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SPECIATE and using the Speciation Tool to prepare VOC and PM chemical speciation profiles for air quality modeling

Madeleine Strum, EPA/OAQPS; Mike Kosusko, EPA/ORD; Tejas Shah, Ramboll Environ

International Emissions Inventory Conference, Baltimore, MD, August 15, 2017

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SPECIATE

TRAINERS

- Mike Kosusko, EPA ORD
- Madeleine Strum, EPA OAQPS
- Tejas Shah, Ramboll Environ

LOGISTICS

COURSE OUTLINE

8:00 SPECIATE, SPECIATE 101

8:45 Speciation Concepts

9:30 Break

10:00 SPECIATE Data Gaps and Future Plan

10:30 The Speciation Tool

11:30 End of Class

CLASS OBJECTIVES

- To introduce you to SPECIATE, its content and use
- To introduce you to the SPECIATE Web Browser and its use
- To provide an opportunity to ask questions about SPECIATE
- To present the Speciation Tool and how to use it

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SPECIATE 101

- What is Speciation?
- What is SPECIATE?
- The SPECIATE Data Browser

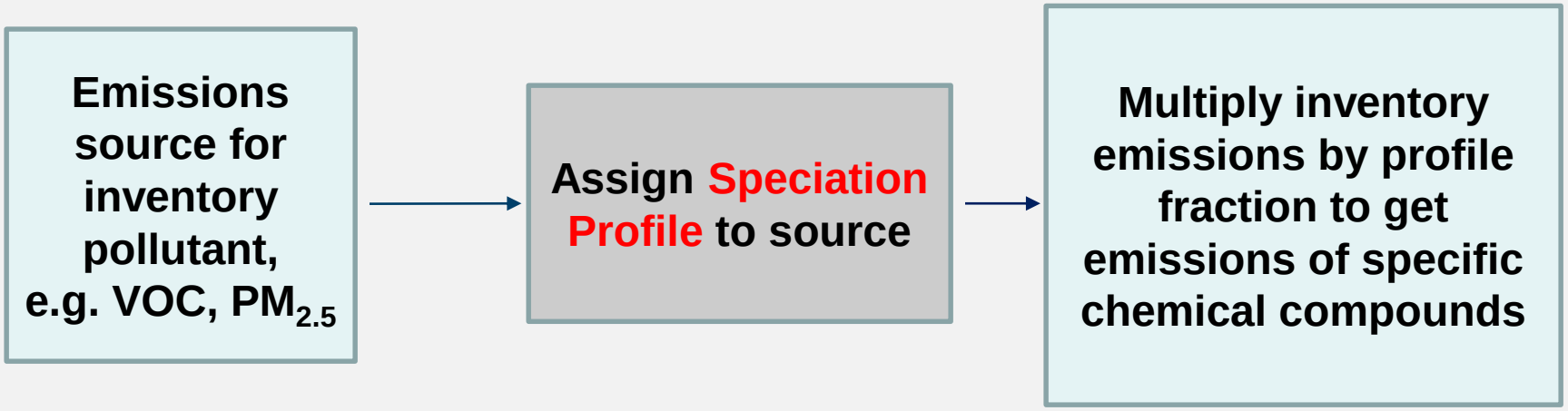
WHAT IS SPECIATION?

Speciation disaggregates inventory species (e.g. VOC, $PM_{2.5}$) into more detailed species

VOC

$PM_{2.5}$

SPECIATION IN GENERAL (STEPS)



100 tons of VOC
Solvent Utilization; Surface Coating; Architectural Coatings; Total: All Solvent Types in Autauga County, AL (SCC = 2401001000)

Profile Code: 8744
Composite Profile - Architectural Coatings: Solvent Borne and Waterborne

50 tons mineral spirits
9 tons texanol
9 tons propylene glycol
5 tons ethylene glycol
etc.

SPECIATION IN GENERAL (SPECIATE)

Assign Speciation Profile to source based on process (SCC)

- SPECIATE  is EPA's repository of speciation profiles.
- SPECIATE 4.5 is the current version.
- Several hundred literature citations to SPECIATE have been found.

WHAT IS SPECIATE?

DATA SOURCES → SPECIATE ⟶ DATA USERS

Peer-reviewed literature

Source testing of speciated emissions

Other

Input to Air Quality Models -- NEI Modeling Platform

Source Apportionment/ Source Receptor Models

Black Carbon Report to Congress

Air Toxics Inventories

Feedback on Data Gaps

WHAT IS SPECIATE? (continued)

- A repository for speciated emissions profiles
- A searchable Microsoft Access database
- Profiles for three air pollution emission types:
  - Particulate Matter (PM)
  - Total Organic Gases (TOG)
  - Other Gases [Hg, NO/NO_2/HONO, semivolatile organic compounds (SVOC)]
- Available on EPA Website: https://www.epa.gov/air-emissions-modeling/speciate-version-45-through-40

WHAT IS SPECIATE? (continued)

- Species include metals, ions, elements, organic and inorganic compounds
- PM profiles are size-segregated (PM_{10}, $PM_{2.5}$)
- Lots of metadata (references, test methods, notes, geographic region…)
- Profiles are rated for quality – judgement (J), vintage (V), number of data points (D)

KEY TABLES IN SPECIATE

- PM_PROFILE
- GAS_PROFILE

List of profiles

- PM_SPECIES
- GAS_SPECIES

Weight percents by profile and species ID

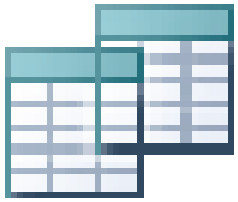
- SPECIES_PROPERTIES

Species ID, name, molecular weight, other IDs, formula, whether it is a HAP, non-VOC

- REFERENCE

Citation or source of data

KEY SPECIATE QUERIES



VIEW_GAS_PROFILES Query

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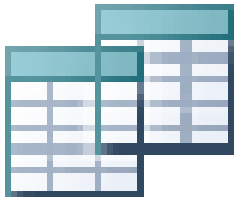

VIEW_PM_PROFILES Query

Date Created: 7/7/2005 8:40:...

Date Modified: 5/11/2017 11:...

EXAMPLES – USING MS ACCESS

1. How do I find a VOC profile that has “Oil and Gas” in the title? (106 of them, example: “95420 Oil and Gas Production - Composite Profile - Glycol Dehydrator, Uinta Basin”)
   A. How do I find the latest profiles?
   B. How would I know if a profile is for a specific geographic region? (Look at Region field for where test was conducted)
   C. How do I get out the weight percentages for any one profile? (View gas profiles or view PM profiles, filter on profile ID)
2. How do I find a PM profile that has "Combustion" in the title? (There are 248 of them, example: 91105, Residential Wood Combustion -- Composite)

KEY METADATA COLUMNS

- NOTES
- REGION
- T_METHOD (Test method)
- DOCUMENT (Reference)
- TEST_YEAR
- P_DATE (Profile date)
- QUALITY
- CONTROLS
- ORIG_COMPO (original or composite)

QUESTIONS?

Are there any questions on what we've covered so far?

THE SPECIATE DATA BROWSER

- Provides database access for the non-MS Access user
  - URL - https://cfpub.epa.gov/speciate/
- On-Line demo
  - Key strength of the browser is the ability to search for profiles,
  - View them, and
  - Download them to MS Excel for further manipulation

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SPECIATE

SPECIATE DATA BROWSER QUERY

- How do I find a VOC profile that has “Oil and Gas” in its title? [Use Keyword Search]
- How would I know if a profile is for a specific geographic region? [View profile information. See 4th row.]
- How do I download profiles to MS Excel? [Add to “Shopping Cart” (but note it’s free) from Search page. Download cart.]
- How do I find a PM profile that has “Combustion” in its title? [Use Keyword Search]

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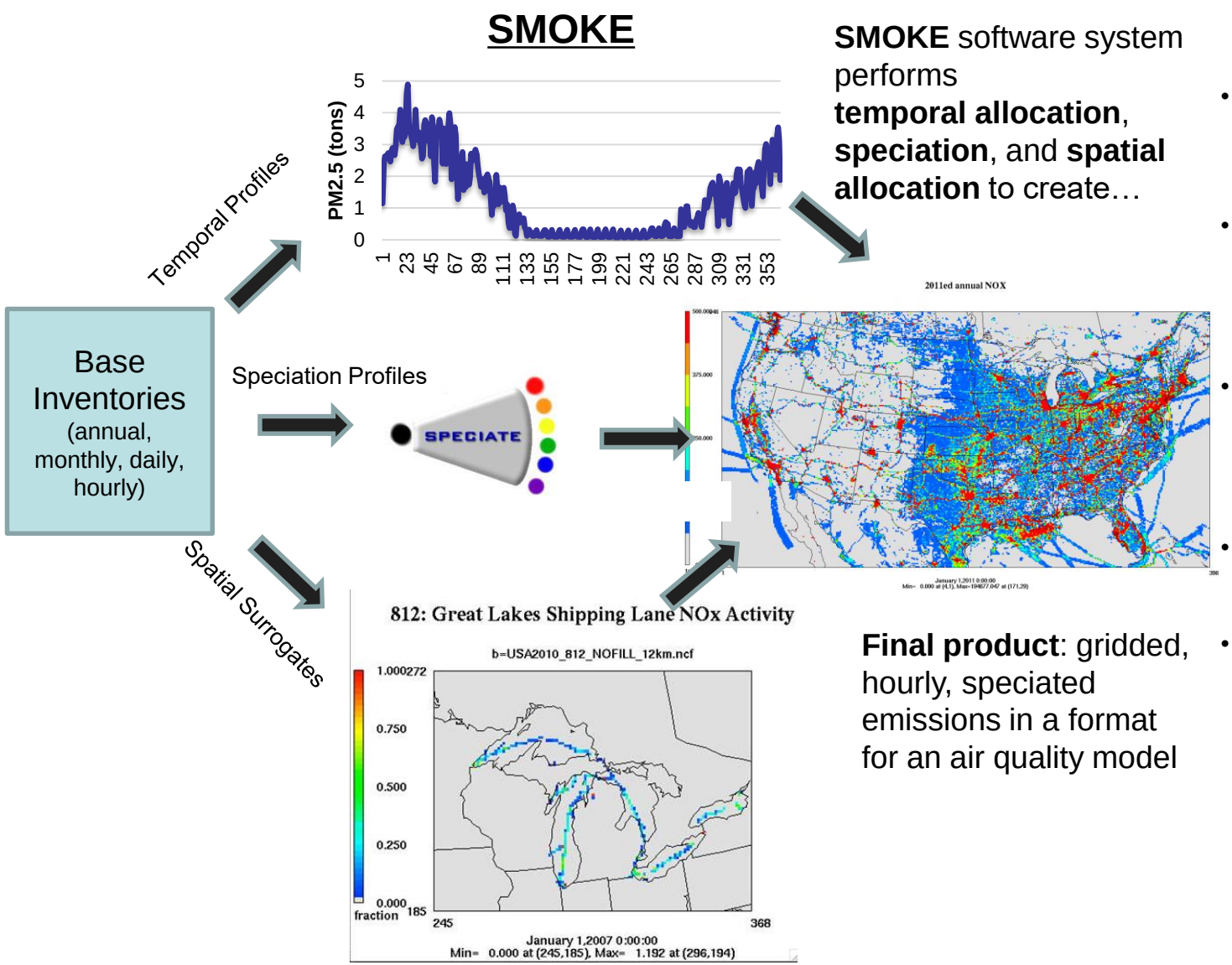
SPECIATE 4.5 HIGHLIGHTS

- New Profiles (September 2016)
  - 182 new PM profiles for a total of 3,782
  - 291 new TOG profiles for a total of 2,170
  - No new Other Gases profiles for a total of 249
  - 2,602 unique species
  - Composite profiles for 85 source categories
- New Profiles cover the following source types:
  - Oil and Natural Gas (RARE with EPA Region 8)
  - Motor Vehicle Exhaust
  - Biomass Combustion
  - Waste Incineration
  - Brake Wear Emission

QUESTIONS?

