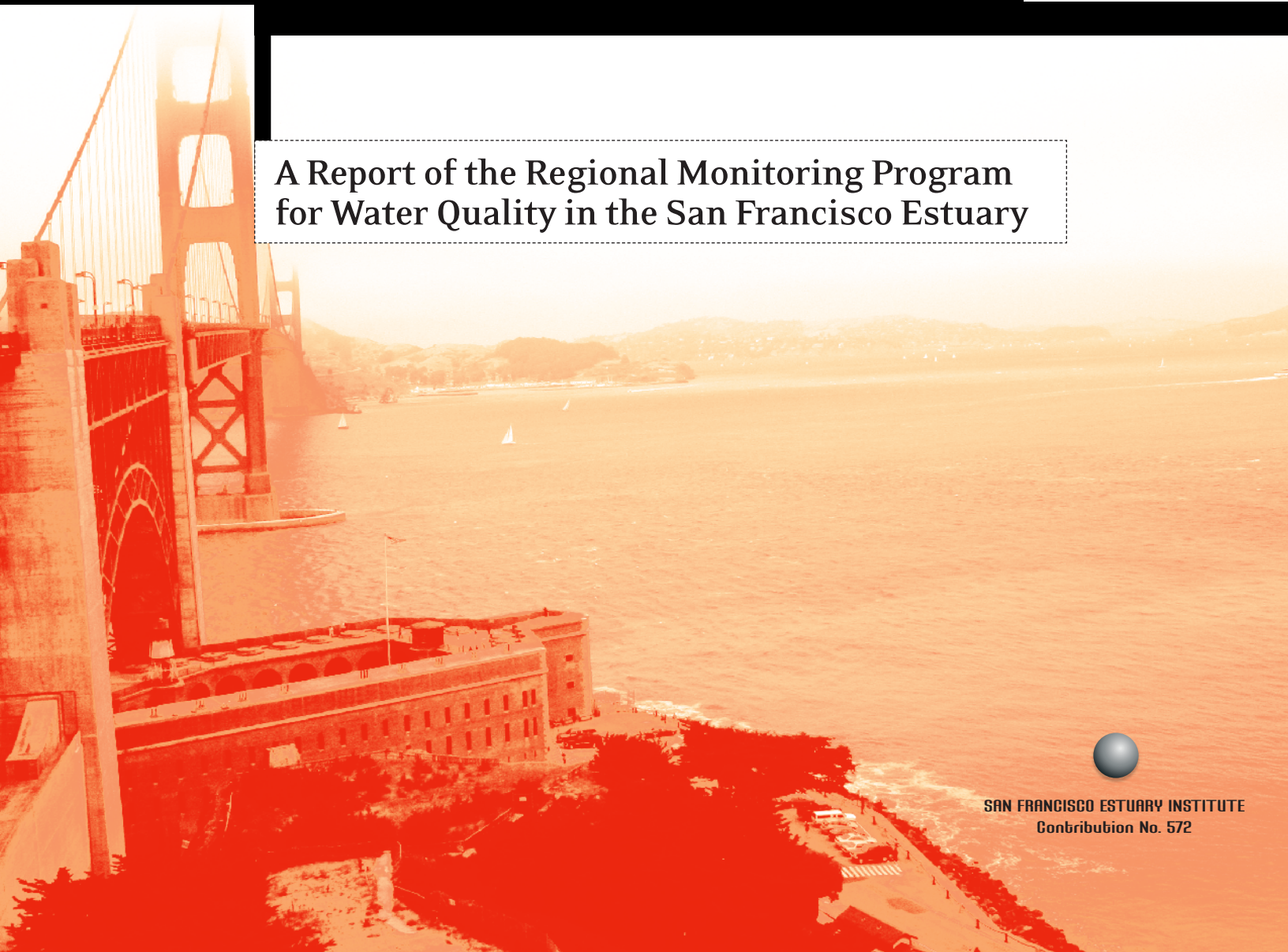
RMP ANNUAL MONITORING RESULTS 2007

A Report of the Regional Monitoring Program for Water Quality in the San Francisco Estuary



SAN FRANCISCO ESTUARY INSTITUTE
Contribution No. 572

THIS REPORT SHOULD BE CITED AS:
San Francisco Estuary Institute (SFEI). 2008. The 2007 RMP Annual Monitoring Results. The Regional Monitoring Program for Water Quality in the San Francisco Estuary (RMP). SFEI Contribution No. 572. San Francisco Estuary Institute, Oakland, CA.

COVER PHOTOGRAPH:
Golden Gate Bridge. San Francisco, CA. Photograph by Linda Wanczyk. 2008.

RMP ANNUAL MONITORING RESULTS 2007

A Report of the Regional Monitoring Program for Water Quality in the San Francisco Estuary

SAN FRANCISCO ESTUARY INSTITUTE
Contribution No. 572

Acknowledgements

The authors would like to thank the Technical Review Committee and the Steering Committee for providing oversight and guidance to the RMP; RMP Contractors and Principal Investigators (Appendix 2) for providing quality analysis in a timely fashion; and the discharger community (Appendix 1) for providing funding. Special thanks are due to SFEI staff for sample collection, data management, quality assurance, and report preparation.

Collaborators
Nicole David, Amy Franz, Cristina Grosso, Katie Harrold, Jennifer Hunt, Michelle Lent, Sarah Lowe, John Oram, John Ross, Meg Sedlak and Don Yee

This report should be cited as: SFEI. 2008. 2007 Annual Monitoring Results. The Regional Monitoring Program for Water Quality in the San Francisco Estuary (RMP). San Francisco Estuary Institute, Oakland, CA

Table of Contents

List of Figures

List of Tables

CHAPTER 1

Introduction

1.0 Introduction

1.1 Program Structure and Objectives

The Regional Monitoring Program for Water Quality in the San Francisco Estuary (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 Program was initiated by the Water Board as a pilot study in 1989 and has been collecting water, sediment, and bivalve tissue data since 1993. The RMP's annual budget is currently approximately $3.7 million, which is primarily funded through wastewater discharge and dredging permits issued by the Water Board (refer to *Appendix* 1 for a current list of participants).

The Technical Review Committee (TRC) and Steering Committee (SC) 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 guidance 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 undergoes a rigorous external review by national science and management experts to ensure that it is adapting to address current regulatory and scientific information needs. This review provides a forum for re-evaluating the programs management questions that guide the long-term Status and Trends Program and more focused Pilot and Special Studies. The second comprehensive five-year review of the RMP was conducted in 2003-2004. The workgroup's findings and recommendations are summarized in the *Report of the 2003 Program Review*.

As suggested by the last Program review, the RMP's management objectives were updated to the following in 2005:

1. Describe the distribution and trends of pollutant concentrations in the Estuary.
2. Project future contaminant status and trends using best understanding of ecosystem processes and human activities.
3. Describe sources, pathways, and loading of pollutants entering the Estuary.
4. Measure pollution exposure and effects on selected parts of the Estuary ecosystem (including humans).
5. Compare monitoring information to relevant benchmarks, such as TMDL targets, tissue screening levels, water quality objectives, and sediment quality objectives.
6. Effectively communicate information from a range of sources to present a more complete picture of the sources, distribution, fate, and effects of pollutants and beneficial use attainment or impairment in the Estuary ecosystem.

In 2007, in an effort to prioritize studies within the workgroups and RMP in general, the management questions and RMP Objectives were revisited. The process of refining the management questions and objectives will continue in 2008 and will be reviewed and approved by the TRC and SC.

The RMP addresses its objectives through the Status and Trends Program, focused workgroups, and pilot and special studies. The Status and Trends Program is comprised of the following four elements:
RMP Program Information

1) *Status and trends long-term monitoring* characterizes the status and trends for contaminants in water, sediment, and bivalves in the Estuary (Objectives 1, 2, 4, and 5).
2) *Sport Fish Contamination Study* triennially screens fish tissue for contaminants of concern to human health (Objectives 1, 2, 4, and 5).
3) *Toxicity studies* investigate episodic toxicity in Estuary tributaries and possible causes of observed toxicity through Toxicity Identification and Evaluation (TIE) methods (Objectives 1 and 3).
4) *USGS studies* collect monthly water quality measurements in the Estuary's deep channels from the Lower South Bay to the confluence of the Sacramento and San Joaquin Rivers, and perform sediment transport monitoring and modeling in the northern Estuary.

The Water Board uses Status and Trends data for regulatory purposes, such as evaluating the Estuary for 303(d) listing of water bodies, calculating National Pollutant Discharge Elimination System (NPDES) permit conditions, estimating Total Maximum Daily Loads (TMDL), and to evaluate whether management actions are successful in reducing contaminant loads to the Estuary through modeling.

Focused workgroups (Sources, Pathways and Loadings, Contaminant Fate, Exposure and Effects, and Emerging Contaminants) address contaminant sources and loadings (Objective 3), additional effects measures (Objective 4), and future contaminant status and trends (Objective 2) and help to develop pilot and special studies. These workgroups meet several times a year to review progress and make recommendations for further study.

Pilot studies 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. Section 1.3 below describes the Pilot and Special Studies conducted by the RMP in 2007. A summary of previous studies conducted by the RMP and specific details on the study development and selection processes are available on the RMP Pilot and Special Studies home page.

The RMP synthesizes and distributes its monitoring and study results (Objective 6) through conferences, workgroups, literature reviews, technical reports, newsletters, and the *Pulse of the Estuary*. This *Annual Monitoring Results* report focuses on the Status

and Trends Program. The RMP publishes separate technical reports for the Sport Fish Contaminant Study and toxicity studies. These reports are available on the web at RMP Documents and Reports. A brief description of those monitoring components and the USGS studies can be found in Section 1.2 below. For more information on the RMP, refer to the RMP home page.

There have been numerous changes over the years to the RMP in order to better address management questions and adapt to changing regulatory and scientific information needs. *Appendix 9* summarizes the major changes since the RMP began in 1993. *Appendix 6 – Appendix 8* provide tables of reported data by matrix for all years. These tables provide a quick overview of the changes in the program and when analytes were added and/or eliminated from the RMP's target parameter reporting list.

1.2 The Status and Trends Program

The 2007 sampling was the sixth year of the new probabilistic sampling design for long-term water and sediment monitoring, which employs the EPA's Generalized Random Tessellation Stratified (GRTS) sample design (Stevens, 1997; Stevens and Olsen, 1999; Stevens and Olsen, 2000). This type of design is more appropriate for addressing the RMP's first objective to describe the spatial and temporal patterns of contamination in the Estuary (Lowe *et al*., 2005). Prior to 2003, a fixed site sampling design was used.

Sampling site information is presented in Appendix 3 for water and Appendix 4 for sediment. Site location maps are included in Chapters 2 and 3. Subcontracting agencies perform the logistical planning, sampling, and laboratory analyses for trace contaminants and ancillary measures. Participating contractors for 2007 are listed in *Appendix 2*. Monitoring data (since 1993) are available for downloading via the RMP website using the *Status and Trends Monitoring Data Query Tool*.

In 2007 as part of the redesign process, the Status and Trends monitoring program was expanded to include the following elements: triennial bird egg monitoring (cormorant and tern); annual small fish monitoring; annual small tributary loading; triennial large tributary loading; and triennial studies of the Guadalupe River. To reduce the financial burden of implementing these new elements they will be phased in over multiple years. In 2007, the Small Fish and Small Tributary Loading Study were implemented.

Cormorant and tern bird egg monitoring will be included in the RMP on a triennial basis beginning in 2009. Substantial monitoring of eggs has previously been conducted through the Exposure and Effects Pilot Studies. Cormorant eggs were collected in 2002, 2003, and 2006 at Wheeler Island, Richmond Bridge, and Don Edwards. In 2009, cormorant eggs will be collected from these previous locations and analyzed for mercury, selenium, PBDEs, perfluorinated compounds, PCBs, dioxin and pesticides. Tern eggs were collected in 2002 and 2003, and were analyzed for mercury as part of the Exposure and Effects Pilot Study. The Status and Trends sampling design for terns is still in development.

RMP small fish monitoring began as part of the Exposure and Effects Pilot Studies in 2005. Small fish were collected as part of the Pilot and Special Studies in 2007, and will be

collected as part of Exposure and Effects Pilot and Special Studies in 2008; in 2009 this study will be incorporated into an annual sampling event as part of Status and Trends.

Tributary loading was added as part of the Status and Trends program in 2006/2007. Tributary studies include small tributary loading to be sampled annually, large tributary loading sampled triennially (Mallard Island studies); and Guadalupe river loading studies sampled triennially. Guadalupe River studies will be conducted in 2009. Mallard Island studies will be conducted in 2010.

1.2.1 Random Sampling Design for Water and Sediment

With a randomized water and sediment sampling design, the RMP can better address Objectives 1 and 5, estimate the statistical basis from which to characterize spatial and temporal patterns of contamination in each region or the Estuary as a whole, determine if the mean contaminant concentrations within a region are above regulatory guidelines, 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 samples for water and sediment monitoring are allocated into five hydrographic regions of the Estuary plus the Rivers region. Those five regions are: Suisun Bay, San Pablo Bay, Central Bay, South Bay, and Lower South Bay. The original 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 2002 redesign effort. Seventy-two random water and sediment sites were allocated into each of the hydrographic regions downstream from the confluence of the Sacramento and San Joaquin Rivers. The sampling frames for water and sediment monitoring are the three-foot and one-foot contour of the Estuary at mean lower low water, respectively (based on NOAA's NAD-83 bathymetry coverage). Each year, a subset of these sites is sampled in sequential order, increasing the spatial coverage of the Estuary over time.

1n 2006, power analysis was performed to evaluate the trend detection ability of the RMP sampling design. Based on the results of the power analysis, the number of water sampling sites was reduced from 31 sites to 22 sites per year while the number of sediment sites was maintained at 47 sites per year.

Several historical fixed water and sediment sites were retained from the original RMP monitoring design to provide continuity between the two sampling designs. Sampling currently occurs once a year during the dry season when Estuary conditions are most consistent on an interannual basis. The sediment sample design incorporates re-sampling of sites for additional trends analyses. The random sites within each region are re-sampled on an annual, five-year, ten-year, and twenty-year basis. The sediment sites sampled annually are labeled XX001 and XX002, the sites sampled every five years are XX003 and XX004, and the sites sampled every 10 years are XX005 and XX006 (where XX stands for the region code). 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.

For more information on the Status and Trends monitoring design, refer to the following articles and technical reports: Power Analysis and Optimization of the RMP Status and Trends Program (Melwani et al., 2008), *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), *2000 Pulse of the Estuary* and *RMP News: Winter 2001/2002*.

1.2.2 Sampling Design for Bivalve Bioaccumulation Monitoring

The bivalve bioaccumulation sample design remains a convenient 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: 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 in 2000 – 2002, only one transplanted bivalve species (*Mytilus californianus*) was deployed in four regions, which makes comparing bioaccumulation results between regions possible. All bivalves are now deployed in cages, rather than mesh bags, to reduce the loss of organisms through predation.

Nine mooring sites (three in the Central Bay and San Pablo Bay regions, two in the South Bay, and one in the Lower South Bay) and two historic sites at the Sacramento River (BG20) and San Joaquin River (BG30) are monitored for bioaccumulative contaminants using transplanted and resident bivalves. Transplanted *M. californianus* are deployed in cages for three months. Resident clams (*Corbicula fluminea*) are collected from the River sites.

Results from 1993 – 2001 indicated that trace metals do not appreciably accumulate in transplanted bivalve tissue at mid-channel locations in the bay. Trace metal analyses were scaled back to a five-year screening study. The next screening will occur in 2008. Tributyltin analysis was discontinued altogether. Since mercury bioaccumulation is included in the Sport Fish Contamination Study, mercury analysis in bivalves was discontinued in 2000.

1.2.3 Water Chemistry and Toxicity

In 2007, the number of water sites was reduced from 31 to 22. Sampling occurred at 3 sites in each of the upper four segments and 5 sites in the Lower South Bay segment (N=17) during the dry season in August. The five annual historic sites were also sampled.

The analyte list for conventional water quality, trace metals, and trace organics was the same as in 2006. See *Appendix* 5 for the 2007 target analyte list. Except for diazinon and chlorpyrifos, which are pending analytical method development, all data are available for reporting at this time.

Water samples were tested for ambient water toxicity in 2007. 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 aquatic toxicity sampling of the Estuary surface waters is scheduled for 2012.

1.2.4 Sediment Chemistry and Toxicity

In 2007, sediment sample collection occurred during the dry season in August at 47 sites throughout the Estuary. Forty random sites and seven historical fixed sites were sampled. See *Appendix* 5 for the 2007 target analyte list. In 2007, BDE 196 and 197 were added to the target analyte list which will result in a more accurate estimate of total PBDEs since these congeners constitute a relatively high percentage of the Deca-BDE mix. All of the data are available for reporting at this time.

Twenty-seven sediment samples were tested for toxicity in 2007. 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. Sediment monitoring is discussed in more detail in Chapter 3.

1.2.5 Bivalve Bioaccumulation

As part of the redesign, bivalves are sampled every other year and were not deployed in 2007. Trace organics in bivalve tissue from 2006 are currently being analyzed as a result of the selection of a new organics laboratory (AXYS Analytical). Bivalve tissue monitoring is discussed in more detail in Chapter 4.

1.2.6 Sport Fish Contaminant Study

Sport fish sampling, which occurs on a three-year cycle, was not conducted in 2007. It will next occur in 2009. The results from sampling popular sport fish species for mercury, PCBs, organochlorine pesticides, and PBDEs in 1994, 1997, 2000, 2003, and 2006 at several fishing locations are available on the RMP Fish Tissue Data Page. For more information refer to the technical reports *Contaminant Concentrations in Fish from San Francisco Bay 2003* and *Contaminant Concentrations in Sport Fish from San Francisco Bay 2006.*

1.2.7 Causes of Sediment Toxicity

The Causes of Sediment Toxicity Study began in 2006 to investigate methods to understand what might be causing the persistent sediment toxicity observed in the

amphipod tests utilized by the Status and Trends program. The 2007 – 2008 study focused on developing Toxicity Identification and Evaluation methods (TIEs) for the 10-day amphipod (*Eohaustorius estuarius)* survival tests employed in the RMP. A TIE is a series of laboratory sample manipulations and toxicity tests that help to identify what contaminant groups or pollutants might be causing a toxic effect observed in an ambient sediment sample.

1.2.8 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. During 2007, it continued to supplement RMP monitoring with 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 six sites using optical backscatter sensors deployed at mid-depth and near the bottom. In 2007, the San Pablo site was replaced with a site at the Richmond Bridge as a result of the deterioration of a pier at the Point San Pablo site. The following six sites were monitored in 2007: five fixed stations (i.e., Alcatraz, Mallard, Benicia, Richmond Bridge, and Dumbarton) and one temporary station located near the Hamilton Army Airfield (San Pablo Bay). The five fixed stations will provide suspended sediment information at four embayments. The temporary site at Hamilton will provide the US Army Corps with information needed to evaluate the impact of the aquatic transfer station. At this point it is not clear whether the temporary station will remain at the Hamilton Army Airfield or whether the funds will be reallocated to another site. Conductivity and temperature data were also collected at some sites. For more information refer to the *2003 Pulse of the Estuary* article Sediment Dynamics Drive Contaminant Dynamics.

Hydrography and Phytoplankton

This study collects 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). Primary production by phytoplankton is the principal source of food for aquatic life in the Estuary. Significant changes in phytoplankton population

dynamics have been observed through this Program's monitoring in recent years, including larger spring blooms, blooms during other seasons, and a progressive increase in the amount of chlorophyll produced in the Estuary. For more information refer to the *2006 Pulse of the Estuary* article What is Causing the Phytoplankton Increase in San Francisco Bay?

With approximately 15,000 acres of salt ponds in the South Bay slated to be restored to wetlands, information on basic water quality such as salinity and dissolved oxygen will be valuable in helping understanding the impact that the restoration will have on the Estuary.

1.3 RMP Pilot and Special Studies

While the Status and Trends is the core component of the RMP, providing long-term contaminant monitoring results, the adaptive management of the RMP is conducted through its Pilot and Special Studies, which allow for shorter-term changes based on the changing regulatory priorities, management of the Estuary, and scientific understanding of the Estuary.

1.3.1 Pilot Studies

Pilot studies augment 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 Program (e.g., Identifying the Cause of Toxicity, Sport Fish Contamination Study).

One pilot study, Exposure and Effects, was conducted by the RMP in 2007.

Exposure and Effects Pilot Study (2000 – 2008)

Applicable RMP Objectives: 1, 4, 5, and 6

Contact: Meg Sedlak (meg@sfei.org)

Beginning in 2000, the RMP implemented this multi-faceted pilot study to develop several indicators of contaminant exposure and effects of beneficial use impairment in the Estuary. 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.

In 2007, EEPS funded the following projects:

Mercury in Small Fish (2005, 2006, 2007, and 2008)
This project examines the uptake of mercury in small fish at seven sites in the Bay. The goal of this study is to better understand the temporal and spatial variation of mercury in biota in the Bay and to quantify exposure to mercury in piscivorous wildlife that may consume benthic or pelagic small fish as prey. In 2007, sampling for trace organic contaminants was added to this study. Additional fish were collected from shoreline areas distributed throughout the San Francisco Estuary and analyzed for PCBs, pesticides, and PBDEs. (Due to budget constraints, this project was funded under Special Studies for 2007. In 2008, the project will return to being funded by EEPS.)

For more information, refer to the project's first year report Mercury in Biosentinel Fish in San Francisco Bay: First-Year Project Report. The report indicates initial spatial and species patterns of mercury in small fish, as well as sampling recommendations for future years of the study.

Development of Forster's Tern Egg Monitoring as an Effects Indicator (2007–2008)
The main objectives of this project are to 1) determine toxic thresholds in Forster's Tern eggs, 2) examine effects of mercury on chick mortality, and 3) link mercury concentrations in eggs to those of down feathers in newly hatched chicks.

Endocrine Disruptors in Shiner Surfperch and Pacific Staghorn Sculpin (2006–2008)
The main objectives of this project are to 1) determine the incidence and magnitude of endocrine disrupting compounds in fish and how they affect stress hormones, growth, reproduction, and thyroid function, 2) look at spatial differences in these responses and contaminant levels, and 3) determine liver contaminant concentrations.

