2008
RMP Annual Monitoring Results

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

March 2010 • Contribution no. 604

RMP STAFF
WATER SAMPLING CRUISE
SUMMER 2009

This report should be cited as: SFEI. 2010. 2008 Annual Monitoring Results. The Regional Monitoring Program for Water Quality in the San Francisco Estuary (RMP). Contribution No. 604. San Francisco Estuary Institute, Oakland, CA.

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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 community of Program participants (Appendix 1) for providing funding. Special thanks are due to SFEI staff for sample collection, data management, quality assurance, and report preparation.

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Table of Contents

Tables and Figures

1

Introduction

1. INTRODUCTION

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 Program participants).

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.

The RMP is overseen by the Technical Review Committee (TRC), the Steering Committee (SC) and four workgroups which consist of invited experts and interested stakeholders. The four workgroups are: the Sources, Pathways and Loadings Workgroup, the Exposure and Effects Workgroup, the Contaminant Fate Workgroup, and the Emerging Contaminants Workgroup.

The four workgroups directly guide planning and implementation of Pilot and Special Studies and provide input on relevant aspects of the annual RMP Status and Trends monitoring. Activities of the Workgroups and the technical content of the RMP as a whole are directed by the TRC. The SC determines the overall budget, allocation of program funds, tracks progress, and provides direction to the Program from a manager's perspective.

Approximately every five years, the RMP undergoes a rigorous external review by national science and management experts to ensure that the program is adapting to address current regulatory and scientific information needs. This review provides a forum for re-evaluating the Program's 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*. Please see the RMP website for more information.

In 2007-2008, an effort was undertaken to prioritize studies within the workgroups and the RMP in general. The management questions and RMP objectives were revisited and a number of programmatic changes were implemented. As a result, the 5-year program review has been deferred while the Steering Committee evaluates the timing, questions, and focus for the next program review.

The RMP is made up of two program elements: the annual Status and Trends Monitoring Program and Pilot and Special Studies. The Status and Trends portion of the program includes long-term monitoring of

San Francisco Bay, including select tributaries, and remains relatively constant from year to year. The Pilot and Special Studies change annually and allow the program to be flexible to changing management priorities.

The RMP management questions were revised in 2007 as part of the RMP's Five-year Program review process and refined and approved by the Technical Review Committee (TRC) and Steering Committee (SC) in 2008. The current Program uses the following management questions to guide changes in the Status and Trends monitoring elements and in deciding which Pilot and Special studies to fund annually:

1. Are chemical concentrations in the Estuary at levels of potential concern and are associated impacts likely?
    a. Which chemicals have the potential to impact humans and aquatic life and should be monitored?
    b. What potential for impacts on humans and aquatic life exists due to contaminants in the Estuary ecosystem?
    c. What are appropriate guidelines for protection of beneficial uses?
2. What are the concentrations and masses of contaminants in the Estuary and its segments?
    a. Do spatial patterns and long-term trends indicate particular regions of concern?
3. What are the sources, pathways, loadings, and processes leading to contaminant-related impacts in the Estuary?
    a. Which sources, pathways, and processes contribute most to impacts?
    b. What are the best opportunities for management intervention for the most important contaminant sources, pathways, and processes?
    c. What are the effects of management actions on loads from the most important sources, pathways, and processes?
4. Have the concentrations, masses, and associated impacts of contaminants in the Estuary increased or decreased?
    a. What are the effects of management actions on the concentrations and mass of contaminants in the Estuary?
    b. What are the effects of management actions on the potential for adverse impacts on humans and aquatic life due to Bay contamination?
5. What are the projected concentrations, masses, and associated impacts of contaminants in the Estuary?
    a. What patterns of exposure are forecast for major segments of the Estuary under various management scenarios?
    b. Which contaminants are predicted to increase and potentially cause impacts in the Estuary?

The RMP addresses its management questions through the Status and Trends Program, focused workgroups, and pilot and special studies.

Status and Trends long-term monitoring characterizes water and sediment quality and contaminants in water, sediment, and bivalves in the Estuary (Objectives 2 and 4). It is comprised of the following elements:

- *Water monitoring* occurs annually during the dry season for analysis of water quality, trace metals, trace organics and ancillary parameters

- *Sediment monitoring* occurs annually during the dry season for the analysis of trace metals, trace organics and ancillary parameters. Beginning in 2010, sediments will be collected in alternate seasons starting with a wet season (winter) collection event followed by a dry season (late summer) collection event in 2011.

- *Bivalve monitoring* occurs biennially for analysis of trace organic parameters and every five years for analysis of trace metal parameters.

- *Toxicity studies* investigate potential water and sediment toxicity in the Estuary and possible causes of observed toxicity through developing Toxicity Identification and Evaluation (TIE) methods (Objectives 1 and 3). The RMP monitors for sediment toxicity annually while water toxicity in the Estuary is monitored on a five-year cycle.

- *Benthic community assessments* were added to the RMP Status and Trends program in 2008 as part of the State's recently approved Sediment Quality Objectives (SQO) methodology to evaluate sediment quality using a triad approach. Benthos samples will be collected during scheduled RMP sediment sampling.

- *Sport Fish Contamination Study* triennially screens fish tissue for contaminants of concern to human health (Objectives 1, 2, 4, and 5).

- *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.

In 2008 two studies that started as Pilot and/or Special studies in previous years became part of the RMP's long-term Status and Trends program. They bring important new information about bioaccumulative substances in higher trophic-level biota and sources and pathways by which contaminants enter the Estuary:

- *Triennial bird egg monitoring* (cormorant and tern) and *annual small fish monitoring* will help us understand spatial patterns of contaminant uptake into the food web and trends in biota over time (Objectives 1, 2, 3 and 4).

- *Loading studies for annual small tributary loading, triennial large tributary loading, and triennial studies of the Guadalupe River* will help us understand the sources of contaminants and the pathways by which they reach the Bay (Objectives 1, 2, 3, and 4.

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 5), and future contaminant status and trends (Objective 5), and help to develop and

review pilot and special studies and provide oversight of Status and Trends elements. These workgroups meet several times a year to review progress and make recommendations for further study. In 2008, the RMP developed five-year plans for each of the four workgroups in order to develop a coherent strategy to address the management questions and objectives that guide the RMP. In addition, the RMP developed strategies for high priority pollutants and select topics of concern. In 2009, workgroup plans, strategy documents, and the Status and Trends program will be synthesized into a five-year master plan for the whole program.

In 2008, at the request of the TRC, the RMP began development of a mercury strategy and created a subcommittee comprised of interested RMP participants, regulators, and scientists to complete this task. The main objectives of the mercury strategy are to address where mercury is entering the food web and) determine which processes, sources, and pathways contribute disproportionately to food web accumulation.

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. Pilot and Special Studies conducted by the RMP in 2008 are discussed later in this chapter. A summary of previous studies conducted by the RMP can be found by going to the RMP Pilot and Special Studies web page and specific details on the study development and selection processes can be accessed via the Selection Process web 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 the section 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 10* provides an overview of changes to the program including: changes to the sampling design, changes in target parameters (analytes added and/or removed), when data were rejected or not available, when stations were added or removed, changes in laboratories who conduct analyses, or significant changes in laboratory methods since the RMP began in 1993. *Appendix 7 – Appendix 9* includes tables of reported analytes by matrix for the long-term Status and Trends monitoring of water, sediment, and bivalve tissue beginning in 1993.

RMP WORK GROUPS

Four workgroups address the major technical subject areas covered by the RMP. Workgroups consist of local scientists, regulators, and stakeholders and invited scientists recognized as leaders in their field. The workgroups directly guide planning and implementation of Pilot and Special Studies and provide input on relevant aspects of the annual RMP Status and Trends monitoring.

Sources Pathways and Loadings

The Sources Pathways and Loadings work group (SPLWG) was formed in 1999 to address the objective developed during the 1997 five-year program review to "describe general sources and loadings of contamination to the Estuary" (Bernstein and O'Connor, 1997). The SPLWG makes recommendations for collection, interpretation, and synthesis of data on general sources and loadings of trace contaminants to the Estuary. Their goal is to create a functional connection between the RMP and efforts to identify, eliminate, and prevent sources of pollution that influence the Bay. The SPLWG ensures that the projects and products are relevant and help to answer ever developing management questions in the context of TMDLs and attainment of water quality standards. For further information, please see the SPLWG web page.

Contaminant Fate

The Contaminant Fate Workgroup's (CFWG) objective is to improve our understanding of physical, chemical, and biological processes that redistribute and transform contaminants in the Estuary, ultimately leading to exposure of biota. Through improved information on Estuary processes, they aim to assist managers in directing limited resources and prioritizing actions for reducing negative impacts, both for new contaminants entering the system, as well as for legacy pollutants already in the Estuary. Please see the CFWG web page for further information.

Exposure and Effects

The Exposure and Effects Work Group (EEWG) was developed in part to create a biological effects pilot study (the Exposure and Effects Pilot Study (EEPS)) that would help address beneficial use management questions developed by the Regional Board. The EEWG designed a five-year plan for addressing biological effects in the Bay. At the end of the five-year pilot study the workgroup was incorporated into the RMP as a permanent workgroup. The EEWG continues to address the biological effects portion of the Status and Trends program and Pilot and Special Studies. See the EEWG web page for more information.

Emerging Contaminants

The Emerging Contaminants Workgroup (ECWG) evaluates the presence of emerging contaminants in the Estuary. Emerging contaminants are defined as chemicals that are not currently regulated and believed to potentially pose significant ecological or human health risks (e.g., pharmaceuticals, flame retardants, and perfluorinated compounds). Because these compounds are not regulated, relatively little information is available on their toxicity or their abundance in the environment, and consequently the magnitude of the risks are not well known at this time. For additional information please see the ECWG web page.

THE STATUS AND TRENDS PROGRAM

Random and Targeted Sampling Design for Water and Sediment

The 2008 sampling was the seventh 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 overarching goal to collect data and communicate information about water quality in the San Francisco Estuary in support of management decisions. An important advantage of random site selection is that estimates of regional condition derived from a probabilistic survey will have a known level of uncertainty associated with them. Prior to 2003, a targeted sampling design was used. The targeted stations were purposefully located along the central axis of the Estuary as far from anthropogenic sources as possible to monitor 'background' concentrations of pollutants of concern. A subset of those historic, targeted water and sediment sites were retained from the original RMP monitoring design, established in 1993, to provide continuity in the long-term monitoring program. With the random sampling design, the RMP can better address their management questions.

The RMP water and sediment monitoring stations are located in six hydrographic regions of the Estuary. Random design sites are located in five of those regions: Suisun Bay, San Pablo Bay, Central Bay, South Bay, and the Lower South Bay. Historic, targeted design sites are located in each of those five regions and at the confluence of the Sacramento and San Joaquin Rivers in the freshwater Rivers region of the Estuary. The sampling frames for water and sediment monitoring (the area within which sites were allocated), are the three-foot and one-foot contours of the Estuary at mean lower low water, respectively (based on NOAA's NAD-83 bathymetry coverage). About seventy-two random water and sediment sites were allocated into the hydrographic regions. Each year, a subset of the water sites are sampled in sequential order, increasing the spatial density of monitoring over time. For sediment, a site re-visit schedule was incorporated into the design to better evaluate trends over time.

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. The sediment sample design incorporates re-sampling of sites for additional trends analyses. Two random sites within each region are re-visited for sediment analysis on an annual, five-year, ten-year, and twenty-year basis. See Appendix 3 for water stations and Appendix 4 for sediment stations sampled during 2008.

The number of Random design sites sampled in each region can change based on management decisions. The initial number of sites sampled in 2002 was based on a power analysis using existing, targeted site data and Water Board management priorities. A power analysis is generally used to evaluate the number of samples needed to detect a change in contaminant concentrations over time with a known level of statistical confidence. The initial random design recommended that 26 water and 40 sediment sites be monitored while maintaining a subset of 5 historic water stations and 7 historic sediment stations (a total of 31 water and 47 sediment sites). A second power analysis was conducted in 2006 using the recently

collected random design data. Based on those results for key contaminants of current concern to environmental mangers of the Estuary, and discussions with the RMP oversight committees (which include Water Board staff), the number of water sites was reduced from 31 sites to 22 sites per year starting in 2007, while the number of sediment sites was maintained at 47 sites per year. Sampling currently occurs once a year during the dry season when Estuary conditions are most consistent on an interannual basis.

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), and the *2000 Pulse of the Estuary*.

2008 Water Sampling

In 2008, 22 sites were sampled for water chemistry during the dry season in July. This includes five historic, targeted stations and seventeen randomly allocated stations: 3 per region in Suisun, San Pablo, Central and South Bays and 5 in the Lower South Bay. Two historic, targeted stations are located in the Rivers Region (one on the Sacramento River and the other on the San Joaquin River) to monitor water quality entering the Estuary from the Delta region. The other historic RMP sites are located in the Central Bay (n=2), and the South Bay and are important monitoring sites used in the Water Board's NPDES permitting process. The water sampling sites are shown in Figure 2.1.

The analyte list for conventional water quality parameters and trace metal parameters remained the same as in 2007. During 2008, the RMP began monitoring trace organic parameters in water biennially with the exception of PBDEs which will continue to be monitored annually. In 2008 water analysis was preformed for PAHs and PBDEs. *Appendix* 6 lists the 2008 target parameters. PCBs and Pesticides will be analyzed, along with PBDEs, in 2009. PAHs and PBDEs will be analyzed again in 2010.

Water samples were last tested for ambient water toxicity in 2007. Since very little aquatic toxicity has been observed in the Estuary by the RMP in past monitoring years, ambient water toxicity testing will take place every five-years. The next aquatic toxicity sampling of the Estuary surface waters is scheduled for 2012.

2008 Sediment Sampling

In 2008, sediment sample collection occurred during the dry season in July and August at 47 sites throughout the Estuary. Forty random sites and seven historic targeted sites were sampled. See figure 3.1 for a map of the 2008 sampling sites.

The analyte list for sediment parameters remained the same as in 2007. See *Appendix* 6 for the 2008 target analyte list. All target analytes were reported with the exception of grainsize. The grainsize data were not reported in 2008 because the fractions were not comparable to previous years since the granule fraction was not analyzed.

Twenty-seven sediment samples were tested for toxicity in 2008 from 20 random sediment chemistry stations and seven historic RMP stations. Toxicity tests included mean percent survival of the amphipod *Eohaustorius estuarius* after exposure to solid-phase sediments for 10 days, and mean percent normal alive for Bay mussel *Mytilus galloprovincialis* larvae after exposure to sediment-water interface cores (SWI) for 48 hours. See figure 3.2 for the 2008 sediment bioassay results.

Sampling Design for Bivalve Bioaccumulation Monitoring

The RMP's bivalve bioaccumulation monitoring effort augments the long-term monitoring effort started by the State Mussel Watch Program. In 2008, bivalves were analyzed for trace metal and trace organic contaminants. The current monitoring design includes the analysis of trace organics in bivalves biennially, and the analysis of trace metals every 5 years.

The bivalve bioaccumulation sample design remains a fixed sample design because deployment of caged bivalves requires secure moorings. Based on the findings from a series of special studies between 2000 – 2005 to redesign and improve technical aspects of the deployed bivalve bioaccumulation monitoring component of the RMP, several changes were made in 2003. These included:

1. Dropping three sites in the northern Estaury: Napa River (BD50) , Petaluma River (BD15) , and Horseshoe Bay (BC21) because only two to three sites were required per region to track long-term changes in contaminant concentrations.
2. Deploying only one bivalve species (*Mytilus californianus*). Because of the reduced salinity range of the study area (because of the dropped sites), the program was able to deploy one, fairly salinity tolerant bivalve species, which makes comparing bioaccumulation results between regions possible.
3. Deploying bivalves in cages, rather than mesh bags, which reduces the loss of organisms through predation.
4. Discontinuing the bivalve maintenance cruise. This was discontinued in 2006 after a study conducted from 2002-2005 showed no significant difference in survival of bivalves in maintained and non-maintained cages.

Mytilus californianus bivalves were collected from Bodega Head in May of 2008 for a three month deployment at nine targeted mooring sites within the Estuary (three in the Central Bay and San Pablo Bay regions, two in the South Bay, and one in the Lower South Bay) for analysis of trace organics, trace elements, selenium, brominated flame retardants (BFRs), growth, and survival. In September 2008, resident bivalves *Corbicula fluminea* were harvested at two historic RMP sites located on the Sacramento and San Joaquin Rivers for analysis of trace organics, BFRs, selenium, trace metals, and growth. At the end of the deployment, *M. californianus* were collected from Bodega Head and analyzed for growth in order to provide a control for interpreting the results from the transplanted bivalves. Bivalve sampling will occur again in 2010.

Water Column Profile Data

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).

Benthic Community Assessments

In 2008, sediment quality objectives (SQOs) for enclosed bays and estuaries were approved by the State. The SQOs are based on sediment chemistry, toxicity, and benthic assessments. To provide the data needed for sediment triad evaluation, the RMP began collecting samples for benthic community assessments in 2008. Samples were collected at 27 sites during the sediment cruise at 20 randomly allocated sites and 7 historic sites. This sampling effort will continue into the future. Because processing benthos samples takes a long time, the SQO triad assessment of the 2008 sediment monitoring results will be reported in a separate technical report under the RMP.

Causes of Sediment Toxicity

In 2008 the RMP concluded a special study on the Causes of Sediment Toxicity Study begun in 2007. The RMP Status and Trends Program has observed persistent, moderate sediment toxicity in the Estaury since the program began in 1993. Understanding the cause(s) of sediment toxicity is one of the primary goals of the RMP because management of contaminants entering the Estuary is most efficient when it targets the key chemicals responsible for biological impacts. The 2007-2008 Causes of Toxicity study goals were to begin developing analytical toxicity identification and evaluation tools to separate contaminants in ambient sediment and sediment elutriate samples in order to determine with contaminant classes were causes an observed toxic response in laboratory toxicity tests using the amphipod *Eohaustorius estuarius*. That study also developed *Eohaustorius estuarius* LC50 effects thresholds for a few key contaminants of concern in the Estaury. The Exposure and Effects Work Group (EEWG) recommended that work to address the causes of the observed toxicity be continued over the next five years, and recommended a workgroup process to develop and oversee new studies. Please see the final report RMP Sediment TIE Study 2007-2008 for a more detailed account of the initial study, and the EEWG website for an update on new RMP special studies addressing current issues related to the causes of toxicity.

Sport Fish Bioaccumulation Monitoring

Sport fish sampling, which occurs on a three-year cycle, was not conducted in 2008. Sport fish sampling includes evaluation of key fish species for long-term trend assessment, combined with follow-up sampling of additional species. The trend assessment species include shiner surfperch, white croaker, striped bass, and white sturgeon. The additional species targeted include anchovies, halibut, and leopard sharks. 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 is available via the Web Query Tool. 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.* Sport fish sampling will be conducted in 2009.

Annual Small Fish Monitoring

Using a randomized design, the small fish program is interested in answering the following questions: (1) What factors (i.e., site characteristics) appear to be important for causing increased mercury concentrations in Bay biota? and (2) Where are the highest mercury concentrations found in the nearshore portions of the system? Each year, 12 sites will be selected based on site characteristics such as enclosed embayments, open bay sites, wetlands with differing mercury concentrations, sites in close proximity to mercury mines, and sites near wastewater treatment facilities.

Triennial Bird Egg Monitoring (Cormorant and Terns)

Cormorant and tern bird egg monitoring were included as part of the Status and Trends Program in 2008. Sampling will occur 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 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, but in 2009, tern eggs will be analyzed for mercury and PBDEs.

Tributary Loading

Tributary loading was added as part of the Status and Trends program in the 2006 water year. Tributary studies include small tributary loading to be sampled annually, large tributary loading to be sampled triennially (Mallard Island studies), and Guadalupe river loading studies to be sampled triennially.

The Tributary Loading objectives are:

1. To improve our knowledge of the magnitude of contaminant loads entering the Bay from local small tributaries (in this case a small industrial watershed with an added mix of commercial and residential use)

2. To provide loadings data to improve our knowledge on processes in the Bay (such as described by the mercury, PCB, PAH, and OC pesticide models for the Bay), thereby assisting in the development of Bay Total Maximum Daily Loads (TMDLs)

3. To demonstrate a methodology for use in other watersheds and make recommendations on how best to sample other watersheds

4. To provide input data for the eventual development of a watershed based model to predict loads on a regional scale

Initially started as a special study in 2006, sampling efforts for a small tributary located in an industrialized area of Hayward (referred to as the Z4LA Project) were incorporated into the Status and Trends program in water year 2007. 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 mercury 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 trends can be assessed over time and provide data for models that describe biological effects in the Bay.

During the water year 2009, samples will be collected at Z4LA and at two locations on the Guadalupe River and at Mallard Island. Refer to the featured article "Advances in Understanding Pollutant Mass Loadings from Rivers and Local Tributaries" in the 2008 Pulse of the Estuary for a detailed discussion of this project.

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 2008, it continued to supplement RMP monitoring with two special studies that address basic hydrographic and sediment transport processes. These monitoring components are described below.

Sediment Dynamics 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 targeted 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 targeted 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 of the 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.

RMP PILOT AND SPECIAL STUDIES

Pilot and Special Studies allow for adaptive management of the RMP by allowing for shorter-term changes based on the changing regulatory priorities, management of the Estuary, and scientific understanding of the Estuary.

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 and the Sport Fish Contamination Study).

Exposure and Effects Pilot Study (2000 – 2008)

Applicable RMP Questions: 1, 2, 4, 5, and 6
Contact: Meg Sedlak (meg@sfei.org)

2008 was the final year of ear-marked funding for the Exposure and Effects Pilot Study (EEPS). 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 2008, the Exposure and Effects Pilot Study funded two new studies: a study on the interaction of mercury and selenium on bird egg hatchability and survival (USGS) and the impact of polyaromatic hydrocarbons (PAHs) on the early life stages of flatfish (NOAA).

THE FOLLOWING STUDIES WERE CONTINUED DURING 2008 UNDER THE EXPOSURE AND EFFECTS PILOT STUDY:

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 was funded by EEPS.) In 2009, this study will be incorporated into an annual sampling event as part of the Status and Trends Program.

Understanding how and where mercury is incorporated into the food web is a high priority for RMP participants. The small fish element initiated in 2008 is planned as a three-year intensive study. The goal of the project is to determine hotspots of methylmercury bioavailability by monitoring mercury concentrations in small fish and sediments. Monitoring will also be performed on mercury isotopes in fish and with Diffusive Gradient in Thinfilm (DGT) devices, in coordination with this program.

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 DISRUPTIONS 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.

AVIAN EXPOSURE AND EFFECTS TO MERCURY AND SELENIUM (2008)

The USGS assisted the RMP by investigating the reproductive success of avians through analysis of individual egg albumin for mercury and selenium and correlating the egg concentrations to hatchability and survival. The results will assist in the development of egg thresholds as well as aid in understanding interactions between mercury and selenium.

EFFECTS OF PAH-CONTAMINATED SEDIMENT ON JUVENILE FLATFISH DEVELOPMENT (2008-2009)

NOAA researchers will assist the RMP by investigating the impacts of pyrogenic (high molecular weight) PAHs on juvenile flatfish development. The first year will focus on a model fish, such as the Zebra fish. After biological endpoints have been identified for the model fish, the second year will focus on a native species.