Are there any questions on what we've covered so far?

SPECIATE AS PART OF EMISSIONS MODELING



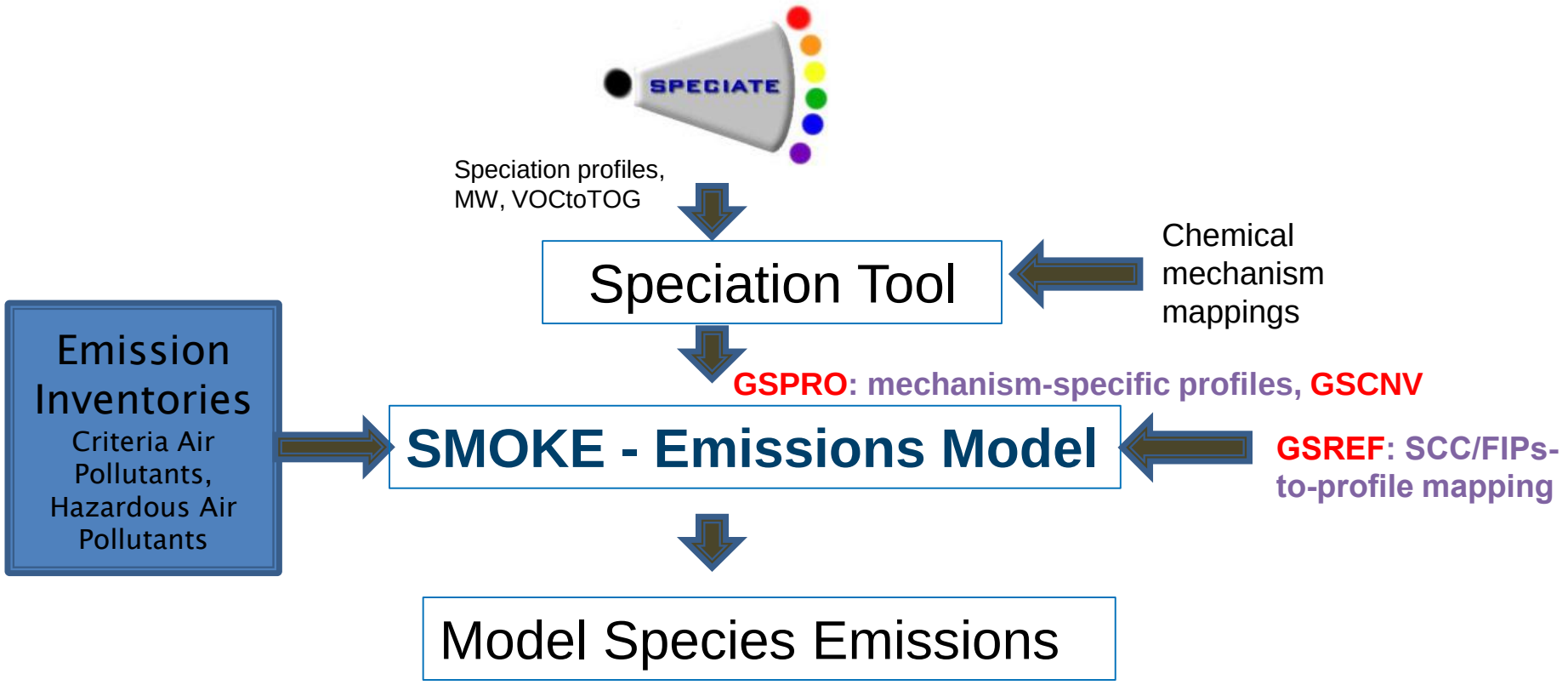
SMOKE software system performs **temporal allocation**, **speciation**, and **spatial allocation** to create…

Final product: gridded, hourly, speciated emissions in a format for an air quality model

- Total VOC and $PM_{2.5}$ need to be speciated into chemical components for photochemical modeling.
- Each speciation profile is cross-referenced to an inventory source by SCC, pollutant, and potentially by region.
- SCC-to-profile mapping is specific to the EPA modeling platform and is separate from the SPECIATE database itself.
- Thousands of SCCs in the NEI are mapped to a few hundred profiles.
- Onroad mobile source emissions species come directly from the EPA MOVES model.

SPECIATION FOR AQ-MODELING

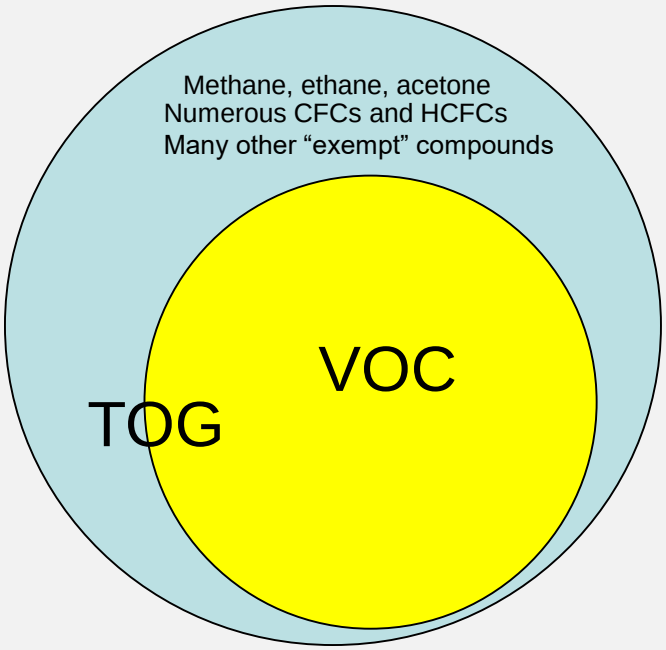
- Develop chemical-mechanism specific profiles from profiles in SPECIATE
- Assign sources to profiles



SPECIATION CONCEPTS

1. TOG (VOC) “Gas" Profiles” Terminology
2. PM Profiles and AE6
3. Assigning Inventory Sources to Profiles
4. VOC Integration
5. Composite Profiles
6. “Gap-Filling” Profiles
7. On-Road Speciation
8. Nonroad Speciation
9. Combination Profiles

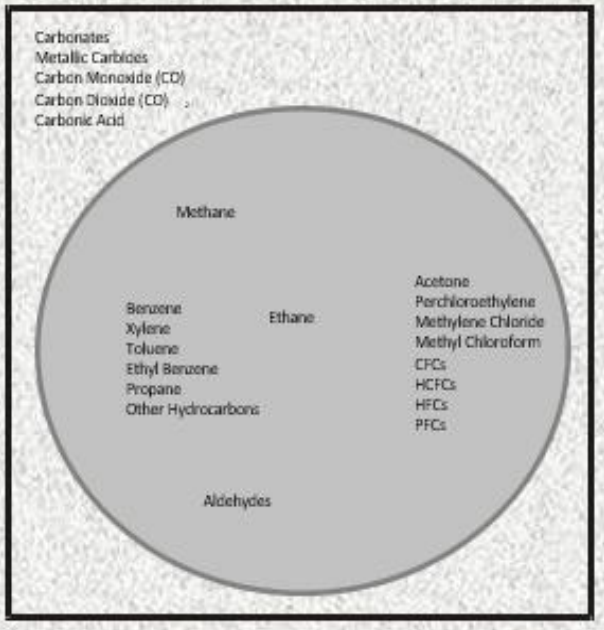
VOC/TOG TERMINOLOGY



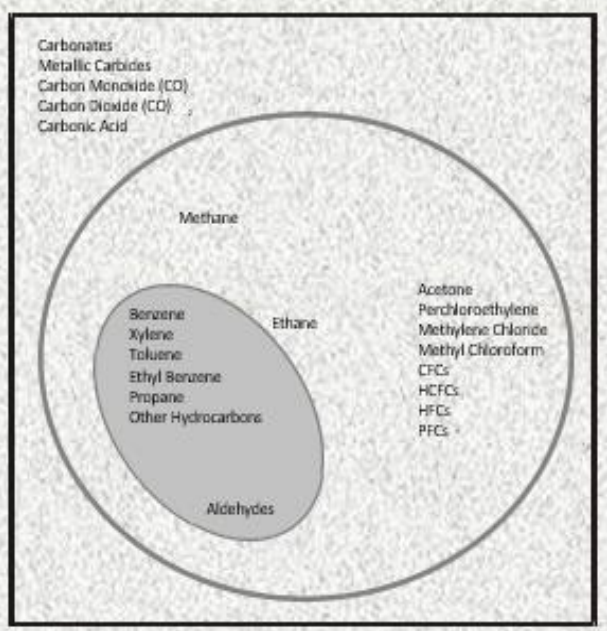
- Gas Profiles in SPECIATE can be based on VOC or TOG
  (see MASTER_POL field)
- Inventories have VOC (regulatory definition)
- TOG is “Total Organic Gases.”
- TOG includes low reactivity and low volatility (low vapor pressure)
- TOG profiles have a factor that allow you to convert VOC to TOG.

Googled and got this from CARB fact sheet

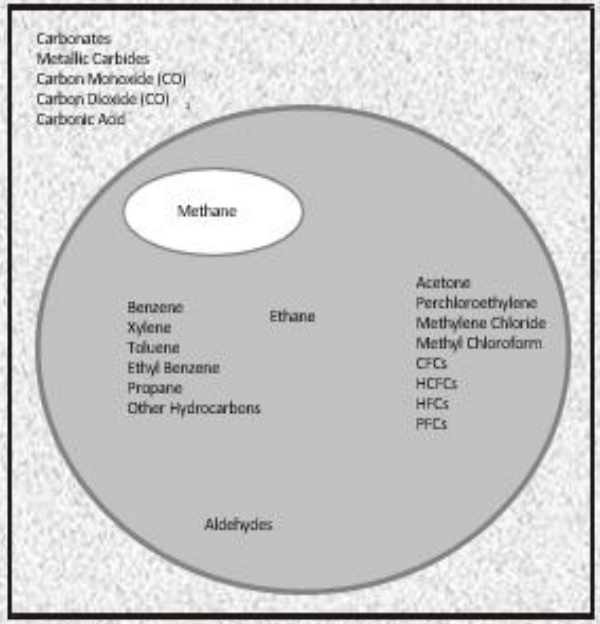
Total Organic Gases (TOG) means "compounds of carbon, excluding carbon monoxide, carbon dioxide, carbonic acid, metallic carbides or carbonates, and ammonium carbonate."



