- |    |   |       |
|----|---|-------|
| 1. | Use perturbations of measured profiles with the FFP   | 09/94 |
| 2. | Study shore range, range dependent media with the PE  | 09/94 |
| 3. | Develop boundary conditions for waves in random media | 03/94 |
| 4. | Model and measure spatial and temporal coherence      | 09/95 |

## Combined Effects Model for Human Response to Noise.

- |    |  |       |
|----|--|-------|
| 5. | Develop plan for Blast/Sonic Boom Effects Studies          | 03/94 |
| 6. | Preliminary consensus National Method for Combined Effects | 09/95 |

### 10. Transition Plan:

Specific research results that result from this program will be incorporated into the USA AICUZ program and into the FIRE-system which is the primary tool used to manage noise and part RFMSS, the day-to-day Army training range management system. The Army Environmental Hygiene Agency will be the primary Army agency to implement technology transfer. In addition, the primary vehicle to transition the results of the proposed research program to the federal system is through FICON, which was established by direction of Congress for this purpose in FY92. The primary vehicle to transition to the private sector is through the American National Standards Institute (ANSI).

### 11. Funding: \$(K)

	FY94	FY95	FY96	Total
SERDP	550	325	0	875

### 12. Performers:

The Department of Defense (DoD) has a coordinated noise program to develop noise mitigation and management technology. The Air Force is responsible for fixed wing aircraft noise and the Army is responsible for artillery and helicopter noise; the Navy relies on the other two services for noise mitigation technology.

The U.S. Army Construction Engineering Research Laboratories (USACERL) will function as the lead laboratory for the physical sound propagation model. Active basic research in this field is done by universities. Penn State, University of Illinois and University of Mississippi publish frequently on topics of this nature. Their work will be integrated into this program. Within the Army, work in sound propagation phenomena is also supported by the Army Tank command and the Army Atmospheric Sciences Laboratory and the US Military Academy, with which we are currently participating with in joint field experiments and in data analysis and theoretical development.

For the Combined Effects Model for Human Response, performing organizations include the USA Construction Engineering Research Laboratories, USAF Armstrong Laboratory, the Federal Aviation Administration, the Department of Transportation, the National Park Service Ranger Activities Division, and NASA Langley Research Center. The U.S. Navy is not an active performer, since they do not actually perform any significant amount of research on the effects of noise on people, however they will participate in the planning and execution of this research. The US Army will be the lead organization.



### **13. Principal Investigators:**

Dr. Paul Schomer and Dr. Michael J. White  
U.S. Army Construction Engineering Research Laboratories  
2902 Newmark Drive, PO Box 9005  
Champaign, IL 61826-9005  
PHONE: (217) 352-6511  
EXTENSIONS: Schomer 7229, White 7436  
FAX: (217) 373-7251

### **14. Keywords:**

Aircraft, Noise, Impulse Noise, Weapons Noise, Environmental Impact, Annoyance, TES, NEPA, ESA, Endangered, Threatened, Fast Field Program, Rifle Ranges, Small Arms, Noise Abatement, Noise Barriers, Shooting Noise.

## SERDP FY95 PROJECT

1. **SERDP Thrust Areas:** Compliance
2. **Title:** Characterizing Open Burning/Open Detonation Emissions
3. **Agency:** U.S. Army Dugway Proving Ground (DPG), Utah
4. **Laboratory:** Dugway Proving Ground
5. **Project ID:** #247
6. **Problem Statement:**

The substantial amounts of energetic materials (propellants, explosives, and pyrotechnics (PEP)) accruing within the Department of Defense (DoD) have become an increasing burden on the military logistics system and subject of growing public concern. Storage facilities are now saturated by a demilitarization inventory exceeding 350,000 short tons and huge amounts of additional unwanted munitions are scheduled for retrograding to CONUS from overseas locations. Despite the critical need to reduce the demilitarization inventory, use of the only available process, OB/OD, has been sharply curtailed. Environmental regulators are demanding item-specific empirical data before granting OB/OD permits under subpart X of the Resource Conservation and Recovery Act (RCRA). These data are not available, and the system for obtaining them has not been fully developed. The Department of Energy (DOE) and defense contractors face a parallel situation at their installations which are accumulating substantial quantities of conventional unwanted energetic materials. Until new permits are granted or existing permits extended, the present dangerous situation will continue to worsen. Moreover, an already skeptical public may perceive that the failure of government agencies to obtain new permits as *prima facie* evidence that OB/OD activities are hazardous to their health and to the environment. The U.S. Environmental Protection Agency (USEPA) has begun closing OB/OD operations (e.g., Ellsworth Air Force Base, South Dakota) and citizens are demanding public hearings addressing risks from nearby OB/OD operations (e.g., Camp Edwards, Massachusetts, a field artillery training area for the Massachusetts Army National Guard).

Limited small-scale testing at DPG indicates that OB/OD-generated emissions of interest are so minute that they pose no hazard to health or the environment. However, the facilities, instruments, and procedures used during this previous testing cannot fully address the broad spectrum of conventional energetic materials awaiting disposal.

The goal of this project is to technologically expand testing facilities, instruments, and procedures so that they can be applied to current and projected disposal permitting-data needs. This includes designing new and larger BangBox testing chambers, characterizing emissions of complete munitions, and grouping munitions into emissions families so that future testing requirements can be abbreviated. During the course of this project, the testing system will be refined to the point where it is suitable for technology transfer to the commer-

cial sector and can be marketed worldwide. Research categories include basic and applied research. The project segment characterizing emissions is an exponential technical progression of a previously funded - and significantly smaller - pilot project.

## **7. Project Description:**

The principal investigator (PI) will chair a technical advisory panel (TAP) which includes expert representatives from DoD, the U.S. Environmental Protection Agency (USEPA), DOE, the National Oceanographic and Atmospheric Administration (NOAA), and defense industries, contractors, and national experts. This panel will provide technical direction for this project and serve as a primary means for interagency coordination. Individual panel members will be selected by the PI.

This project will develop the system to sample, identify, and quantify emissions of environmental interest produced by the OB/OD of PEP end items in the DoD inventory, specialty explosives held by DOE, and PEP manufacturing wastes at DoD, DoD-contractor, and commercial sites. Testing will specifically target criteria gases, semivolatile organic compounds (SVOC), volatile organic compounds (VOC), and metals. The pollutant sampling and analysis systems used in the 1993 BangBox testing at DPG will be refined as the pollutants emitted from the various PEP are identified. New sampling and analysis methods (such as across-the-stack monitors) developed by EPA and the regulated community to measure toxic pollutants from stationary sources will be reviewed frequently to determine if one or more of these methods should be evaluated in the BangBox for use with OB and OD. Pollutant measurement systems evaluated in the BangBox found to be applicable to field and BangBox OB/OD activities will be prepared and standard operation procedures as soon as possible. As laboratory and statistical analyses become available, chemical and ammunition experts will group munitions into families by emissions and relate theoretical projections to empirical data so that testing requirements for the demilitarization inventory can be sharply reduced. Project personnel will use the best available technologies including, but not limited to, the enhanced BangBox test facility located at DPG, supercritical fluid chromatography/mass spectrometry, gas chromatography/mass spectrometry, inductively-coupled plasma mass spectrometry, evacuated and passivated 6-L stainless-steel canisters, and high-volume samplers. The PI, acting in concert with recommendations of the TAP, will direct technological enhancement of these facilities, instruments, and devices as needed. Anticipated detection of most SVOC and VOC emissions will be at the ppt and ng levels, respectively.

This objective also includes design and construction of specialized surface (5000 to 15,000 m<sup>3</sup> with internal support frames and suppressive shields) and ventilated subsurface chambers, the latter having the capability of accommodating the shock, heat, and shrapnel produced by detonating and burning complete munitions containing up to 45 kg of high explosive (HE) material. These specialized BangBoxes will provide the aggregate capability for expeditiously studying the effects of soil type and moisture content, munition and propellant configuration (stacked/unstacked, buried/surface etc), presence or absence of combustion-promoting additives, quantity and type of munitions and propellants, and other variables on the pollutant profile and emission factors resulting from OB/OD operations. They will also provide the means of studying environmental dispersment of SVOCs and metals. If

necessary, field OB/OD testing will be conducted in a manner analogous to those executed at DPG in 1990/1991. An integrated database will collect and track data so that the pollution profiles of buried- or surface-detonated tested items can be compared and selected materials studied in more depth to identify the combustion dynamics and the kinetics of the principle chemical pathway associated with the production of pollutants and residues.

A panel of experts in risk assessment will prepare a guidance document listing the most reliable risk factors for the pollutants released from OB/OD activities and specifying how to use BangBox test results with these factors during the permitting process.

This is a low-risk project. All technologies exist, with only a few requiring moderate enhancement before they can be integrated into a complete testing system capable of fully characterizing emissions produced by the OB/OD of complete conventional energetic munition and propellant end items.

Transferring technologies to the private sector for worldwide commercialization is designed into the project. Contractors will conduct most of the technical work, experts from the private sector will be on the TAP, and reports, when security is not a factor, will be in the public domain. Formation of cooperative agreements with private firms as authorized by the Technology Transfer Act will further facilitate transfer of the technology. Proprietary rights of technologies used in execution of this project will not be included in technology transfer agreements without the express consent of the owner(s).

This project directly supports the DoD objective of avoiding environmental injury during conduct of military-related operations.

The primary technical risk of this project is achieving normal combustion processes while also containing emissions during chamber-testing of munitions with an HE content exceeding 10 kg. The critical path encompasses the design and construction of the advanced BangBoxes described above. However, because the existing BangBox at DPG is adequate for testing of complete munitions containing up to 500 g of HE, initial experiments can be conducted with minimal startup time. Development of the risk assessment guidance document is dependent upon completion of OB/OD-related modeling efforts contained in a companion proposal. Testing of combustion-enhancing additives will be dependent upon results of the identifying and preliminary testing of such oxidizers as contained in a companion proposal.

## **8. Expected Payoff:**

This project will provide the emissions data required by Federal and state regulators for evaluating applications for OB/OD permits under provisions of subpart X, RCRA. Existing OB/OD operations should continue and new permits issued if data indicates that risks to health and the environment are negligible. Because OB/OD destruction techniques are the fastest, safest, most understood, and least expensive means of disposing of conventional energetic materials, stockpiles of unwanted PEP items will be rapidly and inexpensively reduced. Funds will not need to be allocated for developing special facilities or item-peculiar equipment for PEP items identified as being suitable for open-air destruction. Conversely,

funds can be efficiently directed to development of alternate destruction methods for PEP items found not suitable for open-air destruction. Solid scientific data properly presented should allay existing concerns held by public about the safety of OB/OD disposal operations. Adaptation of the TOF mass spectrometer to BangBox testing of conventional energetic materials should result in a considerable reduction of laboratory assay costs.

**9. Milestones:**

The TAP will meet on a quarterly basis unless convened earlier by the PI to address special situations.

- |     |   |       |
|-----|---|-------|
| 1.  | First meeting of the TAP  | 07/94 |
| 2.  | Determination of feasibility of grouping munitions by emission families | 07/95 |
| 3.  | Initiate design of one surface and one subsurface BangBox               | 07/94 |
| 4.  | First FTTA agreements in place  | 01/95 |
| 5.  | Initiate fabrication of BangBoxes                                       | 02/95 |
| 6.  | Draft report on testing and feasibility                                 | 09/95 |
| 7.  | Surface BangBox completed   | 11/95 |
| 8.  | New surface BangBox characterized                                       | 12/95 |
| 9.  | Subsurface BangBox completed  | 03/96 |
| 10. | Initiate experimental testing of five items in new surface BangBox      | 12/95 |
| 11. | Guidance on using risk factors for permit applications released         | 12/95 |
| 12. | Subsurface BangBox characterized  | 04/96 |
| 13. | Initiate experimental testing of five items in subsurface BangBox       | 05/96 |
| 14. | Draft report of first new surface BangBox test                          | 12/96 |
| 15. | Draft report of first subsurface BangBox test                           | 05/97 |

**10. Transition Plan:**

The PI will distribute reports containing results of testing PEP items and manufacturing wastes to agencies having responsibility for obtaining subpart X permits and other interested government agencies. These reports will be submitted to the Defense Technical Information Center where authorized members of the private sector may obtain them. The risk assessment guidance document will be distributed to USEPA and state regulatory agencies, and to DoD organizations involved in the permitting process.

**11. Funding: \$(K)**

	FY94	FY95	FY96	FY97	Total
SERDP	1128	3000	655	2345	8613

**12. Performers:**

This project is a collaborative effort. Government agencies involved in this project include the Department of Defense (DPG, Army Environmental Center plus other military departments as munitions are identified for testing), USEPA Atmospheric Research and Exposure Assessment Laboratory, NOAA, DOE (Sandia National Laboratories), and the private sector (Oregon Graduate Institute of Science and Technology, Alpine West Laboratories, Radian Corporation, ECO LC, Halliburton N.S., and others as TAP requirements expand). This project is part of the SERDP National Program for Open Burning/Open Detonation, for which the U.S. Army is the lead agency.

**13. Principal Investigator:**

MacDonald Johnson  
STEDP-MT-TM-MO  
U.S. Army Dugway Proving Ground  
Dugway, UT 84022-5000  
PHONE: (801) 831-5682  
FAX: (801) 831-5263

**14. Keywords:**

OB/OD, BangBox, Disposal, RCRA, Munition

## SERDP FY95 PROJECT

1. **SERDP Thrust Areas:** Compliance
2. **Title:** Measuring and Modeling for OB/OD Permitting
3. **Agency:** U.S. Environmental Protection Agency (USEPA)
4. **Laboratory:** Atmospheric Research and Exposure Assessment Laboratory (AREAL)
5. **Project ID:** #251
6. **Problem Statement:**

The Department of Defense (DoD), Department of Energy (DOE), defense contractors, and commercial firms all face the problem of disposing of unwanted conventional energetic materials. All have traditionally relied upon open burning/open detonation (OB/OD) techniques which, until recently, have kept a potentially dangerous storage situation manageable. In recent years, all have appreciably reduced their OB/OD disposal operations due to provisions of subpart X of Part 264 of the Resource Conservation Recovery Act which requires OB/OD permits which are issued by USEPA regional headquarters.

Permits have not been issued because none of the affected organizations has all the data required to prepare, review, and approve subpart X permits. There are no credible data available concerning the effect that common environmental variables have on the identities and the quantities of the pollutants released from OB/OD activities. Second, none of the atmospheric dispersion models available have been evaluated to determine if they accurately predict or can be modified to accurately predict how the pollutants released by OB/OD activities will disperse in the atmosphere. Third, there are no reliable chemical dispersion models that predict how the most toxic and long-lived pollutants released will distribute between the air, soil, and water at the site. Fourth, most of the air and soil pollutant measurement systems needed to identify, quantify, and track the pollutants released by OB/OD activities have not been validated. Fifth, there is confusion concerning how to assess the risk that the pollutants emitted from OB/OD activities pose to humans.

The lack of progress in issuing permits has caused the general public to regard OB/OD operations as dangerous to both their health and to the environment. This is unfortunate because recent DoD, DOE, and EPA studies strongly indicate that most munitions, propellants, and their manufacturing wastes can likely be destroyed in an environmentally safe manner through OB/OD procedures. Tests conducted at the U.S. Army Dugway Proving Ground (DPG) and at Sandia National Laboratory (SNL) show that small scale detonations and burns conducted in environmental chambers (BangBoxes) can provide pollutant emission factors representative of full-scale OB/OD operations. These tests have identified candidate air and soil pollutant measurement methods which could be useful for monitoring for the pollutants released at OB/OD disposal sites. On the meteorology side, a new generation of ground-based instruments makes possible the measurement of atmospheric conditions up to

2000 m above ground level. Also, SERDP-funded studies being conducted by NOAA staff at the USEPA facilities in Research Triangle Park are providing the fundamental understanding of how plumes diffuse into the convective boundary layer under different meteorological conditions. Since the plumes released by OB/OD operations can reach this boundary layer, an understanding of how the plume penetrates (diffuses) through this layer is critical to developing reliable atmospheric dispersion models for OB/OD operations.

This project enhances currently-funded DOE, EPA, and NOAA efforts in pollution monitoring and atmospheric dispersion modeling and identifies new efforts in technology demonstration and technology transfer.

## **7. Project Description:**

Due to the close relationship of this project to an OB/OD emissions data acquisition proposal submitted concurrently with this proposal, key members of this project will participate in meetings of the companion project's technical advisory panel. This will facilitate coordination between agencies and departments, and ensure that data acquisition and models are compatible.

This project has four objectives:

The first objective is to develop and validate upper-air meteorological measurement systems. Because the plumes released from OB/OD activities rise quickly, it is important to be able to accurately predict how the pollutants will disperse above ground level. A new generation of instruments will be used to measure, from the ground, continuous profiles of wind, temperature, and some turbulence variables to heights ranging from 100 to 3000 m. An array of these instruments, contained in a mobile platform, will be used in a series of night-time measurements made at about six diverse, non-ideal sites. These should include hillside and hilltop sites in both rolling and quite hilly terrains, shallow and deep valley sites, and sites on inclined tablelands. The mobile instrumentation package will assure uniform quality and completeness of measurements at each site. Instrumentation will include a mini-sodar, radio acoustic sounder, a mini-lidar, a tether sonde with temperature, humidity, wind and turbulence indicators, a portable meteorological mast with several levels of sonic anemometers, microbarographs, and net radiation measurements. These studies will improve our overall understanding of turbulent mixing and provide our first comprehensive understanding of the depth of turbulent mixing at night. They will provide information critical to developing accurate dispersion models for OB/OD permit applications and for identifying the best meteorological situations for conducting such activities.

The second objective is to develop a dispersion model. The dispersion model development part of this project will build on work being done on INPUFF models for EPA by NOAA. An efficient modular puff trajectory model will be developed and validated. The range of applicability will be from tens of meters to several hundred kilometers. Other types of dispersion models may also be examined as the result of the convective boundary layer studies and the upper air measure measurement studies described above.



The third objective is to develop and validate quality assurance and quality control materials and the procedures to use them. These materials/procedures will be needed to document the quality and completeness of the OB/OD test results from the BangBox studies and from open-air OB/OD operations. These materials/procedures will also be needed to quality assure the monitoring data collected during clean-up and closure activities at OB/OD sites. The primary focus will be to develop materials/procedures for semivolatile, volatile organic, and toxic metals.

The fourth objective is to transfer technology. Transferring the technology developed to the private sector for commercialization worldwide is designed into the project since contractors will conduct most of the technical work and experts from the private sector will be on the advisory panel. The formation of cooperative agreements with private firms as authorized by the Technology Transfer Act will also facilitate the transfer of technology developed during this project.

This project directly supports the DoD objective of avoiding environmental injury during conduct of military-related operations.

This is a low-risk project and no delays or technical impediments are anticipated.

### **8. Expected Payoff:**

This project will allow applicants and Federal and state regulators to evaluate the emissions data obtained to support the permitting process for OB/OD permits under provisions of subpart X, RCRA. It complements development efforts to obtain emissions data from a broad spectrum of conventional energetic materials requiring disposal.

### **9. Milestones:**

The following milestone schedule anticipates receipt of initial funds in June 1994 and is compatible with milestones of the OB/OD emissions data acquisition project.

#### Upper Air Measurement System

1.	Work initiated	08/94
2.	Site selection completed	01/95
3.	Mobile instrument package available	06/95
4.	Data from first field test available for use in model development	10/95
5.	Data from second field site available	03/96
6.	SOPs for meteorological equipment available	08/96
7.	Data from all (6) field tests available	11/96

#### Dispersion Model

1.	Work initiated on INPUFF model	07/94
2.	Preliminary users' guide available	07/95
3.	INPUFF model revised based on user comments and meteorological study results	06/96

4. Model refined, new models validated as warranted by test data through FY97 09/97

QA/QC Materials and Procedures

1. Work initiated 11/94
2. QA materials for seven SVOCs available 04/95
3. QA materials for seven additional SVOCs available 10/95
4. Methods and guidance updated through FY97 09/97

Technology Transfer

1. First FTTA agreements in place 01/96
2. Commercialization of technology continues through FY97 09/97

**10. Transition Plan:**

The PI will distribute reports and model information to agencies having responsibility for requesting or approving subpart X permits and to other interested government agencies. All publications generated by this project will be submitted to the Defense Technical Information Center where they can be obtained by authorized members of the private sector.

**11. Funding: \$(K)**

	FY94	FY95	FY96	FY97	Total
SERDP	350	550	575	250	1725

**12. Performers:**

This is a collaborative effort. Government agencies involved in this project include the Department of Defense (DPG, Army Environmental Center), USEPA (Atmospheric Research and Exposure Assessment Laboratory, NOAA, DOE (SNL), and the private sector (Halliburton N.S.). Mr Johnson, as the principal investigator (PI) for the R1 SERDP effort at DPG, will take the lead in overall project direction and management. This project is part of the SERDP National Program for Open Burning/Open Detonation, for which the U.S. Army is the lead agency.

**13. Principal Investigators:**

QA/QC:  
 William Mitchell  
 U.S. Environmental Protection Agency, MD77B  
 Research Triangle Park, NC 27711  
 PHONE: (919) 541-2769  
 FAX: (919) 541-7953

Dispersion modeling:  
William Petersen  
National Oceanographic and Atmospheric Administration  
c/o USEPA, MD 80  
Research Triangle Park, NC 27711  
PHONE: (919) 541-1376  
FAX: (919) 541-1379

**14. Keywords:**

OB/OD, Munitions, Pollution, Modeling, Dispersion

## SERDP FY95 PROJECT

1. **SERDP Thrust Area:** Compliance
2. **Title:** Encapsulation of Hazardous Ions in Smectite Clays
3. **Agency:** U.S. Department of Energy
4. **Laboratory:** Argonne National Laboratory (ANL)
5. **Project ID:** #315

### 6. **Problem Statement:**

The basic initiative under the SERDP Compliance thrust area seeks to develop new and novel materials for the control, treatment, and long term storage of hazardous metal ions, particularly those of toxic heavy metals and radionuclides. This proposal seeks continued funding for the completion of a 3 year program whose first year was supported by the SERDP in FY 1993.

The approach to be used is based on fundamental work on chemically stable organic monolayers at Harvard University and the Weizmann Institute. It involves the long-term encapsulation of ions in a new class of hydrophobic smectite clays, whose properties can be tailored to the specific chemical requirements of a particular hazardous species. Hazardous cations are initially introduced into the matrix of clay minerals, after which the system is encapsulated with hydrophobic agents. Other variations on this theme will also be pursued, including the direct synthesis of hydrophobic clays around a hazardous cation.

Recent research in several laboratories has focused on the use of clays for environmental remediation. Current investigations have sought to develop ways to utilize these materials for the solution of problems in both organic and inorganic environmental contamination. This proposal seeks to combine the results of previous studies with our own expertise in surface modification of inorganic and polymeric substrates to create a new class of materials for use in environmental restoration.

Smectite clays consist of sheets of aluminosilicates which are separated by an interlayer that contains both inorganic cations, such as calcium and potassium, and water molecules. The cations in native clays can be easily replaced by other cations through aqueous ion-exchange processes. Therefore native clays can be readily used as filters for the removal of hazardous heavy metals and radionuclides.

For the remediation of organic materials, clays are traditionally rendered hydrophobic by treatment with quaternary ammonium cations that contain one long chain hydrocarbon tail. The resulting materials have a greater affinity for non-polar and modestly polar organic compounds. This method is, however, inappropriate for hydrophobic encapsulation of hazardous ions. Use of this process after a hazardous metal ion has been exchanged into the

interlayer will only result in the release of the harmful species back into the environment. Clays which simultaneously bind hazardous cations and are hydrophobic are, however, of great interest. Such clays should exhibit an increased resistance to leaching of the hazardous ions out of the interlayer by water. They would therefore require less stringent storage conditions once a hazardous material had been placed within them. Alternative methods, ones which do not rely on ion-exchange, are required to create these desired hydrophobic clays. The development of these methods, and the characterization and testing of the materials which result from them, is the subject of this proposal.

## 7. Project Description:

The research described in this proposal seeks to replace the traditional cationic methods for creating hydrophobic clays with alternative general approaches which do not require the use of charged hydrophobic species. Specifically, we shall covalently bind alkylsilane groups ( $\text{CH}_3(\text{CH}_2)_n\text{Si}-$ ) to the surface of the clay. This approach therefore will satisfy two simultaneous objectives. First, it will maximize the capacity of the clay for the cation of interest. Since clays are electrically neutral, there is a maximum limit to the number of cations which can reside in the interlayer. By covalently binding the hydrophobic species to the surface, all of the cationic charge within the clay's interlayer is reserved for the cation whose encapsulation is desired. Consequently, the volume required by the storage medium for a given amount of hazardous waste will be minimized. Second, the use of a covalent bond to attach the hydrophobic medium to the clay eliminates the possibility that the modified clay can revert by ionic exchange back to the hydrophilic state. The covalent link between an alkyl chain and the surface of a clay, which is the basis of this proposal, is much more stable to the environment than the coulombic interaction present for the alternative quaternary ammonium species.

The proposed method for creating a hydrophobic clay surface is derived from the work of S.R. Wasserman and G.M. Whitesides on monolayers of alkylsiloxanes. Like quaternary ammonium ions, the silanes change a hydrophilic surface into a hydrophobic one. Unlike the ammonium salts, however, the silanes do not carry a positive charge. They therefore can coexist within a clay along with hazardous cations. Both trichloro- ( $\text{RSiCl}_3$ ) and trialkoxy- ( $\text{RSi}(\text{OR}')_3$ ) silanes form covalent bonds to the surface by reaction with surface hydroxyl groups. The resultant silicon-oxygen bonds are stable to strong acids, water, and organic solvents. Although this bond is susceptible to strong base, it resists attack under common environmental conditions. Previous work has demonstrated that dense monolayers containing from 2 to 18 atoms per alkyl chain form on surfaces of amorphous silicon oxide. Since clay minerals also possess surface -OH groups, the techniques developed for the creation of monolayers on silica should also be applicable to these aluminosilicates.

The protective layer on the clay will be polymeric. In addition to their reaction with surface -OH groups, the silanes react with surface water molecules, thereby forming silicon-oxygen bonds between adjacent alkylsilanes. The network of siloxane (-Si-O-Si-) bonds which is formed by this process constitutes a stable cross-linked structure that is held in place by bonds to the substrate and to adjacent silanes. This structure is of high molecular density. Well-formed monolayers of alkylsilanes prevent the penetration of even organic species into

their structure. Therefore, this type of monolayer is expected to be an effective barrier to the entry of both polar and non-polar solvents into the interlayer of clay that contains a hazardous cation.

The presence of the cations in the interlayer of a clay represents a possible complication for the formation of the alkylsilane structures. The characterization of the cation in the hydrophobic medium will therefore be a major part of this project. In most cases, the positively charged species in a clay's interlayer are surrounded by solvating water molecules. During the encapsulation process, some of these water molecules may also react with the alkylsilanes. Such a process would further entrap the cation within the hydrophobic structure.

The nature of this project requires a multidisciplinary approach to the creation, characterization, and testing of this new class of clays. The initial focus of the research will be on the determination of the best experimental conditions for the creation of the hydrophobic clays. One crucial question to be answered is whether solution or vapor phase depositions for the silanes are better for this problem. The traditional techniques for the creation of silane monolayers have relied on the use of solution of the silane in organic solvents. However, using gaseous silanes may enable the silane to penetrate further into the interlayer of the clay and form a more extended network of siloxanes. The greater size of the hydrophobic barrier which results from vapor phase depositions may result in a structure which is even more stable to the environment.

Once the clays have been modified, they will be evaluated to determine how successfully the newly created barriers prevent the migration of the hazardous cations out of the interlayer. For these studies environmental stresses, both chemical and physical, will be simulated. Several analytical techniques, including X-ray powder diffraction and atomic absorption, IR, and UV-visible spectroscopies, will be used to characterize the stability of the hydrophobic layer and the changes which the lattice and interlayer of the clay undergo during the simulations. The results of these measurements will characterize how the clays withstand various stresses and how much material leaves the clay and enters surrounding fluids.

Although it is relatively easy to determine what proportion of the cations leach out of the clay, it is more difficult to quantify the penetration of fluids into the interlayer of a hydrophobic clay. Recent work in this laboratory has demonstrated that it is possible to detect by X-ray absorption spectroscopy (XAS) the interaction between transition metal ions and protic solvents as the ion dissolves in the interior of a clay. This new variation on an established technique will be used to evaluate how effectively the modified clays prevent the entrance of fluid into the clay. These experiments will provide complementary information to that gleaned from studies of the composition of the fluids.

Since much of the clay chemistry outlined in this proposal does not depend on the presence of radioactive materials in the clay lattice, most of the studies will use native, ion-exchanged, and silylated clays which contain representative non-radioactive elements, such as the lanthanides. After most of the technical hurdles have been overcome, the final experiments will apply the best modification protocol to more hazardous species.

## 8. Expected Payoff:

The new and novel clay materials created during this study constitute the development of a new control technology for the treatment and disposal of hazardous wastes. They offer the possibility of improved long term storage for metallic cations whose re-entrance into the environment is undesirable. When native clays are used to filter waste species out of a medium, the resulting immobilized species still require stringent storage. Exposure of such clays to polar solvents which contain other ions can result in the re-exchange of the hazardous waste back into the fluid. Rendering these clays hydrophobic without resorting to charged surfactants will result in materials that are much more resistant to typical environmental stresses. Therefore less rigorous isolation methods will be required for the long-term storage of these hazardous materials.

The modified clays will have a much different affinity for water than unmodified clays and other minerals. This difference should provide an effective means for separation of the hydrophobic materials from native minerals. Should the hydrophobic clays accidentally become remixed with other minerals, re-separation should be simple because of the drastically different flotation properties of the former.

The raw materials for this project, clays and organosilanes, are inexpensive. Clays are a major constituent of the earth, have many industrial uses, and have been proposed for environmental systems where cost minimization is an important consideration. Organosilanes have been used for over three decades for the creation of reverse-phased chromatographic column packings. They are also extremely inexpensive and readily available. Thus novel chemical concepts will be coupled in a rational way to provide a practical solution to a significant environmental problem.

## 9. Milestones:

1. Preparation of hydrophobic smectite clays through the use of alkyltrichlorosilanes. 3/94
2. Preparation of hydrophilic and hydrophobic smectite clays with transition metals in the interlayer. 7/94
3. Characterization of the native and modified clays using powder diffraction, BET absorption measurements, X-ray photoelectron spectroscopy, flotation characteristics, and other physical techniques as appropriate. 9/94
4. Synthesis of new organosilanes as required by the results of Tasks 1, 3, and 4. 9/94
5. Characterization of cations in hydrophobic clays by X-ray Absorption and Anomalous Small Angle X-ray Scattering. 9/95
6. Evaluation of efficacy of hydrophobic clays in resisting leaching 9/96
7. Evaluate direct synthesis of clays about hazardous cations. 9/96

## 10. Transition Plan:

The technology developed under this proposal will be made available to potential users within the Department of Defense and Energy upon successful completion of the study. The creation of hydrophobic clays in bulk will require new, specialized equipment which may be developed under a CRADA agreement. One current supplier of industrial clays, the American Colloid Company of Arlington Heights, IL, has agreed to consult on the creation and use of hydrophobic clays. We shall collaborate with this and other appropriate industrial organizations as the scientific and technical breakthroughs develop.

## 11. Funding: \$(K)

	FY94	FY95	FY96	Total
SERDP	380	200	200	780

## 12. Performers:

The lead organization for this project is the Chemistry Division of Argonne National Laboratory. The principal investigator is a member of the Chemistry Division at ANL. During the testing phase of this program, synchrotron experiments will be performed at the National Synchrotron Light Source and/or the Stanford Synchrotron Radiation Laboratory. The Analytical Chemistry Laboratory of ANL will provide basic analytical services. The analysis of the surface constitution of the modified clays by X-ray Photoelectron Spectroscopy will be performed by an external vendor on a cost for service basis. In future stages of this investigation the personnel and the facilities of the Chemical Separation Science and Heavy Elements Coordination Chemistry groups of the Argonne Chemistry Division will help in the preparation and characterization of clays with tracers and other radioactive constituents.

## 13. Principal Investigator:

Stephen R. Wasserman  
Chemistry Division, Building 200  
Argonne National Laboratory  
9700 S. Cass Avenue  
Argonne, IL 60439  
PHONE: (708) 252-3527  
FAX: (708) 252-9288  
E-MAIL: [wasserman@anlchm.chm.anl.gov](mailto:wasserman@anlchm.chm.anl.gov)

## 14. Keywords:

Encapsulation, Clays, Silanes, Monolayers, Multilayers, Cations



## SERDP FY95 PROJECT

1. **SERDP Thrust Area:** Compliance
2. **Title:** Kinetics of Supercritical Water Oxidation
3. **Agency:** U.S. Department of Energy
4. **Laboratory:** Sandia National Laboratories (SNL)
5. **Project ID:** #364
6. **Problem Statement:**

Supercritical water oxidation (SCWO) is an emerging technology under development by government laboratories, universities, and private industry for the treatment of aqueous wastes. However, the current understanding of the rates and mechanisms of reactions in supercritical water is limited to a handful of empirical mechanisms for very simple chemicals. These mechanisms are of limited use in the formulation of predictive models of SCWO which will be needed in the future for the design and operation of large-scale waste processing equipment. It is also suited for treatment of waste materials best handled in water for environmental or safety reasons such as obsolete munitions, rocket motors, and chemical warfare agents. The process is performed at temperatures and pressures above the critical point of water (typically 450-650°C and 240 bar), and is applicable to waste streams containing 0-20 percent organics in water. The effluent from waste processing can be evaluated for compliance with applicable discharge regulations before release, ensuring protection of the environment.

An early patent for the process included data showing 99.99% destruction of many normal and halogenated hydrocarbons including tetrachloroethylene, DDT, and PCB. Since then, the number of organic and inorganic chemicals, as well as complex mixtures, tested by SCWO has grown considerably. However, the application of SCWO to most DoD and DOE waste treatment needs requires that the technology be advanced beyond its current level of development. These improvements will not be possible without better predictive models for the time, temperature, density, and concentration dependence of the oxidation process.

The current understanding of the rates and mechanisms of reactions in supercritical water is limited to a handful of empirical mechanisms for very simple chemicals. These mechanisms are of limited use in the formulation of a predictive model of SCWO. To be generally applicable and valuable as a design tool, models must be based on elementary reaction steps or at least a detailed quantitative mechanistic description incorporating all the key fundamental reactions. Valuable progress is being made by several research teams but agreement between elementary models and experiment is only qualitative in most cases. In addition, there is a wide variation in experimental results and model predictions from different research efforts as a function of feed concentration, which emphasizes the need for closer collaboration among researchers.

A thorough understanding of operative chemical kinetics at the level of basic science is required to underpin applications of supercritical water oxidation technology. We propose a basic research project that investigates the currently uncertain chemical kinetics of SCWO. This project is a continuation and expansion of SERDP projects funded FY92 and FY93 titled "Kinetic Mechanisms for Supercritical Water Oxidations" which established experimental capability and made initial measurements on fuel species and oxidation products in optically accessible supercritical water oxidation reactors. This project is improving our understanding of SCWO chemistry by directly measuring the time, temperature, and density dependencies of key reacting chemical species and improving the theoretical basis of reaction mechanistic models. This project extends the scope of the mechanistic models beyond the oxidation of simple single carbon organic systems to larger aromatic species and organic molecules containing nitrogen or chlorine.

## **7. Project Description:**

The goal of this project is to produce predictive chemical reaction models to be used to aid the design and operation of large scale SCWO equipment. These engineering design models implicitly center on an accurate description of the chemistry of the key oxidation-resistant species. The insight and understanding needed to develop these models will be generated by coupling an extensive experimental program to a parallel theoretical effort producing quantitative mechanistic descriptions of the oxidation processes. These quantitative mechanisms will then be formalized into predictive computer models.

Actual wastes generated at DoD and DOE facilities are complicated formulations of large organic molecules and inorganic compounds such as paints, dyes, bonded explosives, solvents, and oils. However, work at Sandia and elsewhere has indicated that even at mild SCWO operating conditions, feeds of these complicated materials very rapidly convert to mixtures of simple chemicals. These chemicals are oxidation-resistant molecules such as methane and methanol, simple amines and nitrates, and phenol and other small aromatic ring species. Chlorinated systems represent an exceptionally important waste treatment problem for SCWO where hydrolysis and oxidation reactions are closely coupled. The oxidation rates of these molecules are the limiting processes for the complete destruction of complex feed materials.

This research project has several stages defined by the class of molecules to be studied and how these classes fit into a progression from simpler to more difficult chemical systems to model. Following methane and methanol, for which accurate mechanisms should be available from our current studies by late FY94, experiments and model development will be directed at the first two important classes of molecules: simple aromatics characterized by benzene, phenol, and benzoic acid, and chlorinated organics such as methylene chloride and trichloroethylene. The focus during FY95 and FY96 will be to generate accurate predictive oxidation models for engineering design use. Amines and nitrates, an important class of materials that relate to the treatment of energetic munitions and shipboard wastes such as black water, will be addressed in FY96-FY97 after the models for carbon/hydrogen/oxygen systems are in place.

This work continues the experimental approach from FY93-94 SERDP, extends measurements on key oxidant species, and expands the variety of experimental methods, primarily optical in nature, that can be used to study reactions at SCWO conditions. In this project year we will begin to extend the elementary models developed for methane and methanol to more complicated species and continue to build the experimental data base. We will continue experiments on higher alcohols and chlorinated species, including propanols, phenol, anisole, and methylene chloride. The high density model for methane will be developed to properly account for the pressure dependence the FY94 experiments have revealed.

We will be directly collaborating with Princeton University on the chemistry of aromatic compounds and with MIT on the chlorinated and nitrogen containing species. We will work closely with Dr. K.E. Brezinsky and members of his research group at Princeton to develop the mechanistic description of phenol and toluene oxidation under SCWO conditions. We will collaborate with Prof. J.W. Tester and co-workers at MIT on experiments and model development for halogenated and nitrogen-containing systems.

The experimental portion of the research entails determining the concentration of reactants, stable intermediates, products, and in some cases radical intermediates associated with the oxidation of simple chemical in supercritical water. The time-temperature-concentration profiles that are measured provide the foundation for the mechanistic description of the many stages that even simple organic molecules pass through to completion of oxidation. Measurements of species concentration profiles of key intermediates are critical to developing chemical mechanisms. The experimental profiles of reactants and products provide test and verification of the quantitative capabilities of the predictive models.

Our work to date has proven spontaneous Raman spectroscopy to be a very useful method for measuring concentrations of a variety of chemical species in supercritical water. We have recorded strong signals from  $\text{CH}_4$ ,  $\text{CH}_3\text{OH}$ ,  $\text{CO}_2$ ,  $\text{CO}$ ,  $\text{H}_2$ ,  $\text{O}_2$ , and  $\text{N}_2$  at concentrations below 0.01 mole/liter. Data collected during FY93 on the oxidation of methane have contributed to the understanding of the temperature and concentration dependence of methane oxidation under SCWO conditions. This work demonstrates the power of optical methods for collecting the detailed experimental data that are necessary to completely describe chemical reactivity over wide range of pressure, temperature, and reactant feed concentrations. Measurement of trace species in FY95-FY97 will require application of more sensitive optical methods that will be adapted and applied as a part of this project. The primary experimental difficulty associated with this project is the level of detection sensitivity that will be achievable for reactive intermediates and products of partial oxidation. Consequently, the optical methods will be complemented by the analytical technique of direct sampling and off-line analysis.

The quantitative mechanism and model development will proceed in parallel with the experiments. Initially, predictions from existing elementary reaction mechanisms for low-density, high temperature processes will be compared to results from SCWO experiments. These comparisons will guide the design of new experiments. Subsequently, the results of the experiments will be used to improve the predictive performance of the models. We anticipate that additional steps involving peroxy chemistry will need to be added, as well as high-density corrections to unimolecular rate parameters.

We emphasize that the goal of this project is to produce predictive models for the oxidation of key species in supercritical water and not simply to illustrate the effectiveness of SCWO. The intention is that these models will guide the design of waste treatment equipment for specific DoD and DOE needs and that they will provide the necessary information to overcome critical design issues regarding equipment size, cost, or feed characteristics.

## 8. Expected Payoff:

SCWO is an emerging technology under development at several laboratories and in industry for the treatment of hazardous aqueous waste. Operation at densities two orders of magnitude greater than atmospheric gaseous combustion provides high reaction rates at moderate temperatures. The literature contains results of many studies of SCWO measuring destruction efficiencies for a variety of waste chemicals.

Some of this data can be used to generate empirical global kinetic rate expressions. The in situ measurements used in this project, particularly on unstable intermediates, can lead to valuable information for predictive model development. Data obtained in situ eliminates uncertainties associated with sampling and subsequent off-line analytical techniques. A better understanding of the fundamental reaction rates and the kinetic models this project develops will lead to models for reactor design, predictions of destruction efficiency, and methods for commercial system optimization.

## 9. Milestones:

- |  |       |
|--|-------|
| 1. Complete experimental studies and model development for methane and methanol at industrial process concentrations | 06/95 |
| 2. Identify hydrolysis role in overall role oxidation mechanism for chlorinated organics                             | 10/95 |
| 3. Complete phenol and higher aromatic experiments   | 03/96 |
| 4. Complete mechanism for C,H,O organic oxidation  | 03/96 |
| 5. Complete chlorinated organic oxidation experiments  | 03/96 |
| 6. Initiate nitrogen-containing species experiments  | 01/96 |
| 7. Complete predictive model for C,H,O organic oxidation   | 06/96 |
| 8. Complete chlorinated species oxidation predictive model   | 12/96 |
| 9. Complete nitrogen dioxide kinetics experiments, model nitrogen and nitrous oxide product distribution             | 03/96 |
| 10. Complete amine kinetic experiments, model  | 10/98 |

## 10. Transition Plan:

Sandia National Laboratories is leading the development of technology for the U.S. Army ARDEC effort in SCWO. A contract is currently being negotiated for the fabrication of an approximately 100 ton/year unit. Results generated from this SERDP project will feed directly and immediately into improvements and modifications of production prototype equipment and larger scale systems designed to treat special munitions waste, pyrotechnics, and other military chemicals. The SCWO research team at SNL works in an environment of

open information exchange with research and technology development efforts in universities, industry, and government labs sponsored by the Army Research Office, ARPA, the Naval Civil Engineering Laboratory, and the U.S. Air Force. In addition SNL directly participates in technology development projects in SCWO with the U.S. Army ARDEC, NSWC, and DOE EM-50 Office of Technology Development coordinated through INEL. S.F. Rice serves on the Technical Support Group for the DOE EM-50 project.

**11. Funding: \$(K)**

	FY94	FY95	FY96	FY97	FY98	Total
SERDP	740	300	460	500	200	2200

**12. Performers:**

The lead organization conducting this research project is Sandia National Laboratories, Combustion Research Department, Org. 8361. Mechanistic development for the aromatic molecules to be studied with FY94 and FY95 funding will be conducted in collaboration with Dr. K.E. Brezinsky and co-workers at Princeton University. Experiments and model development for simple chlorinated species will be conducted in collaboration with Prof. J.W. Tester and co-workers at MIT. In addition to mechanistic theoretical contributions and other collaborative research with Prof. Tester and Dr. Brezinsky, this project funds one research associate at MIT, as well as several extended visits to Sandia's Combustion Research Facility by MIT and Princeton researchers to conduct experimental work.

**13. Principal Investigator:**

Dr. Steven F. Rice  
Sandia National Laboratories  
P.O. Box 969  
MS 9052  
Livermore, CA 94551-0969

Street Address:  
MS-9052  
70111 East Ave  
Livermore, CA 94550  
PHONE: (510) 294-1353  
FAX: (510) 294-1004  
E-MAIL: [steve\\_rice@sandia.gov](mailto:steve_rice@sandia.gov)

**14. Keywords:**

Oxidation, Raman spectroscopy, Kinetics, Mechanisms, Supercritical Fluids, Research Modeling

## SERDP FY95 PROJECT

1. **SERDP Thrust Area:** Compliance
2. **Title:** Waste Forms Based on Separations Media
3. **Agency:** U.S. Department of Energy
4. **Laboratory:** Pacific Northwest Laboratory (PNL)
5. **Project ID:** #360

### 6. **Problem Statement:**

A major mission of the DOE complex in general and the Hanford site in particular is the safe disposal of radioactive and mixed wastes. Disposal of such wastes from underground storage tanks will involve partitioning the waste into high-level and low-level components and converting those components into stable solids suitable for long-term storage.

DOE is currently planning to dispose of high-level wastes by converting the most hazardous materials into borosilicate glass. However, existing wastes such as tank sludge contain a range of species including chromates, phosphates, and aluminates which complicate production of borosilicate glass. Given the volume of sludge present (millions of gallons) and the high levels of dilution required to incorporate sludge into glass, it is estimated that direct conversion of existing tank wastes could generate up to 40,000 canisters of high-level waste glass. Not only would such volumes of glass greatly exceed the storage capacity of all known waste repositories, the costs of fabricating the glass alone (\$1M/canister) could exceed \$50 billion.

In order to minimize both waste volumes and costs, chemical separation procedures are under evaluation to concentrate most of the hazardous species into a small volume of high-level waste, allowing for disposal of the bulk of tank contents as low-level waste materials. An important class of chemical separations involves extracting hazardous species (or species which interfere with glass fabrication) using ion exchange procedures. Unfortunately, the separations process and the ultimate waste disposal process are often treated as separate entities. Commercial ion exchange materials are not tailor-made for hazardous waste disposal, and final waste forms are not being designed based on potential feed-streams generated from different separations scenarios. The focus of this proposal is to integrate separations and high-level waste form processing to optimize waste treatment technologies.

The active element in ion exchange is the sorbent material used to pack the ion exchange column. The sorbent material will ultimately be loaded with hazardous species such as radionuclides. Once the ion exchange column is loaded, two options exist to produce high-level wastes:

(1) The loaded ion exchanger could be used directly as the feed material for producing the final loaded high-level waste. Inorganic ion exchangers, in particular, can be (a) melted with other oxides to form a glass or (b) calcined and sintered to form stable ceramics.

(2) Hazardous species could be eluted from the exchange column and converted into a pure product such as a metal salt. The pure compound would then be converted into a glass or ceramic waste.

Option 1 has the advantage that it minimizes the number of processing steps between ion exchange and final waste disposal. However, Option 1 requires that the ion exchanger itself be compatible with the final glass or ceramic waste form. Option 2 requires more processing, but it relaxes the requirement that the exchanger be compatible with the final waste solid. Option 2 might also generate less high-level waste. Both options need to be evaluated to develop optimum processing schemes for treating hazardous tank wastes.

Separations and processing of waste at DOE sites has resulted in a variety of high level waste streams. In the past, separations have produced waste salts such as  $\text{SrF}_2$  and  $\text{CsCl}$ , and currently separations schemes are being considered for removal of Cs, Sr, I, Pu, and Tc from liquid waste streams at several DOE sites. In order to dispose of these various waste streams, an efficient process is needed that results in a stable, durable waste form that is resistant to attack by aqueous solutions. At present, the baseline conversion process involves dissolution of the various waste streams into borosilicate glass. However, many of the candidate separations materials, and the products separations processes, produce a waste streams which is either insoluble or incompatible with the current borosilicate glass formulations. In addition, the extent of dilution required to incorporate many of these wastes (such as phosphates or  $\text{TiO}_2$ ) into borosilicate glass results in prohibitive volumes of expensive borosilicate waste glass. Other options need to be considered for conversion of these problematic waste streams into a stable waste form. The primary objective of this task is to evaluate the feasibility of alternative waste conversion schemes for problem feeds generated as a result of separations. This research will impact needs in both the basic and applied research categories.

## **7. Project Description:**

We propose to examine ion exchangers with potential for removing hazardous cationic and anionic species from tank wastes in the context of conversion into final waste forms. Existing candidate materials for  $\text{Cs}^+$  extraction include: the commercial zeolite IE-96, silicotitanates developed by Bob Dosch at Sandia National Labs, layered zirconium phosphates developed by Professor Abe Clearfield at Texas A&M (and by Allied Signal Corp.), and organic formaldehyde-resorcinol resins developed by Jane Bibler at Savannah River. Inorganic ion exchangers such as layered double hydroxides are under development by the Pacific Northwest Laboratory for removal of anionic species such as the pertechnetate ion. The overall program includes two components:

(1) Synthesis, and/or evaluation of exchangers thought to be effective at removal of species such as  $\text{Cs}^+$ ,  $\text{Sr}^{2+}$ , and  $\text{TcO}_4^-$ . Exchangers will be evaluated for chemical stability, selectivity and ion exchange capacity, and compatibility with existing ion exchange processes. This evaluation will help determine the composition of the loaded exchanger and whether the exchanger is better suited to direct conversion into solid waste or elution to produce a more tractable feed.

(2) Evaluation and development of methods for converting potential feed-stocks produced via ion exchange into solid waste forms. A baseline activity would include determining whether the potential feed is compatible with borosilicate waste glass. However, alternate waste form options will also be explored.

A preliminary analysis of existing  $\text{Cs}^+$  exchangers illustrates some of the trade-offs associated with selecting materials to be optimized for both ion exchange and waste disposal processes. The zeolite IE-96 can be obtained as pellets suitable for ion exchange applications. IE-96 is also soluble in borosilicate glass. Unfortunately, IE-96 has a low selectivity for  $\text{Cs}^+$ , resulting in low  $\text{Cs}^+$  loadings and high volumes of exchanged waste. Silicotitanates and zirconium phosphates have excellent selectivities, minimizing the total volume of exchanged high-level waste. Unfortunately, neither material can be used in ion exchange columns since both consist of nanometer-scale particles which can both clog and escape from columns. In addition, neither material is soluble in borosilicate glass. The organic resin has high  $\text{Cs}^+$  selectivity. However, the material is susceptible to radiation damage, requiring  $\text{Cs}^+$  elution and conversion before excess damage to the column occurs. As the above examples illustrate, most known exchangers have their own unique strengths and weaknesses for solving tank waste problems. The current program is aimed at identifying and mitigating the weaknesses of each of the above materials to provide the optimum solution to the  $\text{Cs}^+$  separation problem.

Work performed in the FY93 SERDP program on zirconium phosphate exchangers illustrates the approach we are following to explore processing and waste form options. While zirconium phosphate shows promise as a  $\text{Cs}^+$  exchanger, the loaded exchanger exhibits a low solubility in normal borosilicate glass due to its high phosphate content. With our SERDP project, we established a collaboration with Professor Delbert Day at the University of Missouri-Rolla to see whether he could develop an alternate host lattice for disposing of zirconium phosphate exchangers. On the SERDP project, Professor Day developed a family of iron phosphate glasses that can be loaded with zirconium phosphate. He was able to show that such a glass can tolerate  $\text{Cs}^+$  loadings at least as high as 30 wt% (compared with 5 wt% for borosilicate glass) and still exhibit a chemical durability to attack by aqueous solutions exceeding that of both borosilicate waste glass and window glass. The new phosphate glass has potential application for treating eluted cesium salts as well as zirconium phosphate exchangers. In fact, the glasses are under evaluation as a means of converting  $\text{CsCl}$  capsules (representing 1/3 of the total radioactive inventory on the Hanford site) into a stable glass waste form.

As noted above, several candidate inorganic ion exchangers, including silicotitanates, zirconium phosphates, and layered double hydroxides, have two major problems associated with them: 1) the nanoparticle exchangers must be consolidated or supported in order to be



used in ion exchange column applications, and 2) the exchangers have a low solubility in the borosilicate waste glass host. Another activity underway in the SERDP project involves the development of porous glass supports to solve both of the above problems. Professor Day has developed two methods for making porous glass supports for waste disposal applications: 1) leaching of phase separated borosilicate glasses, and 2) sol-gel synthesis of porous zirconium silicate glass. With such synthesis routes, glasses can be prepared with interconnected porosities ranging from micron diameters down to nanometer dimensions. Volume fractions of porosity can be as high as 50%. Such porous glasses could be an ideal support for nanoparticle ion exchangers, which could either be synthesized *in situ* via aqueous precipitation or loaded via colloid chemistry techniques. For certain exchange conditions, silane coupling agents could be used to attach the particles to the support. The supported ion exchanger could be configured as porous fibers or beads for use in ion exchange columns. Once loaded with radionuclides, the loaded exchange columns could be hot pressed and/or melted to collapse the porosity in the glass. The resulting waste form would consist of ion exchange particles encapsulated (but not necessarily dissolved) in a highly durable solid glass host. Use of such a composite waste form could reduce waste volumes by as much as a factor of 50 for those exchangers exhibiting poor solubility in current borosilicate glasses. The above technology has yet to be demonstrated, but would be evaluated as part of the SERDP program.

## **8. Expected Payoff:**

As stated above, the fabrication cost per waste glass canister is estimated at near \$1M. Any contribution to the processing of hazardous waste that reduces the number of canisters is valuable. The processing issues addressed in this proposal clearly impact the number of waste canisters that must be fabricated. For example, it is estimated that the maximum allowed Ti content for borosilicate glass is 1 wt%. For a typical silicotitanate ion exchanger, this means that the volume of glass required to convert the exchanger into a solid waste for disposal would be roughly fifty times greater than the volume of the exchanger itself. Even if only 100 canister volumes of exchanger were sufficient to treat the 169 million-gallon tanks at Hanford, the process would generate 5,000 canisters of waste glass requiring disposal. However, if the silicotitanate can be directly converted into a ceramic or encapsulated in a porous glass, only 100-200 waste canisters would be produced for a potential savings to DOE of nearly \$5 billion in processing costs alone. The phosphate glasses developed already in the program could have a similar impact on waste volumes if zirconium phosphates are the Cs<sup>+</sup> exchangers of choice. An analysis of the different exchanger options might provide different solutions to DOE's waste processing problems than might emerge by consideration of the ion exchange step or glass fabrication step alone. For example, although zeolite exchangers are much less selective than silicotitanates for scavenging Cs<sup>+</sup>, the zeolites exhibit much higher solubilities in borosilicate glass. Although the zeolite exchanger would produce more solid waste after the exchange loading step, the net solid waste generated as glass canisters could potentially be less for the zeolite if both materials require disposal in borosilicate glass.

## 9. Milestones:

1. Complete synthesis of  $\text{Na}_2\text{O-Cs}_2\text{O-TiO}_2\text{-SiO}_2$  compositions for phase diagram studies 11/94
2. Determine optimum CsC1 and SrFs loadings for producing stable iron phosphate waste forms 09/96
3. Determine leach properties of select Na, Cs-loaded silicotitanates 09/97

## 10. Transition Plan:

The first objective of this project is to provide DOE with a technical basis for making decisions regarding both its separations and waste disposal options. Results from the program will then be implemented and incorporated into the actual tank clean-up procedures. If the program leads to the development of new exchangers, PNL will identify commercial vendors (such as Allied Signal) who will assume production of sufficient quantities to treat all tank wastes. If the major product of the program involves alternate waste forms, PNL will either work to transfer the waste form technology to existing DOE melt facilities, or will work with both DOE and commercial firms to develop alternate waste form fabrication facilities. If the major impact involves process integration, PNL will work closely with personnel assigned to clean-up of the Hanford tanks to see that optimum processes are implemented in a timely fashion.

## 11. Funding: \$(K)

	FY94	FY95	FY96	FY97	Total
SERDP	200	100	0	400	700
DOE	180	220	200	160	900
TOTAL	380	320	200	560	1600

## 12. Performers:

Organizations performing the work include Pacific Northwest Laboratory (DOE) and the University of Missouri-Rolla.

## 13. Principal Investigator:

Bruce C. Bunker  
Pacific Northwest Laboratory  
Mail Stop K2-45  
P. O. Box 999  
Richland, WA 99352  
PHONE: (509) 375-5969  
FAX: (509) 375-2186  
E-MAIL: BC-BUNKER@PNL.GOV

**14. Keywords:**

Tank Wastes, Radionuclide Separations, Ion Exchange, Glass, Ceramics, Waste Disposal

## SERDP FY95 PROJECT

1. **SERDP Thrust Area:** Compliance
2. **Title:** Shipboard Non-oily Wastewater Treatment System
3. **Agency:** U.S. Navy
4. **Laboratory:** Carderock Division, Naval Surface Warfare Center Annapolis
5. **Project ID:** #29

### 6. **Problem Statement:**

The goal of this project is to provide DoD vessels with the capability to operate in environmentally sensitive areas by meeting current and future national and international effluent discharge standards.

Provisions of the Clean Water Act control the overboard discharge of untreated blackwater (human waste) and graywater within the contiguous zone of the United States. Implementation of Annex IV of the MARPOL Protocol will regulate the discharge of blackwater and graywater from all ocean-going ships. No proven wastewater treatment technology exists today that will reliably meet both the secondary wastewater treatment standards (total suspended solids  $\leq 30$  mg/l, biochemical oxygen demand  $\leq 30$  mg/l, fecal coliform bacteria  $\leq 14/100$  ml and non-toxic) and the operating requirements of DoD vessels (highly reliable, maintainable, supportable, and safe).

DoD vessels today collect and hold only blackwater in collection, holding, and transfer (CHT) tanks for up to 12 hours, or until tank capacity is reached, while transiting the U.S. 3-mile contiguous zone. Graywater is discharged directly overboard. In the future, the 3 mile limit will probably be extended to 12 miles and graywater discharges may also be regulated. Other nations visited by U.S. naval vessels are also expected to impose more strict environmental laws. Ships that rely on holding tanks will be unable to comply.

This project falls into the technology demonstration category in which the feasibility and cost of combining technologies is demonstrated. A product of this research category is proof of the advantage to be gained through application of new technology.

This project is a continuation of an existing FY93 SERDP project. The FY93 effort involves a laboratory demonstration of complete treatment processes at the bench-scale and a subsequent trade-off analysis. That laboratory work will include pre- and posttreatment schemes coupled with membrane filtration to achieve consistent and acceptable effluent. Results from that evaluation will provide system performance data suitable for scale-up to the shipboard prototype.

## 7. Project Description:

This project will demonstrate, first pier-side and then aboard ship, a full-scale (approx. 5 gal./min) process to treat non-oily wastewater to meet EPA recommended wastewater treatment standards prior to discharge. The system is a hybrid membrane-based process, combining aeration pretreatment and membrane ultrafiltration.

The prototype will be designed specifically for a test aboard a CHT equipped ship, but will be initially tested pier-side to insure satisfactory process performance prior to shipboard installation. Following the pier-side demonstration, the prototype, less the aeration chamber, will be incorporated into the test ship's CHT system for a performance demonstration.

The proposed process is designed to treat medium and high strength wastewater, primarily of domestic nature. The process incorporates an aeration chamber followed by tubular membrane ultrafilters. Currently 1-inch bore tubular membranes with a 100,000 molecular weight cutoff (MWCO) are recommended. The process is fully automatic and controlled by a microprocessor. Sludge accumulates in the aeration chamber and is withdrawn once or twice per year. Membrane cleaning is required two to three times a year. The membranes are replaced when minimum flux rate cannot be maintained; membrane life of over five years has been achieved in commercial systems. Energy for the system is entirely electrical. The membrane operation accounts for 60% to 70% of the power requirements. The energy cost per 1000 gallons of wastewater is about 50 kWh.

The risks in this project are related to the impact of actual shipboard wastewater on the aeration chamber, membrane life, and membrane cleaning requirements. This project must demonstrate that aeration/membrane filtration technology will work on actual shipboard generated wastewater under actual shipboard generating conditions. The project must also demonstrate an acceptable membrane life under normal operating conditions of at least one year. Evaluation of the process with graywater and non-oily wastewater has been limited to the laboratory. An extended field trial will be critical to verifying process performance with actual shipboard non-oily wastewater. Additionally, synthetic fibers found in the graywater may accumulate in the aeration chamber and eventually present operational difficulties with pumps, valves, and sensors. The aeration chamber is subject to "upset" due to rapid and large changes in feed stream characteristics such as temperature, pH, aggressive chemical oxidants, and salinity. The demonstration will include planned "spiking" of the feed stream to ascertain the impact of these parameters on the system's performance.

A Navy 6.2 Project on membrane technology for graywater treatment identified ultrafiltration (UF) membranes as the central component to the treatment processes. This effort began in FY89 and will complete in FY94. Bench-scale and trial-scale test stands were fabricated for the evaluation of ceramic and polymeric membranes processing graywater under the 6.2 Exploratory Development Program, Block SC2A, P.E. 62233N, RM 33E60, Task F-8. This effort documented the inability of micro- and ultrafiltration membranes alone to treat graywater to meet secondary discharge standards for five day Biochemical oxygen demand (BOD<sub>5</sub>). Additionally, it was found that polymeric tubular UF membranes provided the best

combination of flux, permeate quality, system simplicity, and reliability in short-term evaluations in the laboratory.

The environmental compliance requirements which are met by this project are identified in the Tri-Service Environmental Quality Strategic Plan as: DoD Pillar 2, Thrust 2.G.2, Non-Oily Waste Emissions from Ships; Requirements 2.II.1.g and 3.II.2.b., Control Blackwater/Graywater from Ships and Integrated Pollution Prevention Systems for Environmentally Sound Ships, respectively.

## **8. Expected Payoff:**

The subsequent advanced development and shipboard evaluation of an Engineering Development Model ensures compliance of every DoD vessel with all current and anticipated graywater and blackwater discharge regulations. Benefits include extended operational time in environmentally sensitive waters, ability to dock in domestic and foreign ports which do not have pier-side waste collection facilities and cost avoidance related to those facilities that do, and a decrease in space and weight on plumbing equipment installations to handle increased graywater holding volume.

## **9. Milestones:**

### **FY93 Funding**

- |    |  |       |
|----|--|-------|
| 1. | Complete contract for the design and fabrication of prototype non-oily wastewater treatment system | 05/94 |
| 2. | Complete trade-off analysis of all successful components and down-select                           | 05/94 |
| 3. | Complete laboratory evaluation of treatment process  | 07/94 |
| 4. | Obligate funds for prototype development contract  | 07/94 |

### **FY94 Funding**

- |     |  |       |
|-----|--|-------|
| 5.  | Select Navy Site for Pier-side Demonstration       | 10/94 |
| 6.  | Complete Preliminary Drawings Package              | 10/94 |
| 7.  | Complete Review of Preliminary Drawing Package     | 11/94 |
| 8.  | Complete First Update of Drawing Package           | 12/94 |
| 9.  | Complete Critical Design Review of First Update    | 01/95 |
| 10. | Complete Final Update of Drawing Package           | 02/95 |
| 11. | Complete Fabrication of Prototype                  | 07/95 |
| 12. | Obligate Funds for Analytical Contract             | 07/95 |
| 13. | Complete Hydraulic Test of Prototype               | 08/95 |
| 14. | Complete Proof-of-Concept Test at Fabrication Site | 08/95 |
| 15. | Deliver Prototype to Navy Site                     | 09/95 |
| 16. | Complete Pier-side Demonstration Test Plan         | 09/95 |

### **FY95 Funding**

- |     |  |       |
|-----|--|-------|
| 17. | Complete Pier-side Installation of Prototype     | 10/95 |
| 18. | Complete System Debugging and Initial Testing    | 11/95 |
| 19. | Complete On-site Assembly of Shipboard Prototype | 06/96 |

20. Complete Pier-side Demonstration of Prototype 08/96

**FY96 Funding**

21. Complete Shipboard System Debugging and Initial Testing 10/96

22. Complete Pier-side Demonstration Report 12/96

**FY97 Funding**

23. Complete Shipboard Demonstration of Prototype 10/97

24. De-install Shipboard Prototype 02/98

25. Complete Final Report 06/98

**10. Transition Plan:**

Upon completion of a successful pier-side and shipboard demonstration, the prototype will be transitioned in FY98 to the Naval Sea Systems Command (SEA 03V) Advanced Development Program, P.E. 63721N. That program will design and fabricate engineering development models for evaluation and ultimate acquisition. Adequate industrial production capability currently exists for all components of the proposed treatment process.

**11. Funding: \$(K)**

	FY94	FY95	FY96	F97	Total
SERDP	700	250	700	400	2850

**12. Performers:**

NSWC/Annapolis is the lead laboratory on this project. Consultation with the U.S. Army Waterways Experiment Station and members of the Interagency Consortium for Desalination and Membrane Separation Research such as NIST (Chemical Science and Technology Division, Boulder, CO) is planned. A separately funded ONR S&T project to be conducted by the Molecular Biology Program (ONR Code 341) has been proposed and directly supports this SERDP project. That ONR project will investigate methods to enhance the biological pre-treatment process and reduce its susceptibility to wastewater perturbations. NSWC/Annapolis and ONR have collaborated on that project's focus. The universities involved in the ONR project are Purdue University and Clemson University. A contract with Westinghouse, Machine Technology Division, for the design and fabrication of pier-side and shipboard prototypes is planned.

**13. Principal Investigator:**

John Benson (Code 634)  
Naval Surface Warfare Center  
Carderock Division Annapolis Detachment  
3A Leggett Circle  
Annapolis, MD 21402-5067  
PHONE: (410) 267-2244  
FAX: (410) 267-4874  
E-MAIL: jbenison@metals.dt.navy.mil

**14. Keywords:**

Graywater, Blackwater, Ultrafiltration, Non-Oily Wastewater, Wastewater Treatment, Hybrid  
Wastewater Treatment Processes



## SERDP FY95 PROJECT

1. **SERDP Thrust Area:** Compliance
2. **Title:** Evaluation of the Use of Waste Energetics as Supplemental Fuels
3. **Agency:** U.S. Army
4. **Laboratory:** U.S. Army Environmental Center (AEC)
5. **Project ID:** #524
6. **Problem Statement:**

The Army, as sole Department of Defense manager for explosives, is currently evaluating and developing safe, environmentally acceptable, alternative disposal and reuse technologies for its stockpile of waste energetic materials. Waste energetic materials are propellants, explosives, and pyrotechnics and are commonly referred to as PEP. Unserviceable PEP materials are generated from the manufacture of PEP materials, assembly of munitions, and demilitarization of obsolete conventional munitions. It is estimated that approximately 2.5 million pounds of scrap and off-specification energetic are generated each year (1985 estimate). In addition there were an estimated 200,000 short tons of conventional munitions requiring demilitarization in 1990.

The disposal alternatives for these unserviceable PEP materials are open burning/open detonation (OB/OD) and incineration. OB/OD is the preferred method of disposal; however its use requires a Resource Conservation recovery act (RCRA) Subpart X permit and due to environmental concerns, OB/OD is only allowed on a case by case basis. The Department of Defense (DoD) is seeking to qualify alternatives to OB/OD by 1995 and to adopt environmentally sound practices by the year 2000. Incineration of energetic materials is uneconomical. To safely burn these materials, energetic are mixed with up to 75% water to form an energetic material/water slurry. The water is required to prevent detonation propagation during the material handling and feed process. The addition of water increases the amount of fuel required to incinerate the energetic materials. Neither OB/OD takes advantage of the energy content of these materials.