1.3.2 Special Studies

Special Studies help the RMP address specific data gaps or management and scientific questions related to contaminants in the Estuary. For example, recent special studies identified and evaluated previously unknown organic contaminants and led to the addition of PBDEs to the RMP target analyte list to determine if they are prevalent in water, sediment, and tissue samples from the Estuary. For more information, refer to RMP Documents and Reports.

The following special studies were conducted in 2007:

- Small Tributary Loading Study – Zone 4 Hayward

- Emerging Contaminants
- Mercury and Trace Organic Pollutants in Small Fish
- Remote Sensing
- Development of a Refined Conceptual Model for Aquatic Food Webs

Small Tributary Loading Study at Zone 4 Hayward (2007 – 2009)

Applicable RMP Objectives: 1, 3, and 6

Contact: Lester McKee (lester@sfei.org)

The objective of this study is to quantify sediment and contaminant loads from a small industrial watershed. Given that historic and current industrialized areas (potentially sources of Hg and PCBs) are found mainly on the lower-rainfall Bay margin, a 4 km^2 watershed in industrial/commercial Hayward will provide valuable information on loads derived from small, low rainfall, but highly impervious, commercial and industrialized "storm drain watersheds" on the Bay margin. This is particularly important for updating regional TMDL estimates of Hg and PCBs loads derived from urban runoff. In addition, loadings studies will provide baseline data so that trends through time can be assessed, and provide data for models that describe biological effects in the Bay.

Emerging Contaminants: Evaluation of Pharmaceuticals in the San Francisco Bay (2007)

Applicable RMP Objectives: 1, 2, and 6

Contact: Meg Sedlak (meg@sfei.org)

The goal of this study is to measure several classes of pharmaceuticals in influent and effluent from two wastewater treatment plants and to determine the concentration of these pharmaceuticals in the Southern portion of the Bay. The RMP does not currently monitor for pharmaceuticals so it is not known which pharmaceuticals are present and at what concentration levels, but there is heightened concern now given that pharmaceutically active drugs have been found to occur in most U.S. water bodies. Therefore, the objective of this study is to evaluate the extent of the concentration levels and occurrence of pharmaceuticals in the San Francisco Bay water column.

Emerging Contaminants: Evaluation of Perfluorinated Chemicals and PBDEs in San Francisco Bay Harbor Seals (2007 and 2008)

Applicable RMP Objectives: 1, 2, 4 and 5

Contact: Meg Sedlak (meg@sfei.org)

The objective of this study will be to determine concentrations of perfluorinated compounds, PBDEs, and hexabromocyclododecane (an alternative flame retardant for PBDEs) in the blood of Pacific harbor seals (*Phoca vitulina richardsi*). As apex predators, harbor seals are an ideal indicator species for persistent bioaccumulative contaminants in the Estuary. Long-lived, they tend to forage for fish in areas that are frequently impacted by contamination (e.g., heavy marine traffic, urban and agricultural runoff, etc.). As a result, they are a good proxy of exposure to contaminants for other apex predators such as humans.

Remote Sensing (2007 and 2008)

Applicable RMP Objectives: 2 and 3

Contact: John Oram (joram@sfei.org)

Monitoring suspended sediment concentrations (SSC) in coastal waters and estuaries is crucial for proper ecosystem management. Such monitoring is traditionally done *in-situ*, with measurements representing SSC at a few discrete points in space and time. However, recent advancement of satellite remote sensing allows for synoptic views of coastal and estuarine dynamics that would otherwise be unavailable. Results are drastically altering our perceptions of coastal ocean transport processes. This project aims to utilize moderate-resolution satellite imagery to investigate episodic sediment transport patterns in San Francisco Bay.

Development of a Refined Conceptual Model for Aquatic Food Webs (2007)

Applicable RMP Objectives: 3, 4 and 6

Contact: Ben Greenfield (ben@sfei.org)

This study will focus on obtaining an improved conceptual understanding of spatial variation in the San Francisco Bay food web. Particular emphasis will be placed on the diets of white croaker and shiner surfperch, as they are important species for understanding of the bay with respect to recovery from impairment by PCB and the results of actions taken to implement the TMDL. The special study will include a combination of literature review and field dietary studies to develop a better understanding of food web transfer pathways for contaminants. It is critical to further our understanding of the diet of target species, specifically to discern between the relative contribution of water column and sediment prey items to the diet of aquatic and other wildlife in and around the Bay. This will help evaluate the relative importance of water and sediment PCBs to white croaker and shiner surfperch, and inform managers on effective implementation actions.
For more information view the report RMP Food Web Analysis; Data Report on Gut Contents of Four Fish Species.

1.4 Annual Monitoring Online Graphics and Data Access Tools

1.4.1 Web Query Tool

The 2007 data are now available online using a dynamic mapping and graphing tool. The online Web Query Tool allows water, sediment, and tissue monitoring results from 1993 to 2007 to be summarized graphically for many trace contaminants and important ancillary measures. The spatial distribution of contaminants is displayed in maps (Figure 1.1) and cumulative distribution function (CDF) plots (Figure 1.2). Simple summary statistics by region are displayed in tabular form (Figure 1.3). The Web Query Tool is available at http://eis.sfei.org/wqt.

Several software programs were used to develop the online graphics. The R statistical analysis software package *spsurvey*, which is designed specifically by EPA for GRTS sample designs was used to calculate estimates of the regional and Estuary-wide contaminant mean, variance, standard deviation, standard error, and CDFs. The R program is an implementation of the S language developed at AT&T Bell Laboratories and can be downloaded for free from the Comprehensive R Archive Network (CRAN). The spsurvey library for the analysis of probability surveys is available from USEPA's Aquatic Resources Monitoring - Monitoring Design and Analysis.

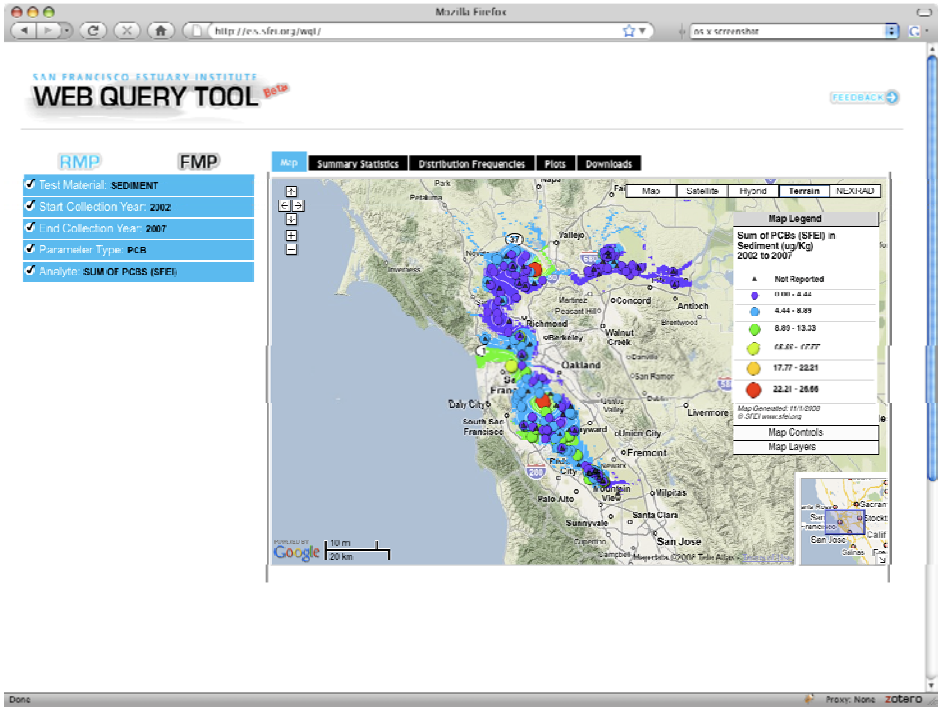


Figure 1.1 - Web Query Tool screenshot

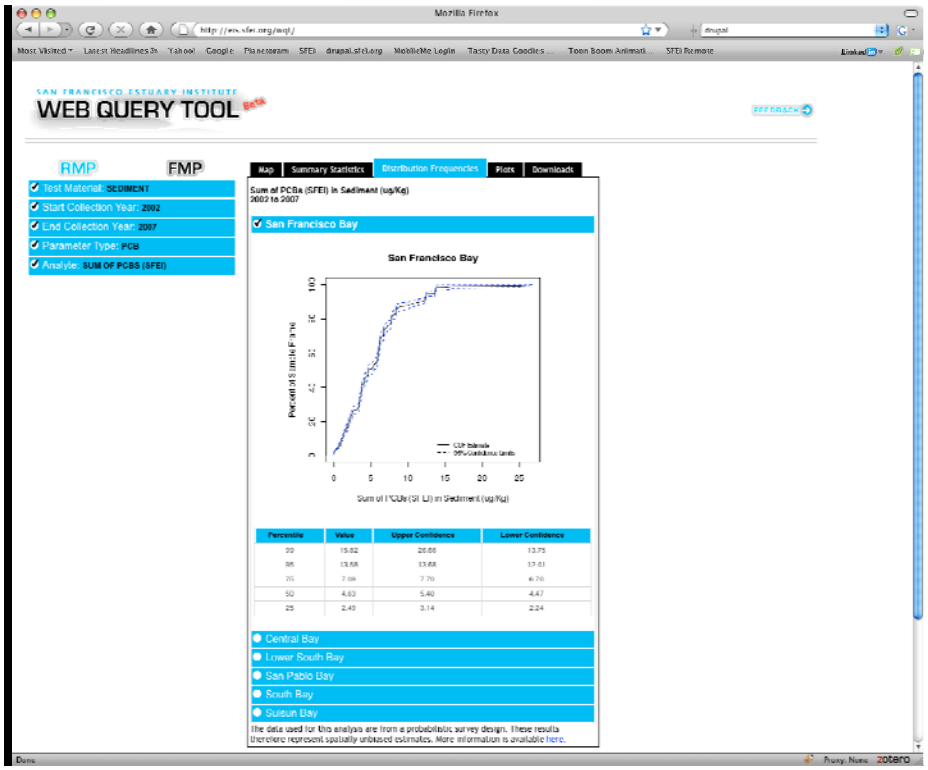


Figure 1.2 - Web Query Tool CDF screenshot.

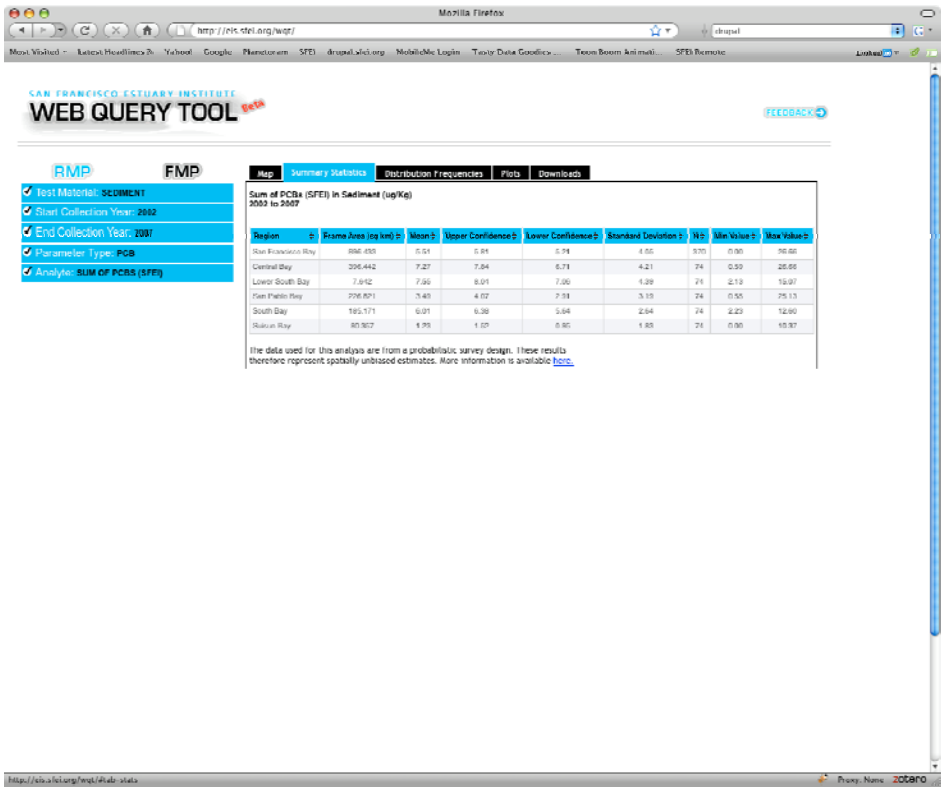


Figure 1.3 - Web Query Tool summary statistics screenshot.

All results, including data from previous years, can be downloaded from the web using the RMP Web Query Tool. The online data includes only those results that have met specific data quality objectives and have passed a rigorous QA/QC evaluation as outlined in the RMP's Quality Assurance Project Plan. 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 target list of RMP congeners (*Appendix 5*) 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.

1.4.2 Water Column Profile Data

In addition, Conductivity, Temperature, and Depth (CTD) profiles of the water column are collected at all RMP water, sediment, and bivalve tissue stations. 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 available through the Web Query Tool, results are available upon request (contact Cristina Grosso cristina@sfei.org).

1.5 References

Lowe, S., B. Thompson, R. Smith, D. L. Stevens, R. Hoenicke, K. Taberski, and J. Leatherbarrow. 2005. Re-design Process of the San Francisco Estuary Regional Monitoring Program for Trace Substances (RMP) Status & Trends Program for Water and Sediment Monitoring. SFEI Contribution #109. San Francisco Estuary Institute. Oakland, CA.

Stevens, Jr., D.L. 1997. Variable density grid-based sampling designs for continuous spatial populations. Environmetrics 8:167-195.

Stevens, Jr., D.L. and A.R. Olsen. 1999. Spatially restricted surveys over time for aquatic resources. Journal of Agricultural, Biological, and Environmental Statistics 4:415-428.

Stevens, Jr., D.L. and A.R. Olsen. 2000. Spatially-restricted random sampling designs for design-based and model-based estimation. In Accuracy 2000: Proceedings of the 4th International Symposium on Spatial Accuracy Assessment in Natural Resources and Environmental Sciences. Delft University Press, the Netherlands, pp. 609-616.

CHAPTER 2

Water Monitoring

2.0 Water Monitoring

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 Regional Monitoring Program for Water Quality in the San Francisco Estuary (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 Field Methods

2.2.1 Water Sampling Field Methods

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 were used in all trace metal and organic sampling procedures (Flegal and Stukas, 1987; U.S. EPA, 1995).

Water samples were collected by pumping water from approximately one meter below the water surface. The sampling intake ports for both the trace organic and trace element samplers were attached to aluminum poles that were oriented up-current from the vessel and upwind from equipment and personnel. The vessel was anchored and the engines turned off before the sampling began. Total and dissolved fractions of Estuary water were collected for trace element analyses. Particulate and dissolved fractions were collected for trace organics analyses.

Changes in Water Sampling

In 2007, one of the major changes to the field sampling protocols was that RMP staff began collecting inorganic water samples in addition to organic samples. In prior years,

UCSC had provided field staff for the collection of inorganic samples. The RMP collected inorganic water samples using the "clean hands" methodology pioneered by UCSC and others. At 9 of the 22 sites, duplicate samples were collected with UCSC to assure comparable results.

During the first four years of the Program, the RMP used a polyurethane foam plug sampler to collect water for trace organics analyses (Risebrough *et al.,* 1976; de Lappe *et al.,* 1980, 1983) and phased in a new, modified, commercially available resin (XAD-2) extraction sampler in 1996, beginning with side-by-side comparisons of both sampling systems. XAD/XAD-2 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 were 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.

Collection of Samples for Trace Organics

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, 3/8 inch outer diameter fluoropolymer tubing, 1 µm glass fiber cartridge particulate filter, and two parallel Teflon® columns filled with XAD-2 resin beads (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. 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 was first passed through a coarse screen before the fluoropolymer intake line. Particles greater than 140 µm were removed by a second inline pre-filter. The water then passed through the pump head and a pressure gauge, before it goes through a four-inch diameter, wound glass fiber filter (1 µm nominal pore size). Flow may be redirected to a second installed filter if the first filter becomes clogged. Material retained on the glass fiber filter (or filters) was designated the particulate fraction. After passing through the filter, the water was split and routed through two Teflon® columns, packed with 75 mL of XAD-2 resin. Two columns were used simultaneously to permit a flow of approximately 1.5 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 (97.5 L per sample) was verified by filling five pre-measured (19.5 L) carboys.

Collection of Field Blanks for Trace Organics

Field blanks were taken for both the resin columns and the glass fiber filters. The two column blanks were collected by opening and closing both ends of a column to simulate

loading of columns into the sampler. Similarly, a glass fiber filter blank was collected by exposing a filter to the air to mimic 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 were collected using a peristaltic pump system equipped with C-Flex tubing in the pump head. Sample containers, which were stored double-bagged, were filled on deck on the windward side of the ship to minimize contamination from shipboard sources (Flegal and Stukas, 1987). Unfiltered (total) water samples were pumped directly into acid-cleaned containers. Filtered (dissolved fraction) water samples were collected through an acid-cleaned polypropylene filter cartridge (Voss Technologies or Micron Separations, Inc., 0.45 μm pore size) on the outlet of the pumping system. Prior to collecting water, several liters of water were pumped through the system and sample bottles were rinsed three times with site water before filling except those for methylmercury. The methylmercury bottles contained a preservative acid, so those samples were collected without rinsing. The bottles were always handled by the "clean hands" collector wearing polyethylene-gloves. The sample tubing and fittings were acid-cleaned polyethylene or fluoropolymer, and the inlets and outlets were kept covered except during actual sampling. Samples were acidified within two weeks in a Class 100 trace metal clean laboratory.

For the analysis of total mercury, water samples (500 mL, minimum) were collected in mercury-clean fluorinated polyethylene (FLPE) bottles, then double-bagged in zip-lock bags. The samples were immediately placed in a cooler on ice. Samples were stored refrigerated at 0 – 4 °C until analysis.

For methylmercury analyses, samples were collected into FLPE bottles (125 to 500 mL). Samples were preserved with 1 – 2 mL sulfuric acid in the field, and stored on ice.

Collection of Field Blanks for Trace Metals

Filtered field blanks were collected prior to the collection of samples using the same acid-cleaned sampling assembly that samples were collected through. Ultra-clean DI water was pumped through the apparatus and an acid-cleaned filter and collected in sample bottles. The field blanks received the same handling and analyses in the laboratory as the field samples.

Collection of Water Quality Samples

Samples for conventional water quality parameters were collected using the same apparatus as for trace metals. Water samples for (dissolved) nitrate and nitrite analyses were frozen on dry ice in the field. Samples for analysis of particulate organic carbon (POC) and chlorophyll/phaeophytin were field filtered on glass fiber filters (GFF) using a vacuum pump. POC samples were filtered on pre-ashed GFF. Chlorophyll/phaeophytin

samples (the residue retained on the filter) were stored in 90% methanol and frozen on dry ice in the field. Bottles for water samples of ammonia, phosphate, and silica were filled without rinsing because the bottles contained pre-measured preservative acid (sulfuric acid for ammonia and phosphate samples and nitric acid for silica samples). The pH of these samples was checked using pH paper to assure that they were appropriately preserved (pH 2 or less).

Collection of Aquatic Bioassay Samples

In 2002, aquatic bioassays (toxicity tests) were only conducted for shallow sites in the Estuary, and the frequency of sampling for aquatic toxicity testing was reduced. No aquatic bioassays were conducted in 2004 and 2005. In March of 2007, the Technical Review Committee decided that aquatic bioassays would be conducted at a five-year interval to assure that any long-term change in toxicity would not be missed. Aquatic bioassay sampling occurred at 9 sites (one per segment and 4 historical sites) in 2007. The next aquatic bioassay sampling will occur in 2012.

2.2.2 Sites

In 2007, RMP Status and Trends Program continued with implementation of the stratified, random sampling design started in 2002 (see Chapter 1, *Introduction*). A total of 26 randomly allocated stations and five historic stations (usually five historic sites per year) in each Bay segment were monitored for contaminants in water between 2002 and 2006. The Status and Trends Program is currently only conducted during the dry season (July/August).

In 2007, 22 sites were sampled for water (Figure 2.1 for site map). Five of these were the historic fixed stations (BA30-Dumbarton Bridge, BC10-Yerba Buena Island, BC20-Golden Gate, BG20-Sacramento River, and BG30- San Joaquin River). The remaining 17 sites were distributed through the five segments as follows: three per segment with the exception of the Lower South Bay which had five sites. Sampling of the 22 sites was successfully completed although one of the random sites (LSB031W) was eliminated due to its proximity to a restricted area (buried water pipeline). This station was replaced with a random oversample site, LSB032W. All other stations were sampled according to the proposed water cruise plan.

Station names, codes, location, and sampling dates for the 2007 monitoring effort are listed in *Appendix 3* and shown in Figure 2.1.