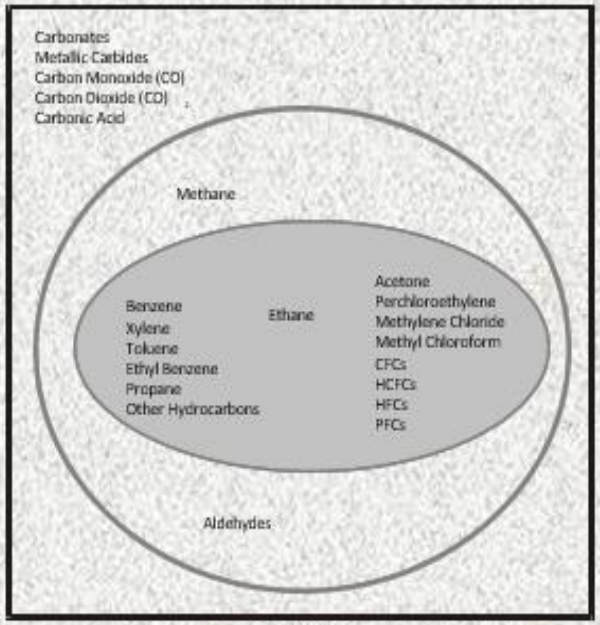
TOG/TOC



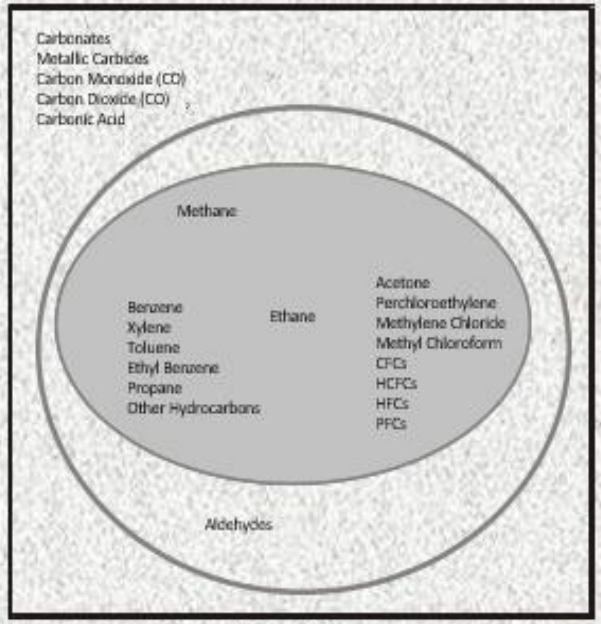
ROG/ROC/VOC



NMOG/NMOC



NMHC



THC/HC

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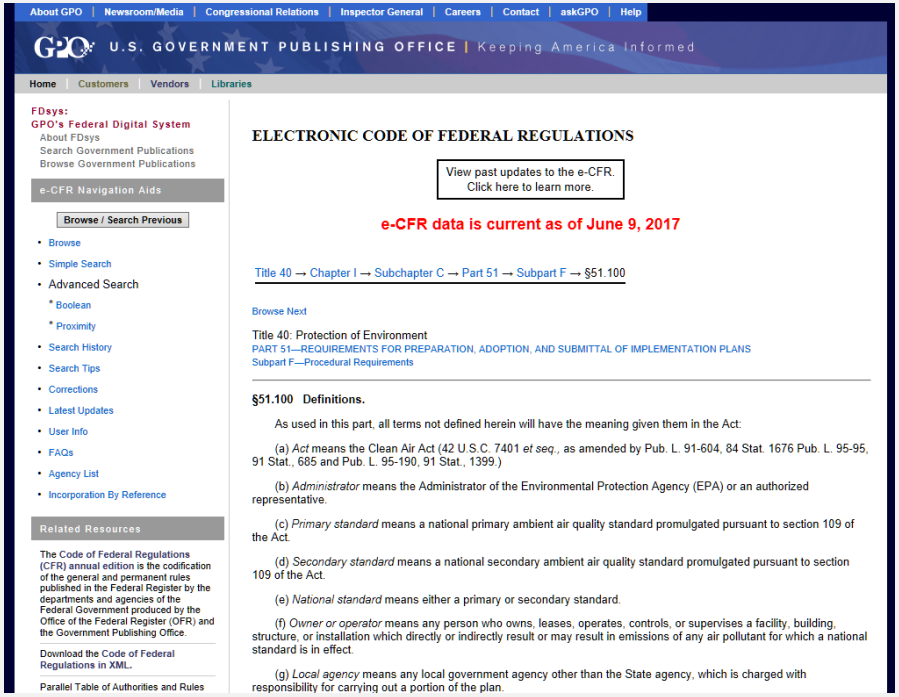
SPECIATE

VOC EXEMPTION INFORMATION

- Electronic Code of Federal Register where the VOC information is available under Title 40 → Chapter I → Subchapter C → Part 51 → Subpart F → § 51.100
- http://www.ecfr.gov/cgi-bin/text-idx?SID=b77fd17146a534c225c8557b5ed4a469&node=40:2.0.1.1.2.3.8.1&rgn=div8



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Related Resources

The Code of Federal Regulations (CFR) annual edition is the codification of the general and permanent rules published in the Federal Register by the departments and agencies of the Federal Government produced by the Office of the Federal Register (OFR) and the Government Publishing Office.

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Parallel Table of Authorities and Rules

ELECTRONIC CODE OF FEDERAL REGULATIONS

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e-CFR data is current as of June 9, 2017

Title 40 → Chapter I → Subchapter C → Part 51 → Subpart F → §51.100

Browse Next

Title 40: Protection of Environment
PART 51—REQUIREMENTS FOR PREPARATION, ADOPTION, AND SUBMITTAL OF IMPLEMENTATION PLANS
Subpart F—Procedural Requirements

§51.100 Definitions.

As used in this part, all terms not defined herein will have the meaning given them in the Act:

(a) *Act* means the Clean Air Act (42 U.S.C. 7401 *et seq.*, as amended by Pub. L. 91-604, 84 Stat. 1676 Pub. L. 95-95, 91 Stat., 685 and Pub. L. 95-190, 91 Stat., 1399.)

(b) *Administrator* means the Administrator of the Environmental Protection Agency (EPA) or an authorized representative.

(c) *Primary standard* means a national primary ambient air quality standard promulgated pursuant to section 109 of the Act.

(d) *Secondary standard* means a national secondary ambient air quality standard promulgated pursuant to section 109 of the Act.

(e) *National standard* means either a primary or secondary standard.

(f) *Owner or operator* means any person who owns, leases, operates, controls, or supervises a facility, building, structure, or installation which directly or indirectly result or may result in emissions of any air pollutant for which a national standard is in effect.

(g) *Local agency* means any local government agency other than the State agency, which is charged with responsibility for carrying out a portion of the plan.

EPA's Regulatory Definition of VOC

List of Compounds exempt from the Definition

(s)*Volatile organic compounds (VOC)* means any compound of carbon, excluding carbon monoxide, carbon dioxide, carbonic acid, metallic carbides orcarbonates, and ammonium carbonate, which participates in atmospheric photochemical reactions.

(1) This includes any such organic compound other than the following, which have been determined to have negligible photochemical reactivity: Methane; ethane; methylene chloride (dichloromethane); 1,1,1-trichloroethane (methyl chloroform); 1,1,2-trichloro-1,2,2-trifluoroethane (CFC-113); trichlorofluoromethane (CFC-11); dichlorodifluoromethane (CFC-12); chlorodifluoromethane (HCFC-22); trifluoromethane (HFC-23); 1,2-dichloro 1,1,2,2-tetrafluoroethane (CFC-114); chloropentafluoroethane (CFC-115); 1,1,1-trifluoro 2,2-dichloroethane (HCFC-123); 1,1,1,2-tetrafluoroethane (HFC-134a); 1,1-dichloro 1-fluoroethane (HCFC-141b); 1-chloro 1,1-difluoroethane (HCFC-142b); 2-chloro-1,1,1,2-tetrafluoroethane (HCFC-124); pentafluoroethane (HFC-125); 1,1,2,2-tetrafluoroethane (HFC-134); 1,1,1-trifluoroethane (HFC-143a); 1,1-difluoroethane (HFC-152a); parachlorobenzotrifluoride (PCBTF); cyclic, branched, or linear completely methylated siloxanes; acetone; perchloroethylene (tetrachloroethylene); 3,3-dichloro-1,1,1,2,2-pentafluoropropane (HCFC-225ca); 1,3-dichloro-1,1,2,2,3-pentafluoropropane (HCFC-225cb); 1,1,1,2,3,4,4,5,5,5-decafluoropentane (HFC 43-10mee); difluoromethane (HFC-32); ethylfluoride (HFC-161); 1,1,1,3,3,3-hexafluoropropane (HFC-236fa); 1,1,2,2,3-pentafluoropropane (HFC-245ca); 1,1,2,3,3-pentafluoropropane (HFC-245ea); 1,1,1,2,3-pentafluoropropane (HFC-245eb); 1,1,1,3,3-pentafluoropropane (HFC-245fa); 1,1,1,2,3,3-hexafluoropropane (HFC-236ea); 1,1,1,3,3-pentafluorobutane (HFC-365mfc); chlorofluoromethane (HCFC-31); 1 chloro-1-fluoroethane (HCFC-151a); 1,2-dichloro-1,1,2-trifluoroethane (HCFC-123a); 1,1,1,2,2,3,3,4,4-nonafluoro-4-methoxy-butane ($C_4F_9OCH_3$ or HFE-7100); 2-(difluoromethoxymethyl)-1,1,1,2,3,3,3-heptafluoropropane ($(CF_3)_2CFCF_2OCH_3$); 1-ethoxy-1,1,2,2,3,3,4,4,4-nonafluorobutane ($C_4F_9OC_2H_5$ or HFE-7200); 2-(ethoxydifluoromethyl)-1,1,1,2,3,3,3-heptafluoropropane ($(CF_3)_2CFCF_2OC_2H_5$); methyl acetate; 1,1,1,2,2,3,3-heptafluoro-3-methoxy-propane (n-C3F7OCH3, HFE-7000); 3-ethoxy-1,1,1,2,3,4,4,5,5,6,6,6-dodecafluoro-2-(trifluoromethyl) hexane (HFE-7500); 1,1,1,2,3,3,3-heptafluoropropane (HFC 227ea); methyl formate (HCOOCH3); 1,1,1,2,2,3,4,5,5,5-decafluoro-3-methoxy-4-trifluoromethyl-pentane (HFE-7300); propylene carbonate; dimethyl carbonate; *trans*-1,3,3,3-tetrafluoropropene; HCF_2OCF_2H (HFE-134); $HCF_2OCF_2OCF_2H$ (HFE-236cal2); $HCF_2OCF_2CF_2OCF_2H$ (HFE-338pcc13); $HCF_2OCF_2OCF_2CF_2OCF_2H$ (H-Galden 1040x or H-Galden ZT 130 (or 150 or 180)); *trans* 1-chloro-3,3,3-trifluoroprop-1-ene; 2,3,3,3-tetrafluoropropene; 2-amino-2-methyl-1-propanol; t-butyl acetate; 1,1,2,2- Tetrafluoro -1-(2,2,2-trifluoroethoxy) ethane; and perfluorocarbon compounds which fall into these classes:

(i) Cyclic, branched, or linear, completely fluorinated alkanes;

(ii) Cyclic, branched, or linear, completely fluorinated ethers with no unsaturations;

(iii) Cyclic, branched, or linear, completely fluorinated tertiary amines with no unsaturations; and

(iv) Sulfur containing perfluorocarbons with no unsaturations and with sulfur bonds only to carbon and fluorine.

(2) For purposes of determining compliance with emissions limits, VOC will be measured by the test methods in the approved State implementation plan (SIP) or 40 CFR part 60, appendix A, as applicable. Where such a method also measures compounds with negligible photochemical reactivity, these negligibility-reactive compounds may be excluded as VOC if the amount of such compounds is accurately quantified, and such exclusion is approved by the enforcement authority.