USAEC, formerly the U.S. Army Toxic and Hazardous Materials Agency (USATHAMA), began investigating the feasibility of reusing the energy content from waste energetic materials to produce steam and/or electricity in 1984. Since explosives are a major waste energetic material in the U.S. Army's inventory, the USAEC began investigating the potential of using TNT, RDX, and Composition B as a supplemental fuel.

## 7. Project Description:

The technical objective of this SERDP proposal is continue work on development of the supplemental fuel technology so that it is ready to be transitioned to the installations/users in order to deal with the burgeoning off-specification and obsolete energetic inventory. Continuing to store these obsolete and unstable materials, while awaiting acceptable technical solutions, imposes great safety hazards. Disposal of waste solvated explosives as a supplemental fuel has been successfully demonstrated from the laboratory (1985), to the bench scale-studies (1988), to the Los-Alamos Pilot-Scale Test (1989), to the conduct of the Hawthorne Pilot-Scale Test (1991). Results of the first pilot scale demonstration at Los Alamos National Laboratory led to a state-of-the-art pilot scale system being designed and constructed for mixing solvated explosives with fuel oil and firing the resulting mixture into a standard industrial boiler to generate steam. The test equipment was designed to meet strict safety standards involved in the handling explosives and volatile solvents. The major process equipment items in the pilot scale system are the explosives dissolving system, the fuel explosives blending tank, the boiler and steam vent system, and boiler management system. The boiler selected for the pilot scale system was a standard Cleaver Brooks Model M4000, 2 million BTU/hr, water tube-type boiler which is one tenth the scale of the majority of the boilers used at Army facilities. Although only 5 of the 18 scheduled test trials were completed during the Hawthorne Pilot-Scale test due to the expiration of Weston's contract and due to some operational problems encountered as a result of operating in the extreme cold temperatures of the desert environment (Hawthorne, Nevada) in winter, the technology once again demonstrated the potential to be an effective method to recover energy from waste explosives. Dilute solutions of TNT (1%) were safely and effectively used to supplement No. 2 fuel oil in an industrial boiler and a removal efficiency greater than 99.99% was achieved. Design modifications made to the system in order to overcome operational problems in extreme cold temperature include: compressed air system improved to provide heated and dry air to the diaphragm pump and other air operated equipment; slurry handling piping and blending tank will be heated and insulated to maintain constant temperature during all ambient conditions; instruments measuring level, flow, and temperature of feed blending system have been upgraded; the burners for fuel oil and slurry have been modified to permit separate supply and control of compressed air to burner nozzles; the control system for combustion air modified to respond stack gas oxygen concentration; and the propane pilot burner was replaced with a pilot using compressed air and propane mixing system.

After significant delays at attempting to resume the previously scheduled tests at Hawthorne Army Ammunition Plant, a Memorandum of Agreement between the USAEC and Indian Head Division, Naval Surface Warfare Center (IHDIVNAVSURFWARCEN), Indian Head, MD., was signed in late 1992 to establish a joint service research and development program for the reuse of waste energetics as fuel supplements. The pilot test equipment was moved to IHDIVNAVSURFWARCEN in Jun 93 where the U.S. Army and Navy shall repeat the original 18 test trials, scheduled for the Hawthorne Pilot-Test, to prove out the equipment modifications and to further develop the technology.

The first part of this SERDP project shall be to conduct the 18 test trial with explosives with the upgraded pilot scale test equipment. Three test sequences are planned. Sequence I consists of No. 2 fuel oil only to characterize the boiler combustion characteristics, particularly nitrous oxide emissions at excess air levels ranging from 20% to 30% (without explosives). Sequence II will evaluate No. 2 fuel oil/solvent/TNT and Sequence III will evaluate No. 2 fuel oil/solvent/Composition B. A matrix of explosives concentrations (TNT: 1%, 10%, 15% ; Composition B: 1%, 4%, 8%) and excess air percentages (20%, 25%, 30%) are scheduled. A final report shall be prepared at the conclusion of the testing as well as an operations manual and a video depicting system operation. Equipment modifications shall be made and "as modified drawings" will be prepared (if necessary). A cost analysis shall then be performed and procurement/fabrication shall be prepared.

A Supplemental Fuels Development Support contract which is scheduled to be awarded in Jan 94 shall be conducted in parallel to this SERDP effort. The main tasks under this support contract shall be as follows: identification of nitrous oxide abatement technologies as they probably will be required based upon the results of firing a dilute solution (1%) of TNT with fuel oil in Hawthorne Pilot-Scale Test; the contractor (Weston) providing consulting support to IHDI VNAV SURFWARCEN personnel during conduct of the demonstrations defined in this SERDP proposal; identification of acceptable slurry nozzles which can be used for firing propellants/fuel oil slurries in an industrial boiler; to conduct of a comprehensive review of all laboratory and bench scale data pertaining to explosives and propellants-supplemented fuels in order to identify any data gaps existing; and then to develop a test plan and execute testing to answer data gaps identified in order to optimize the development of this technology.

After conclusion of the Pilot-Test with explosives at IHDI VNAV SURFWARCEN and the pilot scale system is readied for the Pilot-Test with Propellants (i.e. slurry nozzle identified in "Supplemental Fuels Development Support" contract is installed), a Pilot-Scale Test with Propellants shall be initiated. Propellants investigated in this Pilot-Test shall be AA2 Double-Base Propellant, Nitroguanidine, Nitrocellulose, and another propellant (to be determined after talks with Holston Army Ammunition Plant). A final report shall be prepared at the conclusion of this testing as well as an operations manual and a video depicting system operation. Equipment modifications shall be made and "as modified drawings" shall be prepared (if necessary). A cost analysis shall then be performed and procurement/fabrication guidance shall be prepared.

The third part of this SERDP project shall be to fund a material handling study at Holston Army Ammunition Plant for their off-specification and scrap explosives and propellants and then to assist them in retrofitting an actual scale boiler for the conduct of an Installation Demonstration.

## **8. Expected Payoff:**

The future implementation of this technology could be a cost-effective disposal alternative to incineration and will become an alternative to OB/OD which soon may not be an option due to the environmental concerns associated with the process. Potential safety hazards may also

be mitigated as the large stockpile of these obsolete munitions and scrap and off-specification materials can start to be utilized with this technology for a beneficial end use. This technology will not only benefit the DoD but commercial industry as well.

**9. Milestones:**

- |    |  |       |
|----|--|-------|
| 1. | Initiate Pilot Test on Explosives            | 09/94 |
| 2. | Final Report on Pilot Test with Explosives   | 02/95 |
| 3. | Cost Analysis/Technology Transfer Package    | 09/95 |
| 4. | Finalize Procurement/Fabrication Guidance    | 12/95 |
| 5. | Initiate Pilot Test on Propellants           | 04/96 |
| 6. | Final Report on Pilot Tests with Propellants | 08/96 |
| 7. | Cost Analysis/Technology Transfer Package    | 10/96 |

**10. Transition Plan:**

DERA funding shall be used to used to fund an Installation Demonstration at Holston Army Ammunition Plant in FY97. The transfer of the technology to the Installation level is described in paragraph 7. Holston Army Ammunition Plant was briefed on this program and has expressed an interest in being the first installation that this technology is transitioned to.

**11. Funding: \$(K)**

	FY94	FY95	FY96	FY97	Total
SERDP	800	300	680	900	2680

**12. Performers:**

The USAEC and IHDI VNAVSURFWARCEN shall jointly develop and transition this technology. Sandia National Laboratories (SNL) as part of the Energetics Material Center (EMC) shall be a partner in this effort as they are investigating, under a separate SERDP proposal, tasks on the removal of energetic material and preparation for conversion which will support the material handling portion of this SERDP proposal at Holston Army Ammunition Plant. SNL as part of EMC also has submitted a SERDP proposal on co-firing with coal or waste-to-energy plants in lieu of fuel oil as in this SERDP proposal and programs can complement one another in characterizing boiler process parameters and in the identification of a suitable off-gas handling system.

**13. Principal Investigator:**

Louis Kanaras  
U.S. Army Environmental Center  
SFIM-AEC-TSD/Kanaras (Bldg E4435)  
Aberdeen Proving Ground, MD 21010-5401  
PHONE: (410) 671-1558 DSN 584-1558  
FAX: (410) 671-1680 DSN 584-1680  
E-MAIL: lkanaras@aecl.apgta.army.mil

**14. Keywords:**

Explosives, Propellants, Boiler, Supplemental Fuel, Pollution Prevention, Open Burning/Open Detonation

TABLE XIV  
FY 1995 CONSERVATION PROJECTS

	Funding \$(K) FY95	ID Number	Page Number
Community Ecosystem - Management			
Terrain Modeling and Soil Erosion Simulation (A)	195	752	CS-3
Phased Array Ultrasonic Detection of Cultural Artifacts (A)	120	753	CS-6
Advanced Biotelemetry for Resource Management (A)	270	759	CS-8
Strategic Natural Resource Management Methodology (DOE/A)	50	373	CS-13
Multiple - Risk/Impact Assessment			
Assessment and Management of Risks to Biodiversity and Habitat (EPA)	100	241	CS-18
Species/Genetic - Management			
Threatened, Endangered and Sensitive Resources (A)	300	507	CS-22
Species/Genetic - Resource Characterization			
Integration of Radiotelemetry, Remote Sensing and GIS (DOE)	50	363	CS-27
Fishing Enforcement/Whale Monitoring Using IUSS (N/NOAA)	1,625	48	CS-31
Species/Genetic - Risk/Impact Assessment			
The Effects of Aircraft Overflights on Birds of Prey (AF)	80	89	CS-36
Genetic Diversity Monitoring in Plants and Wildlife (EPA)	0	246	CS-39
Ecological Biomarkers: Monitoring Wild Fauna at DoD Installations (EPA)	0	244	CS-43

TABLE XIV FY 1995 CONSERVATION PROJECTS					Page Number
	Funding \$(K) FY95	ID Number			
Watershed/Landscape - Management					
Ecological Modeling for Military Land Use Decision Support (DOE/A)	260	758			CS-48
<b>Conservation Total</b>	<b>3,050</b>				

## SERDP FY95 PROJECT

1. **SERDP Thrust Area:** Conservation
2. **Title:** Terrain Modeling and Soil Erosion Simulation
3. **Agency:** U.S. Army
4. **Laboratory:** Construction Engineering Research Laboratory
5. **Project ID:** #752

### 6. Problem Statement:

The objective of this basic research project is to develop methods and tools for prediction of spatial and temporal distribution of runoff, soil erosion, and sediment deposition within watersheds. Soil erosion and consequent siltation of waterways have long been major environmental concerns on military installations. Most existing approaches rely on lumped-parameter semi-empirical relationships developed for agricultural fields. Such approaches are unable to provide consistent, accurate results for watershed-scale runoff and erosion processes. Another primary limiting factor is the inability to accurately represent the terrain in a digital form necessary for high resolution watershed-scale erosion and sediment transport modeling. The development of new-generation technical tools to model distributed surface erosion and runoff in complex terrains is a necessity. Such tools will provide a basis for predicting the environmental impacts of military-related activities and for the optimization of land rehabilitation programs for installations.

### 7. Project Description:

The research effort will incorporate the following parallel thrusts: a) Further enhancements of spline interpolation methods to support terrain modeling and processing of field measurements; b) Further development of the unit stream power based modeling of erosion and deposition potential; c) Simulation of rainfall-runoff processes through the application of two-dimensional finite difference technique with the addition of sediment transport routines; d) Development of a vehicle-soil-climate interaction model based on field measurements of soil and hydrologic parameters as consequences of various types and intensities of military vehicular traffic; e) Collection of in-stream sediment concentrations of validation of the proposed models; f) Development of new visualization techniques supporting the design and communication of models of dynamic processes, such as erosion and sediment transport.

The project is focused on the development of computer-based models that will support the determination of the impact of military activities on natural resources and will assist in maximizing availability of military lands with minimal impact to natural resources, especially to soil and vegetation.



## 8. Expected Payoff:

This project will improve the capability to generate accurate digital elevation models and perform topographic analyses for various terrain related applications. There will be improved capability to estimate erosion/deposition potential as an input for choosing the optimal land use management and rehabilitation programs. Modeling of erosion and deposition will assist land managers and trainers in optimizing the training schedules, delineating training areas, and monitoring changes over time. The models will also assist in maximizing availability of military lands with minimal impact to natural resources, especially to soil and vegetation.

## 9. Milestones:

1.	Enhancements to interpolation	02/95
2.	Integration of erosion model within GIS	04/95
3.	Sediment, soil and cover data collection initiated	09/95
4.	Programs to simulate rainfall-runoff-sediment transportation	09/95
5.	Professional journal articles	09/95
6.	Implementation of methods for dynamic cartography	02/96
7.	Evaluation and enhancement of erosion/deposition model using field data	09/96
8.	Calibration and enhancement of rainfall-runoff-sediment transport model using field data	02/97
9.	Incorporation of sediment control practices into models	09/97
10.	Interactive GIS based system for simulation of runoff and erosion processes supporting opt. LU management	09/98

## 10. Transition Plan:

Scientific papers in peer reviewed journals will be published. There will be a release of new programs with updates of GRASS. The information will be integrated into decision support systems and available in World Wide Web documents. Results of this project are used by wide research community at government agencies, universities and military installations using GRASS.

## 11. Funding: \$(K)

SERDP	FY94	FY95	FY96	FY97	FY98	
TOTAL	600	195	190	700	300	1,985

## 12. Performers:

Land Management Laboratory at USACERL and the Geotechnical Laboratory and Hydraulics Laboratory at USAEWES.

### **13. Principal Investigators:**

Dr. Helena Mitasova  
US Army CERL  
Environmental Sustainment Lab  
TIM Team  
PO Box 9005  
Champaign, IL 61826-9005  
PHONE: (217) 352-6511

Dr. Steve Warren  
US Army CERL  
Environmental Sustainment Lab  
TIM Team  
PO Box 9005  
Champaign, IL 61826-9005  
PHONE: (217) 398-5455  
FAX: (217) 398-5470

### **14. Keywords:**

Terrain Modeling, Soil Erosion, Watersheds, Runoff, Sediment, Impacts

## SERDP FY95 PROJECT

1. **SERDP Thrust Area:** Conservation
2. **Title:** Phased Array Ultrasonic Detection of Cultural Artifacts
3. **Agency:** U.S.Army
4. **Laboratory:** Construction Engineering Research Laboratories (CERL)
5. **Project ID:** #753

### 6. Problem Statement:

Currently, the reliability associated with the detection and location of artifacts is minimal. Often, valuable finds are missed only to be found during construction, causing delays and increased costs. The goal of this work is to develop an ultrasonic probe using phased array technology for the subsurface detection and imaging of artifacts. This is an applied research effort and falls under the category of exploratory development.

The development of this technology will include field tests, preferably at known archeological sites. The predictive capability will be compared to actual archeological findings under varying circumstances in order to determine reliability.

### 7. Project Description:

Ultrasonic sound waves exhibit the non-destructive capability of transmission into the ground to probe beneath the surface by reflecting off mediums of higher relative density (i.e. bone, ceramic, stone, glass). Ultrasound techniques are in routine use for medical, engineering, and oil exploration applications. Three-dimensional or two-dimensional (tomographic) imaging of everything from human fetuses to oil fields are now commonplace. The objective of this work is to develop a phased array of ultrasonic transducers which can accurately image subsurface features of differing densities. For example, by analyzing the signal strength returned within specific time windows, precise regions can be examined. By varying these windows, the whole volume can be examined while excluding most interference reflections. Through computer imaging and enhancement, the location of possible artifacts can be identified along with information about their shape and dimension. The main challenges of this work will likely be in the areas of signal attenuation and processing/analysis.

### 8. Expected Payoff:

The expected benefit is to be able to non-destructively probe beneath the earth's surface to locate possible buried artifacts. This would allow for more efficient use of limited excavation resources and help to assure more complete coverage of sites. An additional benefit would be

the avoidance of costly construction delays when unexpected artifacts are encountered. It would also greatly reduce the cost of archeological site assessment for eligibility to the National Registry of Historic Places.

**9. Milestones:**

- |    |   |       |
|----|---|-------|
| 1. | Survey commercial systems and services                                  | 09/94 |
| 2. | Build test bed for transducer and imaging software testing              | 09/94 |
| 3. | Complete characterization of acoustic properties of soils and sub-soils | 09/95 |
| 4. | Build transducer/detector array   | 06/96 |
| 5. | Wire computer interface   | 06/96 |
| 6. | Develop control and imaging software                                    | 03/97 |
| 7. | Test at Controlled Archeological Test Site (CATS)                       | 07/97 |
| 8. | Demonstration of technology   | 06/98 |
| 9. | Report on findings  | 09/98 |

**10. Transition Plan:**

The technology will be transitioned to the Tri-Services Cultural Resource Center. There has been interest expressed by Vista Research, Inc., for commercialization (utility location), and preliminary CRADA discussions have been initiated:

**11. Funding: \$(K)**

SERDP	FY94	FY95	FY96	FY97	TOTAL
	261	120	90	340	811

**12. Performers:**

The lead organization for this effort will be the Engineering and Materials Division of USACERL. Initial coordination with the Cultural Resources Research team and the Tri-Service Cultural Resource Center of USACERL has been initiated.

**13. Principal Investigator:**

Dr. Charles Marsh, FM Division  
USACERL  
P.O. Box 9005  
Champaign, IL 61826-9005  
PHONE: (217)352-6511 ext 7419  
FAX: (217) 373-6732  
E-MAIL: c-marsh@cecer.army.mil

**14. Keywords:**

Cultural Resources, Probe, Ultrasound, Array, Artifacts, Transducer

## SERDP FY95 PROJECT

1. **SERDP Thrust Area:** Conservation
2. **Title:** Advanced Biotelemetry for Resource Management
3. **Agency:** U.S Army
4. **Laboratory:** USAE Waterways Experiment Station
5. **Project ID:** #759
6. **Problem Statement:**

The federal, state, and DoD requirements for research, management, and conservation of natural resources are costly and can impact and disrupt military missions. The object of this proposal is to develop and implement sophisticated remote sensing biotelemetry technology and to develop methodologies to study wildlife on military installations while minimizing disruption to military activities.

The use of advanced technology proposed here will address two difficulties that plague effective research and management of special status species on military land: 1) rare or elusive organisms are difficult to find and study; and, 2) human activity involved in conventional study of these organisms can interfere with military activities.

Threatened and endangered species protection has precluded certain military operations on DoD installations and other federal and state lands. The projected cost in both fiscal and personnel resources for studying threatened and endangered species is significant.

Furthermore, field study activities often place natural resource personnel in situations that interfere with military activities and sometimes may require personnel to enter hazardous impact areas. To address these problems, biotelemetry and specialized survey methods can be used to remotely acquire large quantities of data for long-term studies of wildlife. Biotelemetry can be especially effective for studying threatened and endangered species and migratory organisms that are often indicators of environmental conditions.

This advanced technology can also be useful in addressing other DoD environmental requirements, such as managing for biodiversity and/or neotropical migrants, and monitoring and controlling of environmental contaminants. The application of the proposed technology will streamline data collection and will reduce the personnel investment and interference in the field while demonstrating leadership in DoD natural resource management responsibilities. Our proposal will build on a previously funded DoD technology development project that addressed several protected species while developing natural resource management methodologies and technology. The proposal encompasses basic and applied research, technology demonstration, and technology transfer as specified below:

#### Basic Research:

- Development of environmental sensors and integration with biotelemetry
- Development of enhanced survey and monitoring methods
- Integration of data from remote sensing and surveys with Geographic Information System (GIS) databases for installation resources management

#### Applied Research:

Implementation of the technology and methodologies from basic research to study the effects of military training and other relevant land use activities on natural resources

#### Technology Demonstration:

Demonstration of resource management planning on selected DoD installations integrating the enhanced technology and methodologies

#### Technology Transfer:

Transfer technology and methodologies to U.S. Department of Interior's (DOI) Bureau of Land Management (BLM) and National Biological Survey (NBS) for use in natural resource management

### **7. Project Objectives:**

Our goal is to provide DoD/DOE managers with more effective and efficient ways to meet their environmental objectives. The critical path for the implementation of our proposal requires parallel development in: 1) field methodologies and biometrics; 2) electronics and applied physics; and 3) natural resource research and management. We plan to work with selected installations and their land managers to identify their needs in addressing natural resource problems and then develop innovative methods and technologies required to address their needs. We will include the field testing methods and techniques and the incorporation of them into the natural resource research, planning and management program.

This development and integration of new environmental sensors with conventional and global positioning systems will be carried out in three phases. Phase I will involve the integration of motion, temperature, altitude, and light sensors with globally positioned Argos-Tiros Platform Transmitting Terminals (PTT). Phase II will involve the development of miniature visual and acoustic sensors for use with conventional positioning and tracking systems. Phase III will be the integration of visual and acoustic sensors with the Argos-Tiros PTTs.

Biotelemetry will be used as an animal marking technique in developing new survey and monitoring methods (i.e., mark-recapture). Also, biotelemetry will be used to identify the spatial-temporal use of areas and habitats of interest (e.g., training areas), and to help identify sources of disturbances and contamination. Biotelemetry and survey methods will also be

used in research on potential influence of selected human activities on wildlife.

The proposed work will be integrated with the existing program to maximize exchange of information and minimize duplication. The current program involves several DoD entities: National Guard Bureau (NGB), US Army Construction Engineering Research Laboratories (CERL), and US Army Edgewood Research, Development and Engineering Center (ERDEC); several US Department of Interior agencies; Fish and Wildlife Service (USFWS), National Park Service (NPS), and the National Biological Survey (NBS), Bureau of Land Management (BLM), and several academic institutions: Johns Hopkins University Applied Physics Laboratory (JHUAPL), Virginia Polytechnic Institute and State University (VPI), and the University of Minnesota (UM). By working with NBS's Division of Information and Technology Transfer and CERL, we will maximize our opportunity for technology and methods transfer to other natural resource and conservation efforts ongoing throughout the country.

Potential technical difficulties include: 1) achieving statistical robustness for the study of uncommon organisms; 2) additional miniaturization of telemetry technology for application to small animals; and 3) sensor range and sensitivity applicable to environmental monitoring.

## **8. Expected Payoff:**

The primary benefits of our proposal are cost savings for DoD resource managers, enhanced research and management capabilities, and new technologies for a variety of users.

Cost savings to the military accrue in several ways. First, application of advanced methods and techniques will allow for more effective accomplishment of the study of special status species. Second, application of these methods and techniques will require fewer personnel resources than in the past. Third, fewer persons in the field for shorter periods of time will reduce the interference with military activities.

In addition to more effectively meeting DoD's obligations for natural resource conservation, the technologies we develop will have applications to other military missions. For example, miniaturized telemetry devices can be applied to positioning military assets (e.g., covert devices, search and rescue activities, and "lost" items). Furthermore, sensors developed for monitoring an animal's environment are equally applicable to sampling the environment of troops or other military assets.

These methods will also be applied to basic research on the effects of the military and other anthropogenic stressors on natural resources. The data acquired can be directly applied to resource management planning that is "proactive", whereby we can avoid creating problems and causing species to become threatened or endangered. By preventing disturbance of certain sensitive habitats, DoD and DOE can avoid the expensive, time-consuming, and disruptive responses necessary to manage and mitigate for environmental problems. This approach will also promote better biodiversity management.

Currently, DoD and DOE share with DOI, the Department of Agriculture, and the Department of Commerce many common concerns and responsibilities for the environment.

Furthermore, DoD and DOI are actively involved in the development of international programs to address environmental concerns resulting from their activities and those similar agencies in other nations (e.g., Ministry of Defense, Russian Federation). Our methods and technology are broadly applicable regardless of the user community. This broad application is, in fact, required because the world recognizes the global links among natural systems. These links include such diverse pathways as the migration of birds to and from military lands of many countries, and the circulation of contaminants across political boundaries through the atmosphere and waters of the world. Furthermore, our technology will be available for testing hypotheses, investigating alternative strategies, and monitoring for the predicted effects of global warming.

## 9. Milestones:

1.	Program Start	05/95
2.	Contract award to Johns Hopkins	06/95
3.	Continue program with DOI, NBS	06/95
4.	Demonstrate miniature white light imagery sensor	09/95
5.	Continue system database integration and application with GIS at NBS	09/95
6.	Continue Phase I development and integration of sensors with telemetry system	07/95
7.	Integrate Phase I system for demonstration	06/95
8.	Initiate Phase II development and integration, JHUAPL	07/95
9.	Interim report on sensor/telemetry systems research and development, JHUAPL	10/95
10.	Interim report on systems data analysis and integration, DOI, NBS	10/95

## 10. Transition Plan:

The technical development and integration of new environmental sensors with global/conventional positioning systems for natural resource management and wildlife research will be managed by ERDEC and performed by the JHUAPL working in union with the private sector. In the past, our US Army program, "Bird Borne" (performed by JHUAPL), proved to be a cost effective mechanism for development and rapid transition of technology to industry. Our early research and development in military application resulted in a new generation of miniature PTTs (28gm) which are now available from private industry.

Prototype systems from all three phases of development will be transitioned to several field programs for test and evaluation of performance. These field efforts will be managed by NBS and DoD. The NBS will provide oversight for the development of scientific protocols for the use of the technology for application in select military and DOI natural resource programs. These applications will be with the Idaho Army National Guard (IANG), the Arizona Army National Guard and several wildlife research efforts conducted through the USFWS, BLM, and NPS. Evaluation of the technology, and synthesis and analysis of results will be carried out by the elements of the NBS working with CERL and individual commands/installations and agencies. Integration of developed databases derived from the use of this technology on



several of the fielded programs will be integrated into a GIS capability which is currently under development jointly by CERL, NBS, and IANG.

**11. Funding: (\$K)**

	FY94	FY95	FY96	TOTAL
SERDP	300	270	300	870

**12. Performers:**

The principal performers in this research effort will be the scientists of USAEWES, USACERL, USACRREL, USATEC, and ERDEC. These scientists will coordinate and, when possible, partner activities with Tri-Service installation personnel, with land management agencies such as USFWS, USDA FS, USDA SCS, BLM, and BUREC, with academia, and with the Nature Conservancy and other conservation organizations.

**13. Principal Investigator:**

Dr. William S. Seegar  
ERDEC  
Aberdeen Proving Ground, MD 21010-5423  
PHONE: (410) 671-2586  
FAX: (410) 671-5292  
E-MAIL: WSSEEGAR@CBDCOM.APGEA.ARMY.MIL

**14. Keywords:**

Landscape Planning, Watershed Management, Ecosystem Management, Ecosystem Functions, Integrated Resources Management, Cultural Resources, Natural Resources.

## SERDP FY95 PROJECT

1. **SERDP Thrust Area:** Conservation
2. **Title:** Strategic Natural Resource Management Methodology
3. **Agency:** U.S. Department of Energy
4. **Laboratory:** Argonne National Laboratory (ANL)
5. **Project ID:** #373
6. **Problem Statement:**

Argonne National Laboratory (ANL), in conjunction with the U.S. Army Corps of Engineers, Construction Engineering Research Laboratories (USACERL), proposes to develop a Strategic Natural Resources Management (SNRM) methodology and a decision-support system that will meet planning needs for biological conservation and resource management on military installations and Department of Energy (DOE) sites. This proposed decision-support system, called the Integrated Dynamic Landscape Analysis and Modeling System (IDLAMS), will allow land-use conflicts to be identified and optimally resolved and will determine least-cost solutions to long-term land stewardship issues. This approach will quickly provide pertinent information for determining, evaluating, and resolving natural resource/land-use conflicts, as well as for long-term planning and management of these natural and cultural resources.

The proposed project offers a technology that will enable resource managers responsible for public lands to identify and analyze competing and complementary land uses and to incorporate least-cost, optimization, and "what if" scenarios into their decision-making. The initial emphasis focuses on Army installations; however, the technology will be a tool relevant to the needs of the Navy and Air Force, the Department of Energy, the Bureau of Land Management, the National Park Service, and other federal and state land managing agencies. As such, IDLAMS will be a dual-use technology with the potential for leveraging the Department of Defense funds with those of other agencies for future enhancements and technology transfer.

Background work underpinning this proposal was conducted by ANL at Fort Riley, Kansas, where ANL has developed a dynamic community landscape model that links the installation's training mission with the protection of its natural and cultural resources. This model is being integrated with a rule-based, expert system and geographic information system (GIS) to create a user-friendly interface to be used by the installation's natural resources planning staff. The proposed SNRM methodology will expand and generalize the Fort Riley model to meet the major needs of biological conservation and resource management on military installations and Department of Energy sites.

Relevant USACERL projects have been funded through the Legacy Resource Management Program to develop pilot computer technologies to assist in integrated natural and cultural resource planning and management on military installations. These USACERL projects include XCRIS, an X-windows-based Cultural Resource Information System, and GRASS-PRISM (Planning and Resource Integration Stewardship Modules). These efforts have linked computer tools, including GRASS as a GIS, a relational database management system, and graphic user-interfaces using Xgen for easy-to-use information access and decision support technology. Initial resource "modules" include cultural resources and historic preservation, forestry, endangered species (specifically for the red cockaded woodpecker), and watershed management and erosion control. The SNRM methodology will build upon these efforts by developing a quantitative approach to evaluating land-use alternatives and long-term resource management scenarios.

## **7. Project Description:**

The content of this project addresses several thrusts within the Conservation Pillar of the Tri-Services Reliance R & D Strategic Plan (green book), including Thrust 4A: Natural and Cultural Resource Data Integration and Reporting; Thrust 4B: Range/Training Carrying Capacity; Thrust 4D: Land Management and Scheduling; Thrust 4I: Range/Training Area Revegetation; and Thrust 4K: Sensitive Ecosystem Management.

7.1 Vegetation Dynamics Model: The basis for modeling changes in vegetation is the vital attributes scheme of Noble and Slatyer, which classifies vegetation physiognomically based on its response to different types of disturbance. For example, species respond differently to such disturbances as flooding, fire, trampling, etc. Different vegetation types and successional stages are identified, and a matrix is then developed showing the transition times for natural succession and for responses to disturbance. This matrix identifies the consequences of all possible management actions or disturbances, such as fire, tree planting, fertilization, and tracked-vehicle activity, in terms of changes in vegetation type. This approach allows multiple, spatially distributed disturbances and management activities to be evaluated in terms of their short-term and long-term effects on the vegetation and the landscape. It also allows recovery from disturbance to be modeled.

7.2 Spatial Analysis: In SNRM, GIS is used for far more than mapping alone. First, the interaction between the locations of management actions and their effect on vegetation is explicitly modeled in the GIS, with the GIS acting as the database to store and update vegetation-type changes on a spatial basis. Second, some components of change are modeled in the GIS in an explicitly spatial manner. For example, at Fort Riley, forest has spread rapidly on newly acquired land, but all new forest adjoins existing forest and most occurs in stream valleys. The process of forest spread is being modeled with a spatial contagion model. Other such spatially explicit processes include: fire spread and training damage.

7.3 Biodiversity: A basic problem with the current concept of biodiversity has been that an operational definition does not exist by which biodiversity or habitat integrity may be quantified. A new technique developed at ANL (Loehle and Wein, 1993, Ecol. Mod.) provides such a definition at the landscape scale, based on the similarity of different plant

communities and their spatial arrangement on the landscape. This technique can quantify not only habitat fragmentation (e.g., due to roads) but also the cumulative effects of disturbance on vegetation structure. This approach will be integrated into the GIS as part of the work proposed for funding under SERDP. The U.S. Fish and Wildlife Service and National Biological Survey are developing guidelines for approaches to biodiversity, which we will also incorporate as needed.

**7.4 Optimality Analyses:** Using the vegetation change, spatial analysis, and biodiversity components, the core analysis can then be conducted using optimization approaches. First, the utility function must be defined. This function represents the overall level of management satisfaction that would result from various levels of grassland dominance of the land base. For example, at Fort Riley, Kansas, a simple utility function is:

$$F = w_1xTV + w_2xGV + w_3xWHV$$

where  $x$  = acres of grassland (% of area), TV = Training Value function, GV = Grassland Value function, and WHV = Wildlife Habitat Value function. The weighing  $w$  values represent the relative importance of the different goals. Training value for vehicle maneuvers is maximal at about 80% grassland and declines above and below this value. Grassland value increases as degree of nativeness of the grassland increases. Wildlife habitat value is based on key game species' habitat requirements. More complete utility functions for Fort Riley are under development, but this illustrates the general concept. Given a utility function, the feasible management alternatives are determined by the closest possible achievement of the optimal outcome. By introducing cost of management activities, the least-cost management scenario can be generated. The SNRM methodology generates scenarios that are less likely to incur future ecosystem rehabilitation costs. Thus, stewardship issues are inherently incorporated into the framework.

**7.5 Project Tasks:** The major objective of this proposal is to expand, refine, and integrate the current dynamic landscape community model being developed for Fort Riley into a more generally useful SNRM system for all military installations. The three major tasks to be undertaken are to: (1) model vegetation classes and dynamics, (2) develop utility functions for various landcover configurations, and (3) incorporate appropriate optimization procedures into the SNRM system.

The central functional component of the SNRM system is a model of vegetation (land-use) change, which incorporates both endogenous changes and those resulting from management activities. For the purposes of land management at military bases, it is not necessary to model the fate of every vegetation type, but merely the basic physiognomic classes (forest, grassland, wetland). A basic framework of vegetation types and their transitions will be worked out for SNRM that will apply to most military bases and DOE sites. The second type of transition is that resulting from management actions. For SNRM, a complete list of possible (feasible) management actions and their effects will be compiled, along with their costs. Included in this list will be costs for complete rehabilitation actions, such as restoration of a severely eroded hillslope or wetland.

In order to evaluate tradeoffs in land use and conservation, utility functions are needed. First, the utility functions defining the utility of different land cover configurations for various management purposes (e.g., training) are needed. USACERL will help define these

utility functions. Second, costs are included as a function to be minimized. This helps guide the selection of management scenarios away from those that lead to severe site degradation, with their concomitant high rehabilitation costs. Third, utility functions are needed for Legacy program values, such as wildlife habitat and biodiversity. Utility functions for wildlife habitat will be developed based on general classes of wildlife and their responses to habitat factors. Biodiversity at the landscape level will be quantified using the methods of Loehle and Wein (1993). Other Legacy factors such as special habitats and archaeological sites, will be incorporated by giving a high weight to preservation of these fixed map locations during land-use allocation. Finally, it is necessary to incorporate optimization procedures into the SNRM system.

The entire SNRM methodology will be made compatible with military data systems via work performed at USACERL under this proposal. It will be designed to utilize Land Condition Trend Analysis data, fit with ITAM and the goals of the Legacy program, and provide an integrated tool for the land-use considerations portion of the Carrying Capacity Model.

7.6 Additional Project Tasks: 1) Identify approaches for integrating land-based carrying capacity succession models and other relevant tools, models, and systems being developed by USACERL within the overall dynamic landscape modeling components of IDLAMS; 2) investigate the use of advanced remote sensing technologies to provide large-scale, high resolution images for use in the overall dynamic landscape model; 3) examine additional guidelines and approaches used for evaluating biological diversity; 4) further improve the optimization programming/trade-off analysis by examining artificial intelligence-based approaches such as the more conventional approaches.

## 8. Expected Payoff:

The SNRM system will reduce costs, enhance land-use management responsiveness and effectiveness, disencumber military operations, enhance environmental compliance, and reduce conflicts between competing land uses. The system should also be usable at DOE and other federal facilities and for resource management on federal lands. In this way, dual-use technology will be developed with broad applicability to federal agencies.

## 9. Milestones:

1. Program Start	12/94
2. Meeting between ANL & USACERL	01/95
3. Visit DOE/DoD Test Sites	03/95
4. Data Acquisition (Determine data gaps)	05/95
5. Preliminary Data Development	07/95
6. Initial Model Development	09/95
7. Expert Systems Development	09/95
8. Graphical User Interface	09/95
9. Site Visit to Fort McCoy, WI	10/95
10. Fort McCoy Progress Review	11/95

## 10. Transition Plan:

In order to transfer SNRM analytical tools to the military, ANL will arrange a technology transfer with USACERL. SNRM analytical tools are being designed to be compatible with USACERL systems, such as the GRASS GIS package.

## 11. Funding: \$(K)

	FY94	FY95	FY96	FY97	Total
SERDP	863	50	450	430	1793

## 12. Performers:

Work will be performed by ANL and USACERL. Fort Riley and at least one other military installation will be used as test sites. ANL has extensive experience and expertise in environmental assessment, restoration, conservation, environmental compliance, GIS, and software development. Dr. Sundell has extensive experience in biogeographic research, land-use planning and natural resources management, spatial analysis, and environmental assessment, including the management of large projects funded by the U.S. Army. Dr. Loehle has published over 60 peer reviewed papers and 32 technical reports in ecological modeling, statistics, and environmental assessment and has developed sophisticated software systems. Ms. Sydelko administers the Land Resources Analysis Lab for the Energy Systems Division and has done assessment and applied research projects for the military, utilities, and DOE. Ms. Majerus is currently a Principal Investigator on the USACERL-ECS Spatial Analysis and Systems Team working within the Legacy Resource Management Program. She has administered research and development projects utilizing spatial, relational, and temporal data, spatial analysis and GIS (GRASS) technology, relational database management systems, and graphic user-interfaces for integrated natural and cultural resource management and ecological analyses for computer users on Army installations.

## 13. Principal Investigators:

Dr. Ronald Sundell, Dr. Craig Loehle, Ms. Pam Sydelko  
Argonne National Laboratory  
9700 S. Cass Avenue  
Argonne, IL 60439  
PHONE: (708) 252-5341  
FAX: (708) 252-6407  
E-MAIL: ron\_sundell@qmgate.anl.gov

Kim Majerus  
U.S. Army Corps of Engineers  
Construction Engineering Research Laboratories  
Champaign, Illinois 61820  
PHONE: (217) 352-6511  
FAX: (217) 373-7222

**14. Keywords:**

Conservation, Legacy, Wildlife, Habitats, Geographic Information Systems, Ecological Modeling

## SERDP FY95 PROJECT

1. **SERDP Thrust Area:** Conservation
2. **Title:** Assessment and Management of Risks to Biodiversity and Habitat
3. **Agency:** U.S. Environmental Protection Agency
4. **Laboratory:** Environmental Research Laboratory-Corvallis
5. **Project ID:** #241

### 6. **Problem Statement:**

Biodiversity, in the simplest terms, is the variety of life and its processes. Society recognizes a large variety of aesthetic, economic, conservation, and educational values associated with biodiversity. All of these are dependent on the following "first principles." Biodiversity is a manifestation of genetic diversity. It is the primary raw material that is filtered by natural selection, resulting in evolutionary and ecological adaptation of biota to environmental conditions. Minimizing additional loss of biodiversity will provide the best assurance that biota will adapt to the ever increasing rate and spatial extent of environmental change.

Traditionally, the management of biodiversity has focused on rescuing rare, threatened, or endangered species from the brink of extinction. Huge sums have been spent on recovery programs for a small number of species. While there are strong conservation arguments for preserving these species, the effort expended has been out of proportion to the contribution that these species make to the genetic diversity, and therefore the fitness of the biota as whole to adapt to environmental stress.

The first year of this three year applied research project was funded in FY93. The current proposal requests funding for the third and final year of the project. It is part of a comprehensive interagency research effort to develop the technical information and data bases needed to assess and manage risks to biodiversity. The project specifically addresses Conservation Thrust Research and Development Objective #5, "Develop techniques to assess and predict the impact of military use of the areas on the critical elements of the ecosystem impacting biodiversity." Jointly, the Environmental Protection Agency, Department of Defense, US Fish and Wildlife Service, US Geological Survey, USDA Forest Service, and the Nature Conservancy will develop and test a risk-based paradigm for identifying those areas having species assemblages which contribute the greatest genetic diversity to the biota of their biogeographic regions and then managing those areas to sustain biodiversity.

Initially, this research will quantify relative risks to biodiversity in the west coast transect of states (Washington, Oregon, and California) and then evaluate the specific contribution of several high priority DoD installations to biodiversity along this transect. With SERDP funding, special emphasis will be placed on the contribution of DoD facilities to regional



biodiversity in the pilot study areas. This research will be planned jointly with other SERDP funded research at DoD laboratories.

## **7. Project Description:**

This research will develop and test a new, risk-based paradigm for identifying those areas having species assemblages which contribute the greatest genetic diversity to the biota of their biogeographic regions and then managing those areas to sustain biodiversity. The paradigm is implemented in two stages and at two greatly different spatial scales. First, priorities for management action are identified by comparative risk assessment across spatially extensive biogeographic regions. This permits cost-effective targeting of more intensive diagnostic and remediation efforts, allows accurate evaluation of the many species that have extensive geographic distributions, and avoids the pitfall of instituting protection at the local level, only to have cumulative effects of actions in the surrounding landscape undermine these efforts.

Secondly, specific remedial action plans are developed and implemented at a finer spatial scale (i.e., ecological subregions within a state) than the comparative risk assessment. At this scale, landscape level management approaches are needed. Attention will be directed to ameliorating the adverse effects of habitat fragmentation, reducing other forms of anthropogenic stress, restoring habitat, and evaluating the land management tradeoffs required to sustain biodiversity.

This research will initially categorize and map the species diversity and environmental diversity of sampling units (hexagons) based on the Environmental Monitoring and Assessment Program (EMAP) sampling grid covering the conterminous United States. The process will include (1) compilation of The Nature Conservancy's detailed vertebrate species distribution and attribute data for each hexagon, (2) compilation by hexagon of attributes of environmental diversity from remotely sensed land characterization data [AVHRR, TM or MSS based, depending upon results of pilot studies], and (3) analysis of the species and land characterization data by different ecological weighing methods, spatial analyses, multivariate statistical pattern analyses, and protection optimization methods. This information, along with stressor data compiled from existing databases [TIGER; USGS LUDA; USDA-NASS, ERS, NRI, FIA; USDI BLM] will be evaluated and synthesized to quantify relative risks to biodiversity. Overall patterns that lead to high importance and vulnerability of natural landscapes and biodiversity will be identified. Similar, but higher resolution methods will be used to characterize selected DoD installations. At this scale the emphasis is on the interaction between human activities and species habitat relations. Analyses will include spatially explicit evaluation of the causal mechanisms between landscape characteristics and ecosystem vulnerability to landuse practices. Data layers will include, if possible, 1) ecological characterization (terrain, soils, vegetation, rivers, streams, wetlands, lakes) 2) ecological inventory (species, ecological communities, Threatened and Endangered Species population data), and 3) Ecological Risk Characterization (Activity types, infrastructure, toxic releases, roads, anticipated future developments). This data will be used to develop scenarios of alternative futures for ecological systems, given alternative land management practices.

Methods need to be developed to bridge the hierarchy of space and time scales. Models and decision support systems are needed to allow effective transition between regional prioritization and resource allocation for biodiversity protection and local landuse management consistent with regional priorities. This project will evaluate theoretically based, practical approaches for handling these scale transitions.

### **8. Expected Payoff:**

As managers of large areas of land, the DoD must fully evaluate its role in contributing to regional diversity. Benefits will include (1) establishment of baseline conditions concerning species distributions and their relationships with environmental diversity, (2) comparative risk assessment for biodiversity which identifies priorities for attention by the diversity of public and private land managers whose coordinated efforts will be necessary to sustain biodiversity and (3) testing of methods that hold promise for significantly reducing costs of habitat monitoring, evaluation, and management. Potential users will include virtually all land stewardship organizations concerned with the value of natural biotic resources.

### **9. Milestones:**

Although the program's objectives are national in scope, several scientific issues will be addressed initially and resolved in an integrated series of pilot projects. These pilot studies will be completed over a three-year period (FY93-95). With SERDP funding, special emphasis will be placed on the contribution of DoD facilities to regional biodiversity in the pilot study areas. FY93 was devoted to compilation of data bases and development of analytical methods. Data analysis will occur in FY94, with synthesis and final report preparation in FY96.

1.	Select and access first priority DoD installation	04/94
2.	Select and access second priority DoD installation	11/94
3.	Develop Data for Camp Pendleton	11/94
4.	Develop hierarchial conceptual/analytical approach	09/95
5.	Develop Data bases for West Coast Transect (Species occurrences, AVHRR derived Landscape data, Landscape stresses - by EMAP hexagon for Washington, Oregon, and California)	10/95
6.	Complete analysis for West Coast Transect	04/96
7.	Complete analysis for Camp Pendleton	05/96
8.	Test hierarchical planning framework	06/96
9.	Workshops at selected DoD installations	07/96
10.	Product: Final Report	09/96
11.	Workshops at DoD installations (Tech Transfer)	09/96

**10. Transition Plan:**

This three year effort is a portion of an integrated series of pilot studies designed to develop and evaluate methods for a national assessment to be conducted in 1997 and 1998. On completion of the national assessment, it will be possible to objectively assign priorities for biodiversity protection nationwide.

**11. Funding: \$(K)**

	FY93	FY94	FY95
SERDP	1000	1325	100
EPA	500	500	500
TOTAL	1500	1825	600

**12. Performers:**

In recognition that loss of biological diversity can only be effectively addressed through cooperation of vested interests, EPA has formed a biodiversity research consortium to develop the technical information and data bases needed to assess and manage risks to biodiversity. Membership in the consortium includes the US Fish and Wildlife Service, USDA Forest Service, USDI Geological Survey, and The Nature Conservancy, and the Department of Defense. Additional participants are funded through cooperative research agreements, including: University of California - Santa Barbara, University of Maine, Oregon State University, and Harvard University. The Department of Energy, Oak Ridge National Laboratory participates through Interagency Agreement. The project will be coordinated with DoD's Legacy Biodiversity Task Area, as it develops, to maximize complementarity and avoid redundancy. We propose that the Biodiversity Research Consortium focus on database acquisition and analysis and the DoD have the lead role in developing specific recommendations for biodiversity on the installations studied.

**13. Principal Investigator:**

Dr. David A. Mouat  
U.S. EPA Environmental Research Laboratory  
200 SW 35th Street  
Corvallis, Oregon 97333  
PHONE: (503) 754-4330  
FAX: (503) 754-4716  
E-MAIL: mouat@heart.cor.epa.gov

**14. Keywords:**

Biodiversity, Conservation, EMAP, Ecosystem Stress, Endangered Species, Habitat, Landscape Management, DoD Lands, Land Stewardship

## SERDP FY95 PROJECT

1. **SERDP Thrust Area:** Conservation
2. **Title:** Threatened, Endangered, and Sensitive Resources
3. **Agency:** U. S. Army
4. **Laboratory:** Construction Engineering Research Laboratory (CERL)
5. **Project ID:** #507

### 6. **Problem Statement:**

More than 800 species are protected under the Endangered Species Act (ESA); while thousands more are candidates for listing. Many reside on military lands, resulting in: (1) mission constraints and impediments to land acquisition, potentially leading to reduced defense readiness; (2) lengthy and costly litigation; and (3) criminal and civil penalties. As the number of listed species increases, mission constraints and management burden also increase. Our ability to address this issue is limited because of inadequate information on the effects of mission activities on threatened and endangered species (TES) and supporting ecosystems.

The major objectives of the proposed research are to develop and evaluate protocols to generate threshold models of the impacts of smokes, obscurants, and CS agents on TES, and to initiate research leading to threshold models for habitat disturbance. The requirements addressed here are critical subelements of the Army's highest Conservation Pillar R&D requirement (i.e., Impacts of Military Activities on TES) as determined at a recent Army Conservation Pillar user requirements prioritization workshop. (A third subelement of this requirement focuses on noise impacts. This latter topic is addressed under a separate proposal in the Compliance Pillar.)

### 7. **Project Description:**

Our goal is to establish the Army and participating services as national leaders in proactive conservation of TES and the ecosystems upon which they depend as an integral part of our mission. This research will contribute to an overall programmatic effort to provide capabilities to avoid mission impacts while enhancing efforts to cost-effectively meet national, DoD, and Army TES-related conservation goals. It addresses subelements of the Army's highest Conservation Pillar R&D requirement, "Impact of Military Operations on TES."

Technical Objective: Our objective is to continue research initiated under previous SERDP funding to determine the impacts of military-related chemicals on TES, but narrowed to focus exclusively on smoke, obscurants, and CS agents. This work will also initiate studies to develop threshold models of impact on TES due to maneuver and related habitat disturbance.

Technical Approach: There is a clear need to evaluate the impact of mission activities on TES to meet ESA's biological assessment requirements, and as a basis for defining appropriate levels of TES protection. Direct impacts due to training/testing activities on species as well as indirect impacts due to habitat degradation and fragmentation must ultimately be addressed. Practical approaches and techniques will be developed that can be applied at the installations level.

Smokes, Obscurants & CS Agents: A thorough evaluation of existing documentation on the use of S-O&CS; the known and probable impacts of these materials on plants and animals, including an evaluation of materials currently in development; and research protocols currently applied will be completed. Smoke toxicity thresholds will be determined based on existing documentation and selected laboratory studies. We will determine which species are most likely in jeopardy due to exposure to these materials, and which mission activities are most likely constrained significantly as a result of species sensitivities. Up to two species will be selected for study on one or more installations based on a risk assessment evaluation. A conceptual approach to development of threshold models for the impacts of S-O&CS on TES will be developed. Field research protocols developed shall serve as the basis for preliminary field studies on selected species to be conducted under this work. Complete field evaluations beyond preliminary studies are contingent upon follow-on funding.

Habitat Disturbance: Military activities can adversely affect TES by degrading habitats upon which these species depend. These impacts can be either instantaneous, resulting in immediate site abandonment or mortality, as well as cumulative over time, resulting in a slow degradation of TES carrying capacity and species vigor. Species will differ in their response and resilience to such impacts. The first step in evaluating thresholds of response to habitat disturbance will be to identify an exhaustive list of military activities that may affect TES habitats, followed by an evaluation of the probability that these resulting disturbances will affect species of interest. This assessment will be based on types of military activities in practice and how they are conducted during realistic training and testing scenarios. Species will be selected for follow-on studies based on this analysis. A conceptual approach to development of threshold models applicable to habitat disturbance impacts on TES will be developed.

Relationship to DoD/DOE Environmental Objectives: The proposed work supports many of the Departments' goals and objectives as specified in SERDP guidance documents. Specifically, our intent is to: (1) provide capabilities to unencumber military operations while protecting sensitive resources cost-effectively, (2) contribute leadership in addressing a pressing national environmental problem, (3) facilitate information exchange among governmental and nongovernmental agencies and the private sector, (4) avoid duplication of effort among these groups, (5) investigate potential applications of technologies developed for national defense purposes, and (6) encourage joint interagency R&D and demonstration projects.

Relationship to Similar On-going Work: Related FY93-funded SERDP projects include: "Regional Approaches for Managing TES Habitats on DoD Lands," "Propagation, Translocation, and Reestablishment of TES," and "Identification, Assessment, and Mitigation of Impacts of Military-Related Chemicals and Pollutants on TES." On-going research under

the Army's Long Range Science and Technology Program (LRS&T) includes: "Proactive Mitigation and Management of TES on Army Lands," "TES Enhancements to the U.S. Army LCTA Systems Development," and "Inventory and Monitoring Standards for TES on Army Lands." Several additional TES and related projects are funded under DoD's Legacy Resources Management Program. Close coordination will take place with each of the organizations, activities, and projects identified above in order to avoid duplication of effort.

Tri-Service Environmental R&D Strategic Plan: This work is intricately related to DoD Pillar #4, Conservation. The specific thrusts directly addressed is 4.P: Training/Testing Impact Analysis on T/E.

### 8. Expected Payoff:

These efforts will contribute one piece to a comprehensive, systematic, and integrated approach to TES management on military lands. Resulting products will support the Army's environmental and endangered species management strategies, and aide in efficiently meeting Army TES policies and regulatory requirements. Through this effort, the military will develop and demonstrate scientific and technical leadership in the management of TES. We will thus be better able to integrate TES considerations with military activities while avoiding mission impacts. Expected return on investment is high. On-going interagency coordination will yield benefits at national, regional, and local levels. Potential users include Army and other military elements at installation, MACOM, and DA levels who are responsible for TES management. Products will also transition to interagency and private sector partners.

### 9. Milestones:

#### Regional Habitat Strategies

- |     |   |        |
|-----|---|--------|
| 1.  | Scoping Meeting on T&E study                                | 10/94  |
| 2.  | Select species and habitats for evaluation                  | 06/94  |
| 3.  | Define regions based on selected criteria                   | 06/94  |
| 4.  | Conduct background survey on first set of species           | 09/94  |
| 5.  | Submit concept plan and status report                       | 09/94  |
| 6.  | Conduct scoping meeting for phase II studies                | 10/94  |
| 7.  | Publish TR on concept and strategy plan                     | 07/95  |
| 8.  | Assess habitat requirements of selected species             | 08/95  |
| 9.  | Assess potential impacts of military operations             | 08/95  |
| 10. | Complete draft assessment of selected plant communities     | 09/95  |
| 11. | Assess habitat evaluation and monitoring strategies         | 06/96  |
| 12. | Complete additional community abstracts and faunal profiles | *09/96 |
| 13. | Develop management strategies for selected species          | *04/97 |
| 14. | Complete prototype regional guidebook                       | *09/97 |

### Enhancing Survival and Recovery of TES plants

- |     |  |        |
|-----|--|--------|
| 1.  | Literature review and evaluation report on current methods | 09/94  |
| 2.  | Scoping workshop   | 12/94  |
| 3.  | Report on scoping workshop and research plan               | 02/95  |
| 4.  | Preliminary guidance for installations                     | 06/95  |
| 5.  | Begin greenhouse studies                                   | 06/95  |
| 6.  | Comparative evaluation report of various techniques        | 09/95  |
| 7.  | Preliminary report on field and greenhouse studies         | *06/96 |
| 8.  | Continuation of field and greenhouse studies               | *06/96 |
| 9.  | Final guidelines for TES plant enhancement                 | *09/96 |
| 10. | Complete field and greenhouse studies                      | *03/97 |
| 11. | Final report on field and greenhouse studies               | *09/97 |

### Smokes, Obscurants, & CS

- |    |  |        |
|----|--|--------|
| 1. | Complete evaluation of existing documentation regarding impacts of smokes, obscurants & CS (S-O&CS) on TES | 09/94  |
| 2. | Develop list of species most likely to be impacted by S-O&CS; evaluate probable impacts                    | 09/94  |
| 3. | Select species and sites for field studies   | 02/95  |
| 4. | Conceptual models addressing impact of S-O&CS  | 03/95  |
| 5. | Initiate small-scale field evaluations of protocols in preliminary field trials                            | 08/95  |
| 6. | Determine smoke toxicity levels for selected species   | *03/96 |
| 7. | Complete field work  | *09/96 |
| 8. | Report results of field work; recommendations for follow-on studies  | *03/97 |

### TES Regional Workshop

- |    |  |       |
|----|--|-------|
| 1. | Develop workplan for two regional interagency TES workshops (southeast & southwest)    | 06/97 |
| 2. | Develop/finalize agenda in coordination with NBS and USFWS (CERL and WES coordination) | 07/97 |
| 3. | Prepare and distribute workshop announcement   | 08/97 |

\* Completion of these milestones is contingent upon receipt of funds programmed for FY96-97.

### **10. Transition Plan:**

Technology transfer is an essential element of the proposed work. We are committed to developing useful technology from research projects while reaching out to a broad range of potential users. This includes relevant technologies developed by other TES programs, and distribution of transfer products to government, nongovernment, and private sector entities. A TES Technology Transfer Plan will be prepared and coordinated with related military land management programs under separate funding. Coordination will occur via a high degree of

interaction with the user community through user group workshops, periodic newsletters and information bulletins, and eventual use of alpha- and beta-test sites for technology demonstrations.

Several federal agencies presently conduct TES-related research; much of it applicable across agency lines. Mechanisms will be established to share information, and to coordinate TES R&D with appropriate government and nongovernment agencies and other public and private sector organizations. We will avoid duplication of effort, identify opportunities to leverage limited resources to meet common goals, and maximize transfer and use of the best and most advanced technological capabilities available.

**11. Funding: \$(K)**

SERDP	FY94	FY95	FY96	FY97	TOTAL
	805	300	450	210	1765

**12. Performers:**

The work will be conducted primarily by USACERL with assistance from other COE Labs and Army research elements, with an emphasis on leveraging opportunities. Relevant capabilities exist at Waterways Experiment Station, Cold Regions Research and Engineering Lab, Topographic Engineering Center, and Edgewood Research, Development and Engineering Center. Leveraging opportunities will be also be sought with government and nongovernment agencies and the private sector via interagency cooperation efforts.

**13. Principal Investigator:**

Dr. Dave Tazik  
Natural Resources Assessment & Management Division  
USACERL, PO Box 9005  
Champaign, IL, 61826-9005  
PHONE: (217) 373-4420 Extension 606  
FAX: (217) 373-5420  
E-MAIL: D-TAZIK@CECER.ARMY.MIL

**14. Keywords:**

Threatened and Endangered Species, Military Impacts, Smokes, Obscurants, CS Agents, Habitat Disturbance



## SERDP FY95 PROJECT

1. **SERDP Thrust Area:** Conservation
2. **Title:** Integration of Radiotelemetry, Remote Sensing and GIS Technologies for Habitat Use and Delineation in Support of Risk Assessment and Restoration Activities.
3. **Agency:** U.S. Department of Energy
4. **Laboratory:** Savannah River Technology Center (SRTC)
5. **Project ID:** #363

### 6. Problem Statement:

Historically, habitat use and preference has been very difficult to quantify for many types of organisms. For larger animals, these data are generally collected using radiotelemetry, a method where small radio transmitters are attached to the organisms to be studied. The animals are then located using hand-held antennas connected to portable receivers. Locations of the animals are then surveyed or approximated on a map, or the habitat and cover type are simply recorded. This method requires extensive field time and provides very limited data return for time invested. Organisms available for study are also limited to those large enough to carry radio transmitters. Data for small animals can only be collected through extensive field observation. Current technology in miniaturization is lending itself to much smaller radio transmitters, allowing them to be attached to smaller organisms (i.e. bats, small rodents, snakes, and frogs). There is, however still, the problem of data density, or the amount of information obtained per unit of effort. Automated telemetry systems coupled with existing information technologies could greatly enhance the usefulness of radiotelemetry for habitat use data collection.

### 7. Project Description:

The goal of the proposed program is to integrate existing automated radiotelemetry technology with Global Positioning System (GPS), Geographic Information System (GIS)/Heuristic Optimized Processing Systems (HOPS), and land cover information in a way that will increase efficiency, accuracy, and availability of habitat and land cover use data necessary for a variety of ecological activities including:

- waste site characterization
- ecological risk assessment
- performance and success of ecosystem restorations
- habitat use of animal species of concern, such as those listed as threatened or endangered

Technical Objective:

- Refine the existing automated telemetry system with hardware and software upgrades
- Develop software to use data from the automated telemetry system to calculate locations from triangulation
- Interface triangulation locations with GIS layers of habitat types developed from other remote sensing techniques like GPS and over flight data.
- Field test of upgraded equipment within a potential risk assessment area at SRS

Technical Approach: The principle technical approach is to integrate existing hardware previously developed by SRTC with other available remote sensing (GPS) and information management systems (HOPS). This will be accomplished through further development of the existing hardware and its control software and development of interfaces to integrate the telemetry data with GPS and habitat contour information in an accessible package in HOPS. HOPS is a current Office of Technology Development (OTD, project identifier SR1-4-10-17) program at SRS. It is a server-client information system software managing all types of digital information to provide a system that offers a broad array of functions, among those useful for the current project: Data basing without cryptic query languages; frequently used parametric and nonparametric statistics; easy-to-use translators for different data bases and GIS files, spatial analyses of georegistered data. Full scale field research will provide testing and verification of the technical approach.

Tasks:

- Field test of the existing equipment
- Upgrade of existing hardware to increase capabilities and speed
- Development of triangulation/data analysis software
- Development of GIS interface
- Field test of data acquisition portion of project
- Test of integration algorithms and data analysis
- Publication of results

Relationship to DoD/DOE environmental objectives: This program supports the mission and objective of DoD/DOE to be leaders among government agencies in applying modern technology to ecological risk assessment, restoration, remediation, and the preservation and enhancement of biological diversity. Specifically, this program endeavors to apply new approaches to old problems of determining specific habitat preferences and use by animals within limited areas. By better elucidating how organisms interact with their habitat on a small scale, ecologists will be much better able to determine what risks a waste site may pose to the surrounding ecosystem, or what risks training activities may pose to critical species habitats, for example.

Relationship to other similar ongoing work: The proposed project is a considerable expansion of a program initiated during research supporting proposed actions for continued operation of L and P Reactors at SRS. Lotek Engineering, Inc. was commissioned to design and build an automated radiotelemetry tracking system centered around their very advanced SRX400 receiver. The system is capable of monitoring up to 400 different radio frequencies and can provide automatic relocation of transmitters as often as every five minutes. The system was

intended to monitor movements of fish in response to elevating temperatures during start-up of L and P Reactors. This data was to be an important basis for strategies to minimize fish kills during reactor start-up. Unfortunately, the decision to not restart L or P Reactor obviated the need for the system. Upgrading the existing system and integrating it with other remote sensing and information management technologies will allow more accurate and scientifically defensible characterization and evaluation of waste sites for ecological risk assessment.

**8. Expected Payoff:**

Benefits accrued from the development of automated radiotelemetry and its interface with other remote sensing technologies and GIS could be enormous. The development of very powerful desk top computer data management systems (HOPS for example) will simplify sophisticated analysis of habitat use data. Data collected and analyzed with the proposed system is useful and necessary for many compliance related activities like Natural Resource Damage Assessment (NRDA) activities, characterization of waste sites prior to ecological risk assessment, actual effects and vectors in indicator organisms chosen for ecological risk assessment, and recovery of populations and habitat use within restored ecosystems. The capability of the proposed radiotelemetry system will supply data density on habitat use in order of magnitude greater than that possible with current systems. This will reduce the costs of acquiring necessary information and will provide the benefit of allowing collection of data that is not currently possible to accumulate. Parameters like patterns of habitat use, home range, and behavioral use of space are currently difficult to determine but are important considerations in the evaluation of ecological risk. The ability to precisely evaluate these parameters will greatly improve the accuracy of ecological risk assessment activities.

**9. Milestones:**

- |     |   |       |
|-----|---|-------|
| 1.  | Program start   | 06/95 |
| 2.  | Field test of upgraded telemetry system               | 07/95 |
| 3.  | Begin development of HOPS/GIS data handling software  | 07/95 |
| 4.  | Large scale field test of telemetry system            | 10/95 |
| 5.  | Acquire high resolution GPS unit                      | 01/96 |
| 6.  | Finish first prototype of HOPS/GIS software           | 02/96 |
| 7.  | Status report on field tests of telemetry system      | 03/96 |
| 8.  | Complete software development                         | 04/96 |
| 9.  | Plan remote access telemetry upgrades                 | 06/96 |
| 10. | Demonstrate equipment at non-RSR location             | 08/96 |
| 11. | Publish results of initial tests                      | 12/96 |
| 12. | Integrate applicable developments from ERDEC (Seegar) | 02/97 |
| 13. | Long-term (3 month) deployment of system              | 06/97 |
| 14. | Final program report                                  | 12/97 |

## 10. Transition Plan:

Capabilities of the system will be documented and publicized through publication of the results of the field test of the upgraded system and the analysis of the data collected. Transition of the telemetry system itself will be handled by Lotek Engineering, Inc. through their established private sector marketing network. Transition of the data analysis and GIS interface software will be accomplished cooperatively by the contributors to the program with the assistance of the Technology Transfer organization within WSRC.

## 11. Funding: \$(K)

	FY94	FY95	FY96	FY97	TOTAL
SERDP	0	50	100	200	350
DOE/WSRC	25	25	25		75
TOTAL	25	75	125	200	425

Previous funding: Expenditure by SRTC/ESS for development of the original automated equipment, approximately \$125,000.

## 12. Performers:

Currently the only performers involved in the project are SRTC and Lotek Engineering, Inc. There have, however, been contacts from researchers at Pacific Northwest Laboratory (PNL) and The Institute for Wildlife and Environmental Toxicology (TIWET) at Clemson University regarding the development of the data analysis and GIS interface aspects of the proposed project.

## 13. Principal Investigator:

Lynn D. Wike, Ph.D.  
Senior Scientist A, Ecology Group  
Building 773-42A  
Savannah River Technology Center  
Westinghouse Savannah River Company  
Aiken, South Carolina 29802  
PHONE: 803-725-5210  
FAX: 803-725-7673  
E-MAIL: LYNN.WIKE@SRS.GOV

## 14. Keywords:

Radiotelemetry, Remote Sensing, Ecological Risk Assessment, Habitat Use, Geographic Information Systems, Global Positioning System

## SERDP FY95 PROJECT

1. **SERDP Thrust Area:** Conservation
2. **Title:** Fishing Enforcement/Whale Monitoring Using IUSS
3. **Agency:** U.S. Navy
4. **Laboratory:** Space and Naval Warfare Systems Command
5. **Project ID:** #48

### 6. Problem Statement:

The Integrated Undersea Surveillance System (IUSS) provides a unique resource to monitor the population and movements of several endangered marine mammals -- specifically, the great whales. In no other way can these movements be monitored over the scale of an ocean basin. Exploitation of this resource is vital in complying with the National Environmental Policy Act (NEPA), the Endangered Species Act (ESA), and the Marine Mammals Protection Act (MMPA).

Present utilization of the IUSS to detect and classify marine mammals (and drift net vessels) is a personnel-intensive effort. Projected downsizing will reduce the operational personnel currently monitoring IUSS fixed arrays on a 24-hour basis. One important component of this effort will be to automate the detection and classification processes using neural network signal processing techniques.

Additionally, many of the world's principal fisheries have collapsed or are collapsing. Mitigation measures appear ineffectual, and numerous fishery closures are being considered and/or pursued; some are already in place. Importantly, effective fishery closures require enforcement options, which themselves require some sort of surveillance mechanism. To be successful, any surveillance system must be able to monitor large areas, and must be able to detect, track, and discriminate among fishing vessels.

When this project was presented to the SAB in April, 1994, the Chairman commented that this "was precisely the kind of project Senator Nunn had in mind when he created SERDP." Other panel members were uniformly supportive of the effort.

### 7. Project Description:

The goal of this effort is to continue to apply capabilities of the U.S. Navy Integrated Undersea Surveillance System (IUSS) to support the High Seas Driftnet Fisheries Act (PL102-582) and other national treaty and maritime law enforcement requirements, and to monitor various species of marine mammals to contribute towards conservation and regulations compliance. This work explicitly supports the SERDP Goal to "help solve significant...environmental problems through the application of (DoD's) technical

capabilities...", several SERDP Objectives, all four SERDP Strategy Statements, and Conservation Pillar R&D Objectives 1,3, and 5.