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. The following special studies were conducted in 2008:

- CHARACTERIZATION OF THYROID ENDOCRINE DISRUPTION IN SAN FRANCISCO BAY FISH
- COMPARISON OF CONTAMINANT PATTERNS BETWEEN SAN FRANCISCO ESTUARY AND THE COAST
- GUADALUPE RIVER WATERSHED MODEL – YEAR 1
- NON-PBDE CURRENT USE FLAME RETARDANTS IN BIOTA
- PERFLUORINATED COMPOUNDS IN BIOTA
- REMOTE SENSING OF COASTAL AND ESTUARINE DYNAMICS
- WATERSHED SPECIFIC SEDIMENT LOADS

Characterization of Thyroid Endocrine Disruption in San Francisco Bay Fish (2008)

Applicable RMP Question: 4
Contact: Kevin Kelley, California State University – Long Beach (kmkelley@csulb.edu)

The objective of this work was to characterize the environment-related disruption of the thyroid endocrine system observed in Pacific staghorn sculpin and shiner surfperch. In addition, chemical contaminants in individual fish were measured to determine whether there was a correlation between

contaminants and thyroid effects. The thyroid gland function was assessed, in addition to the hypothalamo-pituitary-interrenal axis (cortisol), in an effort to develop markers of endocrine disruption. This project has been completed and a final project report was submitted to SFEI (Kelley and Reyes, 2009).

Comparison of Contaminant Patterns between San Francisco Estuary and the Coast (2008)

Applicable RMP Questions: 1, 4, 5 and 6
Contact: Aroon Melwani (aroon@sfei.org)

The objective of this study was to compare status and trends in priority contaminants (in fish and sediment) present within San Francisco Bay compared to coastline stations outside the mouth of the Estuary. This study addressed a recommendation by the RMP's Technical Review Committee that the Program integrate data from other monitoring studies. The study evaluated data collected by the City and County of San Francisco, Coastal Fish Contamination Program, and RMP to test two hypotheses: 1. Are contaminant concentrations (Hg, PCBs, and organochlorine pesticides) higher in the Estuary than on the coastline? 2. Are long-term trends in contaminant concentrations similar between the Estuary and the offshore coastline? These data are available through the Web Query Tool and presented in the report Patterns in Mercury and Trace Organic Contamination of Sprot Fish and Sediments in San Francisco Bay Compared to the Offshore Coast.

Guadalupe River Watershed Model – Year 1 (2008-2010)

Applicable RMP Questions: 1, 2 and 6
Contact: John Oram (joram@sfei.org)

The objectives of this project are to begin the development of a numeric model to assist in estimating mass loads of mercury and PCBs; to extrapolate the data to determine long term average loads for the period of extensive rainfall data collection (1973-present); and to determine the proportional sources in the watershed and refine the assumptions of the Guadalupe River mercury TMDL. Ultimately, the model will be used to assess the effects of best management practices and impacts of wetland restoration (e.g., effects of South Bay Salt Pond restoration).

Non-PBDE Current Use Flame Retardants in Bay Sediments and Wildlife (2008-2010)

Applicable RMPQuestions: 1, 2, 4 and 5
Contact: Susan Klosterhaus (susan@sfei.org)

Polybrominated diphenyl ethers (PBDEs) are chemicals used as flame retardants that have been incorporated into a variety of consumer products to comply with fire safety regulations. Environmental and human health concerns have resulted in a ban of the most toxic PBDE mixtures (Penta- and Octa-BDE) in California, which became effective in 2006. The decline in use of PBDEs will result in an increase in the use of non-PBDE flame retardant chemicals since consumer product flammability standards have not changed and a national furniture flammability standard is in development in the United States.

Substantial data gaps exist for non-PBDE flame retardant chemicals in the San Francisco Estuary. Assessment of the current concentrations of these compounds in the Estuary will allow us to determine

the risk of exposure of these chemicals to the estuarine foodweb and to humans consuming sport fish. This study will be the first to determine concentrations of non-PBDE flame retardant chemicals in the San Francisco Estuary and will provide some of the first data on concentrations in an urbanized estuary in North America.

Perfluorinated Compounds in Biota (2007 and 2008)

Applicable RMP Questions: 1, 2, 4 and 5
Contact: Meg Sedlak (meg@sfei.org)

The objective of this study was 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. See the 2007 and 2008 posters presented at SETAC for more information.

Remote Sensing of coastal and estuarine dynamics (2007 and 2008)

Applicable RMP Questions: 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.

Watershed Specific Sediment Loads (2008)

Applicable RMP Questions: 1, 2, 3 and 5
Contact: John Oram (joram@sfei.org)

Suspended sediments supplies to San Francisco Bay are vital for maintaining tidal marsh and mudflat habitats and delivering nutrients and organic carbon to the base of the food web. Prior to human intervention, water, sediment, nutrients, and carbon supplies to the Bay would have been maintained in a quasi-equilibrium state based on climate and tectonic activity. Over the past 150 years, population in the Bay Area has multiplied dramatically. The objective of this project is to bring all the existing data together and use it to estimate suspended sediment loads on a watershed basis and per RMP Bay segment. This information will be useful for:

1. improving our understanding of contaminant distribution and loads and providing a hypothesis on where it might be most appropriate to apply limited Bay Area Stormwater Management Agencies Association (BASMAA) resources to achieving a mass loading target, a loads avoided target, or a sediment concentration target;

2. providing Input into hypotheses about where we are likely to find the most and least contaminated sediment in storm water conveyances and on the Bay margin;

3. providing inputs into watershed and Bay modeling;

4. providing sediment load estimates for salt pond restoration design;

5. providing BASMAA with a data set to use to make decisions about where to apply limited resources to make detailed measurements in relation to permit requirements.

ANNUAL MONITORING ONLINE GRAPHICS AND DATA ACCESS TOOLS

Web Query Tool

The 2008 data are now available online using a dynamic mapping and graphing tool. The online Web Query Tool (available at http://eis.sfei.org/wqt) allows water, sediment, and tissue monitoring results from 1993 to 2008 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).

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.

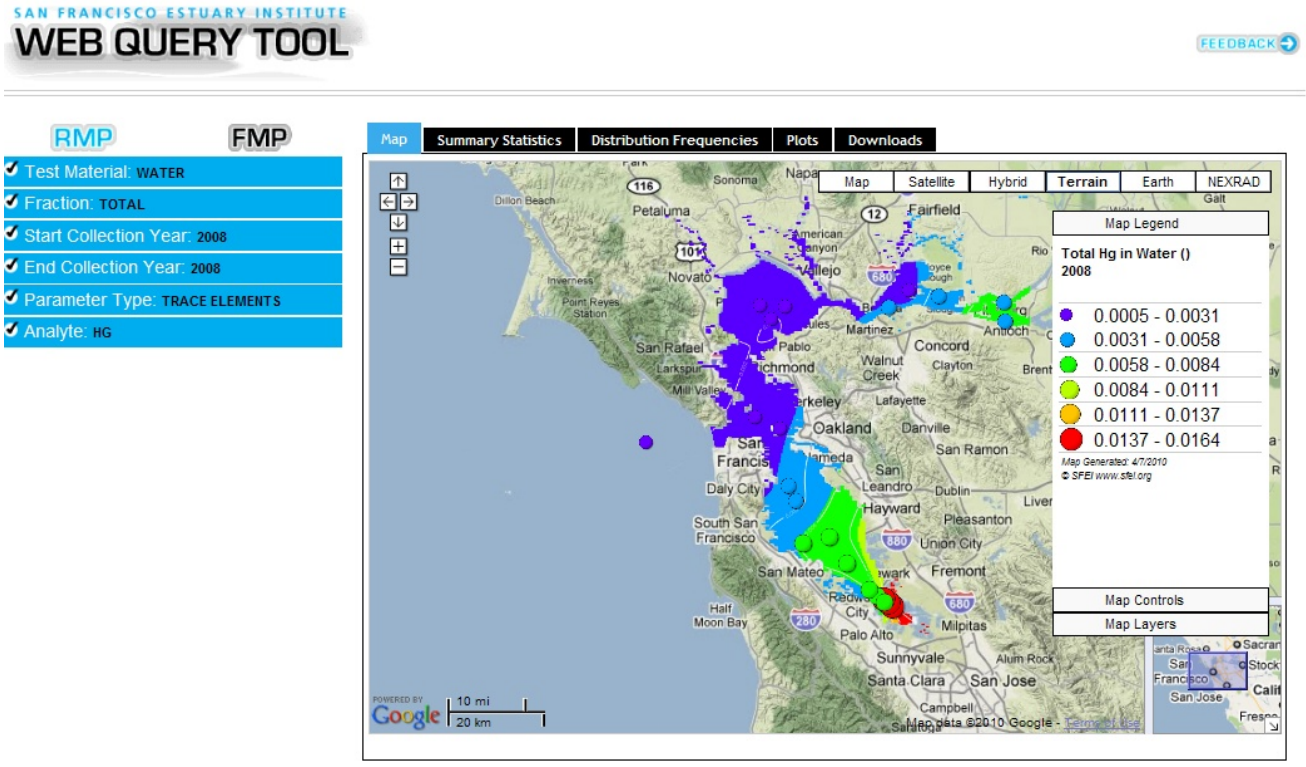

Figure 1.1 Web Query Tool Map Interface

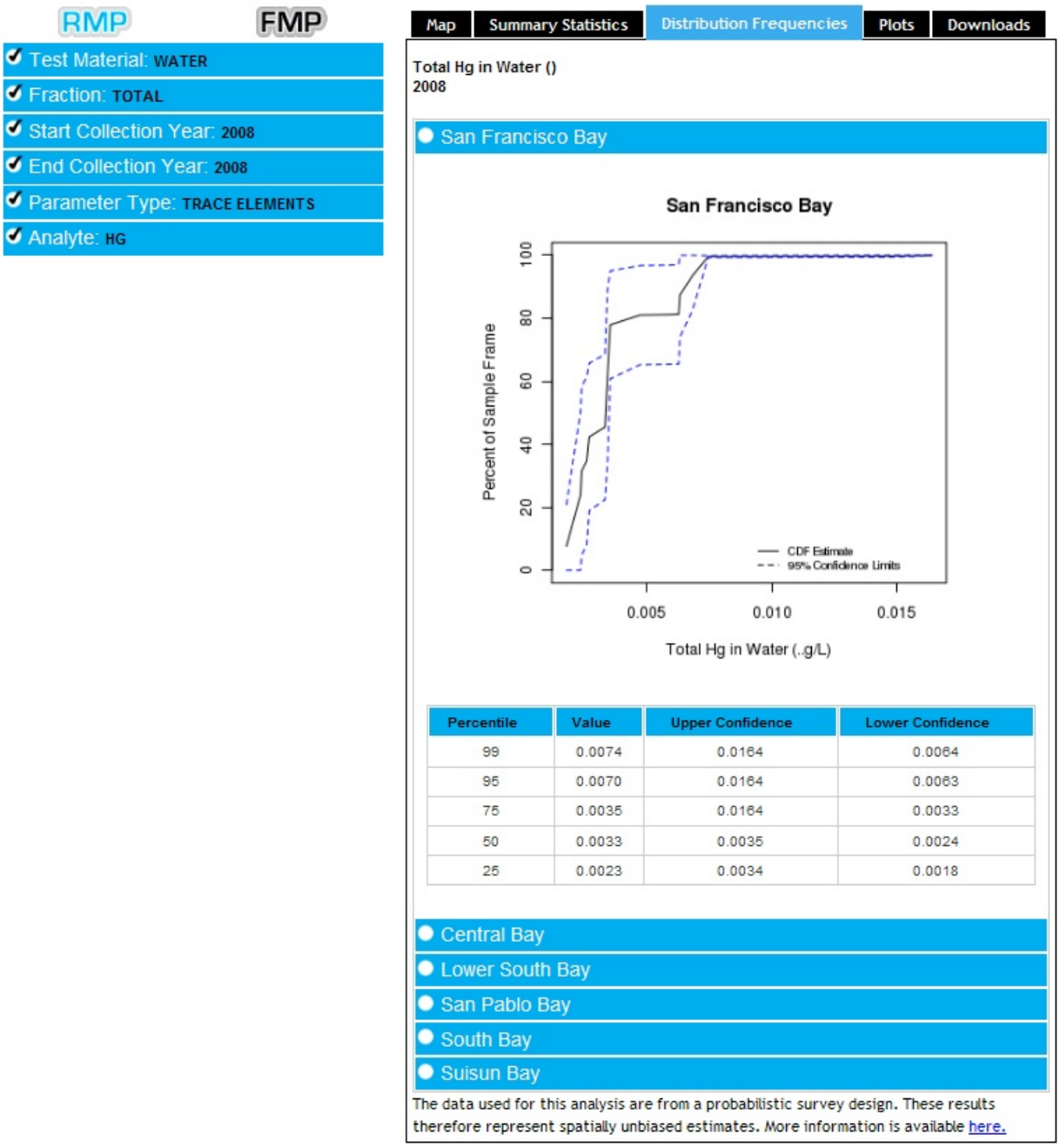

Figure 1.2 Web Query Tool CDF Map Summary

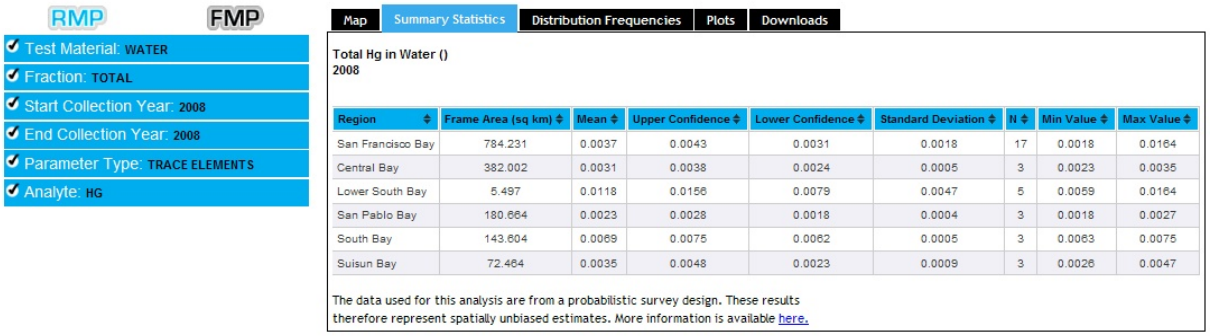

Figure 1.3 Web Query Tool summary statistics

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 6*) 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.

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2

Water Monitoring

2. WATER MONITORING

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 priority management questions listed in the *Introduction*. All water samples were collected aboard the R/V *John Martin* during July 9-18, 2008.

CHANGES IN WATER SAMPLING

The S&T program for water and sediment was revised in 2002 to include a randomized sampling design. In 2007, the number of sites analyzed for water was reduced from 31 to 22. Samples are collected from three sites in each of the upper four segments and five sites in the Lower South Bay segment. The five historic sites continue to be sampled.

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. Whole water samples are collected as ongoing tests to verify the comparability of the Infiltrex solid phase extraction method to more traditional methods of sample extraction and analysis of organic compounds in water samples. Whole water sample results are not included in the site average reported values.

In 2008, based on recommendations from the redesign process, water samples will be analyzed annually for PBDEs and biennially for PCBs, PAHs, and Legacy Pesticides. In 2008, an exception was made to analyze water for PAHs as a result of the Cosco Busan oil spill. The PAH water concentrations in Central Bay (the region most impacted by the spill) in 2008 were generally within range of historical data, indicating no apparent increase due to residual oil from the Cosco Busan spill. PAH analysis will continue to occur biennially. PAHs will be analyzed again in 2010. In

addition, PBDEs extracts (dissolved and particulate) will no longer be combined in order to aid in understanding the partitioning of PBDEs.

SAMPLING SITES

In 2008, 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. In 2007 the number of random sites was reduced from 26 to 17 because power analysis showed that sampling fewer sites per year could still detect trends. Water sampling for the Status and Trends Program is currently only conducted during the dry season (July/August).

In 2008, 22 sites were sampled for water (Figure 2.1 for site map). Five of these were the historic targeted 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 region with the exception of the Lower South Bay, which had five sites. Sampling of the 22 sites was successfully completed although two of the random sites (SB052W and SU027W) had to be replaced. Site SB052W was inaccessible due to its location under the San Mateo Bridge and near infrastructure related to power transmission equipment, and was replaced by random oversample site SB053W. Site SU027W was located within a restricted area around the Mothball Fleet, and was replaced by random oversample site SU029W. All other stations were sampled according to the proposed water cruise plan.

Station names, codes, location, and sampling dates for the 2008 monitoring effort are listed in Appendix 3. A map of the station locations is shown in Figure 2.1.

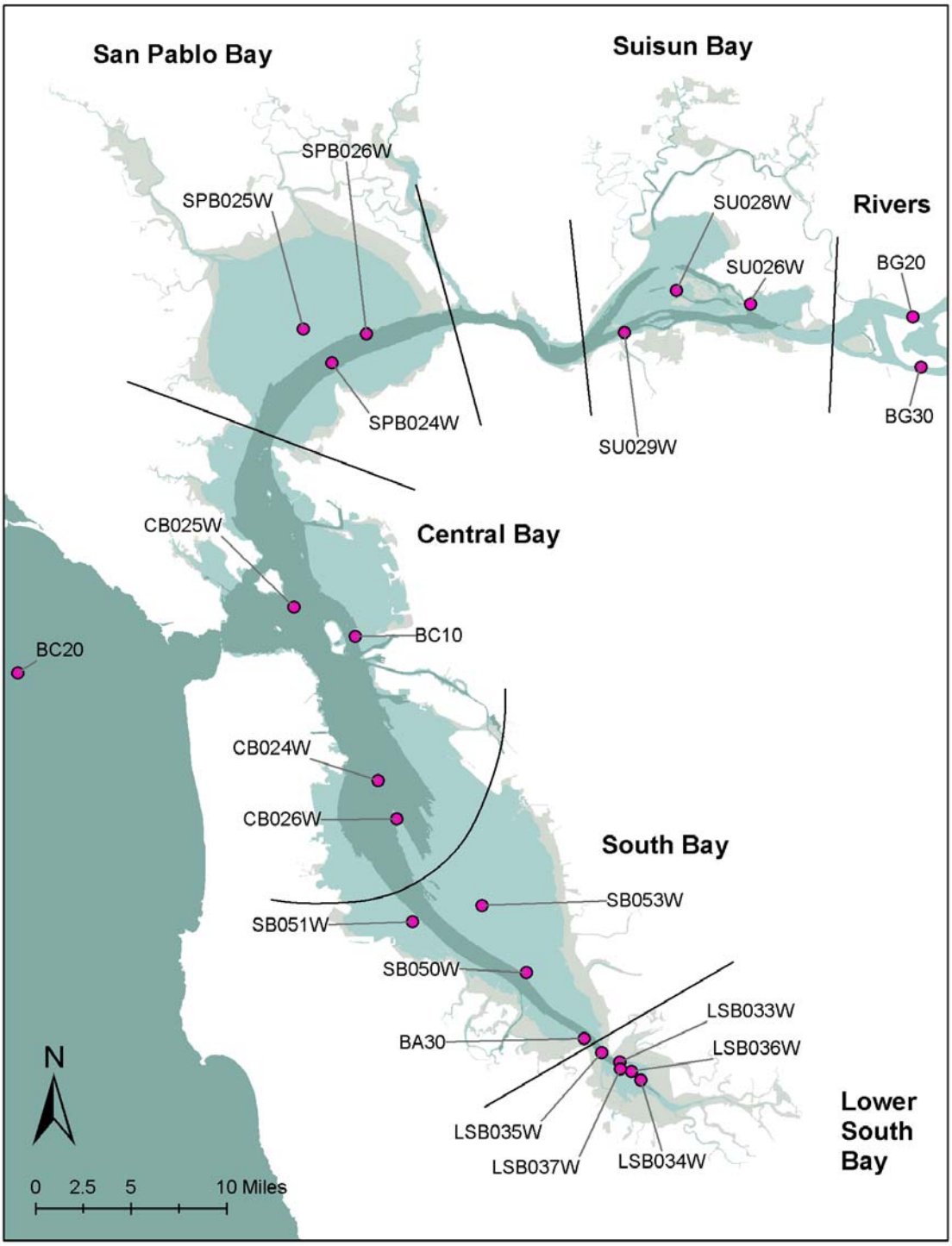

Figure 2.1 Map showing location of 2008 Water Stations

FIELD METHODS FOR WATER SAMPLING

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

Water was collected for trace metal, trace organic, and select water quality analysis (Chlorophyll-a (Chla), Phaeophytin (Phaeo), dissolved organic carbon (DOC), particulate organic carbon (POC)) by personnel from the San Francisco Estuary Institute (SFEI) with assistance from Aquatic Marine Sciences (AMS) using ultra-clean sample handling techniques. AMS collected real-time data at each station over the duration of sampling for conductivity, optical backscatter (OBS), dissolved oxygen (DO), and temperature (1 meter CTD cast for duration of sampling, followed by a full water column profile where water depth allowed). SFEI collected in situ DO, pH, salinity, conductivity, and temperature measurements at each station. Current and recent weather conditions were documented for each site.

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 using an AXYS Infiltrex system. Whole water samples were collected to provide an ongoing check to verify that the Infiltrex results are not biased.

Collection of Samples for Trace Organics

Water for analysis of trace organics was collected 1 m below the surface using the AXYS Infiltrex system consisting 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.

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 were designated as the dissolved fraction. Lastly, the water passed 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 Whole Water Samples for Trace Organics

Whole water samples were collected in clean 4L amber glass bottles for select trace organic analysis using the AXYS Infiltrex System to pump the water (without filters and columns). Once the AXYS Infiltrex system was flushed, the exit tubing was pulled on board and the water samples were collected in 4L amber bottles being careful not to touch the inside of the bottle or neck of the bottle with the tubing (the outside of the tubing is considered to be contaminated – considerable care was taken not to contaminate the sample). The samples were placed on wet ice. Whole water samples collected for analysis of pesticides were transported to SFEI at the end of each day, preserved with Dichloromethane, stored in a refrigerator overnight, and shipped to the lab the following day.

Collection of Samples for Trace Metals

For trace metals, water samples were collected 1 m below the surface 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 samples, several liters of water were pumped through the system and sample bottles were rinsed three times with site water before filling except those containing a preservative, which were filled 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.

For the analysis of total mercury water samples, 250 to 500 ml of estuary water was 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.

For methylmercury analyses, samples were collected into 250 ml FLPE bottles, then double-bagged in zip-lock bags. Samples were preserved with 1 – 2 mL 50% sulfuric acid in the field, and immediately placed on ice in a cooler.

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 deionized (DI) water was pumped through the

apparatus and an acid-cleaned filter and was collected in sample bottles. The field blanks received the same handling and analyses in the laboratory as the field samples.

