The Regional Monitoring Program for Trace Substances in the San Francisco Estuary (RMP)

2003

Annual Monitoring Results

MAY 2005



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1.0 INTRODUCTION

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1.1 Program Structure and Objectives

The San Francisco Estuary Regional Monitoring Program for Trace Substances (RMP) is the primary source for long-term contaminant monitoring information for the Estuary. The RMP is an innovative and collaborative effort between the scientific community, the San Francisco Bay Regional Water Quality Control Board (Water Board), and the regulated discharger community. The RMP's annual budget is currently about \$3 million, which is primarily funded by the discharger community through wastewater discharge permits issued by the Water Board (refer to Table 1.1 for a list of the 2003 RMP participants).

The Status and Trends Monitoring Program is the long-term contaminant-monitoring component of the RMP that was initiated as a pilot study in 1989. The Water Board uses data from the program for regulatory purposes such as evaluating the Estuary for 303(d) listing of water bodies, calculating National Pollutant Discharge Elimination System (NPDES) permit conditions, and estimating Total Maximum Daily Loads (TMDL). Additionally, long-term monitoring data are used to evaluate whether management actions are successful in reducing contaminant loads to the Estuary.

The Technical Review and Steering Committees (TRC and SC, respectively) meet quarterly to provide oversight and guidance to the RMP. The committee members include representatives from the scientific, regulatory, stakeholder, and discharger communities. The TRC and SC assist in program development by prioritizing studies, suggesting new areas of research, and providing constructive comments on existing projects and the overall program. The RMP provides an important forum for collaborative research efforts, encouraging dialogue among scientists, regulators and stakeholders, and facilitating sound environmental management decisions. Approximately every five years, the RMP conducts an external review of the technical and administrative structure and performance to ensure that the RMP remains useful to the regulatory and scientific communities. Nationally prominent scientists and environmental mangers are invited to participate in the review process. The last five-year review was conducted in 2003/2004. The workgroup's <u>Report of the 2003 Program</u> <u>Review</u> includes future recommendations.

The RMP is based on management questions and program objectives that are updated by the Water Board, RMP staff, the TRC, and the SC every five years. The RMP recently updated its management questions and objectives in January 2005 (available on the web at <u>http://www.sfei.org/rmp/RMPproginfo.htm</u>). However, for this report, the program objectives in effect were to:

- 1. Describe patterns and trends in contaminant concentration and distribution.
- 2. Describe general sources and loading of contamination to the Estuary.
- 3. Measure contaminant effects on selected parts of the Estuary ecosystem.

- 4. Compare monitoring information to relevant water quality objectives and other guidelines.
- 5. Synthesize and distribute information from a range of sources to present a more complete picture of the sources, distribution, fates, and effects of contaminants in the Estuary ecosystem.

The Status and Trends Program is comprised of four program elements that collect data to address the RMP Objectives:

- 1) The *Status and Trends Program* consists of long-term contaminant monitoring to characterize the status and trends for contaminants in water, sediment and biota (bivalves) in the Estuary (Objectives 1,3, and 4).
- 2) The *Sport Fish Contamination Study* is a triennial screening of fish tissue for contaminants of concern to human health (Objectives 1,3, and 4).
- 3) The *Episodic Toxicity Monitoring* component investigates potential toxic effects in Estuary tributaries (Objectives 1 and 2).
- 4) The USGS conducts two long-term monitoring efforts partially funded by the RMP, including monthly water quality measurements in the deep channels of the Estuary (from the Lower South Bay to the confluence of the Sacramento and San Joaquin Rivers), and sediment transport monitoring and modeling in the northern Estuary.

Contaminant sources and loadings (Objective 2) and additional effects measures (Objective 3) are addressed through three focused workgroups that help to develop pilot and special studies: the Sources, Pathways and Loadings Workgroup, the Contaminant Fate Workgroup, and the Exposure and Effects Workgroup. These workgroups meet once or twice a year to review progress and make recommendations for further study. The RMP synthesizes and distributes its monitoring and study results (Objective 5) through conferences, workgroups, <u>literature reviews, technical reports, newsletters, and the Pulse of the Estuary</u>.

The RMP also conducts Pilot and Special Studies. Pilot Studies usually are designed to investigate and develop new monitoring measures related to anthropogenic contamination or contaminant effects on biota in the Estuary. Special Studies address specific scientific issues that the TRC, SC, or Water Board identify for further study. These additional studies are developed through an open application process, which starts with an applicant submitting a study idea to the RMP Program Manager for discussion at a TRC quarterly meeting. Specific details on the study development and selection processes are available on the <u>RMP home page</u>. Chapter 1.4 below describes the Pilot and Special Studies conducted by the RMP in 2003. A summary of Pilot and Special Studies conducted by the RMP in available on the <u>RMP home page</u>.

The *Annual Monitoring Results* report focuses on the RMP's Status and Trends Program. The RMP publishes separate technical reports for the Sport Fish Contaminant Study and for the Episodic Toxicity Monitoring effort. These reports are available on the web at <u>RMP's Documents and Reports</u>. A brief description of those monitoring programs, the USGS programs, and the Pilot and Special Studies funded in 2003 can be found in Chapter 1.3 below. For more information on the RMP, refer to the <u>RMP home page</u>.

1.2 The Status and Trends Program (2003)

2003 was the second year that the Status and Trends Program collected water and sediment samples using the EPA's Environmental Monitoring Program (EMAP) Generalized Random Tessellation Stratified (GRTS) sample design (Stevens, 1997; Stevens and Olsen, 1999; Stevens and Olsen, 2000). This type of design is appropriate for addressing the RMP objective (Objective 1) to describe the spatial and temporal patterns of contamination in the Estuary (Lowe *et al.*, 2005).

Sampling site information is presented in Table 1.2, and site location maps are included in Chapters 2.0-4.0. Subcontracting agencies perform the logistical planning, sampling, and laboratory analyses for trace contaminants and ancillary measures. Participating contractors for 2003 are listed in Table 1.3. SFEI maintains current laboratory standard operating procedures (SOPs) for all analyses. A summary of the sampling and analytical methods used by the Status and Trends Program in 2003 are included in Chapter 5.0. SFEI provides technical oversight, participates in field sampling, manages the data, performs a rigorous quality assurance and quality control (QA/QC) evaluation, and synthesizes and reports the information. Monitoring data are available for downloading via the RMP website using the *Status and Trends Monitoring Data Access Tool* at http://www.sfei.org/rmp/data.htm.

1.2.1 Random Sampling Design for Water and Sediment

The GRTS sampling design for water and sediment will allow the RMP to better address Objectives 1 and 4 (above) and will provide the Water Board with a better statistical basis from which to characterize spatial patterns of contamination in each region or the Estuary as a whole.

With the randomized data collected, the RMP can better estimate the spatial and temporal distribution of water and sediment contaminants in the Estuary, determine if the mean contaminant concentration within a region is above a regulatory guideline, estimate what proportion of the Estuary is toxic to laboratory test organisms, and provide a solid foundation for evaluating progress in reducing contaminant concentrations in water and sediment.

The RMP allocated GRTS samples for water and sediment monitoring into five hydrographic regions of the Estuary. Those five regions are: Suisun Bay, San Pablo Bay, Central Bay, South Bay, and Lower South Bay. The number of samples allocated to each region was determined by a power analysis that focused on contaminants and regions of greatest concern to the Water Board at the time of the redesign effort.

Seventy-five water and sediment samples were randomly allocated into the five hydrographic regions in the Estuary downstream from the confluence of the Sacramento and San Joaquin Rivers. The sampling frame for water and sediment monitoring is the 3-foot and 1-foot contour of the Estuary at mean lower low water, respectively (based on

NOAA's NAD-83 bathymetry coverage). Each year, a subset of the seventy-five random sites is sampled in sequential order, increasing the spatial coverage of the Estuary over time.

Several "historical" water and sediment sites were retained from the previous sampling design to provide continuity with the original RMP monitoring design. Sampling occurs once a year during the dry season when Estuary conditions are most consistent on an interannual basis.

The sediment sampling design incorporates repeated measurements at two random sites per region on an annual, five-year, and ten-year cycle to allow additional trends analyses. Repeated sampling reduces within-population variation if a population element retains much of its identity through time. While this is assumed to be true for sediment, it is not true for water due to the constantly moving water masses within the Estuary. Therefore, the water sampling design does not include repeated sampling of randomly allocated sites, and trends in water will be tracked for each region as a whole based on estimates of population statistics. Trends analyses are not attempted in this report for the GRTS design samples as only two years of data are presented.

For more information on the new Status and Trends monitoring design, refer to the following articles and technical reports: *Re-design Process of the San Francisco Regional Monitoring Program for Trace Substances (RMP) Status and Trends Monitoring Component for Water and Sediment* (Lowe *et al.*, 2005), <u>2000 Pulse of the Estuary</u> and <u>RMP News: Winter 2001/2002</u>.

1.3 2003 Annual Monitoring Results

1.3.1 Reporting of Results

Table 1.4 lists all parameters measured in water, sediment, and bivalve tissue samples in 2003. While only a subset of the parameters measured is presented in this report, all results for 2003 and previous years can be accessed and downloaded from the web using the new <u>RMP Data Access Tool</u>. In addition, Conductivity, Temperature, and Depth (CTD) profiles of the water column are collected at all RMP water, sediment, and bivalve tissue stations. In 2003, CTD casts were collected during both the bivalve deployment and retrieval sampling efforts, and both depth and time casts were collected during water sampling. Although these data are not presented in this report, results are available upon request.

Water, sediment, and bivalve tissue monitoring results for many trace contaminants and important ancillary measures are displayed in maps. Schematic box plots and cumulative distribution function (CDF) plots for water and sediment random samples provide simple summary statistics by region. The GRTS sampling design allows several years of data to be combined to provide better spatial coverage of the sample frame. In this report, we combine random sample results from 2002 and 2003, but only show the historic results for the 2003 sampling effort.

The RMP is in the process of synthesizing and reporting on the historical design sampling effort (1993-2001) in a special issue of the scientific journal *Environmental Research*. While time series plots for the historic sites sampled in 2002 and 2003 are presented in this report, detailed trend analyses will be discussed in the peer-reviewed journal articles as part of the Nine-Year Synthesis of Contaminant Status and Trends scheduled for later this year.

The Annual Monitoring Results includes only those results that have met specific data quality objectives and have passed a rigorous QA/QC evaluation as outlined in the <u>RMP's Quality Assurance Project Plan</u>. Values reported as below the method detection limit (MDL) are estimated to be ½ of the MDL in all calculations and graphics. Some organic compounds are summed based on the targeted RMP congeners listed in Table 1.4 for that specific compound group (e.g., PBDEs, PAHs, and PCBs). When laboratory or field replicate data are available, the average of all the replicate concentrations is utilized in this report (consistent with how the web-based data access tool reports the data).

Several software programs were used to develop the graphics for this report. Matlab was used to produce the maps and SAS software to generate the graphics for the schematic box, cumulative distribution function (CDF), and time-series plots.

This year the Status and Trends Program used R statistical analysis software package specifically designed by EPA for GRTS sample designs. The R statistical analysis program is an implementation of the S language developed at AT&T Bell Laboratories and can be downloaded for free through the Comprehensive R Archive Network (CRAN) web site at <u>http://cran.r-project.org/</u>. Estimates of the regional and Estuary-wide contaminant mean, variance, standard deviation, standard error, and CDFs were calculated using the R language and version 2.6 of the psurvey.analysis statistical library. The psurvey analysis library for the analysis of probability surveys is available at the U.S. Environmental Protection Agency Aquatic Resources Monitoring - Monitoring Design and Analysis web site

(http://www.epa.gov/nheerl/arm/designpages/design&analysis.htm).

Maps

A color gradient was used in the maps of this report (Figure 1.1) to depict the range of reported concentrations, from the minimum detected to the maximum values. A circle

symbol (\circ) indicates a random site and a diamond symbol (\diamond) a historic site. Nondetected values are shown by the plus symbol (+). Results that did not pass the QA/QC review process are not shown.

The color scheme of yellow/green indicates results that were below the guideline and blues indicate results above the guideline. The yellow/green color scheme was also used when no guideline was available for comparison (e.g., percent fines, methyl mercury, percent lipids, and total organic carbon).



Figure 1.1. Map of sediment mercury concentrations in the Estuary.

Sample sizes varied by test material and region. The water maps represent data from fifty-four random sites sampled in 2002-2003 and four historic sites (BA30- Dumbarton Bridge, BC10-Yerba Buena Island, BG20-Sacramento River, and BG30-San Joaquin River) sampled in 2003. The reference site at Golden Gate was not sampled in 2003 due to poor weather conditions. In 2002 and 2003, ten and nine sites, respectively, were sampled in the South Bay region, and six and five sites, respectively, in the Lower South Bay region. Four sites were sampled in the Suisun Bay, San Pablo Bay, and Central Bay regions in each year.

In 2003, the RMP reduced the sample size for water by one sample each in the South Bay and Lower South Bay regions in order to add back two historic sites (BA30-Dumbarton Bridge and BC10-Yerba Buena Island) to the monitoring design because those sites (along with BG20-Sacramento River) are currently used by the Water Board for NPDES permit processing.

The sediment maps represent data from eighty random sites from 2002 and 2003 and seven historic sites from 2003. Eight random sites and one historical fixed site were

sampled per region each year, except for the Rivers region where only two historical sites at the Sacramento River (BG20) and San Joaquin River (BG30) were sampled.

The bivalve tissue maps represent 2003 data from nine fixed-mooring sites where caged bivalves were deployed (three per region) and two historical River sites (BG20 and BG30) where resident clams were collected by a trawl. There are no data for San Pablo Bay (BD20) in 2003 due to a lost mooring.

Schematic Box Plots

Figure 1.2 is an example of a schematic box plot used to present results in this report. The horizontal line inside the box represents the median, and the mean is indicated by a blue "+". The top and bottom of the box represent the 3rd quartile (75th percentile) and the 1st quartile (25th percentile), respectively. The distance between these two is the interquartile range (IQR). A whisker is drawn from the upper edge of the box to the maximum value within the upper fence and from the lower edge of the box to the lowest value within the lower fence. The term "fence" refers to the distance from the 25th and 75th percentiles expressed in terms of the IQR.

For example, the lower fence is located at $1.5 \times IQR$ below the 25th percentile, and the upper fence is located at $1.5 \times IQR$ above the 75th percentile. The fences are not displayed in the plots in this report; however, observations that fall beyond these fences (outliers) are indicated by open square symbols. Because there are a variable number of random water samples per segment, the width of the box in the water box plots is proportional to the number of samples reported per region.



Figure 1.2. Illustration of a schematic box plot.

Cumulative Distribution Function (CDF) Plots

Cumulative distribution function plots (Figure 1.3) use the random sample results to show an estimate percentage of the total area sampled in the five Estuary regions

combined (large graph) and each individual region (small graphs) versus individual parameter concentrations. The CDF plot for the total area sampled in the five Estuary regions is adjusted for regional area weights using the R-program function. The CDFs for the individual regions are not.

The total area sampled is different for sediment and water samples because the sample frames were designed to be the 1-foot and 3-foot contour of the Estuary at mean lower low water, respectively. Each region's sample frame area is provided in the table below. No random samples were allocated to the Rivers region, and therefore, that region was not included in the total sample frame.

	Area of Sample	Area of Sample
Region	Frame for Water	Frame for Sediment
Name	(sq. km)	(sq. km)
Rivers	0	0
Suisun Bay	72	80
San Pablo Bay	181	227
Central Bay	382	396
South Bay	144	185
Lower South Bay	5	8
Total Area	784	896

The blue line is the CDF value, while the green lines represent the 95% confidence intervals. A horizontal black line is drawn as a reference to indicate 50% of the area sampled. Guideline values (e.g., TMDL, ERL, fish screening values) are represented as vertical blue-dashed lines when that value is within the range of the results reported. Since the Rivers region does not have random samples, a corresponding CDF plot was not generated.

CDF plots address questions such as what percentage of the Estuary is above a guideline for an analyte. For example in Figure 1.3, approximately 80% of the total sampled area in the Estuary has sediment mercury concentrations above the TMDL target of 0.2 mg/kg. Additionally, the small graphs indicate that most of the San Pablo Bay and Lower South Bay regions and approximately half of the Suisun Bay region are above the TMDL target.

Due to the small sample size (eighty sediment and fifty-four water random sites), the CDFs provide preliminary estimates of the percent area of the Estuary that is above a guideline or has a particular contaminant concentration. However, the power of this analysis will increase as the spatial coverage of the Estuary increases and more samples are collected over time.

In the initial sampling design, area weights were originally calculated for100 sites per region. However, these area weights must be re-calculated each year according to the actual number of sites sampled. Area weights are calculated by dividing the product of the total sample frame area used for sample selection and the original area weights, by the

sum of the original weights for the targeted sites. The targeted sites include sites that could not be sampled for any reason (as one needs to adjust for the area that could not be sampled; for example any site that was not accessible during the sampling cruise), and replacement sites. As the number of sites sampled increases over time, the area weight assigned to each sample will decrease, providing better resolution for the CDF estimates.



Figure 1.3. CDF plot for sediment mercury concentrations.

1.3.2 Water Chemistry and Toxicity

Water sample collection occurred during the dry season in August at 30 sites throughout the Estuary. Twenty-six random sites were sampled (four to nine sites per region) and four historic sites were sampled. Due to weather conditions, the historic reference site at the Golden Gate (BC20) could not be sampled in 2003. Sampling at two sites located at the southern end of the Estuary in Sunnyvale (C-1-3) and San Jose (C-3-0) were discontinued in 2003. Monitoring of trace organics in sediment began at these stations in 1996 as part of the NPDES permit process.

The analyte list for conventional water quality, trace metals, and trace organics was the same as in 2002, including the new classes of compounds (i.e., polybrominated diphenyl ethers (PBDEs), phthalates, and p-nonylphenol). However, not all the results are available for reporting at this time.

No water samples were tested for ambient water toxicity in 2003. Since very little aquatic toxicity has been observed by the RMP in past monitoring years, ambient water toxicity testing will take place on a reduced five-year schedule. The next sampling is scheduled for 2006.

1.3.3 Sediment Chemistry and Toxicity

Sediment sample collection occurred during the dry season in August at 47 sites throughout the Estuary. Eight random sites and one historical fixed site were sampled per region. Sampling at two sites located at the southern end of the Estuary in Sunnyvale (C-1-3) and San Jose (C-3-0) were discontinued in 2003. Monitoring of trace organics in sediment began at these stations in 1996 as part of the NPDES permit process.

The analyte list for sediment quality, trace metals, and trace organics was the same as in 2002, including the new classes of compounds (i.e., PBDEs, phthalates, and p-nonylphenol). However, not all the results are available for reporting at this time.

Twenty-seven sediment samples were tested for toxicity. Toxicity tests included mean percent survival of the amphipods *Eohaustorius estuaries* after exposure to solid-phase sediments for 10 days and mean percent normal development of live Bay mussel *Mytilus galloprovincialis* larvae after exposure to sediment elutriates for 48 hours. Phase I toxicity identification evaluations (TIEs) were conducted at three sites (LSB001, SU011, and SU013) to investigate possible causes of toxicity. Sediment monitoring results are discussed in more detail in Chapter 3.0.

1.3.4 Bivalve Bioaccumulation

The bivalve bioaccumulation sample design remains a convenience sample design because deployment of caged bivalves requires secure moorings. In 2003, several changes were made to the bivalve tissue monitoring component. Because it was determined that only two to three sites were required per region to track long-term changes in contaminant concentrations, three sites were discontinued at Napa River (BD50) and Petaluma River (BD15) in San Pablo Bay and Horseshoe Bay (BC21) in Central Bay. Based on a series of special studies conducted during 2000-2002, only one transplanted bivalve species *Mytilus californianus* was deployed, which will allow for comparing the bioaccumulation of contaminants throughout the Estuary, and all bivalves were deployed in cages to reduce the effects of bivalve predation.

Nine mooring sites (three per region) and two historic River sites (BG20 and BG30) were monitored for potential bioaccumulative contaminants using transplanted and resident bivalves. There are no data for San Pablo Bay (BD20) due to a lost mooring. Transplanted *Mytilus californianus* were deployed in cages for three months and maintained halfway through at 45 days. Resident clams (*Corbicula fluminea*) were collected from the Sacramento and San Joaquin River sites. The analyte list for trace organics was the same as in 2002, including the new classes of compounds (i.e., PBDEs, phthalates, p-nonylphenol, triphenylphosphate, and nitro and aromatic musks). Data from 1993-2001 indicate that trace metals do not appreciably accumulate in transplanted bivalve tissue at mid-channel locations. Therefore, trace metals analyses were scaled back to once every five years as a periodic screening measure, and tributyltin analysis was discontinued. Since mercury bioaccumulation is included in the Sport Fish Contamination Study, mercury analysis in bivalves has been discontinued. Trace metals will be analyzed in bivalve tissue again in 2006. Bivalve tissue monitoring results are discussed in more detail in Chapter 4.0.

1.3.5 Sport Fish Contaminant Study

Sport fish sampling, which occurs on a three-year cycle, was conducted in 2003. Popular sport fish species were sampled at several fishing locations, and tissue samples were analyzed for mercury, PCBs, organochlorine pesticides, and PBDEs. These results will be available on the <u>RMP Fish Tissue Data Page</u> in the Summer of 2005 and a technical report will be made available at the same time on the web at <u>RMP's Documents and Reports</u>.

1.3.6 Episodic Toxicity Monitoring

The RMP is re-scoping the Episodic Toxicity Monitoring component to better address the changing patterns of pesticide usage in urban and agricultural areas. A summary of the Episodic Toxicity Monitoring findings from 1996-2001 was reported in the 2003 Pulse of the Estuary article "Ten Years of Testing for the Effects of Estuary Contamination". In addition, technical reports from this program are available on the web at <u>RMP's</u> Documents and Reports.

During Winter 2002 and Spring 2003, episodic aquatic toxicity monitoring was conducted at five tributaries to the Estuary: Sacramento-San Joaquin Rivers (downstream of the confluence, at Mallard Island), Petaluma River, Sonoma Creek, San Lorenzo Creek, and Coyote Creek. A minimum of five storm events was sampled at each of the tributaries to cover the temporal extent of potential sources of contaminant input (e.g., first flush during October-December, dormant spray runoff during December-February, row crop runoff during March-June, and urban gardening during April-June). Invertebrate and fish-larvae toxicity tests were conducted, as well as toxicity identification evaluations (TIEs) when significant toxicity was present.

Samples were not collected during Winter 2003. In 2004/05, the Episodic Toxicity Monitoring component has turned its efforts to screen bedded sediments entering the Estuary for potential toxic effects and to characterize those sediments for the full suite of RMP contaminants (Table 1.4) and pyrethroids. The Toxicity workgroup is scheduled to meet later this year to discuss the various aquatic and sediment toxicity components of the RMP and make recommendations to the TRC for monitoring toxic effects in the future.

1.3.7 United States Geological Survey Studies

The United States Geological Survey (USGS) has been a collaborating agency in the RMP since the beginning of the Program. In 2003, it continued to supplement RMP

monitoring by conducting two special studies that address basic hydrographic and sediment transport processes.

Factors Controlling Suspended Sediment in San Francisco Bay

This sediment transport study examined the role of several physical factors controlling suspended sediment concentrations in the Estuary for a variety of hydrologic, tidal, and wind conditions and generated time series measurements for calibration and validation of sediment transport models. This monitoring element has taken on added importance because of its close relationship to episodic toxicity due to particle-bound contaminants and its relationship to the special study evaluating particle-associated contaminant load inputs from the Central Valley at Mallard Island. Time series measurements of suspended sediment concentrations were collected at eight sites in each major region of the Bay using optical backscatter sensors deployed at mid-depth and near the bottom. Conductivity and temperature data were also collected at most sites. For more information refer to the 2003 Pulse of the Estuary article Sediment Dynamics Drive Contaminant Dynamics.

Hydrography and Phytoplankton

This study collected monthly measurements of five water quality parameters at 38 stations throughout the Estuary to describe the changing spatial patterns of basic water quality from the lower Sacramento River to the southern limit of the South Bay. Measurements included: salinity, temperature, and dissolved oxygen (which influence the chemical form and solubility of some trace contaminants); and suspended sediments and phytoplankton biomass (which influence the partitioning of reactive contaminants between dissolved and particulate forms). This information is needed to better understand the seasonal changes in water quality and estuarine habitat as they influence biological communities and the distribution and reactivity of trace contaminants. For more information refer to the 2003 Pulse of the Estuary article Lessons from Monitoring Water Quality in San Francisco Bay.

1.4 Other RMP Studies

1.4.1 Pilot Studies

Pilot Studies augment RMP Status and Trends monitoring by focusing on specific topics relating to contamination in the Estuary and provide a proactive approach to addressing management goals and needs. Pilot Studies may eventually be incorporated into the Status and Trends long-term program (e.g., Episodic Toxicity Monitoring, Sport Fish Contamination Study).

Two pilot studies were conducted by the RMP in 2003.

Mercury Deposition Network

This was a collaborative study funded by the City of San Jose and the RMP. Mercury was measured in rain samples at a sampling station in San Jose as part of the total maximum daily load (TMDL) refinement. Data were incorporated into the national

database to evaluate atmospheric mercury contributions from large urban areas and longrange aerial transport from outside the region to surface waters. This is the only remaining component of the Air Deposition Pilot Study that contributed PAH and PCB data for mass budget models. Data collection for this study will continue through 2005. For more information, refer to the final report <u>San Francisco Bay Atmospheric</u> <u>Deposition Pilot Study Part 1: Mercury</u> or contact Donald Yee at <u>donald@sfei.org</u>.

Exposure and Effects Pilot Study

Beginning in 2000, the RMP implemented this five-year pilot study to develop several indicators of contaminant exposure and effects. Using resident species, this study measures exposure and effects at several trophic levels and at different levels of biological organization and spatial scales. Indicators being tested include: diving duck muscle (human exposure indicator); cormorant and Forster's tern eggs (chemical trend indicators); hatchability of Forster's terns, least terns, and clapper rails (effects indicators); blood chemistry and biomarkers in harbor seals (exposure and effects indicators); biomarker studies in fish, aquatic and sediment toxicity testing of resident species (effects indicators); and benthic community evaluations (effects indicators). Linking contaminant bioaccumulation with effects measurements at various levels of the food web can assist with establishing contaminant regulatory priorities and responding to emerging contaminants. For more information, contact Jay Davis at jay@sfei.org.

1.4.2 Special Studies

Special Studies help the RMP address specific data gaps or management or scientific questions related to contaminants in the Estuary. For example, two recent special studies identified and evaluated previously unknown organic contaminants and led to the addition of several new analytes (e.g., PBDEs, phthalates, and p-nonylphenol) to the RMP target analyte list to see if those contaminants are prevalent in the Estuary. For more information, refer to the reports <u>Identification and Evaluation of Unidentified</u> <u>Organic Contaminants in the San Francisco Estuary</u> and <u>Identification and Evaluation of Previously Unknown Organic Contaminants in the San Francisco Estuary (1999-2000)</u>.

Three special studies were conducted by the RMP in 2003.

Contaminant Loads from the Sacramento and San Joaquin Rivers

RMP continued to collaborate with the USGS to monitor suspended solid concentrations at Mallard Island. Sampling will continue through 2004 and contribute to nearly 10 years of continuous data when combined with data collected by the USGS from 1994-98.

The RMP also collaborated with other groups conducting fixed-time and flood-response water sampling (Interagency Ecological Program) to collect sediment-related contaminant concentrations at Mallard Island for the purpose of developing statistical relationships between concentrations and optical backscatter measurements. These relationships can be used to estimate time-continuous concentration data that when combined with estimates of discharge can estimate sediment loads from the Delta and to model contaminant loads entering the Estuary from the San Joaquin Valley. For more information, contact Lester McKee at lester@sfei.org.

Receiving Water Monitoring of the 1977 Priority Pollutant List and Comparisons to California Toxics Rule (CTR) Criteria

The California Toxics Rule (CTR) specifies 129 priority pollutants that may impair beneficial uses in the waters of California. The purpose of this special two-year study was to provide the Water Board with information on contaminants listed in the CTR that were not currently being monitored by the RMP and to comply with an NPDES permit provision for ambient water monitoring for dischargers in the San Francisco Estuary. Similar to the 2002 sampling effort, estuarine water was sampled at three historical RMP sites (Sacramento River, Dumbarton Bridge, and Yerba Buena Island) during the wet (January) and dry (July) seasons. For more information, contact Donald Yee at donald@sfei.org.

Nine-Year Synthesis of Contaminant Status and Trends

Prior to the implementation of the new random sampling design in 2002, the RMP employed a fixed station sampling design from 1993-2001. The RMP is in the process of synthesizing and reporting on those results in a special issue of the scientific journal *Environmental Research*. The articles will address two of the Program's objectives (Objectives 1 and 5) to provide a rigorous evaluation of long-term trends and to synthesize RMP and non-RMP data into an integrated assessment of contamination status and trends in the Estuary. The <u>2004 Pulse of the Estuary</u> was the first part of a two part series highlighting key findings related to the Status and Trends monitoring efforts and synthesizing that information. Please contact Jay Davis at jay@sfei.org for more information.

1.5 References

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Introduction Tables

Table 1.1. RMP Program Participants in 2003.

Municipal Dischargers

Central Contra Costa Sanitary District Central Marin Sanitation Agency City of Benicia City of Burlingame City of Calistoga City of Palo Alto City of Petaluma City of Pinole/Hercules City of Saint Helena City and County of San Francisco City of San Jose City of San Mateo City of South San Francisco/San Bruno Citv of Sunnvvale **Delta Diablo Sanitation District** East Bay Dischargers Authority East Bay Municipal Utility District Fairfield-Suisun Sewer District Las Gallinas Valley Sanitation District Marin County Sanitary District #5, Tiburon Millbrae Waste Water Treatment Plant Mountain View Sanitary District Napa Sanitation District Novato Sanitation District Rodeo Sanitary District San Francisco International Airport Sausalito/Marin City Sanitation District Sewerage Agency of Southern Marin Sonoma County Water Agency South Bayside System Authority Town of Yountville Union Sanitary District Vallejo Sanitation and Flood Control District West County Agency

Industrial Dischargers

C & H Sugar Company Chevron Products Company Dow Chemical Company General Chemical Corporation Martinez Refining Company Rhodia, Inc. TOSCO – Rodeo Refinery Ultramar Inc - Avon Refinery USS – POSCO Industries Valero Refining Company Cooling Water Mirant of California

Stormwater

Alameda Countywide Clean Water Program Caltrans City and County of San Francisco Contra Costa Clean Water Program Fairfield-Suisun Urban Runoff Management Program Marin County Stormwater Pollution Prevention Program San Mateo Countywide Stormwater Pollution Prevention Program Santa Clara Valley Urban Runoff Pollution Prevention Program Vallejo Sanitation and Flood Control District

Dredgers

Benicia Port Terminal Co. CALTRANS - Martinez Bridge Retrofit CALTRANS - San Rafael Bridge Retrofit Chevron City of Benicia Marina City of Vallejo Marina Emerycove Marina **Emerycove Yacht Harbor Entrance** Galilee Harbor Loch Lomond Marina Marin Yacht Club Marina Co. Park District Marina Vista Homeowners Association Port of Oakland Port of San Francisco **TOSCO** Corporation Valero Refining Co. Vallejo Yacht Club

							Site		Type of A	Analysis	
		Historic	;				Depth	Trace	Trace		
Region/Site Name	Site Code	Site	Sample Type	Collection Date	Latitude	Longitude	(m)	Elements	Organics	Ancillary	Toxicity
Sacramento River	BG20	х	Bivalve Tissue	8/18/2003	38.060	121.792	8		Х	Х	
Sacramento River	BG20	х	Sediment	8/18/2003	38.059	121.814	10	Х	х	Х	х
Sacramento River	BG20	х	Water	8/15/2003	38.060	121.811	9	Х	х	Х	
San Joaquin River	BG30	х	Bivalve Tissue	8/18/2003	38.021	121.805	6		х	х	
San Joaquin River	BG30	х	Sediment	8/18/2003	38.023	121.808	8	Х	х	Х	х
San Joaquin River	BG30	х	Water	8/15/2003	38.020	121.806	10	Х	х	Х	
Grizzly Bay	BF21	х	Sediment	8/18/2003	38.116	122.040	2	Х	х	х	х
Suisun	SU001S		Sediment	8/19/2003	38.100	122.046	7	Х	х	Х	х
Suisun	SU002S		Sediment	8/18/2003	38.059	121.980	12	Х	х	Х	
Suisun	SU006W		Water	8/14/2003	38.059	121.944	2	Х	х	Х	
Suisun	SU007W		Water	8/14/2003	38.074	122.085	3	х	х	х	
Suisun	SU009S		Sediment	8/18/2003	38.118	122.048	2	Х	х	Х	Х
Suisun	SU009W		Water	8/14/2003	38.082	122.065	5	Х	х	Х	
Suisun	SU010S		Sediment	8/18/2003	38.069	121.993	0.3	Х	х	Х	
Suisun	SU010W		Water	8/14/2003	38.069	121.991	2	Х	х	Х	
Suisun	SU011S		Sediment	8/19/2003	38.075	122.103	3	Х	х	Х	х
Suisun	SU012S		Sediment	8/18/2003	38.092	122.041	2.5	х	х	х	
Suisun	SU013S		Sediment	8/19/2003	38.056	122.090	7	Х	х	Х	х
Suisun	SU014S		Sediment	8/18/2003	38.065	121.950	2	Х	х	Х	
San Pablo Bay	BD20	х	Bivalve Tissue		١	lot sampled	. Moori	ng lost.			
Pinole Point	BD30	х	Bivalve Tissue	9/26/2003	38.017	122.368	3		х	Х	
Pinole Point	BD31	х	Sediment	8/20/2003	38.024	122.364	7	Х	х	Х	х
Davis Point	BD40	х	Bivalve Tissue	9/26/2003	38.054	122.261	7		х	х	
San Pablo Bay	SPB001S		Sediment	8/19/2003	38.072	122.387	3	Х	Х	Х	Х
San Pablo Bay	SPB002S		Sediment	8/20/2003	38.016	122.341	2.5	Х	х	х	
San Pablo Bay	SPB005W		Water	8/13/2003	38.047	122.397	4	Х	х	Х	