This project will build on the substantial success of the past year and will further enhance the methodologies to exploit the IUSS in support of a variety of national objectives. The Navy demonstration project "WHALES '93" paved the way for the first objective, quantitative analysis of whale populations and migratory movements. Other agencies, particularly NOAA, have become convinced of the need to further the results of that effort in order to refine these capabilities into operational tools. The objectives and work of this proposal have been coordinated with SERDP proposals submitted by NOAA and are complimentary to that proposed work.

This project will focus on four main fronts: (1) a major experimental effort on whales in the Pacific Ocean; (2) accelerating the development of neural net processors; (3) enhancing the interface between the IUSS and potential users; and (4) initiating the surveillance/fishing enforcement task.

On the first objective, the goal is to identify the migratory path(s) of humpback whales (*Megaptera novaeangliae*) in the northeastern Pacific Ocean. The whales are generally known to migrate between feeding grounds along the Pacific coast of North America (SE Alaska to northern California) to breeding grounds off Mexico and Hawaii. (The Hawaiian breeding grounds will be the focus of this effort.) Humpback whales migrate south to the breeding grounds during the fall (Sep-Dec) and return north in the spring (Mar-Jun). During the first round-trip migration, the project will focus on perfecting capabilities using only a few of the fixed arrays. During the second migration, the effort will focus on perfecting the techniques for localization and tracking, and to concentrate on areas of special interest revealed during the first migration. This experiment will be carried out by NRaD Code 51 and will make primary use of the fixed arrays, but will also request the use of mobile IUSS assets (i.e., SURTASS) on a not-to-interfere basis. At both ends of the migratory path there are well-established programs of study (University of West Oahu, Dr. J. Mobely, PI; NOAA National Marine Mammal Laboratory, Dr. M. Dahlheim, PI). These will enable us to link IUSS data to the types of data that have traditionally been gathered by shore-based programs of study.

On the second objective, work on neural network signal processing technology will be enhanced by other work on an improved IUSS beamformer that would give constant beamwidth coverage over the bandwidth of interest, and an improved coherent interarray processing (IAP) capability that will allow more precise localization of specific activities of interest. All of these individual capabilities have been partially developed in a somewhat different form for military applications. The neural network processing capability already exists in a form that could be readily adapted to the marine mammal problem. The design of an improved constant-mainlobe adaptive beamformer has essentially been designed under another effort. The coherent interarray processor (IAP) requires software upgrades that would allow it to work more effectively against the broadband transient signal types which represent most whale vocalizations. The target site for the proposed demonstration will be the Naval Facility (NAVFAC) at Whidbey Island, WA.

For the third objective, full use will be made of the Dual Use Analysis Center (DUAC) which has been built at the Naval Research Laboratory. The DUAC, a secure facility, was created to establish a link between the researcher and the day-to-day operations of the IUSS, with initial emphasis on data acquired during the WHALES '93 Experiment. Initially, significant hardware needs of the DUAC will be met so that the enormous data sets of WHALES '93 can be effectively archived and processed. Then, a system-wide data archiving capability will be developed; i.e., a system that "records everything", as requested by the Environmental Task Force. In the final years of this project, prototype communications links will be established at the DUAC so that users can access IUSS information in an unclassified setting.

For the fourth objective, the IUSS network includes hydrophonic arrays located throughout the major ocean basins that are well placed to monitor large areas and to detect, track, and discriminate among fishing vessels. These arrays can monitor very large areas efficiently with minimal personnel. Further, the system provides "enduring" surveillance, as opposed to intermittent "fixes" or "glimpses." Finally, the system can discern the acoustic signatures of machinery -- like that required to pull in large drift nets -- and record and describe what a target vessel is doing or has done over a specific time period. This project objective includes development of advanced signal processing capabilities and support of several experiments: (1) a series of experiments assessing coverage of Georges Bank, and (2) a drift net surveillance experiment at NAVFAC Whidbey Island.

This proposal addresses several requirements identified in the Tri-Service Environmental Quality R&D Strategic Plan under Conservation Thrusts 4P (Training/Testing Impact Analysis on T/E) and 4Q ((T/E Species Management, Propagation, and Recovery).

## **8. Expected Payoff:**

The benefits of this project come in two main areas. The first is through gains in our understanding of an endangered species with a large range. If the humpback whale's movements and the timing of those movements are known more precisely, the Navy and other users of the range shared with the humpback can plan their activities to minimize impacts on the whales. The development of the automated methods for whale tracking will be of particular value to NOAA and other agencies tasked with protection and management of endangered species. Second, this project will enable the opening up of an ocean-wide network of sensors that is otherwise unattainable by the research community. A primary deliverable of this effort is a user-friendly "portal" to Navy's undersea surveillance system. In a time where "big science" costs are being closely scrutinized, it is particularly attractive to consider access to a system which is already paid for.

## **9. Milestones:**

- |    |  |       |
|----|--|-------|
| 1. | Final Report NMFS SW Fisheries FY 93 MM Survey | 02/94 |
| 2. | Navy Ship Shock trials off Southern California | 04/94 |
| 3. | SURVEYOR ground-truth experiment, NE PAC       | 07/94 |
| 4. | Completed PODS 93 Test Report                  | 07/94 |
| 5. | Final Report, WHALES '93                       | 09/94 |

6.	Final Report, North Pacific Driftnet Experiment	09/94
7.	OREGON II marine mammal cruise/Caribbean	02/95
8.	Workshop to merge Atlantic/Pacific methods	02/95
9.	Monitor humpback whale activity off Hawaii	03/95
10.	Support ATOC California Project playbacks	05/95
11.	Neural net simulation testing	07/95
12.	First NE Pacific ground-truth experiment	09/95
13.	Complete data distribution architecture	09/95
14.	Complete hardware/software installation at DUAC for IUSS data management	10/95
15.	Final report, whale population estimation using automated long-term statistical monitoring	10/96
16.	Complete modification to Inter-Array Processor	02/97
17.	Final Pacific Whale Test	02/97
18.	Final Report, IUSS marine mammal population estimation	10/97
19.	Establish near-real-time communication link for data distribution	08/98

**10. Transition Plan:**

A close working relationship has been established with NOAA, which would be the primary beneficiary of many of the results gained here. A Memorandum of Agreement has been signed by NOAA and Navy on cooperation on environmental issues, and will serve as the umbrella MOA for further agreements which arise from cooperation in this area. In addition to the benefits highlighted with marine mammals (supporting NEPA, ESA and MMPA), the IUSS network will provide the means to monitor fishing activity (in support of national programs and international treaties), mid-ocean seismic and volcanic activity and acoustic tomography studies (in support of global warming studies).

**11. Funding: \$(K)**

FY94	FY95	FY96	FY97	FY98	TOTAL
3000	1625	2000	2500	1000	10125

**12. Performers:**

A. Humpback Migration Task: Naval Research and Development Center (NRaD), Commander, Undersea Surveillance Pacific (CUSP), Lawrence Livermore National Laboratory, NOAA Southwest Fisheries Center, NOAA Marine Mammal Laboratory, NOAA Pacific Marine Environmental Laboratory, University of West Oahu, Woods Hole Oceanographic Institution.

B. Signal Processing Task: Naval Research and Development Center (NRaD), ORINCON Corp., ENSCO Inc.

C. IUSS Interface Task: Naval Research Laboratory, MITRE, MAI, Cornell University.



### **13. Principal Investigators:**

Dr. Dennis M. Conlon, Chief Oceanographer  
Integrated Undersea Surveillance Program (PMW182-OC)  
Space and Naval Warfare Systems Command  
2451 Crystal Drive  
Arlington, VA 22245-5200  
PHONE: (703) 602-1021  
FAX: (703) 602-0123  
E-MAIL: dennis\_conlon@smtp-gw.spawar.navy.mil

The task on humpback whale migration will be managed by:

Dr. Robert Gisiner  
NCCOSC RDT&E Division, Code 511  
49650 Acoustic Rd, Bldg. 112  
San Diego, CA 92152-6250  
PHONE: (619) 553-5592  
FAX: (619) 553-5691

### **14. Keywords:**

IUSS, Acoustics, Whales, Neural Networks, Fisheries, Migration

## SERDP FY95 PROJECT

1. **SERDP Thrust Area:** Conservation
2. **Title:** The Effects of Aircraft Overflights on Birds of Prey
3. **Agency:** U.S. Air Force
4. **Laboratory:** Armstrong Laboratory (AL)
5. **Project ID:** #89

### 6. Problem Statement:

The Air Force is required to assess the impact of proposed aircraft operations on the environment. Many of the assessments accomplished to date contain unsubstantiated remarks concerning the effects of aircraft noise on wildlife. Prior to 1989, noise studies on wildlife were not well controlled or planned. In 1989 the Air Force began performing several 3-4 year studies on the effects of aircraft noise on wildlife species. These studies are beginning to prove useful for environmental planners at the major command and Air Staff level to defend the Air Force's requirements to maintain low altitude Military Training Routes (MTR).

Due to issues raised during public scoping meetings and documented concerns with the US Fish and Wildlife Service (USFWS) and the National Park Service (NPS), there is concern that aircraft overflights may disturb nesting raptors. The Air Force embarked on a project in 1989 to review the current literature regarding the effects and, if feasible, to develop an interim model to predict the effects. The interim model was documented in 1990. Since the model is purely hypothetical, it must be validated with empirical data.

### 7. Project Description:

The goal of this project is to verify predictions of a previous 6.3A effort regarding the effects of aircraft noise on birds of prey or raptors (hawks, eagles, falcons, etc.) and to fill in the technological gaps in the interim model.

The technical objective of this project is to develop a validated dose-response model on the effects of aircraft overflights on birds of prey. The technical approach to accomplish the objective will be to perform field studies on species of interest in an attempt to validate the current model.

Several tasks will accomplish this objective. Task 1, a study protocol will be developed in cooperation with the USFWS to perform valid field studies to detect differences of 5-30% productivity rates in spite of large variances in nest success. The study design will take into account such factors as habituation rates, prey abundance, and changes in parental behavior

that could affect productivity. This first task will examine possible study locations and make a recommendation for the best sites near an Air Force installation to perform such a study.

Task 2 will be designed to make observations of aircraft overflights in the vicinity of nesting raptors. This task should be performed over a two year period as a minimum to determine the effects of noise on productivity.

Task 3 would attempt to address the effects of aircraft overflight noise on threatened or endangered raptor species, such as Peregrine Falcons and Bald Eagles. This task would form a subset of data obtained from Task 2 where nonthreatened and nonendangered species would be studied.

Task 4 will involve making changes to the current dose-response model and inserting the improved model into the latest version of the Assessment System for Aircraft Noise (ASAN). ASAN is a software tool to assist environmental planners assess the impact of aircraft operations on the environment.

This project directly contributes to the objectives identified in the Tri-Service Environmental R&D Strategic Plan, Pillar 4: Conservation; Requirement Thrust 4.K: Sensitive Ecosystem Management and 4.P: Training/Testing Impact Analysis on T/E.

## **8. Expected Payoff:**

The Air Force will benefit by having a validated model to assess the impact of aircraft noise on raptors. This will greatly assist environmental planners in developing timely EIAP documents and providing answers to questions raised by the general public, USFWS, and NPS. Currently, the USFWS can and has stopped proposed actions with formal Section 7 consultations in accordance with the Endangered Species Act. The goal of this project would be to reduce the concerns raised during these formal consultations and speed up the EIAP.

## **9. Milestones:**

1.	Literature review/dose-response model exam	07/94
2.	Research protocol and recommended study sites	07/94
3.	Progress report	10/94
4.	Deliver 2ANM prototypes for testing	12/94
5.	Recruit Graduate student (Task 2&3)	01/95
6.	Obtain all field equipment	04/95
7.	Identify all nest sites to be observed/monitored for productivity	06/95
8.	Perform test flights	08/95
9.	Progress report	12/95

**10. Transition Plan:**

The dose-response model resulting from this effort would replace the current interim model in ASAN. ASAN is scheduled to begin transition in FY94. Since ASAN will accept various effects modules, there will be no risk in changing these two models.

It will be necessary to coordinate aircraft overflights with the nearest operating command to the study site. Since several previous studies similar to this proposal have been accomplished, these procedures are well known.

**11. Funding: \$(K)**

	FY93	FY94	FY95	FY96	FY97	TOTAL
SERDP	80	311	80	350	330	1151

**12. Performers:**

The Air Force Armstrong Laboratory will be the principal agency performing this work with support from the Air Force: AL/OEBN and 11th AF/DOO and 11th AF/LGV. Additionally, the Alaska Fish and Wildlife Cooperative Unit and the University of Alaska along with Alaska Biological Research, Inc. will also participate in this research.

**13. Principal Investigator:**

Capt Michael Carter  
AL/OEBN  
Wright-Patterson AFB, OH 45433-7901  
PHONE: (513) 255-3675  
FAX: (513) 476-7680  
E-MAIL: MCC@OSPREY.AL.WPAFB.MIL

**14. Keywords:**

Raptors, Birds of Prey, Aircraft Noise, Disturbance

## SERDP FY95 PROJECT

1. **SERDP Thrust Area:** Conservation
2. **Title:** Genetic Diversity Monitoring in Plants and Wildlife
3. **Agency:** U.S. Environmental Protection Agency
4. **Laboratory:** Environmental Monitoring Systems Laboratory, Cincinnati, Ohio
5. **Project ID:** #246

### 6. **Problem Statement:**

Undisturbed natural populations tend to maintain a high degree of biological diversity or polymorphism, but any environmental stress that eliminates a large fraction of individuals from the breeding population can eliminate (by pure chance) important genetic variants. This phenomenon, known as a genetic "bottleneck", leads to a reduction of heterozygosity in succeeding generations. The overall effect is populations with greater vulnerability to future stresses. Therefore, quantitative measures of genetic diversity can be useful as indicators of past environmental insult, as well as criteria for targeting potentially sensitive, i.e., genetically homogeneous populations.

Measurement of population genetic diversity directly supports the SERDP Conservation thrust area as an assessment tool to identify vulnerable populations and subpopulations of many species of animals and plants, and to monitor their responses to ongoing conservation and protection efforts. This project has both basic research and applied research components. Enhancement of fingerprinting technologies and statistical evaluations will continue, especially as new species are examined. Once the analytical strategy for a species or genus is established, it will be applied to a myriad of situations confronting member populations. This proposal is for continuation and enhancement of the efforts to develop fingerprinting technologies as genetic diversity measures currently underway in this laboratory with SERDP support.

### 7. **Project Description:**

Goal: The goal of this project is to monitor the genetic diversity of feral populations in ecologically sensitive areas using DNA fingerprinting technologies. Loss of diversity resulting from habitat destruction and pollution is a major concern in wildlife populations. The genetic diversity or total gene ensemble of a population reflects its intrinsic robustness. Loss of genetic diversity leaves a species less able to adapt to new environmental stressors; therefore, loss of population genetic diversity can foreshadow species loss, with resultant loss of biological diversity within an ecosystem.

Technical Objectives: The technique of DNA fingerprinting is being widely used to determine the identity and relatedness of individuals (particularly humans), and is also

attracting attention as a tool for assessment of genetic variations within and between populations. Genetic distinctions between individuals will be demonstrated by analyzing unique differences in DNA, even in species that are otherwise genetically uncharacterized. The summation of DNA fingerprint differences of many individuals will provide a measure of genetic diversity in the population from which those individuals are derived.

Technical Approach: In this laboratory, we are currently adapting two different, but complementary, fingerprinting techniques for use in several species of fish and terrestrial animals. The first method relies on the presence of short repetitive DNA sequences interspersed throughout the genomes of most organisms. These DNA sequences, called VNTRs (variable number of tandem repeats), exhibit high variability within a population. Bands visualized on a Southern blot of target genomic DNA, using radiolabeled probes specific to the repeat sequence, are the genetic identity of an individual. Comparison of the banding patterns among individuals from a population yields a measure of genetic variation within that population. Comparisons across populations yield measures of relative genetic variation and also of the degree of genetic relatedness of the populations. This method is being applied to a test sample of DNAs purified from more than seventy individual brown bullhead catfish representing three populations from both environmentally impacted and clean areas.

The second fingerprint method is based on thermal cycle polymerase chain reaction (PCR). In this procedure, DNA marker bands are biochemically multiplied by a cyclical enzymatic reaction with target DNA. This amplification process occurs when synthetic 10-base DNA molecules, used in the reaction, match exactly with regions in the DNA of interest. This is termed DAF, or DNA Amplification Fingerprinting. DAF reactions, for each of 400 commercially available synthetic 10-base molecules, yield several distinct bands or amplification products - depending on the species surveyed. These products ( $\leq 5,000$  base pairs) from PCR reactions are visually analyzed by gel electrophoresis in agarose or polyacrylamide. Genomic DNA from two individuals within a species often produce disparate amplification banding patterns. A particular DNA band which is generated from the genome of one individual, but absent in a second individual, represents a polymorphism which can serve as a genetic marker. These markers, presumed to be allelic, are inherited in a Mendelian fashion. By statistically analyzing the segregation of these markers among the progeny of a sexual cross, or individual members of a population, genetic maps and indices of heterozygosity of virtually any species can be assembled.

Also, we have developed an ecologically based method of tissue/DNA acquisition for direct use in DNA Amplification Fingerprint reactions. This simple and rapid technique, which is non-intrusive to terrestrial and aquatic animals, obviates the need for radionuclides and isolation, purification, and quantitation of genomic DNA for thermal cycle amplification reactions. This method combines the powerful tools of genetic analysis with an ecologically favorable means of sample acquisition. The strategy is particularly useful when collecting field specimens for population or forensic analysis, or species verification on field specimens and endangered species.

Using the raw fingerprint data from both of these methods, several mathematical treatments for assessing DNA fingerprint diversity are being examined and compared in order to

determine the best statistically valid approach. This part of the effort is being done in conjunction with Dr. Vicki Hertzberg with a Cooperative Agreement funded by SERDP.

Since methods of DNA fingerprinting are under continuous and rapid advancement within the scientific community, we are requesting continuing SERDP support for development of the most efficacious system for each new species to which population genetic diversity measures are applied. Most particularly, we will be expanding our efforts to examine plant population genetics. We intend to use an expanding battery of VNTR probes, such as PCR generated synthetic tandem repeat (STR) probes. We intend to adapt the new non-isotopic probe labeling techniques for use with our fingerprinting methods, which would avoid the use of radioisotopes, thus providing the advantages of standardization due to a long probe shelf-life and portability of methods to laboratories not equipped for radioisotopes usage.

We also will require continuous statistical support in order to tabulate and analyze data generated as each new population and species is examined and to continue to develop and refine the statistical methods required. Each new species will present not only a unique set of banding patterns to be analyzed, but these analyses will also need to take into account characteristic higher-order population dynamics, most notably differences in breeding strategies.

We expect ever-increasing liaison with field ecologists who are experienced with and possess detailed knowledge of each relevant population. When appropriate, these interactions will be formalized as cooperative agreements. This will provide detailed expertise and assistance in field sample collection.

These fingerprint measures of population genetic diversity will directly support the conservation efforts of DoD/DOE by providing assessment tools for monitoring, protecting, and rehabilitating natural ecosystems.

**8. Expected Payoff:**

This method will provide a rapid, non-invasive, and cost effective monitoring method in the form of an assessment of population genetic robustness for virtually any species, animal or plant, aquatic or terrestrial. It is anticipated that it can be modified into a commercially available, field usable tool and marketed via a CRADA.

**9. Milestones:**

1. Validation of Methods: Comparison of fingerprint patterns from inbred and outbred populations of known pedigree. Development of methods for statistical comparison. Test and apply methods with inbred hatchery brown bullheads. Explore methods for plants. 12/94
2. Validation: Comparison of fingerprints of terrestrial plants and animals of known pedigree with those of random field collected individuals of the same species. Continued development and application of statistical methods. 09/95

- |    |   |         |
|----|---|---------|
| 3. | Application of developed methods to field situations. | FY96-97 |
| 4. | Publication of field data.                            | 09/97   |

**10. Transition Plan:**

We anticipate the development of a set of user-friendly, standard field methods for monitoring population robustness that could be transferred to the individual end user or to centralized facilities which would run service samples for the end users. We expect these methods to be potentially marketable via a CRADA.

**11. Funding: \$(K)**

FY93	FY94	FY95	FY96	FY97	TOTAL
200	200	0	190	200	790

**12. Performers:**

U.S. Environmental Protection Agency, Environmental Monitoring Systems Laboratory - Cincinnati, Ecological Monitoring Research Division, Annette C. Roth, Ph.D.; Oak Ridge Institute for Science/Education by Interagency Agreement, David L. Lattier, Ph.D.; Department of Environmental Health, University of Cincinnati, by Cooperative Agreement, Vicki Hertzberg, Ph.D. (Statistical Methods) to be named: by Cooperative Agreement, to explore plant DNA fingerprinting; Biomedical Research and Development Laboratory, Ft. Detrick Department of Army, Dr. Hank Gardner.

**13. Principal Investigator:**

Dr. M. Kate Smith  
 USEPA  
 Ecological Monitoring Research Division  
 Environmental Monitoring Systems Laboratory  
 26 West Martin Luther King Drive  
 Cincinnati, OH 45268  
 PHONE: (513) 569-7577  
 FAX: (513) 569-7609  
 E-MAIL: SMITH.K@EPAMAIL.EPA.GOV

**14. Keywords:**

DNA Fingerprinting, Ecological Monitoring, Genetic Diversity Measures, Heterozygosity Indices, Polymorphism, Population Genetics



## SERDP FY95 PROJECT

1. **SERDP Thrust Area:** Conservation
2. **Title:** Ecological Biomarkers: Monitoring Wild Fauna at DoD Installations (Systemic, genetic, immune and reproductive toxicity evaluation of munitions-impacted terrestrial and aquatic fauna)
3. **Agency:** U.S. Environmental Protection Agency
4. **Laboratory:** Environmental Monitoring Systems Laboratory, Cincinnati, Ohio
5. **Project ID:** #244

### 26. Problem Statement:

The DoD has concerns about the potential ecological consequences associated with soil and water contamination by explosives, and the intermediates and by-products of explosives resulting from the synthesis and degradation of these materials. Munitions products, e.g., hexahydro-1,3,5,2-trinitro-1,3,5-triazine (RDX); octahydro-1,3,5,7-tetranitro,1,3,5,7-tetrazocine (HMX), 2,4,6-trinitrotoluene (TNT) and by-products (e.g., dinitrotoluenes, trinitrobenzene and dinitrobenzene) are frequent contaminants at DoD facilities. They are degraded by microorganisms under anaerobic conditions to numerous by-products; however, the short and long term effects of exposure to these materials on ecological resources are unknown, and data establishing the impacts (or indicating absence of impact) are generally not available. For this reason, DoD is often unable to conduct scientifically defensible, risk-based assessments of the potential impacts imparted by this class of ubiquitous chemicals to feral species and native plants in the vicinity of the affected installations.

This project will assist DoD in developing a quantitative data base for ecological assessments. This project will develop biochemical markers of exposure and effect on widely distributed and ecologically important species. These biomarker data will be evaluated, and the changes will be correlated with existing ecological resources in impacted and reference sites. The results will be used in a diagnostic mode to assess the impacts of the munitions contaminants, to prove or disprove the cause-effect relationships, and to guide cleanup and restoration activities. In conformity to processes presented in the EPA's *Framework for Ecological Risk Assessment*, the project effort will emphasize the definition of assessment and measurement endpoints, their interrelationships, and the characterization of risk across various levels of ecological organization.

## 7. Project Description:

Goal: 1) To apply biomarkers (physiological, biochemical and molecular changes in wild fauna), as tools to assess and monitor impacts of defense-associated chemical production and applications, (e.g. munitions manufacturing, open detonation and open burning, decommissioning and de-arming chemical agents, fuel refining and storage, machine degreasing wastes, and chemical by-products) on sensitive aquatic and terrestrial fauna at selected DoD facilities; and 2) to establish patterns of biomarker changes, via comparative studies of native fauna in contaminated and reference sites, that are useful for demonstrating the probability of ecosystem-level impacts from these materials.

Previous Efforts/Accomplishments: The scientific staff at the U.S. EPA Ecological Monitoring Research Division (EMRD), Environmental Monitoring Systems Laboratory (EMSL), have extensive training, hands-on experience, and expertise in the areas of research that are required to carry out the proposed project successfully. They have a continuous record of peer reviewed publication in research on biomarkers. Currently, EMRD has an interagency agreement with U.S. Army Biomedical Research and Development Laboratory, Fort Detrick, MD to conduct studies on the adduction of nitroaromatic compounds with blood proteins and DNA as biomarkers of exposure. Likewise, EMRD has developed and field tested sets of biomarkers in feral fish for the assessment of exposure and effects of industrial contaminants.

Experimental Overview: This project will: 1) apply and validate, using previously established technology and expertise, an integrated matrix of biomarker endpoints for assessing exposure and effects of munitions-related contamination under laboratory and field settings, and 2) evaluate the utility of this biomarker matrix as a tool to provide DoD with advanced assessments of munitions-related contamination at various ecosystem levels.

Technical Approach: 1) Site selection will be focused on those munitions-contaminated installation(s) which are located in strategic proximity to ecologically appropriate reference site(s). 2) The contaminated and reference sites will be inventoried and lists of ecological assets will be compiled. Suitable measurement endpoints will be selected on the basis of the biomarker methods available and on the ecological resources to be monitored. 3) The biomarker profiles of selected wildlife will be compared in the contaminated and impacted sites and referenced against the status of the ecological assets. 4) Biomarkers that appear useful as predictive of ecosystem impacts will be identified for future assessments at other DoD facilities.

Laboratory studies necessary to support the verification of field results will accompany the field studies. Examples of specific endpoints which can currently be utilized in these biomarker studies include:

- Biochemical Toxicology (e.g., quantitation of DNA and blood protein adducts, bile metabolites, and speciation of altered heme synthesis intermediates (porphyrins) as biomarkers of exposure to selected chemical classes; application of cDNA probes for detection of gene expression (e.g., cytochrome P450Ia1), utilization of hepatic

microsomal enzyme activities indicative of xenobiotic induction. (EROD, AHH, Glutathione))

- Molecular Histopathology (e.g., optical and electron micrography, in combination with computer-assisted image analysis and immunobased, pathology specific histochemistry).
- Molecular Biology (e.g., the detection of genotype distributions within a population and losses of genetic diversity via polymerase chain reaction technology for DNA finger printing and electrophoretic allozyme frequency analysis).
- Cellular and Organ Immunotoxicology (e.g., quantitative measure of phagocytosis and immune suppression, characterization and quantitation of oxidative burst capacity in phagocytic cells via laser activated fluorescence flow cytometry and cell sorting).
- Reproductive Toxicology (e.g., computer assisted sperm motion analysis and flow cytometric characterization of spermatogenesis, sex hormone patterns, gonadal pathology, and developmental anomalies).

Unique Assets Offered: The Ecological Monitoring Research Division (EMRD) of the U.S. Environmental Protection Agency offers the following assets and capabilities: 1) A highly qualified research staff including 14 Ph.D. level scientists (degrees in ecology, toxicology, biochemistry and molecular biology) with substantial records of peer-reviewed publication. 2) State-of-art laboratory instrumentation as well as significant and proven experience in field sampling, sample preservation, transport and logistics. 3) A modern, accredited animal research facility uniquely equipped and a staff experienced in handling animal husbandry for a variety of terrestrial and aquatic species. The Division has developed breeding colonies of terrestrial (field mice, voles, and shrews, invertebrates, and plants), and aquatic (fish, tadpoles, invertebrates and plants) organisms. 4) A fully staffed aquatic research facility with a wide range of aquatic ecotoxicological and bioassessment capabilities.

Innovative Elements: This research is innovative in that traditionally, biologically derived information about ecological impacts have been limited to traditional evaluations of community structure and the direct measurement of tissue residues. Biological markers provide predictive and diagnostic information not only to detect exposure, but also to detect early effects of these exposures and to identify causes. Biomarkers can focus efforts where they are most needed for the protection of wildlife; e.g., on contaminants that are biologically available, which bioaccumulate, and which are biologically active (e.g., toxic).

Relationship to DoD Environmental Objectives: This project will directly support the Conservation Strategy by providing quantitative indicators of the health status of the impacted fauna, leading to enhanced ecological risk assessment. The DoD is in the process of establishing the toxicological and ecological data base for determining the potential environmental effects of munitions chemicals that have been discharged in the environment over years. Technical Issues to Overcome: 1) The selection of appropriate site(s), and coordination with other research organizations dealing with the site studied, 2) the selection, from appropriate existing or new biomarkers, those most appropriate for detection and assessment of exposure to munitions compounds, and 3) development of systematic methods for using biomarker data to assess and predict ecosystem impacts.

## 8. Expected Payoff:

The project will provide five major benefits to DoD: 1) It will provide a quantitative means to prove or disprove cause-effect relationships between munitions byproducts contamination and ecological effects. 2) It will provide baseline data to assess the ecological impact of munitions activities, thus assisting in planning remedial intervention. 3) In terms of impact, (cost/time/efficiency/capability) it will provide means of documenting the cost effectiveness of ecological interventions. 4) It offers the possibility of significant improvements in the timeliness of the ecological assessment process. 5) It will assist in evaluating/reestablishing genetic and biodiversity particularly of sensitive and endangered species at impacted area.

## 9. Milestones:

- |    |  |              |
|----|--|--------------|
| 1. | Commence data collection on initial studies both in EPA (i.e., biomarker development/validation) and with out-of house collaborators   | 10/94        |
| 2. | Initiate program identify contaminants of ecological concern in order to set priorities for biomarker development  | 10/94        |
| 3. | Initiate a process with DoD and others to identify potential field and reference site(s)   | 10/94        |
| 4. | Initiate demonstration level pilot studies for field collection of animal/blood/tissue samples and initiate pilot laboratory support analysis as appropriate for field samples | 4/95 to 8/95 |
| 5. | Initiate studies in data analysis; including data reduction and statistical analysis, approaches utilize biomarker data in ecological risk assessment                          | 9/95         |

## 10. Transition Plan:

DoD/DOE has assisted in the selection of priority site(s) for the study and for the chemical characterization of contaminating agent(s) via a survey of prior DoD/DOE-funded and completed descriptive and analytical efforts. The target species will be identified in the impacted ecological community, and a control population will be identified at appropriate reference site(s). The testing chronology will be defined and coordinated with restoration activities. Biomarker matrix endpoints will be identified based on expected site impacts and via experience with previous industrial studies. In start-up phase validation of the sampling strategy, validation of assays, establishment of baseline reference ranges and quality assurance measures will be verified and reported to DoD. In the initial comparative phase the sampling, assay data collection, and comparative analysis of impacted versus reference sites will be conducted and reported to DoD and the feedback will drive corrective action(s) in conformance with quality assurance standards. Finally, the evaluation phase will cover statistical analysis, peer review and preparation of a final report to DoD.

All of the above phases will require close consultation and coordination with DoD personnel in charge of the sites studied. Such communications will be both verbal and written.

**11. Funding: \$(K)**

	FY93	FY94	FY95	FY96	FY97	FY98	TOTAL
SERDP	900	800	0	400	0	0	2100
USEPA	--	100	200	200	200	200	900

**12. Performers:**

Ecological Monitoring Research Division (EMRD), Environmental Monitoring Research Laboratory (EMSL), U.S. Environmental Protection Agency, 26 West Martin Luther King Drive, Cincinnati, OH 45268; U.S. Army Environmental Hygiene Agency, Aberdeen Proving Ground, MD 21010; U.S. Army Research Development and Engineering Center, Aberdeen Proving Ground, MD 21010.

**13. Principal Investigator:**

F.B. Daniel, PhD. Director,  
Ecological Monitoring Research Division  
26 W. Martin Luther King Drive  
Cincinnati, OH 45268  
PHONE: (513) 569-7401  
FAX: (513) 569-7609  
E-MAIL: DANIEL.B@EPAMAIL.GOV

**14. Keywords:**

2

Ecological Biomarkers, Ecological Risk Assessment, Exposure/Effects Assessment, Munitions, Site Assessment, Wildlife Protection

## SERDP FY95 PROJECT

1. **SERDP Thrust Area:** Conservation
2. **Title:** Ecological Modeling for Military Land Use Decision Support [FY94 title: Strategy for Resource Management on DoD/DOE Lands Combined with decision Support for Disturbed Ecosystem]
3. **Agency:** U.S. Department of Energy
4. **Laboratory:** Oak Ridge National Laboratory (ORNL)
5. **Project ID:** #758
6. **Problem Statement:**

U.S. Department of Defense (DoD) and U.S. Department of Energy (DOE) lands are subjected to a wide variety of uses ranging from military training to hazardous waste disposal to timber production. Nevertheless, these lands are often the last large natural areas in otherwise developed environments. As such, many natural and cultural resources have been preserved, and sites with these attributes can be used as reference sites for conservation, rehabilitation, and mitigation efforts at disturbed sites. For example, the DOE National Environmental Research Parks (NERPs) can provide long-term natural resources data useful for rehabilitating similar DoD and DOE sites where access is limited. The long-term DOE Parks data on various biotic properties have significant value for developing and validating models and management schemes.

Currently, there is no unifying framework for managing these lands that provides decision-makers with a consistent approach to balancing the goals of DoD and DOE operations with the need for resource conservation. We propose to develop and demonstrate such a framework. Our strategy is to use existing data and state-of-the-art technology, with an emphasis on Geographic Information Systems (GIS) and computer modeling, to characterize the natural and cultural resources on selected DoD and DOE sites. We will develop and demonstrate advanced computer-based models to predict incremental and cumulative impacts of agency activities on habitat, biodiversity, and cultural resources and to find solutions that maximize mission-oriented use of the lands while sustaining long-term ecological diversity and preserving cultural resources. The demonstration will involve model predictions of biodiversity subsequent to specific land use activities as compared to in-situ measures after such manipulations on DoD or DOE lands.

The proposed strategy characterizes resources in a risk assessment framework to provide support for DoD and DOE land management that is applicable to levels of organization ranging from species to ecosystems. By risk assessment, we mean to estimate the probability of undesirable (or desirable) outcomes of land management activities in a spatially explicit

fashion. The framework will provide agency decision-makers with a tool for evaluating the effects of alternative land management activities on natural and cultural resources. The model will be useful to land/facility managers and planners for addressing questions such as: What is the relative risk to biotic and/or cultural resources of a set of potential land-use activities? Across a set of potential sites, where would an activity best be placed to minimize the effects on biotic and/or cultural resources? What remedial actions would provide the maximum conservation benefit? What are the impacts on habitats or species of changing the frequency or impact of training exercises at a site?

## **7. Project Description:**

We propose to develop an innovative, spatially-explicit decision model that will be used to assess the impact of DoD and DOE activities on natural and cultural resources. It will focus on the loss/alteration of habitat and the resulting impact on biodiversity. Agency land-use activities will be characterized using a common set of parameters (magnitude, frequency, areal extent, spatial distribution, predictability) that can be applied both to alternative activities and different levels of the same activity. This framework permits the incremental and cumulative effects of diverse activities, such as road building, military maneuvers, grazing, timber harvests, and environmental restoration, to be evaluated. Evaluating the risk posed to habitats, species, and cultural resources is expressed as the probability of a decline or enhancement in the abundance of guilds of species or cultural features. Although the framework is generic, with appropriate databases it can be applied to any site.

Model development will focus initially on two case studies consisting of paired DoD/DOE sites where each pair is within the same physiographic region. The case studies represent two biomes: 1) eastern deciduous forest, which will include the Oak Ridge Reservation (ORR), Tennessee (DOE) and Ft. Knox, Kentucky (DoD); and 2) semi-arid shrub steppe, which will include the Hanford Reservation, Washington (DOE) and the Yakima Training Center (YTC), Washington (DoD). Choice of which study area to be used as the first test of model predictions will be based upon discussions at the first of two workshops. The first field test\ demonstration will begin in 1995 and the second will occur in 1996. The field test\ demonstration will consist of model predictions of biodiversity alternations from a particular land management practice (e.g., forest clearing, grazing, training exercise, etc.). Then the management practice will be applied to a site and the biodiversity before and after the manipulation will be compared to model predictions. These will be field experiments that will be used to test the models. The two pairs of DoD and DOE test sites are sufficiently different to be able to test a range of management practices.

The Oak Ridge Reservation and Ft. Knox respectively encompass 14,000 and 44,700 ha of eastern deciduous and coniferous forest. Large blocks of land have been cleared for low-level radioactive-waste disposal areas on ORR while tank training at Ft. Knox (Ft. Knox's main mission) has denuded scattered blocks of land. The DOE Hanford Reservation and the DoD Yakima Training Center respectively encompass 145,600 ha and 105,800 ha of semi-arid shrub-steppe vegetation dominated by sagebrush/bluebunch wheatgrass. Environmental cleanup activities threaten large tracts of high quality sagebrush community at Hanford while

the Army's need to increase heavy mechanized equipment training at YTC poses a similar threat there.

The proposed project supports both DoD regulations and DOE orders (e.g., A. F. Regulation 126-1, Conservation and Management of Natural Resources, DOE 4320.1B, Site Development Planning) that establish policies for managing and conserving natural resources and for site development and land management planning. As our research approach is implemented, two workshops (one at the start of the project and one just prior to developing the risk assessment framework) will be conducted to establish linkages between decision-makers and scientists; and a peer review advisory board will be established to ensure that the research is responsive to local needs and is consistent with national policies and needs.

Our approach entails five components which integrate existing data, model development and demonstration, and risk assessment.

1) Quantitatively characterize land-use activities. A matrix of characteristics to describe land-use activities on DoD and DOE lands in terms of magnitude, frequency, areal extent, spatial distribution, predictability, and effects on habitat quality and cultural resources will be developed. For example, some types of troop training are low-intensity impacts that are dispersed throughout a site, whereas construction of an industrial facility is a high-intensity activity that occupies a limited area. To assure representation of the selected activities and relevance to each agency, the matrix development will entail a workshop involving representatives from DoD and DOE sites.

2) Develop a land-cover change risk model. A spatially-explicit, land-cover change model will be developed to simulate potential changes in or loss of individual cover types in response to the land-use activities. Inputs to the model will include the matrix of parameters describing land-use activities, and gridded (digital raster) maps of site characteristics, such as present land cover, slope, aspect, soils, etc. The model will simulate the impact of land use activities on land cover. The model will be probabilistic so that stochastic aspects of the land-use activity (e.g., the frequency of training maneuvers) or its effects on the habitat (e.g., the degree to which a forest is damaged by artillery fire) or cultural resources can be represented. Land-use activities that are relatively deterministic and depend on the suitability of the land (e.g., location of new runways) also are easily accommodated within a probabilistic model by setting the appropriate probabilities to 1.0 and fixing specified parameters. From the model, tables and maps of potential land-cover change due to land use activities will be produced for a particular site. The land-cover change projections will be developed for different scenarios of land-use activities and land cover patterns. Stochastic simulations with the model can be replicated many times and the results summarized statistically, thereby providing an estimate of the magnitude and range of potential effects. Most importantly, the stochastic but mechanistic nature of the modeling will allow us to quantify the probability of specific land-cover changes taking into account known uncertainties.

3) Develop a resource-susceptibility model. The second model to be developed will relate characteristics of species, ecosystems, and cultural features to land-cover patterns resulting from land-use activities, as projected by the land-cover change model. Development of this



model will evolve from discussions at a workshop involving DoD and DOE land managers. Long-term NERP data will be especially important in the model development. This resource model will match land cover characteristics (e.g., frequency of land cover types, abundance of suitable habitat, size of habitat patches, frequency of edges, corridors, etc.) to species and ecosystems characteristics (e.g., home range size, vegetation patterns) and to cultural features. For example, activities that cause habitat fragmentation will be detrimental to species that require large blocks of contiguous habitat (e.g., forest-interior species). This model will be probabilistic to ensure its compatibility with quantitative risk assessment. Potential effects on species and ecosystems of no management, alternative land-use activities, environmental restoration, or natural events can be examined. The probability of an undesired or desired outcome (such as loss or increase of a population of interest) is estimated by Monte Carlo simulations of the models under particular scenarios and examination of the frequency distribution of outputs. The visualization that will accompany this spatially-explicit model will also permit managers to "see" the effects of alternative activities on populations or cultural features of interest.

4) Use case studies to field test the modeling approach. The model will be tested by applying it to the paired DoD and DOE sites (Oak Ridge Reservation/ Ft. Knox and Hanford Reservation/Yakima Training Center). To the extent possible, existing land-use/land-cover and resource maps will be used, however some map development may be required. Data available on highly impacted or inaccessible DoD sites can be augmented by the extensive historical data available for the DOE NERPs. Spatial data for each site will be compiled in grid-cell (raster) format into a Geographic Resource Analysis Support System (GRASS), developed by the U.S. Army Corps of Engineers (Construction Engineering Research Laboratory, Champaign, Illinois) GIS (all spatial analyses will be done in accord with the guidelines of the Federal Geographic Data Committee). Converting the existing and acquired information on land-use/land-cover and cultural and natural resources to a GRASS format will assure its compatibility with the land-cover change and resource-susceptibility models. The goal of these case studies is to apply the conceptual framework (i.e., use of the land-use activity matrix, the land-cover change model, and the resource-susceptibility model) to specific sites. For example, collaborators at Pacific Northwest Laboratory will develop a rangeland ecosystem model that incorporates disturbances from military training exercises and environmental restoration options for YTC. This model will i) identify locations to be impacted by training, ii) quantify ecosystem impacts of training, and iii) estimate the economic costs and effectiveness of various environmental restoration activities. Simulations will be conducted for single and combined land-use activities that might occur at each site, and the probability of undesirable or desirable changes in habitats or species will be projected in map and tabular form. To the degree that suitable data are available, predictions will be compared with field data. Biodiversity data collected before and after specific land use activities will be used to test predictions.

5) Conduct risk assessment. A final workshop involving land managers from DoD and DOE sites will be held to consider the applicability of the proposed framework to evaluating risk to biodiversity and cultural resources associated with specific land management practices. The workshop will build upon EPA's Ecological Risk Framework and consider how our model framework contributes to estimation of land-management risks.

## 8. Expected Payoff:

This research will provide a rigorous, quantitative method for conserving and enhancing biodiversity and cultural resources while conducting activities necessary for DoD and DOE missions. The results will include:

- 1) A general risk-based framework that can be used by DoD and DOE land managers and site development planners to analyze the potential impact of selected land-use activities on natural and cultural resources.
- 2) Case study results including tabular projections of percent change in cover and distribution of habitats, species guilds, and cultural features for various land management and site development scenarios at the case study sites along with maps of potential risks to different land cover types under the specified land management scenarios.
- 3) A user-friendly version of the land-cover susceptibility and species-susceptibility models that could be applied at various DoD and DOE sites.

In addition to its use for management of natural and cultural resources, the proposed research is directly applicable to 1) planning for facility closures and realignment (e.g., identification of facility closures that provide the best conservation opportunities), 2) developing environmental restoration and waste management strategies, 3) supporting compliance with the Endangered Species Act, the National Historic Preservation Act, the National Environmental Policy Act, and the Executive Orders for Floodplains and Wetlands, and 4) developing integrated risk assessments that address cumulative effects.

## 9. Milestones:

- |     |  |        |
|-----|--|--------|
| 1.  | Land-use activities workshop   | 05/95  |
| 2.  | Report on land-use activities workshop   | 06/95  |
| 3.  | Plan for field test\demonstration at first site (either deciduous forest or the semi-arid shrub steppe)  | 06/95  |
| 4.  | First field test   | 6-9/95 |
| 5.  | Report on land-cover change risk model   | 06/96  |
| 6.  | Plan for field test\demonstration at second site (either deciduous forest or the semi-arid shrub steppe) | 04/96  |
| 7.  | Second field test  | 5-9/96 |
| 8.  | Report on natural resources susceptibility model   | 12/96  |
| 9.  | Report on framework for land management  | 04/97  |
| 10. | Analysis of field tests\demonstrations on land-use impacts to sites                                      | 02/98  |
| 11. | Risk assessment workshop involving land managers from DoD and DOE sites                                  | 04/98  |
| 12. | Report on risk assessment framework  | 06/98  |
| 13. | User-friendly computer code for applying framework   | 06/98  |
| 14. | Technology training session for DoD and DOE land managers  | 09/98  |

**10. Transition Plan:**

User-friendly codes of the models and land-use management framework developed in this proposal will be transferred to DoD and DOE land managers and site development planners. The inputs of DoD and DOE land managers will be obtained throughout the proposed work via their participation in workshops and on the peer review advisory board.

**11. Funding: \$(K)**

FY94	FY95	FY96	FY97	FY98	TOTAL
500	260	340	700	400	2200

**12. Performers:**

The DOE NERPs (Nevada Test Site, Idaho National Engineering Laboratory, Savannah River Ecology Laboratory, Pacific Northwest Laboratory, FermiLab/Argonne National Laboratory, Los Alamos National Laboratory, and Oak Ridge National Laboratory) and selected DoD facilities (Yakima Training Center, Ft. Knox, Construction Engineering Research Laboratory and others) will participate in the two workshops, Oak Ridge Reservation, Ft. Knox, Hanford Reservation, and Yakima Training Center will participate in the field case studies. This proposal includes funds for workshop participation by DoD/DOE land managers, planners and scientists and for each installation involved in the case studies.

**13. Principal Investigators:**

Virginia H. Dale  
Oak Ridge National Laboratory  
Bethel Valley Road, P.O. Box 2008  
Oak Ridge, TN 37831-6037  
PHONE: (615) 576-8043  
FAX: (615) 576-7287  
E-MAIL: vhd@ornl.gov

Ronald N. Kickert, K6-63  
Battelle Pacific Northwest Laboratory  
P.O. Box 99  
Richland, WA 99352  
PHONE: (509) 372-0814  
FAX: (509) 376-3968

**14. Keywords:**

Biodiversity, Land Use, Habitat, Ecological Risk, Site Development Planning, Species Guilds

TABLE XX  
 FY 1995 ENERGY CONSERVATION/RENEWABLE RESOURCES  
 PROJECTS

FY 1995 ENERGY CONSERVATION/RENEWABLE RESOURCES PROJECTS	Funding (\$K) FY95	ID Number	Page Number
Energy Conservation			
Low Energy Model Installation Program (A/DOE)	500	639	EN-2
Natural Gas Based Air Conditioning Demonstration (A/N)	270	643	EN-6
Renewable Energy			
Fuel Cells for Military Applications (A)	150	641	EN-9
Geothermal Space Conditioning for Large DoD Buildings (DOE)	100	580	EN-13
Utilization of Biomass Technologies on Military Installations (EPA)	580	227	EN-18
Photovoltaics for Military Applications (N/DOE/EPA)	1,600	46	EN-21
<b>Energy Conservation/Renewable Resources Total</b>	<b>3,200</b>		

## SERDP FY95 PROJECT

1. **SERDP Thrust Area:** Energy Conservation/Renewable Resources
2. **Title:** Low Energy Model Installation Program
3. **Agency:** U.S. Army
4. **Laboratory:** Construction Engineering Research Laboratory (CERL)
5. **Project ID:** #639
6. **Problem Statement:**

Current energy policy requires federal and DoD facilities to reduce energy consumption and costs by 30% from 1985 to 2005, by implementing a variety of project and maintenance strategies, maximizing the use of alternative financing. The Energy Policy Act of 1992 requires that all projects that payback within ten years be completed by 2005. Proper analytical tools and methodologies to ensure optimum implementation of the energy program are not available. The DoD also has no example demonstrating all the strategies simultaneously utilizing existing resources available to the engineer community. The DoD Low Energy Model Installation Program at Fort Hood, Texas, will demonstrate the effectiveness of the comprehensive approach while acting as a testbed for the development and technical transfer of tools and methodologies. This project is a combination of applied research, technology demonstration, and technology transfer. The Low Energy Model Installation Program is a continuing effort which received FY 91-93 funding along with DoD and FORSCOM funding. Continued funding is required to complete generic tool development, develop construction design enhancement methodologies, design projects, and complete energy saving and sustainable development demonstration projects at Fort Hood.

### 7. Project Description:

The Low Energy Model Installation Program is twofold effort. The first technical objective is developing a generic methodology for bringing an entire installation up to an energy efficient state. The second technical objective is to implement this methodology at a given installation for demonstrating and validating the process. The two efforts are being conducted simultaneously in a synergistic manner. SERDP funding is intended to pay for the methodology and tool development, project development, minor demonstrations, and project validation. Once the large projects have been identified and the technology demonstrated, other funds will be used to complete them. SERDP leverages other much larger funding requirements.

The program's technical approach is a step by step logical process, shown below:

- (1) establish baseline and existing energy patterns
- (2) improve the existing energy management program
- (3) predict future energy requirements
- (4) optimize MCA and OMA projects to reduce energy
- (5) identify energy conservation opportunities (ECO's)
- (6) develop phased implementation plans
- (7) implement the plans and monitor progress
- (8) develop "Lessons Learned" and modify the program
- (9) document program and accomplish technical transfer

The development of generic analysis tools is designed to formalize the above process and automate it as much as possible. They will provide the DoD and installations with a consistent method and yardstick for evaluating projects and progress. The program builds upon and enhances previous work by Pacific Northwest Labs in the development of the Federal Energy Decision Screening Model (FEDS) and the previous work by Lawrence Berkeley Labs in the development of End-use Disaggregation Algorithm (EDA). It also compliments the separately funded CERL work effort to develop the Renewables and Energy Efficiency Planning (REEP) model to determine the maximum potential and the environmental benefits of energy conservation in the DoD. The final tool that facilitates the process is the Installation Baseline Energy Analysis Model (IBEAM).

IBEAM enables the energy manager to determine the energy flow and consumption trends on the installation. It uses multiple years' input of salient parameters and energy consumption to build an adaptive model of the installation. The model is used to define energy flow and uses and predict consumption based on changes in the salient parameters and to gauge actual progress. It also quantifies the environmental benefits of the energy program. REEP is a basic scoping tool to be used for programming energy funding, evaluating potential, and assessing energy projects on a large scale. FEDS is a project development and prioritizing tool. Results of a level-2 FEDS analysis will provide the detailed information for project documentation and submittal for funding. EDA is a process of developing information from which to build and enhance the models.

Once the tools are finalized, the DoD will have its consistent yardstick for developing projects, determining priorities and assessing progress. This ability has been missing from the energy program and has hindered effective application of scarce resources. The demonstrations at the model installation will provide living proof that the methodology works.

Historically, new technology has had an extremely slow penetration into the DoD infrastructure. Typical lag times are up to fifteen years. The reasons for this are multiple; some are as follows: (1) the construction system is extremely bureaucratic and relies on outdated specification packages, (2) nearly all parties involved in the construction process are extremely conservative by nature and tend to do things the way they have always been done, (3) technology transfer within the DoD is not as effective as it could be, and (4) installation personnel are leery of new technology, do not trust it to perform properly, and therefore,

actively oppose it in their projects. Demonstrations conducted under this program at Fort Hood are intended to overcome these obstacles and show all parties that the current paradigm needs adjustment and that new technology will benefit the installation and the national infrastructure as a whole from both the energy and maintenance perspectives.

The approach to applying new technology in the program is to do small pilot projects to familiarize personnel with new techniques and equipment. These will be followed-up with large, wide-scaled implementation projects funded by the Energy Conservation Investment Program, Military Construction, the DoD Energy O&M Program, or alternative financing.

## **8. Expected Payoff:**

Fort Hood spends about \$23 million per year for facilities energy. Preliminary analysis of the potential savings at the model installation are about 32% of the energy and 24% of the costs. Since the Department of Defense spends about \$2.9 billion per year for facilities energy, savings of this magnitude extrapolated DoD-wide are about \$700 million per year. There are also considerable environmental benefits from such energy reductions such as reduced air emissions and their effects on global climate change. Additionally, external societal savings for such a program are about \$350 million per year. Expected reductions in carbon dioxide from both reduced gas and electrical usage at the model installation are in the 35% range. Demonstrations conducted under this program at Fort Hood are intended to overcome obstacles preventing use of new technology and concepts such as "green buildings" and show all parties that the current paradigm can be adjusted to benefit the installation and the national infrastructure as a whole from both the energy and maintenance perspectives. Developing effective tools for energy analyses and capital investment strategies will enable installations to determine the optimal projects to achieve lasting savings.

## **9. Milestones:**

- |    |  |       |
|----|--|-------|
| 1. | Develop third phase personnel training       | 06/95 |
| 2. | Complete prototype CAPSIZE program           | 09/95 |
| 3. | Complete third phase personnel training plan | 09/95 |
| 4. | Install first phase energy projects          | 09/95 |
| 5. | Refine IBEAM energy predictor model          | 12/95 |
| 6. | Develop water treatment/energy analysis tool | 12/95 |
| 7. | Verify and extrapolate EDA procedure         | 06/96 |

## **10. Transition Plan:**

The results of this program are twofold. The first area is tool and technique development. These will be transferred within the existing structure for energy management within the DoD. The militarized version of FEDS will be incorporated into DOE's training program. The predictor tools and analysis techniques will be incorporated into DoD training programs. The second set of results are the technology demonstrations at the model installation. These projects will fully involve the installation, the local Corps of Engineers District, and the various Corps Centers of Expertise. These results will be transferred using standard DoD

methods such as technical reports, manuals, and bulletins. Since the results of the pilot demonstration projects will show that the technology is applicable to virtually all DoD facilities, they will also be incorporated into training and workshops associated with the energy management programs. Successes at one installation make a given new technology acceptable to others. Demonstrations are an effective way to break the continuing cycle of replacement-in-kind with older, less efficient technology even though the old technology was inappropriate, did not persist, and failed. The technologies being implemented under this program are readily available from industry but have not penetrated the DoD market.

**11. Funding: \$(K)**

	FY91	FY92	FY93	FY94	FY95	FY96	TOTAL
SERDP	1760	940	1400	1650	500	500	6750

**12. Performers:**

This project is being managed and performed by the Construction Engineering Research Laboratories in Champaign, IL. Additional assistance is being provided by the Cold Regions Research and Engineering Laboratory in Hanover, NH; DOE National Labs (Pacific Northwest Laboratory and Lawrence Berkeley Laboratory); the University of Illinois at Urbana/Champaign; the University of North Dakota; Texas A&M University; and various consulting and engineering firms. Huntsville and South Central Divisions of the Corps of Engineers are also program partners.

**13. Principal Investigator:**

US Army Construction Engineering Research Laboratories  
ATTN: CECER-FEM (Mr. Donald Fournier)  
PO Box 9005  
Champaign, IL 61826-9005  
PHONE: (217) 373-7282  
FAX: (217) 373-6740  
E-MAIL: D-FOURNIER@CECER.ARMY.MIL

**14. Keywords:**

Energy Conservation, Global Warming, Demonstration, Renewable Energy, Model Installation, Demand Side Management, Sustainable Development, Renewable Resources



## SERDP FY95 PROJECT

1. **SERDP Thrust Area:** Energy Conservation/Renewable Resources
2. **Title:** Natural Gas Based Air Conditioning Demonstration
3. **Agency:** U.S. Army
4. **Laboratory:** Construction Engineering Research Laboratory (CERL)
5. **Project ID:** #643

### 6. **Problem Statement:**

Many existing chilled water systems within DoD are old and inefficient. Most use chloroflourocarbons (CFCs) or hydrochloroflourocarbons (HCFCs) as the refrigerant and many of these pose an environmental problem by leaking their refrigerant charge. It is becoming expensive to replace CFCs and potential for EPA fines exist when annual leakage rates exceed 15% of the system charge, which is not an uncommon occurrence. Summer air conditioning loads result in an increased peak electrical demand of 30% or more at most installations. This occurs when electricity is the most expensive and electric utilities have the least reserve capacity.

### 7. **Project Description:**

Air conditioning requirements at DoD facilities typically occur when the electric rates are the highest. The demand portion of an installation's electric bill can exceed 50% of the total bill. State-of-the-art natural gas fired cooling systems, such as absorption and engine driven chillers, can be used to reduce electric demand, provide domestic hot water, operate at high coefficients of performance, and avoid the use of environmentally harmful refrigerants. In addition, shifting of cooling from electric driven to natural gas fired equipment offers a significant reduction in the overall environmental impact of the cooling load.

Hospitals, barracks, and other DoD facilities where large cooling and hot water loads exist may be prime candidates for gas cooling technologies. The FY93 Defense Appropriations Act provided \$6 Million of equipment procurement funds to the DoD for "natural gas chillers for the air conditioning of Department of Defense facilities". The FY94 Defense Budget also includes \$16,750,000 to continue with this program. However, no funding was provided with which to identify and evaluate potential implementation sites, develop the equipment purchase documentation, supervise equipment installation and acceptance, monitor equipment performance, or document lessons learned to assess the applicability of these technologies within the DoD as a whole. The proposed project is designed to provide field demonstrations of natural gas chillers at DoD installations and to evaluate their overall applicability within the DoD.

The objective of this project is to evaluate the overall applicability of natural gas fired chiller technology within the DoD through a program of field demonstrations.

**8. Expected Payoff:**

Payoffs from gas cooling come in two forms, environmental and economical. While CFCs are no longer used, HCFCs are still of some concern as a long term solution. Absorption chillers and desiccant dehumidifiers completely eliminate all CFCs and HCFCs. Engine driven chillers typically rely on vapor compression and HCFCs for their cooling process. Current and expected near future equipment costs are somewhat higher than conventional electric driven vapor compression cooling equipment. Therefore areas with large electric - gas cost differentials will initially be targeted for early application in order to minimize the payback period for the incremental cost of the project. Many gas and electric utilities offer rebates, such as on a per ton of installed capacity, in order to 1) reduce peak electric demand, and 2) increase summer gas sales. These rebates can, in some cases more than make up the equipment cost differential. Also, a number of gas utilities offer lower rates for gas cooling. Some applications will allow heat recovery, particularly engine driven chillers, for heating DHW or boiler makeup water. As these applications are identified the cost effectiveness of the system increases. At current equipment costs, modest utility incentives, and gas rates, gas cooling can be cost effective where average electric rates are in excess of \$0.05/kWh. These conditions are met at approximately half of the Army installations.

**9. Milestones:**

- |    |   |       |
|----|---|-------|
| 1. | Phase 1 system performance summary          | 11/95 |
| 2. | Procurement & construction procedure review | 12/95 |
| 3. | Phase 2 construction activities             | 05/96 |
| 4. | Phase 2 systems monitoring                  | 08/96 |
| 5. | Phase 2 system performance summary          | 09/96 |

**10. Transition Plan:**

The final report will be in the FEAP format, published by CERL, and made available for use by the other military services. Procurement and commissioning specifications will be established in Corp of Engineer's Guide Specifications.

**11. Funding: \$(K)**

	FY94	FY95	FY96	TOTAL
SERDP	230	270	270	770

**12. Performers:**

The lead agency will be the U.S. Army Construction Engineering Research Laboratories. Supporting agencies and organizations include: Naval Facilities Engineering and Services Center, Air Force Civil Engineering Services Agency, US Army Construction Engineering Research Laboratory.

**13. Principal Investigator:**

Mr. Michael Brewer  
USACERL  
ATTN: CECER-FE  
P.O. Box 9005  
Champaign, IL 61826-9005  
PHONE: (217) 398-5544  
FAX: (217) 373-3430  
E-MAIL: m-brewer@cecer.army.mil

**14. Keywords:**

Natural Gas, Chillers, Cooling, Engine, Absorption, Desiccant

## SERDP FY95 PROJECT

1. **SERDP Thrust Area:** Energy Conservation/Renewable Resources
2. **Title:** Fuel Cells for Military Applications
3. **Agency:** U.S.Army
4. **Laboratory:** Construction Engineering Research Laboratory (CERL)
5. **Project ID:** #641

### 6. **Problem Statement:**

The majority of central heat plants on U.S. military bases are nearing the end of their useful life and will soon need replacing. This presents an opportunity to replace existing equipment, based on energy concepts developed almost eighty years ago, with current state-of-the-art or near-term emerging technologies. Fuel cells are electrochemical power generators with the potential for attaining very high electrical energy conversion efficiencies while operating quietly with minimal polluting emissions. In addition, by-product thermal energy generated in the fuel cell is available for use for cogeneration of hot water or steam, bringing the overall potential conversion efficiency (electrical plus thermal) to the order of 80%. The extremely low environmental impact associated with fuel cell technology is in direct support of DoD/DOE environmental objectives. Air emissions for key pollutants ( $\text{SO}_2$ ,  $\text{NO}_x$ , and particulates) range from negligible (orders of magnitude below New Source Performance Standards [NSPS] of the Clean Air Act for  $\text{SO}_2$ ) to undetectable (for  $\text{NO}_x$  and particulates) with gas or distillate fuels. Superior environmental performance also can be achieved using coal gas as a fuel. Because of the high energy conversion efficiency, fuel cell power plants also produce lower levels of greenhouse effect pollutants (such as carbon dioxide). Phosphoric Acid Fuel Cells (PAFC) are currently entering the initial stages of commercialization. Molten Carbonate (MCFC) and Solid Oxide (SOFC) fuel cells, offering even higher electrical energy conversion efficiencies and increased cogeneration utility, are expected to become commercially available around the turn of the century. This project is a continuation of an ongoing SERDP program designed to provide a field demonstration of PAFC technology at U.S. military installations, with the resultant lessons learned to be applied to the development of application guidance for the eventual implementation of MCFC and SOFC technologies within the DoD.

### 7. **Project Description:**

The technical objective of this project is to demonstrate of the applicability of fuel cell technology to U.S. military installations. This involves the development of application guidance for PAFC technology, screening of U.S. military installation pertinent data against this application guidance, development of an implementation plan for PAFC installation within DoD, monitoring of the resultant purchase and installation procedures, monitoring of system performance, documentation of lessons learned, and application of lessons learned to

provide guidance for similar implementation plans for use with MCFC and SOFC technologies as they become commercially available.

This project is related to current and outyear COE sponsored R & D work units concerned with advanced electrical supply strategy and the assessment of emerging fuel cell technology for eventual DoD application. It is also related to a DoD funded effort to provide application guidance for PAFC technology within the DoD. In addition, the 1993 Appropriation Act provides for \$18 million (\$6 million each for Army, Navy and Air Force) procurement accounts for non-developmental item natural gas fuel cells currently in production in the U.S. for power generation at military installations, with recommendation for locations in need of enhanced air quality. This funding can be used for system design, purchase of fuel cells and balance of system, and system installation. SERDP funding is primarily requested for the development of the PAFC implementation plan for DoD and for monitoring the resultant acquisitional, installation, and operational aspects involved with fuel cells.

Primary technical risks involved in this project are concerned with the current costs of fuel cell systems. At the present time, fuel cells are not economically competitive with other more conventional energy production technologies. Their primary application must therefore be based on environmental considerations. Current cost projections predict that PAFC systems will become economically competitive within the next 3 - 4 years as market demand increases. This will have to occur before fuel cell technology can be considered as an energy supply alternative based on energy conversion efficiency considerations alone.

Progress on this project to date includes the coordination of the efforts involved in this project with other U. S. Government sponsored fuel cell efforts. Efforts are currently underway to publicize progress and results of this project through established DOE communication pathways. The experience of EPA laboratories (AEERL) in quantifying environmental benefits resulting from the application of fuel cell technology will be used in the assessment of the results of this project. USACERL has also been named as the DoD Technical Stakeholder for a related project being conducted by the National Defense Center for Environmental Excellence (NDCEE) involving a 400 kW air-cooled PAFC. USACERL and representatives from the Tri-Services, acting under the oversight of the Defense Utility Energy Coordinating Council (DUECC), has coordinated efforts to establish a list of potential candidate sites for PAFC demonstrations. Initial PAFC application guidance has been established and pertinent data from the candidate sites is currently being screened against this guidance. A solicitation for the purchase of turnkey PAFC fuel cell systems has been prepared. Responses to this solicitation are currently being evaluated and contract award is expected to proceed shortly.

## **8. Expected Payoff:**

Initial applicability will probably be restricted to DoD installations located in air quality non-attainment regions. The benefit in these cases will be an acceptable level of progress made toward attainment, and reduction or elimination of fines resulting from violations. As production costs decrease, fuel cell technology should prove to be cost-effective based on electrical energy production costs alone. Current industrial projections predict mature market

installed costs for PAFCs to be less than \$2000/kW. With expected natural gas prices at \$4.00/MBtu, these systems should be cost effective in any region in which electric energy costs exceed 5.5 cents/kWh, provided a need for the thermal energy produced exists.

**9. Milestones:**

- |    |   |       |
|----|---|-------|
| 1. | Develop PAFC application guidance for DoD           | 12/93 |
| 2. | Collect pertinent DoD energy consumption/cost data  | 12/93 |
| 3. | Collect pertinent DoD environmental compliance data | 12/93 |
| 4. | Determine Utility Company leveraging opportunities  | 04/94 |
| 5. | Develop PAFC implementation plan for DoD            | 03/94 |
| 6. | Develop RFP for delivery of turnkey PAFC systems    | 02/94 |
| 7. | Develop PAFC performance test plan                  | 12/94 |
| 8. | Complete PAFC purchase/installation process         | 09/95 |

**10. Transition Plan:**

Discussions held with industry representatives indicate that current production capabilities of one commercially available 200 kW PAFC is approximately 5 units per month. This fits easily into the projected project time frame. Increased market demand should be accompanied with increased production capability such as to meet any potential future DoD requirements. Development of the implementation plan and the subsequent monitoring of implementation and operational activities should serve to assure that user requirements are given full consideration. Lessons learned from this project will be incorporated into separately OCE-funded R & D efforts to assess the potential applicability of MCFC and SOFC technologies to DoD facilities.

**11. Funding: \$(K)**

	FY93	FY94	FY95	FY96	TOTAL
SERDP	350	350	150	600	1450

**12. Performers:**

The extensive experience of DOE laboratories and private research organizations (e.g. EPRI, GRI) in fuel cell technology applications will be incorporated. DoD contractors who have demonstrated expertise in the fuel cell technology arena will be employed during the program. The experience of EPA laboratories in quantifying environmental benefits resulting from the application of fuel cell technology will be employed. Selection of the candidate PAFC demonstration sites as part of the implementation plan will be coordinated among the Tri Services. Potential leveraging opportunities available as part of existing or negotiable incentive plans offered by local gas and electric utility companies will be identified and incorporated into the project where applicable. Overall project oversight will be provided by the Defense Utility Energy Coordinating Council (DUECC).