Collection of Samples for Water Quality

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 collected into 500 ml PE bottles and 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 in amber vials and were 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 conducted at a subset of shallow sites in the Estuary and, since then, the frequency of sampling for aquatic toxicity testing was reduced to every five years since no aquatic toxicity had been observed in the Estuary during the summer in many years. The Technical Review Committee decided that aquatic bioassays would be conducted at five-year interval as a screening measure 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. No aquatic bioassay sampling occurred in 2008. The next aquatic bioassay sampling will occur in 2012.

LABORATORY METHODS FOR WATER ANALYSIS

In 2007, the RMP switched from using the UC-Santa Cruz (UCSC) laboratory to a commercial trace metals laboratory. In part this change was driven by elevated methyl mercury quantitation limits in the UCSC laboratory as compared to results that were achieved by commercial laboratories and municipal laboratories. As part of this switch, preliminary data suggest that additional method development and optimization with regard to metal analyses will be needed. SFEI maintains SOPs for all laboratory analyses. Please contact SFEI (cristina@sfei.org) for more details.

Laboratory Methods for Water Quality Parameters

In 2008, conventional water quality parameters were measured for the RMP by Columbia Analytic Services (CAS) and by the East Bay Municipal Utility District (EBMUD, a wastewater treatment facility) laboratory.

CAS analyzed water samples for dissolved organic carbon using EPA Method 9060A. Particulate organic carbon was determined by following the EPA National Exposure Research Laboratory method, NERL 440.0, using elemental analysis.

EBMUD analyzed salinity by Standard Method SM 2520B using electrical conductivity. Hardness as CaCO3 was measured for samples where salinity was found to be less than 5 ppt, using EPA method 130.2, a titrimetric

procedure using EDTA. Ammonium as N was analyzed using EPA method 350.1 by flow injection analysis. Nitirite and Nitrate as N were analyzed by EBMUD using EPA method 353.2 by flow injection analysis. Phosphate as P was analyzed using EPA 365.3 by colorimetry. Pheophytin-a and Chlorophyll-a were analyzed by Standard Method SM 10200 H-2aM and SM 10200 H-2bM, respectively, using spectrophotometric determination. Suspended sediment concentration was measured using Standard Method SM 2540DM by filtering, drying, ashing and weighing. Silica was measured using Standard Method SM 4500-SiO2 C and determined spectophotometrically.

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.

CTD casts were taken by AMS at each site during water cruise using a Sea-Bird SBE19 CTD probe 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 available for download using the Web Query Tool, SFEI maintains these data in a database. Data are available upon request (contact Cristina@sfei.org).

Laboratory Methods for Trace Elements

In 2008, water samples for Trace Elements (Ag, As, Cd, Co, Cu, Fe, Ni, Hg, MeHg, Pb, Se, and Zn) were analyzed by Brooks Rand Laboratories (BRL). All results will be reported for 2008 except total Iron in water which was rejected based on professional judgment, and is discussed below.

On receipt at the lab, all samples that were prepared for analysis by reductive precipitation and analyzed using inductively coupled plasma – mass spectrometry (ICP-MS) were preserved by the addition of pre-tested concentrated HNO_3 to 0.2% (v/v).

BRL determined Fe concentrations in sample water using SM 3500-FeB Standard Methods. The samples were reduced by hydroxylamine hydrochloride and analyzed using colorimetric detection. Concentrations of Ag, As, Cd, Co, Cu, Ni, Pb, and Zn were determined by reductive precipitation, followed by filtration, and measured using inductively coupled plasma-mass spectrometry (ICP-MS) by a modified version of EPA Method 1640. Mn was determined by digestion with HCl and HNO3 in a sand bath and measured using ICP-MS by EPA Method 1638, modified.

The 2007 copper results suggested a discrepancy between reductive precipitation used by the commercial laboratory and the column chelating method used by the City of San Jose(CSJ) and the University of California at Santa Cruz. In 2008, a laboratory intercomparison exercise was conducted for analyses of copper and nickel using

the two different methods by CSJ and BRL. The results showed good agreement between the reductive precipitation method and the column chelating methods. Both labs followed procedures outlined in EPA Method 1640. BRL results for iron in the total water fraction were much lower than previous years (2002-2006) and those data will not be reported based on professional judgment.

Total Mercury Analysis in Water Samples

In 2008, total mercury analysis of water samples was conducted by BRL. Samples were collected in acid-cleaned 250 ml fluorinated polymer (FLPE) bottles and at two stations samples were collected in 500 ml High Density Polyethylene (HDPE) bottles for QA analysis. BRL analyzed total mercury samples using a modified version of EPA Method 1631E. Samples are digested by 24 hour oxidation, reduction, Purge&Trap and detected using cold vapor atomic fluorescence spectrometry.

Methylmercury Analysis in Water Samples

In 2008, total mercury analysis of water samples was conducted by BRL. Samples were collected in acid-cleaned 250 ml fluorinated polymer (FLPE) bottles pre-preserved at the lab with one to two ml 50% sulfuric acid.

BRL analyzed methylmercury in water samples using a modification of EPA method 1630. Samples were analyzed by distillation, aqueous phase ethylation, trapping pre-collection, isothermal gas chromatography (GC) separation, and cold vapor atomic fluorescence spectrophotometer (CVAFS) detection.

Laboratory Methods for Trace Organics

In 2008, trace organics analyses of water samples were conducted by AXYS for PBDE and PAH analytes. PBDE samples are analyzed annually while PAHs, PCBs and Pesticides are analyzed biennially. PCBs and Pesticides will be analyzed in 2009, while PAHs will be analyzed again in 2010. 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 analyzed together, except at three sites the extracts were analyzed separately as dissolved and particulate fractions (three sites plus two duplicates plus one blank). Each XAD-2 column and filter sample was spiked with labeled surrogate standards. The filters were extracted by ambient temperature sonication, and XAD-2 columns with soxhlet extraction. Extract subsamples were subject to different cleanup procedures and analytical instrumentation, depending up on the target analytes.

PAHs were analyzed using a modified version of EPA method 8270. Samples of the dissolved fraction were soxhlet extracted while particulate samples were solvent extracted using Ambient Temperature Extraction (ATX). Analysis was performed using gas chromatography/low resolution mass spectrometry (GC/LRMS).

PBDEs were analyzed using a modified version of EPA 1614. Extraction of aqueous samples was the same as PAHs. The dissolved fraction was soxhlet extracted while the particulate fraction was solvent extracted using Ambient Temperature Extraction (ATX). Extracted samples were analyzed using high-resolution gas chromatograph (HRGC) coupled to a high resolution mass spectrometer (HRMS).

Since 2002, AXYS Analytical Services, Ltd. (AXYS) has 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. AXYS analytical will analyze diazinon and chlorpyrifos in 2009. 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. In 2008, AXYS developed a new method for detecting pesticides in whole water samples, which is able to detect chlorpyrifos and diazinon. The new method uses high resolution gas chromatography and high resolution mass spectrometry (HRGC/HRMS, multi-residue pesticides referred to as MRES). In 2008, the standard suite of RMP pesticide parameters, diazinon and chlorpyriphos were analyzed by AXYS using the new MRES method. An intercomparison study was conducted using samples collected with the Infiltrex high volume system and whole water samples (samples collected with a pump and tubing into a bottle) using the MRES method. Prior to 2008, AXYS used gas chromatography coupled to low resolution mass spectrometry (GC/LRMS) to determine pesticides in water. The results indicated that there was no significant difference between samples collected with the Infiltrex high volume system and whole water samples when analyzed using MRES. Based on these findings, the Technical Review Committee (TRC) approved the use of the MRES method to analyze whole water pesticide samples beginning in 2009. Reportable 2008 results were analyzed using the new MRES method. Oxadiazon cannot be analyzed using MRES and therefore these results were not available in 2008.

Table 2.1 Target Analytes: A summary table of the 2008 target analytes, special field handling requirements and analytical laboratories.

Analyte	Special Field Handling Requirements	Analytical Lab
Dissolved oxygen, conductivity, pH, OBS	None	Collected in field by AMS
Dissolved oxygen, conductivity, pH, salinity	None	Collected in field by SFEI
Trace Elements (Ag, As, Cd, Co, Fe, Mn, Ni, Pb, Se, Zn)	Cooled with wet ice and refrigerated	Brooks Rand Laboratories
Methylmercury	Preserved with sulfuric acid, cooled with wet ice and refrigerated	Brooks Rand Laboratories
Total Mercury	Cooled with wet ice and refrigerated	Brooks Rand Laboratories
Copper and Nickel	Cooled with wet ice and refrigerated	City and County of San Jose
PAHs	Cooled with wet ice and refrigerated	AXYS Analytical Laboratories
PBDEs	Cooled with wet ice and refrigerated	AXYS Analytical Laboratories
POC and DOC	Field filtered, cooled with wet ice and refrigerated	Columbia Analytical Services
Chlorophyll/phaeophytin	Field filtered, filter stored in 90% methanol in amber bottle, frozen on dry ice	East Bay Municipal Utility District
Salinity and hardness	Cooled with wet ice and refrigerated	East Bay Municipal Utility District
Ammonia and phosphate	Preserved with sulfuric acid,	East Bay Municipal Utility District

Analyte	Special Field Handling Requirements	Analytical Lab
	cooled with wet ice and refrigerated	
Nitrate and nitrite	Frozen on dry ice	East Bay Municipal Utility District
Silica	Preserved with nitric acid, cooled with wet ice and refrigerated	East Bay Municipal Utility District
SSC	Cooled with wet ice and refrigerated	East Bay Municipal Utility District

LABORATORY METHODS FOR WATER TOXICITY TESTING

Water Toxicity Testing

Between 1993 and 2002, the Status and Trends Program conducted ambient water toxicity testing on a subset of stations for each monitoring event. Up through 1997 two bioassays were conducted:

1. a chronic (7-Day) survival and growth assay using the mysid shrimp *Americamysis bahia* (EPA-821-R-02-014: the RMP only reports the survival endpoint), and

2. a 48-hour normal development assay on a larval bivalve (*Mytilus edulis*: ASTM Method E724-89).

In 1998, the program dropped the bivalve assay, and reduced the number of Status and Trends stations monitored for aquatic toxicity since little toxicity was observed in the main regions of the Estuary.

In 2002 the RMP Status and Trends program changed their sampling design for water and sediment to a mixed, random and targeted, sampling design and reduced water quality monitoring to the dry-season. Under the new design water toxicity samples are collected at nine stations. Because none of the aquatic toxicity samples were toxic since 1997, the program committees decided to reduce the long-term monitoring for aquatic toxicity to a screening study once every five years. The Status and Trends Program sampled for aquatic toxicity in the Estuary in 2002 and 2007 employing the 7-Day survival and growth bioassay (*Americamysis bahia*) and none of those samples were toxic. The next scheduled aquatic toxicity screening study will occur in 2012.

An overview of toxicity testing in water and sediment over the past ten years of Status and Trends monitoring was summarized by Anderson, Ogle, and Lowe (2003) in the *2003 Pulse of the Estuary*.

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3

Sediment Monitoring

3. SEDIMENT MONITORING

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. The RMP underwent a programmatic change in 2002 and the sediment sampling component was changed from 26 targeted sites sampled annually to a randomized sampling design with 47 sites sampled annually, 40 random sites and 7 targeted historic sites retained from the original sampling design. 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 questions listed in the *Introduction*. All sediment samples were collected aboard the R/V *Lakota* operated by Dixon Marine Services during July 23-August 1, 2008.

FIELD METHODS

Shipboard Measurements

Conductivity, Temperature, and Depth (CTD) Casts were taken by Applied Marine Sciences (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 probe was lowered to approximately one meter below the water surface and allowed to equilibrate to ambient temperature for 3 minutes. Following the sampling, the probe 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 recorded measurements. Although the CTD data are not available via the online Web Query Tool, the RMP maintains these data in a database, and they are available upon request.

Oxidation-Reduction Potential (ORP) and pH 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 at each station. Measurement of sediment 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.

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. Samples were also collected for trace metals archive, trace organics archive, and dioxins archive.

Collection of Ancillary Parameters

In 2008, the RMP analyzed grainsize, percent solids (% Solids), total organic carbon (TOC), and total nitrogen (TN) at 47 sites within the San Francisco Estuary. Moss Landing Marine Laboratories (MLM) conducted the analysis. MLML provided factory cleaned 250 ml high density polyethylene (HDPE) containers for grainsize analysis and plastic scintillation vials for TOC, TN, and % solids analysis. After collection, samples collected for TOC and TN were frozen. Samples collected for grainsize analysis did not have special handling requirements and were not refrigerated.

Collection of Trace Element Parameters

Sediment was collected at 47 sites within the San Francisco Estuary for analysis of the trace elements aluminum (Al), cadmium (Cd), copper (Cu), iron (Fe), mercury (Hg), Manganese (Mn), nickel (Ni), lead (Pb), silver (Ag), zinc (Zn), and % solids by the City and County of San Francisco laboratory (CCSF). CCSF supplied factory cleaned I-Chem 200 series (or equivalent) 250 ml HDPE containers. After collection, samples were placed on dry ice and kept frozen until delivered to CCSF.

Analysis of additional trace elements arsenic (As), mercury (Hg), methylmercury (MeHg), selenium (Se), and % solids was conducted by Brooks Rand Ltd. (BR). BR provided I-Chem 300 series factory cleaned 250 ml HDPE

containers. Due to special handling requirements, samples collected for methyl mercury analysis were placed on dry ice within 20 minutes of collection. All other samples were placed on dry ice as soon as possible. All samples were kept frozen until analyses.

Sediment was collected at 47 sites for trace metal archive. After homogenization, sediment was put into 250 ml HDPE containers and stored on dry ice until they were placed into long term storage at -18°C.

Collection of Trace Organic Parameters

Sediment was collected at 47 sites for the analysis of the trace organics parameters polycyclic aromatic hydrocarbons (PAHs), polybrominated diphenyl ethers (PBDEs), polychlorinated biphenyls (PCBs), and pesticides by East Bay Municipal Utility District (EBMUD). EBMUD provided factory cleaned I-Chem 200 series (or equivalent) 250 ml glass containers. Samples were placed on dry ice immediately after collection and kept frozen until delivered to EBMUD.

Sediment was collected at 27 sites for analysis of pyrethroids at the California Department of Fish and Game Water Pollution Control Laboratory (CDFG-WPCL). Samples were collected in factory cleaned I-Chem 200 series (or equivalent) 250 ml glass containers and stored on dry ice after homogenization. Samples kept frozen until analysis.

As part of the 2008 special studies, sediment was collected for the analysis of dioxins and triclosan. Dioxins were analyzed at three sites by AXYS Analytical and triclosan was analyzed at 12 sites by USEPA. All samples were placed into factory cleaned 250 ml glass containers and kept frozen on dry ice until analysis.

Sediment was collected at 47 sites for trace organics and dioxins archive. After homogenization, sediment was put into 250 ml glass containers and stored on dry ice until they were placed into long term storage at -18°C.

Collection of Sediment for Toxicity Testing

Sediment from 27 of the 47 stations were evaluated for potential toxicity to two different estuarine test species. As in the past, homogenized whole-sediment was tested on the amphipod *Eohaustorius estuarius* in the chronic, 10-day amphipod survival test. In 2008 the RMP reinstated collection of intact sediment cores known as surface-water interface cores (SWI cores) for the acute, 48-hour normal development tests using the bivalve *Mytilus galloprovincialis*. This change in sample collection follows the recommended toxicity test protocols in the State's Sediment Quality Objectives Methods for Enclosed Bays and Estuaries (Beegan 2008).

One liter plastic containers were provided by UC Davis Marine Pollution Studies Laboratory at Granite Canyon (UCD-GC) for the collection of homogenized sediment for the amphipod toxicity tests. Six 3-inch cores were used to collect intact cores (~1.5 inches deep) for the bivalve toxicity tests. Samples were kept upright and stored in a refrigerator or on wet ice until analysis by UCD-GC.

All sampling containers were pre-cleaned by the lab using the following procedures: containers were scrubbed with dilute micro solution, rinsed with deionized water (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.

Collection of Sediment Benthos

In 2008, the RMP also reinstated benthic community sampling into the Status and Trends Program the as part of the Sediment Quality Objectives (SQOs). The SQO assessment methods include sediment chemistry, toxicity, and benthic community evalutions. The RMP collected benthos samples at the same 27 sites where sediment toxicity was tested.

Samples were screened through 0.5 and 1.0 mm nested sieves while on board ship. The material retained on the screen was placed in sample jars, and a solution of relaxant was added to the jar. After approximately 15 minutes, 10% sodium borate buffered formalin was added to fix each sample. Samples were rinsed and transferred from formalin to 70% ethanol 3-14 days after collection.

SITES

In 2008, 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 targeted historical sites (Figure 3.1). Sediments are collected from 20 of the random sites and all seven historic sites for toxicity screening (Figure 3.2). In addition, benthos is collected at the same 27 sites. Station names, codes, coordinates, and sampling dates for the 2008 sediment monitoring effort are listed in *Appendix 4*. A map with the sampling sites is presented in Figure 3.1.

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). These seven historic sites were picked because they have long-term synoptic chemistry and toxicity measures associated with them (SFEI, 2005). Sites ending with 001S or 002S were randomly allocated during the initial restructuring of the sampling scheme in 2002 and are sampled annually while those ending in 003S and 004S are sampled every 5 years.

Every attempt is made to procure acceptable sediments from the target coordinates. Acceptable sediment consists of at least 60% fines and is determined by qualitative analysis. In the event that acceptable sediment is not able to be collected, the vessel is repositioned within a 100 m radius of the given coordinates. If sediment collection is still unsuccessful, the sampling operations will proceed to the next scheduled site and the failed site will be replaced with the next site on the list of available alternative sites, referred to as an oversample site.

In 2008, one of the annual sites, SU001S, located in Suisun Bay, was permanently replaced with oversample site SU073S. Historically, SU001S was a sandy site which resulted in repeatedly failed attempts at getting acceptable grabs. The area was then subject to active dredging which changed the bottom profile significantly.

Two 2008 target sites were not able to be sampled and were replaced with the first available oversample sites. LSB012S was located in a shallow water area and the skipper deemed it too shallow when combined with the strong wind and sea conditions, to safely sample. The first available oversample site, LSB074S, was rejected for similar reasons resulting in LSB075S as the acceptable oversample site for LSB012S. At the other site, SU038S, the

substrate was too sandy to qualify as an acceptable grab. Substrate within 100 m of the site was similarly sandy and SU038S was successfully replaced with oversample site SU080S.

Substrate at two additional sites sampled in 2008, SU037S and SU040S, was too sandy and the vessel had to be repositioned within the acceptable 100 m radius of the target coordinates to get acceptable sediment.

Repeated grabs and repositioning within 100 m of the historic site BG20, located on the Sacramento River, turned up only sandy substrate. Since this is a historic site and an oversample site is not available, it was decided to move outside of the 100 m radius of the target coordinates, as had been done in previous years. Sampling coordinates for this site ended up being approximately 200 m from the targeted 2008 coordinates.

Attempts to collect a benthos sample at BG30 were not successful because the current was so strong that the Ponar grab could not penetrate the sediment. Sampling efforts were abandoned after more than 4 failed attempts to collect a sample.

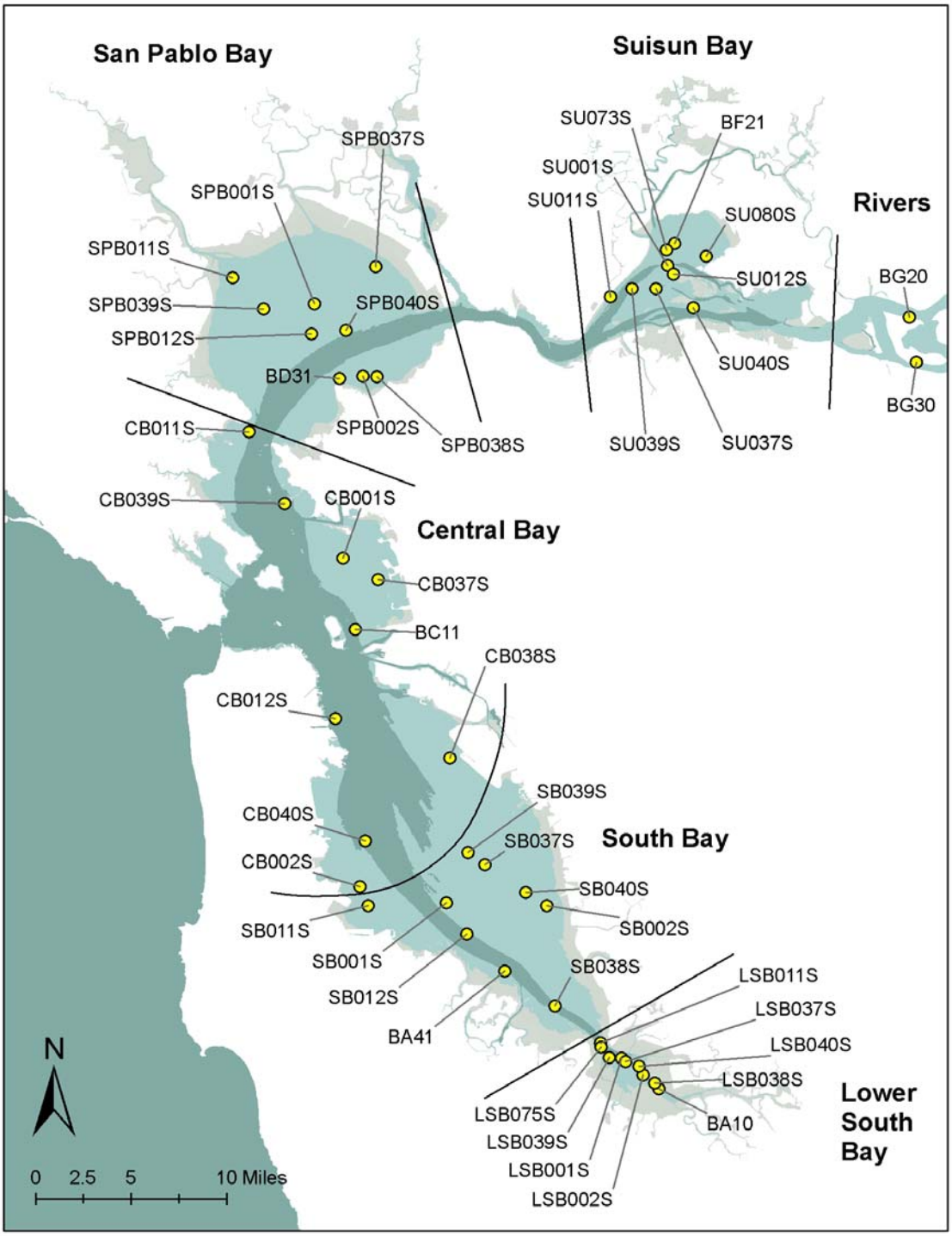

Figure 3.1 Map showing locations of 2008 Sediment Stations

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

Percent solids are the percent content by weight (grams) of solid material in a sediment sample. Brooks Rand LLC (BR) measured percent solids in sediment using EPA Method 160.3. For this method a solid sample was homogenized and an aliquot 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 a modification of EPA method 3050B. When analyzing for trace metals in sediment a separate homogeneous aliquot of the sample must be dried to determine total percent solids.

