San Francisco Estuary
Regional Monitoring Program

EXECUTIVE SUMMARY

This is the second Annual Report of the Regional Monitoring Program for Trace Substances (RMP). It describes concentrations of pollutants in water, sediment, and tissue samples of oysters, mussels, and clams at 15 to 24 sampling locations for three discrete sampling events - during the wet season in February, in April during a period of declining Delta outflows, and during the dry season in August. The sampling stations are located throughout the Estuary and at the major tributaries including the mouths of the Guadalupe River and Coyote Creek in the extreme southern portions of the Estuary to the confluence of the Sacramento and San Joaquin Rivers (Figure 1). In 1994, water samples were also taken at two upstream locations at Rio Vista (Sacramento River) and Manteca (San Joaquin River) to determine river contaminant concentrations during a six-week period in spring.

The RMP is one important component described in a document entitled “Regional Monitoring Strategy” (SFEP 1993). This document was prepared as part of the Comprehensive Conservation and Management Plan for the San Francisco Estuary and is centered around the five key management issues identified in the Plan: pollution prevention and reduction; dredging and waterway modification; biological resources; land use management; and water use. A large number of management actions in these five areas were identified that could contribute to the restoration of a “healthy” Estuary. For most of the five key management issues, some monitoring efforts are already in place so that the outcome of individual management actions taken can be evaluated. The RMP provides information on how contaminant concentrations in the Estuary are responding to pollution prevention and reduction steps and, ultimately, if financial resources spent on these efforts have the desired effects.

The RMP evolved out of a pilot program funded under the State’s Bay Protection and Toxic Cleanup Program, after the Regional Water Quality Control Board had developed a funding and implementation structure. Sixty-three public and private entities that discharge treated waste water and cooling water or are involved in dredging activities contribute the financial resources necessary to conduct the RMP. Many of these program participants also contribute expertise or logistical support. The San Francisco Estuary Institute, as the entity designated to implement the Regional Monitoring Strategy, is administering the program.

The objectives of the Regional Monitoring Program for Trace Substances can be summarized as follows:

1) to describe the condition of the Estuary with respect to toxic and potentially toxic trace elements and organic contaminants in the water, sediment, and the tissue of bivalve mollusks;

2) to develop a long-term data base on trends in trace contaminant concentrations in water and sediments;

3) to determine if water and sediment quality are in compliance with established regulatory objectives; and

4) to provide a data base on trace contaminants which is compatible with data being developed in other ongoing studies.

The Program, as currently designed, does not include elements to determine contaminant sources, mechanisms of contaminant transport and fate, or ecological effects, but may include these additional objectives at some time in the future. The interpretation of RMP data and synthesis of results in the context of the already existing knowledge base is not an explicit objective, although this report is a first attempt at serving that purpose to the extent that available resources allow.

In 1994 more than 100 individual chemical parameters were analyzed in water, sediment and tissue between two and three times per year. Bioassays on water and sediment samples were also conducted to determine possible toxicity to selected organisms. Most of the station locations were chosen so they would be as far as possible from the influence of major contaminant sources and to be as representative as possible of “background” contaminant concentrations. In 1994, two stations adjacent to the wastewater outfalls of the Cities of San Jose and Sunnyvale were added on a trial basis.

Unlike the first sampling year, 1994 was relatively dry and produced only about 40% of the peak runoff that occurred in 1993. As Delta outflow decreased, salinities generally increased with each sampling period. The five parts per thousand isohaline, which the Regional Board has proposed as the dividing line for application of fresh water and marine water quality objectives, moved progressively up the Estuary.

Water Monitoring

Trace contaminant concentrations in Estuary water were far from uniform among the 24 stations and among the three sampling periods in 1994. For example, dissolved and total concentrations of most contaminants typically differed by one to two orders of magnitude. However, dissolved lead differed 10,000-fold among the 22 stations, while dissolved selenium and total arsenic varied by a factor of 6.5 and 2.5, respectively.