							Site		Type of A	nalysis	
		Historic					Depth	Trace	Trace		
Region/Site Name	Site Code	Site	Sample Type	Collection Date	Latitude	Longitude	(m)	Elements	Organics	Ancillary	Toxicity
San Pablo Bay	SPB006W		Water	8/13/2003	38.026	122.298	3	Х	Х	Х	
San Pablo Bay	SPB007W		Water	8/13/2003	38.028	122.448	3	Х	Х	Х	
San Pablo Bay	SPB008W		Water	8/13/2003	38.088	122.317	2	Х	Х	Х	
San Pablo Bay	SPB009S		Sediment	8/20/2003	38.038	122.448	3	Х	Х	Х	х
San Pablo Bay	SPB010S		Sediment	8/20/2003	38.028	122.359	7	Х	х	х	
San Pablo Bay	SPB011S		Sediment	8/19/2003	38.093	122.464	2.3	Х	Х	Х	х
San Pablo Bay	SPB012S		Sediment	8/19/2003	38.050	122.390	1.5	Х	Х	Х	
San Pablo Bay	SPB013S		Sediment	8/19/2003	38.080	122.384	3	Х	х	х	х
San Pablo Bay	SPB073S		Sediment	8/20/2003	38.032	122.437	3.5	Х	Х	Х	
Alameda	BB71	х	Bivalve Tissue	9/24/2003	37.696	122.340	9		х	х	
Yerba Buena Island	BC10	х	Bivalve Tissue	9/24/2003	37.819	122.347	3		х	х	
Yerba Buena Island	BC10	х	Water	8/11/2003	37.821	122.349	7	Х	Х	х	
Yerba Buena Island	BC11	х	Sediment	8/20/2003	37.822	122.349	7	Х	х	х	х
Golden Gate	BC20	х	Water	C	ould not be	e sampled d	ue to w	eather con	ditions.		
Red Rock	BC61	х	Bivalve Tissue	9/24/2003	37.928	122.469	4		Х	Х	
Central Bay	CB001S		Sediment	8/21/2003	37.877	122.361	3	Х	х	х	х
Central Bay	CB002S		Sediment	8/22/2003	37.625	122.347	5	Х	х	х	
Central Bay	CB005W		Water	8/12/2003	37.838	122.341	3	Х	Х	х	
Central Bay	CB006W		Water	8/12/2003	37.694	122.255	3	Х	х	х	
Central Bay	CB007W		Water	8/11/2003	37.917	122.400	2	х	х	х	
Central Bay	CB008W		Water	8/12/2003	37.633	122.367	3	Х	Х	Х	
Central Bay	CB010S		Sediment	8/21/2003	37.691	122.308	11	Х	х	х	
Central Bay	CB011S		Sediment	8/20/2003	37.968	122.451	6	Х	Х	Х	х
Central Bay	CB012S		Sediment	8/21/2003	37.754	122.369	15	Х	Х	Х	
Central Bay	CB013S		Sediment	8/21/2003	37.822	122.360	13	Х	Х	Х	х
Central Bay	CB014S		Sediment	8/21/2003	37.652	122.289	7	Х	Х	Х	

							Site	Type of Analysis			
		Historic					Depth	Trace	Trace		
Region/Site Name	Site Code	Site	Sample Type	Collection Date	Latitude	Longitude	(m)	Elements	Organics	Ancillary	Toxicity
Central Bay	CB074S		Sediment	8/21/2003	37.666	122.327	10.5	Х	х	Х	х
Dumbarton Bridge	BA30	х	Bivalve Tissue	9/25/2003	37.513	122.135	5		х	Х	
Dumbarton Bridge	BA30	х	Water	8/5/2003	37.514	122.135	6	Х	х	Х	
Redwood Creek	BA40	х	Bivalve Tissue	9/25/2003	37.547	122.195	3		х	х	
Redwood Creek	BA41	х	Sediment	8/22/2003	37.559	122.211	3	х	х	х	х
South Bay	SB001S		Sediment	8/22/2003	37.612	122.264	3	х	х	х	х
South Bay	SB002S		Sediment	8/25/2003	37.610	122.167	2	х	х	Х	
South Bay	SB009S		Sediment	8/21/2003	37.678	122.194	2	х	х	х	х
South Bay	SB010S		Sediment	8/22/2003	37.562	122.211	15	Х	х	Х	
South Bay	SB011S		Sediment	8/22/2003	37.610	122.340	4	Х	х	Х	х
South Bay	SB011W		Water	8/8/2003	37.597	122.341	2	Х	х	Х	
South Bay	SB012S		Sediment	8/22/2003	37.589	122.246	15	Х	х	Х	
South Bay	SB012W		Water	8/8/2003	37.650	122.201	2	Х	х	Х	
South Bay	SB013S		Sediment	8/22/2003	37.623	122.247	6	Х	х	Х	х
South Bay	SB013W		Water	8/7/2003	37.594	122.277	2	Х	х	Х	
South Bay	SB014S		Sediment	8/26/2003	37.538	122.174	12	Х	х	Х	
South Bay	SB014W		Water	8/5/2003	37.565	122.169	2	х	х	х	
South Bay	SB015W		Water	8/7/2003	37.626	122.276	4	Х	х	Х	
South Bay	SB016W		Water	8/7/2003	37.608	122.210	3	Х	х	Х	
South Bay	SB017W		Water	8/8/2003	37.616	122.269	3	Х	х	Х	
South Bay	SB018W		Water	8/7/2003	37.596	122.179	2	Х	х	Х	
South Bay	SB019W		Water	8/8/2003	37.637	122.274	6	Х	х	Х	
Coyote Creek	BA10	х	Bivalve Tissue	9/25/2003	37.470	122.064	6		х	Х	
Coyote Creek	BA10	х	Sediment	8/25/2003	37.468	122.064	2	Х	х	Х	х
Lower South Bay	LSB001S		Sediment	8/26/2003	37.492	122.098	7	Х	х	х	х
Lower South Bay	LSB002S		Sediment	8/25/2003	37.479	122.078	9	Х	х	х	

							Site		Type of A	Analysis	
		Historic					Depth	Trace	Trace		
Region/Site Name	Site Code	Site	Sample Type	Collection Date	Latitude	Longitude	(m)	Elements	Organics	Ancillary	Toxicity
Lower South Bay	LSB007W		Water	8/5/2003	37.495	122.108	13	Х	х	Х	
Lower South Bay	LSB008W		Water	8/5/2003	37.488	122.083	4	Х	х	Х	
Lower South Bay	LSB009S		Sediment	8/26/2003	37.492	122.107	3	Х	Х	Х	х
Lower South Bay	LSB009W		Water	8/6/2003	37.497	122.107	15	х	х	х	
Lower South Bay	LSB010S		Sediment	8/25/2003	37.471	122.090	2	Х	х	х	
Lower South Bay	LSB010W		Water	8/6/2003	37.487	122.079	2	Х	Х	Х	
Lower South Bay	LSB011S		Sediment	8/26/2003	37.504	122.119	16	Х	х	х	х
Lower South Bay	LSB011W		Water	8/6/2003	37.504	122.119	15	Х	х	Х	
Lower South Bay	LSB012S		Sediment	8/25/2003	37.471	122.102	2	Х	Х	Х	
Lower South Bay	LSB013S		Sediment	8/25/2003	37.487	122.101	1	х	х	х	х
Lower South Bay	LSB014S		Sediment	8/25/2003	37.475	122.070	5	х	х	х	

Principal Contractor	Mr. Paul Salop and Dr. Andrew Gunther Applied Marine Sciences (AMS), Livermore, CA
BACWA Coordination	Mr. William Ellgas and Ms. Julia Halsne East Bay Municipal Utility District (EBMUD), Oakland, CA
Water Trace Element Chemistry	Dr. Colin Davies and Ms. Misty Mayer Brooks-Rand Ltd. (BRL), Seattle, WA
	Dr. Russ Flegal and Ms. Genine Scelfo UC Santa Cruz (UCSCDET), Santa Cruz, CA
Water Trace Organic Chemistry	Dr. Million Woudneh and Ms. Laurie Phillips AXYS Analytical Services, Inc. (AXYS), Sidney, BC
	Dr. Dave Crane and Mr. Loc Nguyen California Dept. of Fish & Game, Water Pollution Control Laboratory (CDFG-WPCL), Rancho Cordova, CA
Water Hardness	Mr. Jim Chen and Ms. Kathleen Irby Union Sanitary District (USD), Fremont, CA
Sediment Trace Element Chemistry	Dr. Colin Davies and Ms. Misty Mayer Brooks-Rand Ltd. (BRL), Seattle, WA
	Dr. Russ Flegal and Ms. Genine Scelfo UC Santa Cruz (UCSCDET), Santa Cruz, CA
	Mr. Anthony Rattonetti and Mr. Lonnie Butler City and County of San Francisco (CCSF), San Francisco, CA
Sediment Trace Organics Chemistry	Mr. François Rodigari East Bay Municipal Utility District (EBMUD), Oakland, CA
Sediment Toxicity Testing	Mr. John Hunt, Mr. Brian Anderson, and Mr. Bryn Phillips Marine Pollution Studies Lab (MPSL), Granite Canyon, CA
Bivalve Trace Organics	Dr. Dave Crane and Mr. Loc Nguyen California Dept. of Fish & Game, Water Pollution Control Laboratory (CDFG-WPCL), Rancho Cordova, CA
Bivalve Condition and Survival	Mr. Paul Salop Applied Marine Sciences (AMS), Livermore, CA
USGS Water Quality	Dr. James Cloern, USGS, Menlo Park, CA
USGS Sediment Transport	Dr. David Schoellhamer, USGS, Sacramento, CA

Table 1.3. RMP Contractors and Principal Investigators in 2003.

Table 1.4. Parameters analyzed in water, sediment, and bivalve tissuesamples in 2003.

Refer to Table 1.3 for laboratory names.		
Conventional Water Quality Parameters	Lab(s)	Reporting Units
Conductivity	AMS/UCSCDET	µmho
Dissolved Ammonia	UCSCDET	mg/L (N)
Dissolved Nitrate	UCSCDET	mg/L (N)
Dissolved Nitrite	UCSCDET	mg/L (N)
Dissolved Organic Carbon	UCSCDET	µg/L
Dissolved Oxygen	UCSCDET	mg/L
Dissolved Phosphates	UCSCDET	mg/L
Dissolved Silicates	UCSCDET	mg/L
Hardness (when salinity is < 5 ‰)	USD	mg/L (CaCO ₃)
pH	AMS/UCSCDET	pН
Phaeophytin	UCSCDET	mg/m ³
Salinity (by salinometer)	UCSCDET	psu
Salinity (by SCT)	AMS/UCSCDET	‰
Temperature	AMS/UCSCDET	°C
Total Chlorophyll-a	UCSCDET	mg/m ³
Total Suspended Solids	UCSCDET	mg/L
Sediment Quality Parameters	Lab(s)	Reporting Units
% clay (< 4 μm)	UCSCDET	% dry weight
% silt (4 μm–63 μm)	UCSCDET	% dry weight
% sand (63 μm – 2 mm)	UCSCDET	% dry weight
% gravel + shell (> 2 mm)	UCSCDET	% dry weight
% solids	BRL/CCSF/EBMUD	% dry weight
Depth	AMS	m
Hydrogen Sulfide (QAQC measurement)	MPSL	µg/kg
pH (porewater, interstitial sediment)	AMS	рН
Total Ammonia (QAQC measurement)	MPSL	µg/kg
Total Organic Carbon	UCSCDET	%
Total Sulfide (QAQC measurements)	MPSL	µg/kg
Total Nitrogen	UCSCDET	%
Bivalve Tissue Parameters	Lab(s)	Reporting Units
% Lipid	CDFG-WPCL	%
% Moisture	CDFG-WPCL	%
Bivalve Percent Survival	AMS	%
Growth - Change in Internal Shell Volume	AMS	mL
Dry Flesh Weight	AMS	g
Toxicity Tests—Water and Sediment	Lab(s)	Reporting Units
Aquatic Toxicity – <i>Americamysis</i> (shrimp) % Survival	PERL	%
Episodic Aquatic Toxicity –	PERL	%
(Ceriodaphnia, Menidia, Americamysis) % Survival		
Sediment Toxicity – (Amphipod) % Survival	MPSL	%
Sediment Toxicity – (Bivalve) % Normal Development	MPSL	%

	Water	Sediment
Parameter Name	(Dissolved	(dry weight)
	and Total)	
Lab(s) BRL/UCSCDET	BRL/CCSF/ UCSCDET
Aluminum (Al)*	-	mg/kg (200)
Arsenic (As)	μg/L (0.1)	mg/kg (0.2)
Cadmium (Cd)*	µg/L (0.001)	mg/kg (0.001)
Cobalt (Co)	µg/L	-
Copper (Cu)*	μg/L (0.01)	mg/kg (2)
Iron (Fe)*	μg/L (10)	mg/kg (200)
Lead (Pb)*	µg/L (0.001)	mg/kg (0.5)
Manganese (Mn)*	μg/L (0.01)	mg/kg (20)
Mercury (Hg)	µg/L (.0001)	mg/kg (0.00001)
Methylmercury (MeHg)	ng/L (0.005)	µg/kg (0.005)
Nickel (Ni)*	μg/L (0.01)	mg/kg (5)
Selenium (Se)	μg/L (0.02)	mg/kg (0.01)
Silver (Ag)*	µg/L (0.0001)	mg/kg (0.001)
Zinc (Zn)*	µg/L (0.005)	mg/kg (5)

Table 1.4 continued. Parameters analyzed in water, sediment, and bivalve tissue samples in 2003.

- Parameter is not sampled for the matrix.

* Near-total instead of total concentrations are reported for water. Near-total metals are extracted with a weak acid (pH < 2) for a minimum of one month, resulting in measurements that approximate bioavailability of these metals to Estuary organisms.

¹ Beginning in 2002, trace elements in bivalve tissue will be analyzed on a five-year cycle.

Table 1.4 continued. Parameters analyzed in water, sediment, and bivalve tissuesamples in 2003.

Trace organic parameters (lab; reporting units) –							
in water (AXYS; pg/L), sediment (EBMUD; µg/kg), and bivalve tissue (CDFG-WPCL; µg/kg) samples:							
Organochlorines analyzed by GC	Organochlorines analyzed by GC-ECD will be determined using two columns of differing polarity.						
PAHS	SYNTHETIC BIOCIDES	OTHER SYNTHETIC COMPOUNDS					
(Target MDLs: water – 200	(Target MDLs: water – 2 pg/L,	¹ New analytes added in 2002.					
pg/L, sediment and tissue – 5	sediment and tissue – 1	² Constitute Octa-BDEs.					
µg/kg; water PAHs reported in	µg/kg)	³ Constitute Nona-BDEs.					
ng/L)							
1-Methylnaphthalene	Cyclopentadienes	PCB congeners (IUPAC numbers)					
2,3,5-Trimethylnaphthalene	Aldrin	(Target MDLs: water – 2 pg/L, sediment					
2,6-Dimethylnaphthalene	Dieldrin	and tissue – 1 µg/kg)					
2-Methylnaphthalene	Endrin	8, 18, 28, 31, 33, 44, 49, 52, 56, 60, 66,					
Biphenyl		70, 74, 87, 95, 97, 99, 101, 105, 110,					
Naphthalene	Chlordanes	118, 128, 132, 138, 141, 149, 151, 153,					
1-Methylphenanthrene	alpha-Chlordane	156, 158, 170, 174, 177, 180, 183, 187,					
Acenaphthene	cis-Nonachlor	194, 195, 201, 203					
Acenaphthylene	gamma-Chlordane						
Anthracene	Heptachlor	Polybrominated Diphenyl Ethers ¹					
Fluorene	Heptachlor Epoxide	(BDE-IUPAC No., Compound Name)					
Phenanthrene	Oxychlordane	(Target MDLs: water – 1 pg/L, sediment					
Benz(a)anthracene	trans-Nonachlor	and tissue – 1 µg/kg).					
Chrysene		BDE 17 [2,2',4-triBDE]					
Fluoranthene	DDTs	BDE 28 [2,4,4'-triBDE]					
Pyrene	o,p'-DDD	BDE 47 [2,2',4,4'-tetraBDE]					
Benzo(a)pyrene	o,p'-DDE	BDE 66 [2,3',4,4'-tetraBDE]					
Benzo(b)fluoranthene	o,p'-DDT	BDE 82 [2,2',3,3',4-pentaBDE]					
Benzo(e)pyrene	p,p'-DDD	BDE 85 [2,2',3,4,4'-pentaBDE]					
Benzo(k)fluoranthene	p,p'-DDE	BDE 99 [2,2',4,4'5-pentaBDE]					
Dibenz(a,h)anthracene	p,p'-DDT	BDE 100 [2,2',4,4',6-pentaBDE]					
Perylene		BDE 128 [2,2',3,3',4,4'-hexaBDE]					
Benzo(ghi)perylene	НСН	BDE 138 [2,2',3,4,4',5'-hexaBDE]					
Indeno(1,2,3-cd)pyrene	alpha-HCH	BDE 153 [2,2',4,4',5,5'-hexaBDE]					
Dibenzothiophene	beta-HCH	BDE 154 [2,2',4,4',5,6'-hexaBDE]					
	delta-HCH	BDE 183 [2,2',3,4,4',5',6-heptaBDE]					
Alkylated PAHs	gamma-HCH	BDE 190 [2,3,3',4,4',5,6-heptaBDE]					
C1-Chrysenes		BDE 203 ²					
C2-Chrysenes	Other Synthetic Biocides	BDE 204 ²					
C3-Chrysenes	Chlorpyrifos (water only)	BDE 205 ²					
C4-Chrysenes	Dacthal (water only)	BDE 206 ³					
C1-Dibenzothiophenes	Diazinon (water only)	BDE 207 ³					
C2-Dibenzothiophenes	Endosulfan I (water only)	BDE 208 ³					
C3-Dibenzothiophenes	Endosulfan II (water only)	BDE 209					
C1-Fluoranthene/Pyrenes	Endosulfan Sulfate (water	Nitro Musks ¹ (tissue only)					
C1-Fluorenes	only)	Musk ambrette Musk xylene					
C2-Fluorenes	Hexachlorobenzene	Musk ketone					
C3-Fluorenes	Mirex						
C1-Naphthalenes	Oxadiazon (water only)	Polycyclic Musks ¹ (tissue only)					
C2-Naphthalenes		Celestolide Tonalide					
C3-Naphthalenes		Galazolide Versalide					
C4-Naphthalenes							

Table 1.4 continued. Parameters analyzed in water, sediment, and bivalve tissue samples in 2003.

Trace organic parameters (lab; reporting units) continued –							
C1-Phenanthrene/Anthracenes	Other Synthetic Compounds ¹	Phthalates ¹					
C2-Phenanthrene/Anthracenes	(Target MDLs: water – 50 pg/L,	(Target MDLs: water – 50 pg/L,					
C3-Phenanthrene/Anthracenes C4-Phenanthrene/Anthracenes	sediment and tissue – 5 µg/kg)	sediment and tissue – 5 µg/kg)					
	p-Nonylphenol	Bis(2-ethylhexyl)phthalate					
	Triphenylphosphate (tissue only)	Butylbenzylphthalate					
		Di-n-Butylphthalate					
		Diethylphthalate					
		Dimethylphthalate					

CHAPTER 2

Water Monitoring Results

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2.0 WATER MONITORING

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2.1 Background

Trace contaminants are introduced to the water column of the San Francisco Estuary through several major transport pathways, such as runoff from rivers and creeks, atmospheric deposition, municipal and industrial wastewater effluent discharge, and remobilization of contaminants from surface sediments to the overlying water column. Contaminants of current environmental concern in the Estuary primarily originate in areas of the watershed that have been altered or disturbed by human activities through urbanization, industrial development, and agriculture. Historic mining activities have also contributed contaminants to the Estuary (e.g., mercury). The transport of contaminants from these various sources and pathways, coupled with the dynamic nature of water and sediment movement, creates complex and constantly varying conditions of contamination throughout the Estuary. For over a decade, the San Francisco Estuary Regional Monitoring Program for Trace Substances (RMP) has monitored waters of the Estuary for trace elements, organic contaminants, and conventional water quality parameters to develop a better understanding of the cycling and distribution of contaminants in the Estuary and the management actions necessary to reduce their potential exposure to wildlife and humans. Information gained from contaminant monitoring in Estuary water assists the RMP in addressing program objectives listed in the Introduction.

2.2 Approach

2.2.1 Methods

In 2003, RMP Status and Trends Program continued with implementation of the stratified, random sampling design started in 2002 (see Chapter 1, Introduction). Thirty-one stations were monitored for contaminants in water in 2003. The Status and Trends Program is currently only conducted during the dry season (July/August).

In 2003, the Status and Trends Program reduced the random sample size for water by one sample in the South Bay and Lower South Bay regions in order to add back two historic stations (BA30-Dumbarton Bridge and BC10-Yerba Buena Island) to the monitoring design because those stations, along with BG20-Sacramento River, are used by the Regional Water Board for NPDES (National Pollutant Discharge Elimination System) permit processing. As a result, five historic stations (BA30-Dumbarton Bridge, BC10-Yerba Buena Island, BC20-Golden Gate, BG20-Sacramento River, and BG30-San Joaquin River) are part of the continued historic water samples monitored by the Status and Trends Program annually.

Two stations monitored by the Status and Trends Program, part of a local effects monitoring effort since 1996 in sloughs of the Lower South Bay, were discontinued in 2003. Those sites were San Jose (C-3-0) and Sunnyvale (C-1-3)).

In 2003 twenty-six randomly allocated stations and four historic Status and Trends Program stations were sampled within the five major hydrographic regions of the Estuary: Suisun Bay, San Pablo Bay, Central Bay, South Bay, and Lower South Bay (Figure 2.1). (Note: in 2003 the Golden Gate reference site (BC20) was not sampled due to poor weather conditions.) Four random stations were sampled in the Suisun Bay, San Pablo Bay, and Central Bay regions in each year. In 2002 and 2003, ten and nine random stations, respectively, were sampled in the South Bay region, and six and five random sites were sampled in the Lower South Bay region respectively.

Station names, codes, location, and sampling dates for the 2003 monitoring effort are listed in Table 1.2 in the Introduction and shown in Figure 2.1. This Report presents results from the first two years of the new random sampling design (2002-2003). Only the 2003 results for the four historic stations are presented in the map graphics since the 2002 historic station results were reported in the 2002 RMP Annual Monitoring Results (SFEI, 2004). Time-series plots are presented for the five historic stations that have been continued into the new monitoring program to date.

The Status and Trends Program measured 13 trace elements and a variety of organic contaminants, including polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), organochlorine pesticides, polybrominated diphenyl ethers (PBDEs), phthalates, and p-nonylphenol (Table 1.4 in Introduction).

The Status and Trends Program measures trace elements in water as dissolved (0.45 µm filtered) and total (or near-total) concentrations. Trace organic contaminant concentrations were measured in water and reported as dissolved (operationally defined as water fraction that is filtered through a wound glass fiber filter with a nominal pore size of 1 µm) and total (dissolved + particulate) concentrations. The Status and Trends Program also measured conventional water quality parameters to relate contaminant concentrations to general water quality conditions at the time of sampling, (Table 1.4). In addition, the U.S. Geological Survey (USGS) collects water quality data (salinity, temperature, dissolved oxygen, suspended sediments, and phytoplankton biomass) on a monthly basis along a transect of the deep water channels from the Lower South Bay to the confluence of the Sacramento and San Joaquin Rivers. Water quality data from USGS is available on their website at http://sfbay.wr.usgs.gov/access/wqdata/.

Field and analytical methods are described in Chapter 5 – *Description of Methods*. The referred section also provides information on additional Status and Trends Program sampling and analysis reference documentation. Data are available for downloading via the RMP website using the *Status and Trends Monitoring Data Access Tool* @ <u>http://www.sfei.org/rmp/data.htm</u>.

2.2.2 Water Quality Guidelines

To evaluate potential ecological effects, contaminant concentrations were compared to various water quality guidelines. The Regional Board uses Status and Trends Program water contaminant data (and other information) in making recommendations for changes to the state's 303 (d) list of impaired water bodies, and for evaluating "background"

concentrations of regulated contaminants in their 'reasonable potential' analyses (see section 2.2.4 below).

Concentrations of dissolved trace elements and total organic contaminants were compared to the lower of the aquatic life and/or human health (consumption of organisms only) water quality effects thresholds listed in the U.S. Environmental Protection Agency's California Toxics Rule (CTR, U.S. EPA, 2000), the San Francisco Bay Water Quality Control Plan (Basin Plan, SFBRWQCB, 1995), or other sources. Table 2.1 lists the various guidelines used. There are no regulatory effects thresholds for total trace elements (except for mercury and selenium) and comparisons are made in this report for illustrative purposes only.

The CTR lists several effects thresholds aimed at protecting aquatic life or human health. Trace element data were compared to the lowest threshold reported for each contaminant (generally the four-day average aquatic life criteria). Trace organic contaminant concentrations were compared to the human health criteria for the consumption of aquatic organisms only, since Status and Trends Program stations are all downstream of drinking water intakes in the Delta.

Revised Basin Plan objectives in 2004 (and approved by EPA in 2005) clarify the definition of freshwater, marine, and estuarine waters for the Estuary to align with the CTR. These definitions are used to categorize dischargers and determine which set of water quality objectives form the basis of effluent limitations. The CTR defines freshwater as less than 1 part per thousand (‰) at least 95% of the time and marine water as greater than 10 ‰ at least 95% of the time. Anything in between is defined as estuarine water, for which the lower of the marine or freshwater objectives apply. Where applicable, estuarine samples were compared to the lower freshwater or saltwater effects threshold for trace elements (see Defining "Estuarine" Regions in the Estuary section below). Concentrations of six trace elements (cadmium, copper, nickel, lead, silver, and zinc) were compared to the lower of the freshwater or saltwater criteria at sites considered "Estuarine" (see below). Freshwater effects thresholds were calculated for each sample using hardness data that were measured on site or (if data were not available) a hardness factor of 100 mg/L (the default value in the CTR, US EPA, 2000). A hardness cap of 400 mg/L was used for calculating freshwater thresholds (per recommendation of the Regional Water Board staff, 2003).

Regulatory Effects Thresholds

Only a subset of effects threshold comparisons in this report has regulatory implications. This subset consists of nine trace elements and twenty-six trace organic contaminants (Table 2.1). Arsenic, cadmium, copper, lead, silver, nickel, and zinc were compared to the dissolved water quality criteria (WQC) listed in the CTR. The Lower South Bay (south of the Dumbarton Bridge) has site-specific objectives approved for that region for copper, nickel, and mercury (see <u>Site-specific Objectives for the Lower South Bay</u> section below). Total mercury concentrations were compared to the aquatic life objective for total recoverable mercury listed in the Basin Plan (0.025 μ g/L), except for the Lower South Bay where the CTR criterion of 0.051 μ g/L applies (which is the human health
criterion (for the consumption of organisms only)). The CTR lists a selenium criterion of 5 μ g/L for total recoverable selenium that was promulgated for all waters in San Francisco Bay and upstream, including the Delta, in the National Toxics Rule (NTR, U.S. EPA, 1992). Total (dissolved plus particulate fractions) organic contaminants were compared to the CTR human health criterion (for the consumption of organisms only) for those contaminants listed in Table 2.1. Additionally, sum of PAHs were compared to the Basin Plan objective of 15.0 μ g/L.

Non-Statutory/Regulatory Effects Thresholds

Effects threshold comparisons of total trace element concentrations for the seven metals mentioned above (arsenic, cadmium, copper, lead, silver, nickel, and zinc), and total organic concentrations for diazinon, chlorpyrifos, and mirex are strictly for informational purposes and do not have regulatory implications. The total metals effects thresholds used in this report were calculated using the default CTR conversion factors to convert dissolved metals thresholds to total metals thresholds, except for the Lower South Bay where site-specific translators are available for copper and nickel (see below).

Some organic contaminants analyzed by the Status and Trends Program are not listed in the CTR or Basin Plan, but effects thresholds do exist. The following contaminants were compared to effects thresholds from other sources (Table 2.1). Total diazinon concentrations were compared to an effects threshold concentration of 40 ng/L, developed by the California Department of Fish and Game (Menconi and Cox, 1994). Chlorpyrifos and mirex were compared to the EPA recommended thresholds for these contaminants (U.S. EPA, 1999).

Site-specific Objectives for the Lower South Bay

There are site-specific aquatic life water quality objectives for *dissolved* copper and nickel adopted by the State of California in 2003 and approved by the U.S. EPA for Lower South San Francisco Bay (south of the Dumbarton Bridge). The dissolved copper objective changed from 4.8 μ g/L to 10.8 μ g/L acute (exposure for one hour) and from 3.1 μ g/L to 6.9 μ g/L chronic (exposure for four days). The dissolved nickel objectives changed from 74 μ g/L to 62.4 μ g/L acute and from 8.2 μ g/L to 11.9 μ g/L chronic. Additionally there are site-specific translators to convert the objective from dissolved to total. The translators for copper and nickel are 0.53 and 0.44 respectively (dissolved objective / translator value = site-specific total objective).

Defining "Estuarine" Regions in the Estuary

In order to evaluate which regions should be considered estuarine by the new Basin Plan definition, SFEI staff performed a short study of the USGS long-term database for salinity data sampled between 1993 and 2002 for the 2002 RMP Annual Monitoring Results (SFEI, 2004). Results of that study showed that none of the Status and Trends Program sampling sites are located within a freshwater region and that the Rivers, Suisun Bay, San Pablo Bay, and the Lower South Bay regions are estuarine as defined by the revised Basin Plan and the CTR.

2.2.3 Aquatic Toxicity Testing (none in 2003)

Ambient Water Toxicity

Since 1993, the Status and Trends Program has conducted ambient water toxicity testing on seasonal to annual time scales. The Status and Trends Program did not sample water toxicity in the Estuary in 2003. Aquatic toxicity sampling within the Estuary is scheduled to occur in 2006.

2.2.4 Background Concentrations for Total-water-column Contaminants at Three Historic RMP Stations

The State Board adopted the *Policy for Implementation of Toxics Standards for Inland Surface Waters, Enclosed Bays, and Estuaries of California* (SIP) effective as of May 22, 2000 (www.swrcb.ca.gov/iswp/final.pdf). Among other things, the SIP establishes implementation provisions for priority pollutant criteria promulgated by the U.S. EPA through the National and the California Toxics Rules, and for priority pollutant water quality objectives (WQO's) established by the Regional Water Boards in their Basin Plans. The SIP specifies how toxic water quality objectives are translated into effluent limitations.

The Regional Water Board uses the Status and Trends Program's total-water-column data (dissolved plus particulate for organic and total-recoverable for trace element concentrations) to determine "background" contaminant levels in the Estuary. This information serves as a reference for the Regional Water Board in their Reasonable Potential analyses, part of their National Pollutant Discharge Elimination System (NPDES) permitting program. "Reasonable Potential" is defined as the likelihood that the concentration of a pollutant in a discharge would cause or contribute to an exceedance of a water quality guideline. If the Regional Water Board determines that the pollutant has 'reasonable potential', the SIP requires the discharger to have an effluent limit for that pollutant in its NPDES permit (i.e., a limit is "triggered").

Overall, there are three triggers for effluent limits: (1) if the maximum effluent concentration exceeds the WQO, (2) if the maximum background concentration exceeds the WQO, or (3) if there is other information that would require the need for an effluent limit (e.g., 303(d) listing).

Three historic stations (BA30-Dumbarton Bridge, BC10-Yerba Buena Island, and BG20-Sacramento River) are used by the Regional Water Board to estimate background contaminant concentrations in the water-column for determining NPDES effluent limits for Estuary dischargers (trigger 2 above). Following format guidance provided by the permit staff at the Regional Water Board a summary of that data (1993-2003) is provided in *Appendix A*. For each station, the sample size, minimum, maximum (or the lowest reported method detection limit if all samples were non-detects), average, median, and number of samples reported as not detected are reported for all contaminants that have a WQO. The raw total-water-column data are also available on the RMP website through the *Status and Trends Monitoring Data Access Tool @* http://www.sfei.org/rmp/data.htm.

2.3 Results and Discussion

Results from the RMP Status and Trends water monitoring are presented in a series of maps that display the distribution and concentration ranges of salinity (Figure 2.2), dissolved organic carbon (DOC; Figure 2.3), total suspended solids (TSS; Figure 2.4), trace elements (Figures 2.5 - 2.22), and organic contaminants (Figures 2.23 - 2.26) for randomly allocated stations (2002-2003) and historic stations (2003 samples only). Methyl-mercury (MeHg) results were not available at that time of this report. The only organic contaminants available at the time of this report were polyaromatic hydrocarbons (PAHs) and polychlorinated biphinyls (PCBs). As additional 2003 data are finalized, they will be made available through the Status and Trends Monitoring Data Access Tool on the RMP website. The list of parameters measured in water is included in table 1.4 in the *Introduction*.

Additional graphics include box plots with interquartile ranges of contaminant concentrations summarize results from randomly allocated stations (2002-2003) grouped into the five major hydrographic regions of the Bay: Suisun Bay, San Pablo Bay, Central Bay, South Bay, and Lower South Bay. Cumulative Distribution Function (CDF) plots provide an estimate of the square kilometers of the sampled Estuary that have a particular contaminant concentration based on results from the randomly allocated stations (2002-2003). Please see section 1.3.1 in the *Introduction* for additional information about each graphic type.

Temporal trends were not evaluated for the random sampling design results as only two years of data have been collected to date. The RMP is working on a special issue for the journal *Environmental Research* that will include articles synthesizing the ten years of the RMP's Status and Trends Program data (among other topics). That report should be submitted to the journal later this year (2005). We decided to defer any analyses of temporal trends in results from the historic sample design to that reporting effort. However, for reporting continuity, time-series plots were generated and are presented here for the five historic stations that have been continued in the current monitoring program.

2.3.1 Spatial Distribution

Highest contaminant values

Similar to 2002, the highest dissolved concentrations of all dissolved trace element contaminants (except silver) were measured at stations in the southern Estuary regions, the South Bay and Lower South Bay (Figures 2.5 - 2.13). In the five major segments, dissolved concentrations of arsenic, copper, nickel, lead, and zinc were highest at one station in the Lower South Bay (LSB008W), and selenium was highest at LSB0010W compared to other regions. Dissolved mercury concentrations were highest in the South Bay region at SB016W and dissolved cadmium concentrations were highest in both the South Bay and Central Bay regions at SB011W and CB006W respectively. Dissolved silver was highest in the Central Bay at CB006W. Dissolved concentrations of trace elements were operationally defined as the fraction of sample that passes through a 0.45- μ m filter, which also allows smaller particles and colloids to pass through. Thus, dissolved trace element concentrations measured in Status and Trends water samples may

have been influenced by concentrations of DOC (Kuwabara *et al.*, 1989) and colloids (Sañudo-Wilhelmy *et al.*, 1996). DOC concentrations were highest in the Lower South Bay region at LSB008W, the same station that we highest in most dissolved metals concentrations.

The cycling and distribution of many trace elements measured by the Status and Trends Program in Estuary water are greatly influenced by the transport of suspended particles (Schoellhamer, 1996a, Conaway *et al.*, 2003, Schoellhamer *et al.*, 2003). Maximum total concentrations of copper, mercury, nickel, lead, and zinc were measured at SPB005W in San Pablo Bay (Figures 2.16 - 2.22), which also had the highest concentration of TSS (122 mg/L) by at least a factor of two. The highest concentration of total cadmium was measured in the South Bay at SB011W (Figure 2.15), and total silver in the Central Bay at CB006W (Figure 2.21). Total selenium concentrations were highest at LSB008W in the Lower South Bay at the same station that had the highest concentrations of DOC and most dissolved metals. Among the five major Estuary regions, relatively high concentrations of silver, cadmium, copper, mercury, nickel, lead, and zinc were measured in SPB005W San Pablo Bay and were likely influenced by the proportionally high concentrations of TSS in that sample.