CURRENT STATUS OF VOC EXEMPTION

A VOC is exempt based on O_3 formation

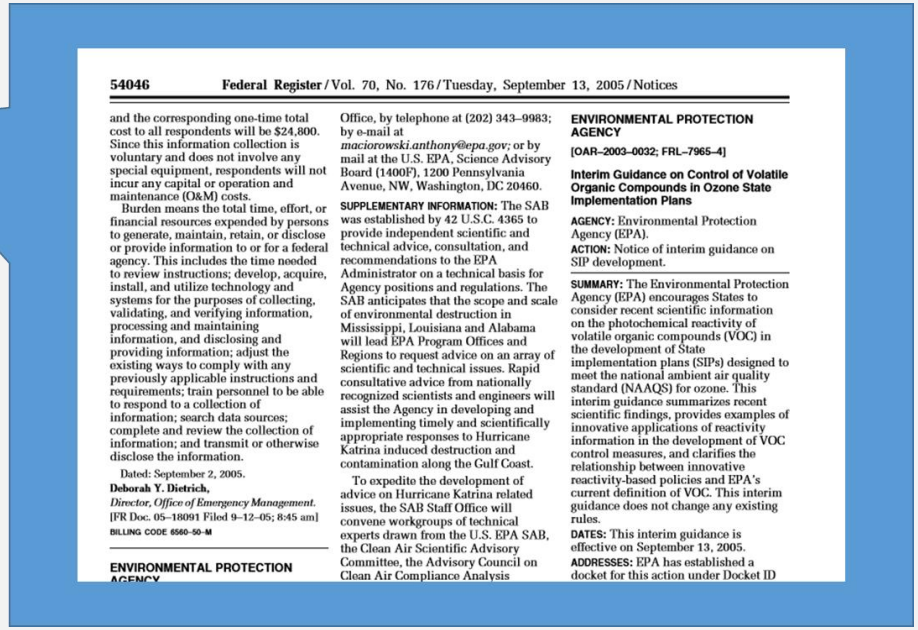
List of Exempt VOC:

1. http://www.ecfr.gov/cgi-bin/text-idx?SID=b77fd17146a534c225c8557b5ed4a469&node=40:2.0.1.1.2.3.8.1&rgn=div8
2. Currently, we have about 68 exempt chemicals including methane and ethane.
3. More chemicals could be added to the list in future assessments.

PROCESS OF VOC EXEMPTION

Interim Guidance of 2005 (70 FR 54046-54051) is the guiding process to assess the viability of a VOC exemption based on:

1. K_{OH}: Reactivity with OH
2. MIR: Maximum Incremental Reactivity to form O_3
3. Toxicity and environmental fate
4. GWP: Global Warming Potential
5. ODP: Ozone Depletion Potential
6. Viability as a better substitute for the same end-uses of other chemicals



54046 Federal Register / Vol. 70, No. 176 / Tuesday, September 13, 2005 / Notices

and the corresponding one-time total cost to all respondents will be $24,800. Since this information collection is voluntary and does not involve any special equipment, respondents will not incur any capital or operation and maintenance (O&M) costs.

Burden means the total time, effort, or financial resources expended by persons to generate, maintain, retain, or disclose or provide information to or for a federal agency. This includes the time needed to review instructions; develop, acquire, install, and utilize technology and systems for the purposes of collecting, validating, and verifying information, processing and maintaining information, and disclosing and providing information; adjust the existing ways to comply with any previously applicable instructions and requirements; train personnel to be able to respond to a collection of information; search data sources; complete and review the collection of information; and transmit or otherwise disclose the information.

Dated: September 2, 2005.

Deborah Y. Dietrich,

Director, Office of Emergency Management.

[FR Doc. 05–18091 Filed 9–12–05; 8:45 am]

BILLING CODE 6560–50–M

ENVIRONMENTAL PROTECTION AGENCY

Office, by telephone at (202) 343–9983; by e-mail at *maciorowski.anthony@epa.gov;* or by mail at the U.S. EPA, Science Advisory Board (1400F), 1200 Pennsylvania Avenue, NW, Washington, DC 20460.

SUPPLEMENTARY INFORMATION: The SAB was established by 42 U.S.C. 4365 to provide independent scientific and technical advice, consultation, and recommendations to the EPA Administrator on a technical basis for Agency positions and regulations. The SAB anticipates that the scope and scale of environmental destruction in Mississippi, Louisiana and Alabama will lead EPA Program Offices and Regions to request advice on an array of scientific and technical issues. Rapid consultative advice from nationally recognized scientists and engineers will assist the Agency in developing and implementing timely and scientifically appropriate responses to Hurricane Katrina induced destruction and contamination along the Gulf Coast.

To expedite the development of advice on Hurricane Katrina related issues, the SAB Staff Office will convene workgroups of technical experts drawn from the U.S. EPA SAB, the Clean Air Scientific Advisory Committee, the Advisory Council on Clean Air Compliance Analysis

ENVIRONMENTAL PROTECTION AGENCY

[OAR–2003–0032; FRL–7965–4]

Interim Guidance on Control of Volatile Organic Compounds in Ozone State Implementation Plans

AGENCY: Environmental Protection Agency (EPA).

ACTION: Notice of interim guidance on SIP development.

SUMMARY: The Environmental Protection Agency (EPA) encourages States to consider recent scientific information on the photochemical reactivity of volatile organic compounds (VOC) in the development of State implementation plans (SIPs) designed to meet the national ambient air quality standard (NAAQS) for ozone. This interim guidance summarizes recent scientific findings, provides examples of innovative applications of reactivity information in the development of VOC control measures, and clarifies the relationship between innovative reactivity-based policies and EPA's current definition of VOC. This interim guidance does not change any existing rules.

DATES: This interim guidance is effective on September 13, 2005.

ADDRESSES: EPA has established a docket for this action under Docket ID

CONVERTING VOC TO TOG

- Ideally, when modeling you want TOG so you get all the species.
- TOG profiles have a factor that allow you to convert VOC to TOG.
- You can compute it

  VOC-to-TOG = 100/(sum of VOC percent)
- These factors are in the GSCNV SMOKE ancillary file.

EXAMPLE TOG SPECIATION PROFILE

(selected fields from the Query "View Gas Profiles")

P_NUMBER	GAS_PROFILE.NAME	CONTROLS	P_DATE	TOTAL	VERSION	VOCtoTOG	SPECIES_ID	SPECIES_PROPERTIES.NAME	WEIGHT_PER	VOC
0051	Flares - Natural Gas	Uncontrolled	05-Jan-89	100	3.2	2	438	Ethane	30	
0051	Flares - Natural Gas	Uncontrolled	05-Jan-89	100	3.2	2	465	Formaldehyde	20	YES
0051	Flares - Natural Gas	Uncontrolled	05-Jan-89	100	3.2	2	529	Methane	20	
0051	Flares - Natural Gas	Uncontrolled	05-Jan-89	100	3.2	2	671	Propane	30	YES

Assume you have 100 lb VOC from Flare – How much propane?

Mass of Propane = 100 lb VOC x (30/100) [lb propane/lb TOG] x [2 lb TOG /1 lb VOC]
= 60 lb

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SPECIATE

QUESTIONS?

Are there any questions on what we've covered so far?

$PM_{2.5}$ SPECIATION– MODELING PROFILE EXAMPLE

Model species definitions

species name	species description	AE5	AE6
POC	organic carbon	Y	Y
PEC	elemental carbon	Y	Y
PSO4	sulfate	Y	Y
PNO3	nitrate	Y	Y
PMFINE	unspeciated PM2.5	Y	N
PNH4	ammonium	N	Y
PNCOM	non-carbon organic matter	N	Y
PFE	iron	N	Y
PAL	aluminum	N	Y
PSI	silica	N	Y
PTI	titanium	N	Y
PCA	calcium	N	Y
PMG	magnesium	N	Y
PK	potassium	N	Y
PMN	manganese	N	Y
PNA	sodium	N	Y
PCL	chloride	N	Y
PH2O	water	N	Y
PMOTHR	unspeciated PM2.5	N	Y

Example modeling speciation profile – AE6

Prescribed Burning – Composite (91109)

pollutant	species	massfrac
PM2_5	POC	0.5019
PM2_5	PEC	0.1093
PM2_5	PSO4	0.0033
PM2_5	PNO3	0.0107
PM2_5	PNH4	0.0034
PM2_5	PAL	0.0005
PM2_5	PCA	0.0007
PM2_5	PCL	0.0024
PM2_5	PFE	0.0004
PM2_5	PK	0.0014
PM2_5	PMN	0.0001
PM2_5	PMOTHR	0.0125
PM2_5	PNA	0.0014
PM2_5	PNCOM	0.3513
PM2_5	PSI	0.0001
PM2_5	PTI	0.0007

HOW DO YOU KNOW THE $PM_{2.5}$ PROFILE HAS WHAT YOU NEED?

- Example1 – 95126 Gas-fired process heater exhaust
  - This one does NOT have what you need for AE6.
- Example 2 – 95462 Composite - Brake Wear
  - This one does.
- Hints
  - Composite profiles from “Emissions Inventory of PM2.5 Trace Elements across the United States, *Environ. Sci. Technol., 43 (15)*, pp 5790–5796, 2009” will have what you need.
  - But, we did add more recent profiles as well (search for PNCOM or PH20).

SIMPLIFIED PROFILES – $PM_{2.5}$ ONLY

- These are legacy profiles.
- They were used from AE5.
- Their function was superceded by the Speciation Tool.

ASSIGNING SOURCES TO PROFILES – GSREF

- Area & Mobile (county level)
  - You can assign profiles based on SCC and/or country/state/county.
  - Provides no sub-county variation - If you want this, you need your source to be inventoried as a point source.
- Point
  - You can assign based on SCC and/or country/state/county and/or facility, unit, process, release point.

NEW-SMOKE4.5

- You can assign a combination of multiple profiles to the same source (10% profile A, 35% profile B, 55% profile C).

Examples of Profile Assignments

SCC 3999999 "Industrial Process, NEC"

Assigned to profile 0000 - Overall Average (the King of Defaults)

SCC 2811015001 Prescribed Forest Burning; Smoldering County=Autauga, AL

Assigned to profile 95421 – Composite Profile - Prescribed fire southeast conifer forest

SCC 2811015001 Prescribed Forest Burning; Smoldering County=Gila, AZ

Assigned to profile 95422 – Composite Profile - Prescribed fire southwest conifer forest

COMPOSITE PROFILES

- Often, a single study may be too specific to apply to an inventory category or that study has multiple test scenarios or different operators.
- A composite profile combines these data into something usable.
- When using a composite of different profiles, one can take the mean or median of each species from the various profiles being composited.
- When compositing individual SPECIATE profiles, see NOTES for the P_NUMBERS used in the composite.
- Issue: Assigning metadata/ratings to composites

"GAP-FILLING" PROFILES

- This is DIFFERENT from "Compositing" – It is adding missing species to a profile.
- Why? – Some profiles may be missing species that are expected. (Be aware of this when assigning profiles.)
- We can create new profiles by filling in these species (gap-filling) from another profile.

profile	pollutant	missing
95242	Poultry Farm - Hen and Animal Waste	Methane Ethane
95241	Swine Farm and Animal Waste	
95240	Beef Cattle Farm and Animal Waste	

+ 70% methane, 20% ethane From profile 0203 (solid waste - animal waste decomposition) → **Three new profiles for SPECIATE**

- We will need to figure out how to indicate which profiles are gap-filled and how (perhaps using the profile number and the NOTES field).