California Department of Fish and Game Water Pollution Control Laboratory (CDFG-WPCL) analyzed percent solids as part of their analysis of pyrethroids. Sediment was weighed and allowed to dry in an oven at 70° C for 24 hours to determine moisture content. This result was later converted into percent solids.

Moss Landing Marine Lab (MLML) analyzed percent solids by drying samples at 60-70 deg. C for 72 hours, recording the dry weight and calculating the percent solids for each sample.

Grainsize

In 2008, RMP switched labs from University of California Santa Cruz Department of Toxicology (UCSC-DET) to Moss Landing Marine Lab (MLML). MLML did not analyze larger grainsize fractions and only fractions <2mm are available. All other grainsize fractions were determined using a Beckman-Coulter laser particle size analyzer.

Total Organic Carbon (TOC) and Total Nitrogen (TN)

Analysis of TOC and TN was performed by Moss Landing Marine Laboratory (MLML) using methods and protocols derived from several published papers, reference procedures and experimental experience. Samples were received frozen and allowed to thaw at room temperature. A subsample was removed from the container and allowed to dry at 60°-70° C for approximately 48-72 hours. The dried sample is homogenized and concentrations of carbon and nitrogen are determined using a modification of the high temperature combustion method in a commercially available instrument. The methods are comparable to the calibration study of EPA method MARPCPN I.

Analysis of Sediment Trace Metals

In 2008, trace metals in sediment were analyzed by the City and County of San Francisco (CCSF) and Brooks Rand Ltd. (BR).

Trace Metals analyzed by CCSF consisted of Al, As, Cd, Ca, Cr, Co, Cu, Fe, Pb, Mg, Mn, Hg, Ni, Se, Ag, and Zn. These metals were measured using a modification of the EPA digest method 3050B, and modified EPA analysis method

6020A. For the digestion of samples, a representative 1 – 2 gram (wet weight) or 1 gram (dry weight) sample was digested with repeated additions of nitric acid (HNO_3) and hydrogen peroxide (H_2O_2). Samples were analyzed using Inductively Coupled Plasma-Mass Spectrometry (ICP-MS).

Brooks Rand analyzed the trace metals As, Hg, MeHg, and Se. Arsenic and selenium samples were analyzed using EPA Method 1638 by ICP-MS. Samples were closed-vessel oven digested with HNO_3 and hydrochloric acid (HCl). Aliquots of digested sample were analyzed using ICP-MS.

Sediments were analyzed for mercury by BR using EPA Method 1631. Samples were digested in HNO_3 and H_2SO_4, and then further oxidized with bromine monochloride (BrCl). Samples were analyzed with stannous chloride ($SnCl_2$) reduction, single gold amalgamation and cold vapor atomic fluorescence spectroscopy (CVAFS) detection using a BR Model III CVAFS Mercury Analyzer. All sample results for low-level mercury analysis were blank corrected.

Methylmercury was analyzed for in the sediment samples by BR using a modified EPA Method 1630. The sediment samples were prepared by acid bromide/methylene chloride extraction. The samples were analyzed by aqueous phase ethylation, Tenax trap collection, gas chromatography separation, isothermal decomposition, and cold vapor atomic fluorescence spectroscopy (CVAFS).

Analysis of Sediment Trace Organics

In 2008, pyrethroids were added to the suite of organic contaminants monitored in sediments by the RMP in order to investigate the potential toxicity of pyrethroids in the bay. Analysis was conducted by California Department of Fish and Game Water Pollution Control Laboratory (CDFG-WPCL). Samples were prepared using an automated extraction system. Dual column gas chromatography with dual electron capture detectors (GC-ECD) and/or gas chromatography with triple quadrupole mass spectrometry (GC-MSMS) were used for analysis.

In 2008, sediment organics were analyzed by EBMUD. Sediment samples are generally analyzed based on the methods followed by the National Oceanic and Atmospheric Administration's (NOAA's) National Status and Trends Program. PAHs were analyzed using gas chromatography/mass spectrometry (GC/MS), and PCBs, PBDEs, and organochlorine (OC) 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; 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 dichloromethane (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, which was slightly modified to provide sufficient sensitivity for PAHs in sediments.

Sediment samples were analyzed for OC pesticides using a modification of EPA method 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 mass-to-charge ratios (m/z's) were monitored throughout a predetermined detention time.

Samples were analyzed for PCBs 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.

Sediments were analyzed for PBDEs using a modification of EPA method 1614. 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.

Table 3.1 Target Analytes: A summary table of the 2008 target analytes, analytical laboratories, reporting units, and method codes.

Parameter	Lab(s)	Reporting Unit	Method Code(s)
Grainsize	MLML	%	Beckman-Coulter Laser Particle Size Analyzer
% solids	BR/CCSF/CDFG/MLML	%	EPA 160.3/ EPA 3050B Mod./EPA 8081B Mod./ MLML-TM %Solids
Depth	AMS-CA	m	NA
pH (porewater, interstitial sediment)	AMS-CA	pH	NA
Total Organic Carbon	MLML	%	MLML-TM TOC/TN
Total Nitrogen	MLML	%	MLML-TM TOC/TN
Sediment Toxicity – (Amphipod) Mean % Survival	UCD-GC	%	EPA 600/R-94-025
Sediment Toxicity – (Bivalve) Mean % Normal Alive	UCD-GC	%	EPA 600/R-95-136
Aluminum (Al)	CCSF	mg/Kg	EPA 6020A Mod.
Arsenic (As)	BR/CCSF	mg/Kg	EPA 1638 Mod./ 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)	BR/CCSF	mg/Kg	EPA 1631/ EPA 6020A Mod.

Parameter	Lab(s)	Reporting Unit	Method Code(s)
Mercury, Methyl (MeHg)	Brooks Rand Laboratory	µg/Kg	EPA 1630 Mod.
Nickel (Ni)	CCSF	mg/Kg	EPA 6020A Mod.
Selenium (Se)	BRL/CCSF	mg/Kg	EPA 1638 Mod/ EPA 6020A Mod.
Silver (Ag)	CCSF	mg/Kg	EPA 6020A Mod.
Zinc (Zn)	CCSF	mg/Kg	EPA 6020A Mod.
PAHs (Low and 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	EBMUD	µg/Kg	EPA 1614 Mod.
Pyrethroids	CDFG-WPCL	µg/Kg	EPA 8081B Mod.

SEDIMENT TOXICITY

Two types of sediment bioassays were conducted at 27 of the RMP stations in 2008 (See Figure 3.2). Homogenized whole-sediment was tested for toxicity using the amphipod *Eohaustorius estuarius* in the 10-day amphipod survival test (EPA 600/R-94-025). Sediment was re-homogenized in the sample jar by placing them on a rolling apparatus and manually stirring with a polypropylene spoon. Samples were then distributed to replicate test beakers. Overlying water was added to the test containers, and sediment and allowed to equilibrate overnight before the amphipods were added. Randomly selected amphipods were placed into replicate containers and allowed to burrow into the test sediments. Amphipods 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.

Surface-water interface (SWI) cores were tested using the bivalve *Mytilus galloprovincialis* in a 48-hour static embryo-larval development toxicity tests (EPA 600/R-95-136). SWI cores were prepared for analysis by adding overlying water and allowing the cores to equilibrate overnight. Bivalve embryos were added by placing a 25 µm screen tube into each core. At the end of each test the larvae were isolated from the cores by removing the screen tube and rinsing the larvae into a 20 ml scintillation vial. The contents were preserved with formalin. The mussel larvae were counted to determine the percentage of embryos that developed into live normal larvae. The negative controls for the *M. galloprovincialis* tests consisted of SWI cores filled with clean home sediment as described above.

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. % survival for amphipods or % normal alive for bivalves was less than the evaluation threshold of effect (the Control minus the MSD). The difference between the mean endpoint value in the control and the mean endpoint value in the test sample was greater than the 90^{th} percentile minimum significant difference (MSD).

A sample must meet both criteria to be considered toxic, because a t-test can often detect small differences between samples when there is low variance among laboratory replicates. 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. MSD values generated from RMP *E. estuarius* and *M. galloprovincialis* tests were used by UCD-GC to establish a 90^{th} percentile MSD threshold. This analysis indicates that the *E. estuarius* test is capable of identifying statistically significant differences in 90% of cases where the difference between the treatment and the control is 18.8%. The threshold is calculated by subtracting 18.8% from the control response. The bivalve larvae 90^{th} percentile MSD is 15.2% (Phillips *et al*., 2001). For the 2008 sediment bioassays, the control responses in the three amphipod tests ranged from 93% to 100%, and the toxicity thresholds from 74.2% to 81.2%. Control responses in the bivalve larvae tests were 93.3% and 102.5%, and the toxicity thresholds 78.1% and 87.3%, respectively.

In 2008 sediments were toxic at 7 of the 27 sites for amphipods (*Eohaustorius estuarius*) and 18 of the 27 sites for larval mussels (*Mytilus galloprovincialis*) (Figure 3.2). A toxic sample indicates 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. Further laboratory tests, Toxicity Identification Evaluations (TIEs), are required to investigate the potential causes of an observed toxic hit.

The RMP only performs TIEs on sediments that have less than 50% survival (or normal-development). The RMP program managers authorize these additional studies on a case-by-case basis based on the annual bioassay results. No sediment TIEs were performed in 2008.

Figure 3.2 shows the results of the 2008 sediment bioassays. Sediments were not toxic (see Sediment Toxicity section) to amphipod, Eohaustorius estuarius, or mussel, Mytilus galloprovincialis, larvae at 8 out of 27 stations. Amphipod toxicity was observed at seven stations: Suisun Bay (Grizzly Bay (BF21)), San Pablo Bay (Pinole Point (BD31) and SPB040S), Central Bay (CB037S), and South Bay (Redwood Creek (BA41), SB039S, and SB040S). Sediment samples from eighteen stations were toxic to larval mussels: Sacramento River (BG20), San Joaquin River (BG30), Suisun Bay (Grizzly Bay (BF21), SU037S, SU040S, and SU080S), San Pablo Bay (Pinole Point (BD31), SPB037S, SPB038S, SPB039S, and SPB040S), Central Bay (Yerba Buena Island (BC11), CB037S, CB038S, and CB039S), and South Bay (Redwood Creek (BA41), SB038S and SB040S).

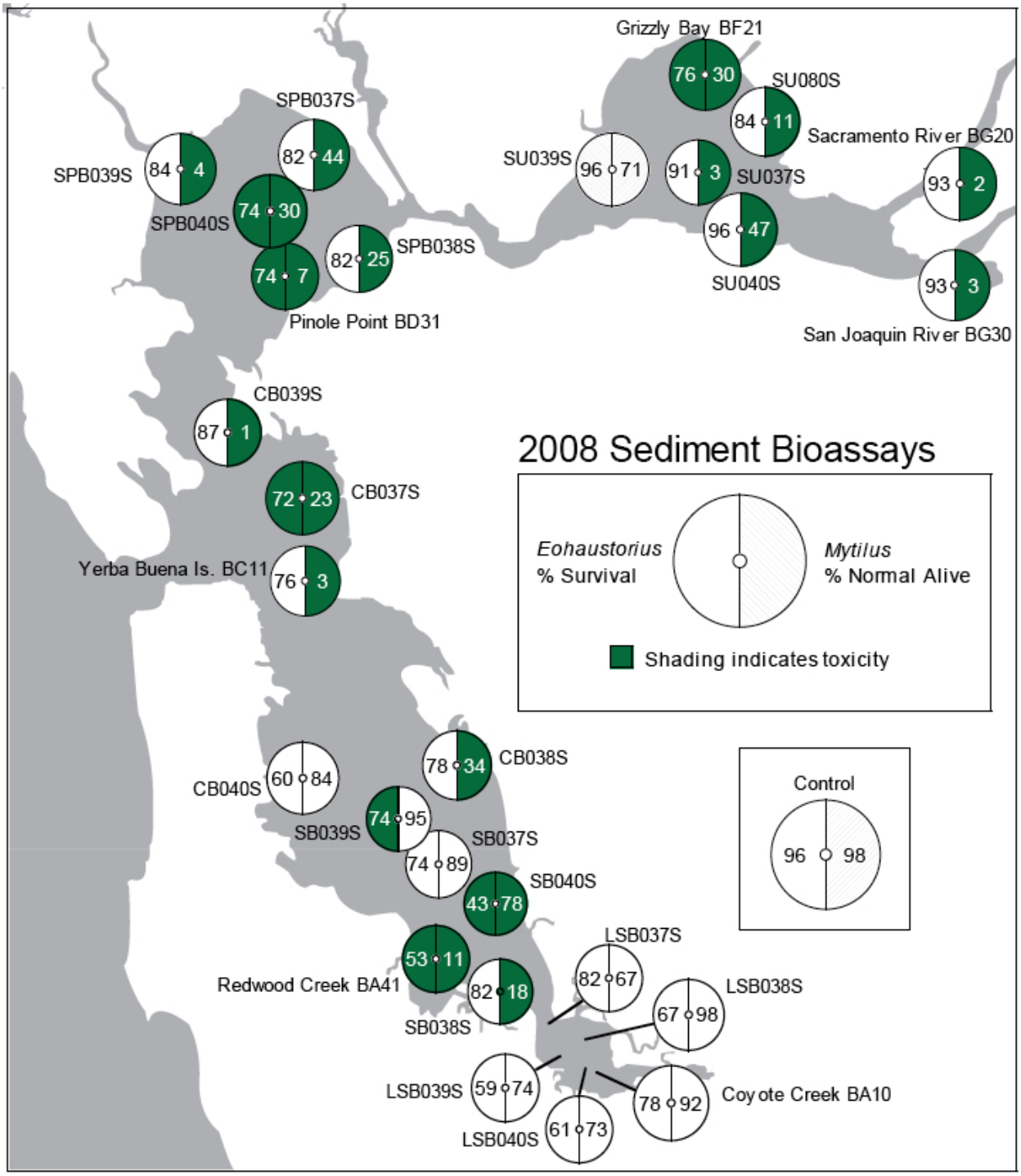

Figure 3.2 Sediment bioassay results for 2008

Assessment of Sediment Quality

Estuary sediments are evaluated through comparisons to several sets of sediment quality guidelines listed in Table 3.2. Although these guidelines hold no regulatory status, they provide concentration guidelines that are useful in assessing the potential for toxic and benthic effects.

Sediment contamination and toxicity results were used to evaluate the quality of the 2008 Regional Monitoring Program samples (Table 3.3). Detailed tables for 2002 – 2007 are available in their respective Annual Monitoring Result reports available online at 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 2008 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 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 2008 sediment samples had at least 20 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 2008 RMP sediment samples for potential adverse ecological effects. Three stations had a mERMq value greater than 0.15 (CB012S, CB040S, and SB011S) and at least 21 results above the ASC guidelines (Table 3.5).

Table 3.2 Sediment Quality Guidelines (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).

In 2008, seven stations were considered potentially toxic by the RMP (CB001S, CB002S, CB012S, CB040S, LSB001S, SB002S, and SB011S) because nine or more contaminant concentrations were above the ERL guidelines. One station sampled in 2008 (CB012S) had four contaminant concentrations above the ERM guidelines, but no stations had greater than four exceedences (Table 3.3).

Table 3.3 Summary of sediment quality for the RMP in 2008

. = not tested

Code	Site Name	Date	% Fines	mERMq	No. of ASC above Guidelines	No. of ERL above Guidelines	No. of ERM above Guidelines	Toxic to Amphipods?	Toxic to Bivalves?
BG20	Sacramento River	7/30/08	58	0.0725	1	7	1	no	yes
BG30	San Joaquin River	7/30/08	71	0.0591	1	4	1	no	yes
BF21	Grizzly Bay	7/31/08	90	0.0749	1	7	1	yes	yes
SU001S	Suisun Bay	7/31/08	68	0.0325	1	4	1	.	.
SU011S	Suisun Bay	7/30/08	79	0.0758	1	6	1	.	.
SU012S	Suisun Bay	7/31/08	77	0.0699	1	7	1	.	.
SU037S	Suisun Bay	7/30/08	86	0.0641	1	6	1	no	yes
SU039S	Suisun Bay	7/30/08	62	0.0375	1	3	1	no	no
SU040S	Suisun Bay	7/30/08	46	0.0637	1	6	1	no	yes
SU073S	Suisun Bay	7/31/08	86	0.0780	1	7	1	.	.
SU080S	Suisun Bay	7/31/08	87	0.0762	1	7	1	no	yes
BD31	Pinole Point	7/29/08	76	0.0813	1	7	1	yes	yes
SPB001S	San Pablo Bay	7/29/08	91	0.0947	1	6	1	.	.
SPB002S	San Pablo Bay	8/1/08	87	0.0771	1	6	1	.	.
SPB011S	San Pablo Bay	7/29/08	87	0.0831	1	6	1	.	.
SPB012S	San Pablo Bay	7/29/08	92	0.0793	1	6	1	.	.
SPB037S	San Pablo Bay	8/1/08	88	0.0760	1	5	1	no	yes
SPB038S	San Pablo Bay	8/1/08	87	0.0771	1	5	1	no	yes
SPB039S	San Pablo Bay	7/29/08	91	0.0914	1	7	1	no	yes
SPB040S	San Pablo Bay	7/29/08	46	0.0485	0	3	1	yes	yes
BC11	Yerba Buena Island	7/28/08	86	0.0897	4	7	1	no	yes
CB001S	Central Bay	7/28/08	78	0.1383	16	15	1	.	.
CB002S	Central Bay	7/25/08	87	0.1348	12	10	1	.	.
CB011S	Central Bay	7/29/08	87	0.0909	1	7	1	.	.
CB012S	Central Bay	7/28/08	64	0.3451	24	18	4	.	.
CB037S	Central Bay	7/28/08	75	0.1045	7	6	1	yes	yes
CB038S	Central Bay	7/28/08	79	0.0494	0	2	1	no	yes
CB039S	Central Bay	7/29/08	58	0.0662	1	5	1	no	yes
CB040S	Central Bay	7/25/08	89	0.1573	21	16	1	no	no
BA41	Redwood Creek	7/28/08	86	0.0943	2	6	1	yes	yes
SB001S	South Bay	7/28/08	90	0.0608	1	4	0	.	.
SB002S	South Bay	7/25/08	83	0.1246	10	11	1	.	.
SB011S	South Bay	7/25/08	88	0.2217	24	19	1	.	.
SB012S	South Bay	7/28/08	94	0.1090	3	7	1	.	.
SB037S	South Bay	7/25/08	89	0.1115	5	7	1	no	no
SB038S	South Bay	7/24/08	93	0.1176	5	6	1	no	yes
SB039S	South Bay	7/25/08	92	0.0842	0	5	1	yes	no
SB040S	South Bay	7/25/08	86	0.1050	3	6	1	yes	yes
LSB001S	Lower South Bay	7/23/08	93	0.1279	11	11	1	.	.
LSB002S	Lower South Bay	7/24/08	96	0.0883	0	5	1	.	.
LSB011S	Lower South Bay	7/23/08	91	0.0940	2	5	1	.	.
LSB037S	Lower South Bay	7/23/08	94	0.1205	3	8	1	no	no
LSB038S	Lower South Bay	7/24/08	96	0.1195	2	8	1	no	no
LSB039S	Lower South Bay	7/23/08	90	0.0967	1	7	1	no	no
LSB040S	Lower South Bay	7/24/08	100	0.0875	0	5	1	no	no
LSB075S	Lower South Bay	7/24/08	78	0.1047	2	7	1	.	.
BA10	Coyote Creek	7/24/08	94	0.0522	0	3	1	no	no

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.

BENTHOS

The benthos samples collected during the 2008 sediment cruise have been processed and reported to SFEI. Samples were sorted into major taxonomic groups and organisms were counted and identified to the lowest practical taxon. Those data will be used in the SQO triad assessment, which includes three lines of evidence to evaluate if estuarine benthic communities are likely to be impacted by contaminated sediments. The 2008 SQO assessment will be a published as a separate RMP technical report.

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4

Bivalve Monitoring

4. BIVALVE MONITORING

BACKGROUND

The RMP has been analyzing bivalve tissue samples for trace contaminants since 1993. Bivalves bioaccumulate chemical contaminants through their food, by ingesting sediment and assimilating contaminants that are sorbed to particles, and by filtering dissolved contaminants directly from the water column. Bivalves act as transfer vectors of contaminants to higher trophic levels of the aquatic and sediment food webs. Contaminant concentrations in living organisms can accumulate to levels much greater than those found in ambient water and sediment due to an organism's inability to metabolize certain contaminants (Vinogradov, 1959) and a high affinity of some contaminants for lipid-rich tissue in bivalves (Stout and Beezhold, 1981). Biomonitoring using bivalves has been widely applied by the California State Mussel Watch Program (Phillips, 1988; Rasmussen, 1994) and other studies (Young *et al.,* 1976; Wu and Levings, 1980; Hummel *et al*., 1990; Martincic *et al.,* 1992, Gunther *et al.,* 1999; O'Connor, 2002). Bivalves are excellent organisms for biomonitoring of contaminants since they accumulate contaminants from the ambient environment, have limited mobility and are fairly resistant to contaminant effects (O'Connor, 2002). The RMP is continuing the long-term monitoring of the State Mussel Watch Program, which monitored sites throughout the Estuary beginning in 1976.

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 objective (see Chapter 1 *Introduction*) of determining long-term trends in contaminant levels. 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.

FIELD METHODS

Bivalve Monitoring Field Methods

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 targeted sites within the Estuary. 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 long-term trend monitoring. 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.

Source of Bivalves

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

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

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

Deployment of Transplanted Bivalves

Three hundred mussels were randomly allocated and placed into predator resistant cages for deployment. The number of individuals was increased from 160 to 300 in 2008 to accommodate additional analysis for PBDEs in tissue. Mussels of approximately the same shell length were used (49-81 mm). The same number was also used for the reference (time zero) sample, which was used to provide a baseline on "pre-deployment" tissue condition before deployment.

The cages were constructed out of rigid plastic mesh and PVC pipe. The mesh overlapped around itself to keep predators from slipping through any gaps between the edges. After the cages were built, they were soaked in water for at least a day to remove any potential signal associated with the adhesives used for the construction.

At each site, a line ran from the bottom of the fixed structure out to the bivalve mooring, which consisted of a large screw (earth anchor) that was threaded into the bottom and was associated with pilings or other permanent structures. A large subsurface buoy was attached to the earth anchor by a one to two meter line. The bivalve cages were attached to the buoy line, which kept the bivalves off the bottom to prevent smothering. Since the beginning of the program, loss of a mooring has occurred on only two occasions, probably due to being ripped out by a vessel anchor. Mooring installation, bivalve deployment, and retrieval were all accomplished by SCUBA divers.

Retrieval of Transplanted Bivalves

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

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

Starting with the 1999 dry season (summer) deployments, CTD profiles were collected at each bivalve site during both deployment and retrieval cruises 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.

SITES

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.

Based on a new biogeographical delineation of the Estuary, it was apparent that the newly defined segments were not represented equally by the 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.

Station names, codes, location, and sampling dates for the 2008 monitoring effort are listed in Appendix 5 and shown in Figure 4.1.