**13. Principal Investigator:**

Dr. Mike Binder  
U.S. Army Construction Engineering Research Laboratories  
ATTN: CECER-FEP  
P.O. Box 9005  
Champaign, IL 61826-9005  
PHONE: (217) 398-5509  
FAX: (217) 373-3430  
E-MAIL: M-BINDER@CECER.ARMY.MIL

**14. Keywords:**

Fuel cell, Electric power, Natural gas, Cogeneration, Alternate energy, Emissions

## SERDP FY95 PROJECT

1. **SERDP Thrust Area:** Energy Conservation/Renewable Resources
2. **Title:** Geothermal Space Conditioning for Large DoD Buildings
3. **Agency:** U.S. Department of Energy
4. **Laboratory:** Sandia National Laboratories (SNL)
5. **Project ID:** #580

### 6. **Problem Statement:**

Electricity production for space conditioning (heating and cooling) and water heating at DoD facilities generates an estimated 18 million tons of CO<sub>2</sub>, 68 tons of SO<sub>x</sub>, and 30 tons of NO<sub>x</sub> annually. In addition, significant amounts of environmentally harmful refrigerants are released to the environment from DoD space conditioning systems. DoD electricity costs alone for heating, cooling and water heating of facilities is estimated to exceed \$700 million annually. The total space conditioning cost to DoD is amplified by major operation and maintenance expenses.

The use of geothermal heating, cooling, and water heating systems - hereafter referred to as "geothermal space conditioning" systems (which include geothermal heat pumps, ground water cooled chillers, heating with geothermal direct use, and water systems used as heat sources and sinks) - has the potential to save 20-50% of the energy and emissions when compared to conventional technologies. For example, geothermal heat pumps (GHPs) use about 30% less electricity compared to air-source heat pumps and 50% less than electric resistance heating. The EPA study (Space Conditioning: The Next Frontier, April 1993) on residential space conditioning and water heating options and notes that geothermal heat pumps have the lowest overall environmental cost and the lowest lifecycle costs of available technologies. GHPs also have the lowest CO<sub>2</sub> emissions of HVAC equipment, reduce refrigerant use up to 75%, reduce utility demand charges for peak loads, and lower maintenance costs substantially. Savings to DoD are estimated at \$200-300 million annually by 2000.

The use of geothermal space conditioning systems will also assist DoD in switching to ozone friendly refrigerants, a key challenge at large buildings. According to the Heating, Piping, & Air-conditioning Journal (April 1993), it is estimated that "some 22,000 low-pressure chillers must be retired from 1996-1998 if chiller owners are to have enough reclaimed CFCs to maintain the remaining installed base of equipment." In addition, the GSA is expected to spend about \$100 million annually over the next 3-5 years to address the CFC issue. The successful implementation of this program will assist DoD in achieving a 20% reduction in energy consumption by the year 2000 as required in Executive Order 12759, and meeting the goal of the National Defense Authorization Act for FY91 which calls for DoD to install 100 MW of renewable technologies.



Major barriers to the accelerated and expanded use of geothermal space conditioning and water heating systems are: 1) lack of awareness about the technologies; 2) availability of data on costs and performance in a DoD context; 3) shortage of sufficiently trained DoD personnel to design, specify, operate and maintain these systems; 4) difficulties in specifying and procuring these systems through the existing DoD procurement process; and 5) higher first - but typically the lowest lifecycle - costs.

## **7. Project Description:**

The initial SERDP funding in FY93 is focused on introducing and rapidly expanding the use of geothermal heat pumps in base housing and small DoD buildings. The DoD Oversight committee on the SERDP Geothermal Space Conditioning Program (which includes representatives of each service, the Defense Energy Policy Office, DoD research organizations, and DOE and EPA) has articulated the overall goal of this program as:

Developing a permanent DoD capability to evaluate, design, install, operate, and maintain geothermal heat pumps to reduce maintenance costs, environmental impacts, and electric power consumption for space heating, cooling, and water heating, saving DoD an estimated \$50 to \$100 million annually by the year 2000.

A Multi-year Work Plan defines program objectives and milestones.

The new FY94-6 proposal will expand the GHP program to target the heating and cooling needs of large DoD buildings (over 50 tons), which constitute the majority of building square footage at DoD facilities. A parallel R&D and performance contracting program aimed at overcoming the higher first cost will be pursued as appropriate. The major objective of the FY94-96 program will be to establish a permanent DoD capability to specify, design, procure, operate and maintain GHP systems and ground water cooled chillers at large buildings. These technologies will be demonstrated and evaluated at DoD facilities within the next three years, and technology transfer completed with widespread DoD acceptance within five years.

Geothermal space conditioning and water heating systems at large buildings will be designed and demonstrated to eliminate the need for cooling towers (a major DoD maintenance consideration requiring skilled personnel and use of chemicals), eliminate the need to shift to more energy intensive air-cooled towers, and reduce the use of ozone damaging CFCs.

The primary technical challenge to ground water cooled chillers will be to determine the collocation of adequate ground water sources with DoD facilities. Water use may be restricted by local regulations, be required to inject most or all the water, or be to warm in a few instances for cost effective cooling.

The critical path to success for this five-year program consists of identifying the best use of these technologies at DoD facilities nationwide, installing, operating and monitoring demonstration projects, documenting the results on a regional basis to factor in climate and geologic variations, developing design criteria and software, and educating and encouraging DoD decision-makers to adopting these geothermal technologies on a widespread scale.

R&D will be performed only if analyses show potential to reduce costs at least 15% within three years. If such R&D needs are not identified, funds will be shifted to field demonstrations at additional sites. DOE, in conjunction with the Electric Power research Institute, National Rural Electric Cooperative Association and others, is currently researching lower-cost ground coupling systems ranging from advance drilled bits or components, to thermally enhanced grouts for wellbores, to granulated backfills for slinkys, to optimizing loop lengths.

## 8. Expected Payoff:

Successful completion of the overall Geothermal Space Conditioning Program (FY93-FY98) will result in: 1) emission reductions at the power plant of approximately 3.6 million tons of CO<sub>2</sub>, 13.6 tons of SO<sub>x</sub>, and 6 tons of NO<sub>x</sub>; 2) a 10% reduction in electricity used in heating, cooling and water heating, saving \$50 to \$100 million annually from the use of geothermal space conditioning and water heating in residential and small DoD buildings; 3) another 10% savings in energy and emissions from the use of geothermal space conditioning and water heating at larger DoD buildings (new FY94-96 program), saving another \$50 to \$100 million annually; 4) reduced refrigerant use by up to 50% for the small building portion and a significant amount for large buildings (at present undetermined due to the wide range of existing equipment); 5) at least a 10% peak electric demand reduction for DoD facilities; 6) significant but unquantified maintenance savings; and 7) opportunity to "fast track" an energy and environmentally beneficial renewable energy technology for Federal Government-wide application.

Base on an extremely conservative annual energy savings of \$50 million for DoD, the benefit-cost ratio for this program would be in excess of 500:1 over ten years. In addition, environmental and cost savings would accrue from reduced power plant emissions and refrigerant releases, reduced maintenance and downtime costs, and improved reliability.

## 9. Milestones:

1.	Select 1-2 new GHP demonstration sites	Deferred
2.	Install and monitor GHP systems at large building sites	Deferred
3.	Sponsor DoD teleconference on technology/case studies	10/95
4.	Develop GHP modules for design software/manuals	05/95
5.	Conduct technical workshops and seminars	2/96
6.	Select 1-2 new geothermally-based systems	10/96
7.	Update data analysis of systems installed over 1 year	12/96
8.	Analyze electric load data & CFC benefits for chillers	12/96
9.	Provide technology transfer, design assistance	94-96
10.	Data reduction and final report	12/96

## 10. Transition Plan:

Transitioning of the geothermal space conditioning and water heater technology from the demonstration stage to end-user and commercial applications is a major and integral aspect

of the proposed effort. The program transition plan targets to distinct audiences: 1) potential DoD decision-makers and end-users of geothermal space conditioning technologies and associated services.

Involvement of key DoD decision-makers and end-user organizations in the entire program planning and execution phases is a fundamental transition strategy. Primary partners in this program are the DOE Geothermal Division - lead organization charged with technology development and demonstration and the U.S. Army Construction Engineering Research Laboratory (CERL) - one of the lead DoD organizations charged with evaluation and information dissemination of HVAC technologies. In addition, involvement of the U.S. Army Cold Region Research and Engineering Laboratory (CRREL), U.S. Navy Engineering Facilities Command (NAVFAC) and the Naval Facilities Engineering Services Center (NFESC), Ft. Polk, and the Patuxent River Naval Air Station in the planning and demonstration stages has already been arranged. This program also has an ongoing working task with the DOE Federal Energy Management Program (FEMP), and the Federal Energy Technology Test Bed Program managed by the Pacific Northwest Laboratories. Tasks on data collection and analysis, technology evaluation, education and awareness, technical training, and procurement process facilitation constitute a major part of the proposed effort. This strategy will ensure that the technology, information, and know-how will be effectively transferred to DoD (and other federal agencies). Appropriate DoD-oriented technology software and modules for design and procurement manuals will also be developed.

Transitioning to the private sector infrastructure will be accomplished by both specific program tasks as well as by early and continuous involvement and consultation with equipment manufacturers, utilities, A&E firms, HVAC installers and servicers, and industry trade groups. These parties will be explicitly involved through participation in cost-sharing demonstration projects, design and installation contracts, and DoD-oriented workshops/seminars/teleconferences, etc. A number of these organizations have already expressed interest in working with DOE and DoD to demonstrate and promote geothermal space conditioning technologies.

**11. Funding: \$(K)**

The SERDP Geothermal Space Conditioning Technology for Large DoD Buildings Program will be implemented in concert with the ongoing DOE Geothermal Heat Pump Program. While the objectives and tasks of the two will be implemented separately, the DOE program will support and enhance the SERDP effort.

	FY93	FY94	FY95	TOTAL
SERDP	800	1050	100	1,950

*Space*

## **12. Performers:**

CERL - program partner, Ft. Hood demonstration/evaluation lead  
Army ASCIM facilities, Ft. Belvoir - design software development  
Sandia National Laboratories - technical/administrative management  
Pacific Northwest Laboratories - Test Bed Program  
Oklahoma State University - GHP technical assistance  
CRREL - management of data collection and technology demonstration (initially at Ft. Polk)  
Naval Shore Facilities Energy Office - data collection and technology demonstration at Naval facilities  
Oregon Institute of Technology - design assistance on geothermally-cooled chillers  
National Ground Water Association - assistance on water well programs  
Trane, Climate Master, Water Furnace, Carrier, etc. - equipment suppliers, technical assistance  
A&E firms, installers, utilities, industry trade group, etc.

## **13. Principal Investigator:**

Lew W. Pratsch  
Department of Energy  
1000 Independence Avenue  
Washington, D.C. 20585  
PHONE: (202) 586-1512  
FAX: (202) 586-5124  
E-MAIL:PRATSCH.LEW@HQ.DOE.GOV

## **14. Keywords:**

Geothermal, Heat Pumps, Ground Source, Chillers, Emissions, Renewable Energy

## SERDP FY95 PROJECT

1. **SERDP Thrust Area:** Energy Conservation/Renewable Resources
2. **Title:** Utilization of Biomass Technologies on Military Installations
3. **Agency:** U.S. Environmental Protection Agency (EPA)
4. **Laboratory:** Air and Energy Engineering Research Laboratory (AEERL)
5. **Project ID:** #227

### 6. Problem Statement:

The goal of this project is to determine the technical, economical, and environmental feasibility of small innovative energy conversion technologies fueled with biomass. The DoD, and numerous other institutions, operates a large number of small energy conversion systems that burn fossil fuels and are in need of repair or replacement. These systems emit substantial amounts of air pollutants (SO<sub>2</sub> and particulate) which must be controlled. Installing biomass fueled systems or converting or replacing existing equipment with systems that utilize biomass would eliminate SO<sub>2</sub> emissions, produce zero net gain of CO<sub>2</sub> emissions, reduce air toxic emissions, and reduce waste disposal problems. The objective of this project is to demonstrate, test, and evaluate a biomass fueled innovative energy conversion technology at a DoD installation. The research category for this project is applied research, and technology demonstration and technology transfer. This project is an enhancement to the previously SERDP funded (FY93) project and continues to be an opportunity for the DoD, EPA, DOE, USDA, AID, national labs, and industry to cooperate in demonstrations that will benefit each organization.

### 7. Project Description:

The technical objective of this project is to demonstrate that small innovative energy conversion technologies fueled with biomass are technically, economically, and environmentally feasible for DoD installations, industries, and developing countries. Existing efforts have focused on large scale systems or mature technologies. The small scale innovative energy conversion technologies have been neglected. The technical approach for this project is to identify interested DoD sites (many military installations have expressed interest and two have offered to be a host site), identify the project cooperators, select the most viable technology, and design, build, and test the system. The coordination between DoD and cooperators would be such that the design of the project would be in the best interest of the host DoD installation. The biomass fuel supply would be generated by activities on-site, in the community, and/or from dedicated feedstock supply systems (DFSS). The technical risks would be minimized by the proper selection of technology based on the available site, size of system, type of fuel, qualifications of operators, and lessons learned by all cooperators. The project would build upon the EPA/OPPE and DoD study "Enhancing Management of Forests and Vegetation on Department of Defense Lands: Opportunities,

Benefits, and Feasibility;" the EPA/AEERL, Southeast and Southwest Regional Biomass Energy Programs, DOE, and National Wood Energy Association funded Sutton/Energeo and Cratech biomass-to-energy projects; the EPA/AEERL, DOE, and AID biomass integrated gasification/gas turbine study; the EPA/AEERL multi-fuel combustor research; the EPRI Distributed Generation Study; the USDA work with a wood fired combustion turbine, utilization of wood pallets and marketing of cull trees; the NREL gasifier scale-up in Hawaii; the Western Research Institute work with co-firing wood and coal in a turbine; the Regional Biomass Program for utilization of biomass; and ORNL research in DFSS. The project relates to the needs of the DoD by supporting Pillar 3 of the Tri-Service Research Plan, Thrust 3.M: Reduce greenhouse gas emissions, (3.V.2.d) Improve efficiencies of mechanical systems and (3.V.3.a) Alternative/renewable energy sources and the DOE by supporting Title XII: Renewable Energy of Energy Policy Act of 1992, H.R. 776/Public Law 102-486, direct combustion or gasification of biomass and biofuels energy systems.

**8. Expected Payoff:**

After successful demonstrations, energy conversion technologies fueled with biomass could be applied in developed or developing countries, industrial sites, rural areas, as well as, DoD installations. The technologies could be modularized to allow for varying fuel supplies, energy demand, and transportability. The benefits for the DoD to install biomass fueled systems are 1) reduce air emissions, 2) minimize on-site and community biomass waste disposal, 3) savings from tipping fees, purchase of fossil fuels, and electricity, 4) energy security at domestic and international military installations, and 5) promotion of exportable technologies.

**9. Milestones:**

1.	Identify host site(s), existing systems, fuel supply	08/93
2.	Cut-off date for Preproposals under solicitation	12/93
3.	Preproposal evaluations completed	02/94
4.	Final application due to EPA Grants	03/94
5.	Award of Competitive Cooperative Agreement	07/94
6.	Identify site/existing utilities, characterize fuel	10/94
7.	Interview technologies	10/94
8.	Select developer	11/94
9.	Contract and begin design	12/94
10.	Begin site preparation & construction	01/95
11.	Complete designs and equipment selections	04/95
12.	Deliver initial equipment module to site	08/95
13.	Complete plant installation & shakedown	07/96
14.	Planned completion date	06/97

**10. Transition Plan:**

The amount of government/industry cooperation required for a project of this type should lead to future CRADA's between government and industry. This project would provide the jump start needed for the development of equipment, design of systems, creation of new markets, and realization of existing untapped markets for biomass fueled energy conversion systems. The potential systems will be comprised of off-the-shelf components or components manufacturable by existing industries. A successful demonstration would allow developing countries to get approval for financing from multi-lateral lenders. Developing countries are in dire need of this type of technology because biomass waste is both a disposal and air pollution (open burning) problem and diesel fuel is too costly to import. Biomass fueled technologies will help provide sustainable energy without being detrimental to the environment.

**11. Funding: \$(K)**

	FY93	FY94	FY95	FY96	TOTAL
SERDP	750	920	580	55	2305

*space*

**12. Performers:**

Demonstration of energy conversion technologies utilizing biomass will be performed through the cooperation of the EPA, DoD, DOE, USDA, AID, national labs, and industries. The EPA/AEERL, the lead organization, has a cooperative agreement with Research Triangle Institute (RTI). With DoD assistance, EPA/AEERL evaluated preproposals and requested RTI to submit an Application Kit to EPA/GAD. A management task force has been formed with representation from EPA/AEERL, RTI, NC Energy Division, and Camp Lejeune. EPA/AEERL and TRI, with assistance from the task force, has selected the technology developer, Mech-Chem Associates, and will proceed with evaluation of environmental and site specific data, and coordinate project participant's activities. The NC Energy Division will enter into a \$100K contract with International Applied Engineering to support the project. Camp Lejeune will provide the demonstration site, specific information to aid the technology selection process, and possibly system operators. Sandia National Lab will be asked to assist with instrumentation, data collection and analysis, etc. DOE's Office of Solar Energy Conversion/Solar Thermal and Biomass Power will be asked to cofund the project. SERBEP, USDA, NREL, and ORNL will provide off-site resource information, including DFSS. Industry will provide system development/design and hardware. AID/Winrock will examine opportunities for transferring technology to international markets.

**13. Principal Investigator:**

Carol R. Purvis (MD-63)  
USEPA, AEERL  
Research Triangle Park, NC 27711  
PHONE: (919) 541-7519  
FAX: (919) 541-2382  
E-MAIL:carol\_purvis@epamail.epa.gov

**14. Keywords:**

Biomass-to-Energy, Energy Conversion, Combustion, Gasification, Gas Turbine, Distributed Power Generation



## SERDP FY95 PROJECT

1. **SERDP Thrust Area:** Energy Conservation/Renewable Resources
2. **Title:** Photovoltaics for Military Applications
3. **Agency:** U.S. Navy
4. **Laboratory:** Naval Air Warfare Center, China Lake
5. **Project ID:** #46
6. **Problem Statement:**

This is a joint proposal from the Department of Defense (DoD) Photovoltaic Review Committee (PVRC), and the Office of Naval Research and the Department of Energy (DOE). The DoD PVRC and DOE jointly executed FY91 and FY93 SERDP activities, and continue to be strongly committed to a joint program.

The program goal is to support and accelerate existing DOE and DoD alternate energy programs to reduce the operational and cost impact of meeting environmental obligations in the DoD and to transfer that technology and information to both the federal and private sectors for widespread implementation.

DoD is the largest single user of energy in the world with annual pollution emissions estimated at 720 million tons of CO<sub>2</sub>, 1.15 million tons of NO<sub>x</sub>, and 740,000 tons of SO<sub>x</sub>. The potential PV application base within DoD is estimated at 50+ MW for small remote systems (less than 25 kW), 200+ MW for intermediate to large remote systems (25 - 1000 kW), and 450+ MW for large grid interactive systems (greater than 100 kW). Small stand-alone systems for the DoD are considered mature and proven. This program targets intermediate to large remote systems and grid interactive systems for remote "island" grids that generate their own power and for load leveling and uninterruptible power for large utility grids.

Program objectives are to leverage DOE's development of innovative PV technologies by demonstrating them in high value applications within DoD. These objectives will reduce emissions to comply with regulations, make progress toward installing 100 MW of renewable energy projects in DoD as directed by the National Defense Authorization Act, help reduce CO<sub>2</sub> emissions, and maintain energy security by reducing dependence on fossil fuels thereby conserving the strategic petroleum reserve. The program is integrated with the PVRC's "fenced" PV Energy Conservation Investment Program (ECIP) and DOE's Balance-of-Systems and Government Agencies PV initiatives to avoid any duplication of effort.

The research category is 6.3. The primary focus will be the integration of existing research/technologies into systems and demonstration in selected field installations thereby preparing the technology for widespread transfer and implementation to the federal and

private sectors. The program is a continuation of the joint DoD/DOE FY91 and FY93 Phase I and II projects.

## 7. Project Description:

The program includes three tasks: 1) Application Evaluation, 2) Hardware Development, and 3) Application Validation. SERDP and ECIP projects are evaluated and selected under Task 1. The FY91 effort initiated a comprehensive data base which will characterize all DoD energy systems, identify potential PV projects, and document the history of projects implemented under ECIP and SERDP. This data base is used to determine energy priorities and needs, and to enhance access to project information and promote information exchange. Projects that meet DoD priorities and needs, are replicable throughout DoD, and expand the PV application base are identified and ranked by the PVRC and SNL. The top ranked projects are evaluated to determine system requirements, specify hardware, and estimate cost and environmental savings. As part of this program, the EPA is developing techniques to quantify the environmental savings. The projects are implemented in order of their ranking. All project information is documented in the data base and widely disseminated.

Any hardware specified under Task 1 that is not off-the-shelf technology is developed under Task 2 through engineering contracts to manufacturers. This effort focuses on integrating existing components and capabilities into field worthy packages. The FY94 effort will use advances from the BOS initiative to develop integrated power processing and control hardware that will operate in both a stand-alone mode (as a voltage source) and in parallel with other sources (as a current source) to serve all potential applications. Out-year development will focus on balance-of-system requirements to use advanced PV collectors, including thin films (multi-junction amorphous Si, CuInSe<sub>2</sub>, CdSe/Te) and concentrators, as they are validated through the DOE program. These lower cost technologies will expand the application base for PV within DoD. Beyond PV collectors, the development will investigate PV compatible alternative energy storage to eventually displace diesel fuel and batteries and avoid their negative environmental consequences. One alternative that will be investigated is hydrogen because it is environmentally benign and can be generated on-site by PV-driven electrolysis.

The applications and systems are validated through demonstrations at DoD facilities. After installation, the systems are evaluated for acceptance and to determine a baseline performance rating. The systems are then evaluated yearly, throughout the life of the program, to develop a technology track record, establish O&M requirements, and identify design improvements.

This approach has now resulted in 8 intermediate size PV systems in various stages of implementation. Seven of these are PV/diesel generator hybrids including one at an electronic warfare range on San Clemente Island (REWS), two at radar facilities at China Lake (Junction Ranch and Shipsite), an artillery range at 29 Palms (Range 500), air combat ranges at Mt. Home Air Force Base (Grasmere Point) and China Lake (Superior Valley), and a mobile power center (MPC) for the Marine Corps. The stationary systems are designed for capacities between 100-200 kW with PV arrays from 50-100 kW. The MPC is designed to

replace 10 kW mobile generators. The 8<sup>th</sup> project is a grid interactive system at Yuma Proving Grounds (Yuma) for demand charge reduction designed for 150-200 kW capacity with 150-200 kW of PV. These projects are on schedule for installation in 1994. The joint efforts of the PVRC and SNL has been a key element in the progress achieved thus far.

Technical risks of the program are moderate. The program is structured to phase in advanced technology so that the majority of the system uses mature technology. Advanced technology is tested and evaluated as necessary at an independent facility before installation. The critical path elements within the program are 1) technical maturity of advanced PV collectors and alternative energy storage, 2) project approval and system procurement, and 3) coordination with the supplier to test non-mature hardware. These risks will be minimized by project phasing based on technology maturing, close interaction with the user, and aggressive project scheduling and execution.

### **8. Expected Payoff:**

If successful, this program will establish viable electrical generation and energy storage technology for widespread applications with the expertise within DoD to implement the technology where appropriate. The long-term benefits include both substantial environmental savings, economic savings, and reduction in consumption of fossil fuels. Current estimates of potential annual savings by using PV are 433,000 tons CO<sub>2</sub>, 10,123 tons of NO<sub>x</sub>, 450 tons of SO<sub>x</sub>, \$495 million. This is a 33% reduction in annual emissions associated with electrical generation. Estimated energy generation indicates that PV can reduce dependence on fossil fuels by 800,000 MWh of electricity per year. PV can also substantially reduce the hazards associated with the transport and handling of liquid fossil fuels as diesel generators are phased out, increase mission capability and reliability, and increase energy security. Note that these benefits will be quantified for all SERDP and ECIP project. The technologies and applications developed and demonstrated under SERDP have direct application and leverage to other government agencies including the National Park Service and National Forest Service. For example, SNL is working with the National Park Service to survey all their diesel generators to examine the potential for cost and environmental savings through PV. There are also a number of near-term benefits beyond the immediate savings provided by the systems themselves. SERDP will provide a means to apply advanced technologies from DoD, DOE, and the private sector, expand the application base for U.S. products and enhance the capability of industry to service these applications, transfer information on the technology and its capabilities throughout DoD, and provide utilities a model for use of PV in "island" grid and value-added utility grid applications.

### **9. Milestones:**

- |    |  |       |
|----|--|-------|
| 1. | Complete evaluation and selection                            | 06/95 |
| 2. | Develop specifications (component of SOW)                    | 07/95 |
| 3. | Develop SOWs (component of RFP)                              | 07/95 |
| 4. | Procure systems  | 09/95 |
| 5. | Engineer, fabricate, and test hardware (test results report) | 12/95 |

6. Install/characterize systems (as-built drawings, system performance rating report)

12/95

## 10. Transition Plan:

SERDP, as well as ECIP, are integral parts of DoD's Photovoltaic Master Plan, developed and documented by the PVRC, to bring about the use of photovoltaics where appropriate and cost-effective. The overall goal of the plan is to realize the full potential of PV in all DoD applications from small remote to intermediate and large hybrids to value-added utility interactive. The Master Plan details a three-pronged strategy to achieving this goal through Outreach, Logistic System Conditioning, and Project Development. Outreach activities are designed to expand the general awareness and knowledge of PV technology and its capabilities. Logistic System Conditioning is designed to integrate PV into the established Federal logistics system to make the procurement of PV systems routine. Project development is designed to identify replicable applications throughout DoD and aid the user in developing the technical and institutional conditions necessary to turn those applications into reality. In addition to the technical aspects, project development activities also investigate other financing avenues like third party capital venture and power purchase/lease agreements with suppliers and utilities.

Project Development activities are used to affect the transition of PV technology from advanced development (6.2/6.3) through engineering development (6.4) to full implementation. SERDP funds provide the vehicle for the transition from advanced to engineering development by demonstrating and validating advanced technologies and applications. "Fenced" ECIP funds provide the vehicle for the transition from engineering development to full implementation by demonstrating that the application is cost-effective and that the technology and industry are prepared for full implementation. Once an application and technology have completed the SERDP and "fenced" ECIP phases, it can be implemented where appropriate through regular ECIP/MILCON or commercial channels.

## 11. Funding: \$(K)

	FY93	FY94	FY95	FY96	TOTAL
SERDP	4000	4000	1600	1775	11375
ECIP	0	5000	5000	5000	15000
DoD	800	800	800	800	3200
DOE	50	150	200	200	600
Total	4850	9950	7600	7775	30175

NOTE: Outyear funding reflects requested SERDP funding and anticipated ECIP funding. Outyear funding for DOE and DoD is unknown.

## **12. Performers:**

The program is managed by the DoD PVRC chaired by Gary D. Smith of the Office of Naval Research (Code 464/12E) and DOE's Photovoltaics Technology Division, directed by James E. Rannels. Technical work is performed by SNL's Photovoltaic Projects, managed by Dr. David Hasti, and the PVRC with contract support from the Global Warming Control Branch of the EPA, Southwest Technology Development Institute, and the Meridian Corporation. DoD facilities that sponsor projects provide substantial support for project development and system procurement. All systems will be supplied by U.S. PV industry through competitive contracts. Although they are not specifically excluded, there are no formal Cooperative Research and Development Agreements (CRADA) contemplated.

## **13. Principal Investigators:**

Gary D. Smith  
Chairman, DoD Photovoltaic Review Committee  
Deputy, Public Works Office  
Code 823AOOD (C8301)  
Naval Air Weapons Station  
China Lake, CA. 93555-6001  
PHONE: (619) 939-2525  
FAX: (619) 939-7366  
E-MAIL:GARY\_SMITH@CL\_SMTP\_GW.CHINALAKE.NAVY.MIL

Mr. Richard Chapman  
Technical Investigator  
Division 6218, Mail Stop 0753  
Sandia National Laboratories  
Albuquerque, N.M. 87185-5800  
PHONE: (505) 844-0859  
FAX: (505) 844-6541

## **14. Keywords:**

Photovoltaics, Renewable Energy, Diesel Generators, Energy Storage, Hybrid, Utility Interactive.

TABLE XXI FY 1995 GLOBAL ENVIRONMENTAL CHANGE PROJECTS		Funding \$(K) FY95	ID Number	Page Number
Atmospheric Research				
Atmospheric Remote Sensing and Assessment Program (ARSAP) (DOE)	13,000	470	GEC-2	
Ocean Research				
Acoustic Monitoring of Global Ocean Climate (ARPA)	3,700	286	GEC-10	
<b>Global Environmental Change Total</b>	<b>16,700</b>			

## SERDP FY95 PROJECT

- 1. SERDP Thrust Area:** Global Environmental Change
- 2. Title:** Atmospheric Remote Sensing and Assessment Program (ARSAP)
- 3. Agency:** U.S. Department of Energy
- 4. Laboratory:** Sandia National Laboratories (SNL)
- 5. Project ID:** #470
- 6. Problem Statement:**

This is a joint DoD/DoE project to investigate, understand, and assess global atmospheric change. The program will develop improved measurements and understanding of the earth's atmosphere and its response to global change. It will utilize and augment 1) existing DoD space-based sensors of the middle and upper atmosphere, 2) ongoing theoretical modeling activities, and 3) will develop DoE sensors and measurement techniques for observing the lower atmosphere. The effort will consist of the application of unique DoD/DoE ongoing research on environmental issues through measurement of key observables, validation of models, and assessment of evidence of global atmospheric change. This DoD/DoE activity will be coordinated with other national environmental programs such as the US Global Change Research Program (USGCRP).

Both natural and anthropogenic agents contribute to global atmospheric change. Subtle variations in the solar irradiance and the periodic injection of dust and gas into the lower stratosphere by volcanoes can profoundly alter climate. The increased emission of CO<sub>2</sub>, methane, CFCs, and pollution resulting from human activity, enhances the natural atmospheric greenhouse effect and depletes the ozone layer. The nature of atmospheric change depends on the region of the atmosphere:

<u>Atmospheric Region</u>	<u>Issues</u>	<u>Characteristics</u>
Lower	Climate	Global warming, UV increase
Middle	Ozone, UV shielding	Ozone depletion, atmospheric cooling, climate impact
Upper	Atmosphere circulation	Global cooling, potential coupling to biosphere

There is ample evidence for global atmospheric change already. The steady increase in atmospheric CO<sub>2</sub>, methane and CFCs is well documented. Global warming of the troposphere has been observed over the last century. Mid-latitude depletion of the ozone layer and the seasonal Antarctic "ozone hole" result from the emission of CFCs. In the middle and upper

atmosphere, there is evidence of a general cooling (at a rate more rapid than predicted by current models) and an increase in the occurrence of polar mesospheric clouds.

## **7. Project Description:**

Because of the strategic decision to de-emphasize global change in SERDP, the Atmospheric Remote Sensing and Assessment Program (ARSAP) has fashioned its plan to achieve an orderly conclusion of the program and transition to sustaining science programs. These science programs will continue using hardware and capabilities developed in SERDP. The portion of ARSAP concerned with ozone depletion has established the following exit criteria.

- Completion of the test and launch of the Orbiting Ozone and Aerosol Monitor (OOAM) mid-latitude stratospheric sensor.
- Completion of a functioning, automated data processing and archiving system for Polar Ozone and Aerosol Monitor (POAM), OOAM, (and the POAM follow-on being funded from other sources) geophysical data. This system to be available to the research community via DoD communications networks. Naval Research Laboratory (NRL) science operations of these systems will be sustained by NRL/Office of Naval Research (ONR) support.
- Completion of two ground-based microwave sensor elements for the Network for Detection of Stratospheric Change plus one back-up/test system. Systems to be operated by NRL with NASA sustaining support.
- Conduct science analysis of all data acquired during FY-95.

### Millimeter-wave Atmospheric Sounder (MAS)

Complete the analysis of MAS ATLAS data including failure analysis of the incident on ATLAS 3. Despite failure of the MAS data system after about 12 hours of operation, the new C10 receivers designed, fabricated, tested and installed gave better data during this short period than the old system did during the entire ATLAS 1 and 2 flights. A zonal survey of C10 will be produced from this data.

In FY95, this portion of the ARSAP program will center on completing the analysis and interpretation of MAS data obtained during ATLAS 1, 2, and 3 flights. Several papers have been written and several more are in preparation on MAS data obtained in these missions. According to current plan, the MAS project will be phased out after FY95, because no more ATLAS missions appear on the shuttle manifest. Owing, in large part, to the generous financial support of SERDP through the ARSAP program, the MAS experiment can be considered a success by greatly increasing our understanding of the distribution of trace constituents in the middle atmosphere.



### Orbiting Ozone and Aerosol Monitor (OOAM)

Complete the OOAM sensor fabrication and test. The OOAM sensor which will make mid-latitude measurements similar to those now being made with POAM is in fabrication. The OOAM is now scheduled for a fourth quarter 1997 launch on the STP STEP4 spacecraft.

The OOAM instrument is now scheduled for delivery in October 1995. Activity on this project will center upon monitoring the final fabrication and planning and aiding in the execution of the instrument characterization tests which must be conducted before instrument delivery. Finally, we need to analyze the data obtained in these instrument characterization tests to ensure that the instrument is performing to specifications and that its operation is well understood before integration onto the STEP4 spacecraft.

### POAM/OOAM Analysis

Construction of the final algorithms for delivery of geophysical data from these sensors is only partially complete. The current status is that ozone and aerosol analysis algorithms are complete, a working NO<sub>2</sub> algorithm has been tested and final H<sub>2</sub>O algorithm is being constructed. A temperature algorithm is being constructed. A temperature algorithm is far behind because of saturation problems in the POAM II sensor and probably will not be built until OOAM comes on line. Data validation with balloon flights continues into 1996.

Owing to the excellent support of the SERDP, the POAM II experiment is returning excellent data and is a complete success. The unique data set obtained from POAM has enabled us to document the dissipation of the 1993 ozone hole, and the formation and dissipation of the FY94 ozone hole in unprecedented detail. Several papers have now been submitted or are in preparation based on POAM II data. FY95 funds will be used to continue to operate the POAM II satellite instrument, and to reduce and operate the POAM II satellite instrument, and to reduce and analyze the data obtained in the experiment. In addition, work will continue in FY95 on improving the POAM retrieval algorithms, especially the retrieval of ozone below about 17 km, and water vapor and nitrogen dioxide throughout the stratosphere.

### Ground-based System Deployment

Cross calibration and test deployment of the ozone and water vapor systems procured by SERDP will continue through 1996. The first fully instrumented Network for Detection of Stratospheric Change (NDSC) site on Hawaii will not be ready until late 1995.

The first and second water and ozone sensors, Water Vapor Monitoring System (WVMS- 1 and -2) are now in the field (Lauder, New Zealand and Table Mountain CA) and are operational. The FY95 SERDP money will be used to complete WVMS-3 and -4, and test them first in the lab at NRL and then in the field. Both of these new instruments should be deployed in the field before the end of FY95. Also this year, several instruments design and data acquisition improvements will be made. These will be directed mainly toward reducing the instrumental spectral baseline in the data (which currently limits the lower altitude measurement range to about 40 km), and on improving the instrument calibration stability.

In addition, WVMS-2 will be moved from the Table Mountain to Mauna Loa to take part in the first official NDSC operations at the Mauna Loa Observatory, now scheduled to begin late summer, 1995.

FY95 will be a transition year for the WVMS program. With the completion of the tasks described above, we will have used SERDP funding to put in place an effective network of ground-based middle atmospheric water vapor measurements. The measurements provided by these instruments have clearly given the highest quality middle atmospheric water vapor data which has ever been obtained, and they will be a very important part of the NDSC program. After FY95, instrument fabrication, and extensive modification, stage of the program will come to an end, and the WVMS project will center upon maintenance of the instruments in the field, and analysis of the data acquired with the instruments.

### Solar Forcing

Research during FY-95 of solar forcing of global change will focus on two primary areas:

1) Collaboration with the Goddard Institute for Space Studies (GISS) to simulate solar forcing of climate change during the past 400 years. Time dependent calculations of the GISS Global Climate Monitoring (GCM) will utilize the solar forcing time series constructed at NRL during previous years of DoD's ARSAP program. This will provide the first ever time dependent simulation of solar forcing of climate change by a GCM, and will provide new information about natural global change during the past 400 years. This information is critical for assessing anthropogenic climate effects during the past 150 years.

2) Determination of the solar soft X-ray forcing of the middle atmosphere using Yohkoh soft X-ray images and a database of solar emission lines already compiled at NRL.

### Middle Atmospheric High Resolution Spectrograph (MAHRSI)

On November 3, 1994, the launch of STS-66 placed MAHRSI and the shuttle payload satellite (CRISTA-SPAS) platform in orbit for eight days of free flight. During that time MAHRSI acquired, for the first time, nearly five complete global maps of the distribution of hydroxyl radicals in the middle atmosphere. These observations are an important first in middle atmosphere research. MAHRSI also recorded one and a half global maps of nitrogen oxide radical (NO), as well as the temperature profile of the altitude region between 40 and 90 km for the entire eight days. During the next year, the effort will be focused on data analysis and publication, and on refurbishing the instrument for the reflight in 1997.

### Map Theory

The 1-d, 2-d, and Mountain Wave models all became operational in the last quarter of CY 1994. This has permitted early validation runs for comparison with WVMS and MAS H<sub>2</sub>O observation, in advance of the processed data from MAHRSI's hydroxyl radical (OH) and NO observations. The work station network is fully established to support these runs. The MAHRSI inversion algorithms are developed and ready for validation using reduced flight data.

## Theoretical and Computational Support

Theoretical and computational support for ARSAP projects on remote sensing of the upper atmosphere has focused on the development of computer algorithms and codes to retrieve composition from limb intensity measurements. Recent accomplishments include the development of robust radiative transport models for estimation of limb intensity measurements during retrieval process. The code for retrieval of dayside neutral density and temperature retrieval now include resonant scattering effects. Version 1.0 of the code for retrieving dayside O<sup>+</sup> concentrations is now available.

The Ultraviolet Remote Sensing (UVRS) Database Systems (DBS) development activity has focused on the development of a generic relational database management system (DBMS) which is appropriate for the various limb-scanning, passive, ultraviolet sensors currently supported by the ARSAP/SERDP project. The initial application is to the Remote Atmospheric and Ionospheric Detection System (RAIDS), for which the Version 1.0 DBMS is complete and is currently undergoing testing and porting to UVRS VAX 4000-600. The UVRS Data Center, which includes both the DBMS and the data analysis system is presently in use.

## Upper Atmosphere

The upper atmosphere portion of the program will be exploring several new technologies that may find their way to advanced DoD sensors. The MAHRSI and HIRAAS instruments provide higher spectral resolution in the middle-UV and far-UV wavelength bands, respectively, than has been achieved in space instruments to date, and thereby provide significantly improved diagnostics of atmospheric constituents and conditions. The Global Imagery Monitor of the Ionosphere (GIMI) instrument on the ARGOS satellite will contain the first space test of electron-bombarded Charge Coupled Devices (CCDs) in electrographic imaging cameras, which yield greatly improved sensitivity for low-light-level detection of far-ultraviolet emissions for the atmosphere.

## DOE

The DOE program is a critical complement to its Atmospheric Radiation Measurement (ARM) program. The ARM ground sites are heavily instrumented with DoE Cloud and Radiation Testbed (CART) instrument as well as from other government programs. However, certain key quantities must be measured in the atmosphere. These quantities include the solar and thermal fluxes at various levels in the troposphere, and especially at the tropopause; properties of cloud tops and layered clouds; and the distribution of upper tropospheric water vapor. Furthermore these measurements must be made up to the tropopause (20 km in the tropics) and for multiple days so as to sample diurnal and synoptic effects. These combined altitude-endurance measurements are beyond the capability of manned aircraft and are best met using unmanned aerospace vehicles (UAVs) that are now under development by industry.

Therefore we are developing the necessary UAV-compatible instrumentation and flying it on rented UAVs to demonstrate and validate the measurement techniques and to obtain early scientific data. In implementing this, we are following a three-phased approach, taking

maximum advantage of the increasing instrument and UAV capabilities as they are developed by ARSAP and by industry. The first phase concentrates on demonstrating the needed accuracy in radiative flux profiling using a low-altitude UAV under clear sky conditions. This phase was completed in a highly successful series of flights in April and constitute the first ever climate measurements from a UAV. The second phase then extends these measurements to mid-altitudes. (40kft--the mid-latitude tropopause) and to cloudy skies. It depends critically on the new UAV-compatible instruments being developed in this program; i.e. a novel net flux radiometer, an imaging cloud radiometer, a cloud detection lidar, and a small interferometer. This phase is more than 50% finished and will be completed even under the new reduced SERDP budgets. The third and final phase provides the full altitude capability (65 kft) needed for the tropics, develops instrumentation for profiling upper tropospheric water vapor, and extends the measurements to other scientific locales and to instruments now under development by the Sciences Team. Most, if not all of this third phase will be sacrificed under early termination of the Global Environmental Change (GEC) pillar now baselined for SERDP.

Given this decision to phase out the GEC, phase out strategy is to maximize the benefit to SERDP and to the broader US Global Change Research Program by: 1) completing the development of the four key instruments cited above; 2) focusing three remaining missions on cloud heating and satellite calibration issues at mid-latitudes, with special attention to the recently observed 'enhanced short-wave absorption' - an effect which can have a dramatic impact on our understanding of atmospheric heating; and 3) insuring that the overall system is as close to operational as possible, so that it can readily be picked up by future users. We will try to, but cannot guarantee, executing a tropical mission as proof-of-principal. More extensive scientific studies in the tropics (nature's greenhouse laboratory) and in the Arctic (predicted to show the largest greenhouse warming) as well as flight testing of some of the instruments now under development by the Science Team will not be possible under this early program termination.

## **8. Expected Payoff:**

The radiation, water vapor, and cloud measurement capabilities will be a major tool in understanding radiation-cloud interactions. These uncertainties drive the magnitude of global warming response and impact policy decisions on energy-related emission and mitigation strategies. The improved measurement capabilities are an important complement to the ARM program and serve as the basis for a future ARM-UAV program to be funded by DOE. This will be a unique capability for long endurance radiative heating measurements up through the tropical tropopause (20 km) and will allow 'indirect calibration' of satellite data, thereby greatly leveraging the use of existing weather satellites. These improvements can also provide the DoD with enhanced weather data, with redundancy in the case of satellite loss during critical operations, and provide improved infrared backgrounds for weapon system sensors. Representatives of both the Defense Meteorological Satellite Program (DMSP) and of NOAA have expressed interest in several of the instruments for weather satellite applications. The UAV demonstrations will be a key step in establishing these platforms as a "better, faster, cheaper" complement to satellite measurements.

The measurements of the upper atmosphere fill an urgent need for space-based atmospheric measurements during the 1995-2000 time frame. The NASA Upper Atmospheric Research Satellite (UARS) was launched in September 1991 and has a projected lifetime of 5-7 years and the Earth Observing System (EOS) atmospheric chemistry missions are scheduled for after the turn of the century. Thus, there is a gap which will be filled by this program during which policy decisions regarding global warming and CFCs must be assessed. Further, a continuation of this program complements the capabilities and global coverage of EOS allowing an uninterrupted series of measurements of the Sun/Earth/atmosphere system for two decades.

A significant benefit to this research activity is the cost savings realized by utilizing existing DoD and DOE observational and theoretical capabilities. Especially important is the leveraged costs of launching sensors into orbit. Existing data centers, Background Data Center (BDC) and Global Change Distributed Information System (GCDIS) will be used for data archiving and management.

### 9. Milestones:

1.	First space-based observations (ATLAS-2)	03/92
2.	Space flight of DoD POAM	09/93
3.	Fly clear sky mission/initial radiometric payload	03/94
4.	Cloudy Sky mission	redefined
5.	3D dynamical/photochemical model	09/94
6.	Shuttle flight of three atmospheric sensors (ATLAS3)	10/94
7.	MAS Failure Analysis Complete	03/95
8.	MAS ATLAS 3 Analysis Complete	05/95
9.	POAM H2O Algorithm Complete	09/95
10.	POAM Data Validation Complete	03/96
WVMS		
1.	Deployment to New Zealand	01/94
2.	Deployment to Mauna Loa	11/95
OOAM		
1.	Flight Sensor Delivery	02/96
2.	Delivery - Integration	09/96
3.	Launch	09/97
MAHRSI		
1.	Data set complete	03/95
2.	Refurbish ICCD Camera	TBD
3.	Deliver to KSC	TBD
4.	CRISTA-SPAS II Flight	TBD
MAP THEORY		
1.	Models operational	09/94
2.	Validation with WVMS	03/95
3.	Validation with MAHRSI and MAS	05/95
4.	CHEM2D with MAHRSI and MAS	TBD

Solar Forcing	
1. Assemble time series	06/95
2. Update line emission database	TBD
UAP	
1. Version 2.0 complete	TBD
2. Version 2.0 validated	TBD
UVRS DBS	
1. GUI Version 1.0 complete	TBD
2. RAIDS upgrade to Version 1.0	TBD
3. Validate Version 1.0	TBD
4. ARGOS upgrade to Version 1.0	TBD
GIMI & HIRAAS Delivery	12/95
GIMOL Delivery	TBD
Launch of ARGOS	12/96
Conduct mid-latitude ozone mission	TBD
Flight test of CDL	08/95
Cloud heating mission/MPIR test	10/95
High altitude long endurance mission	05/96
HONER test	05/96
North slope of Alaska	04/96
Cirrus heating/water vapor mission	11/96

## 10. Transition Plan:

Lower atmosphere measurement techniques will transition to DOE, with DOE paying operating costs when development is complete. In addition to this primary transition path, we will work with NOAA and DMSP to explore transitioning instruments to satellites. All data will be available through the DoD BDC at NRL and the GCDIS center at Oak Ridge. Middle and Upper atmosphere measurement techniques include: the semi-operational POAM sensor, RAIDS and HIRAAs transition to DMSP, and converged weather satellite sensors. Ground-based sensors are commercially marketable meteorological instruments. Data from this and other activities can be used to provide climate data for long term atmospheric change.

## 11. Funding: \$(K)

FY92	FY93	FY94	FY95	FY96	TOTAL
10,000	33,300	24,700	13,000	3,000	84,000

## 12. Performers:

Work will be conducted in-house at NRL, Sandia, Brookhaven, Argonne, Los Alamos, Pacific-Northwest, Lawrence Livermore National Labs. University participants include Penn State, Johns Hopkins, Wisconsin, North Carolina State, Harvard, Maryland, Colorado, Colorado State, California at San Diego, Oklahoma, and Alaska. ARM research is also underway with grants from DOE to scientists at NASA Centers and with cooperative arrangements with

grants from DOE to scientists at NASA Centers and with cooperative arrangements with National Science Foundation and NCAR. Industry participants include Computational Physics Inc, General Atomics, Aurora Flight Services, Thermoelectron Technologies Corp., Research Support Instmts., Millitech Corp., ARTEP, SFA, ATC.

**13. Principal Investigators:**

Dr. Phil Schwartz

Code 7203

NRL

Washington, D.C. 20375

PHONE: (202) 767-2351

FAX: (202) 404-7453

E-MAIL: TETRAULT@NRLSF1.NAVY.MIL

John Vitko

Sandia National Laboratory

MS9056

P.O. Box 969

Livermore, CA 94550

PHONE: (510) 294-2820

FAX: (510) 294-2276

**14. Keywords:**

Global Change, Ozone, Greenhouse, Atmospheric Remote Sensing, Global Warming, Radiation Budget

## SERDP FY95 Project

1. **SERDP Thrust Area:** Global Environmental Change
2. **Title:** Acoustic Monitoring of Global Ocean Climate
3. **Agency:** Advanced Research Projects Agency (ARPA)
4. **Laboratory:** Scripps Institution of Oceanography
5. **Project ID:** #286

### 6. **Problem Statement:**

Conduct a research program to measure and analyze changes in global ocean temperature to advance our understanding of short and long-term ocean variability and its relation to climate trends. The oceans play a key, but still poorly understood, role in the most important processes contributing to climatic changes such as heat and carbon dioxide storage. The main goal of this proposed research is to measure directly global ocean temperature trends using innovative underwater acoustic technologies, based on the fact that the speed of sound in water is proportional to temperature. A further goal is to develop an ocean-atmosphere modeling capability and supporting database to permit skilled forecasts of significant global environmental changes, which are of major impact in global change and climate prediction. Issues are (1) resolving the complex acoustic signal structure in order to track long term trends along specific acoustic paths, and (2) extracting the long-term trends from the background natural variability of the oceanic temperature field. Methods will be developed to incorporate these measurements into climate prediction models, and to merge them with satellite temperature and altimetry data acquired in other research programs. Enhanced ocean-atmospheric circulation models with the capacity to forecast significant global environmental events will be developed. An adjunct effort is the development of predictive stochastic models for evaluating the efficiency of specific realizations of large-scale, ocean, environmental monitoring systems. The currently funded SERDP program initiated studies and demonstration technology developments to establish the feasibility of monitoring global ocean environmental change.

**Background:** Since ocean temperature is a key indicator of global climate change, accurate temperature measurements, spanning the world's ocean basins and sampled over a long period, are essential to complement atmospheric measurements of global climate trends. The capability to make synoptic temperature estimates derived directly from acoustic travel time measurements was demonstrated in the 1991 Heard Island Feasibility Test where acoustic signals were transmitted from a location in the Southern Indian Ocean to 14 receiver stations, manned by nine international scientific teams, in the Atlantic, Indian, and Pacific oceans. The test demonstrated that acoustic signals of moderate intensity can be received over global paths with sufficient signal to noise ratios to measure propagation time and spatial variability.



## **7. Project Description:**

**Status:** The Acoustic Monitoring of Global Ocean Climate program was initially approved by the SERDP Council and the Scientific Advisory Board (SAB) as a Phase I program with the Congress providing initial funding in the Supplemental FY92 legislation. The SAB noted that; "This ambitious proof of concept experiment is a follow-on to the successful three-week long, 'Heard Island' hypothesis testing experiment. Excellent scientists have been associated with this experiment and peer review protocols are used by its management. The ....broad international participation makes technical, economic, and political sense." ARPA competitively selected two university/industry teams for funding. In FY93, the SERDP Council and Congress continued the program.

**Approach:** The initial approach is to deploy acoustic sources near the deep sound channel (800-1000 m) and periodically transmit encoded signals of 20-minute duration at 70 Hz with 20 msec or better timing accuracy. Deep sources direct maximum signal power into the long-range horizontal paths, providing good signal to noise ratios at long range. These sources will require state of the art manufacturing techniques to develop the specified 70 Hz acoustic devices. Both vertical and horizontal arrays will be used to resolve acoustic arrival structures. The program uses the Navy's Integrated Undersea Surveillance System receiver assets and deploys newly developed vertical line arrays (VLA) at strategic points across the Pacific. Moored on the sea floor, each VLA contains 40 hydrophones and advanced signal collection, timing, and processing modules.

In a complementary technology development, the Woods Hole consortium under the direction of Dr. John L. Spiesberger, is developing a unique surface suspended, "drifting" acoustic receiver (SSAR). Through innovative use of satellite telemetry and global positioning system support, these drifting receivers will independently receive acoustic signals, fix their own position, calculate the acoustic path and process received acoustic data onboard; and then transmit all these data to a shore-based center via satellite link. Drifting receivers will push the state of the art in acoustic measurements and will provide the world oceanographic community with a much needed collection instrument. Twelve SSAR receivers will be built and deployed to complement the fixed receivers in locations that best utilize the SSAR's mobility features. The SSARs will also be used extensively in the global network.

## **8. Expected Payoff:**

This effort will directly benefit NOAA, U. S. Navy's oceanographic programs, and the world ocean research community by providing methods to measure and analyze ocean variability at large scales which is the key to global climate change issues.

- The emerging science of acoustic thermometry and the anticipated global network of sources will enable broad ocean climate variability research by the international oceanographic community, since the signal will be available to any country wishing to participate with their own acoustic receiver assets. The emerging global network will provide new techniques and opportunities for understanding ocean variability.

- Advances in methods for merging acoustic thermometry data with existing remote sensing (satellite) ocean data bases will enable research where horizontal and depth resolution are key variables.
- Development and application of coupled ocean/atmospheric modeling and prediction systems will lead to such practical applications as better prediction of "El Nino" effects throughout the Pacific with recommendations on minimizing the economic impact.
- Advances in low frequency sources manufacturing technologies will provide the cost reduction, reliability and system performance needed for long-term ocean data collection programs. The technology advances are pivotal to establishing the long term network reliability in an internationally operated network.
- SSAR receivers and small recording-array technologies offer promise of a low cost method for long-term studies of ocean climate variability, ocean geophysics, monitoring of natural and man-made seismics and environmental monitoring, e.g., pollution tracking. Again, the advance of these technologies provides a principal basis for leveraging US technical leadership in long term monitoring.
- The results of comprehensive marine mammal monitoring will provide benchmark scientific data never before available on the impacts of low frequency sound on marine mammal behavior, to aid in setting better, environmentally safe criteria for noise in the sea.
- Advance Navy understanding of passive/active acoustic detection systems and phenomena.

## 9. Milestones:

All scheduled program milestones to date have been met. The acoustic source, incorporating untried technology and design, has been successfully tested at sea. Network design, mechanical endurance testing of receivers, and the data handling/processing architecture have proceeded through all critical review and approval phases on schedule. Ocean climate models have been developed and in some cases validated with actual data. Finally, permits for network installation and marine mammal research have been submitted. Other major milestones are:

1.	Instrument Barbers Point receiver	06/95
2.	Instrument Guam receiver	06/95
3.	Instrument Kamchatka receiver	06/95
4.	Commence mid Pacific MMRP	06/95
5.	Install mid Pacific source	07/95
6.	Deploy SSAR receivers	08/95
7.	Operational test data collection system	09/95
8.	Complete six month MMRP protocol	01/96
9.	Commence ATOC data collection	01/96

- 10. Preliminary ATOC data analysis 04/96
- 11. MMRP preliminary report 04/96

**10. Transition Plan:**

Funded entirely by SERDP, this is a basic research experiment in the Pacific Ocean to determine the feasibility of climate trend detection. The overall transition plan envisions NOAA assuming funding and management of the long term global monitoring program once all of the elements are in place and functioning.

**11. Funding: \$(K)**

FY92	FY93	FY94	FY95	FY96	TOTAL
7000	24000	20300	3700	2000	57000

**12. Performers:**

Key scientists from the following research institutions and universities are collaborating in the program: Scripps Institution of Oceanography, Woods Hole Oceanographic Institution/Penn State University, Applied Physics Laboratory/University of Washington, University of California/Santa Cruz, Massachusetts Institute of Technology, Cornell University Laboratory of Ornithology, Hubbs-Sea World Research Institute, University of Michigan, Florida State University, Mississippi State University, University of Alaska, Naval Post Graduate School, Naval Research Laboratory/Stennis Space Center, NOAA Laboratories in Boulder and Miami, Research Planning Inc., Marine Acoustics Inc., Southern Methodist University/Mission Research Corp., Science Applications International Corporation, and University of Texas, Austin.

Active collaboration is scheduled with Australian, Canadian, French, German, Indian, Japanese, New Zealand, Russian, South African, and Taiwanese scientists.

**13. Principal Investigator:**

Dr. Ralph Alewine  
 Advanced Research Projects Agency (ARPA)  
 3701 North Fairfax Drive  
 Arlington, VA 22203-1714  
 PHONE: (703) 696-2246  
 FAX: (703) 696-2203

Professor Walter H. Munk  
Scripps Institution of Oceanography  
9500 Gilman Drive  
La Jolla, CA 92093-0210  
PHONE: (619) 534-5671  
FAX: (619) 534-8076

**14. Keywords:**

Global Warming, Acoustic Thermometry, HIFT, Climate Change, SSAR

TABLE XXII  
 FY 1995 POLLUTION PREVENTION PROJECTS

Funding \$(K) FY95	ID Number	Page Number
Paint Stripping/Coatings		
180	304	PP-4
248	65	PP-10
414	756	PP-14
428	81	PP-21
126	429	PP-25
99	067	PP-29
273	139	PP-32
0	121	PP-36
223	134	PP-41
Advanced Materials/Processes		
118	117	PP-44
135	307	PP-49
Other Hazardous Wastes		
300	436	PP-54
169	422	PP-59
68	69	PP-63
0	331	PP-67

TABLE XXI FY 1995 POLLUTION PREVENTION PROJECTS		Funding \$(K) FY95	ID Number	Page Number
Metal Working Process				
Alternate Electroplating Technology (N)		248	71	PP-72
Solid State Metal Cleaning (AF)		100	116	PP-75
Non-Chromate Conversion Coatings and Sealers for Aluminum Alloys (A)		68	673	PP-79
Aircraft Maintenance Chromium Replacement (N)		158	66	PP-83
Non-Chemical Surface Preparation (AF)		274	130	PP-86
Recycling/Purification of Plating/Cleaning Baths (N/AF/EPA)		360	70	PP-90
PVD Coatings and Ion Beam Processing as Alternatives to Electroplating (A)		218	632	PP-94
Ordnance Materials and Processing				
Laser Ignition to Replace Chemical Ordnance Igniters for Propulsion (A)		313	680	PP-101
Extraction and Recycling of LOVA Propellants Using Supercritical Fluids (A)		248	660	PP-104
Recycling Propellants in Nonpolluting Supercritical Fluids: Novel Computational Chemistry Models for Predicting Effective Solvents (A)		158	695	PP-108
Non Ozone Depleting Sealants for Ammunition Applications (A)		113	674	PP-112
Solventless Manufacture of Propellants using Thermoplastic Elastomer Binder (N)		0	867	PP-115
Minimization of Uranium Alloy Waste by Electron Beam Melter (A)		0	872	PP-118
DoD/DOE Clean Agile Manufacturing of Energetic Materials (N/DOE)		600	63	PP-122
Solventless Pyrotechnic Manufacturing (N)		113	757	PP-128

TABLE XXII  
**FY 1995 POLLUTION PREVENTION PROJECTS**

Project Description	Funding \$(K) FY95	ID Number	Page Number
<b>Fire/Explosives Suppression</b>			
Encapsulated Micron Aerosol Fire Suppression Technology (AF)	284	113	PP-133
Chemical and Physical Processes Responsible for Flame Inhibition Using Halon Agents and Their Alternatives (A/NJIST)	203	682	PP-136
Chemistry of Halon Substitutes (A)	200	666	PP-140
Advanced Streaming Agent (AF)	383	158	PP-144
<b>Refrigerants</b>			
Non-Ozone Depleting Refrigerants for Navy Chillers (EPA)	788	309	PP-147
Replacements of Hydrochlorofluorocarbon (HCFC-22) with Non-Ozone Depleting Substitutes in Military Environmental Control Units (ECUs) (A)	236	677	PP-150
<b>Pollution Prevention Total</b>			
	7,846		

## SERDP FY95 PROJECT

1. **SERDP Thrust Area:** Pollution Prevention
2. **Title:** Life Cycle Engineering & Design Program
3. **Agency:** Environmental Protection Agency (EPA)
4. **Laboratory:** Risk Reduction Engineering Laboratory (RREL)
5. **Project ID:** #304
6. **Problem Statement:**

Over the past several years, DoD, DOE and EPA have undertaken independent and joint efforts to develop pollution prevention techniques and technologies for implementation at Federal facilities. Key areas of concern have been addressed through RD&D in painting and repainting, cleaning and degreasing, ozone depleting chemicals, metal fabrication and finishing.

Life Cycle Assessment, Analysis and Design (LCA) is being viewed as the preferred tool for analyzing an operation, system, or activity and designing environmentally benign processes into the base engineering. LCA differs from previous approaches in that it views all resource, energy and cost inputs to a product (inventory analysis), as well as all the associated waste streams (impact analysis), and evaluates and implements opportunities to reduce environmental burdens (improvement analysis) from cradle to grave. This approach is based on the product life cycle, which includes raw material acquisition and processing, manufacturing, use/service, resource recovery and disposal.

The LCA tool meets the SERDP RD&D goal to "address matters of concern to unencumber military operations, enhance military systems' effectiveness, and improve the safety of personnel in meeting the Departments' environmental obligations." Only through the application of a cradle to grave analysis and engineering design approach in the development of military systems can the DoD be assured that a specified system is operating effectively with minimal environmental impacts. Because the projects selected involve technologies with broad applications in public and private sectors, this proposal also supports the SERDP goal to, "help solve significant national and international environmental problems through the application of the Departments' technical capabilities, analytical systems and information."

LCA design emphasizes integrating environmental requirements into the earliest phases of design and successfully balancing these requirements with all other necessary performance, cost, cultural, and legal criteria. Under the Pollution Prevention Thrust Area, LCA design



will enable DoD/DOE/EPA to meet SERDP research and development objectives in: (1) the development of non-hazardous alternate defense unique paints (e.g., CARC), (2) development of cost effective and non-polluting improved industrial processes and low VOC substitute chemicals for depainting, and (3) the development of predictive models and methodology to aid in the development of environmentally sound weapon systems throughout their life cycle and decommissioning.

The Life Cycle Engineering & Design Program will develop projects (identified below) that meet the research category descriptions of applied research and technology demonstration. Technology transfer may be accomplished within the cooperating departments and agencies or through the WREAFS program (Waste Reduction Evaluations at Federal Sites). The WREAFS program is designed to provide technical assistance and support to Federal facilities in conducting pollution prevention research. While the Life Cycle Engineering & Design Program is a new effort, it will build upon LCA methodology and development work already laid down in RREL's LCA, Clean Products and Clean Technologies programs.

## **7. Project Description:**

The thrust of this program will be to take selected innovative technologies and products, applying LCA design analysis to them to determine the net environmental and cost burdens. The LCA will apply methodology and design techniques previously developed under RREL's programs. In FY94, the Life Cycle Engineering & Design Program will develop three LCA design projects:

### **Project #1 -- MEK Substitute in Aircraft Radome Depainting**

Under the WREAFS program, RREL has researched and evaluated substitutes for methyl ethyl ketone (MEK) as cleaners and solvents in aircraft maintenance operations at Tinker Air Logistics Center (ALC) in Oklahoma. Tinker ALC performs maintenance, including structural repair and re-fabrication of USAF aircraft, notably the B-1B and the B-52. Tinker ALC reported using MEK at an annual rate of 5,385 gallons to wipe-down aircraft, and 8,250 gallons to depaint aircraft radomes.

From its research and in cooperation with Texaco, RREL identified solvent formulations based on propylene carbonate and n-methyl pyrrolidone as possible alternatives for MEK. The test focused on the ability of the chemical mixture to accomplish the job required, and meet the same MILSPEC standard as MEK without modifying the operational procedures.

This study determined that a blend of 25% propylene carbonate, 50% n-methyl pyrrolidone and 25% Dibasic ester (PC blend) removed paint in comparable time to the MEK. Hardness tests showed that the PC blend did not embrittle the fiberglass/epoxy substrate of the radome, nor did it effect flexural properties. Scanning with electron microscope indicated no significant damage to the fibers or fiber matrix interface. Test samples were successfully

re-painted and demonstrated complete paint adhesion. For solvent properties, the PC blend compares favorably with MEK. The PC blend has a flash point of 210OF (against MEK's 200F), low toxicity, and lower evaporation rate.

The Life Cycle Engineering & Design Program will evaluate this new formulation in an LCA approach that investigates the energy and environmental impacts of the product as well as the engineering design of the system in which it is used. Methodology laid down in RREL's manual, "Life Cycle Assessment: Inventory Guidelines and Principles," will be applied. The first step will be to conduct an inventory analysis on depainting operations, and the PC Blend, to determine the resources used and actual environmental releases. An impact analysis will determine all the environmental consequences associated with depainting, including the production, use, and disposal of the PC Blend and potential contaminants from the depainting operations. The improvement analysis will focus on evaluating environmental consequences, the PC Blend, other potential alternatives, and MEK. Inherent in this approach will be the standard of meeting mission requirements (e.g., MILSPEC standards and technical order requirements).

In its recently published, "Life Cycle Design Guidance Manual," RREL demonstrates a systems-oriented approach to minimizing environmental impacts and risks via LCA. LCA design includes the application of such concepts as concurrent design, total quality management and cross-disciplinary teams. LCA design principles will be applied to this project to ensure the development of an ecologically and economically sustainable depainting system that fulfills performance requirements.

Project #2 - Improved Chemical Agent Resistant Coating (CARC) Applications Ft. Eustis, Virginia, has completed a base-wide pollution prevention program plan, and has supported previous WREAFS assessments and related studies on-site. During the course of this work, Ft. Eustis identified a need to significantly improve CARC painting and depainting operations, moving to upgrade depainting operations with alumina silicate, separating and recycling grit, and acquiring high-volume, low-pressure (HVLV) painting equipment.

Having made individual upgrades in operations, Ft. Eustis provides the opportunity to conduct an in depth evaluation of CARC painting operations at a typical base painting facility. There are several potential opportunities to test and implement techniques for improved transfer efficiency systems, and integrate them together in a common package designed to meet an individual facility's needs. The purpose of this project will be to conduct an LCA of Ft. Eustis painting and depainting operations, beginning with an inventory analysis of CARC painting and depainting operations to determine the resources used and environmental releases. An impact analysis will determine all the environmental consequences associated with CARC operations, including corrosion control techniques. By evaluating the environmental consequences, the improvement analysis will identify improvement opportunities which will be implemented and evaluated on-site.

As with the previous project, LCA design principles shall be applied to maintain focus on aggregate environmental impact reduction while ensuring performance criteria are fully met. All potential areas of opportunity, from system design to operating procedures and practices, shall be evaluated. For example, because an opened container of CARC cannot be re-sealed and stored, its unused contents must be disposed of properly. One of the objectives of this study will be to design and test a technique to eliminate that waste.

### Project #3 -- DOE Complex-wide LCA Design Case Studies

DOE has depended extensively on the use of process waste assessments in evaluating their technologies and identifying areas of possible environmental improvement. In the area of design and development of weapon systems and the related critical weapon components, the life cycle concept can identify existing or potential environmental problems that may be caused anywhere within the product system, from well head to final disposal. One specific component of particular interest and in which activity has already been started in LCA is related to the Gas Transfer System (GTS), a weapon component currently in production at Rocky Flats, Pinellas, and Savannah River. The purpose of this project is the incorporation of LCA methodology into a major Sandia design group and provide a model for future use leading to the widespread application to other DOE design agencies.

Another area of interest in which DOE/Sandia National Laboratory (SNL) has begun activity relates to total cost assessment (TCA). TCA also incorporates the entire life cycle of a product or process but it focuses on internal and external costs that may be incurred. While LCA provides a range of information to support environmental decision-making, cost information has not typically been integrated with LCA environmental release data. Integration of cost data into the LCA approach will enhance its utility as a decision support tool.

