TOXIC CONTAMINANTS IN THE SAN FRANCISCO BAY-DELTA AND THEIR POSSIBLE BIOLOGICAL EFFECTS

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I. INTRODUCTION

The San Francisco Bay-Delta Aquatic Habitat Institute (AHI) has been requested under the terms of contract WRCB No. 5-290-120-0 to undertake a variety of tasks for the California State Water Resources Control Board. One of these tasks, termed a "Coordination Element," includes a requirement for the following:

> "Prepare a comprehensive report summarizing results of studies that address the effects of pollutants on San Francisco Bay/Delta biota. The report shall include a critical review of the most important research. Whenever possible, summary data shall be presented in an accessible table format and discussed in the text. Conclusions shall address the existing links between pollutant loading and detrimental biological effects with discussion of potential alternative hypotheses."

The present report has been prepared in response to this portion of the contract between AHI and the State Water Resources Control Board.

The San Francisco Bay-Delta is the largest estuary on the western coast of the United States, with a surface area of 1,240 km^2 and a drainage basic of 153,000 km^2, the latter being about 40% of the area of California. Recent general reviews of the estuary were provided by Conomos et al. (1985) and Nichols et al. (1986). The latter authors emphasized the very great historical changes which have occurred in the estuary, particularly since the arrival of white settlers in 1769. These changes include topographic alterations caused by the washdown of debris from hydraulic mining in the Central Valley to the estuary and by the reclamation of land. In addition, much of the natural freshwater inflow to the estuary has been diverted for uses elsewhere, principally in the Central Valley and Southern California. The

increasing human population in the Bay-Delta has also had considerable impacts on the estuary, which receives not only sewage and industrial wastes, but also agricultural drainage fro croplands in the upstream catchment and the Delta itself.

In view of these dramatic changes to the Bay-Delta environment, it might be anticipated that equally drastic effect would have been documented with respect to the biological resources of the estuary. To some extent, this is indeed the case. Thus, massive losses of wetland areas have occurred since the mid-1800s. Benthic communities in the Bay-Delta have been totally altered from historical populations, mainly because of the introduction of exotic species. The fishery resource in the estuary has also undergone long-term changes, and some fish populations appear to be continuing to decline.

It is a popularly-held belief that pollution of the Bay-Delta has contributed (and is contributing) to the changes in biological resources of the estuary. However, incontrovertible evidence of such effects is rare for any ecosystem, and the San Francisco Bay-Delta is no exception. If pollutants are exerting detrimental effects on biota of the Bay-Delta, it is most likely that the contaminants of particular toxicity and persistence in the ecosystem are those with the greatest impact. These so-called "toxics" include trace metals, organochlorines (chlorinated hydrocarbon pesticides and PCBs), and hydrocarbons. The present report concentrates upon data characterizing these groups of contaminants in the estuary. Published data relating to each of these contaminant types are reviewed, conclusions being reached on the existence or otherwise of elevated

concentrations of particular toxicants in components of the Bay-Delta ecosystem. Areas of particular contaminant enrichment are discussed, and where relevant, the estuary is compared to other locations, in order to place local data into a wider context.

In the penultimate section of the report, published data concerning biological effects as such are reviewed, a variety of ecosystem resources being considered. Conclusions and recommendations for future study are presented in the final section.

The demonstration that contaminants in a given aquatic ecosystem are present at significantly elevated levels and are exerting detrimental effects on biological resources is a challenging task. Toxicants are present in such systems in a bewildering variety of physical and chemical forms, and their toxicological significance is highly dependent upon the precise forms present. For example, contaminants may exist in the water column in solution, in chelates or colloidal forms, or in suspension. Each of these categories includes many types of chemical species, displaying unique bio-availabilities and toxicities to biota. Similarly, toxicants in sediments may be more or less available to biota depending on their exact chemical form and method of binding to sediment particles. Both estuaries themselves and the contaminants residing in these areas are under a continual state of dynamic flux; this interferes with the elucidation of cause-and-effect relationships between toxicants and their biological effects.

In most cases, presently-available research and analytical methods provide only a crude picture of the potential for toxic effects of contaminants in aquatic ecosystems. So little is

known of the incidence or significance of different chemical forms of even the better-characterized pollutants that their adverse effects generally have to be dramatic for these to be recognized. Similarly, the control of environmental concentrations of contaminants through the regulation of their mass emissions, to permit the attainment and maintenance of water quality standards or objectives, takes little account of the subtleties of toxicant speciation or bio-availability. The understanding of such matters can be improved only through further research and diligent attempts to enhance present methodologies. Meanwhile, estuarine resources must be protected in the best manner possible, given the available data. This report reviews such data, and suggests conclusions where these are considered scientifically defensible on the basis of present knowledge.

II. TRACE ELEMENTS IN THE BAY-DELTA

Trace element distributions in the Bay-Delta have been studied through the analysis of natural waters, sediments, and biota. There is generally more information available on trace elements in the estuary than on organic contaminants such as organochlorines and hydrocarbons. This may be at least partly due to the relative costs of analysis of inorganic and organic pollutants, but also concerns the degree of sophistication of such analysis.

This section does not seek to exhaustively review all the literature available on trace elements in the estuary. Rather, published material considered to be both reliable and important in improving the overall understanding of metal distributions in the Bay-Delta is discussed and reviewed. Emphasis is given to those elements which are thought to be considerably enriched or of high bio-availability (and potential toxic effect) in the estuary. The metals considered to be of greatest importance are discussed first.

A brief comment is required here with respect to quality control of analysis. It is now well-recognized that many of the older studies of trace elements reported data which were incorrect due to contamination of samples and other problems. This was particularly the case where very low concentrations were present in environmental samples, such as in studies of trace metals in natural waters. The data reviewed in this section have been carefully selected with this in mind, and it is thought that these studies of trace elements in solution are probably largely reliable. However, controversy remains over much of the early

data of this type, and even the results reviewed herein for trace metals in waters of the Bay-Delta should be treated with caution. This problem is generally encountered less frequently in the analysis of sediments or biota for trace elements, as the concentrations in these materials are usually much greater than those found in solution. Further comments on quality control and quality assurance procedures are included in the text below where these are deemed relevant.

A. SILVER

Introduction

Silver is present in both the elemental state and in combined ores in nature. Its global rate of natural mobilization has been estimated as 5,000 tonnes annually; by comparison, anthropogenic activities (mainly mining) mobilize a further 7,000 to 9,000 tonnes a year (MIT, 1970; U.S. Bureau of Mines, 1970). Concentrations of silver in rivers and marine coastal waters are in the submicrogram per liter range.

Contamination of freshwater and marine environments by silver may arise as a result of mining activities and from the discharge of industrial effluents. Industries which are significant potential sources of this element include jewelry, porcelain, and silverware manufacture; photographic, electroplating and food processing industries; and ink and antiseptic manufacture (McKee and Wolf, 1971).

Waldichuk (1974) states that silver ranks very highly among trace elements with respect to pollution hazard, being third after mercury and cadmium. This high ranking is largely a function of the extreme toxicity of silver to freshwater and marine biota. Soyer (1963) found that concentrations as low as 0.36 and 0.57 $\mu g\ L^{-1}$ of silver retarded larval growth of two sea urchin species. Silver causes mortality of embryos of the American oyster Crassostrea virginica at 6 $\mu g\ L^{-1}$ and of hard clam embryos at 13 $\mu g\ L^{-1}$ (Calabrese et al., 1973; Calabrese and Nelson, 1974). A 96-hour LC50 concentration for the stickleback Gasterosteus aculeatus of 10 $\mu g\ L^{-1}$ was reported by McKee and Wolf (1973).

Sublethal effects of silver on enzyme activity in livers of the killifish Fundulus heteroclitus (Jackim et al., 1970; Jackim 19 and oxygen consumption in molluscs (MacInnes and Thurberg, 1973; Thurberg et al., 1974) have also been noted. As a result of such concerns, very low concentrations of silver are proposed for wate quality objectives or standards, in California and elsewhere (e.g Klapow and Lewis, 1979; Linck et al., 1981; U.S. EPA, 1986). The most recent U.S. EPA (1986) standard for silver in marine waters is 2.3 $\mu g\ L^{-1}$; this is also employed as an objective in the Wate Quality Control Plan for the San Francisco Bay Basin.

Silver in Bay-Delta Waters

Little direct information is available on the concentrations of silver in the receiving waters of the San Francisco Bay-Delta. Girvin et al. (1978) studied seasonal and large-scale spatial variations in the levels of silver and other elements in ship channel areas of the Central and South Bays, through the drought years of 1976-77. Sampling and analytical methods were supported by high-quality QA/QC, and these data are considered reliable. A specific method was developed for the analysis of silver, as the standard method used for other elements did not give rise to quantitative extraction. Although in most cases a general enrichment of silver with distance south from the Golden Gate was observed for South Bay waters, this was not always the case (Fig. 1). Temporal variations were also not entirely consistent between stations (Fig. 2), although most sites exhibited maximum silver levels in late 1976. While a general considerable enrichment of silver in South Bay waters compared to waters of

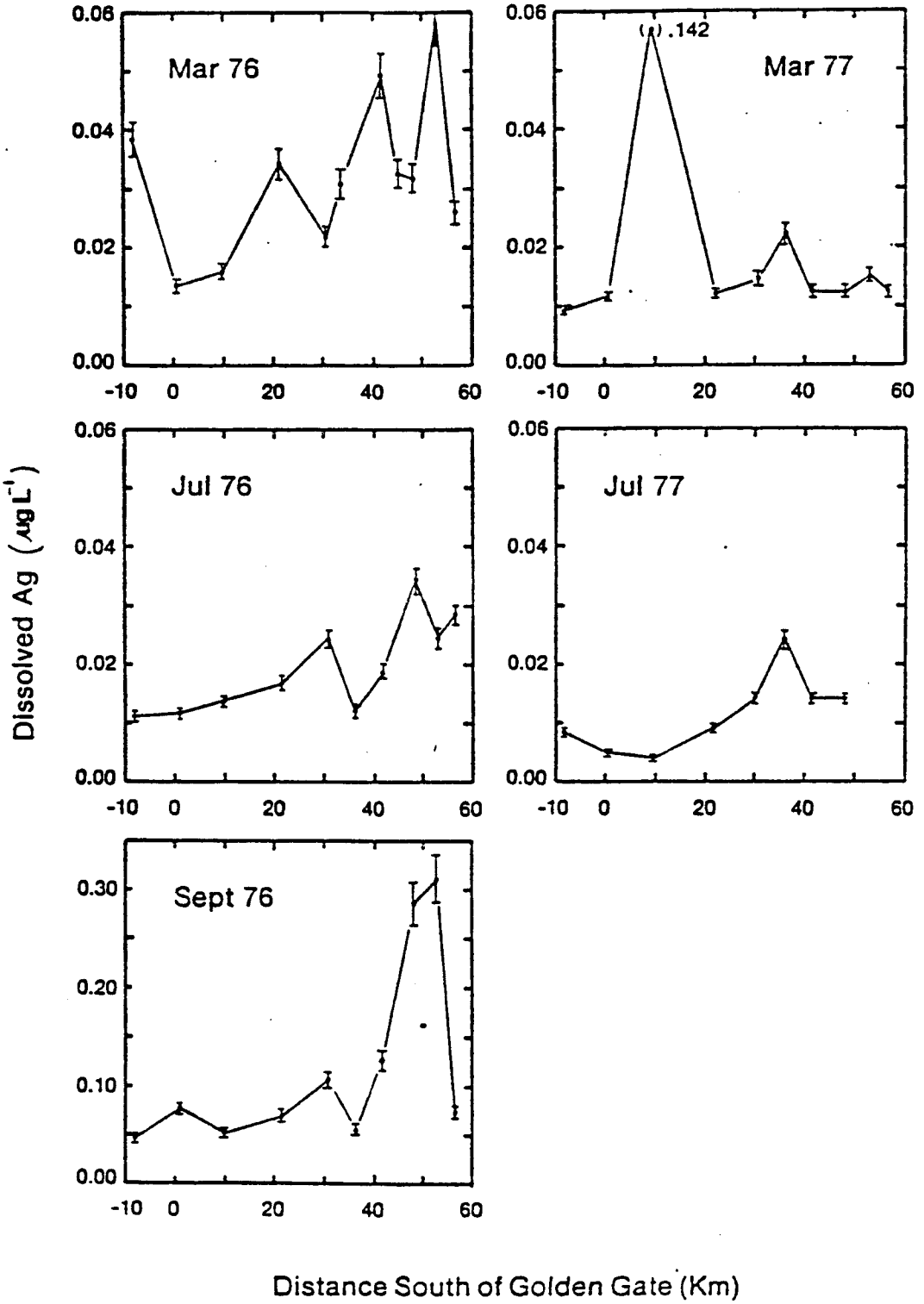


Fig. 1. Spatial variations in concentrations of dissolved silver in waters of central and south San Francisco Bay, 1976-77. The average analytical error of ± 8% is indicated by vertical bars. After Girvin et al. (1978).

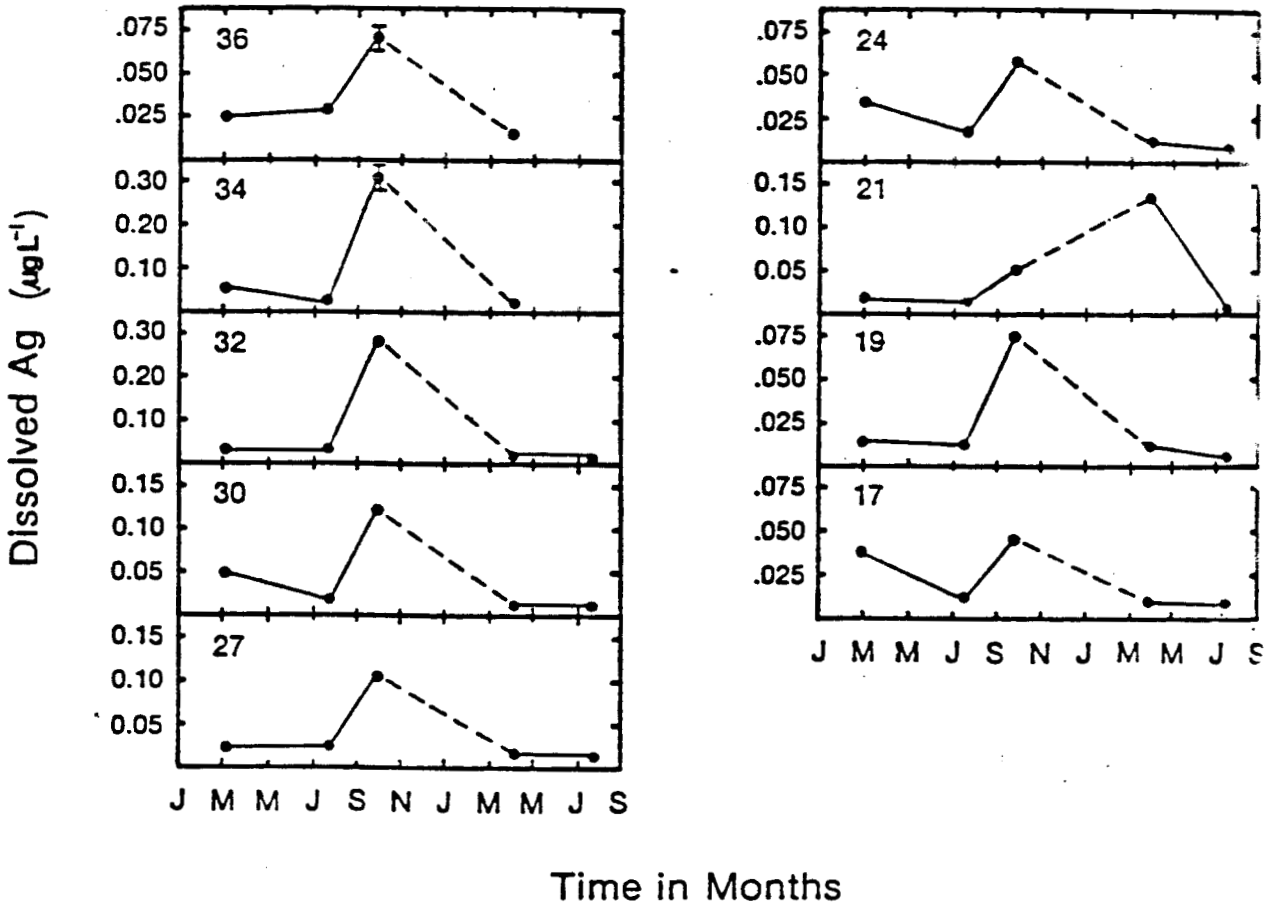


Fig. 2. Temporal variations in dissolved silver in waters of central and south San Francisco Bay, 1976-77, by station. The average analytical error of ±8% is indicated by vertical bars, where this exceeds the width of the data points. After Girvin et al.(1978).

the Gulf of the Farallones was evident (Table 1), the high variability (in Bay locations in particular) masked any statistical difference. It should be noted here that this comparison involved only one sampling time (March 1976) at three sites in the Gulf of the Farallones.

Similarly, Girvin et al. (1978) found that concentrations of silver present in suspended particulates in central and south San Francisco Bay waters were highly variable (range 0.6-28.5 $\mu g\ g^{-1}$ dry weight; mean$\pm$standard deviation of 2.2 $\pm$4.3 $\mu g\ g^{-1}$ dry weight). These levels corresponded to concentrations by water volume of 0.002-3.36 $\mu g\ L^{-1}$ (mean $\pm$S.D. of 0.11$\pm$0.50 $\mu g\ L^{-1}$), indicating that much of the silver in the Bay is particulate-associated, rather than dissolved.

The authors proposed that a source (or perhaps multiple sources) of silver existed in South Bay, but that the discharge of silver to these receiving waters was intermittent. There was no clear correlation of levels of the element with storm run-off; hence wastewater discharges were suspected as the primary source of silver (Girvin et al., 1978). Data from NPDES permits for 1976-77 did little to throw light on probable sources, although some effluent monitoring data did reveal transient increases in discharged silver loads. It was noted that maximum concentrations of dissolved silver in the South Bay (Figs. 1 and 2) closely approached previous long-term water quality objectives for this element (0.45 $\mu g\ L^{-1}$; see Linck et al., 1981). However, the latest U.S. EPA standards for silver in marine waters are significantly greater than the values reported by Girvin et al. (1978), being a maximum of 2.3 $\mu g\ L^{-1}$ for total recoverable silver (U.S. EPA, 1986).

Table 1. Concentrations of dissolved silver ($\mu g\ L^{-1}$) in waters of central and south San Francisco Bay, 1976-77, compared to Gulf of the Farallones water in March 1976. After Girvin et al.(1978).

Parameter	Central/South Bay	Gulf of Farallones
RANGE	0.004-0.310	0.005-0.044
MEAN	0.042	0.019
STANDARD DEVIATION	0.061	0.021

Silver in Bay-Delta Sediments

Rather more data are available on the concentrations of silver in sediments from San Francisco Bay-Delta, although it is notable that no comprehensive surveys have been carried out to date. Girvin et al. (1975) could not detect silver in Bay sediments at 5 locations (Tara Hills, Albany Hill, Bayview Park, Coyote Point North and Foster City; detection limit 2.7 $\mu g\ g^{-1}$ dry weight). Anderlini et al. (1975a, 1975b) reported concentrations of 0.1 to 4.9 ug g^{-1} dry weight for silver in sediments from several locations in the Bay. These data were referred to in Bradford and Luoma (1980), and it was noted that some values at least are enriched in Bay sediments by comparison to data for silver in average shale (about 0.1 $\mu g\ g^{-1}$ dry weight; see Krauskopf, 1967). "Average", "background" or "typical" concentrations of silver in coastal sediments were quoted as 0.01 to 0.5 $\mu g\ g^{-1}$ dry weight by Robertson and Carpenter (1976), and as 0.2 to 0.5 $\mu g\ g^{-1}$ by Katz and Kaplan (1981). The latter authors also suggested that concentrations of silver in sediments of 1-3 $\mu g\ g^{-1}$ indicated moderate to heavy enrichment, while levels of greater than 5 $\mu g\ g^{-1}$ dry weight are extremely enriched.

Hoffman and Meighan (1984) analyzed sediments from the western shore of central San Francisco Bay, in a study of the impact of combined sewer outfalls. Of the 16 sites surveyed, most exhibited only moderate levels of silver (0.4-1.8 $\mu g\ g^{-1}$ dry weight). However, one site at the head of Islais Creek exhibited 9.0 $\mu g\ g^{-1}$ dry weight, and two sites in Mission Creek exhibited silver concentrations of 9.5 and 16 $\mu g\ g^{-1}$ dry weight. These

levels are indicative of severe local contamination by silver.

Additional data on silver in Bay-Delta sediments are available in the reports of Thomson et al. (1984), Chapman et al. (1986), and Luoma et al. (1984; and in press). Thomson et al. (1984) reported data for silver, copper, and zinc in sediments of a small area near the Palo Alto sewage treatment plant outfall. This region was known to be heavily contaminated by silver from previous studies of the deposit-feeding bivalve Macoma balthica (see below). Surface sediments (upper 5mm) were collected at 9 sites around the outfall and in the nearby Palo Alto Yacht Harbor and were digested using a nitric-sulphuric acid reflux technique (this effectively measures total metals in the sample). The results for silver are shown in Fig. 3, and clearly indicate enrichment of surface sediment by the element at the region of the sewage treatment plant outfall. Other possible local sources of silver were not considered to signficantly contribute to the enrichment of this element in sediments at this location. It is notable that silver concentrations varied somewhat seasonally, but were in the range of 2.5 to 4 $\mu g\ g^{-1}$ dry weight close to the outfall, which indicates considerable enrichment. Concentrations decreased more rapidly in a northerly direction than to the south, which may reflect the local hydrology and a propensity for the effluent plume from the treatment plant to move in a southerly direction in most conditions.

The sediment quality triad data of Chapman et al. (1986) involve bulk sediment chemistry at three locations (Islais Creek, Oakland, and San Pablo Bay), with three sites at each

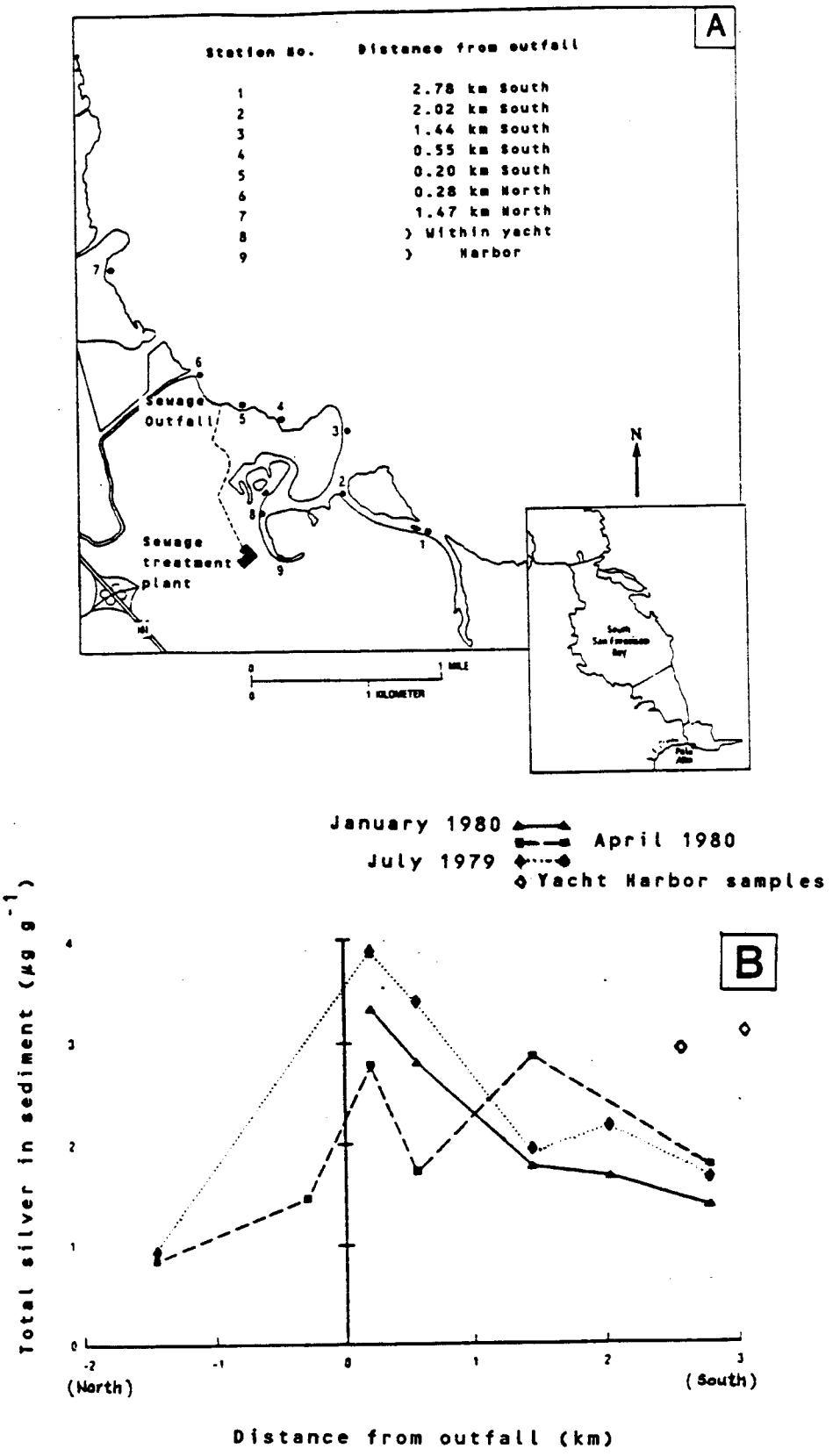


Fig. 3. Location of sampling sites (A) and concentrations of total silver in sediments (B) in $\mu g\ g^{-1}$ dry weight, for studies of silver in the Palo Alto area. After Thomson et al. (1984).

location. Standard EPA analytical methods were employed, with QA/QC of high quality, using recommendations from Keith et al. (1983). Total concentrations of silver at the three locations were 6.9 $\pm$ 2.1 $\mu g\ g^{-1}$ dry weight at Islais Creek, 2.0 $\pm$ 0.3 $\mu g\ g^{-1}$ at Oakland, and 1.2 $\pm$ 0.3 $\mu g\ g^{-1}$ at San Pablo Bay. The Islais Creek samples exhibited evidence of a decreasing gradient in contamination from the inner waterway to the mouth, for silver and several other elements.

Luoma et al. (1984; and in press) reported data for silver in sediments and clams (see below) from the area of Suisun Bay and the Sacramento/San Joaquin Delta. In general, silver levels were low in sediments from this area of the Bay, varying from 0.028 to 0.389 $\mu g\ g^{-1}$ dry weight. The mean value of all samples from 10 sites and several sampling times (n = 29 overall) was 0.150$\pm$0.086 $\mu g\ g^{-1}$ dry weight, indicating little enrichment of these northern Bay and Delta sediments for silver.

The above data provide a general picture of silver in Bay-Delta sediments, which is useful as a background to discussions below of data for this element in biota. Sediments from the north of San Francisco Bay and the Delta exhibit concentrations similar to "background" levels for silver, indicating little anthropogenic contamination from upriver sources. However, within the central and (especially) southern reaches of the Bay, silver is more abundant, and concentrations of the element in sediments are indicative of moderate enrichment in many areas, with heavy enrichment in a few locations (Islais and Mission Creeks and the Palo Alto area are notable in respect to the latter).

Silver in Bay-Delta Biota

Concentrations of silver in biota from the San Francisco Bay-Delta have been quite extensively studied, and these investigations are clearly of particular relevance in respect to many aspects of the potential biological effects of this element within the Bay-Delta ecosystem. Studies on bivalve molluscs are particularly enlightening, as these provide information on the bio-availability of the element, on its bio-accumulation, and on the general spatial distribution of areas of silver enrichment in the Bay-Delta.

Early data on silver in bivalve molluscs in the Bay were reported by Graham (1972), who found levels of 1.3 $\mu g\ g^{-1}$ and 7.3 $\mu g\ g^{-1}$ dry weight in Mytilus edulis and Tapes japonica respectively, both samples being taken from near Coyote Point. Wyland (1975) supplemented these data, reporting concentrations of 5.4 $\mu g\ g^{-1}$ and 4.4 $\mu g\ g^{-1}$ dry weight for silver in Mya arenaria from Coyote Point and Redwood Creek respectively, with levels of 13.4 $\mu g\ g^{-1}$ for Tapes japonica and 1.7 $\mu g\ g^{-1}$ for Mytilus edulis from Redwood Creek.

The first relatively comprehensive survey of silver in Bay bivalves was, however, conducted by Girvin et al. (1975). These authors sampled six species of bivalves at up to nine locations in the Bay, ranging from Tara Hills to Redwood Creek (Fig. 4). All samples other than Crassostrea gigas were subjected to a depuration period to void gut contents (see NAS, 1980). C. gigas was dissected to remove the gills, mantle and hepatopancreas for separate analysis; the whole soft parts of other species were analyzed. Analysis employed the unusual technique of X-ray

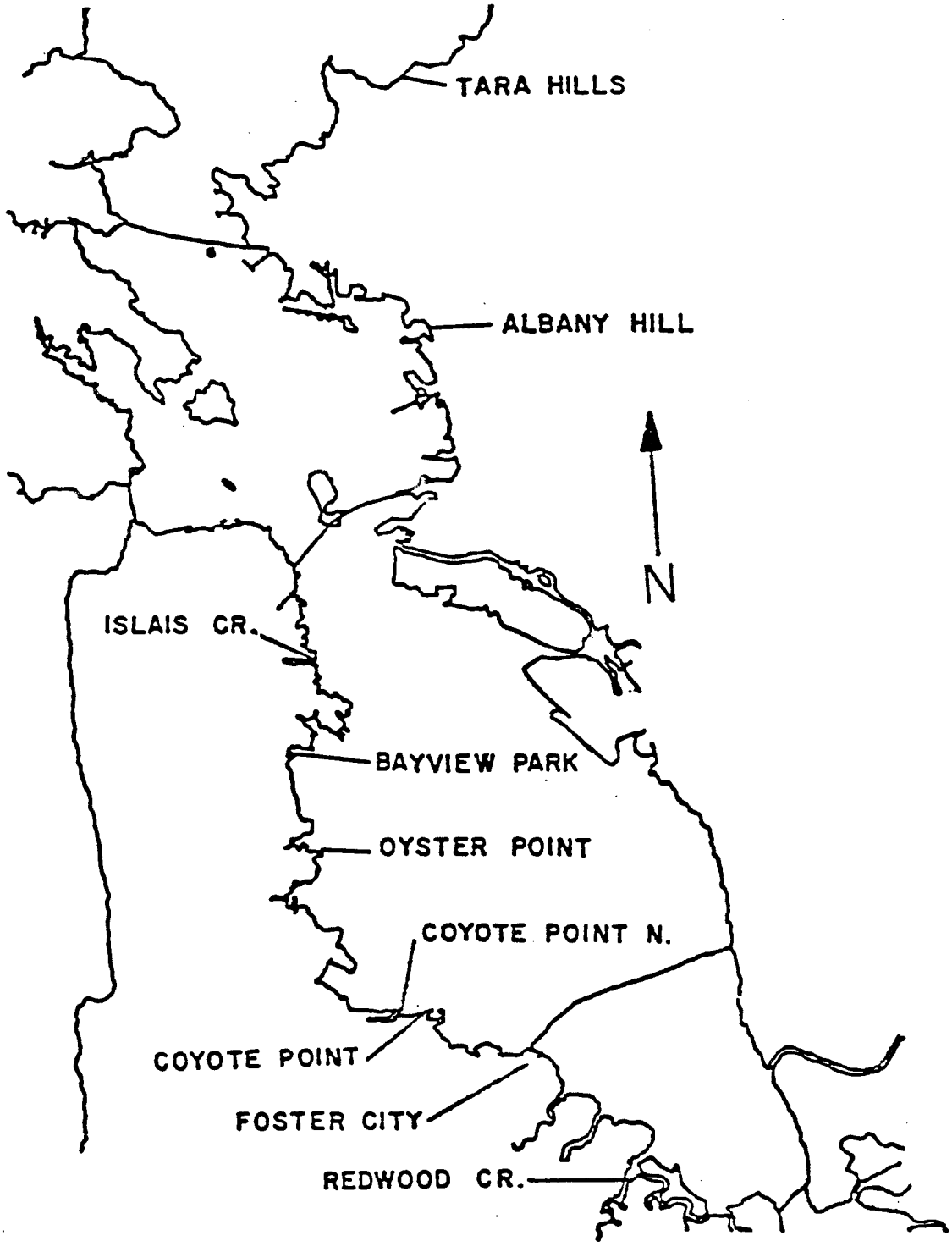


Fig. 4. Map of San Francisco Bay, showing sampling locations for bivalve molluscs in the studies of Girvin et al. (1975).

fluorescence spectrometry for elements other than mercury; the latter was analysed by isotope-shift Zeeman atomic absorption spectrophotometry. Quality control involved the analysis of the orchard leaves standard from the National Bureau of Standards. Two of the six species (Ischadium demissum and Crassostrea gigas) were taken at only one location in the Bay. I. demissum was found only at Tara Hills, and exhibited undetectable silver levels in whole soft tissues (less than 1.5 $\mu g\ g^{-1}$ dry weight). The Pacific oyster, Crassostrea gigas, was taken at Redwood Creek; silver levels in this sample were compared to those in C. gigas from Tomales Bay. These data, shown in Table 2, revealed very considerable enrichment of silver in Redwood Creek oysters compared to the Tomales Bay sample. Enrichment ratios between the two samples were 43 for gill and mantle tissues, and 103 for hepatopancreas tissues. The hepatopancreas is well known as a storage site for excess metals in molluscs, including bivalves.

Silver concentrations in mussels (Mytilus edulis) were reported by Girvin et al. (1975) to be less than the detection limit of 1.5 $\mu g\ g^{-1}$ dry weight at all eight sites sampled for this species. However, the other three species surveyed exhibited at least some data points above detection limits (see Fig. 5). In all cases, a consistent gradient in silver concentrations was found in these species, concentrations increasing with distance south in the Bay towards Redwood Creek. Mya arenaria exhibited mean silver levels of 80 $\mu g\ g^{-1}$ dry weight at Redwood Creek, compared to 33.7 $\mu g\ g^{-1}$ dry weight in Tapes japonica. The considerable differences between the absolute levels of silver accumulated in the different species are not

Table 2. Concentrations of silver (means ± standard deviations, $\mu g\ g^{-1}$ dry weight) in specific tissues of the Pacific oyster, Crassostrea gigas, from Redwood Creek (San Francisco Bay) and Tomales Bay on the California coast. After Girvin et al. (1975).

Tissue	Redwood Creek	Tomales Bay	Enrichment Factor*
Gill	162 + 28.7	3.8 + 0.5	42.6
Mantle	137 + 36.0	3.2 + 0.8	42.8
Hepatopancreas	196 + 12.6	1.9 + 0.5	103.2

*"Enrichment factor" denotes ratio of mean silver concentrations of Redwood Creek oyster tissues to those of Tomales Bay oyster tissues.

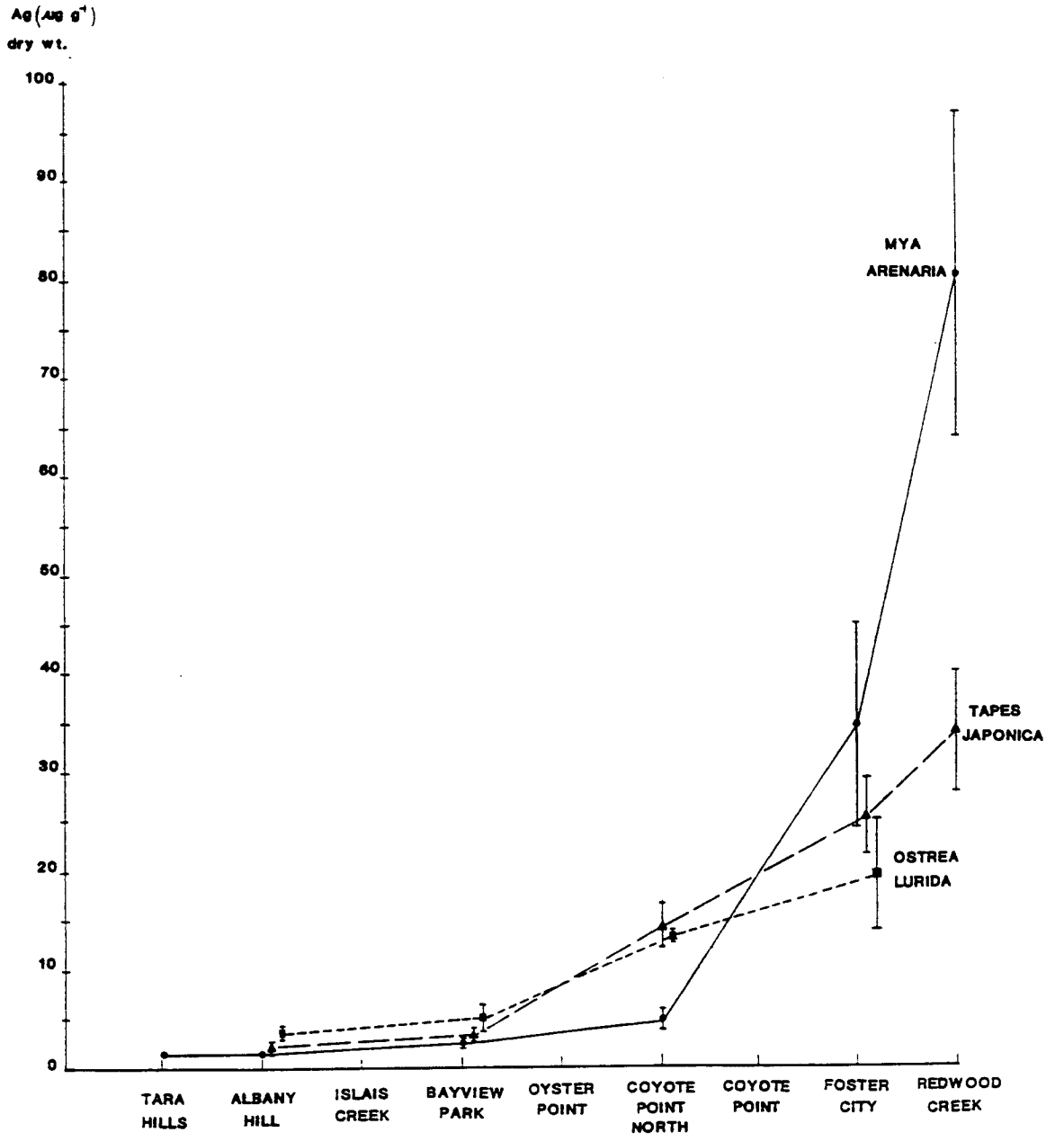


Fig. 5. Concentrations of silver ($\mu g\ g^{-1}$ dry weight) in samples of the eastern softshell clam (Mya arenaria), the Japanese littleneck clam (Tapes japonica) and the Olympic oyster (Ostrea lurida) in San Francisco Bay. After Girvin et al. (1975).

unusual, being found also for other elements and species (e.g. see Segar et al., 1971). However, the concentrations of silver attained in some of the species (M. arenaria, T. japonica and C. gigas in particular) are exceptionally high, and are indicative of extreme contamination of Redwood Creek by silver. These samples were taken within the confined waterway itself (Girvin et al., 1975, page 7), which must have been accepting a highly contaminated industrial effluent discharge at the time of this study. Later data involving other species and authors are discussed below.

In 1976, the EPA commenced funding of a three-year study of pollutants around U.S. coasts, utilizing bivalves as bio-indicators or "sentinel organisms." San Francisco Bay was studied by sampling mussels (Mytilus edulis) at several locations in the northern and the southern reaches of the Bay, and analyzing pooled samples from these two areas. In 1976, composite samples from 11 locations in the north of the Bay and locations in the South Bay were used (Goldberg et al., 1978), but in 1977 only 5 samples in each part of the Bay were collected. In 1978, the north of the Bay was again sampled for metal analysis at 5 sites, but no mussels were collected in south San Francisco Bay (Goldberg et al., 1983). Data for the three years were as follows:

North of the Bay: 0.5 $\mu g\ g^{-1}$ (1976); 0.6 $\mu g\ g^{-1}$ (1977); <0.3 $\mu g\ g^{-1}$ (1978)

South Bay: 2.3 $\mu g\ g^{-1}$ (1976); 2.4 $\mu g\ g^{-1}$ (1977).

The generally greater enrichment of silver in the South Bay is

confirmed by these data, although no specifics on spatial trends in enrichment may be discerned because of the compositing of samples from several locations.

Risebrough et al. (1978) surveyed Mytilus edulis at 28 sites in San Francisco Bay, samples being collected in April 1976. Silver levels in these samples are shown in Fig. 6. In general, a modest enrichment of silver was found in M. edulis from the south of South Bay, in the Redwood City and Dunbarton Bridge areas.

Bradford and Luoma (1980) confirmed the general silver enrichment of South Bay by silver, using Tapes japonica and the snail Nassarius obsoletus. Data for T. japonica are shown in Table 3, and agree tolerably well with those from studies of Girvin et al. (1975), cited above. However, it is clear that seasonal fluctuations occur in the amounts of silver accumulated by T. japonica; this seasonality of silver levels is addressed in greater detail below. Table 4 shows data for silver in the gastropod snail Nassarius obsoletus. Bradford and Luoma (1980) used these data to argue that the primary silver source in the Bay was located close to Palo Alto, rather than at Redwood Creek. The Palo Alto sewage treatment plant was confirmed to be a significant source of silver by Thomson et al. (1984). Data for silver in sediments in this area have been discussed above (see Fig. 3); data for silver in the deposit-feeding bivalve Macoma balthica are shown in Fig. 7. Clear seasonal differences exist in the silver levels attained in clam tissues, although these do not correlate well to data for sediments. It is thus probable that only a portion of the total silver in sediments is available to the bivalve, which probably also accumulates silver from solution.

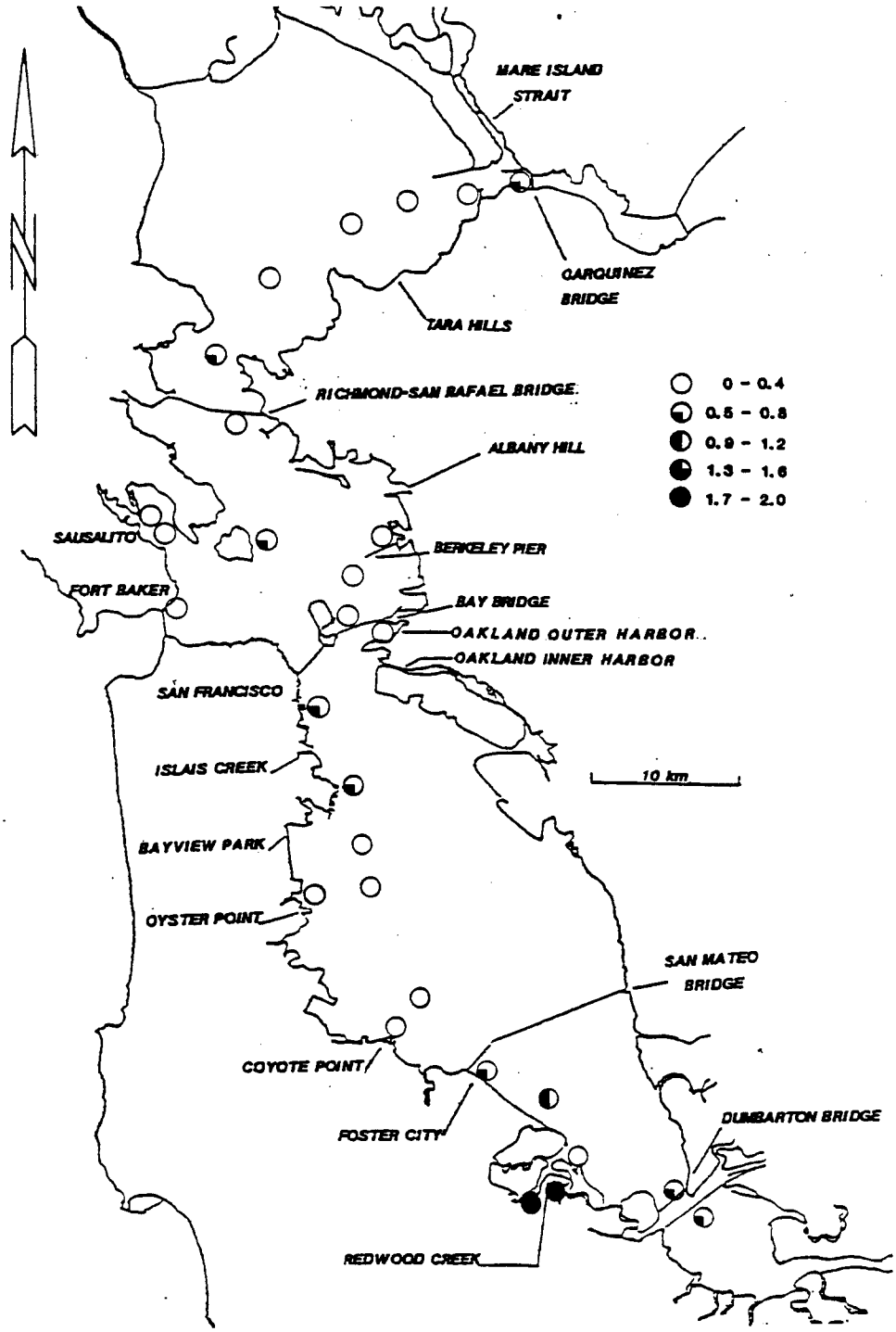


Fig. 6. Concentrations of silver (means, $\mu g\ g^{-1}$ dry weight) in whole soft parts of mussels (Mytilus edulis) from 28 locations in San Francisco Bay. After Risebrough et al. (1978).

Table 3. Concentrations of silver ($\mu g\ g^{-1}$ dry weight) in whole soft tissues of the Japanese littleneck clam (Tapes japonica) from Princeton Harbor on the Pacific coast of California and from San Francisco Bay sites. After Bradford and Luoma (1980).

Station	Date	Silver
Princeton Harbor	January 1977	0.70
San Francisco Bay		
Bayview Park	January 1978	6.7
Bayview Park	March 1976	6.6
Coyote Point	August 1975	2.5
Foster City	March 1976	8.4
Foster City	July 1976	11
Redwood Creek	January 1976	16
Redwood Creek	July 1976	65

Table 4. Concentrations of silver (means, $\mu g\ g^{-1}$ dry weight) in soft tissues of the gastropod snail Nassarius obsoletus from San Francisco Bay. After Bradford and Luoma (198(

Station	Month (1978)	Silver Concentration
North San Pablo Bay	June	22
East Pinole Point	June	49
China Camp	June	50
San Leandro Bay	June	35
Bayview Park	May	47
Redwood Creek	July	150
East Dumbarton Bridge	May	150
Palo Alto	July	320

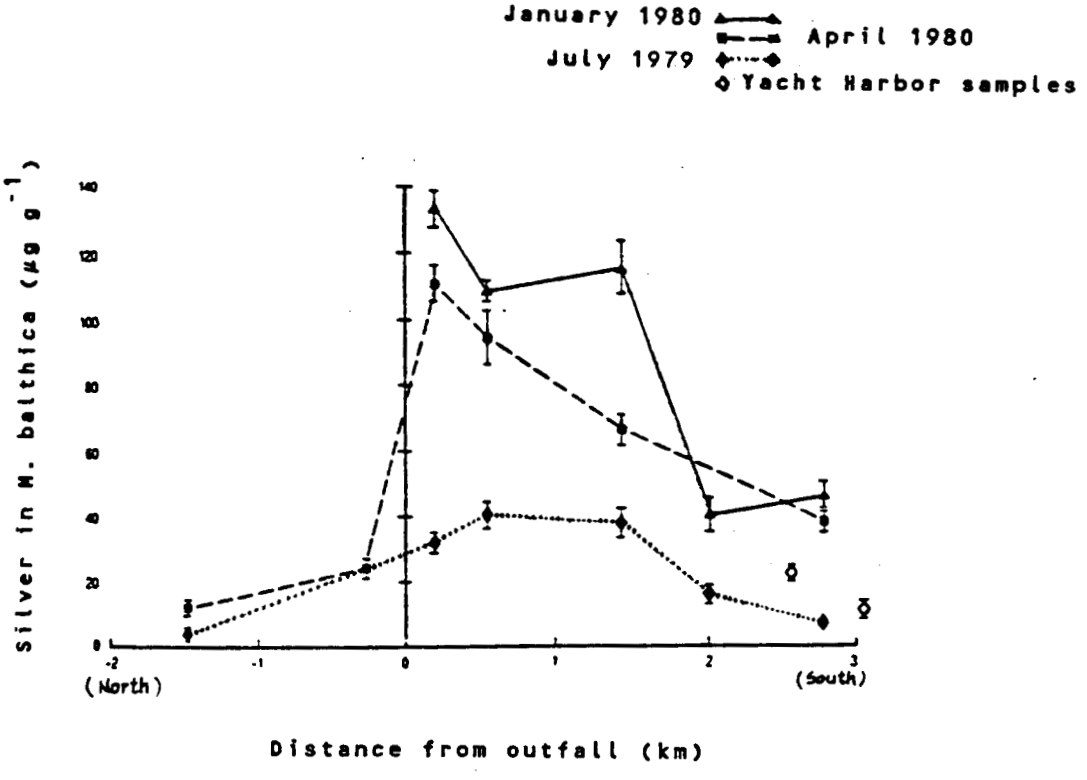


Fig. 7. Concentrations of silver (means and standard deviations, $\mu g\ g^{-1}$ dry weight) in the bivalve Macoma balthica from sampling sites close to the Palo Alto sewage treatment plant. See Fig. 3 for sampling locations. After Thomson et al. (1984).

Additional data relevant to silver in M. balthica are found in the reports of Luoma and Cain (1979) and Luoma et al. (1985). Luoma and Cain (1979) found that silver levels in M. balthica exhibited profiles throughout San Francisco Bay similar to those found in other species by Girvin et al. (1975; see Fig. 5) and by Bradford and Luoma (1980; Tables 3 and 4). Thus, silver concentrations in M. balthica increased substantially with distance from north to south in the Bay; maximum levels were seen at Palo Alto (Table 5). Luoma et al. (1985) reported a long-term data set for silver in M. balthica in the Bay, concentrating on seasonal fluctuations at the Palo Alto site. Silver levels at five sites were studied, the data largely matching those shown in Table 5 (Fig. 8). "Station 7", at Palo Alto, was by far the most contaminated site, silver concentrations in M. balthica varying with season up to maxima approaching 200 $\mu g\ g^{-1}$ dry weight (Fig. 9). The seasonal profiles generally exhibited maxima in winter. There was some evidence that changes in clam tissue weights contributed to the seasonal fluctuations seen (Strong and Luoma, 1981). However, correlations were also evident with parameters involving the Sacramento/San Joaquin Delta outflow. Luoma and Cloern (1982) reported a correlation of minimum summer concentrations in M. balthica from 1975 to 1980 with the ratio of silver discharge by the Palo Alto treatment plant to Delta outflow (Fig. 10A). Similarly, Luoma et al. (1985) reported a correlation of winter maxima in silver concentrations of these clams from Palo Alto with Delta discharge (Fig. 10B). It was hypothesized that Delta outflow rates defined mixing and residence times of contaminated waters in the South Bay, with

Table 5. Concentrations of silver (medians, $\mu g\ g^{-1}$ dry weight) in soft tissues of the clam Macoma balthica from Princeton Harbor on the Pacific coast of California, and from nine sites in San Francisco Bay. After Luoma and Cain (1979).

Station	Silver in M.balthica
Princeton Harbor	1-2
San Leandro Bay	3
Bayview Park	2
Burlingame	4
Hayward Landing	7
Foster City	6
Redwood Creek	13
Dumbarton Point	7
South Dumbarton Bridge	14
Palo Alto	104

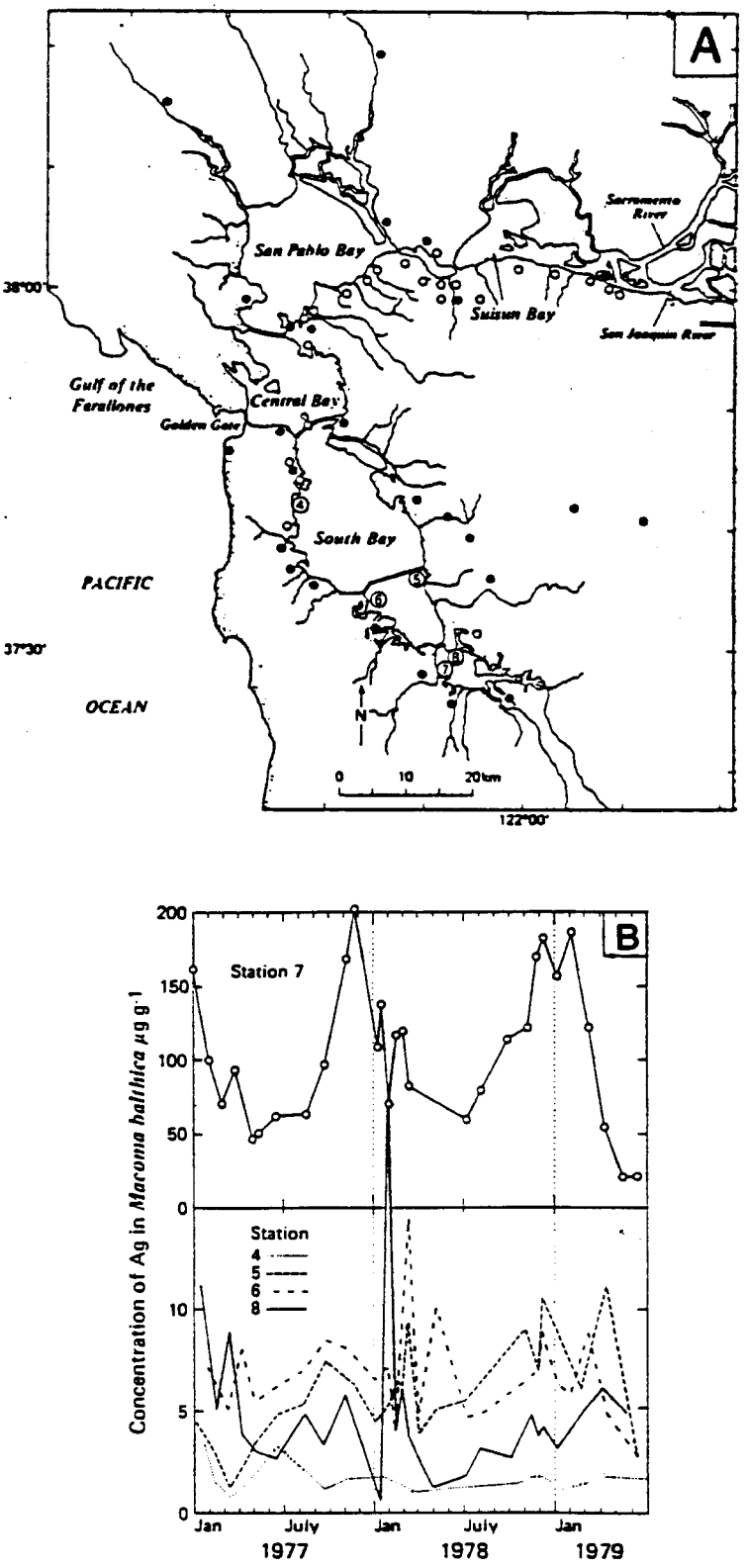


Fig. 8. (A) Sampling sites (numbered 4 to 8) for studies of silver in M. balthica. (B) Concentrations of silver i M.balthica (means, $\mu g\ g^{-1}$ dry weight) from sites 4 to 8. After Luoma et al. (1985).

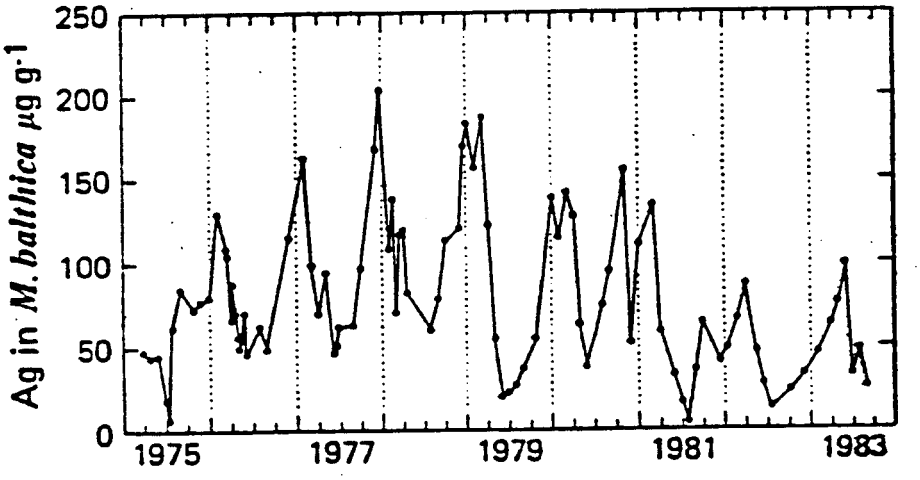
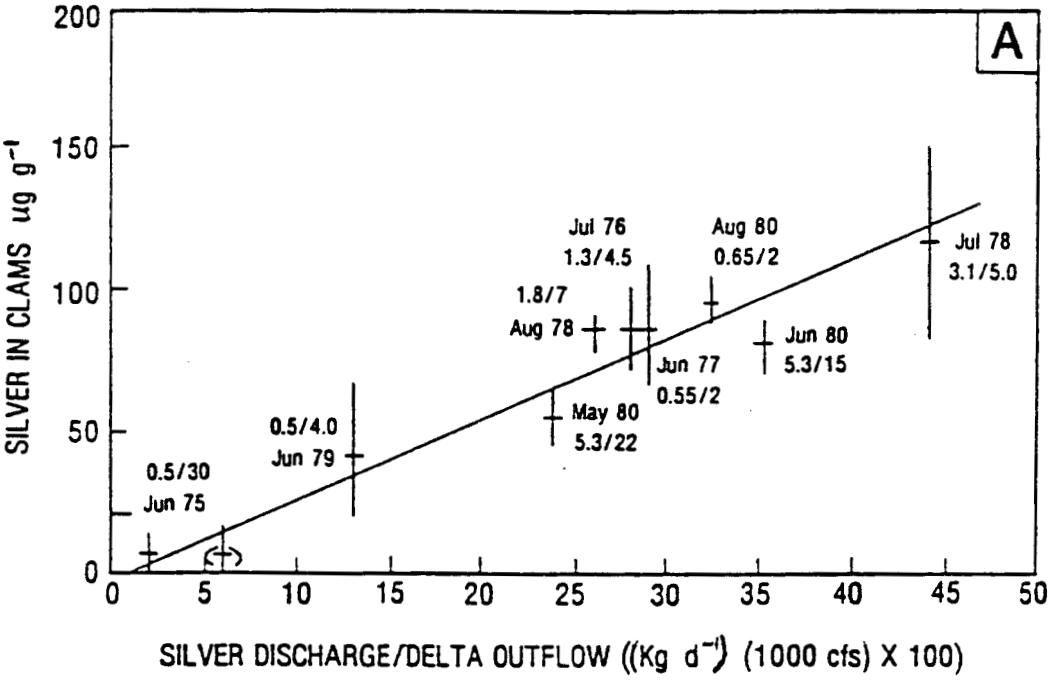


Fig. 9. Mean concentrations of silver ($\mu g\ g^{-1}$ dry weight) in soft tissues of Macoma balthica from station 7 near Palo Alto in South San Francisco Bay, between January 1975 and June 1983. After Luoma et al. (1985).



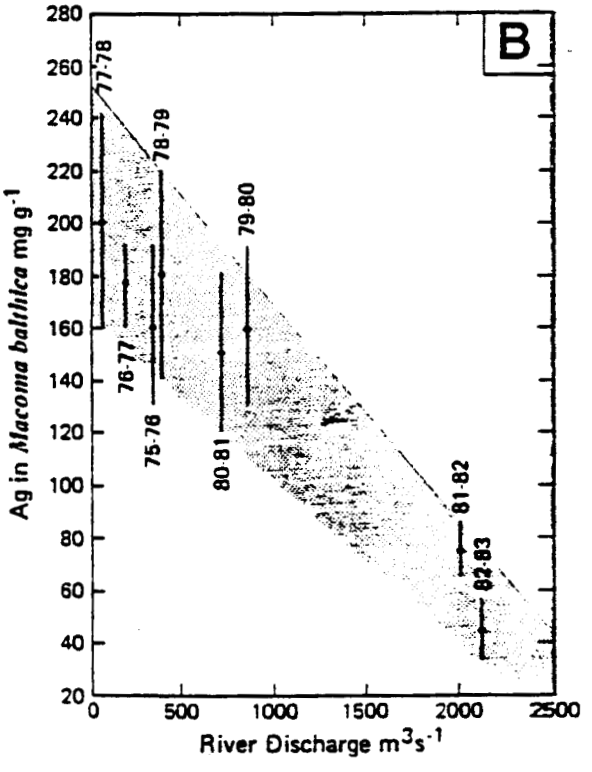


Fig. 10. (A) Correlation between summer minima in silver concentrations in Macoma balthica at Palo Alto and silver discharge at Palo Alto sewage treatment plant normalised to Delta outflow. Date of samples and ratios of discharged silver to Delta outflow are shown. After Luoma and Cloern (1982). (B) Correlatic of winter maxima in silver concentrations in M. balthica from Palo Alto and Delta discharge. After Luoma et al. (1985).

higher Delta outflows leading to greater flushing of South Bay and a reduction in silver contamination. It should be noted that this hypothesis is not proven, and that alternative explanations for the correlation shown in Fig. 10 are possible. For example, the correlation may in fact depend on local inflows (which may also correlate to Delta outflows) rather than to Delta outflows *per se*. However, hydrodynamic models of the Bay provide some support for the dependence of flushing rates in the South Bay on Delta outflow (Conomos, 1979; Walters *et al.*, 1985).

Also of importance with respect to silver levels in bivalve molluscs are data from the California State Mussel Watch Program. This program has been active in the Bay-Delta since the late 1970s. Data are published both in annual reports and (occasionally) in the open literature. The program employs mostly transplanted mussels (*Mytilus californianus*) to monitor pollutants in the Bay, although occasionally samples of native Bay mussels (*Mytilus edulis*) are also taken for analysis. Analyses are performed by the Moss Landing Marine Laboratory, which is a highly respected analytical facility. Quality control and quality assurance procedures are excellent and the data generated are considered of high reliability. The State Mussel Watch data from 1980 to 1986 for silver in Bay mussels are shown in Table 6. It should be noted that values for native Bay mussels (*M. edulis*) should not be directly compared to those for transplanted *M. californianus*, as species commonly differ in absolute levels of elements accumulated (Phillips, 1977, 1980). The 1980-1982 data were recently summarized by Smith *et al.* (1986). Levels of silver found in mussels from these three years

Table 6. Concentrations of silver (means, ug g^{-1} dry weight) in whole soft parts of transplanted Mytilus californianus or native M. edulis[a] at 33 sites in San Francis Bay. All data from the California State Mussel Watch Program (Hayes et al., 1985; Hayes and Phillips, 1986; Stephenson et al., 1986a).

LOCATION	STATION CODE	1980	1981	1982 (J/F)	1982 (O/N/D)	1982 RESIDENT (O/N/D)a	1983	1985
MARE ISLAND	300.20							0.083a
DAVIS POINT	301.00	0.023a			0.147			
POINT PINOLE	302.00	0.022a	0.330	0.090	0.158b		0.155	0.164
RICHMOND BRIDGE	303.00	0.217	1.067	1.133	0.509b			
SANTA FE CH. MOUTH	303.10							
RICHMOND INNER HARBOR	303.60							0.095
STAUFFER'S	304.00			0.333				
ANGEL ISLAND	305.00	0.256	1.040	1.467	0.433b			
FORT BAKER	306.00		1.083		0.481c			
TREASURE ISLAND	307.00	0.427	1.400	1.300	0.554c		0.409	0.687
ALAMEDA YACHT HARBOR	307.20							0.081a
OAKLAND IN. HARBOR WEST	307.30							
OAKLAND IN. HARBOR EMBC.	307.40							
OAKLAND BACK HARBOR	307.60							
HUNTER'S POINT	308.00		1.133	1.333	0.611c	0.315a		
SAN MATEO BRIDGE 8	309.00	1.397	1.860	1.233	0.546c	0.401a	0.295	0.611
SAN MATEO BRIDGE 8A	310.00			0.400				
SAN MATEO OLD BRIDGE	311.00			0.667				
BELMONT SLOUGH	312.00			0.900				
REDWOOD CREEK MOUTH	313.00		4.353	1.133	1.068c	0.549a	0.323	0.957
REDWOOD CREEK 10	314.00			2.933				
REDWOOD CREEK TOWERS	315.00			22.533	1.674b	0.970a		
REDWOOD CREEK TRDWNDS	316.00	0.086a		19.733	0.961b	0.638a		
REDWOOD CREEK STP	317.00				0.762			
SF PETES	318.00				2.133			
SF PULGAS	319.00				0.784			
SF AIRPORT	320.00				1.091			
DUMBARTON BRIDGE 14	321.00	0.273a	2.647	1.733	0.604	0.426a	0.475	0.625
NEWARK SLOUGH	324.00			0.467				
CHANNEL 17	325.00			0.433				
PALO ALTO 8	326.00			2.700		0.267a		
PALO ALTO YACHT	327.00			1.867				
ALVISO SLOUGH	328.00			0.367				

J/F/O/N/D: January/February/October/November/December, all 1982

a Resident Mytilus edulis.

b Mean of two values.

c Mean of three values.

are shown in Fig. 11. A general increase in concentrations of silver with distance south in the Bay was once again seen, from very low levels in San Pablo Bay to moderate-to-high concentrations in the south of South Bay. Exceptionally high levels of silver were found in transplanted M. californianus at two sites in Redwood Creek in January 1982. However, samples of native M. edulis from 1980 and late 1982, and of M. californianus from late 1982, could not confirm these data and no source of silver was identified (Martin, 1985). It is probable that a transient increase in ambient silver occurred in Redwood Creek during the period from October 1981 to January 1982 (corresponding to the period when transplanted mussels were present in the Creek). Smith et al. (1986) reported that silver in the mussels exhibited a significant correlation with station distance from the north of the Bay, in each of the three years (Fig. 12). Data in preparation by Smith on silver concentrations in seawater from the Bay show similar trends (D. Smith, personal communication).

The very low discharge of silver from the Sacramento/San Joaquin system is confirmed by data of Luoma et al. (1984, and in press) on silver levels in clams (Corbicula sp.) from Suisun Bay and the Delta. Concentrations of 0.061 to 0.332 ug g^{-1} dry weight were found, which are similar to levels of the element in Corbicula species from pristine areas. In addition, the Toxic Substances Monitoring Program (which analyzes fish tissues and invertebrates to screen large geographical areas for contaminants) reported low concentrations of silver throughout the Sacramento/San Joaquin catchment, with the occasional

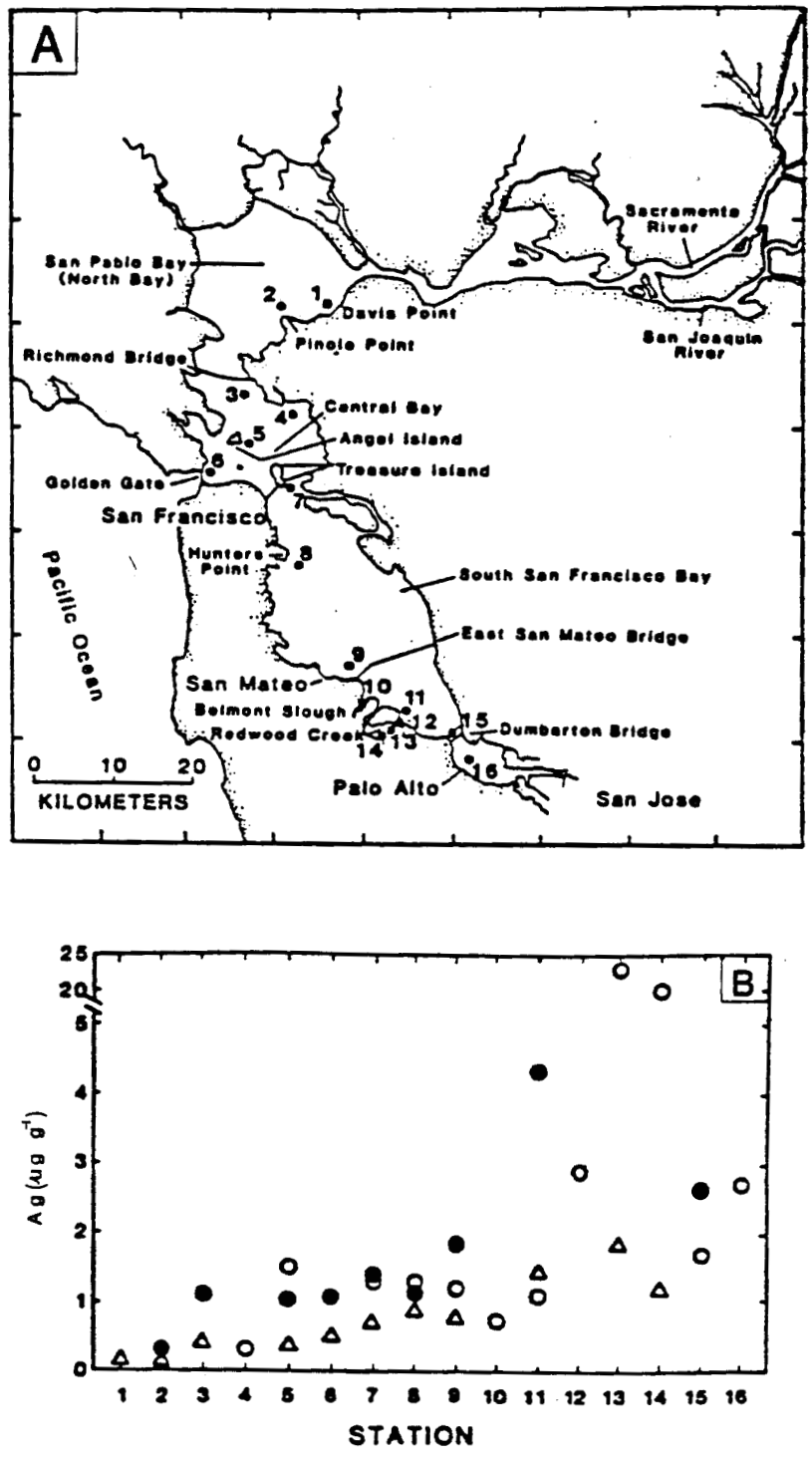


Fig. 11. (A) Locations of 16 State Mussel Watch Program sites in 1980-82. (B) Silver concentrations ($\mu g\ g^{-1}$ dry weight) in transplanted mussels (Mytilus californianus) in 1980-82. 1980 data denoted by filled circles; 1981 data by open circles; 1982 data by triangles. After Smith et al. (1986).

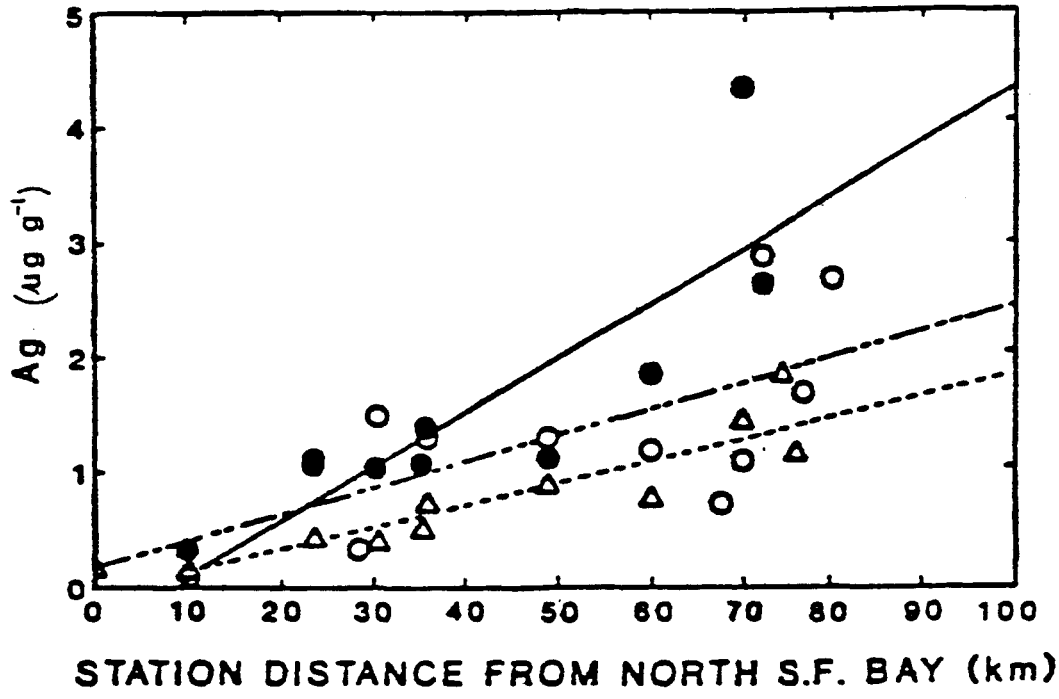


Fig. 12. Correlation between silver in transplanted mussels (Mytilus californianus) in San Francisco Bay in 1980-82 and distance from the north of the Bay. Year 1, closed circles; $y=0.047x-0.365$, $r=0.84$ ($p<0.005$). Year 2, open circles; $y=0.023x+0.174$, $r=0.66$ ($p<0.02$). Year 3, triangles; $y=0.019x-0.048$, $r=0.91$ ($p<0.001$). After Smith et al. (1986).

exception of moderate values in the extreme north of the Sacramento River. The latter area surrounds the Shasta Dam, including the McCloud River, the Pit River, and the Sacramento River at Keswick (e.g. SWRCB, 1986). It is probable that this enrichment arises from mining activities, but little of the released silver appears to reach the Delta or the Bay, or at least if it does so, it is very highly diluted.

Summary

The available data for silver in the San Francisco Bay-Delta ecosystem provide a generally consistent picture of this important and highly toxic element. Very little silver is discharged to the estuary in its northern reaches, and concentrations of the element in the Delta and in Suisun Bay are low, and are consistent with data for pristine environments. However, the central and southern reaches of San Francisco Bay are dominated by silver discharged from at least one major source. The known source is the Palo Alto sewage treatment plant, which is accepting influent industrial effluents containing high levels of silver. Additional sources may be suspected in Redwood Creek (possibly intermittent) and Islais Creek, but the Palo Alto source (and perhaps other sources in lower South Bay) appears to dominate the overall Bay profiles. Considerable contamination of sediments and shellfish has been documented; clearly, the discharged silver is of significant bio-availability. However, very little information exists on the possible transfer of this discharged silver through the food web, or on its toxic effects. Studies of silver levels in harbor

seals in the Bay (Risebrough et al., 1978) produced equivocal results; however, the migration of seals probably prevents their accumulating very high levels of elements in areas of localized enrichment. Ohlendorf et al. (1986c) found high concentrations of silver in livers of diving ducks (greater scaups and surf scoters) from southern San Francisco Bay, particularly in the Redwood City and Dumbarton Bridge area. It is not known whether this accumulation of silver by these ducks implies a toxicological hazard to the birds. There is a clear opportunity for additional research on the presence and toxic effects of silver in South Bay biota, both in respect to invertebrates and vertebrates.

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B. COPPER

Introduction

Copper is mobilized by man's activities at a rate of 10 to 15 times its estimated natural mobilization by geochemical processes, the latter being about 375,000 tonnes annually (Phillips, 1980). The toxicity of copper to aquatic biota is very considerable; generally this element is ranked as the third most toxic of the more common trace metal contaminants, after mercury and silver (Waldichuk, 1974). The precise chemical speciation of copper is important in defining its toxicity to biota. In freshwater ecosystems in particular, complexation and chelation of the element may moderate its toxicity considerably (Mantoura et al., 1978).

Klapow and Lewis (1979), in a review of California marine water quality standards, noted that the margin between reported concentrations of copper in seawater and levels known to be at least chronically toxic to marine biota was very small (Fig. 13). This resulted in problems in identifying an acceptable water quality standard for copper that was greater than average seawater concentrations of the element, but not likely to give rise to chronic toxic effects. A water quality standard of 5 $\mu g\ L^{-1}$ was eventually proposed, and it was noted that reductions in copper contents of effluents might be required to meet this standard in receiving waters. By comparison, the most recent EPA recommendation is that the 1-hour average concentration of copper should not exceed 2.9 $\mu g\ L^{-1}$ more than once every 3 years on the average (U.S. EPA, 1986).

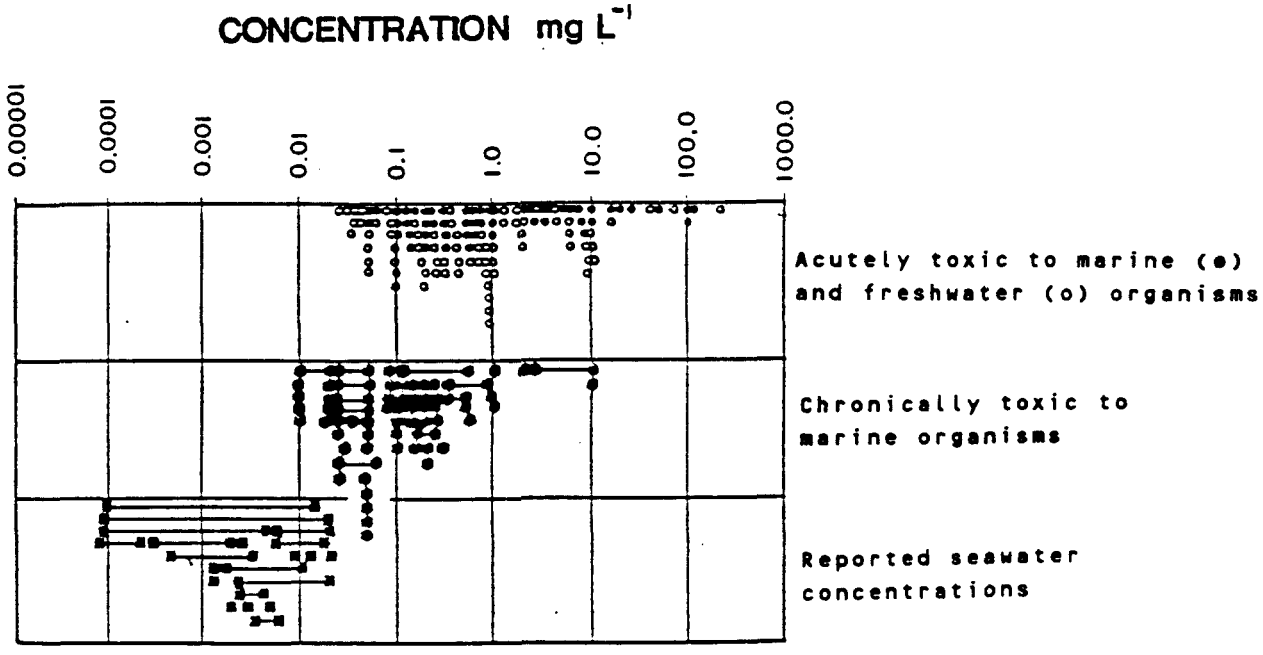


Fig. 13. Concentrations of copper reported in seawater, found to be chronically toxic to marine organisms, and of acute toxicity to aquatic biota. After Klapow and Lewis (1979).

Copper in Bay-Delta Waters

Reliable data for copper in San Francisco Bay-Delta waters have been reported by Girvin et al. (1978), Eaton (1979b) and Gordon (1980). Each of these studies employed sampling and analysis methods designed to avoid extraneous sample contamination, which is of great importance in such investigations. The data of Girvin et al. (1978) on Central and South Bays can be compared to the results of Eaton (1979b) for the northern reach of San Francisco Bay, although it should be noted that certain methodological differences existed between th two studies (e.g. in pore sizes of filters used). Girvin et al. (1978) noted increased concentrations of dissolved copper with distance south from the Golden Gate (Fig.14). There was little variation in profiles between the five survey dates, and maximum concentrations in the South Bay varied between about 2.5 and 4.0 $\mu g\ L^{-1}$. On average, about 60% of the total copper present was i the dissolved form.

In the northern reach of San Francisco Bay, Eaton (1979b) reported remarkably similar data. A mixing profile describing dissolved copper levels and their variation with salinity is shown in Fig. 15. There were indications of non-conservative behavior in the Delta (involving either desorption or adsorption of copper between solution and particulates, and/or copper uptak by biota in the turbidity maximum or null zone), but no consistent effects were observed here. A notable hump in the mixing profile at about 26% salinity indicated copper-containing discharges of significance within the estuary, somewhere in the region of southern San Pablo or northern Central Bays. Data for

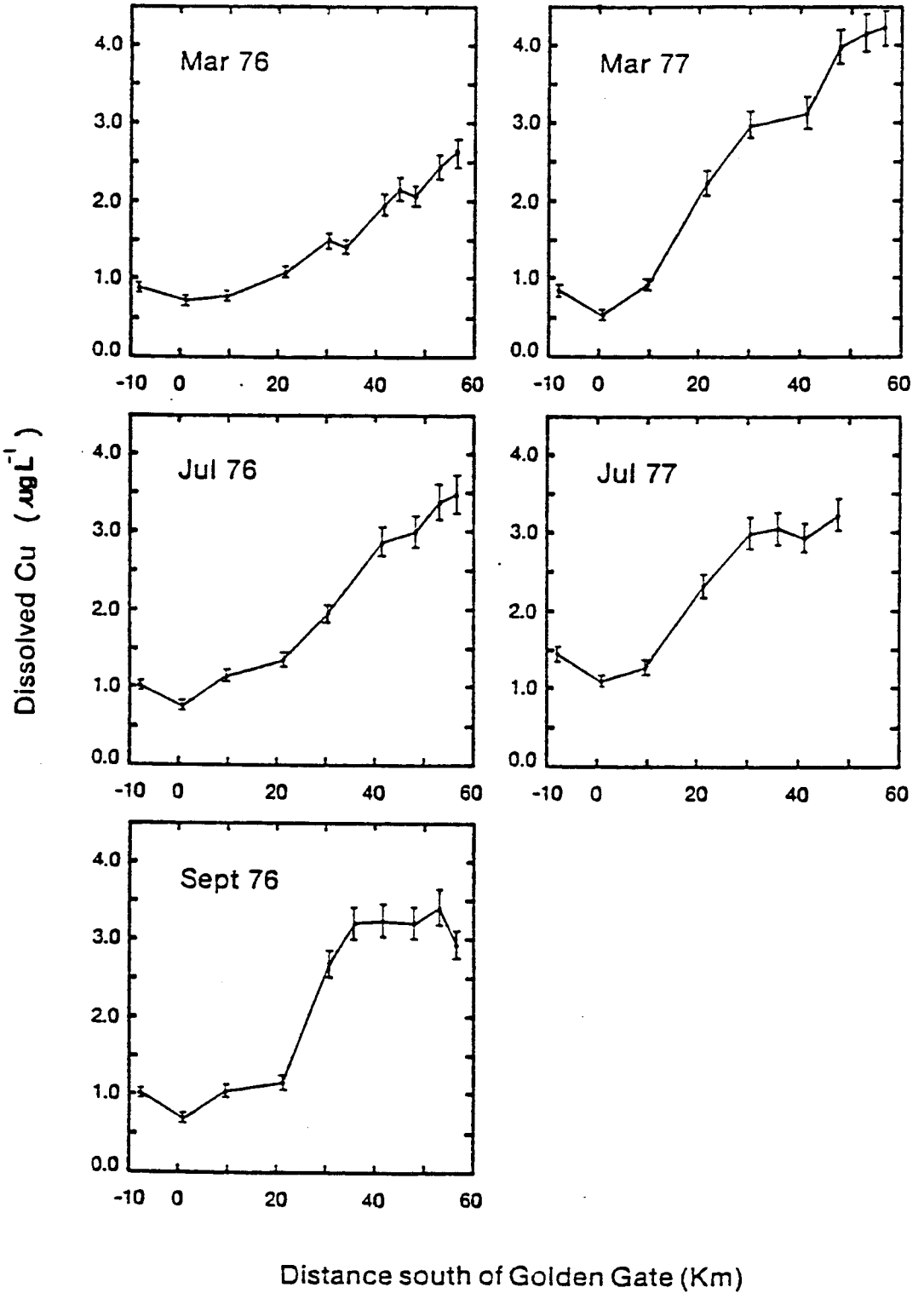


Fig. 14. Concentrations of soluble copper ($\mu g\ L^{-1}$) in Central and South Bay waters, 1976-77. After Girvin et al. (1978).

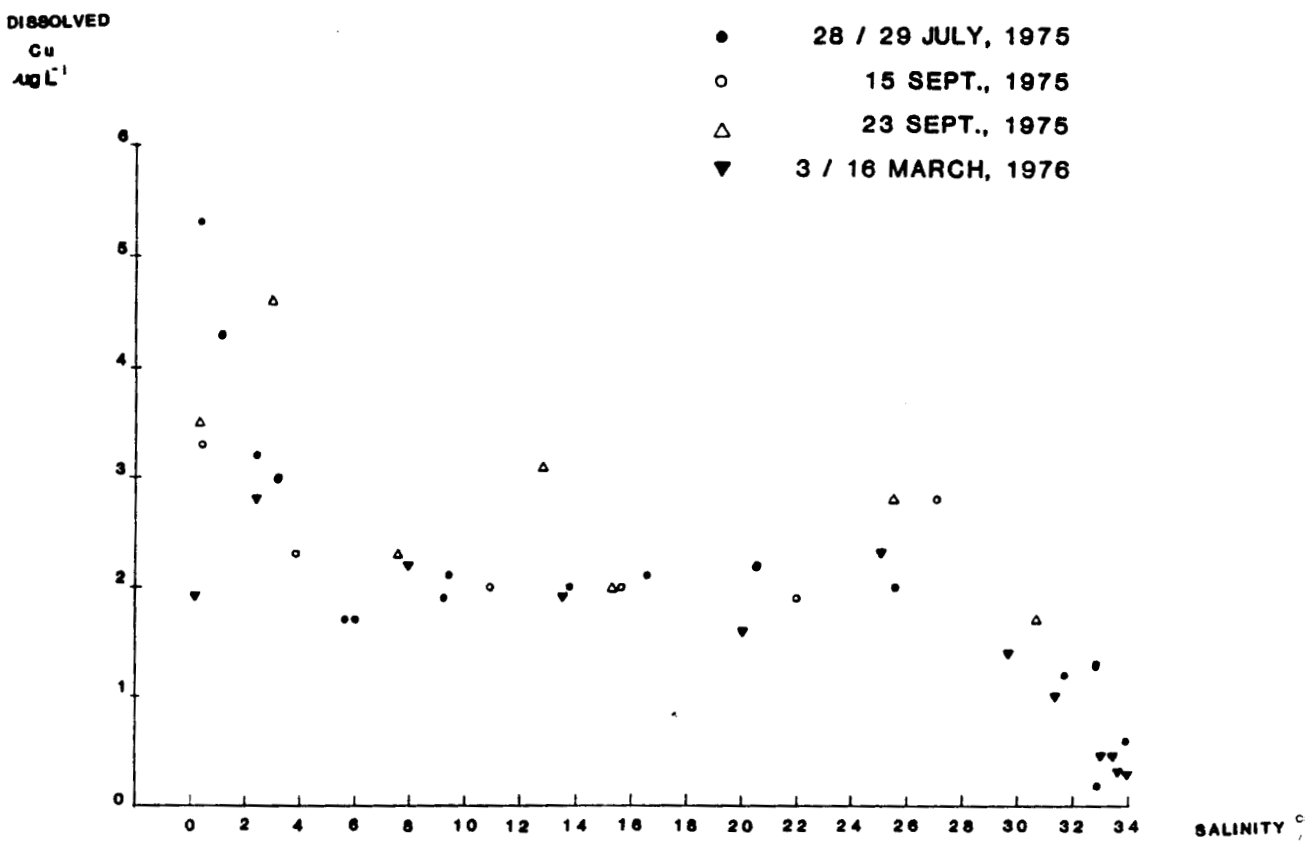


Fig. 15. Concentrations of dissolved copper ($\mu g\ L^{-1}$) in the northern reach of San Francisco Bay, discharge plumes from the Bay, and at the Farallon Islands. After Eaton (1979b).

the Farallon Islands showed very low copper levels of 0.25 to 0.6 $\mu g\ L^{-1}$; these are characteristic of open ocean concentrations in areas of upwelling (Bruland et al., 1977). It is clear from these data and those of Gordon (1980) that San Francisco Bay acts as a significant source of copper to the Pacific coastal waters of California.

Copper in Bay-Delta Sediments

Concentrations of copper in sediments of the Bay-Delta ecosystem have been the subject of numerous studies. Risebrough et al. (1978) summarized the data available to 1977 (Fig. 16), and noted a trend towards copper enrichment in nearshore stations of South Bay and in most of San Pablo Bay, with generally lower levels of copper in sediments of Central Bay and the Golden Gate area. Localized areas of particular copper enrichment were present in the sediments of the eastern San Francisco peninsula, Burlingame, and Palo Alto.

Other authors reported similar data (e.g. see Bradford and Luoma, 1980), and noted that the sediments of most areas of the Bay-Delta were not markedly contaminated by copper compared to some other coastal areas, e.g. Los Angeles Harbor.