Concentrations of dissolved and total sum of PAHs, were highest in the San Pablo and Central Bay regions in 2003 (Figures 2.23, 2.25). Dissolved and Total concentrations of Sum of PCBs were highest in the South Bay and Lower South Bay regions respectively (SB013W, LSB008W; figures 2.24, 2.26).

Concentrations of most trace elements and organic contaminants were highest in southern regions of the Estuary. Much of the South Bay and Lower South Bay lie adjacent to watersheds with regions of urbanization, agriculture, and historic mercury mining. Tributaries that drain local watersheds carry surface runoff with high concentrations of sediment and associated contaminants, including trace metals, PCBs and OC pesticides from urban and agricultural sources, as well as mercury from historic mining (McKee *et al.*, 2004; Thomas *et al.*, 2002). The southern reach also receives treated wastewater effluent from three municipal treatment facilities. In addition, many trace contaminants of concern are persistent in sediment of the South Bay, which receives limited seasonal hydraulic flushing of freshwater from local tributaries compared to the northern reaches of the Estuary. Thus, high concentrations of trace elements and organic contaminants may reflect combined influences of watershed and the treatment plant inputs, as well as the tidal resuspension of persistent contaminants from the sediment of the South and Lower South Bays.

<u>Are the Mean Concentrations Statistically Different Between Regions?</u> Differences in mean contaminant concentrations among regions and between years were examined using a Z-test with a Z score greater than 1.96, or less than -1.96 indicating a statistically significant difference at the 5% significance level. Dissolved contaminant concentrations of arsenic, copper, nickel, selenium, zinc, and PCBs were significantly higher (-1.96< Z>1.96) in the Lower South Bay compared to the Suisun, San Pablo, Central, and South Bays (Table 2.2). Lower South Bay dissolved water samples were also significantly higher in lead compared to the Suisun, Central, and South Bays. Dissolved mercury concentrations were significantly higher in the Lower South Bay and Suisun Bay compared to other regions of the Estuary. Suisun Bay samples were observed to be significantly lower in dissolved cadmium and silver than samples from San Pablo Bay, Central Bay, South Bay and Lower South Bay. South Bay water samples were significantly lower in dissolved PAHs than the San Pablo, Central, and South Bays. Interannual comparisons show that the 2002 samples were significantly higher in dissolved contaminant concentrations of cadmium, lead, mercury, selenium, zinc, and PAHs than the 2003 samples.

Total contaminant concentrations of arsenic and PCBs, like those for dissolved, were significantly higher in the Lower South Bay compared to the other four regions of the Estuary (Table 2.3). Additionally, the Lower South Bay water samples were also significantly higher in total selenium and PAHs than samples from the Suisun and South Bays. Nickel, lead, and zinc total concentrations were significantly lower in the Central Bay and South Bay water samples than those from the Suisun and San Pablo Bays. Central Bay samples were also significantly lower in total concentrations of cadmium and silver than the other Estuary regions. Total mercury concentrations were significantly higher in the San Pablo Bay compared to both the Central and South Bays. Interannual comparisons document that the 2002 water samples were significantly higher in total concentrations of cadmium, and selenium than those collected in 2003.

Are the CDF Results Statistically Different Between Regions?

Cumulative distribution function's (CDFs) were calculated with the R system and the psurvey.analysis statistical library using untransformed contaminant concentrations, normality not being an issue. Differences between two CDFs were examined using a modified version of the Roa-Scott first order corrected (mean eigenvalue corrected) statistic for categorical data (Kincaid, 2004). Overall, significant differences (p<0.05) were observed in 67% (88 out of 132) of the dissolved water comparisons: 69% of the regional and 42% of the interannual (Table 2.4). The greatest number of significant differences was documented for copper, nickel, PCBS, and dissolved organic carbon (DOC) (9 out of 11), and the least for PAHs (3 out of 11). Significant interannual differences in the dissolved water contaminant CDFs were observed for cadmium, mercury, selenium, silver, and PAHs.

Statistical analysis of the CDFs for the total water samples showed significant differences in 50% (61 out of 121) of the comparisons: 55% of the regional and 9% of the interannual (Tables 2.4 and 2.5). Lead and zinc were observed to have the largest number of significant differences, each with 7 out of 11 (64%). Total cadmium was the only contaminant where a significant difference was found in the interannual cumulative distribution functions of the water samples.

2.3.2 Temporal Trends

An objective of the RMP is to determine patterns and trends in contaminant concentrations and distribution in the San Francisco Estuary. A good summary of long-term trends in metal contamination in the Estuary was reported in the 2004 Pulse of the Estuary (Flegal *et al.* 2004).

Temporal trends were not evaluated for the random sampling design at this time as only two years of data have been collected to date. For reporting continuity, time-series plots were generated and are presented in Figures 2.27-2.50 for the five historic stations that have been continued in the current monitoring program. However, analyses and discussion of the contaminant trends at the historic sites is deferred to the special issue of the journal *Environmental Research* to be submitted later this year.

2.3.3 Comparison to Water Quality Guidelines

Various water samples collected in 2003 had contaminant concentrations that were above the water effects thresholds (some of which have regulatory implications, see Table 2.6). Only one sample, BA30 in the South Bay region, was above the regulatory dissolved metals water quality criterion for copper: $3.1 \ \mu g/L$ (or $6.9 \ \mu g/L$ for the Lower South Bay region; Figure 2.7). No other samples were above the regulatory water quality criteria for dissolved metals. In 2003 no samples were above the total mercury criterion of 0.025 $\mu g/L$ (or 0.051 $\mu g/L$ for the Lower South Bay region). However, in 2002, one site in the Lower South Bay and two samples in San Pablo Bay were above the guidelines (Figure 2.18). No stations were above the regulatory total selenium effects threshold of 5 $\mu g/L$ in either year. Only the 2003 PAH and PCB organic contaminants have been reviewed and finalized at the time of this report. Guideline comparisons for those contaminant groups showed that 24 out of the 27 reportable Sum of PCBs results in 2003 were above the CTR criterion of 170 pg/L (Figure 2.26). In 2002 28 out of 33 stations were above the PCB threshold (Figure 2.26). All individual PAH and Sum of PAHs results were below CTR criteria and Basin Plan objectives respectively for both years (Figure 2.25).

Calculated, *non-regulatory* CTR effects thresholds for total metals were compared to total metals concentrations for informational purposes only. In 2003, total copper concentrations were above the non-regulatory threshold of effect of 9.3 μ g/L (or 13.02 μ g/L for the Lower South Bay region) at eight stations: four in Suisun Bay, two in San Pablo Bay, one in the Central Bay, and one in the South Bay (Figure 2.16). In 2002, seven stations were above the thresholds: four in Suisun Bay, two in San Pablo Bay (Figure 2.16). Only one San Pablo Bay station in 2003 was above the non-regulatory total nickel effects threshold of 7.1 μ g/L (or 27.05 μ g/L in the Lower South Bay region), while three stations in 2002 were above the threshold: two in Suisun Bay and one in San Pablo Bay (Figure 2.19). No stations in 2003 were above the non-regulatory salt or freshwater total lead effects thresholds of 5.6 or 3.2 μ g/L respectively (Figure 2.17). However, three stations in 2002 were above the freshwater total lead effects thresholds of 5.6 or 3.2 μ g/L respectively (Figure 2.17). However, three stations in 2002 were above the freshwater total lead effects thresholds of 5.6 or 3.2 μ g/L respectively (Figure 2.17).

2.3.4 Toxicity of Water to Organisms

Ambient Water Toxicity

This measure has been reduced to a periodic screening effort as little ambient aquatic toxicity has been observed in Estuary samples during the dry season. No aquatic toxicity monitoring occurred in 2003. The Status and Trends Program is scheduled to sample aquatic toxicity in the Estuary next in 2006.

Episodic Water Toxicity

Episodic toxicity monitoring in 2003/04 was not conducted as this program is screening for the potential for sediment toxicity in a subset of tributaries in 2005 and will be reviewing study information in an effort to adapt this effects based component of the Status and Trends Program to follow the changing use of pesticides in urban and agricultural environments around the Estuary.

Since episodic toxicity testing began in 1996, there has been an apparent reduction in aquatic toxicity in Estuary waters that has been attributed to reductions in the concentrations of organophosphate (OP) pesticides in the watershed (Ogle and Gunther, 2004). An overview of toxicity testing in water and sediment over the past ten years of Status and Trends monitoring was summarized by Anderson, Ogle, and Lowe (2003) in the 2003 Pulse of the Estuary. <u>http://www.sfei.org/rmp/pulse/pulse2003.pdf</u>

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RMP Annual Monitoring Results 2003

Table 2.1. Water quality guidelines.

California Toxics Rule (CTR) water quality criteria (USEPA, 2000) are listed except where noted. Dissolved trace element criteria are listed (except for mercury and selenium). Total trace element criteria (not shown) were calculated using procedures specified in the CTR. Criteria for organic compounds are listed on a total basis (dissolved + particulate). Bold and italicized concentrations are hardness dependent criteria and were calculated using a hardness concentration of 100 mg/L. Units are μ g/L for all concentrations.

	Aquatic Life				Human Health			
					(10 ⁻⁶ risk fo	or carcinogens)		
Parameter	Fresh	Water	Salt	Water	Fresh Water	Salt & Fresh Water		
	1-hour	4-day	1-hour	4-day	Water & Organisms	Organisms only		
Ag	3.4	·	1.9	·				
As	340	150	69.0	36.0				
Cd	4.3	2.2	43.0	9.3				
Cr VI	16.0	11.0	1100	50.0				
Cu	13.4	9.0	4.8	3.1	1300			
Cu (lower South Bay only)			10.8	6.9				
Hg ^A	2.4	0.025	2.1	0.025	0.05	0.051		
Ni	470	52.0	74.0	8.2	610	4600		
Ni (lower South Bay only)			62.4	11.9				
Pb	64.6	2.5	220	8.1		•		
Se [⊳]		5.0	290	71.0		•		
Zn	120	120	90.0	81.0		-		
Alpha-HCH					0.0039	0.013		
Acenaphthene			-		1200	2700		
Anthracene			•	•	9600	110000		
Benz(a)anthracene			•	•	0.0044	0.049		
Benzo(a)pyrene			•	•	0.0044	0.049		
Benzo(b)fluoranthene				•	0.0044	0.049		
Benzo(k)fluoranthene			•	•	0.0044	0.049		
Beta-HCH			•	•	0.014	0.046		
Chlordane	2.4	0.0043	0.09	0.004	0.00057	0.00059		
Chlorpyrifos ^C	0.083	0.041	0.011	0.0056				
Chrysene			-		0.0044	0.049		
Diazinon ^D						0.04		
Dibenz(a,h)anthracene					0.0044	0.049		
Dieldrin	0.24	0.056	0.71	0.0019	0.00014	0.00014		
Endrin	0.086	0.036	0.037	0.0023	0.76	0.81		
Fluoranthene					300	370		
Fluorene					1300	14000		
Gamma-HCH	0.095	0.08	0.16		0.019	0.063		
Heptachlor	0.52	0.0038	0.053	0.0036	0.00021	0.00021		
Heptachlor Epoxide	0.52	0.0038	0.053	0.0036	0.0001	0.00011		
Hexachlorobenzene	•	•	•	·	0.00075	0.00077		
Indeno(1,2,3-cd)pyrene	•	•	•	·	0.0044	0.049		
p,p'-DDD	•	•	•	·	0.00083	0.00084		
p,p'-DDE			•	·	0.00059	0.00059		
p,p'-DDT	1.1	0.001	0.13	0.001	0.00059	0.00059		
Pyrene				•	960	11000		
		0.001		0.001				
I otal PAHs					0.031	0.031		
Total PCBs	· ·	0.014		0.03	0.00017	0.00017		

^A Mercury guidelines are from the Basin Plan (SFBRWQB, 1995) and are for total recoverable mercury. The Lower South Bay region is compared to the Human Health (organisms only) mercury guideline of $0.051 \mu g/L$.

^E Total PAH guideline is from the footnote in the Basin Plan, 1995 (SFBRWQB, 1995). However the current objective is 15 μg/L.

^B Selenium values are region-specific criteria as outlined in the National Toxics Rule (USEPA, 1992) and are for total recoverable selenium. ^C Chlorpyrifos and mirex criteria from USEPA (1999).

^D Diazinon guideline is from California Department of Fish and Game (Menconi and Fox, 1994).

Table 2.2. Statistical comparisons of mean dissolved contaminant concentrations among regions and between years, 2002-2003.

Significant comparisons shown in bold. * indicates data were log transformed.

					Z-test	Statistic					
Comparison	Ag	As*	Cd*	Cu	Hg*	Ni*	Pb*	Se*	Zn*	PAHs	PCBs*
CB vs LSB	1.05	-14.74	-0.59	-12.79	-4.27	-14.31	-9.10	-5.58	-3.62	-0.13	-3.81
CB vs SB	-0.38	-10.62	-1.51	-5.87	-4.55	-7.13	-2.12	-1.70	-0.68	3.33	-0.02
CB vs SPB	1.03	-2.85	1.51	-2.60	1.15	-3.86		-0.27	0.51	-1.02	1.19
CB vs SU	7.50	-1.03	8.61	-2.59	0.14	0.22	1.83	-0.77	3.65	0.59	6.22
LSB vs SB	-1.82	6.76	-1.77	9.34	1.56	8.95	4.18	5.66	3.04	3.43	3.49
LSB vs SPB	0.31	12.38	2.89	16.09	4.43	13.50	NA	5.60	4.38	-0.93	3.35
LSB vs SU	10.82	14.82	13.42	17.33	3.83	13.80	8.64	5.84	7.02	0.67	8.23
SB vs SPB	1.47	7.73	3.73	5.48	4.23	4.55	NA	1.50	1.28	-3.27	1.15
SB vs SU	10.22	10.53	13.35	6.04	3.45	6.94	2.82	1.23	4.49	-1.69	5.83
SPB vs SU	5.13	2.00	7.84	0.19	-0.85	3.85	-2.53	-0.51	4.10	1.30	2.93
2002 vs 2003	0.54	0.42	5.53	-1.29	6.86	0.76	2.33	3.40	3.02	2.06	1.01
Abbreviations: CB	= Central	Bay, LSB	= Lower	South Ba	y, SB = Sc	outh Bay, S	PB = Sa	n Pablo	Bay, an	d SU = S	uisun Bay

Table 2.3. Statistical comparisons of mean total contaminant concentrations among regions and between years, 2002-2003.

Significant comparisons shown in bold. All parameters were log transformed.

						Z-test	Statistic				
Comparison	Ag	As	Cd	Cu	Hg	Ni	Pb	Se	Zn	PAHs	PCBs
CB vs LSB	-1.45	-10.57	-0.67	-6.23	-1.28	-4.67	-1.33	-1.95	-2.45	-2.19	-2.58
CB vs SB	-0.59	-5.89	-1.15	-3.48	1.12	-1.25	1.49	0.55	0.80	1.00	1.50
CB vs SPB	-1.82	-2.62	-0.54	-3.42	-2.14	-2.88	-2.11	1.21	-2.43	-0.33	1.29
CB vs SU	3.08	-3.52	2.52	-7.36	-2.30	-6.08	-3.43	0.49	-5.78	1.65	6.14
LSB vs SB	1.31	7.30	-0.57	5.37	1.90	5.19	2.61	4.74	3.98	4.72	4.82
LSB vs SPB	-0.26	3.07	-0.11	-0.36	-1.42	-0.36	-1.19	5.30	-1.01	1.69	3.40
LSB vs SU	3.11	9.02	3.40	0.06	0.05	-0.29	-0.89	4.03	-2.27	5.29	9.63
SB vs SPB	-1.72	0.22	0.20	-2.22	-2.41	-2.58	NA	1.93	-2.98	-1.35	0.27
SB vs SU	7.27	2.87	3.92	-9.74	-4.63	-9.59	-10.51	-0.08	-14.78	1.23	5.81
SPB vs SU	3.56	0.86	2.50	0.40	1.56	0.25	0.84	-1.48	0.00	1.95	3.52
2002 vs 2003	-0.39	-0.15	6.63	-0.03	1.18	0.59	-0.08	2.05	-0.12	0.56	0.23
Abbreviations: CB =	Central	Bay, LSB	= Lowe	r South I	Bay, SB	= South Ba	ay, SPB = S	San Pablo	b Bay, and	l SU = Su	iisun Bay

Table 2.4. Statistical comparison of CDF results for dissolved contaminant concentrations among regions and between years, 2002-2003.

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Significant com	narieone	chown	in l	hold
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					Roa-S	cott Test p	o value				
Comparison	Ag	As	Cd	Cu	Hg	Ni	Pb	Se	Zn	PAHs	PCBs
CB vs LSB	0.03	0.00	0.39	0.00	0.00	0.00	0.00	0.00	0.00	0.54	0.01
CB vs SB	0.00	0.00	0.75	0.00	0.00	0.00	0.03	0.00	0.41	0.05	0.42
CB vs SPB	0.70	0.12	0.20	0.00	0.13	0.00	NA	0.80	0.79	0.79	0.00
CB vs SU	0.00	0.77	0.00	0.00	0.04	0.76	0.21	0.22	0.01	0.05	0.00
LSB vs SB	0.06	0.00	0.13	0.00	0.07	0.00	0.00	0.00	0.02	0.00	0.00
LSB vs SPB	0.07	0.00	0.02	0.00	0.00	0.00	NA	0.00	0.00	0.80	0.01
LSB vs SU	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.56	0.00
SB vs SPB	0.01	0.00	0.04	0.00	0.00	0.00	NA	0.23	0.04	0.00	0.00
SB vs SU	0.00	0.00	0.00	0.00	0.04	0.00	0.00	0.61	0.00	0.20	0.00
SPB vs SU	0.00	0.75	0.00	0.43	0.76	0.00	NA	0.54	0.00	0.79	0.01
2002 vs 2003	0.02	0.89	0.00	0.37	0.00	0.30	0.15	0.00	0.05	0.01	0.21

Abbreviations: CB = Central Bay, LSB = Lower South Bay, SB = South Bay, SPB = SanPablo Bay, and SU = Suisun Bay.

Table 2.5. Statistical comparison of CDF results for total contaminant concentrations among regions and between years, 2002-2003. Significant comparisons shown in bold.

					R	ba-Scott	l est p val	ue			
Comparison	Ag	As	Cd	Cu	Hg	Ni	Pb	Se	Zn	PAHs	PCBs
CB vs LSB	0.25	0.00	0.26	0.00	0.74	0.02	0.20	0.01	0.14	0.23	0.14
CB vs SB	0.56	0.00	0.27	0.00	0.03	0.18	0.01	0.78	0.01	0.17	0.53
CB vs SPB	0.35	0.09	0.54	0.09	0.14	0.09	0.05	0.18	0.09	0.49	0.66
CB vs SU	0.04	0.01	0.11	0.00	0.12	0.01	0.00	0.22	0.00	0.18	0.00
LSB vs SB	0.32	0.00	0.54	0.00	0.52	0.00	0.00	0.00	0.00	0.00	0.00
LSB vs SPB	0.11	0.00	0.93	0.00	0.12	0.00	0.08	0.00	0.07	0.80	0.01
LSB vs SU	0.00	0.00	NA	0.78	0.02	0.06	0.00	0.00	0.00	0.00	0.00
SB vs SPB	0.00	0.41	0.74	0.00	0.00	0.00	0.00	0.04	0.00	0.01	0.76
SB vs SU	0.00	0.05	0.00	0.00	0.00	0.00	0.00	0.21	0.00	0.14	0.00
SPB vs SU	0.00	0.05	0.17	0.00	0.01	0.05	0.00	0.11	0.00	0.04	0.00
2002 vs 2003	0.07	0.14	0.00	0.52	0.98	0.66	0.09	0.07	0.67	0.56	0.65

Abbreviations: CB = Central Bay, LSB = Lower South Bay, SB = South Bay, SPB = SanPablo Bay, and SU = Suisun Bay.

Table 2.6. Summary of trace organic and trace element contaminants that were above water

quality guidelines. Only compounds that were above guidelines are listed. Note: only one of the regulatory dissolved trace elements was above the guideline (BA30 in the South Bay region).

dot = above guideline. s = compounds generally comprising a significant portion of the sum were not quantifiable; therefore, the sum was not calculated. Units are $\mu g/L$.

			Σ PCBs (total)	Copper (dissolved)	Copper (total)	Nickel (total)	
	Code	Station Name or Region	0.00017	А	Α	Α	
Rivers	BG20	Sacramento River					
	BG30	San Joaquin River					
Suisun Bav	SU006W	Suisun Bav			•		
···· ·	SU007W	Suisun Bay	•		•		
	SU009W	Suisun Bay	•		•		
	SU010W	Suisun Bay	•		•		
San Pablo Bay	SPB005W	San Pablo Bay	•		٠	•	
,	SPB006W	San Pablo Bay	•				
	SPB007W	San Pablo Bay	•				
	SPB008W	San Pablo Bay	S		•		
Central Bay	BC10	Yerba Buena Islanc	٠				
-	CB005W	Central Bay	•				
	CB006W	Central Bay	•		•		
	CB007W	Central Bay	•				
	CB008W	Central Bay	•				
South Bay	BA30	Dumbarton Bridge	٠	٠	٠		
	SB011W	South Bay	•				
	SB012W	South Bay	S				
	SB013W	South Bay	•				
	SB014W	South Bay	•				
	SB015W	South Bay	•				
	SB016W	South Bay	٠				
	SB017W	South Bay	•				
	SB018W	South Bay	S				
	SB019W	South Bay	•				
Lower South Bay	LSB007W	Lower South Bay	•				
-	LSB008W	Lower South Bay	•				
	LSB009W	Lower South Bay	•				
	LSB010W	Lower South Bay	•				
	LSB011W	Lower South Bay	•				

A. The guidelines used for these comparisons varied by site. The sites within estuarine regions were compared to the lower of the hardness dependent fresh or salt water gudieline and/or the Lower South Bay has a different site specific objective.



Figure 2.1. Map of the 2003 RMP Status and Trends water monitoring effort at 26 randomly selected and five historic sampling sites. 31 stations were sampled in the San Francisco Estuary for analysis of water quality and trace contaminants. The Golden Gate (BC20) historic site was not sampled in 2003 due to poor weather conditions at the time of sampling and is not shown here.



Figure 2.2. Salinity in Water (2002-2003)

a) Map of salinity concentrations in water (practical salinity units - psu) in the six Estuary regions monitored. Fifty-six randomly allocated sites (based on the EMAP sample design) and four historic RMP sites (2003 data only) were sampled and only results that passed QA/QC are reported here. Note that only historic sites were sampled in the Rivers region.

Random sites = \circ , Historic sites = \diamond , Non-detects = +

For further explanations of these graphics please refer to section 1.3.1.



Region Code: LSB=Lower South Bay, SB=South Bay, CB=Central Bay, SPB=San Pablo Bay, Su=Suisun Bay

b) Schematic Box Plot of salinity concentrations in water (psu) for the random sites in five Estuary regions (2002-2003).



c) Cumulative distribution function (CDF) plots for salinity concentrations in water (psu) from the random sites in the five Estuary regions (2002 & 2003).

The large graph shows the percentage of the total area sampled in the five Estuary regions (totaling 784 square kilometers) vs. the salinity concentrations in water.

The small graphs show the same for each individual region (scales are identical to the large graph).

Figure 2.3. Dissolved Organic Carbon (DOC) in Water (2002-2003)



a) Map of dissolved organic carbon concentrations in water (μ g/L) in the six Estuary regions monitored. Fifty-six randomly allocated sites (based on the EMAP sample design) and four historic RMP sites (2003 data only) were sampled and only results that passed QA/QC are reported here. Note that only historic sites were sampled in the Rivers region.

Random sites = \circ , Historic sites = \diamond , Non-detects = +

For further explanations of these graphics please refer to section 1.3.1.



Region Code: LSB=Lower South Bay, SB=South Bay, CB=Central Bay, SPB=San Pablo Bay, Su=Suisun Bay

b) Schematic Box Plot of dissolved organic carbon concentrations in water (μ g/L) for the random sites in five Estuary regions (2002-2003).



c) Cumulative distribution function (CDF) plots for dissolved organic carbon concentrations in water (μ g/L) from the random sites in the five Estuary regions (2002 & 2003).

The large graph shows the percentage of the total area sampled in the five Estuary regions (totaling 784 square kilometers) vs. the dissolved organic carbon concentrations in water.

The small graphs show the same for each individual region (scales are identical to the large graph).





a) Map of total suspended solid concentrations

in water (mg/L) in the six Estuary regions monitored. Fifty-six randomly allocated sites (based on the EMAP sample design) and four historic RMP sites (2003 data only) were sampled and only results that passed QA/QC are reported here. Note that only historic sites were sampled in the Rivers region.

Random sites = \circ , Historic sites = \diamond , Non-detects = +

For further explanations of these graphics please refer to section 1.3.1.



Region Code Region Code: LSB=Lower South Bay, SB=South Bay, CB=Central Bay, SPB=San Pablo Bay, Su=Suisun Bay

b) Schematic Box Plot of total suspended solid concentrations in water (mg/L) for the random sites in five Estuary regions (2002-2003).



c) Cumulative distribution function (CDF) plots for total suspended solid concentrations in water (mg/L) from the random sites in the five Estuary regions (2002 & 2003).

The large graph shows the percentage of the total area sampled in the five Estuary regions (totaling 784 square kilometers) vs. the total suspended solid concentrations in water.

The small graphs show the same for each individual region (scales are identical to the large graph).

Figure 2.5. Dissolved Arsenic (As) in Water (2002-2003)



a) Map of dissolved arsenic concentrations in water (μ g/L) in the six Estuary regions monitored. Fifty-six randomly allocated sites (based on the EMAP sample design) and four historic RMP sites (2003 data only) were sampled and only results that passed QA/QC are reported here. Note that only historic sites were sampled in the Rivers region.

Random sites = \circ , Historic sites = \diamond , Non-detects = +

For further explanations of all graphics and the guideline used to evaluate the reported concentrations, please refer to sections 1.3.1 and 2.2.2 respectively.



Region Code: LSB=Lower South Bay, SB=South Bay, CB=Central Bay, SPB=San Pablo Bay, Su=Suisun Bay

b) Schematic Box Plot of dissolved arsenic concentrations in water (μ g/L) for the random sites in five Estuary regions (2002-2003).



c) Cumulative distribution function (CDF) plots for dissolved arsenic concentrations in water (μg/L) from the

random sites in the five Estuary regions (2002 & 2003).

The large graph shows the percentage of the total area sampled in the five Estuary regions (totaling 784 square kilometers) vs. the dissolved arsenic concentrations in water.

The small graphs show the same for each individual region (scales are identical to the large graph).

The large plot indicates that about 50% of the Estuary regions sampled had dissolved arsenic concentrations of 2.3 μ g/L or greater. The Lower South Bay had the highest concentrations.

Figure 2.6. Dissolved Cadmium (Cd) in Water (2002-2003)



a) Map of dissolved cadmium concentrations in water (μ g/L) in the six Estuary regions monitored. Fifty-six randomly allocated sites (based on the EMAP sample design) and four historic RMP sites (2003 data only) were sampled and only results that passed QA/QC are reported here. Note that only historic sites were sampled in the Rivers region.

Random sites = \circ , Historic sites = \diamond , Non-detects = +

For further explanations of all graphics and the guideline used to evaluate the reported concentrations, please refer to sections 1.3.1 and 2.2.2 respectively.



Region Code: LSB=Lower South Bay, SB=South Bay, CB=Central Bay, SPB=San Pablo Bay, Su=Suisun Bay

b) Schematic Box Plot of dissolved cadmium concentrations in water (μ g/L) for the random sites in five Estuary regions (2002-2003).



c) Cumulative distribution function (CDF) plots for dissolved cadmium

concentrations in water (μ g/L) from the random sites in the five Estuary regions (2002 & 2003). See Section 1.3.1 for an explanation of the CDF plot.

The large graph shows the percentage of the total area sampled in the five Estuary regions (totaling 784 square kilometers) vs. the dissolved cadmium concentrations in water.

The small graphs show the same for each individual region (scales are identical to the large graph).

The large plot indicates that about 50% of the Estuary regions sampled had dissolved cadmium concentrations of 0.08 μ g/L or greater. Suisun Bay had the lowest concentrations.

Figure 2.7. Dissolved Copper (Cu) in Water (2002-2003)



a) Map of dissolved copper concentrations in water (μ g/L) in the six Estuary regions monitored. Fifty-six randomly allocated sites (based on the EMAP sample design) and four historic RMP sites (2003 data only) were sampled and only results that passed QA/QC are reported here. Note that only historic sites were sampled in the Rivers region.

Random sites = \circ , Historic sites = \diamond , Non-detects = + Result above the calculated criterion = dot inside symbol

For further explanations of all graphics and the guideline used to evaluate the reported concentrations, please refer to sections 1.3.1 and 2.2.2 respectively.



Region Code: LSB=Lower South Bay, SB=South Bay, CB=Central Bay, SPB=San Pablo Bay, Su=Suisun Bay

b) Schematic Box Plot of dissolved copper concentrations in water (μ g/L) for the random sites in five Estuary regions (2002-2003).



c) Cumulative distribution function (CDF) plots for dissolved copper concentrations in water (μ g/L) from the random sites in the five Estuary regions

(2002 & 2003). See Section 1.3.1 for an explanation of the CDF plot.

The large graph shows the percentage of the total area sampled in the five Estuary regions (totaling 784 square kilometers) vs. the dissolved copper concentrations in water.

The small graphs show the same for each individual region (scales are identical to the large graph).

The large plot indicates that about 50% of the Estuary regions sampled had dissolved copper concentrations of 1.7 μ g/L or greater. The Lower South Bay had the highest concentrations.





a) Map of dissolved lead concentrations in water (μ g/L) in the six Estuary regions monitored. Fifty-six randomly allocated sites (based on the EMAP sample design) and four historic RMP sites (2003 data only) were sampled and only results that passed QA/QC are reported here. Note that only historic sites were sampled in the Rivers region.

Random sites = \circ , Historic sites = \diamond , Non-detects = +

For further explanations of all graphics and the guideline used to evaluate the reported concentrations, please refer to sections 1.3.1 and 2.2.2 respectively.



Region Code: LSB=Lower South Bay, SB=South Bay, CB=Central Bay, SPB=San Pablo Bay, Su=Suisun Bay

b) Schematic Box Plot of dissolved lead concentrations in water (μ g/L) for the random sites in five Estuary regions (2002-2003).



c) Cumulative distribution function (CDF) plots for dissolved lead

concentrations in water (μ g/L) from the random sites in the five Estuary regions (2002 & 2003). See Section 1.3.1 for an explanation of the CDF plot.

The large graph shows the percentage of the total area sampled in the five Estuary regions (totaling 784 square kilometers) vs. the dissolved lead concentrations in water.

The small graphs show the same for each individual region (scales are identical to the large graph).

The large plot indicates that about 50% of the Estuary regions sampled had dissolved lead concentrations of $0.02 \ \mu g/L$ or greater. However, this plot includes only a few results from the Suisun and San Pablo Bay regions (due to QA/QC issues) and may not be very accurate.

2.25

Figure 2.9. Dissolved Mercury (Hg) in Water (2002-2003)



a) Map of dissolved mercury concentrations in water (μ g/L) in the six Estuary regions monitored. Fifty-six randomly allocated sites (based on the EMAP sample design) and four historic RMP sites (2003 data only) were sampled and only results that passed QA/QC are reported here. Note that only historic sites were sampled in the Rivers region.

Random sites = \circ , Historic sites = \diamond , Non-detects = +

For further explanations of all graphics and the guideline used to evaluate the reported concentrations, please refer to sections 1.3.1 and 2.2.2 respectively.



Region Code: LSB=Lower South Bay, SB=South Bay, CB=Central Bay, SPB=San Pablo Bay, Su=Suisun Bay

b) Schematic Box Plot of dissolved mercury concentrations in water (μ g/L) for the random sites in five Estuary regions (2002-2003).



c) Cumulative distribution function (CDF) plots for dissolved mercury concentrations in water (μg/L) from the random sites in the five Estuary regions

The large graph shows the percentage of the total area sampled in the five Estuary regions (totaling 784 square kilometers) vs. the dissolved mercury concentrations in water.

The small graphs show the same for each individual region (scales are identical to the large graph).

The large plot indicates that about 50% of the Estuary regions sampled had dissolved mercury concentrations of $0.0006 \ \mu g/L$ or greater.



Figure 2.10. Dissolved Nickel (Ni) in Water (2002-2003)



a) Map of dissolved nickel concentrations in

water $(\mu g/L)$ in the six Estuary regions monitored. Fifty-six randomly allocated sites (based on the EMAP sample design) and four historic RMP sites (2003 data only) were sampled and only results that passed QA/QC are reported here. Note that only historic sites were sampled in the Rivers region.

Random sites = \circ , Historic sites = \diamond , Non-detects = +

For further explanations of all graphics and the guideline used to evaluate the reported concentrations, please refer to sections 1.3.1 and 2.2.2 respectively.



All samples were below the CTR 4-day Aquatic Life saltwater criterion of 8.2 ug/L. (The Lower South Bay has a site specific objective of 11.9 ug/L.)

Region Code: LSB=Lower South Bay, SB=South Bay, CB=Central Bay, SPB=San Pablo Bay, Su=Suisun Bay

b) Schematic Box Plot of dissolved nickel concentrations in water (μ g/L) for the random sites in five Estuary regions (2002-2003).



c) Cumulative distribution function (CDF) plots for dissolved nickel

concentrations in water (μ g/L) from the random sites in the five Estuary regions (2002 & 2003).

The large graph shows the percentage of the total area sampled in the five Estuary regions (totaling 784 square kilometers) vs. the dissolved nickel concentrations in water.

The small graphs show the same for each individual region (scales are identical to the large graph).

The large plot indicates that about 50% of the Estuary regions sampled had dissolved nickel concentrations of 1.3 μ g/L or greater. The Lower South Bay had the highest concentrations.

Figure 2.11. Dissolved Selenium (Se) in Water (2002-2003)



a) Map of dissolved selenium concentrations in water (μ g/L) in the six Estuary regions monitored. Fifty-six randomly allocated sites (based on the EMAP sample design) and four historic RMP sites (2003 data only) were sampled and only results that passed QA/QC are reported here. Note that only historic sites were sampled in the Rivers region.

Random sites = \circ , Historic sites = \diamond , Non-detects = +

For further explanations of all graphics and the guideline used to evaluate the reported concentrations, please refer to sections 1.3.1 and 2.2.2 respectively.



b) Schematic Box Plot of dissolved selenium concentrations in water (µg/L) for the random

sites in five Estuary regions (2002-2003).



c) Cumulative distribution function (CDF) plots for dissolved selenium concentrations in water (μ g/L) from the random sites in the five Estuary regions (2002 & 2003).