Two general gradients in total trace metal concentrations were observed in 1994: one gradient, with the highest levels at the southern slough stations decreasing toward the Central Bay, and the other from elevated concentrations in San Pablo Bay to lower levels in the Sacramento and San Joaquin Rivers. Only selenium and mercury were exceptions to these patterns. Selenium exhibited only a slight gradient from the South Bay to the rivers, and mercury had elevated concentrations in the rivers in August. Dissolved copper, mercury, nickel, lead, selenium, and zinc, and total silver and selenium were always highest at the slough stations, located in the bayward ends of Coyote Creek and the Guadalupe River. These tributaries receive treated municipal and industrial effluent, as well as runoff from the Santa Clara Valley. It is not possible from current RMP data to determine which of those possible sources are contributing which contaminants. Dissolved and total (the sum of dissolved and particulate forms) concentrations of most trace elements were generally lowest in the Central Bay, reflecting the influence of oceanic flushing. At times, arsenic, selenium, silver, and zinc were lowest at the two Sacramento and San Joaquin River stations, located just above their confluence.

Organic contaminants were distinctly elevated in the Estuary compared to the reference station outside the Golden Gate. PAHs and PCBs had similar spatial distributions, with relatively high concentrations in the South Bay and the northern Estuary, lower concentrations in the Rivers, and lowest concentrations at the Golden Gate. Compared to the PAHs and PCBs, pesticides tended to have higher concentrations in the northern Estuary and high concentrations in the Rivers. Special sampling on the San Joaquin River at Manteca and the Sacramento River at Rio Vista yielded the highest concentrations of most pesticides in 1994, including DDTs, chlordanes, and dieldrin. The Manteca station had a median concentration of DDTs that was 22 times higher than the median for RMP base stations. Diazinon was found at a high concentration at Coyote Creek during the wet season, suggesting that runoff from the Santa Clara Valley is a source of this insecticide.

Trace elements in both dissolved and particulate phases usually occurred in the highest concentrations at the southern slough stations. Seasonal differences in trace contaminant concentrations may suggest different sources. For example, dissolved zinc, dissolved mercury, and total selenium were higher in February and April than during the dry-season sampling in August, pointing toward runoff as a likely source of these elements. Conversely, elements that are elevated during the dry season, with little surface runoff entering the Estuary, suggest continuous sources, such as waste water outfalls, atmospheric deposition, or mobilization from sediments.

For trace organic contaminants, a switch in contractors between the February and April cruises constrains interpretation of seasonal patterns in contamination. For example, measured diazinon concentrations were much higher in February samples. This pattern might be expected due to seasonal variation in the influence of urban runoff, but methodological differences provide an alternative explanation. Intercalibration exercises between the two contractors for water organics analysis are planned for 1996 to help determine the actual extent of seasonal variation.

The aquatic bioassays showed significant toxicity to the mysid *Mysidopsis* at the Napa River and Red Rock in February. Just which component(s) in the water at those stations caused the observed toxicity is not known.

There were no obvious corresponding elevations in trace contaminants in the water in those samples.

Comparisons to Water Quality Standards

Concentrations of seven of the ten trace elements - silver, cadmium, chromium, lead, selenium, silver, zinc - and total PAHs were below existing water quality criteria or objectives in 1994. However, concentrations for near-total and dissolved copper, total mercury and near-total nickel were often above U.S. EPA criteria. PCBs were well above the criteria at all saltwater stations sampled, similar to the situation reported in March 1993. Seven individual PAH compounds, heptachlor epoxide, dieldrin and p,p'-DDE were above water quality criteria. The insecticide diazinon was above the National Academy of Science guideline of 9,000 ppq at three freshwater stations in February. Despite the numerous exceedances of water quality guidlines throughout the Estuary, only two samples exhibited significant water toxicity.

Sediment Monitoring

The variability of contaminant concentrations in sediments in the San Francisco Estuary reflects the complexity of estuarine geochemical cycles and proximity to the varied sources of contamination. The adsorption of dissolved contaminants onto sediment particles, particle transport by rivers, streams, and storm drains into the Estuary, sediment mixing by currents, tides, and organisms that live in the sediment, and many other factors may affect what is measured by the RMP.

Similar to the spatial gradient observed for trace elements in water, the 1994 sediment samples exhibited the highest concentrations in the southern sloughs. Concentrations decreased into the Central Bay, then increased again in the northern Estuary (except at the coarse sediment stations), and decreased at the Rivers. Concentrations typically ranged over an order of magnitude except for silver and selenium which ranged over two orders of magnitude.