Eaton (1979a) reported the results of differential extraction experiments on metals in sediments from San Francisco Bay. He found that total copper in sediments decreased in the following geographical order of embayments: San Pablo Bay > "North Bay" (Suisun Bay and Carquinez Strait) ≈ South Bay > Central Bay. Differential extractions were performed as follows:

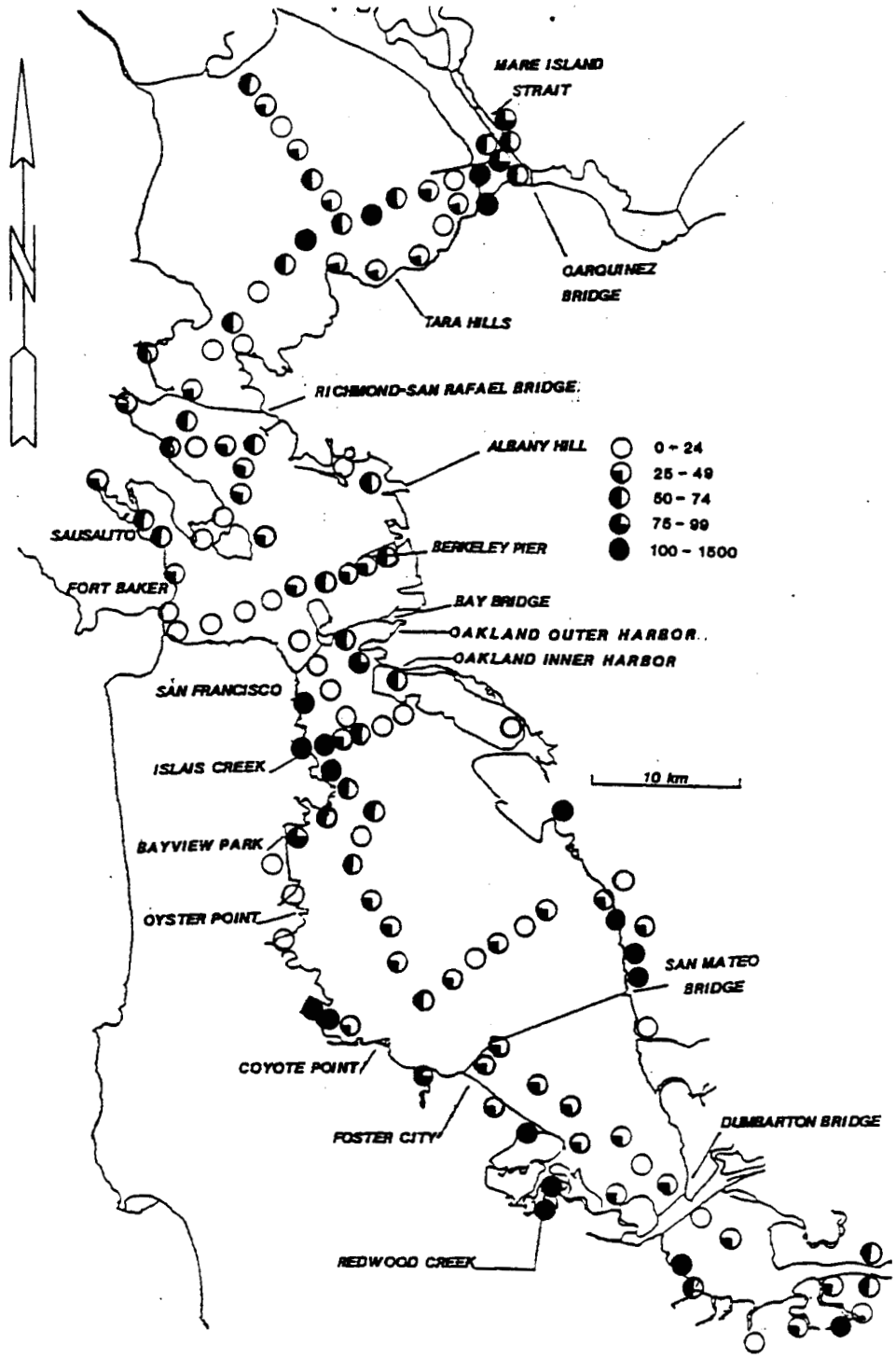


Fig. 16. Concentrations of copper ($\mu g\ g^{-1}$ dry weight) in sediments of San Francisco Bay. Compilation of data from various authors; after Risebrough et al. (1978).

Step 1: 24-hour leach of freeze-dried sediments with 0.1M pyrophosphate solution at pH 10, after Ball and Beaumont (1972). This removes organically bound metals.

Step 2: After centrifuging, the solids were leached for 4 hours in the dark with 0.2M ammonium oxalate-oxalic acid at pH 3.3, after LeRiche and Weir (1963). This treatment removes adsorbed metals or those associated with amorphous iron oxides.

Step 3: Digestion of the residue from Step 2 by $HNO_3/HClO_4/HF$. This measures total residual metals (including those within the crystalline matrix of the sediment particles).

The results of these experiments are shown in Fig. 17. In general, relatively few spatial differences existed in copper distribution among the three fractions of Bay sediments. Thus, residual copper constituted about 50% of total copper in these samples, with organically bound metals constituting approximately an additional 30%. Differences between surface and subsurface sediments were also minor, which probably reflects the high degree of dynamic resuspension/resedimentation of sediments in much of the Bay. Seasonal variations were at least partially related to changes in grain size of the sediments sampled (Eaton, 1979a; Thomson-Becker and Luoma, 1985). It was noted that, by contrast to some elements (Co, Fe, Mn, and Ni), both copper and zinc profiles indicated significant sources within the Bay, as opposed to a complete predominance of riverine sources.

Data on localized enrichment of sediments by copper are useful in indicating probable sources of such within-Bay loads. Luoma and Cain (1979) noted particular enrichment of sediments by copper at Palo Alto, Redwood Creek, and San Leandro Bay. Thomson

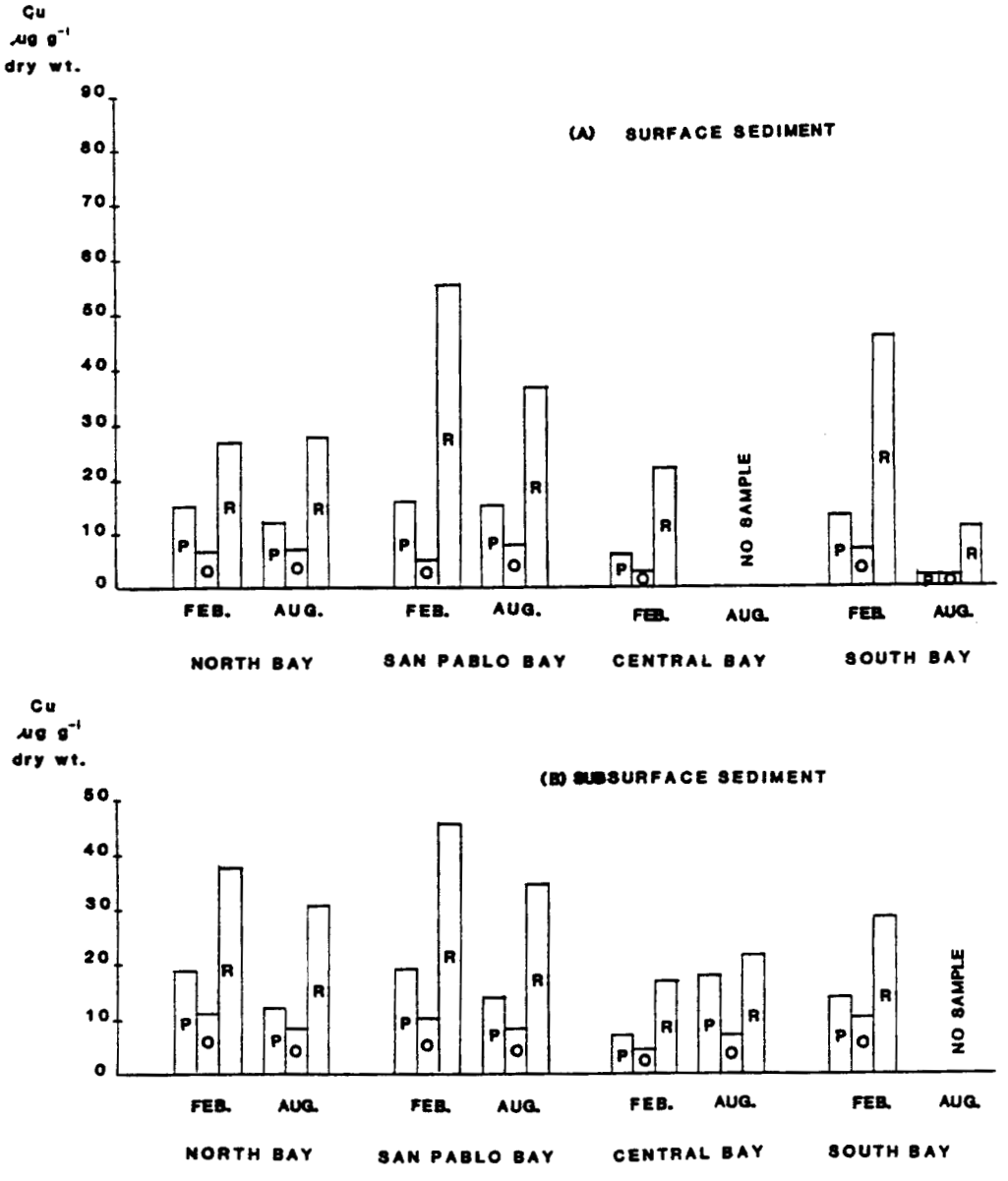


Fig. 17. Concentrations of copper released from sediments by a three-stage differential extraction process. See text for details of methodology.
P: Pyrophosphate leach;
O: Ammonium oxalate-oxalic acid leach;
R: Residual metals.
After Eaton (1979a).

et al. (1984) investigated the comparative importance of four potential sources of the element near Palo Alto, including the Palo Alto sewage treatment plant, a shoreline landfill, a stream receiving urban run-off (San Francisquito Creek), and the Palo Alto Yacht Harbor. Both sediments (Fig. 18) and clams (see below) indicated that the sewage treatment plant outfall constituted the major source of copper in the area.

Hoffman and Meighan (1984) and Chapman et al. (1986) found Islais Creek sediments to be unusually highly contaminated by copper. The former authors reported a concentration of 184 $\mu g\ g^{-1}$ dry weight for copper in sediments from the head of Islais Creek, whereas Chapman et al. (1986) found concentrations of 130, 98, and 68 $\mu g\ g^{-1}$ dry weight of the element at three stations moving sequentially seaward towards the Creek Mouth. Hoffman and Meighan (1984) also found high levels of copper in Mission Creek sediments (172 and 293 $\mu g\ g^{-1}$ dry weight); values at 13 other sites in the Bay ranged from 36 to 83 $\mu g\ g^{-1}$.

Copper in Bay-Delta Biota

Studies on copper in biota of the Bay and Delta have largely employed bivalve molluscs. The mussels Mytilus californianus and M. edulis have been particularly frequently used to monitor copper abundance in the Bay, despite reservations expressed by some authors over the use of at least M. edulis in investigations of copper (Phillips, 1976a, 1980; Davenport, 1977; Davenport and Manley, 1978). Early work by Girvin et al. (1975) showed that M. edulis and Tapes japonica accumulated similar amounts of the element, while Mya arenaria accumulated levels about twofold

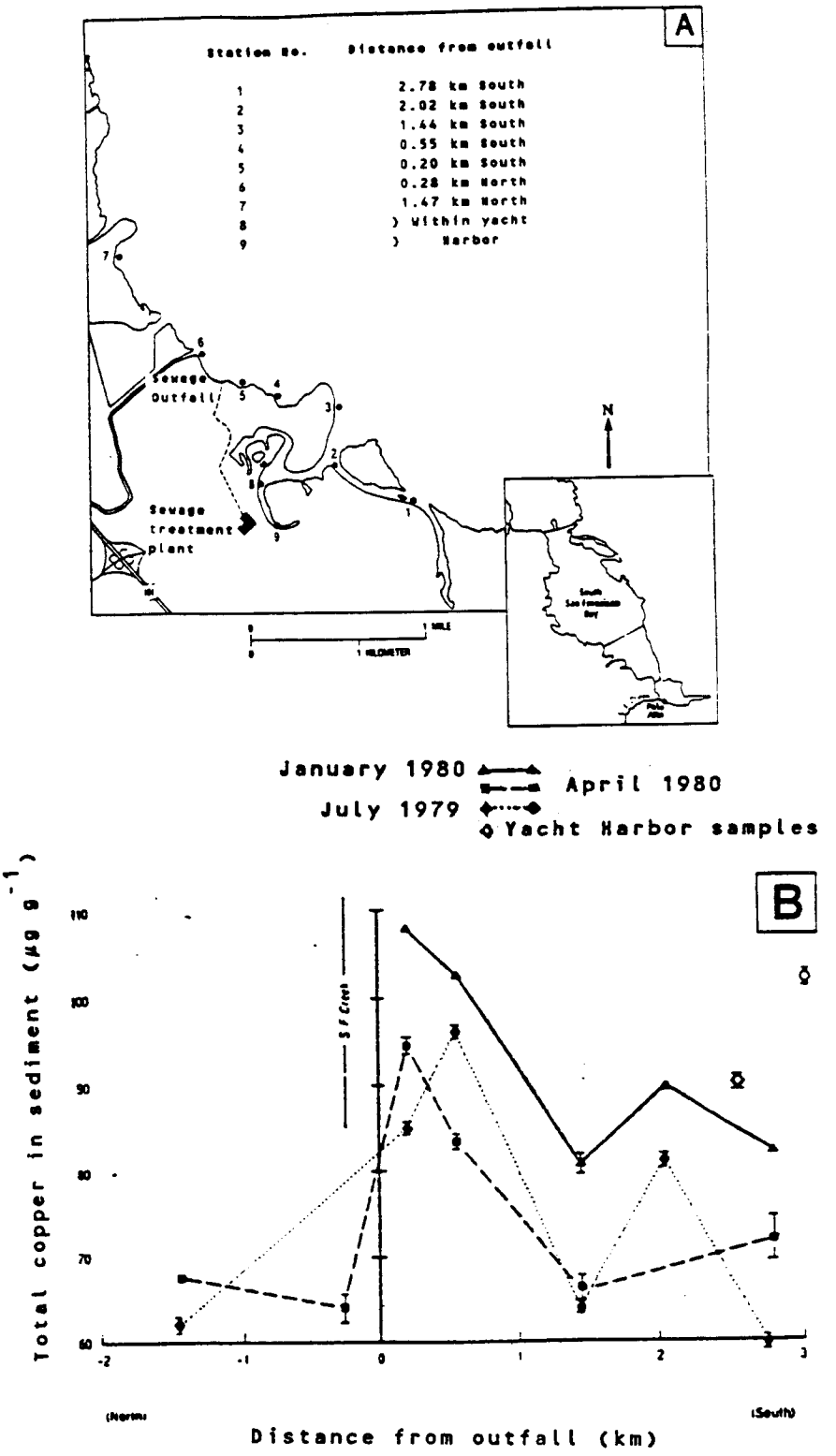


Fig. 18. (A) Locations of sampling sites in studies of copper in sediments and clams. (B) Concentrations of copper (two replicate samples, see bars; µg g^{-1} dry weight) in sediments near Palo Alto. After Thomson et al. (1984).

greater than these. The oysters Ostrea lurida and Crassostrea gigas accumulated very high levels of copper, a trend which is well-documented from many global locations (Eisler, 1981). Comparative data for C. gigas from Redwood Creek and Tomales Bay are shown in Table 7; clearly, Redwood Creek is by far the more contaminated site. Spatial profiles for the other four species studied by Girvin et al. (1975) within San Francisco Bay are shown in Figs. 19 and 20. In general, levels of the element are minimal in areas closest to the Golden Gate; moderate increases are seen in the northern reach of the Bay, and more pronounced increases in the South Bay.

Studies by Risebrough et al. (1978) on copper in Mytilus edulis largely agreed with the data of Girvin et al. (1975) cited above. These results, and those from the State Mussel Watch Program (Hayes et al., 1985; Hayes and Phillips, 1986; Stephenson et al., 1986a; Smith et al., 1986; see Table 8 and Fig. 21) on copper in M. californianus, provide a picture of copper enrichment in the Bay which is largely consistent with data on water and sediment analyses described above. Thus, moderate copper enrichment is seen in both the northern and southern reaches of the Bay, with lower concentrations of the element close to the Golden Gate. The degree of copper enrichment is not extreme, at least in areas reasonably distant from a significant source of the element. The high tidal prism of the Bay and its considerable current velocities (at least in most areas) appear to reduce the effects of local sources of copper and rapidly dilute the element with distance from these sources. These conclusions are also consistent with data reported by Bradford

Table 7. Concentrations of copper ($\mu g\ g^{-1}$ dry weight, means±standard deviations) in tissues of the Pacific oyster *Crassostrea gigas* from Redwood Creek in the South Bay and from Tomales Bay on the Pacific coast of California. After Girvin *et al.* (1975).

Tissue	Redwood Creek	Tomales Bay	Enrichm Factc
Gill	1570±201	155±21	10.1
Mantle	1240±206	109±13	11.4
Hepatopancreas	1680±577	54±4	31.1

[a]Enrichment factor describes ratio of mean copper concentrations at Redwood Creek to those at Tomales Bay.

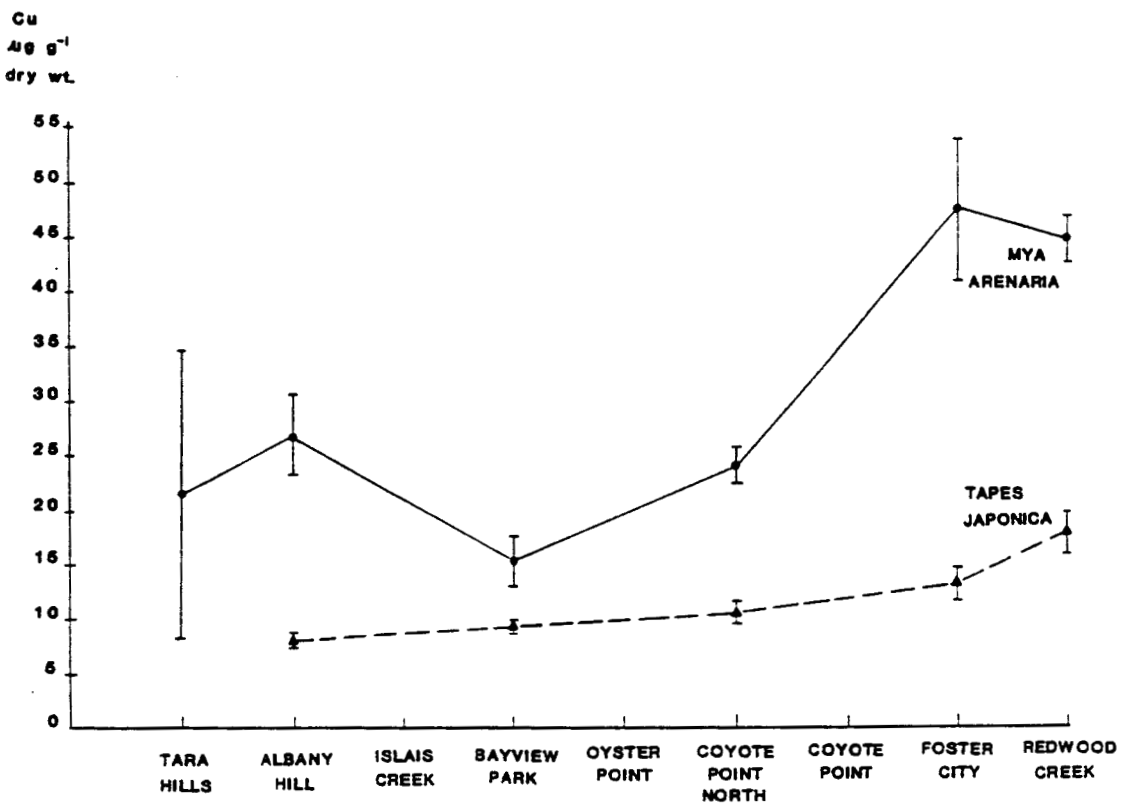


Fig. 19. Concentrations of copper (means±standard deviations, $\mu g\ g^{-1}$ dry wt.) in Mya arenaria and Tapes japonica from sites in San Francisco Bay. After Girvin et al. (1975).

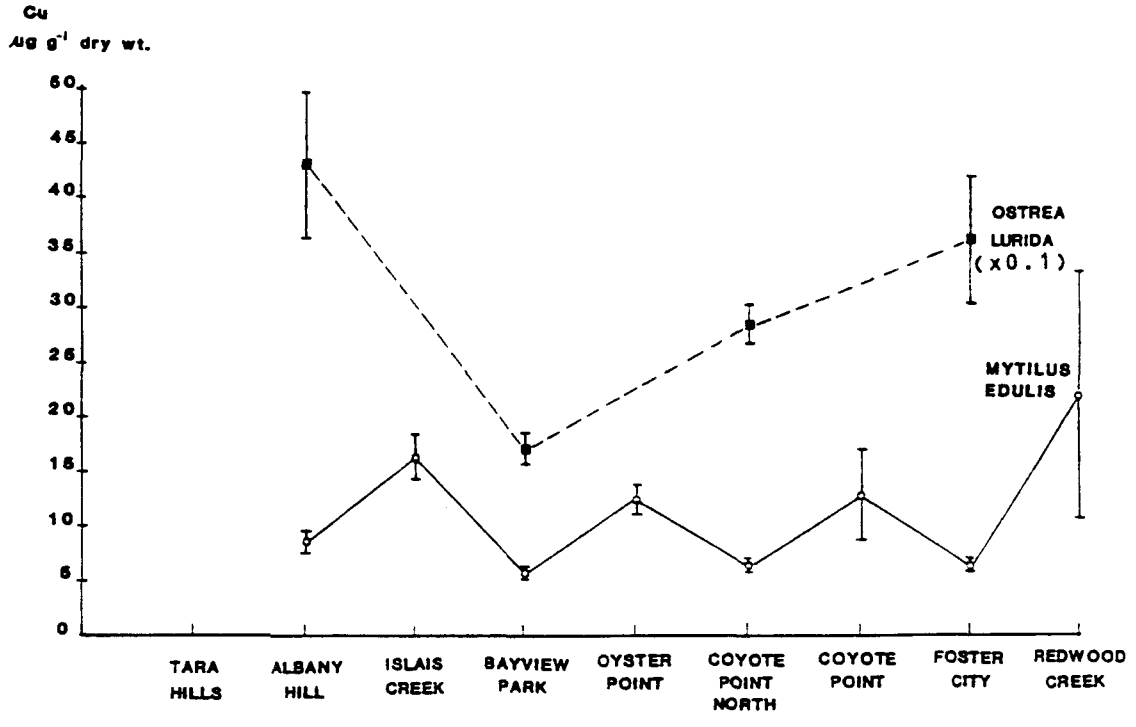


Fig. 20. Concentrations of copper (means±standard deviations, $\mu g\ g^{-1}$ dry wt.) in Mytilus edulis and Ostrea lurida from sites in San Francisco Bay. Note that concentrations in O.lurida are ten-fold higher than shown on vertical axis. After Girvin et al. (1975).

Table 8. Concentrations of copper (means, ug g^{-1} dry weight) in samples of transplanted Mytilus californianus or native M. edulis[a] at 33 sites in San Francisco Bay, 1980-1986. All data from the California State Mussel Watch Program, after Hayes et al. (1985), Hayes and Phillips (1986) and Stephenson et al. (1986a).

LOCATION	STATION CODE	1980	1981	1982 (J/F)	1982 (O/N/D)	1982 RESIDENT (O/N/D)a	1983	1985	1986
MARE ISLAND	300.20							16.3a	8.7
DAVIS POINT	301.00	7.5a			12.7				
POINT PINOLE	302.00	5.3a	14.2	9.7	8.5b		9.6	10.2	8.6
RICHMOND BRIDGE	303.00	6.9	11.2	13.4	10.2b				
SANTA FE CH. MOUTH	303.10								9.2
RICHMOND INNER HARBOR	303.60							16.2	
STAUFFER'S	304.00			10.9					
ANGEL ISLAND	305.00	7.0	10.3	11.1	8.8b				
FORT BAKER	306.00		12.1		8.4c				
TREASURE ISLAND	307.00	7.8	10.5	12.2	10.6c		10.7	10.6	7.4
ALAMEDA YACHT HARBOR	307.20							25.4a	13.3
OAKLAND IN. HARBOR WEST	307.30								10.5
OAKLAND IN. HARBOR EMBC.	307.40								29.1
OAKLAND BACK HARBOR	307.60								15.7
HUNTER'S POINT	308.00		12.2	10.9	11.3c	7.4a			
SAN MATEO BRIDGE 8	309.00	6.4	13.9	10.6	8.1c	8.3a	10.1	13.2	10.6
SAN MATEO BRIDGE 8A	310.00			6.4					
SAN MATEO OLD BRIDGE	311.00			9.2					
BELMONT SLOUGH	312.00			12.3					
REDWOOD CREEK MOUTH	313.00		15.6	9.2	9.6c	6.4a	5.9	14.0	
REDWOOD CREEK 10	314.00			9.8					
REDWOOD CREEK TOWERS	315.00			15.0	11.4b	8.8a			
REDWOOD CREEK TRDWNDS	316.00	7.5a		16.8	12.0b	9.7a			
REDWOOD CREEK STP	317.00				16.9				
SF PETES	318.00				15.0				
SF PULGAS	319.00				11.9				
SF AIRPORT	320.00				13.1				
DUMBARTON BRIDGE 14	321.00	7.2a	16.1	8.3	8.6	6.6a	9.4	8.5	8.5
NEWARK SLOUGH	324.00			6.7					
CHANNEL 17	325.00			8.1					
PALO ALTO 8	326.00			11.1		7.0a			
PALO ALTO YACHT	327.00			10.1					
ALVISO SLOUGH	328.00			8.5					

J/F/O/N/D: January/February/October/November/December, all 1982

a Resident Mytilus edulis.

b Mean of two values.

c Mean of three values.

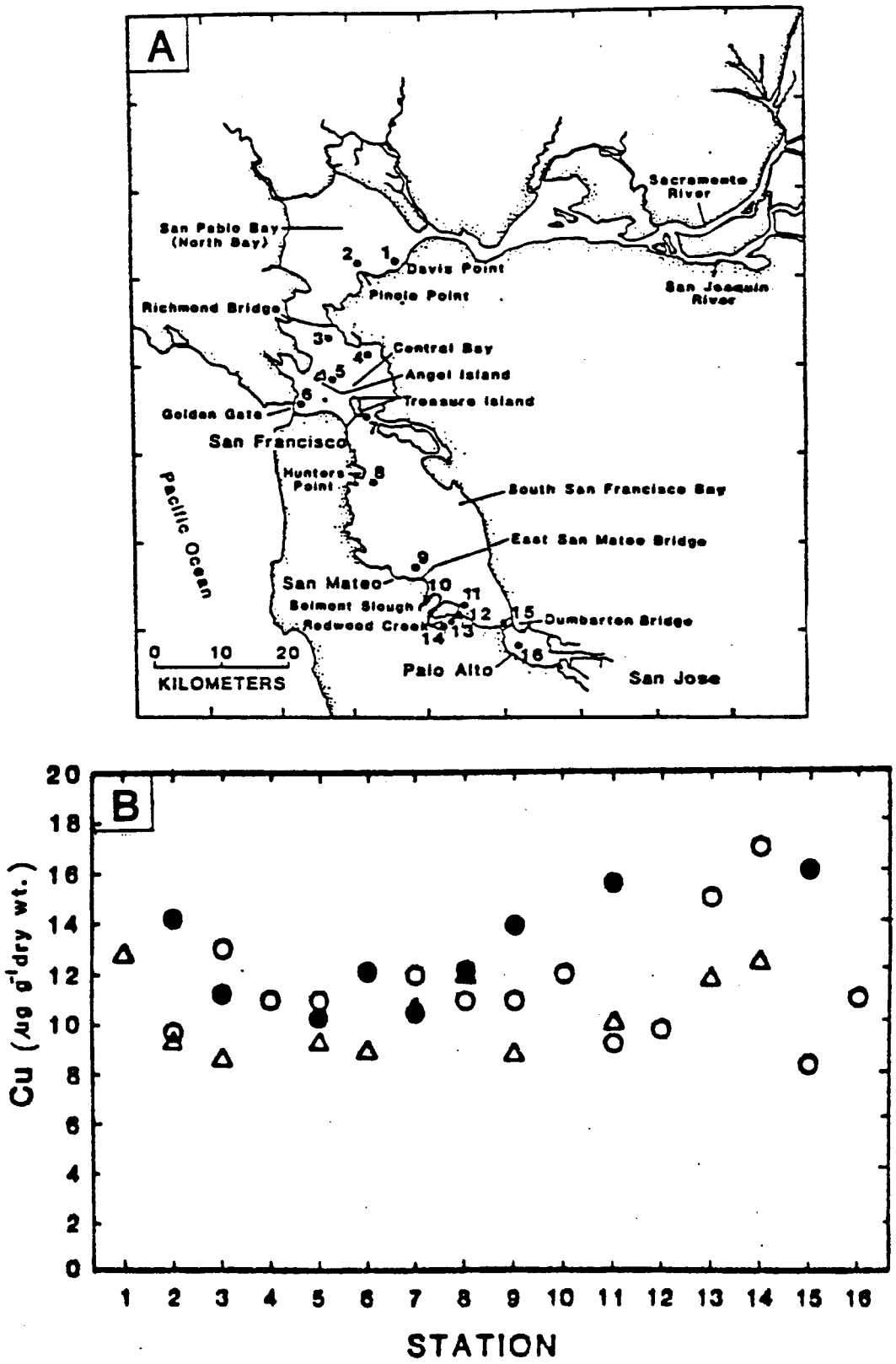


Fig. 21. Mean concentrations of copper ($\mu g\ g^{-1}$ dry weight) in mussels (Mytilus californianus) taken at 16 locations in San Francisco Bay (see map) in 1980-1982. Filled circles; 1980; open circles, 1981; triangles, 1982. After Smith et al. (1986).

and Luoma (1980) on copper in other species of molluscs (Macoma nasuta, Tapes japonica and Nassarius obsoletus) from the Bay.

Data reported for copper in the bivalve Macoma balthica are worthy of particular note here. Thomson et al. (1984) confirmed that copper discharged at the Palo Alto sewage treatment plant was not only contaminating nearby sediments (see above), but was also bio-available, at least to the clam M. balthica. While accumulated copper concentrations in the clam varied with both season and organism size (see also Strong and Luoma, 1981), consistently higher levels of the element were taken up at sites closest to the sewage outfall (Fig. 22; sampling sites shown in Fig. 18A).

The results of analyses of clams by Luoma and Cloern (1982) confirm the impacts of discharges from sewage treatment plants on copper levels in clams. Copper concentrations in M. balthica were studied over a larger area than that used in the work of Thomson et al. (1984) cited above. The variations in copper levels found in clams along this shoreline transect correlated with total loads of copper in the nearest sewage treatment plant discharge (Fig. 23). It was noted that, while copper concentrations were not unusually high in sediments compared to other estuaries, levels of the element were considerable in M. balthica. Luoma and Cloern (1982) suggested that copper discharged to the South Bay may be of unusually high bio-availability, although no mechanism could be found for this. If correct, this conclusion is of particular significance in respect to the need for regulation of copper discharges to San Francisco Bay.

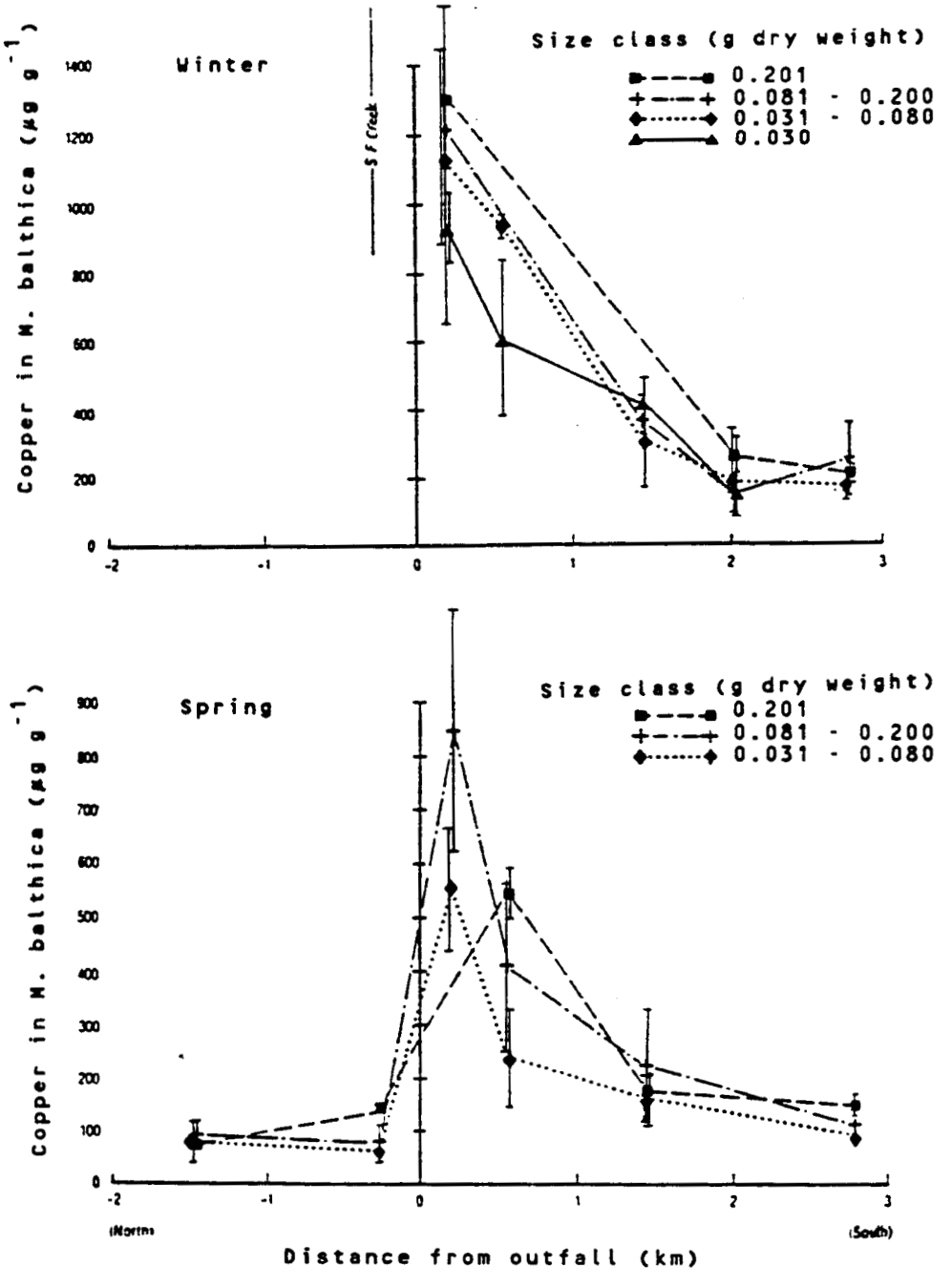


Fig. 22. Concentrations of copper (means±standard deviations, $\mu g\ g^{-1}$ dry weight) in clams, Macoma balthica, of different size classes from the area close to the Palo Alto sewage treatment plant outfall. Winter samples taken in January 1980; spring samples in April 1980. Sampling locations shown in Fig. 18(A). After Thompson et al. (1984).

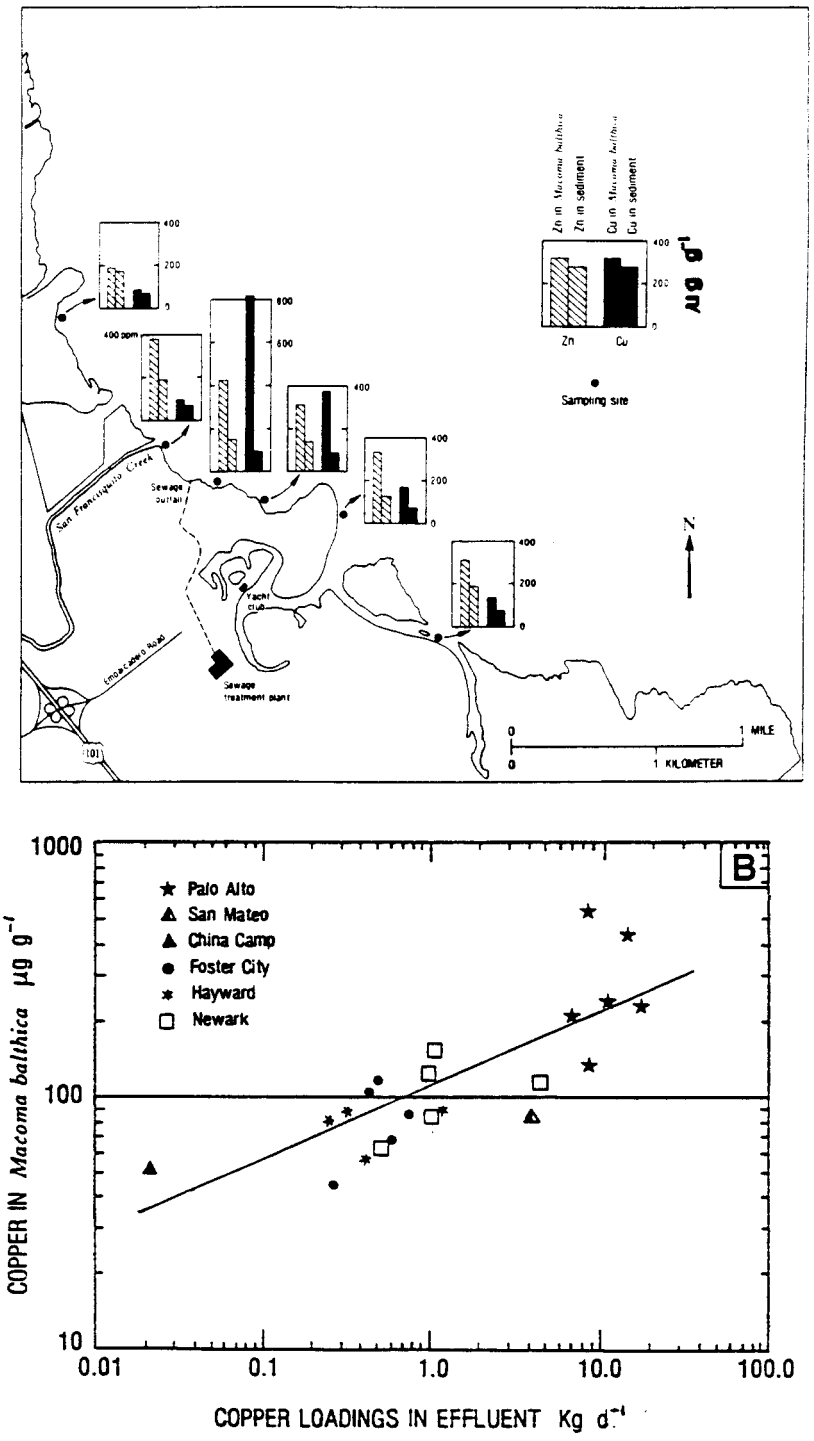


Fig. 23. (A) Mean concentrations ($\mu g\ g^{-1}$ dry weight) of copper and zinc in sediments and soft tissues of the clam Macoma balthica along a 5-km transect near Palo Alto. Samples collected in April 1980. (B) Correlation of copper levels in M. balthica to loads of the element discharged daily at the nearest sewage treatment plants. Stations sampled several times over a three year period. After Luoma and Cloern (1982).

Luoma et al. (1985) reported the results of a long-term study of copper levels in M. balthica at the particularly contaminated Palo Alto site (coded "station 7" in these studies). These data are shown in Fig. 24. Seasonal fluctuations in copper concentrations were considerable, and were at least partly driven by both variations in copper discharged at the sewage treatment plant (Fig. 24) and tissue weight changes in the clam with season (Fig. 25, see also Phillips, 1976a, 1977, 1980; Simpson, 1979; Orren et al., 1980; Lobel and Wright, 1982). However, in addition to these two variables, hydrological changes caused by annual fluctuations in Delta outflow rates were thought to affect copper levels in M. balthica (Luoma and Cain, 1982; Luoma et al., 1985). The correlation of Delta outflow rate to copper in the clams was not as strong as that for silver (see Fig. 10), probably due to the interference of the variations in local discharge rates of copper.

Finally in respect to bivalve molluscs, data for copper in the freshwater clam Corbicula sp. should be discussed. It is notable here that several authors consider this species to be C. fluminea; however, taxonomic uncertainty apparently exists, at least according to some studies (Belanger et al., 1986; Luoma et al., in press). Woodward (1979) reported concentrations of copper in Corbicula sp. from the American River and the Sacramento River (near Sacramento) of 25-80 $\mu g\ g^{-1}$ dry weight. Foe and Knight (1986) reported a median concentration of 94.5 μg (range 66-275 $\mu g\ g^{-1}$) in Corbicula sp. from New York Slough and San Joaquin River sites. Luoma et al. (in press) found average copper levels in Corbicula sp. of 80 $\mu g\ g^{-1}$ at a site near

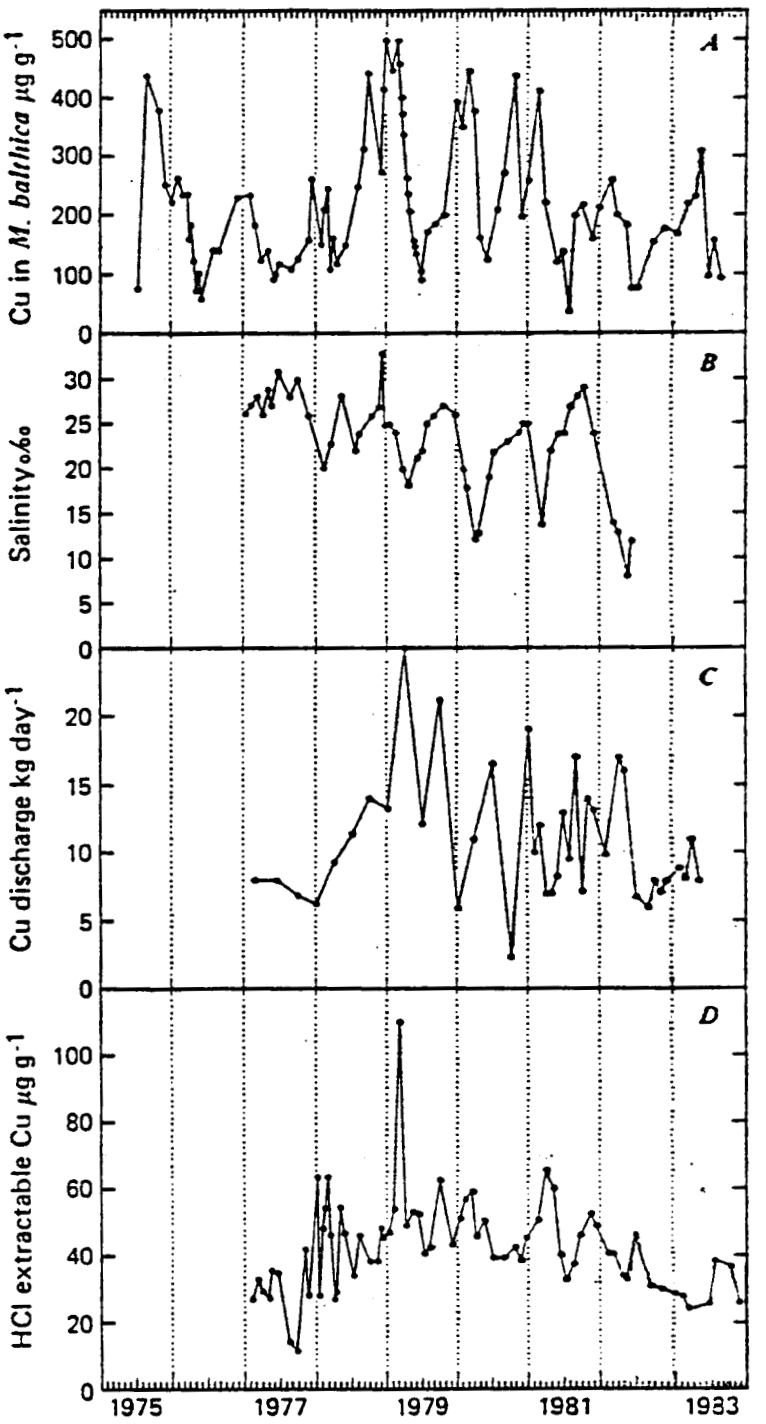


Fig. 24. (A) Mean concentrations of copper ($\mu g\ g^{-1}$ dry wt.) in soft tissues of clams, Macoma balthica, from station 7 near Palo Alto. (B) Salinity at station 7, as measured in bodywater of M. balthica.(C) Copper discharge from the Palo Alto sewage treatment plant, about 1 km north of the sampling site for clams. (D) Copper extracted from surface sediments (<100 um grain size, HCl extraction) at station 7. After Luoma et al. (1985).

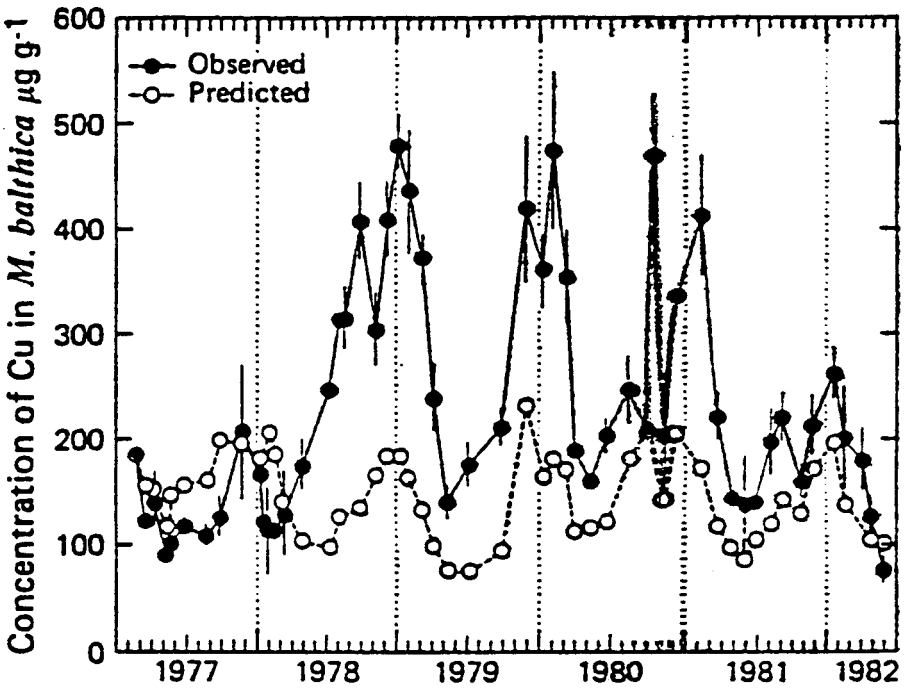


Fig. 25. Fluctuations in copper concentrations (means±standard deviations) in Macoma balthica from station 7 near Palo Alto, compared to predicted fluctuations if bio-available copper had remained constant after January 1977 and tissue weight alone had varied. After Luoma et al. (1985).

Rio Vista in the Sacramento Delta, but higher levels in this species from some sites in Suisun Bay (means of 70 to 120 $\mu g\ g^{-1}$ dry weight). It was suggested that sources of copper existed both in influent rivers and on the margins of Suisun Bay, and that the clams exhibited high levels of copper contamination compared to concentrations in sediments. This supposed high bio-availability of copper to Corbicula sp. is reminiscent of the data of Luoma and Cloern (1982) for South Bay M. balthica (cited above).

The existence of significant sources of copper in the Sacramento and San Joaquin Rivers is confirmed by various data sources. Data from the Toxic Substances Monitoring Program are shown in Fig. 26 (SWRCB, 1986). Particular copper enrichment (concentrations of the element exceeding the elevated data level values) is evident in both the Central Valley catchment and the South Bay catchment. In the Sacramento River at Keswick, high copper values were found in the livers of rainbow trout (Salmo gairdneri). High values at other areas were noted for a variety of species, including livers of striped bass (Morone saxatilis), largemouth bass (Micropterus salmoides), channel catfish (Ictalurus punctatus) and other fish. Reports of high copper levels in water samples from the Sacramento River are also available (SWRCB/CVRWQCB, 1986); the local use of copper-containing pesticides (especially for rice and some orchard crops) and acid mine drainage in the catchment are believed to both be of significance in terms of sources of the element. In some areas, copper concentrations in river waters approach or exceed the EPA national water quality criteria for the protection of aquatic life (4-day average of 6.5 $\mu g\ L^{-1}$ and one-hour average

Fig. 26. Values exceeding "elevated data levels" (EDL 85 and EDL 95) for copper in the Toxic Substances Monitoring Program studies, 1978-1984. After the SWRCB (1986).

of 9.2 $\mu g\ L^{-1}$, both at 50 mg L^{-1} water hardness; see U.S. EPA, 1985, 1986).

Information on copper concentrations in Bay-Delta biota other than bivalve molluscs is sparse. However, Ohlendorf et al. (1986c) found quite high levels of the element in livers of diving ducks from South Bay. Greater scaups (Aythya marila) exhibited higher copper levels ($96.8 \pm 7.6\ \mu g\ g^{-1}$ dry weight) in livers than did surf scoters (Melanitta perspicillata; $49.8 \pm 3.6\ \mu g\ g^{-1}$ dry weight), and this was thought to be a diet-related phenomenon. It is probable that these birds accumulate copper from both algae and molluscs, which are both represented heavily in their diet.

Summary

In summary, the San Francisco Bay-Delta aquatic ecosystem has been clearly documented to be copper-enriched. Moderately elevated concentrations of copper are found in both waters and sediments of the Bay, with local "hot-spots" of particular contamination (e.g. sediments at Palo Alto, Redwood Creek, San Leandro Bay, Islais Creek, and Mission Creek). An overall pattern of contamination can be discerned, with minima at the Golden Gate and increasing levels of the element in both the northern and southern reaches of the Bay. Data from studies of water, sediment and biota suggest significant within-Bay sources of the element. Sewage treatment plant discharges are one documented source of copper in the Bay (see also Young et al., 1981), although it may be expected that direct industrial discharges to Bay-Delta receiving waters also contribute.

Freshwater inflows undoubtedly also enrich the Bay-Delta with copper; it is notable that Eaton (1979a) considered this to be the major source of the element within the Bay (Table 9).

Notwithstanding these known and considerable sources of copper to the Bay-Delta, the concentrations of the element found in local waters and sediments are not remarkable by comparison t other estuaries. Risebrough et al. (1978) thus interpreted the database available to 1977 as showing that there was an "... absence of evidence that copper is a problem in the San Francisco Bay area..." (Risebrough et al., 1978).

However, data available since that time, from both the Bay-Delta itself and other studies, suggest that this may not be the case. The proposals by Luoma and co-workers that copper may be unusually highly bio-available within the Bay-Delta ecosystem (Luoma and Cloern, 1982; Luoma et al., in press) are worthy of serious consideration, even though no specific reasons for this phenomenon have been found. High concentrations of copper certainly occur in biota from some areas of the Bay-Delta. This finding, coupled with the recent improved understanding of the extreme toxicity of this element to aquatic biota (e.g. see Fig. 13), suggests that particular attention should be paid to minimizing discharged loads of copper to local receiving waters. This conclusion is in keeping with the finding that ambient concentrations of copper in Bay-Delta waters sometimes exceed th latest U.S. EPA water quality standards (U.S. EPA, 1986).

Table 9. Estimates of Eaton (1979a) of copper loads to the San Francisco Bay-Delta. Data as metric tonnes discharged annually. After Eaton (1979a); for assumptions, see original author.

Source	Annual Copper Load
Suspended river load	200
Dissolved river load	100
Ocean	16
Aerosol	10
Storm run-off, dissolved	2
Total storm run-off	5
Sewage, dissolved	20
Sewage, oxidizable and desorbable	180
Release from dredging	3
Total	536

C. SELENIUM

Introduction

The chemistry and (especially) biogeochemistry of selenium (Se) are highly complex (Wilber, 1983). This element exists in nature as six stable isotopes (Se^{80} and Se^{78} are the most common), in three allotropic forms, and in a total of five valency states. The latter include states of -2 (hydrogen selenide), 0 (elemental selenium), +2 (selenium dioxide), +4 (selenite, SeO_3^{2-}), and +6 (selenate, SeO_4^{2-}). Changes between the various valency states and between inorganic and organic forms of the element are critical to its environmental behavior, bio-availability, and toxicity.

Selenium is both an essential element (i.e. is required for the maintenance of health) and a toxic element. It is required as an integral part of certain enzymes and other biologically active compounds (Eisler, 1985a). Both terrestrial and marine plants accumulate the element and synthesize selenium-containing amino acids, which are then incorporated into proteins (Wrench, 1978; Wrench and Campbell, 1981). This selenium is bio-available to animals ingesting such plant material, and selenium-containing amino acids are required in the diet by some animals (Lo and Sandi, 1980; Eisler, 1985a). The recommended daily intake of selenium for Man is 50 to 200 $\mu g\ day^{-1}$ (Brooks, 1984). Toxicological data concerning this element are more fully reviewed in later sections of this report.

Uses (and thus, sources) of selenium are diverse. It has been employed in pesticides, in shampoos (as selenium sulfide),

and in the manufacture and production of glass, pigments, rubber, metals and their alloys, medical therapeutic agents, photographic emulsions, and petroleum. The last two of these sources may be particularly significant in San Francisco Bay (see below). Selenium is present in considerable amounts in fossil fuels; their combustion gives rise to release of the element to the atmosphere. The burning of coal produces selenium-rich pulverised fuel ash; at least some portion of the selenium in this ash is bio-available to estuarine bivalve molluscs (Phillips, unpublished data).

Despite the existence of these diverse sources of the element, most authors agree that selenium released from naturally seleniferous soils constitutes potentially the greatest risk to aquatic environments (Eisler, 1985a). Several areas of seleniferous soils exist within the United States. These include parts of the Rocky Mountains and High Central Plains, and various regions in the Pacific northwest and southeast.

The San Joaquin Valley constitutes one such area of seleniferous soil abundance. The original cause of this phenomenon is a function of the geological history of the Coast Ranges (Norris and Webb, 1976; Barnes, 1986; Letey et al.,1986), involving the deposition of marine sediments in the Cretaceous period, followed by uplifting and weathering. The exposed valley floor eventually began to fill with material eroded from the flanking Sierra Nevada and Coast Ranges. Alluvium on the Valley's east side derives from the Sierra Nevada and is generally coarse in texture and poor in minerals or salts. By contrast, the alluvial fan on the west side of the Valley,

generated from the sedimentary Coast Range with Moreno and other types of shale outcrops, contains significant amounts of soluble mineral salts and trace elements, including selenium. Furthermore, the soils of this area are mostly alkaline, and are highly saline. The irrigation of these soils gives rise to leaching out of selenium and the consequent contamination of groundwater and surface waters by the element, present mostly as selenates.

The main area of high selenium concentrations in the Central Valley is the central portion of the San Joaquin catchment, in southern Merced and northern Fresno Counties (DWR, 1986; see Fig.27). The region south of here, in Kings and Kern Counties, generally exhibits lower (but nevertheless significant) levels of selenium in surface and groundwater samples (Fig.28). Sylvester (1986) and CDF&G (1987a) reported high concentrations of selenium in areas providing drainage water to the San Luis Drain. Considerable contamination of this region and the Kesterson Wildlife Refuge by selenium has eventuated, culminating in clean-up and abatement procedures with respect to the Wildlife Refuge, which are ongoing. The relevance of this general outline to the San Francisco Bay-Delta ecosystem is discussed below.

Several aspects of the chemical speciation of selenium in natural waters merit discussion here, as an introduction to the consideration of data reported for the element in the Bay-Delta. As noted above, the biogeochemical cycling of selenium is highly complex; present understanding of this topic is fragmentary and incomplete. Studies have been hampered by analytical difficulties in particular (e.g. see Robberecht and Van Grieken, 1982). Acceptable methods for the differential analysis of the

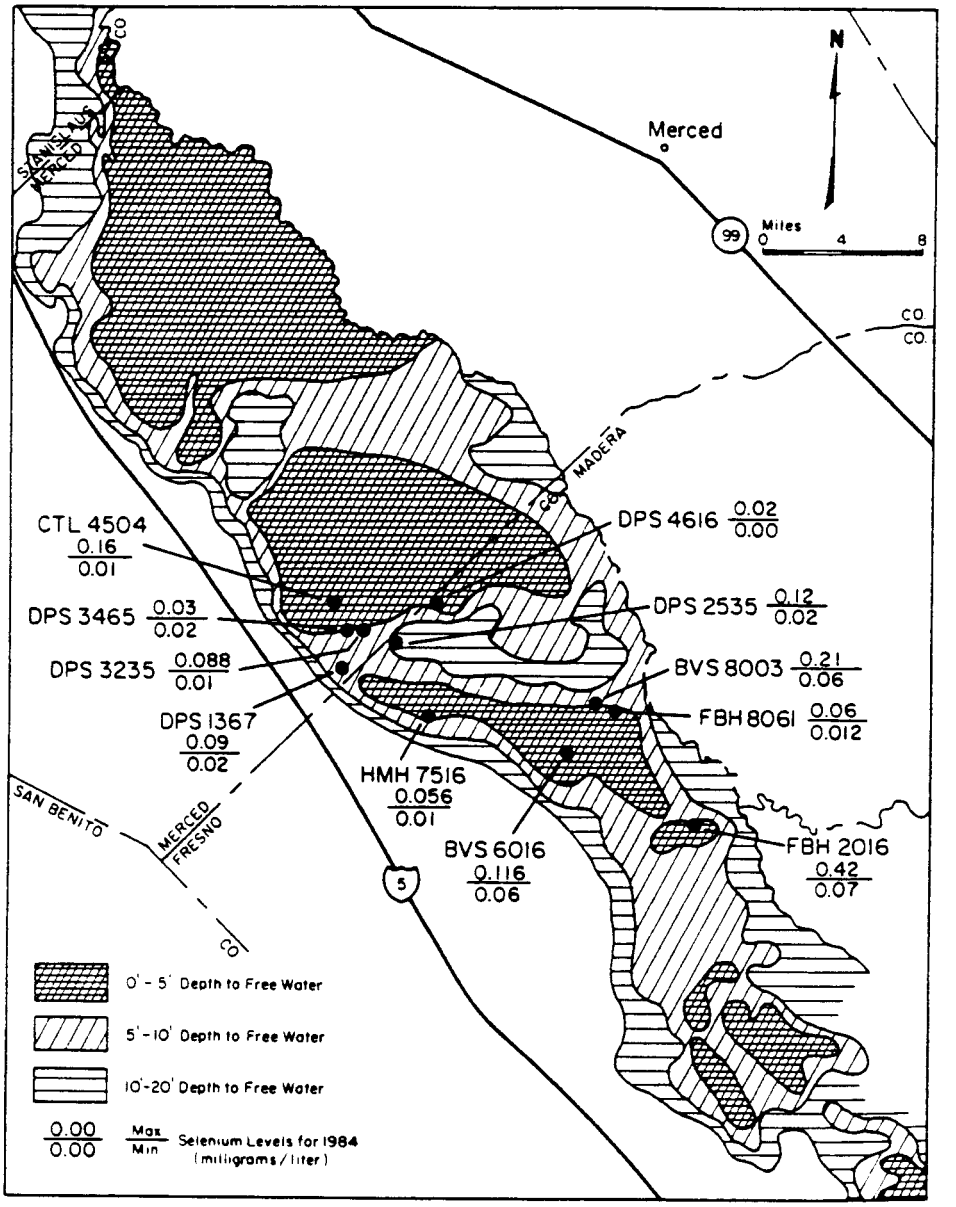


Fig. 27 Concentrations of total selenium (maxima and minima, $\mu g\ L^{-1}$) reported in surface and subsurface waters of the central area of the San Joaquin Valley. After DWR (1986).

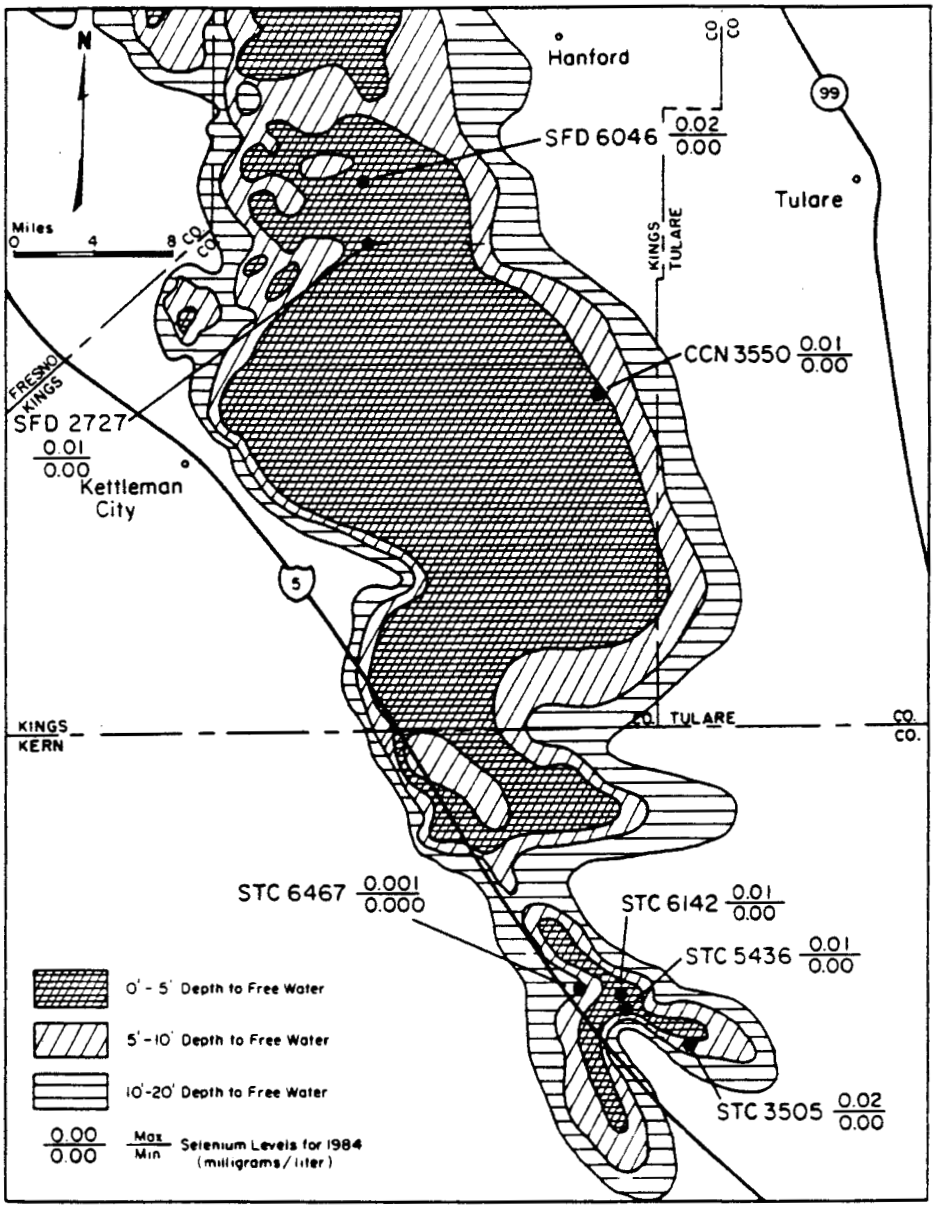
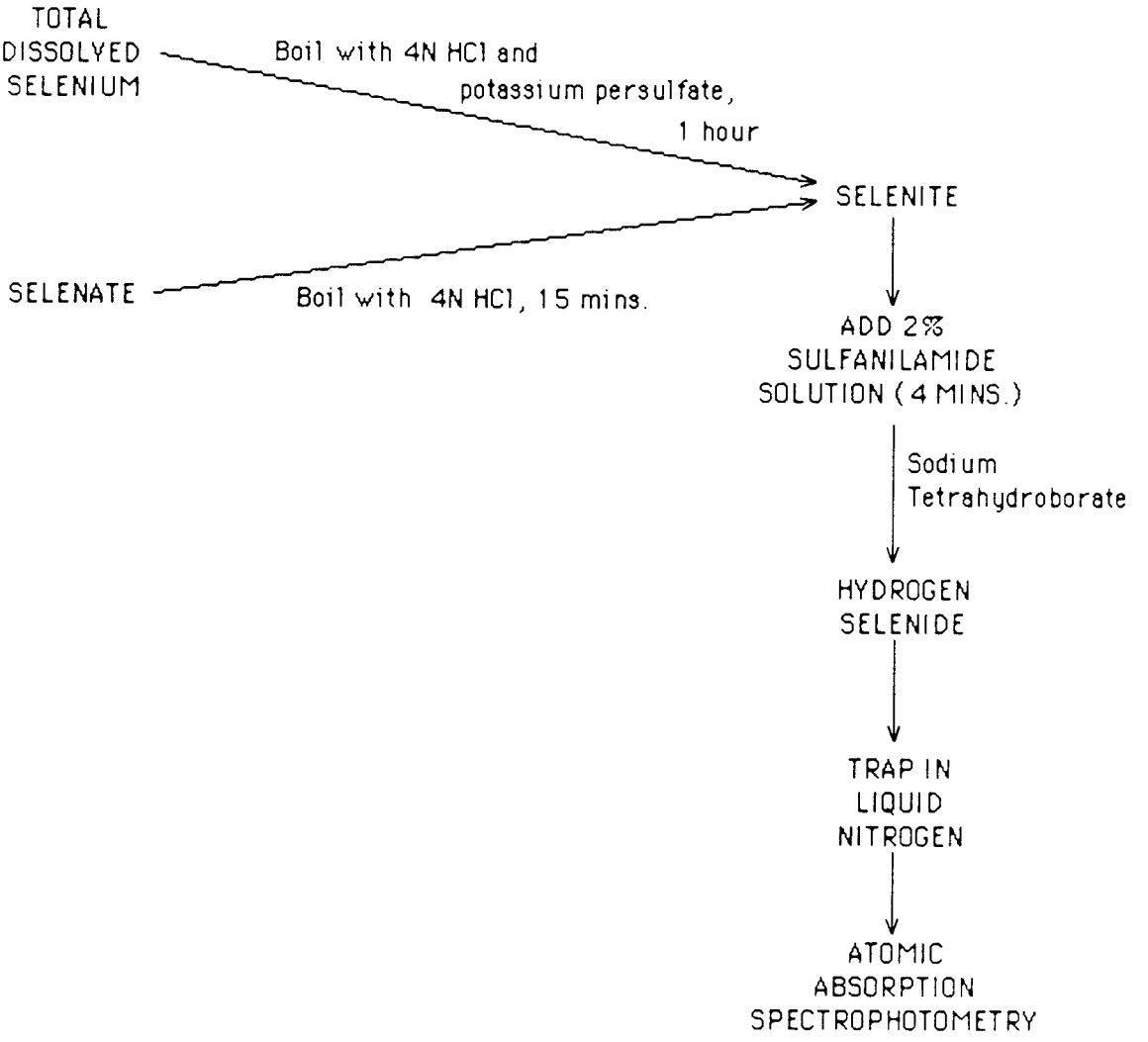


Fig. 28. Concentrations of total selenium (maxima and minima, $\mu g\ L^{-1}$) reported in surface and subsurface waters of the southern area of the San Joaquin Valley. After DWR (1986).

various chemical species of the element in natural waters have only recently become available. Cutter (1978, 1982, 1983, 1985) has been instrumental in the development of these techniques. The basic technique developed by this author involves the reduction of selenite to hydrogen selenide by sodium tetrahydroborate, trapping of the hydride, and quantification by atomic absorption spectrophotometry. Selenate is determined by its reduction to selenite by boiling a 4N HCl acidified sample for 15 minutes, use of the standard selenite procedure, and subtraction of values for selenite. Total selenium analyses involve boiling a 4N HCl acidified sample with the addition of potassium persulfate for one hour, followed by analysis using the selenite procedure. The difference between values for total dissolved selenium and (selenite plus selenate) corresponds to the level of Se (-2+0) in the original sample, operationally termed "organic selenide" by Cutter and Bruland (1984). These analytical procedures are shown in outline in Fig. 29. In more recent work, Cutter (1987) has employed Sep-Pak cartridges to attempt to directly quantify the levels of organic selenium species in aqueous samples.

Using such methods, Cutter and Bruland (1984) re-evaluated the biogeochemical cycling of selenium in marine waters. They proposed a selenium cycle as shown in Fig. 30. In marine surface waters, phytoplankton largely dominate in determining the chemical speciation of the element (Wrench and Measures, 1982). Thus, phytoplankton take up selenite (and to a lesser extent, also selenate) from surface waters and produce "organic selenides", which are largely selenium-containing amino acids and



[Total dissolved selenium = selenite + selenate + Se(-2+0)].

Fig. 29. Schematic representation of the analytical procedure developed for selenium quantification in aqueous samples. After Cutter (1978,1982,1983).

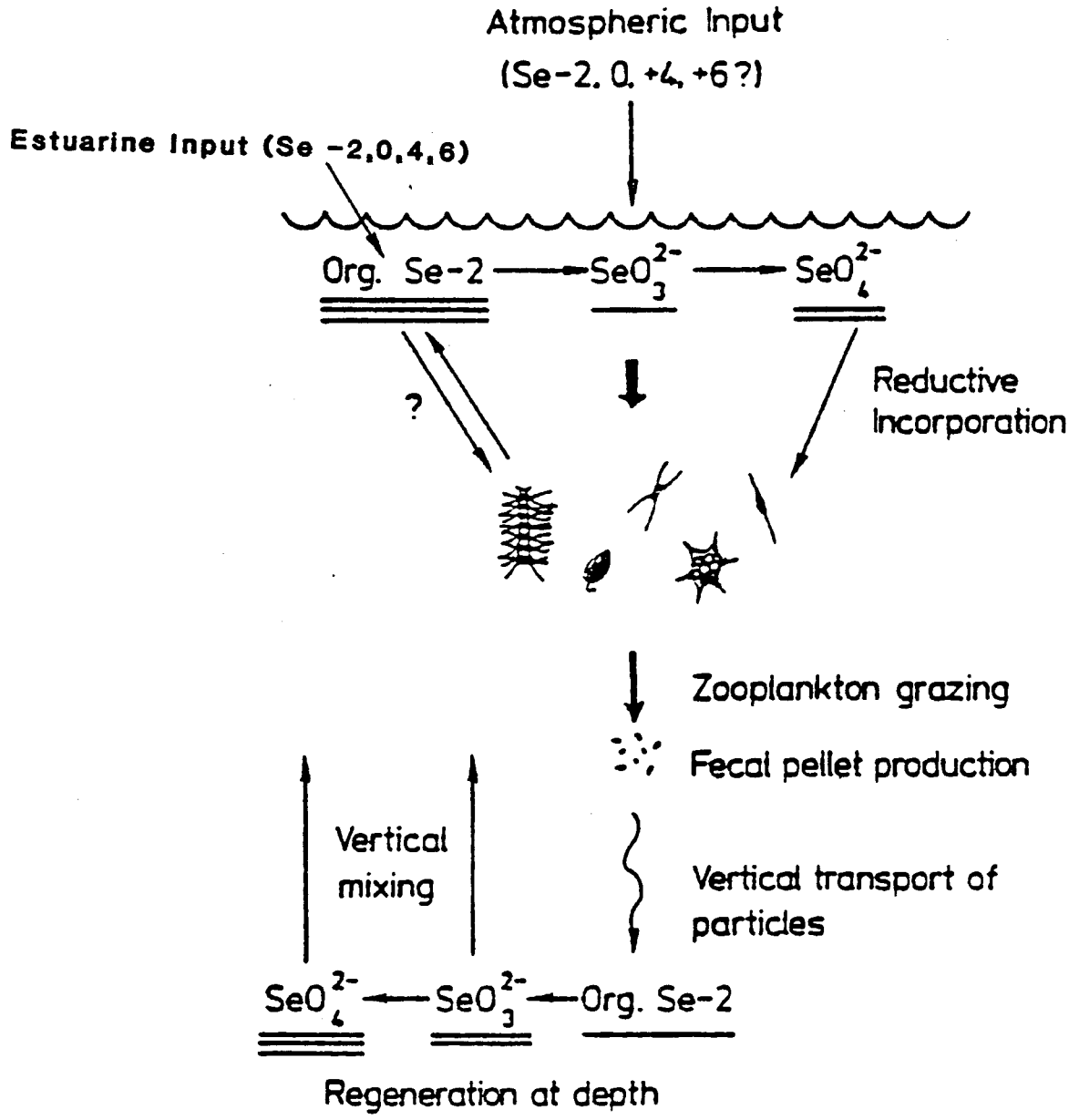


Fig. 30. Schematic representation of the biogeochemical cycling of selenium in marine waters. After Cutter and Bruland (1984).

proteins (Wrench, 1978; Wrench and Campbell, 1981). Organic selenides are thus usually the predominant forms of the element in surface waters of marine environments. The food-chain transfer of organic selenides from primary producers to secondary consumers (zooplankton, etc.) results in a net downward vertical transport of organic selenides to deeper waters, where selenite and selenate are regenerated. Vertical mixing of deep waters resupplies these species to surface waters.

By contrast to this scenario in marine waters, the cycling and speciation of selenium in estuarine environments are more complex and less well understood (Measures and Burton, 1978; Takayanagi and Wong, 1984; Takayanagi and Cossa, 1985; Van der Sloot et al., 1985). No clear and consistent picture of selenium in estuarine waters has emerged from these studies, and the chemical speciation of the element appears to vary between estuaries. This may relate, at least in part, to the influence of phytoplankton (see above).

Selenium in Bay-Delta Waters

The data available for San Francisco Bay and Delta have been reviewed by Cutter (1987). As noted above, the central portion of the San Joaquin Valley is a known source of selenium in the catchment, and this is of concern toxicologically. Various samples of water and (on some occasions) suspended particulates have been analyzed, from cruises in 1984-1986. The later work (1986) is of greatest import, as the entire estuary was included, rather than simply the freshwater inputs or the northern reach. The analytical technique used was as described above (Fig. 29).

Sampling methods were designed to avoid contamination of samples. Analyses were performed in triplicate, and standard addition techniques were employed to calibrate analytical accuracies.

Samples taken in 1984 were from the upper estuary (Suisun Bay and the Delta), with salinities varying up to only 10‰. Very low (or zero) flows from the San Joaquin River were entering the Delta during these surveys, performed in dry periods in July and September 1984. Total selenium levels increased with salinity as a result, and it was clear that the Sacramento River (which provided most or all of the flow during the survey periods) was not a significant source of the element to the estuary. Similar data were reported for the June 1985 survey; although this covered the majority of the salinity range present in the northern reach of the Bay-Delta, riverine inputs were again low and the San Joaquin provided essentially no freshwater input. However, there were indications of a selenium input in the mid-estuary, unrelated to riverine sources (Fig. 31); both selenate and (particularly) selenite concentrations reflected this mid-estuary source.

The very low discharge of selenium from the Sacramento River during low flow periods is in keeping with the lack of seleniferous soils in this catchment. Data reported for the Sacramento River at Green's Landing/Freeport and the San Joaquin River at Vernalis (Fig.32) clearly reflect the impact of the seleniferous areas in the catchment of the San Joaquin River. The predominance of selenate in both river systems is also notable. Interestingly, the highest concentrations of total selenium in the San Joaquin River (in June 1985 and August 1986)

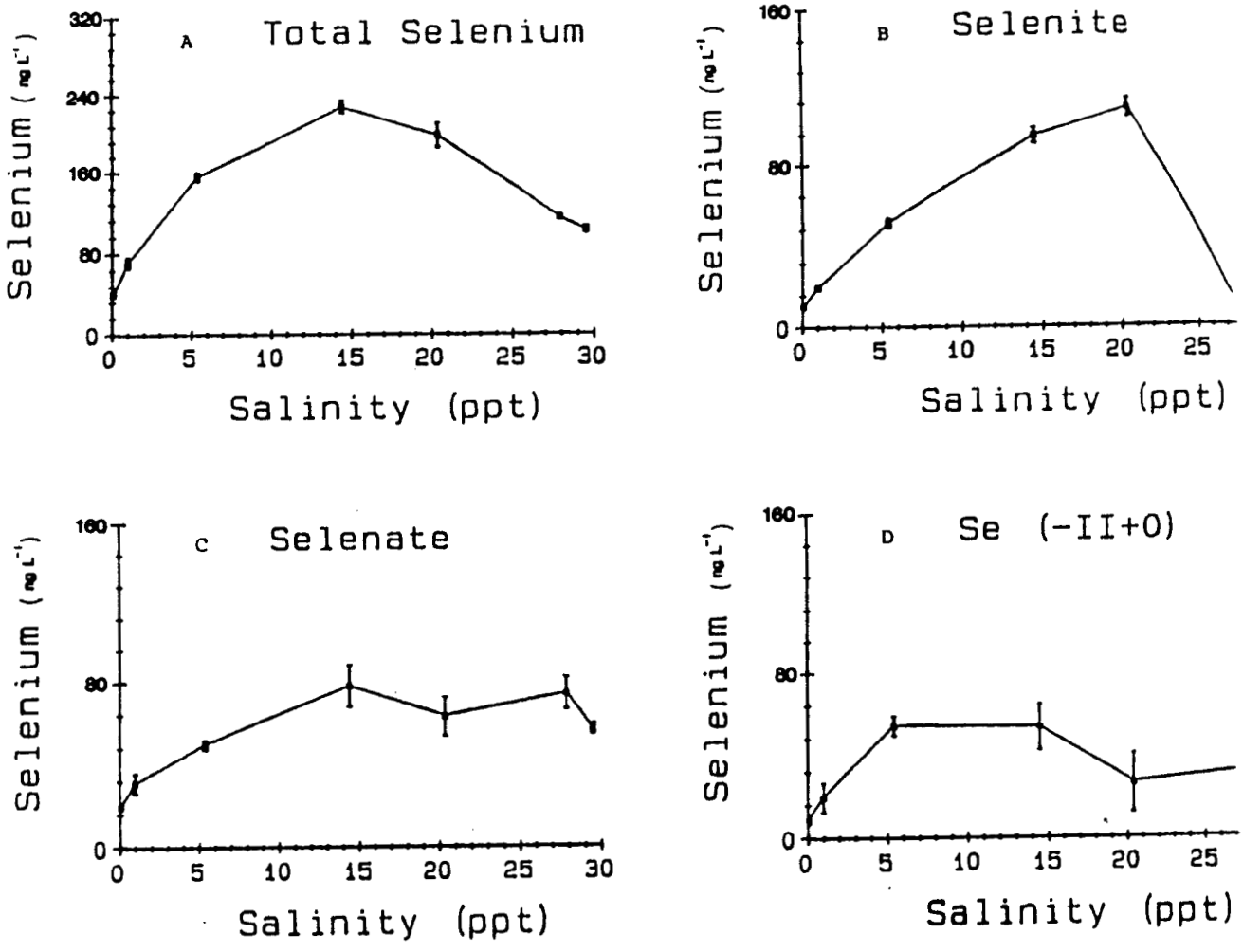


Fig. 31. Concentrations of selenium (ng L^{-1}) in surface waters the northern reach of San Francisco Bay in June 198 Discharge from the San Joaquin River was effective zero. After Cutter (1987).

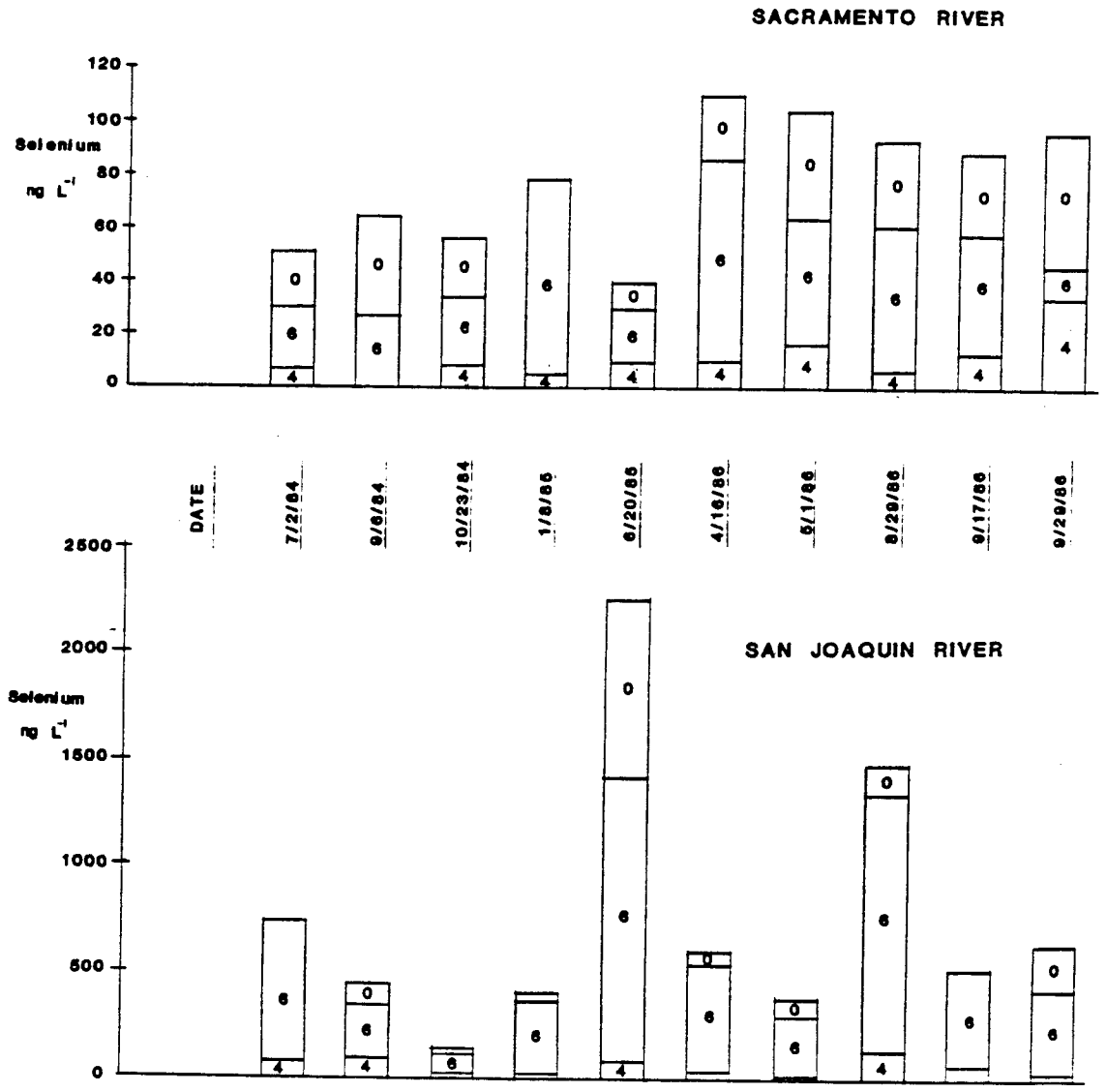


Fig. 32. Concentrations of total selenium (ng L^{-1} or parts per trillion) and the chemical speciation of the element in the Sacramento River at Green's Landing/Freeport, and the San Joaquin River at Vernalis, on several dates from July 1984 to September 1986. "4" represents selenite; "6" refers to selenate, and "0" is "organic selenide". After Cutter (1987). Note difference in vertical scales.

corresponded to times of very low total Delta outflow (Cutter, 1987). However, selenium levels in the combined river outflows at the Delta varied directly with flow rates, i.e. concentrations of the element in combined Delta outflows increased with flow rate. This is the result of increasingly greater amounts of water derived from the San Joaquin catchment contributing to the combined flow in high run-off conditions.

In April 1986, water samples were taken from the Delta and from a variety of locations in the northern and southern reaches of San Francisco Bay. This first geographically comprehensive sampling provided most useful data, particularly as the timing of sampling followed high flows in the Delta caused by winter rains. Profiles of selenium in the waters sampled are shown in Fig. 33 for the northern reach of the bay, and Fig. 34 for South and Central Bays. In the northern reach, total dissolved selenium values exhibited approximately conservative behaviour, but elevated levels of the element were noted close to the Golden Gate, both in respect to selenate and (particularly) organic selenide. These elevated levels were ascribed to selenium originating in the South Bay. Back-extrapolation of the South Bay mixing profiles (Fig. 34) to a freshwater end-member gives rise to an estimated concentration of total selenium of 648 ng L^{-1} with Se (-2+0) comprising 76% of this total. These levels are notably high and clearly reflect a significant source of the element in the South Bay. Cutter (1987) speculated that this source might be from weathering of the Almaden Hills sulfide deposits, or from sewage treatment plants in the South Bay. It is possible that selenium is derived from the Palo Alto sewage

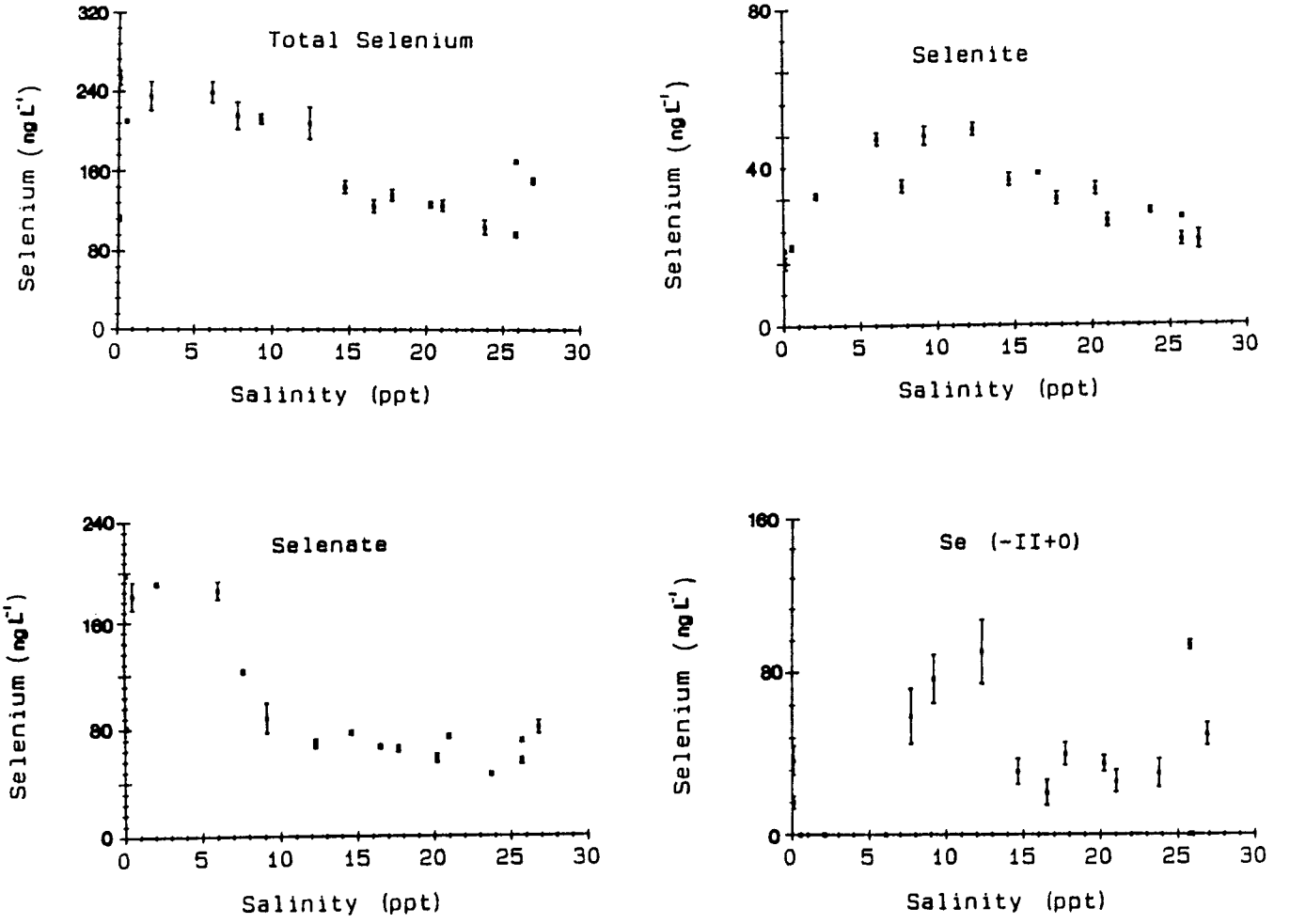


Fig. 33. Concentrations (ng L^{-1} of total dissolved selenium, selenite, selenate and "organic selenide" in the northern reach of San Francisco Bay in April 1986. After Cutter (1987).