The large graph shows the percentage of the total area sampled in the five Estuary regions (totaling 784 square kilometers) vs. the dissolved selenium concentrations in water.

The small graphs show the same for each individual region (scales are identical to the large graph).

The large plot indicates that about 50% of the Estuary regions sampled had dissolved selenium concentrations of 0.08 μ g/L or greater. The Lower South Bay had the highest concentrations.





a) Map of dissolved silver concentrations in water (μ g/L) in the six Estuary regions monitored. Fifty-six randomly allocated sites (based on the EMAP sample design) and four historic RMP sites (2003 data only) were sampled

and only results that passed QA/QC are reported here. Note that only historic sites were sampled in the Rivers region.

Random sites = \circ , Historic sites = \diamond , Non-detects = +

For further explanations of all graphics and the guideline used to evaluate the reported concentrations, please refer to sections 1.3.1 and 2.2.2 respectively.



Region Code: LSB=Lower South Bay, SB=South Bay, CB=Central Bay, SPB=San Pablo Bay, Su=Suisun Bay

b) Schematic Box Plot of dissolved silver

concentrations in water (μ g/L) for the random sites in five Estuary regions (2002-2003).



c) Cumulative distribution function (CDF) plots for dissolved silver

concentrations in water (μ g/L) from the random sites in the five Estuary regions (2002 & 2003).

The large graph shows the percentage of the total area sampled in the five Estuary regions (totaling 784 square kilometers) vs. the dissolved silver concentrations in water.

The small graphs show the same for each individual region (scales are identical to the large graph).

The large plot indicates that about 50% of the Estuary regions sampled have dissolved silver concentrations of $0.005 \ \mu g/L$ or greater. Suisun Bay has the lowest concentrations.





a) Map of dissolved zinc concentrations in water (μ g/L) in the six Estuary regions monitored. Fifty-six randomly allocated sites (based on the EMAP sample design) and four historic RMP sites (2003 data only) were sampled and only results that passed QA/QC are reported here. Note that only historic sites were sampled in the Rivers region.

Random sites = \circ , Historic sites = \diamond , Non-detects = +

For further explanations of all graphics and the guideline used to evaluate the reported concentrations, please refer to sections 1.3.1 and 2.2.2 respectively.



Region Code: LSB=Lower South Bay, SB=South Bay, CB=Central Bay, SPB=San Pablo Bay, Su=Suisun Bay

b) Schematic Box Plot of dissolved zinc

concentrations in water (μ g/L) for the random sites in five Estuary regions (2002-2003).



c) Cumulative distribution function (CDF) plots for dissolved zinc

concentrations in water (μ g/L) from the random sites in the five Estuary regions (2002 & 2003).

The large graph shows the percentage of the total area sampled in the five Estuary regions (totaling 784 square kilometers) vs. the dissolved zinc concentrations in water.

The small graphs show the same for each individual region (scales are identical to the large graph).

The large plot indicates that about 50% of the Estuary regions sampled had dissolved zinc concentrations of $0.5 \ \mu g/L$ or greater.



Figure 2.14. Total Arsenic (As) in Water (2002-2003)

a) Map of total arsenic concentrations in water $(\mu g/L)$ in the six Estuary regions monitored. Fifty-six randomly allocated sites (based on the EMAP sample design) and four historic RMP sites (2003 data only) were sampled and only results that passed QA/QC are reported here. Note that only historic sites were sampled in the Rivers region.

Random sites = \circ , Historic sites = \diamond , Non-detects = +

For further explanations of all graphics and the guideline used to evaluate the reported concentrations, please refer to sections 1.3.1 and 2.2.2 respectively.



Default CTR conversion factors were used to calculate the total effects threshold value. All samples were below the non-regulatory effects threshold of 36 ug/L.

Region Code Region Code: LSB=Lower South Bay, SB=South Bay, CB=Central Bay, SPB=San Pablo Bay, Su=Suisun Bay

b) Schematic Box Plot of total arsenic concentrations in water (μ g/L) for the random sites in five Estuary regions (2002-2003).



c) Cumulative distribution function (CDF) plots for total arsenic

concentrations in water (μ g/L) from the random sites in the five Estuary regions (2002 & 2003).

The large graph shows the percentage of the total area sampled in the five Estuary regions (totaling 784 square kilometers) vs. the total arsenic concentrations in water.

The small graphs show the same for each individual region (scales are identical to the large graph).

The large plot indicates that about 50% of the Estuary regions sampled had total arsenic concentrations of 2.8 μ g/L or greater.

Figure 2.15. Total Cadmium (Cd) in Water (2002-2003)



a) Map of total cadmium concentrations in water (μ g/L) in the six Estuary regions monitored. Fifty-six randomly allocated sites (based on the EMAP sample design) and four historic RMP sites (2003 data only) were sampled and only results that passed QA/QC are reported here. Note that only historic sites were sampled in the Rivers region.

Random sites = \circ , Historic sites = \diamond , Non-detects = +

For further explanations of all graphics and the guideline used to evaluate the reported concentrations, please refer to sections 1.3.1 and 2.2.2 respectively.



Default CTR conversion factors were used to calculate the total effects threshold values. All samples were below the non-regulatory saltwater or calculated freshwater effects threshold values of 9.4 or 2.5 ug/L.

Region Code: LSB=Lower South Bay, SB=South Bay, CB=Central Bay, SPB=San Pablo Bay, Su=Suisun Bay

b) Schematic Box Plot of total cadmium

concentrations in water (μ g/L) for the random sites in five Estuary regions (2002-2003).



c) Cumulative distribution function (CDF) plots for total cadmium

concentrations in water (μ g/L) from the random sites in the five Estuary regions (2002 & 2003).

The large graph shows the percentage of the total area sampled in the five Estuary regions (totaling 784 square kilometers) vs. the total cadmium concentrations in water.

The small graphs show the same for each individual region (scales are identical to the large graph).

The large plot indicates that about 50% of the Estuary regions sampled had total cadmium concentrations of $0.10 \mu g/L$ or greater.





a) Map of total copper concentrations in water $(\mu g/L)$ in the six Estuary regions monitored. Fiftysix randomly allocated sites (based on the EMAP sample design) and four historic RMP sites (2003 data only) were sampled and only results that passed QA/QC are reported here. Note that only historic sites were sampled in the Rivers region.

Random sites = \circ , Historic sites = \diamond , Non-detects = + Result above the calculated criterion = dot inside symbol

For further explanations of all graphics and the guideline used to evaluate the reported concentrations, please refer to sections 1.3.1 and 2.2.2 respectively.



Default CTR conversion factors were used to calculate the total effects threshold value. 15 samples were above the calculated nonregulatory saltwater effects threshold of 3.7 ug/L. (Lower South Bay has a site specific value of 13.02 ug/L.)

Region Code: LSB=Lower South Bay, SB=South Bay, CB=Central Bay, SPB=San Pablo Bay, Su=Suisun Bay

b) Schematic Box Plot of total copper concentrations in water (μ g/L) for the random sites in five Estuary regions (2002-2003).



c) Cumulative distribution function (CDF) plots for total copper

concentrations in water (μ g/L) from the random sites in the five Estuary regions (2002 & 2003).

The large graph shows the percentage of the total area sampled in the five Estuary regions (totaling 784 square kilometers) vs. the total copper concentrations in water.

The small graphs show the same for each individual region (scales are identical to the large graph).

The large plot indicates that about 50% of the Estuary regions sampled had total copper concentrations of 3.0 μ g/L or greater.





a) Map of total lead concentrations in water $(\mu g/L)$ in the six Estuary regions monitored. Fifty-six randomly allocated sites (based on the EMAP sample design) and four historic RMP sites (2003 data only) were sampled and only results that passed QA/QC are reported here. Note that only historic sites were sampled in the Rivers region.

Random sites = \circ , Historic sites = \diamond , Non-detects = + Result above the calculated criterion = dot inside symbol

For further explanations of all graphics and the guideline used to evaluate the reported concentrations, please refer to sections 1.3.1 and 2.2.2 respectively.



Default CTR conversion factors were used to calculate the total effects threshold value. 3 samples were above the calculated nonregulatory freshwater effects thresholds of 3.2 ug/L (applies to estuarine regions of the Estuary).

Region Code: LSB=Lower South Bay, SB=South Bay, CB=Central Bay, SPB=San Pablo Bay, Su=Suisun Bay

b) Schematic Box Plot of total lead

concentrations in water (μ g/L) for the random sites in five Estuary regions (2002-2003).



c) Cumulative distribution function (CDF) plots for total lead

concentrations in water (μ g/L) from the random sites in the five Estuary regions (2002 & 2003).

The large graph shows the percentage of the total area sampled in the five Estuary regions (totaling 784 square kilometers) vs. the total lead concentrations in water.

The small graphs show the same for each individual region (scales are identical to the large graph).

The large plot indicates that about 50% of the Estuary regions sampled had total lead concentrations of $0.5 \ \mu g/L$ or greater.



Figure 2.18. Total Mercury (Hg) in Water (2002-2003)

a) Map of total mercury concentrations in water (μ g/L) in the six Estuary regions monitored. Fifty-six randomly allocated sites (based on the EMAP sample design) and four historic RMP sites (2003 data only) were sampled and only results that passed QA/QC are reported here. Note that only historic sites were sampled in the Rivers region.

Random sites = \circ , Historic sites = \diamond , Non-detects = + Result above the calculated criterion = dot inside symbol

For further explanations of all graphics and the guideline used to evaluate the reported concentrations, please refer to sections 1.3.1 and 2.2.2 respectively.



Region Code: LSB=Lower South Bay, SB=South Bay, CB=Central Bay, SPB=San Pablo Bay, Su=Suisun Bay

b) Schematic Box Plot of total mercury

concentrations in water (μ g/L) for the random sites in five Estuary regions (2002-2003).



c) Cumulative distribution function (CDF) plots for total mercury

concentrations in water ($\mu g/L$) from the random sites in the five Estuary regions (2002 & 2003).

The large graph shows the percentage of the total area sampled in the five Estuary regions (totaling 784 square kilometers) vs. the total mercury concentrations in water.

The small graphs show the same for each individual region (scales are identical to the large graph).

The large plot indicates that about 50% of the Estuary regions sampled had total mercury concentrations of 0.007µg/L or greater.



Figure 2.19. Total Nickel (Ni) in Water (2002-2003)

a) Map of total nickel concentrations in water $(\mu g/L)$ in the six Estuary regions monitored. Fifty-six randomly allocated sites (based on the EMAP sample design) and four historic RMP sites (2003 data only) were sampled and only results that passed QA/QC are reported here. Note that only historic sites were sampled in the Rivers region.

Random sites = \circ , Historic sites = \diamond , Non-detects = + Result above the calculated criterion = dot inside symbol

For further explanations of all graphics and the guideline used to evaluate the reported concentrations, please refer to sections 1.3.1 and 2.2.2 respectively.



Default CTR conversion factors were used to calculate the total effects threshold value. 4 samples were above the non-regulatory effects threshold of 7.1 ug/L. (The Lower South Bay has a site specific objective of 27.05 ug/L.)

Region Code: LSB=Lower South Bay, SB=South Bay, CB=Central Bay, SPB=San Pablo Bay, Su=Suisun Bay

b) Schematic Box Plot of total nickel

concentrations in water (μ g/L) for the random sites in five Estuary regions (2002-2003).



c) Cumulative distribution function (CDF) plots for total nickel concentrations in water (μg/L) from the

concentrations in water (μ g/L) from the random sites in the five Estuary regions (2002 & 2003).

The large graph shows the percentage of the total area sampled in the five Estuary regions (totaling 784 square kilometers) vs. the total nickel concentrations in water.

The small graphs show the same for each individual region (scales are identical to the large graph).

The large plot indicates that about 50% of the Estuary regions sampled had total nickel concentrations of 3 μ g/L or greater.



Figure 2.20. Total Selenium (Se) in Water (2002-2003)

a) Map of total selenium concentrations in water (μ g/L) in the six Estuary regions monitored. Fifty-six randomly allocated sites (based on the EMAP sample design) and four historic RMP sites (2003 data only) were sampled and only results that passed QA/QC are reported here. Note that only historic sites were sampled in the Rivers region.

Random sites = \circ , Historic sites = \diamond , Non-detects = +

For further explanations of all graphics and the guideline used to evaluate the reported concentrations, please refer to sections 1.3.1 and 2.2.2 respectively.



Region Code: LSB=Lower South Bay, SB=South Bay, CB=Central Bay, SPB=San Pablo Bay, Su=Suisun Bay

b) Schematic Box Plot of total selenium concentrations in water (μ g/L) for the random

sites in five Estuary regions (2002-2003).



c) Cumulative distribution function (CDF) plots for total selenium

concentrations in water (μ g/L) from the random sites in the five Estuary regions (2002 & 2003).

The large graph shows the percentage of the total area sampled in the five Estuary regions (totaling 784 square kilometers) vs. the total selenium concentrations in water.

The small graphs show the same for each individual region (scales are identical to the large graph).

The large plot indicates that about 50% of the Estuary regions sampled had total selenium concentrations of $0.01 \mu g/L$ or greater.





a) Map of total silver concentrations in water $(\mu g/L)$ in the six Estuary regions monitored. Fifty-six randomly allocated sites (based on the EMAP sample design) and four historic RMP sites (2003 data only) were sampled and only results that passed QA/QC are reported here. Note that only historic sites were sampled in the Rivers region.

Random sites = \circ , Historic sites = \diamond , Non-detects = +

For further explanations of all graphics and the guideline used to evaluate the reported concentrations, please refer to sections 1.3.1 and 2.2.2 respectively.



Region Code: LSB=Lower South Bay, SB=South Bay, CB=Central Bay, SPB=San Pablo Bay, Su=Suisun Bay

b) Schematic Box Plot of total silver

concentrations in water (μ g/L) for the random sites in five Estuary regions (2002-2003).



c) Cumulative distribution function (CDF) plots for total silver

concentrations in water (μ g/L) from the random sites in the five Estuary regions (2002 & 2003).

The large graph shows the percentage of the total area sampled in the five Estuary regions (totaling 784 square kilometers) vs. the total silver concentrations in water.

The small graphs show the same for each individual region (scales are identical to the large graph).

The large plot indicates that about 50% of the Estuary regions sampled had total silver concentrations of $0.02 \mu g/L$ or greater.



Figure 2.22. Total zinc (Zn) in Water (2002-2003)

a) Map of total zinc concentrations in water $(\mu g/L)$ in the six Estuary regions monitored. Fifty-six randomly allocated sites (based on the EMAP sample design) and four historic RMP sites (2003 data only) were sampled and only results that passed QA/QC are reported here. Note that only historic sites were sampled in the Rivers region.

Random sites = \circ , Historic sites = \diamond , Non-detects = +

For further explanations of all graphics and the guideline used to evaluate the reported concentrations, please refer to sections 1.3.1 and 2.2.2 respectively.



Default CTR conversion factors were used to calculate the total effects threshold value. All samples were below the non-regulatory saltwater effects threshold of 58 ug/L.

Region Code Region Code: LSB=Lower South Bay, SB=South Bay, CB=Central Bay, SPB=San Pablo Bay, Su=Suisun Bay

b) Schematic Box Plot of total zinc

concentrations in water (μ g/L) for the random sites in five Estuary regions (2002-2003).



c) Cumulative distribution function (CDF) plots for total zinc

concentrations in water (μ g/L) from the random sites in the five Estuary regions (2002 & 2003).

The large graph shows the percentage of the total area sampled in the five Estuary regions (totaling 784 square kilometers) vs. the total zinc concentrations in water.

The small graphs show the same for each individual region (scales are identical to the large graph).

The large plot indicates that about 50% of the Estuary regions sampled had total zinc concentrations of $3\mu g/L$ or greater.





a) Map of dissolved sum of PAH

concentrations in water (pg/L) in the six Estuary regions monitored. Fifty-six randomly allocated sites (based on the EMAP sample design) and four historic RMP sites (2003 data only) were sampled and only results that passed QA/QC are reported here. Note that only historic sites were sampled in the Rivers region.

Random sites = \circ , Historic sites = \diamond , Non-detects = +

For further explanations of all graphics and the guideline used to evaluate the reported concentrations, please refer to sections 1.3.1 and 2.2.2 respectively.



Region Code: LSB=Lower South Bay, SB=South Bay, CB=Central Bay, SPB=San Pablo Bay, Su=Suisun Bay

b) Schematic Box Plot of dissolved sum of **PAH** concentrations in water (pg/L) for the random sites in five Estuary regions (2002-2003).



c) Cumulative distribution function (CDF) plots for dissolved sum of PAH concentrations in water (pg/L) from the random sites in the five Estuary regions (2002 & 2003).

The large graph shows the percentage of the total area sampled in the five Estuary regions (totaling 784 square kilometers) vs. the dissolved sum of PAH concentrations in water.

The small graphs show the same for each individual region (scales are identical to the large graph).

The large plot indicates that about 50% of the Estuary regions sampled had dissolved total PAH concentrations of 10300 pg/L or greater.
Figure 2.24. Dissolved Sum of PCBs in Water (2002-2003)



a) Map of dissolved sum of PBC

concentrations in water (pg/L) in the six Estuary regions monitored. Fifty-six randomly allocated sites (based on the EMAP sample design) and four historic RMP sites (2003 data only) were sampled and only results that passed QA/QC are reported here. Note that only historic sites were sampled in the Rivers region.

Random sites = \circ , Historic sites = \diamond , Non-detects = +

For further explanations of all graphics and the guideline used to evaluate the reported concentrations, please refer to sections 1.3.1 and 2.2.2 respectively.



Organic contaminants are compared to the CTR water quality criteria on a total basis only.



b) Schematic Box Plot of dissolved sum of PCB concentrations in water (pg/L) for the random sites in five Estuary regions (2002-2003).



c) Cumulative distribution function (CDF) plots for dissolved sum of PCB concentrations in water (pg/L) from the random sites in the five Estuary regions (2002 & 2003).

The large graph shows the percentage of the total area sampled in the five Estuary regions (totaling 784 square kilometers) vs. the dissolved sum of PCB concentrations in water.

The small graphs show the same for each individual region (scales are identical to the large graph).

The large plot indicates that about 50% of the Estuary regions sampled had dissolved silver concentrations of 160 pg/L or greater.





a) Map of total sum of PAH concentrations in water (pg/L) in the six Estuary regions monitored. Fifty-six randomly allocated sites (based on the EMAP sample design) and four historic RMP sites (2003 data only) were sampled and only results that passed QA/QC are reported here. Note that only historic sites were sampled in the Rivers region.

Random sites = \circ , Historic sites = \diamond , Non-detects = +

For further explanations of all graphics and the guideline used to evaluate the reported concentrations, please refer to sections 1.3.1 and 2.2.2 respectively.



The CTR lists Human Health criteria for ten individual PAHs. None of the samples were above the individual PAH criteria and none of the samples were above the Basin Plan objective for sum of PAHs of 15,000,000 pg/L.

Region Code: LSB=Lower South Bay, SB=South Bay, CB=Central Bay, SPB=San Pablo Bay, Su=Suisun Bay

b) Schematic Box Plot of total sum of PAH concentrations in water (pg/L) for the random sites in five Estuary regions (2002-2003).



c) Cumulative distribution function (CDF) plots for total sum of PAH

concentrations in water (pg/L) from the random sites in the five Estuary regions (2002 & 2003).

The large graph shows the percentage of the total area sampled in the five Estuary regions (totaling 784 square kilometers) vs. the total sum of PAH concentrations in water.

The small graphs show the same for each individual region (scales are identical to the large graph).

The large plot indicates that about 50% of the Estuary regions sampled had total sum of PAH concentrations of 50,000 pg/L or greater.



Figure 2.26. Total Sum of PCBs in Water (2002-2003)

a) Map of total sum of PCB concentrations in water (pg/L) in the six Estuary regions monitored. Fifty-six randomly allocated sites (based on the EMAP sample design) and four historic RMP sites (2003 data only) were sampled and only results that passed QA/QC are reported here. Note that only historic sites were sampled in the Rivers region.

Random sites = \circ , Historic sites = \diamond , Non-detects = +

For further explanations of all graphics and the guideline used to evaluate the reported concentrations, please refer to sections 1.3.1 and 2.2.2 respectively.



Region Code: LSB=Lower South Bay, SB=South Bay, CB=Central Bay, SPB=San Pablo Bay, Su=Suisun Bay

b) Schematic Box Plot of total sum of PCB concentrations in water (pg/L) for the random sites in five Estuary regions (2002-2003).





Dissolved Organic Carbon (DOC) concentrations (µg/L) in water at five historic RMP sites sampled 1993 – 2003.

Figure 2.27. Time Series Plots for





Series Plots for Total Suspended Solid (TSS) concentrations (mg/L) in water at five historic RMP sites sampled 1993 – 2003.

Figure 2.28. Time



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Figure 2.29. Time Series Plots for Dissolved Arsenic (As) concentrations (μg/L) in water at five historic RMP sites sampled 1993 – 2003.

> All samples were below the CTR 4-day Aquatic Life saltwater criterion of 36 ug/L

Historical	<u>Sites:</u>
BG20 Sacra	amento River
BG30 San .	Joaquin River
BC10 Yerb	a Buena Island
BC20 Gold	en Gate
BA30 Dum	barton Bridge



Figure 2.30. Time Series Plots for Dissolved Cadmium (Cd) concentrations (μ g/L) in water at five historic RMP sites sampled 1993 – 2003.

All samples were below the CTR 4-day Aquatic Life saltwater or calculated freshwater criterion of 9.3 or 2.2 ug/L.

Historical Sites: BG20 Sacramento River BG30 San Joaquin River

BG30 San Joaquin River BC10 Yerba Buena Island BC20 Golden Gate BA30 Dumbarton Bridge



Figure 2.31. Time Series Plots for Dissolved Copper (Cu) concentrations

(μ g/L) in water at five historic RMP sites sampled 1993 – 2003. The dashed blue reference line is the CTR 4-day Aquatic Life saltwater quality criterion of 3.1 µg/L.

Four samples, from BA30 in the South Bay region, were above the CTR criterion of 3.1 ug/L. The Lower South Bay has a site specific objective of 6.9 ug/L.

Historical Sites: BG20 Sacramento River BG30 San Joaquin River BC10 Yerba Buena Island BC20 Golden Gate

BA30 Dumbarton Bridge





Figure 2.32. Time Series Plots for Dissolved Lead (Pb) concentrations (µg/L) in water at five historic RMP sites sampled 1993 – 2003.

All samples were below the CTR 4-day Aquatic Life saltwater or calculated freshwater criterion of 8.1 or 2.5 ug/L.



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Mercury is compared to the CTR water quality criterion on a total basis only.



4.0

BG20

Figure 2.34. Time **Series Plots for Dissolved Nickel** (Ni) concentrations (μ g/L) in water at five historic RMP sites sampled 1993 – 2003.

All samples were below the CTR 4-day Aquatic Life saltwater criterion of 8.2 ug/L. (The Lower South Bay has a site specific objective of 11.9 ug/L.)

Historical Sites: BG20 Sacramento River BG30 San Joaquin River BC10 Yerba Buena Island BC20 Golden Gate BA30 Dumbarton Bridge

Sampling Period



Figure 2.35. Time Series Plots for Dissolved Selenium (Se) concentrations

 $(\mu g/L)$ in water at five historic RMP sites sampled 1993 – 2003.

Selenium is compared to the CTR water quality criterion on a total basis only.

Hi	st	10	rical	Sites:



Figure 2.36. Time Series Plots for Dissolved Silver (Ag) concentrations (μ g/L) in water at five historic RMP sites sampled 1993 – 2003.

All samples were below the CTR 1-hour Aquatic Life saltwater criterion of 1.9 ug/L.

Historical Sites:

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Figure 2.37. Time Series Plots for Dissolved Zinc (Zn) concentrations (µg/L) in water at five historic RMP sites sampled 1993 – 2003.

All samples were below the CTR 4-day Aquatic Life saltwater criterion of 81 ug/L

Historical Sites:



Figure 2.38. Time Series Plots for Total Arsenic (As) concentrations (µg/L) in water at five historic RMP sites sampled 1993 – 2003.

Default CTR conversion factors were used to calculate the total effects threshold value. All samples were below the non-regulatory effects threshold of 36 ug/L.

Historical Sites:





Figure 2.39. Time Series Plots for Total Cadmium (Cd) concentrations (µg/L) in water at five historic RMP sites sampled 1993 – 2003.

Default CTR conversion factors were used to calculate the total effects threshold values. All samples were below the non-regulatory saltwater or calculated freshwater effects threshold values of 9.4 or 2.5 ug/L. (2.5 applies to estuarine regions of the Estuary, see section 2.2.2).

Historical Sites:



Figure 2.40. Time Series Plots for Total Copper (Cu) concentrations (μ g/L) in water at five historic RMP sites sampled 1993 – 2003. The dashed blue reference line is the calculated, non-regulatory saltwater effects threshold of 3.7 μ g/L from the CTR.

Samples from the northern estuary Rivers (BG20 and BG30) and the South Bay (BA30) were above the CTR threshold on occasion. (The Lower South Bay has a site specific value of 13.02 ug/L.)

Historical Sites:

RMP Annual Monitoring Results 2003



Figure 2.41. Time Series Plots for Total Lead (Pb) concentrations (µg/L) in water at five historic RMP sites sampled 1993 – 2003.

Default CTR conversion factors were used to calculate the total effects threshold value. All samples were below the calculated nonregulatory saltwater or freshwater effects thresholds of 5.6 or 3.2 ug/L (3.2 applies to estuarine regions of the Estuary, see section 2.2.2).



Figure 2.42. Time Series Plots for Total Mercury (Hg) concentrations (μ g/L) in water at five historic RMP sites sampled 1993 – 2003. The dashed blue reference line is the water quality guideline of 0.025 μ g/L.

One sample at BG20 and four samples at BA30 were above the regulatory total mercury objective of 0.025 ug/L on occasion. (The Lower South Bay has a site specific objective of 0.051ug/L.)

Historical Sites:



Figure 2.43. Time Series Plots for Total Nickel (Ni) concentrations (μ g/L) in water at five historic RMP sites sampled 1993 – 2003. The dashed blue reference line is the water quality guideline of 7.1 μ g/L.

Default CTR conversion factors were used to calculate the total effects threshold value. Two samples at BG20 and four samples at BA30 were above the non-regulatory effects threshold of 7.1 ug/L on occasion. (The Lower South Bay has a site specific objective of 27.05 ug/L.)

Historical Sites:



RMP Annual Monitoring Results 2003

Figure 2.44. Time Series Plots for Total Selenium (Se) concentrations (µg/L) in water at five historic RMP sites sampled 1993 – 2003.

All samples were below the regulatory CTR region specific Aquatic Life criterion of 5 ug/L.

Historical Sites:

RMP Annual Monitoring Results 2003



Sampling Period

Figure 2.45. Time Series Plots for Total Silver (Ag) concentrations (µg/L) in water at five historic RMP sites sampled 1993 – 2003.

Default CTR conversion factors were used to calculate the total effects threshold value. All samples were below the non-regulatory 1hour saltwater effects threshold of 2.3 ug/L.



2.0

RMP Annual Monitoring Results 2003

Figure 2.46. Time Series Plots for Total Zinc (Zn) concentrations (μ g/L) in water at five historic RMP sites sampled 1993 – 2003.

Default CTR conversion factors were used to calculate the total effects threshold value. All samples were below the non-regulatory saltwater effects threshold of 58 ug/L.



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Figure 2.47. Time Series Plots for Dissolved PAH concentrations (pg/L)

in water at five historic RMP sites sampled 1993 – 2003.

Organic contaminants are compared to the CTR water quality criteria on a total basis only.

Historical Sites:



Figure 2.48. Time Series Plots for Dissolved PCB concentrations (pg/L) in water at five historic RMP sites sampled 1993 – 2003.

Organic contaminants are compared to the CTR water quality criteria on a total basis only.



Figure 2.49. Time Series Plots for Total PAH concentrations (pg/L) in water at five historic RMP sites sampled 1993 – 2003.

All samples were below the Basin Plan objective for sum of PAHs of 15,000,000 pg/L.

Historical Sites: BG20 Sacramento River BG30 San Joaquin River BC10 Yerba Buena Island BC20 Golden Gate BA30 Dumbarton Bridge

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Figure 2.50. Time Series Plots for Total PCB concentrations (pg/L) in water at five historic RMP sites sampled 1993 – 2003. The dashed blue line is the water quality guideline of 170 pg/L.

All stations had water samples that were above the CTR Human Health criterion of 170 pg/L on occasion.

Historical Sites: BG20 Sacramento River BG30 San Joaquin River BC10 Yerba Buena Island BC20 Golden Gate BA30 Dumbarton Bridge

c<mark>al Sites:</mark> acramento River

RMP Annual Monitoring Results 2003



CHAPTER 5

Sediment Monitoring Results

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3.0 SEDIMENT MONITORING

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3.1 Background

Since 1993, the San Francisco Estuary Regional Monitoring Program for Trace Substances (RMP) has routinely monitored contaminants in surface sediments (top 5 cm) collected at stations throughout the San Francisco Estuary. Sediments are monitored because they are a fundamental component of the Bay ecosystem, and they play a key role in the fate and transport of contaminants. Sediments serve as contaminant sources and sinks, and most contaminants are usually found in concentrations orders of magnitude higher in the upper few centimeters of sediments than in the water column. Sediment contamination information is used in making decisions related to many important management concerns: the identification of sediment "toxic hot spots" and reference areas; the clean-up of numerous sites in the region that require information about background contaminant levels; and the continued dredging throughout the Estuary that requires testing and comparisons to a reference, or background concentration. Information about sediments addresses several of the RMP Objectives (see Chapter 1.0 Introduction). Patterns in sediment contamination are described (Objective 1) and compared to several sets of sediment quality guidelines (Objective 4), while sediment bioassays address contaminant effects (Objective 3).

3.2 Approach

In 2003, RMP Status and Trends Program continued with implementation of the stratified, random sampling design started in 2002 (see Chapter 1, Introduction). Sediment contaminant monitoring in 2003 was conducted in the dry season (August) at 47 stations, including seven fixed historical stations (Sacramento River (BG20), San Joaquin River (BG30), Grizzly Bay (BF21), Pinole Point (BD31), Yerba Buena Island (BC11), Redwood Creek (BA41), and Coyote Creek (BA10)). At least one historical station was maintained per region to allow for analysis of long-term temporal trends. Monitoring of two stations at the southern end of the Estuary, San Jose (station C-3-0) and Sunnyvale (station C-1-3), was discontinued in 2003. Sediments collected from a subset of 27 random stations were used for conducting sediment bioassays. Station names, codes, location, and sampling dates are listed in Table 1.2 in the *Introduction* and shown in Figure 3.1.

3.2.1 Methods

The complete list of all parameters measured in the 2003 sediment samples is included in Table 1.4 in the *Introduction*. A detailed description of sample collection and laboratory analytical methods is documented in Section 5 *Description of Methods*. Contaminant concentration data can be downloaded from the RMP website using the Status and Trends Monitoring Data Access Tool (http://www.sfei.org/rmp/data.htm).

3.2.2 Sediment Quality Guidelines

Currently, no Basin Plan numerical objectives or other regulatory criteria for sediment contaminant concentrations exist for the San Francisco Estuary. However, sediment quality guidelines are currently being developed for the State of California by staff at the Southern California Coastal Water Research Project (SCCWRP) and the San Francisco

Estuary Institute. Several sets of sediment quality guidelines (Table 3.1) are generally used as informal screening tools for sediment contaminant concentrations, even though they have no regulatory status.

Sediment quality guidelines developed by Long *et al.* (1995) are based on data compiled from numerous studies in the U.S. that included sediment contaminant and biological effects information. The guidelines were developed to identify concentrations of contaminants that were associated with biological effects in laboratory, field, or modeling studies. The effects range-low (ERL) value is the concentration equivalent to the lower 10th percentile of the compiled study data, and the effects range-median (ERM) is the concentration equivalent to the 50th percentile of the compiled study data. Sediment concentrations below the ERL are interpreted as being "rarely" associated with adverse effects. Concentrations between the ERL and ERM are "occasionally" associated with adverse effects. Effects-range values for mercury, nickel, total PCBs, and total DDTs have low levels of confidence associated with them. The effects-range values used for chlordanes and dieldrin are from Long and Morgan (1990). Presently, no effects-range guidelines exist for selenium, but the Regional Board has suggested guidelines of 1.4 mg/kg (Wolfenden and Carlin, 1992), and 1.5 mg/kg (Taylor *et al.*, 1992).

A set of quality guidelines developed by the San Francisco Bay Regional Water Quality Control Board is also used for sediment (Gandesbery, 1998; Gandesbery *et al.*, 1999). Ambient Sediment Concentration (ASC) values are derived from samples collected from the cleanest areas of the Estuary by the RMP (1991-1996) and by the Bay Protection and Toxic Cleanup Program (BPTCP) for their 1995 Reference Site study, and are used to distinguish "ambient" from "contaminated" conditions. Given the fact that virtually no San Francisco Estuary mixed surface layer sediments are free of anthropogenic contaminants this approach was thought to define contemporary ambient contaminant levels. Different ASC values are used for sandy (>60% sand) and muddy (>40% fines) sediments. The ERL guideline values of Long *et al.* (1995) are presented for comparative purposes on the sediment contaminant concentration charts (Figures 3.4–3.14).

The Regional Board is presently developing Total Maximum Daily Loads (TMDLs) which may result in proposed sediment targets for certain contaminants on the State's "Impaired Waters" Section 303(d) list. A sediment target for mercury of 0.2 mg/kg has already been developed and proposed (Johnson and Looker, 2003), and a recent TMDL report proposes 2.5 μ g/kg as a sediment target for PCBs (CRWQCB, 2004). Potentially, these target limits could be used as a new set of sediment quality guidelines, specific to the different regions of the Estuary.

3.2.3 Sediment Toxicity

Sediment bioassays are routinely conducted to determine the potential for adverse biological effects from the exposure to sediment contamination. Two types of sediment bioassays were conducted at 27 of the RMP stations in 2003 (Figure 3.15). Sampling dates are listed in Table 1.2 in Section 1.0 *Introduction*. Amphipods (*Eohaustorius estuarius*) were exposed to whole sediment for ten days with percent survival as the endpoint. Larval mussels (*Mytilus galloprovincialis*) were exposed to sediment elutriates (water-soluble fraction) for 48 hours with percent normal development as the endpoint. The negative control for the *Eohaustorius* (amphipod) solid-phase test consisted of home

sediment, which was clean, well-sorted fine-grained sand collected at the same place and time as the test amphipods. The *Mytilus* (mussel) sediment elutriate test negative control was clean seawater from Granite Canyon, California. Methods of collection and testing are described in Section 5.0 *Description of Methods*, and the relevant quality assurance information is available online (http://www.sfei.org/rmp/data.htm).

When a sample is found to be toxic, it is interpreted as an indication of the potential for biological effects to estuarine organisms. However, since sediments contain numerous contaminants, it is difficult to determine which contaminant(s) may have caused the observed toxicity (see 3.3.3 Sediment Toxicity).