Concentrations of eight of the ten trace elements measured were highest at one or both southern slough stations (silver, cadmium, lead, chromium, copper, mercury, nickel, and zinc) for various sampling periods. Arsenic in sediments was highest at Pinole Point, and selenium was highest at the Napa River station. Excluding the southern slough stations, which are in close proximity to wastewater outfalls, the fine sediment stations in the northern Estuary had the highest average concentrations of arsenic, copper, chromium, mercury, nickel, selenium, and zinc during one or the other sampling periods. Honker Bay had the greatest number of incidents of elevated trace element concentrations in the northern Estuary reach.

Concentrations of all metals were almost always lowest at the coarse sediment stations. In particular, Red Rock, located just south of the San Rafael Bridge, most often had the lowest concentrations of trace elements in sediment. This probably reflects the sandy sediment there.

The elevated sediment concentrations observed in the southern sloughs parallel the patterns in water and reflect the proximity to large urban areas. Coyote Creek and Guadalupe Slough drain runoff, and receive treated industrial and municipal wastewater. The sediments in these sloughs probably function as geochemical sinks for dissolved and particulate contaminants coming into the Estuary.

Only a few of the trace elements were appreciably higher in one or the other sampling period. Silver, copper, and selenium were generally higher in February, and nickel, lead, and zinc were generally higher in August. Mercury concentrations showed no obvious seasonality.

For trace organic contaminants in sediments, the two most obvious patterns in the 1994 RMP data were 1) nearly all trace organic contaminants were highest in the South Bay, and lowest at the coarse sediment stations, and 2) concentrations were usually higher during wet-season sampling (February) than in the dry season (August).

Red Rock and the other coarse sediment stations generally had the lowest concentrations of trace organics. PAH and PCB concentrations at the northern Estuary fine-sediment stations were intermediate between the higher concentrations at stations to the south and the relatively low concentrations at the River stations. In contrast, DDT concentrations at the fine sediment stations in the northern Estuary were generally higher than those measured at the more southerly stations. The elevated p,p'-DDT sampled at Horseshoe Bay during both sampling periods is probably due to a nearby source of fresh DDT.

Total PAHs were comprised of a remarkably constant ratio of individual PAHs at nearly all stations and in both seasons. The homogeneous mixture of PAHs in sediment suggests that the sources also consist of homogeneous mixtures and that the rates of degradation of different PAHs are rather uniform throughout the Estuary. The profile of PAH compounds measured in sediment suggests that automobile exhaust is a primary source.

The most obvious seasonal pattern observed for trace organics was consistently higher PAH concentrations in February at 19 of 20 stations. No general seasonal pattern emerged for total PCBs. Total DDTs were higher in February than August at 13 of the 18 stations where it was measured. Alpha-HCH and dieldrin were also detected at most stations in February but were generally undetected in August.

The elevated trace organics concentrations in February 1994 samples, together with the observed seasonal trends during the previous year, suggest that trace organics contaminants concentrations in the Estuary are influenced by runoff or flows during wet weather. However, the mechanism behind the elevated concentrations is not clear.

Average trace element concentrations in each of the five Estuary reaches over the four RMP sampling periods in 1993 and 1994 were generally similar. There appeared to be very little variation in the South Bay and Rivers stations, with the most variation in the Central Bay and northern Estuary stations.

Sediment bioassays showed that nine of the 12 RMP stations tested indicated toxicity from one of the tests during one or the other of the sampling periods in 1994. The Alameda station was toxic to amphipods and mussel embryos during the February tests, but not in August. Napa River and Grizzly Bay were toxic to amphipods in February and to mussel embryos in August. The River stations were toxic to mussel embryos during both sampling periods. Stations in the northern Estuary (Napa River, Grizzly Bay), and the Rivers were the only stations to indicate toxicity during both sampling periods.

Comparison of the general patterns in sediment contamination with the sediment bioassay results show that both elevated trace contaminant concentrations and significant toxicity were observed in the South Bay and northern Estuary. Sediment contamination was generally low in the Central Bay, and there was no sediment toxicity. More specifically, spikes in sediment PAHs at the Coyote Creek and Alameda stations in February corresponded to amphipod toxicity measured there. However, spikes in PCBs at Yerba Buena Island in February, and DDTs at Horseshoe Bay did not result in significant toxicity. Additionally, significant toxicity to bivalve larvae at the Rivers during both sampling periods did not correspond with any obviously elevated contaminant concentrations, although there were several ERL exceedances in the Rivers. It is not known which contaminants in sediments could have caused the apparent toxicity reported. Because sediment contains mixtures of numerous potential agents, it is difficult using the RMP data alone to determine which ones may have been responsible for the observed toxicity.