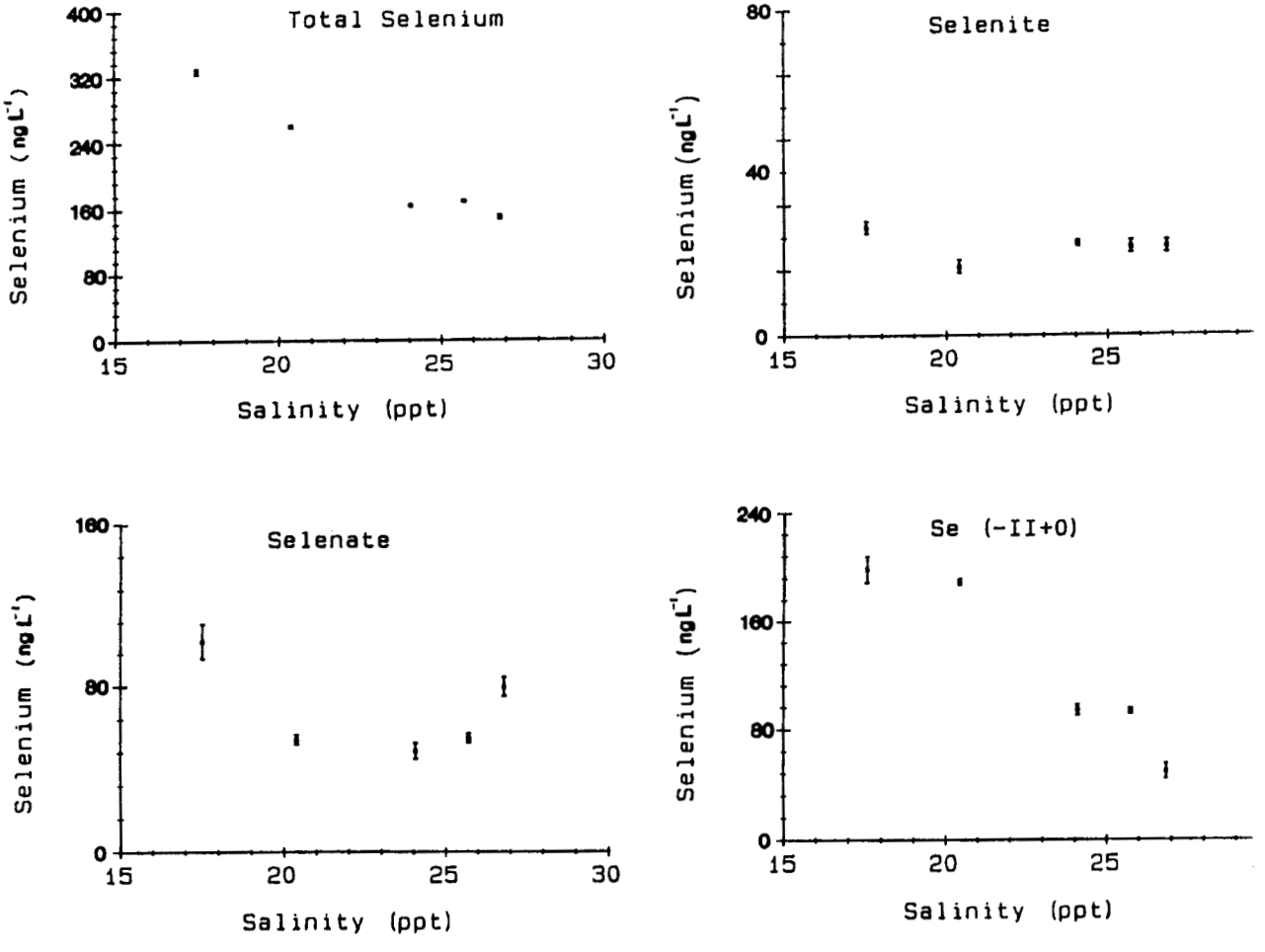


Fig. 34. Concentrations (ng L^{-1}) of total dissolved selenium, selenite, selenate and "organic selenide" in the South and Central Bays, April 1986. After Cutter (1987).

treatment plant, which is documented as a major source of silver to the Bay (see section IIA of this report). Selenium is known to be present in effluents from photographic processing industries, which are likely to be at least a contributor of the silver discharged at Palo Alto.

The April 1986 samples were also analyzed for particulate-associated selenium in the northern reach of the Bay, using the method of Cutter (1985). These data (Fig. 35) show a similar profile to dissolved species of the element, concentrations decreasing from the Delta to the Golden Gate. However, selenium concentrations in suspension averaged only 7% of those in solution.

Finally, Cutter (1987) also reported results of a survey carried out in September 1986 in a period of relatively low Delta outflow. These data were similar to the results of the June 1985 survey. The concentrations of "organic selenide" [Se(-2+0)] in the northern reach correlated to chlorophyll-a levels in the September 1986 work, agreeing with the concept that these chemical species of the element are generated by phytoplankton.

In summary, the studies of Cutter (1987) have provided valuable insight into selenium sources and chemical speciation in the San Francisco Bay-Delta ecosystem. There is clear evidence of the discharge of considerable amounts of selenium (especially selenate) to the upper estuary from the San Joaquin drainage basin. By contrast, the Sacramento River contains low levels of dissolved or suspended selenium, consistent with its geochemistry and soil type. Under conditions of low Delta flow in particular, "mid-estuary" sources of selenium are notable, and these cause a

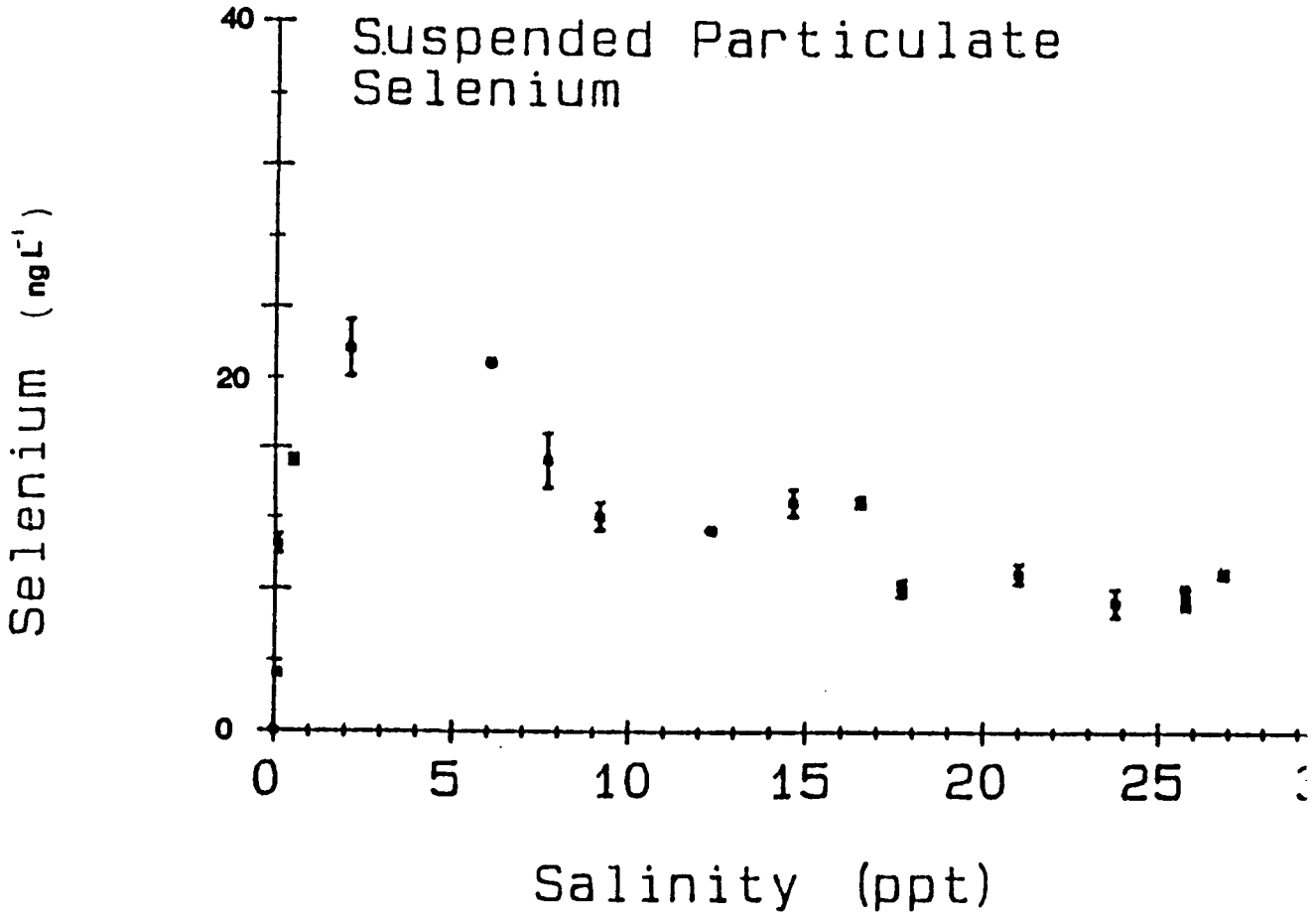


Fig. 35. Concentrations of selenium (all species, ng L^{-1}) present in the water column of the northern reach of San Francisco Bay attached to suspended particulates, April 1986. After Cutter (1987).

hump in the mixing profile for selenium in the northern reach of the estuary. Cutter (1987) shows that the hump is coincident with the Carquinez Strait area. Limited sampling of effluents from oil refineries in this area confirmed the existence of significant loads of the element entering from this source (Table 10). Selenium concentrations in these effluents are likely to vary temporally, and the data in Table 10 can be considered to be indicative only. However, discharged loads of selenium (calculated using these data and average effluent flows for the month of February 1986) total 6.18 kg day^{-1} from these six industrial establishments, which is clearly of significance. By comparison, a Delta outflow of 500 m^3 sec^{-1} (approximately average low flow value) at a total dissolved selenium concentration of 160 ng L^{-1} (similar to flow-weighted concentrations in the Delta measured by Cutter, 1987) would discharge 6.91 kg of the element to the Bay daily.

In addition to the industrial sources of selenium in the northern reach of the estuary, Cutter (1987) has also shown significant sources of the element to exist in the South Bay. However, the precise location and type of these sources are unknown. There is a critical need for additional work in this area, particularly as graphically interpolated concentrations of dissolved selenium in the South Bay discharges appear to be considerable, perhaps even rivalling the San Joaquin River in terms of concentration. Finally, Cutter (1987) also notes that no data are available concerning the role of sediments in selenium flux through the Bay-Delta. Sediments could act as either a source or a sink for the element (or both), and changes

Table 10. Concentrations of total dissolved selenium, selenite selenate, and "organic selenide" [Se(-2+0)] effluents from oil refineries located in the northern reach of San Francisco Bay. Samples were taken on 2 February 1987. After Cutter (1987).

Refinery	Total Selenium	Selenite	Selenate	Se(-2+0)
	-------Selenium concentrations, $\mu g\ L^{-1}$--------			
Chevron, Richmond	13.0	7.9	0.8	4.4
Exxon, Benicia	65.0	55.1	5.0	4.9
Pacific Refining Co.	6.6	ND[a]	3.7	2.9
Shell Oil, Martinez	132.0	95.8	24.4	11.8
Tosco Corp., Avon	21.8	3.2	5.5	13.2
Union Oil, San Francisco	156.3	91.1	61.0	ND[a]

[a]ND: Not detected

in the chemical speciation of selenium may also occur in sediments. It is notable that Seelye et al. (1982) found significant accumulation of selenium by fish from aerated sediments in laboratory tests.

Selenium in Bay-Delta Sediments

By contrast to studies with water and biota, very few data are available concerning selenium levels in the sediments of San Francisco Bay-Delta. Anderlini et al. (1975a, 1975b) noted rather higher levels of selenium in sediments from Mare Island Strait than elsewhere in the Bay. Risebrough et al. (1978) also cited these data, and noted that selenium concentrations in mussels were generally higher than those in sediments. Bradford and Luoma (1980) reported that selenium values in Bay sediments were 3 to 4-fold higher than concentrations in average shales. Given the low affinity of selenium for suspended particulates (Cutter, 1987), it is likely that levels of the element in Bay sediments would not be radically elevated despite the considerable loads of selenium entering the Bay. This does not, however, negate the possible importance of sediments in affecting selenium flux and speciation in the system, noted above.

It should be noted here that recent unpublished analyses of Bay-Delta sediments suggest lower levels than those reported by Anderlini et al. (1975a, 1975b). Additional study is required to confirm these data, which may be indicative of former analytical problems (S. Luoma, personal communication).

Selenium in Bay-Delta Biota

Discussions of selenium levels in biota from the San Francisco Bay-Delta are best prefaced with a note concerning the need for caution in interpreting the significance of selenium concentrations in organisms, at least in respect to their use to reflect point sources of the element. Because the geochemical cycling of selenium is so complex, and so little is known about the bio-availability of the element and the chemical forms of the element present in biota, concentrations found in organisms must be interpreted with extreme caution. In particular, selenium is known to interact with a variety of other elements in biota, and this often influences selenium uptake by organisms. The most common interaction reported to date concerns selenium and mercury. Koeman at al. (1973) first reported that mercury and selenium levels were correlated to each other in marine mammals, being present at 1:1 molar ratios in liver tissues (Fig. 36). Mackay et al. (1975) found a similar co-accumulation of the two elements in the black marlin Makaira indica, which accumulates considerable amounts of both selenium and mercury as it ages. However, although the two elements have been frequently found to influence each other's toxicity to aquatic biota, and have also been shown to affect each other's tissue distribution in organisms, no simple co-accumulation occurs in most invertebrates and finfish (Eisler, 1985a; Pelletier, 1985); rather, the interaction between the elements is more complex. In addition, selenium has been shown to interact (either with respect to bioaccumulation or toxicity) with a wide variety of other contaminants, including arsenic, cadmium, copper, lead, thallium,

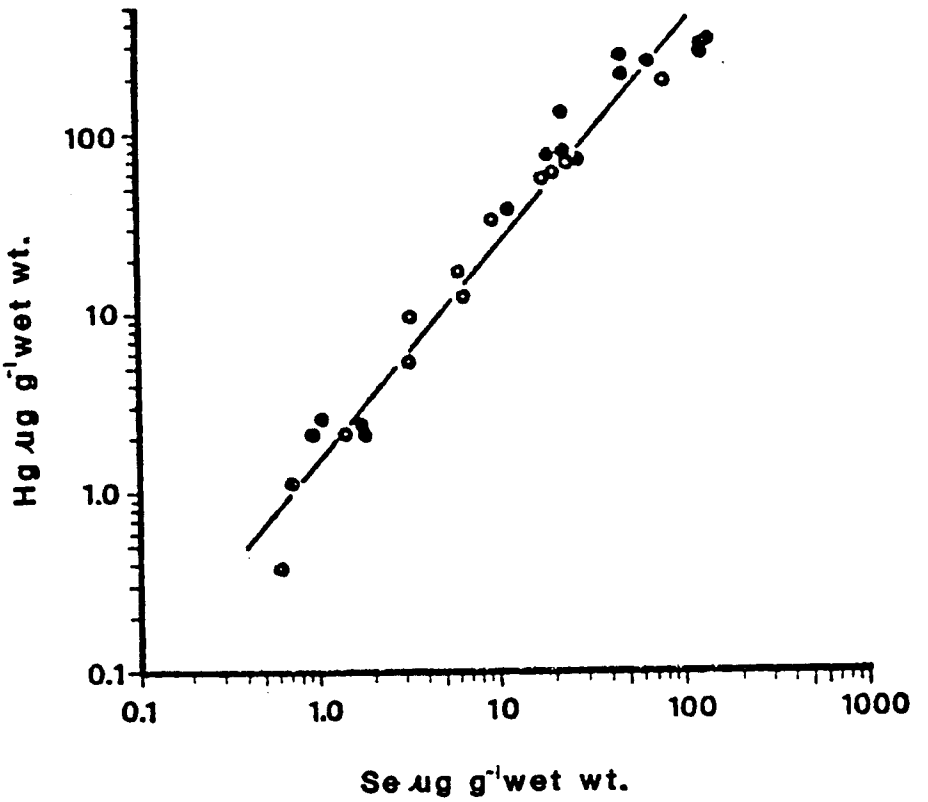


Fig. 36. The correlation between mercury and selenium accumulated in liver tissues of marine mammals. Open circles represent dolphins and porpoises; closed circles represent seals. After Koeman et al. (1973).

and the herbicide paraquat (Eisler, 1985a). As a result of this confused situation and the inadequate present understanding of the factors influencing selenium bio-availability, it has been stated that:

> "Selenium metabolism and degradation are both significantly modified by interaction with various heavy metals, agricultural chemicals, microorganisms, and numerous physicochemical factors, and until these interactions are resolved it will be difficult to meaningfully interpret selenium residues in various tissues". (Eisler 1985a).

Despite these problems, the concentrations of selenium found in Bay-Delta biota are briefly reviewed here, and an attempt is made to relate these to known sources of the element in the estuary. Girvin et al. (1975) analyzed several species of bivalve molluscs for selenium. These data are shown in Figs. 37 and 38. Apart from the high selenium levels in mussels (Mytilus edulis) from Islais Creek, Oyster Point, and Coyote Point (note that no other samples were collected at these sites, and data are consistent with local contamination thereat), these data provide a reasonably consistent profile of selenium in the Bay. Thus, concentrations of the element accumulated by these bivalves generally exhibit minima in the northern portion of South Bay, with higher levels being present in the northern reach of San Francisco Bay and further south in South Bay. This profile agrees well with the data of Cutter (1987) for selenium in water, discussed above, and indicates that the element exhibits higher bio-availabilities in the extremities of the Bay, with minimum values in the central waters of a more marine/oceanic character.

Further data on selenium in Mytilus edulis are available

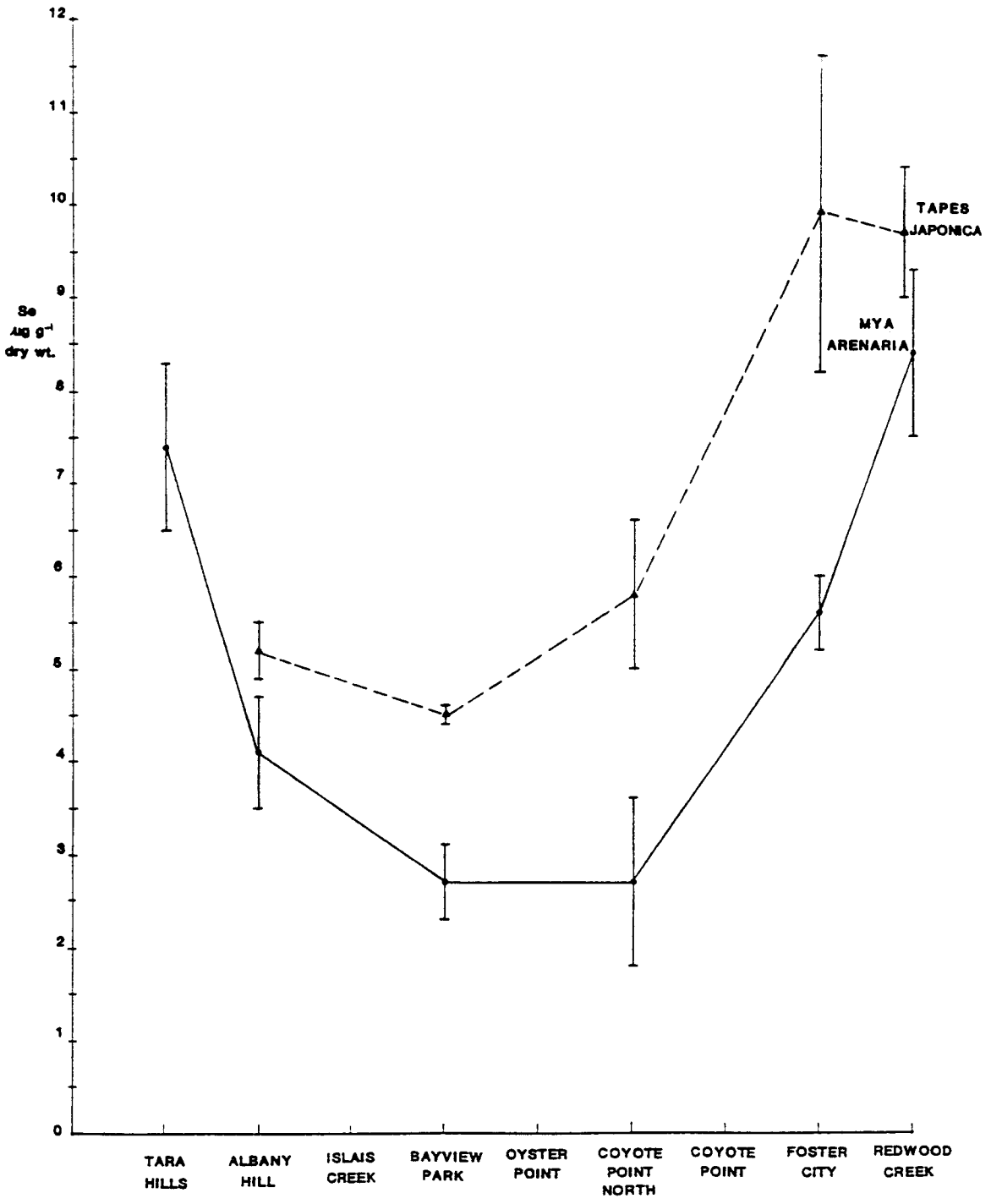


Fig. 37. Concentrations of selenium (means ± standard deviations, $\mu g\ g^{-1}$ dry weight) in the soft shell clam Mya arenaria and the Japanese littleneck clam Tapes japonica from San Francisco Bay sites. After Girvin et al. (1975).

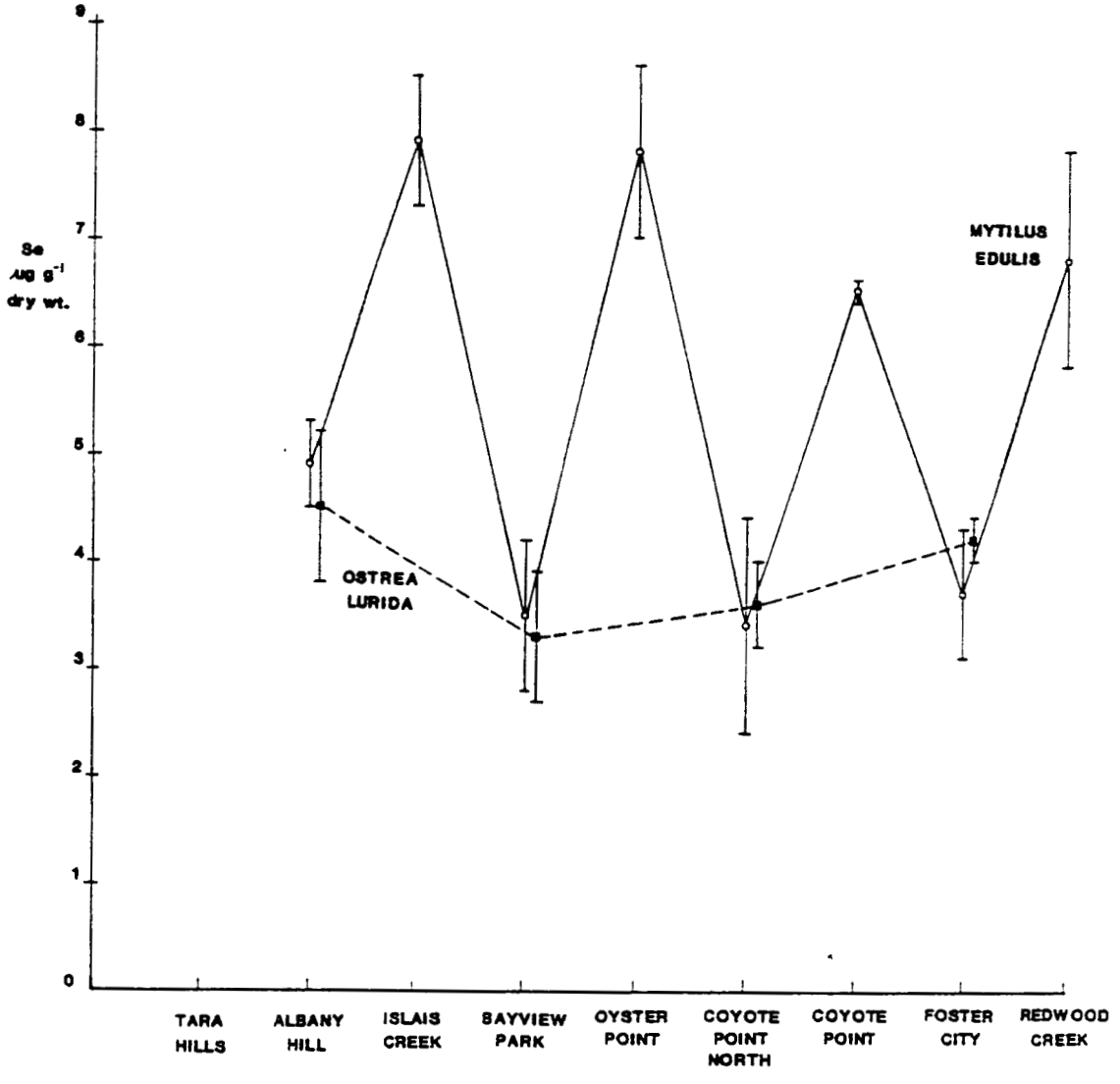


Fig. 38. Concentrations of selenium (means ± standard deviations $\mu g\ g^{-1}$ dry weight) in mussels (Mytilus edulis) and the Olympic oyster Ostrea lurida from San Francisco Bay. After Girvin et al. (1975).

from the report of Risebrough et al. (1978). These results are presented in Fig. 39. It is notable that there is general agreement with the data of Girvin et al. (1975), and that the greatest selenium concentrations were seen in mussels from sites close to the Carquinez Strait. It is probable that these locations are impacted by both selenium derived from the Sacramento/San Joaquin Delta and from discharges from oil refineries (and possibly other industries) in the northern reach of the Bay. The concentrations of selenium reported by Risebrough at al. (1978) for mussels from the South Bay show moderate enrichment only; possibly the sources of the element in this region are temporally variable, as the more recent results of Cutter (1987) clearly show considerable enrichment in this region. Data for selenium in the related mussel Mytilus californianus from the State Mussel Watch studies were reported only for samples taken in early 1982 and 1986, and do not significantly improve the above understanding of the abundance of this element in the Bay.

The Toxic Substances Monitoring Program only commenced analysis of fish samples for selenium in 1984. The 1984 data showed high selenium levels in mosquitofish from the Kesterson area (see also Saiki, 1986), and elevated levels in rainbow trout and brown trout from the most northern portion of the Sacramento River (SWRCB, 1986). In 1985, samples of largemouth bass from Alameda Creek and Lake Herman to the south of South Bay also exhibited significant concentrations of selenium in livers (1.2 and 1.6 $\mu g\ g^{-1}$ wet weight), tending to confirm selenium enrichment in this area, as noted by Cutter (1987). The elevated

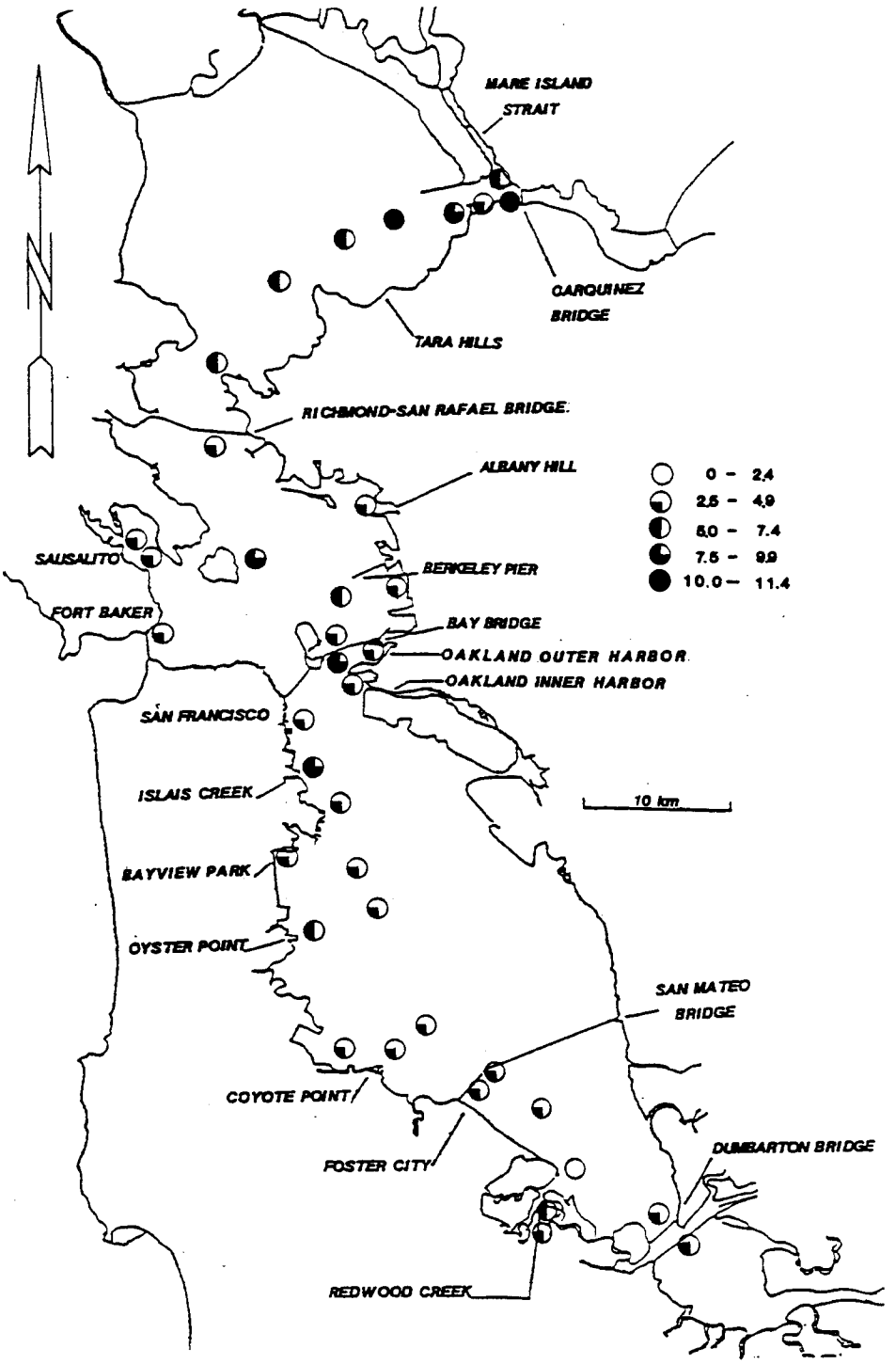


Fig. 39. Mean concentrations of total selenium ($\mu g\ g^{-1}$ dry weight) in native Bay mussels (Mytilus edulis). After Risebrough et al. (1978).

levels of the element in the extreme north of the Sacramento River were also confirmed, and a variety of sites in the San Joaquin catchment were shown to be contaminated by selenium (Linn et al., 1986). It is notable here that selenium is accumulated differentially by fish tissues (e.g. Sager and Cofield, 1984), being concentrated most highly in livers, followed in decreasing sequence by female reproductive tissues, axial muscle, and male reproductive tissues. The toxic effects of selenium on aquatic biota, including fish, will be dealt with in a later section of this report.

CDF&G (1987a) have recently reported the results of extensive studies of selenium in Bay-Delta biota. These investigations were notable for their careful methodology and attention to quality control and assurance. Species taken from Suisun Bay (starry flounder, Platichthys stellatus; Dungeness crab, Cancer magister; Bay shrimp, Crangon spp.) exhibited higher concentrations of selenium than the same species from elsewhere in the Bay-Delta. It was noted that organisms exhibiting such location-based differences were demersal (bottom-dwelling) or fed on benthic species, suggesting that sediments may be a repository and perhaps a source of selenium in Suisun Bay. The diet-related variations between organisms were also seen for important fish species; thus, white sturgeon (Acipenser transmontanus, which feed on benthic shellfish) exhibited significantly higher selenium concentrations than striped bass (Morone saxatilis).

Finally, the presence of selenium in bird populations from the Bay-Delta and its catchment requires discussion. Studies

commenced in 1982 by Ohlendorf and co-workers provided the first indication of high selenium bio-accumulation in the Kesterson region of the central San Joaquin River catchment. In 1983, investigations on birds at the Kesterson Wildlife Refuge commenced (Ohlendorf, 1986; Ohlendorf et al., 1986a). It was soon apparent that high levels of embryonic abnormalities or teratogenic effects were present in the birds nesting at Kesterson (Table 11). The types of abnormalities seen during 1983 are documented in Table 12. Analyses of bird livers and eggs showed that selenium concentrations were about seven times greater for Kesterson birds than for samples from the Volta Wildlife Area, located about 10 km southwest of Kesterson (Table 13). The Volta Wildlife Area is irrigated by water which is uncontaminated by agricultural drainwater (Ohlendorf, 1986), whereas the Kesterson Wildlife Refuge was receiving agricultural drainage waters (containing selenium) from the San Luis Drain. The considerable differences in selenium levels between the two locations were reflected not only in bird tissues, but also in a variety of other plant and animal tissues (Table 14; see also Saiki, 1986).

It is notable here that the concentrations of several other trace metals were also determined in livers of birds from the Kesterson and Volta areas in 1983. These data (Table 15) show little difference between the two areas, with the exception of silver concentrations, which were also higher in Kesterson samples. Ohlendorf et al. (1986a) reported that no significant differences were found between levels of silver in insects from Kesterson and from Volta, although mosquitofish (Gambusia

Table 11. Frequencies of embryonic mortalities and abnormalities in embryos and young of aquatic birds in Kesterson, 1983. After Ohlendorf et al. (1986a).

Species	Total numbers	Dead Embryos		Abnormal embryos or chicks	
		Number	%	Number	%
Coot					
Nests	59	35	59.3	25	42.4
Eggs	487	71	14.6	43	8.8
Ducks					
Nests	30	5	16.7	3	10.0
Eggs	277	7	2.5	11	4.0
Stilt					
Nests	102	17	16.7	18	17.6
Eggs	397	23	5.8	27	6.8
Grebe					
Nests	140	84	60.0	22	15.7
Eggs	457	145	31.7	25	5.5
All species					
Nests	347[a]	141	40.6	68	19.6
Eggs	1681[a]	246	14.6	106	6.3

[a]Totals include 16 avocet nests with 63 eggs in which no abnormalities or mortality occurred.

Table 12. Frequencies of various types of abnormalities in embryos and chicks of aquatic birds at Kesterson in 1983. After Ohlendorf et al. (1986a).

Species	N[a]	Abnormalities[b]					
		Eyes	Legs/Feet	Beak	Hydrocephaly	Exencephaly	Wings
Coot[c]	59 (487)	22 (32)	20 (25)	3 (4)	7 (11)		
Ducks	30 (277)	3 (5)	3 (9)	3 (8)	1 (1)		
Stilt[d]	102 (397)	17 (26)	9 (14)	11 (15)	4 (7)	2 (2)	4 (5)
Grebe[e]	140 (457)	19 (21)	4 (4)	4 (4)	2 (2)	3 (3)	

[a]Number of nests and (eggs) followed through late stages of incubation or hatching.
[b]Number of nests and (eggs) in which an embryo or chick had the abnormalities listed.
[c]Gastroschisis in one coot embryo.
[d]Gastroschisis in one stilt embryo; encephalocele in another.
[e]Encephalocele in one grebe embryo.

Table 13. Concentrations of selenium (geometric means and ranges, $\mu g\ g^{-1}$ dry weight) in livers and eggs of birds from Kesterson and from the Volta area, 1983. After Ohlendorf et al. (1986a).

Species	Volta			Kesterson					
	Livers			Livers			Eggs		
	N	Mean	(Range)	N	Mean	(Range)	N	Mean	(Range)
Coot	3	5.01	(4.4-5.6)	3	37.2	(21-63)	5	54.0	(34-110)
Ducks	2	4.14	(3.9-4.4)	2	28.6	(19-43)	4	9.9	(2.2-46)
Stilt	1	6.1					5	32.7	(12-74)
Avocet[a]							1	9.1	
Grebe				1	130		5	81.4	(72-110)

[a]One egg collected at Volta contained 2.7 μg^{-1} dry weight of selenium.

Table 14. Concentrations of selenium (geometric means and ranges, $\mu g\ g^{-1}$ dry weight) in composite samples of plant and animal tissues collected in May 1983 at Kesterson and the Volta Wildlife Area. After Ohlendorf et al. (1986a).

Sample	Volta			Kesterson		
	N[a]	Mean[b]	(Range)	N	Mean	(Range)
Filamentous algae	0/4	ND[c]		6/6	35.2	(12-68)
Rooted plants	1/1	0.43		18/18	52.1	(18-79)
Net plankton	4/4	2.03	(1.4-2.9)	7/7	85.4	(58-124
Water boatmen (Corixidae)	5/5	1.91	(1.1-2.5)	2/2	22.1	(20-24)
Midge larvae (Chironomidae)	3/3	2.09	(1.5-3.0)	3/3	139	(71-200
Dragonfly nymphs (Anisoptera)	2/2	1.29	(1.2-1.4)	6/6	122	(66-179
Damselfly nymphs (Zygoptera)	2/2	1.45	(1.2-1.7)	3/3	175	(118-21
Mosquitofish (Gambusia affinis)	5/5	1.29	(1.2-1.4)	12/12	170	(115-283

[a]Number with measurable concentrations/number analyzed.

[b]Geometric means; computed only when selenium was measurable in at least 50% of samples. When ony one sample was analyzed the concentration is shown in this column.

[c]ND=not detected.

Table 15. Concentrations of trace metals other than selenium (geometric means and ranges, $\mu g\ g^{-1}$ dry weight) in bird livers and eggs from Kesterson and the Volta area, 1983. After Ohlendorf et al. (1986a).

Metal	Volta[a]			Kesterson[a]					
	Livers			Livers			Eggs		
	N[b]	Mean[c]	(Range)	N	Mean	(Range)	N	Mean	(Range)
Ag[d]	2/2	0.201	(0.15-0.27)	4/4	1.02	(0.61-1.8)	0/4	ND[e]	
As[f]	3/6	0.251	(ND-0.89)	1/6		(ND-0.79)	3/20		(ND-2.9)
Cd[d]	2/2	0.583	(0.34-1.0)	4/4	0.362	(0.12-0.96)	0/4	ND	
Hg[f]	6/6	1.04	(0.48-2.2)	6/6	1.05	(0.35-10)	20/20	0.72	(0.08-4.3)
Pb[d]	2/2	0.255	(0.21-0.31)	1/4		(ND-3.2)	0/4	ND	
Zn[d]	2/2	120	(110-130)	4/4	105	(55-170)	4/4	47.8	(32-84)

[a] One avocet egg from Volta contained < 0.2ppm As and 0.49 ppm Hg. Cr was below the detection limit (0.4ppm, dry weight) in two coot livers from Volta, one mallard and three coot livers from Kesterson, and in three coot eggs from Kesterson; present at 2.7ppm in one coot egg from Kesterson.

[b] Number with measurable concentrations/number analyzed.

[c] Geometric means; computed only when a particular metal was measurable in at least 50% of samples.

[d] Analyzed in coot livers from Volta and in one mallard liver, three coot livers, and four coot eggs from Kesterson.

[e] ND indicates element was not found above the limits of detection (0.04 ppm for Ag and Cd; 0.2ppm for As and Pb).

[f] Analyzed in all liver and egg samples.

affinis) at Kesterson exhibited higher silver concentrations than did those from the Volta area. It was also noted that the concentrations of boron in biota at Kesterson were elevated compared to those in Volta organisms (Ohlendorf et al., 1986a, 1986b). Thus, Kesterson plants exhibited boron levels some 10-fold higher than plants from Volta; differences for insects were about 3-fold, and for mosquitofish, about 4-fold. Compounds of boron produce teratogenicity in birds when injected into eggs (Landauer, 1952; Birge and Black, 1977); further study is required into the possible effects of boron on birds at Kesterson.

Interestingly, mercury levels were not elevated in Kesterson biota compared to organisms from the Volta area. This finding is particularly relevant, in that mercury may afford protection from the toxic effects of selenium, in some organisms at least (Eisler, 1985a).

Ohlendorf et al. (1986b) provided additional data to confirm the link between selenium levels in birds, and the presence of agricultural drainage water. These studies involved not only the Kesterson and Volta areas, but also the Grasslands Water District of Western Merced County. The latter area lies about 25-30 km to the south-east of Kesterson, and is irrigated by a mixture of selenium-contaminated agricultural drainage water and other water with much lower levels of the element. In keeping with the major water source for the areas, eggs from birds exhibited highest concentrations of selenium at Kesterson, intermediate levels at the Grasslands site, and lowest concentrations of the element in the Volta area (Table 16). In addition, it was found that in

Table 16. Concentrations of selenium (geometric means and ranges, $\mu g\ g^{-1}$ dry weight) in randomly-collected eggs of aquatic birds from Kesterson Reservoir (KR), the Grasslands Water District (GWD), and the Volta Wildlife Area (VWA) in 1983 and 1984. After Ohlendorf et al. (1986b).

Species and	1983				1984			
location	N	Mean[a]	Range[b]	Moisture	N	Mean[a]	Range	Moisture[b]
Coot								
KR	15	30.9	17-74	73				
VWA					5	Nd[c]	Nd	75
Stilt								
KR	11	28.2A[d]	14-58	70	37	24.8A	5.2-64.0	71
GWD					6	4.68B	3.8-5.7	73
VWA[e]	3	2.67B	1.3-7.3	70	10	0.386C	Nd-1.9	72
Avocet								
KR[f]	9	6.00A	2.3-22.0	68	26	16.4A	3.4-61	73
GWD					2	5.79A	5.0-6.7	74
VWA[e]	2	1.24B	1.1-1.4	69	5	0.320B	Nd-2.4	72
Eared grebe								
KR	18	69.7	44-130	76				
Pied-billed grebe								
GWD					1	5.6		78
VWA	1	1.9		76	2	0.259	Nd-0.67	76
Gadwall								
KR	6	18.8A	9.6-32.0	67	6	21.4A	18-26	70
GWD					4	4.83B	2.9-6.8	68
VWA	2	0.839B	0.64-1.1	65	1	Nd		68
Mallard								
KR	5	15.2	9.3-31.0	65	5	10.4A	3.6-19.0	71
GWD					7	3.64B	2.1-6.0	69
VWA	1	1.2		66	2	0.152C	Nd-0.23	69
Cinnamon teal								
KR	2	6.85	6.6-7.1	66	5	13.5A	7.7-37.0	69
GWD					4	6.52B	6.2-6.7	69
VWA					1	Nd		70

[a] Geometric mean calculated when two or more samples were analyzed and when >50 percent of samples had detectable (>0.20ppm dry weight) levels of selenium. A value of 0.10ppm was assigned to Nd values to enable computation of some geometric means.
[b] Average moisture content (percentage) in samples.
[c] Nd = Not detectable (limit = 0.20ppm dry weight).
[d] Means followed by same capital letter are not significantly different (P>0.05) between/among sites (within species and year).
[e] Selenium concentration was lower (P<0.001) at VWA in 1984 than in 1983.
[f] Selenium concentration was greater (P<0.001) at KR in 1984 than in 1983.

general, bird species whose eggs accumulated the greatest levels of selenium at Kesterson (eared grebe, coot, and stilt) exhibited the highest incidences of embryotoxicity (Ohlendorf et al., 1986b).

These data provide strong evidence of the impact of selenium (derived from leaching of the element into agricultural drainwater) on the reproductive success of birds in the central portion of the San Joaquin River catchment. Studies in areas not impacted by selenium show much lower levels of embryotoxicity than those found for Kesterson birds. In addition, the experimental feeding of chickens and mallards with selenium-rich diets, or the injection of selenium into eggs, produce similar external deformities in the embryos to those noted at Kesterson (Poley et al., 1937; Palmer et al., 1973; NAS, 1976; Ort and Latshaw, 1978; Ohlendorf et al., 1986a, 1986b). While boron may also be implicated (see above), it is considered that the evidence accumulated to date clearly points to selenium as the probable causative agent for the effects seen on birds at Kesterson.

The above discussion is relevant to the specific area of the San Francisco Bay-Delta for two reasons. Firstly, the central San Joaquin Valley lies within the catchment of the Bay-Delta, and selenium-rich waters are known to drain to the Delta from this area. Secondly, additional sources of selenium exist in both the northern reach of the Bay and in the South Bay. As a result, legitimate concerns exist with respect to the possible impacts of selenium on bird populations within the Bay-Delta area.

In the Bay-Delta region itself, Ohlendorf et al. (1986c) reported data for metals in the tissues of greater scaups (Aythya marila) and surf scoters Melanitta perspicillata) from the South Bay. Livers of scoters contained significantly greater amounts of selenium (34.4±2.58 $\mu g g^{-1}$ dry weight) than did those of scaups (19.3±1.55 $\mu g\ g^{-1}$ dry weight). Interestingly, the opposite was the case for concentrations of copper and zinc, while levels of silver, chromium, mercury, nickel, and lead did not vary significantly between the two species. There appeared to be relatively little variation in selenium levels in the birds with location of sampling. The fact that concentrations of other metals did show site-dependent trends suggests that the ducks do not migrate too extensively, and that the entire southern portion of South Bay (from Redwood City south to Dunbarton Bridge and Newark Slough) is significantly contaminated by bio-available selenium. This is reminiscent of the data of Cutter (1987), which indicate significant sources of the element in freshwater discharges to South Bay.

Interestingly, in these diving ducks, molar concentrations of selenium and mercury in liver tissues were significantly correlated to each other (Fig. 40). However, the molar ratio of mercury to selenium was not 1:1 as observed in mammal livers (Koeman et al., 1973, 1975; Martin et al., 1976), but 1:6 (Ohlendorf et al., 1986c). Eight individual surf scoters exhibited particularly high selenium levels, with average molar ratios about 1:11. If mercury were to protect against selenium toxicity, the latter eight individuals might be expected to exhibit toxic symptoms. It was noted that selenium levels in

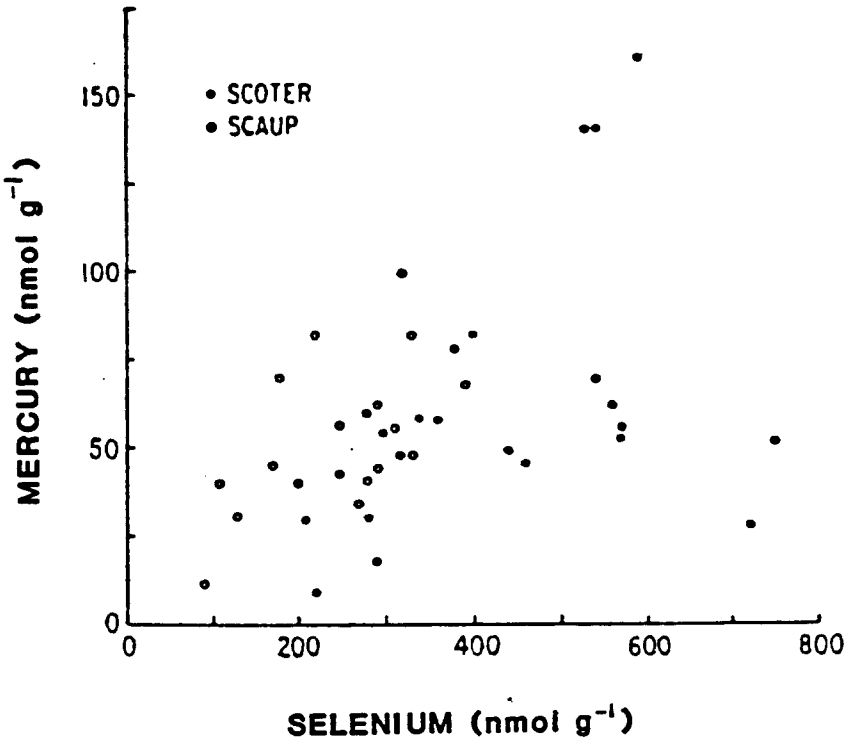


Fig. 40. Correlation of molar concentrations of mercury and selenium in liver tissues of greater scaups (Aythya marila) and surf scoters (Melanitta perspicillata) from South Bay. Correlation coefficient $r=0.422$, $p<0.01$. (Omission of eight scoter values with unusually high selenium increases significance of correlation). After Ohlendorf et al. (1986c).

livers of these ducks were similar to mean concentrations of the element found in dabbling ducks at Kesterson in 1983; however, such cross-species comparisons should be interpreted with caution.

Recent investigations by CDF&G (1987a) have shown that surf scoters and scaups from Suisun Bay also exhibit elevated concentrations of selenium. These data are shown in Table 17. The greater contamination of surf scoters than of scaups, as seen by Ohlendorf et al. (1986c), is confirmed by these results. In addition, the data suggest a general enrichment of selenium within the Bay-Delta, with levels of the element in birds from the entire estuary being rather greater than those in the same species from Humboldt Bay. There is a trend towards higher selenium concentrations in scoters and scaups from the most northern portion of the Bay-Delta. While such data should be interpreted with caution because of the possibility of significant movement of the birds between locations, the trends appear consistent between areas and species. The obvious hypothesis derived from these results is that selenium discharged from the San Joaquin River catchment or from Bay-Delta refineries (or both) gives rise to significant contamination of the northern reach of the estuary in particular.

The similarity of these selenium concentrations to data for birds experiencing reproductive problems at Kesterson in 1983 and 1984 gives rise to legitimate concerns over the possible toxicological impact of selenium on Bay-Delta bird populations. The data of CDF&G (1987a) show that scoters and scaups are generally more contaminated by selenium than are other bird

Table 17. Concentrations of selenium (means, standard deviations, and ranges, $\mu g\ g^{-1}$ wet weight) in muscle and liver tissues of surf scoters (*Melanitta perspicillata*) and greater and lesser scaups (*Aythya marila* and *A. affinis*, grouped together) from various portions of the Bay-Delta, Humboldt Bay and the Salton Sea. After CDF&G (1987a).

		MUSCLE				LIVER			
SPECIES	LOCATION	N	$\bar{x}$	SD	RANGE	N	$\bar{x}$	SD	RANGE
Surf Scoter	Humboldt Bay	10	0.8	0.19	0.5-1.0	10	3.1	0.95	2.4-5.6
	Suisun Bay	10	3.6	1.24	1.6-5.3	10	23	7.7	10-35
	San Pablo Bay	10	1.6	0.21	1.4-2.0	10	15	2.1	12-18
	Central SF Bay	10	2.3	0.86	1.4-4.3	10	12	5.1	6.8-22
	South SF Bay	11	1.9	0.48	1.0-2.8	10	10	3.1	6.9-17
Scaups	Humboldt Bay	2	1.2	0.64	0.7-1.6	2	2.9	1.77	1.7-4.2
	Suisun Bay	10	2.3	1.24	0.9-4.8	10	8.0	4.22	3.6-19
	San Pablo Bay	11	1.4	0.36	1.1-2.4	11	5.0	1.34	3.4-7.1
	Central SF Bay	2	2.8	0.07	2.7-2.8	2	4.9	0.21	4.8-5.1
	South SF Bay	12	1.3	0.51	0.7-2.5	12	3.8	1.13	1.6-5.5
	Salton Sea	12	1.2	0.43	0.4-2.0	12	3.1	1.05	1.5-5.6

species in Suisun marsh. It is therefore possible that only birds with habitat and dietary preferences similar to those of surf scoters and scaups are exposed to high concentrations of the element; this correlates to the comments noted above on the differences between benthic and pelagic species with respect to selenium enrichment. In addition, the effects of the co-accumulation of mercury by birds exhibiting high levels of selenium require clarification. The full significance of these data, and of their toxicological importance, thus remains to be established.

Summary

In summary, the levels of selenium known to be discharged to the receiving waters of San Francisco Bay-Delta generate cause for concern. Demonstrated effects of the element are probable in the Kesterson Wildlife Refuge area, and these are thought to be due to selenium derived from agricultural drainage water, draining naturally seleniferous soils to the western side of the San Joaquin Valley. Selenium (mostly as selenate) drains to the Delta via the San Joaquin River. This source, and additional considerable loads of the element discharged by Bay oil refineries (and perhaps other industries also), give rise to elevated concentrations of selenium in the northern reach of San Franciso Bay. Enrichment is also seen in the South Bay; however, very little is known of possible selenium sources in this area. Generally, concentrations of selenium in biota reflect the levels found in water, although data are notably sparse. It is possible that selenium is heavily concentrated by some specific organisms

in areas of particular abundance. It is also possible that detrimental biological effects occur in Bay-Delta biota due to the high selenium abundance; however, possible interactions with other contaminants (and resulting effects on the element's toxic action) and the general dearth of information preclude strong conclusions at this time. There is no doubt that additional research is needed on selenium in the Bay-Delta ecosystem.

D. MERCURY

Introduction

The natural global rate of mobilization of mercury is only about 3,000 tonnes a year, which is very much less than that of many other trace elements (MIT, 1970). The activities of Man give rise to the release of a further 7,000 to 10,500 tonnes annually (Phillips, 1980). On the basis of these figures, it is perhaps surprising that mercury is considered to be of the greatest pollution hazard of all trace metals (Friberg and Vostal, 1972; Waldichuk, 1974). However, the element is of exceptional toxicity in aquatic environments, effects on biota being evident at the part per billion level ($\mu g\ L^{-1}$) and below (e.g. U.S. EPA, 1986).

The problems caused by mercury contamination of the environment gained notoriety originally through a poisoning episode in Minimata on the island of Kyushu in Japan, in the early 1950s. Symptoms of the poisoning in Man were almost exclusively related to effects on the central nervous system, with both adults and infants *in utero* being affected. A second outbreak of poisoning occurred some years later, also in Japan, at Niigata. Protracted studies in Japan (and later in Sweden and Canada) showed that mercury was the causative agent, and that the chemical speciation of the element was central to its effects. It is now known that the bio-accumulation and toxic effects of mercury vary considerably between a variety of chemical species. The most important form of the element in the environment is the methylated species, which may be produced by microbial

methylation of inorganic mercury in sediments or elsewhere (e.g. intestinal microflora of higher animals). Further details of the toxicities of different chemical species of mercury may be found in Friberg and Vostal (1972); data on bio-accumulation of the various forms of the element were reviewed by Phillips (1980).

In nature, mercury occurs generally in low concentrations in the earth's crust, mostly as sulfides (especially red sulfide or cinnabar). It is notable here that the Coast Range in the Central Valley contains high concentrations of natural mercury deposits, which were mined in the past. The main area of this mining activity was from the Panoche Creek north to the Stony Creek (CVRWQCB, 1987). In addition to inputs from natural weathering of such deposits, mercury is released to aquatic environments from industrial and agricultural sources (Vostal, 1972). Industrial sources include mining and smelting, fossil fuel combustion, chlor-akali plants, the manufacture of electrical equipment, pulp and paper mills, and antifouling or mildew-proofing activities. Mercury sources from agricultural usage are largely related to fungicides, which commonly contain the element (sometimes in unusual chemical forms).

Klapow and Lewis (1979) reported a wide range of acute and chronic toxicities of mercury to aquatic biota, and a very narrow "window" between reported concentrations of the element in seawater and such toxicities (Fig. 41). This emphasizes the considerable pollution hazard from mercury (particularly as many of the toxicity studies relate to the less toxic chemical forms of the element, rather than to methylmercury). Water quality criteria recommended by the U.S. EPA for chronic exposure are

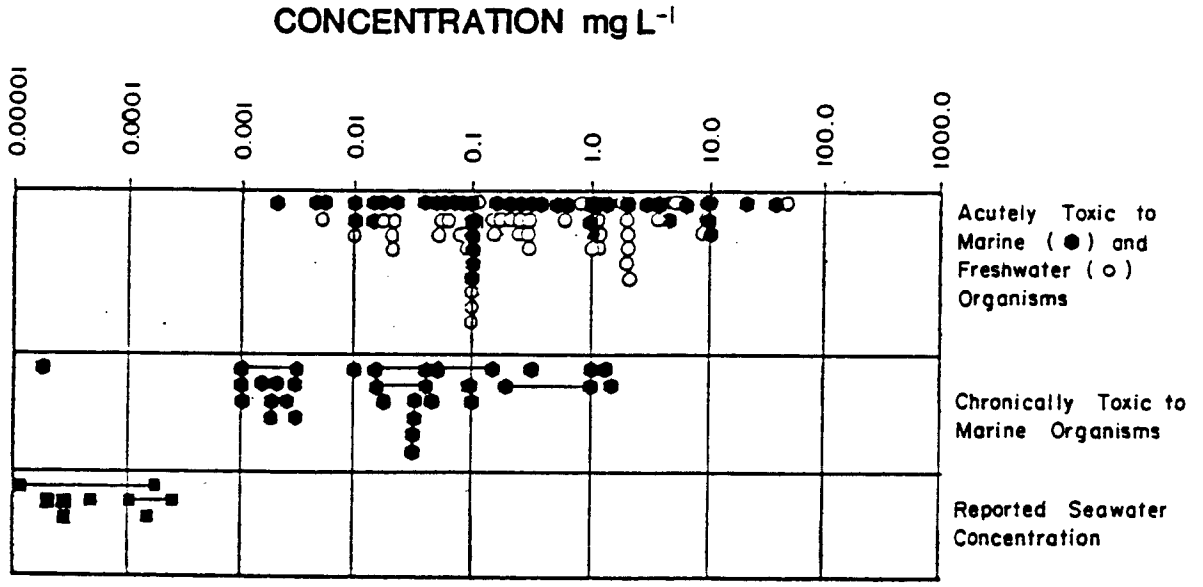


Fig. 41. Concentrations of mercury in seawater, and acute and chronic toxicities of the element (in various chemical forms) reported for aquatic biota. After Klapow and Lewis (1979).

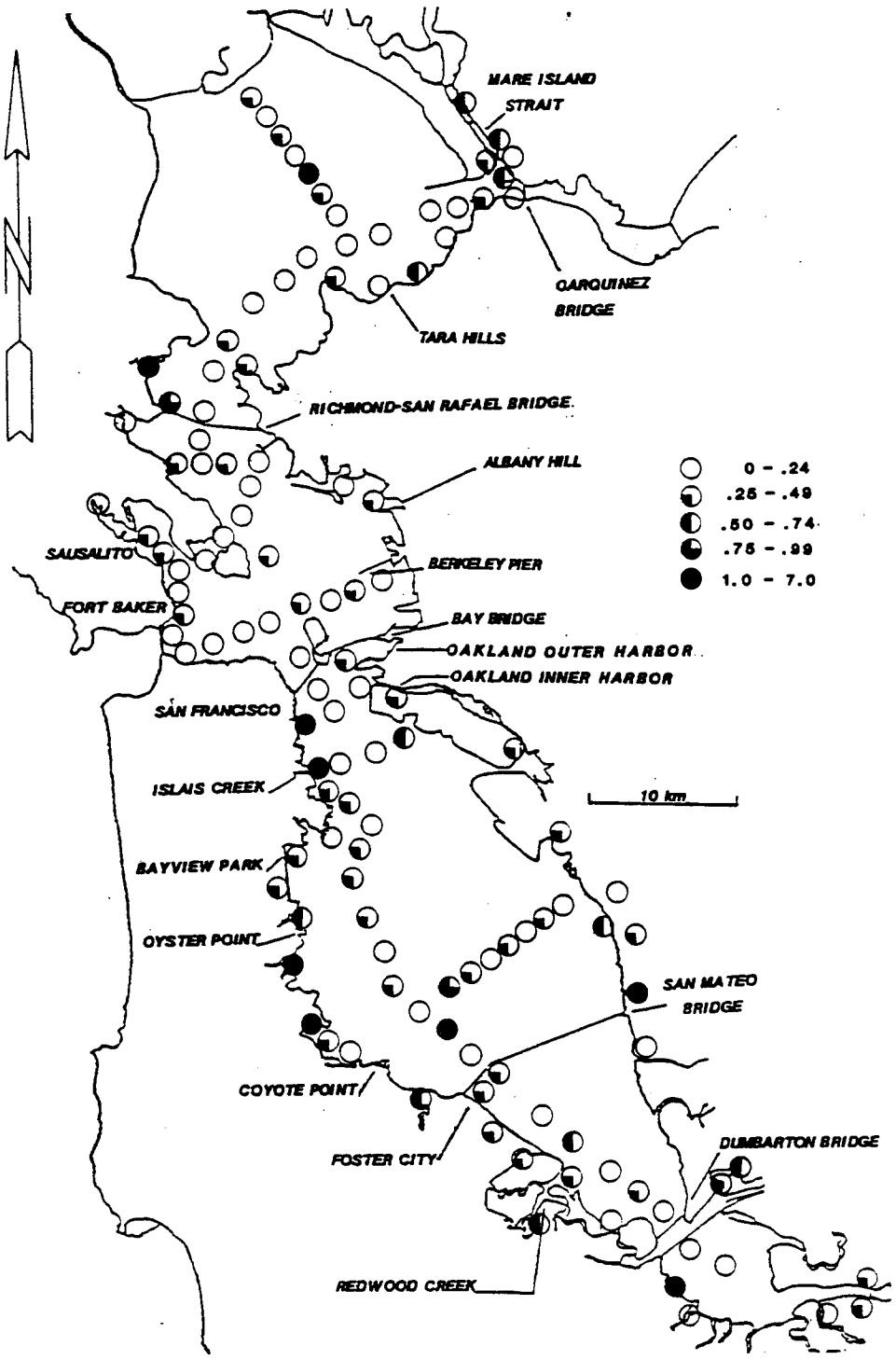


Fig. 42. Mean concentrations of mercury ($\mu g\ g^{-1}$ dry weight) in surface sediments of various sites in the San Francisco Bay. After Risebrough et al. (1978).

emerge from these investigations, although there was some evidence for elevated mercury levels in seston samples from Suisun Bay, and for higher levels of the element in phytoplankton and/or organic detritus than in zooplankton.

Mercury in Bay-Delta Sediments

Girvin et al. (1975) reported concentrations of mercury in sediments from five Bay locations to vary between 0.08 $\mu g\ g^{-1}$ dry weight (Coyote Point North) and 0.46 $\mu g\ g^{-1}$ (Albany Hill). Samples of suspended particulates taken at Albany Hill and Foster City exhibited rather greater levels of the element, at 1.3 and 0.85 $\mu g\ g^{-1}$ dry weight respectively. Data reviewed by Bradford and Luoma (1980) showed broadly similar ranges in concentration for sediments from nine Bay sites, from Mare Island Strait south to Dumbarton Bridge; mean levels at these locations ranged from 0.24 to 0.87 $\mu g\ g^{-1}$ dry weight.

Extensive data were reported by Risebrough et al. (1978) concerning mercury in Bay sediments (Fig. 42). These results show considerable similarities to data for lead in sediments from the same locations (see Fig. 54 in this report). Thus, somewhat elevated mercury levels were seen in sediments from both San Pablo Bay and South Bay compared to those in Central Bay, and nearshore sediments tended to be more contaminated than those from offshore sites. The number of locations exhibiting elevated sediment mercury levels was considerable, suggesting a multiplicity of sources. For lead, such a pattern was correlated to the element's transport atmospherically, its consequent ubiquity, and its presence at high concentrations in run-off. No

data are available on mercury levels in the atmosphere of the Bay-Delta, although these may be appreciable, given that the burning of fossil fuels is an important source of the element (Vostal, 1972). Mercury is present in significant quantitites in urban run-off (e.g. Murphy and Carleo, 1978; Young et al., 1980), and this may partially explain its ubiquity in Bay sediments. Among areas of considerable enrichment are Islais Creek and Mission Creek sediments, which exhibit mercury levels up to 1.2 $\mu g\ g^{-1}$ and 2.5 $\mu g\ g^{-1}$ dry weight respectively (Hoffman and Meighan, 1984; Chapman et al., 1986). Both these creeks receive urban run-off in significant quantities from the surrounding highly urbanized catchments.

In addition to mercury sources in the area local to the Bay, the major drainage basin upstream of the Delta undoubtedly provides considerable quantities of the element to the estuary. Much of this mercury input is likely to be adsorbed to suspended particulates, a large percentage of which settle out in upstream reservoirs, or in the Delta and Bay sediments. Mercury sources in the Central Valley include weathering of the element from naturally rich deposits in the Coast Range (see above) and wash-down of mercury used in historical gold mining activities in the Sierra Nevada Range; some 3,500 tonnes of mercury in total were employed in the latter process. The Central Valley Regional Water Quality Control Board has conducted extensive studies of mercury in these regions, sampling both fish and sediments (CVRWQCB, 1987). Data concerning mercury in fish will be considered below. Concentrations of the element found in a late 1986 survey of sediments are shown in Fig. 43. The relationship

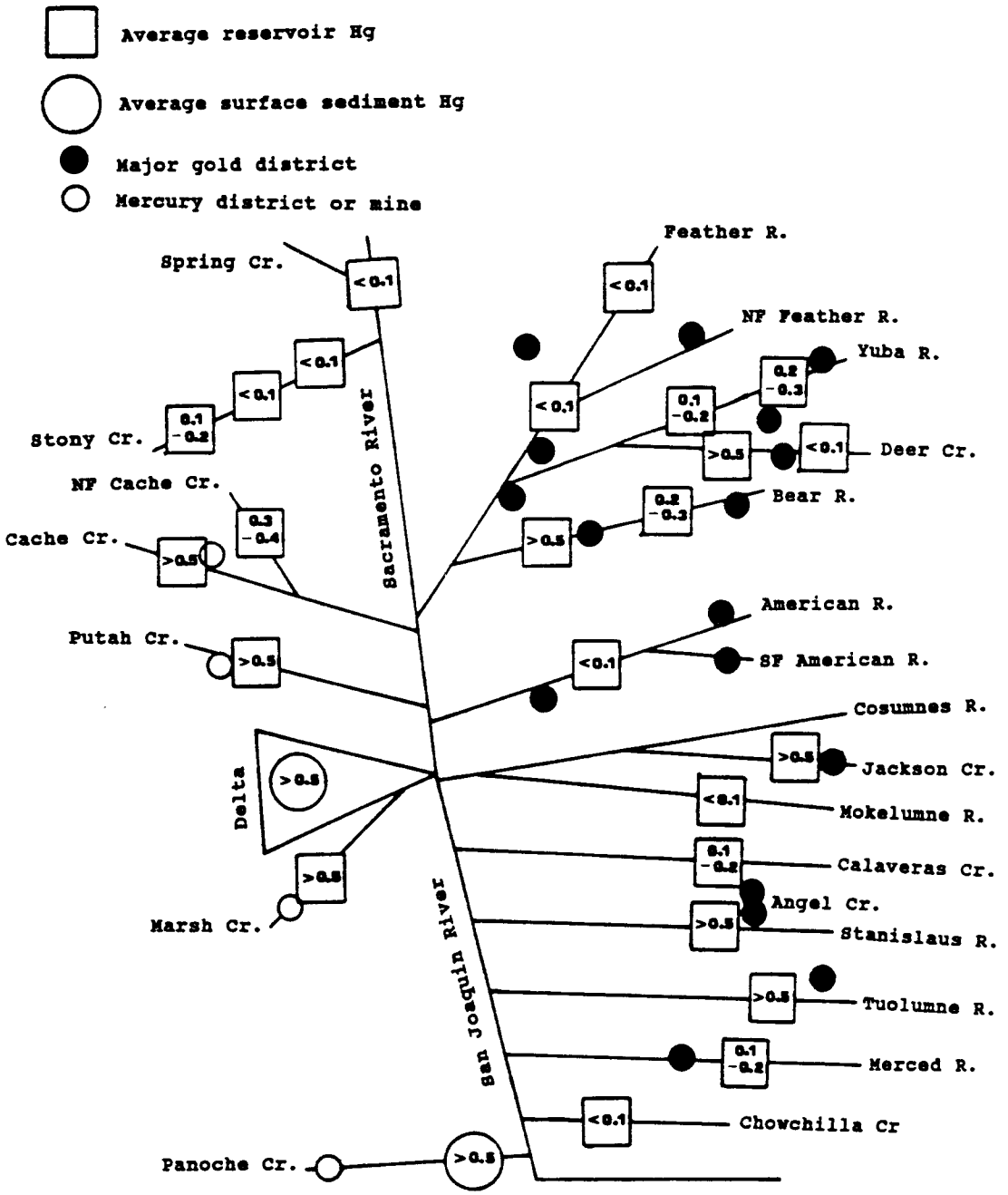


Fig. 43. Concentrations of total mercury ($\mu g\ g^{-1}$ dry weight) in surface sediments of tributaries and reservoirs in the Sacramento and San Joaquin River catchments. After CVRWQCB (1987).

between upstream mercury mining areas and gold mining activities, and downstream contamination of sediments by mercury is particularly well defined in these data. Areas of notable sediment enrichment by the element include Clear Lake, Lake Berryessa, Deer Creek, and Bear River in the Sacramento system. In the San Joaquin catchment, mercury levels are elevated in sediments from Jackson Creek, Angel Creek, Tuolumne River, and Panoche Creek. The Oaks Arm of Clear Lake is exceptionally highly polluted, mainly from the Sulphur Bank Mine. Mercury levels in sediments close to this mine exceed 100 $\mu g\ g^{-1}$ dry weight at the surface, and exceed 1000 $\mu g\ g^{-1}$ at depths of 45 cm, reflecting the magnitude of historical contamination. Concentrations of the element decrease with distance from this major source, but are appreciably elevated in surface sediments throughout the lake. Lower, but nevertheless significant, levels of mercury are found in Lake Berryessa sediments, mainly originating from inflows from the Putah and Pope Creeks, which again receive run-off from inoperative mercury mines. The Marsh Creek reservoir, which drains directly to the Delta south of Jersey Island, also exhibits elevated sediment mercury levels, believed to be due to run-off from the Mount Diablo mine (CVRWQCB, 1987).

This generalized enrichment of mercury in the Central Valley catchment constitutes a source of the element to the upper San Francisco estuary. Contaminated sediments eventually find their way to the Delta and settle out, giving rise to significantly elevated mercury levels in upper estuary sediments. Dredging and dumping activities, and natural resuspension/redeposition

processes in the estuary, will transport the mercury throughout the system.

Finally here, it should be noted that the extreme south of South Bay also exhibits evidence of mercury enrichment, although no data for mercury in sediments appear to be available.

Mercury in Bay-Delta Biota

Mercury is the only trace element for which Federal and State guidelines exist with respect to concentrations in fish tissues (SWRCB, 1986). The Food and Drug Administration has set an action level of 1.0 $\mu g\ g^{-1}$ wet weight for the edible portions of fish and molluscs, to protect human health. The National Academy of Sciences' guideline for predator protection is 0.5 $\mu g\ g^{-1}$ wet weight of total mercury, and the California State Department of Health Services employs this level as an informal standard for protection of human health (SWRCB, 1986). The majority of international standards for total mercury in seafoods are also set at 0.5 $\mu g\ g^{-1}$ wet weight (Nauen, 1983).

Mention should be made here of two factors which may influence either the uptake of mercury by biota, or its toxicity to organisms. The first of these involves the interaction between mercury and selenium in biota (see also section IIC of this report). Since the original reports noting the apparent co-accumulation of these two elements by marine mammals (Koeman et al., 1973, 1975), much research has been carried out to attempt to elucidate the precise relationship between mercury and selenium in aquatic biota (see reviews by Eisler, 1985a; Pelletier, 1985). No truly consistent picture has emerged from

these data, although many reports exist which show that interactions of various types occur in aquatic species, especially fish (e.g. Mackay et al., 1975; Sheline and Schmidt-Nielsen, 1977; Leonzio et al., 1982). Interestingly, such interactions may not occur in at least some species of molluscs (Fowler and Benayoun, 1976). It is possible that this difference relates to the chemical speciation of the mercury present in biota.

The chemical form of mercury in aquatic organisms is of great importance in defining its uptake and toxicity, both to the organism itself and to its predators. As noted previously, methylmercury is by far the most toxic (and most highly bio-available) of the chemical species of this element generally found in the environment. In most instances, mercury in finfish is almost all present in the methylated form. However, in bivalve molluscs, this is not usually the case; thus, organisms such as mussels generally contain only a small percentage of methylmercury among their total accumulated load of the element (e.g. Mikac et al., 1985). It is unfortunate that local studies of mercury in aquatic biota have concentrated only on total levels of the element, without employing differential analysis of the methylated fraction. The only mention of this subject in data relevant to San Francisco Bay appears to be that in studies of mercury in finfish from the Toxic Substances Monitoring Program, where spot checks in 1986 suggested that most of the mercury in fish muscle samples was methylated (SWRCB, 1986). Data reported below on mercury in Bay-Delta biota thus refer to total levels of the element.

Girvin et al. (1975) surveyed several bivalve molluscs from San Francisco Bay for mercury; these data are shown in Figs. 44 and 45. In general, higher levels of the element were seen in samples from the northern and southern extremities of the estuary than in the area of Central Bay and the northern portion of South Bay. Data for M. edulis from Islais Creek and Coyote Point were suggestive of local contamination; for the former site, this agrees with information on sediments (see above). The concentrations of mercury in mussels from Redwood Creek reported by these authors are notably elevated, and are approximately equivalent to a 0.5 $\mu g\ g^{-1}$ wet weight standard for the protection of public health. Contamination of Redwood Creek was confirmed by results for mercury in Pacific oysters (Crassostrea gigas) from this location (see Table 18). Concentrations of the element in Redwood Creek oysters were 16 to 21 times greater than those in Tomales Bay samples, and certainly exceeded a 0.5 $\mu g\ g^{-1}$ wet weight level. As no data are available on the proportion of total mercury present in methylated form in any of these bivalves, the threat to public health from their ingestion is difficult to estimate accurately; however, there is ample cause for concern.

The data of Risebrough et al. (1978) for mercury in native Bay mussels (Mytilus edulis) are presented in Fig. 46. The overall profiles agree well with data from Girvin et al. (1975), showing enrichment of the element in both north-east San Pablo Bay and South Bay, the latter being particularly contaminated in the Islais Creek/Mission Creek area and between Coyote Point and Redwood Creek.

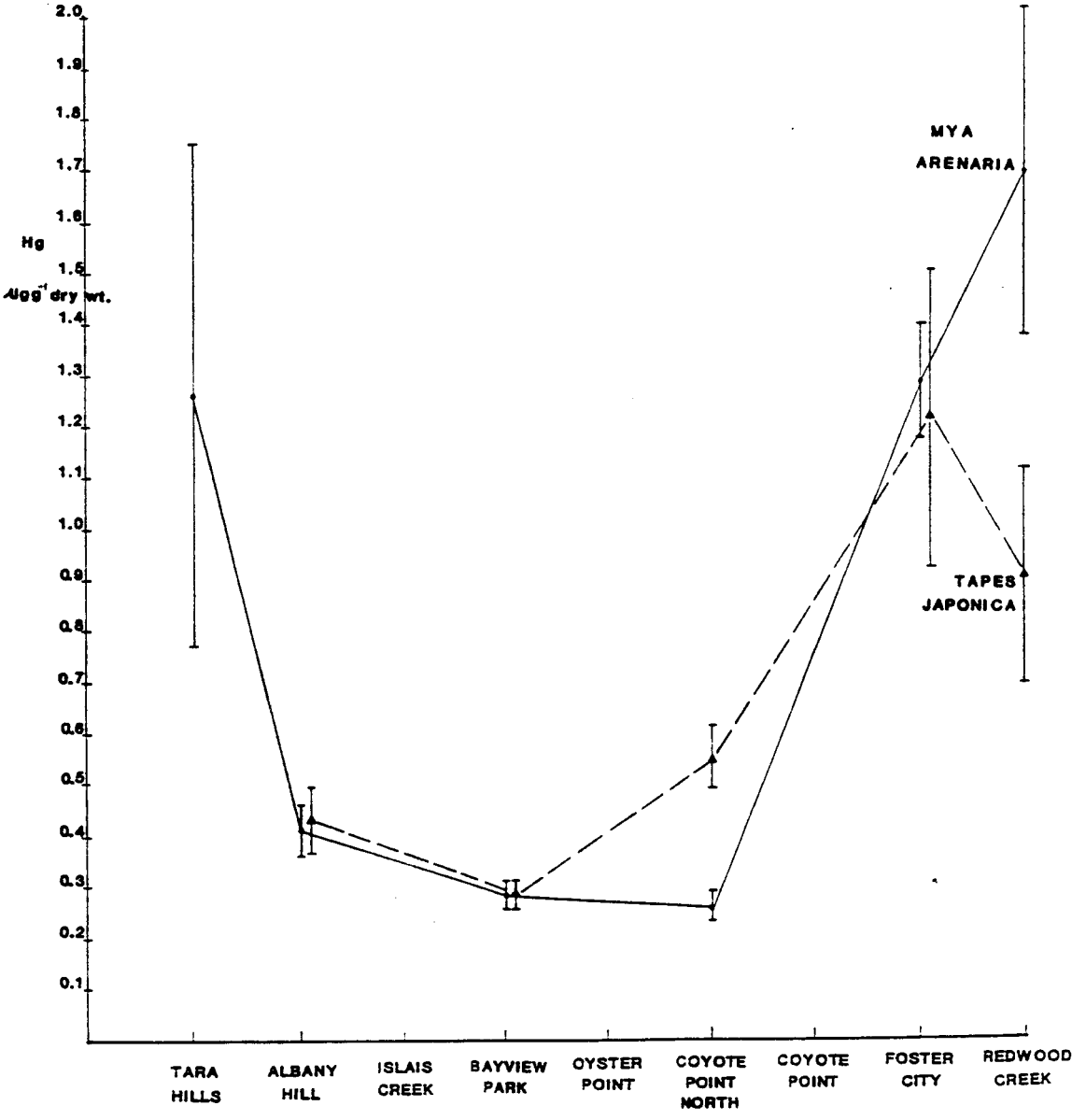


Fig. 44. Concentrations of total mercury (means ± standard deviations, $\mu g\ g^{-1}$ dry weight) in the softshell clam Mya arenaria and the Japanese littleneck clam Tapes japonica from San Francisco Bay. After Girvin et al. (1975).

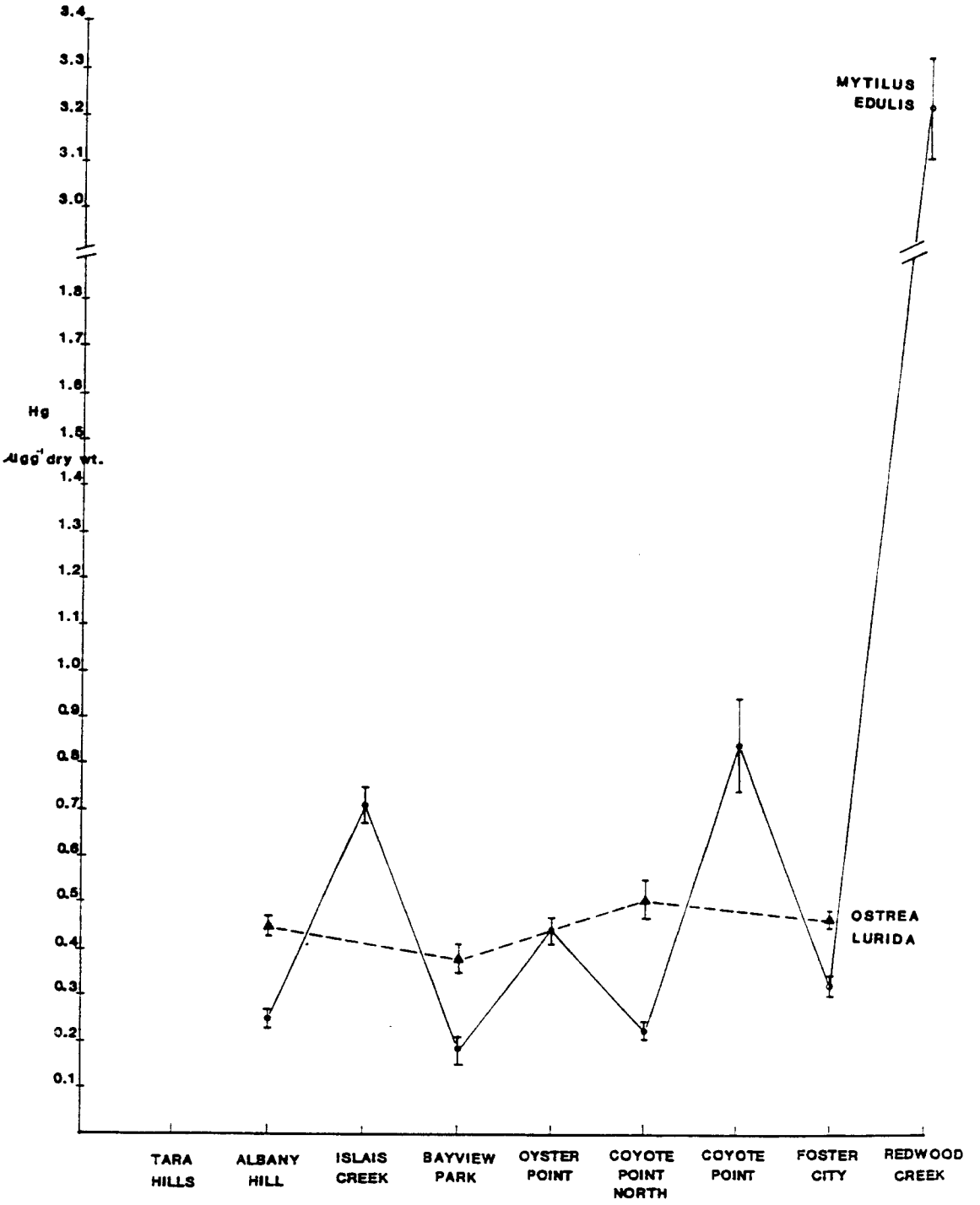


Fig. 45. Concentrations of total mercury (means ± standard deviations, $\mu g\ g^{-1}$ dry weight) in native Bay mussels Mytilus edulis and the Olympic oyster Ostrea lurida fr San Francisco Bay. After Girvin et al. (1975).

Table 18. Concentrations of total mercury (means ± standard deviations, $\mu g\ g^{-1}$ dry weight) in tissues of Pacific oysters, Crassostrea gigas, from Redwood Creek and Tomales Bay. After Girvin et al. (1975).

Tissue	Redwood Creek	Tomales Bay	Enrichment Factor[a]
Gill	8.0±0.24	0.41±0.06	19.5
Mantle	3.1±0.55	0.15±0.02	20.7
Hepatopancreas	3.4±1.03	0.21±0.01	16.2

[a]Enrichment factor denotes the ratio between mean mercury concentrations at the two locations.

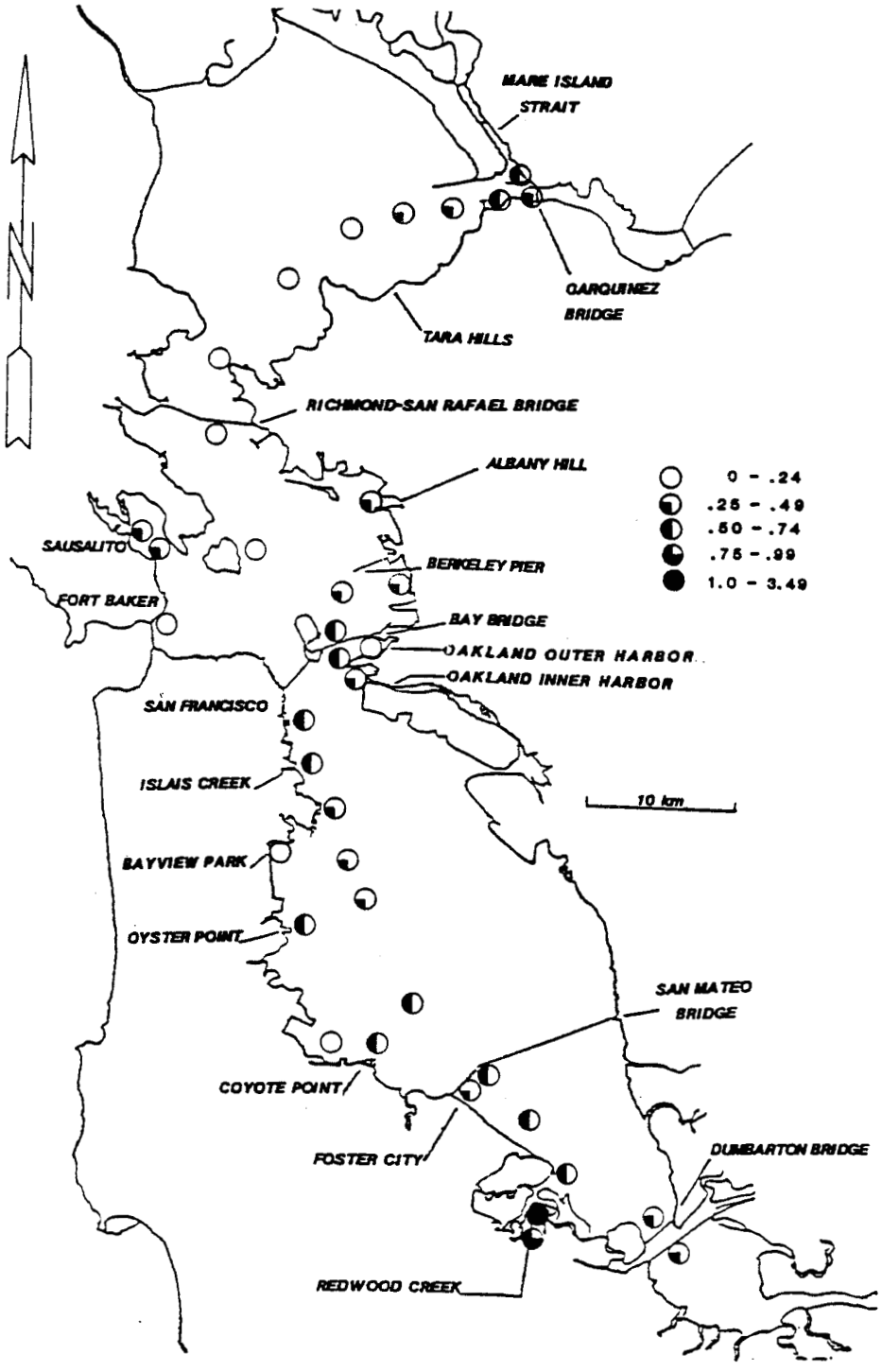


Fig. 46. Mean concentrations of total mercury ($\mu g\ g^{-1}$ dry weight) in native Bay mussels, Mytilus edulis, from San Francisco Bay. Time of sampling for most sites was April 1976. After Risebrough et al. (1978).

Information from the State Mussel Watch Program (Table 19) generally exhibits reasonable agreement with the earlier studies cited above, mercury concentrations tending to be somewhat greater in the northern and southern extremities of the Bay than in Central Bay. The differences are not great, however; this is partly a function of the paucity of control sites near the Golden Gate in the Mussel Watch data. No highly significant temporal trends are notable in this dataset.

Surprisingly, few data are available for mercury in fish from San Francisco Bay itself. However, both the State Water Resources Control Board and the Central Valley Regional Water Quality Control Board have undertaken programs to investigate mercury in fish from the Central Valley catchment. Data from the Toxic Substances Monitoring Program, run by the State Board, are shown in Fig. 47. The widespread enrichment of mercury in the Sacramento and San Joaquin Rivers and their tributaries is clearly evident from these data. In addition, it should be noted that the Guadalupe River and its catchment, to the south of South Bay, also exhibit mercury enrichment. Data from the studies of the Central Valley Regional Board (CVRWQCB, 1987) confirm the high levels of mercury in fish from the Sacramento and San Joaquin basins. Although the correlation of mercury levels in fish tissues to those in sediments was not always evident, in many cases both types of sample reflected local mercury enrichment caused by run-off from old mines or from historical gold mining areas. Mercury levels found in fish are of course dependent on a variety of parameters, including the ambient chemical speciation of mercury (e.g. whether sediment bacteria

Table 19. Concentrations of total mercury (means, ug g^{-1} dry weight) in transplanted mu (Mytilus californianus) or native Bay mussels (M. edulis, as shown[a]) from 33 s in San Francisco Bay. Data from the California State Mussel Watch Program, af Hayes et al. (1985), Hayes and Phillips (1986) and Stephenson et al. (1986a).

LOCATION	STATION CODE	1980	1981	1982 (J/F)	1982 (O/N/D)	1982 RESIDENT (O/N/D)a	1983	1985	1
MARE ISLAND	300.20							0.396a	0
DAVIS POINT	301.00	0.170a			0.305				
POINT PINOLE	302.00	0.165a	0.348	0.477	0.294b		0.500	0.488	0
RICHMOND BRIDGE	303.00	0.234	0.295	0.149	0.337b				
SANTA FE CH. MOUTH	303.10								0
RICHMOND INNER HARBOR	303.60							0.381	
STAUFFER'S	304.00			0.206					
ANGEL ISLAND	305.00	0.166	0.225	0.086	0.302b				
FORT BAKER	306.00		0.261		0.257c				
TREASURE ISLAND	307.00	0.237	0.281	0.226	0.335c		0.471	0.337	0
ALAMEDA YACHT HARBOR	307.20							1.350a	0
OAKLAND IN. HARBOR WEST	307.30								0
OAKLAND IN. HARBOR EMBC.	307.40								0.
OAKLAND BACK HARBOR	307.60								0.
HUNTER'S POINT	308.00		0.385	0.231	0.354c	0.361a			
SAN MATEO BRIDGE 8	309.00	0.345	0.435	0.321	0.366c	0.308a	0.313	0.554	0.
SAN MATEO BRIDGE 8A	310.00			NA					
SAN MATEO OLD BRIDGE	311.00			NA					
BELMONT SLOUGH	312.00			0.334					
REDWOOD CREEK MOUTH	313.00		0.563	0.371	0.442c	0.485a	0.511	0.654	
REDWOOD CREEK 10	314.00			0.329					
REDWOOD CREEK TOWERS	315.00			NA	0.494b	0.691a			
REDWOOD CREEK TRDWNDS	316.00	0.296a		NA	0.327b	0.308a			
REDWOOD CREEK STP	317.00				0.315				
SF PETES	318.00				0.304				
SF PULGAS	319.00				0.398				
SF AIRPORT	320.00				0.317				
DUMBARTON BRIDGE 14	321.00	0.317a	0.575	0.187	0.323	0.401a	0.675	0.447	C
NEWARK SLOUGH	324.00			NA					
CHANNEL 17	325.00			NA					
PALO ALTO 8	326.00			NA		0.337a			
PALO ALTO YACHT	327.00			NA					
ALVISO SLOUGH	328.00			NA					

J/F/O/N/D: January/February/October/November/December, all 1982

a Resident Mytilus edulis.

b Mean of two values.

c Mean of three values.

NA: Not analyzed.