A sample was considered toxic if:

- 1. There was a significant difference between the laboratory control and test replicates using a separate variance t-test (alpha = 0.01), and
- 2. The difference between the mean endpoint value (% survival for amphipods or % normal development for bivalves) in the control and the mean endpoint value in the test sample was greater than the 90th percentile minimum significant difference (MSD).

A sample must meet both criteria to be considered toxic, the reason for this is that in many cases a small among-replicate variance will result in a significant t-test, even though the magnitude of the difference may be small. One way to ensure that statistical significance is determined based on large differences between means, rather than on small variation among replicates, is to use the MSD. MSD is a statistic that indicates the difference between the two means (the mean of the sample and control replicates) that will be considered statistically significant given the observed level of among-replicate variation and the alpha level chosen for the comparison. The detectable difference inherent to a bioassay protocol can be determined by identifying the magnitude of difference detected by the protocol 90% of the time (Schimmel et al., 1991; Thursby and Schlekat, 1993; Phillips *et al.*, 2001). An additional set of t-tests (alpha = 0.05) is conducted and MSD values are calculated for each comparison. The MSDs are ranked in ascending order, and the 90th percentile value is identified. This value is greater than or equal to 90% of the MSD values generated. The 90th percentile MSD value is the difference that 90% of the t-tests will be able to detect as statistically significant and is equivalent to setting the level of statistical power at 0.90. The 90th percentile MSD threshold was established from 119 bioassay results for San Francisco Estuary (Bryn Phillips, Department of Environmental Toxicology, University of California, Davis unpublished data; Hunt et al., 1996). A recalculation in 2003 for the years 1993-2001 confirmed the 90th percentile MSD for *Eohaustorius* was 18.8%, but determined that it should be revised to 15.2% for the bivalve larvae test. For the August 2003 sediment bioassays, an amphipod bioassay was toxic if it had below 69.5% survival while the larval bivalve bioassay was toxic if it had less than 50.7% normal development, and there was a significant difference between the mean of the control and sample replicates using a separate variance t-test (alpha = 0.01).

3.3 Results and Discussion

The geochemistry of sediments is complex, and in order to interpret contaminant concentrations measured in sediments, it is necessary to understand how hydrology and

physical sediment characteristics may affect contaminant concentrations. Conductivity, temperature, and depth (CTD) profiles of the water column were collected at all RMP sediment stations. Although not presented in this report, these data are available upon request from the San Francisco Estuary Institute. Several sediment quality parameters that may affect sediment contaminant concentrations (for example grain-size and total organic carbon (TOC) were also monitored. Percent fines and TOC are presented in Figure 3.2 and Figure 3.3, respectively. The list of parameters measured in the sediment samples is included in Table 1.4 in the *Introduction*. Polychlorinated biphenyls (PCBs), polybrominated diphenyl ethers (PBDEs), and pesticide concentrations were unavailable at time of reporting. Analysis of chromium was discontinued in 2000. Sediment quality parameters, station depths, and all available contaminant concentrations are accessible through the RMP Web Query Tool (http://www.sfei.org/rmp/data.htm).

3.3.1 Spatial Distributions

Sediment contaminant concentrations measured in the San Francisco Estuary exhibit considerable spatial and temporal variation. High contaminant concentrations can reflect proximity to a source, anthropogenic or otherwise, as illustrated by the RMP's Estuary Interface Pilot Study results from Coyote Creek and Guadalupe River in the South Bay (SFEI, 1999; Leatherbarrow *et al.*, 2002). However, complex sediment transport dynamics within the Estuary confound this simplistic model. For example, sediments with more silt- and clay-sized particles contain higher concentrations of most contaminants than coarser, sandier sediments because of their physical properties (Luoma, 1990; Horowitz, 1991). The strength and magnitude of freshwater inflows to the estuary, which transport sediments and contaminants in both the dissolved and particulate fractions of the flows, may radically alter sediment type and contaminant distribution (Krone, 1979). As a consequence, RMP sediment monitoring provides information only about the condition of surface sediments (upper 5 cm) at the time and location of sampling.

In 2003, the highest sediment contaminant concentrations (3 in each region) were measured at stations in San Pablo Bay, Central Bay, and the Lower South Bay (Figures 3.4–3.14). Only one station in the Lower South Bay (LSB014S) had the highest measured concentration for more than one contaminant: silver and zinc. The highest concentration of arsenic (SPB012S), mercury, (SPB011S), and nickel (SPB013S) were measured in San Pablo Bay, whereas the highest concentrations of cadmium (CB010S), methylmercury (CB002S), and PAHs (CB012S) were documented at sampling locations in the Central Bay. Stations in the Suisun (SU011S), South (SB013S), and Lower South Bay (LSB011S) regions had the highest measured concentrations of copper, selenium, and lead, respectively. A majority of the lowest sediment concentrations (8 out of 11 parameters) were measured at stations in the Suisun Bay. The exceptions were copper, nickel, and zinc, which were lowest at one station (SB001S) in the South Bay. Individual stations with coarse sediments (>60% sand: SU002S, SU010S, and SB001S) had the lowest concentrations for all eleven contaminants and are identified in Figure 3.2.

In order to compare sediment contaminant concentrations the RMP sampling stations were grouped into five regions. These regions, each containing eight random stations, are: Lower South Bay (LSB*nnn*S), South Bay (SB*nnn*S), Central Bay (CB*nnn*S), San Pablo Bay (SPB*nnn*S), and Suisun Bay (SU*nnn*S). Non-detects (NDs) were replaced

with a value of one-half the method detection limit (MDL) for trace metals, and for the organic totals NDs were estimated as one-half the average MDL of the summed parameters. The 2002-2003 contaminant concentrations were log (X + 1) transformed, except for arsenic and copper, to correct for the lack of normality and to equalize variances. Estimates of the contaminant mean, variance, standard deviation, and standard errors were then calculated using the R system, and version 2.6 of the psurvey.analysis statistical library. The R statistical analysis program is an implementation of the S language developed at AT&T Bell Laboratories by Rick Becker, John Chambers, and Allan Wilks. R is free software downloadable through the Comprehensive R Archive Network (CRAN) web site at http://cran.r-project.org/. The psurvey.analysis library for the analysis of probability surveys may be obtained from the Monitoring Design and Analysis section of the U.S. Environmental Protection Agency Aquatic Resources Monitoring web site (http://www.epa.gov/nheerl/arm/analysispages/software.htm).

Differences in means among regions and between years were examined using a Z-test with a Z score greater than 1.96, or less than -1.96 indicating a statistically significant difference at the 5% significance level. The contaminant concentrations of lead and zinc were significantly higher (-1.96 < Z > 1.96) in the Lower South Bay compared to the Suisun, San Pablo, Central, and South Bays (Table 3.3). Additionally, Lower South Bay sediments were also significantly higher in silver compared to the Suisun, San Pablo, and Central Bays, and significantly higher in selenium than the Suisun Bay and Central Bay. In contrast, sediments from the Lower South Bay were observed to be significantly lower in cadmium than samples from Suisun Bay, San Pablo Bay, and Central Bay. Sediments from San Pablo Bay were documented as significantly higher in copper and arsenic than samples from the other four regions of the estuary. Mercury sediment concentrations were significantly higher in the San Pablo Bay compared to the Suisun, Central, and South Bays. Significantly lower nickel concentrations were observed in samples from the South and Central Bays than in the San Pablo Bay sediments. Central Bay sediments were significantly higher in PAHs than all other regions, and higher in methylmercury concentrations than the Suisun and San Pablo Bays. Interannual comparisons indicate that the 2002 sediments were significantly higher in measured contaminant concentrations of arsenic, mercury, and silver than the 2003 samples.

Cumulative distribution function's (CDFs) were calculated with the R system and the psurvey.analysis statistical library using untransformed contaminant concentrations, normality not being an issue. Differences between two CDFs were examined using a modified version of the Roa-Scott first order corrected (mean eigenvalue corrected) statistic for categorical data (Kincaid, 2004). Overall, significant differences (p<0.05) were observed in 54% of the comparisons: 55% of the regional and 33% of the interannual (Table 3.3). The greatest number of differences was documented for PAHs (10 out of 11), and the fewest for cadmium (2 out of 11). Significant interannual differences in the CDFs were observed for arsenic, mercury, selenium, and PAH.

The highest numbers of ERL exceedances were observed in the Central Bay (CB012S, CB013S, and CB014S) (see Table 3.2). ERL guideline exceedances and sediment contaminant concentrations tended to be lowest at the coarse sediment stations (>60% sand): Sacramento River (BG20), Suisun Bay (SU001S, SU002S), and Lower South Bay (LSB011S). Low numbers of ERL exceedances were also observed in August 2003 at the non-coarse stations of Suisun Bay (SU013S, SU014S), Central Bay (CB074S),
Redwood Creek (BA41), South Bay (SB001S, SB009S, SB010S, and SB012S), Lower South Bay (LSB001S) and Coyote Creek (BA10).

3.3.2 Temporal Trends

The maintenance of fixed historical sampling stations, at least one per region, permits analysis of long-term temporal trends.

Trace Elements

A method commonly used to improve the comparison of trace element and organic contaminant concentrations in sediments is to normalize them to a sediment component unaffected by anthropogenic activities (Luoma, 1990; Hanson, 1993; Daskalakis and O'Connor, 1995). One conservative tracer that can be used to differentiate natural from anthropogenic sediment components is iron (Schiff and Weisberg, 1999). Linear regression analysis showed all metals had significant positive relationships (p<0.05) with iron, therefore, normalization was considered appropriate (Hebert & Keenleyside, 1995). Arsenic, cadmium, iron, mercury, nickel, selenium, silver, and zinc concentrations were log (X + 1) transformed in an attempt to increase the normality of the linear regression residuals. Residuals of copper and lead were normally distributed, therefore, were not transformed. Analysis of covariance (ANCOVA) showed there was no significant difference between the slopes of the regression lines for each individual station (p>0.05), therefore, the common slopes were used to normalize the data.

Sediment trace element concentrations at each station were normalized for iron using linear regression analysis. Metal concentrations were the independent variables and sediment iron concentrations the dependent variable. Residuals from this analysis represent the variation in contaminant concentration that remains after normalization. Temporal trends were investigated for each station by performing a linear regression analysis using the residuals as the dependent variable, and sampling date as the independent variable. The presence of first-order autocorrelation in the data was examined using the Durbin-Watson test. In cases where first-order autocorrelation was found the data were corrected using the Hildreth-Lu procedure. A significantly positive slope (p<0.05) was assumed to indicate an increase in the concentration of the contaminant at the station over time. Similarly, a significant negative slope assumes a decrease over time, while a lack of significance indicates no change in sediment concentration.

After normalizing for iron content, significant long-term trends for one or more contaminants were found at 6 of 7 historical sites (Figures 3.16-3.25 and Table 3.4). Overall, significant long-term (five to eleven year) trends were observed in 21% of the trace element contaminant analyses. Silver, arsenic, and selenium exhibit significant decreases at six, four, and two stations, respectively. The decline in surface sediment concentrations may be due to the decrease in silver loadings from wastewater treatment plants (Squire *et al.*, 2002). Significant long-term decreases in lead, mercury, and nickel were documented at one station. No long-term increases were detected for any contaminant.

Significant decreases in contaminant concentrations were observed over time at the Yerba Buena Island (BC11) and Coyote Creek (BA10) stations, four and three respectively. Two significant decreases were observed at the Redwood Creek (BA41),

Pinole Point (BD31), Grizzly Bay (BF21), and San Joaquin River (BG30) stations. No significant long-term trends were documented at the Sacramento River (BG20) sampling station.

Trace Organics

Linear regression analysis showed that sum of PAHs had significant positive relationships (p<0.05) with both total organic carbon content (TOC) and percent fines (grain size <63 μ m) expressed as a decimal, therefore, normalization was considered appropriate (Hebert & Keenleyside, 1995). Sum of PAH concentration, percent fines, and TOC were log (X + 1) transformed to normalize the regression residuals. A best subsets regression analysis indicated the best model (one with highest adjusted r² taking standard deviation into account) was the relationship between log-transformed PAHs and log-transformed percent fines. An ANCOVA showed a significant difference between the slopes of the regression lines for each station (F_{6,107}=2.32, p=0.038), therefore, the individual station regression lines were used to normalize the data.

Sediment sum of PAHs at each station was normalized for percent fines using linear regression analysis. Log-transformed percent fines were the independent variables and log-transformed sediment sum of PAH concentration the dependent variable. Residuals from this analysis represent the variation in contaminant concentration that remains after the effect of grain size has been removed. Values falling above or below the regression line have positive or negative residuals, respectively. Residuals were rescaled by adding the grand mean log-transformed sum of PAH concentration to each residual. First order kinetic processes are natural log (ln) - linear with respect to time (Sericano et al., 1996). Therefore, temporal trends were examined for each station by performing a linear regression analysis using the ln (rescaled residual) as the dependent variable, and sampling date as the independent variable. The presence of first-order autocorrelation in the data was examined using the Durbin-Watson test, but no conclusive evidence of firstorder autocorrelation was found in the data. A significantly positive slope (p < 0.05) was assumed to indicate an increase in the concentration of the contaminant at the station over time. Similarly, a significant negative slope assumes a decrease over time, while a lack of significance indicates no change in sediment concentration.

After normalizing for grain size, no significant long-term trends in the sum of PAHs were documented at any of the seven historical stations located throughout the Estuary (Figure 3.25). Concentrations of PCBs for 2002 and 2003, and pesticides for 2003, were unavailable at the time of reporting, and PBDEs have only been measured in sediments since 2002. Therefore, analyses of temporal trends were not conducted for these contaminants.

3.3.3 Sediment Toxicity

Toxicity tests, described in *Section 3.2.3*, were conducted to determine whether sediments were toxic to sensitive benthic organisms. Since these bioassays were conducted using non-resident organisms exposed in laboratory conditions, the results may not necessarily indicate the occurrence of actual ecological impacts.

Estuary sediments were toxic to either amphipods or larval mussels in 14 out of 27 (52%) of the 2003 RMP samples (Table 3.2). Patterns of toxicity for the two test organisms vary within the Estuary (Figure 3.15). Historical stations located in the Rivers and

Suisun Bay regions of the Estuary (Sacramento River (BG20), San Joaquin River (BG30), and Grizzly Bay (BF21)) have been consistently toxic to bivalve larvae since 1994. A pattern documented again in 2003, and strengthened with the observation of toxicity to larval mussels at the Suisun Bay stations of SU009S, SU0011S, and SU013S. Unlike 2002, Central Bay sediments in 2003 did not show evidence of amphipod toxicity. Amphipod toxicity was observed in the San Pablo Bay (SPB001S), South Bay (Redwood Creek (BA41), SB001S, and SB013S), and Lower South Bay (LSB009S). Bioassay results for 2003 indicate sediments from Suisun Bay (SU001S), San Pablo Bay (Pinole Point (BD31), SPB009S, SPB011S, and SPB013S), Central Bay (Yerba Buena Island (BC11), CB001S, CB013S, and CB074S), South Bay (SB009S and SB011S), and Lower South Bay (LSB011S) and LSB013S) were not toxic to either amphipods or larval mussels. Sediments from Grizzly Bay (BF21) were toxic to both amphipods and mussel larvae. Seasonal patterns were not examined due to the discontinuance in 2002 of winter sampling, but prior to 2000 sediments were usually more toxic during the wet season (SFEI 2000; 2001).

Causes of toxicity to the amphipods and bivalve larvae are poorly understood. Analyses using several years of monitoring data suggest that amphipod toxicity is associated with the cumulative effects of mixtures of contaminants (Thompson *et al.*, 1999). Several individual contaminants were identified as probable determinants of toxicity at some sites. For example, toxicity at Grizzly Bay (BF21) was related to covarying patterns of total chlordane, silver, and cadmium from 1991 through 1996. Seasonal variation in PAHs at some stations was related to survival. Sediment elutriates (water soluble fraction) have been observed as being toxic to bivalve larvae for the Sacramento and San Joaquin Rivers, and Grizzly Bay samples since 1993 (SFEI 2000, 2001). Toxicity identification evaluations (TIEs) conducted on the sediment elutriates from the Sacramento and San Joaquin Rivers and Grizzly Bay in 1997 and 1998 indicated that dissolved trace metals, particularly copper, could be partially responsible for the toxicity, but organic contaminants were also identified as possible toxic components from the Sacramento River site (Phillips *et al.*, 2000). These results suggest that sediment toxicity at the different RMP stations may be related to different contaminants and may vary with time.

Studies by RMP investigators demonstrate the complex nature of sediment toxicity due to the numerous contaminant and non-contaminant factors in Estuary sediments. Solid phase sediment toxicity to amphipods has been frequently observed at Redwood Creek (BA41) and Grizzly Bay (BF21). Although exposure to pore water from these sites did not produce toxicity, exposure to bulk sediment did, suggesting that the toxicity is associated with ingestion and assimilation of contaminants in sediment. Amphipods accumulated PAHs, organochlorine pesticides, and PCBs from exposures to both bulk sediment and pore water, but not at levels known to cause mortality. The majority of the contaminants accumulated in amphipods were PAHs, which may have been a key causative agent of the observed toxicity. However, mixtures of contaminants are also believed to be important (Anderson *et al.*, 2000). Anderson *et al.* (2003) summarized ten years of toxicity testing by the RMP (http://www.sfei.org/rmp/pulse/pulse2003.pdf).

3.3.4 Assessment of Sediment Quality

Estuary sediments are evaluated through comparisons to several sets of sediment quality guidelines described in *Section 3.2.2 Sediment Quality Guidelines*. Although these

guidelines hold no regulatory status, they provide concentration guidelines that are useful in assessing the potential for toxic and benthic effects.

Sediment contamination and toxicity results were used to evaluate the quality of the 2003 Regional Monitoring Program samples (Table 3.2). Sediment contamination was estimated for each site by considering the number of contaminants in a sample that exceeded the San Francisco Estuary Ambient Sediment Concentration (ASC: Gandesbery *et al.*, 1999), Effects-Range guidelines (ERL and ERM: Long *et al.*, 1995), and the ERM quotients (Long *et al.*, 1998). The number of sediment contaminants above the ERL or ERM guidelines has been used previously to predict potential biological effects (Long *et al.*, 1998). Long *et al.* (1998) found that samples with more than four ERM exceedances showed toxicity in 68% of amphipod tests, while 51% of samples were toxic to amphipods when more than nine ERLs were above the guidelines. Based on these results the 2003 RMP sediment samples were considered potentially toxic if either four or more ERMs, nine or more ERLs, or half (22) of the ASC values were exceeded. Samples that did not have values for at least 80% of the parameters (32 of 40 for ASC, and 24 of 30 for ERL and ERM) were not included in the calculations.

ERM values were used to calculate a mean ERM quotient (mERMq) for each sample. The mERMq has been used in previous RMP reports and San Francisco Estuary publications, as an index of cumulative sediment contaminant concentrations (Thompson et al., 1999; Hunt et al., 2001a,b; Fairey et al., 2001; Thompson and Lowe, 2004). The primary reason for using the mERMq is that it provides a measure of potential additive contaminant effects. For example, amphipod survival has been found to be significantly and inversely correlated to mERMq (Thompson et al., 1999), suggesting that contaminants individually present in relatively low concentrations in sediments may act together to adversely influence amphipod survival. In these past reports and publications, however, the mERMq has been calculated in several different ways. However, if comparisons to other U.S. estuaries are to be accomplished, a standard method of calculation is necessary. Therefore, the calculation of mERMq was changed in order to make the RMP ERM quotients comparable to other studies from around the U.S. (Hyland et al., 1999; Long et al., 2002; Hyland et al., 2003). In the past, RMP mERMgs were calculated using 13 contaminants, including nickel, but the revised calculations use 24 contaminants (Hyland et al., 1999), excluding nickel (Table 3.1). Samples that did not have values for at least 19 of the 24 parameters were not included in the calculations. The resulting values are considerably lower than the values calculated in previous years, and are heavily weighted with PAHs. Concentrations for chromium, PCBs, and pesticides were unavailable in 2003 and are not included in the calculations.

Long *et al.* (1998) showed that 49% of sediment samples were toxic to amphipods when mERMq values were above 0.5, and 71% of samples were toxic when mERMq values were greater than 1.0. Mean ERM quotients, calculated with 24 contaminants, were used in a previous study of the San Francisco Estuary in which values greater than 0.15 were associated with increased risks of benthic impact (Thompson and Lowe, 2004). These values were used to evaluate the 2003 RMP sediment samples for potential adverse ecological effects. Statistical analysis shows that the mERMq values were significantly higher in the Lower South Bay compared to Suisun Bay, but no significant differences were found among the other regions (Kruskal-Wallis, H=18.72, df=4, p=0.001), a mERMq value above 0.15 was documented for CB012S in 2003 (Table 3.2). Central

Bay stations CB012S, CB013S, and CB014S had six or more contaminants above the ERL guidelines. Fourteen sediment samples were toxic (Sacramento River (BG20), San Joaquin River (BG30), Grizzly Bay (BF21), Suisun Bay (SU009S, SU011S, SU013S, SPB001S), Yerba Buena Island (BC11), Redwood Creek (BA41), South Bay (SB001S, SB013S), Lower South Bay (LSB001S, LSB009S), and Coyote Creek (BA10)); however, all had mERMq values below 0.15 and ERL, ERM, and ASC exceedences below the number considered to be potentially toxic. Sediments from the Central Bay station CB012S had a high number of ASC (25) and ERL (16) exceedences, but were not tested for toxicity.

Sediment evaluations are useful tools that incorporate sediment contamination and toxicity into a weight of evidence assessment of the condition of sediments in the Estuary. Each component is analyzed independently and weighted equally, but although they should be related the results do not always agree. The complexity of sediment evaluations demonstrate the need to consider as much data as possible in assessing the condition of Estuary sediments and the importance of performing future studies to reconcile and understand the observed contradictions.

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Table 3.1. Guidelines to evaluate chemical concentrations in sediment (in dry weight).

Effects Range-Low (ERL) and Effects Range-Median (ERM) values from Long et al. (1995, 1998).

Effects Range-Low, values between this and the ERM are in the possible effects range Effects Range-Median; values above this are in the probable effects range.

San Francisco Bay Ambient Sediment Concentrations (ASC) from Gandesbery et al. (1999). Ambient sediment levels from background sediments in the Estuary allow one to assess whether a site has elevated levels or is "degraded".

Background sediment concentrations for selected trace elements in the San Francisco Bay, from Hornberger et al. (1999) Chromium and nickel concentrations observed throughout the core. All trace elements, except Ag, measured by Inductively Coupled Argon

Plasma Emission Spectroscopy (ICAPES). Ag measured by Graphite Furnace Atomic Absorption Spectrometry (GFAAS).

Near total metals are extracted with a weak acid for a minimun of one month, therefore, concentrations approximate the bioavailability

of these metals to Estuary biota.

Parameter	unit	ERL EF	ERM	ASC-sandy <40% fines	ASC-muddy >40% fines	Background ((Bay wid	Concentrations le ranges)	
						Total	Near Total	
Arsenic	mg/Kg	8.2	70 [†]	13.5	15.3			
Cadmium	mg/Kg	1.2	9.6 [†]	0.25	0.33			
Chromium *	mg/Kg	81	370 [†]	91.4	112	110 - 170	70 - 120	
Copper	mg/Kg	34	270 [†]	31.7	68.1	20 - 55	20 - 41	
Mercury	ma/Ka	0.15	0.71 [†]	0.25	0.43		0.05 - 0.07	
Nickel	mg/Kg	20.9	51.6	92.9	112	70 - 100	50 - 100	
Lead	mg/Kg	46.7	218 [†]	20.3	43.2	20 - 40	10 - 20	
Selenium	mg/Kg			0.59	0.64			
Silver	mg/Kg	1	3.7 [†]	0.31	0.58	0.7 - 0.11	0.7 - 0.11	
Zinc	mg/Kg	150	410 [†]	97.8	158	60 - 70	50 - 100	
Sum of HPAHs (SFEI)	µg/Kg	1700	9600	256	3060			
Fluoranthene	µg/Kg	600	5100 [†]	78.7	514			
Perylene	µg/Kg			24	145			
Pyrene	µg/Kg	665	2600	64.6	665			
Benz[a]anthracene	µg/Kg	261	1600 ⁺	15.9	244			
Chrysene	µg/Kg	384	2800 [†]	19.4	289			
Benzo[b]fluoranthene	µg/Kg			32.1	371			
Benzo[k]fluoranthene	µg/Kg			29.2	258			
Benzo[a]pyrene	µg/Kg	430	1600 ⁺	18.1	412			
Benzo[e]pyrene	µg/Kg			17.3	294			
Dibenz[a,h]anthracene	µg/Kg	63.4	260 [†]	3	32.7			
Benzo[g,h,i]perylene	µg/Kg			22.9	310			
Indeno[1,2,3-c,d]pyrene	µg/Kg			19	382			
Sum of LPAHs (SFEI)	µg/Kg	552	3160	37.9	434			
1-Methylnaphthalene	µg/Kg			6.8	12.1			
1-Methylphenanthrene	µg/Kg			4.5	31.7			
2,3,5-Trimethylnaphthalene	µg/Kg			3.3	9.8			
2,6-Dimethylnaphthalene	µg/Kg		+	5	12.1			
2-Methylnaphthalene	µg/Kg	70	670 '	9.4	19.4			
Naphthalene	µg/Kg	160	2100 '	8.8	55.8			
Acenaphthylene	µg/Kg	44	640 '	2.2	31.7			
Acenaphthene	µg/Kg	16	500 '	11.3	26.6			
Fluorene	µg/Kg	19	540 ⁺	4	25.3			
Phenanthrene	µg/Kg	240	1500	17.8	237			
Anthracene	µg/Kg	85.3	1100 [†]	9.3	88			
Sum of PAHs (SFEI)	µg/Kg	4022	44792	211	3390			
p,p'-DDE **	µg/Kg	2.2	27 †					
Sum of DDTs (SFEI) **	µg/Kg	1.58	46.1 [†]	1.58	46.1			
Total Chlordanes (SFEI) **	µg/Kg	0.5	6	0.42	1.1			
Dieldrin **	µg/Kg	0.02	8	0.18	0.44			
TOTAL PCBs (NIST 18)	µg/Kg	00.7	400 [†]	5.9	14.8			
Sum of PCBs (SFEI) **	µg/Kg	22.7	180 '	8.6	21.6			

* Chromium concentrations were not measured in 2003 sediment samples.

** Concentrations not available for 2003 sediment samples.

[†] Values used to calculate mean ERM quotients (Hyland et al. 1999).

RMP Annual Monitoring Results 2003

Table 3.2. Summary of sediment quality for the RMP in 2003. NA = not available, . = not tested, * indicates number of exceedances above ASC guidelines for sandy samples.

No. of ASC No. of ERL No. of ERM above above above Toxic to Toxic to mERMq Guidelines Guidelines Guidelines Amphipods? **Bivalves?** Code Site Name Date % Fines BG20 Sacramento River 8/18/03 15 0.0266 yes no BG30 San Joaquin River 8/18/03 73 0.0566 0 3 no yes BF21 Grizzly Bay 8/18/03 99 0.0662 0 4 1 yes yes SU001S Suisun Bay 8/19/03 22 0.0227 1* 1 1 no no SU002S Suisun Bay 8/18/03 18 0.0211 1* 1 1 Suisun Bay SU009S 8/18/03 95 0.0647 0 3 no 1 yes SU010S 0.0163 0* Suisun Bay 8/18/03 9 NA NA SU011S Suisun Bay 8/19/03 100 0.0698 1 3 1 no yes SU012S Suisun Bay 8/18/03 93 0.0654 0 4 SU013S Suisun Bay 8/19/03 53 0.0397 0 2 1 no yes SU014S Suisun Bay 8/18/03 57 0.0475 0 2 1 BD31 Pinole Point 8/20/03 91 0.0608 0 3 no 1 no SPB001S San Pablo Bay 8/19/03 98 0.0682 0 4 1 yes no SPB002S San Pablo Bay 8/20/03 95 0.0687 0 3 1 SPB009S San Pablo Bay 8/20/03 96 0.0678 0 3 1 no no SPB010S San Pablo Bay 8/20/03 84 0 4 0.0575 1 98 0 3 SPB011S San Pablo Bay 8/19/03 0.0784 1 no no SPB012S San Pablo Bay 8/19/03 100 0.0708 0 4 1 SPB013S San Pablo Bav 8/19/03 0 0761 0 4 97 1 no no SPB073S San Pablo Bay 8/20/03 97 0.0687 0 4 1 BC11 Yerba Buena Island 8/20/03 70 0.0622 1 3 no yes 1 CB001S Central Bay 8/21/03 71 0.0939 1 5 1 no no CB002S Central Bay 8/22/03 97 0.1187 5 4 1 . CB010S 8/21/03 86 2 3 Central Bay 0.0815 1 CB011S Central Bay 8/20/03 99 0.0762 0 3 1 no no 58 25 CB012S Central Bay 8/21/03 0.2115 16 1 CB013S Central Bay 8/21/03 78 0.0960 1 6 no no 1 CB014S Central Bay 8/21/03 0.1105 5 7 72 1 CB074S 8/21/03 0 2 Central Bay 49 0.0643 no no 1 BA41 Redwood Creek 8/22/03 71 0.0804 0 2 1 yes no SB001S South Bay 8/22/03 47 0.0329 0 1 0 yes no SB002S South Bay 8/25/03 93 0.0701 0 3 1 SB009S South Bay 8/21/03 64 0.0474 0 2 0 no no SB010S South Bay 8/22/03 62 0.0575 0 2 1 2 4 SB011S South Bay 8/22/03 97 0.1115 1 no no 0 2 SB012S South Bav 8/22/03 68 0.0799 1 3 SB013S South Bay 8/22/03 77 0 0739 0 no 1 yes SB014S 8/26/03 100 0.0842 0 3 South Bay 1 LSB001S Lower South Bay 8/26/03 101 0.0709 0 2 no yes 1 LSB002S Lower South Bay 8/25/03 100 0.0769 0 3 LSB009S Lower South Bay 8/26/03 100 0.0771 0 3 yes no 1 0 4 LSB010S Lower South Bay 8/25/03 96 0.0804 1 LSB011S Lower South Bay 8/26/03 40 0 0481 21 2 no 1 no LSB012S Lower South Bay 8/25/03 98 0.0761 0 3 1 LSB013S Lower South Bay 8/25/03 98 0.0780 0 3 1 no no LSB014S Lower South Bay 8/25/03 100 0.0791 0 3 1 BA10 Coyote Creek 8/25/03 0.0501 0 0 no 50 2 yes

RMP Annual Monitoring Results 2003 **Table 3.3. Statistical comparisons among regions and between years, 2002-2003.** A Z score > 1.96, or < -1.96 indicates a statistically significant difference at the 5% significance level. A p value < 0.05 indicates a statistically significant difference to the Dev Control of the States of the State

A p value < 0.05 indicates a statistically significant difference for the Roa-Scott test. * indicates contaminant data were log transformed. Significant comparisons shown in bold.

		Z-test Statistic												
Comparison	Ag*	As	Cd*	Cu	Fe*	Hg*	MeHg*	Ni*	Pb*	Se*	Zn*	PAHs*		
CB vs LSB	-2.94	0.96	2.85	-0.97	-1.65	-2.35	0.04	-2.61	-6.26	-3.98	-3.58	3.65		
CB vs SB	-1.39	0.34	0.95	2.03	2.40	0.72	0.78	2.19	1.02	-1.92	1.73	3.13		
CB vs SPB	1.05	-3.57	-0.46	-5.85	-2.91	-3.39	2.75	-2.78	-1.75	-2.86	-1.95	7.41		
CB vs SU	1.17	0.22	-0.70	-0.15	-1.28	2.23	4.95	-1.64	4.46	0.36	1.98	9.51		
LSB vs SB	1.08	-0.35	-1.33	3.06	3.43	3.06	1.01	3.76	4.74	0.89	3.82	-0.72		
LSB vs SPB	4.40	-4.24	-3.90	-5.65	-0.68	-0.48	3.89	-0.25	7.82	1.47	2.16	3.95		
LSB vs SU	3.79	-0.52	-2.55	0.38	0.52	3.64	7.46	0.49	7.60	2.33	4.55	7.44		
SB vs SPB	2.38	-2.62	-1.41	-7.36	-4.22	-4.24	2.38	-3.87	-2.17	0.07	-2.87	5.01		
SB vs SU	2.31	-0.12	-1.33	-1.44	-3.25	1.77	5.16	-3.18	3.12	1.53	-0.07	7.99		
SPB vs SU	0.35	2.69	-0.47	2.88	1.51	4.13	2.90	0.67	5.56	1.69	3.43	5.65		
2002 vs 2003	2.63	5.83	0.76	-1.18	-0.54	3.29	1.36	-1.93	0.23	0.23	-1.50	-0.06		

	Roa-Scott Test p Value											
Comparison	Ag	As	Cd	Cu	Fe	Hg	MeHg	Ni	Pb	Se	Zn	PAHs
CB vs LSB	0.01	0.00	0.37	0.02	0.04	0.06	0.29	0.00	0.00	0.01	0.00	0.00
CB vs SB	0.90	0.02	0.72	0.12	0.35	0.43	0.19	0.43	0.69	0.07	0.88	0.00
CB vs SPB	0.45	0.00	0.73	0.00	0.04	0.01	0.01	0.00	0.33	0.13	0.33	0.00
CB vs SU	0.08	0.33	0.21	0.03	0.37	0.43	0.00	0.03	0.00	0.19	0.02	0.00
LSB vs SB	0.11	0.89	0.88	0.00	0.00	0.09	0.42	0.00	0.00	0.39	0.00	0.18
LSB vs SPB	0.01	0.01	0.00	0.00	0.90	0.20	0.00	0.19	0.00	0.44	0.01	0.00
LSB vs SU	0.01	0.68	0.01	0.00	0.90	0.06	0.00	0.23	0.00	0.05	0.00	0.00
SB vs SPB	0.36	0.00	0.07	0.00	0.00	0.00	0.01	0.00	0.10	0.32	0.01	0.00
SB vs SU	0.06	0.70	0.12	0.03	0.01	0.44	0.01	0.01	0.01	0.32	0.02	0.00
SPB vs SU	0.05	0.01	0.71	0.01	0.43	0.00	0.05	0.45	0.00	0.03	0.01	0.00
2002 vs 2003	0.62	0.00	0.50	0.96	0.34	0.00	0.16	0.57	0.26	0.03	0.15	0.01

Abbreviations: CB = Central Bay, LSB = Lower South Bay, SB = South Bay, SPB = San Pablo Bay, and SU = Suisun Bay.

RMP Annual Monitoring Results 2003 Table 3.4. Significant trends in iron normalized sediment contaminants, 1993-2003. A significantly positive linear regession slope (p<0.05) was assumed to indicate an increase in the concentration of the contaminant at the station over time. Similarly, a significant negative slope assumes a decrease over time, with a lack of significance indicating no change in sediment contaminant concentration. * indicates contaminant data were log transformed.