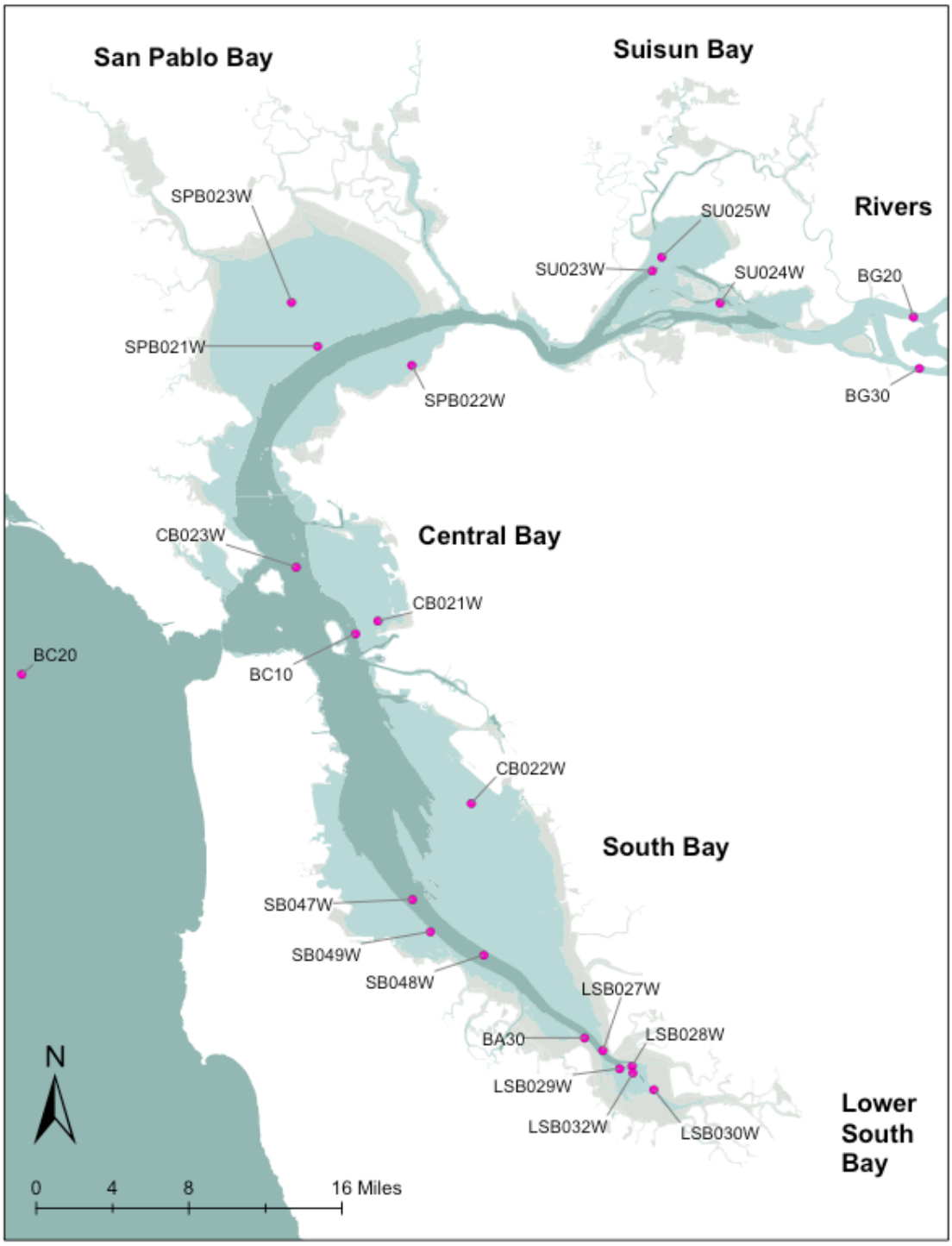


Figure 2.1 - Map of 2007 Water Stations.

2.3 Analysis

2.3.1 Target Analytes

A summary table of target analytes is presented below.

Table 2.1 - Target Analytes

Analyte	Field Prep Code/Method	Analysis Lab
Hg	Acid preserved, field frozen	Brooks Rand Laboratories and UCSC
Dissolved oxygen, conductivity, pH, salinity	None	Collected in field by SFEI
Toxicity	Cooled with wet ice, delivered to lab within 24 hours	Pacific EcoRisk
Trace Elements (Ag, As, Cd, Co, Fe, Mn, Ni, Pb, Zn)	Cooled with wet ice and refrigerated	Brooks Rand Laboratories and UCSC
Selenium	No preservative, chilled	Brooks Rand Laboratories
Methylmercury	Preserved with sulfuric acid (several bottles erroneously preserved with hydrochloric acid)	Brooks Rand Laboratories and UCSC
Mercury	Cooled with wet ice and refrigerated	Brooks Rand Laboratories and UCSC
PAHs	Cooled with wet ice and refrigerated	AXYS Analytical Laboratories
PCBs	Cooled with wet ice and refrigerated	AXYS Analytical Laboratories
Trace organics	Refrigerated	AXYS Analytical Laboratories
POC and DOC	Field filtered, cooled with wet ice, and refrigerated	Applied Marine Sciences, Inc – Texas and UCSC
Chlorophyll/phaeophytin	Field filtered, filter paper stored in 90% methanol, frozen on dry ice	East Bay Municipal Utility District and UCSC
Salinity and hardness	Cooled with wet ice and refrigerated	East Bay Municipal Utility District and UCSC
Ammonia	Cooled with wet ice and refrigerated	East Bay Municipal Utility District and UCSC
Nitrate and nitrite	Frozen on dry ice	East Bay Municipal Utility District and UCSC
Phosphate	Cooled with wet ice and refrigerated	East Bay Municipal Utility District and UCSC
Silica	Cooled with wet ice and refrigerated	East Bay Municipal Utility District and UCSC

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.

2.3.2 Laboratory Methods for Water Analysis

SFEI maintains SOPs for all laboratory analyses. Please contact SFEI for more details.

Laboratory Methods for Water Quality

Beginning in 2007, the RMP began collection of inorganic water samples. The samples were then analyzed by Brooks Rand Laboratories. At 9 of the 22 sites, split samples were collected with and analyzed by UCSC to assure comparable results.

Water Quality Parameters

In 2007, conventional water quality parameters were measured for the RMP by Applied Marine Sciences of Texas (AMS-TX), and the East Bay Municipal Utility District (EBMUD, a wastewater treatment facility) laboratory, with some duplicate samples analyzed by UCSC for intercomparison.

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

Silicates	31-114-27-1
Ammonia	31-107-06-1
Nitrate/nitrite	31-107-04-1
Phosphate	31-115-01-3

EBMUD analyzed dissolved silica, ammonia, and phosphate spectrophotometrically. Silica samples were mixed with molybdate ion in acidic solution, which forms a greenish-yellow color complex in proportion to the amount of dissolved silica in the sample. Ammonia was reacted with alkaline phenol and sodium hypochlorite to produce indophenol blue to which sodium nitroprusside was added. Phosphate samples were reacted with ammonium molybdate and antimony potassium tartrate in acidic conditions to form antimony-phospho-molybdate complex, which turns blue when reduced by ascorbic acid. Reaction products for these analyses were measured by spectrophotometry.

Nitrate-nitrite samples were measured by EMBUD by reaction with sulfanilamide and N-(1-napthyl)-ethylenediamine dihydrochloride to form azo dye, which was measured colorimetrically to determine the concentration of nitrite. The sample was then reacted with granulated copper-cadmium to reduce the nitrate to nitrite, with the procedure repeated to determine a total concentration of nitrate and nitrite. The original concentration of nitrate was determined by subtraction.

UCSC measured chlorophyll and phaeophytin using a fluorometric technique with filtered material from 200 mL samples (Parsons *et al.,* 1984). EBMUD measured chlorophyll and phaeophytin in the filtered material from approximately 1 L of water (ranging 0.5 to 1.5 L) using a similar fluorometric method.

Particulate organic carbon (POC) and dissolved organic carbon (DOC) samples were field filtered with a pre-ashed glass fiber 45 µm filter. The POC sample was retained on the filter and the filtrate was the DOC sample. UCSC measured DOC using high-temperature catalytic oxidation with a platinum catalyst (Fitzwater and Martin, 1993).

AMS-TX measured DOC and POC by combustion with subsequent quantitation of the CO_2 generated (EPA Methods 415.1 and 9060, respectively).

In 2003, total suspended solids (TSS) were replaced by the measurement of suspended sediment concentration (SSC), using method 2540D in Standard Methods for the Examination of Water and Wastewater (APHA, 1992). However, in 2007 EBMUD measured TSS by filtering the sample and drying the retained residue to a constant weight at 103 – 105 °C.

The EBMUD laboratory determined hardness by Method 2340C as described by the 18th Edition of Standard Methods, a titrimetric procedure using EDTA.

In past years, shipboard measurements for temperature, salinity, pH, and dissolved oxygen content were made using a hand-held Solomat 520 C multi-functional chemistry and water quality monitor. Beginning in 2007, shipboard measurements of temperature, salinity, conductivity, pH, and dissolved oxygen were made using a hand-held YSI (556 MPS). Additionally, conductivity, temperature and depth (CTD) casts were taken by AMS at each station (see next section: "Conductivity, Temperature, and Depth (CTD) Casts").

Conductivity, Temperature, and Depth (CTD) Casts

CTD casts were taken by AMS at each site during water, sediment, and tissue sampling. A Sea-Bird SBE19 CTD probe was used to measure water quality parameters at depths throughout the water column. At each site, the CTD was lowered to approximately one meter below the water surface and allowed to equilibrate to ambient temperature for 3 minutes. Following the sampling, the CTD was then lowered to the bottom at approximately 0.15 meters per second and raised. However, only data from the down cast were kept. Data were downloaded onboard the ship and processed in the laboratory using Sea-Bird software.

The CTD probe measured temperature, conductivity, pressure, dissolved oxygen, and backscatter at a sampling rate of two scans per second. These data were 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 from the indicated measures. Although the CTD data are not included in the 2007 RMP Monitoring Results, SFEI maintains these data in a database. Data are available upon request.

Laboratory Methods for Trace Elements

Analysis of Water Samples

Beginning in 2007, the water samples were analyzed by Brooks Rand Laboratories (BRL) for all trace elements reported by the RMP. On receipt at the lab, all samples not previously field-preserved were preserved by addition of pre-tested concentrated HNO_3 to

0.2% (v/v). To assure comparability, UCSC-DET collected and analyzed samples at 9 of the 22 water stations.

BRL analyzed for trace metals using for colorimetric analysis for Fe, inductively coupled plasma-mass spectrometry (ICP-MS) for Mn, reductive precipitation for Cu, Ni, Zn, Cd, Co, Pb, and Ag, and hydride generation-atomic absorption spectrometry (HG-AAS) for As and Se. Methods are briefly described below.

Fe samples were analyzed by reacting Fe(II) with Ferrozine to form a stable violet complex, which was measured colorimetrically. To measure total Fe, Fe(III) was reduced to Fe(II) and analyzed as above; Fe(III) concentrations were then calculated via subtraction.

Mn samples were analyzed via ICP-MS using a Perkin-Elmer ELAN DRC II ICP-MS. Samples were analyzed for Cu, Ni, Zn, Cd, Co, Pb, and Ag by reductively precipitation followed by digestion and oxidation and analysis by ICP-MS using a Perkin-Elmer ELAN DRC II ICP-MS.

Se samples were oxidized to Se(IV) and Se(VI) followed by reduction to Se(IV) and then analyzed by hydride generation-cryogenic trapping-atomic absorption spectrometry (HG-CT-AAS). The methods employed for analysis of As and Se in 2007 were consistent with methods used in 2006, which included slight changes to improve the control of nitrate/nitrite interferences.

UCSC-DET conducted trace metals analyses on field split samples with the exception of As and Se. UCSC-DET used ICP-OES analysis for Fe and Mn and ICP-MS analysis for Cu, Ni, Zn, Cd, Co, Pb, and Ag in 2007. Methods are described below.

Within one week of collection, samples were preserved by acidification to ~ 24 mM with trace metal grade hydrochloric acid (HCl). Acidified samples were then held for a minimum of one week to allow desorption and dissolution. All field and QA (blanks, reference materials) samples were then oxidized with ultraviolet (UV) radiation to degrade any organo-metallic complexes.

Samples for Fe and Mn were analyzed by inductively-coupled plasma - optical emission spectroscopy (ICP-OES). The irradiated field and QA samples were analyzed on a Perkin Elmer ICP-OES (model 430 DV) for Fe and Mn; although UV-digestion was not required for these elements.

The UV-oxidized undiluted samples were analyzed directly by flow-injection inductively-coupled plasma - mass spectrometry (ICP-MS) for the remaining trace metals (Cu, Ni, Zn, Cd, Co, Pb, Ag). The metals of interest are retained by the conditioned column and were eluted off with specific pH buffer prior to entering the analytical system. A cationic resin was used to retain Cu, Ni, Zn, Co, Cd and Pb; an anionic resin column retained Ag.

In some instances, reported dissolved metal concentrations were higher than total (ostensibly including dissolved and particulate fractions) metal concentrations. This was due to expected analytical variation, which was proportionally larger at concentrations near the detection limits. Such results should be interpreted as showing no difference between dissolved and total concentrations, with all the metal in the dissolved phase

Total Mercury Analysis in Water Samples
In 2007, total mercury analysis of water samples was conducted by BRL and by UCSC-DET for a subset of the sampled sites. Samples were collected in acid-cleaned fluorinated polymer (FLPE or PFA) bottles.

BRL analyzed total mercury samples using a modified version of EPA Method 1631E. UCSC-DET also conducted sample digestion and analysis utilizing a modification of EPA Method 1631. Samples were digested by 24 hour oxidation using 0.2N bromine monochloride. Analyses of digests were performed by tin-chloride reduction, purging, gold-amalgamation trapping, thermal desorption, and detection by cold vapor atomic fluorescence spectrometry.

Methylmercury Analysis in Water Samples
In 2007, total mercury analysis of water samples was conducted by BRL and by UCSC-DET at a subset of the sites. Samples were collected in acid-cleaned fluorinated polymer (FLPE or PFA) bottles. Samples for BRL were collected into bottles pre-acidified for preservation,

BRL analyzed methylmercury in water samples by distillation, aqueous phase ethylation, trapping pre-collection, isothermal GC separation, and cold vapor atomic fluorescence spectrophotometer (CVAFS) detection. UCSC-DET analyzed methylmercury in water samples in a similar manner. Prior to analysis of methylmercury by ethylation, distillation separation of methylmercury from the sample matrix was used to reduce interferences during derivitization, particularly from chloride and organic matter. This method is based on Horvat *et al.* (1993a). For samples with low dissolved organic carbon or low ionic strength as well as sulfidic or freshwater samples, additional manipulations were performed to improve extraction.

The analyte solution was adjusted to pH 4.9 using acetate buffer, then ethylated with sodium tetraethyl borate (NaTEB). The ethylated products were purged with nitrogen gas for capture on a Tenax trap and were analyzed by thermal desorption, with gas chromatographic separation, and cold vapor atomic fluorescence spectrometry (CVAFS) detection. The methods are based on Bloom and Fitzgerald (1988) and can be considered variants of EPA Method 1630.

Laboratory Methods for 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) until 2006. Because of inconsistent organophosphate pesticide results in 2006,

water samples were collected and archived for those analytes in 2007, to be analyzed in the future with archived 2006 samples for chlorpyrifos and diazinon. The dissolved and particulate water fractions were combined for all but four sites to reduce the analytical costs for "new" (other than PAHs, PCBs, and organochlorine pesticides) analytes in water.

Analysis of Water Samples

In 2007, trace organics analyses of water samples were conducted by AXYS. 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 or two wound glass filter(s) contained the organic compounds extracted from ~100 L of water at each site. The XAD and the filter samples were generally analyzed together; at three sites the extracts were analyzed separately (three sites plus one duplicate). Each XAD-2 column and filter sample was spiked with labeled surrogate standards, with filter extracted by repeated acetonitrile ambient temperature sonication, and XAD-2 columns with soxhlet extraction. In 2005, this filter extraction method replaced the soxhlet extraction with toluene. The sonication extraction was repeated with hexane, followed by a liquid/liquid extraction. The resulting extracts were split into five portions for separate analyses of PAHs, PCBs, PBDEs, OC pesticides, diazinon and chlorpyrifos. Four of the five portions were analyzed and one was archived. 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.

Extract subsamples were subject to different cleanup procedures and analytical instrumentation, depending up on the target analytes.

PCBs: A florisil chromatographic column was used for the clean-up of the extract 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 Pesticides: A florisil chromatographic column was also used for cleaning the extract 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.

PAHs: PAH extractes were cleaned up on silica and analyzed by high resolution gas chromatography/low resolution mass spectrometry (HRGC/LRMS) using Agilent 6890N GC equipped with an Agilent 5973MSD, an Agilent 7683 Series Autosampler, and a HP Chemstation.

PBDEs: A portion of PBDE extract was cleaned up using gel permeation and separated into two fractions, which were further cleaned using a florisil chromatographic column. Additional cleanup used 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.

Analyses of phthalates and p-nonylphenol were discontinued in 2004. The description of analytical methods remains in this document for informational purposes.

Phthalate Esters: Phthalates were analyzed 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: A portion of the original extract was reserved for p-nonylphenol analysis, with XAD and filter portions combined for p-nonylphenol analysis. The extracts were reduced to dryness and underwent non-aqueous acetylation using pyridine and acetic anhydride. Sample extracts were loaded onto 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.

2.4 Toxicity Testing

Ambient Water Toxicity

Between 1993 and 2002, the Status and Trends Program conducted ambient water toxicity testing on seasonal and annual time scales. A noticeable decline in aquatic toxicity in organisms during this time enabled toxicity testing to be reduced to a five-year cycle. The Status and Trends Program sampled for aquatic toxicity in the Estuary in 2007. The next scheduled aquatic toxicity testing will occur in 2012.

Ambient water toxicity testing was conducted by Pacific EcoRisk. The method used was based on the US EPA Guidelines described in *Short-Term Methods for Estimating the Chronic Toxicity of Effluents and Receiving Waters to Marine and Estuarine Organisms, Third Edition* (EPA-821-R-02-014). This test is based on a 7-day static-renewal exposure of 7-day old *Americamysis bahia* to different concentrations of effluents and/or receiving waters during the life period when eggs are produced by the females. The primary test endpoints are survival and growth (measured as "biomass value" and/or dry weight); an additional fecundity (measured as the number of mature females with eggs in the oviduct and brood sac) endpoint can also be used.

Episodic Water Toxicity

Episodic aquatic toxicity monitoring was conducted in April of 2005 to screen five tributaries that were sampled as part of another study to characterize sediment contamination (RMP analytes plus pyrethroids) and the potential to cause sediment toxicity in tributaries around the Estuary during the wet season. Results of that study are available through the SWRCB PRISM Grant reports (http://www.waterboards.ca.gov/water_issues/programs/grants_loans/prism/). Water samples were collected from the freshwater stations in San Lorenzo Creek, San Mateo Creek, Coyote Creek, Petaluma River, and Suisun Creek and tested using the following short-term chronic toxicity tests: the 3-brood (6-8 day) survival and reproduction test with the crustacean *Ceriodaphnia dubia*; the 7-day shrimp survival and growth test with *A. bahia*; and the 7-day fish survival and growth test with *Menidia beryllina*. None of the water samples showed toxicity using the percent survival endpoint for any test species, which was the endpoint used in previous RMP Episodic Toxicity Monitoring studies. However, a new sub-lethal growth endpoint was also evaluated. San Lorenzo Creek and San Mateo Creek showed significant reduction in *Menidia* growth and Coyote Creek showed a statistically significant reduction in *Ceriodaphnia* growth. Concurrent diazinon and chlorpyriphos results were all below the method detection limit of 0.005 ppb. The full laboratory report is available at SFEI upon request (sarahl@sfei.org).

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 Ten years of testing for the effects of Estuary contamination in the *2003 Pulse of the Estuary*.

2.5 References

Anderson, B., S. Ogle, and S. Lowe. 2003. Ten years of testing for the effects of Estuary contamination. *In*: 2003 Pulse of the Estuary: Monitoring and managing contamination in the San Francisco Estuary. SFEI Contribution 74. San Francisco Estuary Institute. Oakland, CA. http://www.sfei.org/rmp/pulse/pulse2003.pdf

APHA. 1992. Standard Methods for the Examination of Water and Wastewater, 18th Edition. Prepared and published jointly by American Public Health Assoc., American Wastewater Assoc., and Water and Environmental Federation. APHA, Washington, DC.

Bloom, N.S. and Fitzgerald, W.F. 1988. Determination of volatile mercury species at the picogram level by low temperature gas chromatography with cold vapor atomic fluorescence detection. Analytica Chimica Acta, 208, 151–161.

Conaway, C.H., S. Squire, R.P. Mason, and A.R Flegal. 2003. Mercury speciation in the San Francisco Bay Estuary. *Marine Chemistry* 80:199-225.

De Lappe, B.W., R.W. Risebrough, A.M. Springer, T.T. Schmidt, J.C. Shropshire, E.F. Letterman, and J. Payne. 1980. The sampling and measurement of hydrocarbons in natural waters. In Hydrocarbons and Halogenated Hydrocarbons in the Aquatic Environment, B.K. Afghan and D. Mackay, eds. Plenum Press, NY, pp. 29-68.

De Lappe, B.W., R.W. Risebrough, and W. Walker II. 1983. A large-volume sampling assembly for the determination of synthetic organic and petroleum compounds in the dissolved and particulate phases of seawater. *Canadian Journal of Fisheries and Aquatic Sciences* 40:322-336.

Fitzwater, S.E. and J.M. Martin. 1993. Notes on the JGOFS North Atlantic bloom experiment--dissolved organic carbon intercomparison. *Marine Chemistry* 41:179-185.

Flegal, A.R., C.H. Conaway, and S.A. Sañudo-Wilhelmy. 2004. Long-term trends in metal contamination in San Francisco Bay. 2004 Pulse of the Estuary. San Francisco Estuary Institute. Oakland, CA.

Flegal, A.R. and V.J. Stukas. 1987. Accuracy and precision of lead isotopic composition measurements in seawater. *Marine Chemistry* 22:163-177.

Horvat, M., Bloom, N.S. and Liang, L. 1993a. Comparison of distillation with other current isolation methods for the determination of methyl mercury compounds in low level environmental samples, Part 1: Sediments. Analytica Chimica Acta, 281, 135–152.

Infante, A.P., N.C. Guajardo, J.S. Alonso, M.C.M. Navascues, M.P.O. Melero, M.S.M. Cortabitarte, and J.L.O. Narvion. 1993. Analysis of organic water pollutants isolated by XAD-2 resins and activated carbon in the Gallego River, Spain. *Water Research* 7:1167-1176.

Kuwabara, J.S., C.C.Y. Chang, J.E. Cloern, T.L. Fries, J.A. Davis, and S.N. Luoma. 1989. Trace metal associations in the water column of South San Francisco Bay, California. *Estuarine Coastal and Shelf Science* 26:307-325.

Leatherbarrow, J.E., R. Hoenicke, and L.J. McKee. 2002. Results of the Estuary Interface Pilot Study, 1996-1999. RMP Technical Report. SFEI Contribution 50. San Francisco Estuary Institute. Oakland, CA.

McKee, L.J., J.E. Leatherbarrow, R. Eads, and L. Freeman. 2004. Concentrations and loads of PCBs, OC pesticides, and mercury associated with suspended particles in the lower Guadalupe River, San Jose, California. San Francisco Estuary Institute. Oakland, CA.