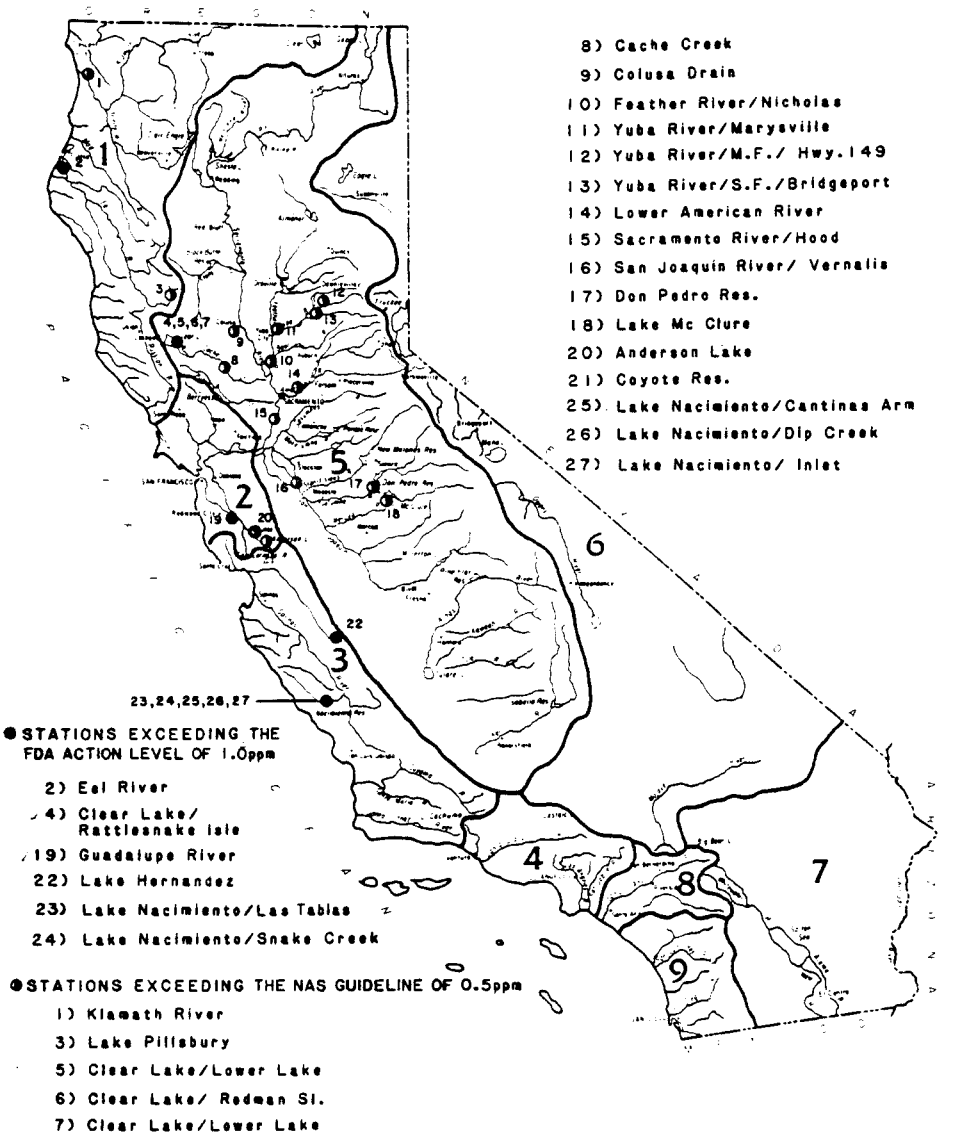


Fig. 47. Locations where sampled fish exhibited elevated levels of total mercury in axial muscle, 1978-1984. Elevations above the FDA action level of 1.0 $\mu g\ g^{-1}$ wet weight, and the NAS guideline of 0.5 $\mu g\ g^{-1}$ wet weight, are shown. Data from the Toxic Substances Monitoring Program, after SWRCB (1986).

significantly methylate the element), and fish length, size, or age (e.g. see Phillips, 1980; Eisler, 1984).

Concentrations of mercury in marine mammals are also highly age-dependent (Phillips, 1980). Risebrough et al. (1978) recognized this factor, and could not find evidence of markedly elevated mercury concentrations in local harbor seals once this age-dependency had been accounted for. Martin et al. (1976) speculated that premature pupping in populations of the California sea lion (Zalophus californianus) in Southern California might relate to a mercury-selenium-bromine imbalance. However, this hypothesis has not been proven, and reproductive problems in seal populations elsewhere in the world have been correlated to high PCB and DDT abundance (Helle et al., 1976a, 1976b). No data appear to be available on the reproductive success of marine mammals in San Francisco Bay.

Finally, Ohlendorf et al. (1986c) found that mercury levels in the livers of dabbling ducks in the South Bay averaged 10.6 to 12.5 $\mu g\ g^{-1}$ dry weight, and correlated to selenium concentrations in these samples (see section IIC of this report). It is possible that mercury is protecting these birds from the effects of selenium poisoning, particularly in view of the fact that Kesterson bird species (which exhibit similar concentrations of selenium in their livers but much lower mercury levels) have shown overt signs of selenium poisoning. One fascinating possibility for research would be the deliberate dosage of Kesterson birds with additional mercury, to attempt to reduce the effects of selenium on their reproductive success.

Summary

Despite the very considerable pollution potential of mercury and its extreme toxicity to aquatic biota, the element has been poorly characterized in the San Francisco Bay-Delta. The paucity of studies is particularly surprising in view of the known mercury enrichment in the Bay-Delta catchment, due to naturally rich mercury deposits (cinnabar) in the Coast Range of the Central Valley and to the use of very considerable amounts of the element in past gold mining activities in the Sierra Nevada. No reliable data are available on mercury in Bay-Delta waters except for some isolated values relating to south-eastern San Pablo Bay.

Data for mercury in sediments of the estuary emphasize the ubiquity of the element within the system, which may correlate to significant atmospheric sources or transport, and to impacts from urban run-off. The latter are suggested by localized enrichment of mercury in sediments of small creeks which flow directly into the Bay. There can be little doubt that large quantities of mercury enter the estuary attached to suspended particulates (and to a minor extent, in solution) through the Delta. While the fate of these mercury loads is not known, both natural and anthropogenic forces (dredging and dumping) undoubtedly contribute to the transport of the element throughout the estuary.

Analyses of biota from the Bay-Delta and its catchment provide a general picture of mercury enrichment at the northern and southern extremities of the system, with somewhat lower levels in the Central Bay area. The gradients of such contamination are not great, however, and this presumably is a

function of the hydrodynamics of the estuary (in particular, its very high tidal prism). Even the South Bay, classically believed to flush poorly except in periods of very high Delta outflow, exhibits only pockets of localized heavy mercury enrichment above a moderately elevated background level of the element. Finally, it should be noted that both the Bay waters and (particularly) influent freshwaters are sufficiently enriched with mercury to cause bio-accumulation of the element by a variety of organisms to levels which may be of concern with respect to public health. Risks associated with the ingestion of such species cannot be presently assessed, however, due to the paucity of data on the chemical speciation of the mercury present, which is central to its toxic effect.

E. CADMIUM

Introduction

Cadmium is produced almost exclusively by the smelting of complex ores and those containing zinc and lead. Cadmium is in essence a by-product of this process. Its biogeochemical cycle is often considered to be related to that of zinc, because of their co-occurrence in ores and the similar transport and properties of the two elements in both terrestrial and aquatic ecosystems (Schroeder et al., 1967; Friberg et al., 1974). Nriagu (1980) noted that the great majority of uses of cadmium (e.g. in paints, alloys, electroplating, dyeing and printing, photography, chemical industries, and glass and battery manufacture) are dissipative in nature; less than 5% of the cadmium presently consumed is reclaimed and recycled. This implies the disposal of cadmium in the environment, and aquatic ecosystems constitute both a transport pathway and a final sink for the element.

Cadmium is considered to be of very great pollution hazard in aquatic environments (Waldichuk, 1974); it is both highly bio-accumulated and of considerable direct toxicity to biota. Its acute and chronic toxicity to aquatic organisms is similar to that of copper; however, ambient concentrations of the element in non-polluted seawater are lower than those of copper by a factor of about five. Bruland et al. (1978, 1979) and Martin et al. (1980) have demonstrated that the concentrations of cadmium in open oceans correlate strongly to those of phosphate and nitrate; this relationship may be useful in defining

anthropogenic enrichment of cadmium in nearshore and estuarine waters. The most recent U.S. EPA water quality standards for cadmium in marine waters are 9.3 $\mu g\ L^{-1}$ as a 4-day average and 43 $\mu g\ L^{-1}$ as a one-hour average (U.S. EPA, 1986). The lower of these concentrations is about three orders of magnitude greater than levels in unpolluted surface waters of marine ecosystems (Martin et al., 1980).

Cadmium is also of exceptional toxicity to mammals, including Man. The symptoms of acute poisoning differ from those due to chronic toxicity (Friberg et al., 1974; Yasumura et al., 1980); the main routes of uptake of the element are usually through inhalation or ingestion. Occupational exposure to cadmium has been a problem in several industries and has resulted in considerable research. Chronic cadmium intake results in both kidney problems and (rarely) bone disorders. The latter were noted in Japan among a relatively small population exposed to high cadmium ingestion rates, largely from contaminated rice. The overt symptoms included brittleness of bones and extreme pain from "pseudofractures" thereof; this gave rise to the celebrated term for this syndrome (Itai-itai or "ouch-ouch" disease). While there remains some doubt as to whether cadmium was the sole causative factor in the Itai-itai syndrome, it was almost certainly heavily implicated (Yasumura et al., 1980). Maximum provisional tolerable weekly intake limits for the element of 400-500 ug have been proposed for humans (FAO/WHO, 1972); however, many populations in both western and developing nations approach or exceed this level of intake. Cadmium has also been implicated as a contributory factor in hypertension, pulmonary

dysfunction, and neoplasia (cancer) in Man (Yasumura et al., 1980).

Cadmium in Bay-Delta Waters

Data for cadmium in waters of the Central and South Bays were reported by Girvin et al. (1978). Contamination profiles are shown in Fig. 48 for dissolved cadmium. It is evident from these that concentrations of the element in solution were found to be low in Central Bay, averaging about 0.1 $\mu g\ L^{-1}$. These data agree well with later studies by Gordon (1980). Soluble levels of the element increased somewhat with distance south from the Golden Gate, suggesting enrichment of the element in South Bay, presumably due to local sources of cadmium in the south of the Bay. Maximum concentrations attained varied seasonally to some degree, peaking at about 0.25 $\mu g\ L^{-1}$ in September 1976. Data for cadmium in suspended particulates through this area varied from 1.2 to 5.0 $\mu g\ g^{-1}$ dry weight, equivalent to weight/volume levels of 0.003 to 0.21 $\mu g\ L^{-1}$. Total concentrations of the element in South Bay are therefore greater than an order of magnitude below the most recent water quality standards cited above (U.S. EPA, 1986).

As noted previously, Gordon (1980) reported similar data to those of Girvin et al. (1978) for cadmium in Central Bay, both with respect to levels in solution and in suspension. Gordon (1980) also showed that dissolved concentrations of the element in the Central Bay were 1.5 to 3 times greater than those offshore in the Gulf of the Farallones. San Francisco Bay may thus be viewed as a source of cadmium to offshore coastal waters.

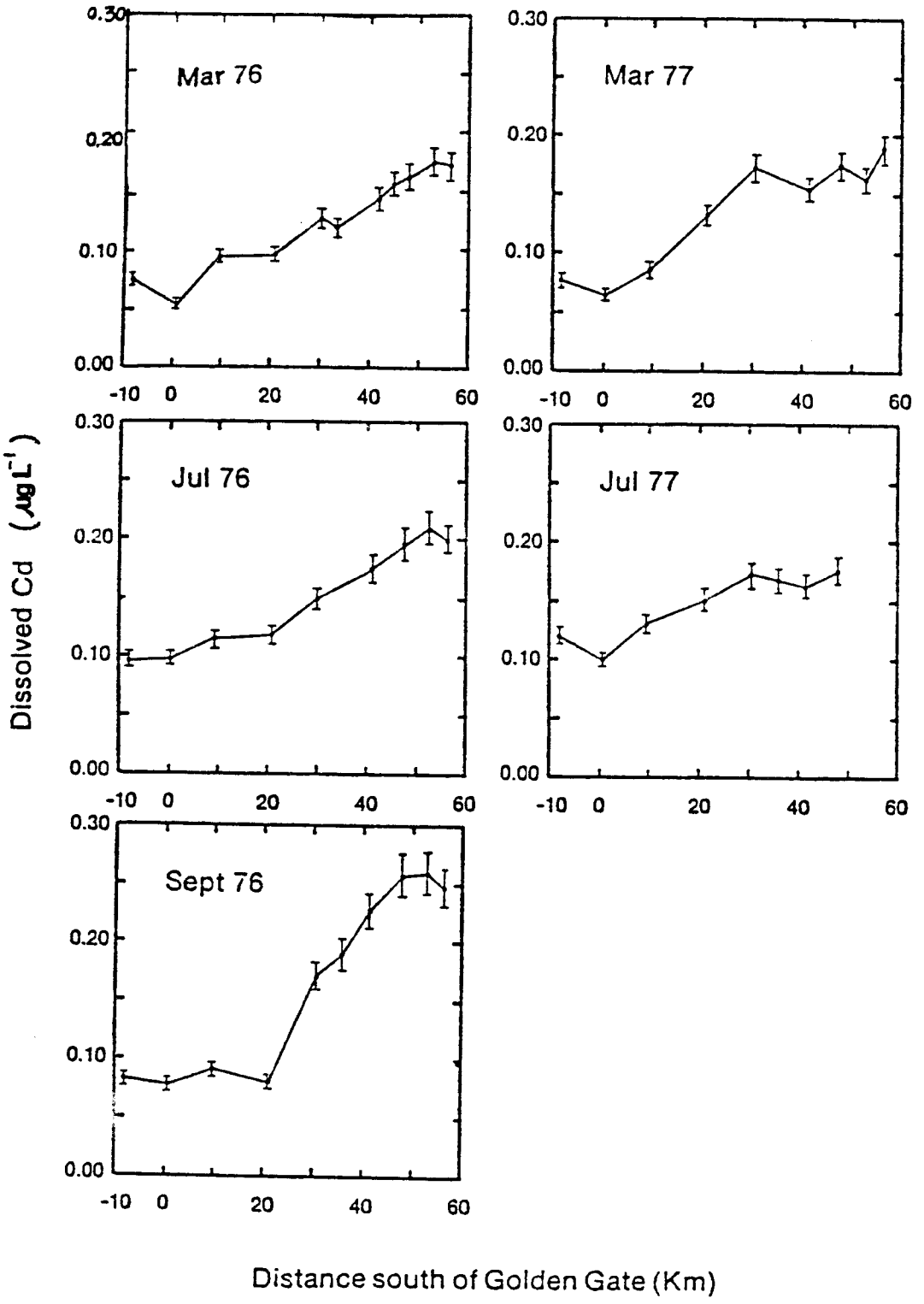


Fig. 48. Concentrations of cadmium ($\mu g\ L^{-1}$) in solution in the waters of Central and South Bays, 1976-1977. The average analytical error of ±7% is indicated by vertica bars. After Girvin et al. (1978).

It is notable that no data are available concerning cadmium levels in waters of the northern reach of the Bay-Delta.

Cadmium in Bay-Delta Sediments

The available data concerning cadmium in sediments of San Francisco Bay-Delta exhibit little evidence of widespread or heavy enrichment by this element. Risebrough et al. (1978) suggested that locally elevated cadmium concentrations in some nearshore sediments in the Bay might be caused by variations in grain sizes of samples. Bradford and Luoma (1980) reviewed the data available from the 1970s, reporting cadmium concentrations of 0.78 to 1.66 $\mu g\ g^{-1}$ dry weight, with only minor site-to-site variability. Hoffman and Meighan (1984) found slightly higher levels than these on average in sediments off the eastern side of the San Francisco peninsula, with minor local contamination evident in Islais Creek and Mission Creek. One site off Brisbane was reported as highly contaminated by cadmium (site 3, 17.3 $\mu g\ g^{-1}$ dry weight) and also showed evidence of mercury enrichment; however, no likely source was suggested and this may be an artifact of post-sampling contamination. Luoma et al. (1984; and in press) found low concentrations of cadmium (generally less than 0.3 $\mu g\ g^{-1}$ dry weight) in Suisun Bay and lower San Joaquin River sediments. Data from the NOAA monitoring programs confirm the generally low levels of cadmium in Bay sediments (Chapman et al., 1986; NOAA, 1987) and show that other locations in California contain sediments exhibiting considerably greater enrichment by this element (NOAA, 1987).

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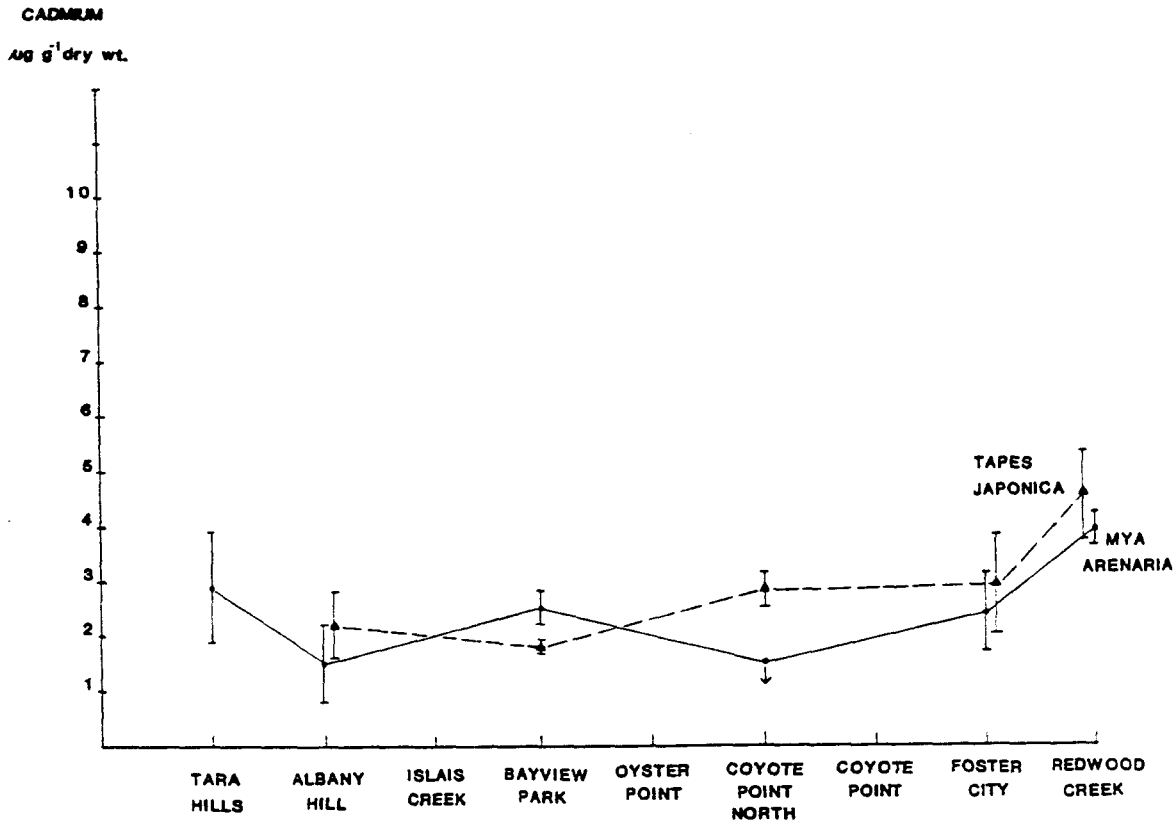
Cadmium in Bay-Delta Biota

The concentrations of cadmium present in organisms from the Bay-Delta are important not only because they may reflect the existence of sources of the element to the estuary, but also because of their implications for public health. Certain types of marine and estuarine organisms are well known to accumulate considerable amounts of cadmium, and this is of concern if they are commercially (or non-commercially) fished for human consumption. Among such organisms are certain bivalve molluscs (particularly oysters) and several crustacean species (especially so-called "brown meats" of crabs; see MAFF, UK, 1973; Phillips, 1980; Eisler, 1981). By contrast, the axial muscle of finfish generally contains low levels of cadmium (e.g. NOAA, 1975; Phillips, 1980), although the element is more concentrated by fish liver tissues. No maximum limit for cadmium in seafoods exists in the United States, although such standards are employed in other countries (SWRCB, 1986). These international standards range from 0.05 to 2.0 $\mu g\ g^{-1}$ wet weight in 10 countries surveyed by Nauen (1983), with median limits of 0.3 $\mu g\ g^{-1}$ wet weight for fish and 1.0 $\mu g\ g^{-1}$ wet weight for shellfish. (It should be noted that such limits are almost always based on wet weights of seafoods; dry weight equivalents may be approximately calculated by multiplying the cited concentrations by a factor of 4 or 5).

Girvin et al. (1975) found very little spatial variation in concentrations of cadmium in four species of bivalves from the Bay (Figs. 49 and 50), with the exception of slightly elevated levels of the element in samples from Redwood Creek. Both native Bay mussels (Mytilus edulis) and Olympic oysters (Ostrea lurida)



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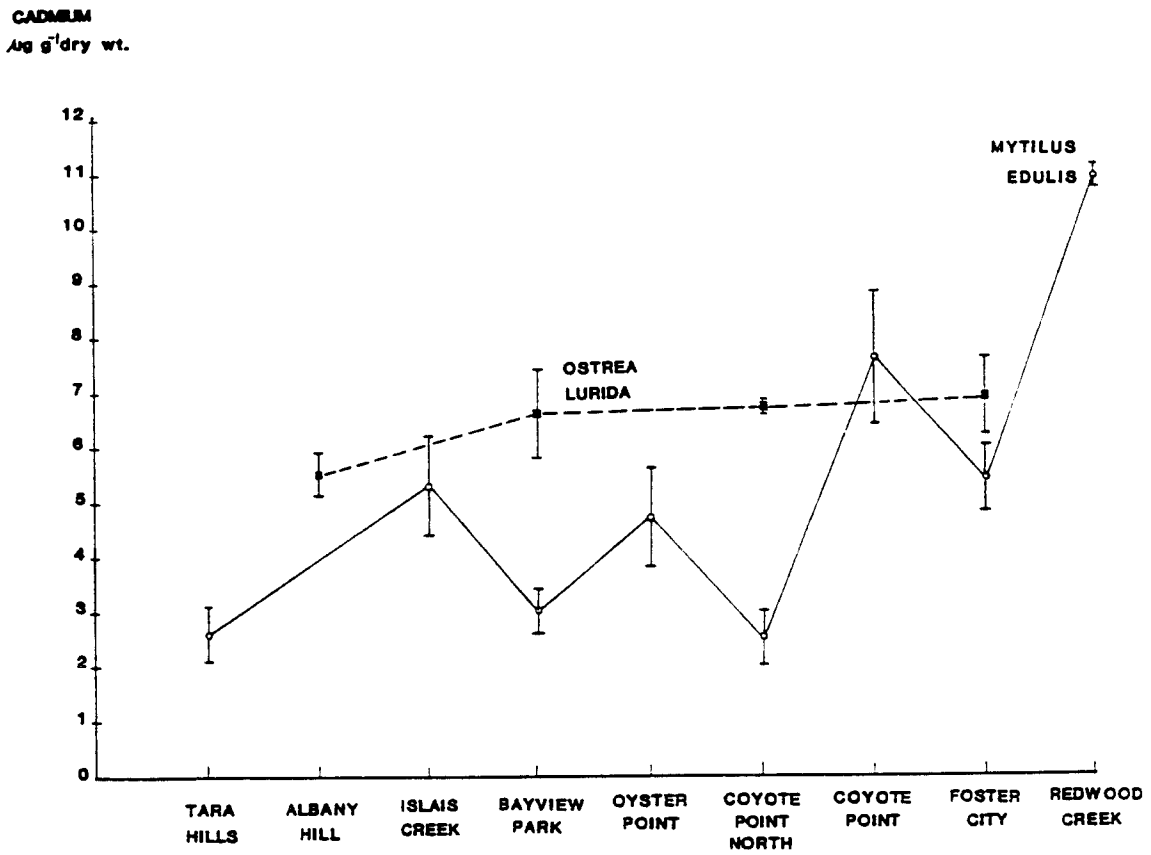

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exhibited concentrations approaching or exceeding 1 $\mu g\ g^{-1}$ wet weight, which is relevant in respect to public health. Tissues of the Pacific oyster (Crassostrea gigas) from Redwood Creek were reported to contain very high concentrations of cadmium (Table 20), by comparison to other species and to C. gigas from Tomales Bay (Girvin et al., 1975). This degree of enrichment is high for C. gigas (Phillips et al., 1982) and worthy of further study.

The data of Risebrough et al. (1978) for cadmium in mussels, Mytilus edulis, from the Bay are shown in Fig. 51. Cadmium enrichment is seen in mussels from the northern and southern extremities of the Bay, with much lower concentrations in the area of Central Bay and the Golden Gate. These authors noted that cadmium levels in mussels from the northern reach of the Bay were inversely correlated to time-averaged salinities. The uptake of cadmium by M. edulis is known to be greater at lower salinities (Phillips, 1976a; Jackim et al., 1977), and this factor will have contributed to the elevated concentrations of the element found in mussels from Carquinez Strait and San Pablo Bay. It should be noted that the concentrations found in these mussels are not extreme by comparison to some locations, but nevertheless suggest moderate levels of contamination of the estuary by cadmium. By comparison, Phillips (1976b) found "background concentrations" of cadmium in M. edulis from Port Phillip Bay (Australia) to be about 2 $\mu g\ g^{-1}$ dry weight, with unusually contaminated samples containing up to about 110 $\mu g\ g^{-1}$ dry weight.

Table 20. Concentrations of cadmium (means±standard deviations, $\mu g\ g^{-1}$ dry weight) in tissues of Pacific oysters, Crassostrea gigas, from Redwood Creek and Tomales Bay. Five replicate samples were analyzed in each case. After Girvin et al. (1975).

Tissue	Redwood Creek	Tomales Bay	Enrichment Factor[a]
Gill	45.7±6.1	11.8±1.6	3.9
Mantle	45.6±5.4	7.6±0.5	6.0
Hepatopancreas	61.7±6.5	8.2±1.2	7.5

[a]Enrichment factor denotes the ratio between mean concentrations of cadmium in oyster tissues at the two locations.

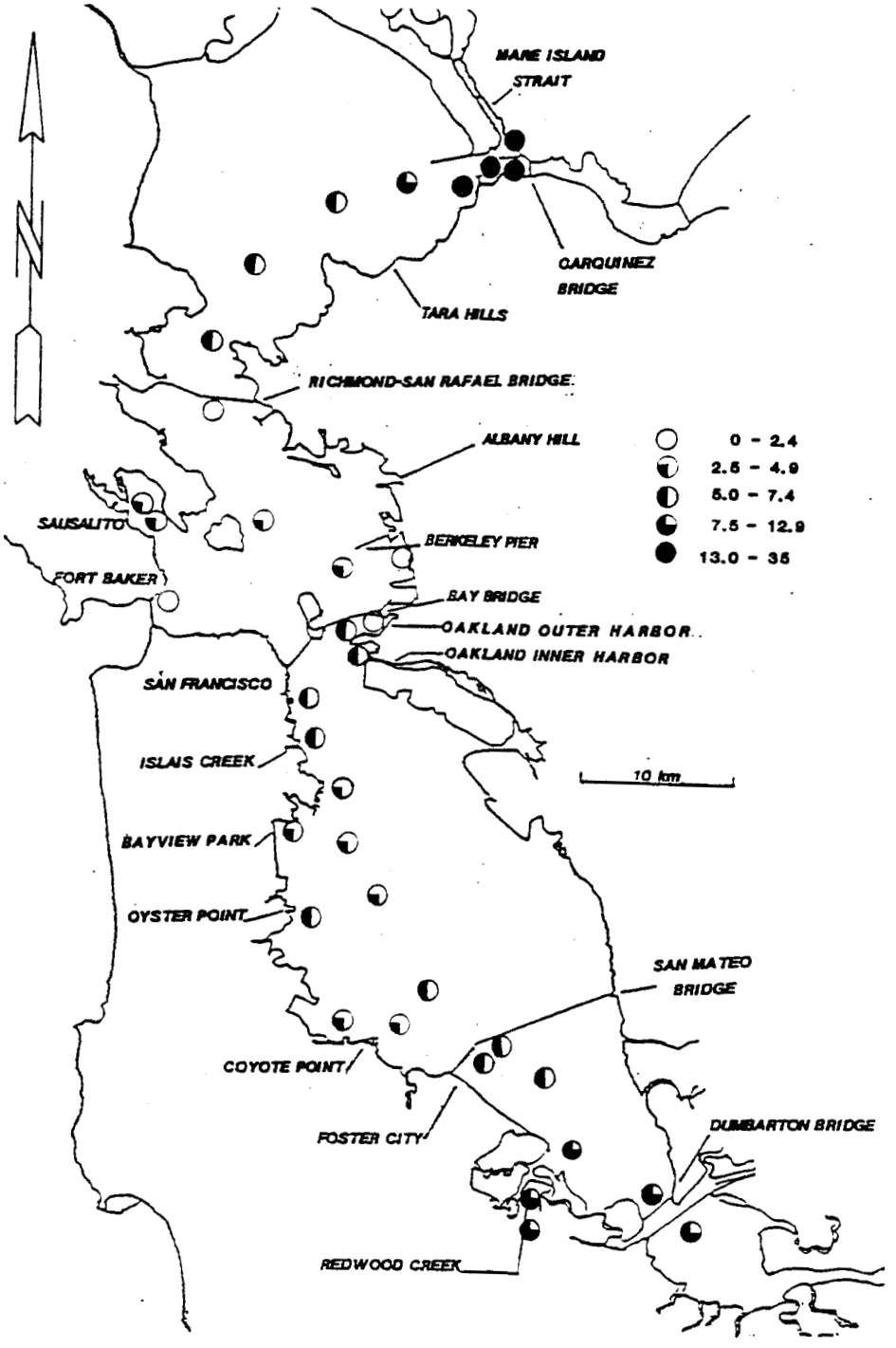

Fig. 51. Concentrations of cadmium (means, $\mu g\ g^{-1}$ dry weight) in native Bay mussels, Mytilus edulis, from San Francisco Bay. Date of sampling was April 1986. After Risebrough et al. (1978).

Data for cadmium in transplanted mussels (M. californianus) are also available, from the studies of the State Mussel Watch Program. These data, shown in Table 21, indicate relatively minor spatial variability in cadmium in M. californianus throughout the Bay. No consistent geographical or temporal trends are evident from the results, and no major sources of cadmium appear to be present in the Bay (Hayes et al., 1985; Hayes and Phillips, 1986; Stephenson et al., 1986a).

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Luoma et al. (1984; and in press) found moderate enrichment of clams (Corbicula sp.) in Suisun Bay and the Delta by cadmium. Although one site in particular may have been influenced by a local cadmium source, the degree of enrichment of the element in Corbicula sp. appeared disproportionate, considering the low levels of the element in sediments of this area. The authors suggested that cadmium might exhibit unusually high bio-availability in the area, similar to observations for copper in parts of the Bay. Very little is known about the uptake of cadmium by Corbicula species, apart from limited studies on the influence of substrate, pH, diet, and temperature (Graney et al., 1984). More data are required on element levels in species of

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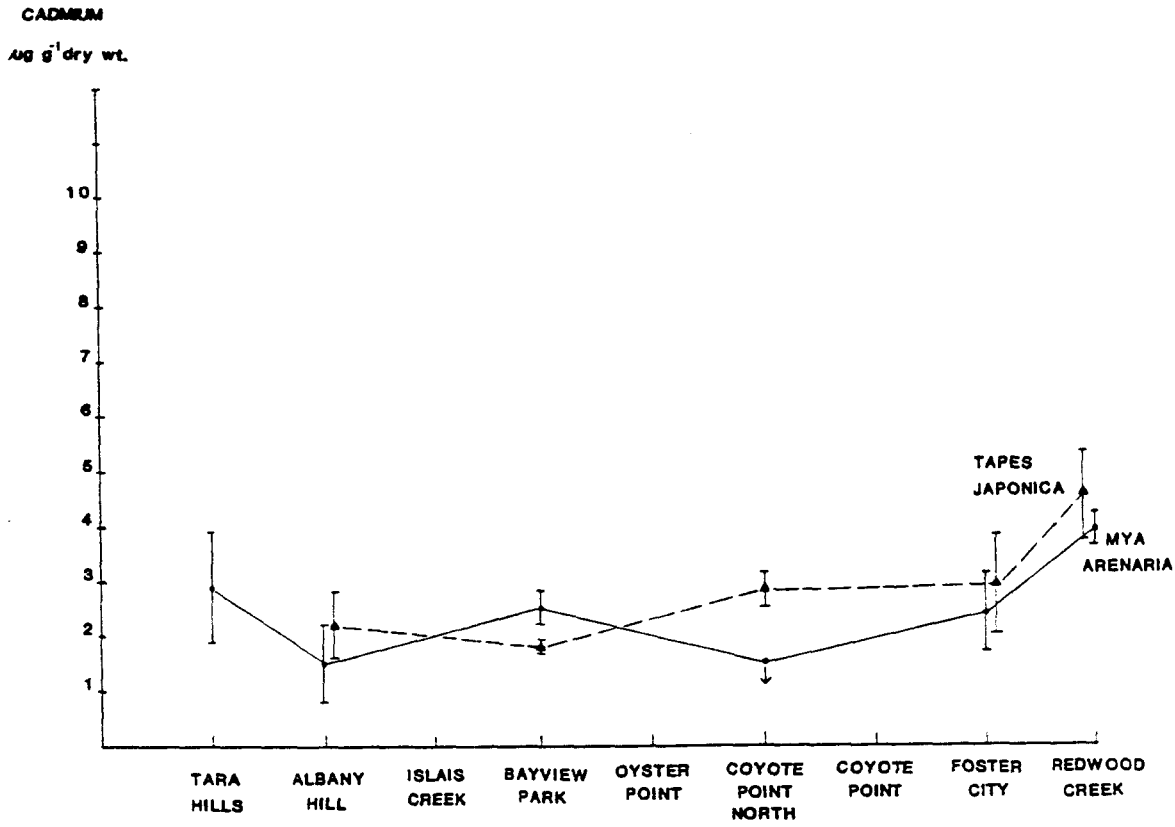

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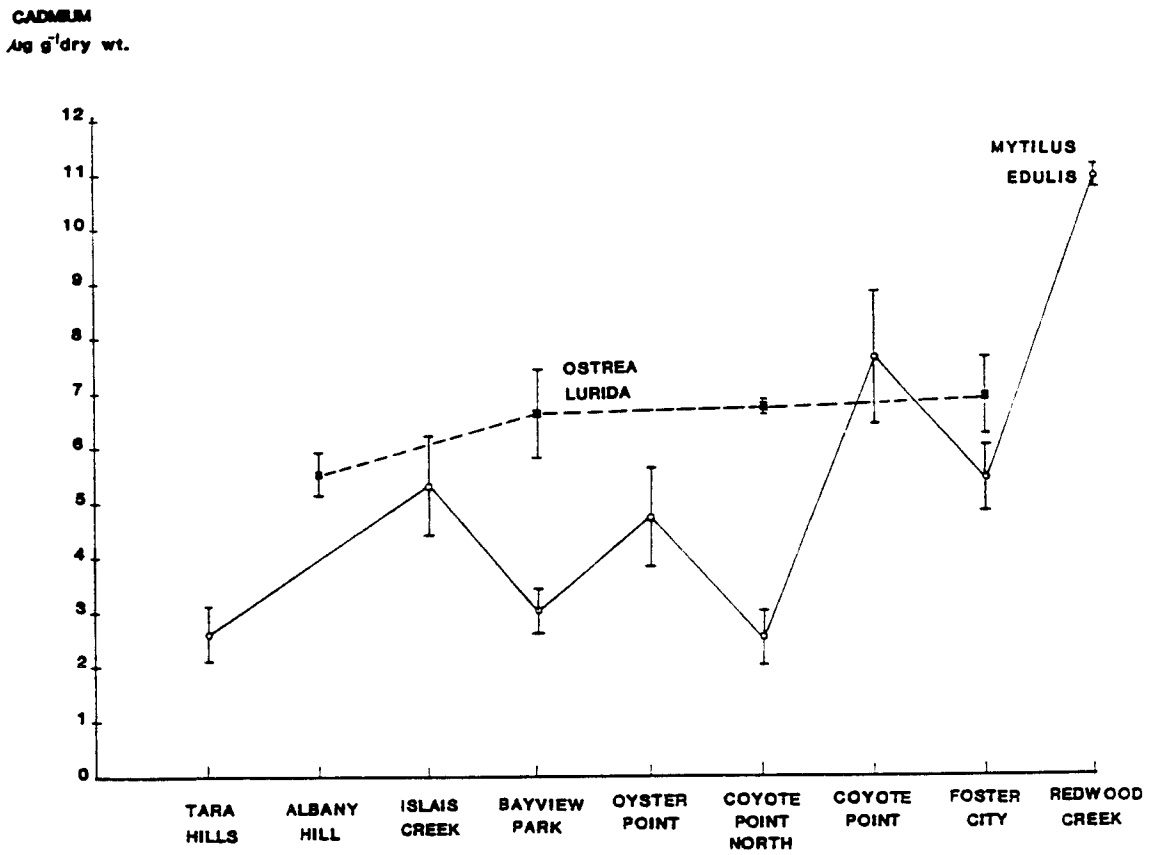

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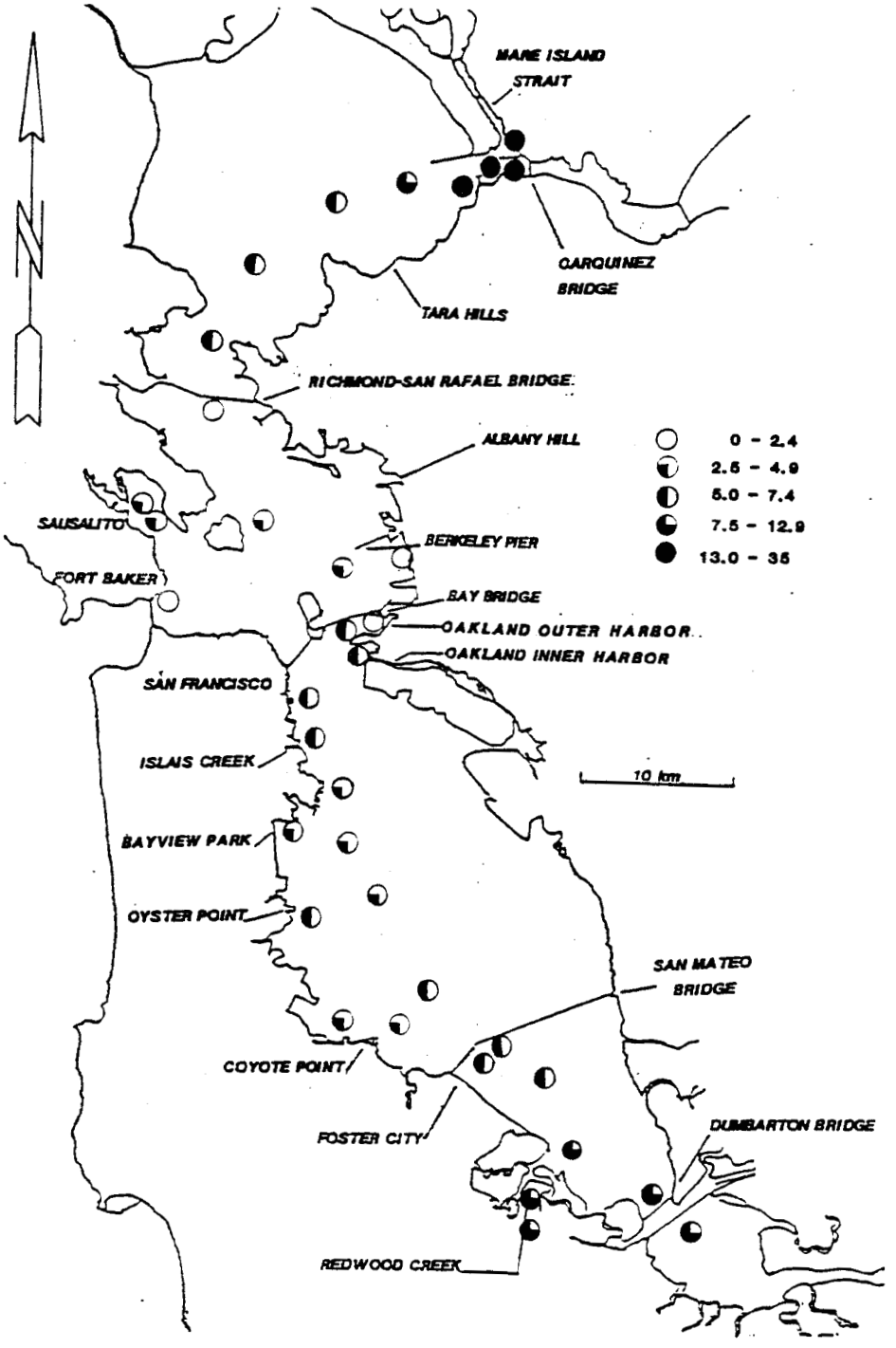

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Table 21. Mean concentrations of cadmium (ug g^{-1} dry weight) in transplanted mussels (Mytilus californianus) or native Bay mussels (M. edulis, as shown[a]) from 33 sites in San Francisco Bay. Data from the State Mussel Watch Program, after Hayes et al. (1985), Hayes and Phillips (1986) and Stephenson et al. (1986a).

LOCATION	STATION CODE	1980	1981	1982 (J/F)	1982 (O/N/D)	1982 RESIDENT (O/N/D)a	1983	1985	1986
MARE ISLAND	300.20							8.2a	5.0
DAVIS POINT	301.00	4.4a			11.7				
POINT PINOLE	302.00	4.3a	19.5	19.9	10.2b		11.8	10.8	5.5
RICHMOND BRIDGE	303.00	11.5	10.8	13.6	9.7b				
SANTA FE CH. MOUTH	303.10								7.5
RICHMOND INNER HARBOR	303.60							5.5	
STAUFFER'S	304.00			7.3					
ANGEL ISLAND	305.00	15.0	7.2	9.4	7.6b				
FORT BAKER	306.00		10.6		8.1c				
TREASURE ISLAND	307.00	12.5	9.4	8.3	8.6c		9.1	7.6	4.3
ALAMEDA YACHT HARBOR	307.20							14.3a	8.6
OAKLAND IN. HARBOR WEST	307.30								5.5
OAKLAND IN. HARBOR EMBC.	307.40								11.7
OAKLAND BACK HARBOR	307.60								4.7
HUNTER'S POINT	308.00		12.1	11.8	11.0c	6.8a			
SAN MATEO BRIDGE 8	309.00	11.3	18.9	12.1	10.9c	6.1a	13.0	9.5	9.9
SAN MATEO BRIDGE 8A	310.00			14.4					
SAN MATEO OLD BRIDGE	311.00			11.3					
BELMONT SLOUGH	312.00			17.2					
REDWOOD CREEK MOUTH	313.00		12.5	13.5	9.2c	6.4a	12.2	11.5	
REDWOOD CREEK 10	314.00			10.3					
REDWOOD CREEK TOWERS	315.00			10.6	7.6b	6.4a			
REDWOOD CREEK TRDWNDS	316.00	5.6a		7.7	7.2b	7.6a			
REDWOOD CREEK STP	317.00				8.2				
SF PETES	318.00				8.5				
SF PULGAS	319.00				9.1				
SF AIRPORT	320.00				7.8				
DUMBARTON BRIDGE 14	321.00	8.6a	16.0	9.9	8.9	8.5a	15.7	7.5	6.1
NEWARK SLOUGH	324.00			12.1					
CHANNEL 17	325.00			12.2					
PALO ALTO 8	326.00			10.4		9.2a			
PALO ALTO YACHT	327.00			10.8					
ALVISO SLOUGH	328.00			13.5					

J/F/O/N/D: January/February/October/November/December, all 1982

a Resident Mytilus edulis.

b Mean of two values.

c Mean of three values.

this genus before conclusions may be made on the significance of the cadmium levels in Delta populations. However, it should be noted that the data of Luoma and co-workers agree well with as yet unpublished values for cadmium in Corbicula sp. from New York Slough (Foe and Knight, in preparation).

Data on cadmium levels in Bay-Delta organisms other than molluscs are rare. Occasional elevated levels of the element are seen in fish livers in the Sacramento and San Joaquin catchments (SWRCB, 1986). Acid mine drainage is probably at least one of the factors responsible for this phenomenon (DWR, 1986). Risebrough et al. (1978) found no evidence for unusually high cadmium concentrations in harbor seals from the Bay. Ohlendorf et al. (1986c) reported higher levels of the element in kidneys of surf scoters than in those of greater scaups (both species being taken from South Bay), which are likely to relate to dietary preferences of these two duck species. The levels found may have been somewhat elevated in relation to other estuaries, but data for comparison are sparse and cross-species comparisons should not be relied upon to draw firm conclusions.

Summary

The available data on cadmium levels in water and sediments of the San Francisco Bay-Delta suggest only minor levels of contamination by this element, with little spatial variation. No major sources of cadmium have been discerned within the Bay, although the existence of many minor sources gives rise to enrichment of the estuary by comparison to offshore waters.

Similarly, data for cadmium in biota of the Bay-Delta

provide little evidence for major sources within the estuary. Thus, concentrations of the element in organisms vary little with location. However, suggestions that the bio-availability of cadmium may be unusually high in the estuary are worthy of further study, as the moderate levels of contamination of biota appear rather disproportionate to the low concentrations of the element in water and sediments. This situation gives rise to appreciable contamination of some species by cadmium; in some instances, such enrichment has implications with respect to public health.

F. LEAD

Introduction

Lead is a non-essential element, but is exceptionally ubiquitous in terrestrial and aquatic environments. Its natural global rate of mobilization (about 180,000 tonnes annually) is exceeded by the Man-induced rate (largely mining) by a factor of about 10-15 (Phillips, 1980).

Lead is unusual among trace elements in that it exhibits only moderate toxicity in aquatic environments, but is highly toxic to mammals. Man accumulates lead by ingestion from food and water, and by the inhalation of atmospheric lead. There has been much controversy over the relative importance of these sources, and over the precise toxic effects of the element in humans. Considerable research has been conducted on lead levels in human tissues (blood and bone in particular), and on the possible correlation between concentrations of lead in the blood of children and intelligence. There can be no doubt that the element is a powerful toxin in humans, principally affecting the neurological system. In view of the non-essential nature of the element, any lead may be too much lead in mammals, although thresholds probably exist in respect to overt toxic symptoms.

It should be emphasized here that very considerable problems have been experienced in the accurate analysis of lead in trace concentrations, particularly in seawater. Patterson and Settle (1976a, 1976b) stated that most data reported for trace amounts of lead in seawater and biological samples to the mid-1970s were grossly inaccurate (often by several orders of magnitude) because

of contamination of the samples during their collection, transport to laboratories, or preparation for analysis. Thus, for example, these authors stated that:

> "It has become apparent that the single most important factor that has been contributing error to past analyses of trace amounts of lead was the inability of the analyst to evaluate properly the true magnitudes of lead contamination from different sources within his laboratory." (Patterson and Settle, 1976b).

This problem was one of the main driving forces for improvement in the techniques for trace metal analysis in the late 1970s and the present decade. It is now widely recognized that sophisticated facilities ("clean labs", ultra-pure reagents, etc.) are required to accurately analyze water samples (and some other samples containing very low element levels). Nevertheless, the literature is replete with reports which emanate from facilities which are unable to control sample contamination adequately, and data for lead are always of greatest potential inaccuracy. The interpretation of data reported for lead in environmental samples is thus fraught with difficulties.

Klapow and Lewis (1979) considered the toxicity of lead to aquatic biota (Fig. 52). These data show that the element is of only moderate acute or chronic toxicity in aquatic environments, and that a very large difference exists between lead levels in uncontaminated seawater and concentrations of the element causing detrimental effects to biota. Data reviewed by the U.S. EPA agree with this; water quality standards for marine waters of 5.6 $\mu g\ L^{-1}$ as a 4-day average and 140 $\mu g\ L^{-1}$ as a one-hour average have been proposed (U.S. EPA, 1986). Receiving water concentrations of the element rarely approach such levels, even in highly

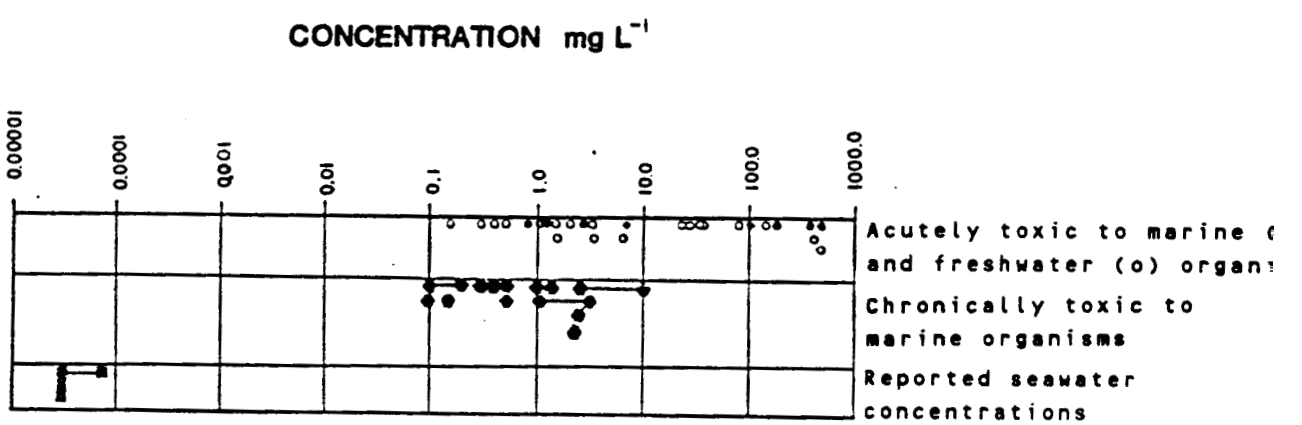


Fig. 52. Concentrations of lead reported in seawater, and concentrations of the element exhibiting acute or chronic toxicity to aquatic biota. After Klapow and Lewis (1979).

polluted environments. However, both effluents and (especially) urban run-off may contain large quantities of lead. Urban run-off is contaminated by the element largely through the deposition of lead onto pavement surfaces. Lead added as an anti-knock agent to gasoline has been the major contributor in the past; however, the advent of unleaded gasoline has reduced loads from this source considerably (e.g. Young et al., 1980), although few reliable data on urban run-off quality are available for the Bay-Delta itself.

Lead in Bay-Delta Waters

Girvin et al. (1978) encountered difficulties in accurately defining the concentrations of lead in waters of the South Bay and Central Bay, because of large errors associated with their analysis of the element. These errors concerned relatively high values for lead in reagent blanks and high variation between replicate samples. This gave rise to considerable total propagated analytical errors, especially in data points for low lead concentrations. Such problems are generally indicative of extraneous contamination of samples, and data for lead from this study should be interpreted with caution. The contamination profiles reported by Girvin et al. (1978) are shown in Fig. 53. Little can be said in a definitive sense concerning these data because of the analytical problems, save that the southernmost site sampled (offshore from the Coyote Creek and Alviso Slough) probably exhibited a degree of lead enrichment. Data for lead in suspended particulates suggested that much of the element present in these waters was particulate-associated rather than in the dissolved phase.

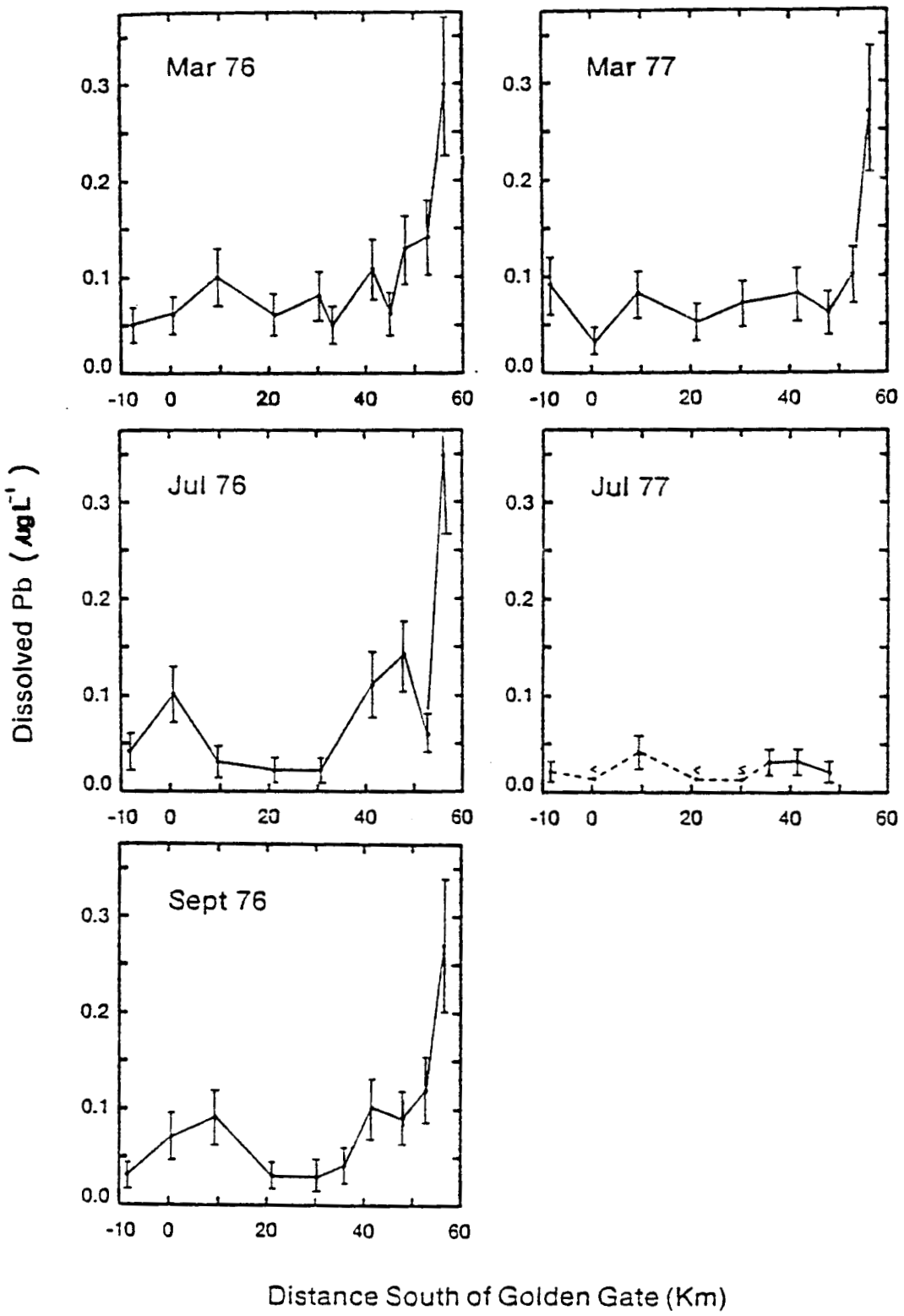


Fig. 53. Concentrations of dissolved lead ($\mu g\ L^{-1}$) in the waters of South and Central Bays, 1976-1977. Analytical erro are indicated by vertical bars. After Girvin et al. (1978).

Gordon (1980) reported somewhat lower values for lead in Central Bay waters than those of Girvin et al. (1978), and this probably reflects the better facilities used by Gordon, permitting the minimization of contamination. Concentrations of dissolved lead found in Central Bay waters by Gordon (1980) averaged 0.018 to 0.033 $\mu g\ L^{-1}$ and varied with season. This may be compared to levels of 0.012 to 0.015 $\mu g\ L^{-1}$ in offshore marine waters of the Gulf of the Farallones. On the basis of these data, it appears that the Bay is a source of lead to offshore waters, although the degree of contamination within Central Bay at least is minor.

Harvey et al. (1982) found that lead was concentrated in the surface microlayer of waters overlying a salt marsh near Palo Alto. This concentration of lead in the microlayer compared to the underlying water column correlated to enrichments of surface layer bacteria ("bacterioneuston"); the entrapment of fine particulates at the microlayer may also have been involved. Enrichment of trace elements and other contaminants in the surface microlayer of natural waters is a well-known phenomenon, although its significance is not yet fully understood. New methods designed to sample large volumes of the microlayer are now available, and our knowledge of the effects of contaminants in the microlayer will hopefully improve in the future.

Lead in Bay-Delta Sediments

Girvin et al. (1975) reported that lead concentrations in sediments from five locations in the Bay varied from 26 to 174 $\mu g\ g^{-1}$ dry weight, highest values being found at Bayview Park and Albany Hill, probably due to local contamination.

Data from the extensive survey of lead in sediments conducted by Risebrough et al. (1978) are shown in Fig. 54. In general, the offshore Central Bay sediments were found to be least contaminated, with patchy higher lead values occurring in both the northern and southern reaches of the Bay. Areas close inshore tended to exhibit greater sediment contamination by the element, and a plethora of local sources appeared to exist. This is in keeping with the ubiquity of lead as a contaminant, and its abundance in run-off. Most data suggest that concentrations of the element in offshore sediments are somewhat elevated over values for average shales (20 $\mu g\ g^{-1}$ dry weight; see Krauskopf, 1967); lead levels of 25-40 $\mu g\ g^{-1}$ dry weight are typical (e.g. see review by Bradford and Luoma, 1980; Hoffman and Meighan, 1984; Chapman et al., 1986; NOAA, 1987). However, nearshore locations (such as harbors and creeks) commonly exhibit greater lead enrichment in sediments (Fig. 54). Particularly elevated levels occur in Islais Creek sediments, where concentrations of the element vary from about 50 $\mu g\ g^{-1}$ at the mouth to 882 $\mu g\ g^{-1}$ dry weight at the head of the Creek (Hoffman and Meighan, 1984; Chapman et al., 1986). Mission Creek is even more contaminated, with highest values being an astonishing 2580 $\mu g\ g^{-1}$ dry weight in sediments (Hoffman and Meighan, 1984).

Less data are available for lead in sediments of the Delta. However, Luoma et al. (1984) reported concentrations of 13-60 $\mu g\ g^{-1}$ dry weight for lead in Suisun Bay sediments. Luoma et al. (in press) found similar levels of 40-62 $\mu g\ g^{-1}$ dry weight in Suisun Bay and 30-38 $\mu g\ g^{-1}$ dry weight in the lower San Joaquin River sediments. While these values are somewhat elevated over

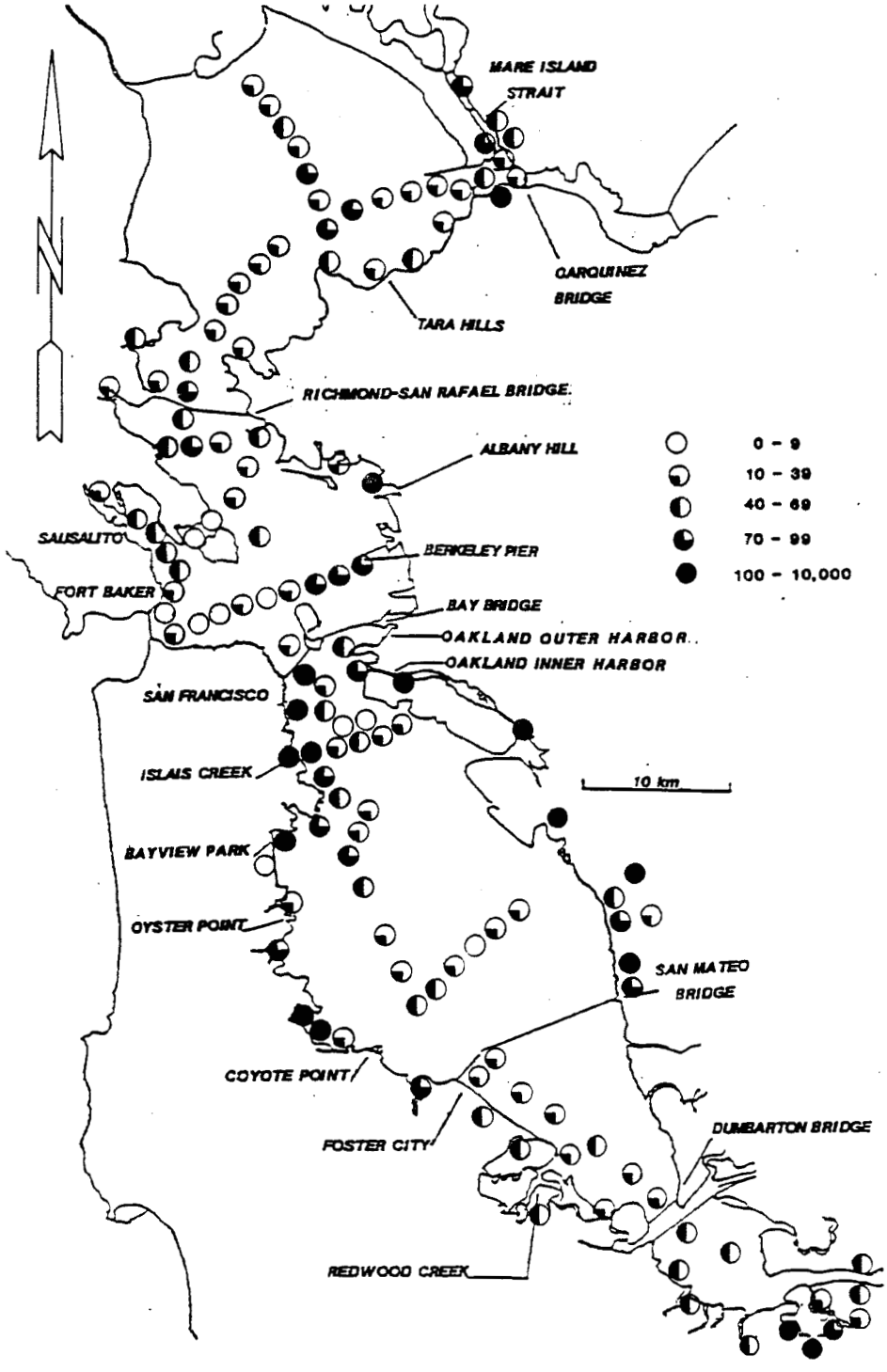


Fig. 54. Concentations of lead (means, $\mu g\ g^{-1}$ dry weight) in the surface sediments of San Francisco Bay. After Risebrough et al. (1978).

the concentrations present in average shales, they do not imply particularly heavy contamination of the upper estuary by the element.

Lead in Bay-Delta Biota

Concentrations of lead in four species of bivalves studied by Girvin et al. (1975) varied little between locations south of Bayview Park to Foster City, with Redwood Creek Samples exhibiting slightly higher values (Figs. 55 and 56). Data for le in tissues of the oyster Crassostrea gigas also suggested marginal enrichment of samples from Redwood Creek compared to Tomales Bay on the California coast (Girvin et al., 1975). However, all bivalves studied at Tara Hills, Albany Hill, and (especially) Islais Creek exhibited considerable lead enrichment, although it is notable that the single value for Tara Hills for Mya arenaria exhibits very high variance. Both Albany Hill and Islais Creek also exhibit lead contamination in sediments (see above), in each case considered to reflect local sources of the element rather than a more general enrichment of large areas of the Bay.

Additional data for species of the genus Mytilus are available from the work of Risebrough et al. (1978) and the results of the California State Mussel Watch Program. Contamination profiles for lead in native Bay mussels (M. edulis) sampled in April 1976 are presented in Fig. 57; these may be compared to similar data for sediments shown in Fig. 54. Local contamination of mussels by lead was noted near Carquinez Strait, Albany Hill, Sausalito, Treasure Island, and Islais and

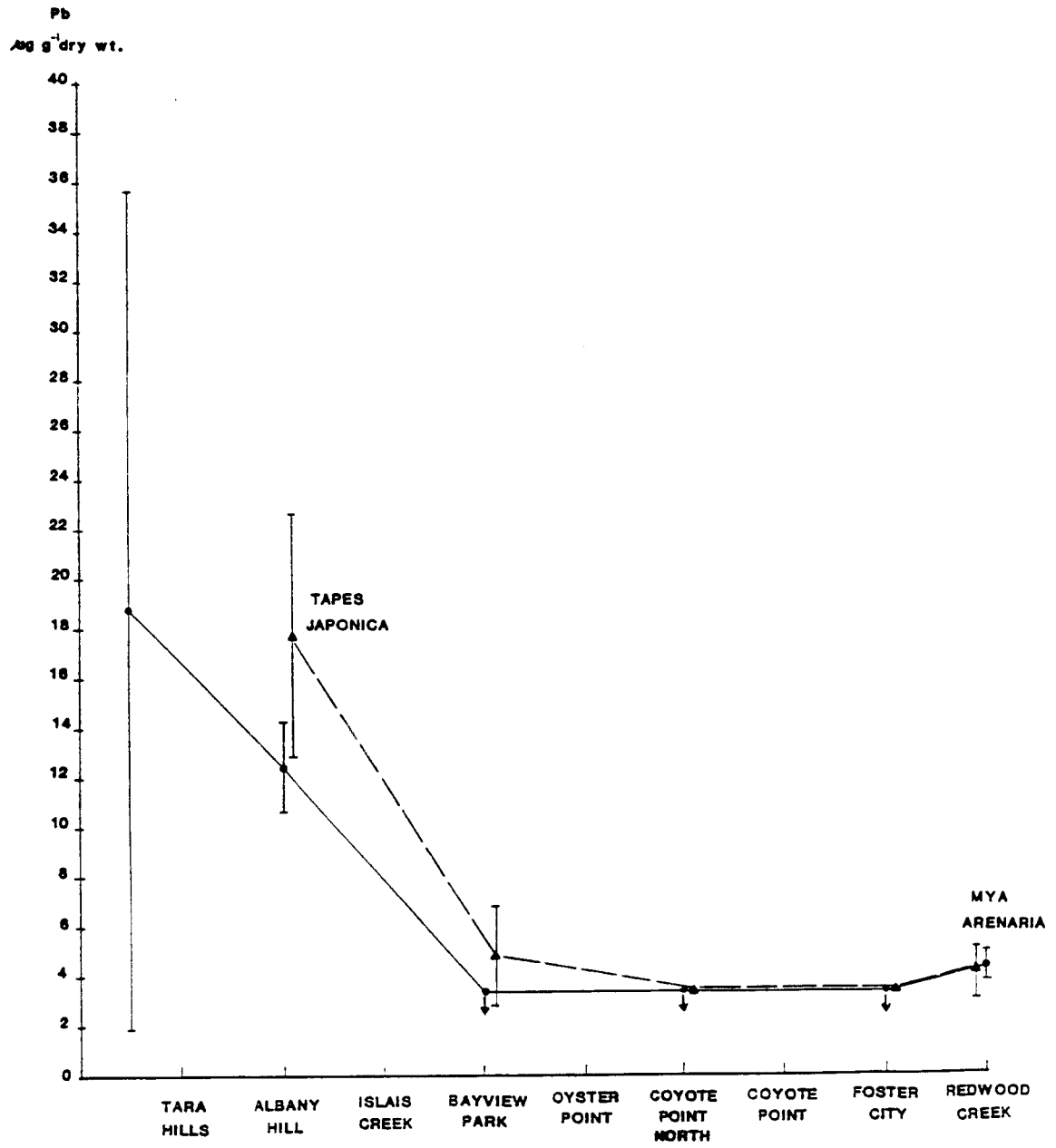


Fig. 55. Concentrations of lead (means ± standard deviations, $\mu g\ g^{-1}$ dry weight) in the softshell clam Mya arenaria and the Japanese littleneck clam Tapes japonica from San Francisco Bay. After Girvin et al.(1975).

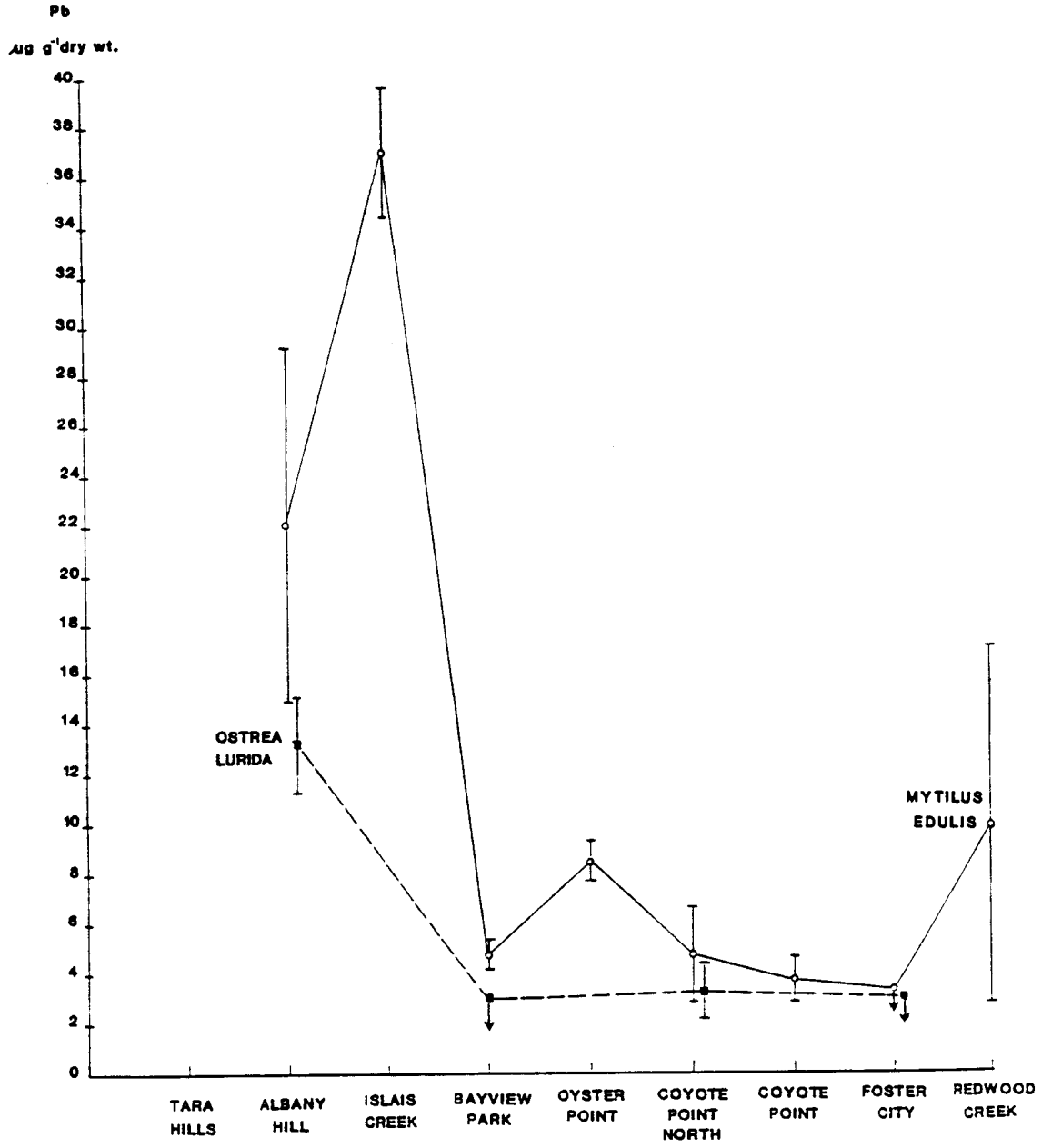


Fig. 56. Concentrations of lead (means ± standard deviations, $\mu g\ g^{-1}$ dry weight) in the native Bay mussel Mytilus edulis and the Olympic oyster Ostrea lurida from San Francisco Bay. After Girvin et al. (1975).

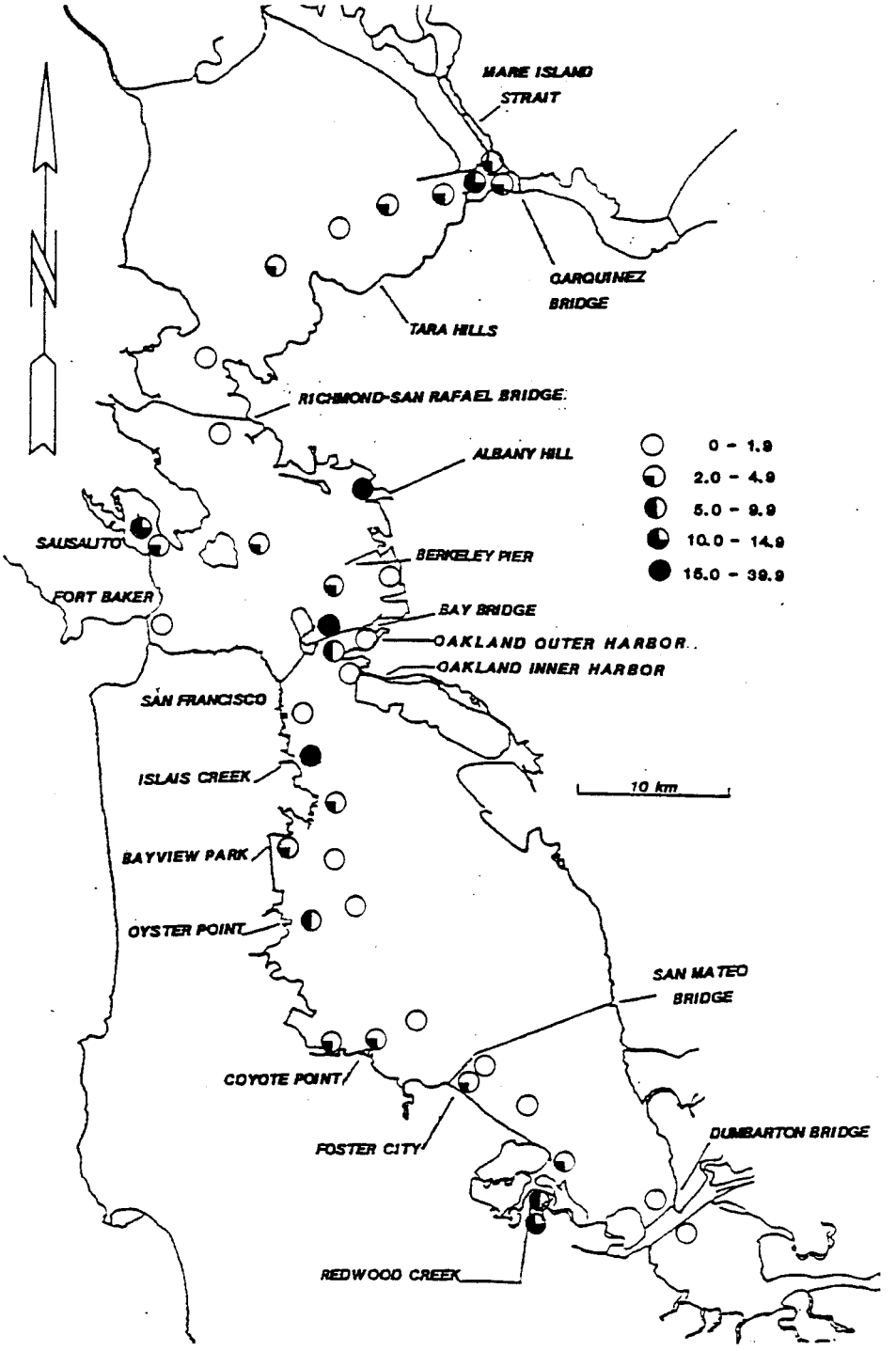


Fig. 57. Concentrations of lead (means, $\mu g\ g^{-1}$ dry weight) in native Bay mussels (Mytilus edulis) from San Francisco Bay; date of sampling was April 1976. After Risebrough et al. (1978).

inner Redwood Creeks. In most cases, reasonable agreement with data for sediments was evident. Lead concentations in transplant mussels (M. californianus) used in the State Mussel Watch Prograr are shown in Table 22. Levels once again vary little through the Bay except for localized "hot-spots", the latter being found at Alameda and Oakland Harbors, the eastern portion of the San Francisco peninsula, and the Redwood Creek area. Considering the differences in species employed, the precise locations sampled, and the timing of these surveys, the agreement between the datasets is high and provides a reasonably consistent picture of lead contamination within the Bay.

In the Delta portion of the estuary, fewer studies have beer completed on lead in biota. However, Luoma et al. (in press) and Foe and Knight (in preparation) both reported quite low values for lead in the asiatic clam (Corbicula sp.) from the lower San Joaquin River and Suisun Bay, agreeing with the pattern for lead in sediments of this region.

Data on lead in organisms other than bivalve molluscs in the Bay-Delta or its catchment show relatively little cause for concern. Occasional elevated values for lead in fish livers have been reported for samples from both the Sacramento and San Joaquin Rivers (SWRCB, 1986). This probably correlates to acid mine drainage in parts of both of the drainage basins (DWR, 1986; SWRCB/CVRWQCB, 1986), but effects again appear to be local. Harbor seals from the estuary contained unremarkable concentrations of lead (Risebrough et al., 1978), as did dabbling ducks from South Bay (Ohlendorf et al., 1986c).

Table 22. Concentrations of lead (ug g^{-1} dry weight) in transplanted mussels (Mytilus californianus) or native Bay mussels (M. edulis, as shown) at 33 sites in San Francisco Bay. Data from the State Mussel Watch Program, after Hayes et al. (1985), Hayes and Phillips (1986) and Stephenson et al. (1986a).

LOCATION	STATION CODE	1980	1981	1982 (J/F)	1982 (O/N/D)	1982 RESIDENT (O/N/D)a	1983	1985	1986
MARE ISLAND	300.20							2.6a	3.4
DAVIS POINT	301.00	1.6a			4.4				
POINT PINOLE	302.00	1.3a	2.5	2.1	1.8b		1.4	3.1	2.7
RICHMOND BRIDGE	303.00	4.0	2.4	2.4	2.0b				
SANTA FE CH. MOUTH	303.10								4.4
RICHMOND INNER HARBOR	303.60							4.0	
STAUFFER'S	304.00			5.7					
ANGEL ISLAND	305.00	3.6	2.5	3.0	2.3b				
FORT BAKER	306.00		3.7		2.6c				
TREASURE ISLAND	307.00	4.3	2.3	3.7	2.1c		3.5	2.4	3.0
ALAMEDA YACHT HARBOR	307.20							50.3a	11
OAKLAND IN. HARBOR WEST	307.30								3.9
OAKLAND IN. HARBOR EMBC.	307.40								13.9
OAKLAND BACK HARBOR	307.60								10.1
HUNTER'S POINT	308.00		2.8	2.9	2.2c	1.3a			
SAN MATEO BRIDGE 8	309.00	3.1	2.6	2.1	1.8c	1.3a	2.0	2.7	2.3
SAN MATEO BRIDGE 8A	310.00			2.3					
SAN MATEO OLD BRIDGE	311.00			2.4					
BELMONT SLOUGH	312.00			2.3					
REDWOOD CREEK MOUTH	313.00		2.8	1.7	1.6c	1.1a	1.7	2.3	
REDWOOD CREEK 10	314.00			2.9					
REDWOOD CREEK TOWERS	315.00			8.7	4.7b	4.9a			
REDWOOD CREEK TRDWNDS	316.00	3.2a		8.0	4.4b	4.6a			
REDWOOD CREEK STP	317.00			10.4					
SF PETES	318.00				5.4				
SF PULGAS	319.00				6.7				
SF AIRPORT	320.00				6.9				
DUMBARTON BRIDGE 14	321.00	1.6a	2.1	1.7	1.5	0.8a	3.1	3.1	2.5
NEWARK SLOUGH	324.00			2.5					
CHANNEL 17	325.00			2.4					
PALO ALTO 8	326.00			2.9		1.2a			
PALO ALTO YACHT	327.00			3.3					
ALVISO SLOUGH	328.00			4.3					

J/F/O/N/D: January/February/October/November/December, all 1982

a Resident Mytilus edulis.

b Mean of two values.

c Mean of three values.

Summary

Lead is not particularly toxic in aquatic ecosystems, although it is of considerable concern toxicologically to mammals, including Man. Concentrations of the element in water, sediments and biota of the San Francisco Bay-Delta are in general not markedly elevated compared to other large estuaries, and no widespread lead contamination problem exists in the catchment. Although no major lead sources are evident in the Bay, a complex mosaic of minor areas of local contamination by the element exists. This pattern is in keeping with the ubiquity of lead in industrialized environments. Most sites exhibiting elevated concentrations of the element are exposed to urban or other types of run-off, which are well documented as lead sources in aquatic ecosystems. The Delta no doubt provides high total loads of lead to the estuary, but these are introduced in highly diluted form, and there is little evidence for significantly elevated lead levels in the upper part of the estuarine system.

G. ZINC

Introduction

The natural rate of mobilization of zinc from the earth's crust is about 370,000 tonnes per year (MIT, 1970). Man's activities mobilize 10 to 15 times this amount annually (U.S. Bureau of Mines, 1970). Man thus influences the concentrations of zinc transported to coastal waters in much the same way as the transport of copper is affected. Most large estuaries exhibit enrichment of both of these elements compared to open oceans. However, zinc is rather less toxic to most aquatic organisms than is copper (compare Fig. 58 to Fig. 13 in this report). The most recent EPA standards propose a 4-day average standard of 86 $\mu g\ L^{-1}$ for zinc in marine waters, and a one-hour average concentration not exceeding 95 $\mu g\ L^{-1}$ (Update number 2, U.S. EPA, 1986).

Zinc in Bay-Delta Waters

Girvin et al. (1978) found a moderate enrichment of zinc in waters of the South Bay on most sampling occasions compared to Central Bay waters (Fig. 59). There was evidence of sources of zinc in both the extreme south of South Bay and the area close to the Bay bridge. The latter source was thought to be the discharge from the East Bay Municipal Utility District sewage treatment plant.

Eaton (1979b) reported similar data for zinc in the northern reach of San Francisco Bay. Concentrations of the element decreased from 2-7 $\mu g\ L^{-1}$ at the Delta to 0.4-2.4 $\mu g\ L^{-1}$ at the Golden Gate, and offshore concentrations outside the Golden Gate were still lower. These data agree well with the results of both

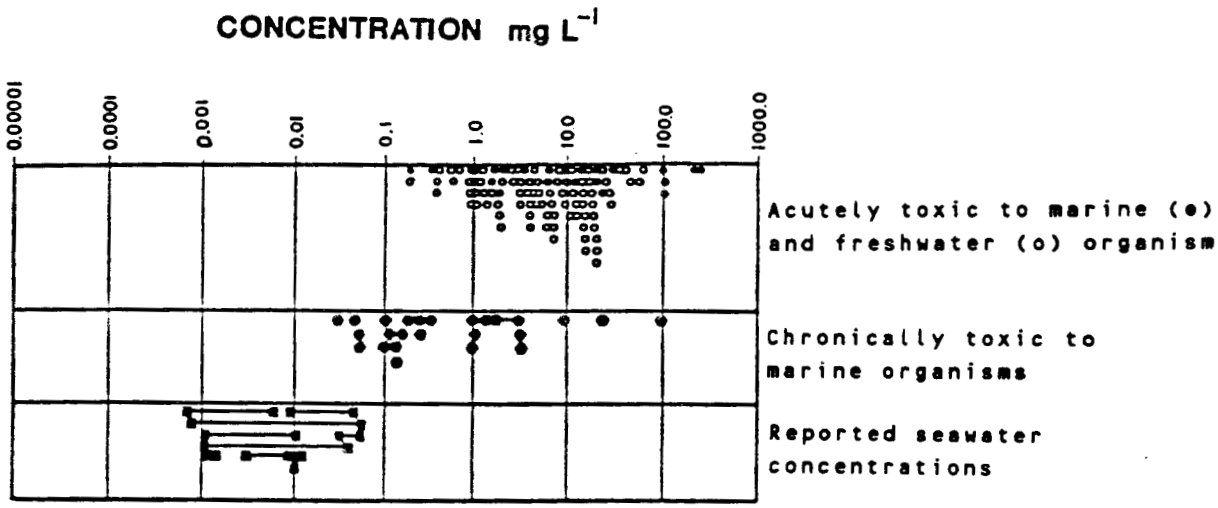


Fig. 58. Reported concentrations of zinc in seawater, and concentrations found to be chronically or acutely toxic aquatic biota. After Klapow and Lewis (1979).

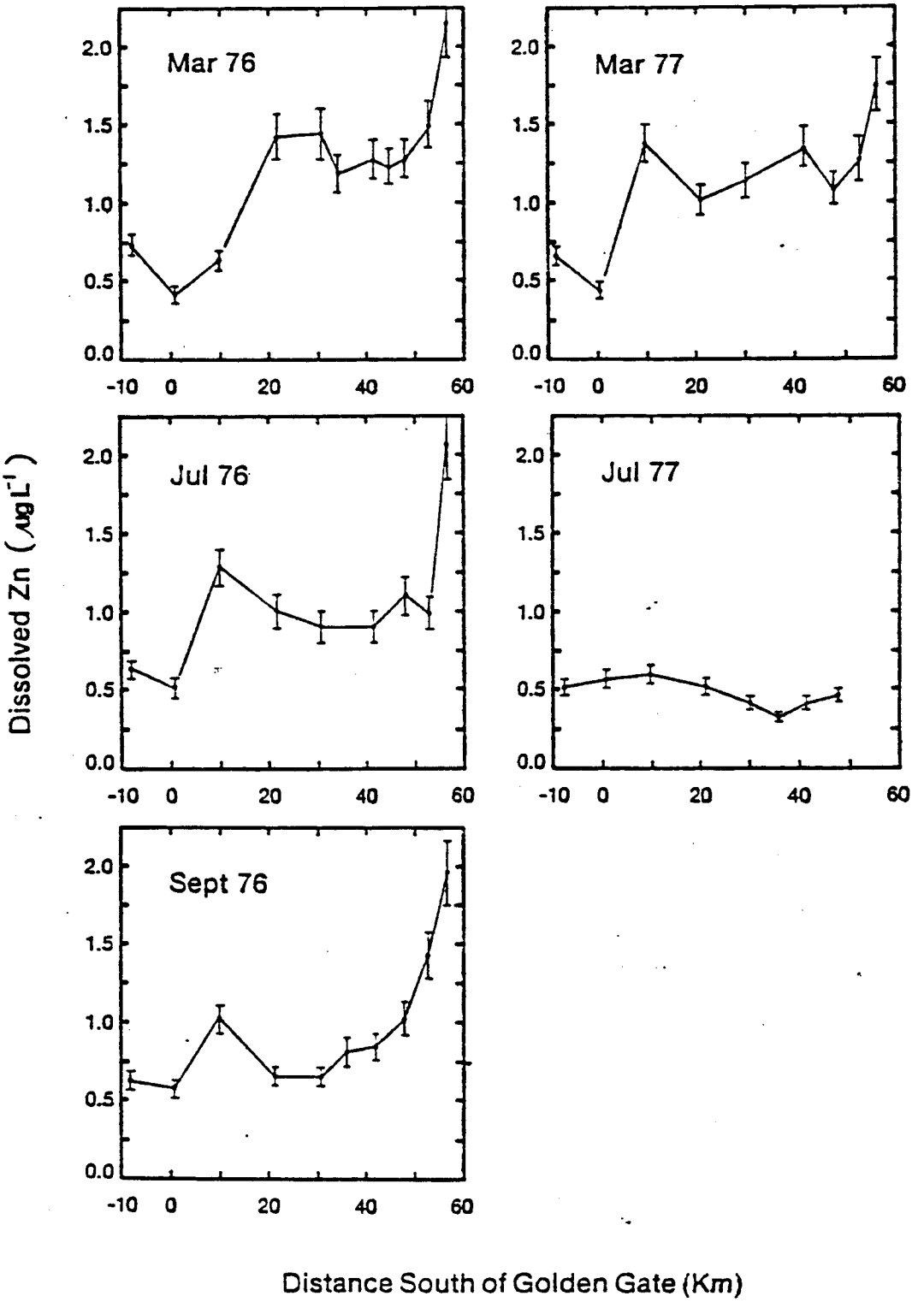


Fig. 59. Concentrations of dissolved zinc ($\mu g\ L^{-1}$) in waters of South and Central Bays, 1976-1977. After Girvin et al. (1978).

Girvin et al. (1978) and Gordon (1980), and show that the estuary is moderately enriched by zinc in both the northern and southern reaches, and that zinc is transported from the Bay to offshore coastal waters outside the Golden Gate. Freshwater inflows appear to provide the majority of the influent zinc to the Bay, although mid-estuary sources are also present; among the latter, sewage treatment plants are likely to be significant (see Young et al., 1981).

Zinc in Bay-Delta Sediments

Data from various authors (e.g. Anderlini et al., 1975a, 1975b; Risebrough et al., 1978; Eaton, 1979a; Bradford and Luoma, 1980; Thomson et al., 1984; Chapman et al., 1986) show that the concentrations of zinc in Bay sediments vary relatively little from area to area, except in the immediate vicinity of sources of the element. Thus, most sediments in the Bay exhibit concentrations of zinc of about 100 $\mu g\ g^{-1}$ dry weight, or a little higher than this. Such levels are not high compared to other coastal embayments (e.g. see Bradford and Luoma, 1980; Katz and Kaplan, 1981), and are only slightly elevated by comparison to values for average shale (Krauskopf, 1967).

In addition, Eaton (1979a) has shown that the majority of the zinc present in both surface and subsurface sediments of the Bay is not released by pyrophosphate or oxalate leaching treatments, but is of a "residual nature", i.e. is tightly bound within the sediment matrix.

A few reports of localized sediment enrichment by zinc deserve mention here. Thomson et al. (1984) found localized

enrichment of zinc in sediments close to the Palo Alto sewage treatment plant outfall; studies on clams (see below) showed that this zinc was bio-available, at least in part. Girvin et al. (1975) reported elevated zinc levels in sediments from Albany Hill (222 ± 51 $\mu g\ g^{-1}$ dry weight), which might have been due to discharges of the element from either sewage treatment plants or industrial sources. Hoffman and Meighan (1984) found very high zinc levels in sediments from the head of Islais Creek (984 $\mu g\ g^{-1}$ dry weight; see also Chapman et al., 1986) and Mission Creek (1255 $\mu g\ g^{-1}$ dry weight), indicating considerable local contamination at these locations.