Station	Name	Ag*	As*	Cd*	Cu	Hg*	Ni*	Pb	Se*	Zn*	PAHs
BA10	Coyote Creek	decrease					decrease	decrease			
BA41	Redwood Creek	decrease	decrease								
BC11	Yerba Buena Island	decrease	decrease			decrease			decrease		
BD31	Pinole Point	decrease	decrease								
BF21	Grizzly Bay	decrease	decrease								
BG20	Sacramento River										
BG30	San Joaquin River	decrease							decrease		



Figure 3.1. Map of the RMP Status and Trends sediment monitoring effort at both randomly selected and historic fixed sampling sites. 47 stations were sampled in the San Francisco Estuary in 2003.



RMP Annual Monitoring Results 2003 Figure 3.2. Percent Fines (<63 um) in Sediments (2002-2003)

> a) Map of percent fines in sediments (%) in the six Estuary regions monitored. Eighty randomly allocated sites (based on the EMAP sample design) and seven historical RMP sites (2003 data only) are represented here. Only historic sites were sampled in the Rivers region. See Section 1.3.1 for further explanation of the map. Number of samples: random =16/region; historic = 1/region except n=2 for the Rivers region.

Random sites = \circ , Historic sites = \diamond , Non-detects = +



Region Code Region Code: LSB=Lower South Bay, SB=South Bay, CB=Central Bay, SPB=San Pablo Bay, Su=Suisun Bay

b) Schematic Box Plot of sediment percent

fines for the random sites in five Estuary regions (2002-2003). See Section 1.3.1 for an explanation of the schematic box plot.



What percent of the Estuary is composed of fine sediments?

c) Cumulative distribution function (**CDF**) plots for sediment percent fines from the random samples in the five Estuary regions (2002-2003). See Section 1.3.1 for an explanation of the CDF plot. n=16/region.

The large graph shows the percentage of the total area sampled in the five Estuary regions (totaling 896 square kilometers) vs. sediment percent fines.

The small graphs show the same for each individual region (scales are identical to the large graph).



Figure 3.3. Total Organic Carbon in Sediments (2002-2003)

a) Map of total organic carbon (TOC) in sediments (%) in the six Estuary regions monitored. Eighty randomly allocated sites (based on the EMAP sample design) and seven historical RMP sites (2003 data only) are represented here. Only historic sites were sampled in the Rivers region. See Section 1.3.1 for further explanation of the map. Number of samples: random =16/region; historic = 1/region except n=2 for the Rivers region.

Random sites = \circ , Historic sites = \diamond , Non-detects = +



Region Code: LSB=Lower South Bay, SB=South Bay, CB=Central Bay, SPB=San Pablo Bay, Su=Suisun Bay

b) Schematic Box Plot of sediment TOC for the random sites in five Estuary regions (2002-2003). See Section 1.3.1 for an explanation of the schematic box plot.



Cumulative distribution of total organic carbon in the Estuary.

c) Cumulative distribution function (CDF) plots for sediment TOC from the random samples in the five Estuary regions (2002-2003). See Section 1.3.1 for an explanation of the CDF plot. n=16/region.

The large graph shows the percentage of the total area sampled in the five Estuary regions (totaling 896 square kilometers) vs. sediment TOC.

The small graphs show the same for each individual region (scales are identical to the large graph).



RMP Annual Monitoring Results 2003 Figure 3.4a-c. Arsenic (As) in Sediments (2002-2003)

> a) Map of arsenic concentrations in sediments (mg/kg dry weight) in the six Estuary regions monitored. Eighty randomly allocated sites (based on the EMAP sample design) and seven historical RMP sites (2003 data only) are represented here. Only historic sites were sampled in the Rivers region. See Section 1.3.1 for further explanation of the map. Number of samples: random =16/region; historic = 1/region except n=2 for the Rivers region.

Random sites = \circ , Historic sites = \diamond , Non-detects = +



Region Code: LSB=Lower South Bay, SB=South Bay, CB=Central Bay, SPB=San Pablo Bay, Su=Suisun Bay

b) Schematic Box Plot of sediment arsenic concentrations for the random sites in five Estuary regions (2002-2003). See Section 1.3.1 for an explanation of the schematic box plot.



What percentage of the Estuary is above the arsenic ERL guideline?

c) Cumulative distribution function (CDF) plots for sediment arsenic concentrations from the random samples

in the five Estuary regions (2002-2003). See Section 1.3.1 for an explanation of the CDF plot. n=16/region.

The large graph shows the percentage of the total area sampled in the five Estuary regions (totaling 896 square kilometers) vs. sediment arsenic concentrations.

The small graphs show the same for each individual region (scales are identical to the large graph).

About 40% of the total sampled area in the Estuary had sediment arsenic concentrations above the ERL guideline of 8.2 mg/kg.



a) Map of cadmium concentrations in sediments (mg/kg dry weight) in the six Estuary regions monitored. Eighty randomly allocated (based on the EMAP sample design) and seven historical RMP sites (2003 data only) are represented here. Only historic sites were allocated to the Rivers region. See Section 1.3.1 for further explanation of the map. Number of samples: random =16/region; historic = 1/region except n=2 for the Rivers region.





Region Code: LSB=Lower South Bay, SB=South Bay, CB=Central Bay, SPB=San Pablo Bay, Su=Suisun Bay

b) Schematic Box Plot of sediment cadmium

concentrations for the random sites in five Estuary regions (2002-2003). See Section 1.3.1 for an explanation of the schematic box plot.



What percentage of the Estuary is above the cadmium ERL guideline?

c) Cumulative distribution function (CDF) plots for sediment cadmium concentrations from the random samples in the five Estuary regions (2002-2003). See Section 1.3.1 for an explanation of the CDF plot. n=16/region.

The large graph shows the percentage of the total area sampled in the five Estuary regions (totaling 896 square kilometers) vs. sediment cadmium concentrations.

The small graphs show the same for each individual region (scales are identical to the large graph).

None of the total sampled area in the Estuary had sediment cadmium concentrations above the ERL guideline of 1.2 mg/kg.



RMP Annual Monitoring Results 2003 Figure 3.6a-c. Copper (Cu) in Sediments (2002-2003)

a) Map of copper concentrations in sediments (mg/kg dry weight) in the six Estuary regions monitored. Eighty randomly allocated sites (based on the EMAP sample design) and seven historical RMP sites (2003 data only) are represented here. Only historic sites were sampled in the Rivers region. See Section 1.3.1 for further explanation of the map. Number of samples: random =16/region; historic = 1/region except n=2 for the Rivers region. Random sites = \circ , Historic sites = \diamond , Non-detects = +



Region Code: LSB=Lower South Bay, SB=South Bay, CB=Central Bay, SPB=San Pablo Bay, Su=Suisun Bay

b) Schematic Box Plot of sediment copper concentrations for the random sites in five Estuary regions (2002-2003). See Section 1.3.1 for an explanation of the schematic box plot.



What percentage of the Estuary is above the copper ERL guideline?

c) Cumulative distribution function (CDF) plots for sediment copper concentrations from the random samples in the five Estuary regions (2002-2003). See Section 1.3.1 for an explanation of the CDF plot. n=16/region.

The large graph shows the percentage of the total area sampled in the five Estuary regions (totaling 896 square kilometers) vs. sediment copper concentrations.

The small graphs show the same for each individual region (scales are identical to the large graph).

About 65% of the total sampled area in the Estuary had sediment copper concentrations above the ERL guideline of 34 mg/kg. The small graphs indicate that San Pablo Bay and the majority of the Lower South Bay are above the guideline, and about half the area of Suisun Bay, Central Bay, and South Bay are above the ERL guideline.



a) Map of lead concentrations in sediments (mg/kg dry weight) in the six Estuary regions monitored. Eighty randomly allocated sites (based on the EMAP sample design) and seven historical RMP sites (2003 data only) are represented here. Only historic sites were sampled in the Rivers region. See Section 1.3.1 for further explanation of the map. Number of samples: random =16/region; historic = 1/region except n=2 for the Rivers region.

Random sites = \circ , Historic sites = \diamond , Non-detects = +



Region Code: LSB=Lower South Bay, SB=South Bay, CB=Central Bay, SPB=San Pablo Bay, Su=Suisun Bay

b) Schematic Box Plot of sediment lead concentrations for the random sites in five Estuary regions (2002-2003). See Section 1.3.1 for an explanation of the schematic box plot.



What percentage of the Estuary is above the lead ERL guideline?

c) Cumulative distribution function (CDF) plots for sediment lead concentrations from the random samples in the five Estuary regions (2002-2003).

See Section 1.3.1 for an explanation of the CDF plot. n=16/region.

The large graph shows the percentage of the total area sampled in the five Estuary regions (totaling 896 square kilometers) vs. sediment lead concentrations.

The small graphs show the same for each individual region (scales are identical to the large graph).

None of the total sampled area in the Estuary had sediment lead concentrations above the ERL guideline of 46.7 mg/kg.



RMP Annual Monitoring Results 2003 Figure 3.8a-c. Mercury (Hg) in Sediments (2002-2003)

> a) Map of mercury concentrations in sediments (mg/kg dry weight) in the six Estuary regions monitored. Eighty randomly allocated sites (based on the EMAP sample design) and seven historical RMP sites (2003 data only) are represented here. Only historic sites were sampled in the Rivers region. See Section 1.3.1 for further explanation of the map. Number of samples: random =16/region; historic = 1/region except n=2 for the Rivers region.

Random sites = \circ , Historic sites = \diamond , Non-detects = +



Region Code: LSB=Lower South Bay, SB=South Bav.

CB=Central Bay, SPB=San Pablo Bay, Su=Suisun Bay

b) Schematic Box Plot of sediment mercury

concentrations for the random sites in five Estuary regions (2002-2003). See Section 1.3.1 for an explanation of the schematic box plot.



c) Cumulative distribution function (CDF) plots for sediment mercury concentrations from the random samples in the five Estuary regions (2002-2003). See Section 1.3.1 for an explanation of the

The large graph shows the percentage of the total area sampled in the five Estuary regions (totaling 896 square kilometers) vs. sediment mercury concentrations.

The small graphs show the same for each individual region (scales are identical to the large graph).

About 80% of the total sampled area in the Estuary has sediment mercury concentrations above the TMDL target of 0.2 mg/kg. The small graphs indicate that both San Pablo Bay and the Lower South Bay regions are above the target, and about half of the area of Suisun Bay is above the TMDL target.



Figure 3.9a-c. Methylmercury (MeHg) in Sediments (2002-2003)

a) Map of methylmercury concentrations in sediments (μ g/kg dry weight) in the six Estuary regions monitored. Eighty randomly allocated sites (based on the EMAP sample design) and seven historical RMP sites (2003 data only) are represented here. Only historic sites were sampled in the Rivers region. See Section 1.3.1 for further explanation of the map. Number of samples: random =16/region; historic = 1/region except n=2 for the Rivers region.

Random sites = \circ , Historic sites = \diamond , Non-detects = +



Region Code: LSB=Lower South Bay, SB=South Bay, CB=Central Bay, SPB=San Pablo Bay, Su=Suisun Bay

b) Schematic Box Plot of sediment methylmercury concentrations for the random sites in five Estuary regions (2002-2003). See Section 1.3.1 for an explanation of the schematic box plot.



Cumulative distribution of methylmercury in the Estuary sediments.





a) Map of nickel concentrations in sediments (mg/kg sry weight) in the six Estuary regions monitored. Eighty randomly allocated sites (based on the EMAP sample design) and seven historical RMP sites (2003 data only) are represented here. Only historic sites were sampled in the Rivers region. See Section 1.3.1 for further explanation of the map. Number of samples: random =16/region; historic = 1/region except n=2 for the Rivers region.

Random sites = \circ , Historic sites = \diamond , Non-detects = +



Region Code: LSB=Lower South Bay, SB=South Bay, CB=Central Bay, SPB=San Pablo Bay, Su=Suisun Bay

b) Schematic Box Plot of sediment nickel

concentrations for the random sites in five Estuary regions (2002-2003). See Section 1.3.1 for an explanation of the schematic box plot.



What percentage of the Estuary is above the nickel ERL guideline?

(CDF) plots for sediment nickel concentrations from the random samples in the five Estuary regions (2002-2003). See Section 1.3.1 for an explanation of the CDF plot. n=16/region.

The large graph shows the percentage of the total area sampled in the five Estuary regions (totaling 896 square kilometers) vs. sediment nickel concentrations.

The small graphs show the same for each individual region (scales are identical to the large graph).

Almost all of the total sampled area in the Estuary had sediment nickel concentrations above the ERL guideline of 20.9 mg/kg.



a) Map of selenium concentrations in sediments (mg/kg sry weight) in the six Estuary regions monitored. Eighty randomly allocated sites (based on the EMAP sample design) and seven historical RMP sites (2003 data only) are represented here. Only historic sites were sampled in the Rivers region. See Section 1.3.1 for further explanation of the map. Number of samples: random =16/region; historic = 1/region except n=2 for the Rivers region.

Random sites = \circ , Historic sites = \diamond , Non-detects = +



CB=Central Bay, SPB=San Pablo Bay, Su=Suisun Bay,

b) Schematic Box Plot of sediment selenium

concentrations for the random sites in five Estuary regions (2002-2003). See Section 1.3.1 for an explanation of the schematic box plot.



What percentage of the Estuary is above the selenium ASC guideline?

c) Cumulative distribution function(CDF) plots for sediment seleniumconcentrations from the random samples

in the five Estuary regions (2002-2003). See Section 1.3.1 for an explanation of the CDF plot. n=16/region.

The large graph shows the percentage of the total area sampled in the five Estuary regions (totaling 896 square kilometers) vs. sediment selenium concentrations.

The small graphs show the same for each individual region (scales are identical to the large graph).

None of the total sampled area in the Estuary had sediment selenium concentrations above the ASC guideline of 0.64 mg/kg.



RMP Annual Monitoring Results 2003 Figure 3.12a-c. Silver (Ag) in Sediments (2002-2003)

a) Map of silver concentrations in sediments (mg/kg dry weight) in the six Estuary regions monitored. Eighty randomly allocated sites (based on the EMAP sample design) and seven historical RMP sites (2003 data only) are represented here. Only historic sites were sampled in the Rivers region. See Section 1.3.1 for further explanation of the map. Number of samples: random =16/region; historic = 1/region except n=2 for Rivers region.

Random sites = \circ , Historic sites = \diamond , Non-detects = +



Region Code: LSB=Lower South Bay, SB=South Bay, CB=Central Bay, SPB=San Pablo Bay, Su=Suisun Bay

b) Schematic Box Plot of sediment silver

concentrations for the random sites in five Estuary regions (2002-2003). See Section 1.3.1 for an explanation of the schematic box plot.



What percentage of the Estuary is above the silver ERL guideline?

c) Cumulative distribution function (CDF) plots for sediment silver concentrations from the random samples

in the five Estuary regions (2002-2003). See Section 1.3.1 for an explanation of the CDF plot. n=16/region.

The large graph shows the percentage of the total area sampled in the five Estuary regions (totaling 896 square kilometers) vs. sediment silver concentrations.

The small graphs show the same for each individual region (scales are identical to the large graph).

None of the sampled area in the Estuary had sediment silver concentrations above the ERL guideline of 1 mg/kg.



Figure 3.13a-c. Zinc (Zn) in Sediments (2002-2003)

a) Map of zinc concentrations in sediments (mg/kg dry weight) in the six Estuary regions monitored. Eighty randomly allocated sites (based on the EMAP sample design) and seven historical RMP sites (2003 data only) are represented here. Only historic sites were sampled in the Rivers region. See Section 1.3.1 for further explanation of the map. Number of samples: random =16/region; historic = 1/region except n=2 for the Rivers region.





Region Code: LSB=Lower South Bay, SB=South Bay, CB=Central Bay, SPB=San Pablo Bay, Su=Suisun Bay

b) Schematic Box Plot of sediment zinc

concentrations for the random sites in five Estuary regions (2002-2003). See Section 1.3.1 for an explanation of the schematic box plot.



What percentage of the Estuary is above the zinc ERL guideline?

c) Cumulative distribution function (CDF) plots for sediment zinc

concentrations from the random samples in the five Estuary regions (2002-2003). See Section 1.3.1 for an explanation of the CDF plot. n=16/region.

The large graph shows the percentage of the total area sampled in the five Estuary regions (totaling 896 square kilometers) vs. sediment zinc concentrations.

The small graphs show the same for each individual region (scales are identical to the large graph).

Only about 5% of the total sampled area in the Estuary had sediment zinc concentrations above the ERL guideline of 150 mg/kg.



RMP Annual Monitoring Results 2003 Figure 3.14a-c. Sum of PAHs in Sediments (2002-2003)

> a) Map of sum of PAH concentrations in sediments (µg/kg dry weight) in the six Estuary regions monitored. Eighty randomly allocated sites (based on the EMAP sample design) and seven historical RMP sites (2003 data only) are represented here. Only historic sites were sampled in the Rivers region. See Section 1.3.1 for further explanation of the map. Number of samples: random =16/region; historic = 1/region except n=2 for the Rivers region.

Random sites = \circ , Historic sites = \diamond , Non-detects = +



Region Code: LSB=Lower South Bay, SB=South Bay, CB=Central Bay, SPB=San Pablo Bay, Su=Suisun Bay

b) Schematic Box Plot of sediment sum of

PAH concentrations for the random sites in five Estuary regions (2002-2003). See Section 1.3.1 for an explanation of the schematic box plot.



What percentage of the Estuary is above the ERL guideline for sum of PAHs?

c) Cumulative distribution function (CDF) plots for sediment sum of PAH concentrations from the random samples in the five Estuary regions (2002-2003). See Section 1.3.1 for an explanation of the CDF plot. n=16/region.

The large graph shows the percentage of the total area sampled in the five Estuary regions (totaling 896 square kilometers) vs. sediment sum of PAH concentrations.

The small graphs show the same for each individual region (scales are identical to the large graph).

About 5% of the total sampled area in the Estuary had sediment sum of PAH concentrations above the ERL guideline of 4022 ug/kg.



Figure 3.15. Sediment bioassay results for 2003. Sediments were not toxic (see Section 3.4 Sediment Toxicity) to either amphipods, *Eohaustorius estuarius*, or mussel, *Mytilus galloprovincialis*, Iarvae at 13 out of 27 stations. Amphipod toxicity was observed at seven stations: Suisun Bay (Grizzly Bay (BF21)), San Pablo Bay (SPB001S), South Bay (Redwood Creek (BA41), SB001S, and SB013S), and Lower South Bay (Coyote Creek (BA10), and LSB009S). Sediment samples from eight stations were toxic to Iarval mussels: Sacramento River (BG20), San Joaquin River (BG30), Suisun Bay (Grizzly Bay (BF21), SU009S, SU0011S, and SU013S), Central Bay (Yerba Buena Island (BC11)), and Lower South Bay (LSB001S). Sediments from Grizzly Bay (BF21) were toxic to both amphipods and Iarval mussels.

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Figure 3.16. Time series plots for arsenic (As) in sediments (mg/kg dry weight) at seven historical sites, arranged from north to south, monitored by the RMP Status and Trends Program (1993-2003). The dashed blue reference line is the ERL guideline of 8.2 mg/kg.

Historical Sites:



Figure 3.17. Time series plots for cadmium (Cd) in sediments (mg/kg dry weight) at seven historical sites, arranged from north to south, monitored by the RMP Status and Trends Program (1993-2003). The ERL guideline is 1.2 mg/kg.

Historical Sites:

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Figure 3.18. Time series plots for copper (Cu) in sediments (mg/kg dry weight) at seven historical sites, arranged from north to south, monitored by the RMP Status and Trends Program (1993-2003). The dashed blue reference line is the ERL guideline of 34 mg/kg.

Historical Sites:



Figure 3.19. Time series plots for lead (Pb) in sediments (mg/kg dry weight) at seven historical sites, arranged from north to south, monitored by the RMP Status and Trends Program (1993-2003). The ERL guideline is 46.7 mg/kg.

Historical Sites:

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Figure 3.20. Time series plots for mercury (Hg) in sediments (mg/kg dry weight) at seven historical sites, arranged from north to south, monitored by the RMP Status and Trends Program (1993-2003). The dashed blue reference line is the TMDL target of 0.2 mg/kg.

Historical Sites:



Figure 3.21. Time series plots for nickel (Ni) in sediments (mg/kg dry weight) at seven historical sites, arranged from north to south, monitored by the RMP Status and Trends Program (1993-2003). The ERL guideline is 20.9 mg/kg.

Historical Sites:

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Figure 3.22. Time series plots for selenium in sediments (mg/kg dry weight) at seven historical sites, arranged from north to south, monitored by the RMP Status and Trends Program (1993-2003). The dashed blue reference line is the ASC guideline of 0.64 mg/kg.

Historical Sites:



Figure 3.23. Time series plots for silver (Ag) in sediments (mg/kg dry weight) at seven historical sites, arranged from north to south, monitored by the RMP Status & Trends Program (1993-2003). The dashed blue reference line is the ERL guideline of 1 mg/kg.

Historical Sites:

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Historical Sites:


Figure 3.25. Time series plots for sum of PAHs in sediment (μ g/kg dry weight) at seven historical sites, arranged from north to south, monitored by the RMP Status and Trends Program (1993-2003). The dashed blue reference line is the ERL guideline of 4022 μ g/kg.

Historical Sites:

BG20 Sacramento River BG30 San Joaquin River BF21 Grizzly Bay BD31 Pinole Point BC11 Yerba Buena Island BA41 Redwood Creek BA10 Coyote Creek

CHAPTER

Bivalve Bioaccumulation Monitoring Results

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4.0 BIVALVE MONITORING

Jennifer Hunt, Sarah Lowe, Paul Salop, and Predrag Stevanovic

4.1 Background

The San Francisco Estuary Regional Monitoring Program for Trace Substances (RMP) has been analyzing bivalve tissue samples for trace contaminants since 1993. Bivalves bioaccumulate chemical contaminants through their food, by ingesting sediment and assimilating contaminants that are sorbed to particles, and by filtering dissolved contaminants directly from the water column. Bivalves act as transfer vectors of contaminant concentrations in living organisms can accumulate to levels much greater than those found in ambient water and sediment due to an organism's inability to metabolize certain contaminants (Vinogradov, 1959) and a high affinity of some contaminants for lipid rich tissue in bivalves (Stout and Beezhold, 1981). Biomonitoring using bivalves has been widely applied by the California State Mussel Watch Program (Phillips, 1988; Rasmussen, 1994) and other studies (Young *et al.*, 1976; Wu and Levings, 1980; Hummel *et al.*, 1990; Martincic *et al.*, 1992, Gunther *et al.*, 1999; O'Connor, 2002).

Bivalves are excellent organisms for biomonitoring of contaminants since they accumulate contaminants from the ambient environment, have limited mobility and are fairly resistant to contaminant effects (O'Connor, 2002). The RMP is continuing the long-term monitoring of the State Mussel Watch Program, which monitored sites throughout the Estuary beginning in 1976. Comparable RMP stations that are still monitored include Pinole Point, Red Rock, Yerba Buena Island, Alameda, Redwood Creek and Dumbarton Bridge. Biomonitoring using bivalves has been thoroughly described in the literature (Luoma and Linville, 1996; Gunther and Davis, 1997; Gunther *et al.*, 1999).

4.2 Approach

Several of the bivalve sampling locations were changed between 2002 and 2003. Based on a review of the bioaccumulation monitoring program by Applied Marine Science (AMS), three sites were discontinued from sampling in 2003. AMS recommended that 2-3 sites per bay segment were required to track long-term changes in contaminant concentrations using biomonitors. Following Technical Review Committee (TRC) approval, Napa River and Petaluma River were discontinued from the San Pablo Bay segment (3 sites remaining) and Horseshoe Bay was discontinued from the Central Bay segment (3 sites remaining). The biomonitoring study area in 2003 ranged from Coyote Creek (BA10) in the Lower South Bay to the Sacramento River (BG20) station in the northern reach of the Estuary (Figure 4.1).

In previous years, bivalves for transplanting included mussels (*Mytilus californianus*) from Bodega Head, mussels (*Mytilus edulis*) from Tomales Bay, and oysters (*Crassostrea gigas*) that were purchased from Hog Island Oyster Company in Tomales Bay. However, in 2003 the RMP began using only one transplanted bivalve mussel species, *M. californianus*, for all sampling locations. To reach this decision the RMP conducted a series of special studies to determine which species could be deployed at all stations since deployment of a single mussel species would allow for comparison of bioaccumulation of contaminants across stations in the Estuary. The bivalves tested were mussels (*M. californianus* and *M. edulis*) and oysters (*C. gigas* and *Ostreola conchaphila*). *M. californianus* and *M. edulis* were the two species that had the highest rates of survival both in the main Estuary (sites along the spine of the Estuary) and at Estuary margin sites (landward sites). A further review of this study can be found in 'Optimizing Transplanted Bivalve Studies for the Regional Monitoring Program for Trace Substances' by AMS. This report will be available in May 2005. Please contact SFEI for status of this report.

Resident clams (*Corbicula fluminea*) were collected from the Sacramento and San Joaquin River stations. Clams from these stations are not transplanted and therefore are exposed to contaminants across their lifetime.

Bivalves were deployed at a total of 9 fixed mooring stations within the Estuary for a period of 90-100 days. Bivalve monitoring was conducted during the dry season months (June through August). The RMP Design Integration Workgroup determined that it is sufficient to analyze tissue concentrations in bivalves only once per year during the dry season, when Estuary conditions are more consistent on an interannual basis. The 2003 bivalve deployment marks the fourth year of annual dry season monitoring.

In 2003 all bivalves were deployed in cages. Three seasons (2000, 2001 and 2002) of side-by-side deployments using a mesh bag deployment method and a cage deployment method showed that the cage deployment method had similar survival rates to the bag method. Cages were also very effective at decreasing bivalve predation at certain sites. Another aspect of the 2003 bioaccumulation study was the deployment of non-maintained cages, in addition to the maintained cages (maintained approximately 45 days into deployment) at all deployment sites to determine if the mid-deployment maintenance cruise was necessary. This pilot study is ongoing and analysis will be completed with the 2004 monitoring results.

Analyses of trace organic contaminant concentrations and bivalve condition were only completed on *M. californianus* that were deployed in maintained cages. Bivalve percent survival was measured in both the maintained and the non-maintained cage deployments. All bivalves collected from reference stations were kept on ice and deployed within 72 hours.

4.2.1 Methods

Table 1.4 in the Introduction lists the parameters measured in bivalve tissue samples in 2003. Section5 – *Description of Methods* summarizes field and analytical methods and provides information on additional RMP sampling and analysis reference documentation. Data are available for downloading via the RMP website using the Web Query Tool at http://www.sfei.org/rmp/data.htm.

Samples were analyzed for synthetic trace organics, which included PAH, PCBs, pesticides, polybrominated diphenyl ethers (PBDEs), nitro and polycyclic musks, phthalates, p-nonylphenol and triphenylphosphate. PBDEs, phthalates, p-nonylphenol, triphenylphosphate, and musks were added in 2002 based on the findings of an RMP special study

(http://www.sfei.org/rmp/reports/unidentified_contaminants/unidentifiedcont.pdf) that identified new organic contaminants from chromatograms generated from previous RMP monitoring efforts.

Contaminant concentrations in tissue of transplanted bivalves were measured before deployment (T-0 or background concentrations) and at the end of the 90-100 day deployment period. Resident clams from the Sacramento River and San Joaquin River stations were collected at the end of the three month period. Survival and growth indices were also measured on the deployed bivalves. Because of potential individual variability in contaminant concentrations and the small tissue mass, composites of up to 30 individual bivalves were made for each species from each deployment site for analyses of trace contaminants. RMP tissue concentrations are reported in ng/g dry weight or ppb. Conversion to dry weight reduces the variability in results that could occur due to variable moisture and lipid content of the samples.

Calculated Measures of Bioaccumulation

Accumulation Factors

In addition to reporting the measured tissue concentrations prior to and following deployment, this report uses accumulation factors (AF) to indicate accumulation or depuration (loss of contaminants from bivalve tissue by metabolism) during the 90-100 day deployment period (Table 4.2). The accumulation factor is calculated by dividing the final contaminant concentration in transplants by the initial bivalve concentration (T-0) for that species. For example, an accumulation factor of 1 indicates that the concentration of a specific contaminant at the end of the deployment period was the same compared to the T-0 contaminant concentration. AFs less than 1 indicate that the bivalves decreased in contaminant concentration during the deployment period due to depuration, while an AF greater than 1 indicates accumulation. Accumulation factors are not calculated in C. fluminea for the Sacramento and San Joaquin River stations, since they were collected as resident species at these stations and not transplanted, like mussels, from a background site outside of the Estuary. For this calculation, if an analyte's concentration was determined to be below the Method Detection Limit (MDL) and reported as not detectable (ND), then one-half of the average MDL was assigned as the final concentration. However, if both the final and initial (T-0) concentrations were ND, then the accumulation factor was not determined.

4.2.2 Biological Growth and Survival

In 2002, the RMP began to measure the mean growth of the deployed bivalves over the 90-100 day deployment period. The growth mean is a measure of growth of the bivalves at a particular station in comparison to the initial T-0 mean dry weight. The growth of each mussel was estimated by subtracting the T-0 mean dry weight from the dry weight

of the individual mussel. The mean of the difference for all the individuals at a particular station (up to 30 individuals/site) was then determined to give the growth mean for that station. A negative growth mean indicates that the deployed bivalves had reduced weight in comparison to the T-0 sample. A negative growth mean could indicate stress in the organism or weight loss due to reproductive processes. Percent lipid and percent moisture measurements were also made before and after deployment.

Percent survival was determined on both maintained and non-maintained caged bivalves. Percent survival is a measure of how many individual bivalves were alive at the end of the 90-100 day deployment period compared to the total number deployed. Mortality can occur from predation and intolerance to water column salinity and temperature regimes. Only bivalves that were alive at the end of the deployment period were included in the composites for contaminant analyses.

4.2.3 Guidelines

The RMP has used various screening values and guidelines to assess contaminant concentrations in bivalve tissue samples. Starting with the 2001 monitoring results, the RMP began using screening values (Table 4.1) developed by Brodberg and Pollock, (1999) for monitoring contaminant concentrations in finfish. These values are, on the whole, more conservative than other screening values previously used by the RMP and are also used by the Office of Environmental Health Hazard Assessment (OEHHA) in screening contaminants in shellfish and finfish for human consumption advisories. These screening values were developed following U.S. EPA guidance (U.S. EPA, 1995) for evaluation of contaminants in fish tissue in a study from two California Lakes and are defined as concentrations of target analytes in fish or shellfish tissue that are of potential public health concern (Brodberg and Pollack, 1999). Exceedance of screening values is considered an indication that more intensive site-specific monitoring and/or an evaluation of human health risk should be conducted. The calculations were based on a 70 kg adult, using a cancer risk of 10⁻⁵ for carcinogens. A consumption rate of 21 grams of fish per day was used. Although these screening values are applied to human consumption of contaminated fish/shellfish, exceedance of the screening value may also indicate the potential for health risks in wildlife that consume contaminated fish/shellfish. The screening values are used for comparison purposes only and do not suggest a possible public health concern. The transplanted bivalves in the RMP are temporary residents of the Estuary and are used as indicators of bioavailable contaminants for status and trends analyses. No follow-up action is triggered when bivalve values exceed guidelines. A wet-to-dry weight conversion was applied to the guideline values for comparative purposes, using a multiplication factor of 7, which is based on average moisture content in bivalves of 85% (SFEI, 1998).

4.3 Results and Discussion

Bivalve monitoring is conducted in the Estuary to measure contaminant accumulation during the dry season as a measure of the potential bioavailability of contaminants of concern. The combination of recent special studies to improve deployment methods and evaluate salinity tolerances of deployed species has helped the RMP refine the bivalve monitoring component of the Status and Trends program. The RMP will continue to use the study results to adjust future bivalve monitoring effort. There were no bivalves available for analysis at the San Pablo Bay site (BD20) due to a lost mooring.

4.3.1 Spatial Distributions

The 2003 sampling period is the first year where one mussel species was deployed at all stations in the Estuary with the exception of Sacramento River (BG20) and San Joaquin River (BG30) stations where resident clams were collected.

Trace Organics

In 2003, transplanted bivalves from Coyote Creek, Dumbarton Bridge, Redwood Creek, Alameda, and Yerba Buena Island stations, exceeded the total PCB concentration screening value (Table 4.2 and Figure 4.2). All other analytes for other stations were below their respective screening values. Note that transplanted bivalves are deployed in the Estuary for a 90-100 day period (except stations BG20 and BG30) and therefore are indicators of bioavailable contaminant accumulation over this time period. High contaminant concentrations indicate the potential for contaminant exposure in the Estuary for resident organisms. Also note that the bivalves collected from the San Joaquin and Sacramento River sites integrate contaminants over a longer time-scale than do the transplanted bivalves. *Corbicula* can live up to seven years (Hall, 1984) but a more average life span is 3-4 years (Sites et al., 1995; McMahon, 1991). Ages of the *Corbicula* collected for this study are not known.

Accumulation factors ranged from 1.0 to 66 for all species and all analytes. The highest accumulation factor, indicating accumulation, was for total PCBs at the Dumbarton Bridge and Redwood Creek stations. The highest calculated AFs were for total PCBs at Dumbarton Bridge, Redwood Creek, Red Rock and Alameda stations. The only trace organic analytes detected in resident clams from the San Joaquin and Sacramento River stations were PCBs, DDTs, and PBDEs. PBDEs (total) (Figure 4.5) ranged from ND (not detected) to 104 ppb with the highest PBDE concentrations found in resident *Corbicula* from the San Joaquin and Sacramento River stations. The PBDE AF at Davis Point decreased by a factor of four from 2002 (AF=60 in 2002 and AF=15 in 2003) possibly due to the deployment of *M. californianus* in 2003 while in 2002 *C. gigas* was deployed. Coyote Creek, which also had *C. gigas* deployed in 2002, did not show this magnitude of change in accumulation with the new species.

Chlordanes (total) were only found in bivalves transplanted at the Redwood Creek, Coyote Creek, Dumbarton Bridge and Yerba Buena Island sites. All other bivalves were below the detection limit. DDTs (total) (Figure 4.3) ranged from 14.3-94 ppb with the two highest concentrations found at the Sacramento and San Joaquin River sites. PCBs (total) ranged from 3.76-212.16 ppb with the two highest concentrations found at Dumbarton Bridge and Redwood Creek. Dieldrin concentrations (Figure 4.4) ranged from ND-9.4 ppb. All stations were below the SV of 14 ppb. Endrin, gamma-HCH, heptachlor epoxide and hexachlorobenzene were not detected at any site. There are a limited number of or no screening values for most of the trace organic analytes measured by the RMP including PBDEs. The emerging contaminants analyzed for 2003 (phthalates, nonylphenol, triphenylphosphate, and musks) were still undergoing analysis at the time of publication. As soon as the data have been approved by the RMP they will be made available to the public. The 2003 PAHs, as well as the 2002 PAHs, are also not available due to an ongoing review of the data and analytical processes. The data will be made available once the analytical issues have been resolved.