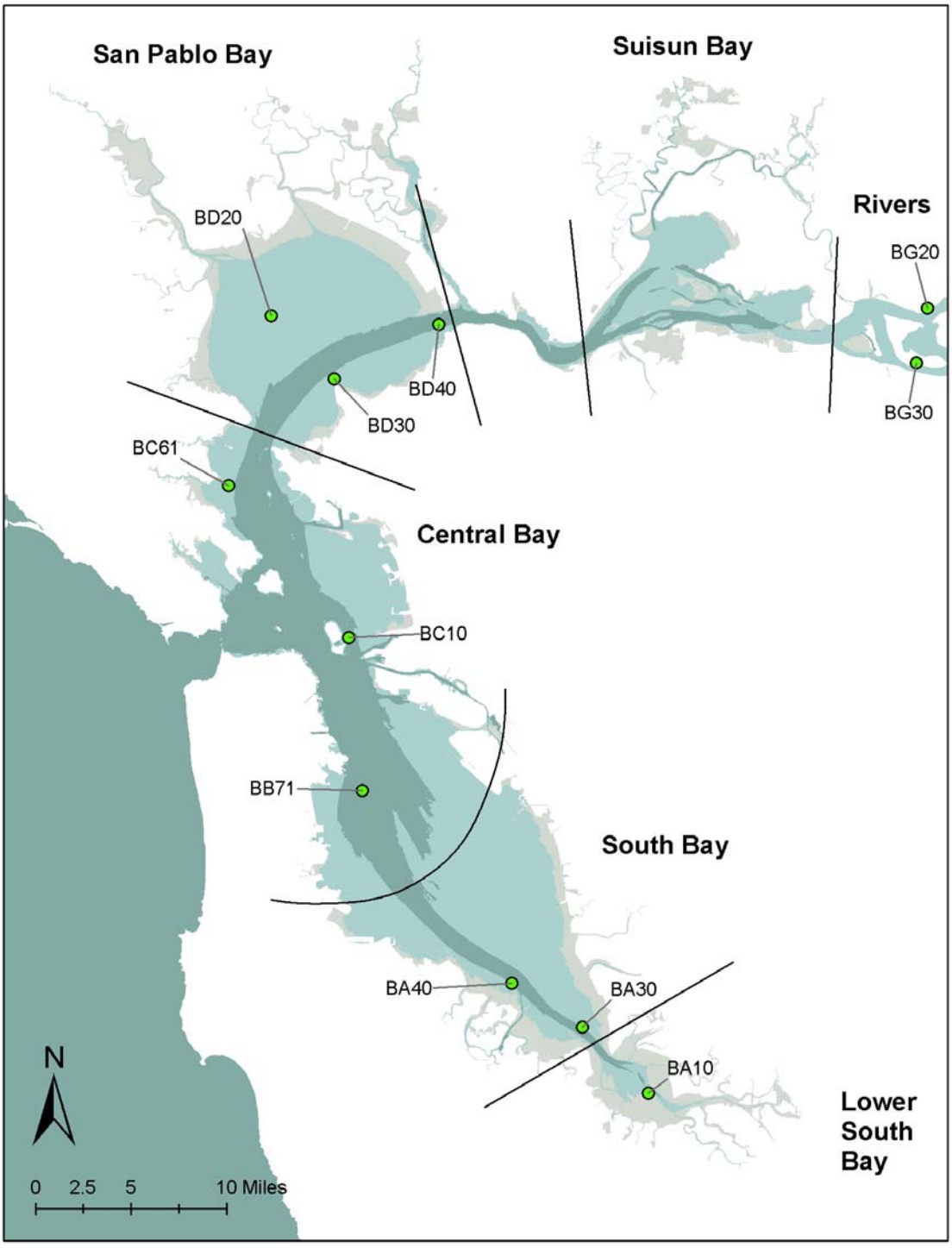


Figure 4.1 Map of 2008 Bivalve Monitoring Stations

ANALYSIS

Target Analytes

A summary table of target analytes is presented below. Refer to Appendix 6 for a more detailed listing of target analytes.

Table 4.1 Target Analytes: A summary table of the 2008 target analytes, analytical laboratories, reporting units, and field preparation code

Analyte	Field Prep Code	Analysis Lab	Reporting Unit
Trace organics	Not rinsed, placed on dry ice	AXYS Analytical Laboratories	ng/g (ppb)
Trace elements	Not rinsed, placed on dry ice	CCSF	µg/g (ppm)
Selenium	Not rinsed, placed on dry ice	Brooks Rand Laboratories	µg/g (ppm)
Brominated flame retardants (BFRs)	Not rinsed, placed on dry ice	AXYS Analytical Laboratories	ng/g (ppb)
Growth	Rinsed in field, placed on dry ice	Applied Marine Sciences	g
Archive	Not rinsed, placed on dry ice	N/A	N/A

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.

In 2006, the RMP Status and Trends program was re-evaluated to determine whether current sampling size and frequency are appropriate for meeting the needs of RMP stakeholders (Melwani et al., 2008). Based on this evaluation, bivalve sampling was modified from an annual to a biennial frequency. Accordingly, bivalve sampling was not performed in 2007. Bivalve sampling occurred in 2008, and is scheduled to next occur in 2010.

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.

Laboratory Methods for Bivalve Analysis

SFEI maintains SOPs for all laboratory analyses. Please contact SFEI (amy@sfei.org) for more details.

Currently, trace organics analyses of bivalve tissue samples are performed by AXYS Analytical Laboratories. In the past, trace organics analyses of bivalve tissue samples were conducted by CDFG-WPCL. A brief overview of the extraction and analyses used for the target trace organics are described below. Extract cleanup and partitioning methods are modifications of the multi-residue methods for fatty and non-fatty foods described in the U.S. Food

and Drug Administration, Pesticide Analytical Manual, Vol. 1, 3rd Edition 1994, Chapter 3, Multi-residue Methods, Section 303-C1. The laboratory SOPs that describe the methods in more detail are on file at SFEI.

Tissue Extraction

Samples were removed from the freezer and allowed to thaw. Prior to extraction, bivalve tissue samples were homogenized using a Büchi B-400 homogenizer. A 10 g sample was mixed with approximately 7 g of pre-extracted Hydromatrix® until the mixture was free flowing. The mixture was then extracted using U.S. EPA Method 3545 (Pressurized Fluid Extraction) with a 50/50 mixture of acetone/dichloromethane. The samples were extracted a second time using the same conditions. The extracts were dried and filtered through a 0.45 µm syringe filter into J2 Scientific AccuPrep 170 (GPC) autosampler tubes. Two milliliters each of the filtered extracts were removed and placed in a pre-weighed aluminum planchet for percent lipid determination.

All sample extracts were cleaned-up using a J2 Scientific GPC (Autoinject 110, AccuPrep 170, DFW-20 Fixed Wavelength Detector, 1" i.d. glass column with 70 g Bio-Beads SX-3 in 100% DCM). For pesticides, PCBs, and PBDEs the GPC purified extracts were then fractionated into 4 separate fractions on a Florisil column using petroleum ether (F1), 6% diethyl ether/petroleum ether (F2), 15% diethyl ether/petroleum ether (F3), and 50% diethyl ether/petroleum ether (F4) elution. For PAHs, the GPC purified extracts were further cleaned-up with silica/alumina column chromatography using DCM:pentane (1:1) as the solvent.

Organochlorine Pesticide, PCB, and PBDE Analyses in Tissue

Cleaned-up extracts were evaporated and fractionated. The fractions were concentrated to an appropriate volume using K-D/micro K-D apparatus prior to analysis by dual column high resolution gas chromatography with electron capture detection. A mixture of synthetic organic standards was eluted through the Florisil 7 column to determine the recovery and separation characteristics of the column.

Analysis of Extractable PAH Compounds in Tissue

Extraction methods for homogenized tissue samples were identical to those for PCBs, PBDEs, and organochlorine pesticides. All samples were then cleaned up using a large (1 inch i.d.) GPC column. The extracts were evaporated using a K-D apparatus to 5 mL. The extracts were then fractionated. The fractions were concentrated to 1 mL using K-D/nitrogen blow down apparatus prior to analysis by gas chromatography/mass spectrometry.

Phthalate, nitro and polycyclic musk, and p-nonylphenol analyses were discontinued in 2004.

Bivalve Growth and Survival

Applied Marine Sciences (AMS) conducted the bivalve health measure evaluations as in previous years.

Analysis of contaminant concentrations was conducted on a subset of the transplanted bivalves (composites contain 40-60 individual bivalves from each site) prior to deployment in Estuary locations (T-0) and after the 100-day deployment period. The differences between pre- and post-deployment concentrations allow determination of contaminant uptake during the period of deployment. A new batch of bivalves were also collected from the

original T-0 transplanted bivalve collection sites at the end of the deployment period to obtain information on uptake variables that may have affected wild populations during the deployment period.

In 2001, AMS began calculating the growth mean in addition to the condition index (CI) for the RMP as an indicator of bivalve health. The CI interpretation of bivalve health can be confounding when ambient conditions (i.e., salinity) are more uniform such as during the summer deployment period. In 2002, the RMP discontinued the condition index measure in favor of the growth mean as the only health indicator. Because the CI is the ratio of dry tissue weight to shell cavity volume, it could be affected by changes in either tissue weight or shell size. For example, either a decrease in tissue weight with stable shell size or an increase in shell size with stable tissue weight could be interpreted as a decrease in CI. Consequently, the interpretation of CI as an indicator of health can be problematic. The growth mean is a measure of growth of the composite of bivalves at a particular site in comparison to the T-0. The growth mean was determined by taking the dry weight of each individual and subtracting the mean dry weight of the T-0 for that species. This calculation was done for each individual bivalve. The mean of the difference of all the individuals at a particular site was then calculated to give the growth mean.

BIVALVE TRENDS

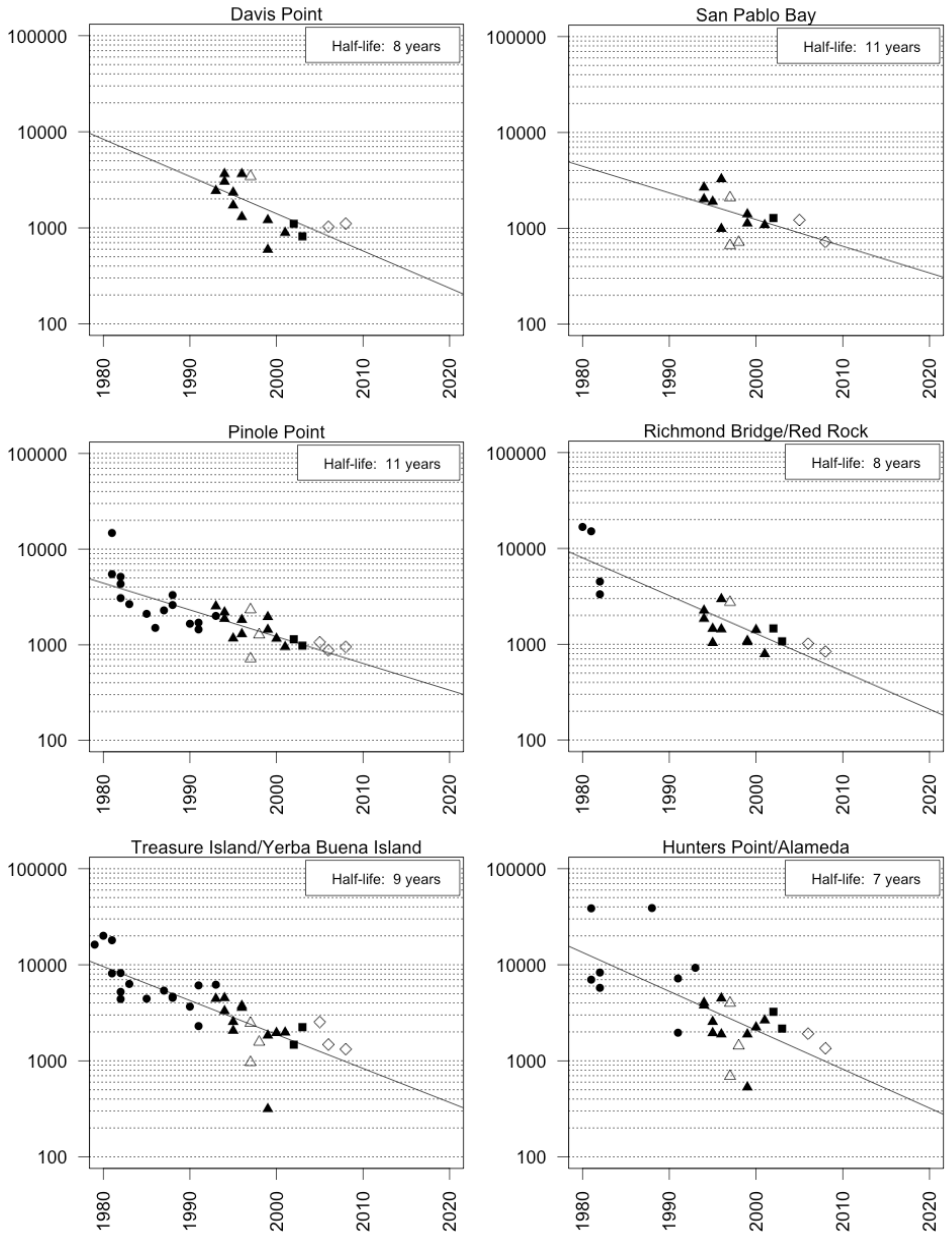
The RMP currently monitors contaminant accumulation in bivalve tissue at nine sites distributed throughout the Bay (Figure 4.1). Many of these sites have been monitored since 1980 by the State Mussel Watch (SMW) program and, consequently, by the RMP. Additionally, the NOAA National Mussel Watch (NMW) program has monitored resident mussel contamination levels at several sites in San Francisco Bay since 1986. Two of the NMW sites are located near RMP bivalve sampling sites. The data from these co-located sites have been included to corroborate trends seen in SMW and RMP bivalve data.

To look at trends of trace organics concentrations in bivalves, linear regressions of log-transformed tissue concentrations over time were generated for the nine sites. The contaminants analyzed were Sum of PCBs, Sum of DDTs, Sum of PAHs, and Sum of PBDEs. Bivalve tissue concentration data from the RMP and the SMW were plotted normalized to lipid weight, while the NMW data were plotted as dry weight (due to high variability in their lipid measurements over the years, making them unreliable). The different data point markers represent different monitoring programs and analysis labs, as shown in the legends. For each linear regression, the slope, significance level and estimated half-life are shown in the tables below. The estimated half-life (if applicable) is also shown on each graph, but is marked with an asterisk when derived from a regression that is not significant at the 0.05 level.

Polychlorinated Biphenyls (PCBs) in Bivalves

The PCB data from the State Mussel Watch Program are sum of Aroclors and the RMP PCB data are sum of congeners. Both datasets were normalized to bivalve lipid content. The PCBs data from the National Mussel Watch Program are sum of congeners in dry weight due to unexplained variation in lipid data obtained from different labs over the years.

RMP and SMW – Sum of PCBs data (ng/lipid g)



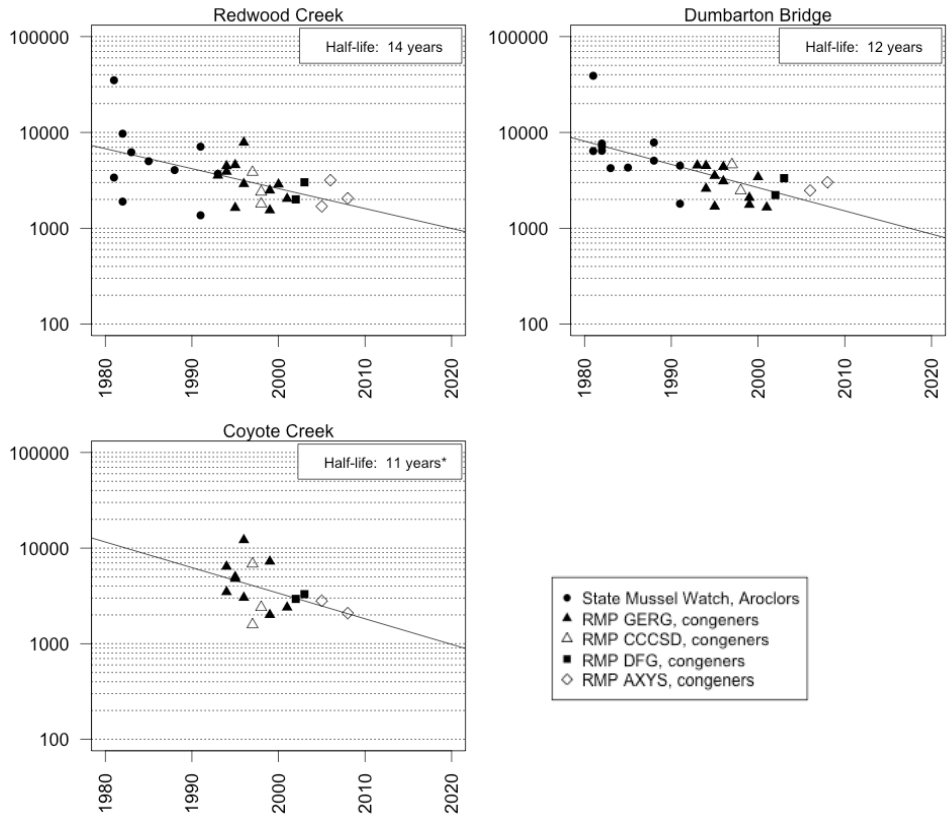


Figure 4.2 concentrations (ng/g lipid) in transplanted mussels (RMP and SMW data), 1979-2008

Table 4.2 Linear regression statistics for PCB concentrations over time (RMP and SMW data)

Code	Site Name	N	Years	Trend	Half-life (years)	Slope	p-value	R2
BD40	Davis Point	15	1993-2008	▼	**8**	**-0.04**	**0.005**	**0.47**
BD20	San Pablo Bay	14	1994-2008	▼	**11**	**-0.03**	**0.050**	**0.28**
BD30	Pinole Point	33	1981-2008	▼	**11**	**-0.03**	**< 0.001**	**0.65**
BC61	Richmond Bridge/ Red Rock	19	1980-2008	▼	**8**	**-0.04**	**< 0.001**	**0.75**

BC10	Treasure Island/ Yerba Buena Island	35	1979-2008	▼	**9**	**-0.04**	**< 0.001**	**0.63**
BB71	Hunters Point/Alameda	25	1981-2008	▼	**7**	**-0.04**	**< 0.001**	**0.47**
BA40	Redwood Creek	29	1981-2008	▼	**14**	**-0.02**	**0.002**	**0.30**
BA30	Dumbarton Bridge	28	1981-2008	▼	**12**	**-0.02**	**< 0.001**	**0.47**
BA10	Coyote Creek	16	1994-2008	**?**	11	-0.03	0.080	0.21

All nine RMP-monitored Bay sites show a decline in PCB concentrations in bivalve tissue, although the decline at the Coyote Creek is not significant at the 0.05 level. The estimated half-lives for bivalve PCB concentrations range from 7 to 14 years by site.

NMW – Sum of PCBs data (ng/dry g)

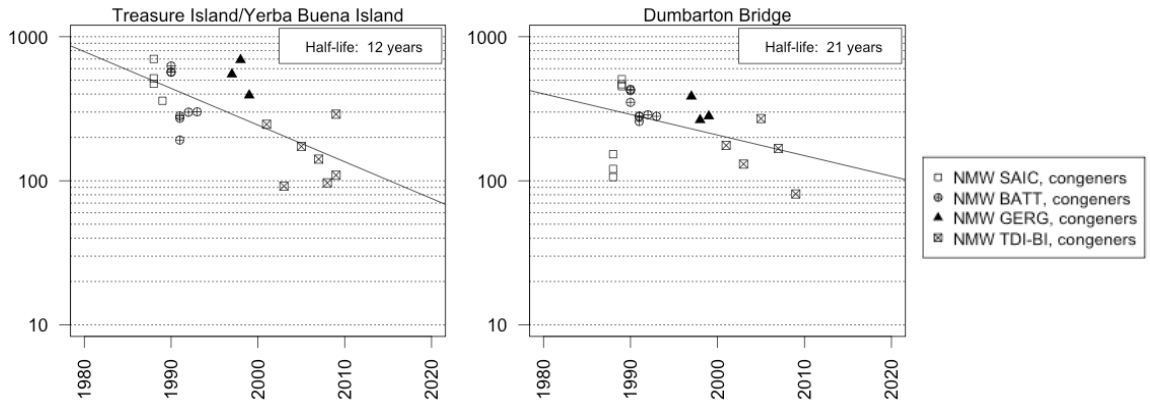


Figure 4.3 PCB concentrations (ng/g dry wt.) in transplanted mussels (NMW data), 1988-2009

Table 4.3 Linear regression statistics for PCB concentrations over time (NMW data)

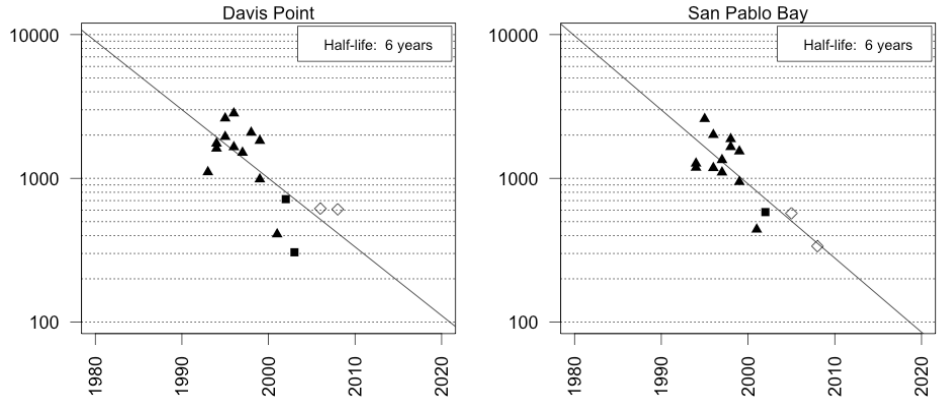
Code	Site Name	N	Years	Trend	Half-life (years)	Slope	p-value	R2
BC10	Treasure Island/ Yerba Buena Island	22	1988-2009	▼	**12**	**-0.03**	**< 0.001**	**0.49**
BA30	Dumbarton Bridge	22	1988-2009	▼	**21**	**-0.01**	**0.048**	**0.18**