This project builds on a current DOE funded project which is developing a technical framework, called Life Cycle Cost Assessment (LCCA), for conducting life cycle cost assessments. This project will take the framework to the next phase of demonstration allowing for further development and refinement.

### **8. Expected Payoff:**

An overriding benefit from all projects would be in the testing and customizing of LCA design approaches for DoD applications, as each project would provide lessons learned in using LCA tools for environmental risk reduction. For each of the three selected projects, the following payoffs are expected:

### Project #1 -- MEK Substitute in Aircraft Radome Depainting

The anticipated benefits include the elimination of a 33/50 toxic chemical, MEK, from the radome depainting operation, along with the VOC air emissions. The WREAFS evaluation of the PC Blend demonstrated a \$30,085 annual savings over MEK usage. We expect broad technology/product transfer opportunities across DoD operations. Follow-on projects would focus on depainting/painting characteristics of a PC blend and alternatives for a variety of thermoplastic and thermoset resins as their use is expanded in aircraft manufacturing.

Project #2 - Improved Chemical Agent Resistant Coating (CARC) Applications Ft. Eustis, Virginia. While CARC material is undergoing tests and reformulation to reduce VOC content and additional research is contemplated, there is an urgent need to address the operational applications of CARC as it is currently available. The model approach proposed here will generate guidance with applicability to facility CARC painting operations throughout the Army and DoD-wide. Costs will be tracked and the payback period will be proven in the implementation. It is anticipated that, through source reduction, more paint will meet the truck, and less will go in the can, generating cost savings and increasing operational efficiency. Lessons learned here will have application to all DoD CARC applications (e.g., vehicles, armor, weaponry, rotorcraft, etc.) in Army, Navy/Marine, and Air Force facilities. EPA's WREAFS program will provide additional support in evaluating the potential for application of lessons learned to marine anti-fouling paints and coatings.

### Project #3 -- DOE Complex-wide LCA Design Case Studies

The largest payoff will be the avoidance of future environmental problems as new or next generation products are developed. This has been seen in various weapon systems which were designed for a specific use but have outlived their usefulness and are now not easily disposed of for various regulatory reasons. These weapons require expensive maintenance until a solution for disposal can be found. This type of problem may have been avoided if the designers had considered end-of-life issues during the development of the product.

## 9. Milestones:

1.	Collect and compile data	12/94
2.	Develop LCA approach and preliminary research plan	01/95
3.	Define life cycle of project operations and refine plan	02/95
4.	Complete LCA/LCD inventories & impact assessment	01/96
5.	Report findings	02/96
6.	Identify alternative materials and engineering designs	03/96
7.	Select technologies/products for evaluation	04/96
8.	Report evaluation, LCA design report	12/96

**10. Transition Plan:**

Technology and information will be transferred through a number of vehicles. EPA and the WREAFS program transfers information through industry contacts and panels, electronic bulletin boards and clearinghouses such as PPIC, the National Technical Information Service (NTIS) and Office of Research and Development mailing lists and networks. With Ft. Eustis being a member of the Tidewater Interagency Pollution Prevention Program (TIPPP), its projects have an added visibility and opportunity for transfer across DoD. Some projects, such as the MEK substitution, shall benefit via CRADAs with industry. Air Force organizations such as AFCEE and AFIT shall participate in technology transfer. Also, DOE networks shall be accessed as appropriate.

**11. Funding: \$(K)**

	FY94	FY95	FY96	FY97	FY98	TOTAL
SERDP	750	180	220	300	300	1750
EPA	200	200	200	200	0	800
TOTAL	950	600	500	500	300	2550

**12. Performers:**

Tinker Air Logistics Center, U.S. Air Force, with Thomas Walker as point of contact, and Texaco Corp. via CRADA agreement shall participate in the MEK replacement (PC Blend) study. Ft. Eustis Army Transportation Command, with Helen Turner as the point of contact, shall participate in the CARC project. And both Sandia National Laboratory and Los Alamos National Laboratory, with Ker Chi Chang as the point of contact, shall support the DOE project.

**13. Principal Investigator:**

Kenneth R. Stone  
USEPA/RREL  
Cincinnati, OH 45268  
PHONE: (513) 569-7474  
FAX: (513) 569-7111  
E-MAIL: STONE.KENNETH@EPAMAIL.EPA.GOV

**14. Keywords:**

MEK, painting, depainting, solvents, computer modeling, LCA

## SERDP FY95 PROJECT

1. **SERDP Thrust Area:** Pollution Prevention
2. **Title:** Organic Protective Coatings and Application Technology
3. **Agency:** U.S. Navy
4. **Laboratory:** Naval Air Warfare Center Aircraft Division - Warminster
5. **Project ID:** #65

### 6. Problem Statement:

To develop high performance, non-toxic, low volatile organic compounds (VOC) content coatings for Navy use. Organic coatings are the primary source of protection against environmental degradation for Navy aircraft (A/C), weapon systems and ground support equipment (GSE). In addition, these materials provide passive countermeasures against many enemy threats. There are a large number of different coating systems currently used by the Navy due to the diverse nature of their functions; the variety of substrates and alloys to which they are applied; and the severe nature of their operational environment. These protective coatings contain toxic inhibitors (i.e. lead, chromates, etc) and high VOC contents. These components are released during painting operations as organic and toxic air emissions. Federal, state and local environmental agencies like the EPA and California Air Quality Management Districts (AQMD) classify these materials as hazardous and restrict their emissions through regulations such as the Clean Air Act, Clean Water Act, CERCLA, Resource Conservation and Recovery Act (RCRA) as well as local EPA and AQMD rules. In addition, OPNAV and CNO directives require significant reductions in the amount of hazardous waste generated by the Navy. Finally, painting operations at maintenance depots are a major contributor to hazardous material and waste generation in the DoD. Therefore, it is necessary to develop new high performance coatings that meet current and future environmental restrictions while allowing the Navy to continue painting operations. This effort is covered under the Tri-service EQ Strategic Plan Area: Pillar 3: Pollution Prevention, Requirement Thrust: 3.B: Coatings and Removal Technology and is a continuation of an existing SERDP 6.2/6.3 effort.

### 7. Project Description:

A full spectrum approach for reducing the VOC and air toxic emissions from protective coatings will be pursued. To begin with, investigation in low VOC polymer technology will be used to produce low VOC binder systems. Reactive monomers/oligomers and diluents will be developed to obtain low viscosity, low VOC binder systems for future organic

coatings. In addition, recent advances in water-borne resin technology will allow for the development of high performance water-borne topcoats which are compliant with these regulations. Coating corrosion resistance, physical performance properties and VOC content will be evaluated to develop the best materials. Furthermore low/no VOC protective coatings (such as electrocoatings, powder coatings, bearing adhesives, fuel cell repair, NDI penetrants, etc) will be investigated for potential aerospace applications. Several recently developed VOC compliant, non-toxic alternative materials will be investigated for this program. These compliant coating systems include Unicoat (a non-lead, non-chromate, low VOC self-priming topcoat); compliant lacquer topcoats and non-toxic inhibitor systems. The non-toxic inhibitor systems will be used to develop replacements for the current lead and chromate containing materials. These materials will be optimized, service evaluated and implemented for Navy use. Finally, conventional air spray equipment used to apply these materials, has a transfer efficiency of only about 28%. Therefore, implementing high transfer efficient spray equipment would significantly reduce the amount of air emissions from painting operations. Application equipment such as air-assisted airless, electrostatic, and high volume low pressure (HVLP) will be evaluated.

**8. Expected Payoff:**

The development of non-toxic, VOC compliant coatings will enable the Navy to meet current and future environmental regulations as well as reduce the total amount of hazardous waste the Navy generates. In addition, these new materials will eliminate the need for the installation of extremely expensive control equipment (i.e. \$1-5M per spray booth for VOC emission control). This effort is in direct support of Navy and DoD hazardous waste minimization policies/directives. In addition to reduced handling and disposal costs, Navy A/C and equipment operational readiness will be maintained by using these new coatings. This is particularly important considering the cost of these A/C, weapon systems and GSE as well as the severely deleterious environment in which the Navy operates. This technology could also be transitioned to many areas of the commercial sector (aerospace, automotive, marine, etc).

**9. Milestones:**

- |    |  |       |
|----|--|-------|
| 1. | Implement TT-P-2756 "Self-Priming Topcoat-Unicoat"   | 07/93 |
| 2. | Develop one-component compliant lacquer coatings   | 09/93 |
| 3. | Service demonstration of compliant lacquer coatings  | 03/94 |
| 4. | Service demonstration of water-borne topcoats  | 04/94 |
| 5. | Transfer high transfer efficiency paint application equipment technology to fleet & depot facilities | 09/94 |
| 6. | Develop low VOC epoxy system A/C coatings  | 09/94 |
| 7. | Resolve discrepancies (rheology) with water-borne topcoat from April demo                            | 11/94 |
| 8. | Develop water-borne aircraft topcoats  | 11/94 |

- |     |  |       |
|-----|--|-------|
| 9.  | Service demonstration of non-toxic inhibited primer coating                          | 03/95 |
| 10. | Resolve discrepancies (outgassing) with water-borne topcoat from April 94 demo       | 05/95 |
| 11. | Service demonstration of optimum water-borne topcoats                                | 11/95 |
| 12. | Initiate service demonstration and technology transfer of non-toxic inhibited primer | 12/95 |
| 13. | Formulate polyurethane coatings based on low VOC additives                           | 12/95 |
| 14. | Characterize non-Cr A/C sealants properties  | 01/96 |
| 15. | Develop/optimize selected powder coatings  | 01/96 |
| 16. | Develop/optimize selected electrocoatings  | 01/96 |
| 17. | Full scale demonstration non-toxic developed coatings                                | 05/96 |
| 18. | Optimize non-Cr A/C sealants   | 06/96 |
| 19. | Initiate Spec revision and technology transfer of water borne topcoats               | 08/96 |
| 20. | Initiate service demonstration of non-toxic powdercoats                              | 02/97 |
| 21. | Initiate service demonstration of non-toxic electrocoats                             | 02/97 |

**10. Transition Plan:**

The best alternative materials identified from the laboratory evaluations will be service demonstrated at a NADEP through the Lead Maintenance Technology Center for Environment. Following demonstration, they will be transitioned to fleet use through specification modification, technical manual revision and design changes. Industry coordination through out the development and evaluation of these materials and processes will insure availability for implementation.

**11. Funding: \$(K)**

	FY94	FY95	FY96	FY97	TOTAL
SERDP	400	248	303	930	1881

**12. Performers:**

Development of non-toxic, low VOC protective coatings is being performed by the Naval Air Warfare Center Aircraft Division Warminster, Naval Aviation Depots and the Lead Maintenance Technology Center for Environment. These efforts are being coordinated with resin/coatings industry (Miles Inc, Air Products, Deft, BASF, Spraylat Courtaulds, etc), Air Force (Tinker AFB, Kelly AFB and Tyndall AFB), Army (ARL, etc), equipment manufacturers (Graco, Binks, etc) and aerospace industry (MDA-E, Boeing, Rohr, etc.).



**13. Principal Investigator:**

Stephen J. Spadafora  
Naval Air Warfare Center Aircraft Division Warminster  
P.O. Box 5156 (Code 4.3.4.1/MS-08)  
Warminster, PA 18974-0591  
PHONE: (215) 441-2704  
FAX: (215) 956-4141  
E-MAIL: spadforas@smtpgate.nadc.navy.mil

**14. Keywords:**

Organic Coatings, Materials Substitution, Paint Application Equipment, Low VOC Polymers,  
Volatile Organic Compounds, Non Chrome/Lead coatings

## SERDP FY95 PROJECT

1. **SERDP Thrust Area:** Pollution Prevention
2. **Title:** Fluorinated Ship-Hull Coatings for Non-Polluting Fouling Control
3. **Agency:** U.S. Navy
4. **Laboratory:** Naval Command, Control and Ocean Surveillance Center (NCCOSC), and Naval Research Laboratory (NRL)
5. **Project ID:** #756
6. **Problem Statement:**

The goal of this project is to develop non-polluting fouling resistant or fouling release hull coatings exploiting the low surface energy of surface oriented perfluorinated alkyl compounds. This project is a continuation of the FY93 funded "Innovative Very Low VOC Antifouling Paints and Processes" SERDP (6.2) program, and includes a new initiative in cooperation with NRL to explore the fouling release properties of low-glass-transition-temperature polyurethanes that have liquid-like surfaces. This project meets SERDP Pollution Prevention Objective 3 and associated with RELIANCE thrust area 3.b (Coatings and Treatment). It addresses the specific Navy requirements 3.I.8.h (Prevention of hazardous discharge from ship in-water hull cleaning).

Protection of ship-hulls from marine fouling organisms is essential for efficient fleet operation and energy conservation. To achieve this protection, ship hulls have been coated with antifouling paints that contain toxic material such as copper or organotin. Conventional antifouling coatings create an environmental hazard due to continuous release of toxic materials. A cruiser size ship (35,000 ft<sup>2</sup> hull area) releases approximately 2 lb copper/day that may bring approximately 5 million gallons of sea water to toxic copper concentrations. Dozens of ships painted with conventional toxic antifouling paints can make a significant environmental impact in an enclosed harbor.

Since the Navy operates both in US and foreign waters, compliance with Federal, State, local environmental regulations as well as with regulations imposed by the host countries is required to ensure unconstrained operation. To meet its needs, the Navy has a strong commitment to develop and maintain an environmentally sound ship for the 21st century. The present proposal is a contribution to this effort with the goal of developing a toxic free coating that resists or reduces the attachment of marine fouling organisms. This proposal takes advantage of the weak adhesion characteristics of materials that have low surface free energies.

All marine fouling organisms use biopolymeric adhesive secretions for attachment. The strength of adhesion, expressed as the work of adhesion (the work required to separate the adhered liquid from the solid surface) ( $W_A$ ) and the liquid ( $Y_l$ ) minus the interfacial tension ( $Y_{sl}$ ) ( $W_A = Y_s + Y_l - Y_{sl}$ , Dupre 1869). From this equation, it is clear that the lower the surface free energy of the solid ( $Y_s$ ), the weaker the adhesion. Hull coatings with sufficiently low surface energy should prevent fouling because organisms would not be able to adhere to it.

The lowest surface free energies can be created by adsorbed monolayers of closely packed perfluorinated compounds. Since adsorbed monolayers are not practical as hull coatings, we propose to simulate them by grafting perfluoroalkyl compounds to surfaces, by embedding such molecules into the surface of polymeric matrices, and by binding the perfluorinated compounds into a polymeric backbone to create comb type polymers with perfluoroalkyl sidechains.

These types of polymeric materials have far lower surface free energies than Teflon and have promising properties for controlling biofouling. The key parameter is the molecular orientation at and immediately under the surface. Therefore, a major part of the proposed work will be dedicated to the elucidation of the molecular orientation of the various experimental systems. This knowledge will assist efforts in optimizing the orientation for minimum surface free energy and maximum performance as well as assessing the stability of the orientation in a seawater environment and the changes caused by the marine environment.

## **7. Project Description:**

The specific objective of this project is to develop a nontoxic, zero discharge coating that protects ship-hulls from marine fouling organisms. Unlike conventional antifouling paints, such coatings will not contain toxic materials, rather they will be designed to resist fouling or allow only weak adhesion of fouling organisms. In order to minimize adhesion we will design materials with the lowest possible surface free energy. Our technical objectives are to: (1) Simulate adsorbed fluorinated monolayers either by grafting perfluoroalkyl molecules to surfaces, by embedding perfluoroalkyl compounds into the surface of polymeric matrices, or by synthesizing comb type polymers with perfluorinated side-chains for maximum effectiveness; (2) Determine the minimum amount of perfluorinated additive needed for optimum performance; (3) Reduce the amount of the expensive perfluorinated moiety by copolymerization of block-polymerization with non-fluorinated monomers to reduce cost; (4) Verify the effectiveness of the perfluorinated polymeric materials against the adhesion of marine fouling organisms.

Elucidation, control and stabilization of the surface orientation of the molecules and polymeric side-chains is a key technical issue. We will systematically optimize the curing and polymerization conditions to achieve consistent low surface free energies and antifouling/fouling-release properties. Additives and copolymerization are also important

issues affecting surface property optimization and coat reduction. In addition to the surface free energy related measurements, the shear strength of a selected series of adhesives, including the mussel adhesive, will be determined. The adhesion strength will indicate the fouling release property of a polymeric surface.

Molecular modeling will help to verify and explain molecular orientations and interactions observed at the polymeric surface. We will use powerful computational chemistry programs such as Gaussian 92, SPARTAN and HyperChem on our Center's Convex C3240 MiniSupercomputer. We will use computational chemistry to calculate surface free energies of model compounds, design low adhesion surfaces, and predict surface effects and molecular interactions at various interfaces.

Long-chain perfluorinated compounds will be prepared from a number of derivatives of perfluoroalkyl iodide homologues. These include acrylates and methacrylates for use as additives or for polymerization to form comb-polymers. Olefins prepared from the iodides will be hydrosilylated to form perfluoroalkylethyl silanes. The silanes are used to form self-assembled chemisorbed monolayers and polysiloxane comb-polymers. The iodides are also used to form perfluoroalkylethyl thiols which are grafted to metal surfaces, such as gold, to also form chemisorbed monolayers. Adsorbed and chemisorbed molecular layers of perfluoroalkyl compounds with various functional groups will serve as model surfaces to study molecular orientation and surface characteristics.

Various techniques will be used to determine the surface configurations of the fluorinated moieties. These techniques include grazing-angle infrared reflectance to calculate molecular orientation, X-ray Photoelectron Spectroscopy (XPS) to determine  $CF_2/CF_3$  ratios on the surface, and visible light and infrared ellipsometry to measure film thicknesses. The molecular depth profile of the surface layer will be determined by variable angle Attenuated Total Reflectance methods. Depth-profiling provides information about the concentration distribution of perfluoroalkyl additives near the surface and also about the conformation of the polymer molecules and orientation of the side-chains at the surface and in the underlying layers.

We will simulate adsorbed molecular layers by mixing perfluorinated amphiphatic compounds into uncured polymeric mixtures. The compounds chosen as additives include perfluoroalkyl acids, alcohols, amines, and esters. The additives migrate to the surface and the hydrophobic portion of the chains extrude from the matrix so that they are immobilized oriented at the polymer surface. The advantage of using additives is simple preparation that requires only small quantities of the expensive perfluoroalkyl compounds to achieve sufficiently low surface energies.

Comb-polymers will be synthesized from monomers with long perfluoroalkyl chains or by grafting perfluoroalkyl chains to existing polymeric backbones. These simulate adsorbed monolayers, producing surfaces with surface energies comparable to those of adsorbed

molecular layers. In addition to the presently explored polymer system, the acrylates/methacrylates and the siloxanes, we will synthesize several new classes of polymers such as urethanes, epoxies and polyethylenes containing long perfluorinated side-chains. We will systematically determine the optimum factors that control the orientation of the perfluorinated moieties at the surface.

Parallel with this effort, basic research (6.1) on fluorinated poly-urethanes with low glass transition temperatures will be initiated at Naval Research Laboratory. The potential advantages of these polymers (1) Low surface energies; (2) Low glass transition temperatures and high elasticity that may inhibit firm attachment of organism; (3) Low release energies that facilitates dislodging of the adherents; (4) Thermoplastic nature that simplifies waste disposal.

A recent development in oxetane chemistry has led to the synthesis of a new family of polyether glycols with fluorinated side-chains. Urethanes based on these new macromers have been successfully prepared at NRL. Results from preliminary tests showed that these urethanes resist attachment of barnacles and preserve the surface properties after a long period of immersion in water.

The goals of the 6.1 part of research are: (1) Incorporate longer fluorinated side-chains into the polymers to reduce the surface energy; (2) Optimize composition and synthesis; (3) Understand the interactions between water and surface during long periods of contact and the relation to release energy.

A new family of fluorinated polyether glycols will be prepared by oxetane chemistry. Fluoroalkoxymethyl-3-methyl-oxetane (FOX) is obtained by reacting 3-bromomethyl-3-methyl-oxetane with fluorinated alkoxides in DMF at 70°C. Ring opening polymerization of FOX monomers is then conducted at 18°C using a lewis acid catalyst. The structure and length of the fluorinated branch can be varied for optimum performance. The fluorinated polyether glycol is reacted with diisocyanates and diols to form polyurethane. By varying the composition, the properties of polymer will be optimized.

The physical properties of the polymers, co-polymers and mixtures prepared both at NCCOSC/RDTE DIV and at NRL will be characterized and optimized for durability and low surface free energy. Low surface energy has been used as the primary design criterion for materials for fouling release. Recent work at NRL with dynamic contact angle analyzer (DCA) provides additional information for characterization. To keep a surface clean, low release energy is required to release the new adherents. A measurement of this release energy is the receding contact angle.

Nanoscale chemical composition and mechanical properties of polymeric materials can vary significantly either laterally or vertically. These variations can be characterized with X-ray photo-electron spectroscopy (XPS) and atomic force microscopy (AFM). It has been shown at

NRL that nanoscale mechanical properties may be quantitatively measured as a function of penetration depth using AFM as a nanoindenter. By obtaining a series of indentations and using a raster scan pattern across a surface, nanoscale three-dimensional mechanical property mapping may be performed on the sample surface. A recently developed algorithm which de-convolute results from XPS measurements can be used to perform corresponding chemical composition mapping. Structure-properties correlations in the surface region can be established.

The experimental coatings will be exposed to the marine environment to determine fouling resistance, fouling release, durability, and possible surface molecular changes caused by seawater, biofilm and fouling organisms.

## 8. Expected Payoff:

Non-polluting, not-toxic antifouling coatings will be synthesized. This new antifoulant will have non-wetting low-energy surface which resists the attachment of the organisms. The low surface energy antifoulant releases no toxic material into the environment; therefore, no environmental hazard will be created. While toxic antifoulants are specific against certain types of fouling, the low energy surfaces prevent any kind of attachment and provide universal protection. More importantly, in the low surface energy coating; since its efficiency is based upon a physical surface phenomenon and not on depletive active substance, long effective lifetime is ensured. Both the Navy fleet and commercial shipping industry are potential users of the non-polluting fouling release coating.

## 9. Milestones:

- |     |   |       |
|-----|---|-------|
| 1.  | Synthesis of perfluoro compounds, including polyfluorooxetanes manual method                  | 03/94 |
| 2.  | Automate polymerization process   | 07/94 |
| 3.  | Automate polymer application process  | 08/94 |
| 4.  | Field exposure testing (1st formulation run)  | 09/94 |
| 5.  | Synthesize 2nd round of polymers  | 01/95 |
| 6.  | Surface characterization studies (1st & 2nd rounds)   | 10/94 |
| 7.  | Determine surface orientation of monolayers   | 06/95 |
| 8.  | Synthesize siloxane networks & block copolymers   | 01/95 |
| 9.  | Synthesize fluoroorgano-oxetane Networks  | 05/95 |
| 10. | Synthesize side-loop architecture optimization cycles   | 07/95 |
| 11. | Conduct three polymerization optimization cycles  | 07/95 |
| 12. | Surface characterization studies with atomic force microscope                                 | 09/95 |
| 13. | Conduct 2 polymerization optimization cycles (progress assessment)                            | 05/96 |
| 14. | Conduct 3 polymerization optimization cycles (progress assessment)                            | 01/96 |
| 15. | Characterize oxetane vs. siloxane vs. side-loop vs. block surface properties of best polymers | 07/96 |

- 16. Optimize surface properties of best acrylate polymers 07/96
- 17. Prepare prime polymer candidates for long-term exposure study 10/96
- 18. Begin long-term exposure study with prime polymer candidates 11/96
- 19. Conduct 4 polymerization optimization cycles (progress assessment) 12/96
- 20. Optimize surface properties of best polymer 01/97
- 21. Scale-up of synthesis of optimized candidates 04/97
- 22. Field exposure testing (latest batch) 06/97
- 23. Correlate long-term field exposure data with predictors from surface characterization 07/97
- 24. Scale-up of synthesis of optimized candidates 09/97
- 25. Optimize large scale coating application parameters 09/97

**10. Transition Plan:**

After successful demonstration, the low-surface-energy non-polluting fouling-release coating will be transferred to suitable private companies (e.g. GenCore Polymer Division) as defense conversion for commercial scale production, and the fleet (NAVSEA) for implementation. Through the NAVSEA/NSWC Advanced Technology Demonstration program on Non-polluting/biodegradable Antifouling Hull Coatings there is a high degree of coordination between performer and user.

**11. Funding: \$(K)**

	FY93	FY94	FY95	FY96	FY97	TOTAL
SERDP	570	895	414	506	930	3315
NAVY	0	75	75	75	0	225
TOTAL	570	970	995	1005	0	3540

**12. Performers:**

The 6.2 portion of the project will be performed at NCCOSC/RDT&E Division Code 521, the 6.1 portion at NRL. The expertise of fluorochemical companies such as DuPont, 3M and GenCore Aerojet (Dr. Aslam Malik) will be recruited for synthesizing the necessary compounds and polymers. The development of the final coating will be performed with the cooperation of the paint companies (GenCore Polymer Division). Professor Joseph A. Gardella, Jr. of SUNY, Buffalo will be in charge of the XPS measurements. This project is coordinated with the ONR 6.1/6.2 Bimolecular Antifouling Program that includes developing and evaluating fouling release materials from industry, NRL and academic research. Also it will be coordinated with NAVSEA/NSWC Advanced Technology Demonstration program on Non-polluting/Biodegradable Antifouling Hull Coatings that started in FY93 and will test and evaluate fouling release and biodegradable natural antifoulant coatings.

**13. Principal Investigators:**

Dr. Sandy Clavell  
NCCOSC/RDT&E Division Code 521  
53475 Strothe Rd.  
San Diego, CA 92152-6325  
PHONE: (619) 553-2775  
FAX: (619) 553-6305  
E-MAIL: clavell@nosc.mil

**Co-Investigator:**

Dr. Ann Mera  
Naval Research Laboratory Code 6127  
4555 Overlook Ave SW.  
Washington DC 20375-5320  
PHONE: (202) 404-8893  
FAX: (202) 767-0594

**14. Keywords:**

antifouling paints, coatings, low surface energy, non-polluting, perfluoroalkyl, fluorinated polyurethane, oxetane, minimally adhesive surfaces, release energy, receding contact angle, nanoscale surface mapping



## SERDP FY95 PROJECT

1. **SERDP Thrust Area:** Pollution Prevention
2. **Title:** Aircraft Depainting Technology
3. **Agency:** U.S. Navy
4. **Laboratory:** Naval Air Warfare Center Aircraft Division Warminster
5. **Project ID:** #81

### 6. **Problem Statement:**

To develop a non-hazardous replacement for chemical paint stripping use on Navy aircraft (A/C), weapon systems (WS) and ground support equipment (GSE). Current chemical paint strippers contain hazardous components like phenols, methylene chloride and chromates. Paint removal operations at maintenance depots has been determined to be a major contributor to hazardous waste generation in the DoD. Federal agencies like the EPA and state agencies like the California Air Quality Management Districts (AQMD) have begun to restrict the use of these hazardous materials. Regulations like the Clean Air and Water Acts, CERCLA, RCRA and local EPA and AQMD rules limit or prohibit the use and disposal of these hazardous materials. In addition, OPNAV and CNO directives require significant reductions in hazardous waste generated by the Navy. Several generic alternative stripping methods to the present chemical removers are being developed. These techniques need to be optimized and evaluated for use at Naval Aviation Depots. Therefore, to comply with existing and future regulations while maintaining aircraft performance and operational readiness, these alternative methods need to be investigated. This effort is covered under the Tri-Service EQ Strategic Plan: Pillar 3 Pollution Prevention, Requirement Thrust: 3.B: Coatings and Removal Technology and is a continuation of an existing SERDP 6.2/6.3 effort.

### 7. **Project Description:**

Alternative methods of coating removal that meet increasing waste disposal constraints, have to be developed to maintain aircraft rework operations while reducing hazardous waste generation. Because there are so many different substrates/alloys and coating systems currently used by the Navy, these non-hazardous paint removal processes will also have to be versatile. Naval aircraft have different load bearing structures (higher strength) to withstand aircraft carrier landings. In addition, the Navy's operational environment can have a seriously deleterious effect on the structural integrity of aircraft skins. This issues complicate the stripping process for naval aircraft. This program will identify the best alternatives from existing and developmental methods such as non-hazardous chemical paint

strippers (i.e. materials that do not contain chromates, methylene chloride, phenol, etc); enzymatic strippers; and mechanical removal procedures (PMB, flash lamp, UV, dry ice stripping, water jet stripping, etc). Procedure efficiency, effects on substrate surface, hazardous waste generation and applicability will be investigated in order to determine the best procedure for Navy applications. Comparison of techniques as well as advantages/disadvantages will also be performed. Mechanical removal procedures eliminate the use of hazardous chemicals, however, several individual mechanical techniques damage the substrate surface during the removal process. Since some sections of aircraft skins are very thin, this is not acceptable. However, if several techniques are combined to remove the coating the surface damage could be eliminated/minimized to an acceptable level. For example, one possible combination is flash lamp/dry ice stripping. The flash lamp would degrade the coating system and the dry ice stripping perform the final removal at a reduced pressure (i.e. reduced surface damage). Finally, the treatment of the blast media used in these mechanical techniques will be investigated for waste reduction.

### 8. Expected Payoff:

The elimination of the majority of chemical paint strippers would significantly reduce the total amount of hazardous materials generated by the Navy. Furthermore, requirements for emission control equipment for methylene chloride (estimated at \$1M/facility) would be eliminated. This effort is in direct support of Navy and DoD hazardous waste minimization policies/directives. In addition to reducing handling and waste disposal costs, Navy aircraft and equipment will be properly maintained. This is particularly important considering the cost of these A/C, weapon systems and GSE as well as the severely deleterious environment in which the Navy operates. This technology could also be transitioned to many areas of the commercial sector (aerospace, automotive, marine, etc).

### 9. Milestones:

- |     |   |       |
|-----|---|-------|
| 1.  | Evaluate Alternative Stripping Processes' Parameters                                | 09/92 |
| 2.  | Characterize Enzyme System Activity/Stability                                       | 09/92 |
| 3.  | Establish Joint Navy/Air Force Investigation of FlashJet                            | 09/92 |
| 4.  | Optimize Alternative Depaint Processes (I Level)                                    | 06/93 |
| 5.  | Evaluate Plastic Blast Media Treatment Processes                                    | 09/93 |
| 6.  | Select Genes for Enzyme Synthesis   | 09/93 |
| 7.  | Evaluate Flash Lamp/Dry Ice Combination Stripping<br>(Joint Navy/Air Force Program) | 11/93 |
| 8.  | Service Demonstration of Optimized Alternative (I Level)                            | 06/94 |
| 9.  | Service Demo Plastic Blast Media Treatment Processes                                | 06/94 |
| 10. | Evaluate water-jet stripping  | 09/94 |
| 11. | Optimize Flash Lamp/Dry Ice Combination Stripping<br>(Joint Navy/Air Force Program) | 12/94 |
| 12. | Production of a Batch of Enzymes for Stripper Studies                               | 03/95 |

- |     |   |       |
|-----|---|-------|
| 13. | Implement Optimized Alternative (I Level)   | 06/95 |
| 14. | Implement Plastic Blast Media Treatment Processes   | 06/95 |
| 15. | Optimize water-jet stripping  | 09/95 |
| 16. | Service Demonstration of Flash Lamp/Dry Ice Combination<br>(Joint Navy/Air Force Program) | 12/95 |
| 17. | Conduct Enzyme Stripping Studies  | 06/96 |
| 18. | Service demo of water-jet stripping   | 06/96 |
| 19. | Implement Flash Lamp/Dry Ice Combination Stripping<br>(Joint Navy/Air Force Program)      | 09/96 |
| 20. | Evaluate/Optimize Enzyme Stripping  | 06/97 |
| 21. | Implement water-jet stripping   | 09/97 |

**10. Transition Plan:**

The best alternative materials identified from the laboratory evaluations will be service demonstrated at a NADEP in coordination with the Lead Maintenance Technology Center for Environment and the National Defense Center for Environmental Excellence (WaterJet & hand held flashjet). These processes will be transitioned to fleet use through specification modification, technical manual revision and design changes. Industry coordination throughout the development and evaluation of these materials and processes will insure availability for implementation.

**11. Funding: \$(K)**

	FY92	FY93	FY94	FY95	FY96	FY97	TOTAL
NAVY	--	--	185				185
DERA	130	250					380
SERDP	261	35	445	428	523	930	2622
TOTAL	391	285	630	428	523	930	3187

**12. Performers:**

Development of alternative stripping processes is being performed by the Naval Air Warfare Center Aircraft Division Warminster, Naval Research Laboratory, Naval Aviation Depots and the Lead Maintenance Technology Center for Environment. This effort is being coordinated with efforts being performed by the Air Force (Tinker AFB, Kelly AFB and Tyndall AFB) and aerospace industry (MDA-E, Boeing, etc.). The University of Maryland (Bioreactor scale-up facility) will collaborate with the enzymatic stripping effort.

**13. Principal Investigator:**

Stephen J. Spadafora  
Naval Air Warfare Center Aircraft Division Warminster  
P.O. Box 5152 (Code 4.3.4.1)  
Warminster, PA 18974-0591  
PHONE: (215) 441-2704  
FAX: (215) 956-4141  
E-MAIL: spadforas@smtpgate.nadc.navy.mil

**14. Keywords:**

Paint stripping, Materials Substitution, Waste Recycling/Reuse, Flashjet, Waterjet, Enzymatic  
Paint Degradation

## SERDP FY95 PROJECT

1. **SERDP Thrust Area:** Pollution Prevention
2. **Title:** High-Performance, Lead-Free Electrical Sealants
3. **Agency:** U.S. Department of Energy (DOE)
4. **Laboratory:** Sandia National Laboratories (SNL)
5. **Project ID:** #429
6. **Problem Statement:**

High-performance, electrical-grade polysulfide (MIL-S-8516F) is used extensively throughout the DoD as a fuel-resistant sealant for electrical components in aircraft; it is also used as a sealant by the DOE to protect warhead arming, jusing, and firing sections, which operate at medium to high voltages. However, electrical-grade polysulfide contains lead oxide, a hazardous material that will be subjected to strict Environmental Protection Agency (EPA) regulations in the near future. A lead-free material meeting the high performance DoD and DOE design requirements needs to be found. Finding such a material will help the Pollution Prevention SERDP Thrust Area achieve its objective of reducing the use of lead, one of the hazardous substances targeted by EPA. Work will also be performed to see if toluene sealant solvents, also targeted by the EPA, can be replaced with nonhazardous solvents.

This program would be a continuation of DOE/ECM-funded seed project. The beginning of the program would be applied research to develop a nonhazardous material substitute. This would be followed by technology transfer to both aerospace and DOE-integrated suppliers, contractors, and repair depots.

### 7. Project Description:

Understandably, it will be challenging to find a lead-free sealant that would be a completely compatible drop-in for MIL-S-8516F. This material has been in use for more than twenty years has had many of its problems ironed out through field experience and constant tweaking. Thus, our first effort for 1994 will be to develop a viscosity envelope for evaluating the flow of both the lead-containing polysulfide and alternative materials such as lead-free polysulfides and thioethers. Understanding sealant rheology is particularly important to insure that the alternative sealants can fill narrow channels and gaps. Long-term reliability testing will also be required for the new lead-free sealants so that they can qualify for the stated high-performance applications. Stability of the formulated production

material needs to be determined in order to determine shelf life, particularly for field repairs. Production lot material identification by "finger printing" should be developed to reduce supplier packaging cost and insure product reliability. We would introduce an innovative procedure for accurately tracking each lot from supplier to government application. This is based on the work of two of the project participants, Keenan and Shepodd, who have developed material tagging procedures for addressing several national security issues. Better material and process characterization information will be used in the rewriting or issuing of a new specification.

In addition to evaluating polysulfide formulations with non-lead additives, this project will investigate the feasibility of using non-polysulfide formulations. For example, extensive work done by Courtaulds, Inc. indicates that polythioether may be a viable candidate as replacement for the standard polysulfides. The cure rate for this material is easier to control than that of polysulfides because moisture is not part of the curing process. Also, available to other sealant manufacturers.

Finally, we plan to investigate encapsulants that do not rely on toluene solvents. Work performed to date indicates that polythioether may not require toluene solvents.

The major technical challenge in this project is identification of suitable lead-free formulations that can be developed into electrical-grade sealants capable of meeting the stringent requirements of MIL-S-8516F. These formulations will be identified as early as possible in the project to determine whether further product testing and development, material fingerprinting development, specification development, and commercial source development should proceed.

## **8. Expected Payoff:**

There is a strong likelihood that lead-containing (8516 type) polysulfides will be difficult or nearly impossible to acquire within the next few years because of stricter requirements placed on hazardous waste minimization. Also, vendors are finding it difficult to obtain the proper grade of the required lead peroxide curative. Another issue is the supplier may have to assume cradle-to-grave responsibility (currently under discussion at EPA) for these materials. This project will cooperate with the interested government agencies and vendors in order to develop an environmentally friendly, drop-in material that can provide solutions to these concerns.

## **9. Milestones:**

- |    |  |       |
|----|--|-------|
| 1. | Viscosity evaluation incorporated to sealant performance specification | 11/95 |
| 2. | Lead-free materials identified for testing*                            | 05/96 |
| 3. | Material compatibility testing   | 11/96 |

- |    |   |       |
|----|---|-------|
| 4. | Material fingerprinting procedure specified as new method to tag vendor production lots | 04/97 |
| 5. | Rewrite MIL-S-8516 (a new specification may be issued)                                  | 08/97 |
| 6. | Develop other commercial sources  | 01/98 |
| 7. | Investigate solvent-free material system  | 04/98 |

\* If suitable candidate lead-free sealants can't be identified, project will end this date.

**10. Transition Plan:**

Instead of having government laboratories develop a new material by themselves, we would work with up to four potential vendors to formulate a new material. The DoD and DOE facilities would provide specification requirements, extensive testing, general guidance for formulation, and methods for material control that will lower their production cost. Because of the high performance nature required of these materials, only small-scale private sector, technical dual-use potential is anticipated. When a solvent-free material (late in the program) is developed, applications for a CRADA would assist in the transfer in the use of new generations of sealants to application like sealing and encapsulating concentrator solar assemblies instead of using silicones. This could realize a large material cost savings.

**11. Funding: \$(K)**

	FY93	FY94	FY95	FY96	FY97	FY98	TOTAL
SERDP	0	110	126	0	450	230	916
DoD	10	50	50	50	30	0	190
DOE	530	200	250	250	200	0	1430
Total	540	360	580	600	460	230	2540

**12. Performers:**

DOE performer is Sandia National Laboratories. DoD performers are the Navy Air Warfare Center in Warminster and the Materials Directorate at Wright Patterson Air Force Base. Also the General Services Administration - Federal Supply, in Auburn, WA.

**13. Principal Investigator:**

Dr. John A. Emerson  
Sandia National Laboratories  
Organic Materials Department, 2472  
Albuquerque, NM 87185-0979  
PHONE: (505) 845-9747  
FAX: (505) 844-1110  
E-MAIL: jaemers@sandia.gov

**14. Keywords:**

Hazardous waste generation, Polysulfide, Polythioether, Lead, MIL-S-8516, Sealant, Fuel resistance, Potting material, Connectors



## SERDP FY95 PROJECT

1. **SERDP Thrust Area:** Pollution Prevention
2. **Title:** Solvent Substitution and Low VOC Cleaners
3. **Agency:** U.S. Navy
4. **Laboratory:** Naval Air Warfare Center Aircraft Division Warminster
5. **Project ID:** #67

### 6. Problem Statement:

To identify low volatile organic compound (VOC) content cleaning solvents for use on Navy aircraft (A/C), weapon systems (WS) and ground support equipment (GSE) and to identify replacements for methylene chloride based chemical paint strippers. Volatile organic solvents such as methyl ethyl ketone (MEK) are used for solvent wipedown of aircraft prior to painting and post-painting cleanup. Other procedures require the use of stoddard solvent for cleaning aircraft parts in solvent tanks. Other degreasing and cleaning methods use high VOC cleaners. In addition, current chemical paint strippers containing hazardous components like phenols, methylene chloride and chromates and paint removal operations at maintenance depots have been determined to be a major contributor to hazardous waste generation in the DoD. Recently, OSHA has reduced the permissible exposure limit for methylene chloride from 400 ppm to 50 ppm, forcing users to make extensive changes in ventilation and personal protection. Regulations like the Clean Air and Water Acts, CERCLA, RCRA and local EPA and AQMD rules limit or prohibit the use and disposal of these hazardous materials. In addition, OPNAV and CNO directives require significant reductions in hazardous waste. Therefore, low VOC non-toxic alternatives to solvent cleaners need to be developed. In addition, there is a need to evaluate alternative chemistries for paint removers for use at Naval Aviation Depots in order to identify a product or a chemistry capable of satisfying existing and future regulations while maintaining aircraft performance and operational readiness. This effort is covered under the Tri-Service EQ Strategic Plan: Pillar 3: Pollution Prevention, Requirement Areas: 3.A.3: Metal Working/Cleaning and Degreasing and 3.B: Coatings and Removal Technology and is a continuation of an existing SERDP 6.2/6.3 effort.

### 7. Project Description:

Solvent cleaners must be effective on a diverse combination of soils from baked on carbon to aircraft greases and lubricants. This program will develop solvent blend formulations and aqueous cleaners which will be evaluated with laboratory performance and cleaning

efficiency tests. The best materials will be further evaluated for vapor pressure, odor, evaporation rate, safety and cost. Enzyme cleaners, lubricant cleaners, low VOC solvent cleaners, and supercritical CO<sub>2</sub> cleaning methods will also be evaluated in this program. Optimized materials will be service tested at a NADEP and transitioned to fleet use through specification modification and design changes. Non-methylene chloride alternatives must exhibit workable performance characteristics while reducing the impact of stripper waste on disposal operations. Because there are so many different substrates/alloys and coating systems currently used by the Navy, non-hazardous paint removers will also have to be versatile. This program will identify the best alternatives for ambient coating removal operations. Procedure efficiency, effects on substrate surface, hazardous waste generation and applicability will be investigated in order to determine the best procedure for Navy applications. The best alternative material will be demonstrated at a NADEP and transitioned to fleet use through specification modification and design changes.

### 8. Expected Payoffs:

The development of low VOC solvents would significantly reduce the total amount of hazardous material emissions generated. In addition, the elimination of the methylene chloride based chemical paint strippers would significantly reduce the total amount of hazardous materials generated by Navy maintenance facilities and eliminate the need for expensive emission control equipment (\$1M/Facility). This effort is in direct support of Navy and DoD hazardous waste minimization policies/directives. In addition to reduced handling and waste disposal costs, Navy aircraft and equipment must be properly maintained. This is particularly important considering the cost of A/C, WS and GSE as well as the severely deleterious environment in which the Navy operates. This technology could also be transitioned to commercial aerospace, automotive, and marine industries.

### 9. Milestones:

1.	Develop no VOC A/C exterior cleaners	06/95
2.	Initiate enzyme cleaner evaluation	07/95
3.	Service evaluation of low VOC wheel well cleaners	09/95
4.	Implementation of optimized non-hazardous strippers (Joint Navy/Air Force Program)	12/95 →
5.	Evaluate/optimize enzyme cleaners	06/96
6.	Service evaluation of no VOC A/C exterior cleaners	06/96
7.	Implement optimized low VOC wheel well cleaners	09/96
8.	Initiate supercritical CO <sub>2</sub> cleaning investigation	09/96
9.	Investigate lubricant low VOC solvent cleaners	12/96
10.	Service evaluation of optimized enzyme cleaners	06/97
11.	Implement no VOC A/C exterior cleaners	09/97
12.	Evaluate/Optimize supercritical CO <sub>2</sub> cleaning methods	09/97
13.	Evaluate/Optimize lubricant low VOC solvent cleaners	09/97

## 10. Transition Plan:

The best alternative materials identified from the laboratory evaluations will be service demonstrated at a NADEP through the Lead Maintenance Technology Center for Environment. These materials will then be transitioned to fleet use through specification modification, technical manual revision and design changes. Industry coordination through out the development and evaluation of these materials and processes will insure availability for implementation.

## 11. Funding: \$(K)

	FY94	FY95	FY96	FY97	TOTAL
SERDP	150	99	121	350	720

## 12. Performers:

Development of non-methylene chloride paint strippers is being performed by the Naval Air Warfare Center Aircraft Division Warminster (NAWCADWAR) and the Air Force (Tyndall AFB) in a joint effort. The solvent substitution and low VOC cleaner efforts are being performed by NAWCADWAR, Naval Aviation Depots and the Lead Maintenance Technology Center for Environment and are being coordinated with efforts by the Air Force (Tinker AFB, Kelly AFB and Tyndall AFB), DOE and aerospace industry (MDA-E, Boeing, etc.).

## 13. Principal Investigator:

Stephen J. Spadafora  
Naval Air Warfare Center  
Aircraft Division Warminster  
P.O. Box 5152 (Code 4.3.4.1)  
Warminster, PA 18974-0591  
PHONE: (215) 441-2704  
FAX: (215) 956-4141  
E-MAIL: spadforas@smtpgate.nadc.navy.mil

## 14. Keywords:

Solvents, Chemical Paint Strippers, Materials Substitution, Cleaners, Volatile Organic Compounds, Methylene Chloride Replacement

## SERDP FY95 PROJECT

- 1. SERDP Thrust Area:** Pollution Prevention
- 2. Title:** Laser Cleaning and Coatings Removal
- 3. Agency:** U.S. Air Force
- 4. Laboratory:** Wright Laboratory, Aeronautical Systems Center (WL)
- 5. Project ID:** #139
- 6. Problem Statement:**

The goal of the proposed effort is to provide a field demonstration of a prototype laser-based facility to demonstrate environmentally acceptable component cleaning and coating removal technology and to transition it to aerospace users, including the following Air Force Logistic Centers:

Oklahoma City Air Logistics Center (OC-ALC)  
San Antonio Air Logistics Center (SA-ALC)  
Warner Robbins Air Logistics Center (WR-ALC)  
Sacramento Air Logistics Center (SM-ALC)  
Ogden Air Logistics Center (OO-ALC)

Cleaning and coatings removal technologies have traditionally depended upon the use of organic solutions, such as, PD 680 (I, II, & III) methyl ethyl ketone (MEK), methylene chloride (MECL), phenol, and strong acids and bases as well as hot potassium permanganate solutions. These materials are hazardous, and include volatile organic compounds (VOCs), ozone depleting chemicals (ODCs) and air toxic emitters which are subject to severe restrictions or are being banned altogether, such as freon (CFC-113). More recently, the trend in cleaning technology is toward the use of water based cleaners (sodium metasilicate bases, terpene/water emulsions or water detergent blends), some of which may be hazardous to some degree. However, technologies are needed which do not involve generation of waste water streams.

Laser-based cleaning and coating removal has been demonstrated to be an environmentally acceptable, affordable and controllable technology. A demonstration facility is needed to facilitate transition of this technology to Air Force, DoD and industry use, targeted to the immediate needs of the Air Logistics Centers.

This is the continuation of an FY93 SERDP funded program.

## **7. Project Description:**

The project objective is to demonstrate the use of laser cleaning and coating removal on components ranging from turbine engine blades to landing gear and radomes.

The project approach is to design, fabricate, test, evaluate and demonstrate a state-of-the-art automated, controllable laser cleaning and coating removal facility. The facility will be designed for carbon dioxide and eximer laser cleaning and coating removal operations. System operation will be fully robotized and computer controlled with on-line instrumentation for component positioning and measuring and controlling laser inputs to the part surfaces.

The project involves the following tasks:

Design system to demonstrate technology on fighter aircraft landing gear and radome components.

Design a subsystem system to handle, treat or capture, as necessary, all gaseous and particulate products of the process.

Purchase or fabricate lasers, computers, robotics, controller, sensors, hardware and software necessary for the operation of the system.

Assemble the demonstration facility system. Make necessary mechanical hardware and software modifications to insure safe, reliable and controllable operations.

Demonstrate system on both metallic and non-metallic specimens.

Test and evaluate adequacy of cleaning and coating removal process for aircraft components.

Operate the facility and make it available for ALC and GOCO engineering evaluation on specific aircraft components.

Qualify facility to applicable specifications for aircraft components cleaning and coating removal.

The proposed effort responds to pollution prevention mandates by DoD and the Air Force. The effort also will enable reduction of risks, compliance costs and liabilities associated with use and release of toxics to the environment. This program supports the DoD objectives to reduce volatile air emissions by 50% by the end of 1999 (1993 baseline).

Extensive test and evaluation work has been completed by the Air Force and the Navy on laser radiation effects on substrate materials and coating removals. What is needed next is a

prototype facility where test and evaluation cost analysis and cleanliness levels can be performed on a variety of aircraft components. The facility would be available to the services as well as the aerospace community for test and evaluation purposes.

The technical risks involved in this project are low. Industrial lasers, both carbon dioxide and eximer are available; controls, robotics sensors, instrumentation are also available. Software will have to be developed/modified to control the production system. Systems design must incorporate all applicable safety devices and features.

Tie to Tri-service Environmental Quality R&D Strategic Plan

Pillar Thrust Area: 3.B.2  
Requirements Category: 3.I.5.a  
Work effort: Tech Base

## **8. Expected Payoff:**

The laser based cleaning and coating removal facility will be applicable to a broad range of aircraft and general equipment cleaning and coatings removal work. Benefits include the complete elimination of the use of toxics and hazardous waste generation in logistic center maintenance and re-manufacturing operations relying on the new technology. The limits of such potential payoff are presently unexplored and remain to be determined. The process is expected to be highly cost effective considering that all costs for hazardous materials management and management of solid, liquid, and vapor waste streams will be eliminated.

## **9. Milestones:**

1.	Project Initiation/begin assessment	04/94
2.	Complete assessment	12/94
3.	Report/document recommendations and findings	04/95
4.	Contract award and begin final design	06/95
5.	Approve Design and initiate hardware procurement/component fabrication	08/95
6.	Initiate life cycle cost study	11/95
7.	Initiate systems assembly and check-out operations	03/96
8.	Complete check-out and de-bug of systems operations	06/96
9.	Initiate test and evaluation with services and industry customers	08/96
10.	Complete life cycle cost studies and economic benefit studies	02/97
11.	Final report and transfer of system to selected DoD facility (ALC)	03/97

## **10. Transition Plan:**

It is planned that the system to be built under this effort will be a prototype demonstration and as such will have many more capabilities than required on an actual production system. Users will perform test and evaluation programs on the prototype and determine the

capabilities needed for their production unit. Cost data will be generated, specific engineering problems will be addressed and production systems design requirements will be generated.

**11. Funding: \$(K)**

	FY93	FY94	FY95	FY96	FY97	TOTAL
SERDP	300	1552	273	1155	950	4230

**12. Performers:**

The project will be performed under the technical leadership and direction of the Air Force Material Command, Aeronautical Systems Center, Wright Laboratory, Materials Directorate, Wright-Patterson AFB, OH 45433.

The Materials Directorate will award one or more research contracts to industry to perform the development and integration.

In order to facilitate generation of public domain information, hands-on government technology assessment and technology transition, the Materials Directorate plans on having the demonstration site to be either an Air Force Material Command Air Logistics Center or the Developmental Manufacturing and Modification Facility (DMMF) at Wright Patterson AFB Ohio.

**13. Principal Investigator:**

Mr. Michael Waddell  
WL/MTPN  
2997 P St., Suite 6  
Wright-Patterson AFB, OH 45433-7739  
PHONE: (513) 255-7277  
E-MAIL: waddelmd@ml.wpafb.af.mil

**14. Keywords:**

Cleaning, Coating removal, Lasers, Methylene chloride, Methyl ethyl ketone, Phenols

## SERDP FY95 PROJECT

1. **SERDP Thrust Area:** Pollution Prevention
2. **Title:** Large Area Powder Coating
3. **Agency:** U.S. Air Force
4. **Laboratory:** Wright Laboratory, Aeronautical Systems Center (WL)
5. **Project ID:** #121

### 6. **Problem Statement:**

Current surface coating technologies for aerospace systems employ spray application processes which use and release volatile organic compounds (VOCs) or isocyanates. Existing primers and topcoats are solvent based systems which have offered excellent protection against corrosion or other operating environment conditions. However, industrial use of solvent based technology has numerous drawbacks: evaporation of toxic volatile organic compounds (VOCs), release of toxic isocyanates, low transfer efficiency, and relatively long cure times. An alternative technology, use of powder coatings, has generated considerable interest within the aerospace industrial community. Powder coating typically involves electrostatic application of powdered metal to a grounded part, followed by a curing cycle to flow the material into a continuous coating. Advantages of powder metal technology include: reduction of toxics use and generation, increased transfer efficiency, and reduced costs of environmental safety and compliance and energy use. Current technology has limitations, however, in use of powder for large parts, such as those on the outer moldline of aircraft. Technology development is needed to obtain the full benefit of powder coatings use in this area of aerospace manufacturing.

### 7. **Project Description:**

**Technical Objective:** Technology for large area powder coating will be developed, optimized, reduced to practice, and qualified for use on Air Force systems.

**Technical Approach:** This program is an integrated program to develop alternatives to solvent based coating systems for large aircraft parts. Considerations in identifying an acceptable technology will include: maintenance or improvement of substrate integrity, effects of part geometries, process quality assurance, and curing specifications. Candidate technologies, including both government and industry initiatives, will be identified and assessed. Development needs will be identified and implemented. Most promising technologies will be developed, optimized, scaled-up, demonstrated and qualified. Needs of



Air Logistics Centers (ALCs) and Government-Owned, Contractor-Operated (GOCO) facilities will be given priority attention.

The planned effort will be coordinated with Wright Laboratory continuing work on advanced low VOC and powder coating programs.

The proposed effort responds to pollution prevention mandates by DoD and the Air Force. The effort will also enable reduction of risks, compliance costs and liabilities associated with use and release of toxics to the environment.

The proposed effort is relevant to various Air Force and industry efforts to develop powder metal technologies for aerospace use. The needs of ALCs are sufficiently urgent to warrant Wright Laboratory participation in the quest for acceptable large area powder coating technology.

Tasks/activities: Process studies will be conducted to identify and assess candidate technologies, including both government and industry initiatives. Studies of development needs will be identified and implemented. The most promising candidate technology will be selected for testing, analysis, development, optimization, scale up, demonstration and qualification. Life cycle cost studies will be performed. The prototype will be transitioned to users for extended production evaluation. The needs of ALCs and GOCOs will be given priority attention.

Technical issues to overcome: Major technical issues include: powder formulation, powder handling and storage, meeting low temperature flexibility and reverse impact requirements, maintenance of proper coating quality and thickness, and curing optimization.

Tie to Tri-service Environmental Quality R&D Strategic Plan

Pillar Thrust Area: 3.B.1  
Requirements Category: 3.I.4.a  
Work effort: Tech Base

## **8. Expected Payoff:**

Availability of acceptable large area powder coating technology will liberate Air Force and industry users from the burdens of using a technology dependent on VOCs and air toxics. The total cost avoidance will be dependent upon the specific applications and the technologies developed. While direct labor, material, and equipment costs may increase, the burdens of environmental compliance and costs of hazardous materials and waste management and response will be entirely eliminated.

The planned effort will not adversely impact system efficiency, capability, or schedule. Experience with detail part technologies suggests that costs may be lower.

## 9. Milestones:

- |    |   |       |
|----|---|-------|
| 1. | Initiate project Initiate studies to define powder coating process mechanisms and requirements for large area coating. Select demonstration site and mobilize R&D team. Design and initiate tests and experiments to determine materials properties | 10/93 |
| 2. | Complete definition studies. Initiate selection of parts and processes to be targeted for development and application of the new technology. Initiate preparation of experimental design for initial technology demonstration                       | 04/94 |
| 3. | Finalize deposition technology demonstration agenda. Select site for deposition demonstration. Initiate preparations for technology demonstration   | 06/94 |
| 4. | Conduct deposition technology demonstration. Initiate analysis of results in concert with research partners and user technical representatives  | 12/94 |
| 5. | Complete review of technology demonstration results. Initiate validation and optimization studies Initiate experiments to determine effects of processes on substrates/parts Evaluate process quality and consistency                               | 02/95 |
| 6. | Complete validation and optimization studies Initiate planning for scale-up studies determine full scale process requirements in terms of equipment, personnel, siting, and operating processes   | 12/95 |
| 7. | Complete scale-up planning Initiate acquisition and positioning of scale-up elements  | 02/96 |
| 8. | Conduct pilot scale demonstration Review results and determine if full scale is appropriate   | 11/96 |

## 10. Transition Plan:

Following the decision to perform full scale demonstration, a demonstration plan will be developed in concert with the user for the selected demonstration site (ALC or GOCO). Performance testing parameters will be developed, equipment and materials procured and positioned, and staffing and support arranged. Full scale demonstration will then be conducted. Findings will be compiled and made available to prospective users for review and evaluation. After evaluation and acceptance, specifications and standards will be prepared or revised to make the new technology available for production or logistics use.

Degree of coordination conducted between performer and user: Potential users will be an integral part of the R&D effort for its duration. Their participation and technical inputs will be utilized throughout the technology development and validation process.

**11. Funding: \$(K)**

	FY93	FY94	FY95	FY96	TOTAL
SERDP	100	315	0	264	697

**12. Performers:**

The project will be performed under the technical leadership and direction of:

Air Force Material Command  
Aeronautical Systems Center  
Wright Laboratory  
Materials Directorate  
Wright-Patterson AFB, OH 45433

The Materials Directorate will award one or more research contracts to industry to perform the development and integration tasks.

In order to facilitate generation of public domain information, hands-on government technology assessment and technology transition, the Materials Directorate plans on having the pilot and full demonstration site to be either an Air Force Material Command Air Logistics Center, the Developmental Manufacturing and Modification Facility (DMMF) at Wright Patterson AFB, Ohio, or a selected Air Force GOCO facility.

**13. Principal Investigator:**

Capt, Martin Whalen/Mr. Michael Halliwell  
WL/MLBP, Bldg 654  
Wright-Patterson AFB, OH 45433-7750  
PHONE: (513) 255-4611  
FAX: (513) 476-3877  
E-MAIL: whalenmt@ml.wpafb.af.mil  
halliwmj@ml.wpafb.af.mil

Wright Laboratory has extensive research and development experience in the area of application and fusing of powdered thermoplastic materials on metallic/non-metallic substrates. Wright Laboratory also has extensive long term research and development experience with powder and other coatings technology. Many of the DoD specifications involving coatings technologies have been developed by and are under the jurisdiction of Wright Laboratory.

**14. Keywords:**

Coating, Powder Metallurgy, VOCs, Isocyanates, Air Pollutants, Painting

## SERDP FY95 PROJECT

1. **SERDP Thrust Area:** Pollution Prevention
2. **Title:** Large Aircraft Robotic Paint Stripping (LARPS)
3. **Agency:** U.S. Air Force
4. **Laboratory:** Wright Laboratory, Manufacturing Technology Directorate (WL)
5. **Project ID:** #134
6. **Problem Statement:**

The Air Logistics Centers primary method to remove organic coatings from aircraft structures is with methylene chloride based chemical stripping compounds. Protective coatings for large aircraft primary and secondary structures consists of thin skin metallic and composite materials which must be removed by environmentally clean processes. The disadvantages of chemical paint stripping are: long processing time, expensive and hazardous chemicals, personnel exposed to hazardous environment, chemicals cause premature degradation of the working areas, and special disposal techniques are required to minimize environmental impact. Methylene chloride and other hazardous chemicals will be banned by the Air Force in 1997 and the Environmental Protection Agency, or federal law by the year 2000. An environmentally safe, high pressure water system, is currently being developed as a Air Force Manufacturing Technology (MANTECH) project. This effort addresses thin skin metallic structures and composite components, but not aircraft radomes. The composite work requirements need to be expanded for radomes. However, radomes must conform to more stringent performance criteria to ensure accurate initial launch coordinates for missiles, artillery, and safe terrain avoidance/mapping information. Depot radome repairs consist of removing or "stripping" multi-layer dielectric coatings, filling and smoothing voids in the radome wall, and then applying new dielectric coatings on to the radome surface. Currently, there are four different coating systems that are applied to aircraft radomes. The overall technical effort of the LARPS will be expanded to address radome coating removal needs. Development actions for large aircraft primary and secondary structures manufactured from thin skin aluminum and composite structures will be continued. This is a previous FY94 SERDP funded program.

### 7. Project Description:

This project enhances the benefits and capabilities of the current Manufacturing Technology Directorate's LARPS program. The LARPS technology is evolving and the system is being developed, but has not yet been demonstrated. This initiative provides an enhanced, fully

automated LARPS system providing an environmentally safe (94% reduction in hazardous waste) paint stripping system which will eliminate personnel exposure to a hazardous working environment. The current development work will be expanded to address composite radome structures. Additionally, the application of medium and high pressure water with various nozzle applications shall be incorporated into existing program requirements. The LARPS high pressure system is planned for KC-135, B-1 and E-3 aircraft applications. Additionally, this effort will address system refinements and expand its application for B-2 and B-52 aircraft. The technical risks are moderate.

Tie to Tri-service Environmental Quality R&D Strategic Plan

Pillar Thrust Area: 3.B.2

Requirements Category: I.5

Work effort: Tech Demo

### **8. Expected Payoff:**

This project eliminates significant quantities of hazardous chemical waste, reduces ALC personnel exposure to hazardous waste environment, and provides high estimated cost savings. The projected savings or cost avoidance is estimated to be \$5.1 million/yr (\$4.6M for aircraft structures and approximately \$500,000 for radomes). This is a high priority project to significantly reduce hazardous waste, personnel exposure to a hazardous environment, cost, and aircraft production flow time.

### **9. Milestones:**

- |                                     |       |
|-------------------------------------|-------|
| 1. Contract modification            | 12/94 |
| 2. LARPS robot subsystem validation | 06/95 |
| 3. Composite process complete       | 06/95 |
| 4. LARPS installation at the OC-ALC | 06/95 |

### **10. Transition Plan:**

This technology will be demonstrated for initial aircraft production application at the Oklahoma City Air Logistics Center (OC-ALC). The technology transfer benefits have wide application for other DoD maintenance centers and the commercial airlines who must transition to chemically free or less hazardous coating removal systems by the year 2000 or earlier if possible.

**11. Funding: \$(K)**

	FY93	FY94	FY95	TOTAL
SERDP	950	1717	223	2890
MANTECH	2950	1724	305	4979
OC-ALC	2529	1141	0	3670
FACILITY	508	0	0	508
SITE PREP	1600	0	0	1600
ACFT COMP	999	0	0	999
NAVY	999	0	0	999
TOTAL	10535	4582	528	15645

**12. Performers:**

The Wright Laboratory, Air Force Manufacturing Technology Directorate will provide technical and contractual management for this program and work in close coordination with the Navy and the OC-ALC. The current contractual effort is being developed by Pratt & Whitney Waterjet Systems, Huntsville, AL, the winner of a competitive AF contract to design and develop the aircraft system for potential DoD and industry applications. The radome coating removal system will be incorporated into existing contract requirements. The system will be demonstrated at Oklahoma City Air Logistics Center. This is a dual use technology applicable to commercial and military aircraft requirements.

**13. Principal Investigator:**

Mr. David See  
WL/MTAP  
Building 653, Area B, 2977 P Street - Suite 6  
Wright Patterson AFB, OH 45433-7739  
PHONE: (513) 255-3612  
FAX: (513) 476-1268  
E-MAIL: seedw@ml.wpafb.af.mil

**14. Keywords:**

Robotics, High Pressure Water, Paint Removal, Methylene Chloride, Hazardous Waste, Phenols

## SERDP FY 95 PROJECT

1. **SERDP Thrust Area:** Pollution Prevention
2. **Title:** Rapid Testing for Acceptable Materials and Processes
3. **Agency:** U.S. Air Force
4. **Laboratory:** Wright Laboratory, Aeronautical Systems Center (WL)
5. **Project ID:** #117

### 6. **Problem Statement:**

The goal of this project is to develop low risk, fast track methodologies and techniques for military qualification of new or modified environmentally benign materials.

Continuing efforts to develop environmentally acceptable materials and processes are constrained by the time-consuming process of qualification testing. Users (customers) must make their decision under conditions of uncertainty and want to take as low as risk possible in the decision. Frequently, substantial testing was conducted in support of the initial product qualification decision or in support of re-qualification for design modification to improve performance or solve problems. The present qualification test process is both time consuming and costly and is often preempted by environmental compliance or enforcement requirements.

There is a real need to develop accelerated and less costly means for qualification testing of alternate, substitute and emerging new materials and processes in order to rapidly introduce environmentally acceptable materials into the military inventory and force structure. Economical means are required in order to preserve a diminishing source base threatened due to costly restrictions.

### 7. **Project Description:**

The objective of this project is to create combined environmental and reliability test techniques with 20:1 time compression ratio in areas such as corrosion, sonic and low-cycle fatigue, adhesive delamination, canopy deterioration, paint aging, and plastic embrittlement.



An integrated product development (IPD) team will be created to conduct a systems engineering analysis of qualification test requirements and provide focus on where material science and research efforts are required. The IPD team will be composed of representatives of Wright Laboratory Materials Directorate, Flight Dynamics Directorate, Propulsion Directorate, Aeronautical Systems Center Systems Engineering Directorate, Air Logistics Center maintenance engineering, and selected representatives from the material supplier base.

Phase I will identify and prioritize materials and processes requiring costly long lead qualification testing requirements such as corrosion, sonic fatigue, and low cycle fatigue.

Phase II will characterize material aging physics and develop the theoretical bridge between real life testing and accelerated testing on selected characteristics and phenomena.

Phase III will formulate methodologies and present technique design concepts to conduct accelerated testing using advanced techniques, assemble historical life testing results in selected material technology areas, and conduct a limited number of accelerated tests to demonstrate the feasibility and viability of the concepts and correlate results with traditional methods.

There are no known comprehensive efforts previously accomplished in this specific research area.

The proposed effort responds to pollution prevention mandates by DoD and the Air Force. The effort will also enable reduction of risks, costs and liabilities associated with use of toxics, and handling, treatment and disposal of hazardous wastes.

The project will provide a method of accelerating qualification of a large number of technology development projects involving development of alternates and substitutes for materials with hazardous or toxic manufacturing wastes.