Menconi, M. and C. Cox. 1994. Hazard assessment of the insecticide diazinon to aquatic organisms in the Sacramento-San Joaquin river system. Administrative Report 94-2. California Department of Fish and Game. Rancho Cordova, CA.

Ogle, R.S. and A. Gunther. 2004. Draft Final Data Report. Episodic ambient water toxicity in the San Francisco Estuary. Prepared for the San Francisco Estuary Regional Monitoring Program. Pacific EcoRisk. Martinez, CA.

Risebrough, R.W., B.W. de Lappe, and W. Walker II. 1976. Transfer of higher-molecular weight chlorinated hydrocarbons to the marine environment. In Marine Pollutant Transfer, H.L. Windom and R.A. Duce, (eds.), D.C. Heath Company, Lexington, Massachusetts and Toronto, pp. 261-321.

SFBRWQCB. 2004. San Francisco Bay Basin, Region 2: Water Quality Control Plan. California Regional Water Quality Control Board, San Francisco Bay Region. Oakland, CA.

SFBRWQCB. 2007. Copper Site-Specific Objectives in San Francisco Bay: Proposed Basin Plan Amendment and Draft Staff Report. California Regional Water Quality Control Board, San Francisco Bay Region, CA.

SFEI. 1999. 1997 Annual Report: San Francisco Estuary Regional Monitoring Program for Trace Substances. RMP Report 37. San Francisco Estuary Institute, Richmond, CA pp. A67-A80.

Sañudo-Wilhelmy, S.A., I. Rivera-Duarte, and A.R. Flegal. 1996. Distribution of colloidal trace metals in the San Francisco Bay estuary. *Geochimica Cosmochimica Acta* 60:4933-4944.

Schoellhamer, D.H. 1996a. Time series of trace element concentrations calculated from time series of suspended solids concentrations and RMP water samples. RMP Contribution #16. The San Francisco Estuary Regional Monitoring Program for Trace Substances. United States Geological Survey. Sacramento, CA.

Schoellhamer, D.H. 1996b. Factors affecting suspended-solids concentrations in South San Francisco Bay, California. *Journal of Geophysical Research* 101:12,087-12,095.

Schoellhamer, D.H., G.G. Shellenbarger, N.K. Ganju, J.A. Davis, and L.J. McKee. 2003. Sediment dynamics drive contaminant dynamics. *In*: 2003 Pulse of the Estuary: Monitoring and managing contamination in the San Francisco Estuary. SFEI Contribution 74. San Francisco Estuary Institute. Oakland, CA. http://www.sfei.org/rmp/pulse/pulse2003.pdf

Squire, S., G. Scelfo, J. Revenaugh, and A.R. Flegal. 2002. Decadal trends of silver and lead contamination in San Francisco Bay surface waters. *Environmental Science and Technology* 36:2379-2386.

Steding. D., C.E. Dunlap, and A.R. Flegal. 2000. New isotopic evidence for chronic lead contamination in the San Francisco Bay estuary system: implications for the persistence

of past industrial lead emissions in the biosphere. *Proceedings of the National Academy of Sciences* 97:11181-11186.

Thomas, M.A., C.H. Conaway, D.J. Steding, M. Marvin-DiPasquale, K.E. Abu-Saba, and A.R. Flegal. 2002. Mercury contamination from historic mining in water and sediment, Guadalupe River and San Francisco Bay, California. *Geochemistry: Exploration, Environment, Analysis* 2:1-7.

U.S. EPA. 1992. Water Quality Standards; Establishment of Numeric Criteria for Priority Toxic Pollutants. 57 Federal Register 60848. December 22, 1992. U.S. Environmental Protection Agency.

U.S. EPA. 1994a. Short-term methods for estimating the chronic toxicity of effluents and receiving waters to marine and estuarine organisms. Second Edition. EPA-600-4-91-003. U.S. Environmental Protection Agency. Environmental Monitoring Systems Laboratory. Cincinnati, OH. 97:11181-11186.

U.S. EPA. 1994b. Short-term methods for estimating the chronic toxicity of effluents and receiving waters to freshwater organisms. Third Edition. EPA-600-4-91-002. U.S. Environmental Protection Agency. Environmental Monitoring Systems Laboratory. Cincinnati, OH.

U.S. EPA. 1995. Method 1669: Sampling ambient water for trace metals at EPA water quality criteria levels. EPA 821-R-95-034, United States Environmental Protection Agency, Washington, D.C.

U.S. EPA. 1999. National recommended water quality criteria – correction. Office of Water. EPA 822-Z-99-001. U.S. Environmental Protection Agency.

U.S. EPA. 2000. Water Quality Standards; Establishment of Numeric Criteria for Priority Toxic Pollutants for the State of California; Rule. Federal Register Vol. 65, No. 97, May 18, 2000. U.S. Environmental Protection Agency.

CHAPTER 3

Sediment Monitoring

3.0 Sediment Monitoring

3.1 Background

Since 1993, the Regional Monitoring Program for Water Quality in the San Francisco Estuary (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 *Introduction*). Patterns in sediment contamination are described (Objective 1) and compared to several sets of sediment quality guidelines (Objective 5), while sediment bioassays address contaminant effects (Objective 4).

3.2 Field Methods

3.2.1 Sediment Sampling Field Methods

Multiple (two to three) sediment grabs were taken at each site, with sediment sub-samples collected for chemical and toxicity analyses. Sediment samples were collected using a Young-modified Van Veen grab with a surface area of 0.1 m^2. The grab is made of stainless steel, and the jaws and doors are coated with Dykon® (formerly known as Kynar®) to make them chemically inert. All scoops, buckets, and stirrers used to collect and homogenize sediments are constructed of Teflon® or stainless steel coated with Dykon®. Sediment sampling equipment was thoroughly cleaned (sequentially with detergent, acid, methanol, and rinsed with ultrapure water) at each sampling location prior to each sampling event. In order to further minimize sample contamination, personnel handling samples wear gloves and employ clean hands techniques.

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. Overlying water was drained off an accepted grab, and a probe was inserted directly into the sediment to measure pH. Using pre-cleaned coring tubes, cores were taken near the sides in the deepest section of the grab for measurement of oxidation-reduction potential (ORP). Sub-samples for special studies requiring unmixed material were also taken. The top 5 cm of sediment was scooped from the remaining area (avoiding portions cored or probed) in each of the grabs and placed in a compositing bucket to provide a single

composite sample for each site. Between sample grabs, the compositing bucket was covered with aluminum foil to prevent airborne contamination. After all sediment grabs (or at least two if complications prevent collection of sufficient material within 20 minutes) were placed into the compositing bucket, the bucket was taken into the ship's cabin and thoroughly mixed to obtain a uniform, homogeneous mixture. Aliquots were subsequently split into appropriate containers for sediment quality, trace metal, trace organics, and toxicity analyses for archive samples.

Collection of Ancillary Parameters

Samples were collected in 250 mL HDPE containers for ancillary analyses by Applied Marine Sciences – Texas (AMS-TX) and UC Santa Cruz (UCSC-DET). AMS-TX supplied factory cleaned I-Chem 200 series (or equivalent) containers. UCSC-DET containers were cleaned at UC Santa Cruz. After collection, AMS-TX samples were refrigerated and subject to a 28-day hold time while UCSC-DET samples were placed in the freezer and remained frozen until delivered to the lab.

Collection of Trace Metal Parameters

Sediments for Trace Metal and Archive Trace Metal analysis were collected for East Bay Municipal Utility District (EBMUD). EBMUD supplied factory cleaned I-Chem 200 series (or equivalent) 250 ml HDPE containers. Samples were placed into the freezer and remained frozen until delivered to the lab.

I-Chem 300 series factory cleaned 250 ml HDPE containers were double bagged and provided by Brooks Rand Ltd. (BRL) for collection and analysis of for analysis of arsenic (As) and selenium (Se) in sediment. Samples were placed in the freezer and remained frozen until analysis.

For methylmercury (MeHg) analysis, sampling and handling procedures are the most important factors influencing the accuracy and uncertainty of MeHg in sediments (Horvat *et al.,* 2004). The transformation and degradation of MeHg can also occur during sample storage and pretreatment, so great care was taken to minimize disturbance and exposure of the sediments to environmental factors that could alter the MeHg concentrations. These factors include light, temperature and atmosphere (Conway *et al.,* 2006). Methylmercury samples were placed on dry ice within 20 minutes of first successful grab collection.

Total mercury (Hg) and MeHg samples were sent to UCSC-DET and BRL for analysis. Sediment was collected for UCSC-DET in 125 mL HDPE containers with screw-cap lids cleaned by the lab using the following procedure. 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 five times to remove all acid residues and then allowed to air dry in a class 100 work area. Containers were stored double bagged. After collection, Hg samples were placed in the freezer and MeHg samples were placed in a cooler on dry ice within 20 minutes of collection. Samples remained frozen while in AMS-CA custody.

I-Chem 300 series factory cleaned 250 ml HDPE containers were double bagged and provided by BRL for collection and analysis of Hg and MeHg in sediment. Within 20 minutes of sediment collection Hg and MeHg samples were placed in a cooler with dry ice and stored frozen while in AMS-CA custody.

Collection of Trace Organic Parameters

Trace Organics and Archive Trace Organics were collected for EBMUD in factory cleaned I-Chem 200 series (or equivalent) 250 ml glass containers. Head space was left at the top of the containers to allow for expanding sediment. Samples were frozen immediately after collection and remained frozen until delivered to the lab.

Collection of Sediment for Toxicity Sampling

Solid-phase amphipod and bivalve elutriate sediment toxicity tests were performed for sediment toxicity. *Eohaustorius estuarius* percent survival and *Mytilus galloprovincialis* percent normal development tests (including ammonia and H_2S measurements) were performed on three liters of sediments sampled from 27 sites:

- 20 random sites (half of the random sampling sites)
- 7 fixed historical samples (BG20, BG30, BF21, BD41, BC11, BA41, and BA10).

One liter plastic containers were provided by University of California, Davis (UCD) for the collection of toxicity samples. The containers were cleaned by the lab using the following procedures: containers were scrubbed with dilute micro solution, rinsed with DI, rinsed with hexane, and rinsed with DI again. The containers were then soaked for 24 hours in an acid bath, rinsed with DI and then soaked for 24 hours in a DI bath. Containers were rinsed again with DI water and placed in a drying oven overnight. Containers were sent to AMS-CA for sample collection.

During the first day of the cruise sediment toxicity samples were collected at the odd-numbered sites within each region (e.g., SU001S, SU003S, SU005S, and SU0035S) as in the past. The collection scheme was altered per SFEI's request for the remainder of the cruise so that toxicity samples were collected from the four lowest numbered sites within a region (e.g., SU001S, SU002S, SU027S, SU028S). This change represents a move toward a sequential sampling design. Mapping of station locations where toxicity samples were collected in previous years showed that the odd number stations clustered in one area of each targeted bay segment while the even numbered stations clustered in the opposite area.

Shipboard Measurements

Conductivity, Temperature, and Depth (CTD) Casts:

CTD casts were taken by AMS-CA at each site. A Sea-Bird SBE19 CTD probe was used to measure water quality parameters at depths throughout the water column. At each site, the CTD was lowered to approximately one meter below the water surface and allowed to equilibrate to ambient temperature for 3 minutes. Following the sampling, the CTD was then lowered to the bottom at approximately 0.15 meters per second and raised.

However, only data from the down cast were kept. Data were downloaded onboard the ship and processed in the laboratory using Sea-Bird software.

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

pH and ORP shipboard measurements:
Two measurements of *in situ* pH were recorded on board the sampling vessel by submerging a Hach™ 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. Measurement of sediment oxidation-reduction potential (ORP) was resumed in 2003, measured in a cored sub-sample of the van Veen by probe inserted (WTW Sentix ORP, KCl electrolyte) to depths of 1 cm and 6 cm from the sediment surface, and 1 cm from the core bottom. The probe was equilibrated for 10 minutes before recording each measurement.

3.2.2 Sites

In 2007, RMP Status and Trends Program continued with implementation of the stratified, random sampling design started in 2002 (see Chapter 1, *Introduction*). Since 2002 sediment contaminant monitoring has been conducted each year during the dry season (July/August) at 47 stations, including seven fixed historical stations.

In order to allow for analysis of long-term temporal trends, repeat sampling of a subset of random sites and continued (yearly) monitoring of historic sites in each of the six regions is conducted. The Rivers Region has two historic sites, the Sacramento River (BG20) and the San Joaquin River (BG30). All other regions have one historic site each: Suisun Bay (Grizzly Bay - BF21), San Pablo Bay (Pinole Point - BD31), Central Bay (Yerba Buena Island - BC11), South Bay (Redwood Creek - BA41) and Lower South Bay (Coyote Creek - BA10). Sites ending with 001S or 002S are randomly allocated sites sampled yearly and those ending in 003S and 004S are randomly allocated sites sampled every 5 years. The seven historic sites were picked because they have long-term synoptic chemistry and toxicity measures associated with them (SFEI, 2005). Sediments collected from a subset of 20 random sites and all seven historic sites were used for conducting sediment bioassays (Figure 3.2). Station names, codes, location, and sampling dates for the 2007 sediment monitoring effort are listed in *Appendix 4*.

Sediment was successfully collected from all seven historic sites with the exception that the Sacramento River site (BG20) had to be repositioned outside of the 100 m radius of the target coordinates in order to collect suitable substrate. SU002S, a site monitored annually, also had to be repositioned outside of the 100 m radius of the target coordinates in order to locate suitable substrate. Three target stations had to be replaced due to

unforeseen issues. SU035S was abandoned before the cruise due to its location within an exclusion zone around a group of WWII Navy Ships known locally as the "Mothball Fleet" located just northeast of the Benicia Bridge. It was replaced with site SU078S. SPB036S was replaced with SPB075S due to the inability to obtain appropriate sediment. SU036S also had inappropriate sediment for a successful sample so it was replaced with oversample site SU079S.

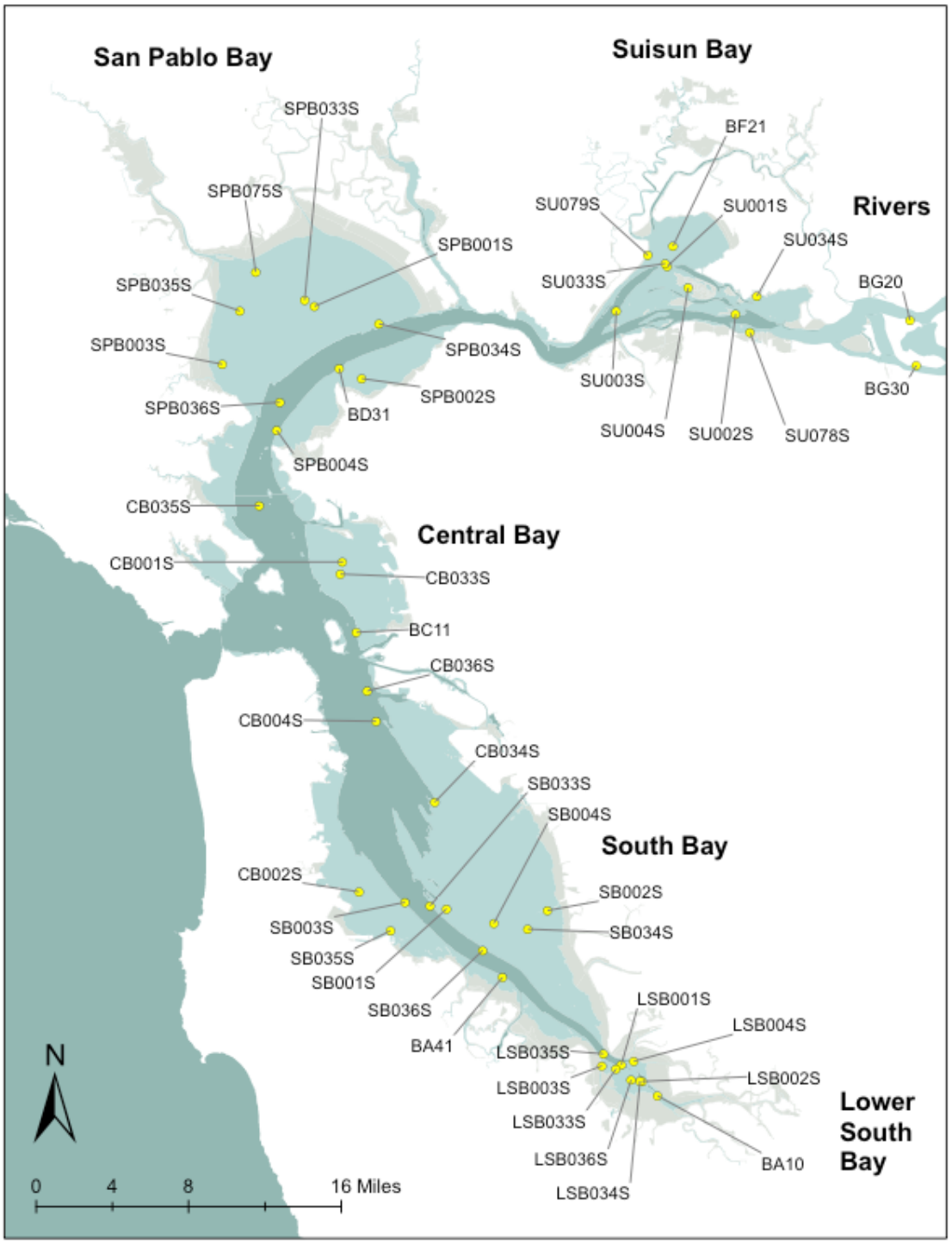


Figure 3.1 - Map of 2007 Sediment Stations.

3.3 Analysis

3.3.1 Target Analytes

In 2007 several different labs analyzed sediment for the RMP. See Appendix tables for data available by year, analyte and matrix.

Table 3.1 - Sediment Quality Parameters and Sediment Toxicity Tests

Sediment Quality Parameters	**Lab(s)**	**Reporting Unit**	**Method Code(s)**
Clay <0.0039 mm	AMS-TX/UCSC-DET	%	Plumb, 1981/ Hibdon, S.H. 1997
Silt 0.0039 to <0.0625 mm	AMS-TX/UCSC-DET	%	Plumb, 1981/ Hibdon, S.H. 1997
Fine <0.0625 mm	AMS-TX/UCSC-DET	%	Plumb, 1981/ Hibdon, S.H. 1997
Sand 0.0625 to <2.0 mm	AMS-TX	%	Plumb, 1981
Granule + Pebble 2.0 to <64 mm	AMS-TX/UCSC-DET	%	Plumb, 1981/ Hibdon, S.H. 1997
% solids	BRL/CCSF/EBMUD	%	EPA 160.3/ EPA 3050B Mod. /EPA 160.3
Depth	AMS-CA	m	
pH (porewater, interstitial sediment)	AMS-CA	pH	
Total Organic Carbon	AMS-TX/UCSC-DET	%	UCD-TOC-TN/EPA 9060A
Total Nitrogen	UCSC-DET	%	UCD-TOC-TN
Nitrogen, Total Kjeldahl	AMS-TX	%	EPA 351.3
Toxicity Tests - Sediment			
Sediment Toxicity – (Amphipod) % Survival	UCD-GC	%	EPA 600/R-94-025
Sediment Toxicity – (Bivalve) % Normal Alive	UCD-GC	%	EPA 600/R-95-136

Table 3.2 - Trace Element Analytes in Sediment

Trace elements analyzed in sediment samples[1]			
Lab(s)	Lab(s)	Reporting Unit	Method Code
Aluminum (Al)	CCSF	mg/kg	EPA 6020A Mod.
Arsenic (As)	BRL/CCSF	mg/kg	EPA 1638/ EPA 6020A Mod.
Cadmium (Cd)	CCSF	mg/kg	EPA 6020A Mod.
Cobalt (Co)	CCSF	mg/kg	EPA 6020A Mod.
Copper (Cu)	CCSF	mg/kg	EPA 6020A Mod.
Iron (Fe)	CCSF	mg/kg	EPA 6020A Mod.
Lead (Pb)	CCSF	mg/kg	EPA 6020A Mod
Manganese (Mn)	CCSF	mg/kg	EPA 6020A Mod.
Mercury (Hg)	BRL/CCSF/ UCSC-DET	mg/kg	EPA 1631/ EPA 6020A Mod/ CVAFS
Mercury, Methyl (MeHg)	BRL/UCSC-DET	µg/kg	EPA 1630/ Ethylation-GC-CVAFS
Nickel (Ni)	CCSF	mg/kg	EPA 6020A Mod.
Selenium (Se)	BRL/CCSF	mg/kg	HGAAS/ EPA 6020A Mod.
Silver (Ag)	CCSF	mg/kg	EPA 6020A Mod.
Zinc (Zn)	CCSF	mg/kg	EPA 6020A Mod.
[1] All sediment samples are reported in a dry weight basis.			

Table 3.3 - Trace Organic Analytes in Sediment

Trace organic parameters analyzed in sediment samples			
Analyte Type[1]	Lab(s)	Unit	Method
PAHs (Low Molecular Weight, High Molecular Weight, Alkylated)	EBMUD	µg/kg	EPA 8270
Cyclopentadienes	EBMUD	µg/kg	EPA 1668A Mod.
Chlordanes	EBMUD	µg/kg	EPA 1668A Mod.
DDTs	EBMUD	µg/kg	EPA 1668A Mod.
HCHs	EBMUD	µg/kg	EPA 1668A Mod.
Other Synthetic Biocides (Hexachlorobenzene, Mirex)	EBMUD	µg/kg	EPA 1668A Mod.
PCBs	EBMUD	µg/kg	EPA 1668A
PBDEs[2]	EBMUD	µg/kg	EPA 1614 Mod.

[1] See *Appendix 5 Target Analytes 2007* for an expanded list of trace organic parameters and a complete list of parameters collected in other matrices.
[2] In 2007 BDE 196 and 197 were added to the target analyte list. These additions will result in a more accurate estimate of total PBDEs since these congeners constitute a relatively high percentage of the Deca-BDE mix.

3.3.2 Laboratory Methods for Sediment Analysis

A brief overview of the laboratory methods used for the target analytes are described below. SFEI maintains SOPs for all laboratory analyses. Please contact Donald Yee donald@sfei.org or Cristina Grosso cristina@sfei.org for more details.