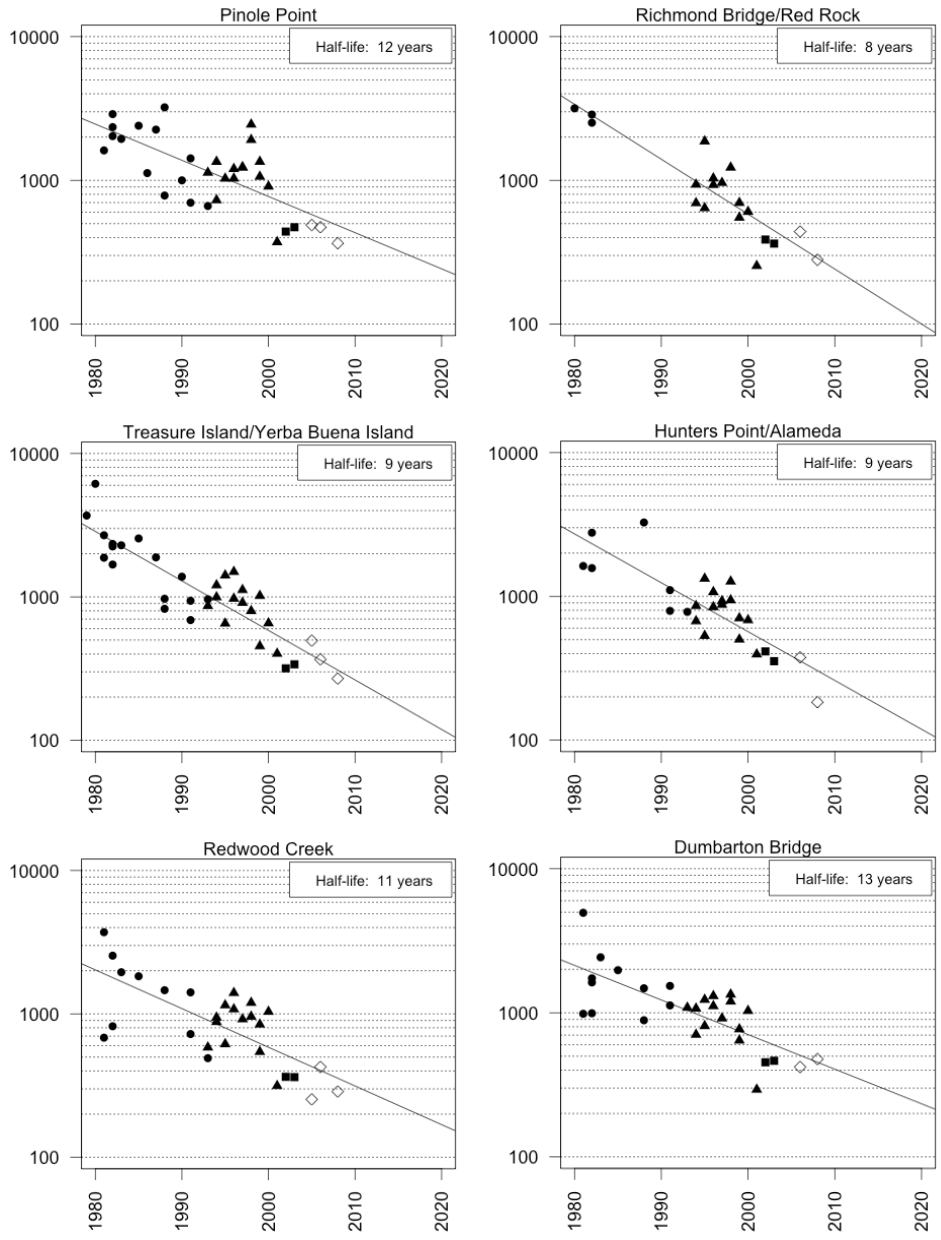
Both National Mussel Watch sites show statistically significant declines in PCBs concentrations in bivalve tissue. However, the NMW data suggest slower rates of decline than the SMW and RMP data. For the Treasure Island site, the NMW data gives an estimated 12 years for bivalve PCBs concentrations to decrease by half versus the 9-year half-life estimated by the combined SMW and RMP data. Similarly, for the Dumbarton Bridge site, the NMW data gives an estimated 21-year half-life versus the 12-year half-life estimated by the SMW and RMP data.

DDTs Trends in Bivalves

The DDTs data from the RMP, the SMW and the NMW are the sum of six DDTs [o,p'-DDD; o,p'-DDE; o,p'-DDT; p,p'-DDD; p,p'-DDE; p,p'-DDT]. The RMP and the SMW DDTs data sets were normalized to bivalve lipid content, while the NMW DDTs data are presented as portion of dry tissue weight.

RMP and SMW – Sum of DDTs data (ng/lipid g)




Pinole Point
Half-life: 12 years
Richmond Bridge/Red Rock
Half-life: 8 years
Treasure Island/Yerba Buena Island
Half-life: 9 years
Hunters Point/Alameda
Half-life: 9 years
Redwood Creek
Half-life: 11 years
Dumbarton Bridge
Half-life: 13 years
10000
1000
100
1980
1990
2000
2010
2020

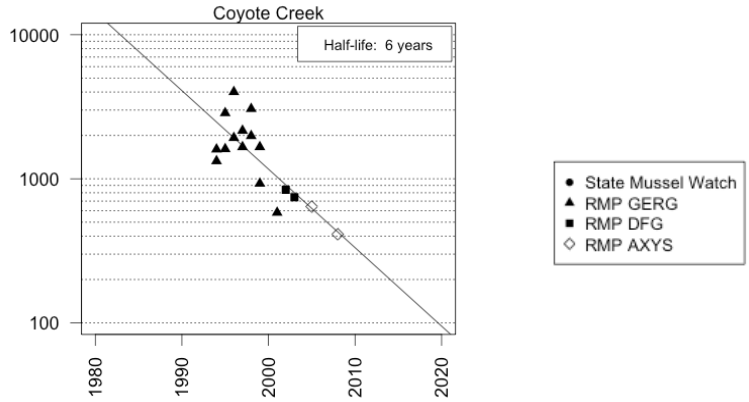


Figure 4.4 DDT concentrations (ng/g lipid) in transplanted mussels (RMP and SMW data), 1979-2008

Table 4.4 Linear regression statistics for DDT concentrations over time (RMP and SMW data)

Code	Site Name	N	Years	Trend	Half-life (years)	Slope	p-value	R2
BD40	Davis Point	16	1993-2008	▼	**6**	**-0.05**	**0.001**	**0.54**
BD20	San Pablo Bay	15	1994-2008	▼	**6**	**-0.05**	**< 0.001**	**0.65**
BD30	Pinole Point	33	1981-2008	▼	**12**	**-0.03**	**< 0.001**	**0.52**
BC61	Richmond Bridge/ Red Rock	19	1980-2008	▼	**8**	**-0.04**	**< 0.001**	**0.80**
BC10	Treasure Island/ Yerba Buena Island	35	1979-2008	▼	**9**	**-0.03**	**< 0.001**	**0.79**
BB71	Hunters Point/Alameda	25	1981-2008	▼	**9**	**-0.03**	**< 0.001**	**0.70**
BA40	Redwood Creek	29	1981-2008	▼	**11**	**-0.03**	**< 0.001**	**0.53**
BA30	Dumbarton Bridge	29	1981-2008	▼	**13**	**-0.02**	**< 0.001**	**0.56**
BA10	Coyote Creek	17	1994-2008	▼	**6**	**-0.05**	**< 0.001**	**0.62**

All of these monitored Bay sites show statistically significant declines in bivalve tissue DDT concentrations. The estimated half-life for bivalve DDT concentrations at these sites ranges from 6 to 13 years.

NMW – Sum of DDTs data (ng/dry g)

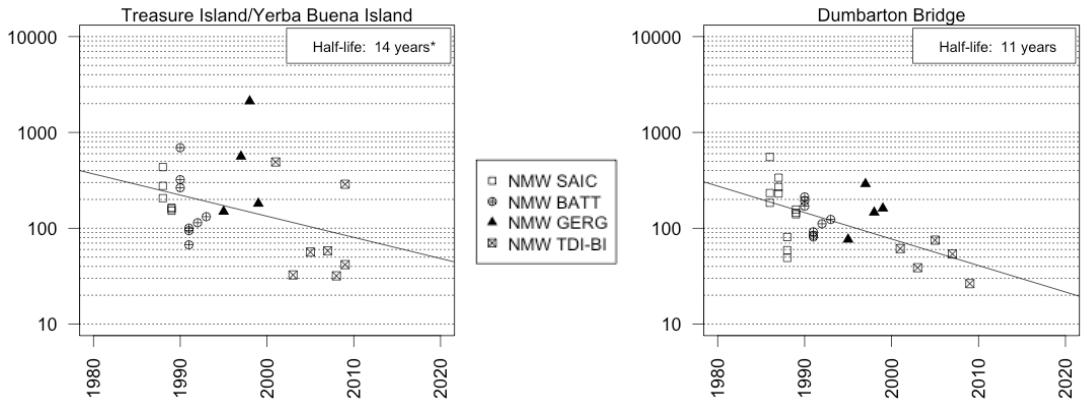


Figure 4.5 DDT concentrations (ng/g dry wt.) in transplanted mussels (NMW data), 1986-2009Table 4.5 Linear regression statistics for DDT concentrations over time (NMW data)

Table 4.6 Linear regression statistics for DDT concentrations over time (NMW data)

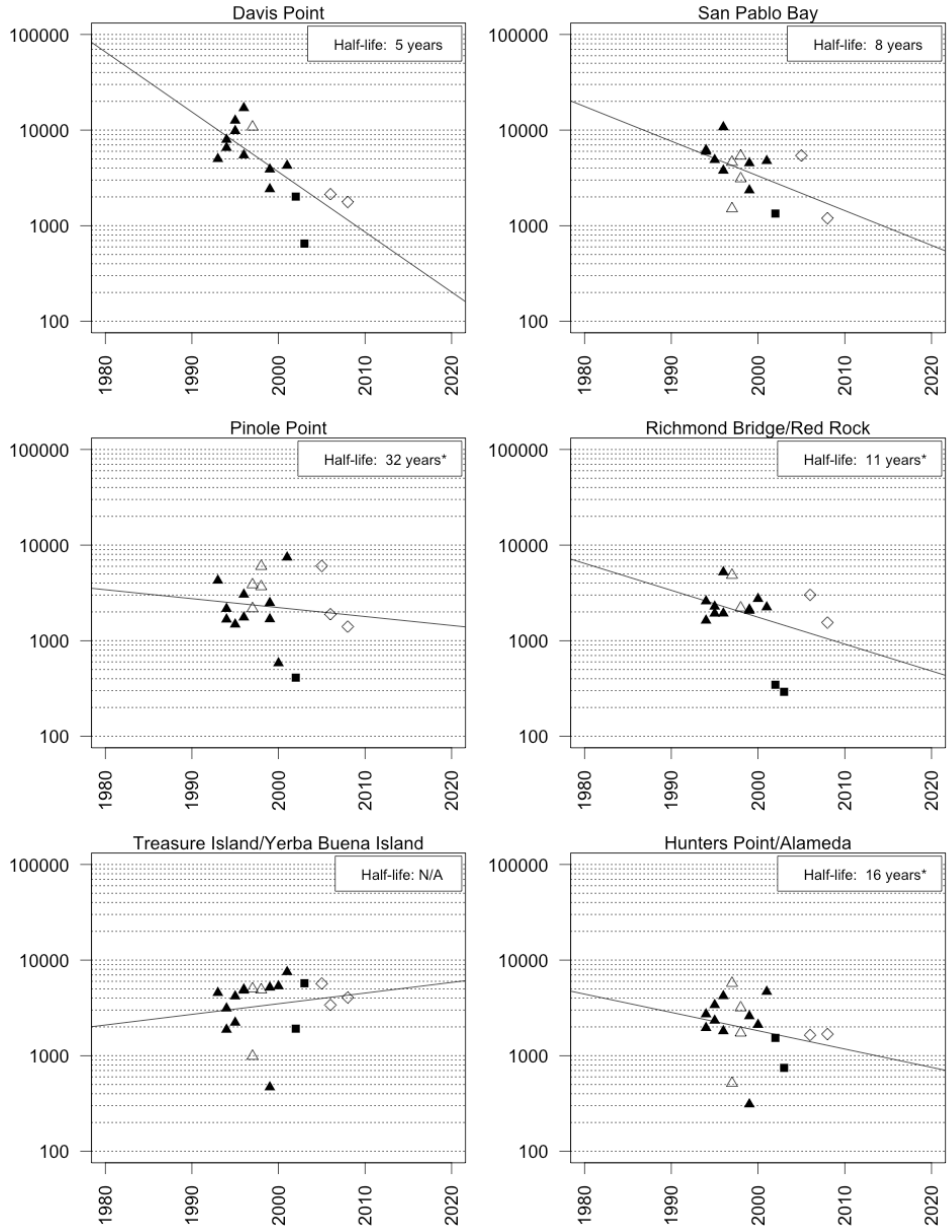
Code	Site Name	N	Years	Trend	Half-life (years)	Slope	p-value	R2
BC10	Treasure Island/ Yerba Buena Island	25	1988-2009	**?**	14	-0.02	0.067	0.14
BA30	Dumbarton Bridge	29	1986-2009	**▼**	**11**	**-0.03**	**< 0.001**	**0.37**

Both of these National Mussel Watch sites show declines in DDTs concentrations in bivalve tissue, but only one trend is statistically significant. The NMW data and the combined RMP and SMW data both give similar half-life estimates for bivalve DDTs concentration at the Dumbarton Bridge site.

Polycyclic Aromatic Hydrocarbons (PAHs) in Bivalves

The RMP PAHs data set was normalized to bivalve lipid content, while the NMW PAHs data are presented as portion of dry tissue weight. No SMW data were available for PAHs. Both the RMP and the NMW data sets consisted of sums over low and high molecular weight PAHs, but not alkylated PAHs.

RMP – Sum of PAHs data (ng/lipid g)



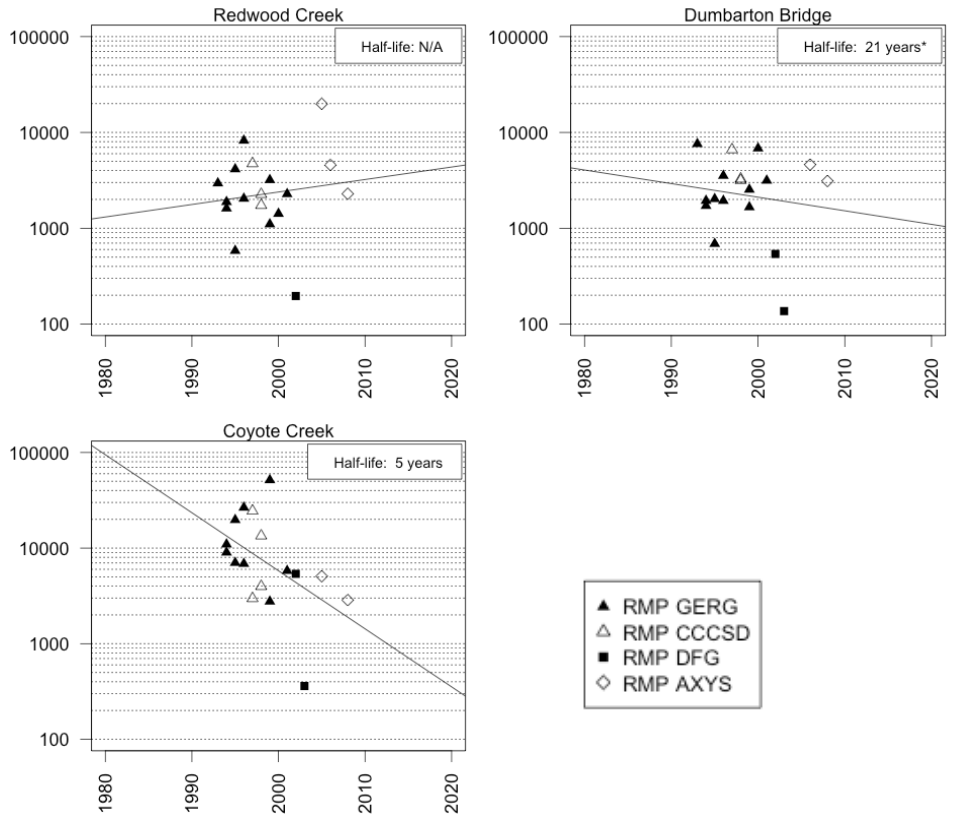


Figure 4.6 PAH concentrations (ng/g lipid) in transplanted mussels (RMP data), 1993-2008Table 4.7 Linear regression statistics for PAH concentrations over time (RMP data)

Table 4.7 Linear regression statistics for PAH concentrations over time (RMP data)

Code	Site Name	N	Years	Trend	Half-life (years)	Slope	p-value	R2
BD40	Davis Point	15	1993-2008	▼	**5**	**-0.06**	**0.001**	**0.57**
BD20	San Pablo Bay	15	1994-2008	▼	**8**	**-0.04**	**0.041**	**0.28**
BD30	Pinole Point	18	1993-2008	**?**	32	-0.01	0.632	0.01
BC61	Richmond Bridge/ Red Rock	16	1994-2008	**?**	11	-0.03	0.179	0.12

BC10	Treasure Island/ Yerba Buena Island	19	1993-2008	?	(-27)	0.01	0.509	0.03
BB71	Hunters Point/Alameda	18	1994-2008	?	16	-0.02	0.348	0.06
BA40	Redwood Creek	18	1993-2008	?	(-23)	0.01	0.604	0.02
BA30	Dumbarton Bridge	18	1993-2008	?	21	-0.01	0.583	0.02
BA10	Coyote Creek	17	1994-2008	▼	**5**	**-0.06**	**0.047**	**0.24**

The RMP data shows mixed trends for PAH concentrations in bivalve tissue. Only three of the monitored Bay sites show statistically significant trends in bivalve tissue PAHs concentrations. For the statistically significant trends, the estimated half-life for bivalve PAH concentrations ranges from 5 to 8 years.

It should be noted that the RMP PAH data set is about a decade shorter than the PCB and DDT data sets.

NMW – Sum of PAHs data (ng/dry g)

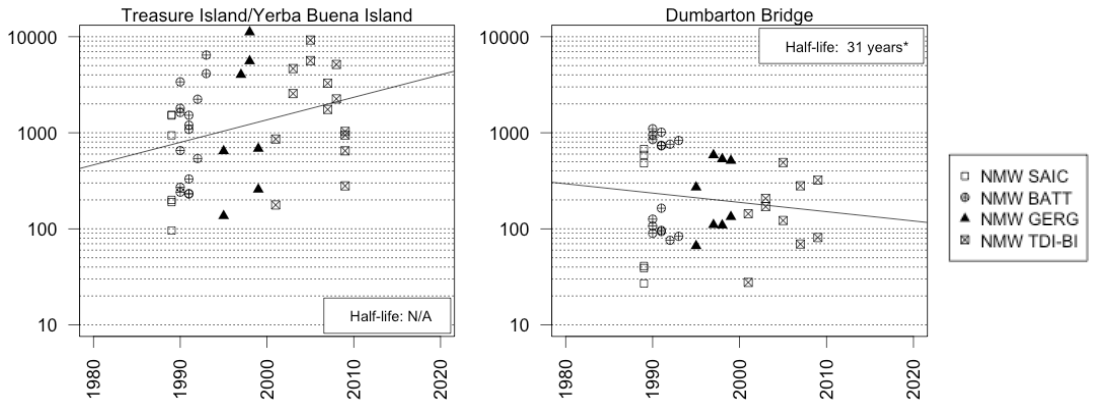


Figure 4.7 PAH concentrations (ng/g dry wt.) in transplanted mussels (NMW data), 1989-2009

Table 4.8 Linear regression statistics for PAH concentrations over time (NMW data)

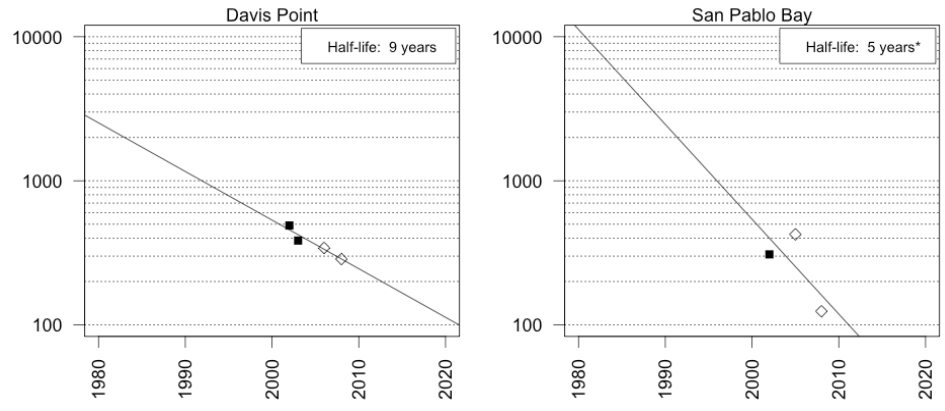
Code	Site Name	N	Years	Trend	Half-life (yrs)	Slope	p-value	R2
BC10	Treasure Island/ Yerba Buena Island	44	1989-2009	**?**	(-13)	0.02	0.051	0.09
BA30	Dumbarton Bridge	40	1989-2009	**?**	31	-0.01	0.417	0.02

The NMW data set, which extends back further in time and includes more many samples per site, also shows mixed trends for PAHs concentrations in bivalve tissue. Neither of the NMW sites shows a statistically significant trend, but the seemingly increasing concentrations at the Treasure Island site are nearly statistically significant (p-value=0.051). Also the ostensible increase in bivalve PAHs levels corroborate with the RMP data set, which also suggests that bivalve PAHs concentrations are increasing at the Treasure Island site. Likewise, neither RMP or NMW data show a statistically significant trend for the Dumbarton Bridge site, but both data sets suggest that PAH concentrations are decreasing.