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SPECIATE

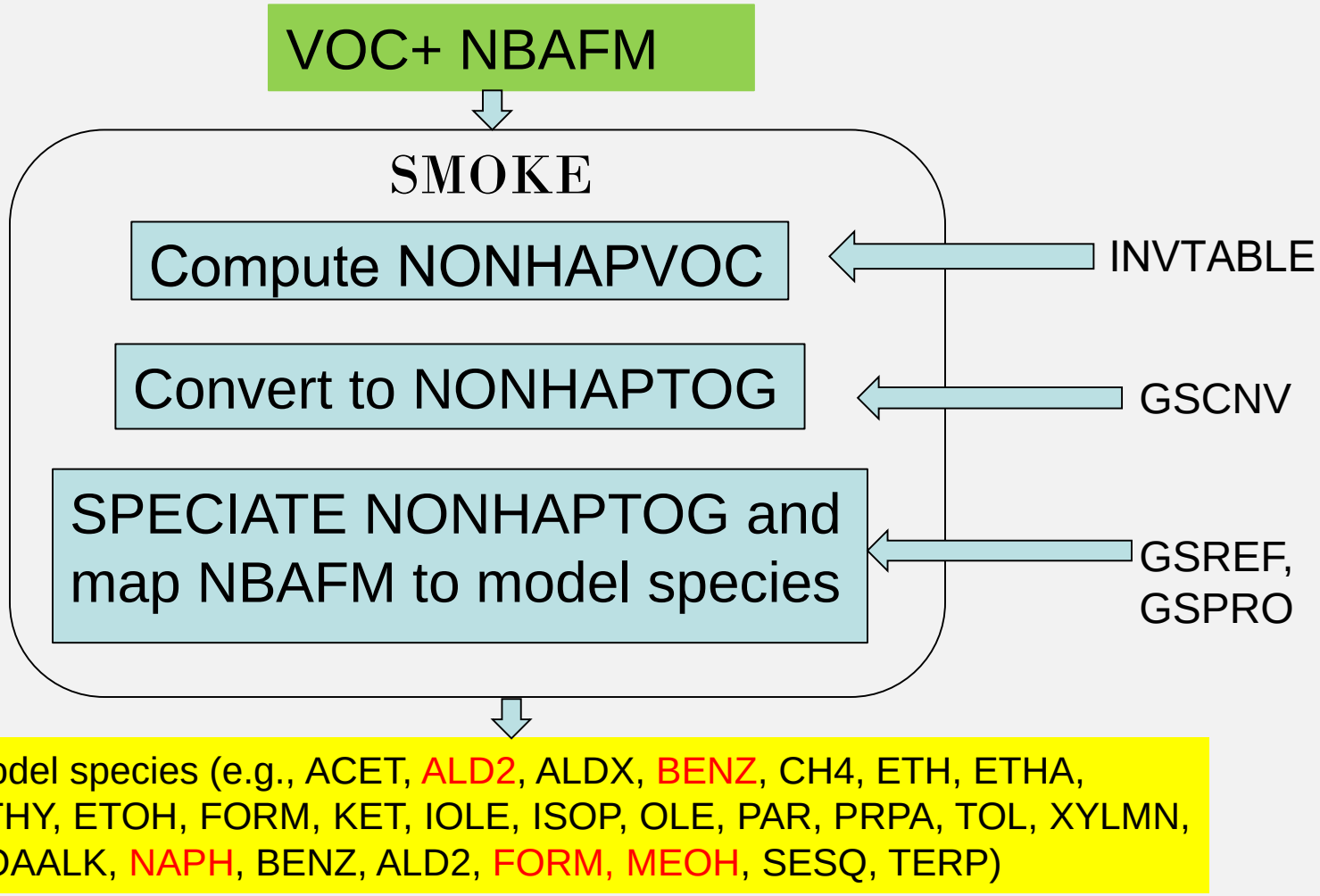
QUESTIONS?

Are there any questions on what we've covered so far?

VOC INTEGRATION - CONCEPT

- Integration
  - Process of taking select VOC HAPs from the HAP inventory and speciating the remaining VOC *because it is generally believed that the HAP inventory is a better source of HAP emissions than the speciated VOC*
  - Want to avoid double counting of HAPs
  - Want to speciate the remaining VOC taking into account HAPs that were removed
- NBAFM chosen as "integration HAPs" in 2014 Modeling Platform
  - Naphthalene, Benzene, Acetaldehyde, Formaldehyde, Methanol
  - These are explicit VOC HAPs in the CB6-CMAQ chemical mechanism.
- NONHAPVOC
  - Remaining VOC after removing explicit VOC HAPs
  - NONHAPVOC = VOC - NBAFM

Integration Steps



EXAMPLE OF INTEGRATED PROFILE

Fireplace wood combustion - pine wood– 4642

No integrate/No use of HAP inventory

pollutant	species	massfrac
TOG	ACET	0.0393
TOG	ALD2	0.0895
TOG	ALDX	0.12
TOG	BENZ	0.0201
TOG	CH4	0.2163
TOG	ETH	0.0588
TOG	ETHA	0.0225
TOG	ETHY	0.0369
TOG	FORM	0.0612
TOG	IOLE	0.014
TOG	ISOP	0.002153
TOG	KET	0.006088
TOG	NAPH	0.0119
TOG	NVOL	0.0115
TOG	OLE	0.0331
TOG	PAR	0.1041
TOG	PRPA	0.008873
TOG	TOL	0.0798
TOG	UNR	0.0437
TOG	XYLMN	0.0203

Integrate

pollutant	species	massfrac
NONHAPTOG	ACET	0.0481
NONHAPTOG	ALDX	0.1468
NONHAPTOG	CH4	0.2647
NONHAPTOG	ETH	0.0719
NONHAPTOG	ETHA	0.0275
NONHAPTOG	ETHY	0.0451
NONHAPTOG	IOLE	0.0172
NONHAPTOG	ISOP	0.002634
NONHAPTOG	KET	0.007449
NONHAPTOG	NVOL	0.0141
NONHAPTOG	OLE	0.0405
NONHAPTOG	PAR	0.1273
NONHAPTOG	PRPA	0.0109
NONHAPTOG	TOL	0.0977
NONHAPTOG	UNR	0.0534
NONHAPTOG	XYLMN	0.0248

WHY NOT INTEGRATE A SOURCE

- Point sources –
  - The State reports HAPs at a different process level than where they reported VOCs. So HAP is at the facility but there is no VOC at that process level to do the subtraction.
  - There is misalignment of VOC and HAP even though both are reported.
- Nonpoint sources –
  - There are no inventory NBAFM emissions at the source.
    - If there really shouldn't be, then remove NBAFM from the profile.
  - NBAFM mass > VOC

TWO APPROACHES TO NO-INTEGRATE

- 1) Don't use any HAPs from the HAP inventory.
  - Use the profile to generate **all** model species - HAPs and nonHAPs.

- 2) Assume HAP inventory is better than speciation:
  - Use the HAP inventory (NBAFM) for model species
  - Create TOG profiles that drop the mass of NBAFM.
  - TOG profiles will have less than 100% of mass if the profile has NBAFM.

VOC INTEGRATION BY SECTOR

Platform Sector *	Approach for Integrating
ptegu	No integration
ptnonipm	No integration
ptfire	No integration
othafdust	No integration
othar	No integration
othon	No integration
ag	N/A – sector contains no VOC
afdust	N/A – sector contains no VOC
biog	N/A – contains specific VOC model species
nonpt	Partial integration (NBAFM)
np_oilgas	Partial integration (NBAFM)
pt_oilgas	No integration
rwc	Partial integration (NBAFM)
nonroad	Full integration (calculated in MOVES)
c1c2rail	Partial integration (NBAFM)
othpt	Partial integration (NBAFM)
c3marine	Partial integration (NBAFM)
onroad	Full integration (calculated in the MOVES model)*

*See Modeling Platform technical support document for sector descriptions (https://www.epa.gov/air-emissions-modeling).

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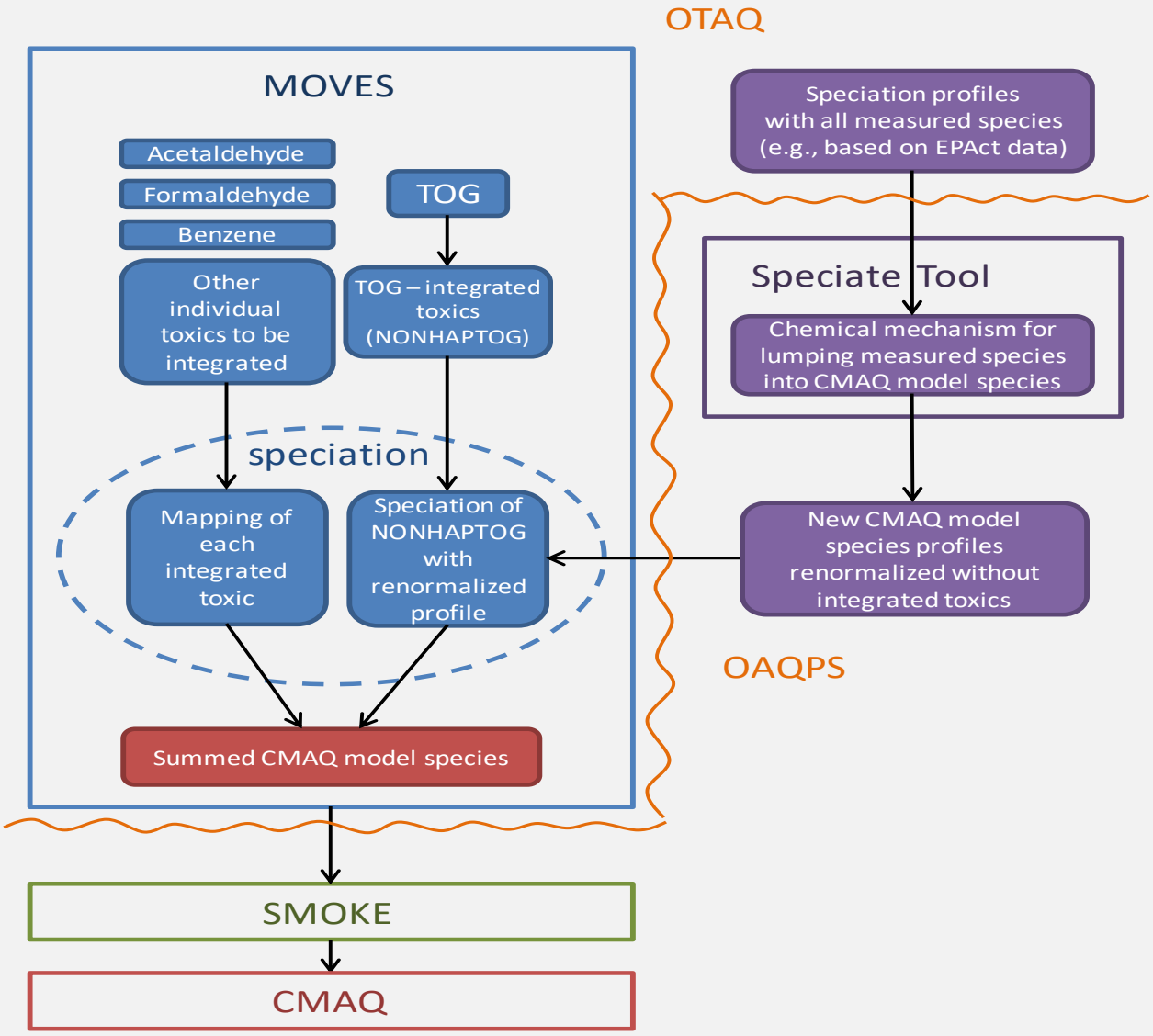
ONROAD SPECIATION

- MOVES2014 does speciation within MOVES for onroad sources
  - Uses inputs from the Speciation Tool
  - Different profiles for different vehicle model years, regulatory classes, fuel types, and emission processes
  - Previously used COMBO files or weighted profiles to approximate, but was a coarse approach
- $PM_{2.5}$
  - AE6 species come directly from MOVES (in mass).
- VOC
  - 16 pollutants are explicit, i.e. integrated.
  - Model species (moles) and inventory pollutants (mass) come directly from MOVES.
  - Need to specify chemical mechanism in the MOVES run

ONROAD SPECIATION IN MOVES



NONROAD SPECIATION

- MOVES2014a provides nonroad emissions that are semi-speciated.
- Also provides individual HAPs - benzene, toluene, etc.
- And provides the remainder along with the profile code
  - e.g. NONHAPTOG_4452
    - NONHAPTOG is the difference between TOG and the sum of the HAPs.
    - 4452 is the profile code to use for NONHAPTOG.
  - Unlike onroad, the speciation is done in SMOKE.
  - Approach allows application of new chemical mechanisms in SMOKE without re-running MOVES.