#### Tasks/Activities

- (1) Select high leverage materials -- those being driven by or forced by legislation
- (2) Characterize time dependent failure modes and test requirements:
- (3) Characterize test modes (fatigue, vibration, corrosion)
- (4) Examine assumptions and rationale behind testing requirements and techniques
- (5) Build theoretical bridge
- (6) Identify most promising acceleration testing methodologies
- (7) Compare and correlate accelerated testing results using traditional materials with those obtained with those using traditional methods (from historical records and qualification test reports)

- (8) Initiate accelerated testing for environmentally benign alternate and substitute materials
- (9) Link with information sources such as the Government/Industry Data Exchange Program (GIDEP) and the USEPA Pollution Prevention Information Exchange System (PPIES) to exchange qualification test results among programs and assess impacts to military specifications and standards

The major technical issues to overcome relate to:

- (1) Acceleration physics, and
- (2) The degree of empirical evidence required to support configuration change decisions

Tie to Tri-service Environmental Quality R&D Strategic Plan

Pillar Thrust Area: 3.J  
 Requirements Category: 3.III.2.f  
 Work effort: Tech Base

## 8. Expected Payoff:

Potential users include aerospace manufacturers (especially those manufacturing dual use civilian/military products), Air Logistics Centers, Integrated Weapon System Program Offices, and DoD industrial operations. Professional societies such as American Society for Testing Materials (ASTM) will be invited to participate in reviewing project plans, progress, and results. The development of an acceptable accelerated testing technology will reduce time for testing, reduce cost of testing, and eliminate costs of environmental compliance and hazardous materials/waste management. These efficiencies and economies will result from elimination of unnecessary or redundant tests and earlier implementation of clean technology.

## 9. Milestones:

- |     |  |       |
|-----|--|-------|
| 1.  | Initiate project - begin studies to select target materials and testing requirements | 03/94 |
| 2.  | Target materials and tests isolated  | 05/94 |
| 3.  | Contract award - initiate studies of failure modes and test modes                    | 08/94 |
| 4.  | Failure modes identified - test modes identified                                     | 11/94 |
| 5.  | Aging physics identified   | 05/95 |
| 6.  | Theoretical bridge established   | 05/95 |
| 7.  | Peer review  | 06/95 |
| 8.  | Contract award - initiate studies on bond strength and aluminum grain structure      | 07/95 |
| 9.  | Advanced testing techniques selected   | 08/95 |
| 10. | Initiate adhesive primer evaluation  | 09/95 |

- 11. Complete bond strength, gain structure and primer evaluations 11/95
- 12. Initiate ATTD/Manufacturing Technology planning as required 12/95
- 13. Refine theoretical bridge, if necessary 12/95
- 14. Demonstration of advanced techniques and correlation of test results with historic data 08/96
- 15. Technology transfer media released 09/96

**10. Transition Plan:**

Users will be participants on the IPD team for needs validation, priority setting, methodology approval, and review of demonstration results.

**11. Funding: \$(K)**

	FY93	FY94	FY95	FY96	TOTAL
SERDP	100	263	118	144	625

**12. Performers:**

The project will be performed under the technical leadership and direction of:

Air Force Material Command  
 Aeronautical Systems Center  
 Wright Laboratory  
 Materials Directorate  
 Wright-Patterson AFB, OH 45433

The Materials Directorate will award one or more research contracts to industry to perform the development and integration.

To facilitate generation of public domain information, hands-on government technology assessment and technology transition, the Materials Directorate plans on having the demonstration site to be either an Air Force Material Command Air Logistics Center or the Developmental Manufacturing and Modification Facility (DMMF) at Wright Patterson AFB Ohio.

**13. Principal Investigator:**

Jim Mazza  
WL/MLSE  
Wright-Patterson, AFB OH 45433-6703  
PHONE: (513) 255-3691  
FAX: (513) 476-4419

Wright Laboratory has extensive Research and Development experience in the area of correlation of laboratory testing of materials and processes with qualification and service testing.

**14. Keywords:**

Qualification testing, Age testing, Corrosion, Fatigue testing

## SERDP FY95 PROJECT

1. **SERDP Thrust Area:** Pollution Prevention
2. **Title:** Model for Facilities Life Cycle Decisions
3. **Agency:** U.S. Environmental Protection Agency (EPA)
4. **Laboratory:** Air and Energy Engineering Research Laboratory (AEERL)
5. **Project ID:** #307

### 6. **Problem Statement:**

**Goal:** The goal of this project is to develop and field test a knowledge-based model of environmental characteristics/attributes to support the decision processes involved in facility design, construction, and operation.

**Background:** Decisions (i.e., design, construction, operation and renovations, and demolition) are made throughout a facility's life cycle which are based primarily on economic and in-place performance. Environmental factors (e.g. energy and resource use, toxic by-products, indoor air quality, waste products, etc.), are not considered in any of the current technical, pricing, or planning data used as the basis for these decisions. The inclusion of environmental factors are essential in optimizing the standard facility decision processes, obtaining the maximum benefits from limited natural and economic resources, and reducing the potential for adverse environmental impacts.

This project is a continuation of a SERDP project initially funded in FY93.

As such, it is enhancement of an existing US Army's Corp of Engineers' Construction Research Laboratories (CERL) Small Business Innovative Research effort to test the feasibility of a Knowledge-Based Model which combines environmental and the standard facility decision factors. The initial prototype advisor incorporated inputs from AEERL's work with the American Institute of Architects. CERL FY92 funds for the prototype totaled \$50K. The demonstration of the prototype was successful and co-funding in FY93 and FY94 from the Corp of Engineers was authorized.

### 7. **Project Description:**

**Previous Efforts:** CERL is currently exploring the feasibility of a Knowledge-based Model that will enable the consideration of environmental factors during the various phases of a facility's life. In addition, CERL performs research to improve and optimize the various

components (e.g., costs, system performance, etc.) of facility construction and operations and to improve construction productivity.

AEERL's Indoor Air Branch (IAB) is involved in research to characterize indoor emission sources and methods of mitigating indoor air quality (IAQ) impacts. IAB has a cooperative agreement with the American Institute of Architects (AIA) to develop environmental life cycle data for materials used in construction. IAB is finalizing a set of catalogs on indoor air emissions sources which assigns SIC Codes, MasterSpec Codes, chemical constituent, and chemical emissions data to those materials typically found in indoor environments. IAB has also completed a data base of emissions factors for those materials identified as potential indoor air sources.

**Technical Objective:** The proposed project will utilize AEERL's experience in materials life cycle and indoor environments and CERL research experience in facility design, construction and operation to expand, enhance and field test CERL's Knowledge-Based Model prototype.

**Technical Approach:** The technical approach will include the following components:

- Expansion of the existing model to include additional data sets (i.e., manager, owner, designer inputs);
- Development of CERL data on facilities such as the performance and costs of various systems;
- Inclusion of IAB's Indoor Air Exposure model and emissions data;
- Modification and application of AIA/IAB's Life Cycle Methodology;
- Expansion of the cataloging activity to include all construction materials;
- Interview/workshops with Experts and Users to establish knowledge base rules and data sets;
- Data gathering and analysis from primary sources; and
- Beta testing.

This project will require close coordination between the sponsoring agencies, facilities managers, designers, general contractors, manufacturers and IAQ experts.

**Relationship to DoD/DOE Objectives:** DoD is potentially the single largest builder and manager of facilities in the world. The proposed Knowledge-Based Model will help DoD to optimize environmental and economic considerations over the life of these facilities.

This project is directly related to DoD/DOE's Pillar 3-Pollution Prevention; Thrust 3.J.: Life cycle Environmental Assessments; item (3.III.2.d): Environmental life cycle cost model. It compliments on-going IAB research in IA emissions and control technology characterization and modified materials life cycle assessments. It also enables CERL to move from its prototype knowledge base to a full-scale, marketable decision making tool.

Relationship to Similar Work: The AIA is currently working with AEERL/IAB to compile information on the environmental impacts of selected materials which can be used by design architects. This information will be made available to the users in an electronic format. There is no existing comparable effort to bring together such a broad array of environmental and construction data into a single expert system which will be available to such a broad range of users.

Task/Activities: Tasks for project completion:

- 1) Incorporation of IAQ Exposure Model
- 2) Beta Test of expanded knowledge base model
- 3) Acquisition/development of pertinent data sets
- 4) Development of pre-production knowledge based model
- 5) Optimization and beta test of model
- 6) General Distribution

Technical issues to overcome involve the restructure of the prototype model to include IAQ components, expansion of the model to accommodate the CERL and IAB data sets, acquisition and development of new data, quality assurance, and optimization of final knowledge base.

## **8. Expected Payoff:**

Potential Users: The Users include architects, engineers (e.g., HVAC engineers), facilities designers, construction managers, public agencies (e.g., GSA, Corp of Engineers, etc.), state and federal policy makers, and materials manufacturers.

Impact: The model will promote environmentally-sensitive decision making throughout a facilities life cycle. The impacts of this approach to decision making to the various components of the life cycle include the following:

Building materials' and equipment manufacture:

- Reduced negative impact on resource consumption;
- Reduced undesirable manufacturing by-products;
- Reduced exposure to hazard (e.g., IA contaminants)

Construction:

- Reduced undesirable waste in terms of quantity and content;
- Reduced pollution generating activities;
- Reduced human exposure to hazard

Operation and Maintenance:

- Reduced operating expenses; energy, and resource consumption;
- Improved service life;
- Reduced undesirable wastes;
- Reduced exposure to hazards (e.g., IAQ impacted from cleaning activities)

Disposal:

Reduced waste and enhanced opportunities for recycle.

### 9. Milestones:

1.	Complete Phase I Environmental Knowledge Base Model	05/93
2.	Initiate Phase II Pre-production Model Development	09/93
3.	Complete Phase II Model	03/94
4.	Initiate data development and workshops	12/94
5.	CERL/ERA review of Phase II model	03/95
6.	Release of model	03/96
7.	Complete data loading and update;final release	09/96

### 10. Transition Plan:

Successful Tech Transfer involves a strong marketing entity, capable of effective implementation in practice and/or a commercial method that sells itself by virtue of its quality and utility. The integration of this product by the Corp of Engineers, DoD, and GSA into its decision matrix for new and existing facilities will act as a driver for the broader usage. In addition, the American Institute of Architects is actively seeking to assume update and distribution responsibilities for this system in FY96 as an extension of the ERG.

### 11. Funding: \$(K)

	FY93	FY94	FY95	FY96	TOTAL
CERL	150	150	0	0	350
EPA	295	295	295	295	1480
SERDP	500	400	135	165	1200
TOTAL	945	845	595	295	3030

\* EPA Funding for FY92-FY96 are funds spent to develop AIA/EPA's LCA materials methodology and to support the transfer of this methodology via the ERG to the User community. In addition, AEERL has spent an estimated \$1,050K in the development of the components necessary to this models success. These expenditures were as follows: \$300K in the development of a LCA materials methodology; \$375K for developing materials catalogs; \$75K in the development of IA emissions data base; and \$300K in the development of IAQ models.



**12. Performers:**

Environmental Protection Agency/Air and Energy Engineering Research Laboratory; US  
Army Corp of Engineers/Construction Engineering Research Laboratory

**13. Principal Investigators:**

James B. White  
Air and Energy Engineering Research Laboratory  
MD-54  
Research Triangle Park, NC 27711  
PHONE: (919) 541-1189  
FAX: (919) 541-2157  
E-MAIL: WHITE.JAMES@EPAMAIL.EPA.GOV

Tom Napier  
US Army Corps of Engineers  
Construction Engineering Research Laboratories  
P.O. Box 9005  
Champaign, IL 61826-9005  
PHONE: (217) 373-7263  
FAX: (217) 373-6724

**14. Keywords:**

Life Cycle Assessment, Expert Advisor, Building Materials, Pollution Prevention,  
Construction costs

## SERDP FY95 PROJECT

1. **SERDP Thrust Area:** Pollution Prevention
2. **Title:** Capacitive Deionization for Elimination of Wastes
3. **Agency:** United States Department of Energy (DOE)
4. **Laboratory:** Lawrence Livermore National Laboratory (LLNL)
5. **Project ID:** #436

### 6. Problem Statement:

Background: Ion exchange is used to remove anions and cations, including heavy metals and radioisotopes, from aqueous streams at Department of Energy (DOE) and Department of Defense (DoD) facilities, as well as at a variety of civilian industrial plants. Such deionization processes generate large volumes of corrosive secondary waste that must be treated, including spent anion and cation exchange resins, and acids and bases contaminated during regeneration. Solutions of  $H_2SO_4$  are used for the regeneration of cation columns in metal finishing and power industries, while  $HNO_3$  is used for regeneration of cation columns in plutonium processing plants. During plutonium processing, resins and solutions of  $HNO_3$  become contaminated with  $PuO_{2++}$  and other radioisotopes. Every pound of cation exchange resin requires approximately 100 lb of 10 wt. %  $H_2SO_4$  or  $HNO_3$  and 2-3 lb of rinse water for regeneration. Solutions of NaOH are used to regenerate anion exchange resins. Given the high cost of disposal in mined geological repositories, there is tremendous incentive for reducing the volume of waste that must be dealt with.

Objective: The objective of this project is to develop an innovative new technology, capacitive deionization, that can be used to replace many existing ion exchangers, thereby eliminating the secondary wastes due to regeneration. In this novel process, ions are retained in the electric double layers formed at the surfaces of two porous electrodes of opposite polarity. Such technology could also be used to treat ground water, surface water, waste water, drinking water, boiler water for power plants, and process water for semiconductor manufacturing. Deionization of boiler water is used as a means of preventing fouling and corrosion of heat transfer surfaces. It may even be possible to use capacitive deionization for the energy-efficient desalination of sea water.

### 7. Project Description:

Principal of Operation: The capacitive deionization process uses a porous-electrode flow-through capacitor to remove cations and anions from water. Conceptually, the construction

and operation of this process is relatively simple. Two porous electrodes with high specific surface area are fabricated from carbon aerogel (or carbon powder) and separated by either a cation exchange membrane or a dielectric microporous sheet. Ions are forced to move to the surfaces of electrodes by an imposed electric field. Cations are concentrated in the electric double layer formed at the surface of the cathode, while anions are concentrated at the surface of the anode. A cation exchange membrane such as Nafion 117 could be used as the electrode separator in a design that is similar to that of the LLNL Aerocapacitor. During the deionization of a NaCl solution with such a device, protons migrate through the ion exchange membrane to balance the anodic charge associated with Cl<sup>-</sup> anions, thereby forming HCl. Since H<sup>+</sup> will also populate the electric double layer formed at the cathode, the presence of HCl in the cathode compartment will reduce the removal efficiency for other cations such as Na<sup>+</sup>. A better design uses a dielectric microporous membrane that allows diffusion of both cations and anions, thereby preventing the formation of HCl. Separators that allow bipolar transport are more desirable than ion exchange membranes.

**Innovative Aspects:** Capacitive deionization is a novel and innovative alternative to ion exchange. The electrode material and proposed mode of operation are entirely new. Carbon aerogels have much higher specific surface areas (600-900 m<sup>2</sup>/gm) than conventional carbon-paste electrodes or activated carbon powders (200-300 m<sup>2</sup>/gm). By using carbon aerogel as the electrode material, instead of carbon paste or powder, the capacity of the deionizer will be increased dramatically (3X). Note that carbon aerogel was developed by Lawrence Livermore National Laboratory (LLNL) and is a "spin-off" of the Strategic Defense Initiative (SDI) Program. Therefore, this project makes use of a technology developed for national defense purposes. The continuous-flow potential-swing mode of operation to be developed during FY94 is also novel.

**Theoretical Model of Capacitive Deionizer:** In addition to process development and demonstration, computer models are being developed that can be used for computational analyses, engineering scale-up, and parametric optimization. Parameters that are being studied include: (1) electrode porosity and thickness; (2) separator porosity and thickness; (3) superficial fluid velocity; (4) charging voltage; and (5) number of electrodes (stages). The original theory for porous-electrode flow-through capacitors was developed by Prof. John Newman of U. C. Berkeley [J. Electrochem. Soc. 118, 3 (1971) 510-517].

**FY93/Proof of Principle:** The effluent from a single capacitive deionizer is being monitored with an on-line conductivity probe, as well as various ion-selective electrodes, and recorded with a strip-chart recorder and/or computerized data acquisition system. This array of sensors is being used to determine removal efficiencies and selectivities for various anions and cations in multicomponent electrolytes. Measured effluent concentrations will be compared to predictions for model validation.

**FY94/Continuous-Flow Pilot Plant:** A continuous-flow pilot plant will be built that consists of two parallel multistage capacitors. This system will be inherently energy efficient since the

current from the discharge of one capacitor will be used to charge the other. One unit will be regenerated (discharged) while the other purifies (charges). This mode of operation will be called potential-swing ion adsorption and is analogous to pressure-swing gas absorption. On-line sensors will also be used to monitor conductivity, pH, and concentrations of cations and anions in the pilot plant. A computer will be used to log data, control flow, and synchronize the charge-discharge cycles of each capacitor.

**8. Expected Payoff:**

This project will minimize waste generation at the source by substituting nontoxic and nonpolluting electricity for the acids and bases that are normally used for regeneration of ion exchange resins. The Pollution Prevention Act of 1990 states that "pollution prevention" means "source reduction" and other "practices that reduce or eliminate the creation of pollutants through: increased efficiency in the use of raw materials including energy, water, and other resources; or materials substitution". In capacitive deionization, we are substituting porous carbon electrodes for ion exchange resins and are substituting electrical current for the chemicals that are normally used to regenerate resins. We believe that this process will reduce the total volume of solid waste from water treatment that will have to be disposed of. Consequently, this process will help extend the life of existing landfills, geological repositories, and other disposal facilities. This innovative process may also prove to be an innovative remediation technology for sites contaminated with heavy metals, radionuclides, and other inorganic contaminants. Ultimately, it may be possible to use this technology as an efficient and effective means of ground water and surface water cleanup.

**9. Milestones:**

1.	Development of computational model	12/94
2.	Design of proof-of-principle capacitive deionization system for batch processing	09/94
3.	Procurement of vessels, valves, pumps, power supplies, conductivity monitors, ion selective, electrodes, and strip-chart recorders	12/94
4.	Preparation of large quantity of carbon aerogel	02/95
5.	Construction of proof-of-principle capacitive deionization system	01/95
6.	Testing of fluid flow systems	01/95
7.	Testing of electrical and electronic systems	06/94
8.	Demonstration with NaCl solution	04/95
9.	Parametric studies with simulation wastes	08/95
10.	Documentation	09/95
11.	License of CDI to US Corporation	12/95
12.	Treatability studies for potential customers	02/96

## 10. Transition Plan:

After a working prototype process is developed, the technology will be made available to engineers who are working on reconfiguration of the DOE Complex. In collaboration with these engineers, tests will be conducted to determine where capacitive deionizers can be used to replace conventional ion exchangers. This new technology will also be important in the private sector. As previously discussed, a capacitive deionizer could be used to produce deionized feed water for boilers in fossil-fired and nuclear power plants. In the future, it may be possible to use such novel technology for the energy-efficient desalination of water for dry, heavily-populated areas like California. Deionized water, free of dissolved organic resin, could also be used for the manufacture of next-generation semiconductors (nanoelectronics). Nanoelectronics will be far less tolerant of impurities introduced by beds of ion exchange resin than microelectronics. This concept (capacitive deionization) was presented to senior level executives of Dow Chemical Company during one of their recent visits to LLNL. They expressed a sincere interest in working with LLNL in a Collaborative Research and Development Agreement (CRADA). It is noteworthy that the Principal Investigator for this project also served as the Principal Investigator for another electrochemical waste treatment project that resulted in the development of technology that has been licensed to a small business in the San Francisco Bay Area.

## 11. Funding: \$(K)

	FY94	FY95	FY96	TOTAL
SERDP	700	300	110	1110

## 12. Performers:

LLNL is a DOE laboratory operated by the University of California and will be responsible for successful completion of the proposed work. This laboratory has recently developed several novel electrochemical processes for the treatment and destruction of mixed wastes [J. C. Farmer et al., J. Electrochem. Soc., 139, 3 (1992) 654-662; Trans. Inst. Chem. Engr., 70B (1992) 158-164; J. Electrochem. Soc., 139, 11, (1992) 3025-3029]. Several patent disclosures have been filed and are being actively pursued by the U. S. Department of Energy. Carbon aerogels with very high surface areas have also been developed by LLNL [R. W. Pekala et al., J. Non-Crystalline Solids, 145 (1992) 90-98]. These materials have unusually high specific surface areas of 600-900 m<sup>2</sup>/gm, much higher than the 200-300 m<sup>2</sup>/gm that is typical of activated carbon powder. LLNL has developed electrolytic supercapacitors for energy storage applications that have carbon aerogel electrodes (known as Aerocapacitors). These new energy storage devices have energy densities of 4-25 Whr/kg, power densities of 0.1-10 kW/kg, and cycle lives greater than 100,000, and are now believed to be essential for load-leveling applications in electric vehicles. As previously discussed, the theory for flow-through porous-electrode electrolytic capacitors was developed and published by Newman over 20 years ago. Little or no work has been done in this area since that time.

**13. Principal Investigator:**

Joseph C. Farmer, Ph.D. L-352  
Chemistry and Materials Science Department  
Lawrence Livermore National Laboratory  
P. O. Box 808  
Livermore, California 94550  
PHONE: (510) 423-6574  
FAX: (510) 422-6892

**14. Keywords:**

Deionization, ion exchange, waste minimization, supercapacitor, aerogel, potential-swing, capacitive deionization.

## SERDP FY95 PROJECT

1. **SERDP Thrust Area:** Pollution Prevention
2. **Title:** Acid Recycle
3. **Agency:** U.S. Department of Energy (DOE)
4. **Laboratory:** Los Alamos National Laboratory (LANL)
5. **Project ID:** #422

### 6. Problem Statement:

Field demonstrations will be conducted at the Los Alamos Plutonium Facility to recycle and reconcentrate nitric and hydrochloric acids from plutonium-containing liquid waste streams.

Nitric acid and hydrochloric dissolution of plutonium-containing solids is a baseline technology for Complex 21 plutonium processing operations. Following removal of plutonium from the acid solutions, previous operations neutralized the acid with caustic and discarded it as waste. Most of the nitric or hydrochloric acid could be separated from the waste solutions and recycled, thus reducing amount of waste generated. This in process technology can also provide major reductions in nitrates and chlorides in effluent streams from processing aimed at cleanup of residues from previous operations.

Recycle of nitric acid will be accomplished via an enhancement of capabilities in the ATLAS (Advanced Testing Line for Actinide Separations) integrated process system. Recycle of hydrochloric acid represents a new program to be implemented using the Los Alamos EXCEL (Experimental Chloride Extraction Line) system.

### 7. Project Description:

We will demonstrate at least 95% recycle of nitric and hydrochloric acid from waste solutions. The recycle acid will be reconcentrated sufficiently to be used for dissolutions, etc. in lieu of makeup acid.

We will demonstrate nitric and hydrochloric acid recycle from actual plutonium processing waste solutions using two operations:

(1) evaporation of acid from a solution containing radionuclides and inorganic salts and (2) fractional distillation of evaporator product to generate concentrated acid. The acids will be separated from the radioactive component of the waste solution by evaporation. The

nonvolatile radioactive residue will be sent to disposal or may receive further treatment (e.g., thermal denitration) before disposal. Evaporated acid will be reconcentrated to a reusable state by fractional distillation. We will develop an integrated process using semi-continuous operation consisting of an evaporator followed by a distillation column.

The existing nitric acid evaporator in the ATLAS system will be operated for additional experience. A nitric acid distillation column will be designed, built, and cold-tested prior to incorporation into ATLAS. Process flow balance and characterization of hydrochloric acid processes will be done. Bench-scale, "cold" evaporation and distillation experiments will be done on hydrochloric acid solutions. An evaporator and a distillation column for hydrochloric acid recycle will be designed, built, and tested. Hydrochloric acid recycle apparatus will be installed and integrated into the EXCEL operation.

Present nitric acid waste solutions from plutonium processing contain both amounts and concentrations of nitrates far above desired levels to meet environmental objectives. Potential leaching of soluble salts (nitrates and chlorides) from cemented radioactive wastes is an unknown which raises major concern. It is very desirable to reduce quantities of TRU wastes to a minimum. Acid recycle promises to provide significant relief in each of these areas.

Nitric acid recycle by evaporation and distillation has been used in uranium operations at Y-12. Savannah River Site has recovered and reconcentrated nitric acid as part of their operation. Pacific Northwest Laboratories has built pilot-scale apparatus for potential acid recycle use at Hanford. New Los Alamos work using freeze-drying for decontamination of nitric acid waste solutions could be integrated with this work.

Recycle of both nitric and hydrochloric acid presents no major technical risks. Evaporation and fractional distillation are both mature technologies. While these have not been applied to recycle of plutonium waste solutions as integrated processes, much industrial production of nitric and hydrochloric acids use this approach.

## **8. Expected Payoff:**

Applicability: Complex 21 processing of plutonium; cleanup of previous plutonium processing residues.

Benefits:

- Reduced number of waste units requiring handling, inspection, packaging, shipping, storage, etc.
- Major reduction in waste disposal costs
- Acid reagent costs reduced
- Potentially leachable nitrates, chlorides in waste reduced



Capability: At least 95% of the acid will be recycled. Acid concentrations will be sufficient for reuse in processing.

Cost-savings example based upon previous Rocky Flats operation:

- Total saltcrete production reduced by 50%
- Waste disposal costs reduced by \$12M/year
- Nitric acid reagent costs reduced by \$100K/year

**9. Milestones:**

1.	Pervaporator received	10/94
2.	Program start	12/94
3.	HNO <sub>3</sub> test column received	02/95
4.	HCL test evaporator construction complete	03/95
5.	HNO <sub>3</sub> test column experiments complete	09/95
6.	Interim report on HNO <sub>3</sub> test column	10/95
7.	HCL test evaporator experiments complete	08/95
8.	Interim report on HCL test evaporator	09/95
9.	Pervaporator tests on HCL complete	09/95
10.	Interim report on HCL pervaporator tests	10/95
11.	Design of full-scale HCL recycle system complete	01/97
12.	Design full-scale HNO <sub>3</sub> column complete	01/97
13.	Construction of full-scale HCL system complete	05/97
14.	Full-scale HNO <sub>3</sub> column received	06/97
15.	Full-scale HCL system installed in "hot" environment	09/97

**10. Transition Plan:**

Following successful demonstration of acid recycle in ATLAS and EXCEL, acid recycle will be applied to all acid effluents from the Plutonium Facility at Los Alamos. Previous nitric acid effluent solutions have amounted to 75,000 L/year. Hydrochloric acid processing has had limited prior use. Both performer and user are the same. No industrial participation is foreseen.

**11. Funding: \$(K)**

	FY94	FY95	FY96	FY97	FY98	TOTAL
SERDP	258	169	0	280	200	907

**12. Performers:**

Department/Agency Laboratory: Los Alamos National Laboratory will conduct the work.

Industry involvement: No industrial involvement is foreseen at present. There has been previous collaboration with the Colorado School of Mines.

Planned cooperative development agreements: There are no planned cooperative development agreements.

**13. Principal Investigator:**

Thomas R. Mills  
Group NMT-6 MS E510  
Los Alamos National Laboratory  
Los Alamos, NM 87545  
PHONE: (505) 665-0631  
FAX: (505) 665-4459  
E-MAIL: trm@lanl.gov

**14. Keywords:**

recycle, reconcentrate, acid, plutonium, nitric acid , hydrochloric acid, effluent

## SERDP FY95 PROJECT

1. **SERDP Thrust Area:** Pollution Prevention
2. **Title:** Recycle Boiler Nitrite Solution
3. **Agency:** U.S. Navy
4. **Laboratory:** Naval Facilities Engineering Service Center (NFSEC); formerly Naval Civil Engineering Laboratory (NCEL)
5. **Project ID:** #69
6. **Problem Statement:**

The nitrite solutions used for marine boiler tube hydroblast, lay-up, hydrostatic testing, and rinsing must be recycled to the extent possible and then treated for NPDES disposal with minimal nitrate conversion. The Navy uses nitrite extensively as a rust-preventing fluid in marine boiler maintenance. Because it oxidizes readily to nitrate, it will support surface water eutrophication and is therefore treated as a "de facto" hazardous waste regardless of whether contaminants are taken up in its usage. This has resulted in high disposal costs.

NFESC has been working on this problem since FY90 and has developed a highly successful treatment process, based on sulfamic acid, that converts nitrite to nitrogen gas with little or no conversion of the nitrite to nitrate being caused by the treatment itself. Working with the Naval Station, Treasure Island, CA, it has been determined that the nitrite solutions can be recycled a number of times as long as they are stored under an oxygen free head gas and are treated and disposed of before the nitrate concentrations acquired from hydroblasting, lay-up or hydrostatic testing do not reach unacceptable levels. The challenge now is one of bringing these technical requirements into a cost-effective and dockside acceptable system that will eliminate the need for exporting nitrite wastewater.

This is an enhancement to an on-going 6.3 technology demonstration project. It addresses SERDP Thrust 3.A.2.b: Metal working Process/Cleaning & Degreasing, and it supports a SERDP goal to minimize or eliminate hazardous wastes at the source.

### 7. Project Description:

The goal of this project will aim at: (1) full scale design and demonstration testing of the sulfamic acid process at a selected Naval shipyard; (2) designing an oxygen-exclusive, conditioning process for bringing the used nitrite solutions back to specification quality;

(3) development of a practical procedure for long-term storage of recyclable nitrite solutions without head-gas caused nitrate formation; and (4) evaluation of an alternative biological treatment process suggested by EPA.

Full scale sulfamic acid process demonstration will be accomplished preferably at the Long Beach Naval Shipyard using the NFESC plant that was erected there and successfully tested in FY92. This will be an operational demonstration using shipyard personnel and nitrite wastewater solutions from ship(s) being serviced there. Samples will be taken to fully characterize the wastewater before and after denitrification process. These data will be used to determine the processing necessary to restore the liquid to specification quality. Previous data obtained by NCEL show that reconstitution should be quite practical. A system will then be designed, fabricated, and tested. The final process step will be the design of a system that will permit the oxygen-free storage of the reworked nitrite solution. Operating procedures will then be defined that will govern the use of the nitrite solution in a manner that will ensure extended cycles of service.

The Risk Reduction Engineering Laboratory of EPA, Cincinnati, will team with NFESC on this effort. Their primary interest is to evaluate a biological system that will convert both nitrite and nitrate to nitrogen gas. If such a process proves successful, it would greatly extend the useful cycles before disposal is required and significantly reduce the costs entailed in chemical treatment.

The technical risk is very low. The project addresses Tri-Service Environmental R&D Strategic Plan, Requirement (I.2.b): Non-polluting, Non-toxic Cleaning and Degreasing Technology.

### **8. Expected Payoff:**

Take Long Beach Naval Shipyard as an example, the average cost of disposing of the approximately 500,000 gallons of nitrite wastewater generated annually is about \$1,500,000 at \$3.00/gallon.

After successfully implementing the NCEL hydroblast recycling process, it has been estimated that the total volume of sodium nitrite wastewater generated by all Naval shipyards to still be about 3 million gallons each year, and by Navy-wide boiler maintenance operations to be 10 million gallons per year. The proposed chemical denitrification process has the potential of reducing the disposal cost by at least 90 percent (reduced from \$3.00/gallon to \$0.30/gallon operating cost) or \$8M savings per year for Naval shipyards and \$17M savings per year for the Navy-wide boiler maintenance operations.

The proposed chemical process will not produce hazardous waste and the effluent produced can be safely discharged to the sanitary sewer.

This project should have very high transition opportunities because of the high payoffs.

**9. Milestones:**

- |    |   |       |
|----|---|-------|
| 1. | Program Start   | 10/94 |
| 2. | Complete Test & Evaluation Plan and permit application at test site                   | 07/95 |
| 3. | Complete full scale denitrification process design & fabrication                      | 12/95 |
| 4. | Complete full scale demonstration   | 04/96 |
| 5. | Complete design, fabrication, and testing of nitrite recycle system                   | 07/96 |
| 6. | Complete development and testing of nitrite storage procedure                         | 10/96 |
| 7. | Complete evaluation of a biological system converting nitrite/nitrate to nitrogen gas | 10/96 |
| 8. | Complete development of User Data Package and final reports                           | 03/97 |

**10. Transition Plan:**

At the conclusion of this project, the proven full-scale demonstrated system will be left at the host site for continuous operation. Implementation throughout the Navy will be done through the cooperation with Naval Ship Systems Engineering Station (NAVSEES). The technology transfer documentation (User Data Package) will be published as a final deliverable. This UDP will contain information on system design & specification, O&M, permitting, training, and safety plan. The other DoD agencies and private industry will have access to the information developed and, with it, will be able to apply the technology thus described as desired.

**11. Funding: \$(K)**

	FY94	FY95	FY96	FY97	TOTAL
SERDP	475	68	0	200	743

**12. Performers:**

NAVY/NAVSEA/NFESC and EPA. The Risk Reduction Engineering Laboratory of EPA, Cincinnati, will team with NFESC on this effort and has proposed to the SERDP Executive Director the evaluation of a biological system that will convert both nitrite and nitrate to nitrogen gas.

**13. Principal Investigator:**

Dr. Richard Lee, Code ESC421  
Naval Facilities Engineering Service Center  
560 Center Drive  
Port Hueneme, CA 93043-4328  
PHONE: (805) 982-1670  
FAX: (805) 982-1409  
E-MAIL: RLEE@NFESC.NAVY.MIL

**14. Keywords:**

Nitrite, nitrate, denitrification, sulfamic acid, nitrogen gas, boiler

## SERDP FY95 PROJECT

1. **SERDP Thrust Area:** Pollution Prevention
2. **Title:** Integrated Expert Solvent Substitution Data Base
3. **Agency:** U.S. Environmental Protection Agency (EPA)
4. **Laboratory:** HQ and Air and Energy Engineering Research Laboratory (AEERL)
5. **Project ID:** #331
6. **Problem Statement:**

The goal of this project is to build an integrated solvents substitutes data base from existing data bases and high-light potentially redundant activities underway in each of the participating and other agencies. The resultant expert tool would combine priority information from each existing data base such as compatibilities and performance, and fill gaps by providing economic analyses and vendors information. It would be targeted for direct use by all DoD depots, logistics centers, defense contractors, small and medium industries as well as State Technical assistance offices, NIST Manufacturing and Technology Centers, and universities implementing the EADS program. This data base could provide an important technology transfer function for Federal Agencies, states, and small and medium industries to advance the reduction of hazardous waste releases/emissions in meeting the Executive Order on Federal Compliance's (12856) 50% reduction of TRI toxics by 1999, and the Clean Air Act/SNAP hammer deadlines. It will assist in the redevelopment of many Mil Spec Standards under executive Order 12856, and will assist each agency and the US in meeting its ozone depletion reduction, and toxics use reduction goals. The project will also demonstrate federal cooperation and environmental leadership by promoting and making publicly available the successes and lessons learned by the participating agencies.

### 7. Project Description:

Develop an integrated expert solvent substitutes data base that will combine related data base efforts across agencies and expand those efforts in depth and breadth. Objectives would include targeting related solvent data base tools for integration; develop expert front end for expanded PIES solvent umbrella; integrate compatible platforms, conduct research and develop system architecture for non-compatible platforms; develop strategy for the testing of new alternatives; validate that information through existing test bed centers; conduct deployment/feedback program.

This proposal is strengthened by the full life cycle design of the expert tool including deployment by State Technical Assistance Centers and update/expansion through generation of new alternatives through its own research testing and validation program, and a self expanding industrial feedback loop. The tasks of this project will be closely guided and prioritized by a technical review board comprised of participating agencies, labs, test bed facilities, industry and State P2 Technical Assistance Programs.

This project promotes the SERDP objective of maximum exchange of information via several deployment mechanisms. It is designed to assist government agencies and industry as an information exchange data base to be linked with the PIES, DENIX, EPIC, and LINKS networks over INTERNET for widespread electronic access. This array of electronic dissemination of DoD and DOE solvent alternatives knowledge and leadership meets a second objective of SERDP, to provide appropriate access (to federal, state, and local governments and industry) to data available to DoD and DOE relevant to environmental matters. The National Center for Manufacturing Sciences and the National Roundtable of State Pollution Prevention Programs are committed to networking the final product throughout their membership. The Roundtable, NIST MTC's, and the academic institutions of the EADS program represent a massive hands-on deployment mechanism. More than 70 technical assistance centers operated by these programs will use the tool in on-site assessment visits to industries within their jurisdictions.

This project implements a third objective of SERDP by minimizing the duplication of environmentally related research. The purpose of this project is to integrate similar solvent substitute data bases and focus on growth of the integrated tool through a coordinated, monitored effort by representatives of a technical review board. This project will further coordinate alternatives being validated at a number of existing test centers. Participation of these centers in the validation portion of this project will promote coordination of activities at these centers. We intend to use the following test bed centers for the validation function of this project: DoD's National Defense Center for Environmental Excellence (NDCEE); DOE's Idaho National Engineering Laboratory; University of Tennessee's Center for Industrial Services; and the Illinois Hazardous Waste Resource Information Center. Other validation test bed facilities will be considered for inclusion.

This project meets a fourth objective of SERDP, by spurring three tiers of development and demonstration activities. These three tiers include research and development to design a system architecture for non-compatible data base tools; the development of an expansion strategy that will operate a testing regime to generate new data for the integrated data base; and the implementation of a validation program which will use existing test bed centers (as neutral third parties) to verify the utility of new substitutes or process alterations.

By deploying this expert data base through the depots and logistics centers, national labs, State, NIST and EADS technical assistance centers we are providing governmental and nongovernmental entities with analytical assistance in reducing toxics use and meeting the



bans of ozone depleting substances under the Clean Air Act the Montreal Protocol, and Executive Order 12856. We are therefore meeting a fifth objective of SERDP, providing analytical assistance in reducing military and industrial ODS impact on the stratospheric ozone layer. This objective will be met by networking this expert tool throughout all service bases and joint depot maintenance shops. More massive impacts will be seen with widespread application of the tool to the small and medium businesses of the plating, fabrication, electronics and maintenance and repair industries.

The project will build on the EPA's Solvent Alternatives Guide (SAGE), and PIES Vendor data bases; DOE/INEL's HSSDS and SHSD databases; the National Center for Manufacturing Sciences (NCMS) Solvent and Materials Compatibility data bases; and others as identified. Ultimately the system will be comprised of a fully integrated data base that builds on aspects of SAGE to assist users in identifying alternative technologies and chemical groups based on their knowledge of the application. The system will be supported by compatibility and chemical test data (from INEL HSSDS, SHDS, and NCMS) to assist users in identifying suitable replacement chemicals/technologies for their application; vendor information (from PIES and NCMS) to identify sources for alternatives; and case study information (from PIES) to provide information on effectiveness, payback and potential problems with the alternative selected. The data base developed under this project will focus exclusively on solvents and will serve as a model for subsequent expansion efforts to address other industrial sector applications.

The project will enhance the technology transfer work of the PIES expansion project under SERDP in 1993 where information umbrellas are established within the P2 network, as well as on the GUI programming research initiated under that project.

**Project Tasks:** The tasks involved in this project encompass:

1. Establish a Technical Advisory Board/User group: This board, representing participating Agencies and targeted users, will guide each stage of this project. It will set the priorities in the testing and validation phases, design requirements of the final system, and beta test various project accomplishments.
2. Identify information sources and relationships: This task will involve an exhaustive search to identify other data bases that should be considered in the integration. This task will evaluate: function; data gaps; relationships between data bases; areas of duplication; and data formats and file structures.
3. Expand the PIES information umbrella: This builds on FY93 SERDP funding which establishes information umbrellas pointing to several tools under a single network. These will be expanded to house other solvent systems from federal and private sectors.
4. Create an expert front end and integrate compatible tools: Compatible systems will be integrated and combined. This will reduce duplication of information and provide a seamless, integrated data environment. The user will be able to navigate easily through several tools without the need to learn separate operating command structures.
5. Develop system architecture for non-compatible platforms: Those systems having

incompatible data structures will be integrated into the system. A system architecture that can access the differing systems based on the previously implemented intelligent front end will be developed to provide seamless, intelligent access to all the information available.

6. Generate new information: The technical advisory board will develop a strategy to initiate testing and research of new alternate technologies and substitutes. This strategy shall combine chemical reduction, process, and regulatory hammer priorities. Test bed centers such as the NDCEE, INEL and the University of Tennessee shall be used for testing.

7. Establish continuous feedback loop including site visits by State TAPs: State technical assistance centers will determine what substitutes were made as a result of using the tool. This will be added into the data base as an implementing user resource. NCMS will assist workshops directed at supplier networks with participation of United Technologies and Texas Instruments.

8. Deployment/marketing/training: The system will be deployed using the Depot/logistics centers, State Technical Assistance Programs, NIST MTC's and the EADS universities in their on-site industry assessments. EPA and States will directly network with local Chambers of Commerce. Use of INTERNET for access to PIES/DENIX/EPIC integrated solvents tool will promote further interface with the National Information Infrastructure including Enterprise Integration Net, Product Data Exchange Standards, CALS, and others.

## 8. Expected Payoff:

The benefits of this effort for DoD, DOE, and EPA include better centralized access to pertinent information to reduce the use of toxic and ozone depleting solvents; and a reduction of redundant research efforts. The benefits to industry include easier access to technical information that will allow them to implement alternatives and reduce the emissions of ODS and other toxics; and assist in meeting the bans under the Clean Air Act. Industrial benefits include monetary savings and liability reduction due to implementing P2 alternatives. The project will provide a measurable indicator of its impact on industrial facilities in terms of cost savings and ODS reduction gained through options implemented.

## 9. Milestones:

1.	Establish technical advisory board	05/94
2.	Create GUI/Mosaic platform for PIES	08/94
3.	Identify information sources/relationships/gaps	09/94
4.	Expand PIES/DENIX/EPIC solvent information umbrella	10/94
5.	Generate new info via board strategy; quarterly adds	11/94
6.	Expand Umbrella to include other Fed. dbs	06/95
7.	Develop Expert system for solvent info synthesis	09/95
8.	Initiate validation testing & industrial feedback loop	01/96
9.	Initiate State/NIST/MTC TAP deployment & implemented feedback	01/96
10.	Augment State TAP training based on system progress	05/97

- 11. Conduct testing & validation for generation of new information throughout project 09/97
- 12. Conduct on-site verification as feedback mechanism throughout project 09/97

**10. Transition Plan:**

The expert system will be accessed by industrial users directly through Internet. Also, the State TAPs, NIST MTCs, and the universities implementing DOE's EADS Program, will network the system through their on-site P2 assessment visits. Industrial access will also be gained through a direct networking/training effort for local Chambers of Commerce and Trade Associations.

**11. Funding: \$(K)**

	FY94	FY95	FY96	TOTAL
SERDP	3000	0	1520	4520

**12. Performers:**

DoD: Navy: Naval Facilities Engineering Service Center, Larry Hill. Army: Corps of Engineers, Defense Environmental Corporate Information Management Program Office (DECIM), Connie Watts. Air force: Center for Environmental Excellence Brooks AFB, Steve Green. National Defense Center for Environmental Excellence, Jack Adams. DOE: ER Arnold Edleman. INEL: Kevin Twitchel. NIST/MEP: Dave Gold, EPA: AEERL, Charles Darwin. Nat. Cent. for Man. Sciences, Mike Wixom. Univ. Tenn: George Smelcer; WRRRC: Vic Young.

**13. Principal Investigator:**

Myles Morse  
 US EPA  
 Office of Research and Development  
 Office of Environmental Engineering and Technology Demonstration  
 401 M Street, S.W.  
 Washington, DC 20460  
 PHONE: (202) 260-3161  
 FAX: (202) 260-3861/4524

**14. Keywords:**

Solvent, Network, ODS, P2, Compatibility, Vendors

## SERDP FY95 PROJECT

- 1. SERDP Thrust Area:** Pollution Prevention
- 2. Title:** Alternative Electroplating Technology
- 3. Agency:** U.S. Navy
- 4. Laboratory:** Naval Air Warfare Center Aircraft Division, Warminster
- 5. Project ID:** #71

### **6. Problem Statement:**

To replace hazardous plating processes (chromium, cadmium, cyanide, etc) currently used on Naval aircraft (A/C), weapon systems (WS) and ground support equipment (GSE). Chromium and Cadmium are heavy metal pollutants and carcinogens. Cyanide is hazardous to human health. The Clean Air Act Amendment of 1990 (Electrolytic Chromium National Emission Standard for Hazardous Air Pollution (NESHAP), etc.) as well as other EPA and state Departments of Environmental Resources regulations restrict the emissions from these processes. In addition, OPNAV and CNO directives require reductions in hazardous waste. Presently, these plating processes are used in production and Depot level maintenance operations. Therefore, in order to comply with these regulations while maintaining aircraft performance and operational readiness, alternative plating processes need to be developed and validated. This effort is covered under the Tri-Service EQ Strategic Plan Area: Pillar 3: Pollution Prevention, Requirement Thrust: 3.1.3 Metal Working/Plating and Finishing (e-h) and is a continuation of an existing SERDP 6.2/6.3 effort.

### **7. Project Description:**

Chrome plating and cadmium plating are common inorganic corrosion preventive coatings. Chrome plating is also used to build up worn components when they no longer meet tolerance levels. Cadmium plating is frequently used for fasteners and other very tight tolerance parts because of the dual qualities of lubricity at minimal thickness and superior sacrificial corrosion protection. Replacements for chromium and cadmium will require similar mechanical and performance properties over the full spectrum of applications for which they are currently used. Tin-zinc and zinc-nickel electroplating both offer potential to fulfill all of the requirements of Cadmium plating. These processes provide characteristics which would meet the majority of the corrosion resistance and lubricity requirements of Cadmium plating. A joint Navy industry effort will optimize and demonstrate this capability. Another alternative to Cadmium plating which has potential to fulfill all of these requirements is aluminum-manganese (Al-Mn) electroplating from a molten salt bath. This process differs from the traditional aqueous electrolytic plating bath. Optimum Al-Mn concentrations for Naval aircraft use will be isolated through a test program which examines the varied choices of Al-Mn systems on test coupons of various materials and sizes. This

bath formulation will then be established as a full size prototype at a selected NADEP. Following full scale tests Al-Mn will be transitioned to the fleet through specification modification and design changes. In addition, ion vapor deposited (IVD) aluminum is another demonstrated alternative for certain applications that will be pursued for Navy use. Other alternatives to hexavalent chrome plating and cadmium plating that will be investigated include electroless nickel plating and hard chrome plating as well as alternative application techniques with non-chrome/cadmium materials (physical vapor deposition, spray casting, flame spray/high velocity oxygen fuel, etc). Finally, cyanide strippers have been used to remove metallic coatings. Non-cyanide strippers will be evaluated based on an Air Force investigation.

## 8. Expected Payoff:

The elimination of chromium and cadmium plating significantly reduces the total amount of hazardous materials emitted from Navy operations. Elimination of chrome plating also eliminates the need for expensive emission control equipment required by CAA and AQMD legislation (estimated at several \$M per Depot facility). Furthermore, these alternatives significantly reduce disposal costs of chromium and cadmium from Navy operations. This effort is in direct support of Navy and DoD hazardous waste minimization policies/directives. In addition, without the use of adequate replacements, aircraft operational readiness could be curtailed by excessive environmental degradation. This is particularly important considering the cost of Navy A/C, WS and GSE as well as the severely deleterious environment in which the Navy operates. This technology could also be transitioned to commercial airlines and automotive industries, equipment manufacturers, fastener manufacturers, etc.

## 9. Milestones:

1.	Investigate IVD Aluminum for specific navy applications	09/92
2.	Initiate Al-Mn investigation	06/93
3.	Initiate Zinc-Nickel electroplating investigation	09/93
4.	Demonstrate initial Zn-Ni and Sn-Zn plating bath processes	07/94
5.	Fabricate test samples for cadmium replacement process evaluation	12/94
6.	Initiate coating of test samples for chromium replacement	11/94
7.	Issue multiyear contract for transition of Al-Mn molten salt bath (cadmium replacement) to commercial technology	12/94
8.	Zn-Ni and Sn-Zn tank line increased	02/95
9.	Initiate complete test matrix coating application for 6 potential cadmium replacements	02/95
10.	Release contract for test of chrome alternative plated samples	03/95
11.	Cadmium replacement candidates testing completed	09/95
12.	Evaluate Zinc-Nickel Electroplating	06/95
13.	Evaluate Tin-Zinc Electroplating	06/95
14.	Evaluation of Al-Mn Molten Salt Bath Electroplating	12/95
15.	Electroless Ni Optimization/Demonstration	09/95
16.	Optimize Zinc-Nickel Electroplating	03/96

- |     |   |       |
|-----|---|-------|
| 17. | Optimize Tin-Zinc Electroplating                    | 03/96 |
| 18. | Optimization of Al-Mn Molten Salt Bath Plating      | 05/97 |
| 19. | Implementation of Electroless Ni Electroplating     | 08/97 |
| 20. | Service demonstration of Zinc-Nickel Electroplating | 05/97 |
| 21. | Service demonstration of Tin-Zinc Electroplating    | 08/97 |

**10. Transition Plan:**

The best alternative materials identified from the laboratory evaluations will be service demonstrated at a NADEP through coordination with the Lead Maintenance Technology Center for Environment. These processes will then be transitioned to fleet use through specification modification, technical manual revision and design changes. Industry coordination through out the development and evaluation of these materials will insure availability for implementation.

**11. Funding: \$(K)**

	FY92	FY93	FY94	FY95	FY96	FY97	TOTAL
SERDP	138	460	360	248	303	400	1909

**12. Performers:**

Evaluation/demonstration of Chromium and Cadmium Plating alternatives is being performed by the Naval Air Warfare Center Aircraft Division Warminster, Naval Aviation Depots and the Lead Maintenance Technology Center for Environment. The Cadmium replacement efforts (Zn-Ni & Sn-Zn) also have Boeing, Peter Gumm and McGean Rhoco as industry partners. This effort is being coordinated with the Air Force (Tinker ALC, Tyndall AFCEA), the Army and aerospace industries (Boeing, Grumann, MDA-E, etc.).

**13. Principal Investigator:**

Stephen J. Spadafora  
 Naval Air Warfare Center Aircraft Division Warminster  
 P.O. Box 5156 (Code 4.3.4.1)  
 Warminster, PA 18974-0591  
 PHONE: (215) 441-2704  
 FAX: (215) 956-4141  
 E-MAIL: spadforas@smtpgate.nadc.navy.mil

**14. Keywords:**

Electroplating Processes, Materials Substitution, Chromium Replacement, Cadmium Replacement, Alternative Plating Technologies, Non-Cyanide Processes

## SERDP FY95 PROJECT

1. **SERDP Thrust Area:** Pollution Prevention
2. **Title:** Solid State Metal Cleaning
3. **Agency:** U.S. Air Force
4. **Laboratory:** Wright Laboratory, Aeronautical Systems Center (WL)
5. **Project ID:** #116
6. **Problem Statement:**

The goal of this project is to develop innovative metal cleaning processes that do not require the use of water or volatile organic compounds (VOCs).

Cleaning of metals is a mandatory step in the processing of aircraft components, including wing skins, fuselage panels and bulkheads, etc., prior to surface preparation, such as anodizing, and subsequent priming in preparation for coating or adhesive bonding. State-of-the-art cleaning processes now involve the use of PD 680 type solvents, chlorinated solvents, or water based cleaning systems to remove oil, waxes and particulates from the surface of component surfaces.

### 7. Project Description:

There are two technical objectives to be achieved by this project:

- (1) To develop and transition to a using customer a cleaning process for large (and small) aircraft components that do not require the use of water or VOCs.
- (2) To develop a process that will allow components to proceed directly to the next step in the process for surface without the need for subsequent treatments involving water or organic solvents.

Research and development (R&D) will be performed to study the mechanisms and kinetics of solid state soil (oils, waxes, particulates and metallic oxides) removal processes. Various processes will be studied including activated particulates or polymers, carbon, starch, CO<sub>2</sub> and various inorganic particulates including carbonates and phosphates. Studies will include assessment of how clean components really need to be before they proceed to the next step in their particular processing track. Components proceeding to inspection or other intermediate process steps do not have to meet the cleanliness standards required for surface preparations such as alodine and anodize or those going into a plating or metal deposition process. Laboratory testing will be accomplished to define and measure surface cleanliness levels needed for various subsequent processing steps in order to maintain/improve the performance of subsequent operations.

Feasibility studies have been performed using activated carbon/starch/CO<sub>2</sub>/air and other cleaning media for the removal of various types of soil and particulates. Preliminary research has established the feasibility of this approach for the removal of a number of oily, waxy and particulate contaminants.

The proposed effort responds to pollution prevention mandates by DoD and the Air Force. The effort will also enable reduction of risks, costs and liabilities associated with use of toxics, and handling, treatment and disposal of hazardous wastes. The project will assist in meeting Air Force pollution prevention objectives to reduce volatile air emissions by 50% by the end of 1999 (1993 baseline).

No government sponsored work is presently ongoing/planned in this technology area.

The project encompasses these major tasks:

- Experiments to define/delineate mechanisms/kinetics of solid state soil particulates and oxides removal as a function of cleaning media, energy levels, temperatures and times, etc.
- Process studies to select/optimize cleaning process parameters and influence on substrates, mechanics, and physical properties.
- Studies to define, measure and validate cleanliness levels required for components proceeding to the next stop of their process track.
- Testing and analysis to validate that processing changes do not degrade components performance. Factors such as corrosion resistance, coating adhesion/performance, adhesive bond durability/strength and metal plating adhesion/performance will be comprehensively studied.
- Scale-up to pilot size process to determine scalability of processing parameters previously established.
- Demonstrate/validate process on customer-designated components. Establish and approve process specifications and standards. Perform life cycle cost analysis on process.
- Transition prototype to user/customer for extended production evaluation.

Technical Issues to Overcome:

- Removal of soils/contaminants from simple/complex geometry components without using liquid.
- Ability of solid cleaners to provide wide spectrum cleaning capability under conditions not detrimental to substrate.
- Develop a safe, environmentally sound and affordable/economical process.
- Obtain adequate cleanliness levels in order to eliminate the need for follow-on cleaning operations.

Tie to Tri-service Environmental Quality R&D Strategic Plan:

Pillar Thrust Area: 3.A.2.a  
Requirements Category: I.2.b and I.2.g  
Work effort: Tech Base



## 8. Expected Payoff:

If successful, the scope of this effort will cover the gamut of industrial cleaning operations used throughout the industrialized world. Water waste streams and VOC emissions will be eliminated from industrial cleaning operations. The goal will be to do at least the same (if not better) cleaning job than is now being accomplished using liquids, at a cost equal to or less than today's cost (with no waste streams).

## 9. Milestones:

1. Project initiation/start date.  
Initiate experiments to select cleaning media and define process mechanisms, and critical process parameters. 08/94
2. Complete media testing and process parameters definitions. 07/95
3. Initiate process parameters optimization and substrate sensitivity testing.  
Initiate experiments to define, measure and validate surface cleanliness levels required. 08/95
4. Complete process sensitivity studies and substrate sensitivity testing Initiate coating, bonding plating performance validation studies. 10/95
5. Complete process optimization and initiate scale-up and assemble pilot size process. 01/96
6. Optimize and demonstrate pilot scale operation in cooperation with user/customers. 05/96
7. Complete all performance testing. Write up draft specifications and standards  
Transfer prototype to user/customer for extended production operation. 02/97

## 10. Transition Plan:

This (R&D) program will be conducted in concert with the Air Logistic Centers and will provide engineering data and process information to allow each user to design and implement a systems and processes which will meet their specific requirements.

Potential users will be an integrated part of the R&D team so that their inputs will be incorporated on a continuous basis into the product development cycle.

## 11. Funding: \$(K)

	FY93	FY94	FY95	FY96	FY97	TOTAL
SERDP	350	900	100	578	200	2128

## **12. Performers:**

The project will be performed under the technical leadership and direction of:

Air Force Material Command  
Aeronautical Systems Center  
Wright Laboratory, Materials Directorate  
Wright-Patterson AFB, OH 45433

The Materials Directorate will award one or more research contracts to industry to perform the development and integration.

To facilitate generation of public domain information, hands-on government technology assessment and technology transition, the Materials Directorate plans on having the demonstration site to be either an Air Force Material Command Air Logistics Center or the Developmental Manufacturing and Modification Facility (DMMF) at Wright Patterson AFB, Ohio.

## **13. Principal Investigator:**

Dr. Phil D. Mykytiuk  
WL/MLSE Building 652  
2179 12th Street, Suite 1  
Wright, Patterson AFB, OH 45433-7718  
PHONE: (513) 255-3953  
FAX: (513) 476-4378  
E-MAIL: MYKYTIPD@ML.WPAFB.AF.MIL

## **14. Keywords:**

Cleaning, Coating, Adhesive bonding, VOCs, Ozone depleting substances, Non-aqueous cleaning media

## SERDP FY95 PROJECT

1. **SERDP Thrust Area:** Pollution Prevention
2. **Title:** Non-Chromate Conversion Coatings and Sealers for Aluminum Alloys
3. **Agency:** U.S. Army
4. **Laboratory:** Army Research Laboratory Materials Directorate (ARL)
5. **Project ID:** #673
6. **Problem Statement:**

The development and implementation of (1) a non-chromate conversion coating for aluminum alloys and (2) an alternative sealing treatment to the currently used sodium dichromate in the anodizing process for use in combat and tactical vehicles, munitions, and aircraft.

Background: Chromate conversion coatings such as the currently specified Alodine treatment have been identified as a large unacceptable source of hazardous waste generation and danger to worker health and safety. Chromate conversion coatings have been utilized to promote adhesion and corrosion resistance of organic coating systems (primer-topcoat), but efforts to develop finishing systems that do not incorporate a pre-treatment have not demonstrated comparable performance. This project which is aimed at reducing production and disposal of hexavalent chromium hazardous waste received support (\$50K) in FY91 under the EAMTP (Environmentally Acceptable Materials Treatment Processes - MANTECH) program but remained unfunded in FY92 and FY93 due to limited availability of funds.

Another source of unacceptable hexavalent chromium is the sodium dichromate seal used in the aluminum anodizing process. Removal and disposal of the additional hexavalent chrome from the process waste water exacerbates the cost and the potential health safety problem. The use of non-chromate sealing system will permit an anodizer to eliminate one hazardous constituent.

### 7. Project Description:

Preliminary laboratory testing at ARL Watertown (previously MTL) based on salt fog and electrochemical impedance spectroscopy showed that a Sanchem Boehmite non-chromate conversion coating was promising for several aluminum alloys. The technical objective of the proposed project is to demonstrate the efficacy of non-chromate conversion coatings and sealers for aluminum alloys without compromising corrosion resistance for Army applications and environments. Limited test results of a non-chrome sealer, nickel acetate, for anodized aluminum indicated that this seal system could provide comparable corrosion resistance to the chrome sealer.

Because of the high performance alloys used throughout Army weapons and ammunition, and the harsh environments/extremes encountered in military service, test programs to evaluate these coatings for Army-specific applications are required. Successful completion of the project will contribute to the DA and DoD goal of a significant reduction in hazardous waste generation in the 1995-1997 time frame.

#### Technical Approach:

- (1) Evaluate by a comprehensive characterization of candidate non-chromate conversion coatings (industrial sources and in-house development) for aluminum alloys 5083, 2519, 7039 for comparison with the currently used Alodine chromate conversion coatings. Test protocol includes Auger, ESCA and IR spectroscopy analyses, salt fog, Electrochemical Impedance Spectroscopy, adhesion, stress corrosion cracking, outdoor exposure and field tests to simulate battlefield environments. This project is considered to be low risk. This effort will leverage work being performed by the National Center for Manufacturing Sciences (NCMS) on similar coatings on Al alloys 356, 2024, 3003, 6061, 7075.
- (2) Several sources of supply for the non-chrome sealer will be identified and evaluated in the laboratory with respect to corrosion resistance, abrasion resistance adhesion, fatigue life. Comparable tests will be conducted in the actual production environment to demonstrate performance equivalent to chromium sealers. Nonchrome sealers for the aluminum anodizing process have been available; however, their performance has been inadequate for application requiring maximum corrosion resistance. Some recent formulations of nonchrome sealers claimed comparable performance. The FY93 funding covered the lab evaluation of several nonchrome sealers. This proposal covers the tech-demo and production trials to "prove out" the nonchrome technology on production equipment at production rates.

#### 8. Expected Payoff:

Potential users include MSCs, RDECs, Depots, DoD industrial base. The P.I. of the project is a member of the Aerospace Chrome Elimination Group comprised of Army, Navy, Air Force, and industry participants (Boeing, Grumman, McDonnell Douglas, Northrop, Rockwell, Lockheed, Hughes). Use of the non-chromate conversion coating and sealing system will allow government and industry facilities to eliminate one source of hazardous waste with concomitant cost savings associated with reduction of waste treatment and disposal costs. Though an exact cost benefit analysis is not yet available, the minimal implementation costs foreseen produce a high potential for significant cost savings. In 1991 the Army's cost of safe handling and disposal of hazardous waste was estimated to be \$335M. The same cost was projected to be \$75B throughout the industrial base.

## 9. Milestones:

### Non-chromate conversion coating

- |    |   |       |
|----|---|-------|
| 1. | Complete industry survey                        | 02/94 |
| 2. | Obtain coated coupons for laboratory evaluation | 05/95 |
| 3. | Complete initial laboratory analysis            | 03/95 |
| 4. | Downselect conversion coatings for field trials | 12/94 |
| 5. | Outdoor exposure tests, field tests             | 09/95 |

### Non-chromate sealing system

- |    |                                   |       |
|----|-----------------------------------|-------|
| 1. | Industry survey system            | 02/94 |
| 2. | Complete feasibility testing      | 05/94 |
| 3. | Complete laboratory testing       | 10/94 |
| 4. | Complete technology demonstration | 10/95 |
| 5. | Complete production trial         | 09/96 |

## 10. Transition Plan:

Coordination with MSCs, RDECs, Depots through membership in corrosion Prevention Advisory Teams (CPATS) and the Aerospace Chrome Elimination (ACE) Group; Project Reliance sub-panel AM-6.2 on Paints, Coatings and Cleaning Materials; introduce specification for non-chromate conversion coating for aluminum alloys early in the acquisition cycle of weapon system and insure flow-down to contractors, sub-tier suppliers and vendors.

Once a nonchrome sealing system has been successfully demonstrated in the production environment, the technical agency will direct the contracting officer to permit the use of the qualified nonchrome sealing system on aluminum components. Transition to the nonchrome sealing system will require draining and cleaning of the current sealing tank, to remove any residual chromium, and refilling the tank with the designated nonchrome solution.

## 11. Funding: \$(K)

	FY93	FY94	FY95	FY96	TOTAL
SERDP	245	300	68	172	795

## 12. Performers:

Department of the Army, Army Research Laboratory (formerly MTL) Materials Directorate, AMSRL-MA-MA, Watertown, MA. Member of the ACE Group, cooperative development agreements with DoD and industrial base. U.S. Army, ARDEC, ATTN: SMCAR-CCH-P, Picatinny Arsenal, NJ and Production Installations

**13. Principal Investigator:**

Dr. John H. Beatty  
Corrosion Science-Army Research Lab  
102 Maryland Hall  
Johns Hopkins University  
Dept. of Materials Science & Engineering  
3400 N. Charles Street  
Baltimore MD 21218  
PHONE: (410) 516-4648  
FAX: (410) 516-5298  
E-MAIL: jbeatty@arl.mil or jbeatty@aol.com

**14. Keywords:**

Conversion coatings, aluminum alloys, hexavalent chromium reduction, Sanchem Boehmite

## SERDP FY95 PROJECT

1. **SERDP Thrust Area:** Pollution Prevention
2. **Title:** Aircraft Maintenance Chromium Replacement
3. **Agency:** U.S. Navy
4. **Laboratory:** Naval Air Warfare Center Aircraft Division, Warminster (NAWC)
5. **Project ID:** #66
6. **Problem Statement:**

To replace chromates (Cr) currently used in aerospace materials and processes on Navy aircraft (A/C), weapon systems (WS) and ground support equipment (GSE). Chromium VI is a carcinogen. Federal, state and local environmental agencies (EPA, California's Air Quality Management Districts (AQMD), etc.) are restricting the use and disposal of this hazardous material through regulations such as the Clean Air and Water Acts, CERCLA, and RCRA along with local EPA and AQMD rules. In addition, OPNAV and CNO directives require significant reductions in the amount of hazardous waste generated by the Navy. Chromated materials used in production and depot level maintenance operations are a large contributor to this overall waste generation. Therefore, in order to comply with these regulations while maintaining aircraft performance and operational readiness, chrome-free alternatives have to be developed. This work is covered under the Tri-Service EQ Strategic Plan Pillar 3: Pollution Prevention: Requirement Thrust: 3.A.3: Metal Working/Processes Plating/Finishing and is a continuation of an existing SERDP 6.2/6.3 environmental effort.

### 7. Project Description:

Non-chromate alternative materials and processes will be investigated for current anodizing, pretreating, sealing, adhesive and corrosion preventive processes. The approach taken for the development of non-chromate materials will be identification, development, test and evaluation, demonstration and implementation. Chromic acid anodizing (CAA) is a common inorganic coating for pretreating aluminum prior to painting. As an example, this program identified the best alternatives to CAA from existing and developmental coating methods. These alternatives included thin sulfuric, phosphoric acid anodizing and Boeing Aerospace Corp's Sulfuric-Boric Acid Anodize (SBAA). Selected alloys were processed and tested to determine which replacement systems provided equivalent corrosion resistance and paint adhesion while maintaining the existing mechanical properties provided by CAA. After lab optimization, a SBAA production process was demonstrated at the Naval Aviation Depot (NADEP) at North Island. After successful completion of the service demonstration, the MIL-A-8625 Anodize specification was modified and the process is being transitioned to full fleet implementation. This approach will be taken for the development of non-chromate pretreating materials (alkaline cleaners & deoxidizers, etc.), adhesives, sealants, and other aerospace chrome containing corrosion preventive materials.

## 8. Expected Payoff:

The elimination of chromic acid anodizing, chromated alkaline cleaners and deoxidizers, and sealants and adhesives, significantly reduces the total amount of chromium emitted from Navy operations. Elimination of chromic acid anodizing also eliminates the need for expensive emission control equipment (estimated at \$1M per Depot facility) required by CAA and AQMD legislation. Non-chromated alkaline cleaners and deoxidizers, developed under a Pollution Abatement funded program have been implemented at three NADEPs to meet these new regulations. NADEP Jacksonville has reported an annual cost savings of \$23K and a reduction of 3 tons of chromium waste per year from the use of the non-chromate deoxidizer. Furthermore, these alternatives significantly reduce rising disposal costs of chromium from Navy operations. This effort is in direct support of Navy and DoD hazardous waste minimization policies/directives. In addition, without the use of adequate replacements, aircraft operational readiness could be curtailed by excessive environmental degradation. This is particularly important considering the cost of Navy A/C, WS and GSE as well as the severely deleterious environment in which the Navy operates. This technology could also be transition to commercial airlines, automotive industries, equipment manufacturers, etc.