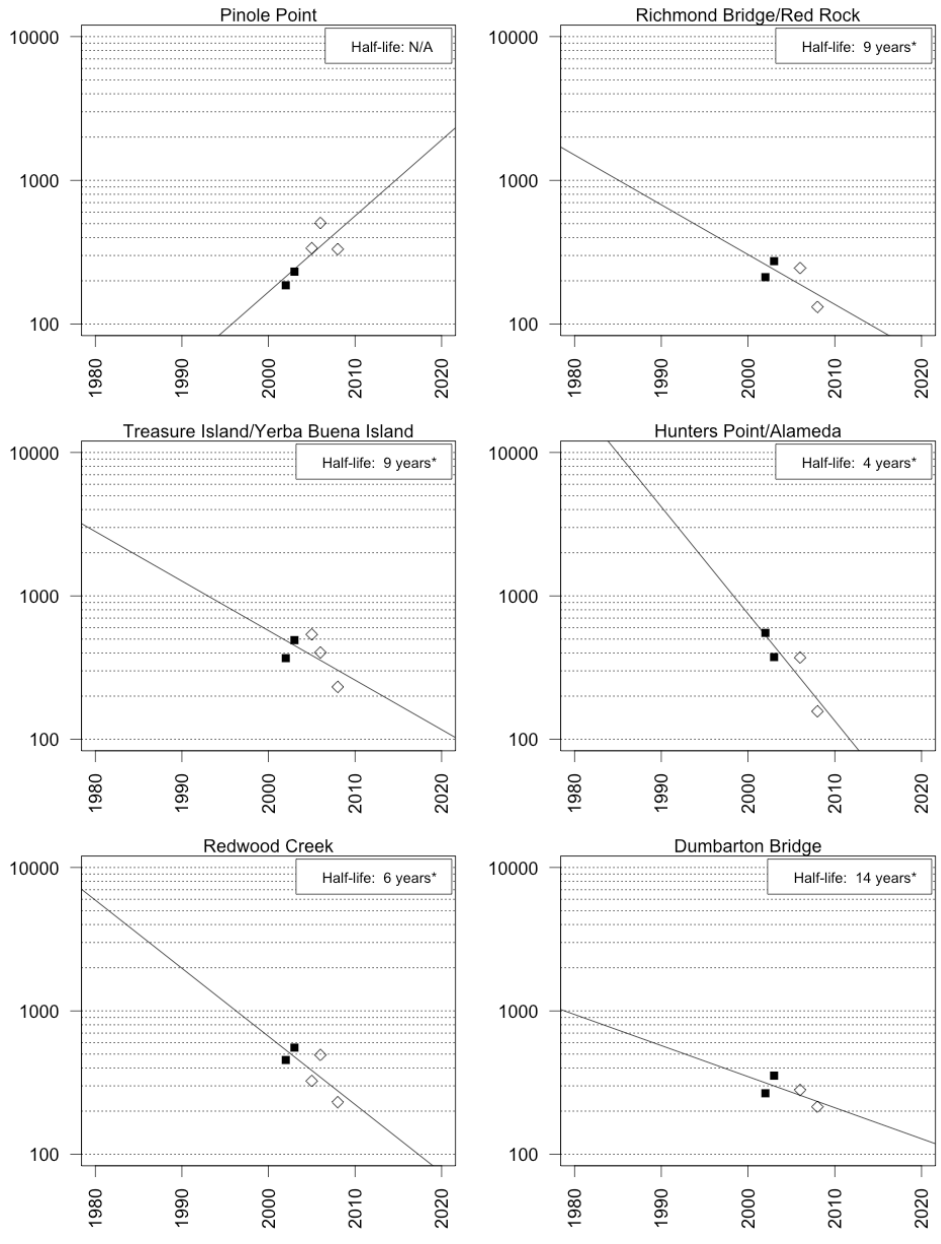
Polybrominated Diphenyl Ethers (PBDEs) Trends in Bivalves

The RMP PBDEs data set was normalized to bivalve lipid content. No SMW data were available for PBDEs, and NMW data were not included since only one data point was available for each NMW site. The RMP Sum of PBDEs data set consists of the sum of over 50 different PBDE compounds.

RMP – Sum of PBDEs data (ng/lipid



g)


Pinole Point
Half-life: N/A
Richmond Bridge/Red Rock
Half-life: 9 years*
Treasure Island/Yerba Buena Island
Half-life: 9 years*
Hunters Point/Alameda
Half-life: 4 years*
Redwood Creek
Half-life: 6 years*
Dumbarton Bridge
Half-life: 14 years*
10000
1000
100
1980
1990
2000
2010
2020

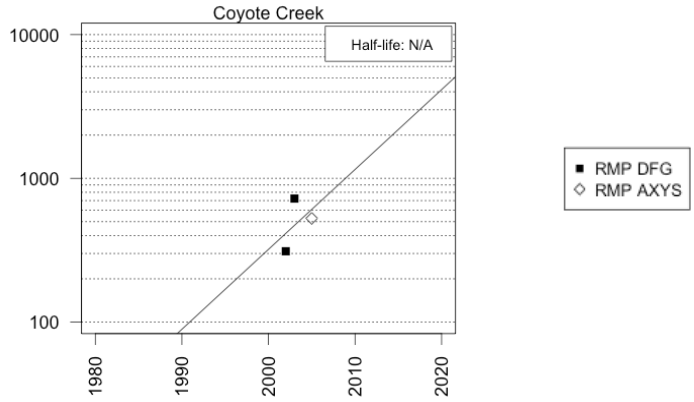


Figure 4.8 PBDE concentrations (ng/g lipid) in transplanted mussels (RMP data), 2002-2008Table 4.8 Linear regression statistics for PBDE concentrations over time (RMP data)

Table 4.99 Linear regression statistics for PBDE concentrations over time (RMP data)

Code	Site Name	N	Years	Trend	Half-life (yrs)	Slope	p-value	R2
BD40	Davis Point	4	2002-2008	▼	**9**	**-0.03**	**0.047**	**0.91**
BD20	San Pablo Bay	3	2002-2008	**?**	5	-0.07	0.495	0.51
BD30	Pinole Point	5	2002-2008	**?**	(-6)	0.05	0.139	0.57
BC61	Richmond Bridge/ Red Rock	4	2002-2008	**?**	9	-0.03	0.319	0.46
BC10	Treasure Island/ Yerba Buena Island	5	2002-2008	**?**	9	-0.03	0.308	0.33
BB71	Hunters Point/Alameda	4	2002-2008	**?**	4	-0.07	0.111	0.79
BA40	Redwood Creek	5	2002-2008	**?**	6	-0.05	0.16	0.53
BA30	Dumbarton Bridge	4	2002-2008	**?**	14	-0.02	0.331	0.45
BA10	Coyote Creek	3	2002-2005	**?**	(-5)	0.06	0.697	0.21

The RMP began sampling PBDEs in 2002, and currently the bivalve PBDE data sets are too short (N=3 to 5 per site) to say much with confidence. Surprisingly, one site, Davis Point, does show a statistically significant decline despite having only four data points.

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5

Appendix Tables

5. APPENDIX TABLES

APPENDIX 1 RMP PROGRAM PARTICIPANTS IN 2008

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 (SD#1)
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
Sewer 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

Cooling Water

Mirant of California, Pittsburgh and Potrero
Mirant Delta

Other

Coyote Point Marina
Marin Co. Service Area 29
Marin Rowing Association

Industrial Dischargers

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

Dredgers

BAE Systems
Chevron Richmond Long Wharf
City of Benicia
Conoco Phillips Company
Corinthian Yacht Club
Larkspur Ferry Terminal
Paradise Cay Yacht Harbor
Point San Pablo Yacht Club
Port of Oakland
Port of San Francisco
Strawberry Channel
Valero Refining Co.

Storm Water

Alameda Countywide Clean Water Program
California Department of Transportation
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 2008

Logistical Coordinator; Shipboard Conductivity, Temperature, and Depth (CTD) Readings	Mr. Paul Salop Applied Marine Sciences (AMS), Livermore, CA
Ship Captain	Mr. Brian Shore Captain, *RV Lakota* Dixon Marine Services
Water Trace Element Chemistry	Mr. Colin Davies and Ms. Tiffany Stilwater Brooks-Rand Ltd. (BR), Seattle, WA
Water Trace Organic Chemistry	Ms. Candice Navaroli AXYS Analytical Services, Inc. (AXYS), Sidney, BC
Water Ancillary Measurements	Water Cognates: Ms. Julia Halsne and Ms. Nirmela Arsem East Bay Municipal Utility District (EBMUD), Oakland, CA
	Water DOC and POC: Mr. Howard Borse and Mr. Pradeep Divvela Columbia Analytical Services (CAS), Kelso, WA
Sediment Trace Element Chemistry	Sediment As, Se, Hg, and Methyl Mercury Mr. Colin Davies and Ms. Tiffany Stilwater Brooks-Rand Ltd. (BR), Seattle, WA
	Sediment Al, Ag, Cd, Cu, Fe, Hg, Mn, Ni, Pb,and Zn 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. Ivano Aiello and Ms. Autumn Bonnema Moss Landing Marine Labs (MLML), Moss Landing, CA
USGS Water Quality	Dr. James Cloern, USGS, Menlo Park, CA
USGS Sediment Transport	Dr. David Schoellhamer, USGS, Sacramento, CA

APPENDIX 3 SUMMARY OF 2008 RMP WATER SAMPLING STATIONS

Region	Site Code	Historic Site	Collection Date	Latitude	Longitude	Site Depth (m)
Central Bay	CB024W		7/15/2008	37.71083	-122.32917	12.1
Central Bay	CB025W		7/14/2008	37.84330	-122.40835	36
Central Bay	CB026W		7/15/2008	37.68150	-122.31153	4.2
Central Bay/Golden Gate	BC20	X	7/14/2008	37.79403	-122.67355	30.0
Central Bay Yerba Buena Island	BC10	X	7/15/2008	37.82097	-122.34962	6.7
Lower South Bay	LSB033W		7/18/2008	37.49570	-122.10013	9.6
Lower South Bay	LSB034W		7/16/2008	37.48152	-122.08063	6.7
Lower South Bay	LSB035W		7/16/2008	37.50267	-122.11740	15.9
Lower South Bay	LSB036W		7/16/2008	37.48828	-122.08903	6.7
Lower South Bay	LSB037W		7/16/2008	37.49005	-122.10000	5.3
Rivers/Sacramento River	BG20	X	7/9/2008	38.05948	-121.81180	9.0
Rivers/San Joaquin River	BG30	X	7/9/2008	38.02128	-121.80448	8.8
San Pablo Bay	SPB024W		7/11/2008	38.02870	-122.37042	10.4
San Pablo Bay	SPB025W		7/14/2008	38.05432	-122.39763	3.9
San Pablo Bay	SPB026W		7/11/2008	38.05073	-122.33733	7.6
South Bay	SB050W		7/17/2008	37.56407	-122.18867	4.2
South Bay	SB051W		7/17/2008	37.60330	-122.29723	3
South Bay	SB052W		NS	NS	NS	NS
South Bay	SB053W		7/17/2008	37.61522	-122.23027	2.8
South Bay/Dumbarton Bridge	BA30	X	7/18/2008	37.51338	-122.13397	5.9
Suisun Bay	SU026W		7/10/2008	38.07075	-121.96730	4.3
Suisun Bay	SU027W		NS	NS	NS	NS
Suisun Bay	SU028W		7/10/2008	38.08162	-122.03840	3.5
Suisun Bay	SU029W		7/10/2008	38.05002	-122.08882	15.5

NS: Not Sampled, site replaced with next available alternate sample site

APPENDIX 4 SUMMARY OF 2008 RMP SEDIMENT SAMPLING STATIONS

Region	Site Code	Historic Site	Collection Date	Latitude	Longitude	Site Depth (m)
Central Bay/Yerba Buena Island	BC11	X	7/28/2008	37.82211	- 122.3496	6.7
Central Bay	CB001S		7/28/2008	37.87678	-122.3611	3.3
Central Bay	CB002S		7/25/2008	37.62508	-122.34706	4.4
Central Bay	CB011S		7/29/2008	37.97385	-122.45069	5.4
Central Bay	CB012S		7/28/2008	37.75389	-122.3692	13.9
Central Bay	CB037S		7/28/2008	37.8601	-122.32757	3.2
Central Bay	CB038S		7/28/2008	37.7231	-122.2604	3
Central Bay	CB039S		7/29/2008	37.91894	-122.41687	14.3
Central Bay	CB040S		7/25/2008	37.66017	-122.34196	7
Lower South Bay/Coyote Creek	BA10	X	7/24/2008	37.46825	-122.06334	4.1
Lower South Bay	LSB001S		7/23/2008	37.49185	-122.09854	5.8
Lower South Bay	LSB002S		7/24/2008	37.47904	-122.07801	8.1
Lower South Bay	LSB011S		7/23/2008	37.50372	-122.11871	14.2
Lower South Bay	LSB037S		7/23/2008	37.48938	-122.09466	6.4
Lower South Bay	LSB038S		7/24/2008	37.47266	-122.06693	5.1
Lower South Bay	LSB039S		7/23/2008	37.4926	-122.11026	2.1
Lower South Bay	LSB040S		7/24/2008	37.48562	-122.08216	5.3
Lower South Bay	LSB075S		7/24/2008	37.50047	-122.11808	9.4
Rivers/Sacramento River	BG20	X	7/30/2008	38.05703	-121.81516	9.1
Rivers/San Joaquin River	BG30	X	7/30/2008	38.02274	-121.80852	8.1
San Pablo Bay/Pinole Point	BD31	X	7/29/2008	38.01457	-122.3634	6.8
San Pablo Bay	SPB001S		7/29/2008	38.07177	-122.3868	3.7
San Pablo Bay	SPB002S		8/1/2008	38.01619	-122.34087	2
San Pablo Bay	SPB011S		7/29/2008	38.09237	-122.46526	1.8
San Pablo Bay	SPB012S		7/29/2008	38.04863	-122.39017	4.5
San Pablo Bay	SPB037S		8/1/2008	38.09975	-122.32797	1.4
San Pablo Bay	SPB038S		8/1/2008	38.0157	-122.32717	1.3
San Pablo Bay	SPB039S		7/29/2008	38.06816	-122.43565	2.8

Region	Site Code	Historic Site	Collection Date	Latitude	Longitude	Site Depth (m)
San Pablo Bay	SPB040S		7/29/2008	38.05142	-122.35695	3.8
South Bay/Redwood Creek	BA41	X	7/28/2008	37.55917	-122.20932	4.3
South Bay	SB001S		7/28/2008	37.61226	-122.2645	3.6
South Bay	SB002S		7/25/2008	37.60903	-122.16861	2
South Bay	SB011S		7/25/2008	37.61023	-122.33955	3.6
South Bay	SB012S		7/28/2008	37.58799	-122.24543	15.7
South Bay	SB037S		7/25/2008	37.64102	-122.22755	3.5
South Bay	SB038S		7/24/2008	37.53251	-122.16184	13.2
South Bay	SB039S		7/25/2008	37.65057	-122.24372	3.4
South Bay	SB040S		7/25/2008	37.6194	-122.18856	2.3
Suisun Bay/Grizzly Bay	BF21	X	7/31/2008	38.11554	-122.03993	1.5
Suisun Bay	SU001S		7/31/2008	38.09882	-122.04675	5.6
Suisun Bay	SU011S		7/30/2008	38.07532	-122.10228	3.4
Suisun Bay	SU012S		7/31/2008	38.09192	-122.04144	1.7
Suisun Bay	SU037S		7/30/2008	38.08103	-122.05818	3.5
Suisun Bay	SU039S		7/30/2008	38.08125	-122.08118	8.9
Suisun Bay	SU040S		7/30/2008	38.06619	-122.02248	3.9
Suisun Bay	SU073S		7/31/2008	38.11083	-122.04779	1.9
Suisun Bay	SU080S		7/31/2008	38.10552	-122.00948	1.9

APPENDIX 5 SUMMARY OF 2008 RMP BIVALVE MONITORING STATIONS

Region	Site Code	Historic Site	Collection Date	Latitude	Longitude	Site Depth (m)
Bodega Bay	T-0	X	5/7/2008	38.30477	-123.06563	0
Bodega Bay	T-1	X	9/17/2009	38.30477	-123.06563	0
Central Bay / Alameda	BB71	X	9/11/2009	37.69955	-122.33967	10.1
Central Bay / Red Rock	BC61	X	9/11/2009	37.92833	-122.46883	4.5
Central Bay / Yerba Buena Island	BC10	X	9/11/2009	37.81363	-122.35896	4.0
Lower South Bay / Coyote Creek	BA10	X	9/09/2009	37.46983	-122.06383	3.0
Rivers / Sacramento River	BG20	X	9/12/2008	38.07212	-121.77973	6.0
Rivers / San Joaquin River	BG30	X	9/12/2008	38.01902	-121.80488	6.0
San Pablo Bay / Davis Point	BD40	X	9/10/2009	38.05443	-122.26050	6.5
San Pablo Bay / Point Pinole	BD30	X	9/10/2009	38.01667	-122.36750	5.5
San Pablo Bay / San Pablo Bay	BD20	X	9/10/2009	38.04533	-122.42850	3.5
South Bay / Dumbarton Bridge	BA30	X	9/09/2009	37.51333	-122.13467	6.4
South Bay / Redwood Creek	BA40	X	9/09/2009	37.54700	-122.19500	4.2

APPENDIX 6 RMP TARGET PARAMETER LIST IN 2008

Field Measures – CTD Meter (Water, Sediment and Bivalve Cruises)	**Reporting Units**
Backscatter	Ftu
ElectricalConductivity	S/m
Temperature	°C
Density	kg/m3
Oxygen, Dissolved	mg/L
Pressure	Db
Salinity	psu
Field Measures - Shipboard (Water Cruise)	Reporting Units
Oxygen, Dissolved	mg/L
pH	pH
Salinity	ppt
SpecificConductivity	µmhos/cm
Temperature	°C
Field Measures - Shipboard (Sediment Cruise) *pH from interstitial water in undisturbed section of sediment grab	**Reporting Units**
pH*	pH
Eh	mV

Conventional Water Quality Parameters	**Reporting Units**	**Basis**
Ammonium as N	mg/L	ww
Chlorophyll a	mg/m3	ww
Dissolved Organic Carbon	µg/L	ww
Hardness as CaCO3	mg/L	ww
Nitrate as N	mg/L	ww
Nitrite as N	mg/L	ww
Oxygen, Dissolved	mg/L	ww
Particulate Organic Carbon	µg/L	ww
pH	pH	ww
Pheophytin a	mg/m3	ww
Phosphate as P	mg/L	ww
Salinity	psu	ww
Silica	mg/L	ww
SpecificConductivity	µmho	ww
Suspended Sediment Concentration	mg/L	ww
Temperature	°C	ww
Sediment Quality Parameters	Reporting Units	Basis
% Solids	%	dw
Depth	m	
Total Nitrogen	%	dw
Total Organic Carbon	%	dw

Grainsize Parameters [Sum of Clay and Silt]**	**Reporting Units**	**Basis**
Clay <0.0039 mm	%	dw
Fine <0.0625 mm**	%	dw
Granule + Pebble 2.0 to <64 mm	%	dw
Sand 0.0625 to <2.0 mm	%	dw
Silt 0.0039 to <0.0625 mm	%	dw
Sediment Toxicity Parameters – Homogenate for EOHA & HYAL SD = Standard Deviation	Reporting Units	Basis
Mean % Survival; SD - Mean % Survival	%	dw
Sediment Toxicity Parameters - Surface Water Interface for MCAL	Reporting Units	Basis
Mean % Normal Alive; SD - Mean % Normal Alive	%	dw
Bivalve Tissue Parameters 1. Reported with Trace Metals 2. Reported with Trace Organics	**Reporting Units**	**Basis**
% Solids[1]	%	dw
% Survival per Species	%	dw
% Survival per Species (caged)	%	dw
Dry Weight	g	dw
Dry Weight Standard Error	g	dw
Growth Mean	g	dw
Growth Standard Error	g	dw
Lipid	%	dw
Moisture[2]	%	dw

Trace elements analyzed in water, sediment, and tissue samples:
Target Method Detection Limits (MDLs) are in parentheses following the reporting units.
Basis codes: dw=dry weight, ww=wet weight.
- Parameter is not sampled for the matrix.
* Dry and wet weight mercury concentrations are reported for fish tissue.

	Water	Sediment	Bivalve Tissue
Basis	ww	dw	dw
Aluminum	-	mg/Kg (200)	µg/g (1)
Arsenic	µg/L (0.1)	mg/Kg (0.2)	-
Cadmium	µg/L (0.001)	mg/Kg (0.001)	µg/g (0.01)
Cobalt	µg/L (.0005)	-	-
Copper	µg/L (0.01)	mg/Kg (2)	µg/g (0.2)
Cyanide	µg/L (0.4)	-	-
Iron	µg/L (10)	mg/Kg (200)	-
Lead	µg/L (0.001)	mg/Kg (0.5)	µg/g (0.01)
Manganese	µg/L (0.01)	mg/Kg (20)	-
Mercury*	µg/L (.0001)	mg/Kg (0.00001)	-
Mercury, Methyl	ng/L (0.005)	µg/Kg (0.005)	-
Mercury, Acid Labile	µg/L	-	-
Mercury, Reactive	µg/L	-	-
Nickel	µg/L (0.01)	mg/Kg (5)	µg/g (0.2)
Selenium	µg/L (0.02)	mg/Kg (0.01)	µg/g (0.01)
Silver	µg/L (0.0001)	mg/Kg (0.001)	µg/g (0.001)
Zinc	µg/L (0.005)	mg/Kg (5)	µg/g (10)

Trace organic parameters (reporting units) analyzed in water (pg/L), sediment (µg/Kg), and bivalve tissue (ng/g) Note: PAHs, Pesticides and PCBs are reported biennially in water. Sums calculated by SFEI. Organochlorines in tissue from CDFG analyzed by GC-ECD will be determined using two columns of differing polarity.		
Polycyclic Aromatic Hydrocarbons (PAHs) *(Target MDLs: water – 200 pg/L, sediment -- 5 µg/Kg, tissue – 5 ng/g)* *[1]Sum of LPAHs and HPAHs* *[2]Reported in sediment only*		
Low molecular weight PAHs Acenaphthene Acenaphthylene Anthracene Biphenyl Dibenzothiophene Dimethylnaphthalene, 2,6- Fluorene Methylnaphthalene, 1- Methylnaphthalene, 2- Methylphenanthrene, 1- Naphthalene Phenanthrene Trimethylnaphthalene, 2,3,5- Sum of LPAHs (SFEI)	High molecular weight PAHs Benz(*a*)anthracene Benzo(*a*)pyrene Benzo(*b*)fluoranthene Benzo(*e*)pyrene Benzo(g,h,i)perylene Benzo(*k*)fluoranthene Chrysene Dibenz(*a,h*)anthracene Fluoranthene Indeno(1,2,3-c,d)pyrene Perylene Pyrene *Sum of HPAHs (SFEI)* *Sum of PAHs (SFEI)[1]*	Alkylated PAHs Benz(a)anthracenes/Chrysenes, C1- Benz(a)anthracenes/Chrysenes, C2- Benz(a)anthracenes/Chrysenes, C3- Benz(a)anthracenes/Chrysenes, C4- Chrysenes, C1[2] Chrysenes, C2[2] Chrysenes, C3[2] Chrysenes, C4[2] Dibenzothiophenes, C1- Dibenzothiophenes, C2- Dibenzothiophenes, C3- Fluoranthene/Pyrenes, C1 - Fluorenes, C1 - Fluorenes, C2 - Fluorenes, C3 - Naphthalenes, C1 - Naphthalenes, C2 - Naphthalenes, C3 - Naphthalenes, C4 - Phenanthrene/Anthracene, C1 - Phenanthrene/Anthracene, C2 - Phenanthrene/Anthracene, C3 - Phenanthrene/Anthracene, C4 -

SYNTHETIC BIOCIDES (Target MDLs: water – 2 pg/L, sediment - 1 µg/Kg, tissue – 1 ng/g) [+] Parameter reported for water matrix only. Sums calculated by SFEI.				
Cyclopentadienes Aldrin Dieldrin Endrin	Chlordanes Chlordane, alpha- Chlordane, gamma- Heptachlor Heptachlor Epoxide Nonachlor, cis- *Nonachlor, trans-* *Oxychlordane* Sum of Chlordanes (SFEI)	DDTs DDD(o,p') DDD(p,p') DDE(o,p') DDE(p,p') DDT(o,p') DDT(p,p') Sum of DDTs (SFEI)	HCH HCH, alpha HCH, beta HCH, delta HCH, gamma Sum of HCHs (SFEI)	Other Synthetic Biocides Chlorpyrifos[+] Dacthal[+] Diazinon[+] Endosulfan I[+] Endosulfan II[+] Endosulfan sulfate[+] Hexachlorobenzene Mirex