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COMBINATION PROFILES

- SMOKE now has a method of combining two or more speciation profiles for a specific SCC/FIPS.
- Examples:
  - Combine E0 and E10 fuel profiles
  - Combine flare profile with oil & gas process profile

COMBINATION PROFILES (cont.)

- Combine flare profile with oil & gas process profile
  - Based on output from the Oil and Gas Tool (software & data that is used to develop EPA Oil and Gas estimates for the NEI)

SCC	PROFILE CODE	POLLUTANT	FIPS	FACTOR
2310021010 (Oil & Gas:On-Shore Gas Prod;Cond. Storage Tank)	SWFLA_R (Oil and Gas -SW Wyoming Basin Flash Gas Composition for Condensate Tanks)	NONHAPVOC	56045	0.0456
2310021010	FLR99 (Natural Gas Flare Profile with DRE >98%)	NONHAPVOC	56045	0.9544

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SPECIATE

QUESTIONS?

Are there any questions on what we've covered so far?

BREAK

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SPECIATE

SPECIATE DATA GAPS AND FUTURE PLANS

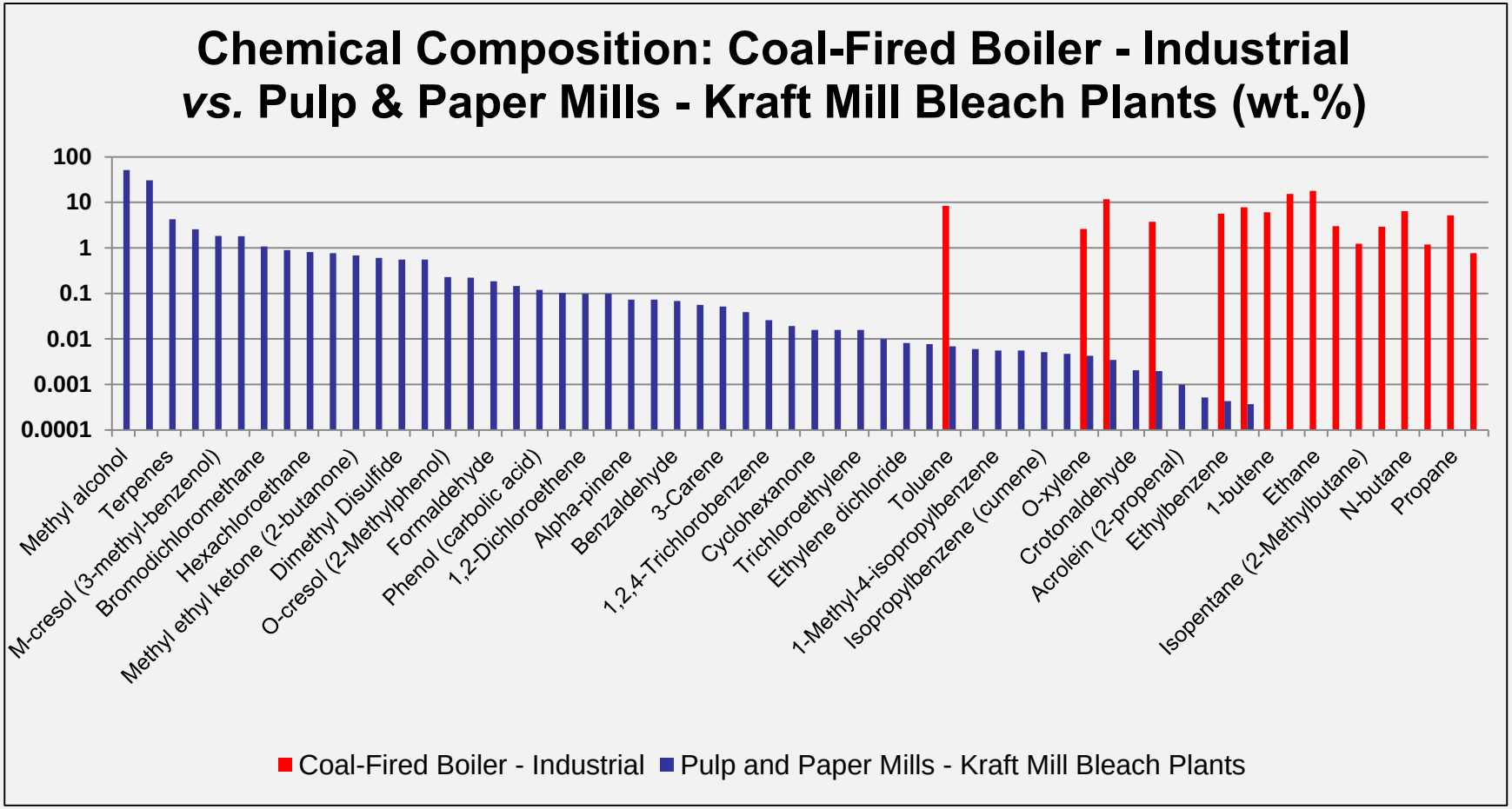
DATA GAP ANALYSIS – AN ONGOING PROCESS

- Goal: Every inventory source is assigned to a good profile that best fits its source category.
  - Are assignments appropriate?
  - How good are the available profiles?
  - What research is needed to meet the goal?
- Past Efforts: Analyses leading toward 2011 NEI Modeling Platform improvements
- Current Efforts: Gaps and needs analysis

PAST EFFORT: 2008 NEI (2013 VOLUNTEER)

- Found low-hanging fruit in the 2008 NEI Platform
- Reviewed VOC emission profiles applied to SCCs that are the largest sources of VOCs
- Identified opportunities for Pulp & Paper
  - Over 200 source operations linked to generic profiles
  - Profile 1185: Coal Fired Boiler – Industrial linked to eight largest operations (43 of 144 kTpy)
- The 2008 NEI had > 500 kTpy of TOG speciated with the default profile (0000).

IMPACT OF MISMATCHED PROFILES



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PAST EFFORTS: 2011 NEI MODELING PLATFORM IMPROVEMENTS

- EPA developed and applied appropriate composite source profiles for the Pulp & Paper and Chemical Manufacturing sectors from SPECIATE emissions profiles.
- Pulp and Paper: 97 of 121 kTpy (80%) reassigned from profiles 0000 and 1185
- Chemical Manufacturing: 20 of 90 kTpy (22%) reassigned from profile 0000
- Composite profiles were added to SPECIATE 4.5.

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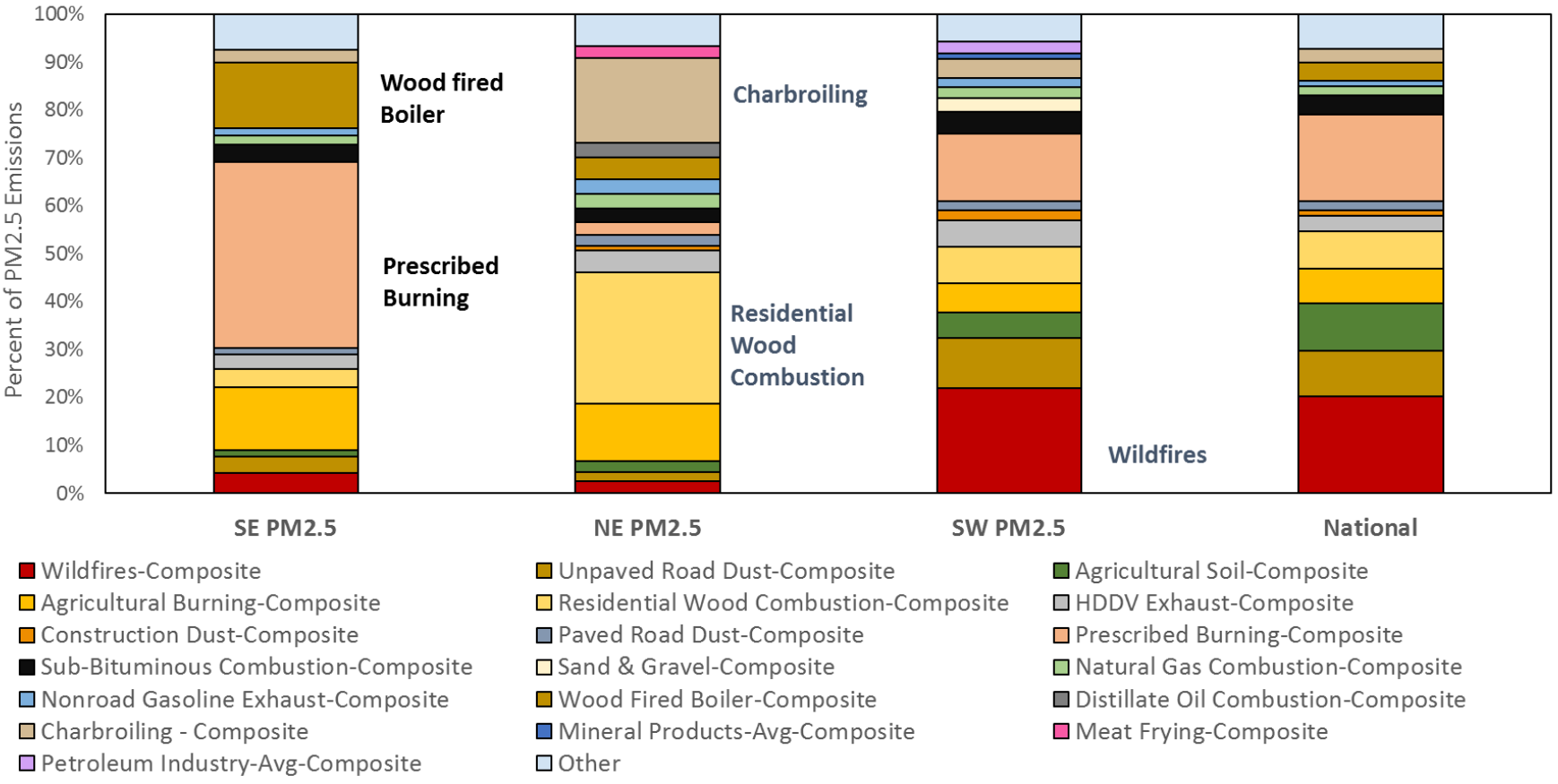
Assessment of Important SPECIATE Profiles in EPA's Emissions Modeling Platform and Current Data Gaps

- Casey Bray, NC State & EPA/ORD Intern
- Goals
  - Elucidate profiles/categories of most importance for air quality modeling purposes
  - Evaluate current profiles
  - Identify and articulate research needs

Come to Casey's talk FRIDAY @ 8 am

Major $PM_{2.5}$ Profiles (% of mass assigned in 2014 EPA modeling platform)* - from Bray's work