## 9. Milestones:

1.	Optimize non-Cr adhesive pretreatments	07/95
2.	Evaluate non-Cr adhesive bond primers and conversion coat process	09/95
3.	Service demonstration of non-Cr aluminum pretreatment	12/95
4.	Advanced development of non-Cr conversion coatings	12/95
5.	Optimize non-Cr adhesive bond primers	02/96
6.	Optimize water-borne non-Cr adhesives	03/96
7.	Initiate non-Cr pretreatment strippers development	05/96
8.	Service demonstration of non-Cr conversion coatings	05/96
9.	Transition of non-Cr pretreatments	08/96
10.	Service demonstration of non-Cr adhesive bond primers	09/96
11.	Initiate water displacing corrosion preventatives	10/96
12.	Transition water-borne non-Cr adhesives	06/97
13.	Evaluate water displacing corrosion preventatives	05/97
14.	Transition of non-Cr adhesive bond primer	06/97
15.	Initiate water-borne non-Cr adhesives evaluation	06/97
16.	Service demo water displacing corrosion preventatives	06/97
17.	Service demonstration water-borne non-Cr adhesives	09/97
18.	Transition of water displacing corrosion preventatives	09/97

## 10. Transition Plan:

The best alternative materials identified from the laboratory evaluations will be service demonstrated at a NADEP and transitioned to fleet use through specification modification, technical manual revision and design changes. Industry coordination through out the development and evaluation of these materials will insure availability for implementation.



For example, non-chromated alkaline cleaners and deoxidizers have been fully implemented at three NADEPs to meet these new environmental regulations. The SBAA process has been successfully demonstrated at NADEP North Island and is currently being transitioned to fleet use.

**11. Funding: \$(K)**

	FY94	FY95	FY96	FY97	TOTAL
SERDP	180	158	193	350	881

**12. Performers:**

Evaluation/demonstration of Chromium-free alternatives is being performed by the Naval Air Warfare Center Aircraft Division Warminster, Naval Aviation Depots and the Lead Maintenance Technology Center for Environment. This effort is being coordinated with the Army Research Laboratory (Watertown, MA), the Air Force (Tinker ALC and Tyndall AF Civil Engineering Services Center), National Defense Center for Environmental Excellence (Non-Chromate conversion coating demo) and aerospace industries (Boeing, Rohr, Grumann, MDA-E, Lockheed, etc.).

**13. Principal Investigator:**

Stephen J. Spadafora  
Naval Air Warfare Center Aircraft Division Warminster  
P.O. Box 5156 (Code 6062E)  
Warminster, PA 18974-0591  
PHONE: (215) 441-2704  
FAX: (215) 441-1925  
E-MAIL: spadforas@smtpgate.nadc.navy.mil

**14. Keywords:**

Chromium Elimination, Pretreatments, Materials Substitution, Surface Preparation, Anodizing, Adhesive bonding

## SERDP FY95 PROJECT

1. **SERDP Thrust Area:** Pollution Prevention
2. **Title:** Non-Chemical Surface Preparation
3. **Agency:** U.S. Air Force
4. **Laboratory:** Wright Laboratory, Aeronautical Systems Center (WL)
5. **Project ID:** #130

### 6. **Problem Statement:**

Conventional cleaning and surface treatment processes used in the aerospace industry often involve use of toxic materials and solvents and generation of aqueous hazardous waste streams. These processes involve toxic hazards in the workplace, risk of uncontrolled releases of hazardous substances, and treatment and disposal procedures which are costly, administratively burdensome, and attended by serious legal and financial liabilities. In addition, many traditional materials, such as ozone depleting chemicals, are subject to bans on production and use.

The development of advanced metal surface preparations that do not require use or generation of hazardous substances is needed.

### 7. **Project Description:**

**Technical Objective:** The objective is to identify, develop, and optimize non-wet chemistry approaches for the formation of stable morphologies on the surface of aluminum, titanium and copper materials that will allow performance of high quality coating or adhesive bonding.

**Technical Approach:** This program will involve laboratory R&D, process scale-up, specifications development, and technology transition in two specific technical areas. These areas are: (1) laser surface preparation of aluminum and titanium alloys. The feasibility of the use of the eximer laser to grow oxides on aluminum has been shown, and the bondability to both coatings and adhesives has been demonstrated; (2) non-chemical surface morphologies for coating and bonding to aluminum, titanium, and copper can be achieved via non-chemistry based processes including plasma spray, flame spray, and vapor deposition. These approaches are based on new technology and initial feasibility has been demonstrated. Processes currently in use are based on wet chemistry and require use of soluble chromate, strong acids and bases and large amounts of water. The use and generation of toxics is an increasingly risky and expensive proposition. The new approaches represent a radical, but environmentally benign, departure from existing technology. There are no serious technological roadblocks foreseen in the scale-up of these processes.

Previous efforts/accomplishments in this area within and outside the organization: This technical effort will build on recent efforts in cooperation with EOARD to develop CO<sub>2</sub> laser surface modification technology.

The proposed effort responds to pollution prevention mandates by DoD and the Air Force. The effort will also enable reduction of risks, costs and liabilities associated with use of toxics, and handling, treatment and disposal of hazardous wastes. In some instances, elimination of ozone depleting chemicals (ODCs) may be achieved. This project will support the Air Force goal to reduce hazardous waste generation by 50% by the end of 1999 (1992 baseline).

Related activities include work on solid state cleaning of metals and thin film deposition technology, the AF Civil Engineering Support Activity (AFCESA) spray casting program and thin film (including sol gel) deposition technology developed for the electronic and commercial construction industry.

Tasks/activities: Experiments will be conducted to determine the feasibility of developing surface oxide morphologies that are thermodynamically stable, mechanically strong, and resistant to corrosion (chemically stable).

Technology areas to be investigated will include sol gel films, thin film deposition of SiC, SiN, SiO, sputtered and enhanced ion-beam deposition coatings as well as laser enhanced oxide formation.

- Surface laser characterization will be accomplished using various surface analysis techniques.
- Chemical and thermodynamic stability of coatings will be determined.
- Corrosion resistance and performance of coatings and adhesive bonded joints will be studied.
- Bench top process equipment will be developed and process parameters optimized.
- Testing and analysis will continue and life cycle cost studies will be performed.
- Scale up to pilot size equipment will be accomplished.
- Specifications and standards will be written.
- Processes will be optimized.
- Pilot scale equipment will be operated so that users may have short production runs performed on components prior to more extensive field\service applications.

Technical issues to overcome: The technical risks include the ability to produce the desired oxide morphology with the requisite thermodynamic and chemical stability and the needed mechanical strength without degrading the substrate mechanical properties. Attending these risks are the challenges of developing technology that will be environmentally acceptable and affordable.

Tie to Tri-service Environmental Quality R&D Strategic Plan

Pillar Thrust Area: 3.B.1  
Requirements Category: I.4  
Work effort: Tech Base

## 8. Expected Payoff:

Breakthrough technologies to prepare metal surfaces in various stages of manufacturing and remanufacturing will be of enormous benefit to aerospace and other industries in the US and worldwide. The total cost avoidance will be dependent upon the specific applications and the technologies developed. While direct labor, material, and equipment costs may increase, they may be offset by eliminating the costs of hazardous materials and waste management and environmental compliance and response.

## 9. Milestones:

1.	Project go-ahead	08/94
2.	Initiate laboratory development and tests of candidate materials and processes Define processes to be replaced and applicable specifications and standards. Define process mechanisms and critical process parameters	10/94
3.	Select candidate processes for more extensive testing	12/94
4.	Select most promising materials and processes for more extensive testing.	04/95
5.	Initiate large laboratory scale process studies Initiate process parameter sensitivity studies	06/95
6.	Initiate studies on surface stability and strength Initiate coating and bonding studies	09/95
7.	Complete all preliminary tests and studies. Initiate scale-up to pilot scale process facility	12/95
8.	Initiate optimization of pilot scale process. Begin treatment of customer furnished components for extended service evaluation. Prepare or revise specifications and standards	03/96

## 10. Transition Plan:

The proposed R&D program will be accomplished in an integrated program development mode. The pilot plant will be operated at the Developmental Manufacturing and Modification Facility (DMMF) at Wright-Patterson AFB, OH or at one of the Air Logistics Centers in cooperation with a user team. Successful service experience along with specifications and standards will enable each prospective user to implement processes meeting their specific needs. Potential users will be an integral part of the R&D team to ensure that their inputs will be incorporated on a continuous basis into the technology development cycle.

## 11. Funding: \$(K)

	FY93	FY94	FY95	FY96	TOTAL
SERDP	300	998	274	641	2213

## **12. Performers:**

The project will be performed under the technical leadership and direction of the Air Force Material Command, Aeronautical Systems Center, Wright Laboratory, Materials Directorate (WL\ML), Wright-Patterson AFB, OH 45433.

The Materials Directorate will award one or more research contracts to industry to perform the development and integration.

In order to facilitate generation of public domain information, hands-on government technology assessment and technology transition, the Materials Directorate plans demonstration to be conducted either at an Air Force Material Command Air Logistics Center or the Developmental Manufacturing and Modification Facility (DMMF) at Wright Patterson AFB, Ohio.

## **13. Principal Investigator:**

Mr. James Mazza  
WL/MLSE, Bldg 652  
2179 12th Street, Suite 1  
Wright-Patterson AFB, OH 45433-7718  
PHONE: (513) 255-7778  
E-MAIL: mazzajj@ml.wpafb.af.mil

## **14. Keywords:**

Coating, Bonding, VOCs, Hazardous Air Pollutants, Corrosion Protection, Ozone depleting substances

## SERDP FY95 PROJECT

- 1. SERDP Thrust Area:** Pollution Prevention
- 2. Title:** Recycling/Purification of Plating/Cleaning Baths
- 3. Agency:** U.S. Navy
- 4. Laboratory:** Naval Facilities Engineering Service Center (NFESC)
- 5. Project ID:** #70
- 6. Problem Statement:**

The goal of this effort is to develop innovative techniques for prolonging process bath life and for recycling hazardous materials from spent process baths to reduce the generation of hazardous wastes (HWs). DoD electroplating shops use process solutions containing hazardous materials for plating, metal stripping, acid etching, alkaline cleaning, anodizing, and other metal finishing operations. The effective life of these solutions is limited by the increasing levels of contaminants that are dragged in from the parts being plated or cleaned. These contaminants reduce plating and cleaning efficiency and will eventually adversely affect the quality of the metal finishing operation. As a result of this contamination, the "spent" bath must be periodically dumped. Large volumes of concentrated HWs are generated from these process solutions that become spent due to buildup of contaminants.

Based on Navy data collected for CY-90, the largest volumes of spent process baths in decreasing order included sodium hydroxide, chromic acid/sodium dichromate, hydrochloric acid, cyanides, sulfuric acid, nitric acid, electroless nickel and nickel sulfamate. While ongoing RDT&E efforts to develop new technologies for eliminating chromium and cadmium (cyanide) plating operations will reduce the use of these particular process baths, many of the alternative processes will require purification of contaminants (i.e. replacement of chromic acid anodizing with sulfuric-boric acid anodizing, replacement of cadmium plating with zinc-nickel plating, use of electroless nickel coatings in place of hard chromium plating). Development of alternative application techniques such as spray casting which eliminate the use of chemical process solutions are in the developmental stages and not currently available. Cleaning and stripping solutions will continue to be used. In addition, many new aqueous cleaning solutions are being used to eliminate solvent cleaning with CFCs. These cleaning solutions will require purification to maximize the solution life.

Separation technologies such as ultrafiltration, carbon absorption, ion exchange, electrolysis, membrane electrolysis, electrodialysis, and diffusion dialysis will be investigated for use in removing contaminants from plating/metal cleaning process baths. This effort will address a variety of process solutions and removal of different contaminants that buildup. The process baths requiring purification will be prioritized based on DoD volumes of solution waste generated, disposal costs, toxicity, and continued use. The impact of ongoing RDT&E efforts to eliminate chromium and cadmium plating will be considered as well as anticipating

requirements for purification of alternative process baths. Several technologies will be developed for specific applications as required. Test and evaluation of purification technologies with applicability to a variety of process baths will be given the most emphasis. Purification of alternative plating solutions will be considered in the test program.

This project is an ongoing SERDP effort. The Navy effort was enhanced under FY93 funding as a joint Navy/Air Force/EPA project. It addresses SERDP Thrust 3.A.3.a Pollution Prevention for Metal Working/Plating and Finishing. It supports the SERDP goal to minimize or eliminate hazardous wastes through improved in-process treatment technologies for key industrial operations, including metal preparations.

## **7. Project Description:**

The objective of this effort is to develop effective methods and on-line systems for purification/rejuvenation of electroplating (chrome, nickel, electroless nickel, copper, etc), anodizing, and metal cleaning solutions (acids, alkalis). Data will be collected from DoD plating shops to identify the contaminant levels for major process baths and current bath maintenance practices. Contaminant buildup in alternative process baths under test demonstration will also be investigated. Separation technologies such as membrane electrolysis, electrodialysis, ion exchange, carbon absorption, and ultrafiltration will be investigated for removal of metal and/or organic contaminants from plating and cleaning solutions. Chemical/electrochemical destruction technologies for removal of residual organic contaminants will also be investigated. An assessment of technologies completed by the Navy in FY92 will be updated and expanded to identify the status and applicability of emerging technologies for purification/rejuvenation of Navy and Air Force process solutions.

Laboratory tests will be conducted as needed to evaluate alternative technologies. The most promising technologies will be identified for each major process solution disposed by Navy and Air Force plating operations. Field testing of selected technologies will be performed to determine the effectiveness and to optimize design and operational parameters for each purification system developed for specific process baths. Appropriate planning, design, operation, and maintenance criteria will be developed for technology transfer of each system to DoD plating operations and coordinated with American Electroplating and Surface Finishing (AESF) society for transfer to private industry. The technical risk of this effort is low. The project addresses the Tri-Service EQ Strategic Plan, Requirement I.3.b. Reuse/recycling of hazardous wastes generated from electroplating operations.

## **8. Expected Payoff:**

Development and demonstration of bath purification technologies will provide in-process treatment of plating, acid etching, pickling, alkaline electrocleaning, chromating, anodizing, and other solutions. Hazardous wastes generated from these metal finishing processes could be reduced by 75% with the extension of process bath life. Navywide hazardous wastes could be reduced by 375,000 gal/yr providing a saving of \$1.3M per year or more depending on the cost for disposal. In addition, cost savings for chemical replacement is estimated at \$1.5 M/yr. DoD-wide savings would be at least tripled. The anticipated non-economic

benefits include improved product quality of finished parts by reducing contamination in the plating/cleaning processes. Users include Navy and DoD plating shops as well as many potential users of this technology in the public and private sectors. As there are many thousand electroplating and surface finishing facilities in the US, there would be high interest and potential for transfer to industry.

**9. Milestones:**

- |     |   |       |
|-----|---|-------|
| 1.  | Collect DoD Plating Shop Data   | 01/94 |
| 2.  | Complete review of advanced and emerging separation and organicdestruction technologies.  | 03/94 |
| 3.  | Identify technology alternatives for each major process bath and prepare updated technology assessment report   | 09/94 |
| 4.  | Develop experimental design for laboratory and field evaluations to address technology/process bath matrix  | 06/94 |
| 5.  | Conduct feasibility studies to assess the effectiveness and performance of alternative bath purification systems - Alkaline cleaner recycling and electroless nickel rejuvenation | 08/95 |
| 6.  | Complete feasibility studies - Chrome purification and acid recovery  | 11/95 |
| 7.  | Prepare feasibility reports   | 11/95 |
| 8.  | Optimize designs  | 11/95 |
| 9.  | Conduct field testing - Alkaline cleaner recycle  | 02/96 |
| 10. | Select field site for electroless nickel rejuvenation   | 08/95 |
| 11. | Contract award to A.D.L. for electroless rejuvenation test  | 10/95 |
| 12. | Complete prototype design of diffusion dialysis system for EN rejuvenation  | 12/95 |
| 13. | Diffusion dialysis installation   | 12/95 |
| 14. | Test of electroless nickel rejuvenation complete  | 03/96 |
| 15. | Prepare test report on diffusion dialysis   | 04/96 |
| 16. | Select site/coordination of crossflow microfiltration   | 04/96 |

**10. Transition Plan:**

Documentation covering planning, design, operation, and maintenance of bath purification systems will be prepared for technology transfer to Navy and DoD activities. This technology transfer package will be published as a final deliverable. The technology transfer package will be provided to appropriate Navy, Army, and Air Force activities for implementation including Air Force's System Program Office and the Technology Transfer Division of Air Force's Center for Environmental Excellence. Private industry will have access to the information developed and, with it will be able to apply the technology as desired. In addition, the capabilities of EPA's Center for Environmental Research (CER) will be used to provide technology transfer of information to private industry.



**11. Funding: \$(K)**

	FY93	FY94	FY95	FY96	TOTAL
SERDP	600	800	360	440	2200

**12. Performers:**

The performers include the Naval Facilities Engineering Service Center with joint participation from Air Force's Wright Laboratory, Manufacturing Technology Division and EPA's Risk Reduction Engineering Laboratory. Wright Laboratory will assist in the collection of plating shop data, development of contracted efforts for pilot and field testing, and identification and coordination of field tests at selected Air Logistic Centers. RREL will assist in laboratory and bench scale studies of advanced membrane technologies that could be applied to process bath purification and in transfer of technology to private industry. The POCs for partners in this effort are Mr. Roger Wilmoth, RREL, Toxics Control Branch, (513)569-7509 and Mr. Dan Brewer, WL/MTX, (513)255-36701 x208.

**13. Principal Investigator:**

Ms. Jennie Koff, Code 421  
Naval Facilities Engineering Service Center  
560 Center Drive  
Port Hueneme, CA 93043-5003  
PHONE: (805) 982-1674  
FAX: (805) 982-1409  
E-MAIL: JKOFF@NFESC.NAVY.mil

**14. Keywords:**

Electroplating, Metals Removal, Membrane Separations, Purification

## SERDP FY95 PROJECT

1. **SERDP Thrust Area:** Pollution Prevention
2. **Title:** PVD Coatings and ION Beam Processing as Alternatives to Electroplating
3. **Agency:** U.S. Army
4. **Laboratory:** Army Research Laboratory - Watertown (ARL)
5. **Project ID:** #632

### 6. **Problem Statement:**

Goal: Conduct applied research and development to demonstrate that metal or ceramic coatings deposited by physical vapor deposition (PVD), and/or ion-beam-modified surfaces are equivalent or superior in performance and are a cost-effective alternative to electroplated chromium and cadmium for military applications.

Background: Hard chrome is primarily used in DoD related manufacturing to (1) coat high wear surfaces such as bearing shafts and hydraulic components and is principally performed by Original Equipment Manufacturers (OEM's) and (2) rebuild and remanufacture out-of-tolerance components, such as worn shafts and corroded hydraulic components, with the work being performed by maintenance depots. For the former, the use of hard chrome has actually been increasing because the general requirement for coatings has also been increasing due to enhanced performance requirements. For example, one engine manufacturer currently applies hard chrome to 1192 different engine components. For the latter application, many pieces of military hardware are returned to the depots for refurbishment with components that are worn, corroded, or eroded by use. Rather than replacing them, they are reworked by removing the damaged metal, stripping off any old hard chromium coatings, building them up with hard-chrome, and then machining them to final tolerance. As an example of usage, at the Corpus Christi Army Depot, where most of the Army's helicopters are serviced, annually more than 10,000 separate types of components are coated with hard-chrome for this purpose. It should be noted that most of these components are reworked and re-plated several times. To provide an indication of costs associated with chrome plating, it is estimated that for each plating line the cost of waste disposal is \$10,000 per month with the total cost associated with installation of a new plating shop that meets EPA and OSHA regulations ranging from \$5M to \$15M.

Gun tube wear and erosion have been a long-standing military unique problem. A practical objective has been to achieve gun tube wear life comparable to fatigue life. The unexpectedly short tube life for the new 8" and 155 mm gun systems was revealed by wear and erosion test late in the development cycle. Further, the Army has a strong interest in pushing towards higher gun performance to extend the range of its artillery and to obtain higher velocities and shorter times of flight for rapid-fire anti-aircraft guns. The problem remains to obtain acceptable tube life with higher performance. Modern high performance guns require

erosion protection, and advanced gun systems under development (such as Liquid Propellant and Rail Guns) will push these requirements to even higher standards. Chromium plating of gun tubes has provided a finite improvement in tube life depending on gun operating conditions. But the mechanical stability of Cr electroplate (due to numerous microcracks) is limited and new protective coatings with even higher melting points (refractory metals) are needed to challenge the use of more energetic propellants which have higher flame temperatures. Reduction in the use of electroplated chromium will result in an appreciable reduction of the Army's cost of safe handling and disposal of hazardous waste (estimated to be greater than \$335M in 1991).

Cadmium electroplating is also used by both OEM's and by DoD maintenance depots to impart corrosion resistance and lubricity to a wide variety of parts, although substitute coating processes have been more fully developed for this than for the hard-chrome plating. These alternatives include electrodeposited Zn alloys and ion vapor deposited (IVD) aluminum. The Air Force has taken the lead in the actual implementation of these alternatives. At other facilities, such as the Cherry Point Naval Aviation Depot, which has had an IVD system for almost 10 years, the ratio of Cd-plated to IVD-coated parts is more than 10 to 1. The Anniston Army Depot, Anniston, Alabama, has recently installed two IVD systems and is replacing cadmium with IVD aluminum for certain components of armored vehicles other than fasteners. The Air Force acknowledges that IVD-Al will not replace more than about 50% of the Cd-plating requirements. The Army has authorized electroplated zinc as an alternative to cadmium for grade 8 fastener application. Concurrence by the Air Force and Navy to accept zinc as a legitimate alternative to cadmium for these fasteners has also been obtained. Exceptions include selected electrical or electronic applications where cadmium-plated fasteners are required or preferred and high-strength steels for certain helicopter components. A recent preliminary laboratory study by the Army Research Laboratory, Watertown Site, showed a Zn-Ni alloy provided better resistance than zinc and exhibited a comparable coefficient of friction. Thus there still exists the strong need for further coating development efforts.

## **7. Project Description:**

**Previous Efforts:** Most previous efforts in this area have been the investigation of alternative electroplated coatings, such as Zn alloys to replace cadmium. The only significant exception to this is the development of IVD aluminum. It is interesting to note that large-scale IVD-Al systems have been available for over 15 years, yet DoD is still funding R&D work to investigate and implement this process. Electroless nickel coatings are also being investigated as a replacement for chrome, but nickel is on the EPA "toxic enemies" list so it should only be considered as an interim replacement process.

**Technical Objective:** Demonstrate PVD coating techniques and ion beam processing as effective environmentally acceptable alternatives to chromium and cadmium electroplating. Demonstrate applicability to advanced military systems, and the ability to withstand severe military service conditions.

**Technical Approach:** Vacuum-based PVD coating techniques are known to produce the highest quality coatings, with widespread use of high vacuum techniques in the microelectronics industry having broadened the industrial base for large scale systems with a concomitant reduction in cost. The most advanced types of PVD coating techniques utilize what can be called "ion-assist" whereby energetic charged particles are incident on the workpiece during the coating process. Two variations on ion-assisted PVD are (1) ion-beam-assisted deposition (IBAD) whereby a directed beam of energetic particles from an ion gun are coincident on the workpiece with the depositing vapor atoms, and (2) magnetron sputtering whereby vapor atoms are produced by sputtering from an electrode with ions being accelerated from a plasma by application of a negative bias to the workpiece. These two techniques produce coatings that are highly adherent, fine grained, generally pin-hole free and fully dense, and which can be deposited at relatively low temperatures on virtually any type of solid material. The deposition rates for these types of coating techniques are sufficiently high that they could be expected to economically replace both chrome platings deposited by OEM's and electroplated cadmium. For these applications, the types of coatings to be investigated would be TiN, (Ti, Al) N, CrN, Ta and diamondlike carbon, all of which have been previously investigated for corrosion and wear applications. However, the deposition rates are not high enough to replace the chrome plating operations in military depots which are intended for re-build of components. For this application, the proposed solution is to rebuild the component using an alternative electroplating technique such as electroless nickel, machine it to final tolerance, and then apply one of the above PVD coatings which should provide significant wear and corrosion resistance leading to a reduced requirement for future rework.

Ion implantation has been shown to significantly improve the corrosion and wear behavior of a variety of materials. With this technique near-surface alloys or compounds can be produced, with no discrete interface between the modified layer and underlying material that could lead to delamination problems as is possible with coatings. Virtually any element can be implanted into substrate materials although only a few will be selected for this program. Previous research conducted at ARL has shown that nitrogen implantation into hard-chrome coatings increases the surface hardness and significantly reduces the tendency of the coatings to form microcracks when subjected to loads or stresses. This will be further investigated under this program as well as ion implantation of thin-dense-chrome coatings, a proprietary process of Armoloy, Inc., which is an electroplating process that does not produce toxic effluents.

**Relationship to DoD Environmental Objectives:** This program addresses the objectives of eliminating airborne toxic emissions and hazardous waste streams associated with chromium and cadmium electroplating. The treatment of these hazardous effluents at the many installations utilizing these processes is estimated to cost DoD tens of millions of dollars each year.

Relationship to Other Similar Ongoing Work: In November 1992, the Basic Industry Research Laboratory (BIRL) at Northwestern University was notified by ARPA that they will be awarded a substantial contract (\$1.5M over two years) entitled, "Hard-Chrome Coatings: Advanced Technology for Waste Elimination." A major portion of this contract will be to investigate methods for reclaiming or recycling effluents from the plating operations. Another significant portion is the investigation of alternative coating processes. These include HVOF plasma spraying, laser cladding, laser-assisted chemical vapor deposition, and sputtering. The Surface Modification Branch at NRL will have a small effort under the ARPA program (\$30K per year) to perform ion-beam modification of some of the coatings. This proposed SERDP program is designed to investigate other coating techniques and thus there would be virtually no duplication of effort. One of the POC's (BDS) on this proposal has previously collaborated with the PI on the ARPA contract in other areas and it is anticipated that there would be extensive collaboration between the two programs to ensure that DoD would obtain the optimum solution(s) to this problem.

Tasks/Activities: Since it will not be necessary to demonstrate that the coating techniques to be investigated under this program are environmentally acceptable, the focus of the project will be the characterization and evaluation of the coatings in comparison to electroplated chromium and cadmium coatings. Evaluation of coating performance must include laboratory simulation of the conditions to which coated components will be subjected to in battlefield and global environments, with a baseline comparison with hard-chrome coated components. Properties such as hardness, adhesion, and density will be determined for all of the coatings. Measurements related to actual performance will be correlated with the type of electroplated coating intended to be replaced and the actual end use application. Thus, appropriate tests could include (1) sliding wear tests with realistic loads, speeds, and use of lubricants, (2) erosion tests, (3) corrosion tests using electrochemical and/or salt spray methods, and (4) low-cycle or high-cycle fatigue, or rolling-contact fatigue, and (5) Hothardness tests.

In addition to evaluation of coated test coupons, actual components will be selected for coating and evaluation in rig tests at appropriate depots. The POCs have assembled a team that can address all of the tasks related to coating deposition, characterization, and evaluation. The following correlates the tasks with the activities expected to perform them. An (A) or (N) following the activity denotes whether the Army or the Navy will be the primary contact with the activity.

1. Corrosion Science Group, ARL(A): Deposition of IBAD and plasma sprayed coatings; cohesion, adhesion, and porosity measurements on all coatings; surface analytical measurements; corrosion by electrochemical impedance spectroscopy, galvanic corrosion studies; erosion tests; coefficient of friction measurements; rolling contact fatigue measurements.
2. Surface modification branch, NRL(N): Deposition of IBAD coatings; hardness, density, and adhesion measurements on all coatings; composition measurements on compound coatings and determination of impurities, if any; other surface analytical measurements; sliding wear tests; electrochemical corrosion tests.
3. BIRL, Northwestern University: Deposition of magnetron sputtered coatings; high temperature wear tests using Falex tester; deposition of HVOF coatings (A).

4. Jet Process Corporation, New Haven, CT: Deposition of PVD coatings (N).
5. Armoloy of Connecticut, Inc.: Deposition of TDC coatings (A)
6. Naval Air Warfare Center, Trenton, NJ: Fatigue testing of coated samples (N).
7. Corpus Christi Army Depot (CCAD): Deposition of cadmium and chromium coatings onto test specimens selection of two helicopter engine or transmission components (in consultation with ARL) for coating; rig testing of coated components (A).

In addition, in the latter stages of the project, attempts would be made to perform actual flight tests on coated and surface modified components. The arrangements for these would have to be made in cooperation with the Army Aviation Systems Command and the Naval Air Systems Command.

Technical Issues to Overcome: An important issue in developing new types of coatings in any system is whether it will have any effect on any other system components. As an example, a part that is currently chromium-plated may be in sliding contact with another part in an aircraft engine. If the chromium coating is replaced with another coating which demonstrates superior performance in laboratory tests, will it have a detrimental effect on its mating part? This potential problem will be considered in the selection and evaluation of actual components. This overall program is considered to be of medium technical risk.

**8. Expected Payoff:**

Impact: The costs of alternative coating technologies should not be compared with the previous cost of chrome and cadmium coating, but with the expected future costs associated with the processes, taking into account regulations projected into the future. The Basic Industry Research Lab has performed a detailed cost analysis based on information provided by CCAD and McClellan AFB and on their own calculations related to PVD coating operations and have concluded that for operations that would produce equivalent throughput, the total annual operating cost for a PVD facility would be approximately 20% less than for a plating operation.

Coatings developed under this project should demonstrate performance that exceeds that of electroplated coatings, thus reducing the frequency of rework necessary. This will further reduce the costs associated with the new processes. As an example, if a 2.5 X increase in service life by using ion implantation can be achieved, estimates based on CCAD data show these re-work savings on only three bearings and gears used in the AH-1/UH-1 helicopter drive trains would total over \$1.2 M yearly. The potential on a DoD wide basis would be many times greater.

**9. Milestones:**

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|---|--|
| <ol style="list-style-type: none"> <li>1. Test coupon fabrication</li> <li>2. Coating application to coupons</li> <li>3. Lab. wear evaluation</li> <li>4. Lab. electrochemical evaluation</li> <li>5. Fatigue evaluation</li> </ol> | <p>11/94<br/>01/95<br/>06/95<br/>06/95<br/>09/95</p> |
|---|--|

- |     |                                     |       |
|-----|-------------------------------------|-------|
| 6.  | Salt-Spray evaluation               | 09/95 |
| 7.  | Component selection                 | 08/94 |
| 8.  | Coating optimization identification | 08/95 |
| 9.  | Coating components                  | 09/96 |
| 10. | Rig testing                         | 09/96 |
| 11. | Develop transition plan             | 09/96 |
| 12. | Flight testing                      | 10/96 |

### 10. Transition Plan:

There are an extremely large number of potential users of the technology developed under this program. Virtually all military that overhaul aircraft, land vehicles, or ships perform chromium and/or cadmium electroplating. In addition, many OEM's can benefit from this technology since chromium and cadmium are still being applied to components during the manufacturing process. It is also intended to spin-off this technology into areas related to armaments, e.g., gun tubes which are routinely electroplated with chromium to provide wear resistance to portions of the bore.

### 11. Funding: \$(K)

	FY93	FY94	FY95	FY96	TOTAL
SERDP	485	550	218	267	1520

In addition, from the above amounts, funds would be provided to the other organizations listed above in the Tasks/Activities Section on a service basis. In general, the amounts would range from \$10K to \$30K per year for each organization. It is anticipated that approximately 67% of the total funding would remain in-house at ARL and NRL, with the remaining 33% distributed to the other organizations.

Based on the results of the work performed under this project, a detailed transition plan would be developed early in 1995. This would be done in close cooperation with the field activities, CCAD and CPNAD, that took part in the program. In addition, there would be the coordination with other activities such as Army MSC's and RDEC's, NAWC's as well as the Joint Technology Exchange Group and the Aerospace Chrome Elimination Group (government and industry). Additional components beyond those evaluated in the project would be selected and then pilot production quantities of all components would be coated, with some subjected to additional rig testing (e.g., engine evaluations on a test stand) and the remainder installed in actual operating aircraft. Cherry Point NAD expects to install a large PVD coating system in early 1995, which should coincide well with the transitioning of the technology. Since it will not be possible to individually evaluate (qualify) the replacement coatings for every component that is currently electroplated, a key aspect of the transition plan would be to provide information and data, including coating deposition specifications, to agency engineers so that new coating technologies can be certified for use in broad areas.

## **12. Performers:**

See the Tasks/Activities section above. Since there is intended to be mutual sharing of information between this project and the ARPA project, and since many OEM's are facing the same hazardous effluent emission restrictions as military installations, it is believed that by the time of completion of this program, there should be a strong possibility for implementation of Cooperative Research and Development Agreements (CRADA's) with some of the OEM's.

## **13. Principal Investigators:**

John H. Beatty  
AMSRL-MA-MA  
Army Research Laboratory  
Watertown, MA 02172-0001  
PHONE: (617) 923-5212/5331  
FAX: (617) 923-5219  
E-MAIL: jbeatty@watertown-emhl.army.mil

Bruce D. Sartwell  
Surface Modifications Branch  
Naval Research Laboratory  
Code 6675  
Washington, D.C. 20375-5345  
PHONE: (202) 767-4800  
FAX: (202) 767-5301

## **14. Keywords:**

Hard chrome, physical vapor deposition, metal coatings, ceramic coatings, electroplated chromium, ion-beam-modified surfaces, zinc alloys, tin alloys



## SERDP FY95 PROJECT

- 1. SERDP Thrust Area:** Pollution Prevention
- 2. Title:** Laser Ignition to Replace Chemical Ordnance Igniters for Propulsion
- 3. Agency:** U.S. Army
- 4. Laboratory:** Army Research Laboratory, Aberdeen Proving Ground, MD (ARL)
- 5. Project ID:** #680

### **6. Problem Statement:**

**Goal:** To reduce production of waste and unnecessary energetics material in manufacturing for guns and rockets. To completely eliminate inventories of high explosives (RDX, HMX, PETN, TNT), pyrotechnics (blackpowder, lead styphnate, azides) and nitrocellulose-based igniter materials from the inventory of energetic materials used in propulsion through the use of laser radiation as the primary ignition source. To avoid pollution problems associated with the demilitarization/incineration of these materials. One laser can replace thousands of lbs of this material in the life cycle of a gun system.

**Background:** The chemical ignition materials used in gun propulsion consist of various high explosive, blackpowder, nitrocellulose-based propellants, benite, BKN03 and other pyrotechnics. Demilitarization of the vast inventories of these sensitive materials via incineration is dangerous and can produce pollutants, carcinogens and toxic agents. There are also safety considerations in the manufacture, handling, storage, disposal or recycling of these energetic materials which greatly impact cost. This proposal addresses a means to negate all of these concerns through the development of technology by which propellant ignition materials will be eliminated from DoD inventories. Rather than initiating research to understand or minimize the hazards associated with incineration, advanced laser technology will be utilized as a replacement for large caliber gun propulsion. Problems associated with the disposal of ignition materials will no longer exist when lasers are integrated as the primary gun ignition source.

### **7. Project Description:**

**Previous Efforts:** The concept of the use of lasers as an ignition source for propulsion applications where the primary purpose is to eliminate stockpiles of energetic materials in order to completely avoid demilitarization and pollutant formation problems which arise through incineration has not been previously considered.

**Technical Objective/Approach:** Set up laboratory-scale experiments for propellant ignitions using our in-house state-of-the-art laser laboratory with full electro-optics

diagnostics capability. Design laser-based ignition systems for propulsion using laser energy distributed through optical fibers. Perform parametric investigations of laser parameters such as wavelength, pulse width, repetition rate to optimize performance. Test ignition configuration in simulators. Transfer ignition technology to large caliber gun and rocket motor designers for integration into current and future systems. All chemical propellant ignition material will be eliminated from energetic materials inventories.

## 8. Expected Payoff:

Potential Users: DOE, DoD, ARDEC, MICOM, Benet, AFAS, Navy, NASA, Air Force, Industry will use technology to eliminate these dangerous and unnecessary materials from their inventories. Dual Use Technology developed such as laser systems, optical components, optical feedthroughs will benefit both military and civilian markets. Four ongoing SBIR programs to develop technology are in place.

Impact: Removal of these materials from current inventories, eliminate environmental pollution, waste and hazard from disposal, immense cost savings from safety considerations in all aspects of manufacture, production waste in manufacturing, storage and handling, benefit to the soldier in the field from a safer and simpler weapons system (less vulnerable).

## 9. Milestones:

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|----|--|-------|
| 1. | Determine ignition thresholds of propellants and energetic materials using laser   | 09/94 |
| 2. | Design optics package for breech spindle, test ignition in small scale ballistics simulator, begin large scale ballistic simulator testing with laser ignited charge | 12/94 |
| 3. | Development of Mil-Std optical fiber connector, sapphire window materials study testing  | 08/95 |
| 4. | Lab testing, range tests and data analysis   | 12/95 |
| 5. | Optical fiber manufacturing, feedthrough fabrication, three compact laser developmental efforts  | 09/96 |
| 6. | Final report   | 09/97 |

## 10. Transition Plan:

Technology will be transferred to ARDEC and coordinated with Benet Labs through 6.3 program.

Relationship to DoD/DOE: To reduce production of waste and unnecessary energetic materials in manufacturing. This proposal seeks to eliminate pollution hazards from propellant materials demilitarization, incineration and recycling by eliminating their need in current applications.

Relationship to Ongoing Work: Participants: ARDEC, MICOM, Benet, PM-AFAS, Navy, China Lake, NASA, Air Force. The defense industry, international defense institutions (Germany, UK) and the US DoD community are utilizing lasers as a means of augmenting propulsion. This represents the first effort to design a propulsion system with the central purpose being the elimination of stockpiles of energetic materials to avoid pollution from demilitarization and incineration. Our preliminary work has demonstrated that the laser can achieve these goals.

**11. Funding: \$(K)**

	FY94	FY95	FY96	FY97	TOTAL
SERDP	200	313	138	180	831

**12. Performers:**

This work will be performed at ARL. Demonstration testing will be done at ARDEC.

**13. Principal Investigator:**

Dr. Brad E. Forch, ARL  
US Army Research Laboratory  
AMSRL-WT-PC  
Aberdeen Proving Ground, MD 21005-5066  
PHONE: (410) 278-7067  
FAX: (410) 278-6150  
E-MAIL: BFORCH@ARL.MIL

**14. Keywords:**

Laser, Ignition, Propulsion, Primer, Gun, Optical Fibers

## SERDP FY95 PROJECT

- 1. SERDP Thrust Area:** Pollution Prevention
- 2. Title:** Extraction and Recycling of LOVA Propellants Using Supercritical Fluids
- 3. Agency:** U.S. Army
- 4. Laboratory:** U.S. Army Research Laboratory (ARL)
- 5. Project ID:** #660

### 6. Problem Statement:

**Objective:** Solid gun propellants are currently destroyed by open pit burning or incineration; supercritical fluid (SF) recycling, rather than destruction, would have both economic and environmental advantages. Unfortunately, the ingredients of composite LOVA (nitramine) propellants have insufficient solubility in non-reactive SFs (e.g.,  $\text{CO}_2$ ). The objective of this new program is to identify suitable SF solvents for use in extracting and recycling the ingredients of solid LOVA gun propellants being developed for AMC munitions development programs.

**Background:** Supercritical fluids (SFs) have two potential environmental-related applications related to energetic materials demilitarization: destruction via oxidation in SFs (HAZMAT destruction), and "solventless" SF extraction/separation for purposes of recycling (pollution prevention). The first area is being actively pursued (see C&E News, Dec. 23, 1991): the DoD has established a pilot plant that uses supercritical water to destroy military toxic wastes. For the long term, however, recycling should be the preferred approach. There is a fundamental dilemma, however. While the energetic material (RDX) and polymeric binder of LOVA propellants tend to be highly soluble in the (polar) SF solvents used for destructive oxidation (e.g., supercritical  $\text{H}_2\text{O}$ ,  $\text{TC}=374^\circ\text{C}$ ), the solubilities in "inert" solvents (e.g., supercritical  $\text{CO}_2$ ,  $\text{TC}=31^\circ\text{C}$ ) that one would like to use for extraction/recycling are too low for the process to be economically feasible. (This is not a problem for double base propellants, since the energetic plasticizer nitroglycerine is soluble in SF  $\text{CO}_2$ , and therefore easily soluble from the nitrocellulose binder.)

### 7. Project Description:

The research involves experimental and theoretical investigations of the effectiveness of polar "modifiers" in increasing the solubility of energetic materials (e.g., HMX, RDX) in supercritical  $\text{CO}_2$ . The goal is the identification of polar "modifiers" that a) significantly increase solubility of the solid propellant components in SF  $\text{CO}_2$ , b) do not result in hydrolysis or other chemical degradation of the propellant ingredients, and c) can either themselves be recycled (SF extractors can operate closed-cycle), or are as close as possible to neat  $\text{CO}_2$  in having negligible environmental impact. In

addition to polar modifiers, several alternative (to CO<sub>2</sub>) supercritical solvents have been identified and are being investigated; these are fluids with significant dipole moments, but that are not ozone-depleters.

For other systems/applications, CO<sub>2</sub> modifiers at the 1-5% level have increased solubilities by up to several hundred percent. This research is probing the relationship between modifier molecular structure and its effect on solubility of nitramine energetic materials and other propellant ingredients. The research also involves finding the optimum SF conditions (e.g., temperature, pressure/density) for promising CO<sub>2</sub>-polar modifier supercritical solvents.

The experimental work involves measurement of nitramine (and other ingredient) solubilities in supercritical solvents using a variety of polar modifiers, and under several supercritical conditions (e.g., both close to- and far from- the critical point). Two experimental techniques are being used to measure solubility. One involves spectroscopic detection using an optical (windowed) supercritical cell; the other involves use of a supercritical fluid extractor (SFE) interfaced to a supercritical fluid chromatograph (SFC). During FY93, the effect of a series of polar modifiers on the rate of RDX extraction from LOVA M43 propellant was investigated. For P = 5,000 to 10,000 psi and T from 31 to 50° C, enhancement factors of up to 120,000-fold have been measured, compared to neat CO<sub>2</sub>. Dissolution rates and solubilities for several alternative SFs (primarily non-ozone-depleting fluorocarbons) were also measured during FY93.

The theoretical work serves to guide the experimental effort: theoretical solubility predictions are being used to identify promising solvent-modifier systems,<sup>2-3</sup> with other theoretical techniques <sup>4 5</sup> being used to generate the complex "phase diagram" from a limited number of solubility measurements, thus increasing the number of modifiers that can be investigated in a reasonable amount of time. The theoretical solubility prediction techniques involve ab initio methods, as well the use of molecular modeling software (BioSym's Insight 11 operating on a Silicon Graphics workstation) for predicting solubilities. This is apparently the first application of these techniques for prediction of SF solubilities.

## 8. Expected Payoff:

Prevention of pollution associated with disposal of Army (and Navy) gun propellants; associated reduction of life-cycle cost of munitions.

## 9. Milestones:

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|----|---|-------|
| 1. | Develop molecular modeling techniques   | 06/94 |
| 2. | Survey of polar modifiers - extraction of RDX from M43  | 06/94 |
| 3. | Measure RDX solubilities in alternative supercritical solvents  | 09/95 |
| 4. | Measure full solubilities diagrams for RDX in most promising polar modified CO <sub>2</sub> systems and alternate SF solvents | 06/95 |

- 5. Design and test (lab-scale) extraction/recycling schemes for M43 based on results from 6.1 program 09/95
- 6. Larger scale experiments; explore & optimize M43 propellant extraction/recycling schemes; begin work on new (explosive or propellant) formulation 09/96

**10. Transition Plan:**

Progression is from 6.1 research into solubility relationships and modifiers (through FY94), then 6.2 research into extraction/recycling schemes beginning in FY95. If successful, technology transfer would take place via a pilot plant demonstration at a LOVA manufacturing site; this would be a venture jointly funded with SERDP by PM-TMAS and/or the Naval Surface Warfare Center, Indian Head (NSWC-IH), where LOVA gun propellant is currently manufactured.

**11. Funding: \$(K)**

	FY93	FY94	FY95	FY96	TOTAL
SERDP	400	450	248	303	1401

**12. Performers:**

Most research (6.1, 6.2) is being carried out in-house, with technical interactions involving ARO contractors, Battelle Northwest, University of Delaware, University of Wisconsin, and University of Texas (Austin). During FY93 and FY94, there were small contracts for technical support and instrument development with the CECOM Group (Wilmington, DE) and CCS Instrument Systems, Inc. (Avondale, PA). During FY95 (using FY94 SERDP funds), a somewhat larger technical support contract is anticipated, perhaps with Phasex Corp. (Lawrence, MA); they would then be involved in design and construction of the "scale-up" facility to be used in the technical demonstration. Joint sponsorship will be sought from PM-TMAS or the LOVA manufacturer (Navy/NSWC-IH) for the 6.3 portion of the program. Related Activities: This project is being closely coordinated with related projects at MRDEC (MICOM) and RMP (AP-based, and NC-based propellants, respectively). For example, discussions are under way with Bill Melvin of MRDEC so that cost and other comparisons can be made with the MRDEC liquid ammonia process once an optimum supercritical fluid solvent system (and optimum conditions) has been established.

**13. Principal Investigator:**

Dr. Jeffrey B. Morris  
Weapons Technology Directorate Army Research Laboratory  
AMSRL-WT-PC ARL  
Aberdeen Proving Ground, MD 21005-5066  
PHONE: (410) 278-6148  
DSN 298-6148  
FAX: (410) 278-6150  
E-MAIL: morris@arl.army.mil

**14. Keywords:**

Propellant, LOVA, Demil, Extraction, Recycling, Supercritical Fluid

## SERDP FY95 PROJECT

- 1. SERDP Thrust Area:** Pollution Prevention
- 2. Title:** Recycling Propellants in Nonpolluting Supercritical Fluids: Novel Computational Chemistry Models for Predicting Effective Solvents
- 3. Agency:** U.S. Army
- 4. Laboratory:** Army Research Laboratory, Aberdeen Proving Ground (ARL-APG)
- 5. Project ID:** #695
- 6. Problem Statement:**

Waste solid gun propellants are destroyed primarily by open pit burning or incineration. Because of environmental concerns, the DoD has recently established a pilot plant to destroy military toxic wastes by oxidizing the solids in non-polluting polar reactive supercritical fluids (SFs) such as SF H<sub>2</sub>O at  $T_c=374^\circ\text{C}$ . Extraction and subsequent recycling of the propellant, as opposed to destruction, using a non-polluting, inert SF solvent would have obvious economic and environmental advantages. The components of composite solid LOVA propellants (an energetic material [RDX] and polymeric binder) have very low solubilities in an inert sf solvent such as CO<sub>2</sub>, making the extraction process economically infeasible. A proven method for enhancing the solubility of the propellant in SF CO<sub>2</sub> is addition of simple polar modifiers at levels as low as 1-5%. The solubilities have been shown to increase up to several hundred percent upon this small addition. The object of this research is to complement an experimental effort at the ARL to determine the optimal physical conditions and chemical makeup of an effective SF CO<sub>2</sub>/modifier solvent using well-established computational chemistry techniques and high performance computers. Computer simulation is an inexpensive and safe method of filtering a wide assortment of chemical systems, leading the experimentalist more quickly to successful candidate solvents.

### 7. Project Description:

The research will be divided into two complementary parts that will be worked on in parallel. The first part will give insight into the actual dynamical event of the first step in the SF solvation process, the dissolution of an RDX crystal into SF solvent. The second part will be more rigorous quantum chemical study on the relative abilities of real modifiers to stabilize an RDX molecule in the SF solvent.

Part 1. The simulation model will consist of an RDX crystal immersed in SF CO<sub>2</sub> doped with model modifier molecules (MMs). The CO<sub>2</sub>, MMs and the crystal will all be described by purely classical potential energy function that includes hydrogen



bonding, dispersion forces, and electrostatic interactions. The description of the MMs will be flexible enough to span a wide range of both polarity and polarizability, since these characteristics are often associated with dissolution capability of a solvent. Constant pressure, constant temperature, rigid body molecular dynamics simulations will provide a dynamical picture of the molecular micro-environment of the system as it dissolves, as well as indicate relative ability of each different SF mixture to break up the lattice. This qualitative picture can lead to selection of modifiers with specific chemical and physical properties that should maximize the dissolution of RDX in the SF solvent.

Parameters that will accurately describe the intermolecular interactions can be obtained through the use of recently developed quantum chemical techniques such as nonlocal density functional theory (NDFT)<sup>2</sup> and symmetry adapted perturbation theory (SAPT)<sup>3,4</sup>. The molecular structure of each compound will be determined by doing geometry optimizations of each isolated molecule using NDFT. These molecular structures will then remain fixed. The intermolecular interactions will be fitted to pairwise interactions between the different compounds using the SAPT method developed specifically for this task. In addition, the intermolecular interaction terms will include the ability of the partial charges, and hence the multiple moments of each molecule, to adjust to the electric field around it as the molecular dynamics proceeds.

Part 2. This part of the modelling combines quantum and classical methods to produce a more quantitative prediction of solubility by attempting to calculate the free energy of solvation, i.e.,  $\Delta F = \Delta H - T\Delta S$ , for one or more RDX molecules in SF CO<sub>2</sub> as a function of the specific modifier molecules included in solution. The solution space will be divided into two zones; 1) an inner "action" zone, and 2) an outer "bath" zone. The action zone will consist of an RDX molecule, the first and second treated purely quantum chemically for the determination of changes in the enthalpy,  $\Delta J$ , using a combination of NDFT and SAPT. The action zone will be surrounded by the bath zone made of a layer of CO<sub>2</sub> molecules described by a classical potential for the quantum chemical action zone. Such a combined quantum/classical approach has already been used to study catalysis on zeolites<sup>5</sup>.

The total quantum chemical energy calculated for the action zone will give the enthalpy of the (RDX + SF CO<sub>2</sub> + MMs) solution. This will be calculated for each of the proposed modifier compounds. The change in enthalpy,  $\Delta H$ , needed as part of the free energy, can then be obtained by a thermodynamic calculation and the sum of the enthalpies from each isolated molecules will be approximated by calculating the full vibrational spectrum of the action zone. The  $\Delta S$  will be calculated as the difference between the sums of the vibrational energies over the action zone first with the modifier molecules included, then excluding the modifier molecules. This difference in total vibrational energies should give the contribution of the MMs to  $\Delta S$  for solvation of RDX in the SF mixture.

## 8. Expected Payoff:

Timely development of a method for recycling solid propellants to keep the Army in compliance with EPA standards for reducing atmospheric, ground, and water pollutants. Computer modelling has been widely recognized by the chemical and pharmaceutical industries as a cost cutting technique in the pursuit of chemical properties for systems of interest to the manufacturer (see; "Promise of Rich Payoffs Drives Computer-Aided Chemistry" in *Research & Development Magazine*, p. 28, September 1993; and "The Question Is Not Whether But When To Go For Computer Aids", in *Today's chemist At Work*, vol. 2, p. 20, 1993). The same cost cutting needs are obvious in today's environment of shrinking DoD budgets. Furthermore, computer modelling will reduce both the personal and environmental risks associated with experiments involving military hazardous materials.

## 9. Milestones:

- |    |   |       |
|----|---|-------|
| 1. | Develop potential energy function for solid RDX   | 01/95 |
| 2. | Develop classical pairwise interaction functions for RDX - CO <sub>2</sub> - Modifier(s)                                    | 02/95 |
| 3. | Complete molecular dynamics for solid RDX + Solution  | 06/96 |
| 4. | Complete free energy calculations on 4 modified solutions   | 07/96 |
| 5. | Complete quantum chemical dimer interactions  | 03/96 |
| 6. | Predict solubility enhancement for candidate modifiers; consider new alternate SF's; study temperature and pressure effects | 01/97 |
| 7. | Enhance model to include new energetic materials and/or SF's  | 02/98 |

## 10. Transition Plan:

Once the theoretical chemistry models are in place and verified, calculations on various model modifier/CO<sub>2</sub> SF solvents will begin. These calculations will give a microscopic description of the physical state of the system at the various stages of the solvation process. The results of these simulations will rank the modifiers according to their ability to increase the solubility of solid propellants in SF CO<sub>2</sub> and possibly other supercritical fluids. This information will build a data base useful by experimentalists in selecting new modifiers and supercritical fluids.

## 11. Funding: \$(K)

	FY94	FY95	FY96	FY97	FY98	TOTAL
SERDP	350	158	0	450	450	1408

## **12. Performers:**

Dr. George Adams, Army/US Army Research Laboratory, APG, MD; Professor Krzyatof Szalewic, Depts of Chemistry and Physics, University of Delaware - Assist in studies of intermolecular interaction energies using his SAPT methods; Professor Donald L. Thompson Department of Chemistry, Oklahoma State University - Assist in the classical molecular dynamics simulations.

Coordinated with the POC for the experimental research - Dr. Jeffrey Morris, Army/US Army Research Laboratory, APG, MD.

## **13. Principal Investigators:**

Dr. Betsy Rice  
US Army Research Laboratory  
AMSRL-WT-PC  
Aberdeen Proving Ground, MD 21005-5066  
PHONE: 410-278-6183  
FAX: 410-278-6150  
E-MAIL: betsy@arl.mil

Dr. Cary Chabalowski  
US Army Research Laboratory  
AMSRL-WT-PC  
Aberdeen Proving Ground, MD 21005-5066  
PHONE: 410-278-6094  
FAX: 410-278-6150  
E-MAIL: cary@arl.mil

## **14. Keywords:**

Supercritical Fluid Extraction, Propellant Recycling; Solid Propellant Extraction

## SERDP FY95 PROJECT

- 1. SERDP Thrust Area:** Pollution Prevention
- 2. Title:** Non Ozone Depleting Sealants for Ammunition Applications
- 3. Agency:** U.S. Army
- 4. Laboratory:** U.S. Army Armament, Research, Development, and Engineering Center (ARDEC)
- 5. Project ID:** #674

### **6. Problem Statement:**

**Goal:** The goal of this program is to eliminate and replace the currently used series of ozone depleting case mouth sealants, for small and medium caliber ammunition, with environmentally safe alternatives. These materials would also be applicable for threaded and fitted material components such as fuzes.

**Background:** Currently, the Army, Navy, Air Force, Special Forces, and other military organizations have mandated the elimination of Ozone Depleting Chemicals (ODC's). Unfortunately, most of the military's small and medium caliber ammunition, currently in the inventory, uses solvent rich, highly toxic, ozone depleting chemicals (1,1,1 trichloroethane, keytones, etc.). It is essential that these materials be replaced with solvent-free or solvent-safe case mouth sealants. This is necessary because the commercial equipment and practices currently available have been found to be relatively ineffective in controlling VOC emissions.

### **7. Project Description:**

**Technical Objective:** This research program is aimed at investigating alternate solvent-free or solvent-safe case mouth sealants for military ammunition. This will be accomplished by evaluating state-of-the-art, commercially available non ozone depleting sealants.

**Technical Approach:** Efforts will be aimed at testing and documenting the compatibility, reliability, and durability of non-ozone depleting sealants that will also meet all of the ammunition acceptance requirements. Promising candidates then will be subjected to functional testing and characterization, as well as lot acceptance evaluation. Initial selection of commercial materials will be based on a study of mechanical, chemical, and physical property data as well as manufacturers recommendations.

Tasks:

- Document sealant properties relevant to ammunition applications
- Conduct compatibility and long term evaluations
- Conduct functional testing
- Evaluate on line application techniques
- Document data for technology transfer

Relationship to DoD/DOE Environmental Objectives: DoD/DOE has mandated the reduction/elimination of ozone depleting chemicals from military material.

Other Work: The reduction/elimination of ozone depleting chemicals is a relatively new requirement, and similar/prior R&D efforts in this field have not been found.

Technical risks are minimal for this proposed effort.

### 8. Expected Payoff:

A payoff is expected in several specific areas. First and foremost is that significant amounts of sealants with ozone depleting, toxic solvents, such as 1,1,1, trichloroethane, ketones, etc., will be eliminated; yielding a notable environmental benefit. As an example, the yearly usage of ODC sealants that would be eliminated at the Lake City Army Ammunition Plant is estimated at 2,000 gallons of 1,1,1 trichloroethane (5.56mm, 7.62mm, and .50 cal rounds) and 700 gallons of other assorted ODC solvents (20mm rounds). Economic benefits include reduced costs (elimination of toxic ODC environmental protection activities), increased production rates, reduced scrap ammunition (estimated at \$2 million per year), and reduced lot rejection rate (which currently averages 6% per year). Other benefits include reduced ODC health/ safety problems, reduced misfires/hangfires, decreased damage to weapon systems/vehicles, and improved personnel safety.

### 9. Milestones:

1.	Program start	10/94
2.	Prepare SOW for contractor participation	11/94
3.	Procure candidate sealants	01/95
4.	Contract awarded	01/95
5.	Review data on candidate sealants	02/95
6.	Initiate "fast track" testing	02/95
7.	Solicit quotes for vendor participation	04/95
8.	Contract task revision	04/95
9.	Select best candidate	09/95
10.	Initiate production for quality tests	10/95
11.	Evaluate cost estimates for quality tests	10/95
12.	Interim report	12/95
13.	Finalize production for quality tests	01/96
14.	Initiate quality tests	02/96

15.	Complete quality tests	07/96
16.	Developmental material specifications	07/96
17.	Generate ECP	08/96
18.	Final report	09/96

**10. Transition Plan:**

Acceptable materials will be commercially produced sealants that are readily available for immediate use. Project R&D personnel will be working closely with users and producers to ensure that useful needed sealants are selected and are readily available to the production arena.

**11. Funding: \$(K)**

	FY94	FY95	FY96	TOTAL
SERDP	250	113	337	400

**12. Performers:**

The Adhesives Section of the Armament Engineering Directorate, U. S. Army Armament Research, Development and Engineering Center will perform the study, working in close coordination with industrial manufacturers/suppliers and with other government organizations: Close Combat Armament Center (CCAC), ARDEC (all rounds); Olin Corp., Lake City Army Ammunition Plant (LCAAP) (5.56mm, 7.62mm, .50 cal, M50, GPU); Ballistic Services Office (LCAAP) (test & evaluation); McAllister Army Depot (M90); Weapons System Laboratory Navy (M50); Hill Air Force Base (M50, M90, PGU); Elgin Air Force Base (M50, M90, PGU).

**13. Principal Investigators:**

Donald T. Rorabaugh and Dean Martinelli  
 SMCAR-AET-M  
 Building 183  
 Adhesives Section  
 ARDEC  
 Picatinny Arsenal, NJ 07806-5000  
 PHONE: (201) 724-4482 / (201) 724-5333  
 FAX: (201) 724-2864  
 E-MAIL: DEANMARTIN@PICA.ARMY.MIL

**14. Keywords:**

Ozone Depleting Substances, TCE, Case Mouth Sealants

## SERDP FY95 PROPOSAL

1. **SERDP Thrust Area:** Pollution Prevention
2. **Title:** Solventless Manufacture of Artillery Propellant Using Thermoplastic Elastomer Binder
3. **Agency:** U.S. Navy
4. **Laboratory:** Naval Air Warfare Center/Weapons Division (NAWC)
5. **Project ID:** #867
6. **Problem Statement:**

The goal of this project is to develop and evaluate artillery propellant formulations which can reduce or eliminate use of solvents containing volatile organic compounds (VOCs). The Army Single Manager for Conventional Ammunition (SMCA) has a model plant initiative for the Radford Army Ammunition Plant (AAP). The goal is to bring the polluting emissions from this plant as close to zero as practical. In 1991 the volatile air emissions from this plant average 12.5 tons per day. The SERDP project on Clean Agile Manufacturing of Energetics (CAME) is demonstrating solventless processing of thermal plastic elastomer (TPE) binders in propellants. Use of solventless process TPE propellants from the CAME SERDP project in artillery propellant will contribute to achieving the goal of the Radford model plant initiative. Further, TPE based artillery propellants can be reprocessed into other products (rather than destroyed) at the end of their useful life. This project proposes to develop and evaluate TPE based artillery propellant formulations which might be manufactured at Radford AAP for specific Army applications.

### 7. Project Description:

Technical Objective: The objective is, using TPE materials and solventless processes demonstrated in the CAME SERDP project, to measure data the Program Executive Officer for Field Artillery Systems (PEO/FAS) requires from the energetic materials community prior to evaluating or developing further new materials for specific applications.

Technical Approach: This project will measure, for specific modular charge formulations appropriate for a 155mm howitzer, burning rates at high pressure, mechanical properties at high strain rates, safety data, thermal stability, chemical properties, sensitivity, processing (rheological) properties, and pollutants produced during manufacture. The formulations will be evaluated for proof of principal testing and melt processability.

Relationship to the DoD/DOE Environmental Objective: This project is responsive to the DoD Environmental Technology Requirements Strategy, Reduce VOC's in Ordnance Manufacture.

Relationship to Similar/Related Projects: The SERDP CAME project is demonstrating solventless processing technologies using TPE binders and is quantifying their benefit, from a pollution perspective. The CAME project is not developing or evaluating formulations for specific applications. TPE solventless processing methods successfully demonstrated by the CAME project will be made ready for consideration by PEO/FAS in specific formulations (artillery propellant) for specific applications (155mm howitzer) by this joint Army and Navy project.

The Tank Main Armament System (TMAS) program office is funding a 6.1 effort to develop gun propellant formulations, including TPE based formulations. The formulations will not be produced using solventless processes. All three projects (TMAS, CAME, this proposed project) will share data.

The CRUSADER project is developing a modular charge for 155-mm howitzer ammunition using M30 propellant. This is a triple-based propellant produced at Radford using solvent. This project might provide an alternate artillery propellant which can be manufactured in a solventless process.

## **8. Expected Payoff:**

Elimination of the use of solvents in the manufacture of artillery propellants will contribute to: (1) achieving an ordnance goal included in the DoD Environmental Technology Requirements Strategy; (2) enabling the Army to achieve the goal of its Radford model plant initiative; and (3) provide an artillery gun propellant for consideration in programs under the cognizance of PEO/FAS.

## **9. Milestones:**

- FY95 Choose artillery propellant formulation
  - Measure sensitivity properties
  - Measure mechanical, chemical, and burn rate properties
  - Measure processing (rheological) properties
- FY96 Grain design
  - Gun firings
- FY97 Optimize formulation and charge design
- FY98 Demonstrate propellant manufacture in a twin screw extruder such as the one at the Flexible Manufacturing Facility for Energetic Materials at the Longhorn Army Ammunition Plant



**10. Transition Plan:**

Transfer technology results to:

Radford Army Ammunition Plant  
PEO/FAS for PALLADIN, CRUSADER, TMAS

<b>11. Funding:</b> \$(K)	FY96	FY97	FY98	TOTAL
SERDP	300	300	300	900
NAWC/WD	40	40	40	120
NSWC/IHD	60	60	60	180
ARDEC	200	200	200	600
TOTAL	600	600	900	1800

Additional funding will be sought from Army sources for FY96-FY97. We have no commitment from Army sponsors at this time.

**12. Performers:**

Naval Air Warfare Center/Weapons Division (Tom Stephens)  
Naval Surface Warfare Center/Indian Head Division (Connie Murphy)  
Armaments Research, Development, and Engineering Center (Lee Harris)

**13. Principal Investigator:**

Dr. Thomas Stephens  
Naval Air Warfare Center/Weapons Division  
474230D  
China Lake, CA 93555-6001  
PHONE: (619) 939-1643  
FAX: (619) 939-1617  
E-MAIL: stephenst@scfe.chinalake.navy.mil

**14. Keywords:**

Thermoplastic Elastomer Binder, Propellant, VOC's, Solventless Manufacture

## SERDP FY95 PROPOSAL

- 1. SERDP Thrust Area:** Pollution Prevention
- 2. Title:** Minimization of Uranium Alloy Waste by Electron Beam Melting
- 3. Agency:** U.S. Army
- 4. Laboratory:** Army Armament Research, Development & Engineering Center (ARDEC)
- 5. Proposal ID:** #872
- 6. Problem Statement:**

Depleted uranium metal is used in the manufacture of armor piercing penetrators for military use as well as for a variety of civilian applications. Most of the bulk scrap generated during the manufacturing process is currently recycled using conventional Vacuum Induction Melting (VIM) techniques. Current VIM practice has the disadvantage of introducing carbon contamination from graphite crucibles. The amount of low specific activity (LSA) waste which is generated in the processing of uranium metal from uranium hexafluoride and disposed of through burial, adds a significant cost to a pound of uranium metal. One fourteen (14) ton cylinder of uranium hexafluoride contains 17,600 pounds of uranium. Reduction of one cylinder of uranium hexafluoride to uranium tetrafluoride generates twenty-five gallon drums of contaminated calcium fluoride. Calcium is used to neutralize the hydrogen fluoride process stream. This equates to 187.5 cubic feet of LSA waste. Reduction of uranium tetrafluoride to uranium metal generates fifteen and four-tenths fifty-five gallon drums of contaminated magnesium fluoride which equates to 115.5 cubic feet. The total volume of LSA waste, 303 cubic feet, at a burial cost of \$300 per cubic foot, adds a cost of \$5.16 per pound to the uranium metal. If uranium metal usage is approximately 500,000 pounds per year, recycling material vs. reduction of uranium hexafluoride realizes a cost avoidance in excess of \$2.5 million.

Low grade scrap such as machining chips, are presently disposed of as radioactive waste, adding to the overall cost of the product. Likewise, spent penetrators from firing ranges and fields of operations cannot currently be recycled due to contamination pick-up during use, and the inability of the VIM process to remove these contaminants.

By applying conventional electron beam melting and refining techniques to uranium metal, however, much of what is currently considered scrap can be recycled to usable product. Processing via Electron Beam Cold Hearth Melting and Refining (EBCHR) in non-reactive, cooled copper containment vessels under high vacuum, volatilized high vapor pressure contaminants such as copper, chromium, and iron, while floating out oxides such as SiO<sub>2</sub>. Electron beam melting and ingot production has the potential to produce high quality ingots in a single process step.

Uranium alloys used for penetrators, such as 0-0.75%Ti, are sensitive to alloy chemistry segregation in the ingot: strength and toughness properties may vary with local Ti content in

the forged product. These chemistry variations can be caused by inconsistent feed stock or by fluctuations in the melting process and ingot solidification. It is important to optimize the overall process to maintain uniformity. Models which predict evaporation losses of important alloying constituents and alloy segregation during ingot solidification are needed to fully characterize the process, particularly for scale-up to industrial operation.