Percent Solids

Brooks Rand LLC (BRL) measured percent solids in sediment using EPA Method 160.3. For this method a solid sample is homogenized and an aliquot is measured, dried, and measured and the percent of dried solid material is calculated.

City and County of San Francisco (CCSF) analyzed percent solids as part of their analysis of trace metals using EPA 3050B Mod. When analyzing for trace metals in sediment a separate homogeneous aliquot of the sample must be dried to determine total percent solids.

Grainsize

Applied Marine Sciences (AMS-TX) measured grainsize in 2007 according to Plumb (1981). Sediment samples were wet-sieved through a No. 230 (0.0625 mm) U.S. Standard Sieve. The fine fraction (silt and clay) was collected in a 1-L graduated cylinder. Sediment retained on the No. 230 sieve was washed with distilled water into a pre-labeled and pre-weighed beaker and oven dried for 24 hours at 105 °C. After drying, the soil was passed through a No. 10 U.S. Standard Sieve to determine the percent gravel and a No. 230 sieve to determine the percent sand. Sediment passing the No. 230 sieve was added to the fine fraction in the graduated cylinder. The fine fraction was stirred and aliquots secured using a pipette for determination of the percent silt (<0.0625 mm to 0.0039 mm) and percent clay (< 0.0039 mm). Sample results were reported in percent gravel, sand, silt, and clay on a dry-weight basis. Samples were grouped into batches of 15 or less. In each batch, the following QA samples are analyzed: Sample Duplicate –

replicate aliquots prepared and analyzed independently to quantify method performance. RPD of the replicate results must be ≤ 25%.

University of California, Santa Cruz – Department of Environmental Toxicology (UCSC-DET) measured grainsize as part of the Intercomparison study with AMS-TX in 2007. Samples are thawed and organic matter is removed by H_2O_2 digestion. Salts are removed by washing several times using a centrifuge. The fine and course fractions are separated by wet sievieng through a 63µm sieve and receiver. The fine fraction is analyzed on a Sedigraph 5100. This is then dried and weighed to give the clay and silt fraction. The dry coarse fraction is weighed and passed through a 2mm sieve to separate the sand and gravel fractions. The sand fraction is obtained from the difference of the total coarse and gravel fractions.

TOC and Total Nitrogen

UCSC-DET analyzed sediments for total organic carbon (TOC) and total nitrogen (TN). The sediment samples are dried and finely ground to completely homogenize the sample. TOC is determined by acidifying the sediment to remove the inorganic carbon fraction (Nieuwenhuize, et al. 1994). Acidification does not affect TN measurements (Nieuwenhuize, et al. 1994). An aliquot is analyzed for TOC and TN with a Carlo Erba 2500 Elemental Analyzer. The sediment is combusted at 1030 °C in a quartz tube containing layers of chromium oxide and silver cobaltous-cobaltic oxide, with oxygen acting as the oxidizing agent. The reaction products (CO_2 and nitrogen oxides) are swept by a continuous He flow into a second quartz tube filled with active copper granules where nitrogen oxides are reduced into elemental nitrogen at 650 °C. The gas mixture (CO_2, N_2, and water) is separated by a 2 m (6 mm o.d. and 4 mm i.d.) stainless steel column packed with Poropack QS and detected by a thermal conductivity detector. Instrument standards are alanine and pugel. At least 10 % of the sediment samples are processed in triplicate to evaluate precision. Method blanks are measured by processing a clean, acidified silver capsule. Equipment blanks are measured by analyzing a clean silver capsule, without acidification (silver capsules are cleaned by baking in 450 °C – 500 °C muffle furnace). Standard Reference Materials were measured to determine accuracy. Accuracy of carbon measurements is evaluated by the analysis of MESS-2, Beaufort Sea marine sediment reference material (National Research Council Canada). Accuracy of nitrogen measurements is evaluated by analysis of CP-1, compost (AgroMAT).

AMS-TX analyzed sediments for TOC. Organic carbon is measured using a carbonaceous analyzer. This instrument converts the organic carbon in a sample to carbon dioxide (CO_2) by either catalytic combustion or wet chemical oxidation. The CO_2 formed is then either measured directly by an infrared detector or converted to methane (CH_4) and measured by a flame ionization detector. The amount of CO_2 or CH_4 in a sample is directly proportional to the concentration of carbonaceous material in the sample. One blank was analyzed per sample batch and calibration was verified with an independently prepared check standard every 15 samples. One spike duplicate sample was analyzed for every 10 samples. A duplicate sample is a sample brought through the whole sample preparation and analytical process.

AMS-TX analyzed sediments for Total Kjeldahl Nitrogen (TKN) using EPA Method 351.3. TKN is defined as the sum of free-ammonia and organic nitrogen compounds which are converted to ammonium sulfate $(NH_4)_2SO_4$ when the sample is heated in the presence of concentrated sulfuric acid, K_2SO_4 and $HgSO_4$ and evaporated until SO_3 fumes are obtained and the solution becomes colorless or pale yellow. The residue is cooled, diluted, and is treated and made alkaline with a hydroxide-thiosulfate solution. The ammonia is distilled and determined by EPA Method 3251.3. Three alternatives are listed for the determination of ammonia after distillation: the titrimetric method which is applicable to concentrations above 1 mg N/liter; the Nesslerization method which is applicable to concentrations below 1 mg N/liter; and the potentiometric method applicable to the range 0.05 to 1400 mg/L.

Analysis of Sediment Trace Metals

In 2007, trace metals in sediment were analyzed by the City and County of San Francisco (CCSF), BRL and UCSC-DET.

CCSF Trace Metals analysis consisted of Al, As, Cd, Ca, Cr, Co, Cu, Fe, Pb, Mg, Mn, Hg, Ni, Se, Ag, and Zn. These metals were measured using digest method EPA 3050BM and analysis method EPA 6020AM. For the digestion of samples, a representative 1 – 2 gram (wet weight) or 1 gram (dry weight) sample is digested with repeated additions of nitric acid (HNO_3) and hydrogen peroxide (H_2O_2). For Inductively Coupled Plasma-Mass Spectrometry (ICP-MS) analysis, the resultant digestate is reduced in volume while heating and then diluted to a final volume of 100 mL. ICP-MS measures ions produced by a radio-frequency inductively coupled plasma. Analyte species originating in a liquid are nebulized and the resulting aerosol is transported by argon gas into the plasma torch. The ions produced by high temperatures are entrained in the plasma gas and extracted through a differentially pumped vacuum interface and separated on the basis of their mass-to-charge ratio by a mass spectrometer. The ions transmitted through the mass spectrometer are quantified by a channel electron multiplier or Faraday detector and the ion information is processed by the instrument's data handling system. Interferences must be assessed and valid corrections applied or the data qualified to indicate problems. Interference correction must include compensation for background ions contributed by the plasma gas, reagents, and constituents of the sample matrix.

BRL analyzed As, Hg, MeHg, and Se. Arsenic samples were analyzed using EPA Method 1638 by ICP-MS. Samples are closed-vessel oven digested with HNO_3 and hydrochloric acid (HCl). Aliquots of digested sample are pipetted into 15-mL centrifuge tubes, diluted to 10-mL with reagent water, and then analyzed using ICP-MS with 74Ge internal standardization. Detection is based on the mass-to-charge ratio of the ions.

BRL analyzed mercury samples using EPA Method 1631. Samples were digested in HNO_3 and H_2SO_4, and then further oxidized with bromine monochloride (BrCl). Samples are analyzed with stannous chloride ($SnCl_2$) reduction, single gold amalgamation and cold vapor atomic fluorescence spectroscopy (CVAFS) detection

using a BRL Model III CVAFS Mercury Analyzer. All sample results for low-level mercury analysis are blank corrected.

BRL analyzed methylmercury samples using EPA Method 1630 Modified. The sediment samples are prepared by acid bromide/methylene chloride extraction. The samples are analyzed by aqueous phase ethylation, Tenax trap collection, gas chromatography separation, isothermal decomposition, and cold vapor atomic fluorescence spectroscopy (CVAFS).

BRL analyzed selenium using hydride generation atomic absorption spectroscopy (HGAAS). Sample aliquots of approximately 1000 mg are measured into flasks and digested with a nitric/hydrochloric acid (HNO_3:HCl) mixture. Samples are then diluted with deionized water and potassium persulfate ($K_2S_2O_8$) and heated in a water bath at 150 ºC for 1 hour. Prior to cooling, 100 mg of sulfanilamide is added to each sample to remove potentially interfering nitrates. Analysis is performed using hydride generation with sodium borohydride ($NaBH_4$) addition, cryogenic trap precollection, hydrogen/air flame quartz furnace decomposition, and atomic absorption spectroscopy (HGAAS).

UCSC-DET analyzed methylmercury and total mercury in sediment. The analysis for total mercury was based on Bloom and Crecelius *(1987)*. Sediments were prepared in the lab by freeze drying and were stored in a well-sealed dessicator until analysis. Samples were digested using a weak acid (60:40 solution of HNO_3:H_2SO_4) and oxidized with bromine monochloride (BrCl). Samples were analyzed by cold vapor atomic fluorescence spectrometry using a Tekran 2600 automated water analysis system.

Methylmercury in sediment was first separated by acid digest-organic extraction. A known mass of sediment was digested in a Teflon centrifuge tube using an acidic mixture of potassium chloride (KCl), copper sulfate ($CuSO_4$), and sulfuric acid (H_2SO_4). An organic solvent, methylene chloride/dichloromethane (CH_2Cl_2), was added to the mixture, into which MeHg and other organomercury species (and other organic compounds), preferentially partition. This acid-organic extraction was 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 was transferred to a glass centrifuge tube containing ultra-pure water for back-extraction into an aqueous phase. The organic solvent was volatilized by placing samples in a warm sand bath and bubbling with inert Hg free gas (N_2 or Ar). The soluble MeHg remained in the aqueous phase and was analyzed by Aqueous Phase Ethylation using a method based on the Bloom and Fitzgerald (1988) method. The analysis the pH of the analyte solution was adjusted to 4.9 using acetate buffer. The solution was then ethylated using sodium tetraethyl borate (NaTEB) and allowed to react for 15 minutes. Following reaction with NaTEB the solution was purged with nitrogen gas (N_2) for 15 minutes, and the MeHg was collected on a Tenax trap after which tubes were dried for 15 minutes. Mercury species were 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).

Analysis of Sediment Trace Organics

In 2007, sediment organics were analyzed by EBMUD (the RMP lab for sediment organics since 1997). Sediment samples are generally analyzed based on the methods followed by NOAA's National Status and Trends Program. PAHs were analyzed using gas chromatography/mass spectrometry (GC/MS) and PCBs, PBDEs, and organochlorine pesticides were analyzed using high resolution gas chromatography – mass spectrometry (HRGC-MS).

Samples were homogenized and then extracted using a Dionex Accelerated Solvent Extraction, ASE (U.S. EPA Method 3545). The sample extracts were dried with anhydrous granular Na_2SO_4. Extracts were cleaned up with an alumina/copper column and concentrated to 1 ml in DCM. This extraction and concentration procedure was used for all trace organic compounds of interest in the sediment samples.

Just prior to analysis of PAHs 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 PAHs in sediments.

Organochlorine (OC) pesticide samples were analyzed using a modified method of EPA 1668A. Just prior to analyses, injection internal standards were added to the sample extracts, and then an aliquot of the extract was injected into the gas chromatograph. The analytes were separated by the gas chromatograph and detected by a high resolution (>8,000) mass spectrometer (HRMS). Two exact m/z's were monitored throughout a predetermined detention time.

PCB samples were analyzed using EPA Method 1668A. A cleanup standard was spiked into the extract prior to analyses. The extract was then put through a drying column and concentrated. After drying and concentrating, the samples were cleaned up using gel permeation and activated alumina column chromatography. After cleanup, the solvent was exchanged to hexane. Injection internal standards were added to each extract before injection into the gas chromatograph. The analytes were separated by gas chromatography and detected by a high-resolution (>10,000) mass spectrometer (HRMS). Similar to the oc-pesticide analyses, two exact m/z's were monitored throughout a predetermined detention time.

PBDE samples were analyzed using EPA 1614M. A cleanup standard was spiked into the extract, which was then dried and concentrated. The samples were then purified using an activated alumina column, and the solvent in the samples was exchanged to hexane. Just prior to the analysis, injection internal standards were added to each extract and an aliquot was injected into the gas chromatograph. Similar to OC pesticides and PCB analyses, the PBDE congeners were separated by the gas chromatograph and detected by a high-resolution (>5,000) mass spectrometer (HRMS) with two exact m/z's monitored for each compound.

3.4 Toxicity Testing

Toxicity tests 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. In 2007, sediment bioassays were conducted by UC Davis - Marine Pollution Studies Laboratories (UCD-MPSL) as in previous years. Two types of sediment bioassays, % survival for amphipods and % normal alive for bivalves, were conducted at 27 of the 47 RMP stations (Figure 3.2).

Amphipods (*Eohaustorius estuarius*) were analyzed for toxicity using EPA 600/R-94-025. 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. Twenty randomly selected amphipods were placed into replicate container and allowed to burrow into the test sediments. Samples were exposed to whole sediment for ten days with percent survival 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.

Larval mussels (*Mytilus galloprovincialis*) were analyzed for toxicity using EPA 600/R-95-136. Samples were exposed to sediment elutriates (water-soluble fraction) for 48 hours with percent normal alive as the endpoint. Elutriate solutions were prepared by adding 50 g of sediment to 200 mL of Granite Canyon seawater 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 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. The *Mytilus* (mussel) sediment elutriate test negative control was clean seawater from Granite Canyon, California and *E. estuaries* home sediment.

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.

Toxicity in sediments was found at 18 of the 27 sites for larval mussels (*Mytilus galloprovincialis*) and 10 of the 27 sites were found to be toxic to amphipods (*Eohaustorius estuarius*) (See Fig. 3.2 for 2007 amphipod and bivalve toxicity).

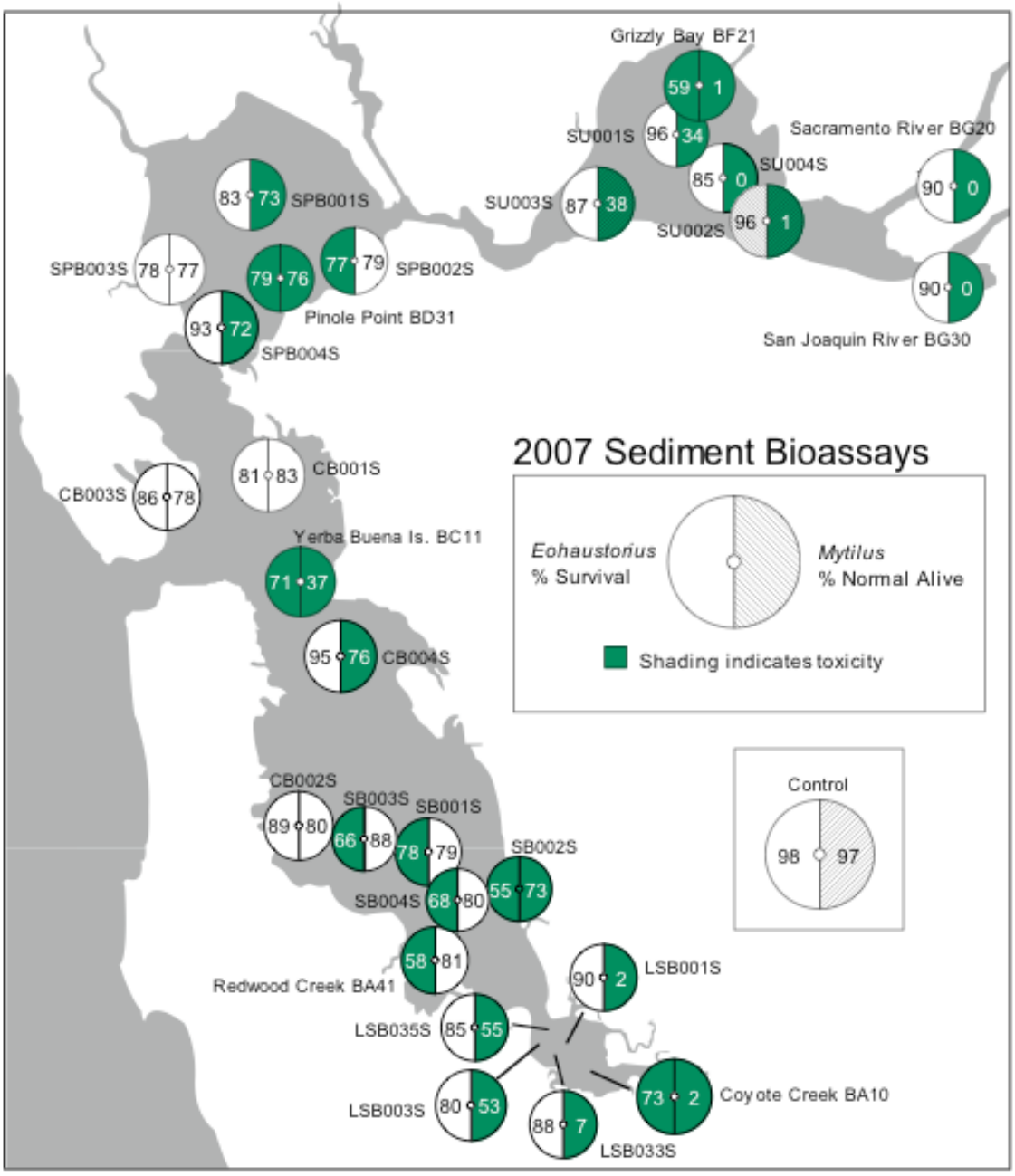


Figure 3.2 - Sediment bioassay results for 2007.

Sediments were not toxic to either amphipods, *Eohaustorius estuarius*, or mussel, *Mytilus galloprovincialis*, larvae at 23 out of 27 stations. Amphipod toxicity was observed at ten stations: Suisun Bay (Grizzly Bay (BF21)), San Pablo Bay (Pinole Point (BD31) and SPB002S), Central Bay (Yerba Buena Island (BC11)), South Bay (Redwood Creek (BA41), SB001S, SB002S, SB003S, and SB004S), and Coyote Creek (BA10). Sediment samples from eighteen stations were toxic to larval mussels: Sacramento River (BG20), San Joaquin River (BG30), Suisun Bay (Grizzly Bay (BF21), SU001S, SU002S,

SU003S, and SU004S), San Pablo Bay (Pinole Point (BD31), SPB001S, and SPB004S), Central Bay (Yerba Buena Island (BC11) and CB004S),South Bay (SB002S), Lower South Bay (LSB001S, LSB003S, LSB033S, and LSB035S), and Coyote Creek (BA10).

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 alive 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 2007 sediment bioassays, an amphipod bioassay was toxic if it had below 79.2% survival while the larval bivalve bioassay was toxic if it had less than 81.3% normal alive. In both years there also had to be a significant difference between the mean of the control and the sample replicates using a separate variance t-test (alpha = 0.01).

In 2005 it was decided to perform Toxicity Identification Evaluations (TIEs) only when sufficient toxicity was observed as method development is underway and needed to aid in understanding the toxicity found in the bay sediment. TIEs were not conducted in 2007. A summary of ten years of toxicity testing by the RMP can be found on our website Anderson *et al.* (2003) (http://www.sfei.org/rmp/pulse/pulse2003.pdf).

3.5 Assessment of Sediment Quality

Estuary sediments are evaluated through comparisons to several sets of sediment quality guidelines listed in Table 3.4. Although these guidelines hold no regulatory status, they provide concentration guidelines that are useful in assessing the potential for toxic and benthic effects.

Table 3.4 - 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	ERM	ASC-sandy <40% fines	ASC-muddy >40% fines	Background Concentrations (Bay wide 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	mg/Kg	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			5.9	14.8		
Sum of PCBs (SFEI)	µg/Kg	22.7	180 †	8.6	21.6		

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

Table 3.5 - Summary of sediment quality for the RMP in 2007.

NA = not available, . = not tested, * indicates number of exceedances above ASC guidelines for sandy samples.

Code	Site Name	Date	% Fines	mERMq	ASC above Guideline	No. of ERL above Guidelines	No. of ERM above Guidelines	Toxic to Amphipods Eohaustorius?	Toxic to Bivalves Mytilus?
BA10	Coyote Creek	8/21/2007	100	0.0906	0	8	1	Yes	Yes
BA41	Redwood Creek	8/22/2007	65	0.0844	0	5	1	Yes	No
BC11	Yerba Buena Island	8/23/2007	93	0.0793	1	6	1	Yes	Yes
BD31	Pinole Point	8/27/2007	82	0.0694	1	6	1	Yes	Yes
BF21	Grizzly Bay	8/28/2007	99	0.0693	1	7	1	Yes	Yes
BG20	Sacramento River	8/29/2007	21	0.0319	4*	3	0	No	Yes
BG30	San Joaquin River	8/29/2007	66	0.1030	7	8	1	No	Yes
CB001S	Central Bay	8/24/2007	78	0.0970	0	7	1	No	No
CB002S	Central Bay	8/22/2007	99	0.1008	5	7	1	No	No
CB003S	Central Bay	8/24/2007	97	0.0744	0	6	1	No	No
CB004S	Central Bay	8/23/2007	21	0.0345	12*	3	0	No	Yes
CB033S	Central Bay	8/24/2007	87	0.0919	1	7	1	.	.
CB034S	Central Bay	8/23/2007	82	0.1461	21	18	1	.	.
CB035S	Central Bay	8/24/2007	20	0.0199	1*	2	1	.	.
CB036S	Central Bay	8/23/2007	95	0.0958	1	7	1	.	.
LSB001S	Lower South Bay	8/21/2007	100	0.0846	0	6	1	No	Yes
LSB002S	Lower South Bay	8/21/2007	99	0.0933	1	8	1	.	.
LSB003S	Lower South Bay	8/21/2007	100	0.0924	0	6	1	No	Yes
LSB004S	Lower South Bay	8/21/2007	99	0.0790	0	6	1	.	.
LSB033S	Lower South Bay	8/21/2007	100	0.0966	0	7	1	No	Yes
LSB034S	Lower South Bay	8/21/2007	100	0.0867	0	6	1	.	.
LSB035S	Lower South Bay	8/21/2007	98	0.0877	0	7	1	No	Yes
LSB036S	Lower South Bay	8/21/2007	100	0.0776	0	5	1	.	.
SB001S	South Bay	8/22/2007	31	0.0478	21*	2	1	Yes	No
SB002S	South Bay	8/22/2007	97	0.0662	0	5	1	Yes	Yes
SB003S	South Bay	8/22/2007	60	0.0700	0	5	1	Yes	No
SB004S	South Bay	8/22/2007	41	0.0548	0	3	1	Yes	No
SB033S	South Bay	8/22/2007	70	0.0689	0	5	1	.	.
SB034S	South Bay	8/22/2007	66	0.0820	0	6	1	.	.
SB035S	South Bay	8/22/2007	83	0.0952	1	6	1	.	.
SB036S	South Bay	8/22/2007	100	0.1065	2	7	1	.	.
SPB001S	San Pablo Bay	8/27/2007	100	0.0575	1	5	1	No	Yes
SPB002S	San Pablo Bay	8/24/2007	97	0.0704	1	6	1	Yes	No
SPB003S	San Pablo Bay	8/27/2007	99	0.0769	1	6	1	No	No
SPB004S	San Pablo Bay	8/24/2007	70	0.0625	1	6	1	No	Yes
SPB033S	San Pablo Bay	8/27/2007	99	0.0663	1	6	1	.	.
SPB034S	San Pablo Bay	8/27/2007	25	0.0357	7*	3	0	.	.
SPB035S	San Pablo Bay	8/27/2007	100	0.0696	0	6	1	.	.
SPB075S	San Pablo Bay	8/27/2007	95	0.0776	0	6	1	.	.
SU001S	Suisun Bay	8/28/2007	20	0.0142	2*	1	0	No	Yes
SU002S	Suisun Bay	8/28/2007	29	0.0411	4*	4	1	No	Yes
SU003S	Suisun Bay	8/28/2007	61	0.0390	1	4	1	No	Yes
SU004S	Suisun Bay	8/28/2007	95	0.0954	4	8	1	No	Yes
SU033S	Suisun Bay	8/28/2007	33	0.0466	12*	4	1	.	.
SU034S	Suisun Bay	8/28/2007	98	0.0912	5	8	1	.	.
SU078S	Suisun Bay	8/29/2007	98	0.1028	7	7	1	.	.
SU079S	Suisun Bay	8/28/2007	99	0.0966	4	7	1	.	.