Zinc in Bay-Delta Biota

Girvin et al. (1975) found that the concentrations of zinc present in four bivalve species in the Bay (Mya arenaria, Tapes japonica, Mytilus edulis, and Ostrea lurida) varied relatively little with location, although there was some evidence of zinc enrichment at Albany Hill and Tara Hills (the two most northerly sites), and a high concentration in the mussel M. edulis from Islais Creek. Pacific oysters (Crassostrea gigas) from the Redwood Creek area exhibited higher zinc levels than did those from Tomales Bay, although this difference was not as marked as for some other elements, such as silver or copper.

Risebrough et al. (1978) confirmed the high levels of zinc in M. edulis from Islais Creek and its surrounds, and noted moderate contamination in mussels from Mare Island Strait, the Berkeley area, Coyote Point, and inner Redwood Creek. However, no greatly elevated concentrations were found, and these authors

noted that the amounts of zinc present in Bay mussels were not exceptional compared to locations elsewhere. Data from the California State Mussel Watch Program (Table 23) confirm this for both M. edulis and M. californianus (Hayes et al., 1985; Hayes and Phillips, 1986; Stephenson et al., 1986a; Smith et al., 1986).

This general picture of moderate elevations of zinc levels throughout the Bay, with no unusually high contamination and relatively little variation between sites has been seen by other authors also, utilizing different species. Thus, Bradford and Luoma (1980) reported that zinc levels in the clam Tapes japonica from San Francisco Bay were only slightly higher than in those from Princeton Harbor, Half Moon Bay. The same authors found little variation in zinc concentrations in the snail Nassarius obsoletus from eight sites in the Bay. Similarly, Luoma et al. (in press) found no evidence of high zinc levels in either sediments or clams (Corbicula sp.) from Suisun Bay and the Delta. Data for zinc in the deposit-feeding clam Macoma balthica (Luoma and Cloern, 1982; Thomson et al., 1984; Luoma et al., 1985) also show no evidence of being particularly elevated, although clams from the area close to the Palo Alto sewage treatment plant exhibited moderate increases in zinc levels.

Few data are available on zinc concentrations in organisms other than molluscs from the Bay-Delta. A few elevated levels of zinc in fish livers have been found in samples from lower tributaries of the Sacramento River and from the metal-enriched area around Shasta Dam (SWRCB, 1986). However, zinc from the Sacramento and San Joaquin Rivers is highly diluted upon its

Table 23. Concentrations of zinc (means, ug g^{-1} dry weight) in transplanted mussels (Mytilus californianus) or native Bay mussels (M. edulis, as shown[a]) at 33 sites in San Francisco Bay. Data from the State Mussel Watch Program, after Hayes et al. (1985), Hayes and Phillips (1986) and Stephenson et al. (1986a).

LOCATION	STATION CODE	1980	1981	1982 (J/F)	1982 (O/N/D)	1982 RESIDENT (O/N/D)a	1983	1985	1986
MARE ISLAND	300.20							158a	169
DAVIS POINT	301.00	62a			209				
POINT PINOLE	302.00	89a	184	272	209b		237	239	188
RICHMOND BRIDGE	303.00	190	152	232	237b				
SANTA FE CH. MOUTH	303.10								251
RICHMOND INNER HARBOR	303.60							241	
STAUFFER'S	304.00			214					
ANGEL ISLAND	305.00	175	125	199	201b				
FORT BAKER	306.00		116		188c				
TREASURE ISLAND	307.00	197	137	227	204c		257	219	202
ALAMEDA YACHT HARBOR	307.20							651a	348
OAKLAND IN. HARBOR WEST	307.30								226
OAKLAND IN. HARBOR EMBC.	307.40								404
OAKLAND BACK HARBOR	307.60								317
HUNTER'S POINT	308.00		160	229	228c	137a			
SAN MATEO BRIDGE 8	309.00	157	198	321	205c	128a	285	253	232
SAN MATEO BRIDGE 8A	310.00			244					
SAN MATEO OLD BRIDGE	311.00			224					
BELMONT SLOUGH	312.00			236					
REDWOOD CREEK MOUTH	313.00		162	223	205c	138a	240	249	
REDWOOD CREEK 10	314.00			288					
REDWOOD CREEK TOWERS	315.00			317	237b	111a			
REDWOOD CREEK TRDWNDS	316.00	103a		272	228b	132a			
REDWOOD CREEK STP	317.00				239				
SF PETES	318.00				227				
SF PULGAS	319.00				215				
SF AIRPORT	320.00				234				
DUMBARTON BRIDGE 14	321.00	82a	200	207	195	129a	332	245	161
NEWARK SLOUGH	324.00			230					
CHANNEL 17	325.00			253					
PALO ALTO 8	326.00			244		115a			
PALO ALTO YACHT	327.00			223					
ALVISO SLOUGH	328.00			244					

J/F/O/N/D: January/February/October/November/December, all 1982

[a] Resident Mytilus edulis.

[b] Mean of two values.

[c] Mean of three values.

entry to the Delta; thus, concentrations of the element are quite low, even though total loads from this source are considerable (Eaton, 1979a, 1979b). Finally, data from Ohlendor et al. (1986c) on zinc in the livers of diving ducks from the South Bay suggest moderate elevations of the element, but are no considered of great toxicological import.

Summary

The available data on zinc in the San Francisco Bay-Delta ecosystem show that, while the estuary is a source of the element to offshore marine waters outside the Golden Gate, the degree of contamination of Bay-Delta waters by zinc is relativel minor, and is similar to that found in many other estuaries. Neither water nor sediments exhibits unusually high levels of zinc, except in a few areas of highly localized contamination (e.g. Islais Creek and Mission Creek sediments). Water quality standards for zinc appear to be attained in all parts of the receiving waters of the Bay. While there is evidence for zinc discharges in the area of the Bay itself (as opposed to from Delta outflow), these loads (which probably derive from sewage treatment plants and industrial effluents entering the Bay directly) are not unusually great and probably do not harm Bay resources measurably. Biota from the Bay exhibit unexceptional levels of zinc, indicative of a minor degree of contamination, and with little site-to-site variation.

H. CHROMIUM

Introduction

The natural rate of mobilization of chromium from the earth's crust is far outweighed by its mobilization due to the activities of Man. In the United States, chromium is used principally in metallurgical and chemical industries (Langard and Norseth, 1979). Most of the chromium discharged by industry to the environment enters the atmosphere; much less is discharged directly to aquatic environments through aqueous emissions (Ecological Analysts, 1981; Eisler, 1986a). The most important direct sources of chromium in aquatic ecosystems are discharges from metal finishing industries and sewage treatment plants. Other (generally more minor) sources include iron and steel works, chemical industries, tanneries, textile manufacturers, and urban run-off (Towill et al., 1978; Eisler, 1986a).

Chromium exists in nature in valency states ranging from Cr(-2) to Cr(+6), but the most common forms are the trivalent and hexavalent states. The element in its trivalent form is essential in mammals, required for a variety of enzymes. Organic forms of chromium exist in the environment, but almost nothing is known of their abundance or effects. The hexavalent form of the element is generally considered to be of higher toxicity than the trivalent state. The biogeochemical cycle of chromium has been poorly characterized, however, and there has been little agreement on appropriate water quality standards. The latter have been altered significantly by the U.S. EPA in various proposed standards, the 1980 standard for hexavalent

chromium of 0.29 $\mu g\ L^{-1}$ as a 24-hour average being increased to 50 $\mu g\ L^{-1}$ as a 4-day average in the recent guidelines (U.S. EPA, 1986). The proposed standard for freshwaters is 11 $\mu g\ L^{-1}$ as a 4-day average (U.S. EPA, 1986). Klapow and Lewis (1979) and Eisler (1986a) noted that while chromium did not generally exhibit acute toxicity to aquatic biota at low concentrations, chronic effects spanned several orders of magnitude in concentration. Eisler (1986a) considered levels of 5 $\mu g\ L^{-1}$ to be associated with measurable bioaccumulation of the element, and 10 $\mu g\ L^{-1}$ to cause detrimental effects on biota, in both freshwater and marine ecosystems.

By comparison with other metals, chromium has been poorly characterized in the San Francisco Bay-Delta. The available data are considered below.

Chromium in Bay-Delta Waters

No direct measurements of dissolved chromium concentrations in the receiving waters of the Bay-Delta are available. However, Gordon (1980) reported slightly higher mean concentrations of total chromium in suspended particulates from the Central Bay than from surface or deep waters in the Gulf of the Farallones. Chromium has also been detected at significantly elevated concentrations in the waters of the Sacramento River (e.g. SWRCB/CVRWQCB, 1986) and the San Joaquin River (DWR, 1986). The main source of the element in the Sacramento River is believed to be acid mine drainage from the Spring Creek near Redding and the Squaw and Little Backbone Creeks near the Shasta Dam. Less is known of the sources in the San Joaquin catchment, but both mine

run-off and chromium-containing pesticides may be implicated (SWRCB, 1986). It is likely that the Delta transports appreciable quantities of chromium to the Bay, in both dissolved and particulate-associated forms. However, direct measurements of this transport are not available.

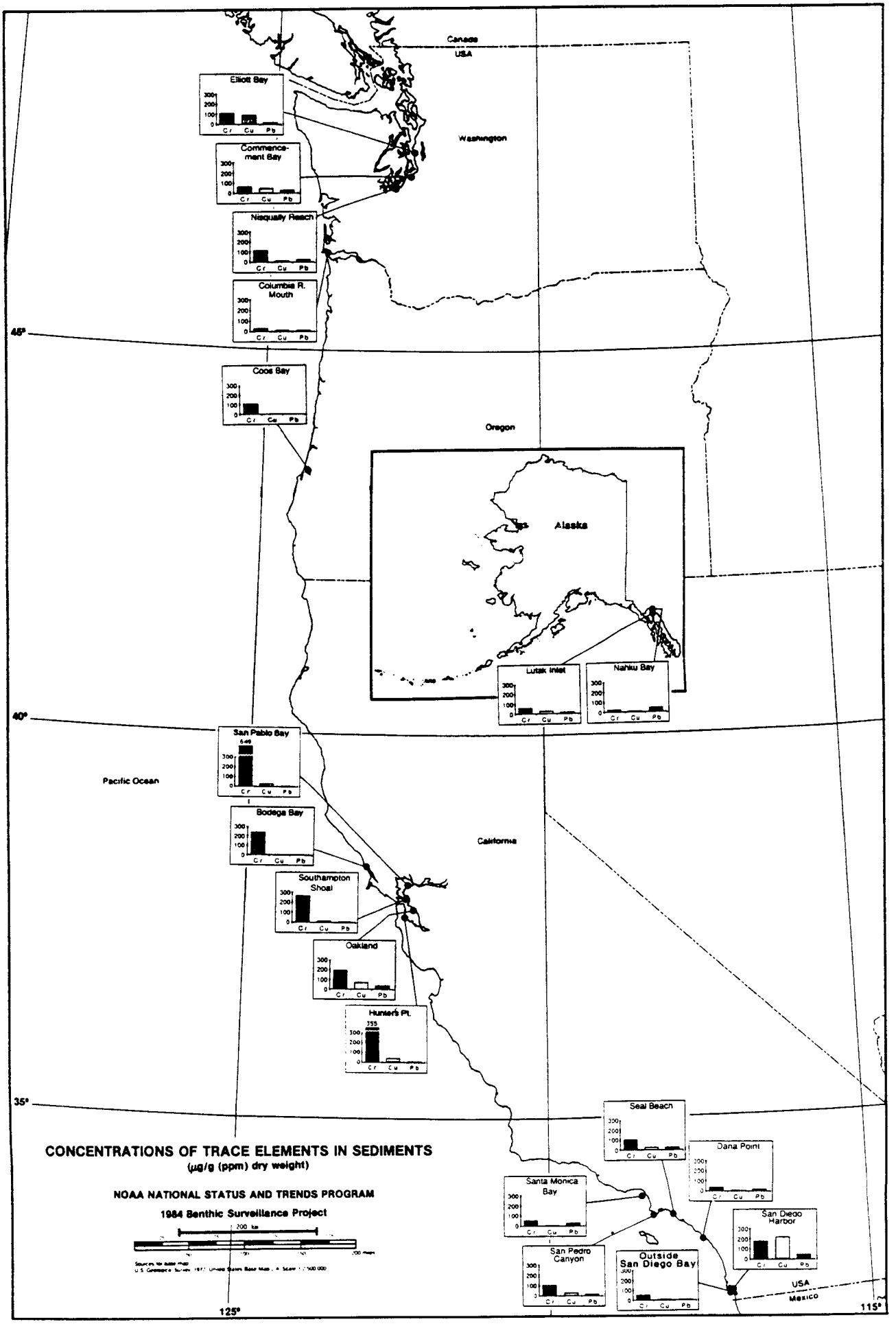
Chromium in Bay-Delta Sediments

Several authors have reported data for chromium in Bay-Delta sediments. Girvin et al. (1975) reported concentrations of total chromium between 234 and 464 $\mu g\ g^{-1}$ dry weight for sediments from five sites in the Bay, between Tara Hills and Foster City. Bradford and Luoma (1980) cited similar concentrations for Alcatraz and the Oakland Harbor area. Data from the benthic surveillance project of the National Status and Trend Program (NOAA, 1987) also indicate high concentrations of chromium for sediment samples taken in the Bay at five sites in 1984 (Fig. 60). It is notable that the levels of chromium found in Bay sediments in this project were generally higher than those reported for samples from elsewhere in California.

By contrast, Hoffman and Meighan (1984) reported generally lower levels of the element (126-173 $\mu g\ g^{-1}$ dry weight) in sediments from the eastern side of the San Francisco peninsula, with the exception of Islais Creek sediments, which reflected a local source of chromium (195 $\mu g\ g^{-1}$ dry weight at the mouth, increasing to 534 $\mu g\ g^{-1}$ at the head of the Creek). Chapman et al. (1986) found chromium concentrations of only 72-93 $\mu g\ g^{-1}$ dry weight in sediments of San Pablo Bay, concentrations at Oakland being 85-95 $\mu g\ g^{-1}$ and those for Islais Creek 110-146 μg^{-1} dry weight.

Fig. 60.

Mean concentrations ($\mu g\ g^{-1}$ dry weight) of chromium, copper, and lead in sediments from the west coast of the USA. Data from the 1984 benthic surveillance project of the National Status and Trends Program. After NOAA (1987).



CONCENTRATIONS OF TRACE ELEMENTS IN SEDIMENTS
(µg/g (ppm) dry weight)

NOAA NATIONAL STATUS AND TRENDS PROGRAM

1984 Benthic Surveillance Project

It is not known whether the more recent tendency towards lower reported concentrations of chromium in Bay sediments reflects a real trend in decreased discharges of the element over the last decade (perhaps correlating to the instigation of improved treatment methods for sewage and industrial effluents) or is due to recent improvements in analytical techniques and quality control. The differences between concentrations of chromium reported by NOAA (1987) and by Hoffman and Meighan (1984) and Chapman et al. (1986) are particularly difficult to interpret; in general, quality control is excellent in the studies of NOAA (1987). It is possible that Bay sediments are particularly heterogeneous with respect to levels of this element. Further studies are required to clarify whether Bay sediments exhibit chromium levels greater than those in average shales (100 $\mu g\ g^{-1}$ dry weight; see Krauskopf, 1967). The investigation of chromium levels in sediment cores might be useful to indicate the past record of contamination by the element within the Bay.

Chromium in Bay-Delta Biota

Girvin et al. (1975) could not detect chromium in any of the five species of bivalve molluscs they analyzed (detection limits ranged from 6.6 to 10.2 $\mu g\ g^{-1}$ dry weight). Risebrough et al. (1978), using more standard methods with much improved detection limits for chromium, produced the contamination profile shown in Fig. 61 for the element in native Bay mussels, Mytilus edulis, sampled in April 1976. This profile is interesting, in that it suggests very low levels of the element in the northern reach of

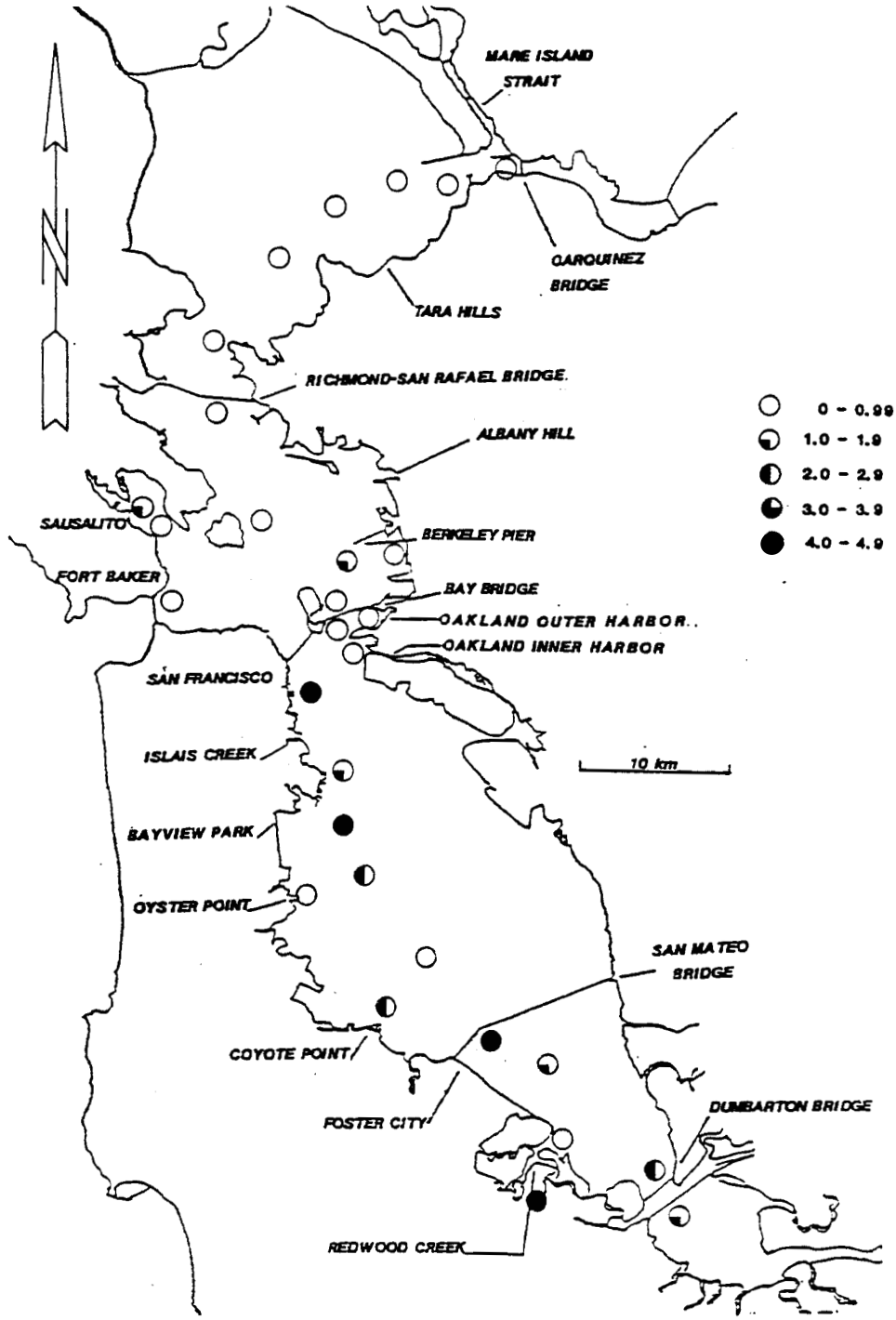


Fig. 61. Concentrations of chromium (means, $\mu g\ g^{-1}$ dry weight) in native Bay mussels (Mytilus edulis) from various locations in San Francisco Bay. Sampling time was April 1976. After Risebrough et al. (1978).

the Bay, elevated concentrations occurring only in South Bay locations. To some extent, this is reminiscent of profiles for silver contamination in the Bay, although greater local variability is seen for chromium in mussels.

Later data from the California Mussel Watch Program (Hayes et al., 1985; Hayes and Phillips, 1986; Stephenson et al., 1986a; see also Martin et al., 1984; Smith et al., 1986) are shown in Table 24. It should be noted that most of these data refer to transplanted M. californianus rather than native Bay mussels (exceptions as shown), and that caution should be exercised in attempting to compare these values with data for M. edulis, as species differences may exist in the bio-accumulation of chromium (Phillips, 1980). However, qualitative differences appear to be present between the profiles reported for chromium in M. edulis by Risebrough et al. (1978) and those found for either this species or M. californianus in the State Mussel Watch Program. Thus, the data in Table 24 suggest no tendency toward higher chromium concentrations in South Bay mussels, but a rather homogeneous distribution of the element within the Bay. These differences may be related to the temporal trends in reported concentrations of chromium in sediments noted above; however, no firm conclusion is possible given this restricted database. The need for improvements in monitoring long-term changes in trace elements in the Bay-Delta ecosystem is clear.

Finally with respect to bivalves, studies on the freshwater asiatic clam Corbicula sp. require mention. Luoma et al. (in press) analyzed this species, taken from Suisun Bay and several sites in the Delta, for chromium. The data revealed considerable

Table 24. Concentrations of chromium (means, ug g^{-1} dry weight) in transplanted Mytilus californianus or native M. edulis (as shown [a]) analyzed in the State Mussel Watch Program. After Hayes et al. (1985), Hayes and Phillips (1986) and Stephenson et al. (1986a).

LOCATION	STATION CODE	1980	1981	1982 (J/F)	1982 (O/N/D)	1982 RESIDENT (O/N/D)a	1983	1985	1986
MARE ISLAND	300.20							7.4a	3.8
DAVIS POINT	301.00	2.3a			6.1				
POINT PINOLE	302.00	1.5a	3.0	2.7	2.2b		4.0	4.4	4.4
RICHMOND BRIDGE	303.00	1.7	2.5	2.8	2.7b				
SANTA FE CH. MOUTH	303.10								3.4
RICHMOND INNER HARBOR	303.60							3.5	
STAUFFER'S	304.00			2.6					
ANGEL ISLAND	305.00	2.3	2.4	2.6	1.4b				
FORT BAKER	306.00		1.7		1.9c				
TREASURE ISLAND	307.00	2.2	2.6	3.6	2.1c		6.5	2.9	3.1
ALAMEDA YACHT HARBOR	307.20							4.0a	4.7
OAKLAND IN. HARBOR WEST	307.30								3.8
OAKLAND IN. HARBOR EMBC.	307.40								5.4
OAKLAND BACK HARBOR	307.60								4.6
HUNTER'S POINT	308.00		2.8	3.8	2.1c	1.9a			
SAN MATEO BRIDGE 8	309.00	2.6	3.0	2.7	2.0c	2.7a	4.1	3.6	4.7
SAN MATEO BRIDGE 8A	310.00			2.1					
SAN MATEO OLD BRIDGE	311.00			1.9					
BELMONT SLOUGH	312.00			2.6					
REDWOOD CREEK MOUTH	313.00		3.6	2.6	2.2c	2.0a	2.7	4.4	
REDWOOD CREEK 10	314.00			2.0					
REDWOOD CREEK TOWERS	315.00			2.4	2.1b	1.6a			
REDWOOD CREEK TRDWNDS	316.00	1.3a		2.6	1.6b	1.4a			
REDWOOD CREEK STP	317.00				2.2				
SF PETES	318.00				2.1				
SF PULGAS	319.00				2.2				
SF AIRPORT	320.00				2.2				
DUMBARTON BRIDGE 14	321.00			2.5	2.1	1.6a	5.2	5.1	3.1
NEWARK SLOUGH	324.00	2.7a	3.3	2.4					
CHANNEL 17	325.00			2.3					
PALO ALTO 8	326.00			2.6		2.2a			
PALO ALTO YACHT	327.00			2.7					
ALVISO SLOUGH	328.00			5.2					

J/F/O/N/D: January/February/October/November/December, all 1982

[a] Resident Mytilus edulis.

[b] Mean of two values.

[c] Mean of three values.

enrichment of chromium in clams from the area of Antioch; a point source of the element of some magnitude was suspected to exist at this location. Concentrations of chromium were about 13 $\mu g\ g^{-1}$ dry weight at this site, which suggests considerable enrichment. Similar elevated levels of the element were found by Foe (C. Foe, personal communication) in Corbicula sp. from New York Slough, near Pittsburg (Foe and Knight, in preparation). It is evident from these data that industrial point sources of chromium of some magnitude are present in the lower Delta area.

The Toxic Substances Monitoring Program provides data for chromium levels in fish liver from the Bay-Delta catchment. Elevated data levels covering the results from 1978 to 1984 are shown in Fig. 62. The EDL 85 corresponds to a concentration of 0.03 $\mu g\ g^{-1}$ wet weight; the EDL 95 corresponds to a level of 0.1 $\mu g\ g^{-1}$ wet weight. It is clear that both the Sacramento and San Joaquin river catchments contain significant amounts of chromium. As noted above, this enrichment is thought to arise mainly from acid mine drainage and perhaps from the application of chromium-containing pesticides.

Summary

The abundance of chromium within the Bay-Delta ecosystem has been poorly characterized by past studies. No direct measurements on chromium in Bay-Delta receiving waters exist, although the monitoring of both effluents and rivers entering the estuary reveals significant amounts of the element. The database for chromium in both sediments and biota is patchy, with disagreement between studies. It is not possible to discern

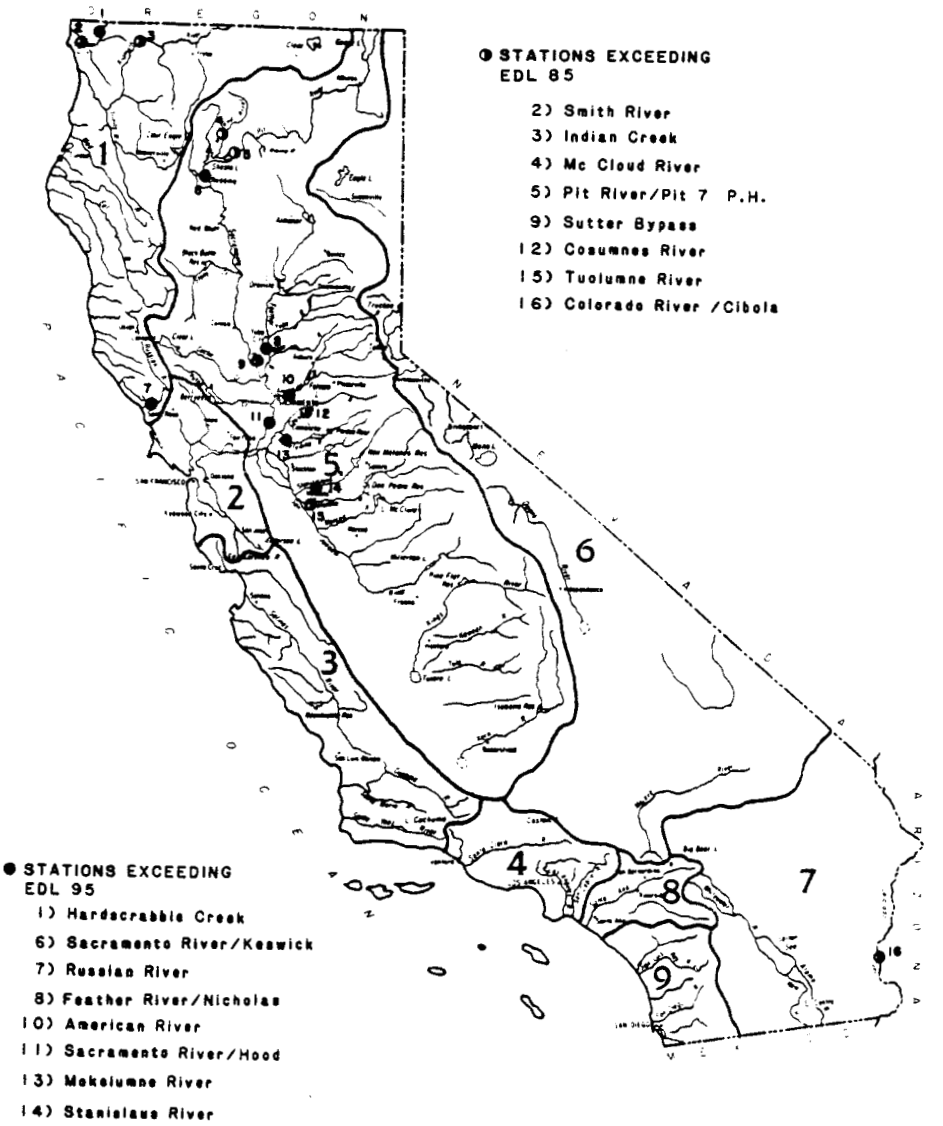


Fig. 62. Locations at which elevated data levels (EDL 85 and EDL 95) were exceeded for chromium concentrations in livers of finfish, in studies conducted under the Toxic Substances Monitoring program, 1978 to 1984. After SWRCB (1986).

long-term temporal trends in abundance of the element with confidence. However, there is a suggestion from data for both sediments and mussels that the levels of chromium may have decreased in the Bay over the last decade. Nevertheless, point sources of the element remain, augmented no doubt by loads of chromium reaching the estuary from non-point sources. Given the toxicity of chromium (including mutagenic, teratogenic, and carcinogenic activities at high dosage), there appears to be a need for improved monitoring of the element in the Bay-Delta.

I. NICKEL

Introduction

Nickel is of only moderate toxicity in aquatic environments, ranking after elements such as mercury, cadmium, silver, and copper. Its natural rate of mobilization from the earth's crust is about 300,000 tonnes annually, which is approximately doubled by the activities of Man (MIT, 1970; Waldichuk, 1974; Phillips, 1980).

The main sources of nickel loads in aquatic environments arise from metal finishing industries, although a variety of other industrial sources exists. Nickel is present in appreciable quantities in both urban run-off and municipal effluents (e.g. Young et al., 1981).

Data on the toxicity of nickel to aquatic biota are rather more sparse than information on some other elements, especially for chronic bioassays. However, the available information clearly shows the lower toxicity of nickel compared to mercury, cadmium, silver, or copper, and also suggests that toxic concentrations of nickel are markedly greater than ambient concentrations measured in aquatic environments (Fig. 63). The most recent U.S. EPA guidelines propose maxima of 8.3 $\mu g\ L^{-1}$ as a 4-day average for nickel in marine waters, and 75 $\mu g\ L^{-1}$ as a one-hour average (Update number 2, U.S. EPA, 1986).

Data on nickel in San Francisco Bay exist for water, sediments, and biota, although the element has not been as extensively studied in the Bay-Delta as some other trace metals.

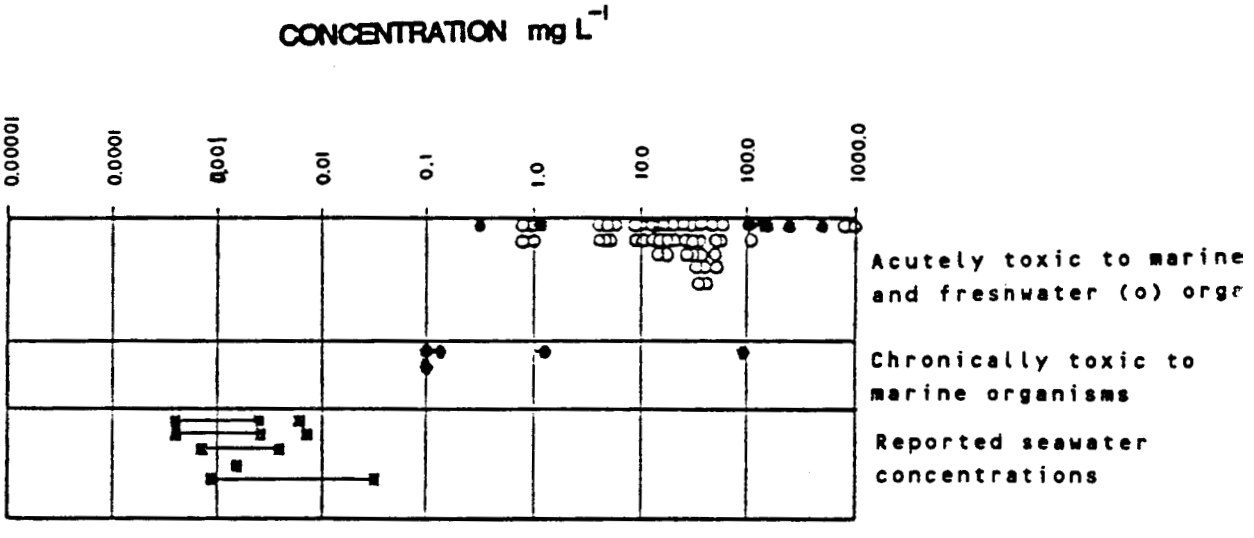


Fig. 63. Concentrations of nickel found in seawater, and concentrations documented as chronically or acutely toxic to aquatic biota. After Klapow and Lewis (1979).

Nickel in Bay-Delta Waters

Girvin et al. (1978) reported a strong longitudinal gradient for nickel in waters of the South and Central Bays. Such a gradient was evident at all sampling times employed in this investigation, and reflected increasing concentrations of dissolved nickel in the study area with distance south from the Golden Gate (Fig. 64). The data indicate a source of nickel in the southern extremity of South Bay; there was little evidence of mid-Bay sources. Maximum concentrations of about 8 $\mu g\ L^{-1}$ were noted, similar to the most recently proposed guidelines of the U.S. EPA (1986), discussed above. Girvin et al. (1978) also noted a mean concentration of nickel in the Gulf of the Farallones of 0.36 $\mu g\ L^{-1}$, suggesting that the Bay is a source of the element to offshore marine waters.

Eaton (1979b) reported rather lower contamination of the northern reach of San Fancisco Bay by nickel than that noted above for South Bay. The Delta outflow constituted a nickel source to the northern reach of the estuary, but maximum concentrations of dissolved nickel in the influent freshwaters were only about 2 $\mu g\ L^{-1}$ on average. The mixing profile indicated the existence of secondary sources of nickel within the Bay, probably from industrial and municipal effluents. This study and the data of Gordon (1980) agree that the Bay is a significant source of nickel to offshore marine environments. Thus, concentrations of nickel decrease from the northern and southern extremities of the Bay to levels around 1 $\mu g\ L^{-1}$ in the Central Bay, through dilution of influent loads by inflowing marine waters. By comparison, the offshore marine waters in the

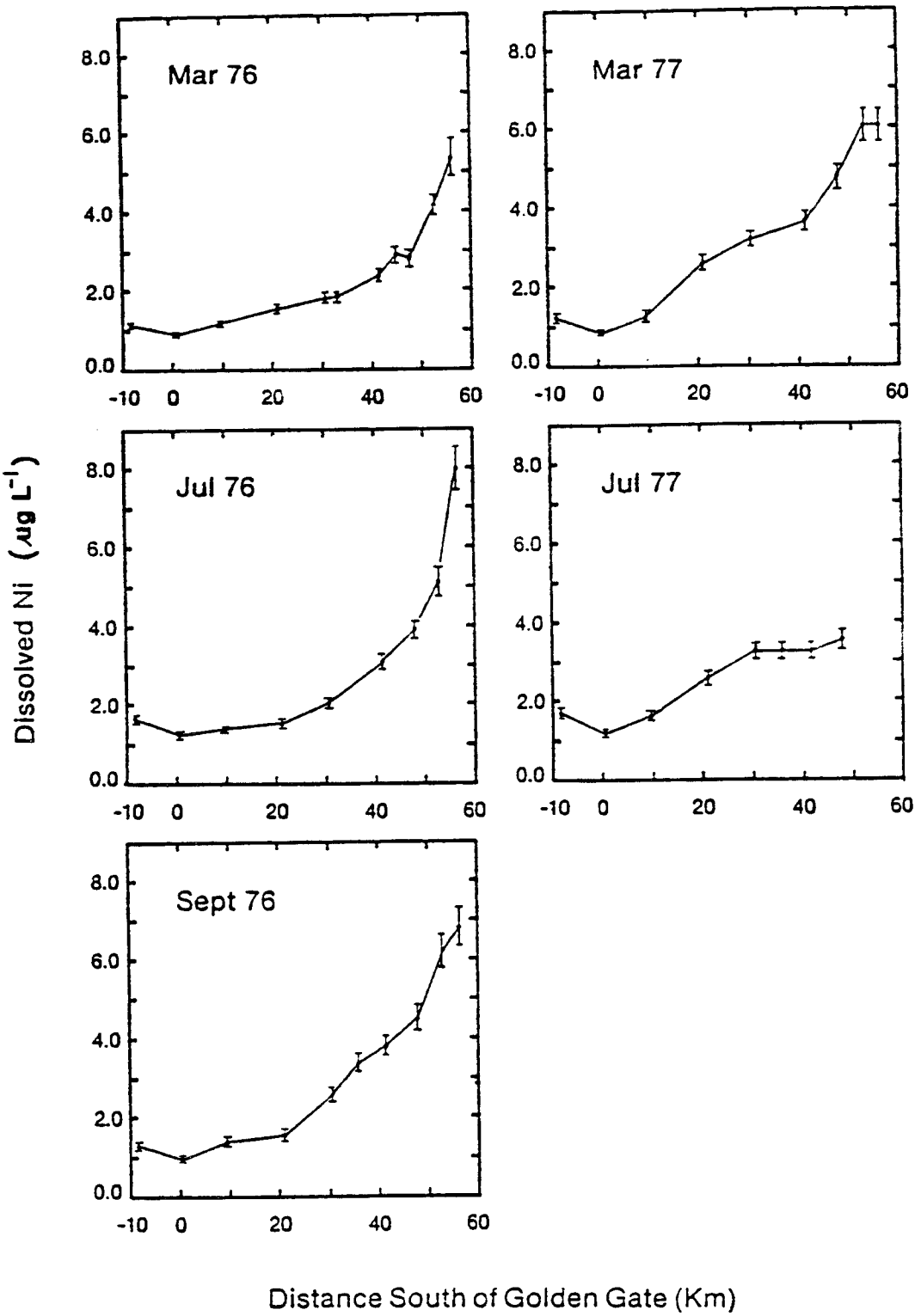


Fig. 64. Concentrations of dissolved nickel ($\mu g\ L^{-1}$) in waters o the Central and South Bays, March 1976 to July 1977. The average analytical error of $\pm$ 7% is indicated by vertical bars. After Girvin et al. (1978).

Gulf of the Farallones exhibit nickel concentrations in solution of only 0.2 to 0.4 $\mu g\ L^{-1}$.

Nickel in Bay-Delta Sediments

Like zinc, there is apparently relatively little spatial variation in the concentrations of nickel in San Francisco Bay sediments. Bradford and Luoma (1980) summarized data from several previous studies, which indicated that nickel concentrations varied from 84 $\mu g\ g^{-1}$ dry weight in Carquinez Strait to 189 $\mu g\ g^{-1}$ in Oakland Inner Harbor. These data may be compared to levels in average shale of 95 $\mu g\ g^{-1}$ dry weight (Krauskopf, 1967). A similar range in concentration of nickel in sediments was noted by Girvin et al. (1975). Samples from this study for both sediments and suspended particulates at Foster City showed a degree of nickel enrichment, agreeing with data on nickel in solution in South Bay, cited above. The data of Hoffman and Meighan (1984) and Chapman et al. (1986) also show nickel levels in Bay sediments to be generally close to 100 $\mu g\ g^{-1}$ dry weight, with little variability between sites. Interestingly, neither Islais Creek nor Mission Creek sediments was significantly nickel-enriched, which contrasts markedly to data for many other trace elements at these locations.

Eaton (1979a, 1979b) reported that, while significant total amounts of nickel entered the Bay through the Sacramento/San Joaquin estuary (mostly adsorbed to suspended particulates), concentrations of the element in Bay-Delta sediments were not markedly elevated. Extractions of nickel using a progressive leaching technique revealed that most of the element (mean of

85%) was present in the residual fraction, i.e. was bound within the sediment matrix. This suggests that a relatively small fraction of the total nickel present in Bay-Delta sediments or suspended particulates is likely to be available to biota.

Nickel in Bay-Delta Biota

As for most other elements, the great majority of information on nickel in Bay-Delta biota comes from studies of bivalve molluscs. However, some of these data are difficult to interpret (or have been subject to varying interpretations), and no truly consistent pattern emerges.

Girvin et al. (1975) found only minor nickel enrichment in bivalves from the northern reach of San Francisco Bay, consistent with data from studies of water and sediments in this area (Figs. 65 and 66). However, in the South Bay, contamination profiles differed according to the species used. Analyses of Mya arenaria, Mytilus edulis, and Ostrea lurida revealed no major contamination of the South Bay by nickel. However, data for the Japanese littleneck clam Tapes japonica showed high nickel bio-availabilities in the South Bay, at Coyote Point, Foster City, and Redwood Creek (Fig. 65). Presumably, T. japonica was responding to a nickel load in the South Bay which was not available to the other three species. Such a phenomenon has been documented elsewhere, and disagreements between contamination profiles generated from the study of several biological indicators such as these are not particularly uncommon (Phillips, 1980). Risebrough et al. (1978) analyzed native Bay mussels (Mytilus edulis) from various locations in San Francisco

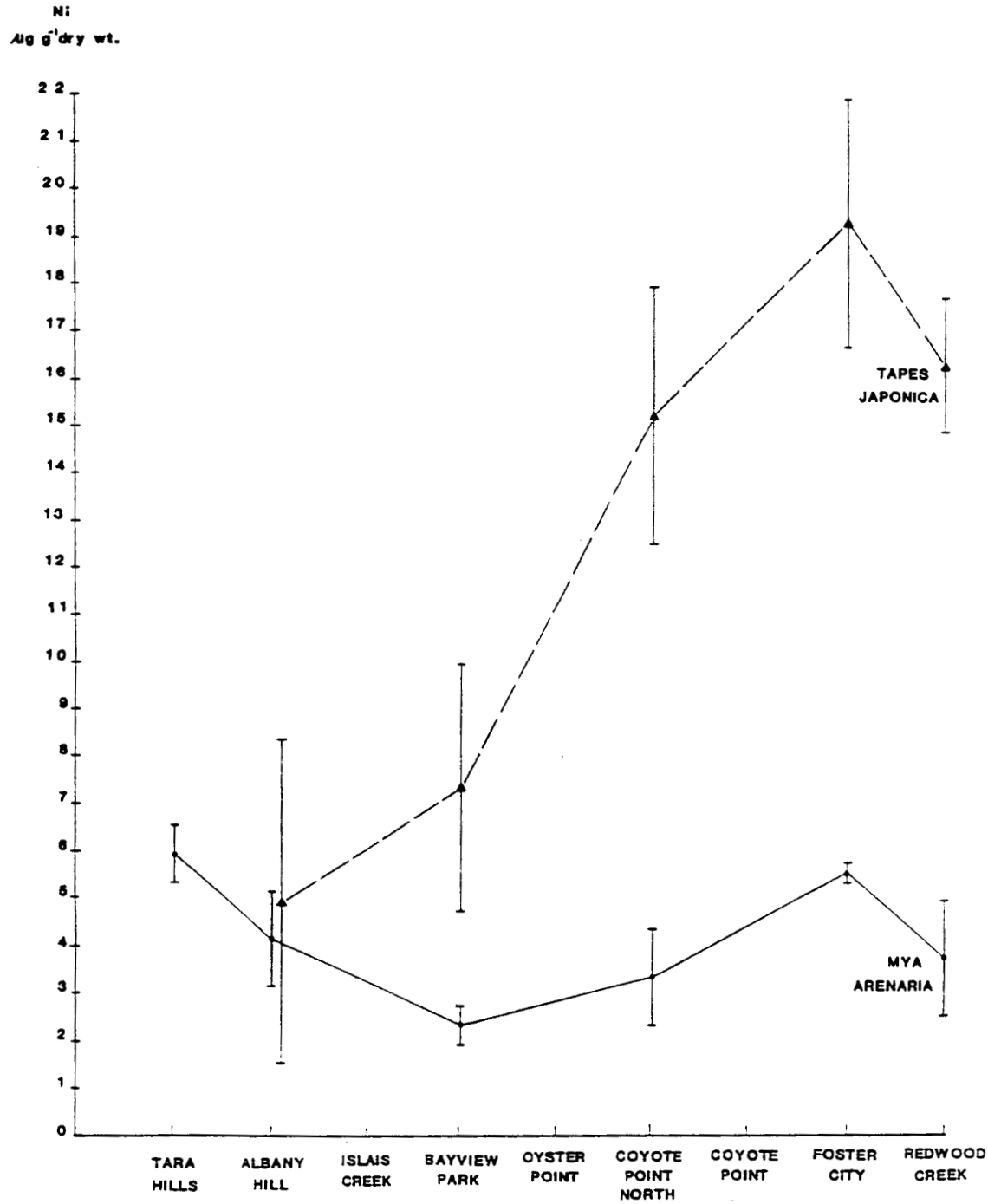


Fig. 65. Concentrations of nickel (means ± standard deviations, $\mu g\ g^{-1}$ dry weight) in the softshell clam Mya arenaria and the Japanese littleneck clam Tapes japonica from San Francisco Bay. After Girvin et al. (1975).

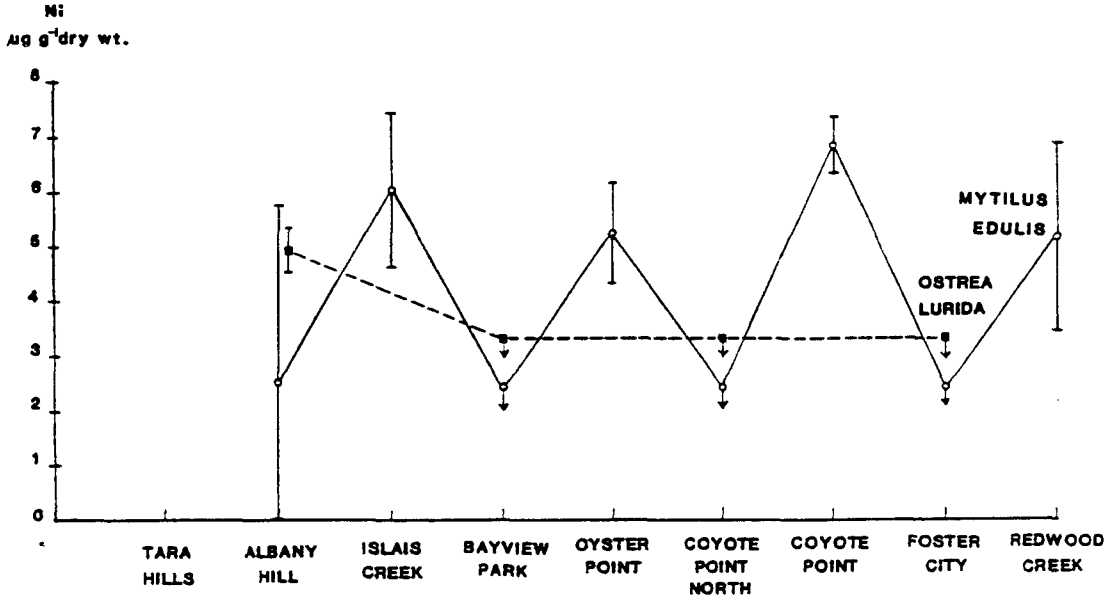


Fig. 66. Concentrations of nickel (means ± standard deviations, $\mu g\ g^{-1}$ dry weight) in the native Bay mussel Mytilus edulis and the Olympic oyster Ostrea lurida from San Francisco Bay. After Girvin et al. (1975).

Bay, ranging from the Carquinez Strait Bridge to the Dumbarton Bridge. The resulting contamination profile for nickel (Fig. 67) was patchy, reflecting no large areas of extensive enrichment, but rather more localized contamination in a few areas only. The latter included Carquinez Strait and surrounds, Islais Creek, and Redwood Creek; somewhat lower nickel concentrations were found in mussels from Oyster Point, Coyote Point, and Foster City. Most concentrations reported were below 5 $\mu g\ g^{-1}$ dry weight. Risebrough et al. (1978) considered the levels found to be unremarkable, although Luoma and Cloern (1982) thought the highest concentrations (noted for Carquinez Strait, Islais Creek, and Redwood Creek) indicative of extreme contamination. There is little doubt that Mare Island Strait and the nearby Carquinez Strait area is significantly enriched by nickel. Anderlini et al. (1975a) found high nickel concentrations in Macoma balthica at this location, although once again there was considerable spatial variability among the data.

Information from the California State Mussel Watch throws little light on this rather confused situation. Nickel was surveyed only in 1980 in this program, and little variability was noted among stations.

Data from studies of fish and ducks in the San Francisco catchment also reveal no consistent pattern of unusual nickel enrichment. The results of the Toxic Substances Monitoring Program (SWRCB, 1986) show only occasional high nickel values in fish livers from the Bay-Delta catchment, although higher values have been noted in samples from elsewhere in California. Finally, Ohlendorf et al. (1986c) found nickel above the

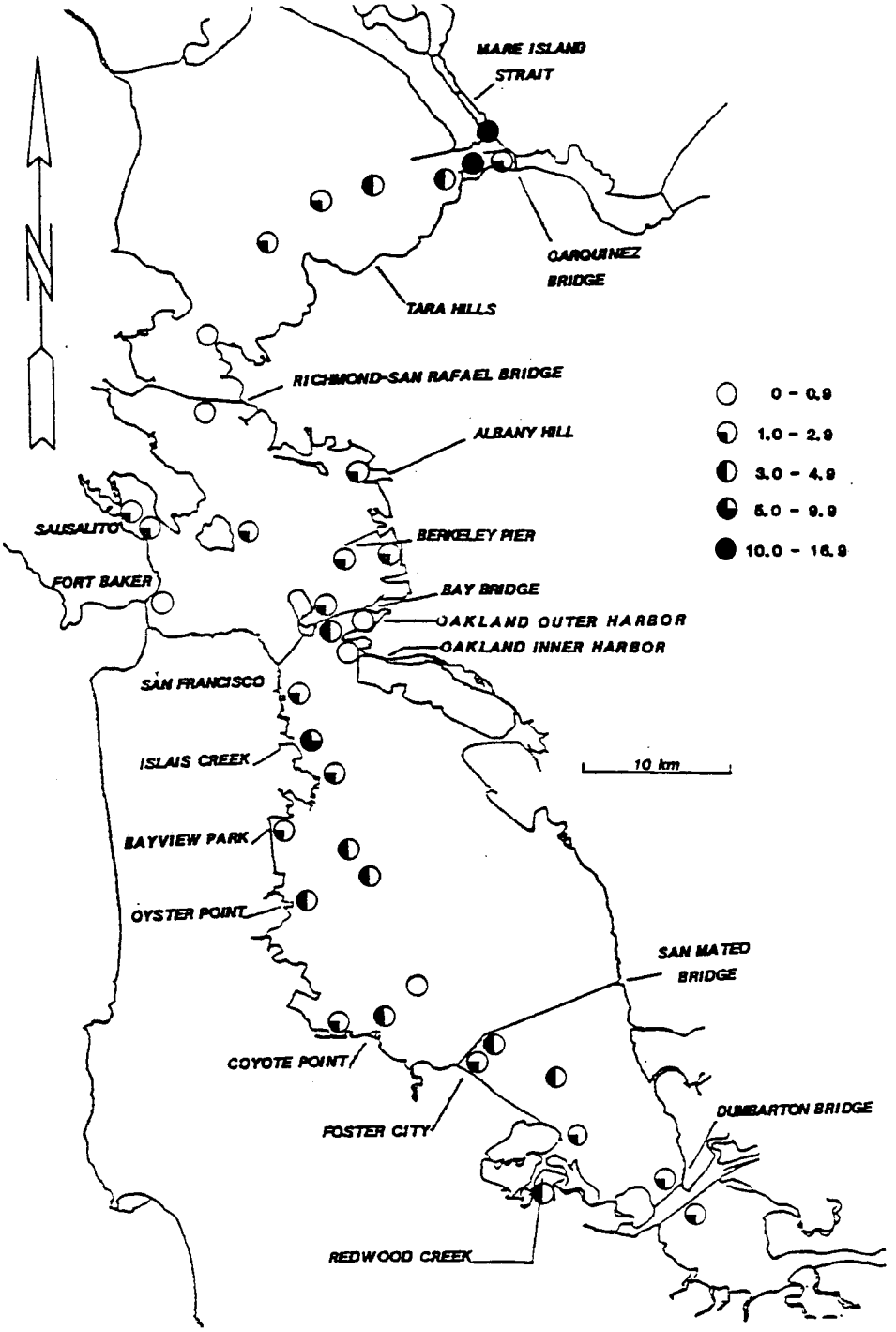


Fig. 67. Mean concentrations of nickel ($\mu g\ g^{-1}$ dry weight) in native Bay mussels, Mytilus edulis, from various sites in San Francisco Bay. After Risebrough et al. (1978).

detection limit (0.1 $\mu g\ g^{-1}$ wet weight) in the livers of only 27% of surf scoters and 22% of greater scaups examined in South Bay; this element is thus not highly concentrated by ducks in the Bay.

Summary

Nickel concentrations are known to be somewhat elevated in waters of both the northern reach and (especially) southern reach of San Francisco Bay compared to offshore marine waters. In the South Bay, ambient levels of nickel are similar to the most recent water quality standard for this element proposed by the U.S. EPA (1986). Most sediments in the Bay-Delta exhibit concentrations of nickel similar to, or slightly greater than, the levels in average shale; there is little evidence for marked enrichment of nickel in sediments, even on a local scale.

Nickel concentrations in Bay-Delta biota have been poorly characterized in general, and there is disagreeement between species and confusion among authors in the interpretation of the data. A few areas of nickel enrichment (Mare Island Strait, Islais Creek, Redwood Creek) appear to exist, but the elevations in nickel concentrations seen are localized and unlikely to pose a major threat to the Bay-Delta ecosystem.

J. TIN

Introduction

The activities of Man radically increase the mobilization of tin from the earth's crust, from a natural rate of 1,500 tonnes annually to about 200,000 tonnes a year (MIT, 1970; Phillips, 1980). However, until recently, the impact of tin on aquatic ecosystems received little attention, as inorganic forms of the element were known to exhibit low toxicities in freshwater and marine environments (e.g. Smith, 1970; Waldichuk, 1974; Brown and Holley, 1982).

This situation altered dramatically with the advent of widespread organotin usage as an antifouling agent in the 1970s. Organotins had been used in a variety of industries prior to this time, for stabilizing PVC polymers, and as bactericides, fungicides, and insecticides (Champ, 1986). However, their development as antifouling agents for vessels gave rise to their direct introduction to aquatic environments in large quantities. It soon became clear that organotins were not only highly potent as antifouling compounds, but also exerted toxic effects on non-target organisms.

Much of the pioneering work on the effects of tributyltin and related compounds was undertaken in France by Alzieu and co-workers (e.g. Alzieu *et al.*, 1980, 1982, 1986; Alzieu, 1986), following the discovery in 1976 of shell thickening defects and spawning problems in the local oyster culture industry (His and Robert, 1985). It is now clear that tributyltin exerts effects on *Crassostrea gigas* and other species of molluscs at very low

waterborne concentrations, to as low as 50 ng L^{-1} (Waldock and Thain, 1983; Alzieu et al., 1986; IEEE, 1986). A recent conference provided comprehensive coverage of the present state of our knowledge on organotins in aquatic environments (IEEE, 1986) and these data will not be exhaustively reviewed here. However, it is notable that tributyltin has been found to be toxic at levels close to 100 ng L^{-1} not only to molluscs, but also to species of several other phyla (Champ, 1986). Relatively little is known in detail of the biogeochemical cycling of tributyltin, although studies to date suggest it is broken down to dibutyl and monobutyl species relatively rapidly under some conditions (e.g. Lee, 1985, 1986; Seligman et al., 1986; Olson and Brinkman, 1986). It may also be noted that the methylation of tin by aquatic microorganisms has excited some interest (Hallas et al., 1982; Tugrul et al., 1983; Donard and Weber, 1985), although in most environments, butylated species of the element outweigh methylated forms (Maguire et al., 1986). Finally here, it is relevant that while all the various chemical forms of tin are known to accumulate in sediments (Maguire, 1984), the available analytical methods for tin in sediment samples are still in need of development (D. Young, personal communication) and very little is known of the bio-availability of the element from sediments.

Tin in San Francisco Bay-Delta

The only studies known on tin in the San Francisco Bay-Delta are those of Goldberg (1987), performed under contract to the State Water Resources Control Board. Samples of water and

sediment were collected from 10 locations in the Central Valley and 18 sites in San Francisco Bay, mostly in harbors or marinas. The data for tin in the water column are summarized in Table 25. It is evident that tributyltin was present at higher concentration than dibutyl or monobutyl species at almost all sites in water samples, and that the concentrations of each form varied widely between locations. The highest levels of tributyltin recorded in water were 230 ng L^{-1} at Oxbow Marina in the Central Valley, and 350 ng L^{-1} at Antioch Yacht Club.

These levels are not unusual, by comparison to other published data for organotins in areas with heavy boat traffic. Thus, Cleary and Stebbing (1985) reported levels of organotins up to 880 ng L^{-1} in waters of the United Kingdom. Alzieu et al. (1986) found concentrations of up to 900 ng L^{-1} of organotins in the waters of Arcachon Bay, France, where the Crassostrea gigas fishery had beeen severely affected by tin contamination. Concentrations of organotins decreased following the introduction of controls on tributyltin usage as an antifouling agent in France in January 1982. In a survey of 265 locations in Canada, Maguire et al. (1986) found that tributyltin species were generally more prevalent in waters than the dibutyl and monobutyl forms of the element; levels of tributyltin varied greatly, with the most contaminated locations exhibiting more than 2 μg L^{-1} of this chemical species. Valkirs et al. (1986) showed significant contamination of San Diego Bay by tributyltin, concentrations in water varying up to 930 ng L^{-1}. Stephenson et al. (1986b) have shown effects of tributyltin on transplanted mussels and oysters in San Diego Bay. Finally, Hall et al. (1987) found that some

Table 25. Mean concentrations (ng L^{-1}) of tributyltin (TBT), dibutyltin (DBT) and monobutyltin (MBT) in the dissolved phase of the water column at 10 sites in the Central Valley and 18 locations in San Francisco Bay. After Goldberg (1987).

LOCATION	TBT	DBT	MBT
Central Valley			
Sacramento Turning Basin	4	14	8
Oxbow Marina, Isleton (a)	230	17	5
Stockton Yacht Club (a)	51	34	16
Stockton, Paradise Point (b)	11	3	10
Stockton, Tower Park (c)	ND	ND	ND
Bethel Is. Yacht Sales (a)	15	5	8
Village West, Stockton (a)	145	22	12
Rio Vista Delta Marina (a)	90	12	5
Stockton, Ladds Marina (a)	61	12	9
Tiki Lagoon Resort(a)	5	2	3
San Francisco			
Vallejo, near Mare Island (a)	2	ND	7
Pittsburg Marina	69	16	8
Martinez Marina (a)	140	13	11
Antioch Yacht Club (a)	350	18	10
San Rafael Yacht Club (a)	31	27	10
Richardson Bay, Clipper Y.H. (a)	31	19	5
Richardson Bay, Sausalito (a)	59	29	25
Coyote Point Marina (a)	41	17	14
St. Francis Yacht Club (a)	58	17	7
Fort Mason East (north) (a)	46	17	12
Fort Mason South (west) (a)	41	16	3
Berkeley Marina (a)	62	33	37
Pier 39, San Francisco (a)	6	4	10
Petes Harbor (a)	180	52	54
Peninsula Marina (a)	105	28	15
Oakland, London Marina (a)	82	37	48
Oakland, Alameda Marina (a)	82	22	11
Emeryville Cove Marina (a)	37	27	8

[a] Means of two samples.

[b] Means of four samples.

[c] Means of three samples.

ND: Not detected.

locations in Chesapeake Bay exhibited levels of tributyltin approaching 1 $\mu g\ L^{-1}$ in the water column; it was also noted that tin species concentrated preferentially in the microlayer, which is in keeping with the high octanol/water partition coefficient for tributyltin (Laughlin et al., 1986).

Data from the studies of Goldberg (1987) for sediments from the Central Valley and San Francisco Bay sites are more difficult to interpret, because of the analytical problems referred to previously. These problems relate largely to interferences from other contaminants, principally sulfur and hydrocarbons, in the GC-flame photometric analysis (D. Young, personal communication). The data of Goldberg (1987) are in any event again not unusual, showing that monobutyltin is generally more prevalent in sediments than the more highly butylated species, and that heavily contaminated locations may contain some tens of parts per million of these contaminants. These data are comparable to results from other locations (e.g. Maguire, 1984; Maguire et al., 1986).

Summary

Inorganic tin is not a contaminant which generates great cause for concern in aquatic environments, as it is of low toxicity to biota. However, it is known to be methylated by sediment microorganisms, and this may increase its pollution potential, particularly as methyltins appear to be highly bio-available to some organisms (Tugrul et al., 1983). More information is needed on the significance and biogeochemical cycling of tin species in aquatic environments.

The main thrust of present research on tin concerns butylated forms of the element, especially tributyltin, which is of very considerable toxicity to aquatic biota. The principal source of this compound is its use in antifouling paints for vessels, although a variety of other unrelated sources exist and should not be overlooked.

The only data available on tin in San Francisco Bay-Delta are those from the survey of Goldberg (1987). These show elevated levels of butylated tin species in marinas and harbors of both the Central Valley and San Francisco Bay. The degree of contamination of these sites no doubt relates to the density of vessel traffic and to the extent of flushing of the water bodies concerned (flushing is often poor in harbors and marinas, permitting a build-up of contaminants). While the concentrations of butyltins are not unusual in the Bay-Delta by comparison to other locations, they are nevertheless sufficiently elevated to give rise to toxic effects on sensitive species. The latter could include algae, crustaceans, molluscs, and possibly fish. Partial bans or restrictions on tributyltin usage in antifouling agents have been introduced in several countries (such as France and the United Kingdom). Similar legislative controls have been passed in the State of Virginia recently (EDF, 1987) and are pending in California, Alaska, Maryland, Oregon, and Washington.

K. OTHER TRACE ELEMENTS

For the sake of completeness, brief discussion is required here of trace elements not covered by the previous sections. These elements are not covered in individual sections because very little information is available on them, or because present available data do not permit conclusions on their significance in the Bay-Delta with respect to possible biological effects.

Antimony

Antimony is very toxic to mammals, including Man, and is thus subject to controls in several countries, in order to protect public health from possible detrimental effects due to seafood ingestion (Nauen, 1983; SWRCB, 1986). However, very little is known concerning the abundance of this element in San Francisco Bay-Delta. Its analysis is not included in either the Toxic Substances Monitoring Program or the State Mussel Watch Program. Problems relating to antimony in marine products have been very rare worldwide and there is little reason to suppose that the Bay-Delta is significantly contaminated by this element.

Arsenic

By contrast to antimony, considerable amounts of data exist for total arsenic levels in the Bay-Delta, both for sediments and biota. Total arsenic is quantified in both the Toxic Substances Monitoring Program and the State Mussel Watch Program, providing a long-term database.

However, while the analytical methods employed to determine total arsenic in biota are appropriate (dry ashing and hydride generation), no differential analyses of the inorganic and

organic forms of the element have been undertaken. Arsenic exists in a variety of chemical forms in marine and estuarine ecosystems, including inorganic species, methylated forms, arseno-lipids, arseno-sugars, arsenobetaine, and arsenocholine (see review by Phillips and Depledge, 1985). Data relating to total arsenic cannot be adequately interpreted, either in relation to overall abundance of the element or its effects, because of the multiplicity of chemical species involved. Differential analysis of inorganic and organic forms of the element (e.g. Lunde, 1973; Brooke and Evans, 1981; Maher, 1983; Phillips and Depledge, 1986) is vital to adequately estimate the toxic effects of arsenic.

Cobalt

Very little is known about cobalt in the San Francisco Bay-Delta ecosystem. Eaton (1979a) noted that cobalt levels in Bay sediments varied little with location and were similar to data for average shale (Krauskopf, 1967). About 50-70% of the cobalt present in sediments was found in the "residual fraction", i.e. tightly bound to the matrix of the particulates. Influx of cobalt from the Delta was thought to predominate over sources of the element within the Bay.

Other Elements and Radionuclides

Insufficient data are available on other elements to permit useful discussion of their abundance or significance in the Bay-Delta. Radionuclides are not considered in this report.

III. ORGANOCHLORINES IN THE BAY-DELTA

The organochlorines (or chlorinated hydrocarbons) discussed in this section include a range of compounds used mainly as pesticides, and the polychlorinated biphenyls (PCBs), which are of industrial origin. These contaminants share a range of properties which set them apart from other types of pollutants. They are generally of relatively low water solubility (although considerable differences exist between the solubilities of individual compounds, even when they are closely related chemically). This low water solubility may be quantified in terms of the octanol:water partition coefficient of each contaminant (Butler, 1971; Neely et al., 1974; Ernst, 1977, 1979, 1980; Phillips, 1980, 1986). In general terms, the degree of bio-accumulation of organochlorines is correlated to both their water solubilities and their octanol:water partition coefficients (Ernst, 1980; Phillips, 1986; see Fig. 68). These correlations are largely due to the dependence of organochlorine uptake by biota on their body lipids, i.e. are a function of the hydrophobic and lipophilic nature of the various compounds (Phillips, 1978, 1980, 1986).

The persistence of organochlorines in the environment is a consequence of their resistance to metabolic or chemical degradation. Thus, most such compounds are broken down very slowly either abiotically or by organisms. This sets the organochlorines apart from other types of pesticides or agricultural agents, which are mostly far more labile.

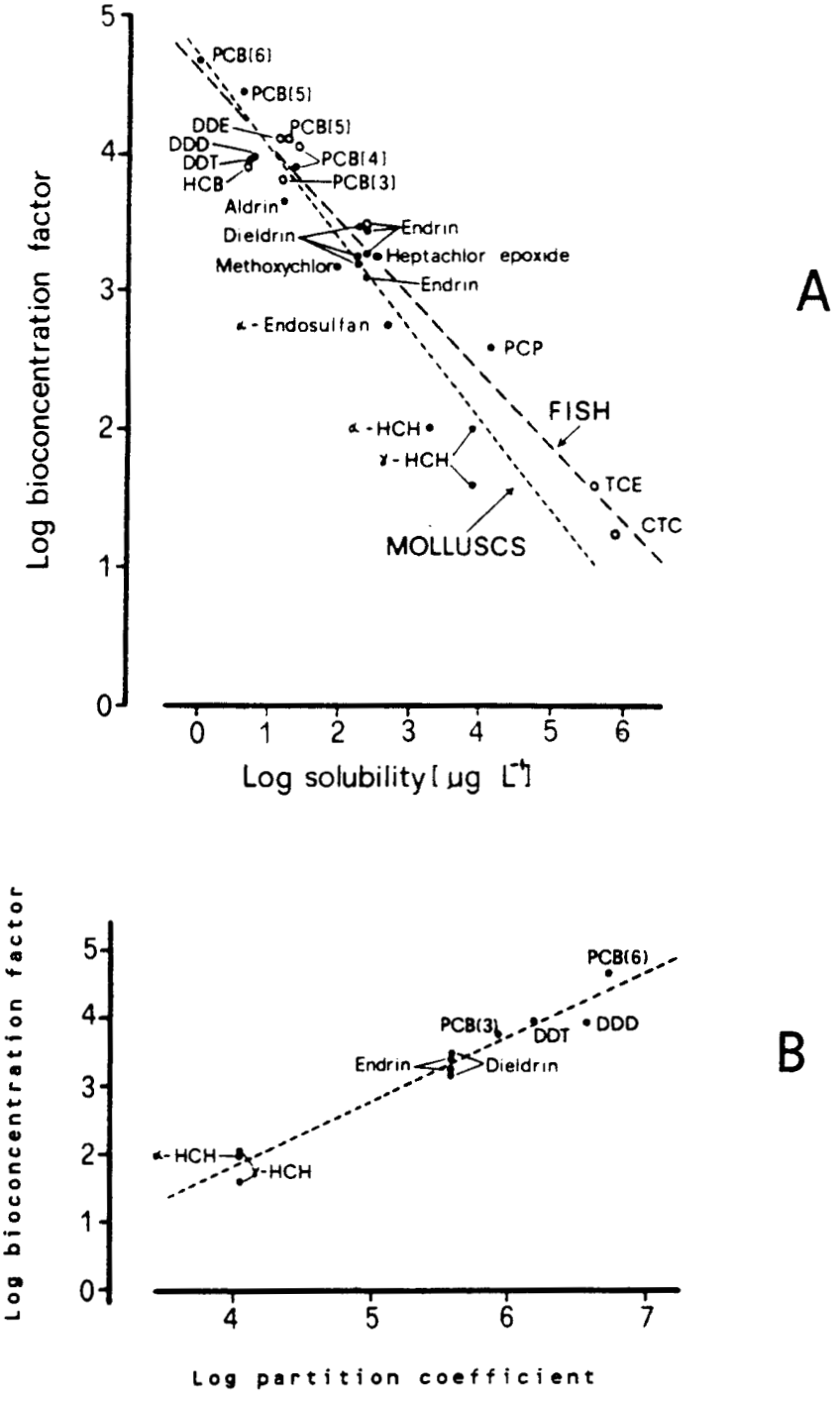


Fig. 68. Correlations between the bioconcentration of organochlorines by organisms (concentrations in biota / concentrations in water) and the (A) solubilities of the compounds in water, or (B) octanol:water partition coefficients of each compound. TCE is tetrachloroethylene; CTC is carbon tetrachloride; numbers in parentheses after PCBs indicate degree of chlorination. After Ernst (1980) and Phillips (1986).

As a result of both their hydrophobic nature and their resistance to degradation, organochlorines exhibit a considerable tendency to accumulate in biota, being concentrated most highly by tissues rich in lipids (Phillips, 1980). Once taken up by biota, these compounds exert a wide variety of toxic effects, upon both plants (e.g. Mahanty, 1986) and animals (Holden, 1972; Ghirelli et al., 1983; Harding and Addison, 1986). These range from effects on primary production due to toxicity to phytoplankton, to impacts on fish, marine mammals, and birds (e.g. Fuller and Hobson, 1986; Peakall, 1986). The effects of chlorinated hydrocarbons on higher organisms vary in type, but diminished reproductive success is often involved (e.g. Helle et al., 1976a, 1976b).

The abundance of chlorinated hydrocarbons in particular discrete environments is a function of their local use as pesticides, or (in the case of PCBs, in particular) by industry. Certain types of compounds have been subject to restrictions or bans in much of the developed world, although residues often continue to persist in soils and aquatic sediments. Those compounds considered to be of particular importance in the San Francisco Bay-Delta are considered individually in the following sections.

A. POLYCHLORINATED BIPHENYLS

Introduction

The polychlorinated biphenyls (PCBs) are a group of compounds based on the biphenyl ring, chlorine atoms occupying any of the ten available substitution positions. They were first produced commercially in 1929 in the United States. Over a million tonnes have been produced worldwide to date, about 50% of this in the USA by the Monsanto Chemical Company. The first indication that PCBs were accumulating in the environment and impacting biota come from their discovery in 1966 in Swedish wildlife by Soren Jensen (Jensen, 1972). They were soon found to be ubiquitous in the biota of aquatic environments worldwide. Voluntary restrictions on sales by Monsanto in 1971 were followed by the introduction of controls on PCB use and manufacture in the USA under the Toxic Substances Control Bill of 1976. Previous dissipative uses of PCBs for a wide variety of purposes (carbonless copying paper, antifouling paints, heat transfer fluids, etc.) were banned by this legislation, and the use of PCBs in transformers and capacitors was phased out. Despite a decade of restrictions, PCBs remain a problem in many parts of the world, due to their abundance, very great persistence, and considerable toxicity to aquatic biota. Recent reviews of PCBs in the environment include those of Eisler (1986b) and Waid (1986).

As commercially produced, PCBs exist as a range of mixtures of compounds differing in their precise chemical composition and

their overall degree of chlorination. The basic compositions of Aroclors 1242 and 1254 (produced by the Monsanto Chemical Company) are shown in Table 26 as an example (Hutzinger et al., 1974). Within each class of component (monochlorobiphenyls, dichlorobiphenyls, etc.), a variety of isomers or homologues may be present, differing in the pattern of chlorine substitution around the biphenyl ring. These differences are of considerable importance in defining the persistence of residues in the environment and in individual organisms (see review by Phillips, 1986). In addition, recent evidence suggests that so-called coplanar PCBs (those with chlorines in non-ortho substitution patterns) may be of the greatest biological activity and toxicity (Tanabe et al., 1987). Several of these compounds (e.g. 3,3',4,4' tetrachlorobiphenyl and 3,3',4,4',5,5' hexachlorobiphenyl) resemble the dioxins in both activity and toxic symptoms. It has become apparent that the PCBs cannot realistically be considered en masse in respect to their impact on biota, but that individual congeners should be quantified (Phillips, 1980, 1986; Tanabe et al., 1987). Unfortunately, this calls for very sophisticated (and expensive) analysis, which is frequently not available. The data on PCBs in San Francisco Bay-Delta biota do not generally provide such information, most estimates being based on less sophisticated methodologies. This constrains the interpretation of local data on PCBs. It might also be noted here that very few reliable data exist for PCBs in water from the Bay-Delta. Schmidt et al. (1971) reported significant amounts of PCBs in wastewater effluents entering the Bay, which is probable for that period prior to restrictions on

Table 26. The molecular compositions of Aroclors 1242 and 1254. After Hutzinger et al. (1974).

Component	Abundance (% by weight) Aroclor 1242	Aroclor 1254
$C_{12}H_{10}$	<0.1	<0.1
$C_{12}H_9Cl$	1.0	<0.1
$C_{12}H_8Cl_2$	16.0	0.5
$C_{12}H_7Cl_3$	49.0	1.0
$C_{12}H_6Cl_4$	25.0	21.0
$C_{12}H_5Cl_5$	8.0	48.0
$C_{12}H_4Cl_6$	1.0	23.0
$C_{12}H_3Cl_7$	<0.1	6.0
$C_{12}H_2Cl_8$	ND	ND

ND: Not detected.

PCB usage. Surface run-off is also a known source of PCBs, whic are significantly transported atmospherically, despite their relatively low vapor pressures (e.g. Young et al., 1980). Limited analyses by Anderlini et al. (1975b) found PCB concentrations in Bay waters approaching the part per trillion (ng L^{-1}) level around experimental dredge spoil disposal sites, although these values should be intepreted with caution, as should the limited data reported by Risebrough et al. (1976) on PCB levels in Bay waters. It is generally believed that PCB quantitation in seawater suffers from many of the same problems associated with the analysis of trace elements in that medium. As a result, researchers have largely concentrated on the analysis of biota and sediments for PCBs. Work in San Francisco Bay to date is no exception to this, most data being available o PCBs in Bay-Delta fauna.

PCBs in Bay-Delta Sediments

Surprisingly little information is available on PCBs in sediments from the San Francisco estuary. Law and Goerlitz (1974) surveyed sediments from 26 streams flowing into the Bay and found significant PCB contamination in several of these samples. In the northern reach, the San Rafael Creek and parts of the Napa River were contaminated. Streams flowing to the South Bay containing high PCBs in sediments included the San Francisquito Creek, Stevens Creek, Los Gatos Creek, and Alamitos Creek. Guadalupe River sediments were found to contain polychlorinated naphthalenes (compounds related to PCBs chemically and of similar properties and uses).

In the Bay itself, Risebrough et al. (1978) reviewed data available to that time, reporting only five data points. Sediments from Albany Hill and the Oakland area showed evidence of elevated PCB levels.

The most reliable and most recent data on PCBs in Bay sediments arise from studies associated with the National Status and Trends Program of NOAA. Unfortunately, however, this work covers few sites in the Bay and none close to the Delta. Chapman et al. (1986) reported considerable within-site and between-site variability in PCB concentrations in sediments from San Pablo Bay, Oakland, and Islais Creek (Table 27). This spatial heterogeneity is interesting, especially as studies on PCBs in starry flounder (see below) also show evidence of such variability in sediment contamination over short distances in the Bay. Coastal sediments are often highly heterogeneous (Phillips, 1980, 1986) and it is difficult to take representative samples in such environments. The data in Table 27 also show that inner Islais Creek (sites SP02 and SP05) is significantly contaminated by PCBs, dilution occurring towards the Creek mouth (SP09).

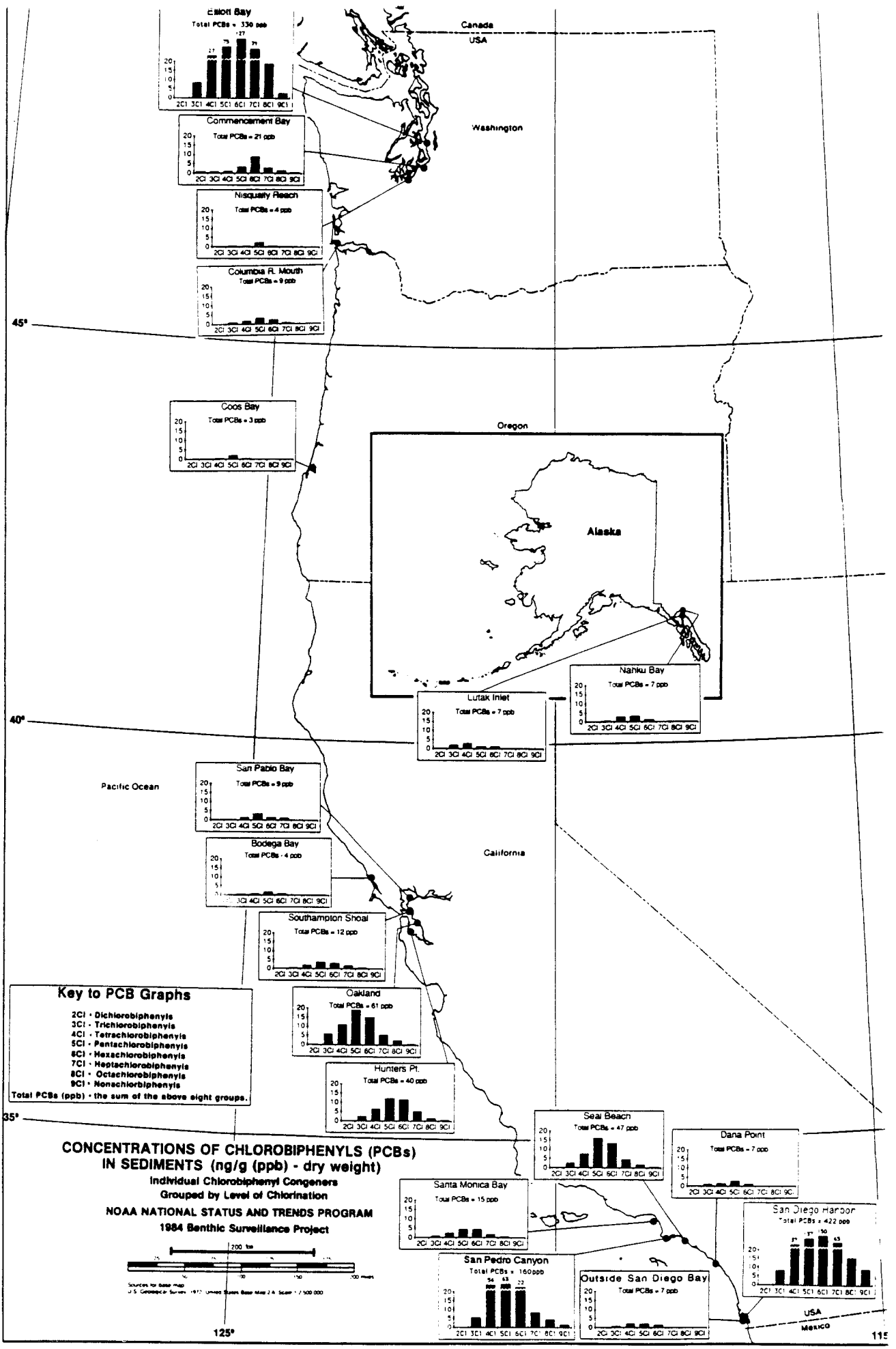
The contamination of local sites by PCBs is placed into context by studies in the Benthic Surveillance Project of NOAA (1987), which is an integral part of the National Status and Trends Program. As noted for trace elements, these data are considered reliable, as they are subject to high levels of quality assurance and control. Data for PCBs in west coast sediments taken in 1984 are shown in Fig. 69. It is clear from these results that San Francisco Bay constitutes one of three general areas of PCB enrichment on the west coast. Sediments

Table 27. Concentrations of PCBs (ng g^{-1} dry weight) in sediments from three locations in San Francisco Bay. After Chapman et al. (1986).

Location	Station	Total PCB (ng g^{-1} dry weight)
San Pablo Bay	SP02	5.71
	SP05	11.14
	SP09	17.45
Mean±S.D.		11.43±4.80
Oakland	OA02	36.84
	OA05	26.57
	OA09	26.95
Mean±S.D.		30.12±4.75
Islais Creek	IS02	179.81
	IS05	255.26
	IS09	57.31
Mean±S.D.		164.13±81.57

Fig. 69. (Overpage).

Concentrations of PCBs (ng g^{-1} dry weight) in sediments from the west coast of the USA. Data are shown as sums of individual chlorobiphenyl congeners, with total PCBs given above the bars. After NOAA (1987).


Elliott Bay
Total PCBs = 330 ppb
Commencement Bay
Total PCBs = 21 ppb
Nisqually Reach
Total PCBs = 4 ppb
Columbia R. Mouth
Total PCBs = 9 ppb
Coos Bay
Total PCBs = 3 ppb
San Pablo Bay
Total PCBs = 9 ppb
Bodega Bay
Total PCBs = 4 ppb
Southampton Shoal
Total PCBs = 12 ppb
Oakland
Total PCBs = 61 ppb
Hunters Pt.
Total PCBs = 40 ppb
Seal Beach
Total PCBs = 47 ppb
Santa Monica Bay
Total PCBs = 15 ppb
San Pedro Canyon
Total PCBs = 160 ppb
Outside San Diego Bay
Total PCBs = 7 ppb
Dana Point
Total PCBs = 7 ppb
San Diego Harbor
Total PCBs = 422 ppb
Nahku Bay
Total PCBs = 7 ppb
Lutak Inlet
Total PCBs = 7 ppb
2Cl 3Cl 4Cl 5Cl 6Cl 7Cl 8Cl 9Cl
Canada
USA
Washington
Oregon
California
Alaska
Pacific Ocean
Mexico
45°
40°
35°
125°
115
Key to PCB Graphs
2Cl - Dichlorobiphenyls
3Cl - Trichlorobiphenyls
4Cl - Tetrachlorobiphenyls
5Cl - Pentachlorobiphenyls
6Cl - Hexachlorobiphenyls
7Cl - Heptachlorobiphenyls
8Cl - Octachlorobiphenyls
9Cl - Nonachlorbiphenyls
Total PCBs (ppb) - the sum of the above eight groups.
CONCENTRATIONS OF CHLOROBIPHENYLS (PCBs)
IN SEDIMENTS (ng/g (ppb) - dry weight)
Individual Chlorobiphenyl Congeners
Grouped by Level of Chlorination
NOAA NATIONAL STATUS AND TRENDS PROGRAM
1984 Benthic Surveillance Project

from Elliot Bay (off Seattle, Washington State) exhibited total PCBs of 330 ng g^{-1} dry weight, heavily dominated by hexachlorobiphenyls. Various sites in southern California also contained sediments with significantly elevated total PCB concentrations (San Pedro Canyon, 160 ng g^{-1} dry weight; Seal Beach, 47 ng g^{-1}; San Diego Harbor, 442 ng g^{-1}), nearby less polluted sites containing 7-15 ng g^{-1} dry weight. In San Francisco Bay, San Pablo Bay sediments contained 9 ng g^{-1} total PCBs, Southampton Shoal 12 ng g^{-1}, Oakland sediments 61 ng g^{-1}, and Hunter's Point samples 40 ng g^{-1} dry weight. By contrast, the Bodega Bay "reference site" exhibited only 4 ng g^{-1} total PCBs in sediment. All profiles in the San Francisco Bay were dominated by pentachlorobiphenyls, similar to an Aroclor 1254 mixture (Table 26). This is generally consistent with data from the State Mussel Watch Program on PCBs in transplanted or native mussels from the Bay (see below).

These data thus provide a general picture of significant PCB enrichment in San Francisco Bay sediments. While levels of contamination locally are not as great as those in certain other west coast locations, they remain cause for concern. However, data for sediments are insufficient to delineate current sources of PCBs in the Bay-Delta, with the probable exception of Islais Creek.

PCBs in Bay-Delta Biota

Information on PCBs in biota from the estuary is available for bivalve molluscs, some fish species, harbor seals and birds. These data are discussed in turn below.

Bivalve Molluscs

Girvin et al. (1975) analyzed four species of bivalves from up to three locations in the Bay (Albany Hill, Coyote Point North, Foster City; see Fig. 4) for PCBs. Relatively little variation was found in PCBs accumulated at the different locations by any one species (Table 28), but native Bay mussels (Mytilus edulis) and oysters (Ostrea lurida) contained considerably greater concentrations of these contaminants than clams (Mya arenaria and Tapes japonica). It is notable that some of these data refer to small numbers of individuals per sample. The clam samples from each location constituted only 3 or 5 individuals, while 10 mussels and 15 oysters were analyzed in each sample. Most studies (e.g. NAS, 1980; Phillips, 1980) have shown that at least 10 and possibly up to 25 individuals should be combined to overcome the so-called "inherent variability" of contaminants in bivalves and accurately characterize mean concentrations in bulked samples. These results should thus be interpreted with caution.

Data from the U.S. Mussel Watch Program have been reviewed by Goldberg et al. (1978) and Farrington et al. (1982, 1983). As noted in Section II(A) of this report, samples of mussels (Mytilus edulis) from San Francisco Bay were composited to produce only one sample from each of the northern reach and the South Bay, so no spatial trends within the Bay can be discerned. Only the sample from South Bay was analyzed for PCBs, concentrations recorded being 590 ng g^{-1} dry weight in 1976 and 990 ng g^{-1} in 1977.

Table 28. Concentrations of total PCBs (means, ng g^{-1} wet weight) in the whole soft parts of four species of bivalve molluscs from three Bay locations. After Girvin et al. (1975).

Species	Albany Hill	Coyote Point North	Foster City
Mya arenaria	39.2	55.1	52.6
Tapes japonica	38.1	35.2	29.1
Mytilus edulis	138	108	152
Ostrea lurida	No data	201	118

Risebrough et al. (1978) produced a much more detailed data-set for PCBs in M. edulis from the Bay, most samples being taken in April 1976 (Fig. 70). These data confirm the relatively high levels of PCBs in mussels from the South Bay, particularly from coastal sites from Islais Creek south to Redwood Creek. Elevated concentrations of PCBs were also found in mussels off Richmond, Albany Hill, and Oakland.

The State Mussel Watch Program serves to update these values to the 1980s. Results for PCBs are shown in Table 29. Several aspects of these data are worthy of note. Firstly, the entire Bay from northern San Pablo Bay to South Bay shows evidence of generalized PCB contamination; multiple sources may be suspected. Secondly, these data agree well with previous studie of PCBs in bivalves cited above, and no highly significant long-term trends are evident in the data, despite the imposition of restrictions on PCB usage in 1976. Clearly, residual PCB contamination exists in the Bay catchment. Thirdly, data for 1981 samples show particular PCB enrichment throughout the Bay. Samples taken outside San Francisco Bay in 1981 did not generally exhibit such a marked enrichment, and these samples were not analyzed in any different fashion to those from other years (M. Martin, personal communication). It is thus considered that this difference is unlikely to be an artifact of sampling or analysis, but may reflect a PCB spill of some magnitude occurring in late 1980 or early 1981 when the transplanted mussels were present in the Bay. No record of such a spill could be found, although PCB spills from a storage facility in Richmond in February 1980 and

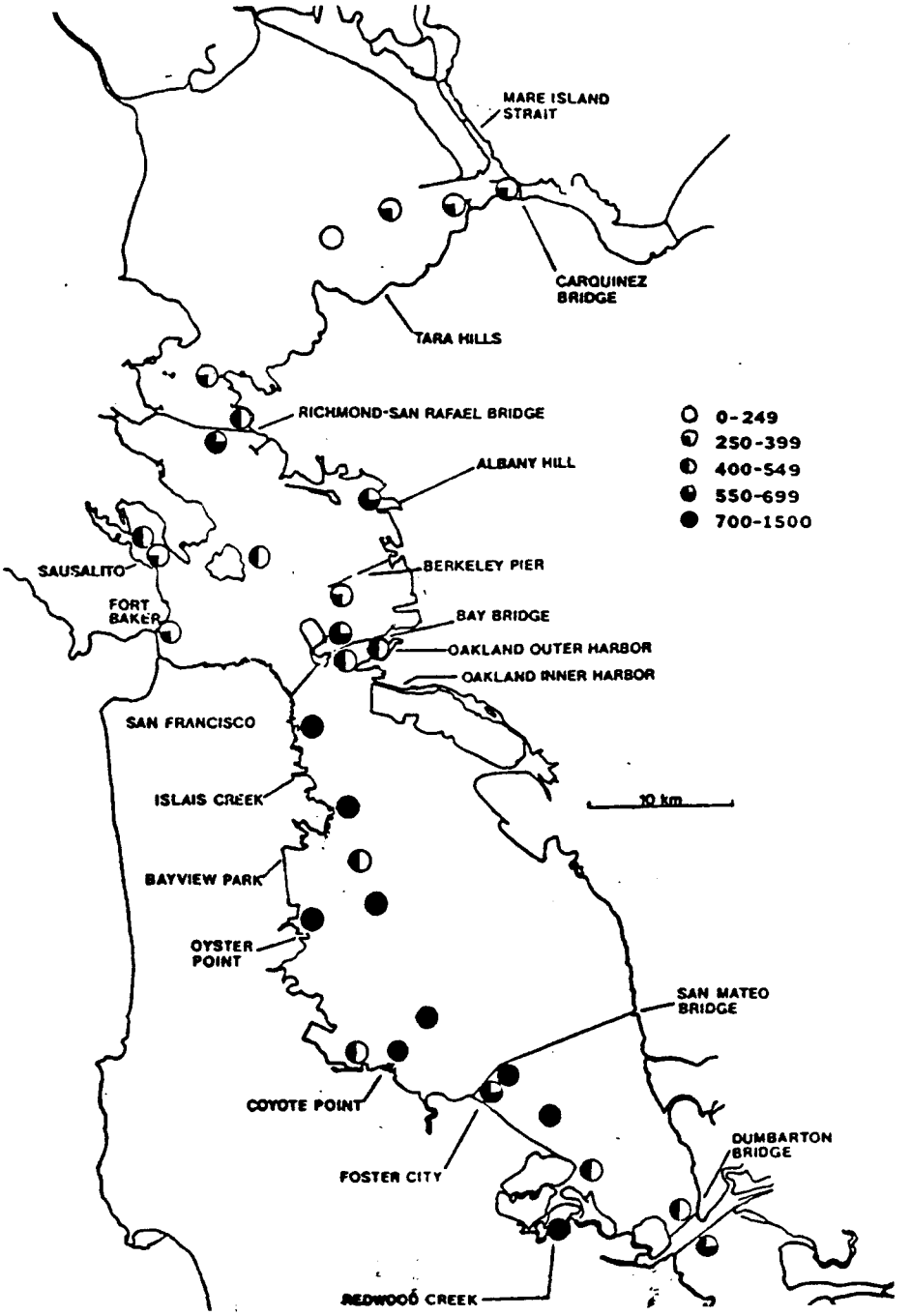


Fig. 70. Concentrations of total PCBs (means, ng g^{-1} dry weight) in whole soft parts of native Bay mussels (Mytilus edulis) from San Francisco Bay. Sampling was undertaken in April 1976. After Risebrough et al. (1978).