Growth and Survival

2003 marks the first year that all transplanted bivalves were all one species. *M. californianus* was deployed at all transplant stations. 2003 was also the first year that all bivalves were deployed in cages. After analyzing side-by-side deployment methods of mesh bags vs. cages it was decided that cages would be the optimal deployment method since caged bivalve survival was similar to mesh bag survival and bivalve mortality due to predation was lower in the caged samples. Both maintained and non-maintained cages where deployed in a side-by-side study. Maintained cages are cleaned once during the deployment period, mid way through the deployment period, while non-maintained cages are not cleaned. Survival for both maintained and non-maintained cages were all above 90% suggesting no major differences in survival based on maintenance for 2003. A full analysis of the maintenance study will be completed with the analysis of the 2004 bivalve data which will include 3 years of side-by-side data.

4.3.2 Bivalve Trends

Long-term trend evaluation has been deferred to the RMP's synthesis of information from the past ten years (1993-2002) of bivalve tissue monitoring in the Estuary.

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Table 4.1. California Screening Values calculated according to U.S. Environmental Protection Agency guidance (U.S. EPA, 1995). Calculations were based on a 70 kg adult and a fish consumption value of 21 g/day. Guidelines were specifically developed for a California lake fish study and should be used as reference values in bivalve tissue concentrations only (Brodberg and Pollack, 1999). No follow-up actions are associated with bivalve tissue concentrations above these screening values. Screening values have been converted to dry weight using a conversion factor of 7, which is based on an 85% average moisture content in bivalves.

PARAMETER	Screening Value (dry weight)	unit
Cd	21	ppm
Se*	14	ppm
Dieldrin	14	ppb
Endrin	7,000	ppb
gamma-HCH	210	ppb
Heptachlor Epoxide	28	ppb
Hexachlorobenzene	140	ppb
Total Chlordanes (SFEI)	210	ppb
Total DDTs (SFEI)	700	ppb
Total PCBs (SFEI)	140	ppb

* The RMP uses the selenium screening value recommended by the California Office of Environmental Health Hazard Assessment from Fan et al., 1988. All other analyte screening values are from the California lake fish study (Brodberg and Pollack, 1999). The Se SV for the lake study is 140 ppm dry weight. Table 4.2. 2003 bivalve accummulation factors (AF) and final contaminant concentrations (ng/g dry weight) that were above the method detection limit (MDL) and had screening values. Endrin, gamma-HCH, Heptachlor Epoxide, and Hexachlorobenzene were not detected (ND) at all sites. If both the final concentration and T-0 reference concentrations were ND, no AF was calculated and the result is reported as ND. If either the final concentration or the T-0 was ND, then 1/2 the MDL was used to calcualte the AF. Results are in ng/g dry weight. Growth mean (g) is determined by subtracting the average. T-0 dry weight from each individual bivalve at each station and then taking the mean of the differences.

ND=not detected, NA=not availablele=analyte was detected but not quantifiable therefore value is estimated.

The mooring for BD20 was lost and there is no analytical data for this site in 2003.

									Dieldri	n	Ch	Sum	S	um DTs	S P(ium CBs	Sum PBDF	s
					ırvival	oids	oisture	⁄th Mean		iiiiiiiiiiiiiiiiiiiiiiiiiiiiiiiiiiiiii		<u> </u>		±		H H		lt It
CODE	SITE NAME	DATE	NUMBER	MATRIX	% Sı	% Lip	% Mc	Grow	ΑF	Resu	AF	Resu	AF	Resu	ΑF	Resu	ЧF	Resu
BA10	Coyote Creek	9/25/2003	2003-09	MCAL	100	4.27	90.3	-0.3788	1.232227488	le 7.8	2	4.39	2	32	37	141	19.4245283	31
BA30	Dumbarton Bridge	9/25/2003	2003-09	MCAL	99	6.37	88.1	-0.1072	1.347551343	le 8.53	7	14.3	2	30	56	212	14.16352201	23
BA40	Redwood Creek	9/25/2003	2003-09	MCAL	NA	7.01	88.2	0.046	1.344391785	le 8.51	4	8.96	2	25	56	212	24.45283019	39
BB71	Alameda	9/24/2003	2003-09	MCAL	96	8	85.3	0.2664	1.069510269	le 6.77	NA	ND	2	28	46	173	18.8490566	30
BC10	Yerba Buena Island	9/24/2003	2003-09	MCAL	90	8.89	84.2	0.6256	1.104265403	le 6.99	3	7.2	2	30	53	199	27.47798742	44
BC61	Red Rock	9/24/2003	2003-09	MCAL	98	8.29	85.3	0.244	1.206951027	le 7.64	NA	ND	2	30	24	89	14.28930818	23
BD20	San Pablo Bay				NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
BD30	Pinole Point	9/26/2003	2003-09	MCAL	91	6.95	87.6	0.066	1.197472354	le 7.58	NA	ND	2	33	18	68	10.12578616	16
BD40	Davis Point	9/26/2003	2003-09	MCAL	98	6.08	90.4	-0.256	1.488151659	le 9.42	NA	ND	1	19	13	50	14.71069182	23
BG20	Sacramento River	8/18/2003	2003-09	CFLU	NA	9.64	91.6	NA	NA	ND	NA	ND	NA	94	NA	107	NA	96
BG30	San Joaquin River	8/18/2003	2003-09	CFLU	NA	8.32	94.4	NA	NA	ND	NA	ND	NA	67	NA	135	NA	104
T-0	Bodega Head	5/19/2003	2003-09	MCAL	NA	5.22	87.3	NA	NA	le 6.33	NA	ND	NA	14	NA	4	NA	ND

¹ T-0 samples were collected from the reference/source sites and archived for later growth & chemical analysis

Table 4.3. 2003 bivalve percent survival by site and species for maintained caged deployment methods and unmaintained caged methods.

Species include: transplanted mussels *Mytilus californianus* (MCAL) and resident clams *Corbicula fluminea* (CFLU).

SITE_CODE	SITE_NAME	SPECIES	COLLECTION_DATE	Survival per Species Caged Maintained (%)	Survival per Species Caged Unmaintained (%)
Coyote Creek	BA10	MCAL	9/25/2003	96	90
Dumbarton Bridge	BA30	MCAL	9/25/2003	100	100
Redwood Creek	BA40	MCAL	9/25/2003	98	98
Alameda	BB71	MCAL	9/24/2003	99	100
Yerba Buena Island	BC10	MCAL	9/24/2003	91	98
Red Rock	BC61	MCAL	9/24/2003	98	93
San Pablo Bay	BD20	MCAL		NA	NA
Pinole Point	BD30	MCAL	9/26/2003	96	98
Davis Point	BD40	MCAL	9/26/2003	90	90
Sacramento River	BG20	CFLU	8/18/2003	NA	NA
San Joaquin River	BG30	CFLU	8/18/2003	NA	NA



Figure 4.1 Map of 2003 RMP Status and Trends bivalve monitoring sites at 10 locations in the San Francisco Estuary.

Mytilus species were deployed in cages for a three-month period at mooring locations within the Estuary, while resident *Corbicula* species were collected using a trawl at the end of the deployment period.



Figure 4.2 Bivalve tissue concentrations for Total PCBs at 10 sites sampled in the San Francisco Estuary in 2003. Blue triangles denote concentrations above the screening value (140 ng/g).





All concentrations were below the screening value (700 ng/g).





All concentrations were below the screening value (14 ng/g).



Figure 4.5 Bivalve tissue concentrations for Total PBDEs at 10 sites sampled in the San Francisco Estuary in 2003. There is no screening value for PBDEs.



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5.0 DESCRIPTION OF METHODS

Nicole David, Daniel Oros, Sarah Lowe, Cristina Grosso

The purpose of this chapter is to provide brief descriptions on the sample collection and analytical methods used in Status and Trends Monitoring component of the Regional Monitoring Program for Trace Substances (RMP) and to highlight any changes that may occur each year. Water, sediment and bivalve tissue samples are collected and analyzed for trace elements, trace organics, and conventional water and sediment quality parameters, and tested for sediment toxicity. Information on sampling methods and analytical procedures for RMP pilot and special studies and fish contamination monitoring are provided in separate technical reports available on the RMP Reports and Publications page at http://www.sfei.org/rmp/reports.htm, or by contacting the RMP Manager.

Other resources related to the RMP field and analytical methods include:

- 1. <u>Field Sampling Manual for the Regional Monitoring Program for Trace</u> <u>Substances</u> provides standard operating procedures for sampling of water, sediment, and bivalve tissue (http://www.sfei.org/rmp/documentation/fom/FOM2001.pdf).
- <u>Quality Assurance Project Plan for the Regional Monitoring Program for Trace</u> <u>Substances</u> describes the quality assurance and quality control (QA/QC) protocols and requirements for RMP field sampling and laboratory analyses

(http://www.sfei.org/rmp/reports/1999 QAPP/1999 QAPP.pdf).

3. Standard Operating Procedures for each analytical laboratory are on file at SFEI.

5.1 Field Sampling Methods

Logistical planning and field sampling for the RMP is implemented by Applied Marine Sciences Inc. who have systematically improved the field sampling logistics and sampling methods each year since the inception of the program in 1993.

5.1.1 Water Sampling

One of the RMP objectives is to evaluate if water quality guidelines are being met in the Estuary. Therefore, the sampling and analytical methods must be able to detect and, when analytically possible, quantify substances below guideline levels. In order to attain the low detection limits used in the RMP, ultra-clean sampling methods are used in all trace metal and organic sampling procedures (Flegal and Stukas, 1987; U.S. EPA, 1995).

Water samples are collected approximately one meter below the water surface using peristaltic and gear-driven pumps. The sampling intake ports for both the trace organic and trace element samplers are attached to aluminum poles that are oriented up-current from the vessel and upwind from equipment and personnel. The vessel is anchored and the engines turned off before the sampling begins. Total and dissolved fractions of Estuary water are collected for trace element analyses. Particulate and dissolved fractions are collected for trace organics analyses.

Collection of Samples for Trace Organics

Background

The RMP used a polyurethane foam plug sampler to collect water for trace organics analyses during the first four years of the Program (Risebrough *et al.*, 1976; de Lappe *et al.*, 1980, 1983) and phased in a new, modified, commercially available resin extraction sampler in 1996, beginning with side-by-side comparisons of both sampling systems. XAD resins have been used throughout the world to measure synthetic organic contaminants in both water and air (Infante *et al.*, 1993). The sampler comparisons were continued in 1997, and results from both years are presented in the RMP 1997 Annual Report (SFEI, 1999).

Since 1997, an Axys Infiltrex system (Axys Environmental Systems, Ltd., Sidney, B.C.) has been used to collect all RMP water samples for analysis of trace organic contaminants. It consists of a constant-flow, gear-driven positive displacement pump, 1/2 inch Teflon® tubing, 1 µm glass fiber cartridge particulate filter, and two parallel Teflon® columns filled with XAD-2 resin with a particle size range of 300-900 µm. Amberlite XAD-2 resin is a macroreticular, styrene-divinyl benzene copolymer, nonionic bead, and each bead is an agglomeration of microspheres. This sponge-like structure offers excellent physical and chemical stability. The discrete pores allow rapid mass transfer of analytes, and the mesh size ensures very little, if any, back pressure during use. The hydrophobic nature of the resin leads to excellent capability of concentrating hydrophobic contaminants.

Collection of Particulate and Dissolved Fractions

To remove large debris that may interfere with sample collection, the sample water is first passed through a coarse screen before the Teflon® intake line. Particles greater than 140 μ m are removed by a second inline pre-filter. The water then passes through the pump head and a pressure gauge, before it goes through a four-inch diameter, wound glass fiber filter (1 μ m). Flow may be redirected without interruption to a second installed filter if the first filter becomes clogged. Material retained on the glass fiber filter (or filters) is designated the particulate fraction. After passing through the filter, the water is split and routed through two Teflon® columns, packed with 75 mL of XAD-2 resin. Two filters are used simultaneously to increase the flow to approximately 1.3 L/min. The compounds adsorbed to the XAD-2 resin are designated as the dissolved fraction. Lastly, the water passes through a flow meter and out the exit tube, where the extracted water volume (100 L per sample) is verified by filling five calibrated 20 L carboys.

Collection of Field Blanks for Trace Organics

Field blanks are taken for both the resin columns and the glass fiber filters. The two column blanks are collected by leaving both ends of a column open while the filled sample columns are being loaded into the sampler. Similarly, the two glass fiber filter blanks are collected by exposing a filter to the air while loading the sample filters into the cartridges. The field blanks receive the same analytical treatment in the laboratory as the field samples.

Collection of Samples for Trace Metals

Collection of Total and Dissolved Fractions

For trace metals, water samples are collected using a peristaltic pump system equipped with C-Flex tubing in the pump head. Sample containers are filled on deck on the windward side of the ship to minimize contamination from shipboard sources (Flegal and Stukas, 1987). Filtered (dissolved fraction) water samples are obtained by placing an acid-cleaned polypropylene filter cartridge (Micron Separations, Inc., 0.45 µm pore size) on the outlet of the pumping system. Unfiltered (total) water samples are pumped directly into acid-cleaned containers. Prior to collecting water, several liters of water are pumped through the system, and sample bottles are rinsed five times with site water before filling. The bottles are always handled with polyethylene-gloved "clean hands". The sample tubing and fittings are acid-cleaned polyethylene or Teflon[®], and the inlets and outlets are kept covered except during actual sampling. Samples are acidified within two weeks in a Class 100 trace metal clean laboratory.

For the analysis of total mercury, water samples (500 mL, minimum) are collected into a Hg-clean Teflon bottle, then double-bagged in zip-lock bags. The samples are immediately placed in a cooler with dry ice. Samples are stored frozen until analysis. For methylmercury analysis, PFA Teflon (125 to 500mL) are used for sample containers. Samples may be stored frozen or not and preserve with 0.2% sulfuric (v/v). They should be stored in the dark but will last up to 1 yr. sitting out on the counter top.

Collection of Field Blanks for Trace Metals

During the collection of one sample, a pre-cleaned bottle filled with a diluted acid is opened and exposed to the air. Field blanks are collected during the sampling of both the total (unfiltered) and dissolved (filtered) fractions and receive the same analytical treatment in the laboratory as the field samples.

Collection of Water Quality Samples

Samples for conventional water quality parameters are collected using the same apparatus as for trace metals. However, containers are rinsed only three times, and the "clean hands" procedure is unnecessary.

Collection of Aquatic Bioassay Samples

In the previous year, aquatic bioassays were only conducted for shallow sites in the Estuary, and it was also decided to reduce the sampling years for aquatic toxicity testing. No aquatic bioassays were conducted in 2003, and the Technical Review Committee will determine a new sampling frequency at the end of 2005.

5.1.2 Sediment Sampling

Sediment sampling is conducted using a Young-modified Van Veen grab with a surface area of 0.1 m². The grab is made of stainless steel, and the jaws and doors are coated with Dykon[®] (formerly known as Kynar[®]) to achieve chemical inertness. All scoops, buckets, and stirrers used to collect and homogenize sediments are also constructed of Teflon[®] or

stainless steel coated with Dykon[®]. Sediment sampling equipment is thoroughly cleaned at each sampling location prior to each sampling event. In order to further minimize sample contamination, personnel handling samples wear gloves.

If the sediments at a station are considerably fine, plastic floats may be attached to the grab frame and secured so they do not interfere with grab operation. Likewise, if the sediments are considerably coarse, weights are added to the grab frame to assist penetration of the sediments. To ensure the quality of the sediment samples, each grab must satisfy several criteria in order to be accepted: complete closure, no evidence of sediment washout through the doors, even distribution of sediment in the grab, minimum disturbance of the sediment surface, and minimum overall sediment depth appropriate for the sediment type.

Collection of Sediment Samples

Two grabs are taken at each site, and sediment sub-samples are removed for toxicity tests. Overlying water is drained off an accepted grab, and using pre-cleaned glass cores, three 5 cm deep cores are taken from each side of the grab. Starting in 2002, porewater hydrogen sulfide analyses of field samples were no longer performed in the S&T component of the RMP, as those data were most relevant for interpreting potential benthic community effects.

The remaining top 5 cm of sediment is scooped from each of two replicate grabs and mixed in a compositing bucket to provide a single composite sample for each site. Between sample grabs, the compositing bucket is covered with aluminum foil to prevent airborne contamination. After two sediment samples have been placed into the compositing bucket, the bucket is taken into the ship's cabin and thoroughly mixed to obtain a uniform, homogeneous mixture. Aliquots are subsequently split into appropriate containers for sediment quality, trace metal, trace organics, and toxicity analyses for archive samples.

For total mercury analysis, high density polyethylene wide mouth jars (60mL) with screw-cap lids were used. New bottles/caps were soaked for one week in micro-soap to remove oils associated with manufacture. Bottles and caps were thoroughly rinsed with Tap/DI water to remove all soap residues. Jars were soaked in 6 N hydrochloric acid bath for at least one week. Bottles were rinsed with ultra-pure (MQ) water 5x, to remove all acid residue and then allowed to air dry in HEPA area. The batch of jars was double bagged.

Sediment samples were collected by Applied Marine Sciences. Samples were immediately placed in a cooler with dry ice. Samples were stored frozen until analysis.

For methylmercury analysis, sampling is the most important factor influencing the accuracy and uncertainty of mmHg in sediments (Horvat, et. al., 2004). The transformation and degradation of mmHg can also occur during sample storage and pretreatment. Great care should be taken to minimize disturbance and exposure of the sediments to environmental factors that may alter the mmHg concentrations. These

factors include light, temperature and atmosphere. The following protocol may be revised depending on updated research. As there is only one mmHg analysis per sample, multiple smaller volume samples should be collected.

Sample Containers (glass is preferable)

- Borosilicate glass vials; clear 40mL, Teflon lined solid screw-caps (I-Chem 100)
- Or Polypropylene (PP) screw cap jars, 30mL
- Sample Container Preparation
- New glass vials: rinse with deionized (DI) water and oven-dry.

• Recycled glass vials: scrub clean w/ Nessler tube brush, DI rinse (5x), Formula 409 soak (overnight), DI rinse (5x), oven-dry

• PP jars: acid clean in weak HCl (reagent grade) acid bath, DI rinse (5x), air or oven dry. Sample Collection

- Collect bottom sediments with a Van Veen grab; single grab only, do not mix.
- Obtain 5+ samples from center portion of the undisturbed sediment grab.
- Quickly scoop sediment from top 5 cm into the containers.
- Label vials and individually bag in ziplock bags.
- Freeze immediately. Keep samples dark and frozen until analysis.

Collection of Sediment Cores for Toxicity Sampling

Solid-phase amphipod and bivalve elutriate sediment toxicity tests were performed for sediment toxicity.

Eohaustorius % survival and *Mytilus* % normal development tests (including ammonia and H₂S measurements) were performed on 3 liters of sediments sampled from 27 sites:

- 20 random sites (1/2 of the random sampling sites; one from each panel in each segment)
- 7 fixed historical samples (BG20, BG30, BF21, BD41, BC11, BA41, & BA10).

2 amphipod and 3 bivalve TIEs, and TIE chemistry studies, were included on samples that showed the most toxicity (e.g. less than \sim 50 % survival or normal development (for amphipod and bivalve tests respectively).

Solid-phase samples were prepared as described in the amphipod protocols (U.S. EPA 1994, U.S. EPA 2000). Sediment was re-homogenized in the sample jar with a polypropylene spoon, and then distributed to replicate test beakers. Overlying water was added to the test containers, and sediment and overlying water was allowed to equilibrate overnight before the amphipods were added.

Elutriate solutions were prepared by adding 50 grams of sediment to 200 mL of Granite Canton seawater in a clean 250 mL borosilicate glass jar with a Teflon-lined lid (1:4 volume to volume ratio; U.S. EPA/ACOE 1991). The 250 mL elutriate mixture was shaken vigorously for 10 seconds and then allowed to settle for 24 hours (Tetra Tech 1986). The elutriate solution was pipetted into replicate containers for testing.

Mussel test containers were inoculated with 231 ± 16 (n = 5 initial counts) embryos for a 48-hour exposure. All mussel larvae were counted in each test container at the end of the exposure to determine the percentage of embryos that developed into live normal larvae. This value was determined by dividing the observed number of live embryos inoculated at the beginning of the test.

5.1.3 Bivalve Tissue Sampling

Source of Bivavles

Bioaccumulation is evaluated by collecting mussels (*Mytilus californianus*) from uncontaminated "background" sites of known chemistry and deploying these bivalves at 12 locations in the Estuary for approximately 100 days. Resident clams (*Corbicula fluminea*) are also collected from one site on the Sacramento River and another site on the San Joaquin River. Bivalves are deployed once each year during the dry season, usually in June. Starting in 2003, *Mytilus californianus* was the only transplanted species in the Estuary to ensure higher comparability between sites. *Mytilus californianus* is a salt tolerant species that can also handle salinities as low as 15ppt (Bayne, 1976). Trace element and trace organic tissue concentrations are more comparable throughout the San Francisco Estuary when they are accumulated by the same species because metabolism rates are similar in all deployed organisms.

Mussels (*Mytilus californianus*) are collected from Bodega Head and stored in running seawater at the Bodega Marine Laboratory until deployment at stations in San Pablo Bay, Central Bay, South Bay, and Lower South Bay, which are expected to have the highest salinities. *Mytilus californianus* will survive short-term exposure to salinities as low as 5 ppt (Bayne, 1976).

Resident freshwater clams are now collected from near the RMP historic bivalve deployment sites in the Sacramento River and San Joaquin River. Resident clams are collected using a clam dredge approximately two feet wide by three feet long and 50 pounds in weight. The dredge is deployed from a boat and is dragged along the bottom. When brought to the surface, the clams are placed into a clean plastic container and packaged for organics analysis.

Deployment of Transplanted Bivalves

160 mussels are randomly allocated and placed into predator resistant cages for deployment. Animals of approximately the same shell length are used (49-81 mm). The same number is also used for the reference (time zero) sample, which is analyzed for tissue condition before deployment.

A pilot study conducted in 2001 and 2002 showed that survival rates were generally higher in cages than in the originally used mesh bags. Based on these results, deployment in mesh bags was discontinued in 2003. The cages now used are fairly similar to the original bags with rigid plastic mesh around sections of PVC. The mesh overlapped around itself to keep predators from slipping through any gaps between the edges. After the cages are built they are soaked in water for at least a day to remove any potential signal associated with the adhesives used for the construction.

At each site, a line runs from the bottom of the fixed structure out to the bivalve mooring, which consists of a large screw (earth anchor) that is threaded into the bottom and is associated with pilings or other permanent structures. A large subsurface buoy is attached to the earth anchor by a 1-2 meter line. The bivalves are in enclosures (mesh bags or cages) attached to the buoy line, which keeps the bivalves off the bottom to prevent smothering. In one hundred and fifty individual deployments, loss of a mooring has occurred on only two occasions, probably due to being ripped out by a vessel anchor. Mooring installation, bivalve deployment, maintenance, and retrieval are all accomplished by SCUBA divers.

Maintenance of Transplanted Bivalves

The deployed samples are checked approximately 50 days after deployment to ensure consistent exposure. Moorings and enclosures are checked for damage and repaired if necessary, and fouling organisms are removed. The comparison between maintained cages and un-maintained cages continued in 2003 to evaluate whether results regarding survival rates are significantly different and to determine whether the maintenance work can be discontinued.

Retrieval of Transplanted Bivalves

Upon retrieval, the bivalve enclosures are placed into polyethylene bags and taken to the surface. On the vessel, the number of dead organisms is recorded. Twenty percent of the live organisms are allocated for condition measurement, and the remainder is equally split for analyses of trace metal and organic compounds. Bivalves used for trace organic analyses are rinsed with reagent grade water to remove extraneous material, shucked using a stainless steel knife (acid-rinsed), and homogenized (until liquefied) in a combusted mason jar using a Tissumizer[®] or Polytron[®] blender. Bivalves used in trace element analyses are shucked with stainless steel knives, and the gonads are removed. The remaining tissue is rinsed with ultrapure water and placed in acid-cleaned, plastic coated, glass jars. The sample is then homogenized (until liquefied) using a Brinkmann homogenizer equipped with a titanium blade.

Based on findings by Stephenson (1992) during the RMP Pilot Program, bivalve guts are not depurated before homogenization for tissue analyses, although the gonads are removed from organisms for trace metal analyses. With the exception of lead and selenium, no significant differences exist in trace metal concentrations between mussels depurated for 48 hours in clean Granite Canyon seawater before homogenization and undepurated mussels. However, sediment in bivalve guts may contribute to the total tissue concentration for trace organic contaminants.

5.2 Laboratory Methods

For a list of analytes measured in 2003 please refer to the Table 1.4 in the Introduction. SFEI maintains SOPs for all laboratory analyses. Please contact SFEI for more details.

5.2.1 Water and Sediment Quality

No significant changes were made to the analytical methods in 2003 for water or sediment quality.

Water Quality Parameters

In 2003 conventional water quality parameters were measured by the University of California Santa Cruz, Department of Environmental Toxicology (UCSCDET) and by Applied Marine Sciences (AMS). Hardness was measured by the Union Sanitary District, which is part of the Bay Area Clean Water Agencies (BACWA).

Dissolved nutrients in samples are analyzed using the Lachat QuikChem 800 System Nutrient Autoanalyzer (Ranger and Diamond, 1994). The QuickChem methods used are:

silicates	31-114-27-1
ammonia	31-107-06-1
nitrate/nitrite	31-107-04-1
phosphate	31-115-01-3

Chlorophyll and phaeophytin are measured using a fluorometric technique with filtered material from 200 mL samples (Parsons *et al.*, 1984). Shipboard measurements for temperature, salinity, pH, and dissolved oxygen content are made using a hand-held Solomat 520 C multi-functional chemistry and water quality monitor. Dissolved organic carbon (DOC) is measured using high-temperature catalytic oxidation with a platinum catalyst (Fitzwater and Martin, 1993). Total suspended solids (TSS) are determined using method 2540D in Standard Methods for the Examination of Water and Wastewater (APHA, 1992). Hardness was determined by Method 2340C as described by the 18th Edition of Standard Methods, a titrimetric procedure using EDTA.

Sediment Quality Parameters

UCSCDET measured sediment quality parameters in 2003.

Sediment size fractions are determined with a grain-size analyzer based on x-ray transmission (Sedigraph 5100). Total organic carbon is analyzed according to the standard method for the Coulometrics CM 150 Analyzer made by UIC Inc., which determines light transmitted through a cell containing the carbon dioxide evolved from a combusted sample. Two measurements of *in situ* pH were recorded by submerging a HachTM pH probe directly into the sediment sample to approximately 1" in depth after the Van Veen grab was brought on deck. A total of four measurements were recorded for each station. Starting in 2002, porewater hydrogen sulfide analyses of field samples are no longer performed.

Conductivity, Temperature, and Depth (CTD) Casts

CTD casts are taken by AMS at each site during water, sediment, and tissue sampling. A Sea-Bird SBE19 CTD probe is used to measure water quality parameters at depths throughout the water column. At each site, the CTD is lowered to approximately one meter below the water surface and allowed to equilibrate to ambient temperature for 3 minutes. Following the sampling, the CTD is then lowered to the bottom at approximately 0.15 meters per second and raised. However, only data from the down

cast are kept. Data are downloaded onboard the ship and processed in the laboratory using Sea-Bird software.

The CTD probe measures temperature, conductivity, pressure, dissolved oxygen, and backscatter at a sampling rate of two scans per second. These data are compiled and averaged into 0.25 m depth bins during processing. At this time, salinity (based on conductivity measurements), and depth (based on pressure) are calculated measures. Although the CTD data are not included in the 2003 RMP Monitoring Results, SFEI maintains these data in a database. Data are available upon request.

5.2.2 Trace Elements

Starting in 2001/2002 UCSCDET's analytical methods for water trace metals changed as described below. Tissue trace metals were not analyzed in 2003 as the Redesign Workgroup decided to reduce analyses to every five years.

Analysis of Water Samples

As in previous years, trace metals analyses were conducted by UCSCDET and Brooks Rand Ltd. (BRL). UCSCDET used ICP-OES analysis for Fe and Mn and ICP-MS analysis for Cu, Ni, Zn, Cd, Co,Pb, and Ag in 2003. Methods are described below.

Sample Preservation:

Within one week of collection, samples are acidified to ~ 24 mM with trace metal grade hydrochloric acid (HCl).

Ultraviolet Digestion:

The field and QA (blanks, reference materials) samples are oxidized with ultraviolet (UV) radiation to 'digest' any organo-metallic complexes.

Inductively-coupled plasma - optical emission spectroscopy (ICP-OES) analysis for Fe and Mn:

The irradiated field and QA samples are analyzed on the Perkin Elmer ICP-OES (model 430 DV) for Fe and Mn; although UV-digestion is not required for these elements.

Inductively-coupled plasma - mass spectrometry (ICP-MS) analysis for Trace Metals (Cu, Ni, Zn, Cd, Co, Pb, Ag):

The UV-oxidized undiluted samples samples are analyzed directly by ICP-MS. The metals of interest 'stick' on the conditioned column and are eluted off with specific pH buffer prior to entering the analytical system. A cationic resin is used to retain Cu, Ni, Zn, Co, Cd and Pb; an anionic resin column retains Ag.

In some instances, reported dissolved metal concentrations are higher than total (ostensibly including dissolved and particulate fractions) metal concentrations. This is due to expected analytical variation, which is proportionally larger at concentrations near the detection limits. Such results should be interpreted as no difference between dissolved and total concentrations, or that the total fraction of metals is in the dissolved phase.

Arsenic and selenium are analyzed by BRL. The same methods as in the past are employed. Samples are analyzed by both U.S. EPA Method 200.9 Graphite Furnace Atomic Absorption (GFAA) and by Brooks Rand SOP BR-0020 Hydride Generation Atomic Absorption (HGAA). The U.S. EPA method includes the digestion of samples with nitric acid and hydrochloric acid and heating by U.S. EPA Method 200.2. Samples are analyzed by Stabilized Temperature Platform-Graphite Furnace Atomic Absorption (STP-GFAA) Spectrometry by U.S. EPA Method 200.9. The Brooks Rand method uses sample aliquots digested using an 80:20 HNO₃:HClO₄ acid mixture with heating. Analysis is performed using hydride generation with NaBH₄ addition, cryogenic trap precollection, H₂/Air flame quartz furnace decomposition, and Atomic Absorption (HGAAS) detection.

Total Mercury Analysis in Water Samples

In 2003, total mercury analysis of water samples was conducted by UCSCDET. Samples were collected in acid-cleaned Teflon (PFA) bottles.

Sample digestion and analysis is accomplished utilizing a modified EPA 1631 method. Samples are digested by 24 hour oxidation using 0.2N bromine monochloride. Analyses of digests are performed by tin-chloride reduction, gold-amalgamation, and detection by cold vapor atomic fluorescence spectrometry.

Methylmercury Analysis in Water Samples

Methylmercury Separation from Water by Distillation

Prior to analysis of MeHg by ethylation, separation of MeHg from the sample matrix is required to reduce interferences during derivitization, particularly from chloride and organic matter. The method outlined below is appropriate for seawater or estuarine samples with sample concentrations as low as roughly 10pg/L.

Samples are distilled by heating the solution to a low boil in acid (and chloride) under inert gas in Teflon vessels. Steam is released through Teflon lines and distillate is trapped in receivers chilled on ice. Matrix modifiers may be added to distillations for some sample types. This method is based on Horvat et al. (1993a).

Note:

For samples with low dissolved organic carbon or low ionic strength as well as sulfidic or freshwater samples, additional manipulations are performed to improve extraction.

Analysis of Methylmercury by Aqueous Phase Ethylation

UC-Santa Cruz WIGS Laboratory Standard Operating Procedure for the Determination of Methyl Mercury by Aqueous Phase Ethylation Room Temperature Trapping, Followed by Gas Chromatography Separation and Cold Vapor Atomic Fluorescence Spectrometry Detection (GC-CVAFS).

Scope and Application:

This method may be used to determine methylmercury (MeHg) concentrations in a variety of matrices, including water, sediment, and tissue. Because of potential chloride

interference at the part per million level, and because the aqueous phase must be adjusted to a specific pH in this method, extraction or distillation methods are usually required to remove MeHg from the original matrices before use of this method.

Summary of Method:

The pH of the analyte solution is adjusted to 4.9 using acetate buffer. The solution is then ethylated using sodium tetraethyl borate (NaTEB) and allowed to react for 15 minutes. Following reaction with NaTEB the solution is purged with nitrogen gas (N2) for 15 minutes and the MeHg is collected on a Tenax trap after which tubes are dried for 15 minutes. Mercury species are thermally desorbed from the Tenax trap, separated using a gas chromatography (GC) column, reduced using a pyrolytic column, and detected by cold vapor atomic fluorescence spectrometry (CVAFS). The method is based on the Bloom and Fitzgerald (1988) method.

Analysis of Sediment Samples

In 2003, trace metals in sediment were analyzed by the City and County of San Francisco (CCSF), which is part of the Bay Area Clean Water Agencies (BACWA), and BRL. No changes were made in methodology compared to previous years.

Homogenized sediments are digested in nitric/hydrochloric acids to obtain "near-total" concentrations of trace metals using a method comparable to U.S. EPA Standard Methods (Tetra Tech, 1986) that does not decompose the silicate matrix of the sediment. Because of this, any element that is tightly bound as a naturally occurring silicate may not be fully recovered. Extracts are analyzed for silver by Graphite Furnace Atomic Absorption Spectrophotometry (GFAAS) and for aluminum, cadmium, copper, iron, manganese, nickel, lead, and zinc by inductively coupled plasma atomic emission spectrometry (ICP-AES) with cyclonic nebulization.

BRL digested sediment samples with nitric acid and hydrochloric acid and heated by EPA Method 200.2. Samples were analyzed by Stabilized Temperature Platform Graphite Furnace Atomic Spectrometry (STP-GFAA) by EPA Method 200.9. For selenium analysis, sample aliquots were digested with a HNO₃:HClO₄ acid mixture in a heated sand bath. The samples were then diluted with HCl and deionized water. The samples were reduced with NH₂-OH-HCl, heated in a water bath at 95°C for 20 minutes and then allowed to cool prior to analysis. Analysis was performed using hydride generation with NaBH₄ addition, cryogenic trap precollection, H₂/Air flame quartz furnace decomposition, and Atomic Absorption detection (HGAAS).

UCSCDET analyzed methylmercury and total mercury in sediment. High density polyethylene jars, pre-cleaned with micro-soap and hydrochloric acid, were used to collect samples for total mercury analysis. Sediment samples were freeze dried and stored until analysis. Samples were digested using a weak acid (60:40 solution of HNO₃:H₂SO₄) and oxidized with bromine monochloride (BrCl).
Analysis of sediment digests is accomplished utilizing a modified EPA 1631 method, using tin-chloride reduction, gold-amalgamation, and detection by cold vapor atomic fluorescence spectrometry.