Sediment contamination and toxicity results were used to evaluate the quality of the 2007 Regional Monitoring Program samples (Table 3.5). Detailed tables for 2002 – 2006 are available in their respective Annual Monitoring Results available online SFEI: Documents & Reports. 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 2007 RMP sediment samples were considered potentially toxic if either four or more ERMs, nine or more ERLs, or half (20) 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). The 2007 mERMqs were calculated using 24 contaminants as indicated in Table 3.4 per the Hyland method (Hyland *et al.*, 1999). Samples that did not have at least 19 of the 24 parameters were not included in the calculations. All 2007 sediment samples had between 21 and 24 parameters reported.

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 2007 RMP sediment samples for potential adverse ecological effects. There were no stations with a mERMq value greater than 0.15 see Table 3.5.

In 2007, one station was considered potentially toxic by the RMP (CB034S) because it had nine or more contaminants above the ERL guidelines. There were no stations sampled in 2007 that showed ERM exceedances greater than 4 (Table 3.5).

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.

3.6 References

Anderson, B., S. Ogle, and S. Lowe. 2003. Ten years of testing for the effects of estuary contaminants. *In:* The Pulse of the Estuary: Monitoring and Managing Contamination in

the San Francisco Estuary. SFEI Contribution 74. San Francisco Estuary Institute, Oakland, CA. pp. 27-31.

Anderson, B., J. Hunt, B. Phillips, and J. Sericano. 2000. Investigations of chemicals associated with amphipod mortality at two Regional Monitoring Program stations. Draft RMP Technical Report. San Francisco Estuary Institute, Richmond, CA. 16 pp.

Conway, C.H., G.Scelfo and A. Luengen. 2006. Standard Operating Procedure for the Analysis of Mercury and Methylmercury in Environmental Samples (Draft 6/15/06). University of California at Santa Cruz, WIGS Laboratory, Santa Cruz, CA. 29 pp.

CRWQCB. 2004. PCBs in San Francisco Bay: Total maximum daily load project report. California Regional Water Quality Control Board, San Francisco Bay Region.

Fairey, R., E. R. Long, C. A. Roberts, B. S. Anderson, B. M. Phillips, J. W. Hunt, H. R. Puckett, and C. J. Wilson. 2001. An evaluation of methods for calculating mean sediment quality guideline quotients as indicators of contamination and acute toxicity to amphipods by chemical mixtures. *Environmental Toxicology and Chemistry* 20:2276–2286.

Gandesbery, T. 1998. Ambient concentrations of toxic chemicals in sediments. Memorandum: Water Boards Staff, from Tom Gandesbery, March 1998, File No: 1150.00.

Gandesbery, T., F. Hetzel, R. Smith, and L. Riege. 1999. Ambient concentrations of toxic chemicals in San Francisco Bay sediments: Summary. In 1997 Annual Report: San Francisco Estuary Regional Monitoring Program for Trace Substances. San Francisco Estuary Institute, Richmond, CA. pp. 140–147.

Horowitz, A. 1991. A Primer on Sediment-Trace Element Chemistry, 2nd rev. ed. Lewis Publishers/CRC Press, Inc. Boca Raton, FL. 136 pp.

Horvat, M., Logar, M., Ogrinc N., Fajon, V., Logen, S., Akagi, H., Ando, T., Tomiyasu, T., Matsuyama, A., 2004. The effect of sampling and sample pretreatment on MeHg concentration in coastal marine sediments. *RMZ-Materials and Geoenvironment* 51(3).

Hunt, J.W., B. S. Anderson, S. Tudor, M. D. Stephenson, H. M. Puckett, F. H. Palmer, and M. Reeve. 1996. Marine Bioassay Project, Eighth Report: Refinement and implementation of four effluent toxicity testing methods using indigenous marine species. Report #94-4. State Water Resources Control Board, Sacramento, CA. pp. 85–104.

Hunt, J. W., B. S. Anderson, B. M. Phillips, J. Newman, R. S. Tjeerdema, R. Fairey, H. M. Puckett, M. Stephenson, R. W. Smith, C. J. Wilson, and K. M. Taberski. 2001a. Evaluation and use of sediment toxicity reference sites for statistical comparisons in regional assessments. *Environmental Toxicology and Chemistry* 20:1266–1275.

Hunt, J. W., B. S. Anderson, B. M. Phillips, R. S. Tjeerdema, K. M. Taberski, C. J. Wilson, H. M. Puckett, M. Stephenson, R. Fairey, and J. Oakden. 2001b. A large-scale categorization of sites in San Francisco Bay, USA, based on the sediment quality triad, toxicity identification evaluations, and gradient studies. *Environmental Toxicology and Chemistry* 20:1252–1265.

Hyland, J. L., R. F. van Dolah, and T. R. Snoots. 1999. Predicting stress in benthic communities of southeastern U.S. estuaries in relation to chemical contamination of sediments. *Environmental Toxicology and Chemistry* 18:2557-2564.

Hyland, J. L., W. L. Balthis, V. D. Engle, E. R. Long, J. F. Paul, J. K. Summers, and R. F. Van Dolah. 2003. Incidence of stress in benthic communities along the U.S. Atlantic and Gulf of Mexico coasts within different ranges of sediment contamination from chemical mixtures. *Environmental Monitoring and Assessment* 81:149-161.

Johnson, B., and R. Looker. 2003. Mercury in San Francisco Bay: Total maximum daily load (TMDL) project report. California Regional Water Quality Control Board, San Francisco Bay Region.

Kincaid, T. M. 2004. Testing for differences between cumulative distribution functions from complex environmental surveys. *Survey Methodology* (in revision).

Krone, R. 1979. Sedimentation in the San Francisco Bay system, In: San Francisco Bay, the Urbanized Estuary. T. Conomos, ed. Pacific Div. of the Amer. Assoc. for the Advancement of Science, San Francisco. pp. 85-96.

Leatherbarrow, J. E., R. Hoenicke, and L. J. McKee. 2002. Results of the Estuary Interface Pilot Study: 1996-1999. RMP Technical Report. SFEI Contribution 50. San Francisco Estuary Institute. Oakland, CA.

Long, E. R. and L. G. Morgan. 1990. The potential for biological effects of sediment-sorbed contaminants tested in the National Status and Trends Program. NOAA Tech. Memo NOS OMA 52. National Oceanic and Atmospheric Administration, Seattle, WA. 175 pp.

Long, E. R., D. D. MacDonald, S. L. Smith and F. D. Calder. 1995. Incidence of adverse biological effects within ranges of chemical concentrations in marine and estuarine sediments. *Environmental Management* 19:18–97.

Long, E. R., L. J. Field, and D. D. MacDonald. 1998. Predicting toxicity in marine sediments with numerical sediment quality guidelines. *Environmental Toxicology and Chemistry* 17:714-727.

Long, E. R., M. J. Hameedi, G. M. Sloane, and L. B. Read. 2002. Chemical contamination, toxicity, and benthic community indices in sediments of the lower Miami River and adjoining portions of Biscayne Bay. *Estuaries* 25:622-737.

Luoma, S. N. 1990. Processes affecting metal concentrations in estuarine and coastal marine sediments. In: Heavy metals in the marine environment. R. W. Furness and P. S. Rainbow, (eds.). CRC Press, Inc., Boca Raton, FL.

Nieuwenhuize, Joop., Maas, Yvonne E.M., Middelburg, Jack J. , 1994. Rapid Analysis of Organic Carbon and Nitrogen in Particulate Materials. *Marine Chemistry*, 45:217-224

Phillips, B., B. Anderson, and J. Hunt. 2000. Investigations of sediment elutriate toxicity at three estuarine stations in San Francisco Bay, California. Draft Regional Monitoring Program Technical Report. San Francisco Estuary Institute, Richmond, CA. 16 pp.

Phillips B. M., J. W. Hunt, and B. S. Anderson. 2001. Statistical significance of sediment toxicity test results: threshold values derived by the detectable significance approach. *Environmental Toxicology and Chemistry* 20:371-373.

Plumb, R. H., 1981. Procedure for Handling and Chemical Analysis of Sediment and Water Samples. U.S. Army Engineers Waterways Experiment Station, CE, Vicksburg, MS. EPA Technical Report CE 81-1 for Grainsize analysis.

Schimmel, S., B. Melzian, D. Campbell, C. Strobel, S. Benyi, J. Rosen, H. Buffum, and N. Rubenstein. 1991. Statistical summary: EMAP-Estuaries, Virginian Province. EPA/620/R-94/005.

SFEI. 1999. 1997 Annual Report: San Francisco Estuary Regional Monitoring Program for Trace Substances. San Francisco Estuary Institute, Richmond, CA.

SFEI. 2000. 1998 Annual Report: San Francisco Estuary Regional Monitoring Program for Trace Substances. San Francisco Estuary Institute, Richmond, CA.

SFEI. 2001. 1999 Annual Report: San Francisco Estuary Regional Monitoring Program for Trace Substances. San Francisco Estuary Institute, Richmond, CA.

SFEI, 2005. Re-design Process of the San Francisco Estuary Regional Monitoring Program for Trace Substances (RMP) Status & Trends Monitoring Component for Water and Sediment. SFEI Contribution 109. San Francisco Estuary Institute, Oakland, CA.

Taylor, K., W. Pease, J. Lacy, and M. Carlin. 1992. Mass Emissions Reduction Strategy for Selenium. San Francisco Regional Water Quality Control Board, Oakland, CA. 61p.

Tetra Tech. 1986. Recommended protocols for measuring selected environmental variables in Puget Sound. Prepared for the Puget Sound Estuary Program by Tetra Tech, Inc., Bellevue, WA.

Thompson, B., B. Anderson, J. Hunt, K. Taberski, and B. Phillips. 1999. Relationships between sediment contamination and toxicity in San Francisco Bay. *Marine Environmental Research* 48:285-309.

Thompson, B. and S. Lowe. 2004. Assessment of macrobenthos response to sediment contamination in the San Francisco Estuary, California, USA. *Environmental Toxicology and Chemistry* 23:2178-2187.

Thursby, G. and C. Schlekat. 1993. Statistical analysis of 10-day solid phase toxicity data for amphipods. Abstract, 14th Annual Meeting, Society of Environmental Toxicology and Chemistry.

U.S. EPA. 1994b. Methods for assessing the toxicity of sediment-associated contaminants with estuarine and marine amphipods. C.I. Weber (ed.). EPA/600/R-94/025. Office of Research and Development, Washington, D.C.

U.S. EPA and ACOE. 1991. Evaluation of dredged material proposed for ocean disposal (testing manual). EPA-503/8-91/001, USEPA Office of Water (WH-556F), U.S. Army Corps of Engineers, Washington, D.C.

U.S. Environmental Protection Agency. 2000. Methods for measuring the toxicity and bioaccumulation of sediment-associated contaminants with freshwater invertebrates. EPA/600/R-99/064. Office of Research and Development, Washington D.C.

Wolfenden, J. D. and M. P. Carlin. 1992. Sediment screening criteria and testing requirements for wetland creation and upland beneficial reuse. California Environmental Protection Agency and California Regional Water Quality Control Board.

CHAPTER 4

Bivalve Monitoring

4.0 Bivalve Monitoring

The History of the RMP Bivalve Bioaccumulation Monitoring Program: Using Adaptive Management to Better Understand Contaminant Bioaccumulation in the Estuary

4.1 Introduction

Since its inception in 1993, the RMP Bivalve Bioaccumulation Monitoring Program has undergone numerous changes in response to program findings and identified needs. This report summarizes and documents the various changes that have occurred in the Program, presents justification for these changes and identifies ongoing investigations that may result in changes to the Program in the near term.

There are currently no new bivalve contaminant data for this edition of the Annual Monitoring Results. Bivalves were not deployed in 2007. In 2006 bivalves were deployed at nine fixed locations and collected from two river stations; however, samples are in storage and are pending chemical analysis.

4.2 Objectives of the Bioaccumulation Program

The objectives of the RMP Bioaccumulation Monitoring Program are to:

- Describe the distribution and trends of pollutant concentrations in the Estuary,
- Measure pollution exposure and effects on selected parts of the Estuary ecosystem, and
- Compare monitoring information to relevant benchmarks, such as TMDL targets, tissue screening levels, water quality objectives, and sediment quality objectives.

These general goals implicitly address the RMP objectives of determining seasonal and long-term trends in chemical and biological water quality. This program component also complements the water and sediment sampling. Unlike the water quality sampling, which gives an indication of water quality at one particular point in time, contaminant concentrations measured in transplanted bivalves serve to integrate water quality over the period of deployment (typically 90 to 100 days). Also, while measurement of contaminant concentrations in water and sediment are useful for trend monitoring over time, they do not reveal the extent to which various contaminants are able to transfer into the food web and pose risks to consumers.

4.3 Initial Program Design

The RMP Bivalve Bioaccumulation Monitoring Program was initiated in 1993 as a transplant study in which bivalves were collected from "clean" locations (i.e., those with relatively low concentrations of specific pollutants) and transplanted to fixed sites within the Estuary. Due to substantial spatial and temporal variation in salinity, the program

initially used three bivalve species, which were deployed according to the salinity range expected at each site:

- *Mytilus californianus*, the California mussel, deployed at the most saline sites;
- *Crassostrea gigas*, the Japanese oyster, deployed at sites of intermediate salinity;
- *Corbicula fluminea*, a freshwater clam, deployed at sites of lowest salinity.

Bivalves were initially deployed at eleven sites throughout the Estuary to represent both the spine and margins of the Estuary. In 1994, four deployment sites were added, for a total of 15. Specific site locations were heavily influenced by the availability of a fixed structure to easily relocate the subsurface moorings.

Bivalves were deployed for 90 to 100-day periods with deployment beginning in February and June. These deployment periods were chosen to encompass the range of hydrographic conditions in the Estuary and to allow comparisons of within-season variation in addition to trend monitoring over time. At the conclusion of deployments, bivalves are retrieved, processed using clean techniques, and aliquoted for eventual analysis. Generally, 30–40 bivalves are composited from each site for each type of analysis, although high bivalve mortality sometimes reduces the number of organisms in a composite sample.

4.4 Bivalve Bioaccumulation Monitoring Program Changes

The Program has evolved since its inception in 1993. The number of transplant stations, species deployed, deployment apparatus, and parameters measured have changed over the years. Below is a summary of the changes that have occurred (based on a report by Applied Marine Sciences (Hardin *et al*., 2005)), as well as the current status of the Program:

- From 1999 to 2002, several bivalve species were deployed in side-by-side experiments to evaluate which species had the best survival and growth across all sites during dry-season deployments. Results from the study showed that the mussel *M. californianus,* was the best candidate for Estuary wide deployment. This change was instituted in 2003. The main factors in the decision included the following:
    - Lower survival of the oyster *C. gigas*,
    - Essentially equivalent survival between *M. californianus* and *M. edulis* across all sites,
    - Better growth at many sites for *M. californianus*, and
    - Extensive historic data for transplanted *M. californianus* in San Francisco Bay.
- Based on a new biogeographical delineation of the Estuary, it was apparent that the newly defined segments were not represented equally by the original 15-station bivalve deployment design. Consequently, an analysis was undertaken to determine the optimum number and distribution of bivalve deployment sites needed to track trends in bioavailable contaminants in the Estuary. Based on this analysis, several sites were removed from the project and, in 2003, the design of the Program study

sites was modified to its current configuration, consisting of three transplant sites within the Lower South Bay-South Bay, Central Bay and San Pablo Bay Estuary segments, respectively, and collection of resident bivalves at two sites within the Rivers segment.

- A side-by-side study was conducted from 1999 – 2002 in order to assess the effectiveness of a new bivalve deployment structure. Initially, transplanted bivalves were deployed in plasticized nylon mesh bags, attached to mooring systems on the Estuary bottom. At times, predation, as indicated by torn mesh bags and broken mussel shells, led to an insufficient number of bivalves to support all desired analyses and at other times causing loss of entire deployments at a site. Deployment cages were tested during this period and showed reduced mortality at two of the most predated sites. Beginning in 2003, all transplanted bivalves were deployed in cage-type structures.
- The original design of the RMP transplanted bivalve program implemented in 1993 included a maintenance cruise near the midpoint of the deployment period to reduce mooring loses by checking their integrity and to improve bivalve survival and health by removing biological and physical fouling. From 2002 – 2005, a side-by-side comparison between maintained and un-maintained cages indicated only slight differences in the survival or growth of *M. californianus*. Since differences were minimal the maintenance cruise was discontinued in 2006.
- Starting with the 1999 dry season (summer) deployments, CTD profiles were collected at each bivalve site to help determine how ambient environmental factors affect the transplanted bivalves. Salinity, dissolved oxygen, temperature, and total suspended solids impact bivalve health and could affect contaminant bioaccumulation rates.
- In 1999, a comparison of growth and condition was begun to investigate whether growth was a more appropriate measure of bivalve health during deployment. Condition is a ratio of tissue mass to shell volume. Using condition as a metric of health can be confounded by changes in mass or volume that aren't necessarily tied to health. Growth is a more direct measurement which compares the pre- and post-deployment weight of the individual mussel. As a result of this study, the health indicator was changed from condition to growth in 2002.
- In 2000, the wet-season bivalve deployment was discontinued since long-term temporal trends in contaminant concentrations were more consistently observed in dry-season data than in wet-season data.
- In 2000, the analysis of mercury and arsenic in bivalves was discontinued since concentrations were similar in the transplanted bivalves and in the reference bivalves. In the case of mercury, there is evidence that bivalves are not the best indicators of bioavailability, especially for methylmercury.
- In 2001, trace metals measurements in bivalves were reduced from every year to every fifth year as a cost reduction measure for metals not on the 303(d) list or the Water Board's "pollutants of concern" for San Francisco Bay list.

4.5 Conclusions

Further optimization of the program under consideration includes re-instituting a wet-season deployment of transplanted *M. californianus* at Yerba Buena Island. Salinity remains relatively high during the wet season at this site, which would enable monitoring of the effect of delta outflow on contaminant concentrations in transplanted mussels, while minimizing the effects of wet-season salinity variation on mussel survival and growth. The Program will continue to use adaptive management to review and refine the questions we are asking and to further optimize our sampling regime by continuing short-term comparison studies.

4.6 References

Hardin, D. Salop, P. and B. Bemis. 2005. Optimizing Transplanted Bivalve Studies for the Regional Monitoring Program for Trace Substances. Applied Marine Sciences. Livermore, CA.

CHAPTER 5

Appendix Tables

5.0 Appendix Tables

Appendix 1 RMP Program Participants in 2007

Municipal Dischargers
Burlingame Waste Water Treatment Plant
Central Contra Costa Sanitary District
Central Marin Sanitation Agency
City of Benicia
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/Santa Clara
City of San Mateo
City of South San Francisco/San Bruno
City of Sunnyvale
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 Sanitation District
Sewerage Agency of Southern Marin
Sonoma County Water Agency
South Bayside System Authority
Town of Yountville
Union Sanitary District
Vallejo Sanitation & Flood Control District
West County Agency

Industrial Dischargers
C & H Sugar Company
Chevron Products Company
ConocoPhillips Company
Crockett Cogeneration
Dow Chemical Company
General Chemical Corporation
Rhodia, Inc.
Shell – Martinez Refining Company
Tesoro Golden Eagle Refinery
USS – POSCO Industries
Valero Refining Company

Cooling Water
Mirant California
Mirant Delta

Dredgers
Alameda Point
Arques Shipyard and Marina
Benicia Port Terminal Co. Pier 95
Chevron Richmond Long Wharf
City of Benicia
City of San Rafael
Clipper Yacht Club
ConocoPhillips Company
Corinthian Yacht Club
Paradise Cay Yacht Harbor
Port of Oakland
Port of San Francisco
Richmond Yacht Club
Strawberry Channel
U.S. Coast Guard, Fort Baker
Valero Refining Co.