Comparisons to Sediment Quality Guidelines

Only two trace elements, cadmium and lead, were below both the “effects range low” (ERL) and “effects range median” (ERM) values at all stations during both sampling periods. ERL values were compiled from the literature as sediment concentrations at which effects on biota are “possible”. ERM values are contaminant concentrations above which effects are “probable”. As in 1993, nickel was the only trace metal that exceeded the ERM values for sediments, and it was above the ERM (51.6 ppm) at all but three stations in February. However, the ERM value for nickel has low confidence (Long and Morgan 1990), thus making evaluation difficult. Concentrations of silver and zinc were above the ERL at only one and three stations, respectively, but the remaining trace elements were above the ERL values at 11 to 22 stations in each sampling period.

Total PCBs were above the ERL in eight samples, six in February and two in August. Concentrations of total PAHs and many individual PAHs were above ERLs. Total PAHs exceeded the ERL in 10 samples, nine of which were collected in February. Two low-molecular weight PAHs, fluorene and acenaphthene, had the largest number of ERL exceedances. Total DDTs were above the ERL in 31 samples, but they were evenly divided between the two sampling periods. Nearly all of the instances where trace organics were above the ERLs occurred in February samples.

These results indicate that the background concentrations of the major classes of contaminants in sediments of the Estuary are generally within the range in which biological effects could be occurring. Further, additive effects of numerous contaminats may occur. None of the five trace organic compounds for which the EPA has proposed sediment quality objectives were above their guidelines.

Bivalve Monitoring

Monitoring the accumulation of trace substances in transplanted bivalves integrates water quality conditions over time because bivalves are exposed to ambient water continuously. This component of the RMP identifies compounds bioavailable that accumulate above levels found in the tissue of clams, oysters, and mussels from "clean" locations after transplanting them into the Estuary.

Tissue concentrations were higher for three trace metals - chromium, lead, and nickel - in all three species after transplanting them to the Estuary from presumably clean locations. Of these metals, only lead showed consistently high bioaccumulation factors throughout the Estuary. Chromium and nickel concentrations were considerably higher than pre-deployment levels at five of the 15 stations. Arsenic, cadmium, and selenium did not accumulate in any species above pre-deployment concentrations.

Interannual differences are apparent between 1994 and 1993 results. For those metals exceeding background concentrations by a great amount, dry-season levels were more likely to be higher than wet-season concentrations in the southern portion of the Estuary, while 1993 showed the opposite pattern. The observation made in 1993 that chromium, nickel, copper, lead, and zinc concentrations in bivalve tissue were much higher at various locations throughout the Estuary than they were at "reference" sites generally holds true for 1994.

Some spatial and temporal patterns were evident in trace organic concentrations in bivalves. In oysters, elevated wet-season concentrations of PAHs, PCBs, DDTs, chlordanes, and dieldrin, were observed at the Petaluma River and Napa River stations, suggesting that these tributaries were sources of these compounds in late winter and spring. These elevated concentrations corresponded with "spikes" in water at the Petaluma River during the corresponding sampling period. PAHs, PCBs, chlordane, and dieldrin in oysters were also relatively high in both May and September at the Coyote Creek station, another location under the influence of freshwater runoff to the Estuary. Temporal trends were not apparent in trace organics in oysters.

Broader spatial patterns in trace organic concentrations were observed in mussels. Concentrations of PCBs from Yerba Buena Island into the South Bay were uniformly higher than in the Central Bay or the northern Estuary. This difference was most apparent for a specific PCB congener (PCB180), which had average concentrations in the South Bay that were four times higher than in the Central Bay and the northern Estuary. The elevated PCB concentrations are consistent with water measurements. Concentrations within the South Bay were fairly uniform. The South Bay also had elevated concentrations of total chlordanes. Total chlordane concentrations were also relatively high in mussels at the Petaluma River station. In contrast to the high concentrations of DDTs in sediment at Horseshoe Bay, this station had the lowest concentrations of DDTs (and chlordanes) found in mussels, suggesting that the DDT is not entering the water column.