Table 29. Concentrations of PCBs (means, ng g^{-1} dry weight, as Aroclor 1254 with additional residues as noted) in transplanted mussels, Mytilus californianus, or native Bay mussels (M. edulis, as shown) in San Francisco Bay. Data from the State Mussel Watch Program, after Hayes et al. (1985), Hayes and Phillips (1986) and Stephenson et al. (1986a).

LOCATION	STATION CODE	1979	1980	1981	1982 (J/F*)	1982 (D*)	1983	1985
MARE ISLAND	300.20							100a
DAVIS POINT	301.00					230		
POINT PINOLE	302.00			690	140	330	180	78
RICHMOND BRIDGE	303.00		370	1100	220	280		
SANTA FE CH. MOUTH	303.10							
SANTA FE CH. L.C.	303.20							660b
SANTA FE CH. L.C. END	303.30							
SANTA FE CH. END	303.40							860c
RICHMOND INNER HARBOR	303.60							
ANGEL ISLAND	305.00		770	830		230		
FORT BAKER	306.00			510		270		
TREASURE ISLAND	307.00	790	630	1500	220	300	280	200
ALAMEDA YACHT HARBOR	307.20							
OAKLAND IN. HARBOR WEST	307.30							
OAKLAND IN. HARBOR EMBC.	307.40							880
OAKLAND BACK HARBOR	307.60							690d
HUNTER'S POINT	308.00			1800	230	340		
SAN MATEO BRIDGE 8	309.00			1300	180	430	180	
SAN MATEO BRIDGE 8A	310.00				140			
REDWOOD CREEK MOUTH	313.00			1200	200	390	210	
REDWOOD CREEK TRDWNDS	316.00		850a					
DUMBARTON BRIDGE 14	321.00			1300	250		180	

*J/F/D: January/February/December, all 1982.

[a]Native M. edulis

[b]Also 68 ng g^{-1} Aroclor 1248.

[c]Also 100 ng g^{-1} Aroclor 1248.

[d]Also 32 ng g^{-1} Aroclor 1260.

[e]Also 100 ng g^{-1} Aroclor 1248.

[f]Also 180 ng g^{-1} Aroclor 1248.

[g]Also 160 ng g^{-1} Aroclor 1248.

[h]Also 180 ng g^{-1} Aroclor 1248.

from Bethel Island in Contra Costa County in July and August 1982 are documented. No doubt many such spills go unreported at other times.

The existence of multiple sources of PCBs within the Bay is also suggested by variabilities in PCB relative peak heights in discrete samples. Thus, several samples of mussels taken in both 1985 and 1986 showed evidence of lower chlorinated isomers characteristic of Aroclor 1248, rather than the more usual Aroclor 1254. By contrast, the mussels taken in 1985 from Oakland Back Harbor contained more highly chlorinated PCBs, similar to Aroclor 1260; this was the only sample ever taken in California waters to exhibit such an isomer profile (Hayes and Phillips, 1986). These varying components of the PCB mixtures provide clues to possible sources of PCBs in each location, as the different PCB mixtures are often employed for slightly different industrial applications (Ghirelli et al., 1983; Hayes and Phillips, 1986).

It should be noted here that while the data for San Francisco Bay undoubtedly point to the existence of local contamination by PCBs, the concentrations attained by mussels in the Bay are considerably lower than those in highly polluted locations elsewhere. Areas of particularly elevated PCB concentrations in mussels include New Bedford Harbor in Buzzards Bay, Massachusetts (Farrington et al., 1983), and Newport Harbor, San Pedro Harbor, and San Diego Harbor in California (Goldberg et al., 1978; Martin, 1985). These data thus provide general support to the conclusions reached concerning PCBs in sediments; San Francisco Bay exhibits high levels of these contaminants

throughout, but levels are not as extreme as some sites elsewhere. Presumably, PCBs introduced from the numerous point sources around the Bay and its catchment are rapidly diluted and dispersed throughout the system by the considerable tidal prism and high sediment mobility.

Fish

PCBs have been shown to have a variety of sublethal and lethal effects upon bony fish, ranging from the induction of hepatic mixed function oxidases, through hormonal and (especially) reproductive effects (Ghirelli et al., 1983; Eisler, 1986b; Harding and Addison, 1986). As a result, PCB concentrations in fish have been the subject of much study. However, these data can rarely be used to identify sources of PCBs except in a very general sense. Thus, it may be possible to infer from datasets for PCBs in certain fish species that San Francisco Bay is more contaminated than offshore marine waters of the Pacific. However, it is rarely (if ever) possible to unequivocally show the existence and location of point sources of such pollutants by the use of fish samples. This is because most fish move considerable distances in even short periods, and their contaminant levels are a complex function of their exposure in space and time (Phillips, 1980).

The available information on PCBs in fish from the Bay-Delta is reviewed in the light of this problem, and is used here simply to confirm data from studies of bivalve molluscs (which do not suffer from the same difficulties, as most bivalves are sessile).

Data from the Toxic Substances Monitoring Program on PCBs in fish are presented in Fig. 71. This depicts locations within the State at which samples exceeded the EDL 85 (170 ng g^{-1} wet weight), or either the National Academy of Science's guideline for predator protection (500 ng g^{-1} wet weight) or the Food and Drug Administration tolerance level for PCBs (2,000 ng g^{-1} wet weight). The correspondence between these data and those for PCBs in sediments off the west coast (Fig. 69) is striking. Clearly, many sources of PCBs exist in the Bay-Delta catchment, both in the Central Valley and in the south of the Bay. It should be noted here that the discovery of particularly high PCB levels in fish from the South Fork of the Feather River at Forbestown was followed in 1980 by detailed investigations of this area (SWRCB, 1981). PCB residues were found at high levels in soils, and a previous unreported spill and chronic pollution from powerhouse sumps were identified as the primary causes of the high local contamination; clean-up action was taken, and reported residues in fish from this site have decreased in follow-up monitoring.

Several species of fish from the Bay-Delta itself have also been analyzed for PCBs. Spies and co-workers and NOAA (1987) have reported data for the starry flounder, Platichthys stellatus. Studies of the former group deal mainly with the effects of PCBs and other organic contaminants on liver mixed function oxidase (MFO) activities, and on the relationship between these parameters and reproductive success (Spies et al., 1984, 1985a, 1985b, in press; Rice et al., unpublished manuscript; Spies and Rice, in press). These data will be

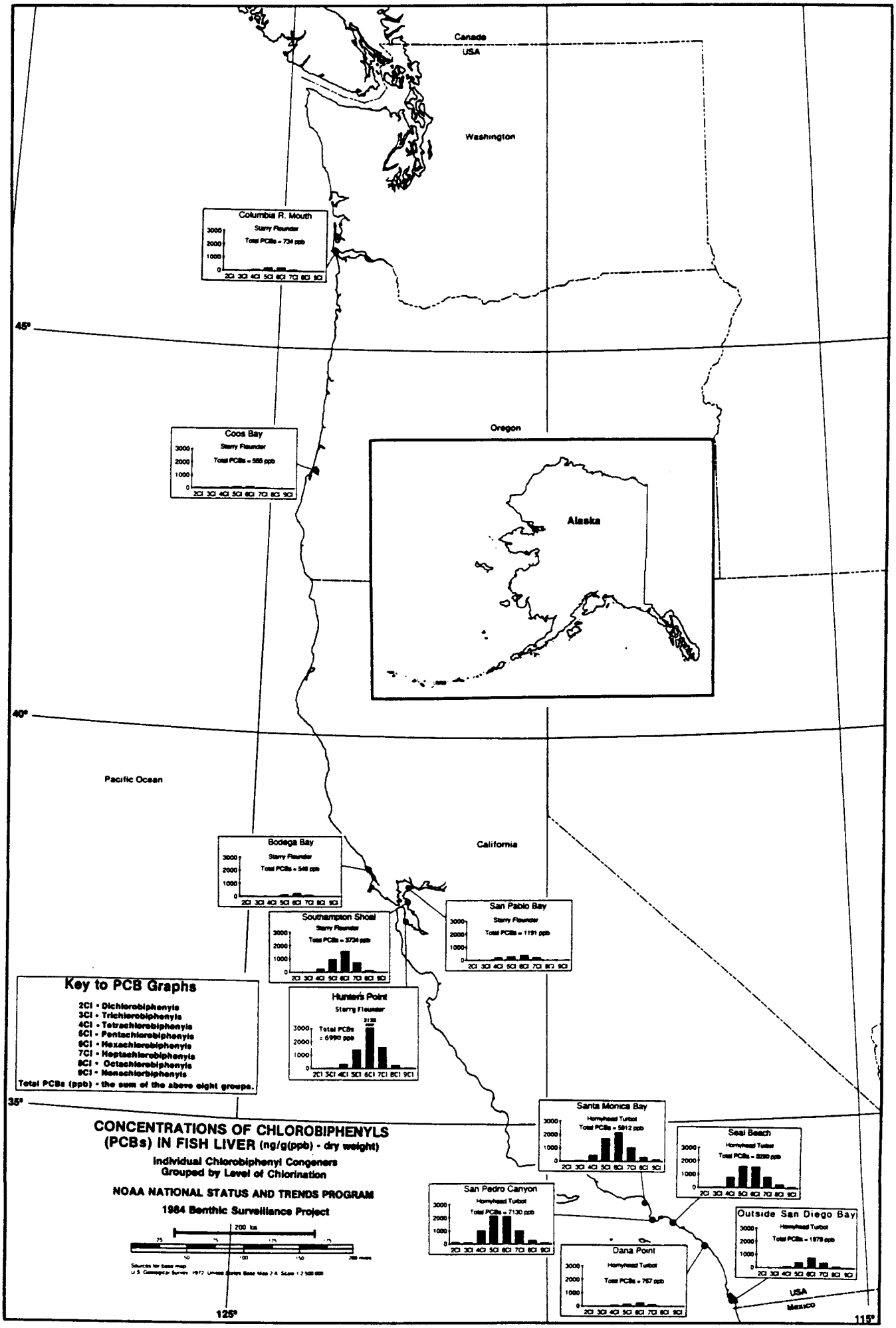
Fig. 71. Locations at which samples of fish livers exhibited total PCB levels above the 1978-84 EDL 85 (170 ng g^{-1} wet weight), the NAS guideline for predator protection (500 ng g^{-1} wet weight) or the FDA tolerance level (2,000 ng g^{-1} wet weight). Data from the Toxic Substances Monitoring Program. After SWRCB (1986).

considered further in section V of the present report. However, it may be noted here that PCB concentrations in the livers of P. stellatus are generally greater in the Richmond and Berkeley areas of the Bay than in fish from offshore regions of San Pablo Bay. NOAA (1987) have also documented such differences, and have shown that livers of San Francisco Bay starry flounder (from Southampton Shoal and Hunters Point) are considerably more contaminated by PCBs than are those from P. stellatus taken from the Columbia river mouth, Coos Bay, or Bodega Bay. These data are shown in Fig. 72. Similar enrichment of PCBs in livers of white croaker from Oakland was demonstrated compared to such samples from Bodega Bay (NOAA, 1987).

The levels of PCBs in striped bass (Morone saxatilis) from the San Francisco estuary have also been a subject of study, particularly as local populations of this species have declined in the last 25 years (see section V of this report). Stevens (1980) reported concentrations of 5.49 $\mu g\ g^{-1}$ (wet weight, presumably) for PCBs in flesh of striped bass from the Delta in 1972, and of 0.51 $\mu g\ g^{-1}$ for similar samples in 1976. However, later data show that concentrations vary greatly between individuals (e.g. Whipple, 1984), and sample numbers in this study were not sufficient to confirm the apparent temporal decrease in PCB levels. Whipple et al. (1983) showed that striped bass from the Sacramento and San Joaquin Rivers exhibited elevated levels of PCBs in gonads, liver, and muscle tissues compared to the same species from Coos River, Oregon. Pesticides such as DDT and metabolites, chlordane, dieldrin, toxaphene, and others showed similar differences. In addition, differences

Fig. 72.

Concentrations of PCB components and total PCBs (ng g^{-1} dry weight) in livers of starry flounder (Platichthys stellatus) and hornyhead turbot (Pleuronichthys verticalis) from various sites on the U.S. west coast in 1984. After NOAA (1987).


Canada
USA
Washington
Columbia R. Mouth
Starry Flounder
Total PCBs = 734 ppb
45°
Coos Bay
Starry Flounder
Total PCBs = 555 ppb
Oregon
Alaska
40°
Pacific Ocean
California
Bodega Bay
Starry Flounder
Total PCBs = 548 ppb
Southampton Shoal
Starry Flounder
Total PCBs = 3734 ppb
San Pablo Bay
Starry Flounder
Total PCBs = 1191 ppb
Hunter's Point
Starry Flounder
Total PCBs = 6990 ppb
Key to PCB Graphs
2Cl - Dichlorobiphenyls
3Cl - Trichlorobiphenyls
4Cl - Tetrachlorobiphenyls
5Cl - Pentachlorobiphenyls
6Cl - Hexachlorobiphenyls
7Cl - Heptachlorobiphenyls
8Cl - Octachlorobiphenyls
9Cl - Nonachlorbiphenyls
Total PCBs (ppb) - the sum of the above eight groups.
35°
CONCENTRATIONS OF CHLOROBIPHENYLS
(PCBs) IN FISH LIVER (ng/g(ppb) - dry weight)
Individual Chlorobiphenyl Congeners
Grouped by Level of Chlorination
NOAA NATIONAL STATUS AND TRENDS PROGRAM
1984 Benthic Surveillance Project
200 km
125°
Santa Monica Bay
Hornyhead Turbot
Total PCBs = 5812 ppb
Seal Beach
Hornyhead Turbot
Total PCBs = 5290 ppb
San Pedro Canyon
Hornyhead Turbot
Total PCBs = 7130 ppb
Outside San Diego Bay
Hornyhead Turbot
Total PCBs = 1979 ppb
Dana Point
Hornyhead Turbot
Total PCBs = 767 ppb
USA
Mexico
115°

between the sexes in PCB accumulation were noted; gonads of female pre-spawning M. saxatilis always exhibited higher levels of PCBs than did gonads of male fish. Similar data were reported by Crosby et al. (1983) for female striped bass taken in early 1981 from the Sacramento River and Coos River (Fig. 73). More recent data, reviewed by Brown et al. (1987), could not confirm any temporal decreases in PCB concentrations in striped bass through the 1980s, although recent data from Knudsen and Kohlhorst (1987) are suggestive of such reductions. The high variability encountered between individual fish, which no doubt relates to a variety of factors (migration pattern, time spent in contaminated areas, reproductive condition, lipid content, age or size, etc.; see Cahn et al., 1977; Phillips, 1980, 1986) masks any marginal long-term trends in the data, at least unless highly stratified samples can be taken. There is, however, no doubt that the local striped bass population exhibits high levels of organochlorines, including PCBs. While the PCB levels in Bay-Delta fish are not as great as those in the particularly contaminated Hudson River population (e.g. see Horn et al., 1979; Califano et al., 1982), they are nevertheless elevated compared to many other areas, such as the Coos River or Chesapeake Bay (Eisenberg et al., 1980; Brown et al., 1987). It is probable that anadromous fish such as striped bass are exposed to cyclical contamination in the Bay-Delta each year during their spawning run. Presumably residues accumulate in striped bass in the Bay-Delta in spring and early summer and are slowly lost when the fish return to less contaminated offshore waters. However, a recent report of Melzian et al. (in press) raises concerns about PCB

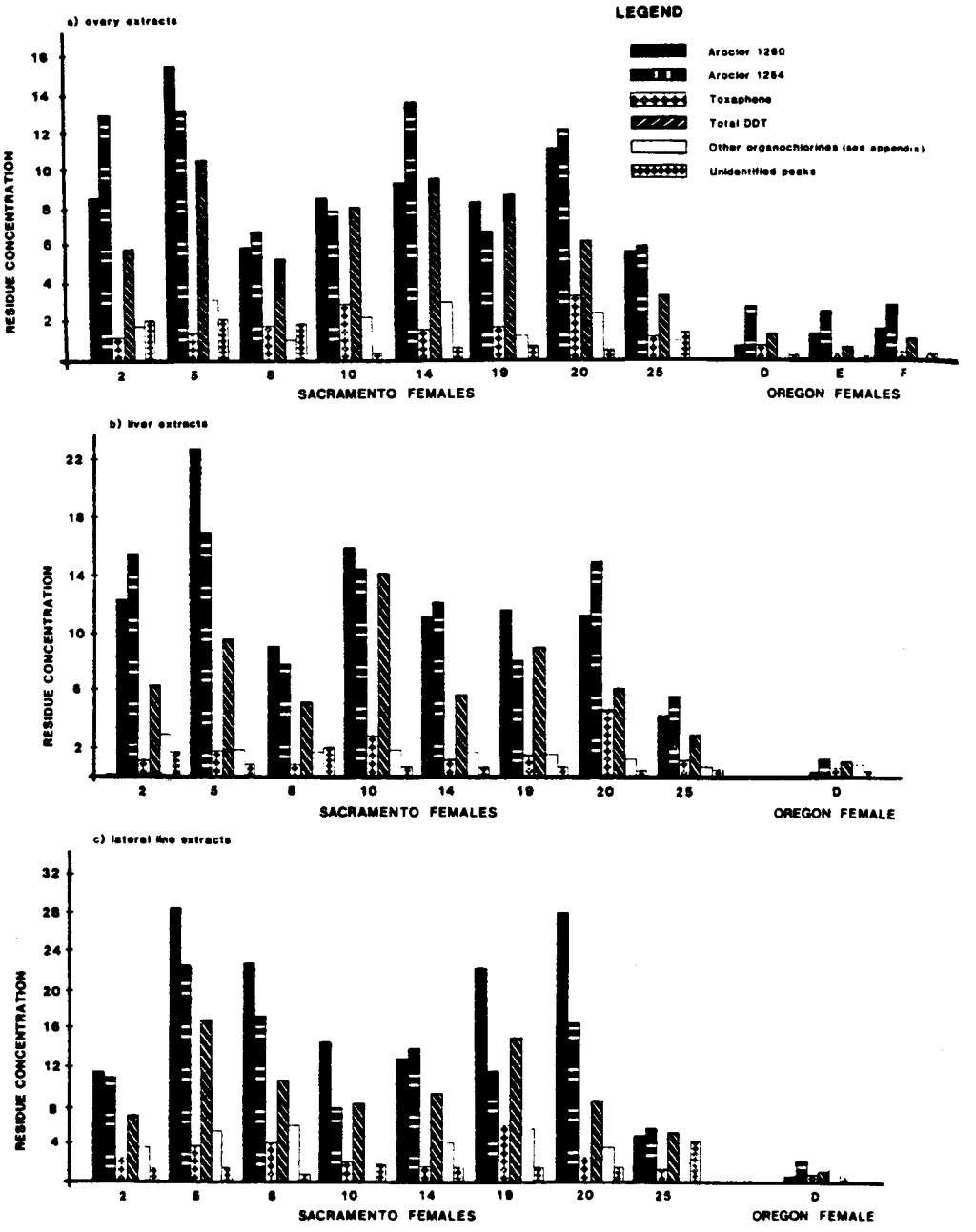


Fig. 73. Concentrations of PCBs (quantified as Aroclors 1260 and 1254), toxaphene, total DDT, "other organochlorines" and unidentified peaks in ovaries, liver extracts and lateral line extracts of striped bass (Morone saxatilis) females taken in 1981 from the Sacramento River and Coos River, Oregon. All data as $\mu g\ g^{-1}$ lipid weight. After Crosby et al. (1983).

levels in fish even in the Pacific waters near the Farallon Islands, which may be impacted by contaminants from toxic chemical dumping areas. Much remains to be learned about PCB dynamics in fish which migrate significant distances.

Marine Mammals

The problems encountered in interpreting data on PCBs in fish because of their movement or spawning migrations are also evident in attempting to interpret such data for marine mammals. In addition, organochlorine levels in such species vary considerably between the tissues and are a complex function of age and sex (Phillips 1980, 1986). Data for PCBs in marine mammals from the Bay-Delta are limited to those of Risebrough et al. (1978) on harbor seals (Phoca vitulina). The individuals analyzed were found dead in 1975-1976; this further complicates data interpretation. One individual (coded REJ 865) from Richardson Bay was exceptionally heavily contaminated by PCBs, exhibiting concentrations of 500 $\mu g\ g^{-1}$ lipid weight in blubber, 12,000 $\mu g\ g^{-1}$ in liver and 31,000 $\mu g\ g^{-1}$ lipid weight in muscle. Other individuals contained PCBs at concentrations approaching or occasionally exceeding 100 $\mu g\ g^{-1}$ lipid weight. Such levels are not dissimilar to those believed to affect reproduction in ringed seals (Pusa hispida) in the Bothnian Bay (Helle et al., 1976a, 1976b). However, such cross-species comparisons are fraught with complications. No data on the reproductive success of local marine mammal populations have been reported, although there has been concern over premature pupping of Californian sea lions (Zalophus californianus californianus) in the San Miguel and San Nicolas Islands off southern California (Delong et al.,

1973; Martin et al., 1976). This appears to be a topic worthy of further study, particularly as Reijnders (1980) has speculated that PCBs may be a contributory factor to reductions in the Wadden Sea harbor seal population.

Birds

Few data are available on PCB levels in Bay-Delta bird populations. Ohlendorf and Miller (1984) analyzed four species of waterfowl (northern pintails, Anas acuta; northern shovelers, Anas clypeata; canvasbacks, Aythya valisineria; and lesser scaups, Aythya affinis) from wintering areas in California for organochlorines. In general, the levels of most organochlorines studied were considered to be quite low. However, increases in concentrations were seen from north to south in the State, and birds wintering in the Delta and Central Valley appeared to accumulate contaminants (DDT and metabolites, HCB, and probably PCBs) during this period. It was considered unlikely that entire populations of these species were being adversely affected by organochlorines, although certain particularly contaminated individuals might have suffered sublethal effects, such as impaired reproduction.

More definitive data were produced by Hoffman et al. (1986) on PCBs in black-crowned night herons from the San Francisco Bay National Wildlife Refuge on Bair Island in South Bay. Unpublished observations on several bird species at this location in 1981 and 1982 suggested the existence of problems commonly associated with organochlorine contamination (egg breakage, hatching failure, and chick mortality in Caspian terns Sterna caspia, and reproductive problems in both great blue herons Ardea

herodias and black-crowned night herons Nycticorax nycticorax). Hoffman et al. (1986) found that both PCBs and DDE were present at elevated concentrations in eggs of N. nycticorax from Bair Island compared to controls from the Patuxent Wildlife Research Center. The PCB levels (log transformed) correlated negatively with embryo weights of the night herons, although levels of DDE showed no such correlation. Impaired growth of the Bair Island birds was also suggested by low mean embryo weights and reduced crown-rump lengths and femur lengths, compared to control birds from Patuxent, Maryland. While these differences may have been due to varying nutrition of the two groups of birds, PCBs were suspected as a primary cause. However, the considerable variability between bird species in sensitivity to PCBs permits no definitive conclusion in the absence of direct cause and effect studies; these have not been carried out. It is also unclear whether the growth reduction observed would have persisted through hatching of the birds.

Summary

PCBs are of exceptional persistence and wide-ranging toxic effect in aquatic environments due to their high bio-accumulation and resistance to abiotic or metabolic degradation. Their widespread use in dissipative applications has given rise to considerable contamination in many urban estuaries; San Francisco Bay-Delta is no exception to this general rule. There is little evidence of significant reductions in PCBs in aquatic ecosystems since restrictions on their use were introduced in the USA in 1976.

Few data are available on PCBs in Bay-Delta waters. However, sediments from influent streams and from the Bay itself exhibit generally elevated PCB levels. Such enrichment is also indicated by analyses of bivalve molluscs in the Bay; these data suggest the existence of multiple sources of PCBs and a widespread moderate to high abundance and bio-availability of these compounds within the entire Bay. Analyses of fish confirm such trends and also show that significant PCB sources exist in the Central Valley basin and South Bay catchment. The contamination of other biota including marine mammals and birds in the Bay-Delta has received less study, although the available data suggest that PCBs may be exerting detrimental biological effects. While certain other areas of the U.S. coastline exhibit even greater contamination by PCBs, the levels in the San Francisco Bay-Delta are of concern and deserve further study. In particular, future studies should be designed to both elucidate cause-and-effect relationships between PCB abundance and detrimental biological effects, and to quantify individual PCB components (especially coplanar PCBs, which are of extreme toxicity to biota).

B. DDT AND METABOLITES

Introduction

The worldwide production of DDT approximates 100,000 tonnes annually, used principally for agricultural pesticide and anti-malarial purposes (Phillips, 1980). Total worldwide usage rates have been relatively constant over the last two decades, despite the introduction of stringent controls on DDT use for agricultural purposes in many developed nations (including the USA) in this period. This fact caused Goldberg (1975) to hypothesize a "southward tilt" in the use and abundance of DDT globally, as tropical underdeveloped countries increased their usage of the compound concomitant to reductions in the temperate regions of the northern hemisphere. DDT is thus still of considerable concern as a global contaminant, particularly as it is significantly transported through the atmosphere from regions of usage to distant locations (NAS, 1971).

In general, it is believed that DDT is rather less persistent in aquatic environments than are PCBs. DDT is broken down to DDE and DDD; of these, DDE is the more commonly encountered contaminant in most cases, and exhibits the more persistent and refractory nature. Further metabolic breakdown products (DDMU, DDMS) are not highly cumulative in biota and are of relatively short environmental half-life.

Like PCBs, DDT and its metabolites have wide-ranging effects on aquatic biota (e.g. Holden, 1972). Direct toxic effects are exerted over a very wide range in ambient concentration (Klapow and Lewis, 1979), and may affect many phyla. This is especially

the case in rivers or estuaries receiving agricultural run-off where DDT is employed as a pesticide. However, both DDT and DDE (in particular) are highly bio-accumulated, and residues taken up by biota may also exert toxic effects. The octanol:water partition coefficients of these compounds are similar to those of PCBs with 4 or 5 chlorine atoms (Fig. 68); it is thus not surprising that they also preferentially accumulate in tissues rich in lipids. The precise mode of toxic action of these compounds remains largely unknown, but their effects on aquatic biota are frequently similar to those of PCBs. Controversy continues over the question of food chain amplification of these contaminants (Phillips, 1980), although there is little doubt that high-ranking predators such as fish-eating birds or marine mammals are at risk from their effects.

The use of DDT for almost all purposes was banned in California in 1970 and in the USA in 1971. While this compound and its metabolites are known to persist in soils for considerable periods after their application to crops, it would be expected that levels present in coastal environments of the USA would have decreased substantially since the early 1970s. Unfortunately, no adequate long-term database exists to accurately test this hypothesis. Although many authors consider that such reductions in abundance of DDT and its metabolites have occurred (e.g. Matta et al., 1986), significant amounts of residues remain, which may still be exerting detrimental effects on sensitive species (e.g. Risebrough et al., 1978).

Data for DDT and related compounds in San Francisco Bay-Delta are restricted to sediments and biota, and are reviewed

below. Where both DDT and its metabolites are considered as a group, the notation "ΣDDT" is employed. Unless otherwise specified, the residues referred to will be the p,p' isomers, which are the most common.

ΣDDT in Bay-Delta Sediments

Law and Goerlitz (1974) reported significant quantities of DDT, DDE, and DDD in the sediments of streams flowing into San Francisco Bay. These data are shown in Table 30, which includes results for both o,p'-DDT and p,p'-DDT, in addition to p,p'-DDE and p,p'-DDD. Stream sediments were significantly contaminated in Belmont, San Francisquito, Los Gatos, and Coyote Creeks in the South Bay, and in the Napa river and streams near Tiburon in the northern reach. While such data cannot be considered to be necessarily representative of the current situation, it is clear that widespread and significant contamination of the Bay by DDT and related compounds has occurred in the past.

More recent data are available from the studies of Chapman et al. (1986) and NOAA (1987). These results are shown in Table 31 and Fig. 74. It will be noted that much lower concentrations of ΣDDT were found in Bay sediments in these investigations than those shown in Table 30 for influent stream sediments. This is probably a function both of proximity of sampling sites to sources of these compounds, and of the timing of the studies relative to the introduction of controls on DDT use. In general, the recent data reveal only minor contamination of sediments in open areas of the Bay by DDT and metabolites; levels of ΣDDT ranged from less than 1 ng g^{-1} dry weight in San Pablo Bay and

Table 30. Concentrations of DDT and metabolites (ng g^{-1} dry weight) in sieved sediments of streams entering San Francisco Bay. (Numbering commences at the San Francisco peninsula and runs anti-clockwise round the Bay to Marin County). Values underlined indicate that residues were confirmed by mass spectrometry. After Law and Goerlitz (1974).

		Concentration (ng g^{-1} dry weight)			
SITE NO.	STREAM	DDD	DDE	o,p'-DDT	p,p'DDT
1	Colma Creek	3.0	2.0	1.7	3.2
2	Colma Creek	4.1	1.8	0.80	5.3
3	Belmont Creek	41	17	89	200
4	Cordilleros Creek	3.8	3.5	4.0	13
5	Cordilleros Creek	17	6.1	5.2	39
6	Redwood Creek	8.4	5.2	4.2	24
7	San Francisquito Creek	2.2	2.1	0.96	7.1
8	San Francisquito Creek	160	43	20	150
9	Los Trancos Creek	10	5.5	1.3	5.6
10	Stevens Creek	0.0	0.0	0.0	12.3
11	Stevens Creek	19	25	11	33
12	Los Gatos Creek	1.8	0.87	0.28	2.2
13	Los Gatos Creek	33	24	11	32
14	Guadalupe River	3.5	2.3	0.87	3.2
15	Guadalupe River	3.1	1.8	0.52	1.6
16	Alamitos Creek	18	26	2.2	14
17	Coyote Creek	86	40	5.7	31
18	Coyote Creek	17	11	2.6	4.3
19	Alameda Creek	5.6	4.5	0.16	0.57
20	Alameda Creek	12	9.2	2.4	2.1
21	Arroyo de la Laguna	27	23	4.5	7.3
22	Arroyo de la Laguna	3.5	4.3	0.77	1.3
23	San Lorenzo Creek	7.0	7.5	0.0	1.7
24	Wildcat Creek	18	4.1	2.7	6.5
25	Wildcat Creek	8.8	6.1	1.8	9.7
26	San Pablo Creek	2.0	3.4	2.0	3.6
27	Union Creek	45	16	2.6	2.8
28	Green Valley Creek	1.9	2.3	0.36	0.86
29	Napa River	2.2	2.7	0.78	2.3
30	Napa River	46	0.0	9.7	73
31	Napa River	16	11	2.8	8.4
32	Sonoma Creek	0.98	1.0	0.25	1.9
33	Petaluma River	8.3	5.5	3.8	2.7
34	Navato Creek	3.5	3.6	2.4	10
35	Miller Creek	16	11	13	8.4
36	San Rafael Creek	120	61	38	51
37	Corte Madera Creek	12	11	8.7	48
38	Corte Madera Creek	42	42	6.7	41
39	Arroyo Corte Madera del Persidio	34	7.6	11	16

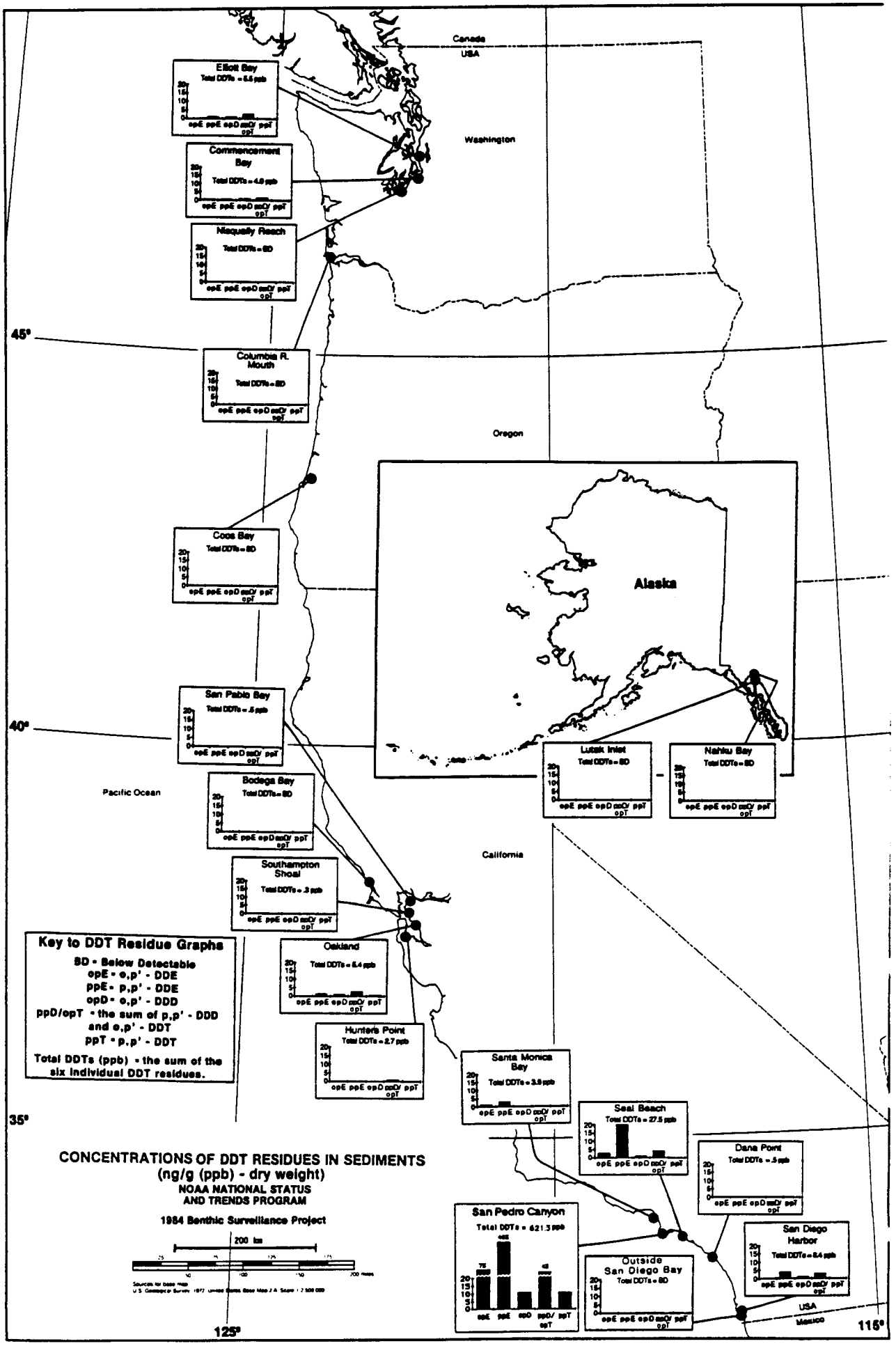
Table 31. Concentrations of DDT, DDE, and DDD (ng g^{-1} dry weight) in sediments from three areas of San Francisco Bay. Three sites were sampled for chemical analysis within each area. After Chapman et al. (1986).

Location	Site	DDT	DDE	DDD	ΣDDT*
San Pablo Bay	SP02	<0.10	0.21	0.21	0.42
	SP05	<0.10	0.27	0.53	0.80
	SP09	<0.10	0.26	0.45	0.71
Oakland	OA02	0.24	0.29	1.00	1.53
	OA05	<0.10	0.24	0.82	1.06
	OA09	<0.10	0.22	0.65	0.87
Islais Creek	IS02	0.63	1.32	0.98	2.93
	IS05	0.87	1.29	1.44	3.60
	IS09	0.40	0.46	1.38	2.24

*Sum of DDT, DDE and DDD; non-detectable residues taken as zero.

Fig. 74. (Overpage).

Concentrations of DDT and metabolites (ng g^{-1} dry weight) in sediments from the US west coast. Data for ΣDDT(total DDT) given above the bars. After NOAA (1987).


Canada
USA
Washington
Oregon
Alaska
Pacific Ocean
California
45°
40°
35°
125°
115°
Elliott Bay
Commencement Bay
Nisqually Reach
Columbia R. Mouth
Coos Bay
San Pablo Bay
Bodega Bay
Southampton Shoal
Oakland
Hunters Point
Santa Monica Bay
Seal Beach
Dana Point
San Pedro Canyon
Outside San Diego Bay
San Diego Harbor
Lutak Inlet
Nahku Bay
Key to DDT Residue Graphs
BD = Below Detectable
opE = o,p' - DDE
ppE = p,p' - DDE
opD = o,p' - DDD
ppD/opT = the sum of p,p' - DDD and o,p' - DDT
ppT = p,p' - DDT
Total DDTs (ppb) = the sum of the six individual DDT residues.
CONCENTRATIONS OF DDT RESIDUES IN SEDIMENTS
(ng/g (ppb) - dry weight)
NOAA NATIONAL STATUS AND TRENDS PROGRAM
1984 Benthic Surveillance Project
200 km

Southampton Shoal to about 3 ng g^{-1} at Hunter's Point and Islais Creek. The Oakland sediments may be spatially heterogeneous, as the two data sets differ in reported levels of ΣDDT, Chapman et al. (1986) finding lower concentrations than did NOAA (1987). The latter studies also found much higher amounts of ΣDDT in the area of San Pedro Canyon in southern California; this residual contamination is from previous industrial sources and has received much study in the past.

ΣDDT in Bay-Delta Biota

Most of the investigations to date on DDT and metabolites in the Bay-Delta concern either bivalve molluscs or finfish. Such data are reviewed below.

Bivalve Molluscs

Early data on ΣDDT in Bay-Delta bivalves were provided by studies undertaken as part of a national program on pesticides in coastal environments (Butler, 1966, 1969, 1973; Modin, 1969). Data for 1966 and 1967 are shown in Tables 32 and 33 as examples of these investigations. Concentrations of DDT and metabolites in Pacific oysters (Crassostrea gigas) from the Bay varied with time, but these temporal trends were not consistent between the two years (Table 32). Mean levels of ΣDDT were 157±60 ng g^{-1} wet weight in 1966 and 186±54 ng g^{-1} wet weight in 1967. In both years, DDT made up about 10-25% of total DDT residues in these oysters, and DDD was generally predominant over DDE. Concentrations of these compounds in asiatic clams (Corbicula fluminea) from the Delta region (Table 33) in 1967 were higher than those found in oysters, suggesting that the Central Valley

Table 32. Concentrations of DDT and metabolites (ng g^{-1} wet weight) in Pacific oysters (Crassostrea gigas) from San Francisco Bay in 1966 and 1967. After Modin (1969).

Month	1966 Samples				1967 Samples			
	DDT	DDE	DDD	ΣDDT*	DDT	DDE	DDD	ΣDDT
January	14	12	20	46	88	52	130	270
February	13	30	37	80	49	34	65	148
March	19	47	60	126	49	30	59	138
April	23	52	83	158	70	42	75	187
May	45	69	120	224	34	23	55	112
June	38	59	62	159	64	39	85	188
July	24	37	47	108	89	45	120	254
August	43	52	82	177	63	53	130	246
September	49	57	90	196	38	30	74	142
October	33	51	88	172	36	31	68	135
November	40	55	84	179	85	100	50	235
December	98	55	110	263	45	45	84	174
MEANS	37	48	74	157	59	44	83	186
±S.D.	23	15	29	60	20	20	29	54

*Sum of DDT, DDE, and DDD

Table 33. Concentrations of DDT and metabolites (ng g^{-1} wet weight) in Asiatic clams (Corbicula fluminea) sampled in the Delta at West Island and False River in 1967. After Modin (1969).

Month	WEST ISLAND				FALSE RIVER			
	DDT	DDE	DDD	ΣDDT*	DDT	DDE	DDD	ΣDDT*
January	210	280	250	740		No sample		
February	300	330	370	1000		No sample		
March	320	320	350	990		No sample		
April	250	270	250	770	1000	470	410	1880
May	260	320	250	830	910	460	320	1690
June	270	230	210	710	640	320	200	1160
July	150	170	130	450	780	420	260	1460
August	130	140	93	363	500	270	180	950
September	230	170	150	550		No sample		
October	270	180	150	600		No sample		
November	1100	690	490	2280		No sample		
December	770	390	310	1470	210	400	350	960
MEANS	355	291	250	896	673	390	287	1350
±S.D.	285	148	115	525	290	79	89	389

*Sum of DDT, DDE, and DDD

was a significant source of DDT. Ratios between the compounds in clams were also distinct from those in oysters, with DDT generally predominating and DDE levels being similar to or slightly greater than DDD. This is consistent with a Central Valley source of DDT which is progressively metabolized to DDE and DDD as it is transported through the Delta and into the Bay. It is notable that in general, Modin (1969) considered the San Francisco Bay-Delta to be only of moderate contamination by DDT and metabolites, higher levels of these compounds being found in some of the other west coast estuaries. He ascribed this to large dilutions of contaminants in the Bay, by both freshwater inflows and exchange through the Golden Gate. However, the Bay-Delta may have been acting as a significant source of ΣDDT to the west coast; Dungeness crab (Cancer magister) samples were found to contain more DDE at Point Bonita near the Bay entrance than at sites further north (Double Point and Bodega Bay).

Girvin et al. (1975) reported data for ΣDDT in four species of bivalves from three Bay locations (Table 34). These samples were taken in April 1975, after restrictions on DDT use in the USA had come into force. While direct comparisons cannot be made as Crassostrea gigas was not included in the later studies, there is evidence of a general reduction in ΣDDT levels in Bay bivalves between the studies of Modin (1969) cited above and those of Girvin et al. (1975). It may also be noted that the concentrations of ΣDDT found by the latter authors in Ostrea lurida from Coyote Point were lower than any previously recorded for that species at this location (Butler, 1973; U.S. EPA, 1974).

Table 34. Concentrations of DDT and metabolites (ng g^{-1} wet weight) in the eastern softshell clam Mya arenaria, the Japanese littleneck clam Tapes japonica, the native Bay mussel Mytilus edulis and the Olympic oyster Ostrea lurida from three San Francisco Bay locations. After Girvin et al. (1975).

Species	Location	p,p'-DDE	p,p'-DDD	p,p'-DDT	o,p'-DDT	Total DDT
Mya arenaria						
	Albany Hill	6.02	4.84	2.27	ND	12.8
	Coyote Pt. N.	5.90	2.26	1.96	ND	10.1
	Foster City	5.00	1.80	1.35	1.94	10.1
Tapes japonica						
	Albany Hill	6.91	5.00	3.46	Trace	14.9
	Coyote Pt. N.	4.27	1.52	1.43	ND	7.22
	Foster City	4.73	1.83	Trace	ND	6.56
Mytilus edulis						
	Albany Hill	16.4	10.6	7.27	3.41	34.3
	Coyote Pt. N.	11.8	3.34	6.29	7.79	24.8
	Foster City	15.0	3.28	1.53		24.3
Ostrea lurida						
	Coyote Pt. N.	16.0	4.00	3.49	5.68	29.2
	Foster City	10.3	3.52	3.62	3.14	20.6

ND: Not detected.

Goldberg et al. (1978) and Farrington et al. (1982, 1983) reported data from the national Mussel Watch program, which included a composite sample of mussels (Mytilus edulis) derived from several South Bay locations. Levels of total DDT were not reported as such, but DDE and DDD concentrations totalled about 50 to 90 ng g^{-1} dry weight in 1976 and 1977 samples. The more extensive and recent data from the State Mussel Watch Program, covering up to 22 sites in San Francisco Bay and employing both transplanted M. californianus and native M. edulis, are shown in Tables 35 to 38. Comparison of the total DDT data in Table 38 to previous studies suggests that concentrations of these compounds have probably diminished slightly since the studies of Girvin et al. (1975), but there is little evidence for continued decreases since the late 1970s. It is also clear from the latest work that significant sources of DDT remain in the Bay, particularly in the area of the Santa Fe Channel, off Richmond Harbor. The primary source of this contamination is believed to be the site of the former United Heckathorn Company plant, which is located on the east bank of the Lauritzen Canal (which drains to the Santa Fe Channel; see Hayes and Phillips, 1986; Stephenson et al., 1986a). Soils on the site and sediments in the Lauritzen Canal both exhibited exceptionally high levels of DDT in 1984; various aquatic organisms were likewise highly contaminated (Harding Lawson Associates, 1984a, 1984b; Hayes and Phillips, 1986). It is notable that this area is also a hot-spot for chlordane and dieldrin, which were also formulated and packaged by the former company.

Table 35. Concentrations of p,p'-DDT (means, ng g^{-1} dry weight) in transplanted mussels, Mytilus californianus, or native Bay mussels (M. edulis, as shown) in San Francisco Bay. Data from the State Mussel Watch Program, after Hayes et al. (1985), Hayes and Phillips (1986) and Stephenson et al. 1986a).

LOCATION	STATION CODE	1979	1980	1981	1982 (J/F*)	1982 (D*)	1983	1985	1986
MARE ISLAND	300.20							NAa	ND
DAVIS POINT	301.00					5.6			
POINT PINOLE	302.00			NA	ND	7.8	ND	4.6	ND
RICHMOND BRIDGE	303.00		8.0	NA	11.0	10.0			
SANTA FE CH. MOUTH	303.10								30.0
SANTA FE CH. L.C.	303.20							NA	880
SANTA FE CH. L.C. END	303.30								6800
SANTA FE CH. END	303.40							1200	160
RICHMOND INNER HARBOR	303.60								14.0
ANGEL ISLAND	305.00		270	11.0		12.0			
FORT BAKER	306.00			NA		7.1			
TREASURE ISLAND	307.00	24.0	20.0	13.0	ND	8.8	ND	6.4	
ALAMEDA YACHT HARBOR	307.20								18.0
OAKLAND IN. HARBOR WEST	307.30								5.8
OAKLAND IN. HARBOR EMBC.	307.40							41.0	42.0
OAKLAND BACK HARBOR	307.60							NA	17.0
HUNTER'S POINT	308.00			NA	4.9	4.8			
SAN MATEO BRIDGE 8	309.00			NA	ND	5.2	ND		
SAN MATEO BRIDGE 8A	310.00				ND				
REDWOOD CREEK MOUTH	313.00			7.4	ND	4.9	ND		
REDWOOD CREEK TRDWNDS	316.00		13.0a						
DUMBARTON BRIDGE 14	321.00			5.2	ND		8.0		

ND: Not detected.
NA: Not analyzed.
*J/F/D: January/February/December, all 1982.
aNative M. edulis

Table 36. Concentrations of p,p'-DDE (means, ng g^{-1} dry weight) in transplanted mussels, Mytilus californianus, or native Bay mussels (M. edulis, as shown) in San Francisco Bay. Data from the State Mussel Watch Program, after Hayes et al. (1985), Hayes and Phillips (1986) and Stephenson et al. 1986a).

LOCATION	STATION CODE	1979	1980	1981	1982 (J/F*)	1982 (D*)	1983	1985
MARE ISLAND	300.20							NAa
DAVIS POINT	301.00					95		
POINT PINOLE	302.00			NA	46	78	64	35
RICHMOND BRIDGE	303.00		56	NA	63	50		
SANTA FE CH. MOUTH	303.10							
SANTA FE CH. L.C.	303.20							NA
SANTA FE CH. L.C. END	303.30							
SANTA FE CH. END	303.40							960
RICHMOND INNER HARBOR	303.60							
ANGEL ISLAND	305.00		1900	71		48		
FORT BAKER	306.00			NA		38		
TREASURE ISLAND	307.00	56	72	69	41	41	51	33
ALAMEDA YACHT HARBOR	307.20							
OAKLAND IN. HARBOR WEST	307.30							
OAKLAND IN. HARBOR EMBC.	307.40							66
OAKLAND BACK HARBOR	307.60							NA
HUNTER'S POINT	308.00			NA	31	46		
SAN MATEO BRIDGE 8	309.00			NA	30	55	38	
SAN MATEO BRIDGE 8A	310.00				20			
REDWOOD CREEK MOUTH	313.00			52	26	52	44	
REDWOOD CREEK TRDWNDS	316.00		94a					
DUMBARTON BRIDGE 14	321.00			99	44		48	

ND: Not detected.
NA: Not analyzed.
*J/F/D: January/February/December, all 1982.
[a]Native M. edulis

Table 37. Concentrations of p,p'-DDD (means, ng g^{-1} dry weight) in transplanted mussels, Mytilus californianus, or native Bay mussels (M. edulis, as shown) in San Francisco Bay. Data from the State Mussel Watch Program, after Hayes et al. (1985), Hayes and Phillips (1986) and Stephenson et al. 1986a).

LOCATION	STATION CODE	1979	1980	1981	1982 (J/F*)	1982 (D*)	1983	1985	1986
MARE ISLAND	300.20							NAa	32
DAVIS POINT	301.00					110			
POINT PINOLE	302.00			NA	53	78	61	40	22
RICHMOND BRIDGE	303.00		ND	NA	93	80			
SANTA FE CH. MOUTH	303.10								200
SANTA FE CH. L.C.	303.20							NA	2600
SANTA FE CH. L.C. END	303.30								1400
SANTA FE CH. END	303.40							5400	980
RICHMOND INNER HARBOR	303.60								160.0
ANGEL ISLAND	305.00		190	100		120			
FORT BAKER	306.00			NA		35			
TREASURE ISLAND	307.00	65	72	110	58	64	44	60	
ALAMEDA YACHT HARBOR	307.20								62
OAKLAND IN. HARBOR WEST	307.30								20
OAKLAND IN. HARBOR EMBC.	307.40							70	64
OAKLAND BACK HARBOR	307.60							NA	32
HUNTER'S POINT	308.00			NA	27	55			
SAN MATEO BRIDGE 8	309.00			NA	28	56	17		
SAN MATEO BRIDGE 8A	310.00				12				
REDWOOD CREEK MOUTH	313.00			46	55	39	22		
REDWOOD CREEK TRDWNDS	316.00		73a						
DUMBARTON BRIDGE 14	321.00			34	13		47		

NA: Not analyzed.
*J/F/D: January/February/December, all 1982.
[a]Native M. edulis

Table 38. Concentrations of total DDT (DDT and all metabolites, means, ng g^{-1} dry weight) in transplanted mussels, Mytilus californianus, or native Bay mussels (M. edulis, as shown) in San Francisco Bay. Data from the State Mussel Watch Program, after Hayes et al. (1985), Hayes and Phillips (1986) and Stephenson et al. 1986a).

LOCATION	STATION CODE	1979	1980	1981	1982 (J/F*)	1982 (D*)	1983	1985
MARE ISLAND	300.20							NAa
DAVIS POINT	301.00					238		
POINT PINOLE	302.00			NA	113	186	131	89
RICHMOND BRIDGE	303.00		70	NA	214	176		
SANTA FE CH. MOUTH	303.10							
SANTA FE CH. L.C.	303.20							NA
SANTA FE CH. L.C. END	303.30							
SANTA FE CH. END	303.40							10700
RICHMOND INNER HARBOR	303.60							
ANGEL ISLAND	305.00		2659	258		213		
FORT BAKER	306.00			NA		101		
TREASURE ISLAND	307.00	180	193	265	122	140	102	121
ALAMEDA YACHT HARBOR	307.20							
OAKLAND IN. HARBOR WEST	307.30							
OAKLAND IN. HARBOR EMBC.	307.40							216
OAKLAND BACK HARBOR	307.60							NA
HUNTER'S POINT	308.00			NA	70	113		
SAN MATEO BRIDGE 8	309.00			NA	65	126	55	
SAN MATEO BRIDGE 8A	310.00				32			
REDWOOD CREEK MOUTH	313.00			149	86	102	66	
REDWOOD CREEK TRDWNDS	316.00		197a					
DUMBARTON BRIDGE 14	321.00			178	57		103	

NA: Not analyzed.
*J/F/D: January/February/December, all 1982.
[a]Native M. edulis

Fish

DDT and its metabolites have been measured in most of the samples of fish studied for PCBs and discussed in section IIIA of this report above. However, while PCBs have been implicated in reproductive impairment of starry flounder in the Bay (and may also contribute to other problems in the Bay-Delta, such as effects on birds), DDT and its related compounds are not thought to contribute to such effects locally. However, it should be noted here that both DDE and PCBs are known to have significant impacts on fish reproduction (e.g. see Burdick et al., 1964; Anderson and Everhart, 1966; Hansen et al., 1985), and DDT is also of considerable direct toxicity to fish such as striped bass (Korn and Earnest, 1974).

Earnest and Benville (1971) reported correlations between DDT, DDE, and DDD contents of fish from San Francisco Bay and their lipid contents. Phillips (1978, 1980) has reviewed the effects of lipid on organochlorines in aquatic biota, and concluded that this parameter is of considerable importance in defining contaminant levels. Most fish sampled in the Bay by Earnest and Benville (1971) in the late 1960s (before DDT usage was restricted in the USA) contained ΣDDT levels of about 100-200 ng g^{-1} wet weight (whole body basis).

Data from the Toxic Substances Monitoring Program (1978-1984) are shown in Fig. 75. The EDL 85 for total DDT in this dataset corresponds to 823 ng g^{-1} wet weight; the National Academy of Science's guideline for predator protection is 1,000 ng g^{-1}, and the Food and Drug Administration action level is 5,000 ng g^{-1}. It may be seen that several locations in the

Fig. 75. Locations at which sampled fish exceeded the EDL 85 (823 ng g^{-1} wet weight), the NAS guideline for predator protection (1,000 ng g^{-1} wet weight), or the FDA action level (5,000 ng g^{-1} wet weight) for total DDT. Data from the Toxic Substances Monitoring Program, 1978-1984. After SWRCB (1986).

Central Valley supported fish with ΣDDT concentrations exceeding either the EDL 85 or the NAS guideline, although the FDA action level was not breached by fish from this area. Temporal trends for fish sampled by this program are shown in Fig. 76. There is little evidence for significant changes in ΣDDT abundance through the 1980s; this agrees with the data of the State Mussel Watch Program cited above. Studies of isomer abundance in the Salinas River region and elsewhere in California (Mischke et al., 1985; Agee, 1986; SWRCB, 1986) have suggested that washout of residual DDT from soils may be the primary ongoing source of contamination of aquatic biota. However, illegal use of DDT as a pesticide may also occur. In any event, significant amounts of DDT and its metabolites continue to be present in fish from much of the Bay-Delta catchment area.

Stevens (1980) reported a long-term dataset for ΣDDT levels in striped bass (Morone saxatilis) from the Sacramento/San Joaquin estuary (Table 39). It should be noted that many factors may affect ΣDDT levels in striped bass (as stated for PCBs above) and that interpretation of these data is fraught with difficulties. Anderson and Fenderson (1970) recommended the use of stratified sampling techniques to monitor insecticide residues in Atlantic salmon (Salmo salar), and this would be of value in studies of striped bass also. More recent studies of ΣDDT in striped bass suggest that concentrations of about 0.5 to 1.0 $\mu g\ g^{-1}$ wet weight were commonly encountered in muscle samples taken in the early 1980s (Crosby et al., 1983; Whipple et al., 1983; Brown et al., 1987), with livers and (especially) ovaries exceeding these values somewhat. Data for 1984 and 1985 agree

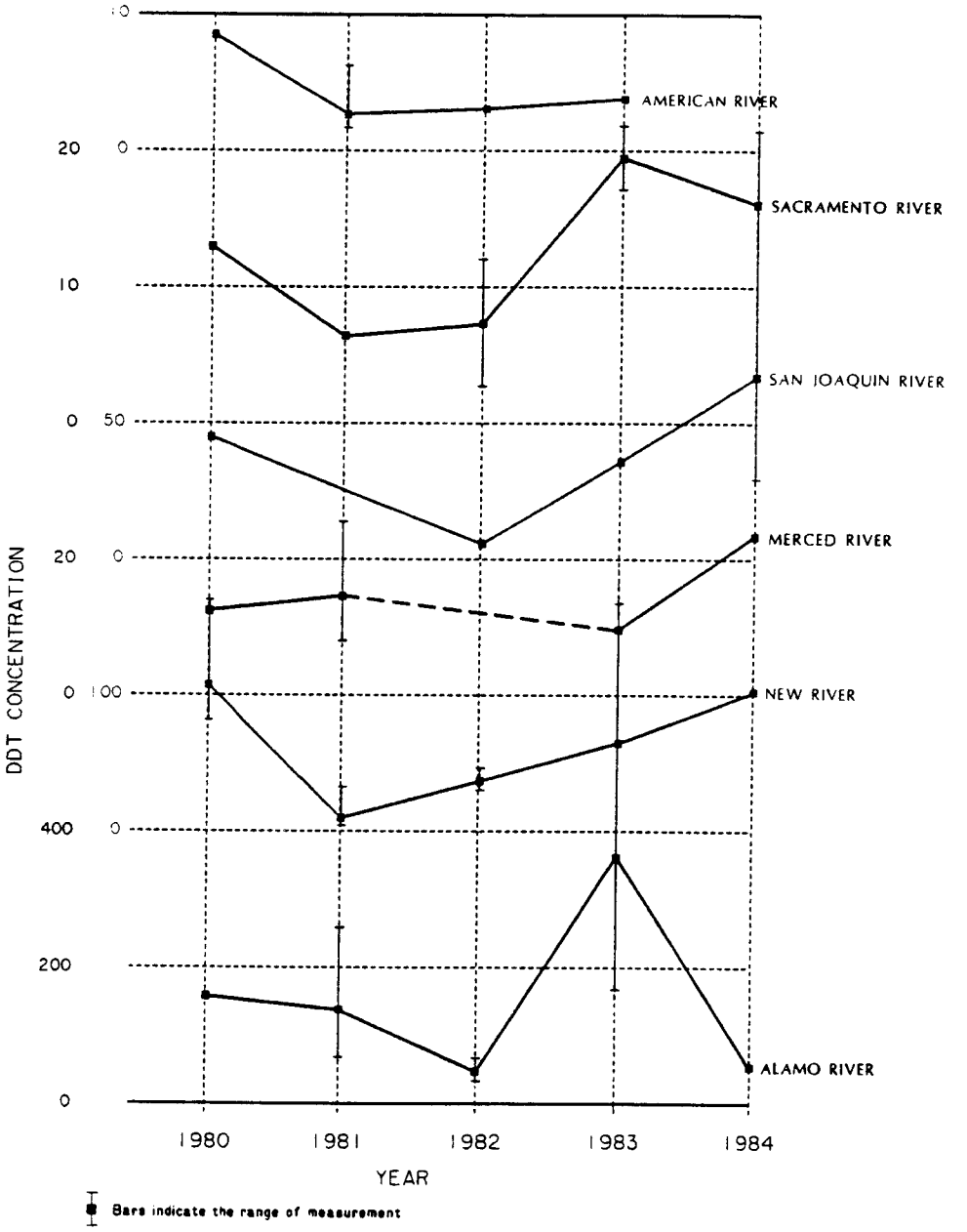


Fig. 76. Temporal trends in levels of total DDT (means and ranges, $\mu g\ g^{-1}$ lipid weight) in fish from six California Rivers, 1980-1984. After SWRCB (1986).

Table 39. Concentrations of total DDT ($\mu g\ g^{-1}$ wet weight) in muscle tissues of striped bass (Morone saxatilis) from the Sacramento/San Joaquin estuary. After Stevens (1980).

Year	Number	ΣDDT
1964	7	0.62
1965	6	0.54
1967	2	1.62
1969	29	1.72
1970	49	1.69
1971	18	1.45
1972	22	1.80
1974	8	0.59
1975	13	0.21
1976	9	0.12

tolerably with these estimates (Knudsen and Kohlhorst, 1987). In the absence of sufficient samples and analyses to account for the effects of external variables on ΣDDT levels in striped bass, the elucidation of long-term trends appears impossible. Nevertheless, it may be concluded that if such trends do indeed exist, they are unlikely to be dramatic in nature. It should also be emphasized that M. saxatilis from the Bay-Delta are undoubtedly more contaminated by DDT and metabolites than are fish of the same species from the Coos River, Oregon (Crosby et al., 1983; Whipple et al., 1983; Jung et al., 1984), although differences between Bay-Delta fish and those from estuaries on the U.S. east coast are less marked (Brown et al., 1987).

Finally here, the data of NOAA (1987) deserve mention. These studies reported that total DDT in livers of starry flounder (Platichthys stellatus) from three sites in the Bay (San Pablo Bay, Southampton Shoal, Hunter's Point) ranged between 1.0 and 1.3 $\mu g\ g^{-1}$ dry weight. Similar concentrations were found for livers of P. stellatus from Bodega Bay, but fish from the Coos River and Columbia River mouth exhibited much lower levels of these compounds (0.02 and 0.29 $\mu g\ g^{-1}$ dry weight respectively). Livers of hornyhead turbot (Pleuronichthys verticalis) from sites in southern California contained highly elevated total DDT concentrations (3.2 to 18.7 $\mu g\ g^{-1}$ dry weight), in keeping with the known extreme historical contamination of sediments in this area by DDT and its metabolites.

Marine Mammals

Data on ΣDDT levels in marine mammals from the Bay-Delta are restricted to those of Risebrough et al. (1978) on harbor seals.

As noted above in section IIIA, it is not possible to draw firm conclusions from most studies of this nature, as it is impossible to know where and when contaminants were accumulated by an animal which is migratory in nature. The only highly significant result among these data was the discovery of very high ΣDDT levels (mostly as DDE) in a seal found dead in Richardson Bay. This individual (code REJ 865) also exhibited very high PCB levels.

Birds

The concentrations of DDT and metabolites in birds have received a great deal of attention in the past, mainly because bio-accumulation of these compounds (especially by birds of prey) caused reproductive impairment in many wild populations (Miller and Berg, 1969). However, the introduction of controls on DDT usage in the USA and elsewhere in the early 1970s has been followed by the gradual recovery of many bird populations.

In the Bay-Delta, Ohlendorf and Miller (1984) found little evidence of problems from ΣDDT accumulation in four waterfowl species (sampled in the Delta and the Central Valley). Similarly, DDE was not considered to be a primary causative factor of reproductive impairment in birds of the San Francisco National Wildlife Refuge on Bair Island in the South Bay (Hoffman et al., 1986). Reproductive problems in birds at Kesterson Wildlife Refuge in the San Joaquin catchment are thought to relate to selenium enrichment rather than organochlorines (see section IIC of this report).

Such negative reports on ΣDDT impacts on birds in the San Francisco catchment are heartening, as several portions of the catchment are of exceptional importance as migration and

wintering areas for a variety of bird species on the so-called Pacific Flyway.

Summary

The usage of DDT in the San Francisco Bay-Delta catchment was considerable prior to 1970. Data from that time show that the estuary was significantly contaminated by DDT and metabolites, although levels of these compounds in local biota were not as great as in some other estuaries, presumably due to the high flushing of the Bay by freshwater and tidal inflows.

The controls placed on DDT usage in California in 1970 probably gave rise to short-term reductions in the amounts of these compounds in biota in the Bay-Delta, although the available database is poor. Such reductions may have continued more gradually through the mid-1970s, but since then it appears that ΣDDT levels in Bay-Delta organisms have remained relatively stable. There can be little doubt that DDT and its metabolites continue to enter the estuary from soils in the catchment (Martin, 1985). It is also possible that illegal usage of DDT exists, augmenting residues washing down to the Bay from areas of historical use in agriculture.

Overall, current levels of DDT and metabolites within the Bay are relatively low and are unlikely to exert highly significant detrimental effects on biota.

C. OTHER ORGANOCHLORINES

PCBs and the DDT group of compounds have been more extensively studied in the San Francisco Bay-Delta ecosystem than have other organochlorines; the latter are therefore discussed as a group in this section.

The relative paucity of data on organochlorines other than PCBs and ΣDDT in the estuary is somewhat surprising, as many of these compounds are highly toxic to aquatic biota. Comparative acute toxicity data are shown in Fig. 77; it is evident that endrin rivals DDT in direct toxicity, with chlordane, heptachlor, methoxychlor, toxaphene, and the other cyclodienes (aldrin and dieldrin) also exhibiting significant toxic action (Klapow and Lewis, 1979). Certain organochlorines, such as mirex, are not included here, as their local usage is minor and they are unlikely to be abundant in the Bay-Delta (see Eisler, 1985b). However, compounds such as chlordane and toxaphene are more abundant locally, despite restrictions on their use introduced by the EPA in the 1970s and early 1980s. Although toxaphene is generally not a threat to warm-blooded animals (Eisler, 1985c), it is nevertheless of very significant toxicity to aquatic biota (especially fish), and was present a considerable proportion of the time in agricultural drainage water until restrictions on its usage were introduced in 1982 (Cohen et al., 1982). The available data on organochlorines other than PCBs and DDT and metabolites are reviewed below.

Sediments of the Bay-Delta

Law and Goerlitz (1974) found significant amounts of

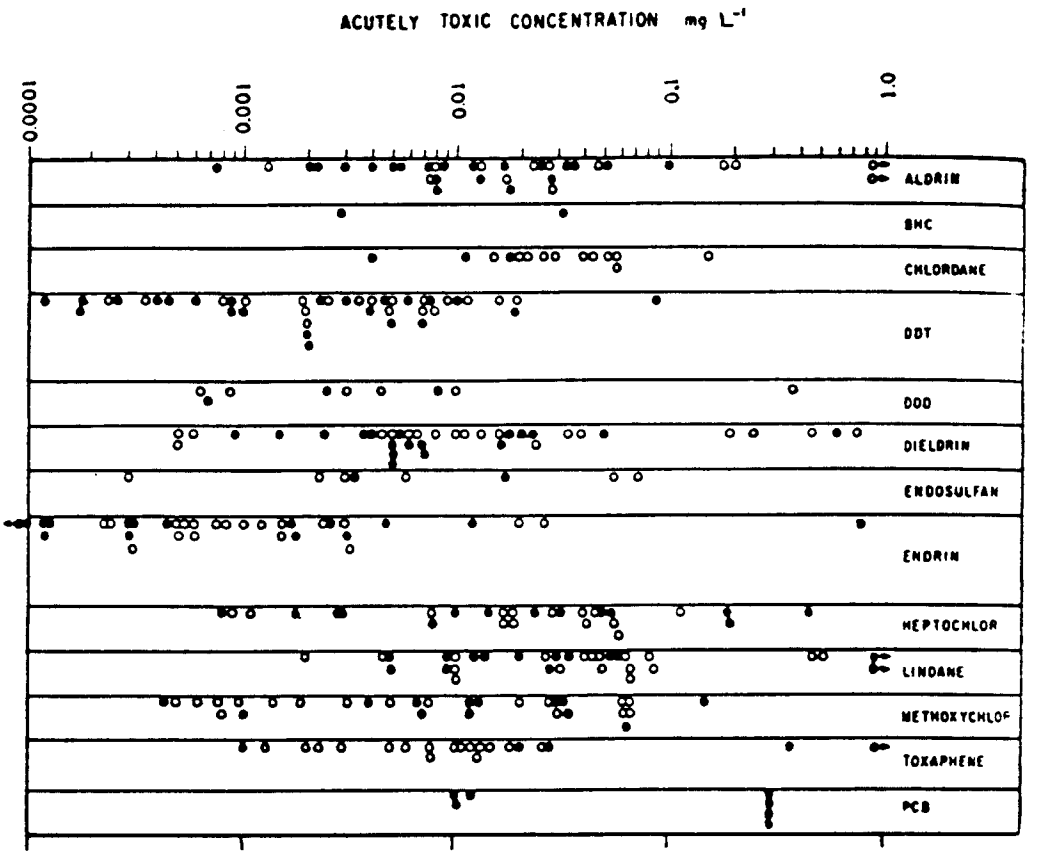


Fig. 77. Acutely toxic concentrations (24-hour, 48-hour or 96-hour LC50 values, mg L^{-1}) of various organochlorines in solution. Closed circles refer to marine species; open circles to freshwater biota. After Klapow and Lewis (1979).

chlordane in the sediments of streams flowing to San Francisco Bay. These data, shown in Table 40, emphasized the widespread abundance of chlordane in the estuary; concentrations of this chemical rivaled those of PCBs in sediments, and generally exceeded ΣDDT levels in such samples.

Significant amounts of trans-chlordane and cis-chlordane were also found more recently by Chapman et al. (1986) in the sediments of Islais Creek, although samples from Oakland and San Pablo Bay exhibited undetectable levels (<0.14 and <0.11 ng g^{-1} dry weight respectively) of these compounds. Islais Creek sediments were also contaminated by trans-nonachlor. These (and PCBs and ΣDDT) were the only organochlorines reported for the samples studied. The National Status and Trends studies in 1984 (covering sites at San Pablo Bay, Southampton Shoal, Oakland and Hunter's Point) detected hexachlorobenzene in Oakland sediments (mean of 0.57 ng g^{-1} dry weight), but lindane, heptachlor, aldrin, dieldrin, chlordane, nonachlor, and mirex were not detected (unpublished data; personal communication from NOAA).

Biota in the Bay-Delta

Modin (1969) reported dieldrin concentrations of 10 to 23 ng g^{-1} wet weight in Pacific oysters, Crassostrea gigas, from San Francisco Bay. Asiatic clams (Corbicula fluminea) from two sites in the Delta exhibited similar dieldrin levels of <10 to 28 ng g^{-1} wet weight, and one clam sample from West Island in the Delta also contained detectable concentrations of endrin (10 ng g^{-1} wet weight). Dieldrin was also found (at 6.7 ng g^{-1} wet weight) in 1985 in C. fluminea from the San Joaquin River at Newman, but

Table 40. Concentrations of chlordane (ng g^{-1} dry weight) in sieved bottom sediments of influent streams to San Francisco Bay. Stream numbers run anti-clockwise from the San Francisco peninsula to Marin County. Values underlined indicate that residues were confirmed by mass spectrometry. After Law and Goerlitz (1974).

SITE NO.	STREAM	CHLORDANE
1	Colma Creek	39
2	Colma Creek	19
3	Belmont Creek	660
4	Cordilleros Creek	20
5	Cordilleros Creek	33
6	Redwood Creek	40
7	San Francisquito Creek	7.1
8	San Francisquito Creek	670
9	Los Trancos Creek	21
10	Stevens Creek	7.8
11	Stevens Creek	190
12	Los Gatos Creek	0.0
13	Los Gatos Creek	280
14	Guadalupe River	17
15	Guadalupe River	9.6
16	Alamitos Creek	46
17	Coyote Creek	83
18	Coyote Creek	71
19	Alameda Creek	13
20	Alameda Creek	52
21	Arroyo de la Laguna	200
22	Arroyo de la Laguna	22
23	San Lorenzo Creek	15
24	Wildcat Creek	87
25	Wildcat Creek	45
26	San Pablo Creek	65
27	Union Creek	200
28	Green Valley Creek	0.0
29	Napa River	10
30	Napa River	0.0
31	Napa River	97
32	Sonoma Creek	4.3
33	Petaluma River	130
34	Navato Creek	62
35	Miller Creek	310
36	San Rafael Creek	800
37	Corte Madera Creek	140
38	Corte Madera Creek	66
39	Arroyo Corte Madera del Persidio	140

other clam samples exhibited levels below the detection limit of 5 ng g^{-1} wet weight (Linn et al., 1987). Data from the State Mussel Watch Program for dieldrin are shown in Table 41. The most recent studies discovered a significant source of dieldrin in the Lauritzen Canal/Santa Fe Channel; this is believed to be a result of contamination from a previous pesticide formulation and packaging plant at this location (Hayes and Phillips, 1986; Stephenson et al., 1986a). It should also be noted here that Martin et al. (1984) correlated the scope for growth of mussels (M. californianus) from the Bay with dieldrin and chlordane levels in their tissues, as well as with covarying trace element concentrations. The organochlorine data are presented in Table 42; interestingly, PCB levels in mussels did not correlate to scope for growth in these studies. It should be emphasized that these results do not necessarily confirm a cause-and-effect link between contaminant levels and mussel physiology, as many other covarying parameters exist (Martin et al., 1984).

The recent inclusion of analysis of Corbicula fluminea in the Toxic Substances Monitoring Program (Linn et al., 1987) augments data for pesticides in fish tissues (discussed below). Clams sampled in late 1985 at Vernalis, Newman, Fremont Ford, and Salt Slough all showed evidence of contamination by pesticides other than DDT and its metabolites; chlordane, chlorpyrifos, dieldrin, endosulfan, and toxaphene were present in one or more samples. These data compare well to information from the State Mussel Watch Program, which includes analysis of a wide range of organochlorines in mussels from the Bay. Apart from PCBs, ΣDDT, and dieldrin (discussed above), data from this program indicate

Table 41. Concentrations of dieldrin (means, ng g^{-1} dry weight) in transplanted mussels, Mytilus californianus, or native Bay mussels (M. edulis, as shown) in San Francisco Bay. Data from the State Mussel Watch Program, after Hayes et al. (1985), Hayes and Phillips (1986) and Stephenson et al. (1986a).

LOCATION	STATION CODE	1979	1980	1981	1982 (J/F*)	1982 (D*)	1983	1985
MARE ISLAND	300.20							NAa
DAVIS POINT	301.00					28		
POINT PINOLE	302.00			24	8	27	40	26
RICHMOND BRIDGE	303.00		18	26	21	31		
SANTA FE CH. MOUTH	303.10							
SANTA FE CH. L.C.	303.20							NA
SANTA FE CH. L.C. END	303.30							
SANTA FE CH. END	303.40							800
RICHMOND INNER HARBOR	303.60							
ANGEL ISLAND	305.00		29	34		40		
FORT BAKER	306.00			20		29		
TREASURE ISLAND	307.00	NA	32	24	11	41	43	32
ALAMEDA YACHT HARBOR	307.20							
OAKLAND IN. HARBOR WEST	307.30							
OAKLAND IN. HARBOR EMBC.	307.40							47
OAKLAND BACK HARBOR	307.60							NA
HUNTER'S POINT	308.00			27	54	62		
SAN MATEO BRIDGE 8	309.00			50	32	100	82	
SAN MATEO BRIDGE 8A	310.00				18			
REDWOOD CREEK MOUTH	313.00			44	55	81	64	
REDWOOD CREEK TRDWNDS	316.00		36a					
DUMBARTON BRIDGE 14	321.00			35	24		68	

NA: Not analyzed.
J/F/D: January/February/December, all 1982.
[a]Native Mytilus edulis

Table 42. Scope for growth and concentrations of organochlorines (ng g^{-1} dry weight) in transplanted mussel (*Mytilus californianus*) from San Francisco Bay. After Martin *et al.* (1984).

Location	Scope for Growth Jh^{-1}	Total chlordane	Dieldrin	PCB[a]
Tomales Bay (reference)	43.8	4	4.7	27
San Francisco Bay				
Fort Baker	31.8	39	20	510
Treasure Island	26.3	67	24	1500
Hunter's Point	21.2	51	27	1800
San Mateo Bridge	15.9	83	50	1300
Redwood Creek	3.8	78	44	1200
Linear Regression (r)		-0.89	-0.91	-0.67
Level of significance		0.05	0.05	NS[b]
Degrees of freedom		4	4	4

[a] Quantified as Aroclor 1254.
[b] Not significant.

low-level contamination of the Bay by such toxicants as chlorbenside, dacthal, endosulfan, hexachlorobenzene, isomers of HCH, and heptachlor and its epoxide. Concentrations of total chlordane are of significantly elevated abundance and are shown in Table 43. Chlordane is principally employed for the control of termites in California (Hayes and Phillips, 1986). The Lauritzen Canal site is a notable hot-spot for total chlordane, most being present as the cis- and trans-chlordane isomers and as trans-nonachlor (Hayes and Phillips, 1986; Stephenson et al., 1986a).

Data on organochlorines other than PCBs and ΣDDT in fish from the Bay-Delta and its catchment are available on striped bass and on several species in the Central Valley. Selected results from the Toxic Substances Monitoring Program are shown in Figs. 78 to 83. These show a consistent pattern of elevated pesticide residues in California between 1978 and 1984, with areas of contamination of fish being present in the Central Valley, the Monterey Bay catchment, and a variety of streams between Los Angeles and San Diego in southern California. Fish from the Central Valley region exhibited elevated levels of chlordane, dieldrin, endosulfan, isomers of HCH, hexachlorobenzene, and toxaphene. These data agree well with the results of the State Mussel Watch Program cited above, and clearly show that pesticides used in the Central Valley eventually drain to the Bay, where they become available to the estuarine biota. It is notable that in many cases, fish from the Central Valley exceeded the relevant National Academy of Science's guideline or FDA action level.

Table 43. Concentrations of total chlordane (means, ng g^{-1} dry weight) in transplanted mussels, Mytilus californianus, or native Bay mussels (M. edulis, as shown) in San Francisco Bay. Data from the State Mussel Watch Program, after Hayes et al. (1985), Hayes and Phillips (1986) and Stephenson et al. (1986a).

LOCATION	STATION CODE	1979	1980	1981	1982 (J/F*)	1982 (D*)	1983	1985	1986
MARE ISLAND	300.20							NAa	31
DAVIS POINT	301.00					65			
POINT PINOLE	302.00			69	47	55	39	28	31
RICHMOND BRIDGE	303.00		36	60	46	36			
SANTA FE CH. MOUTH	303.10								27
SANTA FE CH. L.C.	303.20							NA	121
SANTA FE CH. L.C. END	303.30								440a
SANTA FE CH. END	303.40							226	43
RICHMOND INNER HARBOR	303.60								27
ANGEL ISLAND	305.00		236	67		40			
FORT BAKER	306.00			41		30			
TREASURE ISLAND	307.00	NA	61	71	48	40	29	33	
ALAMEDA YACHT HARBOR	307.20								107
OAKLAND IN. HARBOR WEST	307.30								29
OAKLAND IN. HARBOR EMBC.	307.40							116	128
OAKLAND BACK HARBOR	307.60							NA	76
HUNTER'S POINT	308.00			54	22	28			
SAN MATEO BRIDGE 8	309.00			88	43	66	40		
SAN MATEO BRIDGE 8A	310.00				26				
REDWOOD CREEK MOUTH	313.00			83	58	67	42		
REDWOOD CREEK TRDWNDS	316.00		176a						
DUMBARTON BRIDGE 14	321.00			102	32		70		

NA: Not analyzed.
J/F/D: January/February/December, all 1982.
[a]Native Mytilus edulis

Fig. 78. Locations at which sampled biota (generally fish livers) exceeded the elevated data level (EDL 85, 43 ng g^{-1} wet weight) for total chlordane, or exceeded the NAS guideline of 100 ng g^{-1} or the FDA action level of 300 ng g^{-1} wet weight. Data from the Toxic Substances Monitoring Program, 1978-84, after SWRCB (1986).

Fig. 79. Locations at which sampled biota (generally fish livers) exceeded elevated data levels (EDL 85, 12 ng g^{-1} wet weight; EDL 95, 42 ng g^{-1} wet weight) or the NAS guideline of 100 ng g^{-1} wet weight for dieldrin. Data from the Toxic Substances Monitoring Program, 1978-84, after SWRCB (1986).

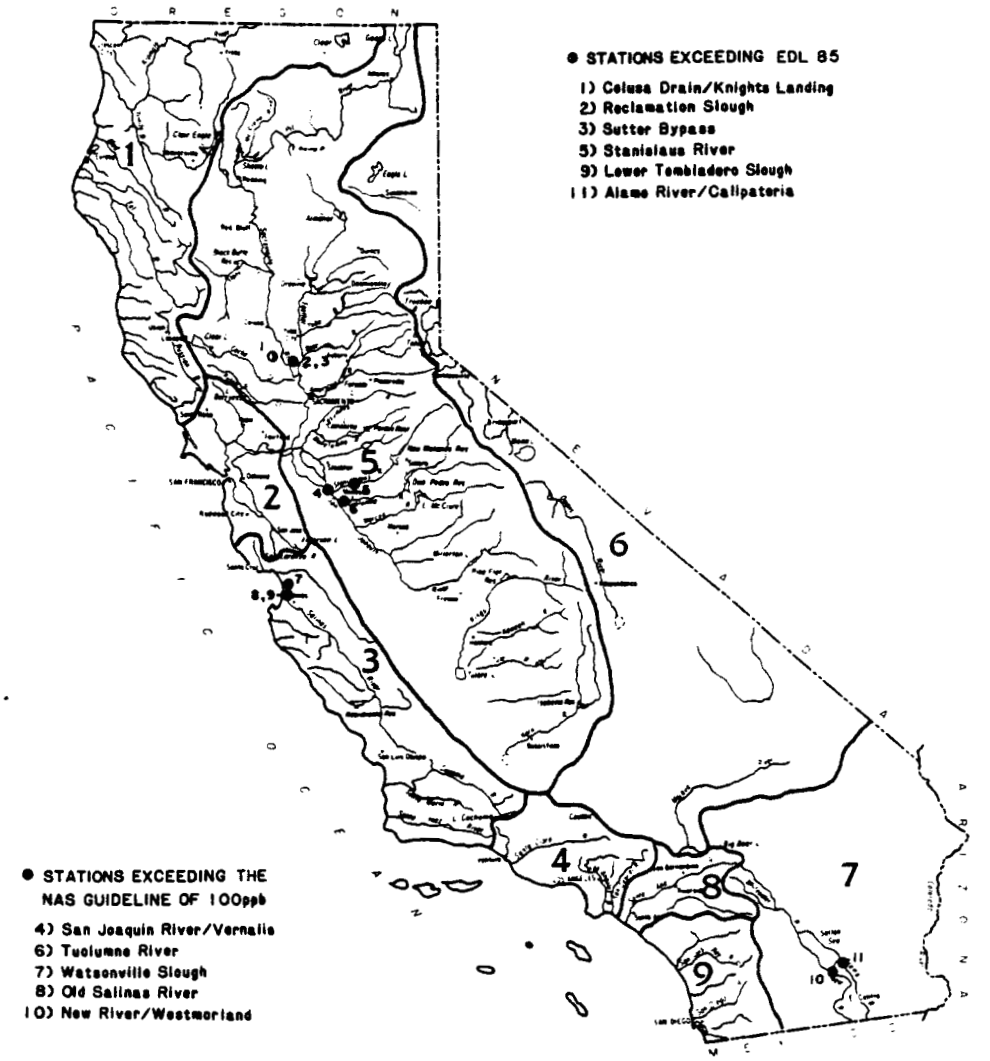


Fig. 80. Locations at which sampled biota (generally fish livers) exceeded the elevated data level (EDL 85, 5 ng g^{-1} wet weight) for total endosulfan, or exceeded the NAS guideline of 100 ng g^{-1} wet weight. Data from the Toxic Substances Monitoring Program, 1978-84, after SWRCB (1986).

Fig. 81. Locations at which sampled biota (generally fish livers) exceeded elevated data levels (EDL 85, 2 ng g^{-1} wet weight; EDL 95, 4 ng g^{-1} wet weight) for lindane (gamma-HCH). Data from the Toxic Substances Monitoring Program, 1978-84, after SWRCB (1986).

Fig. 82. Locations at which sampled biota (generally fish livers) exceeded elevated data levels (EDL 85, 2 ng g^{-1} wet weight; EDL 95, 7 ng g^{-1} wet weight) or the NAS guideline (100 ng g^{-1} wet weight) for hexachlorobenzene. Data from the Toxic Substances Monitoring Program, 1978-84, after SWRCB (1986).

Fig. 83. Locations at which sampled biota (generally fish livers) exceeded the NAS guideline of 100 ng g^{-1} wet weight or the FDA action level of 5000 ng g^{-1} wet weight for toxaphene. Data from the Toxic Substances Monitoring Program, 1978-84, after SWRCB (1986).

Striped bass also reflect the general pattern of pesticide use in the Central Valley, exhibiting elevated concentrations of aldrin, dieldrin, chlordane, hexachlorobenzene, dacthal (Whipple et al., 1983), and toxaphene (Crosby et al., 1983) compared to the same species from Coos River, Oregon. Korn and Earnest (1974) have shown that 96-hour LC50 values for striped bass for many of these compounds are below 10 $\mu g\ L^{-1}$, with endrin, endosulfan, DDT, and dursban exhibiting LC50 values below 1 $\mu g\ L^{-1}$. The possible local impacts of pesticides on striped bass are further considered in section V of this report.

Finally, it is notable here that Ohlendorf and Miller (1984) detected dieldrin and hexachlorobenzene in relatively small amounts in waterfowl from the Delta and San Joaquin Valley. This is not surprising, in view of the data on fish cited above.

Summary

Organochlorines other than PCBs and the DDT group of compounds have been generally poorly characterized in the Bay-Delta. The few studies which are available clearly indicate that the past or present use of pesticides in the Bay catchment gives rise to significant contamination of the estuary currently. The compounds which are most commonly identified to be enriched in the Bay-Delta or its catchment include dieldrin (although its precursor aldrin is less often found), chlordane, and toxaphene. Smaller but significant amounts of various other pesticides (e.g. hexachlorobenzene, endosulfan, chlorbenside, dacthal, heptachlor and HCH isomers) are also present. The Lauritzen Canal constitutes a continuing Bay-side source of several of these

contaminants; this is believed to be residual pollution from the United Heckathorn Company plant, which formulated and packaged a range of pesticides at this site in the past.

It is hardly surprising that the San Francisco Bay-Delta is significantly contaminated by organochlorine pesticides, given its huge catchment area (153,000 km^2; see Conomos et al., 1985) and high proportion of agricultural land. In general, the level of contamination is relatively minor within the Bay-Delta itself (with the exception of PCBs and DDT and metabolites), and system-wide effects on biological resources are unlikely. Such profiles of contamination are reminiscent of those for trace metals, and presumably depend largely on the high tidal prism of the Bay and residual freshwater inflows, both of which serve to flush the Bay and reduce contaminant levels within the system. Nevertheless, it should be noted that in areas of particular organochlorine enrichment, adverse effects on biological resources of the estuary are likely, as this group of compounds is of great direct toxicity to biota and of high bio-accumulative capacity.

IV. HYDROCARBONS IN THE BAY-DELTA

A. INTRODUCTION

Hydrocarbons are important contaminants of aquatic environments, with respect to both acute pollution (from spills) and low-level chronic contamination. Discussion of hydrocarbons in the San Francisco Bay-Delta ecosystem is prefaced here by brief notes on the classes of these compounds present in aquatic environments and on the difficulties encountered in their analysis in environmental samples.

Classes of Hydrocarbons

Hydrocarbons enter aquatic ecosystems from a variety of sources, which mostly relate to the use, transport, and combustion of fossil fuels. Hydrocarbon compounds arising from petroleum, gas, coal, oil shales and their products or combustion, in addition to compounds which are derived from these in the environment, are the subject of this section. Petroleum hydrocarbons *per se* are emphasized somewhat, because of the large quantities of these reaching the world oceans (5 to 10 million tonnes annually; see NAS, 1975).

Crude petroleum contains a highly complex mixture of hydrocarbons, in addition to smaller amounts of asphaltenes; organic compounds containing nitrogen, sulfur, and oxygen; and trace metals in complexed and uncomplexed forms (Kallio, 1976; Posthuma, 1977). The hydrocarbons are present in two main forms, comprising the aliphatic and aromatic compounds. Blumer *et al.* (1972) and various other authors (e.g. Farrington *et al.*, 1976; Connell and Miller, 1984) further separated the hydrocarbons into

several categories, as discussed below (see Fig. 84). Structures of some of the more important compounds are shown in Fig. 85. The following discussion emphasizes the origin of each class of hydrocarbon, as this is relevant to whether its existence in aquatic environments is due to the activities of Man or is a natural phenomenon.