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

Appendix 2 RMP Contractors and Principal Investigators in 2007

Logistical Coordinator; Shipboard Conductivity, Temperature, and Depth (CTD) Readings	Mr. Paul Salop Applied Marine Sciences (AMS), Livermore, CA
Ship Captain	Mr. Nick Sakata US Bureau of Reclamation Captain, *RV Endeavor*
Water Trace Element Chemistry	Mr. Colin Davies and Ms. Tiffany Stilwater Brooks-Rand Ltd. (BRL), Seattle, WA
Water Trace Organic Chemistry	Ms. Pam Riley and Mr. Richard AXYS Analytical Services, Inc. (AXYS), Sidney, BC
Water Ancillary Measurements	Water Cognates: Ms. Julia Halsne East Bay Municipal Utility District (EBMUD), Oakland, CA
	Water DOC and POC: Mr. Kenneth Davis Applied Marine Sciences Inc. (AMS), League City, TX
Aquatic Toxicity	Dr. Scott Ogle Pacific Eco Risk (PER), Fairfield, CA
Sediment Trace Element Chemistry	Mr. Colin Davies and Ms. Tiffany Stilwater Brooks-Rand Ltd. (BRL), Seattle, WA
	Mr. Anthony Rattonetti and Mr. Lonnie Butler City and County of San Francisco (CCSF), San Francisco, CA
Sediment Trace Organics Chemistry	Mr. François Rodigari and Ms. Saskia van Bergen East Bay Municipal Utility District (EBMUD), Oakland, CA
Sediment Toxicity Testing	Mr. John Hunt, Dr. Brian Anderson, and Dr. Bryn Phillips Marine Pollution Studies Lab (MPSL), Granite Canyon, CA
Sediment Ancillary Measurements (Grainsize, TOC, TN)	Mr. Kenneth Davis Applied Marine Sciences Inc. (AMS), League City, TX
USGS Water Quality	Dr. James Cloern, USGS, Menlo Park, CA
USGS Sediment Transport	Dr. David Schoellhamer, USGS, Sacramento, CA

Appendix 3 Summary of 2007 RMP Water Sampling Stations

Region	Site Code	Historic Site	Collection Date	Latitude	Longitude	Site Depth (m)
South Bay / Dumbarton Bridge	BA30	X	8/16/2007	37.51373	-122.13392	8
Central Bay / Golden Gate	BC20	X	8/10/2007	37.79307	-122.67012	30
Central Bay / Yerba Buena Island	BC10	X	8/13/2007	37.82250	-122.34975	7
Rivers / Sacramento River	BG20	X	8/7/2007	38.05943	-121.81108	10
Rivers / San Joaquin River	BG30	X	8/7/2007	38.02010	-121.80613	16
Central Bay	CB021W		8/13/2007	37.83242	-122.32848	2
Central Bay	CB022W		8/13/2007	37.69293	-122.24027	4
Central Bay	CB023W		8/10/2007	37.87353	-122.40627	16
Lower South Bay	LSB027W		8/16/2007	37.50410	-122.11653	15
Lower South Bay	LSB028W		8/15/2007	37.49210	-122.08892	3
Lower South Bay	LSB029W		8/15/2007	37.49000	-122.10063	4
Lower South Bay	LSB030W		8/15/2007	37.47377	-122.06837	7
Lower South Bay	LSB031W		-	NS	NS	NS
Lower South Bay	LSB032W		8/16/2007	37.48662	-122.08825	7
South Bay	SB047W		8/14/2007	37.62012	-122.29715	13
South Bay	SB048W		8/14/2007	37.57740	-122.22950	16
South Bay	SB049W		8/14/2007	37.59557	-122.28032	2
San Pablo Bay	SPB021W		8/9/2007	38.04160	-122.38430	5
San Pablo Bay	SPB022W		8/9/2007	38.02670	-122.29420	3
San Pablo Bay	SPB023W		8/9/2007	38.07502	-122.40913	3
Suisun Bay	SU023W		8/8/2007	38.09682	-122.06193	10
Suisun Bay	SU024W		8/8/2007	38.07170	-121.99723	3
Suisun Bay	SU025W		8/8/2007	38.10725	-122.05275	3

NS: Not Sampled

Appendix 4 Summary of 2007 RMP Sediment Sampling Stations

Region	Site Code	Historic Site	Collection Date	Latitude	Longitude	Site Depth (m)
Lower South Bay	BA10	X	8/21/2007	37.46798	-122.06387	4
South Bay	BA41	X	8/22/2007	37.55927	-122.21095	3
Central Bay	BC11	X	8/23/2007	37.82283	-122.34870	7
San Pablo Bay	BD31	X	8/27/2007	38.02395	-122.36330	6
Suisun Bay	BF21	X	8/28/2007	38.11513	-122.04085	2
Rivers / Sacramento River	BG20	X	8/29/2007	38.05657	-121.81323	8
Rivers / San Joaquin River	BG30	X	8/29/2007	38.02215	-121.80780	6
Central Bay	CB001S		8/24/2007	37.87672	-122.36163	3
Central Bay	CB002S		8/22/2007	37.62513	-122.34758	5
Central Bay	CB003S		8/24/2007	35.86798	-122.48552	2
Central Bay	CB004S		8/23/2007	37.75495	-122.33032	11
Central Bay	CB033S		8/24/2007	37.86732	-122.36347	4
Central Bay	CB034S		8/23/2007	37.69308	-122.27467	7
Central Bay	CB035S		8/24/2007	37.92002	-122.44112	13
Central Bay	CB036S		8/23/2007	37.77818	-122.33875	12
Lower South Bay	LSB001S		8/21/2007	37.49172	-122.09803	7
Lower South Bay	LSB002S		8/21/2007	37.47903	-122.07827	8
Lower South Bay	LSB003S		8/21/2007	37.49098	-122.11655	2
Lower South Bay	LSB004S		8/21/2007	37.49433	-122.08607	2
Lower South Bay	LSB033S		8/21/2007	37.48863	-122.10325	2
Lower South Bay	LSB034S		8/21/2007	37.47925	-122.08037	2
Lower South Bay	LSB035S		8/21/2007	37.50028	-122.11498	16
Lower South Bay	LSB036S		8/21/2007	37.48022	-122.08882	2
South Bay	SB001S		8/22/2007	37.61178	-122.26427	4
South Bay	SB002S		8/22/2007	37.60977	-122.16750	2
South Bay	SB003S		8/22/2007	37.61685	-122.30397	11
South Bay	SB004S		8/22/2007	37.60048	-122.21877	3
South Bay	SB033S		8/22/2007	37.61410	-122.27992	12
South Bay	SB034S		8/22/2007	37.59592	-122.18648	3
South Bay	SB035S		8/22/2007	37.59537	-122.31775	3
South Bay	SB036S		8/22/2007	37.57975	-122.23002	14

Region	Site Code	Historic Site	Collection Date	Latitude	Longitude	Site Depth (m)
San Pablo Bay	SPB001S		8/27/2007	38.07160	-122.38678	4
San Pablo Bay	SPB002S		8/24/2007	38.01608	-122.34162	3
San Pablo Bay	SPB003S		8/27/2007	38.02777	-122.47598	2
San Pablo Bay	SPB004S		8/24/2007	37.97718	-122.42398	11
San Pablo Bay	SPB033S		8/27/2007	38.07623	-122.39610	4
San Pablo Bay	SPB034S		8/27/2007	38.05770	-122.32492	6
San Pablo Bay	SPB035S		8/27/2007	38.06837	-122.45892	3
San Pablo Bay	SPB036S		8/24/2007	37.99865	-122.42088	16
San Pablo Bay	SPB075S		8/27/2007	38.09792	-122.44302	2
Suisun Bay	SU001S		8/28/2007	38.09970	-122.04663	6
Suisun Bay	SU002S		8/28/2007	38.06263	-121.98115	4
Suisun Bay	SU003S		8/28/2007	38.06593	-122.09600	9
Suisun Bay	SU004S		8/28/2007	38.08325	-122.02653	2
Suisun Bay	SU033S		8/28/2007	38.10175	-122.04845	5
Suisun Bay	SU034S		8/28/2007	38.07625	-121.96033	2
Suisun Bay	SU035S		-	NS	NS	NS
Suisun Bay	SU036S		8/28/2007	35.06245	-122.03965	9
Suisun Bay	SU078S		8/29/2007	38.04867	-121.96763	6
Suisun Bay	SU079S		8/28/2007	38.10833	-122.06497	2

NS: Not Sampled

Appendix 5 RMP Target Parameter List in 2007

See Appendix 2 for laboratory names

Conventional Water Quality Parameters	**Lab(s)**	**Reporting Units**
Conductivity	AMS-CA	µmho
Ammonium as N	CAS/UCSC-DET	mg/L
Nitrate as N	CAS/UCSC-DET	mg/L
Nitrite as N	CAS/UCSC-DET	mg/L
Dissolved Organic Carbon	AMS/UCSC-DET	µg/L
Dissolved Oxygen	AMS-CA	mg/L
Phosphate as P	CAS/UCSC-DET	mg/L
Silica	CAS/UCSC-DET	mg/L
Hardness as CaCO3 (when salinity is < 5 ‰)	EBMUD	mg/L
PH	AMS-CA	pH
Pheophytin a	UCSC-DET	mg/m^3
Salinity (by salinometer)	UCSC-DET	psu
Salinity	EBMUD	‰
Suspended Sediment Concentration	UCSC-DET	mg/L
Temperature	AMS-CA	°C
Chlorophyll a	UCSC-DET	mg/m^3
Toxicity Tests - Water	**Lab(s)**	**Reporting Units**
Water Toxicity – (Amphipod) % Survival	PER	%
Water Toxicity – (Bivalve) % Normal Alive	PER	%
Sediment Quality Parameters	**Lab(s)**	**Reporting Units**
Clay <0.0039 mm	AMS/UCSC-DET	%
Silt 0.0039 to <0.0625 mm	AMS/UCSC-DET	%
Fine <0.0625 mm	AMS/UCSC-DET	%
Sand 0.0625 to <2.0 mm	AMS	%
Granule + Pebble 2.0 to <64 mm	AMS/UCSC-DET	%
% solids	BRL/CCSF/EBMUD	%
Depth	AMS-CA	m
pH (porewater, interstitial sediment)	AMS-CA	pH
Total Organic Carbon	AMS/UCSC-DET	%
Nitrogen, Total Kjeldahl	AMS	%
Total Nitrogen	UCSC-DET	%
Toxicity Tests - Sediment	**Lab(s)**	**Reporting Units**
Sediment Toxicity – (Amphipod) % Survival	UCD-GC	%
Sediment Toxicity – (Bivalve) % Normal Development	UCD-GC	%

RMP Target Parameter List in 2007 (cont'd).

Trace elements analyzed in water and sediment samples[1] 2007				
	Water[2]		Sediment[3]	
	Lab	Units	Lab	Units
Aluminum (Al)	-	-	CCSF	mg/kg
Arsenic (As)	BRL	µg/L	CCSF/BRL	mg/kg
Cadmium (Cd)*	BRL/UCSC-DET	µg/L	CCSF	mg/kg
Cobalt (Co)	BRL/UCSC-DET	µg/L	CCSF	mg/kg
Copper (Cu)*	BRL/UCSC-DET	µg/L	CCSF	mg/kg
Iron (Fe)*	BRL/UCSC-DET	µg/L	CCSF	mg/kg
Lead (Pb)*	BRL/UCSC-DET	µg/L	CCSF	mg/kg
Manganese (Mn)*	BRL/UCSC-DET	µg/L	CCSF	mg/kg
Mercury (Hg)	BRL/UCSC-DET	µg/L	CCSF/BRL/UCSC-DET	mg/kg
Mercury, Methyl (MeHg)	BRL/UCSC-DET	ng/L	BRL/UCSC-DET	µg/kg
Nickel (Ni)*	BRL/UCSC-DET	µg/L	CCSF	mg/kg
Selenium (Se)	BRL	µg/L	CCSF/BRL	mg/kg
Silver (Ag)*	BRL	µg/L	CCSF	mg/kg
Zinc (Zn)*	BRL/UCSC-DET	µg/L	CCSF	mg/kg

- 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, 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.

[2] All water samples are analyzed for the total and dissolved fractions and results are reported in a wet weight basis.

[3] All sediment samples are reported in a dry weight basis.

RMP Target Parameter List in 2007 (cont'd).

Trace organic parameters (lab; reporting units) analyzed in water (AXYS; pg/L) and sediment (EBMUD; µg/kg):		
Polycyclic Aromatic Hydrocarbons* (PAHS)		
Low molecular weight PAHs	**High molecular weight PAHs**	**Alkylated PAHs**
1-Methylnaphthalene	Benz(*a*)anthracene	C1-Chrysenes
1-Methylphenanthrene	Benzo(*a*)pyrene	C2-Chrysenes
2-Methylnaphthalene	Benzo(*b*)fluoranthene	C3-Chrysenes
2,6-Dimethylnaphthalene	Benzo(*e*)pyrene	C4-Chrysenes
2,3,5-Trimethylnaphthalene	Benzo(*ghi*)perylene	C1-Dibenzothiophenes
Acenaphthene	Benzo(*k*)fluoranthene	C2-Dibenzothiophenes
Acenaphthylene	Chrysene	C3-Dibenzothiophenes
Anthracene	Dibenz(*a,h*)anthracene	C1-Fluoranthene/Pyrenes
Biphenyl	Fluoranthene	C1-Fluorenes
Dibenzothiophene	Indeno(*1,2,3-cd*)pyrene	C2-Fluorenes
Fluorene	Perylene	C3-Fluorenes
Naphthalene	Pyrene	C1-Naphthalenes
Phenanthrene		C2-Naphthalenes
		C3-Naphthalenes
		C4-Naphthalenes
		C1-Phenanthrene/Anthracenes
		C2-Phenanthrene/Anthracenes
		C3-Phenanthrene/Anthracenes
		C4-Phenanthrene/Anthracenes
SYNTHETIC BIOCIDES		
Cyclopentadienes	**DDTs***	**Other Synthetic Biocides**
Aldrin	o,p'-DDD	Chlorpyrifos *(water only))*
Dieldrin	o,p'-DDE	Dacthal *(water only)*
Endrin	o,p'-DDT	Diazinon *(water only)*
	p,p'-DDD	Endosulfan I *(water only)*
Chlordanes*	p,p'-DDE	Endosulfan II *(water only)*
alpha-Chlordane	p,p'-DDT	Endosulfan Sulfate *(water only)*
cis-Nonachlor		Hexachlorobenzene
gamma-Chlordane	**HCH***	Mirex
Heptachlor	alpha-HCH	Oxadiazon *(water only)*
Heptachlor Epoxide	beta-HCH	
Oxychlordane	delta-HCH	
trans-Nonachlor	gamma-HCH	

RMP Target Parameter List in 2007 (cont'd).

OTHER SYNTHETIC COMPOUNDS

Polychlorinated Biphenyls* (PCBs)

IUPAC numbers listed.

PCB 008	PCB 066	PCB 118	PCB 170
PCB 018	PCB 070	PCB 128	PCB 174
PCB 028	PCB 074	PCB 132	PCB 177
PCB 031	PCB 087	PCB 138	PCB 180
PCB 033	PCB 095	PCB 141	PCB 183
PCB 044	PCB 097	PCB 149	PCB 187
PCB 049	PCB 099	PCB 151	PCB 194
PCB 052	PCB 101	PCB 153	PCB 195
PCB 056	PCB 105	PCB 156	PCB 201
PCB 060	PCB 110	PCB 158	PCB 203

Polybrominated Diphenyl Ethers* (PBDEs)

IUPAC number - compound name listed.

007 - [2,4-diBDE]	100 - [2,2',4,4',6-pentaBDE]
008 - [2,4'-diBDE]	105 - [2,3,3',4,4'-pentaBDE]
010 - [2,6-diBDE]	116 - [2,3,4,5,6-pentaBDE]
011 - [3,3'-diBDE]	119 - [2,3',4,4',6-pentaBDE]
012 - [3,4-diBDE]	120 - [2,3',4,5,5'-pentaBDE]
013 - [3,4'-diBDE]	126 - [3,3',4,4',5-pentaBDE]
015 - [4,4'-diBDE]	128 - [2,2',3,3',4,4'-hexaBDE]
017 - [2,2',4-triBDE]	138 - [2,2',3,4,4',5'-hexaBDE]
025 - [2,3',4-triBDE]	140 - [2,2',3,4,4',6'-hexaBDE]
028 - [2,4,4'-triBDE]	153 - [2,2',4,4',5,5'-hexaBDE]
030 - [2,4,6-triBDE]	154 - [2,2',4,4',5,6'-hexaBDE]
032 - [2,4',6-triBDE]	155 - [2,2',4,4',6,6'-hexaBDE]
033 - [2',3,4-triBDE]	166 - [2,3,4,4',5,6-hexaBDE]
035 - [3,3',4-triBDE]	181 - [2,2',3,4,4',5,6-heptaBDE]
037 - [3,4,4'-triBDE]	183 - [2,2',3,4,4',5',6-heptaBDE]
047 - [2,2',4,4'-tetraBDE]	190 - [2,3,3',4,4',5,6-heptaBDE]
049 - [2,2',4,5'-tetraBDE]	196 - [2,2',3,3',4,4',5',6-octa-BDE]
051 - [2,2',4,6'-tetraBDE]	197 - [2,2',3,3',4,4',6,6'-octa-BDE]
066 - [2,3',4,4'-tetraBDE]	203 - [2,2',3,4,4',5,5',6-octa-BDE]
071 - [2,3',4',6-tetraBDE]	204 - [2,2',3,4,4',5,6,6'-octaBDE]
075 - [2,4,4',6-tetraBDE]	205 - [2,3,3',4,4',5,5',6-octaBDE]
077 - [3,3',4,4'-tetraBDE]	206 - [2,2',3,3',4,4',5,5',6-octaBDE]
079 - [3,3',4,5'-tetraBDE]	207 - [2,2',3,3',4,4',5,6,6'-octaBDE]
085 - [2,2',3,4,4'-pentaBDE]	208 - [2,2',3,3',4,5,5',6,6'-octaBDE]
099 - [2,2',4,4'5-pentaBDE]	209 - [2,2',3,3',4,4',5,5',6,6'-decaBDE]

*Sum of these compounds refers to the particular subsets listed above as opposed to complete sets of all congeners in that category. Elsewhere in this report these sets are referred to as Sum of [compound] (SFEI).

Appendix 6 Regional Monitoring Program Analytes Reported in Water Samples (1993-2007)

Parameter	Parameter Type	1993	1994	1995	1996	1997	1998	1999	2000	2001	2002	2003	2004	2005	2006	2007
Ammonia as N	ANC	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■
Chlorophyll a	ANC	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■
Conductivity	ANC	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■
Dissolved Oxygen	ANC	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■
Dissolved Organic Carbon	ANC	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■
Hardness as CaCO3	ANC	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■
Nitrate as N	ANC	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■
Nitrite as N	ANC	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■
pH	ANC	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■
Pheophytin a	ANC	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■
Phosphate as P	ANC	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■
Particulate Organic Carbon	ANC												■	■	■	
Salinity (by salinometer)	ANC	■		■	■	■	■	■	■	■	■	■	■	■	■	■
Salinity (by SCT)	ANC	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■
Salinity (by Solomat)	ANC					■										
Silica	ANC	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■
Suspended Sediment Concentration	ANC										■	■	■	■	■	■
Total Suspended Solids	ANC	■	■	■	■	■	■	■	■	■				■	■	
Temperature	ANC	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■
PAHs	ORG	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■
PAHs Alkylated	ORG						■	■	■	■	■	■	■	■	■	■
Alkanes (C10-C34)	ORG	■	■	■												
PBDEs	ORG										■	■	■	■	■	■
PCBs	ORG	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■
Phthalates	ORG										■	■				
Chlordanes	PEST	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■
Chlorpyrifos	PEST	■	■	■	■	■	■	■	■	■	■	■	■	■		
Cyclopentadienes	PEST	■	■	■	■	■	■	■	■	■	■	■	■	■	■	
Dacthal	PEST	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■
DDTs	PEST	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■
Diazinon	PEST	■	■	■	■	■	■	■	■	■	■	■	■	■		
Endosulfan I	PEST	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■
Endosulfan II	PEST	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■
Endosulfan Sulfate	PEST	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■

Parameter	Parameter Type	1993	1994	1995	1996	1997	1998	1999	2000	2001	2002	2003	2004	2005	2006	2007
HCHs	PEST	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■
Hexachlorobenzene	PEST	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■
Mirex	PEST	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■
Oxadiazon	PEST	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■
p-Nonylphenol	SYN										■	■				
Triphenylphosphate	SYN										■					
Arsenic	TE	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■
Cadmium	TE	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■
Cyanide	TE	■	■													
Cobalt	TE								■	■	■	■	■	■	■	■
Chromium	TE	■	■	■	■	■	■	■		■						
Copper	TE	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■
Iron	TE							■	■	■	■	■	■	■	■	■
Mercury	TE	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■
Mercury, Methyl	TE							■	■	■	■	■	■	■	■	■
Manganese	TE							■	■	■	■	■	■	■	■	■
Nickel	TE	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■
Lead	TE	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■
Selenium	TE	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■
Silver	TE	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■
Zinc	TE	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■
Cell Count	WaterTox	■														
Mean % Normal Development	WaterTox	■	■	■	■	■										
Mean % Survival	WaterTox	■	■	■	■	■	■	■	■	■	■					

Gray = Analyte Reported for RMP Status and Trends Sampling.