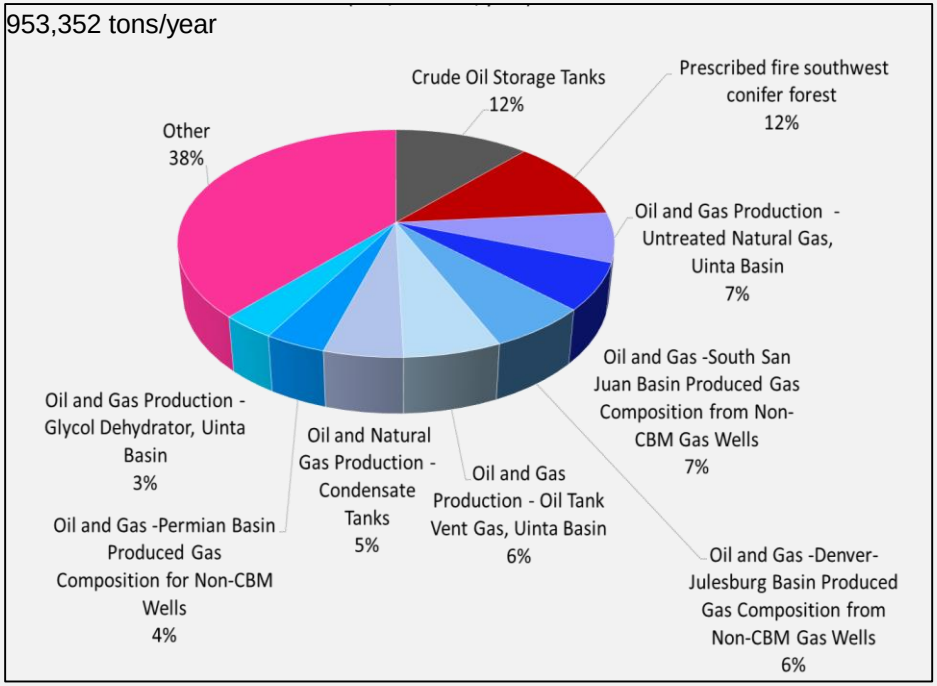
*excludes emissions from the onroad mobile sector

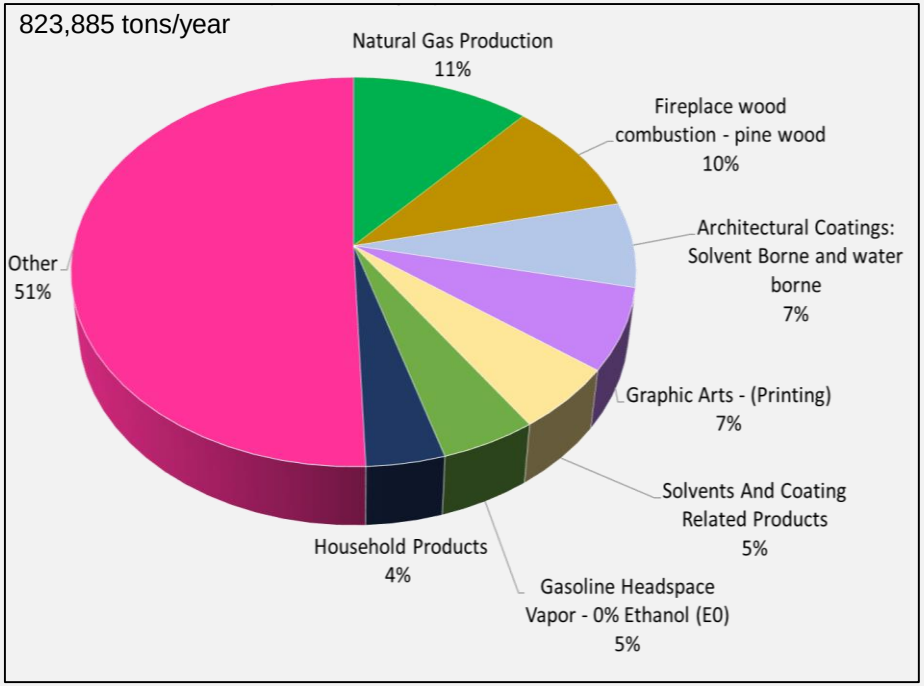
VOC PROFILES – REGIONAL DIFFERENCES*

(From Bray)

Southwest: UT, CO, AZ, NM

Northeast: ME, NH, VT, RI, CT, NY, NJ, DE, PA, MD





*excludes emissions from the onroad and nonroad mobile sectors

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THE SPECIATE WORKGROUP AND FUTURE PLANS

- EPA's SPECIATE Workgroup
- Modelers tell us what is important
- Ongoing literature searches
- Peer-reviewed journal articles preferred
- The "Master List" of references
- Needs Analysis Project - data gaps
- Please let us know if you've got data that could be added!

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FUTURE SPECIATE PLANS

- Develop Standard Operating Procedure (SOP) for SPECIATE Profile Selection, Collection, and Entry
  - Allow In-House Processing of Profiles
  - Improve Documentation of Metrics and Processes
  - Identify Key Metrics for Quality Profiles
  - Formalize Prioritization Process
- ACCESS database structure improvements (including use of forms to add to profiles)
- Continue Oil and Natural Gas Emissions profiles started with Region 8 RARE
- Comparison of Emissions Inventory HAPs vs. those from speciated VOC to improve VOC/HAP integration

THE SPECIATION TOOL

ACKNOWLEDGEMENTS

- Greg Yarwood – Ramboll Environ
- Madeleine Strum EPA/OAQPS
- Zac Adelman – Institute for the Environment – UNC
- Michele Jimenez – Ramboll Environ

DEFINITIONS

- AQM – Air Quality Model
  - CMAQ, CAMx, etc.
- Model Species – Model species are used in the AQM
  - e.g., OLE, PAR, etc. in CB mechanisms
- Profile – list of mass fractions (or wt. %) of compounds
- Organic Compounds – Organic compounds included in SPECIATE profiles
  - e.g., 1-Methylcyclopentene, isomers of hexane, etc.
- SPECIATE – EPA's SPECIATE database
- SPTOOL – The stand-alone Speciation Tool

ATMOSPHERIC CHEMISTRY IN AQM

- Atmospheric chemistry consists of millions of reactions among many thousands of chemical compounds

- AQMs use a condensed chemical mechanism with a manageable number of reactions and model species
  - CB05, CB6r2, CB6r4
  - SAPRC99, SAPRC07, SAPRC11
  - RACM2
  - CRIv2r5
  - etc.

ATMOSPHERIC CHEMISTRY IN AQM

- An integral part of any condensed chemical mechanism is the assignment from real organic compounds to model species of the condensed mechanism

- Chemical mechanism provides a basis for computer modeling studies of ozone, particulate matter (PM), visibility, acid deposition and air toxics issues

PREPARING EMISSIONS FOR MODELING

- Emissions processing converts from inventory pollutants to chemical mechanism model species, e.g., total VOC converted to CB OLE, PAR etc.
  - Emissions processing step referred to as '<u>speciation</u>'
- AQMs require emitted gaseous species in molar and PM species in mass units

PREPARING EMISSIONS FOR MODELING

- SMOKE ancillary files GSPRO and GSCNV are used for speciation

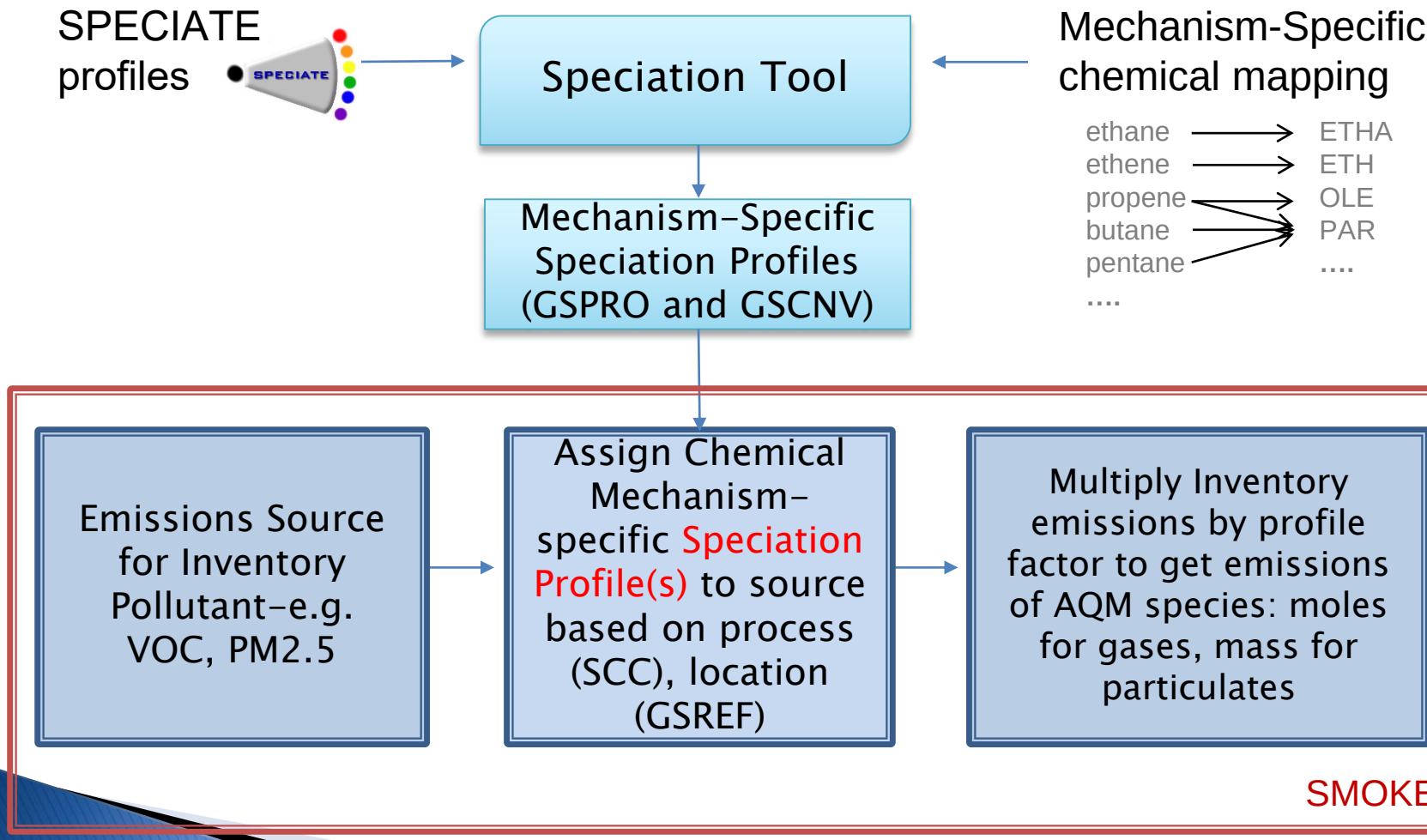
- GSPRO contains factors to speciate inventory pollutants
  - Split Factor: numerator for mole-based speciation
  - Divisor: denominator for the mole-based speciation
  - Split Factor/Divisor = moles of model species per ton of TOG
  - For PM, divisor = 1

- GSCNV contains VOC-to-TOG conversion factors to convert inventory VOC (or ROG) to TOG to apply TOG-based speciation profiles

SPECIATION STEPS IN MODELING TOOLS

- Speciation Tool: creates SMOKE ancillary files GSPRO and GSCNV
  - Uses SPECIATE profiles
  - Uses mechanism-specific chemical mapping, e.g., CB6 different from CB05
- SMOKE: assigns profiles to sources and uses ancillary files GSPRO and GSCNV to compute AQM emission files
- Emissions Modeling Framework: can be used as an interface for managing inventories and related data (profiles), and interface for running the Speciation Tool and SMOKE

SPECIATION FOR AQ MODELING



SMOKE GSPRO and GSCNV files

GSPRO sample profile					
Speciation profile number	Pollutant ID (name)	Species ID (name)	Split factor	Divisor	Mass Fraction
0051	TOG	CH4	0.2	16.042	0.2
0051	TOG	ETHA	0.3	30.069	0.3
0051	TOG	FORM	0.2	30.026	0.2
0051	TOG	PRPA	0.3	44.096	0.3
GSCNV sample profile					
Name of pollutant converting from	Name of pollutant converting to	Speciation profile code	Conversion factor		
VOC	TOG	0051	2		