* n-Alkanes in petroleum hydrocarbons are present as a series of compounds from C_1 to beyond C_{60}, with a ratio of approximately one between components with odd numbers of carbon atoms and those with even numbers. Biogenic n-alkanes are synthesized by many organisms; generally, compounds with odd numbers of carbon atoms predominate in these naturally-produced hydrocarbons, although bacteria, sponges, and corals do not exhibit this preference. In phytoplankton, n-alkanes with 15,17,19, and 21 carbons predominate.
* Petroleum also contains branched alkanes or iso-alkanes, with a variety of isomers being present. These compounds are also found in organisms; for example, pristane is moderately abundant in fish.
* The last aliphatic group is the cycloalkanes or naphthenes, which comprise a complex mixture of compounds with both substituted and unsubstituted rings. The former ring type is more common than the latter, and so-called "terpenes" (hydrocarbons with between one and three non-aromatic rings) are present in terrestrial plants.
* Aromatic hydrocarbons exist as naphthaeno-aromatics (with mixed subunits, which may include aromatic and cycloalkane rings), and as mono-, di-, and poly-aromatic compounds, which

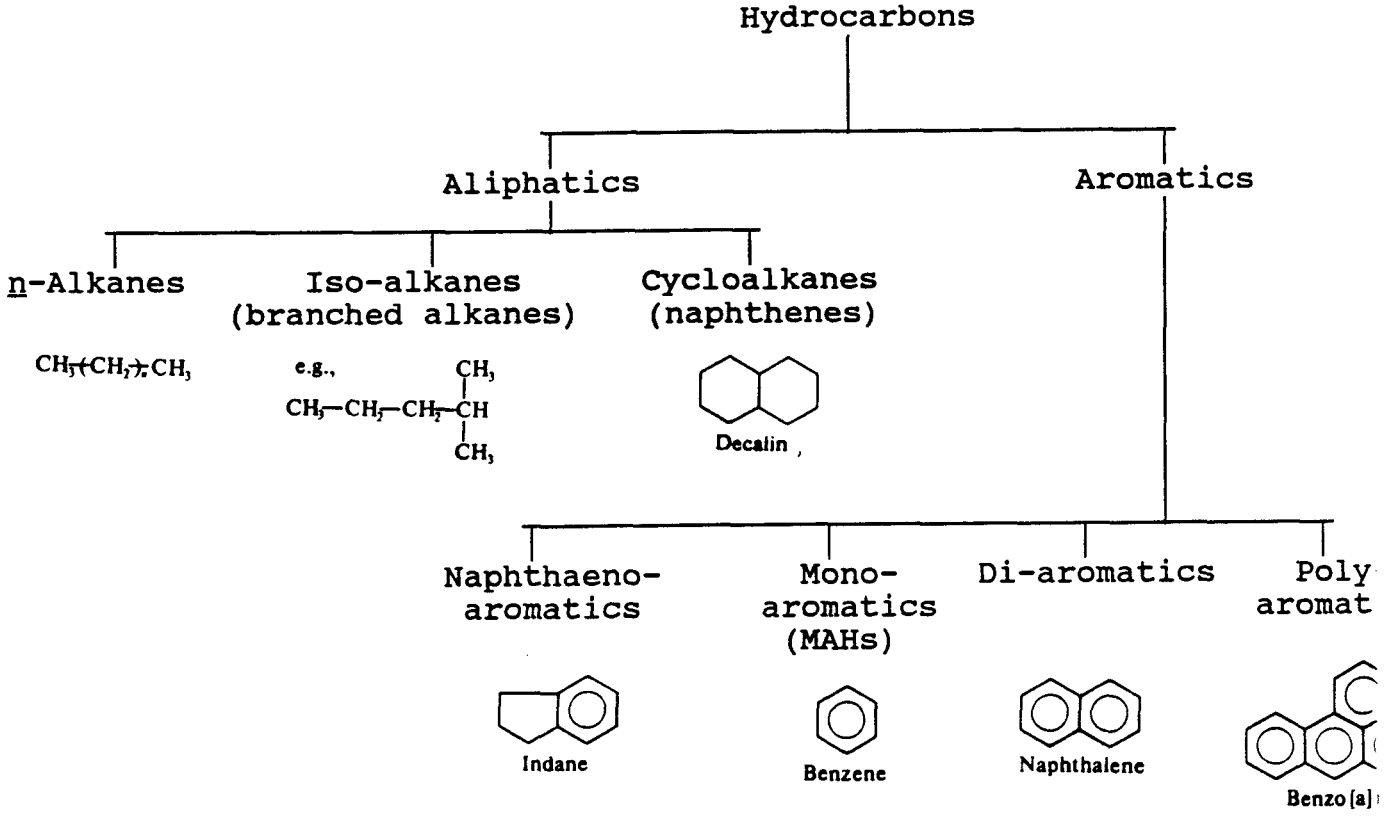


Fig. 84. Major classes of hydrocarbons and generic or specific examples of their structures. The di-aromatics are often included in PAHs as a single class. After Connell and Miller (1984).

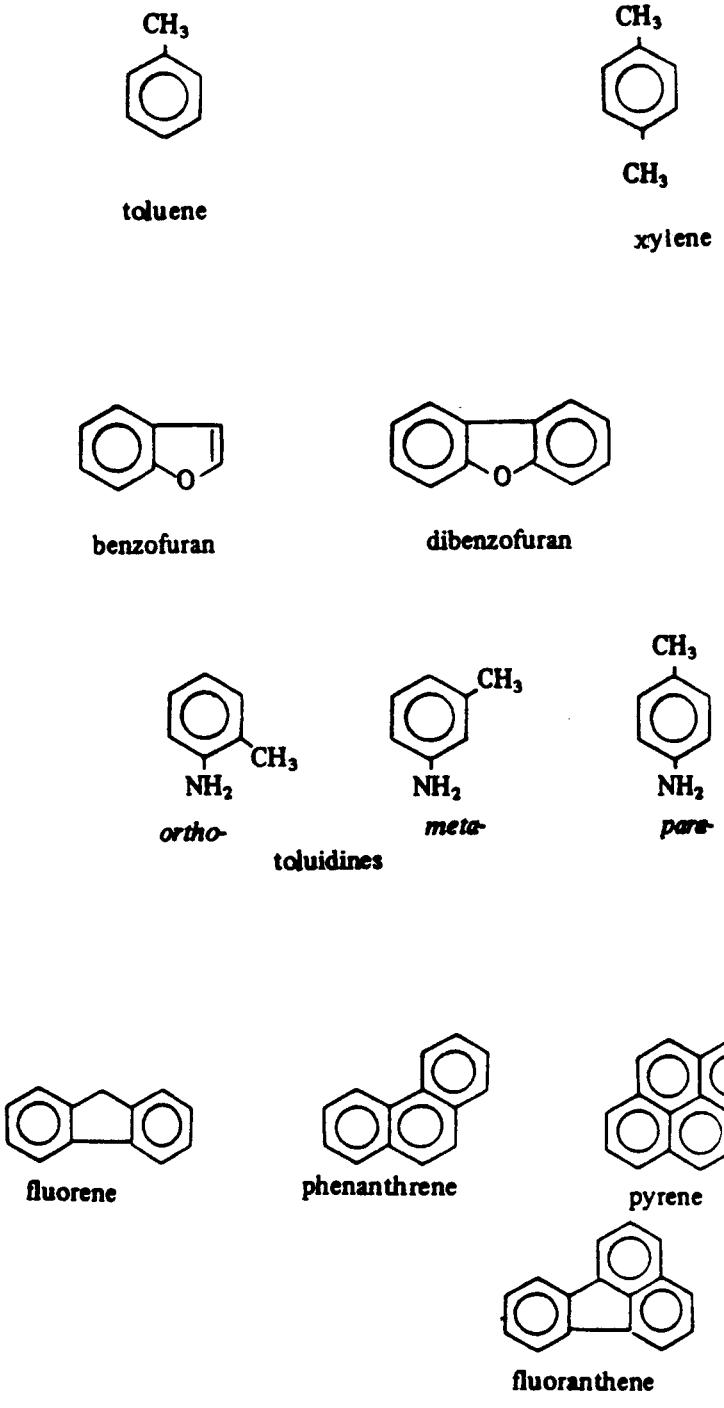


Fig. 85. Chemical structures of some hydrocarbons which are of significance as contaminants of aquatic ecosystems.

differ in the number of rings present. Alkyl substitutions on these various rings give rise to a large number of compounds, the analytical separation of which is highly taxing. Some terrestrial plants contain aromatic hydrocarbons naturally, but polyaromatic hydrocarbons (PAHs) are not synthesized by most marine organisms, at least in quantity.

* The alkenes or olefins should also be mentioned. These are generally not found in crude oils, but are formed by the "cracking" process used to refine such oils. Alkenes are common in aquatic biota, being found naturally in many phyla. Squalene (found in shark and fish livers in particular) is one example of this group of compounds.

The Analysis of Hydrocarbons

There are three principal problems in the analysis of hydrocarbons in aquatic environments. These relate to the separation of compounds for their accurate analysis; to the availability of standards permitting the quantification of individual compounds; and to the identification of hydrocarbons as anthropogenic rather than natural in source.

It is evident from the discussion above on the classes of hydrocarbons present in aquatic ecosystems that a great number of closely-related compounds may be present. Thus, for example, Malins et al. (1982, 1984) found over 500 aromatic hydrocarbons in sediments from Puget Sound, in addition to large numbers of halogenated compounds. The separation of these compounds must occur prior to their quantification. Despite improvements in techniques in the last decade (largely through the introduction

of glass capillary gas chromatography and high performance liquid chromatography), considerable problems remain to be solved in this area (NAS, 1975, 1980; Farrington et al., 1976; Connell and Miller, 1984; Malins et al., 1984). Many authors thus continue to report data concerning "unresolved complex mixtures" (UCM) of hydrocarbons, due to inadequate separation of components. The interpretation of the toxicological significance of such data is impossible in many cases. It should also be noted here that these analytical problems continue to give rise to quality control and quality assurance difficulties. Intralaboratory precision in hydrocarbon analysis frequently exhibits coefficients of variation of 25-50% (Malins et al., 1984), and comparisons between laboratories give rise to a large scatter in reported values, even when similar or identical techniques are employed.

Although many individual compounds can be adequately separated for analysis using newly developed techniques (for an example, see Fig. 86), their precise quantification may be impossible due to the lack of commercial standards. Only a few hundred such standards are presently available, to provide reference mass spectra against which the spectra of compounds isolated from environmental samples may be matched. This constrains the ability of the chemist to interpret data; many of the hydrocarbons found in gas chromatographic analyses simply cannot be fully identified.

In some cases, however, certain hydrocarbons can be both adequately separated from other related compounds and accurately quantified against available standards. Nevertheless, an

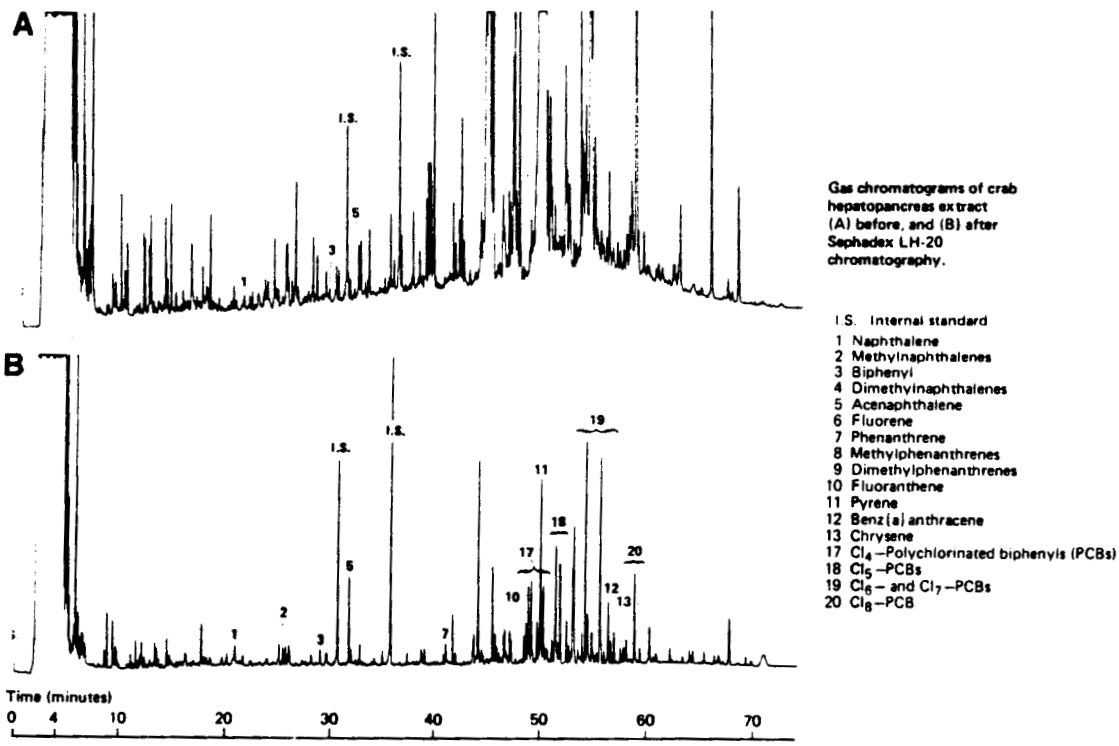


Fig. 86. Example of high resolution glass capillary gas chromatogram of unsaturated hydrocarbons extracted from the hepatopancreas of the crab Cancer gracilis. (A) Analysis after isolation by silica gel chromatography, showing overlapping peaks and generally inadequate separation of compounds. (B) Analysis subsequent to further chromatography on Sephadex LH-20 column, showing improved separation of compounds. After Malins et al. (1984).

additional problem frequently frustrates data interpretation at this stage. Thus, it is often difficult to be certain that a hydrocarbon present in an environmental sample is derived from an anthropogenic source (combustion of fossil fuels, petroleum hydrocarbon spill, etc.). Many hydrocarbons are found in quantity both naturally and through environmental contamination by Man, and the assignation of such compounds found in environmental samples to anthropogenic or biogenic sources is frequently a matter of judgement rather than exactitude. While certain clues to the origin of hydrocarbons can be used (e.g. odd-carbon to even-carbon ratios among the n-alkanes; the presence of certain types of triterpenes or steranes), it is often the case that both natural sources and those related to contamination by fossil fuels exist, giving rise to intermediate patterns of relative hydrocarbon abundance which are difficult to interpret.

B. HYDROCARBONS IN THE SAN FRANCISCO ESTUARY

General

Given the considerable problems inherent in the accurate analysis of environmental samples for hydrocarbons, it is not surprising that this group of contaminants has in general received less attention than either the trace metals or organochlorines. However, several factors suggest that hydrocarbons are likely to be important contaminants in the San Francisco Bay-Delta. The first of these is the very high transport of crude oil through the Bay. Risebrough et al. (1978) reported that petroleum refineries in the Bay receive some

3 to 4% of the total crude oil transported annually by tankers throughout the world. While it has been demonstrated by several authors (e.g. NAS, 1975; Connell, 1982; see Table 44 for an example) that neither oil spills nor refinery effluents contribute very large percentages to overall hydrocarbon budgets, either globally or in most coastal embayments, the existence of such an industry within the Bay is undoubtedly accompanied by the potential for both chronic contamination by hydrocarbons and catastrophic spill-related pollution.

As shown in Table 44, the main sources of hydrocarbons in estuaries are frequently urban run-off, sewage treatment effluents, and industrial discharges. The first of these sources has received considerable study in Narragansett Bay (e.g. Van Vleet and Quinn, 1978; Hoffman et al., 1982, 1983, 1984) and elsewhere (e,g, Hunter et al., 1979; Eganhouse et al., 1981; Brown et al., 1985), but has not been extensively investigated in the San Francisco estuary. Similarly, there are no highly detailed data available to document the concentrations or total loads of individual hydrocarbons discharged to the Bay-Delta from sewage treatment plants or industrial discharges. Most such analyses concern "oil and grease" measurements, which are inadequate as a basis for the consideration of hydrocarbons in any detail.

The general paucity of quality information on hydrocarbon sources in the Bay-Delta is largely matched by data on these compounds in water, sediments, or biota. Most studies to date have concentrated on aromatic hydrocarbons of two types, the monoaromatics (MAHs) and the polyaromatics (PAHs). These

Table 44. Estimates of petroleum hydrocarbon discharges (kg day^{-1}) to the Hudson Raritan Estuary from various sources. After Connell (1982).

Source	Hydrocarbon load (kg day^{-1})	Reliability[a]
Sewage treatment effluents	35,000	Moderate
Oil refinery discharges	1,300	Moderate
Industrial discharges other than refineries	17,000	Low
Oil spills	1,500	Moderate
Atmospheric deposition	2	Low
Urban and rural run-off	37,000	Moderate
Total	92,000	

[a]Reliability based on amount and quality of available concentration and flow data.

fractions are generally the most toxic and most persistent of the components of crude oils, and MAHs in particular are also the most water-soluble. Whipple et al. (1981) reviewed the effects of MAHs on fish, emphasizing data on compounds such as benzene, toluene, and xylenes. It was noted that MAHs are extensively used in industry (e.g. in the synthesis of chemical products, including pesticides; as solvents; and as automotive and aviation fuels). Crude oils vary in their content of aromatic hydrocarbons from 0.2 to 7.4% (Jewell et al., 1972; Connell and Miller, 1984), and MAHs may constitute 20-50% of the water-soluble fraction of crude oil. These compounds are accumulated directly from the water column by biota, with accumulation from food being minor. Their half-lives are generally short in organisms, i.e. they are excreted (and in some cases also metabolized) rapidly in uncontaminated conditions. Data concerning tissue distributions and toxicities of MAHs will be discussed in section V of this report, specifically in relation to striped bass (Morone saxatilis) and starry flounder (Platichthys stellatus).

PAHs are obviously closely related to MAHs, differing in the number of rings present. Some authors differentiate di-aromatics (with two rings) from polyaromatics (with three or more rings), but as used here, PAHs will include both these classes. These compounds have diverse origins, but are mostly produced by the pyrolysis of organic matter and by generation in sedimentary organic material and fossil fuels. Neff (1979) has discussed PAH formation by the pyrolysis and incomplete combustion of organic matter; Connell and Miller (1984) provided a more general

overview of PAH sources in the environment. The two major sources of PAHs may be differentiated to some extent by considering the degree of alkyl substitution of individual compounds (e.g. Risebrough et al., 1980). PAHs in petroleum are generally substituted in nature, containing one or more methyl or ethyl groups (Blumer and Youngblood, 1975). By contrast, PAHs formed as combustion products (e.g. by automobiles, forest fires, burning of fossil fuels) contain greater amounts of the unsubstituted compounds.

Data on hydrocarbons in the Bay-Delta are mostly limited to recent analyses of these contaminants in sediments and biota, especially fish. Risebrough et al. (1978) noted the paucity of adequate information on hydrocarbons available to the late 1970s, but considered that these compounds were nevertheless likely to be important in the estuary.

Hydrocarbons in Bay-Delta Sediments

The concentrations of hydrocarbons in Bay-Delta sediments have not been well characterized. Guard et al. (1983) reviewed early data, which mostly involved "total hydrocarbon" measurements. These authors also reported the existence of a variety of hydrocarbon types in sediments from the Pinole Point and Point San Pablo areas of the Bay. The hydrocarbons found included both biogenic and probable anthropogenic compounds; n-alkanes and PAHs were well represented, but no compounds were individually quantified. It was also noted that crabs from San Francisco Bay generally contained higher levels of n-alkanes and aromatic hydrocarbons than did those from other coastal areas of

California (Table 45), but the lack of resolution of individual components and the use of several species in the various locations constrains interpretation of these data.

Chapman et al. (1986) analyzed sediments from three sites in the Bay (San Pablo Bay, Oakland, and Islais Creek) for PAHs; in total, 17 individual compounds were quantified. This is the most complete and reliable database on sediment hydrocarbons published to date for the Bay; the results are shown in Fig. 87. It is evident that for all hydrocarbons studied, Islais Creek samples were the most contaminated, followed by Oakland and San Pablo Bay in descending order of concentration. The levels of enrichment of a number of compounds (phenanthrene, chrysene, benzopyrenes, benzo(a)anthracene, fluoranthene, and pyrene) were generally indicative of considerable contamination of the Bay, particularly at Islais Creek. At least some of these compounds [e.g. benzo(a)pyrene and benzo(a)anthracene] have been found to be carcinogenic to laboratory mammals (Neff, 1979). It is also notable that many of these PAHs found to be enriched in Bay sediments are known to be present at significant levels in urban run-off. The Nationwide Urban Runoff Program found phenanthrene, chrysene, anthracene, fluoranthene, and pyrene to be the most frequently reported PAHs in samples of urban run-off (Cole et al., 1984).

NOAA (1987) reported data for hydrocarbons in sediments only as "total aromatics", without information for individual compounds. Nevertheless, these data serve to place the Bay-Delta in perspective with respect to its degree of contamination by aromatic hydrocarbons. The results of the 1984 Benthic

Table 45. Concentrations (means, $\mu g\ g^{-1}$ dry weight) of n-alkanes and aromatic hydrocarbons in whole crabs or their tissues for a variety of crab species from sites in California. After Guard et al. (1983).

Location	Species	Tissue	n-Alkanes	Aromatic hydrocarbons
California coast				
Santa Cruz Pier	Cancer antennarius	Hepatopancreas	<7	<7
Pigeon Point	Cancer antennarius	Hepatopancreas	52	26
		Muscle	18	<7
Farallon Islands	Cancer magister	Hepatopancreas	80	43
		Muscle	14	11
Tomales Bay	Hemigrapsus oregonensis	Whole Crab	<1.4	ND[a]
	Hemigrapsus oregonensis	Whole Crab	14	2
San Francisco Bay				
Oakland Harbor	Cancer antennarius	Hepatopancreas	231	81
		Muscle	30	8
North Bay	Cancer antennarius	Hepatopancreas	75	43
		Muscle	30	11
North Bay	Cancer antennarius	Hepatopancreas	193	57
North Bay shore	Hemigrapsus oregonensis	Whole Crab	20	7
Point San Pablo	Pagarus samuelis	Egg mass	1540	1460

[a]ND: No Data.

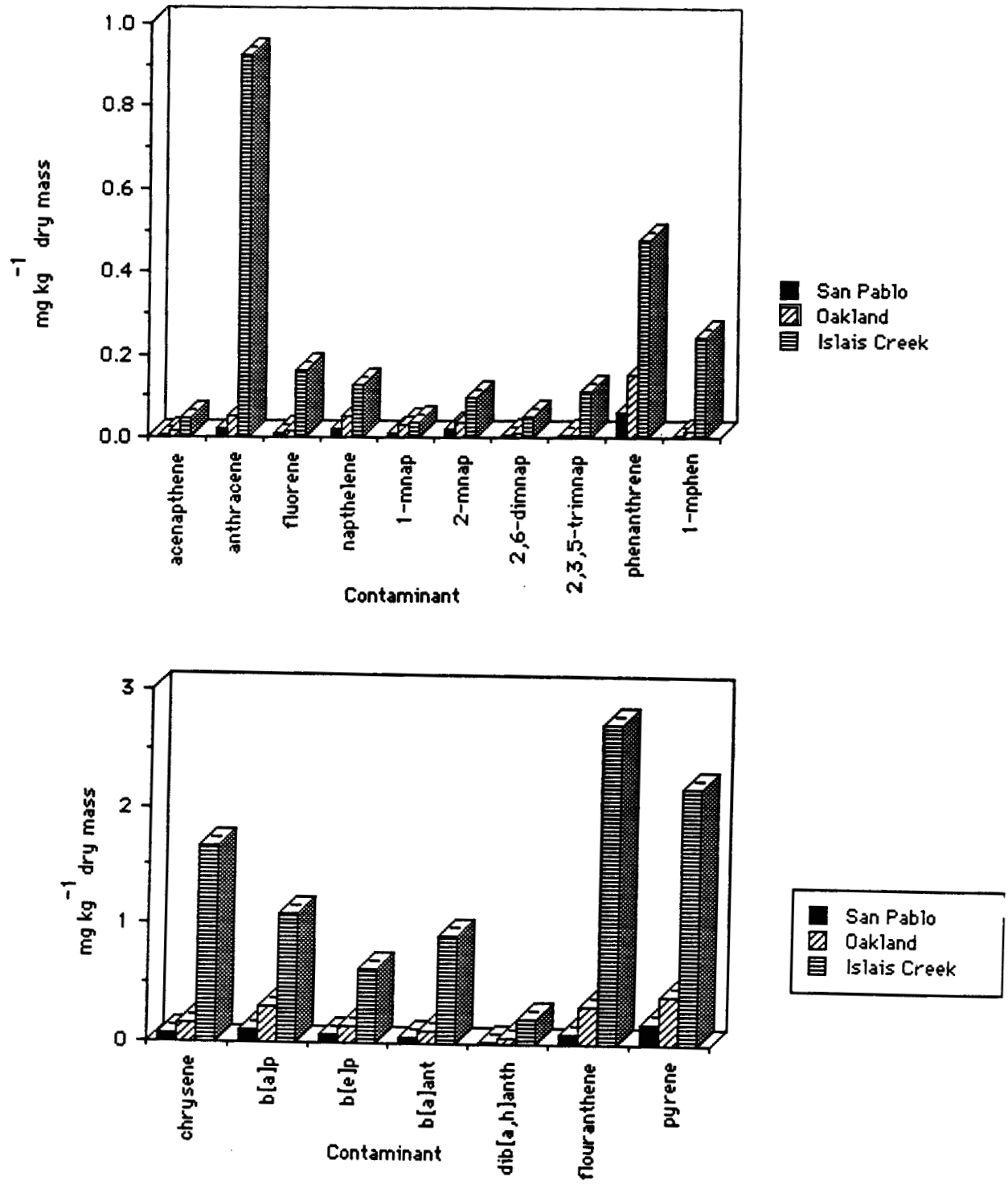


Fig. 87. Concentrations of PAHs (ng g^{-1} dry weight, means±standard deviations) in surface (upper 2 cm) sediments of San Pablo Bay, Oakland and Islais Creek After Chapman et al. (1986).

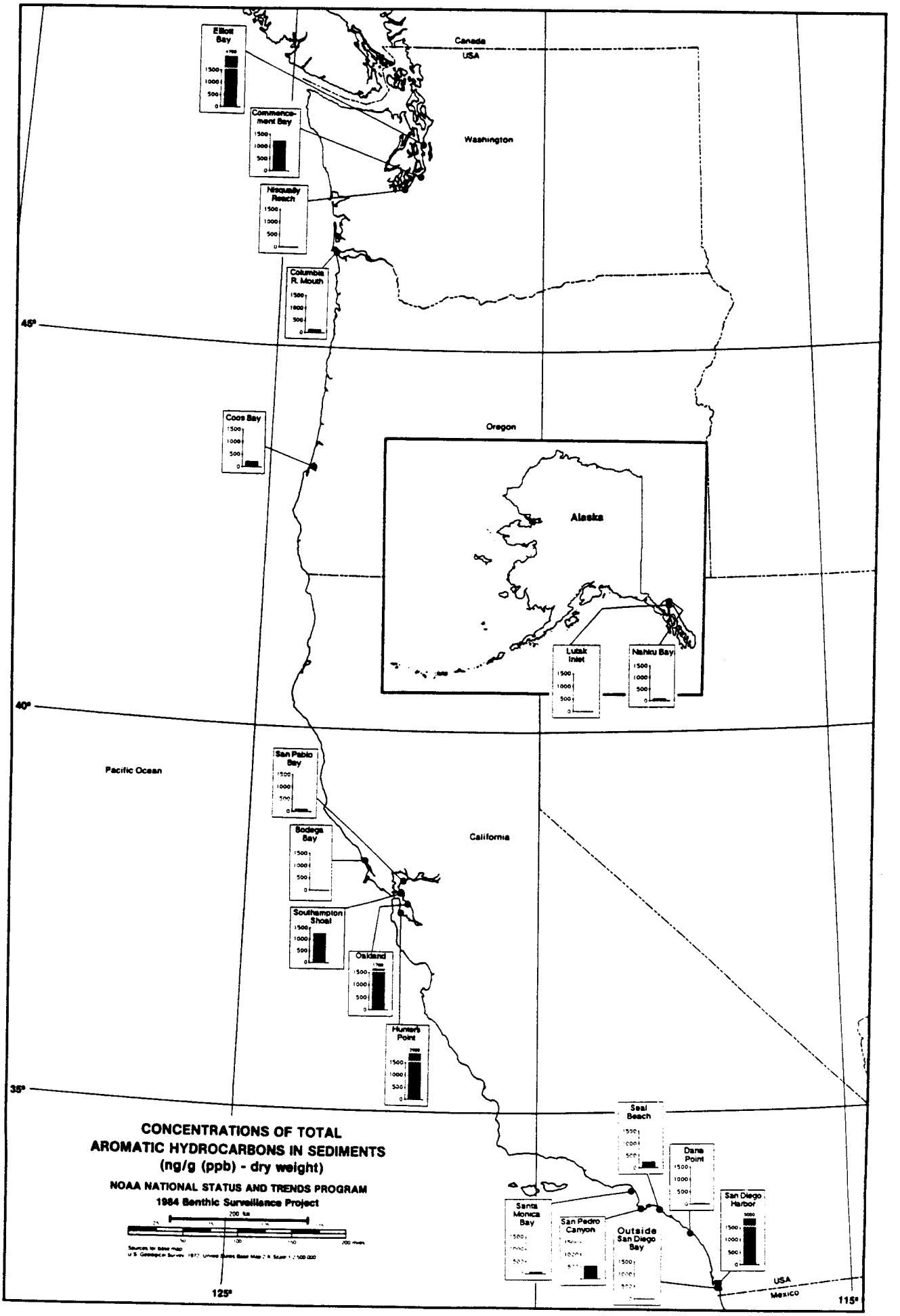
Surveillance Project for Pacific coast sediment samples are shown in Fig. 88. A general agreement with the data of Chapman et al. (1986) cited above is evident, San Pablo Bay sediments being less contaminated by total aromatics than sediments from sites further south (Southampton Shoal, Oakland, Hunter's Point). The latter three sites exhibited total aromatic levels exceeding 1000 ng g^{-1} dry weight, which should be considered indicative of considerable contamination. Only 34% (15 of 44) of the sites surveyed throughout the USA by NOAA (1987) for aromatic hydrocarbons exceeded this level in sediments.

It should also be noted here that Spies et al. (1985a, 1985b) have reported data for PAHs in sediments from the San Pablo Bay, Richmond, Berkeley, Oakland, and Alameda regions. Considerable intra-location variation between samples was found for individual PAHs, suggesting that the Bay sediments are spatially heterogeneous over small distances in respect to their hydrocarbon content. Similar differences between samples from closely-spaced locations were noted for organochlorine levels (ΣDDT and PCBs). If this is generally the case, improving the characterization of hydrocarbon distributions within Bay-Delta sediments does not promise to be a simple task.

One final dataset concerning PAHs in Bay sediments may be mentioned here. These results are as yet unpublished, but concern analyses of PAHs in sediments from 10 sites in South Bay, performed by the EPA laboratory in Newport, Oregon (Baumgartner et al., unpublished manuscript). The results are summarized in Fig. 89, as sums of low molecular weight PAHs (those with three rings or less) and of high molecular weight PAHs (those with four

Fig. 88.

Concentrations (ng g^{-1} dry weight) of total aromatic hydrocarbons in surface sediments of locations on the Pacific coast of the USA. After NOAA (1987).


Elliot Bay
Commencement Bay
Nisqually Reach
Columbia R. Mouth
Coos Bay
Lutak Inlet
Nahku Bay
San Pablo Bay
Bodega Bay
Southampton Shoal
Oakland
Hunters Point
Seal Beach
Dana Point
San Diego Harbor
Santa Monica Bay
San Pedro Canyon
Outside San Diego Bay
Canada
USA
Washington
Oregon
Alaska
California
Pacific Ocean
Mexico
48°
40°
35°
125°
115°
CONCENTRATIONS OF TOTAL
AROMATIC HYDROCARBONS IN SEDIMENTS
(ng/g (ppb) - dry weight)
NOAA NATIONAL STATUS AND TRENDS PROGRAM
1984 Benthic Surveillance Project

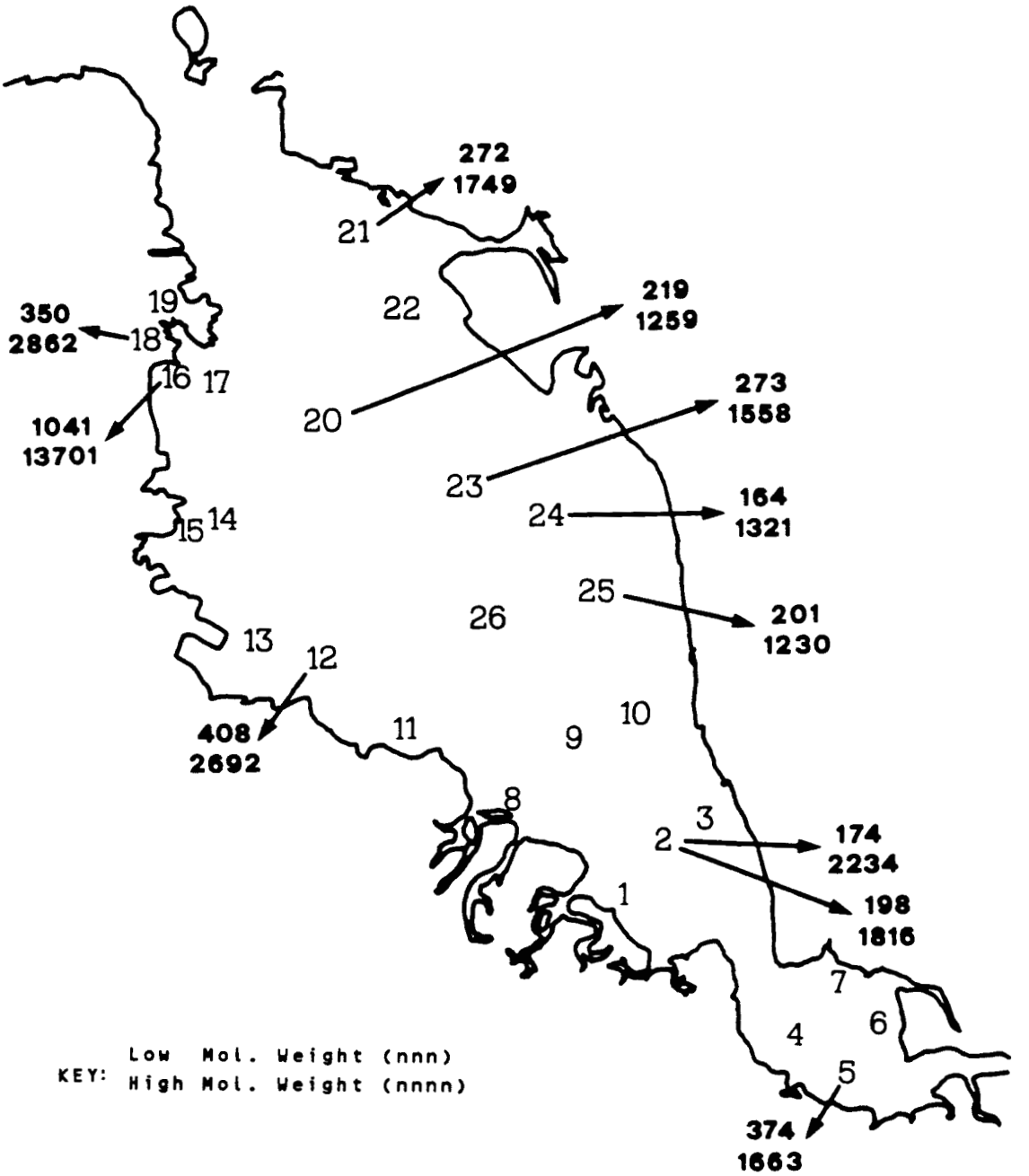


Fig. 89. Map of South Bay, showing concentrations of low and high molecular weight PAHs (ng g^{-1} dry weight) in sediments from 10 sites. Replicates taken at site 2. Unpublished data from the EPA laboratory, Newport, Or (Baumgartner et al., unpublished manuscript).

rings or more). The ratio between these two groups of compounds was generally similar at all sites. Sediments from site 16 near Bayview Park were particularly contaminated, but significant levels of PAHs were found at all sites studied. The data compare well to the results of Chapman et al. (1986) and NOAA (1987) cited above. PAHs of highest abundance were generally fluoranthene, pyrene, benzo(a)anthracene, chrysene, benzofluoranthenes, benzo(a)pyrene, and benzo(g,h,i)perylene.

Hydrocarbons in Bay-Delta Biota

Data for hydrocarbons in Bay-Delta biota are restricted to analyses of bivalve molluscs and fish, except for the details discussed above concerning crab analyses.

Little useful data on hydrocarbons in San Francisco Bay mussels were reported in the U.S. Mussel Watch studies between 1976 and 1978 (Goldberg et al., 1978; Farrington et al., 1982, 1983), and hydrocarbons are not analyzed for routinely in the State Mussel Watch Program. However, Risebrough et al. (1980) reported data for the 1977-78 mussel watch studies along the California coast. Mussels (Mytilus edulis) from San Francisco Bay sites exhibited quite high levels of hydrocarbons. The pattern of contamination, as determined by consideration of the unresolved complex mixture, of odd:even carbon ratios in n-alkanes, and of phytane levels, suggested that petroleum compounds were a likely source of these elevated levels. It was estimated that about 500 kg of petroleum-related compounds were discharged to Bay waters daily from sewage treatment plants and industrial dischargers. In addition, Risebrough et al. (1980)

noted that mussels from several sites in the Bay contained detectable levels of PAHs, including phenanthrene, fluoranthene, pyrene, and chrysene. Particularly high concentrations of some PAHs in a mussel sample from Treasure Island may have been due to their uptake from creosote on the pilings to which they were attached. It is unfortunate that no later published data based upon improved analytical techniques (high performance liquid chromatography) exist for mussels, as these early studies do not adequately characterize hydrocarbons in the samples taken.

Studies on hydrocarbons in fish from the Bay-Delta generally confirm the conclusions reached in investigations of sediments and bivalves, cited above, showing significant contamination of the estuary by a range of these compounds. Most data are available on starry flounder, Platichthys stellatus, and striped bass, Morone saxatilis. Whipple et al. (1978) exposed P. stellatus to the water-soluble fraction of Cook Inlet crude oil, and demonstrated significant uptake of various hydrocarbons. MAHs (benzene and substituted benzenes, toluene, and xylene isomers), various cyclohexanes, and dicyclic aromatics related to naphthalene were all significantly accumulated by both liver tissues and mature ovaries of the flounders. Female flounders concentrated these hydrocarbons in ovaries, and levels in these tissues exceeded exposure concentrations by greater than two orders of magnitude. There was evidence of histological damage in both livers and ovaries, the latter involving accelerated maturation and the production of abnormal or dead eggs.

More recently, Spies et al. (1985a, 1985b) have analyzed starry flounders for PAHs, as part of extensive investigations on

the relationships between mixed-function oxidase activities in these fish, organic contaminants in fish tissues and sediments from the Bay, and reproductive success in P. stellatus. Levels of total PAHs were determined in flounder livers, using combined extracts from several individuals taken at each site. The analytical method employed (EPA method 610) involves a fluorescent detector in a high performance liquid chromatograph. Total PAHs (including their metabolites) were found in P. stellatus livers at concentrations of 0.14 $\mu g\ g^{-1}$ wet weight for San Pablo Bay samples, 2.6 $\mu g\ g^{-1}$ for fish from Berkeley, 1.4 $\mu g\ g^{-1}$ for Oakland fish, and 14.0 $\mu g\ g^{-1}$ wet weight in a small sample (4 individuals) from Alameda. These data cannot be strictly interpreted to reflect the relative environmental contamination at each site, as starry flounder are known to move around the Bay. However, it is clear that significant amounts of PAHs are present in the Bay, and it may be assumed that these are derived from anthropogenic sources.

The focus of most of the research on striped bass in the Bay-Delta has concerned MAHs, rather than PAHs. Both MAHs and cycloalkanes are known from laboratory studies to be toxic to striped bass when they are present at high concentrations in ambient waters (Benville and Korn, 1977; Benville et al., 1985). The kinetics of benzene and other MAHs have also been widely studied in striped bass and other species (e.g. Korn et al., 1976; Eldridge et al., 1978; Whipple et al., 1981), as have the physiological effects of MAHs on fish (e.g. Brocksen and Bailey, 1973; Eldridge et al., 1977, 1978; MacFarlane and Benville, 1986). The possible toxicological significance of MAHs in

striped bass from the Bay-Delta will be discussed in section V of this report; data considered here are only those which relate to contaminant concentrations found in the fish.

Analytical results for benzene (alone), total MAHs (including benzene), and cycloalkanes in striped bass from the main Delta rivers and Coos River in Oregon were reported for the years 1978-1980 by Whipple et al. (1983) and Jung et al. (1984). These data are shown in Tables 46 to 48 (liver tissues) and 49 to 51 (gonads); the same results are summarized diagramatically in Fig. 90. It is clear from these results that very considerable variation was noted between individual fish sampled in any one year at any of the three locations. In many cases, the number of striped bass exhibiting hydrocarbon levels above the detection limits was a small percentage of the total number of fish analyzed. Those individuals exhibiting detectable concentrations of hydrocarbons often contained unusually elevated levels, however, and were thus "outliers" in the population sampled. It was noted that correlations existed between classes of hydrocarbons in the fish sampled, i.e. those individuals exhibiting high levels of benzene or total MAHs generally also contained elevated concentrations of cycloalkanes. However, the very widespread scatter in detected values among locations, and between years at each location, seriously hampers any attempt to confirm statistical differences in the datasets.

Striped bass are of course anadromous in nature, i.e. adults migrate annually from offshore marine waters through estuaries to the lower reaches of rivers to spawn. Little is known of the actual pathways taken by individual fish during this process, or

Table 46. Concentrations of benzene ($\mu g\ g^{-1}$ wet weight) reported for livers of prespawning adult striped bass (Morone saxatilis) in 1978-1980 at three locations. After Whipple et al. (1983).

Location	Year	Number analyzed	Number detected	Mean±S.D. of detected values	Range
San Joaquin River, CA	1978	71	48	0.256±0.303	ND-1.997
	1979	43	0	-	ND
	1980	32	0	-	ND
Sacramento River, CA	1979	43	2	2.282±1.848	ND-3.588
	1980	35	0	-	ND
Coos River, OR	1980	34	0	-	ND

ND: Not detected (detection limit not quoted, but about 0.01 or 0.02 $\mu g\ g^{-1}$ wet weight).

Table 47. Concentrations of monoaromatic hydrocarbons (MAHs, $\mu g\ g^{-1}$ wet weight) reported for livers of prespawning adult striped bass (Morone saxatilis) in 1978-1980 at three locations. After Whipple et al. (1983).

Location	Year	Number analyzed	Number detected	Mean±S.D. of detected values	Range
San Joaquin River, CA	1978	71	53	0.651±1.121	ND-5.735
	1979	43	2	3.539±4.344	ND-6.610
	1980	32	11	0.305±0.369	ND-1.246
Sacramento River, CA	1979	43	6	0.961±1.327	ND-3.588
	1980	35	19	0.765±1.936	ND-8.649
Coos River, OR	1980	34	21	1.878±2.232	ND-7.293

ND: Not detected (detection limit not quoted, but about 0.01 or 0.02 $\mu g\ g^{-1}$ wet weight).

Table 48. Concentrations of cycloalkanes ("alkyl cyclohexane", $\mu g\ g^{-1}$ wet weight) reported for livers of prespawning adult striped bass (Morone saxatilis) in 1978-1980 at three locations. After Whipple et al. (1983).

Location	Year	Number analyzed	Number detected	Mean±S.D. of detected values	Range
San Joaquin River, CA	1978	71	45	0.267±0.361	ND-1.567
	1979	43	16	1.259±0.680	ND-2.219
	1980	32	0	-	ND
Sacramento River, CA	1979	43	21	1.691±1.299	ND-5.030
	1980	35	1	5.039[a]	ND-5.039
Coos River, OR	1980	34	1	2.506[a]	ND-2.506

[a]Single value.
ND: Not detected (detection limit not quoted, but about 0.01 or 0.02 $\mu g\ g^{-1}$ wet weight).

Table 49. Concentrations of benzene ($\mu g\ g^{-1}$ wet weight) reported for gonads of prespawning adult striped bass (Morone saxatilis) in 1978-1980 at three locations. After Whipple et al. (1983).

Location	Year	Number analyzed	Number detected	Mean±S.D. of detected values	Range
San Joaquin River, CA	1978	71	2	0.854±1.179	ND-1.687
	1979	40	1	12.883[a]	ND-12.883
	1980	34	0	-	ND
Sacramento River, CA	1979	41	0	-	ND
	1980	33	0	-	ND
Coos River, OR	1980	37	0	-	ND

[a]Single value only.
ND: Not detected (detection limit not quoted, but about 0.01 or 0.02 $\mu g\ g^{-1}$ wet weight).

Table 50. Concentrations of monoaromatic hydrocarbons (MAHs, $\mu g\ g^{-1}$ wet weight) reported for gonads of prespawning adult striped bass (Morone saxatilis) in 1978-1980 at three locations. After Whipple et al. (1983).

Location	Year	Number analyzed	Number detected	Mean±S.D. of detected values	Range
San Joaquin River, CA	1978	71	30	0.139±0.376	ND-1.687
	1979	40	7	3.424±5.197	ND-12.883
	1980	34	13	0.161±0.098	ND-0.437
Sacramento River, CA	1979	41	12	0.235±0.260	ND-0.962
	1980	33	8	0.447±0.216	ND-0.674
Coos River, OR	1980	37	7	4.047±5.576	ND-12.725

ND: Not detected (detection limit not quoted, but about 0.01 or 0.02 $\mu g\ g^{-1}$ wet weight).

Table 51. Concentrations of cycloalkanes ("alkyl cyclohexane", $\mu g\ g^{-1}$ wet weight) reported for gonads of prespawning adult striped bass (Morone saxatilis) in 1978-1980 at three locations. After Whipple et al. (1983).

Location	Year	Number analyzed	Number detected	Mean±S.D. of detected values	Range
San Joaquin River, CA	1978	71	13	0.093±0.075	ND-0.208
	1979	40	4	4.203±3.985	ND-8.665
	1980	34	0	-	ND
Sacramento River, CA	1979	41	3	32.319±44.631	ND-83.690
	1980	33	0	-	ND
Coos River, OR	1980	37	0	-	ND

ND: Not detected (detection limit not quoted, but about 0.01 or 0.02 $\mu g\ g^{-1}$ wet weight).

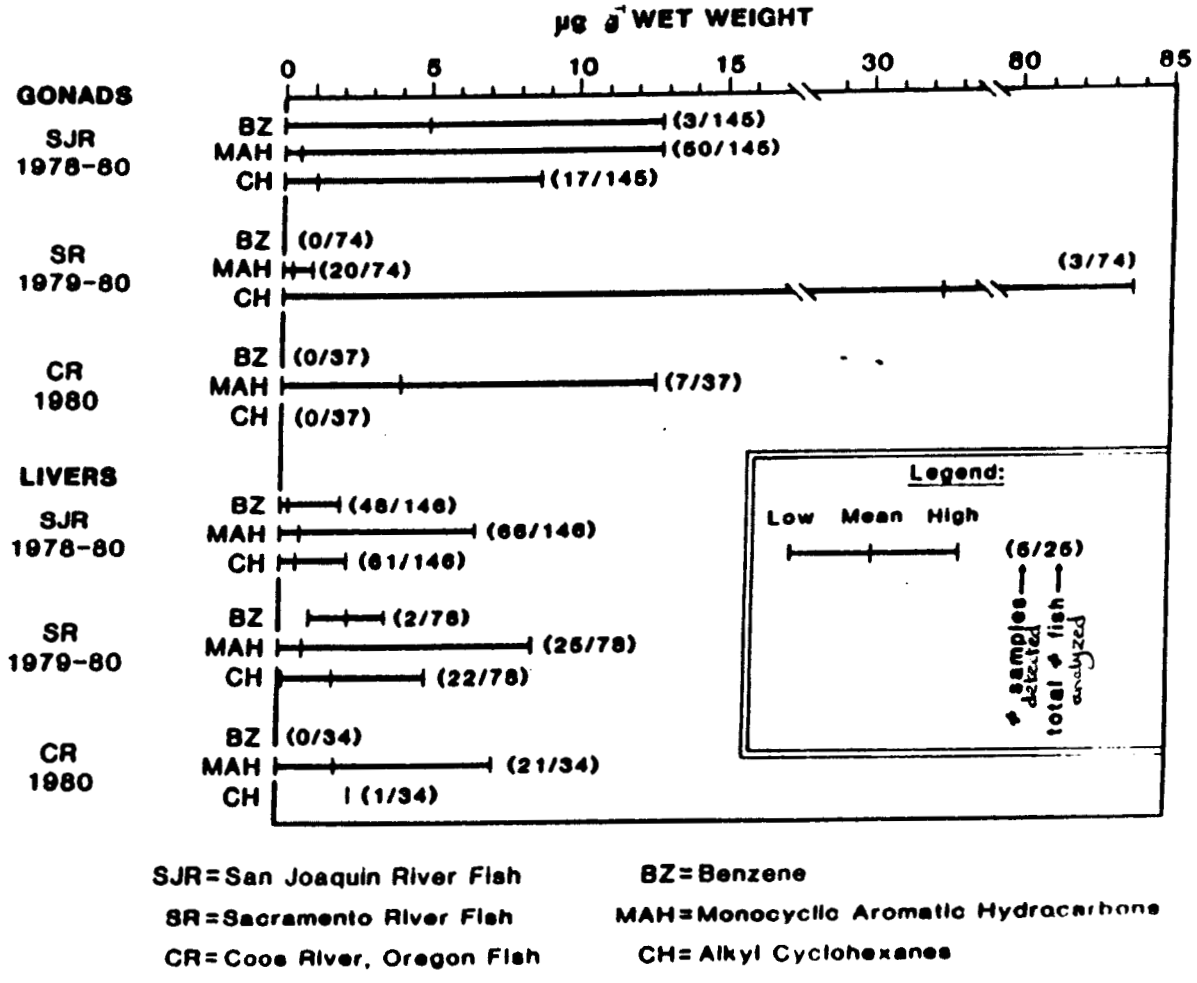


Fig. 90. Diagrammatic representation of the concentrations of benzene, total MAHs (including benzene), and cycloalkanes in livers and gonads of striped bass (Morone saxatilis) from three locations. (Data as in Tables 46-51, but presented diagrammatically). After Jung et al. (1984).

of variations between individuals in the length of time taken to migrate through the estuary. As noted elsewhere in this report, the concentrations of contaminants found in non-sedentary species are a complex function of their accumulation through space and time. Migratory species are an extreme case of this scenario, and the interpretation of the data shown in Tables 46-51 is exceptionally challenging. It is possible that the highly contaminated individuals were exposed to transient enrichment of MAHs prior to their capture, perhaps as a result of swimming through plumes of MAHs created by a spill or an effluent discharge. This might occur either during the spawning migration or in the lower reaches of the rivers. There seems to be no consistent difference among locations (even comparing Coos River fish to San Francisco individuals) or between years.

It must also be noted here that no details of analytical methodology or quality control could be found in publications concerning these data. The problems associated with hydrocarbon analysis in environmental samples have already been alluded to above. It is perhaps relevant that MAHs have been considered by some authors to be particularly difficult to accurately quantify (e.g. Cole et al., 1983, 1984).

C. SUMMARY

In general, hydrocarbons have received much less study in the San Francisco ecosystem than have trace elements or organochlorines. The paucity of data is related more to the difficulties inherent in the characterization of hydrocarbons in aquatic environments than to their potential importance. The

Bay-Delta receives and processes very large quantities of petroleum; this factor, coupled with the generally urbanized margins of the Bay, suggests that hydrocarbon contaminants are likely to be of significance locally.

Such data as are available on hydrocarbons in the Bay-Delta tend to corroborate the notion that elevated levels of these compounds are present, in both sediments and biota of the estuary. Concentrations of aromatic hydrocarbons (and particularly PAHs) are moderate to high in Bay-Delta sediments and organisms compared to other areas. It is unfortunate that no recent data are available on hydrocarbons in bivalve molluscs, as these would add significantly to our present understanding of the bio-availability of such contaminants in local waters. While the published analyses of certain fish suggest the presence of bio-available aromatic hydrocarbons, the possible or known movement of these species around or through the estuary constrains attempts to concisely interpret data with respect to defining local sources of these contaminants. It nevertheless remains possible that hydrocarbons are exerting detrimental effects on biological resources within the Bay-Delta. The possibility that such effects exist is considered further in the final section of this report, which follows below.

V. BIOLOGICAL EFFECTS OF BAY-DELTA CONTAMINANTS

It will be apparent from the foregoing review that much effort has been expended to document the concentrations of contaminants in the waters, sediment and biota of San Francisco Bay-Delta. There is clear evidence that certain contaminants are present at significantly elevated levels within the estuary.

However, the question of greatest importance concerns the impacts of these elevated toxicant levels on the biological resources of the Bay-Delta. Direct studies of this nature have been much less common than monitoring activities for contaminants. Nevertheless, some data are available, and these are reviewed in the present section.

Contaminants may exert impacts on one or more of a variety of resources in the estuary. This review considers possible effects on benthic infauna (i.e. sediment-dwelling organisms), on populations of fish and invertebrates, on birds, and on mammals, including Man. Finally, data from bioassays of effluents and sediments in the Bay-Delta are discussed.

A. THE BENTHOS OF THE BAY-DELTA

Studies of biological communities in the substrates of aquatic environments have long been considered a most useful tool in elucidating the "health" of marine or estuarine ecosystems, and in defining local or regional impacts due to effluent discharges or other disturbances. Classically, healthy benthic communities are expected to exhibit moderate biomass and high species diversity. Increasing stress due to organic enrichment is generally reflected in the benthos by a transition to reduced species diversity, often with higher biomass and numerical dominance by one or a few hardy or tolerant species. The effects of more toxic contaminants on benthic communities may vary from this classical pattern, and may be represented by the loss of sensitive species, leading to reduced biomass and lower species diversities. Such patterns become more extreme as stress on the benthos increases further; eventually, partial or complete defaunation occurs in severely degraded benthic environments.

The instability of estuarine environments is usually considered the prime factor leading to reduced numbers of benthic species in such areas compared to marine ecosystems. San Francisco Bay-Delta is no exception to this general rule. In addition, however, the Bay-Delta is relatively young in geological terms (Atwater, 1979), and is both geographically and faunistically isolated from other estuaries on the Pacific coast (Hedgpeth, 1968; Nichols and Thompson, 1985a). These factors are likely to further depress the numbers of benthic species present in the estuary.

It is known that great changes have occurred historically in

the benthos of the Bay-Delta (Nichols, 1979). Shellfish populations are believed to have been considerable until a few hundred years ago, when they declined (Nelson, 1909; Skinner, 1962). Hydraulic mining in the period between 1853 and 1884 gave rise to massive siltation of the upper catchment of the Bay, and eventually of the Bay-Delta itself (e.g. Hedgpeth, 1979; Nichols et al., 1986). This process, and the deliberate filling of marginal areas of the Bay-Delta for a variety of purposes, gave rise to radical alterations in the topography of the estuary (e.g. see Atwater, 1979; Atwater et al., 1979). The effects on tidal marshes have been particularly dramatic (Fig. 91). There can be no doubt that benthic communities were greatly affected by these changes, but no quantitative data exist to confirm this.

An additional factor which has given rise to massive changes in Bay-Delta benthos is the introduction of exotic species to the estuary. Carlton (1978, 1979) has documented the deliberate or accidental introduction of almost 100 species to the estuary since the mid-1800s. Most of these are benthic in nature, and now represent the great majority of individuals found on Bay substrates, accounting for an astonishing 95% or more of the biomass present in at least some areas (Nichols, 1979; Nichols and Thompson, 1985a; see Table 52 for an example).

It is thus clear that the present-day benthos of the Bay-Delta is very dissimilar to historical communities, having undergone major changes throughout the last several hundred years. Documentation of such changes essentially commenced in 1912, with the benthic surveys undertaken by the Albatross expedition (Nichols, 1973; 1979). A variety of surveys was

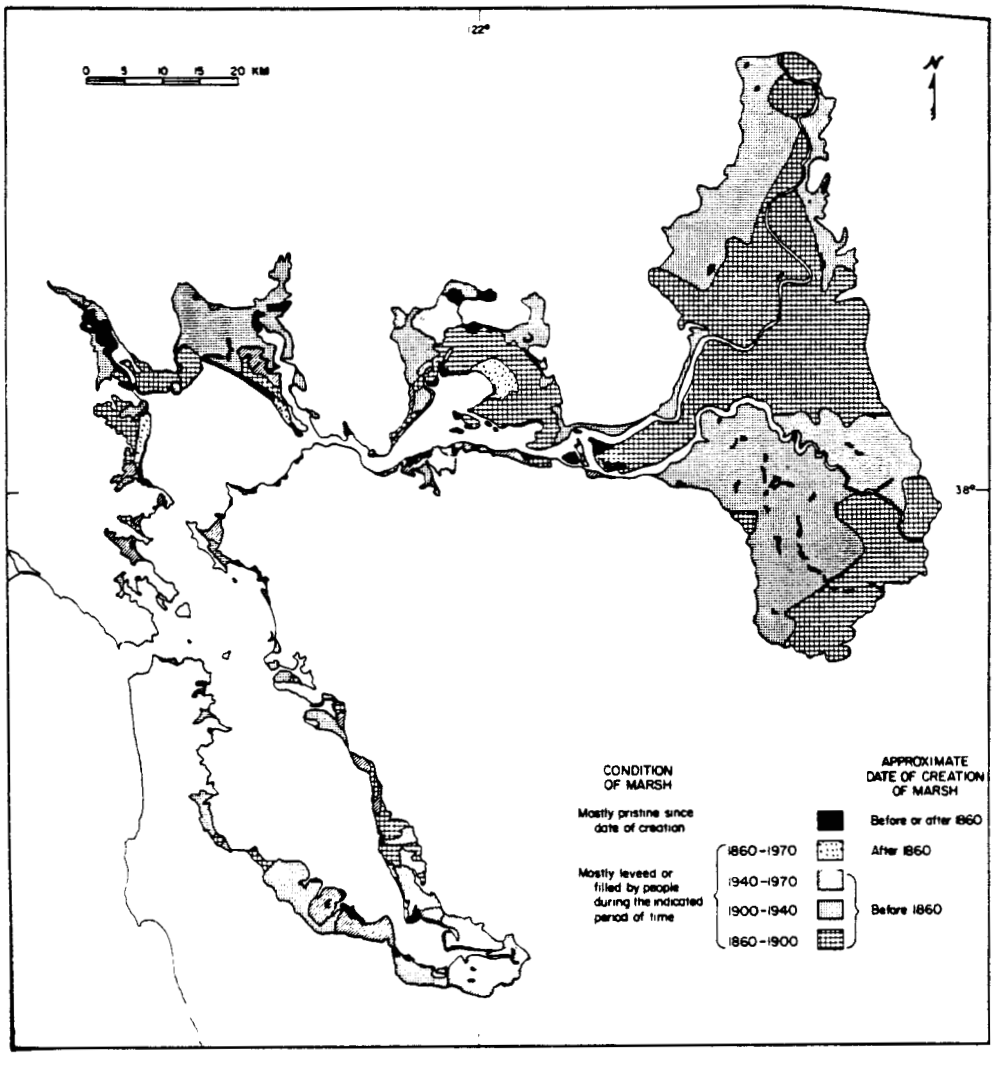


Fig. 91. Approximate historic changes in the aerial distribution of tidal marshes in the Bay-Delta. After Atwater et al. (1979).

Table 52. Macrobenthic species identified in a mudflat at Palo Alto, with notes on whether the species listed are native to the Bay-Delta or introduced from elsewhere, and on general abundance of each species. *common; **uncommon; ***rare; n, native; i, introduced; i?, possibly introduced; ? not known. After Nichols and Thompson (1985a).

Species	Status	Status reference	Comments
ANNELIDA			
Harmothoe imbricata***	n		
Eteone californica*	i?	Carlton 1978; Pettibone 1954	Probably E.
Sphaerosyllis sp.**	i?	Nichols unpubl.	Probably S. er
Nereis succinea*	i	Carlton 1978	
Glycinde sp.***	n		G. armigera/po
Marphysa sanguinea***	i	Carlton 1978	
Polydora ligni**	i	Carlton 1978	
Pseudopolydora kempi**	i	Carlton 1978	
Pygospio elegans***	n		
Streblospio benedicti*	i	Carlton 1978	
Tharyx sp.**	?		
Chaetozone sp.***	?		
Capitella capitata**	i	Carlton 1978	Possibly sibling
Heteromastus filiformis*	i	Carlton 1978	
Tubificoides brownae*	?		
Limnodriloides monothecus*	?		
Oligochaeta spp.***	?		
CRUSTACEA			
Ampelisca abdita*	i	Carlton 1978,1979	= A. miller
Corophium acherusicum*	i	Carlton 1978,1979	
Corophium insidiosum**	i	Carlton 1978,1979	
Corophium spp.*	i		Unident. fem
Grandidierella japonica*	i	Chapman and Dorman 1975	
Cyprideis sp.*	?		
Sarsiella zostericola*	i	Kornicker 1975	
Balanus improvisus***	i	Carlton 1978	
Cumella vulgaris***	?		
Tanais sp.***	i	Carlton 1978	
Synidotea laticauda**	i	Carlton 1978,1979	
MOLLUSCA			
Boonea bisuturalis*	i	Carlton 1978,1979	= Odostomia = M
Ilyanassa obsoleta**	i	Carlton 1978,1979; Hanna 1966	
Urosalpinx cinerea**	i	Carlton 1978,1979; Hanna 1966	
Gemma gemma*	i	Carlton 1978,1979; Hanna 1966	
*Macoma balthica**	n	Carlton 1978,1979	
Musculista senhousia**	i	Carlton 1978,1979; Hanna 1966	= Musculus
Mya arenaria**	i	Carlton 1978,1979; Hanna 1966	
CNIDARIA			
Anthozoa***	?		
PLATYHELMINTHES			
Turbellaria***	?		

undertaken between that time and the early 1970s (e.g. Sumner et al., 1914; Packard, 1918a, 1918b; Filice 1954a, 1954b, 1958, 1959; Painter, 1966; Storrs et al., 1969; Daniel and Chadwick, 1971). These early studies have been comprehensively reviewed by Nichols (1973), who points out a range of methodological deficiencies in the resulting data which seriously constrain their interpretation (see also Risebrough et al., 1978). Most of these concern variations or errors in sampling, taxonomic identification, and data interpretation. There can be no doubt that Nichols (1973) is correct in his opinion that these early data are only semi-quantitative at best; this is particularly the case where samples from different locations were collected non-synoptically.

However, the early studies nevertheless reached certain conclusions concerning the benthos of the estuary which remain broadly valid today. These relate largely to the effects of salinity and substrate texture and mobility in determining benthic community structures within the Bay-Delta. In addition, the data of Filice (1954a, 1954b, 1958, 1959) are persuasive that industrial outfalls and sewage discharges in Castro Cove were (then) significantly contaminating local areas of the Bay, leading in extreme cases to defaunation (and in less extreme cases to alterations of benthic diversities and species dominance patterns). Such effects are not documented at present in the Bay, at least in most areas. Luoma and Cloern (1982) provided convincing evidence of the general improvements in Bay-Delta water quality, subsequent to the introduction of adequate sewage treatment facilities in the 1960s and 1970s. As noted (somewhat

wistfully) by Nichols (1979), the present greater attention to effluent treatment has reduced local effects on benthic communities around outfalls considerably, although combined sewer overflows may still exert effects around the San Francisco peninsula (Hoffman and Meighan, 1984; Chapman et al., 1986).

Nichols (1979) provided reliable data on the general status of benthic communities in the Bay-Delta. Some of these results are summarized in Figs. 92 and 93. It is evident that the number of species present (Fig. 92) was greatest in Central Bay and offshore marine sediments, intermediate numbers being found in South Bay, and generally few species being present in the northern reach of the Bay. The low numbers of species in the latter area are a function of the high salinity fluctuations experienced in San Pablo Bay, Suisun Bay and the Delta. This pattern is standard for most estuaries (Boesch, 1977). The low species number in sediments near the Golden Gate is related to scouring effects of currents through this region.

In terms of biomass (Fig. 93), South Bay benthic communities exhibited the highest levels (although these were spatially highly variable), Central Bay being intermediate, and low biomass being found in benthos from the northern reach of the Bay. As noted by several authors (e.g. Conomos, 1979; Walters et al., 1985), South Bay is a generally more stable environment than the northern reach of the estuary. Its relatively poor flushing and high waste loading (Conomos, 1979) lead to moderate enrichment of primary producers (Cloern, 1979), which support members of the benthic communities. By contrast, phytoplankton abundance may be regulated in the northern reach of the Bay by benthic grazing (Nichols, 1985

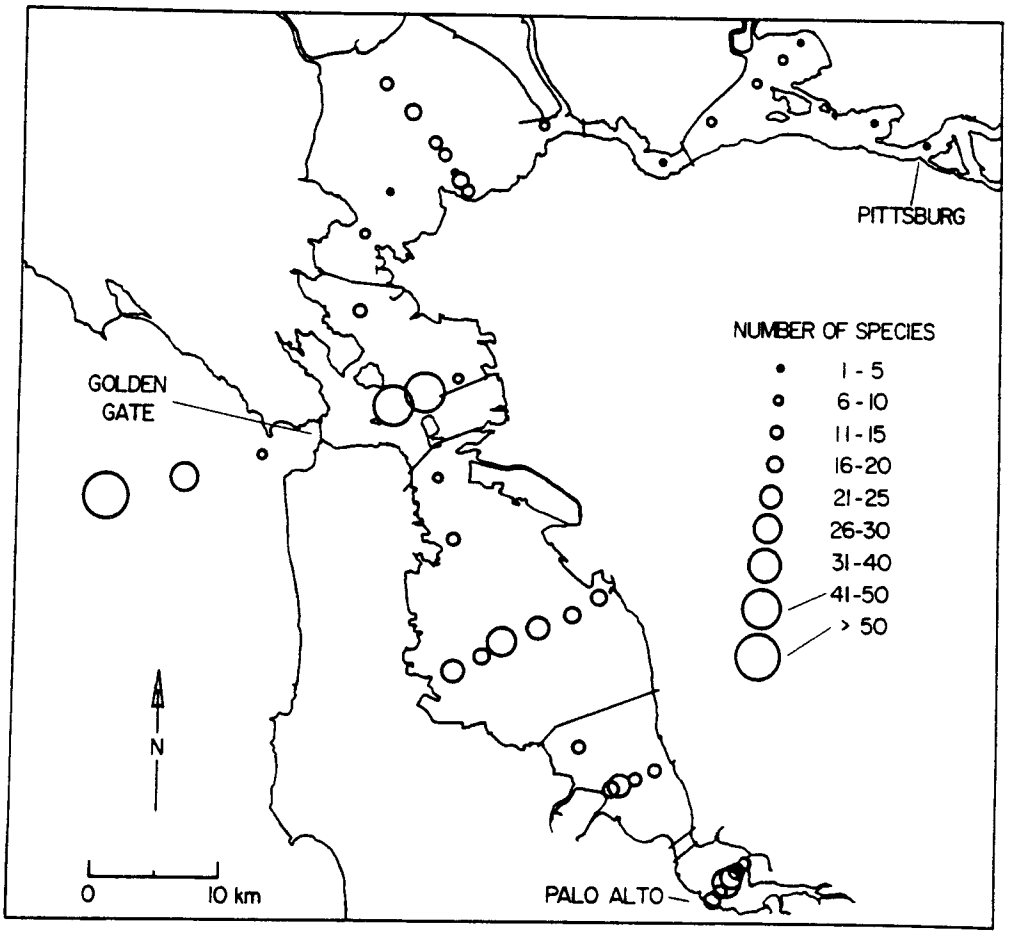


Fig. 92. Total numbers of benthic macrofauna species found in surveys of the Bay-Delta in February and August 1973. Replicate 0.1m^2 samples collected using a van Veen sampler, synoptically at all stations; 1.0mm screen employed for sorting. After Nichols (1979).

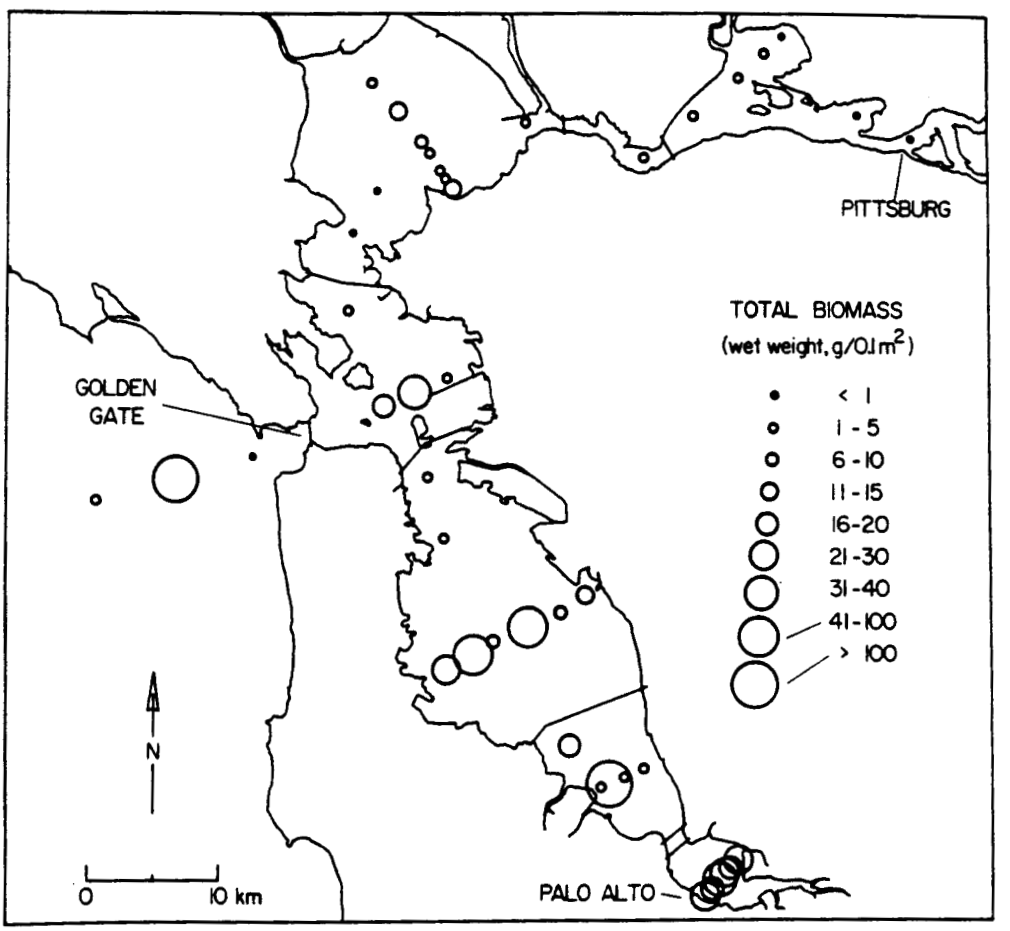


Fig. 93. Total biomass (g wet weight per 0.1 m^2) of benthic macrofauna in samples taken in February and August 197 Details as in Fig. 92. After Nichols (1979).

Nichols (1979) discussed the data in Figs. 92 and 93 in relation to the influence of natural factors, emphasizing salinity fluctuations, sediment texture and stability, and biotic disturbances (e.g. bat ray effects on sediments) as important determining factors. Sediment stability is of unusual importance in the Bay-Delta (Krone, 1979; Rubin and McCulloch, 1979), partly because the area is so shallow. However, even some deeper areas such as the San Pablo Bay shipping channel exhibit high-energy substrates which are suitable only for certain types of benthic fauna. Substrate type also largely defines the distribution of macroalgae in the estuary, although factors such as turbidity, nutrient availability, salinity fluctuations, and (perhaps) pollutant abundance are probably also operative in certain parts of the Bay (Silva, 1979; Josselyn and West, 1985).

Against this general background, Nichols and co-workers have conducted intensive studies to attempt to differentiate between the effects of natural factors and anthropogenic disturbances on Bay-Delta benthos. These investigations are described in detail by Nichols (1985b) and Nichols and Thompson (1985a, 1985b). The database involves benthic invertebrate abundance over a ten year period (1974-1984) at a mudflat in Palo Alto. This very considerable effort has added greatly to our knowledge of the benthos of the Bay-Delta, but has been largely unsuccessful in differentiating anthropogenic effects from natural variations in species composition and abundance in bottom-dwelling communities. The estuary benthos is dominated by introduced opportunistic species (see above and Table 52), with flexible lifestyles and a wide-ranging habitat tolerance. Changes in abundance of the

However, even in these obvious areas of anthropogenic impacts, there are no precise data on causative factors of the defaunation, as many contaminants co-vary in distribution. Thus, for example, both Islais and Mission Creeks are considerably contaminated by a wide range of trace elements and organic pollutants, the latter including (in Islais Creek at least) organochlorines and aromatic hydrocarbons (Hoffman and Meighan, 1984; Chapman et al., 1986). It is therefore concluded that surveys of benthic infauna are a generally imprecise tool to employ in the Bay-Delta as a means of identifying possible impacts from toxic contaminants on the biological resources of the estuary.

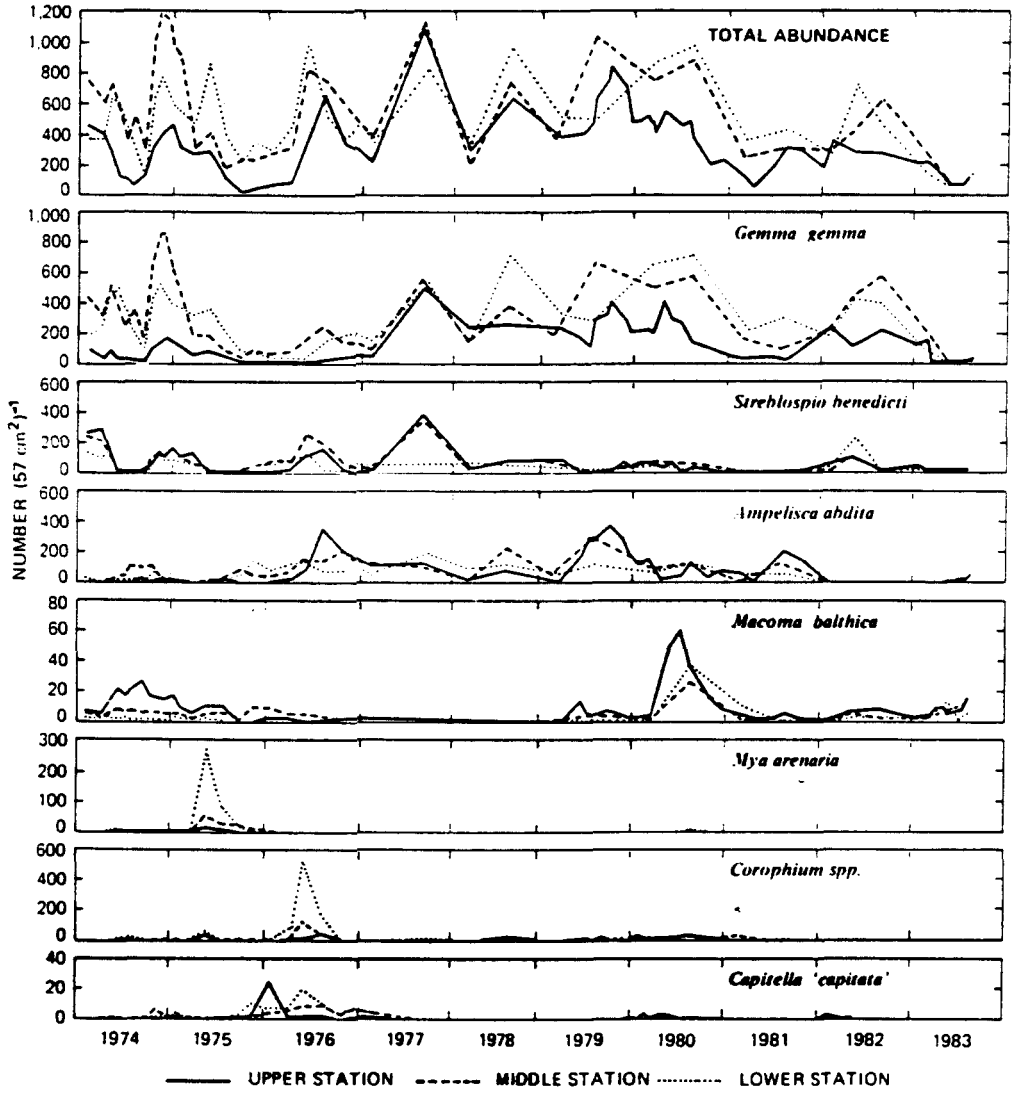


Fig. 94. Total mean abundance of specimens, and mean abundances of numerically dominant species (G. gemma, S. benedicti and A. abdita), the native species with greatest biomass (M. balthica), and three irruptive species (M. arenaria, Corophium spp. and C. capitata) in the mudflat at Palo Alto. After Nichols and Thompson (1985a).

B. FISHERIES OF THE BAY-DELTA

A vast amount of information is available concerning the fishery resource of the San Francisco Bay-Delta. The present report does not seek to comprehensively review this mass of information, but provides a brief overview of the status of fish and invertebrate populations in the estuary and discusses specific populations (especially striped bass, Morone saxatilis, and starry flounder, Platichthys stellatus) which are thought to possibly be affected by toxicants. The incidence of external lesions and neoplasms in fish from the Bay-Delta is also reviewed.

Status of Fishery Populations

Many authors have reviewed the status of fish and invertebrate populations in the estuary (for recent examples, see Smith and Kato, 1979; Tasto, 1979; Stevens, 1979, 1980; Cannon, 1982; Luoma and Cloern, 1982; SWRCB, 1982; Herrgesell et al., 1983; Wild and Tasto, 1983; Armor and Herrgesell, 1985; Brown, 1986; Dowgiallo et al., 1986; Miller, 1986; CDF&G, 1987b). In general, these authors concur that many fish populations within the estuary have suffered long-term declines. Some species, such as chinook salmon (Oncorhynchus tshawytscha) and sturgeon (Acipenser transmontanus and A. medirostris) are thought to have declined over very long time periods (Fig. 95), whereas the major reductions in the numbers of other species such as striped bass (Morone saxatilis) have apparently occurred more recently (e.g. see Stevens et al., 1985). Fig. 95 shows data for landings of four species and the timing of bans on their commercial harvesting. Interestingly, the timing of the local decline in striped bass numbers is matched very well by similar

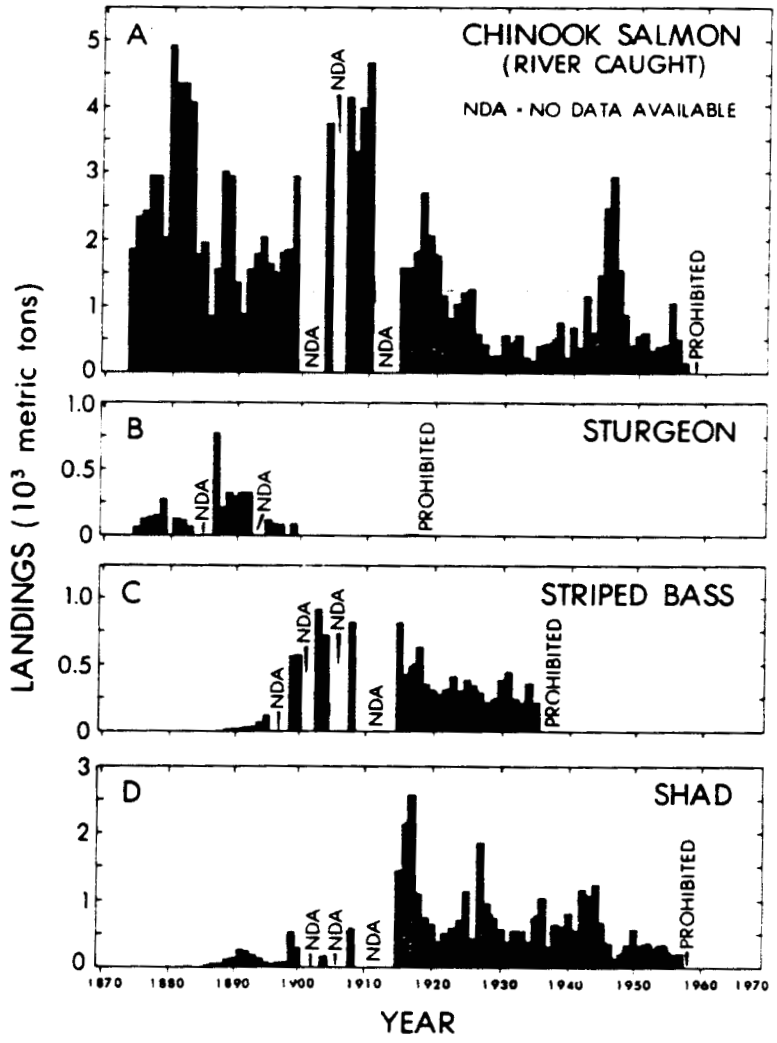


Fig. 95. Commercial fish catches in the Bay-Delta and adjacent tributary streams. (A) Chinook salmon in the Sacrament and San Joaquin Rivers; (B) Sturgeon in the Bay-Delta; (C) Striped bass in the Bay-Delta; (D) Shad in the Bay-Delta. After Smith and Kato (1979).

population reductions of M. saxatilis in Chesapeake Bay (Florence, 1980), although other populations of this species have not shown this pattern (McIlwain, 1980).

The declines in fish populations within the Bay-Delta have been matched to some extent by similar changes in invertebrates. Thus, for example, the California oyster industry thrived in the late 1800s, Crassostrea virginica being produced (after its introduction in the 1860s from the east coast of the USA) in large quantities in San Francisco Bay, despite its inability to reproduce successfully in Bay waters (Barrett, 1963). However, the fishery collapsed in the early 1900s, and the Bay gradually became less important as a growing area for the surviving oyster industry (Fig. 96), Tomales Bay and other areas being preferred. This is reported by Barrett (1963) to have been mainly due to widespread industrial and sewage pollution of the Bay, which both hampered oyster growth and contaminated the meat. The introduction of the Pacific Oyster Crassostrea gigas from Japan in the 1930s was not successful in San Francisco Bay, as growth was poor (Bonnot, 1935), although this species was cultured elsewhere in California (Barrett, 1963). Various other species of native or introduced bivalves were also the subject of culture or capture fisheries in the Bay-Delta in the past. These include softshell clams Mya arenaria (introduced accidentally in 1870 with an oyster shipment; landings dropped markedly between 1910 and 1930), Japanese littleneck clams Tapes japonica (introduced in the early 1930s, also with oysters), the native Bay mussel Mytilus edulis, and the introduced ribbed mussel Ischadium demissum (Smith and Kato, 1979). However, none of these species is presently commercially cultured or harvested within the Bay-

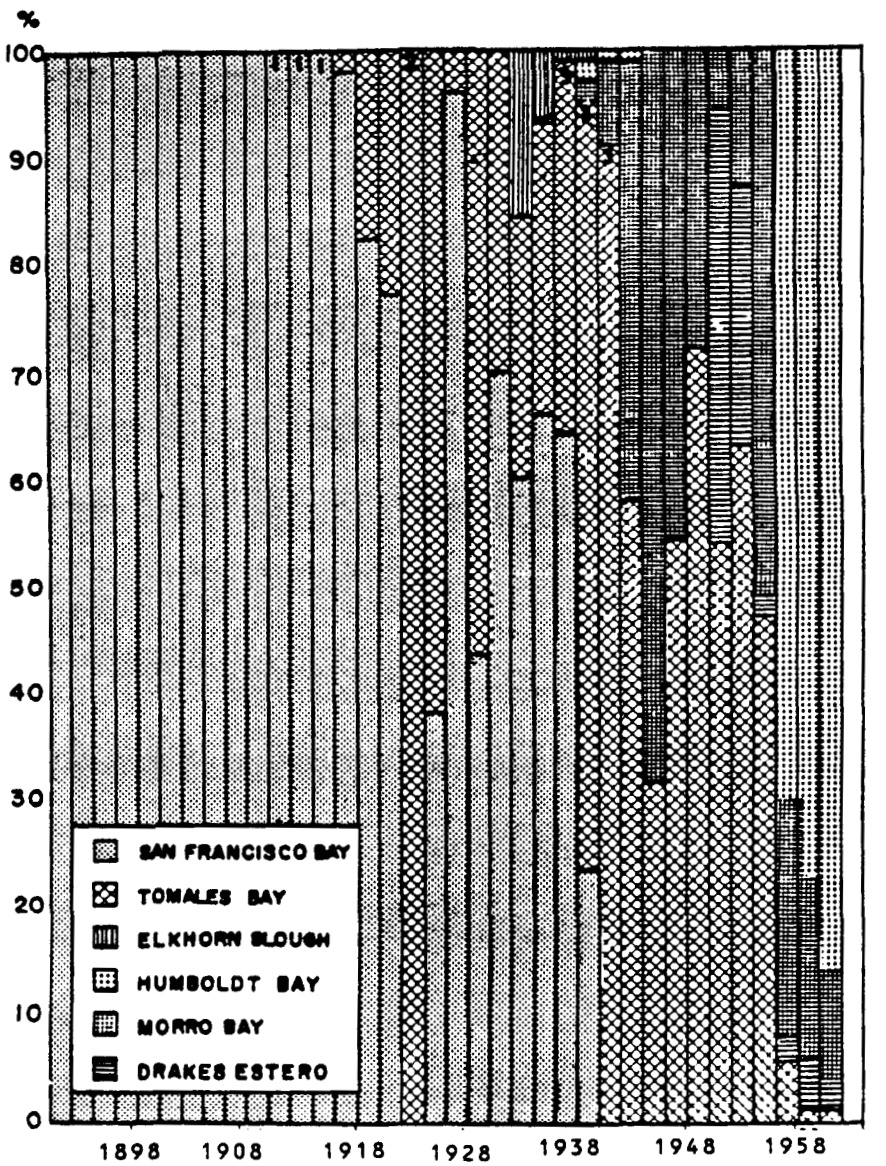


Fig. 96. The production of oysters in California by major growing area, 1888 to 1959. Data shown as percentage of total biennial production in each area. After Barrett (1963).

Delta. Although the introduction of improved treatment methods for sewage and industrial effluents in the 1960s and 1970s might now permit adequate growth of certain species of bivalves in the Bay-Delta to support a culture industry, concerns remain over public health issues. The latter include possible exposure to paralytic shellfish poisoning (PSP) toxins, chemical contaminants, and microbial agents (see section VD below), and continued concern is justified, given the propensity of bivalves to accumulate such toxins or contaminants.

San Francisco Bay is also an important nursery area for the Dungeness crab, Cancer magister (see review by Wild and Tasto, 1983). The commercial fishery outside the Bay on the Pacific coast collapsed in the early 1960s. Subsequent research investigated several potential reasons for this decline in local C. magister populations, including parasitism of eggs (Wickham, 1979), seawater temperature (Wild, 1983), chlorinated wastewater effluents (Russell and Horne, 1977; Horne et al., 1983) and organic contaminants (Guard et al., 1983; Haughen, 1983). No consensus has been reached on this issue to date, although it should be noted that data involving contaminant concentrations in C. magister are not generally thought to be persuasive that this factor is a major influence in determining population levels.

The various similarities and contrasts between present-day benthic populations in the Bay-Delta (see above) and current viable sport or commercial fisheries are of great interest as part of a "natural experiment in ecology". The present benthic communities are dominated heavily by tolerant opportunist species with flexible lifestyles and often wide habitat preferences, and most of these were originally introduced to the Bay. Introduced

fish have largely fared less well to the present, although there are exceptions to this general rule. Some authors have drawn parallels between the two groups, suggesting that the restriction of present-day commercial fisheries in the Bay to herring (Clupea harengus pallasi), northern anchovy (Engraulis mordax), and shrimp (Crangon franciscorum, C. nigricauda and the introduced Palaemon macrodactylus) represents a shift from longer-lived species to these opportunists with rapid reproduction and reduced adult longevity. This is sometimes interpreted as evidence of the effects of pollution in the estuary, mitigating against the longer-lived species (which are often of greater commercial importance, at least potentially; see Meyer Resources, 1985). There has been much speculation among the scientific community concerning possible effects of contaminants in the estuary on biota (see, for example, references cited above for C. magister; also Luoma, 1977; Luoma et al., 1983; Greenberg and Kopec, 1986). As noted in previous sections of this report, elevated levels of some trace metals and organic contaminants certainly exist in the Bay-Delta, and many of these are known from laboratory studies to exert detrimental effects on biota, at least at high ambient concentrations.

However, the success or otherwise of populations of any given species in the Bay-Delta is undoubtedly an exceptionally complex phenomenon, depending upon many factors which are often inter-related. These include the reduction in freshwater discharge to the estuary (with its consequent effects on salinity distributions, flushing, and gravitational circulation, all of which affect biota), alterations in Bay-Delta habitats (e.g. the massive loss of wetlands, which are important

nursery areas for some aquatic species), the effects of introduced species (which may prey upon or compete with native species), and several other factors in addition to pollution of the estuary. The interaction of these parameters is also complex. For example, it is certain that the historical reduction in freshwater inflow to the Bay-Delta from the Central Valley catchment influences the amounts of contaminants present in the estuary and their distribution and bio-availability. However, far too little is known of the dynamics of contaminants in the system to predict such effects quantitatively, at least with any accuracy. It is unfortunate that the historical database on contaminant levels in the estuary is generally so poor, as even the effects of previous diversions of freshwaters on these cannot be accurately quantified, to act as a basis for future decisions.

As a result of the complexity of the estuary and the inter-related nature of many of the most important parameters affecting its biological resources, the demonstration of cause-and-effect relationships is a particularly challenging task. Correlations between Delta outflows and fish abundance (e.g. see Rozengurt and Herz, 1981, 1986; Rozengurt et al., 1985) may be interpreted in different fashions. For example, Delta outflows affect both productivity of the upper estuary and contaminant levels therein, and either of these parameters may significantly impact fish populations.

There is thus no single dataset which establishes with reasonable certainty that toxic contaminants within the Bay-Delta environment are reducing entire populations of important aquatic species in the estuary. However, certain results (particularly

those relating to striped bass and starry flounder) are suggestive of such effects. The data for striped bass and starry flounder are reviewed below.

Striped Bass

Striped bass (Morone saxatilis) were introduced to San Francisco Bay in 1879, when 132 individuals from the Navesink River, New Jersey, were released at Carquinez Strait. In 1882, an additional 300 fish from the Shrewsbury River, New Jersey, were released to the Bay (Stevens, 1980). By 1890, these introduced fish had spread to the Russian River and Tomales Bay; four years later, their distribution had extended to southern California (Skinner, 1962), and a decade thereafter they were present along the Pacific coast from British Columbia to northern Mexico (Miller and Lea, 1972). By contrast to this rapid initial success, the only populations of M. saxatilis of consequence at present on the west coast of USA are in the Bay-Delta and surrounding marine waters, and in the Coos and Umpqua Rivers in Oregon (Parks, 1978; Stevens, 1980).