Appendix 7 Analytes Reported in Sediment Samples (1993-2007)

Parameter	1993	1994	1995	1996	1997	1998	1999	2000	2001	2002	2003	2004	2005	2006	2007
% Solids															
Ammonia															
Clay <0.005 mm															
Fine <0.0625 mm															
Silt 0.0039 to <0.0625 mm															
Sand 0.0625 to <2.0 mm															
Granule + Pebble 2.0 to <64 mm															
Hydrogen Sulfide															
pH															
TOC															
Total Nitrogen															
Total Sulfide															
PAHs															
PAHs Alkylated															
PBDEs															
PCBs															
Phthalates															
Chlordanes															
Cyclopentadienes															
DDTs															
HCHs															
Hexachlorobenzene															
Mirex															
Mean % Normal Alive															
Mean % Survival															
p-Nonylphenol															
Silver															
Aluminum															
Arsenic															
Cadmium															
Cromium															
Copper															
Iron															
Mercury															
Mercury, Methyl															
Manganese															
Nickel															
Lead															
Selenium															

Appendix 8 Analytes Reported in Bivalve Tissue Samples (1993-2007)

Parameter	ParameterType	1993	1994	1995	1996	1997	1998	1999	2000	2001	2002	2003	2004	2005	2006*	2007**
% Moisture	ANC		■	■	■	■	■	■	■	■	■	■	■			
% Survival per Species	ANC	■	■	■	■	■	■	■	■	■	■	■	■			
Condition Index (CI)	ANC	■	■	■	■	■	■	■	■							
Growth Mean	ANC							■	■	■	■	■	■			
Dry Weight	ANC	■	■	■	■	■	■	■	■	■	■	■	■			
Gonad Index CI Mean	ANC							■	■							
Musks	ORGS										■	■	■			
PAHs	ORGS	■	■	■	■	■	■	■	■	■	■	■				
PAHs Alkylated	ORGS	■	■	■	■	■	■	■	■	■	■	■				
Alkanes (C10-C34)	ORGS	■	■	■												
PBDEs	ORGS										■	■		■		
PCBs	ORGS	■	■	■	■	■	■	■	■	■	■	■		■		
Phthalates	ORGS										■	■	■			
Chlordanes	PESTs	■	■	■	■	■	■	■	■	■	■	■		■		
Cyclopentadienes	PESTs	■	■	■	■	■	■	■	■	■	■	■		■		
DDTs	PESTs	■	■	■	■	■	■	■	■	■	■	■		■		
HCHs	PESTs	■	■	■	■	■	■	■	■	■	■	■		■		
Hexachlorobenzene	PESTs	■	■	■	■	■	■	■	■	■	■	■		■		
Mirex	PESTs	■	■	■	■	■	■	■	■	■	■	■		■		
p-Nonylphenol	SYN										■	■	■			
Triphenylphosphate	SYN										■	■	■			
Silver	TE	■	■	■	■	■	■	■	■	■						
Aluminum	TE		■	■		■	■	■	■	■						
Arsenic	TE	■	■	■	■	■	■	■								
Cadmium	TE	■	■	■	■	■	■	■	■	■						
Chromium	TE	■	■	■	■	■	■	■								
Copper	TE	■	■	■	■	■	■	■	■	■						
DBT (Dibutyltin)	TE	■	■	■	■	■	■	■	■	■						
Iron	TE						■	■								
Mercury	TE	■	■	■	■	■	■	■								
MBT (Monobutyltin)	TE	■	■	■	■	■	■	■	■	■						
Methyl Mercury	TE	■														
Manganese	TE						■	■								
Nickel	TE	■	■	■	■	■	■	■	■	■						
Lead	TE	■	■	■	■	■	■	■	■	■						
Selenium	TE	■	■	■	■	■	■	■	■	■						
TBT (Tributyltin)	TE	■	■	■	■	■	■	■	■	■						
Tetrabutyltin	TE		■	■	■	■	■	■	■	■						
Zinc	TE	■	■	■	■	■	■	■	■	■						

Gray = Analyte Reported for RMP Status and Trends Sampling.
*2006 Bivalve data was not analyzed pending analytical issues.
**Bivalves were not deployed in 2007.

Appendix 9 Summary of Changes, 1993-2007

Action Code A= Analyte added or removed from sampling design; D= Data rejected or not available; L= Change in laboratory conducting analysis or in laboratory methods; P= Change in program or sampling design; S= Station added or removed from sampling design.

Action Code	Year	Action	Detail/Rationale
P	1993	Implemented Regional Monitoring Program for Trace Substances in the San Francisco Estuary (RMP). Samples collected three times per year for conventional water quality parameters and trace analytes	Samples were collected during the wet season (March), during declining Delta outflow (May), and during the dry season (Aug - Sept).
P	1993	Implemented Regional Monitoring Program for Trace Substances in the San Francisco Estuary (RMP.) Samples. Samples collected twice a year for sediment quality parameters and trace analytes	Samples were collected during the wet season (March) and during the dry season (Aug-Sept).
P	1993	Implemented Regional Monitoring Program for Trace Substances in the San Francisco Estuary (RMP). Bivalve samples collected twice a year for transplanted, bagged bivalve bioaccumulation and condition	Samples were deployed during the wet season (March-May) and during the dry season (Aug-Sept) and retrieved between 90 and 100 days after deployment.
P	2007	Modified sediment toxicity sampling design.	During 2002-2006, every other sediment sample was analyzed for toxicity, which spatially biased the samples to the Lower South Bay
S	1993	Collected samples along the spine of the estuary at 16 set stations for water and sediment; Toxicity was measured at 8 of these stations for each matrix. Bivalves were deployed at 11 of the stations.	Original RMP sampling design.
S	1994	Added 6 stations for water and sediment sampling (previously 16): San Bruno Shoal (BB15), Alameda (BB70), Red Rock (BC60), Honker Bay (BF40), Petaluma River mouth (BD15), Coyote Creek mouth (BA10)	Sites selected to fill large areas in Estuary where no samples were taken and to better monitor areas around tributaries. Stations = 22.
S	1994	Added 2 stations for water and sediment sampling (previously 22) as part of the Local Effects Monitoring Program (LEMP): C-1-3 (Sunnyvale) and C-3-0 (San Jose)	Sites located by water pollution control plants. Added on a trial basis by Water Board. Sites were to be treated identically as RMP stations. Stations =24.
S	1994	Added 4 stations (previously 11) for bivalve tissue sampling	Stations = 15.
A	1996	Added trace organics analysis for Southern Slough stations Sunnyvale (C-1-3) and San Jose (C3-0)	Trace organics were not analyzed for Sunnyvale (C-1-3) during the 1996-07 or 1997-08 wet season cruises however samples were analyzed for trace metals and ancillary parameters. .
S	1996	Added 2 stations for water and sediment sampling (previously 24) as part the Estuary Interface Pilot Study: Standish Dam (BW10) and Guadalupe River (BW15)	Added as part of the Estuary Interface Pilot Study. Stations = 26.
S	1996	1996-04 Corbicula fluminea (CFLU) clams were collected from Putah Creek.	1996-04 Corbicula fluminea (CFLU) couldn't be retrieved from Lake Isabella so clams were collected from Putah Creek. Due to concerns with contamination, both pre- and post-depuration analysis was performed, but only the post-depurated results

Action Code	Year	Action	Detail/Rationale
			were reported. In 1996-09, only post-depurated analysis was performed.
A	1997	Identified 40 target PCB congeners for labs to report: PCB 008, 018, 028, 031, 033, 044, 049, 052, 056, 060, 066, 070, 074, 087, 095, 097, 099, 101, 105, 110, 118, 128, 132, 138, 141, 149, 151, 153, 156, 158, 170, 174, 177, 180, 183, 187, 194, 195, 201, 203	Analysis of RMP data collected from 1993-1995 showed 40 congeners consistently quantified in Bay samples. It was found that 40 congeners would be a good representation (~80% representative) of the total mass of PCBs in the bay.
D	1997	Total salinity measurements taken in the field are not available for the April cruise.	Measurements not available.
L	1997	Changed analytical lab for analysis of PCBs and PAHs in bivalve tissue samples	Central Contra Costa Sanitary District began analysis of PCBs and PAHs in bivalve tissue.
P	1997	Implemented Sport Fish Contaminant Study - Sport Fish are to be collected on a three year cycle and analyzed for mercury, PCBs, legacy pesticides (DDT, dieldrin, chlordane), and Se	Study implemented as a follow up to a 1994 study conducted by the San Francisco Bay Regional Water Quality Control Board (SFBRWQCB).
A	1998	T-1 samples analyzed for trace organics and trace elements	While T-0 samples have bee consistently analyzed throughout the years, T-1 samples were analyzed for only two cruises: 1998-04 and 2001-09. The decision to analyze was because a lot of the implants died during deployment.
S	1998	Removed 1 station (previously 15) for bivalve tissue sampling BF20 (Grizzly Bay)	A bivalve reference site could not be found for *Corbicula fluminea* (CFLU). Stations = 14.
L	1999	Changed analytical lab for analysis of mercury in water samples	University of Maryland, Center of Environmental Studies began analysis of Hg in water.
A	2000	Removed Mercury (Hg) and Arsenic (As) analysis in bivalve tissue samples	RMP results (1993-99) indicated that there was very little bioaccumulation of Hg beyond background concentrations and there was an absence of serious As contamination.
A	2000	Added gonadal index and growth analysis in bivalve tissue samples	Growth analysis calculated by SFEI in 2000 and 2001. AMS started calculating growth analysis in 2002.
A	2000	Added Cobalt (Co) analysis in water and sediment samples	Co is a useful marker of geochemical processes in the Estuary, particularly as an indicator of metal fluxes from sub-oxic sediments. Added as part of the Fe/Mn/Co group.
A	2000	Added Methyl Mercury analysis in water and sediment samples	Ratios of Methyl Mercury to Total Mercury can be used to determine environments that methylation is most likely to occur in.
L	2000	Changed analytical lab for analysis of PCBs and PAHs in bivalve tissue samples	Texas A&M Geochemical and Environmental Research began analysis of PCBs and PAHs in bivalve tissue.
P	2000	Changed frequency of sediment sampling to once a year for ancillary, trace metal and organic analytes	Samples collected during the dry season (Aug-Sept).
P	2000	Changed frequency of water sampling to twice a year for ancillary and trace metal analytes	Discontinued sampling during declining Delta outflow (May). Samples were collected during the wet season (March) and during the dry season (Aug-Sept). It was determined that samples collected during the dry season were most indicative of ambient concentrations.

Action Code	Year	Action	Detail/Rationale
P	2000	Changed frequency of water sampling to once a year for organic analytes	Samples collected during the dry season were analyzed for organic contaminants. Most organic contaminants are legacy pollutants which degrade slowly so analyzing more that once a year for these analytes was found to be unnecessary.
A	2001	Removed Gonadal Index analysis in bivalve tissue samples	Unable to obtain sufficient level of precision in separating somatic and gonadal tissue.
A	2001	T-1 samples analyzed	While T-0 samples have bee consistently analyzed throughout the years, T-1 samples were analyzed for only two cruises: 1998-04 and 2001-09. No rational was found for analyzing these samples.
A	2002	Removed chromium analysis in water, sediment and bivalve tissue samples	Technical Review Committee made decision based on findings by Khalil Abu-Saba that stated that the chromium found in the estuary was mostly of the trivalent form and none of the hexavalent form was detected. The concentrations in water and sediment were found to be essentially the same as those from the soils in the watersheds draining into the estuary.
A	2002	Added PBDEs, phthalates, and p-nonylphenol analysis in water and sediment samples	Added potential persistent pollutants with the ability to bioaccumulate and cause toxicity.
A	2002	Added PBDEs, phthalates, p-nonylphenol, triphenylphosphate and nitro and polycyclic musks analysis in bivalve tissue samples	Added potential persistent pollutants with the ability to bioaccumulate and cause toxicity.
A	2002	Reduced bivalve Trace Metals (Ag, Al, Cd, Cu, Ni, Pb, Se, Zn) analysis in bivalve tissue samples to 5 year cycle and removed tributyltin analysis in bivalve tissue samples	RMP results indicated that Trace Metals and tributyltin do not appreciably accumulate in bivalve tissue. Report link: http://www.sfei.org/rmp/Technical_Reports/RMP_2002_No109_RedesignProcess.pdf
A	2002	Changed health indicator from Condition Index Mean to Growth Mean in bivalve tissue samples	Condition index is the ratio of tissue mass to shell volume and may be affected by factors other than health. Growth compares the pre- and post-deployment weight of each mussel and is a more direct measurement of health.
D	2002	Data unavailable/rejected for PCB 132 analyzed in bivalve tissue samples	PCB 132 not analyzed in the lab due to co-elution problems.
D	2002	Data unavailable/rejected for BDEs 82, 128, 203, 204, 205, 206, 207, and 209 for bivalve tissue samples	BDEs 82, 128, and 209 not part of standard mix reported by lab. BDEs 203, 204, 205, 206, 207 and 209 do not elute off of the GC-ECD columns.
L	2002	Changed analytical lab for analysis of mercury and methyl mercury in water	University of California, Santa Cruz Dept. of Environmental Toxicology began water Hg and MeHg analysis (formerly conducted by University of Maryland).
L	2002	Changed analytical lab for analysis of trace organics in bivalve samples	California Dept. of Fish and Game, Marine Pollution Control Laboratory began analysis of trace organics in bivalve tissue (including pesticides, PAHs, and PCBs).
L	2002	Changed method for analysis of Total Suspended Solids (TSS) in water to Suspended Solid Content (SSC) in water	The SSC method analyzes the whole sample while TSS is a subsetting method. SSC poses less variability by human interference and attains better precision because heavier sand and sticky clay particles are not lost during analysis.
L	2002	Changed analytical lab for water trace organics to AXYS	Analysis formerly conducted by University of Utah Energy and Geoscience Institute (UUEGI)

Action Code	Year	Action	Detail/Rationale
P	2002	Implemented new random sampling design. Random sampling design based on spatially balanced probabilistic sampling design. The bay was divided into 5 hydrographic regions plus the Rivers segments. 7 Historic RMP sites were maintained in the program for sediment trends analysis and 3 (now 5) historic sites were maintained for water analysis	Sampling design will provide better statistical basis to answer regulatory questions. Will provide unbiased estimate of ambient conditions.
P	2002	Changed Aquatic Toxicity Testing from yearly to a five year cycle	From 1993 to 2002, a noticeable decline in aquatic toxicity to organisms was observed, especially during the dry season.
A	2003	CTD casts were not taken during 2003 bivalve tissue maintenance cruise	The water and bivalve maintenance cruise occurred concurrently and it was decided that it was more important to take casts on the water cruise.
A	2003	Added PBDE analysis in sport fish samples collected for the Sport Fish Contaminant Study	Increasing PBDE concentrations in the bay area coupled with concern about the health effects on humans and wildlife led to adding PDBEs.
D	2003	Data unavailable/rejected for pesticide, PCB, and PBDE sediment samples	Samples are to be reanalyzed using HRGC/MS since there has been a change in analytical method.
D	2003	Data rejected for PAHs in bivalve tissue	Data was rejected by SFEI QA Officer due to many samples being qualified as Non Detect.
P	2003	Stopped deployment of bivalves *Corbicula fluminea* (CFLU) in the estuary. CFLU collection was continued in the delta by trawling at the Rivers sites BG20 (Sacramento River) and BG30 (San Joaquin River)	Findings from 2000-2002 special studies concluded that bioaccumulation of contaminants in the estuary could be monitored using only one species *Mytilus californianus* (MCAL).
P	2003	Changed container for bivalves deployed from bags to cages. Some of the cages were maintained and some were un-maintained at each site	Findings from side by side deployment of bivalves in cages and in bags indicated that cages reduced the effects of bivalve predation. Report link: http://www.sfei.org/rmp/reports/431_AMS_bivalvestudies.pdf.
S	2003	Removed water sampling from one random site in the South Bay segment and one random site in the Lower South Bay segment in order to add water sampling at historic sites BA30 (Dumbarton Bridge) in the South Bay and BC10 (Yerba Buena Island) in the Central Bay	Dropping these two random sites enabled the two historic sites to be added back into the sampling design at no additional cost to the program. These sites, along with BG20 (Sacramento River) are used by the Water Board for NPDES permit processing
S	2003	Removed two water and sediment stations (previously 24) C-1-3 (Sunnyvale) and C-3-0 (San Jose), part of the Local Effects Monitoring Program (LEMP)	Funding ended for monitoring of trace organics in water and sediment which began in 1996 at these stations as part of the NPDES. Stations = 24.
S	2003	Removed three stations (previously 14) BD50 (Napa River), BD15 (Petaluma River in San Pablo Bay), and BC21 (Horseshoe Bay in Central Bay) for bivalve tissue monitoring	Findings indicated that only 2-3 stations were required to track long term changes in contaminant concentrations in bivalves. Stations = 11.
A	2004	Added Particulate Organic Carbon (POC) analysis in water samples	Began analyzing for POC in order to be able to calculate Total Organic Carbon values (DOC+POC).
A	2004	Removed phthalates and p-nonylphenol analysis in water and sediment samples	These analytes posed low levels of concern for the San Francisco Bay Region based on current literature.
A	2004	Removed PBDEs, phthalates, p-nonylphenol,	These analytes posed low levels of concern for the

Action Code	Year	Action	Detail/Rationale
		triphenylphosphate and nitro and polycyclic musks analysis in bivalve tissue samples	San Francisco Bay Region based on current literature.
A	2004	Data unavailable for pesticides, PAHs, PCBs, and PBDEs in bivalve tissue samples	Samples will be reanalyzed.
D	2004	Bivalve Organics data are not available	Samples may be reanalyzed
A	2005	Removed Toxicity Identification Evaluations (TIEs) from sediment toxicity analysis	Method development is needed to aid in understanding the toxicity found in the bay sediments. Toxicity Identification Evaluations (TIEs) will be conducted using contingency funds when sufficient toxicity is observed.
A	2005	Expanded target BDE analyte list for sediment and water samples	Based on results from BDEs sampled in previous years and capabilities of the RMP laboratories, increased number of analytes.
A	2005	Data unavailable for PAHs in bivalve tissue samples	Samples will be reanalyzed.
A	2005	2005-09 archived bivalve tissue samples reanalyzed for organics by AXYS in 2007	Data located RMP\2005\Work\2005-09_Bivalve\AXYS_ReanalyzedArchives
D	2005	Bivalve PAHs data are not available	Data received but not formatted since may be reanalyzed.
L	2005	Changed method for extraction of organic analytes in water samples	High blank contamination in 2003 PAH samples led to a change from the Soxhlet extraction method to an ambient temperature extraction method.
A	2006	Removed BDE 82 from target analyte list	BDE 082 is not in any commercial mixtures and its rationale for reporting it was unclear as it is not a major congener.
A	2006	Began collecting hardness data for all water stations where salinity <5ppt	Previously hardness data was collected at riverine stations where salinity <1ppt and estimated for estuarine sites.
A	2006	Data unavailable for all analytes in bivalve tissue samples	Not analyzed pending a decision on an analytical lab.
A	2006	Data unavailable for chlorpyrifos and diazinon water samples	Not analyzed pending a decision on an analytical lab.
D	2006	Bivalve Organics data are not available	Samples collected – analysis pending.
D	2006	Water diazinon and chlorpyrifos data are not available	Samples were not analyzed – pending method development
L	2006	Changed method for analysis of arsenic in water samples	Method changed from HGAA to ICP-MS as a cost saving measure for method development.
L	2006	Changed lab for the water diazinon an chlorpyrifos analysis from CDFG to AXYS	Changed labs based on new method development for this analysis.
P	2006	Stopped collecting the dissolved water fraction for analysis of organic analytes in water	California Toxics Rule (CTR) has only been established for the total fractions of organic contaminants. The dissolved fraction was removed as a cost saving measure.
P	2006	Changed program name to Regional Monitoring Program for Water Quality in the San Francisco Estuary	Previous name was the Regional Monitoring Program for Trace Substances in the San Francisco Estuary. This change is intended to more adequately express the objectives of the RMP.
S	2006	Changed bivalve tissue site BD20 (San Pablo Bay) by a nautical mile. BD20 will be renamed.	USGS replaced the channel marker where bivalve mooring BD20 was attached. The site was moved from Petaluma Light 1 to Petaluma Light 4. A new mooring will be installed at that sight.
A	2007	Nitrogen results will be reported as "Nitrogen, Total Kjeldahl" in sediment. This	Lab changed from UCSCDET to AMS-Texas.

Action Code	Year	Action	Detail/Rationale
		is different from the historical RMP data.	
A	2007	Added BDE 196 and 197 to target analyte list for water and sediment.	This will provide a more accurate estimate of total PBDEs since these congeners constitute a relatively high percentage of the Deca-BDE mix.
D	2007	Bivalve Organics data are not available	Bivalves were not deployed in 2007. Sampling was changed to every other year.
D	2007	Water diazinon and chlorpyrifos data are not available	Samples were not analyzed – pending method development
D	2007	Dissolved salinity measurements taken in the lab are not available	Switched labs; measurement not taken.
L	2007	Changed lab from UCSCDET to AMS-Texas for analysis of sediment quality samples	Changed labs based on an evaluation of turn around time, cost, and analytical capabilities.
L	2007	Changed lab for the bivalve tissue analysis from CDFG to AXYS	2006 tissue analysis is presently being done by AXYS. 2005 archive bivalves were reanalyzed by AXYS in 2007 and results much improved.
L	2007	Intercomparison study with UCSC and BRL for trace metals in water samples	UCSC sampled 9 of the 22 sites, BRL sampled all 22 sites.
L	2007	Intercomparison study with UCSC (POC only) and AMS-Texas (POC/DOC) for ancillary analytes in water	UCSC sampled 9 of the 22 sites, AMS-Texas sampled all 22 sites.
L	2007	Intercomparison study with UCSC and EBMUD for analysis of SSC, Pigments Nutrients, salinity, and hardness in water	UCSC sampled 9 of the 22 sites, EBMUD sampled all 22 sites. (Pigments (Chlorophyll & phaeophytin) & Nutrients (ammonia, phosphate, nitrate/nitrite, silica))
L	2007	Intercomparison study with UCSC and AMS-Texas for grainsize, Total Organic Carbon and Total Nitrogen in sediment	UCSC sampled 9 of the 47 sites; AMS-Texas sampled all 47 sites.
P	2007	Water toxicity sampling occurred in 2007. Toxicity sampling has been changed to a screening effort approximately every five years	RMP S&T aquatic toxicity monitoring in the Estuary has shown little toxicity over the past several years. No toxicity was observed in 2007. Next scheduled sampling will occur in 2012.
P	2007	The S&T monitoring program was expanded to include the following elements: triennial bird egg monitoring (cormorant and tern); annual small fish monitoring; annual small tributary loading; triennial large tributary loading; and triennial studies of the Guadalupe River	Part of the redesign process implemented in 2006.
P	2007	Bivalves were not deployed in 2007.	Sampling was changed to every other year.
P	2007	The number of water sites was changed from 31 to 22. Sampling will occur at 3 sites in each of the upper 4 segments and 5 sites in the Lower South Bay segment. The 5 historic sites will continue to be sampled.	The power analysis from San Jose suggests that this change will be able to detect about a 1 ug/L change (give or take) in dissolved copper in every segment at a very high 99% power.

> For a PDF of this report, please go to

www.sfei.org/rmp/annualmonitoringresults/index.htm