Clams at the River stations had considerably higher concentrations of PCBs, DDTs, chlordanes, and dieldrin than clams at another Estuary site, suggesting that the Rivers are measurable sources of these compounds to the Estuary. This observation is consistent with the striking concentration gradient of pesticides in water at the upstream river stations.

A few trace organics showed consistent seasonal variation across stations. Mussels had higher concentrations of carcinogenic PAHs in the wet season at all stations, similar to the seasonal contrast between wet- and dry-season sediment samples. Chlordanes and dieldrin concentrations in tissue were slightly higher in May at almost all stations.

These data on bioaccumulated trace organics support some hypotheses regarding sources. Elevated concentrations of all trace organics in tissue relative to other stations were observed at the Petaluma River, Napa River, and Coyote Creek stations, indicating either re-mobilization of these contaminants from the sediment or the presence of continuing sources of these compounds within the watersheds of these tributaries. Investigations as part of the 1996 RMP may further elucidate this question. Similarly, the Sacramento and San Joaquin Rivers appear to be sources of PCBs, DDTs, chlordanes, and dieldrin. Concentrations of PAHs, chlordanes, and dieldrin were higher in bivalves deployed during the wet season, suggesting that runoff is a source. Strong correlations among individual PAHs and individual pesticides are consistent with them having similar sources. Urban runoff is a likely source of the uniform PAH mixture that is distributed throughout the Estuary. Pesticide inputs from a multiplicity of sources in watersheds might be responsible for the consistent mixtures of chemicals found in RMP, as indicated by strong correlations among individual pesticides.

Comparisons to Tissue Quality Guidelines

Seven of the ten metals were accumulated above background concentrations by one or more bivalve species in 1994. Tissue concentrations were higher than Median International Standards (MIS) for one or more metals at all stations measured, including the three reference sites. Mercury, selenium, and arsenic had most of the incidences of being higher than the MIS, followed by cadmium, chromium, zinc, and copper. Lead was the only metal that was consistently lower than the MIS throughout the Estuary. Although none of the measurements of trace organic contaminants in tissue exceeded the Food and Drug Administration's action levels or National Academy of Sciences guidelines, tissue levels at all Estuary locations were higher than the Maximum Tissue Residue Levels (MTRLs) developed by the State Water Resources Control Board for most of the trace organics groups. PCB, PAH, and total chlordane concentrations were consistently higher than MTRLs. For a detailed description of guidelines used to compare RMP tissue concentrations, see Bivalve Bioaccumulation and Condition section in the report.

Trace Contaminant Patterns

For two years in a row, PCBs were identified as a group of contaminants that cause concern in the Estuary. Concentrations exceeded water quality guidelines at all stations during all three sampling periods each year. In both years, the South Bay exhibited the highest mean concentrations of total PCBs in water, although sediment and tissue concentrations did not reflect this pattern nearly as strongly. Bivalve tissue measurements corresponded much better with elevated dissolved PCBs at the Coyote Creek station. At the Petaluma River, wet-season spikes in near-total chromium, copper, nickel, silver, total PCBs, PAHs, and DDTs in water generally corresponded with elevated wet-season tissue concentrations. However, other stations did not necessarily reflect the same contaminant patterns across all three media.

Tissue concentration patterns corresponded better with total concentrations of metals in water, rather than with the dissolved fraction. Station comparisons with respect to bioaccumulation are difficult, because species differences frequently obscure station contamination characteristics.

RMP scientists have begun to work on developing a meaningful index that summarizes the contaminant information obtained from water, sediment, and tissue analyses in a concise way. An index is envisioned that would reflect which stations and Estuary reaches had the most exceedances of water quality standards, as well as sediment and tissue guidelines. Effects information, such as bioassay results, and benthic community data should also be included and perhaps even more heavily weighted, since they reflect actual biological responses to contaminant levels. This Estuary Contamination Index would serve to track progress toward environmental improvement goals and could be combined with other ecological measurements to evaluate overall Estuary health.

SFEI staff will work with risk assessment experts and others to refine these initial thoughts. Ultimately, the Estuary Contamination Index could become part of a set of "health indicators" for the San Francisco Estuary that cover all of the five key management areas outlined in the Comprehensive Conservation and Management Plan.

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List of Figures

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