The Bay-Delta striped bass population fared well until the 1960s. Commercial fishing for this species was banned in California in 1935, mainly because of conflicts between sport and commercial fisheries; the population was stable at this time (Clark, 1933; Stevens, 1980). Trends in the M. saxatilis population since the late 1950s have been calculated using a variety of statistical methods. These include: Petersen estimates, based on tagging and recapture data (Bailey, 1951); assessments on a catch-per-effort (CPE) basis using California Department of Fish and Game (CDF&G) data, generated when bass are

caught by gill nets and fyke traps in the Delta and Sacramento River for tagging; an estimate from charter boat data of total catch and catch per angler day; an assessment based on inspection of catches by local anglers, inspections being carried out by CDFG; and a young-of-the-year index. These various methods are discussed in publications of SWRCB (1982), Stevens (1980), Stevens et al. (1985), and CDF&G (1987b). They all suffer from certain disadvantages; in particular, only Petersen estimates include any data on the precision of the assessment. Stevens (1977, 1980) noted that the best long-term statistics were those based on charter boats, although these take only 14% of the total catch on average. Trends in the Bay-Delta striped bass population between 1938 and 1977, based on these estimates, are shown in Fig. 97 (Stevens, 1980). It appears from these data that catch per angler day declined gradually from 1940 to 1956, recovered briefly in the period 1957 to 1963, and declined thereafter, with the possible exception of better years in 1972 and 1974 (see below). The considerable variation from year to year renders strict interpretation of these data difficult, however.

Other estimates of striped bass abundance have been available only since the late 1960s. CDF&G (1987b) have calculated the most up-to-date information, which is presented in Figs. 98 and 99. It is clear that each estimate shows a general decline in the striped bass population since the 1960s. However, few conclusions can be drawn beyond this general statement, as the details of each estimate do not agree. Thus, for example, the improved catches by charter boats in 1972 and 1974 are not reflected in Petersen estimates or the CPE index.

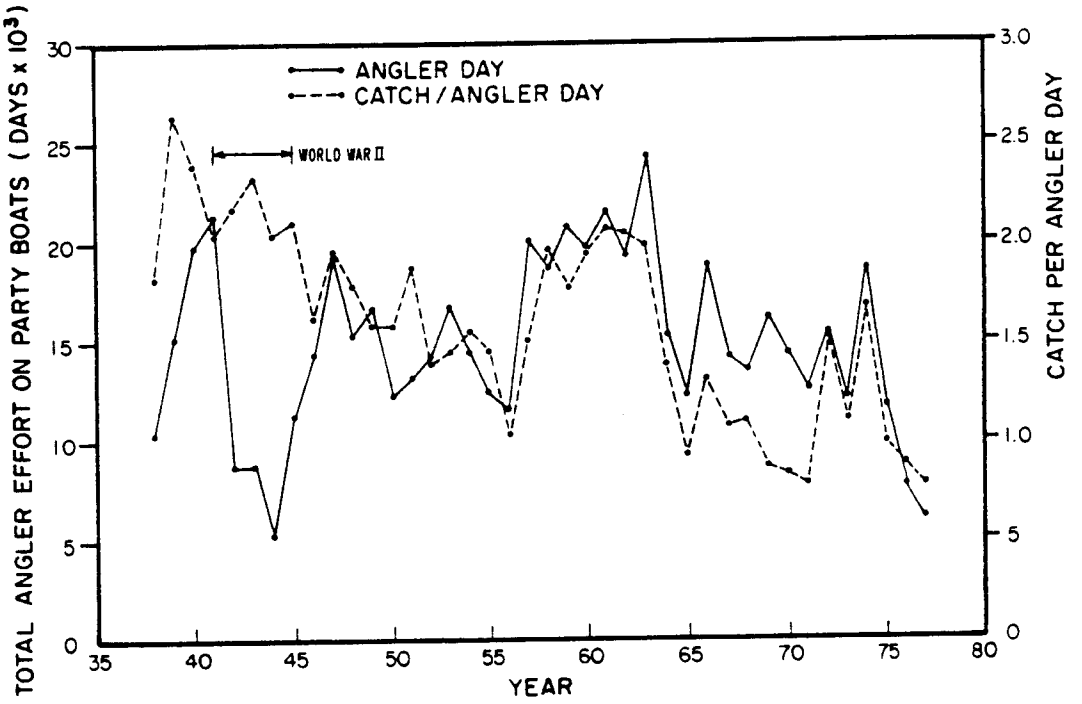


Fig. 97. Trends in catch per angler day from charter boats for striped bass (Morone saxatilis) in the Bay-Delta. After Stevens (1980).

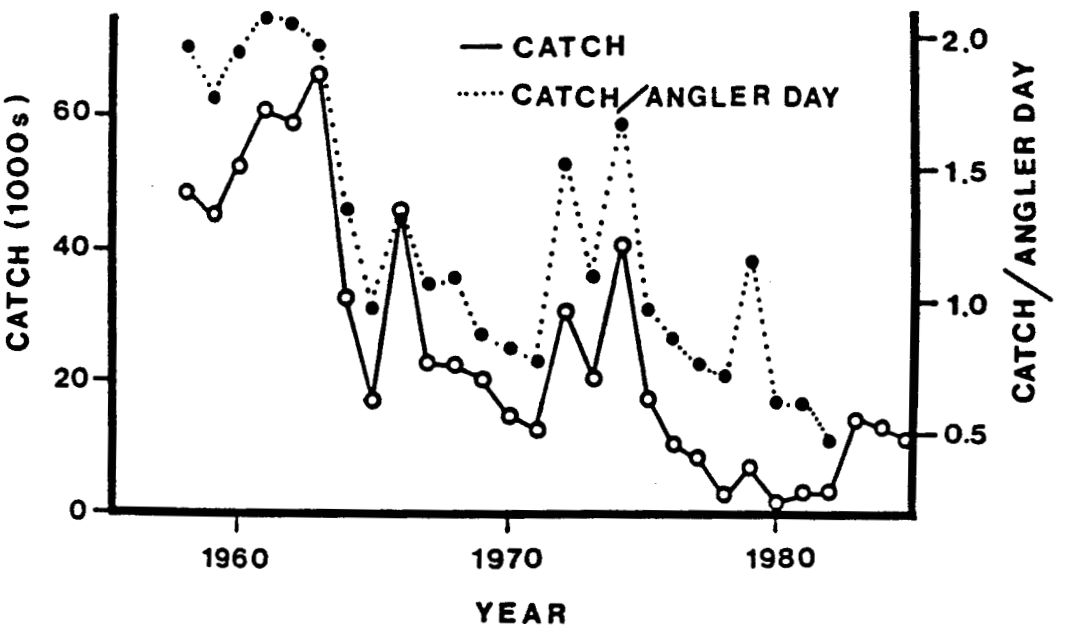


Fig. 98. Updated trends in total catch and catch per effort (catch per angler day) for charter boat data concerning striped bass (Morone saxatilis) in the Bay-Delta. After CDF&G (1987b).

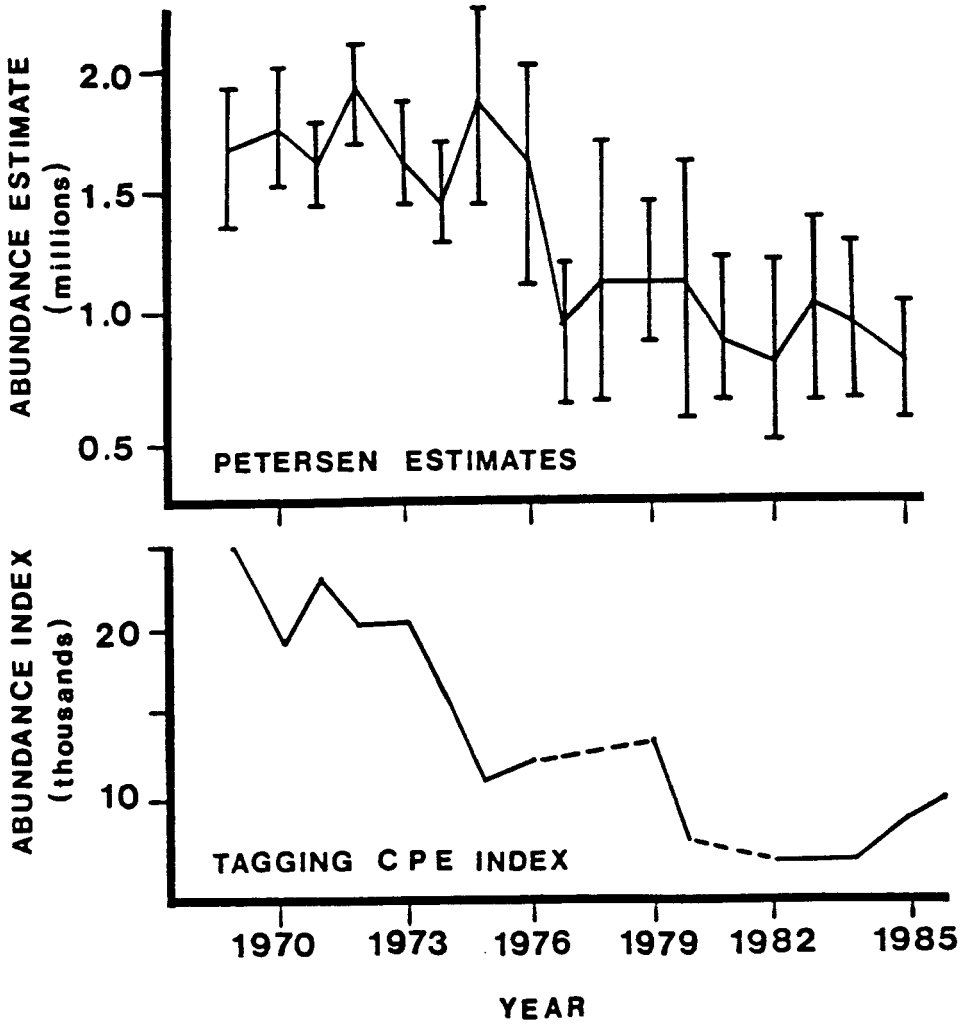


Fig. 99. Updated trends in Petersen estimates and the so-called CPE index (based upon catch per effort statistics generated by CDF&G during tagging exercises) for striped bass (Morone saxatilis) in the Bay-Delta. After CDF&G (1987b).

Similarly, the considerable reductions in Petersen estimates of striped bass abundance in the drought years of 1976 and 1977 (continuing at low levels to the present) are not confirmed by data from the CPE index, which suggest population reductions occurred in the period from 1973 to 1975. While some authors (e.g. Stevens et al., 1985) have speculated that the unusually dry years of 1976 to 1977 may have been instrumental in the decline of M. saxatilis in the estuary (and such a conclusion may be intuitively satisfying; see below), it is considered that the data may be insufficient to warrant such a judgement.

To complete this discussion of population estimates for striped bass in the Bay-Delta, data on young-of-the-year assessments are presented. CDF&G sample these fish every two weeks between late June and early August in the Delta and Suisun Bay, to provide estimates of young fish entering the population each year; data are available since 1959. There is a bias in these estimates in wet years, as high Delta flows occurring during May to July wash fish further into the northern reach of the Bay, where sampling is less reliable (Stevens, 1977, Stevens et al., 1985). However, these estimates are nevertheless generally a useful indication of spawning success and of the potential for later recruitment into the adult M. saxatilis population. The observed indices for young-of-the-year striped bass for the period 1959 to 1986 are shown in Fig. 100, data again being taken from CDF&G (1987b). The overall profile shows low abundance of young fish in the early years of sampling, higher but variable numbers in the period from 1962 to 1974, and reductions thereafter to very low levels of abundance. Surprisingly, data for 1986 suggested considerable improvement

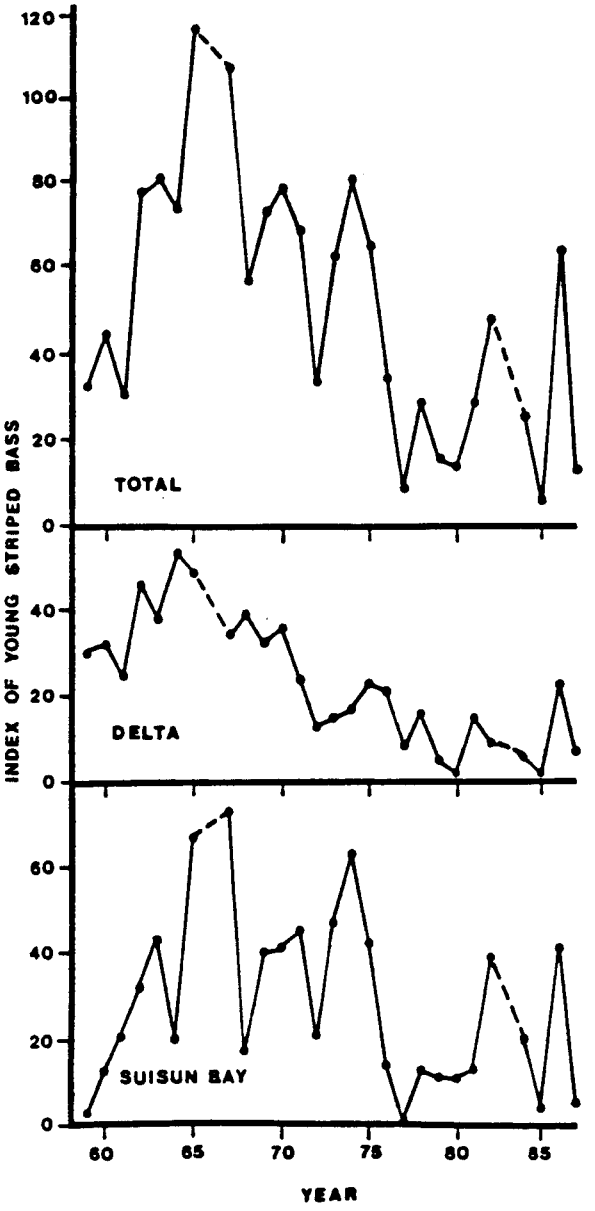


Fig. 100. Index of young-of-the-year striped bass (Morone saxatilis) for the Delta and Suisun Bay, 1959 to 1986. (No sampling was conducted in 1966). After CDF&G (1987b).

over the previous decade, large numbers of young fish being found. There was no obvious correlation of this event to Delta flows or to food availability; it appeared that unusually high survival rates of eggs, larvae, and fry had occurred in 1986 (D. Stevens, personal communication). This is of interest, as several authors have suggested striped bass populations to be dependent on an influx of large numbers of recruits from particularly successful years (e.g. Florence, 1980), rather than on sustained moderate reproductive success in all years. However, the late 1986 trawl survey of striped bass in the northern reach of the Bay and the Delta suggested that the initial high abundance of young-of-the-year fish had declined considerably by the end of the calendar year, very poor survival (7%) being estimated between September and December (CDF&G, 1987b). It thus appears unlikely that recruitment to the adult population from the 1986 year-class will be above normal.

Many difficulties exist in the interpretation of the available data concerning the abundance of striped bass in the Bay-Delta, and no consensus has been reached to date on the principal factors acting on the population. The disagreement between abundance estimates (discussed above) gives rise to problems in attempting to test hypotheses as to the causative factors for population reductions. However, many such hypotheses have nevertheless been advanced; these are briefly reviewed below, prior to discussion of the possible impacts of contaminants on M. saxatilis in the estuary.

The main two parameters which are thought by many to affect striped bass numbers in the estuary are closely inter-related. These are the flow of freshwater into the Delta, and the

diversion of a significant portion of overall flows out of the Delta for uses elsewhere (largely by agriculture in the Central Valley and south thereof, but also as potable supplies in southern California). Several authors (e.g. Turner and Chadwick, 1972; Chadwick et al., 1977; Stevens, 1980; Stevens et al., 1985) have published various correlations between Delta outflow rates in June and July of each year and abundance of young-of-the-year striped bass. Similar correlations also exist between fish abundance and the percentage of the flow which is diverted, as Delta outflow is obviously a function of the amounts of water diverted from the estuary (Fig. 101). The volume of fresh water entering the Delta is thought to affect striped bass in a number of ways, as follows:

* Young striped bass are carried to feeding areas in the Delta by freshwater inflow. This process may be more rapid and effective, and predation on the larvae and fry may be reduced, if flows are high.

* High Delta outflows may also disperse the young fish more widely, thereby reducing intraspecies competition for food (Chadwick et al., 1977; Stevens, 1977).

* Delta outflows also define the position of the null zone (turbidity maximum, or entrapment zone) in the upper estua Some authors (e.g. Arthur and Ball, 1978, 1979; Ball and Arthur, 1979) have suggested that primary productivity in the upper estuary is defined by Delta outflow, as the null zone must be pushed downstream by the outflow from the Delta channels, to the shallows in upper Suisun Bay

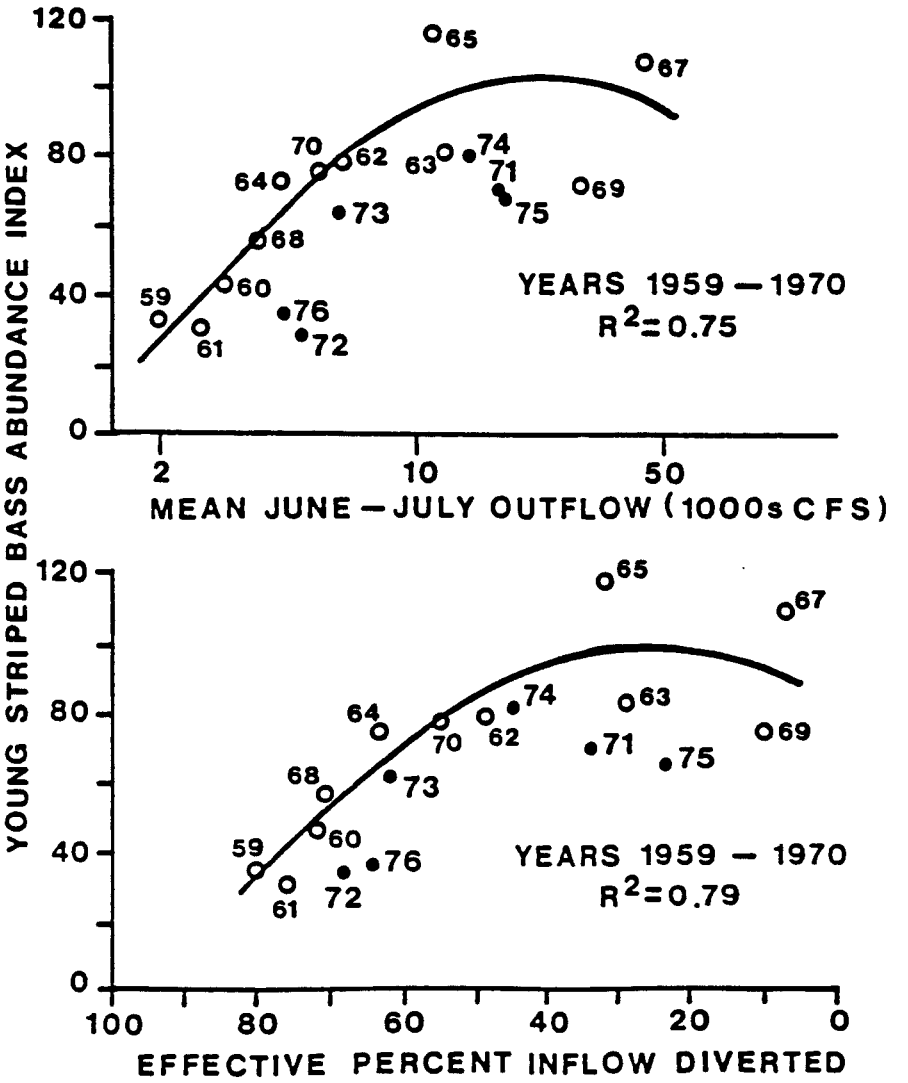


Fig. 101. Example of correlation between the index of abundance of young striped bass (Morone saxatilis) in the Sacramento/San Joaquin estuary and Delta outflow rates in June and July (top) or percentage of inflows diverted away from the estuary (bottom). Curves fitted to 1959-1970 data only. After Stevens et al. (1985).

for high productivity to occur. This high primary productivity should in turn generate large numbers of shri (Neomysis mercedis) in the area for young striped bass to feed on (Heubach et al., 1963; Kost and Knight, 1975; Orsi and Knutson, 1979; Knutson and Orsi, 1983).

* Water diversions from the Delta not only reduce Delta outflow volumes but also physically remove fish (including eggs, larvae, and young striped bass) and their food items from the Delta channels. Power plants in the Delta have similar effects, although biota entrained in cooling waters are returned to the estuary (after exposure to physical disturbances and potentially lethal temperature fluctuations). Several authors have attempted to calculate the effects of these factors on the survival of young M. saxatilis in the Delta (e.g. Chadwick et al., 1977; Stevens and Finalayson, 1977; SWRCB, 1982; Stevens al., 1985); conclusions as to their significance have vari (e.g. compare SWRCB, 1982, to Stevens et al., 1985).

It is generally considered likely that the reductions in Delta outflow have contributed to the striped bass decline in the estuary. The correlations between the abundance of young M. saxatilis and Delta outflow or percent diversions from the estuary (Fig. 101 and citations above) are convincing evidence for such effects. However, the existence of this correlation does not necessarily imply a direct cause and effect phenomenon. Evidence is perhaps particularly persuasive for certain years. Thus, the drought years of 1976 and 1977 (which may have been associated with marked declines in adult striped bass; see above)

are likely to have produced poor conditions for the survival of young M. saxatilis. Stevens (1980) noted that abundance indices found for young-of-the-year striped bass were particularly low in the years 1977, 1978, and 1979; the indices for these years averaged 32% lower than expected from prior relationships between fish abundance and Delta outflows or water diversion rates. In these years, phytoplankton productivity was also low, and the numbers of shrimp (Neomysis mercedis) were consequently depressed (see also Knutson and Orsi, 1983). It thus seems that the drought years of 1976 and 1977 started a period of generally low primary and secondary productivity in the upper estuary (perhaps as least partly due to the position of the null zone; see above), and that survival of striped bass larvae and fry (which feed on the shrimp N. mercedis, as well as on Corophium spp. and other organisms) may have been reduced because of this. Hypotheses involving the nutritional status of fish populations are difficult to test, however. Recent studies on the use of RNA: DNA ratios as an index of nutritional status in striped bass (Horne et al., 1987) appear to be worthy of further development.

Apart from freshwater inflows and food availability, there are additional factors which may influence striped bass populations. One of these is the annual die-off of M. saxatilis, occurring in the Suisun Bay-Carquinez Strait-San Pablo Bay region in late spring and early summer, when the adults return to marine waters after spawning (Kohlhorst, 1975). Some authors have speculated that this may be due to a combination of pollutant stresses and osmoregulatory stress (Stevens, 1980), but there is little strong evidence for such hypotheses. Recent evidence indicates that liver dysfunction may be involved, however (G.

Young, personal communication), and studies are ongoing. A further factor which may have a significant impact on striped bass populations locally concerns the drastic changes in habitat which have occurred in the Bay-Delta (particularly the upper estuary). Quantification of the effects which such changes have on fish populations would be exceedingly difficult, but the fact that tidal wetlands are generally considered to be important nursery areas for fish suggests that such impacts have probably occurred, and may have been quantitatively significant.

Another factor which may influence striped bass when they are in the Delta region concerns pesticide use in the Delta and Central Valley. This is known to lead to the contamination of drainage waters, which find their way back to the rivers and streams where striped bass spawn. Insecticides are of course of considerable direct toxicity to juvenile striped bass (e.g. Korn and Earnest, 1974), and local effects in such areas of agricultural drainage may be expected. Studies by the Central Valley Regional Water Quality Control Board have shown significant toxicity in ambient waters in the catchment rivers (J. Bruns, personal communication), although the contaminants causing such toxic effects are rarely identified. Faggella and Finlayson (1987) have concluded that herbicides such as molinate and thiobencarb are unlikely to significantly affect larval or juvenile striped bass in the Delta, although N. mercedis may be affected in low flow conditions, when agricultural drainage waters are poorly diluted by receiving waters in the rivers. However, neither molinate nor thiobencarb is as toxic to striped bass as many other pesticides in use in the Delta and Central Valley regions (compare Korn and Earnest, 1974, to Faggella and

Finlayson, 1987).

The various factors which may be involved in the decline of striped bass in the estuary, and their inter-relationships, are shown in Fig. 102. The complexity of the system is clearly evident, and there can be little wonder that single causative parameters have not been identified as of over-riding importance.

The levels of contaminants found in striped bass have been addressed in previous sections. To recap briefly, it has been shown that elevated concentrations of a variety of contaminants (PCBs, DDT and other organochlorine pesticides, selenium, zinc, and possibly monoaromatic hydrocarbons) exist in M. saxatilis from the Bay-Delta compared to certain populations elsewhere (the Coos River population was used for comparison by most authors). At least some of these contaminants accumulate preferentially in female reproductive tissues (e.g. Sager and Cofield, 1984; Greenberg and Kopec, 1986); in the case of the organic contaminants, this is largely due to their lipophilic nature (Phillips, 1978, 1980, 1986). Whipple et al. (1983) and Jung et al. (1984) have summarized the data on MAHs and striped bass, and have noted correlations between MAH levels in tissues of contaminated fish and egg resorption, as well as other sublethal effects (such as external lesions caused by parasitism by the metacestode Lacistorhynchus tenuis; see also Moser et al., 1984; Wellings and Lindstrom, 1986). Crosby et al. (1983, 1986) have summarized data on chlorinated hydrocarbon residues in M.saxatilis.

As noted previously, these data are exceptionally difficult to interpret in respect to their possible significance to the striped bass population. A variety of reasons exist for this:

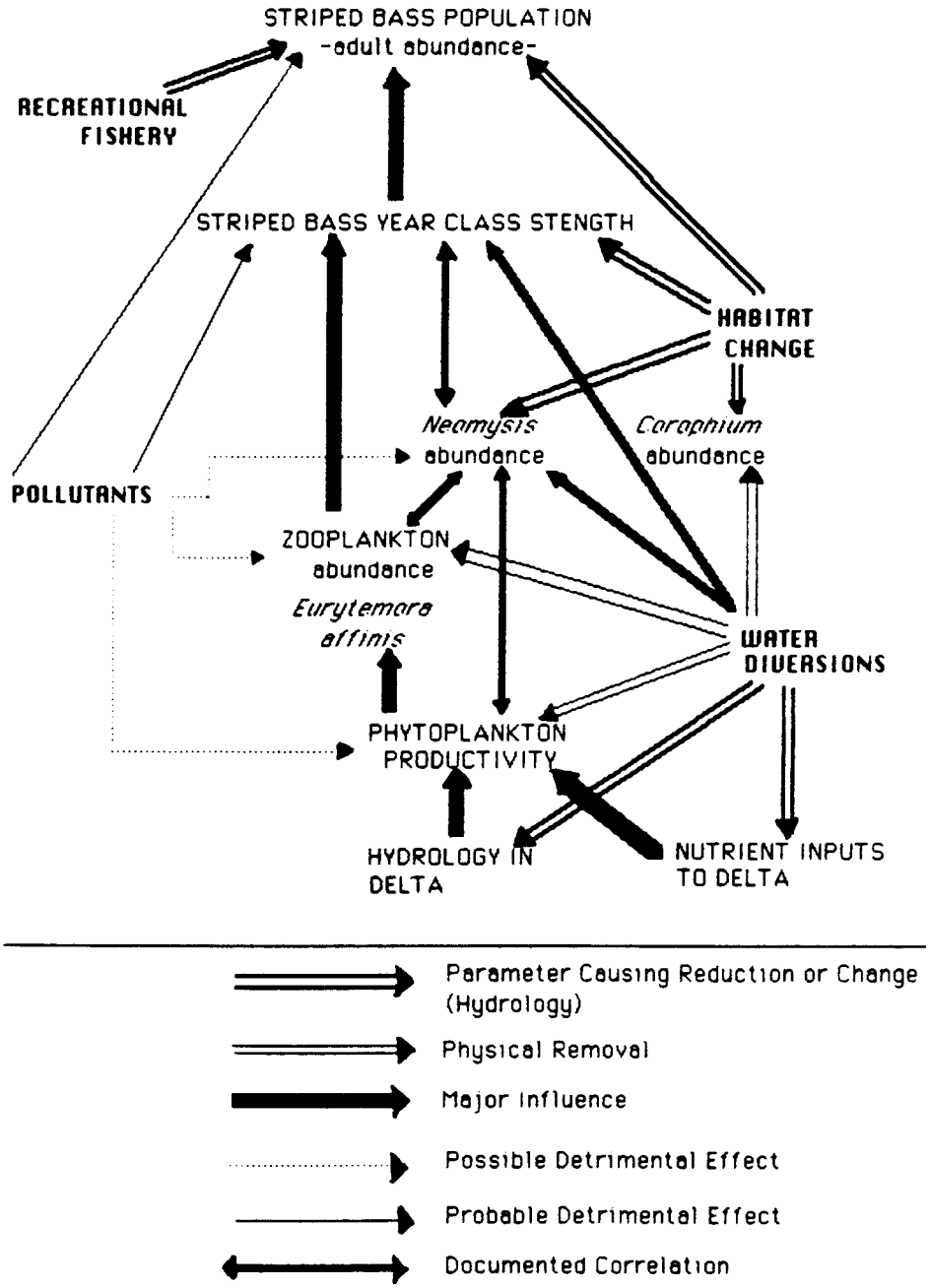


Fig. 102. Diagrammatic representation of the factors likely to influence populations of striped bass (Morone saxatilis) in the Bay-Delta.

* The concentrations of contaminants in fish tissues are a complex function of the exposure of the fish to the contaminants in space and time. Striped bass migrate through the estuary, and individuals are likely to vary greatly in their exposure to at least some contaminants. MAHs are a prime example, particularly as they may be introduced to the estuary episodically (in spills, etc.) and are of short half-life in fish.

* Individual fish have been shown to exhibit highly varied concentrations of contaminants. This not only correlates to their probable difference in exposure noted above, but also to a host of other variables, which have been reviewed in detail by Phillips (1977, 1978, 1980, 1986). Among these variables are condition of the fish (e.g. lipid content), age, and sex, all of which have been demonstrated to be of significance in defining contaminant levels in striped bass (e.g. see Whipple et al., 1983). Notwithstanding this, no stratified samples of striped bass have been taken for analysis; this severely constrains comparison of data from different locations or time periods.

* In some cases, large numbers of individual fish exhibited contaminant levels which were below the detection limits of the methods employed for analysis, while a few individuals were apparently highly contaminated (see Tables 46-51 for examples). The accurate characterization of contaminant concentrations (either means or ranges) in such populations is extremely difficult, as much depends

on the chance sampling of highly contaminated individuals This situation is exacerbated for contaminants such as MAHs, which are of very short half-life in fish. It is highly possible that individual fish would be exposed to MAHs at some point in the spawning migration, suffer toxi effects from this, but not be sampled for analysis until after the MAHs have been excreted. As a result, even if MAHs or other contaminants of short half-life in M. saxatilis were exerting toxic effects, it would be difficult to demonstrate a correlation between the effect and elevated levels of the contaminant in the fish.

* Striped bass appear to contain elevated concentrations oı many different contaminants. The generally greater contamination of Bay-Delta M. saxatilis compared to Coos River fish extends to PCBs, DDT and metabolites, several other chlorinated hydrocarbon pesticides, some types of hydrocarbons, and probably certain trace elements. It is also thought (e.g. see Whipple et al., 1983) that organic contaminant levels correlate to each other in striped bass, i.e. individual fish will exhibit high levels of a range of contaminants rather than any single compound. The same appears to be true for organochlorines (e.g. Crosby et al., 1983, 1986). In such situations it is often impossible to adequately demonstrate that an individual contaminant is responsible for any particular (sublethal or lethal) effects. This is due to the covariance of contaminants, and the problem has been noted in other studies also (e.g. see Martin et al., 1984

concerning the sublethal effects of contaminants in the South Bay on mussels). It is even possible that detrimental biological effects are in fact due to contaminants which are not even being measured in the populations studied, especially if these covary with contaminants which are analyzed. The unequivocal establishment of a cause-and-effect phenomenon requires extensive laboratory studies of contaminant impacts on individuals and populations of a species, and these have not been undertaken to date for any contaminant/species pair. It is not sufficient to compare local data on contaminant levels in striped bass to published information from elsewhere on other fish species (e.g. see Crosby et al., 1986), as different species have been shown to vary widely in sensitivity to contaminants (e.g. see Hogan and Brauhn, 1975; Von Westernhagen et al., 1981; Eisler, 1986b).

In summary, it is concluded that, although evidence exists for a decline in striped bass numbers in the Bay-Delta over the last two decades, the precise timing of major declines between years has not been fully established. Similarly, the causes of the population reduction are not completely understood. Many factors may have contributed, including the reduction in freshwater inflow to the estuary; the removal of eggs, larvae, fry, and food items from the Delta by water diversions; habitat changes in the upper estuary; and contaminant effects on reproduction. It is also possible that as yet unstudied factors have played a role in the decline of M. saxatilis in the estuary. These may include

exotic contaminants not yet quantified in the fish, or biological effects such as competition or predation by introduced species; the threadfin shad (Dorosoma petenense), introduced to the estuary in 1959 and 1960, is one possible candidate with respect to the latter (Heubach et al., 1963). Additional carefully-designed research, both in the laboratory and the field, is required before firm conclusions may be reached concerning the impacts of contaminants on striped bass populations in the Bay-Delta. This conclusion is not new, having been voiced by many previous reviewers of this complex problem (e.g. SWRCB, 1982; Stevens, 1980; Stevens et al., 1985). It is notable that Goodyear (1985) could not distinguish well between the effects of fishing-related mortality and toxicant-induced impacts on striped bass populations in Chesapeake Bay, using modeling techniques. He nevertheless concluded that the population would be likely to improve if fishing mortality were reduced (whatever the primary cause of the population decline). The recreational fishing of M. saxatilis was banned in Chesapeake Bay recently in an attempt to allow the population to recover; perhaps similar measures should be considered for the San Francisco estuary.

Starry Flounder

Data concerning the possible impacts of PCBs on starry flounder (Platichthys stellatus) in the Bay-Delta are discussed only briefly here, as some of these are as yet unpublished. Permission to cite certain material in the present report was kindly given by Dr. Robert Spies of the Lawrence Livermore National Laboratory.

Spies et al. (1984) first noted that P. stellatus females from San Francisco Bay exhibited a correlation between their fertilization success and the activity of mixed-function oxidase (MFO) enzymes in their liver tissues (Fig. 103). No such correlation was found between MFO activities and either hatching success or percentage of normal larvae. Fish from Berkeley exhibited the highest MFO activity and lowest fertilization success, while P. stellatus from San Pablo Bay had lowest MFO activities and highest rates of fertilization. Later studies (Spies et al., 1985a, 1985b) confirmed these differences and also documented the existence of histopathological changes in liver, gill, and kidney tissues, which may be related to the toxic effects of polyaromatic hydrocarbons (found at elevated levels in Bay sediments). The MFO activity of P. stellatus taken from the Bay was inhibited by 7,8-benzoflavone, showing that such activity was largely due to cytochrome P-450 enzymes. The synthesis of these enzymes is induced by both coplanar PCBs and certain PAHs (Spies et al., in press).

The poor fertilization success noted for flounders in parts of the Bay was directly correlated to PCB levels in later studies also, embryological success varying inversely to PCB concentrations in the eggs (Spies and Rice, in press). Several possible modes of toxic action were discussed, including effects of organic contaminants on hormone metabolism in P. stellatus. Laboratory studies delineated the major sources of variability in spawning success of starry flounder spawned in the laboratory (Rice et al., unpublished manuscript).

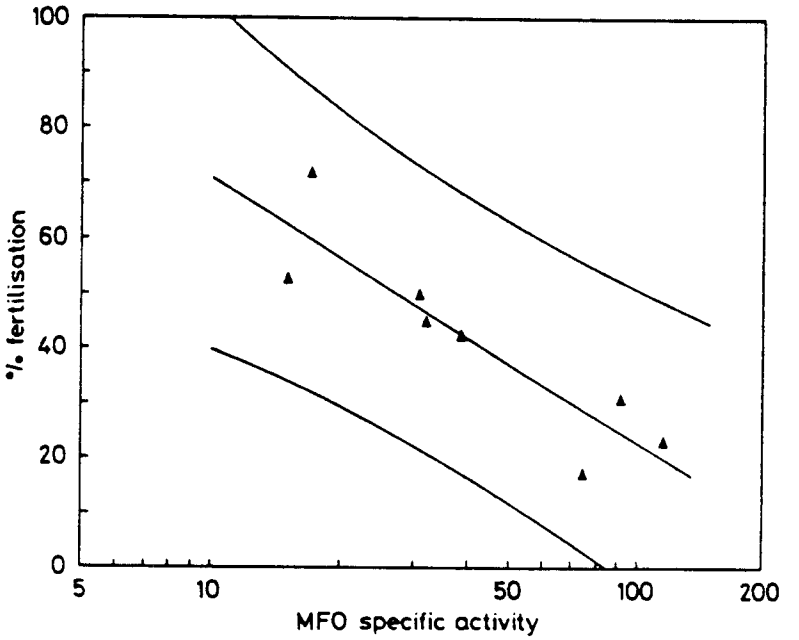


Fig. 103. Correlation between the specific MFO activity in livers of starry flounder (Platichthys stellatus) females and their percentage fertilization. Data cover the period from December 1982 to February 1983. Confidence interva of 95% are also shown. After Spies et al. (1984).

Despite these highly promising results, certain questions remain to be answered with respect to the effects of organic contaminants on P. stellatus. Firstly, some results have indicated the existence of high variability in contaminant levels in sediments over small areas of the Bay (e.g. Table 6 in Spies et al., 1985a). This reduces confidence in correlations between the effects on fish and location of their capture. It is possible that such problems underlie the lack of complete agreement between the incidence of histopathological abnormalities in P. stellatus and the degree of contamination of sediments at their capture site. Secondly, the degree of movement of starry flounders around the Bay is not known. It cannot necessarily be assumed that a fish captured at a given site has been in that general area for long periods, and this tends to weaken any conclusions relating fish physiology to contamination of sediments at its site of capture, although correlations between PCB concentrations in flounders and reproductive success remain significant regardless of the location of capture of the fish. Finally, despite indications in the literature of similar problems from PCBs in other fish species (e.g. Von Westernhagen et al., 1981; Hansen et al., 1985), it cannot be assumed that PCBs are the only (or even the major) causative factor involved in reducing fertilization success of P. stellatus in the absence of direct cause-and-effect studies. These would involve laboratory investigations of fertilization success in the presence of sediments which are deliberately enriched by PCBs but otherwise are unchanged from field conditions.

It is nevertheless concluded that these data provide strong evidence for the existence of sublethal effects of both PCBs and PAHs in a natural fish population in the Bay-Delta. There is no reason to suppose that P. stellatus should be the only species so affected. Additional studies on other demersal fish in the Bay-Delta would be most worthwhile.

External Lesions and Neoplasms in Fish

A brief note is required here concerning the incidence of external lesions and neoplasms in fish. Such morphological abnormalities have been reported from many global locations, particularly in recent times, but also from historical records. Sindermann (1979) and Mix (1986) reviewed these abnormalities and considered the evidence for their association to pollution.

The incidence of external lesions in striped bass (Morone saxatilis) from San Francisco Bay has already been mentioned. These lesions have been shown to be due to an unusual immune response to infection of the fish by the trypanorhyncan metacestode Lacistorhynchus tenuis (see Moser, 1983; Whipple et al., 1983; Jung et al., 1984; Moser et al., 1983; Moser et al., 1984; Moser, 1986; Wellings and Lindstrom, 1986). The life cycle of L. tenuis involves elasmobranchs (sharks and rays), copepods or other microcrustaceans, and striped bass. Moser et al. (1984) have described the effects on striped bass, which involve formation of a raft of fibrous tissue encapsulating dead metacestodes which have penetrated the intestinal wall (after ingestion of infected crustaceans) and become embedded in the muscle, usually on the right side of the fish (the left side is protected by the liver and stomach, the dorsal surface by the

swimbladder). When the raft touches the peritoneum, an inflammatory response produces reddening of the right side of the fish. The action of lymphocytes and fibroblasts encapsulates the raft, which is commonly expelled through an open lesion in the right-side muscle. The lesion thus formed is prone to secondary infection by bacteria (Aeromonas and Bacillus species) and by a fungus, and this no doubt affects the vitality of the fish. However, Wellings and Lindstrom (1986) did not consider this to be a major factor in the summer die-off of striped bass in the Bay. The incidence of lesions in M. saxatilis from the Bay-Delta has been suggested to be correlated to MAH levels in the fish (Whipple et al., 1983). It is possible that many factors combine to increase the susceptibility of striped bass to infestation, by both L. tenuis and other parasites such as larval nematodes (Anasakis sp.), as suggested by Sakanari et al. (1986).

Other morphological abnormalities have also been detected in fish from the Bay-Delta. Cooper and Keller (1969) reported the existence of papilloma-like tumors on the epidermis of English sole (Parophrys vetulus) from the Bay. This condition had also been noted by Harold and Innes (unpublished material, cited by Cooper and Keller, 1969), as early as 1922 in P. vetulus from the Bay. The incidence of papillomas was recorded by Cooper and Keller (1969) to be high and to be species-specific for P. vetulus, which is in direct contrast to other areas. It was also reported that papillomas were more common in fish from the northern reach than in those from South Bay, but a later survey could not confirm this (Kelly, 1971). Recent evidence (see review by Mearns, 1985) suggests that the cause of these papillomas, which are commonly reported in pleuronectid and cod-

like fishes of the north-east Pacific, is an amoeba (Dawe et al., 1979); however, an association with pollution has not been completely ruled out, at least by some authors (Cross, 1984).

Finally here, it should be noted that reports of fin erosion in fish from San Francisco Bay are rare compared to other areas of the Pacific coast or elsewhere (e.g. see Sindermann, 1979; Mearns, 1985). However, Anatec Laboratories (1987a) reported a high incidence of fin erosion in juvenile striped bass and other fish captured by trawling close to the effluent outfalls of the Chevron (USA) Richmond refinery. In addition, fin erosion was induced in the laboratory by exposure of striped bass and shiner perch to diluted effluents from the refinery (diluted using water from the Bodega Bay Marine Laboratory). These data are further discussed in the section below on bioassays.

C. BIRD POPULATIONS

The available data concerning contaminant concentrations in birds of the Bay-Delta and its catchment have been reviewed in previous sections. Almost all the information published to date is the result of studies by Ohlendorf and co-workers.

It is worth reiterating here that the Delta and Central Valley are exceptionally important areas with respect to both resident and (especially) migratory bird species on the so-called Pacific Flyway. California as a whole provides wintering and migration habitat for 60-90% of the Pacific Flyway waterfowl population, and three of the five areas of greatest importance (the Klamath Basin, the Sacramento and San Joaquin Valleys, the Delta, and the Imperial Valley) are in the catchment of the Bay-Delta (Gilmer et al., 1982; Ohlendorf and Miller, 1984). The gross changes in habitat which have occurred in the region (e.g. see Fig. 91) have undoubtedly played a major role in regulating bird populations in the past, and these effects are in general thought to have had a greater impact than any problems related to contaminants.

However, isolated problems in respect to contaminant effects on bird populations in the Bay-Delta and its catchment have been documented. The effects of selenium on Kesterson populations are reviewed in section IIC of this report, and it is noted that although selenium has not been conclusively proven to be the causative agent of the effects seen at Kesterson, it is considered that this is most likely to be the case. Presumably, such effects are declining in incidence because of the recent discontinuance of the use of the San Luis Drain; however, ongoing

studies of birds at Kesterson are apparently not being undertaken. The impacts of selenium on birds elsewhere in the catchment are also open to doubt, although the report of Ohlendorf et al. (1986c) concerning levels of this element in diving ducks from the South Bay is disquieting. It remains possible that mercury plays a role in this scenario, and there is much potential for further research on this aspect.

Mercury itself is generally not found at sufficiently high levels in the Bay-Delta to be likely to give rise to effects on birds. However, the Central Valley area is extensively contaminated by past use of the element in mining activities and by run-off from metalliferous areas. The only data known suggesting a mercury problem in the area concern western grebes (Aechmophorus occidentalis) in Clear Lake (which is the most contaminated area in the Central Valley with respect to mercury; see section IID above). Unpublished analyses of the California Department of Fish and Game found high mercury concentrations in both livers and muscle tissues of A. occidentalis from Clear Lake (see CVRWQCB, 1987). By contrast, American coots from the same location exhibited low levels of mercury. The species differences are almost certainly a function of diet; coots are herbivorous, while A. occidentalis is piscivorous. It is interesting that the same conclusion was reached in studies of ΣDDT residues in western grebes from this location almost two decades ago. The problem at that time was largely caused by DDD use to control midges (Chaoborus astictopus); a total of almost 55 tonnes of DDD was applied directly to the Lake between 1949 and 1957 for this purpose (Herman et al., 1969).

The impacts of organochlorines on bird populations in the Bay-Delta have similarly been the subject of few studies. Risebrough et al. (1978) considered that organochlorine levels at that time were sufficiently high to cause reproductive problems in raptors, although no data were cited to support this contention. Ohlendorf and Miller (1984) demonstrated that pesticides and PCBs were accumulated in waterfowl wintering in the Bay-Delta, but felt that the residue levels attained were insufficient to give rise to population-wide problems, although individual birds might be affected. Hoffman et al. (1986) provided evidence for sublethal effects of PCBs on black-crowned night herons (Nycticorax nycticorax) on Bair Island in South Bay.

The general paucity of local data on contaminants in birds does not permit strong conclusions on their effects in the Bay-Delta, or on the comparison between these and the impacts due to habitat alteration or destruction. It would appear that further studies of this nature are worthwhile.

D. MAMMALIAN POPULATIONS, INCLUDING MAN

Little information is available on the impacts of contaminants on mammalian populations in the Bay-Delta. Risebrough et al. (1978) found little evidence that either trace elements or organochlorines in harbour seals (Phoca vitulina) were causing detrimental effects, although the documented impacts of PCBs on aquatic mammals elsewhere (Helle et al., 1976a, 1976b; Reijnders, 1980) would suggest that further research on local populations might be worthwhile.

Documentation of potential public health problems due to contaminants in the Bay-Delta and its catchment is not seen as the major thrust of the present report. However, certain problems are worth highlighting briefly here, as follows:

* As noted by SWRCB (1986), the U.S. Food and Drug Administration (FDA) does not promulgate standards for trace elements in aquatic biota, with the exception of mercury. The U.S. FDA standard for methylmercury is 1.0 $\mu g\ g^{-1}$ wet weight, which is generally less stringent than most international standards for this element (Nauen, 1983). However, the California Department of Health Services (CDHS) employs a standard of 0.5 $\mu g\ g^{-1}$ wet weight for total mercury when issuing health advisory notices (SWRCB, 1986). Median international standards used by other countries for trace elements are shown in Table 53; these may be used for comparison with published data to indicate whether concerns exist with respect to public health. However, it should be noted that not all the standards quoted in Table 53 were set

Table 53. Median international standards and ranges in such standards ($\mu g\ g^{-1}$ wet weight) for trace elements in freshwater fish and marine shellfish. Afer Nauen (1983), as cited by the SWRCB (1986).

Element	Median Standards Fish	Shellfish	Range	Number of Countries With Standards
Antimony	1.0	1.0	1.0 to 1.5	3
Arsenic	1.5	1.4	0.1 to 5.0	11
Cadmium	0.3	1.0	0.05 to 2.0	10
Chromium	1.0	1.0	1.0	1
Copper	20.0	20.0	10.0 to 100	8
Fluoride	150.0	---	150	1
Fluorine	17.5	---	10.0 to 25	2
Lead	2.0	2.0	0.5 to 10	19
Mercury	0.5	0.5	0.1 to 1.0	28
Selenium	2.0	0.30	0.30 to 2.0	3
Tin	150.0	190.0	50 to 250	8
Zinc	45	70.0	40 to 100	6

specifically to protect human health, some being intended for the protection of biological resources.

* Mercury concentrations exceeding 1.0 $\mu g\ g^{-1}$ wet weight in fish have been recorded in the Toxic Substances Monitoring Program at Clear Lake and the Guadalupe River (SWRCB, 1986; see Fig. 47 in this report). Levels of total mercury above 0.5 $\mu g\ g^{-1}$ wet weight have been found in fish from many Central Valley locations, in addition to the South Bay catchment (Fig. 47; also CVRWQCB, 1987). Girvin et al. (1975) also found high concentrations of mercury in mussels (Mytilus edulis) and Pacific oysters (Crassostrea gigas) from Redwood Creek (Fig. 45 and Table 18 in this report). The CDHS has issued health advisories regarding mercury in several fish species from Clear Lake, and for mercury in striped bass (Morone saxatilis) from the Bay-Delta.

* Health advisories have also been issued by CDHS in respect to selenium in fish from the Grassland area, Merced County. This is presumably due to the existence of selenium levels greater than 2.0 $\mu g\ g^{-1}$ wet weight (see Table 53) in some fish from the Kesterson area and surrounds (e.g. Greenberg and Kopec, 1986; Saiki, 1986; SWRCB, 1986; Linn et al., 1986, 1987). Some bivalve molluscs in the Bay-Delta also approach or exceed this concentration (see section IIC of this report).

* Cadmium is rarely accumulated to high levels by fish, but several species of bivalve mollusc concentrate this element

to great extents (e.g. see Phillips, 1980; Eisler, 1981). Cadmium is of exceptional toxicity to mammals, including Man (Friberg et al., 1974), and is of great persistence in mammals once it is accumulated (FAO/WHO, 1972). Girvin et al. (1975) found unusually high levels of this element in oysters (C. gigas) from Redwood Creek, and mussels in the Bay approach or exceed the concentrations favored in public health regulations (e.g. Risebrough et al., 1978; Hayes et al., 1985; Hayes and Phillips, 1986; Stephenson et al., 1986a; see section IIE of this report).

* Present concentrations of lead in Bay-Delta biota (section IIF) are generally below levels which would generate concern with respect to public health. The same is true of copper and zinc, which are metabolically regulated by mammals and are relatively non-toxic compared to the elements discussed above. Similarly, chromium levels in aquatic biota are not considered problematical from a public health aspect. The potential impact of arsenic in local aquatic organisms on public health cannot be assessed presently, as no differential analyses have been undertaken to elucidate the chemical speciation of this element in local biota. Evidence from elsewhere has shown that the inorganic form of arsenic (thought to be of greatest toxicity) constitutes a small fraction of total levels of the element in most aquatic organisms (e.g. see Phillips and Depledge, 1986).

* The effects of organic contaminants on public health are much less well understood in general than are those of trace elements. However, the U.S. FDA has prescribed a variety of standards for organochlorines in aquatic organisms, essentially to protect against health effects in humans. Results from the Toxic Substances Monitoring Program (SWRCB. 1986) have shown that fish from the Central Valley rivers occasionally exceed FDA standards for various organochlorines. These data are reviewed in section III of this report. It is also notable that some of the polyaromatic hydrocarbons (PAHs) are known to exert mutagenic, teratogenic, carcinogenic, or other toxic effects on mammals. However, the toxicological significance to Man of PAHs or other types of hydrocarbons in aquatic biota from the Bay-Delta is unknown.

* Microbial contamination of biota in the estuary is not a basic concern of the present report, which deals with anthropogenic chemical contaminants. The same is true of neurotoxins such as that causing paralytic shellfish poisoning. It may be noted that both these topics are worth of attention in respect to Bay-Delta shellfish, however. Public health concerns relating to the transmission of parasites to Man from the ingestion of aquatic biota are also not addressed in the present report.

E. BIOASSAY DATA

General

Bioassays are employed to determine the effects of environmental conditions (including individual contaminants or mixtures thereof) on organisms. A wide range of bioassay techniques exists, and these methods are under continuing development worldwide. Most early bioassays were conducted under stable conditions in the laboratory (often selected as optimal conditions for the test species used), employing single toxicants introduced through their simple addition to the test waters in solution. These early versions of bioassays were static in nature (i.e. test solutions were not changed) and were generally of short duration, calculating organism lethality as an end point, usually after 24, 48, or 96 hours of exposure.

The first significant improvement to such protocols was the introduction of the flow-through test, in which the test solution is continually replaced throughout the bioassay. This reduces the build-up of metabolites of the test species (which may contribute to observed toxicities in static bioassays), and also maintains toxicant concentrations at the desired level (in static tests, toxicant uptake by organisms can significantly reduce the ambient exposure concentrations). The stressing of test organisms by their handling is also reduced in flow-through bioassays compared to "renewal tests", the latter being static tests with periodic replacement of solutions.

The flow-through bioassay, employed to ascertain direct acute toxicities of contaminants, remains a mainstay of contaminant screening today. Most bioassays of this type report

as results a 96-hour LC50 value, this being the concentration of a toxicant in solution which is lethal to 50% of the test organisms over a 96 hour period. There are, however, many drawbacks with the use of this standard method. Briefly, these are as follows:

* Test species are often selected because they are hardy organisms, easy to sample and maintain live in the laboratory, both in acclimation periods and during testing. These attributes may correlate with an insensitivity to toxicants, at least in some cases. The use of the stickleback (Gasterosteus aculeatus) in local testing of effluent toxicities is a case in point here.

* Many factors may interfere with the acute toxicity of contaminants to organisms. These include test conditions (salinity, temperature, pH, aeration, etc.) and biological attributes of the species used (life stage, condition, size, sex, etc.). It is difficult to produce standardized protocols for many of these factors, and even more difficult to relate bioassay results to toxicities of contaminants in the field.

* Organisms in the environment are exposed to fluctuating natural conditions, multiple stresses, and a very large range of contaminants in combination with each other. Interaction between contaminants in respect to their toxic action or effect is common; effects may be simply additive, less than additive ("antagonistic"), or more than additive ("synergistic") in nature. Laboratory tests cannot hope to

cover all combinations of toxicants which will be encountered in the environment.

* Contaminant toxicity in natural conditions is generally not likely to be a simple function of the uptake of a toxicant from solution. Rather, organisms accumulate contaminants from a variety of sources (solution, food, perhaps sediments or suspended particulates). Standard flow-through laboratory bioassays do not reflect such conditions.

* The chemical speciation of contaminants is of great importance in defining their acute (and chronic) toxicities. Bioassays generally employ simple salts of trace metals, and may add organic chemicals in acetone or other such carrier solvents to encourage their dissolution. This does not reflect environmental conditions.

Even in the absence of the above problems, serious difficulties would be encountered in relating acute toxicities of contaminants, documented from laboratory testing, to acceptable environmental levels. A so-called "application factor" has been much employed, and is intended as a margin relating acutely toxic levels of a contaminant to those which have no discernible sublethal effect on an organism. There has been much controversy over this matter; many scientists consider application factors to be of arbitrary magnitude. There is no doubt that published data relating no-effect levels or maximum acceptable toxicant concentrations (MATCs) to LC50 levels generated from acute bioassays provide little support for the use of a standard application factor. Thus, toxicants differ in respect to the

concentration range between their sublethal and their lethal effects on species. This relates to their degree of bio-accumulation and to other factors.

The recognition of these various problems involved in the use of acute bioassays of specific species has given rise to a slow and continuing revolution in bioassay techniques. Much greater attention has been paid recently to the direct study of sublethal effects of contaminants (both in the laboratory and in field studies). A wider range of organisms is now being employed, and most authorities consider that any toxicity testing program should include several test species. Other new methods are being introduced, including the use of sediment bioassays. Some of these new methods are beginning to be employed in studies of the Bay-Delta. Results of these recent investigations are reviewed below. It is emphasized that although these newly developed methods are considered to be a great improvement over previous techniques, few studies have been completed to date in the estuary.

Bioassay Data in the Bay-Delta

Direct testing of the toxicities of industrial and municipal effluents in the Bay-Delta has until recently relied mainly upon simple testing of species such as the stickleback (Gasterosteus aculeatus). At best, such data provide only a crude indication of the effects of contaminants in effluents. However, more appropriate bioassay methods are now being introduced and these will radically improve our understanding of the local (and perhaps regional) effects of effluent discharges upon the Bay-Delta environment. Anatec Laboratories (1987a) provided

interesting data on bioassays of the effluents from the Chevron USA refinery at Richmond, as part of an Environmental Impact Report concerned with the possible need to relocate the outfall of the refinery. Behavioral response tests were conducted on rainbow trout (Salmo gairdneri) and striped bass (Morone saxatilis). Effluent dilutions of 10:1, 30:1, 100:1 and 500:1 were employed. Although behavioral responses were somewhat variable, statistically significant preferences for the effluent (i.e. non-avoidance) were noted for both species, particularly at low concentrations of the effluent. Data variability may have been due to alterations in chemical composition of the effluent between tests; territorial behavior of large S. gairdneri also affected some results.

Other studies by Anatec Laboratories (1987b) on the same Environmental Impact project concerned bioassays of a range of organisms; both lethal and sublethal effects of the effluent were investigated (Table 54). The species tested varied considerably in sensitivity (Table 55), sanddabs (Citharichthys stigmaeus) and striped bass (Morone saxatilis) showing the greatest effects. C. stigmaeus exhibited 30% mortality in only 10% effluent (effluent percentage in test solution); M. saxatilis exhibited both fin erosion (down to 10% effluent), and lethal responses at effluent concentrations greater than 32%. The dose-response relationships suggested the possible presence of cumulative forms of toxicity. Surprisingly, the crustaceans tested were found to be quite insensitive compared to some of the fish. Embryo-larval tests were thought to be more sensitive than incipient lethal studies, although problems were encountered in survival rates for controls in some cases. Ratios between effluent dilutions

Table 54. Species employed and type of study for bioassay investigations of the effluent of the Chevron USA plant in Richmond, CA. After Anatech Laboratories (1987b).

Common Name	Taxonomic Name	Type of Study
Striped bass	Morone saxatilis	Incipient leth
White sturgeon	Acipenser transmontanus	Incipient leth
Rainbow trout/steelhead	Salmo gairdneri	Incipient let.
Sanddab	Citharichthys stigmaeus	Incipient leth
Mississippi silverside	Menidia beryllina	Incipient leth
Shiner perch	Cymatogaster aggregata	Incipient let.
Stickleback	Gasterosteus aculeatus	Incipient leth
Sheepshead minnow	Cyprinodon variegatus	Incipient leth Embryo-larval
Bay shrimp	Crangon franciscorum	Incipient leth
Korean prawn	Palaemon macrodactylus	Incipient leth
Mud crab	Rithropanopeus harrissii	Range finding Embryo-larval
Opossum shrimp	Neomysis mercedis	Incipient leth
Dungeness crab	Cancer magister	Range finding
Diatom	Skeletonema costatum	14 day algal a

TABLE 55. Estimates of LC50 values, expressed as % effluent for effects of a mixture of refinery effluent and Ortho blowdown. Data refer to toxicity tests on effluents from the Chevron USA refinery in Richmond, CA. After Anatech Laboratories (1986b).

Common Name (Species)	Day 4	Day 7	Day 14	Day 21	Final
Sanddab (Citharichthys stigmaeus)	>100	>100	45.6 (34.8-58.3)[a]	18.8 (12.5-25.2)	17.4 (Day 25) (11.2-23.4)
Striped Bass (Morone saxatilis)	>100	>100	65.6 (55.5-78.3)	42.3 (35.6-50.3)	33.1 (Day 27) (27.9-39.2)
Shiner perch (Cymatogaster aggregata)	47.9 (42.9-53.1)	38.9 (34.3-44.1)	35.3 (30.9-40.4)	---	---
Steelhead (Salmo gairdneri)	74.8 (56.0-100.0)	74.8 (56.0-100.0)	---	---	---
Stickleback (Gasterostreus aculeatus)	>100	>100	---	---	100 (day 9)
Sheepshead minnow (Cyprinodon variegatus)	>100	>100	---	---	>100 (day 8)
Silversides (Menidia beryllina)	>100	95.0 (85.2-108.1)	---	---	74.8 (day 11) (56.0-100.0)
Bay shrimp (Crangon francisorum)	>100	>100	---	---	>100 (day 8)
Prawn (Palaemon macrodactylus)	>100	>100	---	---	>100 (day 8)
Opossum shrimp (Neomysis mercedis)	>100	>100	61.1 (46.1-84.8)	---	---
Algae (Skeletonoma costatum)	---	---	57.9 (52.7-63.2)	---	--
White sturgeon (Acipenser transmontanus)	88.1 (74.6-109.51)	75.6 (65.0-89.2)	---	---	72.6 (day 9) (62.6-85.1)

[a] 95% confidence interval in parentheses.

causing acute and chronic effects, and consideration of the probit plots for mortality in the acute studies, suggested that the effluent might exert significant effects on biota in the field at concentrations as low as 0.5 to 2.0%. It was also noted that striped bass (M. saxatilis) taken from the area close to the outfall exhibited fin erosion.

These data are a useful demonstration of the power of multi-species bioassays in characterizing effluent toxicity. It will be noted from Table 54 that the stickleback Gasterosteus aculeatus was highly tolerant to effects of the effluent, compared to some of the other species tested. Clearly, the present trend away from the use of acute bioassays of this species to a range of lethal and sublethal tests (SFBRWQCB, 1987) will greatly improve our understanding of the direct impacts of effluents upon the living resources of the Bay-Delta. This effort should be both applauded and encouraged.

The evolution of methods designed to assay the toxicity of marine and estuarine sediments has been reviewed by Chapman (in press). He notes that neither benthic infaunal surveys nor chemical analyses of sediments provide a full picture of contaminant bio-availability in sediments. Techniques have thus been developed which demonstrate the toxicity of sediments to biota. As noted above for effluent bioassays, a range of methods is becoming available, including responses at the lethal and sublethal levels and various ancillary techniques. Inter-laboratory comparison tests have shown acceptable levels of variability, and Chapman (in press) pleads for the standardization of sediment bioassay methods and for the adoption of the amphipod bioassay (using Rhepoxynius abronius, formerly

called Paraphoxus epistomus) as a means of calibrating data from different researchers. There can be no doubt that such standardization is needed; its introduction at the present stage of evolution of such studies would greatly aid in the overall development of these important techniques.

Few studies using these methods have been undertaken in the Bay-Delta. However, those which have been completed lend credence to the oft-repeated view that sediments of the estuary contain significantly elevated levels of contaminants which are likely to exert detrimental effects on infaunal and demersal biota.

Chapman et al. (1986) reported the results of field trials for the use of the so-called "sediment quality triad" (benthic infauna, sediment chemistry, and sediment bioassays) in San Francisco Bay. These trials were carried out to determine the usefulness of these methods with a view to their possible inclusion in the National Status and Trends Program of NOAA. Four bioassay techniques were employed on sediments from three locations in the Bay (San Pablo Bay, Oakland, and Islais Creek). The techniques used were:

* The 10-day Rhepoxynius abronius amphipod bioassay, which measures both sublethal (avoidance of sediments) and lethal effects (Swartz et al., 1982, 1985).

* Sublethal (abnormal development) and lethal responses of larvae of the native Bay mussel Mytilus edulis (Mitchell et al., 1985).

* Behavioral responses of clams, Macoma balthica, measured as rate of reburial in sediments. (McGreer, 1979).

* Reproductive impairment investigations, using the harpacticoid copepod Tigriopus californicus (Misitano, 1983).

Details of the methods employed are given in full in Chapman et al. (1986) and will not be repeated here. Results of these studies are shown in detail in Tables 56 to 59, and differences between the results for each site are summarized in Fig. 104. In general, the agreement between the four techniques was good. The amphipod and mussel larvae bioassays both suggested high toxicity in Islais Creek sediments, and some data from the other two tests also reflected this. The clam Macoma balthica is not present in sediments from inner Islais Creek, and this agrees with its reburial times noted for these sites (IS02 and IS05). There was less agreement between the techniques concerning the ranking of Oakland and San Pablo Bay sediments in respect to their toxicity. This may reflect the abundance of particular contaminants at each site and their bio-availability and/or toxicity to each organism. Other sediment properties (grain size, redox potential, etc.) may also be relevant in determining the precise responses of organisms in such bioassays. The effects of grain size in particular deserve further study.

Additional sediment bioassay data were produced by Marine Bioassay Laboratories (1987) as part of an Environmental Impact Statement on the homeporting of U.S. Navy vessels in the Bay. Several species and techniques were employed in these studies. Suspended particulate phase bioassays (elutriate tests) were

Table 56. Rates of survival and avoidance of sediments for bioassays of the amphipod Rhepoxynius abronius, using sediments from 10 sites at each of three Bay locations: (San Pablo Bay (SP), Oakland (OA), and Islais Creek (IS)). After Chapman et al. (1986).

Station	Mean Values ± S.D.[a]	
	Survival[b]	Avoidance[c]
SP01	17.6 ± 2.3	0.5 ± 0.3
SP02	18.2 ± 1.6	1.1 ± 0.9
SP03	17.4 ± 1.5	0.8 ± 0.3
SP04	16.0 ± 4.4	0.8 ± 0.6
SP05	19.2 ± 0.8	0.5 ± 0.7
SP06	18.4 ± 1.3	0.4 ± 0.4
SP07	16.8 ± 0.4	0.4 ± 0.3
SP08	14.2 ± 7.0*	0.3 ± 0.2
SP09	15.2 ± 2.2	0.5 ± 0.3
SP10	17.8 ± 1.8	0.4 ± 0.2
SP Overall (n=10)	17.1 ± 1.5	0.6 ± 0.2
SP02/05/09 Overall (n=3)	17.5 ± 2.0	0.7 ± 0.3
OA01	18.0 ± 1.6	0.5 ± 0.4
OA02	18.2 ± 0.8	0.7 ± 0.3
OA03	18.4 ± 1.5	0.5 ± 0.3
OA04	16.0 ± 2.3	0.6 ± 0.4
OA05	17.4 ± 0.9	0.4 ± 0.4
OA06	16.0 ± 2.3	1.1 ± 1.1
OA07	15.6 ± 1.1	0.6 ± 0.4
OA08	17.6 ± 2.1	0.8 ± 0.4
OA09	17.4 ± 0.5	1.9 ± 0.8
OA10	17.8 ± 2.4	0.4 ± 0.5
OA Overall (n=10)	17.2 ± 1.0	0.8 ± 0.4
OA02/05/09 Overall (n=3)	17.7 ± 0.5	1.0 ± 0.8
IS01	1.0 ± 1.2*	9.1 ± 1.8*
IS02	1.0 ± 1.2*	7.4 ± 0.9*
IS03	10.4 ± 6.0*	4.8 ± 3.3*
IS04	0.0 ± 0.0*	7.0 ± 5.8*
IS05	15.2 ± 0.4	1.7 ± 0.5
IS06	15.8 ± 2.3	0.4 ± 0.2
IS07	14.2 ± 2.0*	0.7 ± 0.5
IS08	13.8 ± .6*	2.7 ± 0.8
IS09	12.6 ± 3.8*	0.6 ± 0.5
IS10	10.0 ± 2.4*	0.2 ± 0.1
IS Overall (n=10)	9.4 ± 6.3*	3.5 ± 3.4
IS02/05/09 Overall (n=3)	9.6 ± 7.6*	3.2 ± 3.6
Control	18.8 + 1.6	1.3 + 1.6

a. n=5

b. 20.0=100% survival. Asterisks denote values significantly less than (P=0.05) the control (West Beach, Whidbey Island, Washington), and are based on comparisons among 30 stations.

c. Number of amphipods on the surface per jar per day (out of a maximum of 20.0). Asterisks denote values significantly greater than (P=0.05) the control.

Table 57. Percentage survival and percentage of abnormal larvae found in bioassays of larvae of the native Bay mussel *Mytilus edulis*, using sediments from three sites at each of three Bay locations. Codes as in Table 56. After Chapman *et al.* (1986).

	Mean Values + S.D.(a)		
Station	Number of Larvae(b)	Percent Survival(c)	Percent Abnormal(d)
SP02	288±43*	56.9±8.4	13.4±2.8
SP05	418±43	82.7±8.6	7.7±1.5
SP09	258±60*	50.9±11.8	15.3±5.4
SP Overall (n=3)	321±85	63.5±16.9	12.1±4.0
OA02	248±46*	49.1±9.0	14.5±2.6
OA05	122±26*	24.0±5.2	24.7±6.8*
OA09	170±24*	33.5±4.7	18.7±8.4*
OA Overall (n=3)	180±64*	35.5±12.7	19.3±5.1
IS02	30±18*	6.0±3.5	67.7±8.9*
IS05	16±16*	3.2±3.0	65.9±19.8*
IS09	70±27*	13.9±5.3	31.9±5.2*
IS Overall (n=3)	39±28*	7.7±5.5	55.2±20.2*
Seawater Control	506±35	100.0±6.9	5.6±1.2
Sediment Control	371±80	73.4±15.8	7.4±0.6

a. n=5
b. Numbers of larvae surviving at the end of the test, which are used to determine relative survival and percent abnormal larvae. All values are significantly less than (P=0.05) the seawater control except SP Overall; asterisks denote values significantly less than (P=0.05) the sediment control.
c. Relative to the seawater control, which is assigned a mean value of 100%.
d. All values are significantly greater than (P=0.05) the seawater control except SP02, SP05, SP Overall, OA Overall, and the sediment control; asterisks denote values significantly greater than (P=0.05) the sediment control.

Table 58. Median reburial times for clams, Macoma balthica, in sediments of three sites at each of three Bay locations. Codes as in Table 56. After Chapman et al. (1986).

Sample	Replicate	ET50 (min)	Mean ± S.D.
SP02	A	3.0	
	B	1.5	
	C	3.0	
	D	3.5	
	E	5.5	
			3.3±1.4
SP05	A	2.0	
	B	5.0	
	C	3.0	
	D	6.5	
	E	2.0	
			3.9±1.8
SP09	A	2.0	
	B	2.0	
	C	2.0	
	D	5.5	
	E	4.5	
			3.2±1.7
OA02	A	4.5	
	B	2.5	
	C	4.0	
	D	4.0	
	E	3.0	
			3.6±0.8
OA05	A	4.5	
	B	5.0	
	C	2.0	
	D	4.0	
	E	4.0	
			3.9±1.1
OA09	A	2.5	
	B	5.0	
	C	6.0	
	D	9.0	
	E	6.5	
			5.8±2.4
IS02	A	7.0	
	B	8.0	
	C	5.5	
	D	11.0	
	E	6.0	
			7.5±2.2
IS05	A	7.0	
	B	7.5	
	C	5.0	
	D	10.0	
	E	5.5	
			7.0±2.0
IS09	A	3.0	
	B	5.0	
	C	3.5	
	D	4.0	
	E	5.5	
			4.0±1.2
Sediment Control	A	13.0	
	B	5.0	
	C	1.0	
	D	3.0	
	E	2.0	
			4.8±4.8 (2.8±1.7 for reps B-E)

Table 59. Reproductive success of harpacticoid copepods, Tigriopus californicus, exposed to sediments from three sites at each of three Bay locations. Codes as in Table 56. After Chapman et al. (1986).

Station	Mean Number of Young ±S.D. Produced Per Adult Over 4 Weeks	Number of Adults Surviving To 4 Weeks(
SPO2	107.5 ± 44.2*	5
SPO5	121.2 ± 36.8	8
SPO9	62.9 ± 33.1*	7
SP Overall (n=3)	97.2 ± 44.6*	6.7
OAO2	112.0 ± 54.6	7
OAO5	113.9 ± 52.6	8
OAO9	118.8 ± 78.0	8
OA Overall (n=3)	114.9 ± 60.1	7.7
ISO2	96.9 ± 37.3*	7
ISO5	103.8 ± 48.6*	6
ISO9	84.0 ± 35.3*	7
IS OVERALL (n=3)	95.3 ± 40.0*	6.7
Seawater Control	181.0 ± 132.6	7

a. Asterisks denote values significantly less than the control (P=0.05).
b. n=8 adults at start of testing

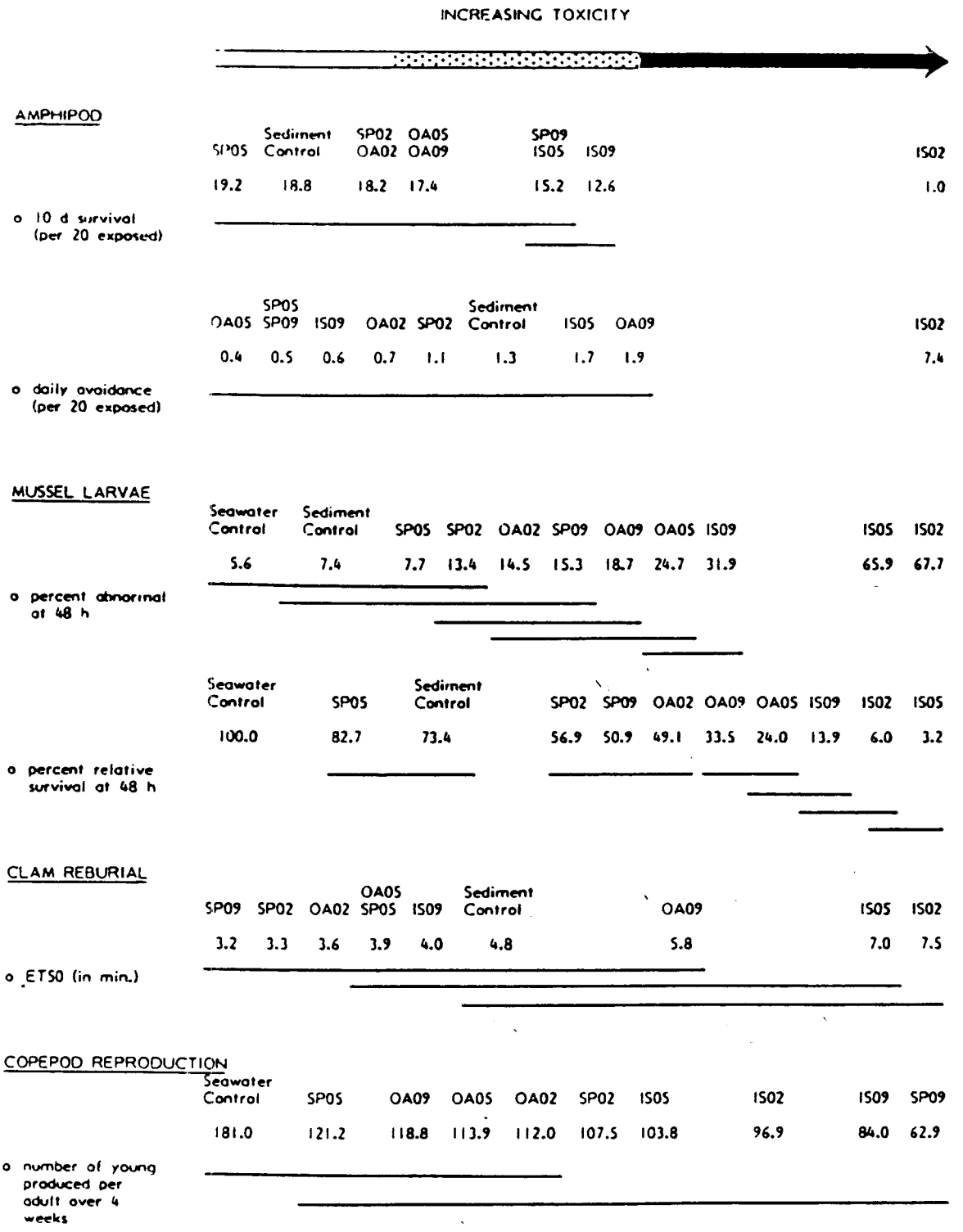


Fig. 104. Summary of mean values of sediment bioassay data from Tables 56 to 59. Treatments not underlined by the same line are significantly different at $P<0.05$. After Chapman et al. (1986).

carried out using sanddabs (Citharichthys stigmaeus), the mysid shrimp Acanthomysis sculpta, and larvae of the Pacific oyster Crassostrea gigas. Solid phase bioassays employed mysid shrimp, the clam Macoma nasuta, the polychaete worm Nephtys caecoides, and the amphipod Rhepoxynius abronius. Sediments from several sites at Hunter's Point, the eastern side of Treasure and Yerba Buena Islands, and Alameda were used in the bioassays. Briefly, the results were as follows:

* No significant mortality of sanddabs was noted in elutriate tests. However, effects were noted for mysids exposed in suspended particulate phase bioassays to sediments from Hunter's Point or Treasure Island, and for oyster larvae exposed to particulates from sediments of any of the three locations.
* No significant mortalities of mysids, clams or polychaetes occurred in solid phase bioassays. However, in some tests, control mortalities at unacceptable rates occurred, for both mysids and polychaetes. These data should thus be interpreted with caution.

* Survival of amphipods (Rhepoxynius abronius) was reduced upon exposure to sediments from some sites at each of the three locations studied; this effect was statistically significant by comparison to control survival (in Yaquina Bay sediment, from which the amphipods were originally collected). No significant differences existed between emergence and reburial rates of amphipods in test sediments and controls, except for a greater emergence rate for sediments from a few sites at Treasure Island and Alameda.

These data again emphasize the usefulness for a multi-species approach to bioassay studies. It is clear that Bay sediments are of significant toxicity in a variety of locations.

Finally, mention is required of some recent (as yet unpublished) data on standard 10-day bioassays conducted by the EPA laboratory, Newport, Oregon, on survival of R. abronius after exposure to sediments from 26 sites in the South Bay (Baumgartner et al., unpublished manuscript). The sites sampled are shown in Fig. 89 in section IV of this report; survival data are presented in Table 60. Significant toxicity is evident in sediments from most of these locations. Interestingly, the poorest rates of survival were found using sediments from offshore locations in the east of the central section of South Bay. The data for Hunter's Point sediments (locations 18 and 19) agree well with those of Marine Bioassay Laboratories (1987), cited above.

In summary, recent data from both direct effluent toxicity bioassays and sediment toxicity tests have provided indications of significant effects on Bay-Delta biota due to the discharge of industrial and municipal effluents and the existence of elevated concentrations of contaminants in sediments of the estuary. The new techniques which are now beginning to be used to study toxicological problems in the Bay-Delta show considerable promise; their continued and expanded use should be accorded high priority, such that the overall anthropogenic impacts on the estuary may be more fully understood in the future.

Table 60. Survival of the amphipod Rhepoxynius abronius after 10-day exposure to surficial sediments from 26 South Bay locations. Sampling sites shown in Fig. 89. After Baumgartner et al. (unpublished manuscript).

Location Number	Number of Survivors[a]	Percent Survival
1	16	80
2	10	50
3	15	75
4	15	75
5	11	55
6	12	60
7	14	70
8	11	55
9	14	70
10	16	80
11	15	75
12	10	50
13	7	35
14	12	60
15	8	40
16	6	30
17	14	70
18	13	65
19	15	75
20	9	45
21	11	55
22	11	55
23	0	0
24	10	50
25	0	0
26	12	60

[a] 20 individuals initially

VI. CONCLUSIONS

This broad-ranging report covers many facets of the abundance of contaminants and their potential effects in the San Francisco Bay-Delta. A variety of conclusions may be reached from a review of the existing database in this area. These conclusions may be stated both in general terms and in relation to specific problems; such a subdivision is employed in the listings below.

A. GENERAL CONCLUSIONS

1. The quality of the existing database which may be employed to elucidate the abundance of contaminants in the Bay-Delta ecosystem is poor. Few contaminants have been studied in sufficient detail to adequately characterize their distribution in the Bay-Delta on regional or local scales, and the temporal trends therein. This is the case with respect to toxicant levels in water, sediments and biota of the estuary. Data on biota rely largely on the analysis of bivalve molluscs. The transfer of contaminants through Bay-Delta food chains has been ignored to date.
2. There are many reasons for the inadequate characterization of contaminant abundance in the estuary. These include the fact that present analytical techniques are in some cases insufficiently robust to fully separate or quantify individual pollutants of concern. Little can be done to improve such matters in advance of general enhancements of such techniques.
3. In certain instances, however, the current state of knowledge of contaminant abundance in the estuary is not constrained by analytical methodologies. In these cases, the

present rudimentary understanding is due to the inadequate design of monitoring programs, or the poor application of available techniques. Inattention to basic quality control and quality assurance procedures is particularly notable. There is an urgent need for improvement of such matters if contaminants are to be better characterized in components of the Bay-Delta ecosystem.

4. Studies of the biological effects of contaminants in the estuary have been few. While it is true that many of the techniques which may be employed to monitor the impacts of toxicants on aquatic biota have only been recently developed, their use in investigations of the Bay-Delta has been inadequate to date. In some instances, this is now changing; recent attempts to employ new methods for toxicity testing of effluents discharged to the estuary and of Bay-Delta sediments are cases in point, and should be encouraged.

5. Investigations of the effects of contaminants on Bay-Delta biota have suffered from many of the same problems as toxicant monitoring studies, discussed above. In addition, however, most research to date has dealt only with correlations of parameters, rather than being specifically designed to demonstrate cause-and-effect phenomena. As a result, the existing database is largely <u>suggestive</u> of detrimental effects due to toxicants in the estuary, but not <u>conclusive.</u> This should be redressed by undertaking specific studies on cause-and-effect relationships.

6. Portions of the Bay-Delta ecosystem which are particularly

contaminated have been inadequately studied, either with respect to toxicant concentrations or their effects. For example, research on microlayer pollutants has been almost completely ignored to date. Very few studies of the biological effects of contaminants have been undertaken in known toxicant "hot-spots." Clearly, contaminants will be likely to exert their most extreme effects in areas of their greatest abundance; the latter areas thus deserve particular attention.

B. SPECIFIC CONCLUSIONS

1. Additional research on the sources, general abundance, and toxic effects of silver in the South Bay is recommended. Existing data show this region to be the major source of silver to the Bay-Delta as a whole. The concentrations of silver present in the South Bay appear sufficiently high to be likely to exert toxic effects on biota, at least in areas close to discharges of the element.
2. Both copper and cadmium have been suggested to be of unusually high bio-availability in the Bay-Delta. This is particularly relevant with respect to regulatory controls required in the estuary. Further studies of this specific aspect of bio-availability should be undertaken.
3. The sources of selenium within the estuary itself have been particularly poorly characterized. Existing data suggest these are significant in both the northern reach of the Bay and in the South Bay. In addition to further characterization of sources of selenium, its effects on Bay-Delta biota deserve additional attention.

4. Very little information exists on tin in the estuary. Levels of butyltin compounds measured to date suggest the possibilit of detrimental biological effects from these highly toxic compounds, particularly in poorly-flushed harbors or marinas. Additional studies of an effect-related nature (perhaps utilizing the Pacific oyster, Crassostrea gigas) are needed.
5. The presently-available information on arsenic in Bay-Delta biota is restricted to data for total arsenic, as no differential analyses of the various chemical forms of this element have been undertaken. Quantification of the inorganic form of the element in Bay-Delta organisms is required, to assess the toxicological significance of arsenic in the estuary. The same criticism may be made with respect to studies of mercury in the Bay-Delta to date.
6. Consideration of the general abundance of polychlorinated biphenyls (PCBs) in the Bay-Delta suggests that it is likely that these compounds are exerting sublethal effects on some estuarine species. Cause-and-effect studies should be undertaken to investigate this possibility further. PCBs in biota should be quantified in terms of individual components (homologues), particular attention being given to the levels and effects of coplanar PCBs.
7. The impacts of organochlorine pesticides on biota of the Sacramento and San Joaquin Rivers and the Delta are virtually unknown. Given the high rate of past and present use of these compounds in the Bay-Delta catchment, their effects are worthy of further study.
8. The State Mussel Watch Program does not presently include

the analysis of hydrocarbons in mussels from the Bay-Delta. This is unfortunate, as this Program provides much useful data on other types of contaminants in the estuary. Consideration should be given to the inclusion of hydrocarbon analysis in this Program in the future. The results of the Program would also be of greater use in trend analysis if certain locations were consistently employed in data collection.

9. There is generally a dearth of information on hydrocarbon distributions in the Bay-Delta. This should be redressed, particularly with respect to the levels of polyaromatic hydrocarbons (PAHs), which are of considerable toxicity in the aquatic environment.

10. No conclusion may be reached at present with respect to the cause(s) of the apparent decline in certain fish populations in the estuary. The impacts of contaminants on this resource may be significant, but present data are not conclusive in this regard. Additional cause-and-effect studies are required, on striped bass (Morone saxatilis) and other species. Investigations of demersal species of fish would be of particular benefit.

11. Few studies exist on the impacts of contaminants in the Bay-Delta on birds or aquatic organisms of high trophic levels. It is likely that such species will accumulate particularly high concentrations of certain contaminants, which may thus exert detrimental effects on the species concerned. Additional research is needed on this aspect; non-migratory species should be preferred as the subjects of such studies.

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VI. CONCLUSIONS

This broad-ranging report covers many facets of the abundance of contaminants and their potential effects in the San Francisco Bay-Delta. A variety of conclusions may be reached from a review of the existing database in this area. These conclusions may be stated both in general terms and in relation to specific problems; such a subdivision is employed in the listings below.

A. GENERAL CONCLUSIONS

1. The quality of the existing database which may be employed to elucidate the abundance of contaminants in the Bay-Delta ecosystem is poor. Few contaminants have been studied in sufficient detail to adequately characterize their distribution in the Bay-Delta on regional or local scales, and the temporal trends therein. This is the case with respect to toxicant levels in water, sediments and biota of the estuary. Data on biota rely largely on the analysis of bivalve molluscs. The transfer of contaminants through Bay-Delta food chains has been ignored to date.
2. There are many reasons for the inadequate characterization of contaminant abundance in the estuary. These include the fact that present analytical techniques are in some cases insufficiently robust to fully separate or quantify individual pollutants of concern. Little can be done to improve such matters in advance of general enhancements of such techniques.
3. In certain instances, however, the current state of knowledge of contaminant abundance in the estuary is not constrained by analytical methodologies. In these cases, the

present rudimentary understanding is due to the inadequate design of monitoring programs, or the poor application of available techniques. Inattention to basic quality control and quality assurance procedures is particularly notable. There is an urgent need for improvement of such matters if contaminants are to be better characterized in components of the Bay-Delta ecosystem.

4. Studies of the biological effects of contaminants in the estuary have been few. While it is true that many of the techniques which may be employed to monitor the impacts of toxicants on aquatic biota have only been recently developed, their use in investigations of the Bay-Delta has been inadequate to date. In some instances, this is now changing; recent attempts to employ new methods for toxicity testing of effluents discharged to the estuary and of Bay-Delta sediments are cases in point, and should be encouraged.

5. Investigations of the effects of contaminants on Bay-Delta biota have suffered from many of the same problems as toxicant monitoring studies, discussed above. In addition, however, most research to date has dealt only with correlations of parameters, rather than being specifically designed to demonstrate cause-and-effect phenomena. As a result, the existing database is largely <u>suggestive</u> of detrimental effects due to toxicants in the estuary, but not <u>conclusive.</u> This should be redressed by undertaking specific studies on cause-and-effect relationships.

6. Portions of the Bay-Delta ecosystem which are particularly

contaminated have been inadequately studied, either with respect to toxicant concentrations or their effects. For example, research on microlayer pollutants has been almost completely ignored to date. Very few studies of the biological effects of contaminants have been undertaken in known toxicant "hot-spots." Clearly, contaminants will be likely to exert their most extreme effects in areas of their greatest abundance; the latter areas thus deserve particular attention.

B. SPECIFIC CONCLUSIONS

1. Additional research on the sources, general abundance, and toxic effects of silver in the South Bay is recommended. Existing data show this region to be the major source of silver to the Bay-Delta as a whole. The concentrations of silver present in the South Bay appear sufficiently high to be likely to exert toxic effects on biota, at least in areas close to discharges of the element.
2. Both copper and cadmium have been suggested to be of unusually high bio-availability in the Bay-Delta. This is particularly relevant with respect to regulatory controls required in the estuary. Further studies of this specific aspect of bio-availability should be undertaken.
3. The sources of selenium within the estuary itself have been particularly poorly characterized. Existing data suggest these are significant in both the northern reach of the Bay and in the South Bay. In addition to further characterization of sources of selenium, its effects on Bay-Delta biota deserve additional attention.

4. Very little information exists on tin in the estuary. Levels of butyltin compounds measured to date suggest the possibilit of detrimental biological effects from these highly toxic compounds, particularly in poorly-flushed harbors or marinas. Additional studies of an effect-related nature (perhaps utilizing the Pacific oyster, Crassostrea gigas) are needed.
5. The presently-available information on arsenic in Bay-Delta biota is restricted to data for total arsenic, as no differential analyses of the various chemical forms of this element have been undertaken. Quantification of the inorganic form of the element in Bay-Delta organisms is required, to assess the toxicological significance of arsenic in the estuary. The same criticism may be made with respect to studies of mercury in the Bay-Delta to date.
6. Consideration of the general abundance of polychlorinated biphenyls (PCBs) in the Bay-Delta suggests that it is likely that these compounds are exerting sublethal effects on some estuarine species. Cause-and-effect studies should be undertaken to investigate this possibility further. PCBs in biota should be quantified in terms of individual components (homologues), particular attention being given to the levels and effects of coplanar PCBs.
7. The impacts of organochlorine pesticides on biota of the Sacramento and San Joaquin Rivers and the Delta are virtually unknown. Given the high rate of past and present use of these compounds in the Bay-Delta catchment, their effects are worthy of further study.
8. The State Mussel Watch Program does not presently include

the analysis of hydrocarbons in mussels from the Bay-Delta. This is unfortunate, as this Program provides much useful data on other types of contaminants in the estuary. Consideration should be given to the inclusion of hydrocarbon analysis in this Program in the future. The results of the Program would also be of greater use in trend analysis if certain locations were consistently employed in data collection.

9. There is generally a dearth of information on hydrocarbon distributions in the Bay-Delta. This should be redressed, particularly with respect to the levels of polyaromatic hydrocarbons (PAHs), which are of considerable toxicity in the aquatic environment.

10. No conclusion may be reached at present with respect to the cause(s) of the apparent decline in certain fish populations in the estuary. The impacts of contaminants on this resource may be significant, but present data are not conclusive in this regard. Additional cause-and-effect studies are required, on striped bass (Morone saxatilis) and other species. Investigations of demersal species of fish would be of particular benefit.

11. Few studies exist on the impacts of contaminants in the Bay-Delta on birds or aquatic organisms of high trophic levels. It is likely that such species will accumulate particularly high concentrations of certain contaminants, which may thus exert detrimental effects on the species concerned. Additional research is needed on this aspect; non-migratory species should be preferred as the subjects of such studies.

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