OTHER SYNTHETIC COMPOUNDS						
Polychlorinated Biphenyls (PCBs) (Target MDLs: water – 2 pg/L, sediment - 1 µg/Kg , tissue – 1 ng/g) IUPAC numbers listed. Sums calculated by SFEI.						
PCB 008	PCB 049	PCB 074	PCB 105	PCB 141	PCB 170	PCB 194
PCB 018	PCB 052	PCB 087	PCB 110	PCB 149	PCB 174	PCB 195
PCB 028	PCB 056	PCB 095	PCB 118	PCB 151	PCB 177	PCB 201
PCB 031	PCB 060	PCB 097	PCB 128	PCB 153	PCB 180	PCB 203
PCB 033	PCB 066	PCB 099	PCB 132	PCB 156	PCB 183	Sum of 40 PCBs (SFEI)
PCB 044	PCB 070	PCB 101	PCB 138	PCB 158	PCB 187	

Polybrominated Diphenyl Ethers (PBDEs) (Target MDLs: water – 1 pg/L, sediment – 1 µg/Kg, tissue – 1 ng/g) IUPAC number listed. Only analyzed in sediment.			
PBDE 007	PBDE 035	PBDE 105	PBDE 183
PBDE 008	PBDE 037	PBDE 116	PBDE 190
PBDE 010	PBDE 047	PBDE 119	PBDE 196
PBDE 011	PBDE 049	PBDE 120	PBDE 197
PBDE 012	PBDE 051	PBDE 126	PBDE 203
PBDE 013	PBDE 066	PBDE 128	PBDE 204
PBDE 015	PBDE 071	PBDE 138	PBDE 205
PBDE 017	PBDE 075	PBDE 140	PBDE 206
PBDE 025	PBDE 077	PBDE 153	PBDE 207
PBDE 028	PBDE 079	PBDE 154	PBDE 208
PBDE 030	PBDE 085	PBDE 155	PBDE 209
PBDE 032	PBDE 099	PBDE 166	
PBDE 033	PBDE 100	PBDE 181	

Pyrethroids (Target RDLs: sediment – 1 to 10 µg/kg) *Sum of individual isomers. Sums calculated by SFEI.		
Allethrin	Deltamethrin	Phenothrin
Bifenthrin	Esfenvalerate/Fenvalerate, total*	Prallethrin
Cyfluthrin, total*	Fenpropathrin	Resmethrin
Cyhalothrin, lambda, total*	Permethrin-1	Tetramethrin
Cypermethrin, total*	Permethrin-2	Tralomethrin
		Sum of Pyrethroids (SFEI)

APPENDIX 7 ANALYTES REOPRTED IN WATER SAMPLES (1993-2008)

Shaded areas indicate that results are available for RMP Status and Trends Sampling.
Parameter Type Codes: ANC = Ancillary Parameters, ORGS = Organic Parameters, PESTs = Pesticide Parameters, SYN = Synthetic Parameters, TE = Trace Metal parameters, WaterTOX = Toxicity Parameters

Reportable Water Parameter	Parameter Type	1993	1994	1995	1996	1997	1998	1999	2000	2001	2002	2003	2004	2005	2006	2007	2008
Ammonium as N	ANC	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■
Chlorophyll a	ANC	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■
SpecificConductivity	ANC	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■
Oxygen, Dissolved	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	ANC	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■
Silica	ANC	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■
Suspended Sediment Concentration	ANC										■	■	■	■	■	■	■
Total Suspended Solids	ANC	■	■	■	■	■	■	■	■	■				■	■		
Temperature	ANC	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■
PAHs	ORGS	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■
PAHs Alkylated	ORGS						■	■	■	■	■	■	■	■	■	■	■
PBDEs	ORGS										■	■	■	■	■	■	■
PCBs	ORGS	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	
Phthalates	ORGS										■	■					
Chlordanes	PESTs	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■

Reportable Water Parameter	Parameter Type	1993	1994	1995	1996	1997	1998	1999	2000	2001	2002	2003	2004	2005	2006	2007	2008
Chlorpyrifos	PESTs																
Cyclopentadienes	PESTs																
Dacthal	PESTs																
DDTs	PESTs																
Diazinon	PESTs																
Endosulfan I	PESTs																
Endosulfan II	PESTs																
Endosulfan Sulfate	PESTs																
HCHs	PESTs																
Hexachlorobenzene	PESTs																
Mirex	PESTs																
Oxadiazon	PESTs																
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																

Reportable Water Parameter	Parameter Type	1993	1994	1995	1996	1997	1998	1999	2000	2001	2002	2003	2004	2005	2006	2007	2008
Cell Count	WaterTox	■															
Mean % Normal Development	WaterTox	■	■	■	■	■											
Mean % Survival	WaterTox	■	■	■	■	■	■	■	■	■	■						

APPENDIX 8 ANALYTES REPORTED IN SEDIMENT SAMPLES (1993-2008)

Shaded areas indicate that results are available for RMP Status and Trends Sampling.
Parameter Type Codes: ANC = Ancillary Parameters, EC=Emerging Contaminants, ORGS = Organic Parameters, PESTs = Pesticide Parameters, SedTOX = Toxicity Parameters SYN = Synthetic Parameters, TE = Trace Metal parameters

Reportable Sediment Parameter	Parameter Type	1993	1994	1995	1996	1997	1998	1999	2000	2001	2002	2003	2004	2005	2006	2007	2008
% Solids	ANC		■	■	■	■	■	■	■	■	■	■	■	■	■	■	■
Ammonia	ANC			■	■	■	■	■	■	■							
Clay <0.0039 mm	ANC																■
Clay <0.005 mm	ANC	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	
Eh	ANC											■	■	■	■	■	■
Fine <0.0625 mm	ANC	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■
Granule + Pebble 2.0 to <64 mm	ANC	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	
Hydrogen Sulfide	ANC			■	■	■	■	■	■	■							
pH	ANC	■	■	■	■	■	■	■	■	■	■					■	■
Sand 0.0625 to <2.0 mm	ANC	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■
Silt 0.0039 to <0.0625 mm	ANC	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■
Total Nitrogen	ANC	■					■	■	■	■	■	■	■	■	■	■	■
Total Organic Carbon	ANC	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■
Total Sulfide	ANC			■	■	■	■	■	■	■							
Benthos	Benthos																■
PCNs	EC																■
Triclosan	EC																■

Reportable Sediment Parameter	Parameter Type	1993	1994	1995	1996	1997	1998	1999	2000	2001	2002	2003	2004	2005	2006	2007	2008
209 PCBs	ORGS																
40 PCBs	ORGS																
PAHs	ORGS																
PAHs Alkylated	ORGS																
PBDEs	ORGS																
Phthalates	ORGS																
Chlordanes	PESTs																
Cyclopentadienes	PESTs																
DDTs	PESTs																
HCHs	PESTs																
Hexachlorobenzene	PESTs																
Mirex	PESTs																
Mean % Normal Alive	SedTox																
Mean % Survival	SedTox																
p-Nonylphenol	SYN																
Aluminum	TE																
Arsenic	TE																
Cadmium	TE																
Copper	TE																
Cromium	TE																
Iron	TE																
Lead	TE																
Manganese	TE																
Mercury	TE																
Mercury Isotopes	TE																
Mercury, Methyl	TE																
Nickel	TE																
Selenium	TE																
Silver	TE																
Zinc	TE																

APPENDIX 9 ANALYTES REPORTED IN BIVALVE TISSUE SAMPLES (1993-2008)

Shaded areas indicate that results are available for RMP Status and Trends Sampling.

[1]2006 Bivalve data was not analyzed pending analytical issues.

[2]Bivalves were not deployed in 2007. Beginning in 2007, bivalve monitoring occurs biennially for trace organics and every 5 years for trace metal parameter

Parameter Type Codes: ANC = Ancillary Parameters, ORGS = Organic Parameters, PESTs = Pesticide Parameters, SYN = Synthetic Parameters, TE = Trace Metal parameters

Reportable Tissue Parameter	Parameter Type	1993	1994	1995	1996	1997	1998	1999	2000	2001	2002	2003	2004	2005	2006[1]	2007[2]	2008
% Lipids	ANC																■
% Moisture	ANC		■	■	■	■	■	■	■	■	■	■	■		■		■
% Solids	ANC	■	■	■	■	■	■	■	■	■	■	■	■				■
% Survival per Species	ANC	■	■	■	■	■	■	■	■	■	■	■	■				■
% Survival per Species (caged)	ANC	■	■	■	■	■	■	■	■	■	■	■	■		■		■
Condition Index (CI)	ANC	■	■	■	■	■	■	■	■								■
CTD	ANC							■	■	■	■	■	■		■		■
Dry Weight	ANC	■	■	■	■	■	■	■	■	■	■	■	■		■		■
Gonad Index CI Mean	ANC							■	■	■							
Growth Mean	ANC							■	■	■	■	■	■		■		■
Alkanes (C10-C34)	ORGS	■	■	■													
Musks	ORGS										■	■	■				
PAHs	ORGS	■	■	■	■	■	■	■	■	■	■	■		■	■		■
PAHs Alkylated	ORGS	■	■	■	■	■	■	■	■	■	■	■			■		■
PBDEs	ORGS										■	■		■	■		■
PCBs	ORGS	■	■	■	■	■	■	■	■	■	■	■		■	■		■
Phthalates	ORGS										■	■	■				
Chlordanes	PESTs	■	■	■	■	■	■	■	■	■	■	■		■	■		■
Cyclopentadienes	PESTs	■	■	■	■	■	■	■	■	■	■	■		■	■		■
DDTs	PESTs	■	■	■	■	■	■	■	■	■	■	■		■	■		■
HCHs	PESTs	■	■	■	■	■	■	■	■	■	■	■		■	■		■
Hexachlorobenzene	PESTs	■	■	■	■	■	■	■	■	■	■	■		■	■		■
Mirex	PESTs	■	■	■	■	■	■	■	■	■	■	■		■	■		■

Reportable Tissue Parameter	Parameter Type	1993	1994	1995	1996	1997	1998	1999	2000	2001	2002	2003	2004	2005	2006[1]	2007[2]	2008
p-Nonylphenol	SYN																
Triphenylphosphate	SYN																
Aluminum	TE																
Arsenic	TE																
Cadmium	TE																
Chromium	TE																
Copper	TE																
DBT (Dibutyltin)	TE																
Iron	TE																
Lead	TE																
Manganese	TE																
MBT (Monobutyltin)	TE																
Mercury	TE																
Methyl Mercury	TE																
Nickel	TE																
Selenium	TE																
Silver	TE																
TBT (Tributyltin)	TE																
TTBT (Tetrabutyltin)	TE																
Zinc	TE																

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APPENDIX 10 SUMMARY OF CHANGES, 1993-2009

Action Codes: 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/sampling design; S= Station added or removed.

Action Code	Year	Action	Detail/Rationale
D	1993-1998	Conductivity, temperature, and depth (CTD) data are not available for tissue	CTD cast was not deployed.
D	1999-2001	CTD data are available for Deployment, maintenance and retrieval tissue cruises	Began deploying CTD casts during tissue cruises.
D	1998-1999	Iron in bivalves is a non-target analyte and not reported via WQT	Iron in bivalves reported by lab, but is not available via WQT.
A	1993	MeHg in bivalve tissue samples was only analyzed in 1993.	This was part of a pilot study. Total mercury was analyzed each year through 1999.
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.
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),	Sites selected to fill large areas in Estuary where no samples were taken and to better monitor areas around tributaries. Total water stations = 22.

Action Codes: 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/sampling design; S= Station added or removed.

Action Code	Year	Action	Detail/Rationale
		Honker Bay (BF40), Petaluma River mouth (BD15), Coyote Creek mouth (BA10)	
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 treated identically as RMP stations. Total water stations =24.
S	1994	Added 4 stations (previously 11) for bivalve tissue sampling	Total bivalve stations = 15.
A	1996	Added trace organics analysis for Southern Slough stations Sunnyvale (C-1-3) and San Jose (C-3-0)	Trace organics were not analyzed for Sunnyvale (C-1-3) during the July 1996 or August 1997 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. Total water and sediment 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 were reported. In September 1996, 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 will 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).

Action Codes: 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/sampling design; S= Station added or removed.

Action Code	Year	Action	Detail/Rationale
A	1998	T-1 bivalve 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 transplants died during deployment.
D	1998	Tissue results are not available for Sept. 1998 for BF20 (Grizzly Bay)	The bivalves *Corbicula fluminea* (CFLU) could not be found at the reference site Lake Chabot
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.
S	1999	Removed 1 station (previously 15) for bivalve tissue sampling BF20 (Grizzly Bay)	A bivalve reference site could not be found for *Corbicula fluminea* (CFLU). Total bivalve tissue stations = 14.
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.
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.

Action Codes: 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/sampling design; S= Station added or removed.

Action Code	Year	Action	Detail/Rationale
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	CTD casts were not taken during 2002 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.
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 Codes: 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/sampling design; S= Station added or removed.

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.
P	2002	Stopped Bivalve Maintenance Cruise	Cruise was found to be unnecessary.
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	Funding ended for monitoring of trace organics in water and sediment which began in 1996 at these stations

Action Codes: 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/sampling design; S= Station added or removed.

Action Code	Year	Action	Detail/Rationale
		(previously 24) C-1-3 (Sunnyvale) and C-3-0 (San Jose), part of the Local Effects Monitoring Program (LEMP)	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, triphenylphosphate and nitro and polycyclic musks analysis in bivalve tissue samples	These analytes posed low levels of concern for the 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.
D	2006	Tissue data are unavailable for San Pablo Bay	Mooring was removed during deployment period

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Action Code	Year	Action	Detail/Rationale
		(BD20)	
D	2006	Tissue data are unavailable for Coyote Creek (BA10)	Nearly full mortality (1% survival) due to heavy biofouling and sedimentation
D	2006	2006 bivalve trace organics data were analyzed in 2008	Analysis was pending decision on analytical lab
D	2006	Water diazinon and chlorpyrifos data are not available	Initially, samples were not analyzed due to analytical issues. These issues were resolved. In 2010, the TRC decided to cancel the analysis due to the high cost and the lack of a pressing need for the data
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.
P	2006	Bivalve Maintenance Cruise discontinued	TRC approved dropping the maintenance cruise after a study conducted from 2002-2005 showed no significant difference in survival of bivalves in maintained and non-maintained cages
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 site.
A	2007	Nitrogen results will be reported as "Nitrogen, Total Kjeldahl" in sediment. This is different from the historical RMP data.	Lab changed from UCSCDET to AMS-Texas.
A	2007	Added BDE 197 to target analyte list for water and sediment and BDE 196 for sediment only.	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	Initially, samples were not analyzed due to analytical issues. These issues were resolved. In 2010, the TRC decided to cancel the analysis due to the high cost and the lack of a pressing need for the data
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.

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Action Code	Year	Action	Detail/Rationale
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.
L	2007	SFEI begins taking shipboard total salinity measurements.	Switched labs for water ancillary data; new lab does not participate in cruises. UCSC used to also report salinity by SCT along with their analytical measurements.
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
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. The TRC approved this change in December 2006.
A	2008	Added pyrethroids analysis in sediment by CDFG	To investigate the potential toxicity of pyrethroids in the bay.

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Action Code	Year	Action	Detail/Rationale
A	2008	Added selenium analysis in tissue by BRL	Added to provide information for the Selenium TMDL
A	2008	Added benthos analysis by CCSF and MLML	The addition of benthos collection will enable sediment assessments in accordance with the SQOs which use three lines of evidence, benthos, sediment chemistry and sediment toxicity
A	2008	PCBs were not analyzed in water. PAHs and Pesticides in water were not scheduled to be analyzed but were added into the sampling plan.	PCBs, PESTS, PAHs will be sampled every other year in water (on a biennial basis) based on recommendations from the redesign process. PAHs were analyzed because of the Cosco Busan oil spill, and PESTS were analyzed in order to check the detection level for AXYS Analytical Laboratory's MRES method using both whole water samples and 100L High volume extracts. Pesticide results were not reported because they were part of the Intercomparison study.
D	2008	Oxadiazon was not reported	The MRES method cannot analyze for Oxadiazon and since the 2008 demonstration project used only the MRES method, it was not possible to collect this data.
D	2008	Missing % Lipids for the trace metals bivalve analysis	Lab could not analyze for this.
D	2008	2008 Grainsize Granule fraction is not available	Granule fraction was not analyzed. In 2008, RMP switched labs from UCSC-DET to MLML-Aiello. MLML did not analyze larger grainsize fractions and only fractions <2mm are available.
D	2008	Water pesticide data is not available on the Web Query Tool	The 2008 samples were part of a demonstration project for the MRES method and were conducted on a subset of stations using whole water grabs (7 samples). These results were then compared to the extracts from the 100-liter infiltrex samples at the same location. These results will not be reported on the web.
D	2008	Pyrethroid tralomethrin not analyzed in sediment samples	Tralomethrin was not analyzed in 2008 by CDFG, but will be in the future.
D	2008	Manganese and iron in bivalves are non-target analytes and not reported via WQT	Manganese and iron are not reported as target analytes via WQT.
L	2008	Changed principle lab for trace metals in water from UCSC to BRL and changed principle lab for trace metals in tissue from UCSC to BRL (Se) and CCSF (other metals)	Changed labs based on an evaluation of turn around time, cost, and analytical capabilities such as elevated methyl mercury quantitation limits. Due to BRL's method, metals (Al, Cd, Cu, Fe, Pb, Mn, Ni, Ag, and Zn) are no longer reported as near-total concentrations. UCSC extracted with a weak acid (pH < 2) for a minimum of one month, resulting in measurements that approximate bioavailability of these metals to Estuary organisms, while BR used reductive precipitation.
L	2008	Intercomparison study with BRL and City and County of San Jose for Copper and Nickel in water	Samples were taken for both labs at all 22 sites.
L	2008	Changed lab for POC and DOC analysis from UCSC and AMS-Texas to Columbia Analytical Services	Changed labs based on an evaluation of turn around time, cost, and analytical capabilities/ AMS-Texas went out of business.
L	2008	Changed lab for analysis of SSC, Pigments, Nutrients, salinity, and hardness in water from	Changed labs based on an evaluation of turn around time, cost, and analytical capabilities.

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Action Code	Year	Action	Detail/Rationale
		UCSC to EBMUD	
L	2008	Changed lab for analysis of grainsize in sediment from UCSC to MLML - Aiello	Changed labs based on an evaluation of turn around time, cost, and analytical capabilities.
L	2008	Changed lab for analysis of Total Organic Carbon and Total Nitrogen in sediment from UCSC to MLML – Hunter	Changed labs based on an evaluation of turn around time, cost, and analytical capabilities.
L	2008	Changed toxicity testing method for bivalve larval (*Mytilus galloprovincialis*) from elutriate testing to sediment-water interface exposure (SWI). Sediment-water interface cores (SWICS) will be analyzed for toxicity by UCD-GC.	The Sediment Quality Objectives recommend using sediment–water interface exposure (SWI) for bivalve larva toxicity instead of elutriate testing for toxicity. Toxicity testing for amphipods will continue to be done with the elutriate method. TIEs will be conducted in samples that show significant toxicity.
L	2008	Intercomparison study pesticide water analysis conducted by AXYS was performed using MRES method on samples collected on 100L infiltrix system. In previous years pesticides were analyzed using GC/LRMS which could not detect chlorpyrifos/diazinon.	The MRES method is able to detect the standard suite of RMP pesticides including chlorpyrifos/diazinon (Oxadiazon is not tested for using MRES). These results are not reported on the Web Query Tool.
P	2008	Benthos sampling was added as part of the sediment sampling cruise	With all three lines of evidence (i.e., benthos, sediment chemistry and sediment toxicity), it will be possible to conduct sediment assessments in accordance with the Sediment Quality Objectives (SQOs), which are scheduled to be promulgated in 2008.
P	2008	Began reporting water particulate trace organic results.	New design of web query tool makes it easier to post particulate results.
A	2009	The RMP PCB list was expanded from 40 congeners to 209 congeners	The non-Aroclor PCB, PCB 11, was unexpectantly found in air samples, prompting the expansion of the RMP PCB congener list to include all possible congeners
A	2009	Whole water samples were collected at 22 sites for analysis of pesticides	Whole water samples are collected for the analysis of pesticides using MRES methods.
A	2009	Cyanide was analyzed in water	New site specific objective was developed for cyanide in water in SF bay
A	2009	Dioxins were analyzed for all 22 water stations, all 47 sediment stations, and in sportfish	Data will fill the dearth of information that currently exists for dioxin. Not part of S&T. 5 year special study.
A	2009	Dioxins were added as part of the Small Tributary Loading Study	Data will fill the dearth of information that currently exists for dioxin. Not part of S&T. 5 year special study.
A	2009	PFC samples were collected at a subset of	Special Study - Added because of concern over elevated concentrations found in Bay Area environmental

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Action Code	Year	Action	Detail/Rationale
		water stations	samples as compared to reference samples.
A	2009	PFC analysis was added to bird samples	Part of Exposure and Effects Pilot Study.
A	2009	PFC analysis was added to sportfish samples	Part of Emerging Contaminants Pilot Study.
A	2009	Water PAHs were not analyzed	Due to the Cosco Busan oil spill, PAHs were analyzed in 2008. Since no significant changes in the water column were identified, PAH sampling was skipped in 2009 and the biennial sampling schedule was resumed. Water PAHs are scheduled to be sampled again in 2010.
A	2009	Oxadiazon was dropped from the RMP target analyte list	The different MRES method for analyzing pesticides in water adopted by the RMP doesn't analyze for oxadiazon. Since concentrations of oxadiazon have remained relatively constant over time, the TRC approved removing it from the target list in July 2009.
D	2009	Water PBDEs 196, 201, and 202 are not available.	AXYS has not developed a method for analyzing these PBDEs.
L	2009	Contra Costa Sanitation District will analyze water for cyanide	New analyte for analysis in water only
P	2009	Dioxins were analyzed in water, sediment, sediment core, bird egg, small tributary loading, and sportfish samples	The Dioxin Pilot Study is not part of the S&T component but samples were collected during regular RMP sampling events.
P	2009	Changed the statistical design for sediment sampling from five-year panels to six-year panels	Changed to incorporate wet weather sediment sampling which will occur every other year starting in 2010. Wet weather sampling will occur at 20 random sites and 7 historic sites. Dry weather sampling will continue to occur at 40 random sites and 7 historic sites.
D	2010	TRC cancelled scheduled analysis of archived 2006 and 2007 water samples for Diazinon and Chlorpyrifos	Initially, water samples were stored during method development, to be analyzed once analytical issues were resolved. These issues have since been resolved. In 2010, TRC decided to cancel the analysis due to the high cost ($60,000) and the lack of a pressing need for the data
P	2010	Sediment samples will be collected in alternate seasons starting with a wet season (winter) sampling event in February 2010.	There appears to be a seasonal element to sediment toxicity with winter sampling exhibiting higher toxicity. 27 samples will be collected during the dry season and 47 samples will be collected during the wet season.

RMP

Regional Monitoring Program
for Water Quality
in the San Francisco Estuary

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