SPECIATION TOOL – SPTOOL

- SPTOOL is a stand-alone tool that was developed to generate the GSPRO and GSCNV ancillary data SMOKE uses for speciation
- SPTOOL implemented using open source PostgreSQL database and Perl interface
- The latest SPTOOL install and User Guide can be downloaded from the EPA/CMAS website https://www.cmascenter.org/help/documentation.cfm?MODEL=speciation_tool&VERSION=4.0

SPTOOL SOFTWARE REQUIREMENTS

- PostgreSQL can be downloaded from http://www.postgresql.org
- Perl and the database drivers can be downloaded from http://www.perl.com
- User must have database create privileges in PostgreSQL to run the Speciation Tool

SPTOOL QUICK START

1. Create a Speciation Tool directory

2. Extract the Speciation Tool installation files
   a) Change to the Speciation Tool directory
   b) Copy the Speciation Tool package to this directory
   c) Extract the zipped file

3. Verify required software packages are available.
   a) Run ./spool_reqd_checks.sh

4. Set environment variables
   a) Edit Assigns.sptool; Set SPTOOL_HOME
   b) Source Assigns.sptool

SPTOOL QUICK START

5. Initialize the Speciation Tool database
   a) Execute ./init_sptooldb_v4.0.csh

6. Execute the provided test case
   a) Change to the run directory; cd /run
   b) Run ./test_all.job

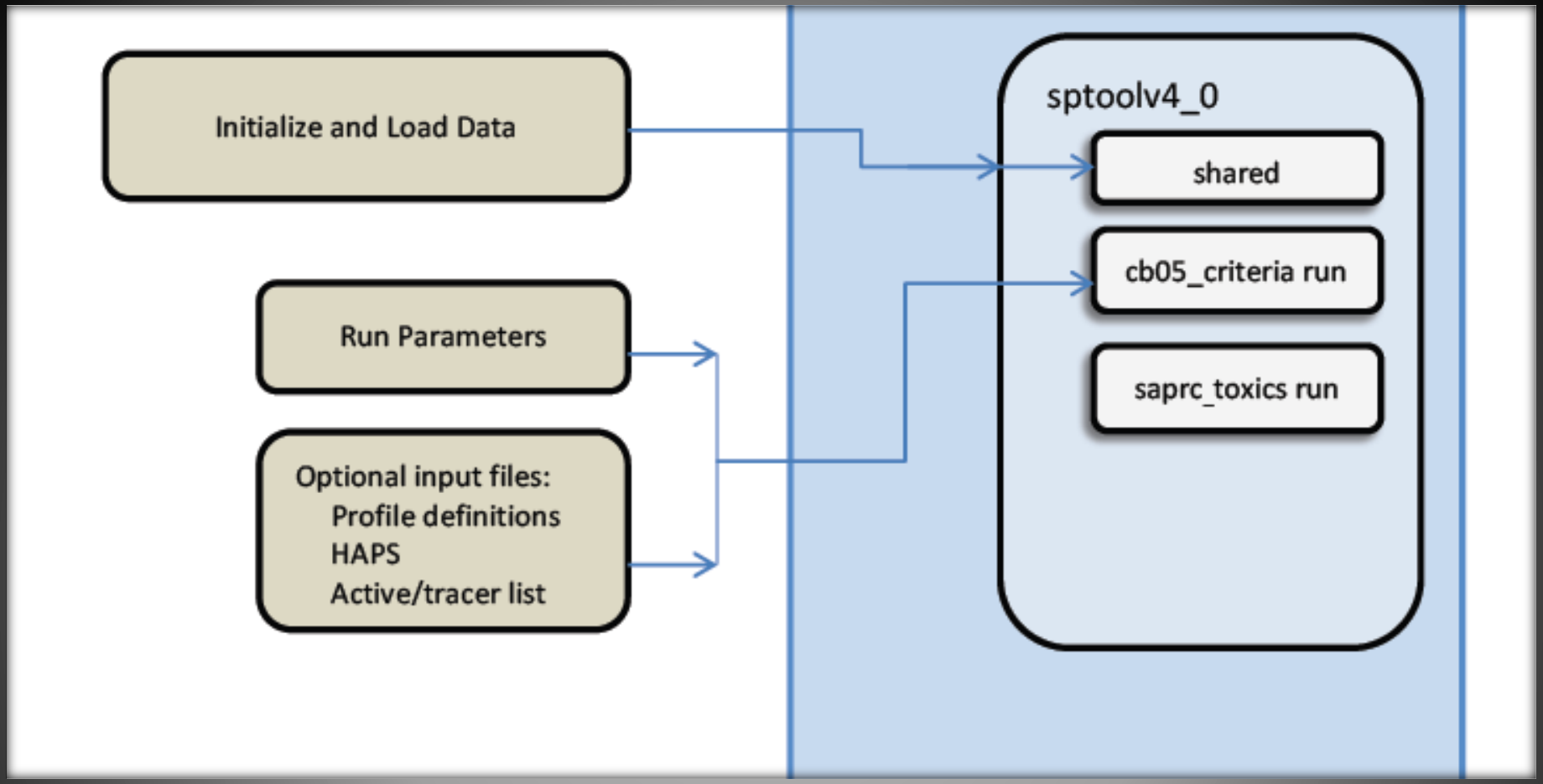
7. Review results
   a) Change to output directory; cd ../output

SPTOOL INSTALLATION

- Create SPTOOL home directory with any valid directory name
- Copy the installation file to home directory and extract
  - tar -xvzf tar_Speciation_Tool_v4.0_11jan2017.tgz
- Run script to check for required software and verify user PostgreSQL authorizations
  - Run sptool_reqd_checks.sh

SPTOOL DATABASE INITIALIZATION

- Speciation Tool must be initialized prior to making any runs. Initialization steps include:
  - Update and source the assigns file **Assigns.sptool**
    - Set the home directory
  - Run the initialization script
    - ./init_sptooldb_v4.0.csh
- What happens during the SPTOOL initialization?
  - Create database, set permissions, create the *shared* schema and table definitions for the tool data, and import data to the *shared* schema.



SPECIATION TOOL INITIALIZATION

Initialization creates the sptoolv4_0 PostgreSQL database with schema shared. Each run will create an additional named schema based on the user specs.

SPTOOL ASSIGNS FILE

- **Assigns.sptool** file can be found in the top level SPTOOL home directory
  - Update and source the **Assigns.sptool** file

- Assigns file sets environment variables that are required for the database initialization
  - SPTOOL home directory
  - Database name
  - File names of input speciation data

SPTOOL INPUT FILES

- PROFILES_GAS – gas profile description and documentation
- WEIGHTS_GAS – organic gas mass fraction profiles (in weight percent)
- PROFILES_PM – PM profile description and historical information
- WEIGHTS_PM – PM mass fraction profiles (in weight percent)

SPTOOL INPUT FILES

- SPECIES_PROPERTIES – properties of individual organic compound, including molecular weight
- MECHANISM – mechanism mappings
  - moles model species / mole organic compound
- MECHANISMPM – PM2.5 mechanism mappings
  - mass model species / mass PM2.5
- CARBONS – number of carbon atoms in each model species

SPTOOL OUTPUT FILES

- SPLITS_OUT (GSPRO) – SMOKE speciation profiles
  - Split Factor: numerator for mole-based speciation
  - Divisor: denominator for the mole-based speciation
  - Split Factor/Divisor = moles of model species per ton of TOG
  - For PM, divisor = 1
- CNV_OUT (GSCNV) – SMOKE VOC-to-TOG conversion factor file

RUNNING SPTOOL

- First source the **Assigns.sptool** file to set the required environment variables SPTOOL_HOME and SPTOOL_DB
- SPTOOL must be initialized prior to making any runs
- Run script – The perl program **run_sptool.pl** creates output SMOKE profile files – GSPRO and GSCNV
- The run script requires the SPTOOL database name, a name to uniquely label the database schema, and a run control file name as input
  - perl $SPTOOL_SRC_HOME/run_sptool.pl $SPTOOL_DB cmaq_cb6_criteria RUNCTL

SPTOOL RUN CONTROL FILE

- The run control file indicates run parameters and run-specific data files required for the Speciation Tool run.

- The format of the run control file is

  <keyword>, <option>

  Examples,

  MECH_BASIS, CB05

  OUTPUT, VOC

  RUN_TYPE, CRITERIA

  AQM, CAMX

RUN PARAMETERS

- MECH_BASIS – select chemical mechanism to use
- OUTPUT – select which output profiles to generate. Options are “VOC” for gas species and “PM” for particulates
- RUN_TYPE – The RUN_TYPE options are: CRITERIA, INTEGRATE, NOINTEGRATE, HAPLIST, and VBS
- AQM – this parameter selects model-correct species names for output files
- TOLERANCE – specifies acceptable deviation from 100% for the sum of weight percentages (default is 5%)

SPTOOL FAQ

- What happens when an organic compound used by a profile lacks a defined molecular weight?
  - Any detailed organic compound with an undefined molecular weight is dropped from the profile because a molecular weight is required to compute splits factors. Dropped mass fraction due to missing molecular weights may takes the profile sum outside the selected tolerance, causing the profile to be dropped. This problem should be resolved by specifying missing molecular weights in the species properties.

SPTOOL FAQ

- What happens when an organic compound used by a profile lacks an assignment in the mechanism mapping?
  - SPTOOL issues a warning and the compound is assigned to UNK

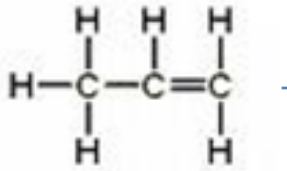
- When does SPTOOL renormalize a profile?
  - If the sum of mass fractions for a profile is not 100%, and nothing is done to correct the profile, subsequent SMOKE processing will not conserve mass. SPTOOL renormalizes all gas profiles whose sum is within the tolerance thereby preserving VOC mass. Profiles outside the tolerance are dropped and a warning is issued.
  - For the AE6 PM profiles, when sum of AE6 PM species is less than 100%, the remaining mass gets assigned to PMOTHR (=100% - sum of AE6). When the sum is greater than 100%, the profiles are dropped with a warning.

Extra Slides

CARBON BOND MECHANISM

- Carbon Bond (CB) mechanisms represent some organic compounds explicitly
  - e.g., ethane (ETHA), ethene (ETH), ethyne (ETHY), etc.
  - more explicit species in CB6 than CB05

- CB mechanisms lump other organic compounds according to carbon bonding type
  - alkanes (paraffins) to PAR
  - alkenes (olefins) to OLE or IOLE
  - aromatics to TOL or XYL

- example: propene:  PAR + OLE

CARBON BOND MECHANISM

Organic Compound	Mole Fraction	CB6 Mapping (mol/mol)	CB6 Profile (mol/mol TOG)
ethane	0.2	1 ETHA	0.2 ETHA
butane	0.1	4 PAR	0.4 PAR
ethene	0.05	1 ETH	0.05 ETH
propene	0.1	1 PAR + 1 OLE	0.1 PAR + 0.1 OLE
formaldehyde	0.1	1 FORM	0.1 FORM
acetaldehyde	0.15	1 ALD2	0.15 ALD2
toluene	0.1	1 TOL	0.1 TOL
ethylbenzene	0.05	1 PAR + 1 TOL	0.05 PAR + 0.05 TOL
xylene	0.15	1 XYL	0.15 XYL
TOG	1.0		0.2 ETHA + 0.55 PAR + 0.05 ETH + 0.1 OLE + 0.1 FORM + 0.15 ALD2+ 0.15 TOL + 0.05 XYL

- Example profile (first two columns) of organic compounds
- CB6 mapping in third column
- Right column shows CB6 model species per mole of TOG emitted