In 1993, Lawrence Livermore National Laboratory (LLNL) converted an existing uranium qualified vacuum processing system into an electron beam melting furnace. In 1994, in a program partially funded by SERDP, LLNL demonstrated the ability of the EBCHR process to produce a uranium 6% Niobium alloy meeting Y-12 specifications, and the ability of the process to recycle bulk scrap. For the past 20 years, LLNL has been involved in the processing of uranium metal using electron beams in high vacuum. Through LLNL's Atomic Vapor Laser Isotope Separation Program, LLNL has gained experience in equipment design, safe handling procedures, and administrative controls required to meet current environmental, safety and health requirements for uranium metal. In recent years, LLNL has pioneered the development of techniques to produce net-shape or near net-shape parts via electron beam, physical vapor deposition.

Sandia National Laboratories (SNL), under SERDP funding for two projects in 1994 and 1995, performed electron beam melting process development and optimization using appropriate surrogate alloys. Evaporative losses of alloying elements from the electron beam furnace hearth were directly measured, and initial models were developed to predict alloying loss rates for varying furnace operating conditions. SNL also experimentally characterized and modeled ingot solidification and micro structures using a surrogate alloy for U-6% Niobium.

## **7. Project Description:**

The first year of this project will determine the optimum EBCHR melting conditions and Ti alloy additions to produce high quality U-0.75%Ti ingots from scrap material. Three ingots will be produced. Uranium penetrators, supplied by the US Army, Armament Research, Development and Engineering Center, Picatinny Arsenal, will be remelted in LLNL's existing EBCHR furnace, utilizing an existing scrap feed system, and cast into 5.5" diameter, 24" long ingots. Both the starting penetrators and the resulting ingots will be characterized as to titanium, carbon, and tramp impurity content.

It is expected that a certain amount of titanium will be volatilized during the melting process, and the first ingot produced will be used to determine extent of Ti loss within the ingot. If necessary, techniques will be developed to add titanium to the melt to maintain the required chemistry, and these will be verified in a second ingot. It will be sectioned and examined micro structurally and by x-ray fluorescence analysis to evaluate uniformity of the Ti composition. A third optimized ingot will be produced as demonstration material available to be fabricated into penetrators by the Army.

Sandia's task will be to provide process development and optimization and participate in ingot analyses. Hearth evaporation experiments will be performed on surrogate alloys to improve the existing models for loss of alloying elements; these will be benchmarked using results from the LLNL uranium ingots. Again, using a surrogate alloy, ingots will be

produced to optimize melt processing and modeling for ingot micro structure and chemistry uniformity of U-0.75%Ti alloy. Variations of Ti content produced in the second LLNL ingot will be measured on the sectioned ingot using an X-Ray Fluorescence Macro analyzer at SNL, CA.

In follow-on years, additional scrap forms and/or alloys will be processed, with the final goal of transferring the technology to a commercial supplier. Spent penetrators from firing ranges are expected to contain significant quantities of miscellaneous contamination from sand, dirt, etc. Using the information gained from initial melting studies, a quantity of such material will be obtained and techniques developed to recycle the material via EBCHR. There is interest in this technology within the Air Force to minimize waste from production/demilitarization of depleted uranium alloy rounds and participants from Elgin AFB will assess the EBCHR process for those needs.

Machining scrap obtained from commercial producers of depleted uranium will be obtained, and techniques developed to recycle this material. It is expected that much of the required development here will center around development of cleaning techniques to remove machining fluids and surface oxides. A similar program was developed for the recycling of titanium metal machining scrap in the mid 1970s which resulted in a very successful industry built around recycling what was formerly low value titanium scrap. Techniques developed to clean and melt titanium will be used as a starting point in the development of uranium recycling.

## **8. Expected Payoff:**

Reduce disposal costs for uranium metal producers. Environmentally friendly - lowers quantity of hazardous radioactive waste. Potential to recover and consolidate scrap from the field. Reduce the need for virgin material - avoids approximate \$5 per pound cost to uranium metal at burial costs of \$300/cu. ft. Due to classification of production numbers, we can only illustrate this as follows: if uranium metal usage is approximately 500,000 pounds per year, recycling material vs. reduction of uranium hexafluoride realizes a cost avoidance in excess of \$2.5 million.

## **9. Milestones:**

1. Ship penetrators to LLNL
2. Melt and cast 3 ingots from army supplied U-.75%Ti scrap (LLNL)
3. Develop models for Ti evaporation and ingot solidification (SNL)
4. Characterize ingots (LLNL and SNL)
5. Produce in-spec ingot via Ti wire feed to hearth (LLNL)

## **10. Transition Plan:**

Solicit participation from industrial partners beginning in FY96. Assist in the procurement and commissioning of a production furnace at industrial site. Transfer developed processes to industrial partners in FY97.

**11. Funding: \$(K)**

	FY95	FY96	FY97	FY98	TOTAL
SERDP	0	400	650	200	1250

**12. Performers:**

Picatinny Arsenal, Eglin AFB, LLNL, SNL

**13. Principal Investigator:**

Kenneth Willison  
Us Army Armament Research, Development & Engineering Center  
2AMSTA-AR-AET-M, Bldg 355  
Picatinny Arsenal, NJ 07806-5000  
PHONE: (201) 724-2879  
FAX: (201)724-7378

Dr. Thomas Shepp  
Lawrence Livermore National Lab  
PO Box 808,L-470  
Livermore, CA 94551  
PHONE: (510) 422-6724  
FAX: (510)422-6724

Dr. Frank Zanner  
MS-1134  
Sandia National Lab  
PO Box 5800  
Albuquerque, NM 87185  
PHONE: (505) 845-3185  
FAX: (505) 845-3430

**14. Keywords:**

Depleted Uranium, Electron Beam Melting, Vacuum Induction Melting

## SERDP FY95 PROJECT

- 1. SERDP Thrust Area:** Pollution Prevention
- 2. Title:** DoD/DOE Clean Agile Manufacturing of Energetics Materials
- 3. Agency:** U.S. Navy
- 4. Laboratory:** Office of Naval Research (ONR)
- 5. Project ID:** #63
- 6. Problem Statement:**

Approximately 100 million pounds of energetic materials (propellants, explosives, and pyrotechnics (PEP)) are produced each year for DoD, DOE, and NASA as main charge explosives, solid rocket propellants, and flares/illuminators. Many are based on energetic materials that could negatively impact the environment during an item's life cycle.

Under Executive Order 12856, Federal facilities are required to achieve a 50% reduction of hazardous wastes by 1999. PEP chemicals and products are produced in government operated, GOCO, and defense contractor facilities. Ever stricter environmental regulations and waste restrictions are curtailing production of some PEP chemicals (for instance TNT). Department of Energy and NASA also have PEP waste reduction requirements.

Past waste reduction has been accomplished by cleaning up individual PEP production processes. Future waste reduction can be achieved by pollution prevention measures throughout the PEP product life-cycle. The product life-cycle includes synthesis of PEP chemicals; formulation of chemicals into a product; chemical processing, loading, and unloading of the product; combustion emissions; and methods to reclaim and recycle or reuse excess material.

In his Earth Day speech last April and his recent Executive Orders, President Clinton demonstrated that the Government should lead by example and that Federal facilities should become the leader in applying pollution prevention to policies and daily operations. Similarly DoD has raised "environment" to the Deputy Under Secretary level, has re-emphasized life-cycle environmental and cost considerations early in the acquisition cycle, and has stressed partnerships with industry and the R&D community in this area. Additionally, there are significant parallel efforts by different groups outside the Government that share common goals and objectives in life-cycle assessment (LCA) and in modeling and simulation of industrial processes.

### **7. Project Description:**

**Technical Objective:** The objective of this program is to develop integrated product/process development (IPPD) technologies and tools to achieve concepts for reconfiguring existing PEP life-cycle facilities into a clean, agile enterprise that will function economically with total life-

cycle wastes reduced by 90%. In the context of this proposal, life-cycle facilities are defined to be the set of existing, geographically separate, PEP facilities that design, develop or produce PEP products, recycle the production by-products into usable products, or recycle PEP parts returned as excess from the ordnance inventory. Many facilities operate under the oversight of the Army Single Manager for Conventional Ammunition.

Significant advances have been made synthesizing new PEP chemicals (e.g., ADN, CL-20, NTO, TNAZ). These new chemicals could enable significantly lower pollution PEP products. Since processes or facilities that produce and handle these new materials have not yet been specified, designed or built, they are prime candidates for demonstration of the IPPD approach that will enable design of the clean, agile facilities that will be able to comply with future environmental regulations.

The Environmental Protection Agency (EPA) has established a Life-Cycle Assessment guidelines to evaluate environmental effects consistent with criteria established by the Society for Environmental Toxicology and Chemistry (SETAC). This EPA guideline, including Peer Review Panel, will be followed to identify phases of the PEP life cycle where considerable pollution is generated. Simulations coupled with the life-cycle assessment can be used to test alternative routes for preventing pollution.

**Technical Approach:** Government and industry PEP R&D labs, pilot plants, and production facilities will be organized into a program network. Models and simulations will predict life-cycle pollution. Pollution prevention technologies and new facility concepts will be experimentally tested in existing facilities available to members of the program network. When use of existing facilities is not practical, a special demonstration testbed may be built. Facility design concepts will be developed, addressing chemical engineering unit operations, mass/energy balances, regulatory requirements, safety, pollution prevention and costs.

**Life-Cycle Assessment Simulation Tool:** A Process Modeling System enterprise simulation framework will be used to organize the PEP environmental life-cycle assessment following EPA guidelines. For example, this project might exploit the G2 simulation tool used in a Technology Reinvestment Project (TRPO). The simulation will test a variety of facility concepts. It will also be used to assess the complete pollution picture for the PEP product life-cycle. Models and simulations will be validated by existing data and experiments done throughout the program network.

**New Materials and Processes to Prevent Pollution:** The synthesis practice is well understood for various new energetic ingredients such as: ammonium dinitramide (ADN), hexanitrohexaazaisowurtzitane (CL-20), nitrotriazolone (NTO), energetic polymers with polyether backbones (glycidyl and oxetane backbones), and energetic plasticizers for formulation into advanced energetic formulations. Energetic monomer and polymer scale-up in continuous flow reactors have been initiated at Thiokol and Aerojet. Synthesis of ADN in laboratory and small pilot facilities is being supported by SDIO, NASA, MICOM and ONR at SRI International, NSWC-IH and Thiokol. An alternate synthesis approach for HMX production was developed by the Army and Lawrence Livermore National Laboratory in the MUSALL project. These new materials and synthesis methods make practical a search for production methods that reduce pollution through the PEP life-cycle.

Reclamation of PEP formulations can be done using solvents in the super critical state. ADN offers an unusual reclamation opportunity. ADN is a chlorine free oxidizer which could replace ammonium perchlorate, eliminating the ozone depletion and acid rain Space Shuttle launch issues. ADN decomposes to ammonium nitrate and N<sub>2</sub>O (laughing gas) in an acidic aqueous environment. This property makes possible the conversion of future ADN based PEP into ammonium nitrate for use as a commercial fertilizer.

Program demonstrations will include a solventless or reduced solvent technique in place of conventional solvents to process PEP and supercritical fluid extraction techniques to reclaim and reuse PEP returned from the arsenal.

The Army Production Base Modernization Activity (of the Army Single Manager) supports development of improved production capability at GOCO facilities. They have a demonstration testbed in the design stage, called the Flexible Manufacturing Facility for Energetic Materials, which could be adopted for the mixing, processing and loading phase of this effort.

Demonstration of Critical Pollution Prevention Technologies by the Program Network: Various processes and products will be evaluated in a test program utilizing laboratories and pilot plants in an experimental network. These experiments will demonstrate new PEP chemicals, products, and processes that are practical for safe, cost effective, environmentally clean implementation during the PEP life-cycle, and satisfy ordnance performance requirements.

Relationship to the DoD/DOE Environmental Objectives: This effort directly supports Pillar 3 (Pollution Prevention) of the Tri-Service Users Requirements, Items I.6.a-f and I.6.h: Reduction of hazardous waste by 50% in ordnance manufacture. The reconfigured processing of new PEP chemicals should produce significantly less waste than the Pillar 3 objective. It also supports accomplishment of Pillar 3 Item III.2.d-f: Methods for developing environmentally sound weapons systems. This effort also supports the DOE Defense Programs Waste Minimization/Pollution Prevention Program (DOE Order 5400.1) strategy.

## **8. Expected Payoff:**

This program will result in new PEP materials, processes and concepts for reconfiguring existing PEP facilities to reduce hazardous wastes by a factor of ten, almost twice the 1999 national goal for pollution prevention. The output of this program is intended to mitigate price increases for future PEP products due to cost of complying with environmental regulations. Satisfying regulations will help curtail facility shutdowns or unscheduled retirement of ordnance systems.

Utilizing the program network of existing laboratories, pilot plants, and production facilities will:

1. Preclude duplication of existing facilities;
2. Reduce construction funds needed for new plants; and
3. Allow each unit to contribute to the life-cycle phase in which it is most knowledgeable.



At the end of the program, a PEP life-cycle simulation tool will be available to the Army Single Manager to assist in reducing life-cycle pollution as the PEP production base continues to be modernized. The models and simulations will provide an understanding of current operations, assist in evaluating alternative processes to surpass the national goal, and quantify future environmental gains which might be achieved through clean and agile facility design.

In addition, this program will provide the basis for evaluation of the potential for using the modeling tools for commercial/dual-use applications (e.g., energetic polymers and anti-fouling coatings for ships produced using the same facilities; reusing PEP in commercial blasting products).

### 9. Milestones:

FY93 SERDP funds available since November, 1993 are being used as follows:

- |    |   |           |
|----|---|-----------|
| 1. | Technology transition plan and program network established  | 6 Months  |
| 2. | Pollution prevention product/process surveys complete   | 9 Months  |
| 3. | Life-cycle simulations of two RDX products (PBX N109 in GBU-24 bomb and M43 propellant in the M-900 cartridge for a tank round) | 12 Months |

FY94 SERDP funds now requested will be used to:

- |    |  |           |
|----|--|-----------|
| 1. | Initial pollution prevention technology prioritization   | 15 Months |
| 2. | Complete initial EPA Life-Cycle Assessment   | 18 Months |
| 3. | Select and develop/apply priority PEP materials and processes, e.g:  | 24 Months |
| 4. | Clean crystalline explosives, polymers, plasticizers, oxidizers and binders; Clean life-cycle, high performance propellant<br>Supercritical processing to avoid solvents Reuse/recycle of energetics Life-cycle simulation of clean, agile operation of pilot plants | 24 Months |

To be achieved with FY95-97 SERDP funds:

- |    |   |           |
|----|---|-----------|
| 1. | Simulation and experimental validation of reduction of  | 30 Months |
| 2. | Pollution for selected PEP products and new materials and processes<br>Life-cycle trade-off analysis complete for selected products and new materials and processes | 36 Months |
| 3. | Demonstration of the program network of life-cycle pollution prevention, product safety and performance for selected products                                       | 36 Months |
| 4. | Estimate life-cycle waste reduction relative to 1992 baseline   | 60 Months |
| 5. | Dual-use life-cycle assessment simulation tools for Army Single Manager   | 60 Months |

## 10. Transition Plan:

The beneficiaries of this program are existing development, production and reclamation facilities operated for the Army Single Manager and DOE, GOCOs and commercial industry. Introduction of the new PEP chemicals and processes into the existing facilities will achieve the Pillar 3 ordnance DoD/DOE environmental objectives.

The Defense Conversion Armament Retooling and Manufacturing Support Program (ARMS), the NASA propellants production programs, and the DOE's complex reconfiguration program are potential customers.

The life-cycle modeling and simulation software will be transferred to the Army Single Manger, DOE, and GOCOs as well as commercial industries through the Cooperative Research and Development Agreements (CRADA).

Standards to support modeling and simulation will be integrated with industry standardization processes.

## 11. Funding: \$(K)

SERDP

FY93	FY94	FY95	FY96	FY97	TOTAL
2000	3700	600	5121	3260	14681

## 12. Performers:

This program will be jointly managed by DoD and DOE. The Program Manager resides at the Office of Naval Research. A program advisory panel of government and industry PEP R&D and production managers will be formed. The panel will provide guidance to the program so as to ensure that the program products will transition into the DoD and commercial PEP production bases. The performers in the program network will include DoD ordnance laboratories (e.g., Naval Surface Warfare Center, Naval Air Warfare Center/Weapons Directorate, Army Research Development Engineering Center, Production Base Modernization Activity, Wright Laboratory Armaments Directorate), DOE National Laboratories (Los Alamos, Lawrence Livermore, Sandia), Army owned GOCO plants (e.g., Holston, Milan, McAlester), industry R&D labs (e.g., Thiokol, Aerojet), not for profit research institutes (e.g., Battelle Columbus), university consortia (e.g., Environmental Risk Reduction Center situated at the New Jersey Institute of Technology), universities (e.g., University of North Carolina), and small businesses (e.g., GENSYM). A peer review panel as described in the EPA Life-Cycle Assessment procedure will provide objective oversight.

**13. Principal Investigator:**

Dr. Richard S. Miller  
Office of Naval Research  
800 North Quincy Street  
Arlington, VA 22217-5000  
PHONE: (703) 696-4404  
FAX: (703) 696-5383  
E-MAIL: MILLER@onr-hq.navy.mil

**14. Keywords:**

propellants, explosives, pyrotechnics, environmental life-cycle assessment, pollution prevention.

## SERDP FY95 PROJECT

1. **SERDP Thrust Area:** Pollution Prevention
2. **Title:** Solventless Pyrotechnic Manufacturing
3. **Agency:** U.S. Navy
4. **Laboratory:** Naval Surface Warfare Center, Crane Division (NSWC, Crane)
5. **Project ID:** #757
6. **Problem Statement:**

Because the manufacturing use of volatile organic compounds (VOC)'s as processing solvents is a major source of the nation's pollutant waste streams, it is important to modify or replace processes in order to minimize or eliminate the use of VOC's. In our work we will focus on processes for manufacturing energetic materials that are concerned with pyrotechnic materials that are used, for example, as grain materials for air-countermeasures (infra-red decoys) and as igniters in Jet Assisted Take Off (JATO) and tactical rocket motors. These devices play major roles in certain defense areas, infra-red decoys being critical in the countermeasures suites deployed on tactical aircraft, while tactical rocket motors find important air defense and air-to-air interception applications.

The majority of these pyrotechnic compositions are currently manufactured using a crash precipitation method called the "shock-gel" process. The process generates large amounts of hazardous waste and constantly releases VOC's and toxic air pollutants (TAP's) to the environment. In the case of magnesium-Teflon-Viton (MTV), one such pyrotechnic used for solid rocket igniters, 1 lb of material generates from 0.3 to 1.5 gallons of waste solvent, depending on the processing facility.

Increasingly stringent environmental legislation, such as, the Clean Air Act Amendments of 1990, are increasing the manufacturing costs of these critical pyrotechnics by forcing the producers to reduce the hazardous air emissions and minimize the waste generated. Pollution abatement techniques alone will not be adequate to satisfy those restrictions. The obvious solution is to eliminate the solvents from the production process.

The Solventless Pyrotechnic Manufacturing project is aimed at eliminating all the hazardous solvents and associated emissions from current and future pyrotechnic formulations used in these critical applications. This 6.2/6.3 research will be performed concurrently at two separate divisions of the Naval Surface Warfare Center. Each division has unique expertise, facilities and equipment which will ensure success of the project.

The program is a combination of two separate efforts and as such would be composed of two phases. The first phase of the program would demonstrate a solventless cryogenic production process for the manufacture of MTV. This phase of the project would be a continuation of previous SERDP work (under the same title) which dealt solely with

cryogenic processing of MTV and the installation of a pilot scale facility at the Indian Head Division. The second phase would develop castable pyrotechnic formulations based on modern polymeric binder systems. This phase of the project would be a follow on to the previously funded work and would be directed toward the modification of a decoy composition now under development and toward appropriately modifying the in-service composition to make it castable. Currently the developmental work being conducted at the Crane Division is funded under a NAVAIR air-countermeasures PIP program and on ONR Electronic Warfare (Infrared Countermeasures) 6.2 research program.

Both phases of the proposed work are complemented by similar efforts from U.S. Army Armament Research, Development and Engineering Center (ARDEC). In the cryogenic phase ARDEC is investigating the cryogenic processing of magnesium-Teflon-Hytemp (MTH) pyrotechnics. A joint effort in 1989 between the Indian Head Division and ARDEC resulted in two separate areas of investigation each focused on resolving the unique processing difficulties of each binder system. In the castable pyrotechnic phase ARDEC is developing a modification of the decoy composition as part of an ARMY AIRCMM project.

## **7. Project Description:**

The objective of the Solventless Pyrotechnic Manufacturing project is to demonstrate two alternative approaches as methods of eliminating the hazardous waste and VOC emissions caused by the solvents used in the manufacture of MTV and similar pyrotechnic materials. Both the phase 1 cryogenic approach and the phase 2 castable pyrotechnic approach offer unique solutions to the pollution problems associated with the current solvent manufacturing process. Once both phases are completed they will provide the Navy and other DoD facilities with a full spectrum method to eliminate solvents and prevent VOC emissions from in-service and future pyrotechnic formulations. The project is listed under heading 3C5 of the Tri-Service Environmental R&D Strategic Plan (Green Book).

The cryogenic process for manufacturing MTV is a solventless process that has been demonstrated on a small scale. In the cryogenic process the Viton is cryogenically ground to a fine particle size using inert liquid nitrogen (LIN), Magnesium and Teflon are then chilled to LIN temperatures. Once the ingredients have reached equilibrium, they are mixed in a slurry of ground Viton and LIN. When a uniform distribution of the ingredients has been attained the temperature of the slurry is increased and the LIN is vaporized. Once the LIN has vaporized, the relatively free flowing pyrotechnic powder can be pressed or extruded into the appropriate size and shape using conventional molding technology. In terms of environmental liabilities, there are none. Nitrogen is an environmentally benign gas that makes up 79% of the air we breathe every day. Upon completion of Phase 1, the Navy will have a pilot plant capable of manufacturing solventless MTV and investigating other pyrotechnic applications.

The technical approach to demonstrate the solventless manufacture of pyrotechnics on a production scale is to: (1) develop material handling techniques necessary to process the extremely cold material in a moisture free state, (2) install a pilot scale cryogenic MTV processing facility, and (3) apply the cryogenic approach to other energetic materials manufactured by the solvent process.

The second phase of this project will use modern polymeric binder materials to formulate pyrotechnic compositions emphasizing their use for castable grains for decoy devices. Rocket composition formulating has driven the development of curable polymeric materials for application in energetic composites. We propose to formulate candidate pyrotechnic flare materials that employ binders of this type. The major technical challenge will be to find binder material that will cure to give pyrotechnic grains that perform in their decoy function as required. We feel that there is great potential for application in developmental composition system of binder material candidates from the general class of azide-containing, curable pre-polymers. These binder materials are currently available in limited commercial quantities from at least two manufactures.

For the standard, in service composition, the curable binder material must have a high content of fluorine atoms. Significant U.S. Navy funding for the development of one such material at Aerojet/Gencorp (Sacramento, CA) comes from ONR 6.1 programs, MIMI and MEQ. Potential non-military coatings applications will make the future availability of these materials less vulnerable to cuts in defense spending. Aerojet material can be obtained immediately for initial testing, but it is probable that Aerojet and/or other industry involvement will be contracted to develop materials tailored for our application.

Major tasks to be carried out in phase 2 include material procurement, laboratory scale formulating, functional testing, scale-up and performance testing. Some of the laboratory scale formulating and functional testing has already begun. Most performance testing will be carried out at the Crane Division using facilities and equipment elaborated specifically for the ground-based testing needed in their decoy development.

## **8. Expected Payoff:**

Solventless pyrotechnic manufacturing will result in an environmentally compliant process which is safer and less costly than the current solvent manufacturing process. Both the cryogenic and the castable pyrotechnic processing approaches can eliminate the large quantities of hazardous solvent waste and VOC emissions currently generated in production. The elimination of waste streams from any process eliminates the need to install expensive solvent recover and recycling systems which will require additional energy usage, constant maintenance and possible upgrades to remain in compliance as regulators lower discharge thresholds.

The potential payoff in terms of hazardous waste elimination can be readily estimated from procurement figures for FY95. The Navy is planning on procuring some 100,000 lbs of flare decoy composition, the Army about half that and the Air Force approximately 5 times that of the Navy, totalling 650,000 lbs per year. This estimate only represents one family of decoy compositions, however, this amount of material will generate anywhere from 195,000 to 975,000 gallons of hazardous waste solvent. The current cost of disposing of waste solvent at the Indian Head Division is 600 dollars per 55 gallon drum. Based on this figure the total cost savings from the solvent elimination alone is anywhere from 2.1 to 10.6 million dollars. When everything is considered such as procurement costs of alternative materials these numbers are probably high.

Based on the cryogenic approach, the Army has estimated a potential cost saving of \$900,000.00 if their current 600,000 lbs per year "shock-gel" production process for flare decoys were replaced with the cryogenic process. The cost savings realized from not installing solvent reclamation and recovery systems have not been included.

Additional benefits may be realized in the area of product improvement. The use of curable polymers will give castable, curable compositions. Casting compositions into molds has the potential advantage over pressing grains from solids that it is easier to fabricate grains with complex shapes.

## 9. Milestones:

- |     |  |       |
|-----|--|-------|
| 1.  | Select poly(oxetane) systems for trails  | 6/94  |
| 2.  | Procure fluorinated materials  | 6/94  |
| 3.  | Evaluate ingredient precoolers and feeders   | 12/94 |
| 4.  | Procure ingredient precoolers and feeders  | 2/95  |
| 5.  | Procure large scale cryogenic mixing vessel  | 3/95  |
| 6.  | Install cryogenic equipment in MTV processing facility                               | 5/95  |
| 7.  | Complete Lab-scale work  | 6/95  |
| 8.  | Select castable decoy system for scale-up  | 6/95  |
| 9.  | Debug and start up cryogenic equipment   | 6/95  |
| 10. | Demonstrate cryogenic technology on a production scale.                              | 8/95  |
| 11. | Prepare final report, phase 1.   | 9/95  |
| 12. | Complete preparation of 1-10 lb batches of materials for full size grain testing     | 12/96 |
| 13. | Complete ground-based performance testing and select systems for further development | 6/98  |
| 14. | Complete final report, phase 2   | 9/98  |

## 10. Transition Plan:

The transition plan for first phase transition of the project cryogenic process expected to occur at the end of FY95 and the second phase will deal with the transition of the castable pyrotechnic technology. We expect that the Indian Head Division will convert their MTV igniter production to the new process having proofed the technology in MK 22 igniter systems. Their low production requirement will enable the Navy to use the equipment as a test bed to investigate other applications for cryogenic pyrotechnic manufacture. Transition of the second phase to advanced development will take place concurrently with flight testing or after initial flight testing of the candidate decoy device and occur at the Crane Division. The funding for this transition is expected to come from a product improvement program for a particular (in-service) decoy device. It is hoped that new pyrotechnic materials developed in this phase of the project may well be selected as candidates for the Air Forces Advanced Strategic and Tactical Expendables (ASTE) program and/or the Navy's Advanced Technology Expendables and Dispenser System (ATEDS) program both of which are seeking to improve the current in service decoy device configurations.

**11. Funding: \$(K)**

	FY93	FY94	FY95	FY96	FY97	FY98	TOTAL
SERDP	355	500	113	100	300	200	1568
NAVY	0	270	200	250	250	0	970
TOTAL	355	770	313	350	550	200	2538

**12. Performers:**

The major performer for the castable pyrotechnic (phase 2) approach as well as the SERDP program management is the Naval Surface Warfare Center Crane Division. The cryogenic (phase 1) process development work will be performed by the Naval Surface Warfare Center Indian Head Division. We plan cooperative development of advanced fluorinated binder systems through contacts with industry.

**13. Principal Investigator:**

Dr. Norris J. Caldwell  
Code 4073, Bldg. 2540  
Naval Surface Warfare Center Crane Division  
300 Highway 361, Crane, IN 47522-5001  
PHONE: (812) 854-2815  
FAX: (812) 854-1711

**14. Keywords:**

Pyrotechnics, Flares, Binders, Hazardous Waste minimization, Solventless manufacture



## SERDP FY95 PROJECT

1. **SERDP Thrust Area:** Pollution Prevention
2. **Title:** Encapsulated Micron Aerosol Fire Suppression Technology
3. **Agency:** U.S. Air Force
4. **Laboratory:** Wright Laboratory (WL/FIVCF, Tyndall AFB, Florida)
5. **Project ID:** #113

### 6. **Problem Statement:**

This project seeks to develop and test a new fire suppression concept leveraged on Soviet aerosol technology for use in a wide variety of facility and aircraft protection roles. Halons, while powerful fire suppressants, cause ozone depletion and are being eliminated. Halon 1301 replacement candidates identified thus far are 2-3 times less effective than Halon 1301 in fire suppression efficiency. Known replacement agents would require major modifications to piping, nozzles, and other components of the delivery systems. Suitable replacements resulting from existing programs and technologies are not available or projected to be available in the near term. A class of environmentally safe agents that can fulfill some of these fire suppression roles is badly needed and required to maintain the operational readiness and capability of the Air Force. Encapsulated Micron Aerosol Agents (EMAA) may provide the Air Force with an environmentally and occupationally safe agent that has 6 times the fire suppression capability of Halon 1301 by weight. It requires no piping or pressure cylinders and will be a fraction of the cost of Halon 1301 in installation and life cycle costs. It also allows delivery strategies other than total flood and can be placed locally in high fire risk locations within a facility. FY95 SERDP funding will be used to continue a program initiated with FY93 SERDP and USAF funds.

### 7. **Project Description:**

Various EMMA formulations will be tested for fire suppression efficiency, materials compatibility, storage stability and lifetime, packaging, toxicity, electrical conductivity, corrosion, and combustion products. The results of these analyses will be utilized in the engineering of delivery systems for both total-flood and local fire suppression strategies. Several delivery packages and methods containing both non-electrical and electrical initiation will be designed, fabricated, and tested to determine the best practical methods for delivering fire suppression aerosols. Ultimately, large scale testing against scenario fires will be conducted to determine the final configuration of EMMA delivery systems. A CRADA with Spectrex, Inc. will result in the basic aerosol compositions and chemistry being assessed. Applications for EMMA will center around local delivery systems that can be used without the need to resort to a total flooding of the space being protected. Possible strategies include placing an EMMA device directly in equipment that is a potential source of fire. The risks of this program are moderate. The major difficulties are the corrosion potential of the EMMA solids in a humid atmosphere, toxicological effects of lung penetration of the micron and

submicron sized particles, and the handling of high temperatures and energy developed in the creation of the aerosol. The technical program addresses each of these areas and provides for detailed analysis of each of these potential problem areas.

Tie to Tri-service Environmental Quality R&D Strategic Plan

Pillar Thrust Area: 3.H

Requirements Category: II.4

Work effort: Tech Demo

## 8. Expected Payoff:

The successful development of pyrotechnically generated aerosols as envisioned in this program will provide the Air Force with a badly needed option in the drive to replace Halon 1301 with non-ozone depleting fire suppressants. In addition to removing the threat of an environmentally unacceptable chemical, EMAA actually provides superior performance on a weight and volume basis. The result will be new applications such as fire protection systems that can be easily built into deployable shelters, hand thrown and remotely launched devices that can be used to provide "first-aid" to begin the process of extinguishment, and the potential to protect large fuel storage tanks from destruction via compact fire suppression systems. The Air Force also stands to benefit economically from the development of EMAA applications because the provisions of the CRADA call for royalties to be paid to the Air Force for products created and sold as a result of the Air Force research and development investment.

## 9. Milestones:

1.	Selection of Aerosol Formulations	03/94
2.	Particle Characterization	08/94
3.	Extinguishment Mechanisms	10/94
4.	Completion of Corrosion Studies	06/94
5.	Thermal Characterization	11/94
6.	Ignition Methods	11/94
7.	Energy Absorption Methods	09/94
8.	Fire Suppression Effectiveness	12/94
9.	Toxicity Testing	12/94
10.	Stability Testing	06/95
11.	Hand Thrown Device Testing	05/95
12.	Remote Launch Device Testing	07/95
13.	Medium Scale Facility Tests	10/95
14.	Delivery System Design/Testing	06/96
15.	Large Scale Tests	01/97
16.	Final Report	10/97

## 10. Transition Plan:

A CRADA merges the efforts of Air Force laboratories with Spectrex, Inc. to produce a powerful yet low cost fire protection system. Provisions in the CRADA create devices that are suitable for Air Force applications and create a licensing scheme that will allow multiple source commercialization of the end products. The CRADA requires that the Air Force receive royalties that, if the project is fully successful, will more than recover the development investment of the Air Force.

## 11. Funding: \$(K)

	FY93	FY94	FY95	FY96	FY97	TOTAL
SERDP	650	630	284	347	740	2651
USAF	200	0	0	0	0	200
TOTAL	850	630	284	347	740	2851

## 12. Performers:

This project will be managed by the Air Base Fire Protection and Crash Rescue Systems Section (WL/FIVCF), Wright Laboratory, at Tyndall Air Force Base, Florida. Extensive coordination and cooperation will be accomplished with Spectrex, Inc. Spectrex will handle issues of agent composition whereas WL/FIVCF is responsible for technical issues such as corrosion assessment, initial toxicological assessment, particle size measurements, thermal characterization, thermal absorption studies, calorimetry, and applications engineering. Several contractors will be utilized to accomplish the tasks under this effort to include Applied Research Associates (ARA), the New Mexico Engineering Research Institute (NMERI), the University of Massachusetts (Lowell), and the University of Florida. Extensive coordination will be conducted with the Army, Navy, and the FAA due to their interest in possibly utilizing this technology for their own purposes.

## 13. Principal Investigator:

Dr. Charles J. Kibert  
WL/FIVCF (Stop 37)  
139 Barnes Drive, Suite 2  
Tyndall AFB, FL 32403-5323  
PHONE: (904) 283-3745  
DSN: 523-3745  
FAX: (904) 286-6763  
E-MAIL: kibert@nervm.nerdc.usc.edu

## 14. Keywords:

Halon 1301, Encapsulated Micron Aerosol, Fire Suppressants, Ozone Depleting Substances, HCFCs, Aerosols

## SERDP FY95 PROJECT

- 1. SERDP Thrust Area:** Pollution Prevention
- 2. Title:** Chemical and Physical Processes Responsible for Flame Inhibition Using Halon Agents and their Alternatives
- 3. Agency:** U.S. Army
- 4. Laboratory:** Army Research Laboratory (ARL)
- 5. Project ID:** #682
- 6. Problem Statement:**

The presently used Halons 1301 and 1211 fire extinguishing agents are being phased out due to their role in the catalytic destruction of the stratospheric ozone layer. There is a major effort underway within the DoD to find environmentally acceptable Halon replacement compounds. The goal of this research project is to develop a detailed flame chemistry computer model which will be able to predict the relative flame extinguishment properties of new Halon alternative compounds as well as to identify the possible formation of toxic flame products resulting from the use of the agent. This model, once fully verified and tested, will become a very important predictive tool for the RDT&E organizations for screening new compounds, or mixtures of compounds, and for interpreting results of full-scale testing.

This project is primarily a 6.2 effort since it builds upon a large body of basic research in combustion science. It will transition into 6.3a as the model is simplified to include only the important overall reactions. Ultimately, this reduced/simplified flame chemistry model is expected to be run on advanced PCs, rather than on the workstations which are presently required for running the full chemistry.

### 7. Project Description:

This project is a continuation of a project that was funded under SERDP Phase II during FY93, and which will continue to be funded during FY95. The full year's of research funding in FY93 has yielded many results thus far. We have already obtained a set of flame structure profiles for methane/oxygen flames doped with various hydrofluorocarbon (HFC) compounds as well as Halon 1301. A flame model has been developed at NIST (largely with AF funding) for fluorine-containing inhibitor compounds which includes over 700 reactions.

Our basic approach involves a tightly coordinated research program of flame model development coupled with experimental verification. The flame experiments involve the use of a low pressure burner apparatus which contains a premixed laminar flow flame. The different flame zones are spread out at low pressure so that spatially-resolved profiles of the temperature and major/minor species can be made. We use two diagnostic techniques for the flame profile studies. These include the Molecular Beam/Mass Spectrometric (MB/MS) sampling as well as the Tunable Diode Laser (TDL) absorption techniques. Each of these

methods has its inherent advantages and disadvantages. The detailed chemical flame mechanisms are tested on the basis of agreement with the experimental results. The modeling work typically involves many hundreds of elementary chemical reactions as well as nearly 100 flame species. Due to the magnitude of the required computation, this work is typically performed on workstations or larger computers. However, after the complete reaction set is verified, then the number of reactions can be significantly reduced through the use of sensitivity analysis. The detailed kinetic models are based on accurate knowledge of thermodynamic and kinetic properties of the relevant species and reactions. For those reactions where previous data does not exist, an estimate has to be determined through the use of computational chemistry tools such as the BAC- MP4 and Transition State Theory programs.

After completion of the initial stage of model development and verification with the laboratory low pressure burner experiments, we will proceed to modify the models so that they can mimic, and ultimately predict, the large-scale fire extinguishment tests as carried out by TARDEC, NRL, and Wright-Pat. Also, we will adapt and test the models for the scenario where a combination/mixture of agents may be used. Our major goal is to develop such a high degree of confidence in the detailed chemistry models so that we can move to the next logical step, which is the reduction of the size of the model to include only the important reactions. This model simplification step will allow for (a) the models to run much more rapidly on the present workstations and (b) the models to be run on advanced PCs. Thus, these models will become much more readily available, and more generally useful, to the survivability engineers. We should reemphasize our position that we will continue to be very closely coordinated with the survivability organizations throughout this project, something that we believe will be very important in this urgent and rapidly developing Halon replacement program. Strat Plan Area: 3.H Fire Fighting Agents

## **8. Expected Payoff:**

The successful execution of this research program will benefit all organizations concerned with survivability of military platforms involved in a fire scenario. The DoD organizations working in this area include TARDEC, ATCOM, Wright-Pat, and NRL. A flame chemistry model that includes fluorine, bromine, as well as iodine chemistry will be particularly useful as a screening tool for a wide range of candidate fire extinguishing agents. The ultimate development of the reduced chemistry flame model which can predict fire extinguishment behavior for mixtures of agents as well as the possible formation of toxic products, and which can be run on an advanced PC, will be a powerful tool for the survivability engineers.

## **9. Milestones:**

1. Experimental decomposition kinetics for iodine and fluorine compounds, work performed at NIST 05/94
2. Kinetic data base development to include iodine and bromine reactions, work performed at NIST 07/94
3. Thermochemical calculations to estimate rate constants for key iodine reactions, work performed at NIST 07/94
4. Experimental flame structure studies and modeling performed at ARL 09/94

- |     |   |       |
|-----|---|-------|
| 5.  | Complete low-pressure premixed flame structure studies of PFC and HFC flames  | 07/95 |
| 6.  | Complete detailed kinetic modeling of PFC and HFC flames  | 07/95 |
| 7.  | Complete experimental studies and kinetic data base development to include iodine and bromine reactions, work performed at NIST | 09/95 |
| 8.  | Expand model development to predict results of large-scale testing  | 09/95 |
| 9.  | Develop and test models for mixtures of agents  | 09/96 |
| 10. | Develop reduced chemistry models to be run on advanced PCs  | 09/96 |

**10. Transition Plan:**

This research will continue to be closely coordinated with the survivability organizations (TARDEC, Wright-Pat, NRL) and the work will be coupled with these organizations as we develop models to predict large-scale testing of individual as well as mixtures of agents. Ultimately, once the reduced chemistry models are successfully developed so they can be run on advanced PCs, then these models will be transferred to the survivability organizations for more extensive use.

**11. Funding: \$(K)**

	FY93	FY94	FY95	FY96	TOTAL
SERDP	300	400	203	248	1151

**12. Performers:**

This project will be performed at both the Army Research Laboratory and the National Institute of Standards and Technology. The work at both ARL and NIST will concentrate on extinguishment model development and verification and will be closely coupled with the larger-scale fire extinguishment tests conducted by TARDEC and Wright-Pat.

**13. Principal Investigators:**

Dr. Andrzej W. Miziolek  
 Army Research Laboratory  
 AMSRL-WT-PC  
 Aberdeen Proving Ground, MD 21005-5066  
 PHONE: (410) 278-6157 DSN: 298-6157  
 FAX: (410) 278-6150  
 E-MAIL: miziolek@brl.mil

Drs. Wing Tsang, Donald Burgess, and  
Michael R. Zachariah (Partners)  
Chemical Kinetics and Thermodynamics  
Division  
National Institute of Standards and  
Technology  
Gaithersburg, MD 20899  
PHONE: (301) 975-2507  
FAX: (301) 926-4513

Mr. Steve McCormick (Partner)  
TARDEC  
Survivability Technology Center  
Warren, MI 48397-5000  
PHONE: (313) 574-5948  
FAX: (313) 574-6674  
E-MAIL: MCCORMIC@CC.TACOM.ARMY.MIL

**14. Keywords:**

Halons, Fire Extinguishment, Flame Modeling, Chemical Mechanisms, Vehicle Survivability,  
Flame Research

## SERDP FY95 PROJECT

- 1. SERDP Thrust Area:** Pollution Prevention
- 2. Title:** Chemistry of Halon Substitutes
- 3. Agency:** U.S. Army
- 4. Laboratory:** Research Laboratory, Weapons Technology Directorate (ARL)
- 5. Project ID:** #666

### **6. Problem Statement:**

Goal: Identify the potential halon replacement agents which are efficient in extinguishing fuel fires without producing excessive amounts of toxic by-products. The cost, space and weight claims of agents will be considered in assessing efficiency.

Background: While Halon 1301 has been universally accepted as a non-toxic fire extinguishing agent, certain toxic acids (HF and HBr) are produced when Halon 1301 is used to extinguish flames. The amounts of these acids are generally low enough to be considered merely a nuisance. However, in studies that the Army has conducted using Halon 1301 to extinguish crew compartment fires (mist fireball explosions) the acids have been analyzed in higher than acceptable concentrations. Potential halon replacements may well be less chemically effective than the halons. It is possible that even higher quantities of toxic gases may be produced from these materials than are produced from the halons. This information should be available before expensive full scale vehicle tests are conducted.

### **7. Project Description:**

Previous Efforts: Private industry has initiated a program to identify acceptable substitutes for the halons. Industry's criteria of acceptability is somewhat different than the Army's. The severe space and weight constraints found in fielded combat vehicles, as well as the mist fireball explosion scenario are Army problems not addressed by industry. Likewise, the Air Force projects to find halon replacements for engine nacelle fires does not have the toxic gas production limitation that Army crew compartment fires have. The Navy is addressing the occupied volume fire problem, but not the mist fireball explosion problems.

Technical Objective: Identification of fire extinguishing agents which will be useful in controlling fires in Army combat vehicles. These agents must be non-ozone depleting and have minimal weight and space impacts on the vehicles. Any toxic gases formed during the fire extinguishing process must be at acceptable levels.

Technical Approach: Non-ozone depleting candidate for extinguishing agents will be studied for their ability to extinguish JP-8 fuel fires. The study will be conducted in a chamber whose interior volume is approximately that of a generic combat vehicle. A comparison of the amounts required to extinguish various size JP-8 fire will be made for different agents.



Analyses of gases inside the chamber will be conducted to rank agents on bases of toxic gases produced during extinguishment.

Relationship to DoD Environmental Objectives: Removal of Halon 1301 from Army combat vehicle is a DoD requirement. Any replacement agent must be a non-ozone depleter. Identification of suitable replacement agents will contribute useful information to test programs for qualifying new agents on Army combat vehicles.

Relationship to Other Ongoing Work: The Navy and Air Force have active halon replacement programs. Several members of HARC (Halon Alternatives Research Corporation) have active programs in this area. Information gained will be shared with others interested in the halon replacement problem.

Tasks/Activities: Input from our 6.1 program, consultation with other DoD and private industry will be used to identify potential replacement agents for testing in a generic system. Agents will be ranked according to their ability to extinguish various sized JP-8 fuel fires. Analyses of gases produced during the extinguishment process will be carried out. Another ranking of agents will be made according to toxic gas production. An overall ranking of potentially useable agents will be made and the information disseminated to interested parties.

Technical Issues to Overcome: The halons are very efficient fire extinguishing agents because they contain bromine. But it is the bromine which causes the halons to have ozone depletion potential problems. Replacement agents will probably not contain bromine. Therefore, they may well be less efficient than the halons. This probably translates to extra volume of agents required for fire protection. It is very difficult to find any extra storage room on a fielded combat vehicle. An agent with a lower efficiency than halon may well produce more toxic gases during fire extinguishing scenarios due to longer time in the flame ozone. Toxic gases can be a major problem in crew compartments.

## **8. Expected Payoff:**

Potential Users: Both DoD and private industry would welcome a non-ozone depleting, low cost, efficient fire extinguishing agent with acceptable toxic gases production. There is a potential payoff for all of DoD and the world in general.

Impact: The removal of halon from combat vehicles must be carried out independent of cost considerations. The identification of acceptable replacement agents at low cost would be very beneficial. The quicker the changeover from halon to a new agent in our combat vehicles, the better from an environmental point of view. There will be fewer accidental discharges of halon if it is removed quickly.

## **9. Milestones:**

- |    |   |       |
|----|---|-------|
| 1. | Order placed with metal shop for construction of fire' test box                     | 11/94 |
| 2. | Order placed for stainless steel hardware for gas transfer into and out of test box | 12/94 |

- |     |   |       |
|-----|---|-------|
| 3.  | Purchase order placed for agents  | 11/94 |
| 4.  | Some agents acquired  | 12/94 |
| 5.  | Literature review updated   | 12/94 |
| 6.  | A 95-liter fire test box built for fire-extinguishing experiments using liquid and gaseous agents                               | 01/95 |
| 7.  | Instrumentation installed for analysis of carbon monoxide and carbon dioxide produced by JP-8 fires and extinguishing processes | 02/95 |
| 8.  | Initial tests performed using four water-based extinguishing agents delivered through a spray nozzle onto JP-8 pan fires        | 03/95 |
| 9.  | Equipment in place for large scale fires using misting technology for extinguishing fires                                       | 08/95 |
| 10. | Analysis of toxic gases from large fires  | 01/96 |
| 11. | Rating of various agents as to effectiveness and toxic gas production using misting technique                                   | 12/96 |

**10. Transition Plan:**

Transfer: TECOM, which is responsible for the testing of TACOM's vehicles, will be kept informed continuously of our results in testing new agents. TECOM will be responsible for vehicle testing for the most promising agents. Member of HARC will be informed of our results through regular HARC technical committee meetings.

Coordination: TECOM, TACOM, the Navy and the Air Force will be continuously informed. The Navy and the Air Force will share all information with the Army to solve this common halon replacement problem.

**11. Funding: \$(K)**

	FY94	FY95	FY96	FY97	TOTAL
SERDP	155	200	0	160	515

**12. Performers:**

In-house work will be performed at the Army Research Laboratory/Weapons Technology Directorate, Aberdeen Proving Ground, MD. Involvement by Universities, a non-profit Research Institute and industry will be determined from an Army Research Office study of potential partners.

Cooperative Development Agreements: To be determined from an Army Research Office study.

**13. Principal Investigator:**

Dr. Anthony E. Finnerty  
U.S. Army Research Laboratory  
Weapons Technology Directorate  
Aberdeen Proving Ground, MD  
PHONE: 410-278-6572  
FAX: 410-278-8736  
E-MAIL: Finnerty@arl.army.mil

**14. Keywords:**

halons, fire extinguishment, JP-8 fuel fires, flame chemistry model, flame research, toxic gases, crew compartment fires

## SERDP FY95 PROJECT

**1. SERDP Thrust Area:** Pollution Prevention

**2. Title:** Advanced Streaming Agent

**3. Agency:** U.S. Air Force

**4. Laboratory:** Wright Laboratory (WL)

**5. Project ID:** #158

### **6. Problem Statement:**

Although extensive research has been conducted by both industry and the Department of Defense (DoD), a suitable replacement for Halon 1211 used in flightline and aircraft portable fire extinguishers has not been found/developed. Prior efforts to find a replacement concentrated on currently in-production chemicals and were directed at finding a chemical that had a low to zero ozone depletion potential (ODP), was non-corrosive, left little to no residue, had low toxicity, and had a fire suppressant effectiveness close to that of Halon 1211. Extensive research and testing efforts by the Air Force's Wright Laboratory (WL/FIVCF) identified perfluorohexane ( $C_6F_{14}$ ) as the recommended candidate replacement agent for the DoD. Perfluorohexane, meets all performance requirements, but has a long atmospheric lifetime, which means it could contribute to global warming. Therefore, the US Environmental Protection Agency tentatively approved perfluorohexane for military fire fighting use only. Air Force Headquarters (AF/CE/LGM) subsequently decided not to recommend fielding of this chemical in view of this and possible future more stringent restrictions. As a result, WL/FIVCF has initiated a preliminary research effort to develop a second generation fire suppressant which will meet the original Halon 1211 replacement agent requirement as well as having a low to zero global warming potential (GWP). This proposal provides for continuation of this preliminary effort.

### **7. Project Description:**

The prior research work identified several classes of chemical compounds not in commercial production that exhibit fire suppressant characteristics equal to or better than halons. The most promising of these include bromofluoroalkenes, fluoroiodocarbons, aromatic bromine-containing halocarbons, polar-substituent bromocarbons, and non-volatile precursors. The objective of this effort is to develop a "drop-in" clean, environmentally safe streaming fire suppressant to replace Halon 1211 used in flightline and aircraft portable fire extinguishers. The candidate compounds will be examined for their global environmental impact to insure that those that are filtered through to advanced testing have low/zero ODP and GWP. The major uncertainties at present are their toxicity and manufacturability. The primary focus in the initial screening of these compounds will be to perform preliminary toxicity evaluations. A manufacturing/synthesis assessment will be conducted in the initial evaluation to insure that the emerging candidates are able to be manufactured at reasonable cost. The best candidates to emerge from screening will be manufactured in a small pilot plant to create

sufficient quantities for medium and large scale testing, materials compatibility testing, and validation testing. Coordination with manufacturers for technology transfer in the latter stages of the program will be an important consideration for matching Air Force demand to private sector capacity. The Air Force is taking the lead in exploring this class of chemicals. Close coordination and collaboration with the Army, Navy, industry and academia is being exercised to avoid possible duplication and to take advantage of synergistic opportunities.

Tie to Tri-service Environmental Quality R&D Strategic Plan:

Pillar Thrust Area: 3.H  
Requirements Category: 3.II.4.c  
Work effort: Tech Demo

## 8. Expected Payoff:

The successful completion of this research effort will provide the Air Force and other DoD components with a replacement for Halon 1211, a heavy ozone depleter. A Halon 1211-like agent is required for use in Air Force and other DoD component flightline and portable aircraft fire extinguishers due to that agent's excellent fire suppression capability and zero residue and non-corrosive characteristics. These characteristics are essential for fighting aircraft engine and manned compartment fires. Due to the widespread use of Halon 1211 fire extinguishers in the civilian community, the agent developed in this research effort will also be of significant benefit to that sector.

## 9. Milestones:

1.	Complete survey compounds/fire suppression mechanisms	03/94
2.	Complete manufacturing/synthesis assessment	05/94
3.	Complete global environmental impact assessment	09/94
4.	Complete preliminary toxicity evaluations	12/94
5.	Complete initial laboratory testing	03/95
6.	Complete stability evaluations	09/95
7.	Complete medium Scale Tests	03/96
8.	Complete pilot plant studies: synthesis	09/96
9.	Complete materials compatibility	12/96
10.	Complete toxicity studies	01/97
11.	Complete large scale testing	06/97
12.	Complete operational validation	12/97

## 10. Transition Plan:

The effort will produce a streaming agent purchase specification and technical documentation covering materials compatibility, combustion products, and fire extinguisher performance tests results. These products will be transitioned to the Air Force Material Command, Aeronautical Systems Center (ASC/YOC) for the Engineering Manufacturing Development (EMD) phase. The EMD effort will, if necessary, develop and test any modifications to flightline and aircraft portable fire extinguishers to accept the new agent and will implement an agent change-out program. The same data will be provided to the Army, Navy, and

industry for application, as appropriate. Industry has the capability to produce the chemical compounds of interest in laboratory quantities. It is believed that a cost effective volume production capability can be established for the selected compound(s). This should be confirmed by the manufacturability assessment to be conducted as part of the currently on-going effort.

**11. Funding: \$(K)**

	FY94	FY95	FY96	FY97	FY98	TOTAL
SERDP	850	383	0	850	500	2583

**12. Performers:**

This project is being managed by the Air Base Fire Protection and Crash Rescue Systems Section (WL/FIVCF), Wright Laboratory, at Tyndall AFB, Florida. A SETA Subtask has been awarded to accomplish the first phase of the research effort, i.e., through initial laboratory testing. A task order contract and/or additional SETA Subtasks, as appropriate, will be used for the follow-on phases. The SETA contractor, Applied Research Associates, has subcontracted the initial research work to the New Mexico Engineering Research Institute. Preliminary toxicity efforts are being conducted by the Armstrong Laboratory (AL/OET). An expert panel will be established to conduct initial and periodic reviews of the technical approach; data collection procedures; interpretation of results; and environmental, regulatory, and safety issues that may have a impact on agent viability. Throughout the program , actions by standards making organizations involved in fire protection, including the National Fire Protection Association (NFPA), and by environmental regulatory agencies - in particular, the US Environmental Protection Agency - will be reviewed to ensure that agents developed are in full compliance with planned standards and regulations. Other players in the fire research arena that will be used or consulted include, but are not limited to, the University of Florida, chemicals manufacturers, and fire extinguishing equipment manufacturers. Close coordination, to include joint testing, will be maintained with the Army and Navy to ensure the selected agent meets their mission requirements.

**13. Principal Investigator:**

Dr. Charles J. Kibert  
WL/FIVCF (Stop 37)  
139 Barnes Drive, Suite 2  
Tyndall AFB, FL 32403-5323  
PHONE: (904) 283-3745 DSN 523-3745  
FAX: (904) 286-6763  
E-MAIL:kibert@nervm.nerdc.usc.edu

**14. Keywords:**

Halon 1211, Fire Suppression, Halocarbons, Bromocarbons, Fluoroiodocarbons, Bromofluoroalkenes

## SERDP FY95 PROJECT

1. **SERDP Thrust Area:** Pollution Prevention
2. **Title:** Non-Ozone Depleting Refrigerants for Navy Chillers
3. **Agency:** U.S. Environmental Protection Agency (EPA)
4. **Laboratory:** Air and Energy Engineering Research Laboratory (AEERL)
5. **Project ID:** #309
6. **Problem Statement:**

The Navy currently has approximately 900 shipboard chillers using CFC-114 refrigerant for purposes of vital equipment cooling and comfort air-conditioning. By law, production of CFC-114 must cease by December 31, 1995. The Navy must, therefore, find a suitable alternative refrigerant to retrofit all of its CFC-114 chillers as the supply of CFC-114 dwindles or convert the entire fleet to entirely different cooling plants. Retrofitting existing chillers instead of replacing these units would save the Navy in excess of \$500 million. Projected unavailability of CFC-114 requires that the Navy commence retrofitting the fleet in the 1997 to 1998 time frame.

The EPA (Environmental Protection Agency) has been researching potential CFC-114 alternatives since 1988. Through this program, two non-ozone depleting, low global warming candidate alternatives (i.e., HFC-236ea and HFC-236fa) have emerged which appear to be especially promising. The Navy, through its own evaluation of several possible alternatives, has also concluded that HFC-236ea and HFC-236fa are among the most viable retrofit candidates. However, in order to meet the stringent retrofit deadlines, further evaluations of HFC-236ea and HFC-236fa must be completed prior to 1998. Toxicity testing of the chemicals is now recognized as that element of the development program which requires the greatest time to complete and which, therefore, defines the critical path to success. Additionally, further laboratory performance and materials evaluations of the chemicals are required to identify which of the two candidates is superior.

### 7. Project Description:

In anticipation of meeting the Navy's retrofit needs, the EPA requested and received FY91, FY92, and FY93 SERDP funds for acquisition and laboratory evaluation of HFC-236ea. Work is progressing satisfactorily in concert with the Navy's performance testing of both HFC-236ea and HFC-236fa in a 125-ton chiller of the type used on ships. This proposal is to continue and expand the evaluations of both chemicals along a parallel path until such time as one chemical can be clearly identified as superior to the other. When a preference for one of the chemicals is decided, further work will concentrate on the preferred alternative.

Completion of toxicity testing sufficient to enable the Navy to safely commence retrofit of shipboard chillers with the selected alternative refrigerant will be the main thrust of the

proposed project. Initial acute inhalation toxicity tests such as determination of the LC<sub>50</sub>, cardiac sensitivity threshold, and developmental toxicity have been conducted for HFC-236ea with FY92 SERDP funds. FY93 SERDP funds have been utilized for determination of the genetic toxicity and 90-day subchronic inhalation toxicity of HFC-236ea.

The proposed 4-year project would complete genetic toxicity and 90-day subchronic inhalation toxicity tests for HFC-236fa and complete all required toxicological evaluations for the one preferred chemical, including evaluations imposed by the Navy as regards use of the chemical in confined spaces such as submarines.

Requested FY95-FY97 SERDP funds will also be used to procure quantities of HFC-236ea and HFC-236fa needed for the toxicity testing and for laboratory performance investigations which have been planned by the Navy. The Navy has recently established a laboratory facility and installed seven shipboard-type air conditioning plants for performance investigations of CFC-114 alternatives. These air-conditioning plants are the same designs which are currently installed on the Navy's most sophisticated aircraft carriers, surface combatants, and submarines. The Navy also has developed plans to procure 6 additional shipboard-type air-conditioning plants for a second phase of laboratory performance investigations. It has been estimated that up to 10,000 pounds of each chemical (HFC-236ea and HFC-236fa) will be required for the toxicity and performance investigations.

Engineering materials and lubricants compatible with the alternative refrigerants will be identified via AEERL in-house laboratory tests for use in the Navy's refrigerant performance investigations. Expansion of the thermophysical property database and determination of the heat transfer coefficients for HFC-236fa will also be accomplished with the requested FY94-97 funds.

This work directly supports the goals of Pillar 3 (Pollution Prevention) in the Tri-Source Research Plan which has a goal to eliminate the use of ODS (ozone-depleting substances) as soon as possible. Specifically, the project supports work under Thrust 3F to identify safe, affordable chemical substitutes for ODS refrigerants.

## **8. Expected Payoff:**

Building upon the success of previous work, it appears very likely that HFC-236ea or HFC-236fa will be selected to replace CFC-114 in Navy shipboard chillers. This would enable the Navy to quickly eliminate the use of CFC-114 without incurring the major expense of converting all existing chillers to new equipment. Once implemented by the Navy, it is anticipated that additional uses of HFC-236ea or HFC-236fa would be identified in the private sector to further eliminate the Nation's dependence on ODS's.

## **9. Milestones:**

- |    |   |       |
|----|---|-------|
| 1. | Determine developmental toxicity and cardiac sensitivity        | 12/94 |
| 2. | Complete additional HFC-236fa subchronic genetic toxicity tests | 06/95 |
| 3. | Procure additional quantities of HFC-236ea, and HFC-236fa       | 01/96 |
| 4. | Complete balance of toxicity tests for preferred chemical       | 09/96 |



## 10. Transition Plan:

Toxicity testing must be completed prior to commercialization of any chemical. Results of such tests will be reported to the Navy and chemical producers to allow timely decisions to be made regarding selection of preferred retrofit chemical, any equipment design or construction modifications, and commercialization. Every attempt will be made to meet the retrofit deadlines set by the Navy.

## 11. Funding: \$(K)

	FY91	FY92	FY93	FY94	FY95	FY96	FY97	TOTAL
SERDP	500	500	300	1000	125	410	0	2835
EPA	50	50	150*	50*	0	0	0	300
TOTAL	550*	550	450	1050	125	410	0	3135

\* Most of these funds were for performance related activities not toxicity.

## 12. Performers:

Primary: EPA/AEERL with contracts to toxicity testing laboratories and chemical suppliers.

Other: Naval Medical Research Institute, Robert Carpenter  
Naval Sea Systems Command, Joel Krinsky

## 13. Principal Investigator:

William J. Rhodes (Overall Coordinator)  
US Environmental Protection Agency  
AEERL, Mail Drop 62B  
Research Triangle Park, NC 27711  
PHONE: (919) 541-2853  
FAX: (919) 541-7885  
E-MAIL: RHODES.BILL@EPAMAIL.EPA.GOV

## 14. Keywords:

Refrigerant, Chillers, Ships, Stratospheric Ozone, CFC-114, toxicity

## SERDP FY95 PROJECT

1. **SERDP Thrust Area:** Pollution Prevention
2. **Title:** Replacement of Hydrochlorofluorocarbon (HCFC-22) with Non-Ozone Depleting Substitutes in Military Environmental Control Units (ECUs)
3. **Agency:** U.S. Army
4. **Laboratory:** U.S. Army Belvoir Research, Development, and Engineering Center
5. **Project ID:** #677

### 6. Problem Statement:

Goal: Evaluate HCFC-22 non-ozone depleting alternative refrigerants in existing military ECUs and develop optimized retrofit designs using the best of the refrigerant substitutes.

Background: An international treaty, the "Montreal Protocol on Substances that Deplete the Ozone Layer," and the Clean Air Act Amendment of 1990 require that the production and consumption of chlorofluorocarbons, hydrochlorofluorocarbons, halons, carbon tetrachloride, and methyl chloroform be phased out early in the 21st century. The Department of Defense procures significant quantities of ozone-depleting chemicals each year. The present inventory of ECUs within DoD represents approximately 125,000 pounds of ozone depleting chemicals.

Industry and Government agencies have been working to identify refrigerant replacements for HCFC-22. In 1991, the Air Conditioning and Refrigeration Institute (ARI) formed a Task Force to launch a cooperative research effort to identify alternatives to HCFC-22. Although the final results will not be published until July 1994 the preliminary results indicate that eight possible substitutes for HCFC-22 will be identified. ARI's role will be limited to providing basic thermophysical, material compatibility, and toxicological data to refrigeration manufacturers; "selecting the alternative fluid(s) most appropriate for a specific application and the designing of optimized equipment are tasks left to individual developers and manufacturers" (ARI quote). The Army therefore must ensure that its unique requirements and equipment are matched with the proper refrigerant.

### 7. Project Description:

Technical Objective: Develop a knowledge of the performance of drop-in refrigerants to allow for the update of MIL-STD ECU technical data packages with non-ODS refrigerants.

Technical Approach: Select leading candidate HCFC-22 refrigerant replacements for testing based on ARI studies and computer analysis. Perform baseline performance tests on MIL-STD ECUs with HCFC-22. Convert to selected drop-in refrigerants and conduct performance tests at normal commercial rating points and at high temperatures required for military ECUs. Down-select to one or two refrigerants and conduct extended life tests to determine long term effects of drop-in refrigerants. Concurrently with ECU testing, work to update

existing software simulation codes to reflect thermophysical properties are being developed by the National Institute of Science and Technology (NIST) and heat transfer properties are being developed by the Electric Power Research Institute. The simulation software will be validated against the actual testing and used to optimize military ECU designs/component selection with the new refrigerants.

Tasks:

- Select leading replacement fluids for MIL-STD ECUs
- Update vapor cycle simulation code
  - thermophysics data
  - advanced heat transfer surface data
- Establish baseline performance profiles with HCFC-22
- Modify candidate ECUs based on ADEP material compatibility research
- Install new refrigerant and compatible lubricant
- Conduct reliability/ASHRAE-16 capacity tests
- Validate simulation model against test data
- Conduct component inspection and analysis
- Simulate and characterize performance across the family of military ECUs
- Identify deficiencies and determine corrective actions to retrofit military ECUs

Relationship to DoD/DOE Environmental Objectives: This program directly addresses the DoD directive to accelerate actions to phase out use of ODCs, by giving priority attention to revising specifications and requirements to eliminate the use of these chemicals (DoD directive, dated August 11, 1992, signed by Mr. Don Yockey, Under Secretary of Defense). This effort also supports the 1990 Clean Air Act Amendment and the Montreal Protocol international treaty.

Technical Risks: The risks are considered low to moderate that a refrigerant will be found that has suitable characteristics for use in military ECUs. Performance degradation of drop-in refrigerants may require system component engineering to compensate for degradation.

**8. Expected Payoff:**

Payoff will be reflected in the savings of not having to replace the existing inventory of approximately 26,000 Army ECUs worth \$150 million.

**9. Milestones:**

- |    |   |       |
|----|---|-------|
| 1. | Down-select "best" candidate refrigerant HCFC-22 replacement(s) for military applications | 11/94 |
| 2. | Complete computer simulations   | 03/95 |
| 3. | Complete material compatibility evaluation  | 06/95 |
| 4. | Complete prototype modifications  | 09/95 |
| 5. | Complete unit testing   | 09/96 |
| 6. | Complete development of hardware changes  | 03/97 |

- 7. Complete validation of model vs test results 09/97
- 8. Complete documentation of conversion process 03/98

**10. Transition Plan:**

Roadmap for transfer to the next stage through implementation: The subject proposal will result in a selection of a best HCFC-22 replacement for MIL-STD ECUs. It is envisioned that drawing and specification changes required to support the new refrigerant will be implemented through Engineering Change Proposals (ECPs) and Modification Work Orders (MWOs).

Coordination between performer and user: Coordination is being conducted with the user representative, i.e., the Ordnance Center and School, on improvements to the Army Environmental Control Unit family.

Industry ability to assume production: Through the ARI Alternative Refrigerant Evaluation Program (AREP) industry is working to develop manufacturing capabilities and practices to support each of the eight refrigerants comprising the replacement family for HCFC-22.

**11. Funding: \$(K)**

	FY94	FY95	FY96	FY97	FY98	TOTAL
SERDP	250	236	0	300	150	936

*spacing*

**12. Performers:**

Department/Agency Laboratory: Work will be performed by the Environmental Equipment Development Team at the Belvoir Research, Development and Engineering Center.

Industry involvement: The Air-Conditioning and Refrigeration Institute is coordinating industrial involvement within the United States. ARI has established a Task Force Committee and a Technical Committee which have representatives from the leading refrigerant manufactures within the United States. International coordination is conducted through the European Committee of Manufactures of Refrigeration Equipment (CECOMAF) and the Japan Refrigeration and Air Conditioning Industry Association (JRAIA).

Planned cooperative development agreements: As part of ARI's coordination effort an automated database of industry and Government research and development has been established. All work performed under the subject proposal will be submitted for review and coordination to this technical database.

**13. Principal Investigator:**

Chris W. Bolton  
U. S. Army Belvoir  
Research Development and Engineering Center  
Attn: SATBE-FED  
Fort Belvoir, Virginia 22060-5606  
PHONE: (703) 704-1995  
FAX: (703) 704-2005  
E-MAIL: cbolton@belvoir.army.mil

**14. Keywords:**

HCFC-22, alternative refrigerants, hydrofluorocarbons, ozone depleting substances,  
1environmental control units (ECUs)

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