Methylmercury in Sediment Samples

Methylmercury Separation from Sediment by Acid Digest-Organic Extraction A known mass of sediment is digested in a Teflon centrifuge tube using an acidic mixture of potassium chloride (KCl), copper sulfate (CuSO4), and sulfuric acid (H2SO4). The mixture comes in contact with added organic solvent, methylene chloride (CH2Cl2) a.k.a. dichloromethane (DCM), into which organic species, including mmHg and other organomercury species, preferentially partition. This acid-organic extraction is performed for one hour using a wrist shaker to agitate samples. After centrifugation to separate the aqueous, sediment, and organic phases, an aliquot of the organic phase is transferred to a glass centrifuge tube containing ultra-pure water for back-extraction into an aqueous phase. The organic solvent is volatilized by placing samples in a warm sand bath and bubbling with inert Hg free gas (N2 or Ar). The soluble mmHg remains in the aqueous phase. For analysis of methylmercury by Aqueous Phase Ethylation, please see above (methylmercury in water samples).

Analysis of Bivalve Tissue Samples

In previous years trace metals in bivalve tissue samples were analyzed by CCSF and BRL. However, in 2002 and 2003 trace metals in tissue were not analyzed. The next trace metal monitoring will be conducted 2006. Analytical methods described here are for informational purposes for samples from prior years.

Bivalve tissue samples are homogenized and then digested with aqua regia to obtain neartotal concentrations of trace elements. Digestion techniques are similar to the California State Mussel Watch Program (Flegal *et al.*, 1981; Smith *et al.*, 1986) and consistent with the RMP Pilot Program (Stephenson, 1992). Sample aliquots are extracted with dichloromethane using a Tissumizer[®]. Extracts are then concentrated and purified by various chromatographic techniques prior to instrumental analyses.

The trace metals are quantified by Inductively-coupled plasma - atomic emission spectrometry (ICP-AES) or Inductively-coupled plasma - mass spectrometry (ICP-MS). Selenium is quantified by hydride generation coupled with atomic absorption spectroscopy. Arsenic is analyzed by U.S. EPA Method 200.9 (stabilized temperature platform graphite furnace atomic absorption spectrometry, STP- GFAA) (U.S. EPA, 1994a). Butyltins are measured following NOAA's National Status and Trends Mussel Watch Project methods (NOAA, 1993). This technique involves extracting the sample with hexane and the chelating agent tropolone and then measuring the butyltin residues by capillary gas chromatography. Concentrations are expressed in total tin per gram of tissue dry weight.

5.2.3 Trace Organics

Since 2002, AXYS Analytical Services, Ltd. (AXYS) analyzed water samples for trace organics with the exception of diazinon and chlorpyrifos, which were analyzed by the California Department of Fish and Game – Water Pollution Control Laboratory (CDFG-WPCL). CDFG-WPCL also analyzed the tissue organics since 2002. Sediment organics were analyzed by EBMUD. The dissolved and particulate fractions were combined for all but three sites to economize the analytical costs for the "new analytes".

Analysis of Water Samples

In 2003, trace organics analyses of water samples were conducted by AXYS. Because the RMP is performance based, the analytical methods used by AXYS followed the strict protocols of the RMP's Quality Assurance Project Plan (QAPP). A brief overview of the extraction and analytical methods used for the target trace organics are described below. The SOPs that describe the laboratory methods in more detail are on file at SFEI.

Two parallel XAD-2 resin columns and one glass fiber filter contain the organic compounds extracted from 100 L of water at each site. The XAD columns and the filter samples were analyzed separately. Each XAD-2 column and filter sample was spiked with labeled quantification standards and Soxhlet extracted in solvent. The resulting extract was split into five portions for separate analyses of PAHs and Phthalates, PCBs, Diazinon and chlorpyrifos, PBDEs, OC pesticides and nonylphenol. Target concentrations were determined by isotope dilution or internal standard quantification against the labeled surrogate compounds added at the beginning of the analysis, a procedure that yields recovery corrected results. The recoveries of the labeled surrogates were determined against the labeled internal standards and were used as general indictors of data quality.

PCB Extraction: A florisil chromatographic column was used for the extraction of PCBs. The analytical procedure was in accordance with US EPA Method 1668, Revision A. Analysis was performed using a Micromass Ultima high resolution MS equipped with a Hewlett Packard 6890 GC and a CTC autosampler.

Organochlorine Pesticide Extraction: A florisil chromatographic column was also used for the extraction of chlorinated pesticides. High resolution gas chromatography/high resolution mass spectrometry (HRGC/HRMS) analysis was conducted using a VG 70 VSE HRMS equipped with a HP 5890 gas chromatograph.

PAH Extraction: Polycyclic Aromatic Hydrocarbons (PAH) were extracted, and a small portion of the original abstract was cleaned up on silica and analyzed by high resolution gas chromatography/low resolution mass spectrometry (HRGC/LCMS) using Agilent 6890N GC equipped with an Agilent 5973MSD, an Agilent 7683 Series Autosampler, and a HP Chemstation.

PBDE Analysis: For Polybrominated Diphenyl Ethers (PBDE) analyses, a portion of the extract was cleaned up using gel permeation and then separated into two fractions using a Florisil chromatographic column. The extract was further cleaned up using layered

acid/base silica and alumina chromatographic columns. The extraction and cleanup procedures were in general accordance with U.S. EPA Method 1668 Revision A, followed by instrumental analysis in accordance with AXYS Method MLA-025. Samples were analyzed by HRGC/HRMS on an AUTOSPEC ULTIMA high resolution MS equipped with an HP 6890 gas chromatograph, a CTC autosampler, and an Alpha data system running Micromass software.

Phthalate Ester Analysis: The phthalate ester analyses were conducted using the same portion of the original extract that was used for PAH analyses. The extract was cleaned up on silica and analyzed by HRGC/LRMS using either: an Agilent 5973 MSD equipped with an Agilent 6890N GC, an Agilent 7683 autosampler and a HP Chemstation; or a Finnigan Incos 50 MS equipped with a Varian 3400 GC, a CTC autosampler, and a HP Chemstation.

p-Nonylphenol Extraction and Analyses: A portion of the original extract was reserved for p-nonylphenol analysis. From each sampling site, one half of the raw XAD extract and one half of the raw filter extract were combined for p-nonylphenol analysis. The extracts were reduced to dryness and underwent non-aqueous acetylation using pyridine and acetic anhydride. Sample extracts were then loaded onto prepared 5% deactivated silica for chromatographic cleanup. Instrumental analysis was conducted by HRGC/LRMS using an Agilent 5973 mass spectrometer equipped with an Agilent 5890 gas chromatograph, a CTC autosampler, and an Agilent Chemstation data system.

Extraction and analytical methods for diazinon and chlorpyrifos were not available at the time of publication.

Analysis of Sediment Samples

In 2003 trace organics analyses of sediment samples was conducted by the East Bay Municipal Utility District (EBMUD, Oakland, CA), which is a part of BACWA. Because the RMP is performance based, the analytical methods used by EBMUD followed the strict protocols of the RMP's Quality Assurance Project Plan (QAPP). A brief overview of the extraction procedures and analyses used for the target trace organics are described below. The laboratory SOPs, which describe the methods in detail, are on file at SFEI. Sediment samples are generally analyzed based on the methods followed by NOAA's National Status and Trends Program.

Although the same analytical methods were utilized in 2002 and 2003 as in the past by EBMUD (the RMP lab for sediment organics since 1997), results for PCBs, PBDEs and OC pesticides in 2003 were below detection limits. As a result, data are not reported in 2003. Samples will be re-analyzed, and a new method with lower detection limits is in development.

Sediment Extraction: The sample was homogenized, and the mixture was then extracted using U.S. EPA Method 3545 (Accelerated Solvent Extraction, ASE). The sample extracts were then dried with anhydrous granular Na₂SO₄. Extracts were cleanup up with an alumina/copper column and concentrated to 1 ml in DCM. This extraction and

concentration procedure is applicable to the extraction of all trace organic compounds of interest in the sediment samples.

Organochlorine Pesticides and PCB Analyses: Just prior to analysis the sample extracts were exchanged to hexane and then spiked with the internal standard tetrachloro-mxylene. Organochlorine pesticides and PCBs were then analyzed using U.S. EPA Method 8080 (Organochlorine Pesticides and Polychlorinated Biphenyls by Gas Chromatography), which includes dual column gas chromatography with electron capture detection (GC-ECD).

Polycyclic Aromatic Hydrocarbons (PAH) Analyses: Just prior to analysis the sample extracts were spiked with deuterated internal standards (fluorine-d10 and benzo[a]pyrene-d12). PAHs were then analyzed using U.S. EPA Method 8270 (Semi-volatile Organic Compounds by Gas Chromatography), which was slightly modified to provide sufficient sensitivity for PAH in sediments.

PBDEs, Phthalates, and p-Nonylphenol Analyses: The organochlorines extract was used without any additional cleanup for this analysis. PBDEs, phthalates, and p-nonylphenol were analyzed using a GC-MS equipped with a DB5-MS fused silica capillary column (15 m length, 0.25 mm i.d., 0.25 µm film thickness, J&W Scientific).

Analysis of Bivalve Tissue Samples

In 2003 trace organics analyses of bivalve tissue samples was conducted by CDFG-WPCL. Because the RMP is performance based, the analytical methods used by the CDFG-WPCL followed the strict protocols of the RMP's Quality Assurance Project Plan (QAPP). A brief overview of the extraction and analyses used for the target trace organics are described below. The laboratory SOPs that describe the methods in more detail are on file at SFEI.

Tissue Extraction: Prior to extraction, bivalve tissue samples were homogenized using a Büchi B-400 homogenizer. A 10 g sample was mixed with approximately 7 g of preextracted Hydromatrix[®] until the mixture was free flowing. The mixture was then extracted using U.S. EPA Method 3545 (Pressurized Fluid Extraction). The samples were extracted a second time using the same conditions. All sample extracts were cleaned-up using a J2 Scientific GPC (Autoinject 110, AccuPrep 170, DFW-20 Fixed Wavelength Detector, 1" i.d. glass column with 70 g Bio-Beads SX-3 in 100% DCM). For pesticides, PCBs, and PBDEs the GPC purified extracts were then fractionated into 4 separate fractions using Florisil and petroleum ether (F1), 6% diethyl ether/petroleum ether (F2), 15% diethyl ether/petroleum ether (F3), and 50% diethyl ether/petroleum ether (F4). For PAHs the GPC purified extracts were further cleaned-up with silica/alumina column chromatography using DCM:pentane (1:1) as the solvent.

Organochlorine Pesticide, PCB, and PBDE Analyses in Tissue: These procedures are applicable when low parts per billion analyses are required to monitor differences between burdens in organisms from relatively uncontaminated reference areas and

contaminated areas. In addition, the procedures are applicable when low detection limits are required for the estimation of potential health effects of bioaccumulated substances.

Summary of Method

Sets of 12-16 homogenized tissue or sediment samples are scheduled for extraction by the project lead chemist. Extraction methods employed were developed and validated by the Water Pollution Control Laboratory (WPCL). Extract cleanup and partitioning methods are modifications of the multi-residue methods for fatty and non-fatty foods described in the U.S. Food and Drug Administration, Pesticide Analytical Manual, Vol. 1, 3 rd Edition 1994, Chapter 3, Multi-residue Methods, Section 303-C1. Homogenized tissue or sediment samples are removed from the freezer and allowed to thaw.

A 1-5 g (tissue homogenate) sample is weighed into a pre-weighed aluminum planchet and placed in a 70 °C oven for 48 hours to determine moisture content. A 10 g sample is mixed using a clean glass stirring rod with approximately 7 g of pre-extracted Hydromatrix 7 in a 250 mL Trace Clean Wide Mouth Jar until the mixture is free flowing. The extractor cells (maximum are placed on the ASE 200 autosampler rack and the samples are extracted with a 50/50 mixture of acetone/dichloromethane (DCM) using heat and pressure.

The extracts are dried and filtered through a 0.45 µm syringe filter into J2 Scientific AccuPrep 170 (GPC) autosampler tubes. Two milliliters each of the filtered extracts are removed and placed in a pre-weighed aluminum planchet for percent lipid determination.

The GPC autosampler tubes are then placed on the GPC autosampler for initial sample cleanup.

The cleaned-up extracts are evaporated and fractionated. The fractions are concentrated to an appropriate volume using K-D/micro K-D apparatus prior to analysis by dual column high resolution gas chromatography. A mixture of synthetic organic standards is eluted through the Florisil 7 column to determine the recovery and separation characteristics of the column.

The analysis of synthetic pyrethroids was conducted with the same extraction and analysis method used for organochlorine pesticides, PCBs, and PBDEs.

Analysis of Extractable PAH Compounds in Tissue: Extraction methods for homogenized tissue samples were developed and validated by the Water Pollution Control Laboratory. Extract cleanup and partitioning methods are modifications of the multi-residue methods for solids described in EPA Method 3500B-3545 from EPA Test Methods for Evaluating Solid Waste Vol. 1B.

Homogenized tissue samples are removed from the freezer and allowed to thaw.

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A 1-5 g (tissue homogenate) sample is mixed using a clean glass stirring rod and weighed into a pre-weighed aluminum planchet and placed in a 70° C oven for 48 hours to determine moisture content. A 10 g sample is weighed using a clean glass stirring rod and mixed with approximately 7 g of twice pre-extracted Hydromatrix until the mixture is free flowing. The samples are extracted twice with a 50/50 mixture of acetone-dichloromethane (DCM) using heat and pressure.

The extracts are combined and dried and evaporated to approximately 5 mL. The extracts are then evaporated to approximately 1 mL using nitrogen. The extracts are then diluted and filtered.

All samples are cleaned up using the large (1 inch i.d.) GPC column. The extracts are evaporated using a K-D apparatus to 5 mL. The extracts are then fractionated. The fractions are concentrated to 1 mL using K-D/nitrogen blow down apparatus prior to analysis by gas chromatography/mass spectrometry.

Phthalates Analyses: Phthalates were analyzed by liquid chromatography-mass spectrometry (LC-MS) using API-electrospray (+ mode) with sodium acetate buffer used to form the sodium adduct of the individual phthalates. The quantitation ion used was the phthalate molecular weight plus sodium. Details of the analyses were not available at time of publication.

Nitro and Polycyclic Musks Analyses: The musks were analyzed by GC-MS using negative chemical ionization. Details of the analyses were not available at time of publication.

p-Nonylphenol Analyses: p-Nonylphenol was analyzed by liquid chromatography-mass spectrometry (LC-MS) using API-electrospray (- mode). Details of the analyses were not available at time of publication.

5.2.4 Toxicity Testing

Sediment Bioassays

In 2003 sediment toxicity was tested by UC Davis - Marine Pollution Studies Laboratories (UCD-MPSL), similar to previous years.

The RMP uses three sediment bioassays: (1) a ten-day acute mortality test, where the estuarine amphipod *Eohaustorius estuarius* is exposed to whole sediment using ASTM method E 1367 (ASTM 1992), (2) a sediment elutriate test, where larval bivalves (*Mytilus spp.*) are exposed to the material dissolved from whole sediment in a water extract using ASTM method E 724-89 (ASTM 1991) and percent normally developed larvae measured as the endpoint, and (3) sediment-water interface core (SWIC) test, where *Mytilus galloprovincialis* larvae are exposed to SWI for 48 hours and percent normally developed larvae measured as the endpoint.

Solid-phase samples were prepared as described in the amphipod protocol (U.S. EPA, 1994b). Sediment was re-homogenized in the sample jar with a polypropylene spoon and then distributed to form a layer 2 cm deep in each of five one-liter replicate beakers. Overlying water was added to the test containers, and sediment and overlying water were allowed to equilibrate overnight before the amphipods were added.

Elutriate solutions are prepared by adding 50 g of sediment to 200 mL of Granite Canyon seawater or freshwater in a clean 250 mL borosilicate glass jar with a Teflon-lined lid (1:4 volume to volume ratio; U.S. EPA and ACOE, 1991). The elutriate mixture was shaken vigorously for 10 seconds and allowed to settle for 24 hours (Tetra Tech, 1986) before being transferred into replicate containers for testing.

5.2.5 Bivalve Growth and Survival

Applied Marine Sciences (AMS) conducted the bivalve health measure evaluations as in previous years.

Analysis of contaminant concentrations is conducted on a subset of the transplanted bivalves (composites contain 40-60 individual bivalves from each site) prior to deployment in Estuary locations (T-0) and after the 100-day deployment period. The differences between pre- and post-deployment concentrations allow determination of contaminant uptake during the period of deployment. A new batch of bivalves are also collected from the original T-0 transplanted bivalve collection sites at the end of the deployment period to obtain information on uptake variables that may have affected wild populations during the deployment period.

In 2001 AMS began calculating the growth mean in addition to the condition index (CI) for the RMP as an indicator of bivalve health. The CI interpretation of bivalve health can be confounding when ambient conditions (i.e., salinity) are more uniform such as during the summer deployment period. In 2002, the RMP discontinued the condition index measure in favor of the growth mean as the only health indicator. Because the CI is the ratio of dry tissue weight to shell cavity volume, it could be affected by changes in either tissue weight or shell size. For example, either a decrease in tissue weight with stable shell size or an increase in shell size with stable tissue weight could be interpreted as a decrease in CI. Consequently, the interpretation of CI as an indicator of health can be problematic. The growth mean is a measure of growth of the composite of bivalves at a particular site in comparison to the T-0. The growth mean is determined by taking the dry weight of each individual and subtracting the mean dry weight of the T-0 for that species. This calculation is done for each individual bivalve. The mean of the difference of all the individuals at a particular site is then calculated to give the growth mean. The 2003 survival results include survival of both maintained and un-maintained bivalve cages.

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Appendix A.

Contaminant summary statistics for three historic Status and Trends Program stations used by the Regional Water Board for 'reasonable potential analyses' (1993-2003). See Chapter 2, section 2.2.4 for more information.

Туре	Parameter	Site Code	No.Of Measures	No. Of NDs	Begin Date	End Date	Units	Median	Avg	StDev	Min	Max
PAH	Sum of PAHs (SFEI)	BA30	19		1993-03	2003-08	pg/L	54062	76378	79237	16357	384331
PAH	Sum of PAHs (SFEI)	BC10	19		1993-03	2003-08	pg/L	20050	21931	10802	8993	51449
PAH	Sum of PAHs (SFEI)	BG20	20		1993-03	2003-08	pg/L	9688	9100	4212	3032	16197
LPAH	Sum of LPAHs (SFEI)	BA30	20		1993-03	2003-08	pg/L	7120	7301	5219	640	18100
LPAH	Sum of LPAHs (SFEI)	BC10	19		1993-03	2003-08	pg/L	4420	5449	4487	800	17079
LPAH	Sum of LPAHs (SFEI)	BG20	20		1993-03	2003-08	pg/L	1492	2312	2089	407	7073
LPAH	Acenaphthene	BA30	14	2	1996-02	2003-08	pg/L	634	770	664	140	2640
LPAH	Acenaphthene	BC10	13	2	1996-02	2003-08	pg/L	973	971	480	130	1500
LPAH	Acenaphthene	BG20	13	8	1996-07	2003-08	pg/L	240	565	748	154	1900
LPAH	Anthracene	BA30	19	2	1993-03	2001-08	pg/L	300	549	642	57	2300
LPAH	Anthracene	BC10	17	9	1993-03	2001-08	pg/L	127	206	195	8	498
LPAH	Anthracene	BG20	20	15	1993-03	2002-07	pg/L	65	81	69	24	197
LPAH	Fluorene	BA30	12	1	1996-02	2001-08	pg/L	1190	1493	1414	290	5450
LPAH	Fluorene	BC10	13		1996-02	2003-08	pg/L	1100	1115	610	240	2078
LPAH	Fluorene	BG20	13	2	1996-02	2002-07	pg/L	420	418	153	180	720
HPAH	Sum of HPAHs (SFEI)	BA30	21		1993-03	2003-08	pg/L	46337	66952	72775	15426	366231
HPAH	Sum of HPAHs (SFEI)	BC10	21		1993-03	2003-08	pg/L	14418	16623	8198	7433	41144
HPAH	Sum of HPAHs (SFEI)	BG20	23		1993-03	2003-08	pg/L	5304	6273	3783	1440	15790
HPAH	Benz(a)anthracene	BA30	17		1993-03	2003-08	pg/L	2540	3704	3003	467	11250
HPAH	Benz(a)anthracene	BC10	17		1993-03	2003-08	pg/L	1138	1302	1246	63	5315
HPAH	Benz(a)anthracene	BG20	19	2	1993-03	2003-08	pg/L	630	540	301	34	1100
HPAH	Benzo(a)pyrene	BA30	21	11	1993-03	2003-08	pg/L	897	5855	13858	26	45000
HPAH	Benzo(a)pyrene	BC10	20	14	1993-03	2003-08	pg/L	36	312	576	19	1469
HPAH	Benzo(a)pyrene	BG20	23	16	1993-03	2003-08	pg/L	89	277	305	30	822
HPAH	Benzo(b)fluoranthene	BA30	21		1993-03	2003-08	pg/L	7830	10735	11543	1727	57200
HPAH	Benzo(b)fluoranthene	BC10	21		1993-03	2003-08	pg/L	1800	1971	1089	800	4590
HPAH	Benzo(b)fluoranthene	BG20	23	1	1993-03	2003-08	pg/L	655	757	482	155	1900
HPAH	Benzo(k)fluoranthene	BA30	21		1993-03	2003-08	pg/L	2600	3840	4288	553	21048
HPAH	Benzo(k)fluoranthene	BC10	21	1	1993-03	2003-08	pg/L	620	775	396	310	1508
HPAH	Benzo(k)fluoranthene	BG20	23	5	1993-03	2003-08	pg/L	271	332	218	83	928
HPAH	Dibenz(a,h)anthracene	BA30	21	1	1993-03	2001-08	pg/L	781	1422	1950	48	8800
HPAH	Dibenz(a,h)anthracene	BC10	20	5	1993-03	2001-08	pg/L	250	278	188	25	640
HPAH	Dibenz(a,h)anthracene	BG20	22	15	1993-03	2002-07	pg/L	200	223	210	17	670
HPAH	Fluoranthene	BA30	20		1993-03	2003-08	pg/L	7150	8714	7690	2180	38960
HPAH	Fluoranthene	BC10	20		1993-03	2003-08	pg/L	4137	4935	2112	2520	10855
HPAH	Fluoranthene	BG20	21		1993-03	2003-08	pg/L	1231	1592	698	830	3000
PCB	Sum of PCBs (SFEI)	BA30	21		1993-03	2003-08	pg/L	829	1094	799	370	4046
PCB	Sum of PCBs (SFEI)	BC10	20		1993-03	2003-08	pg/L	321	437	326	203	1462
PCB	Sum of PCBs (SFEI)	BG20	22		1993-03	2003-08	pg/L	165	231	186	54	792

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Appendix A (continued). Contaminant summary statistics for three historic Status and Trends Program stations

Туре	Parameter	Site Code	No.Of Measures	No. Of NDs	Begin Date	End Date	Units	Median	Avg	StDev	Min	Max
DDT	Sum of DDTs (SFEI)	BA30	18		1993-03	2001-08	pg/L	400	492	411	109	1850
DDT	Sum of DDTs (SFEI)	BC10	17		1993-03	2001-08	pg/L	221	251	121	106	546
DDT	Sum of DDTs (SFEI)	BG20	16		1993-03	2002-07	pg/L	602	657	369	283	1769
DDT	p,p'-DDD	BA30	18		1993-03	2001-08	pg/L	141	185	177	4	770
DDT	p,p'-DDD	BC10	17		1993-03	2001-08	pg/L	95	118	75	12	313
DDT	p,p'-DDD	BG20	16		1993-03	2002-07	pg/L	133	156	81	45	347
DDT	p,p'-DDE	BA30	19		1993-03	2001-08	pg/L	168	199	142	67	678
DDT	p,p'-DDE	BC10	19		1993-03	2001-08	pg/L	76	112	144	32	693
DDT	p,p'-DDE	BG20	21		1993-03	2002-07	pg/L	304	365	229	96	920
DDT	p,p'-DDT	BA30	16	2	1993-03	1999-07	pg/L	47	70	63	9	202
DDT	p,p'-DDT	BC10	18	4	1993-03	2001-08	pg/L	28	39	42	2	167
DDT	p,p'-DDT	BG20	18		1993-03	2002-07	pg/L	34	59	91	6	349
CHLR	Sum of Chlordanes (SFEI)	BA30	18		1993-03	2001-08	pg/L	213	245	137	79	574
CHLR	Sum of Chlordanes (SFEI)	BC10	18		1993-03	2001-08	pg/L	102	101	46	38	180
CHLR	Sum of Chlordanes (SFEI)	BG20	18		1993-03	2002-07	pg/L	111	130	72	25	302
CHLR	alpha-Chlordane	BA30	18		1993-03	2001-08	pg/L	6	66	45	15	177
CHLR	alpha-Chlordane	BC10	19		1993-03	2001-08	pg/L	6	25	13	5	51
CHLR	alpha-Chlordane	BG20	18	1	1993-03	2002-07	pg/L	4	26	14	8	58
CHLR	gamma-Chlordane	BA30	17		1993-03	2001-08	pg/L	40	60	38	8	146
CHLR	gamma-Chlordane	BC10	18		1993-03	2001-08	pg/L	16	20	9	2	36
CHLR	gamma-Chlordane	BG20	18		1993-03	2002-07	pa/L	20	21	11	5	53
CHLR	Heptachlor	BA30	16	9	1994-04	2001-08	pg/L	54	8	7	2	22
CHLR	Heptachlor	BC10	17	11	1994-04	2001-08	pg/L	27	8	7	2	19
CHLR	Heptachlor	BG20	15	9	1994-04	2002-07	pg/L	24	5	4	1	11
CHLR	Heptachlor Epoxide	BA30	17	2	1994-01	2001-08	pg/L	47	52	51	1	174
CHLR	Heptachlor Epoxide	BC10	17	2	1994-01	2001-08	pg/L	22	26	24	3	94
CHLR	Heptachlor Epoxide	BG20	18		1994-04	2002-07	pg/L	18	26	23	2	97
HCH	Sum of HCHs (SFEI)	BA30	17		1993-03	2001-08	pg/L	810	1032	720	184	2559
HCH	Sum of HCHs (SFEI)	BC10	19		1993-03	2001-08	pg/L	501	589	334	155	1284
HCH	Sum of HCHs (SFEI)	BG20	17		1993-03	2002-07	pg/L	152	329	396	27	1506
HCH	alpha-HCH	BA30	17		1993-03	2001-08	pg/L	190	280	217	40	662
HCH	alpha-HCH	BC10	19		1993-03	2001-08	pg/L	223	242	122	81	496
НСН	alpha-HCH	BG20	17	1	1993-03	2002-07	pg/L	38	81	94	5	347
HCH	beta-HCH	BA30	17		1994-01	2001-08	pg/L	152	187	140	11	607
НСН	beta-HCH	BC10	19		1993-03	2001-08	pg/L	130	148	105	16	413
HCH	beta-HCH	BG20	17		1994-04	2002-07	pg/L	18	28	28	6	118
НСН	delta-HCH	BA30	15	5	1994-04	2001-08	pa/L	14	34	42	2	133
НСН	delta-HCH	BC10	17	6	1994-04	2001-08	pa/L	7	16	18	4	53
HCH	delta-HCH	BG20	15	4	1994-04	2001-08	pa/L	13	14	10	4	38
HCH	gamma-HCH	BA30	19	1	1993-03	2001-08	pa/l	443	545	408	63	1667
НСН	- gamma-HCH	BC10	19	1	1993-03	2001-08	pa/l	157	204	154	53	703
HCH	- gamma-HCH	BG20	18		1993-03	2002-07	pg/L	94	210	278	9	1003

Туре	Parameter	Site Code	No.Of Measures	No. Of NDs	Begin Date	End Date	Units	Median	Avg	StDev	Min	Max
OTHER	Dieldrin	BA30	19	2	1993-03	2001-08	pg/L	75	91	83	2	292
OTHER	Dieldrin	BC10	20	3	1993-03	2001-08	pg/L	55	76	71	4	264
OTHER	Dieldrin	BG20	17		1994-04	2002-07	pg/L	89	127	114	2	380
OTHER	Endrin	BA30	16	8	1994-08	2001-08	pg/L	41	50	41	5	120
OTHER	Endrin	BC10	16	9	1994-08	2001-08	pg/L	14	17	15	2	40
OTHER	Endrin	BG20	16	13	1994-08	2002-07	pg/L	4	8	9	2	19
OTHER	Diazinon	BA30	17		1994-01	2001-08	pg/L	5600	6227	4750	610	18469
OTHER	Diazinon	BC10	17	1	1994-04	2001-08	pg/L	2050	3089	3388	370	13000
OTHER	Diazinon	BG20	18		1994-04	2002-07	pg/L	2350	6291	9873	520	37690
OTHER	Chlorpyrifos	BA30	17	1	1993-03	2001-08	pg/L	108	210	283	6	1005
OTHER	Chlorpyrifos	BC10	16	1	1993-03	2001-08	pg/L	137	321	593	4	2185
OTHER	Chlorpyrifos	BG20	19	1	1993-03	2002-07	pg/L	327	339	280	21	950
OTHER	Hexachlorobenzene	BA30	18	1	1993-03	2001-08	pg/L	15	51	116	5	480
OTHER	Hexachlorobenzene	BC10	17	1	1993-03	2001-08	pg/L	9	11	6	2	22
OTHER	Hexachlorobenzene	BG20	18		1993-03	2001-08	pg/L	21	30	25	3	109
OTHER	Mirex	BA30	18	15	1994-04	2001-08	pg/L	1.1	1.2	0.5	0.7	1.7
OTHER	Mirex	BC10	17	17	1994-04	2001-08	pg/L					
OTHER	Mirex	BG20	19	18	1994-04	2002-07	pg/L	54.0	54.0		54.0	54.0
TE	Ag	BA30	23		1993-03	2003-08	ug/L	0.019	0.024	0.024	0.006	0.119
TE	Ag	BC10	23		1993-03	2003-08	ug/L	0.007	0.010	0.010	0.003	0.052
TE	Ag	BG20	23	1	1993-03	2003-08	ug/L	0.007	0.009	0.012	0.001	0.057
TE	As	BA30	26		1993-03	2003-08	ug/L	2.8	3.2	1.0	1.7	5.1
TE	As	BC10	26		1993-03	2003-08	ug/L	1.9	1.9	0.3	1.1	2.5
TE	As	BG20	27	1	1993-03	2003-08	ug/L	2.0	2.0	0.6	1.2	3.7
TE	Cd	BA30	26		1993-03	2003-08	ug/L	0.10	0.09	0.03	0.05	0.17
TE	Cd	BC10	26		1993-03	2003-08	ug/L	0.07	0.07	0.03	0.02	0.13
TE	Cd	BG20	26		1993-03	2002-07	ug/L	0.03	0.03	0.01	0.02	0.05
TE	CN	BA30	3	3	1993-03	1993-09	ug/L					
TE	CN	BC10	3	3	1993-03	1993-09	ug/L					
TE	CN	BG20	3	3	1993-03	1993-09	ug/L					
TE	Со	BA30	5		2000-02	2003-08	ug/L	0.51	0.99	0.98	0.45	2.74
TE	Со	BC10	5		2000-02	2003-08	ug/L	0.27	0.34	0.15	0.21	0.58
TE	Со	BG20	6		2000-02	2003-08	ug/L	0.74	0.82	0.21	0.60	1.14
TE	Cr	BA30	21		1993-03	1999-07	ug/L	4.6	5.4	3.8	1.3	14.7
TE	Cr	BC10	21		1993-03	1999-07	ug/L	1.4	1.7	1.1	0.6	4.4
TE	Cr	BG20	21		1993-03	1999-07	ug/L	5.2	10.2	17.1	1.4	80.4
TE	Cu	BA30	26		1993-03	2003-08	ug/L	4.0	4.4	1.3	3.0	8.6
TE	Cu	BC10	26		1993-03	2003-08	ug/L	1.8	1.8	0.4	0.8	2.5
TE	Cu	BG20	26		1993-03	2003-08	ug/L	3.4	3.9	1.6	2.2	9.9
TE	Fe	BA30	5		2000-02	2003-08	uq/L	665	1910	2628	555	6588
TE	Fe	BC10	5		2000-02	2003-08	uq/L	425	591	382	244	1183
TE	Fe	BG20	6		2000-02	2003-08	ug/L	1456	1475	444	883	2052

Appendix A (continued). Contaminant summary statistics for three historic Status and Trends Program stations

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Туре	Parameter	Site Code	No.Of Measures	No. Of NDs	Begin Date	End Date	Units	Median	Avg	StDev	Min	Max
TE	Hg	BA30	25		1993-03	2003-08	ug/L	0.009	0.016	0.016	0.005	0.068
TE	Hg	BC10	25		1993-03	2003-08	ug/L	0.004	0.004	0.002	0.000	0.009
TE	Hg	BG20	26		1993-03	2003-08	ug/L	0.006	0.008	0.007	0.001	0.038
TE	MeHg	BA30	6	1	1999-04	2001-08	ng/L	0.084	0.098	0.062	0.018	0.171
TE	МеНд	BC10	5	1	1999-04	2001-08	ng/L	0.050	0.081	0.079	0.025	0.197
TE	МеНд	BG20	7	1	1999-02	2002-07	ng/L	0.097	0.149	0.125	0.043	0.332
TE	Mn	BA30	5		2000-02	2003-08	ug/L	92	110	60	61	213
TE	Mn	BC10	5		2000-02	2003-08	ug/L	16	19	6	15	29
TE	Mn	BG20	6		2000-02	2003-08	ug/L	37	38	7	31	49
TE	Ni	BA30	26		1993-03	2003-08	ug/L	4.7	6.3	3.0	3.6	15.8
TE	Ni	BC10	26		1993-03	2003-08	ug/L	2.3	2.3	0.7	1.1	3.7
TE	Ni	BG20	27		1993-03	2003-08	ug/L	4.2	5.3	3.8	2.5	21.8
TE	Pb	BA30	26		1993-03	2003-08	ug/L	0.8	1.2	1.0	0.3	4.2
TE	Pb	BC10	26		1993-03	2003-08	ug/L	0.3	0.3	0.2	0.1	0.8
TE	Pb	BG20	27		1993-03	2003-08	ug/L	0.6	0.8	0.5	0.3	2.3
TE	Se	BA30	26		1993-03	2003-08	ug/L	0.27	0.30	0.12	0.05	0.63
TE	Se	BC10	26	2	1993-03	2003-08	ug/L	0.12	0.15	0.09	0.04	0.39
TE	Se	BG20	27	1	1993-03	2003-08	ug/L	0.12	0.14	0.06	0.02	0.30
TE	Zn	BA30	26		1993-03	2003-08	ug/L	5.1	6.6	4.0	2.6	21.3
TE	Zn	BC10	26		1993-03	2003-08	ug/L	2.3	2.5	1.0	1.2	5.1
TE	Zn	BG20	27		1993-03	2003-08	ug/L	5.0	6.3	3.8	2.6	18.2

Appendix A (continued). Contaminant summary statistics for three historic Status and Trends Program stations