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

2009
RMP ANNUAL MONITORING RESULTS

San Francisco Estuary Institute Contribution No. 629

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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 among the scientific community, the San Francisco Bay Regional Water Quality Control Board (Water Board), and the regulated discharger/dredging 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 $3.9 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 Status and Trends portion of the program includes long-term monitoring of San Francisco Bay, while Pilot and Special Studies change annually in response to changing management priorities and stakeholder needs.

The RMP is overseen by the Technical Review Committee (TRC), the Steering Committee (SC) and five workgroups, which consist of scientists who are currently studying the Bay, invited scientists who are nationally recognized experts in their field, and federal and state regulators. The TRC oversees the activities of the workgroups and the technical content of the RMP as a whole. The SC determines the overall budget, allocation of program funds, tracks progress, and provides direction to the Program from a manager's perspective. The five workgroups, the Sources, Pathways and Loadings Workgroup, the Exposure and Effects Workgroup, the Contaminant Fate Workgroup, the Emerging Contaminants Workgroup, and the Sport Fish Workgroup directly guide planning and implementation of Pilot and Special Studies and provide input on relevant aspects of the annual RMP Status and Trends monitoring. These workgroups meet several times a year to review progress and make recommendations. In 2009, strategy documents and long-term work plans were developed that articulated the priority questions to be answered and the longer-term information needs. Strategy documents have been developed for a number of topics including: small tributaries, modeling, mercury, polychlorinated biphenyls (PCBs), and dioxins. RMP Workgroups have also developed long-term plans for studies of emerging contaminants and contaminant exposure and effects. These strategy documents and work plans lay the foundation for future environmental monitoring. These information needs and priorities have been summarized in the RMP Master Plan.

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 TRC and 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?
    d. What contaminants are responsible for observed toxic responses?
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?

Status and Trends monitoring characterizes water and sediment quality and contaminants in water, sediment, and tissue in the Estuary. The Water Board uses Status and Trends data for regulatory purposes, such as evaluating the Estuary for 303(d) listing of water bodies, calculating National Pollutant Discharge Elimination System (NPDES) permit conditions, estimating Total Maximum Daily Loads (TMDL), and evaluating whether management actions are successful in reducing contaminant loads to the Estuary through modeling. For questions regarding the RMP Status and Trends contact Meg Sedlak , Meg@sfei.org.

Status and Trends monitoring 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. Water toxicity is monitored on a five-year cycle and was last conducted in 2007. For details of the 2009 water sampling event see the Water Chapter or visit the Status and Trends web page.

- 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. The RMP monitors for sediment toxicity annually. For details of the 2009 sediment sampling event see the Sediment Chapter or visit the Status and Trends web page.

- The RMP's bivalve bioaccumulation monitoring effort augments the long-term monitoring effort started by the State Mussel Watch Program. The current monitoring design includes the analysis of trace organics biennially and trace elements every 5 years. Bivalves were last analyzed for both trace element and trace organic parameters in 2008. Refer to the Bivalve Chapter in the 2008 AMR or visit the Status and Trends web page.

- 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 with three lines of evidence (i.e., benthos, sediment chemistry and sediment toxicity) to conduct sediment assessments. Benthos samples are collected during scheduled RMP sediment sampling events at 27 sites (20 random sites and 7 historic sites).

- The Sport Fish Contamination Study triennially screens fish tissue for contaminants of concern to human health. Sport fish sampling includes evaluation of key fish species for long-term trend assessment, combined with follow-up sampling of additional species. The 2009 RMP sport fish sampling was part of a two-year statewide evaluation of bioaccumulation in sport fish along the entire coast of California by the State Water Board's Surface Water Ambient Monitoring Program (SWAMP). Year 1 of the program focused on the Southern California Bight and the northern California coast near San Francisco Bay. Year 2 will cover the remaining areas of the State. A similar sampling design to that used in the Bay by the RMP will be used for the entire State, allowing comparison of RMP data to results for similar species across California. The SWAMP report is expected to be available to the public in the spring of 2011. The results from sampling popular sport fish species for mercury, PCBs, organochlorine pesticides, and PBDEs in 1994, 1997, 2000, 2003, and 2006 at several fishing locations are available 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.

- The United States Geologic Survey (USGS) has collaborated with the RMP since the beginning of the Program. During 2009, it continued to supplement RMP monitoring with two on-going studies that address basic hydrographic and sediment transport processes. The Hydrography and Phytoplankton study collects 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. Details on this study can be found on our web site. For more information refer to the *2006 Pulse of the Estuary* article What is Causing the Phytoplankton Increase in San Francisco Bay?

  The Sediment Dynamics in San Francisco Bay study examines the role of several physical factors controlling suspended sediment concentrations in the Estuary for a variety of hydrologic, tidal, and wind conditions and generates time series measurements for calibration and validation of sediment transport models. Time series measurements of suspended sediment concentrations are collected at six sites using optical backscatter sensors deployed at mid-depth and near the bottom. Details on this study can be found on our web site and in the *2003 Pulse of the Estuary* article Sediment Dynamics Drive Contaminant Dynamics and the *2009 Pulse of the Estuary* article Suspended Sediment in the Bay: Past a Tipping Point.

In 2007, the RMP's long-term Status and Trends was expanded to include bird egg monitoring, providing much needed information about bioaccumulative substances in higher trophic-level biota.

- Triennial bird egg monitoring (cormorant and tern) took place in 2009. This element of the Status and Trends Program will help us understand spatial patterns of contaminant uptake into the food web and trends in biota over time. Cormorant and tern bird egg monitoring was included as part of the Status and Trends Program in 2008, with triennial sampling beginning in 2009. Cormorant eggs were analyzed for mercury, selenium, PBDEs, perfluorinated compounds, PCBs, and pesticides. Tern eggs were analyzed for mercury, selenium and PBDEs. Analysis of dioxin in bird eggs is deferred until 2012.

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 2009 are discussed later in this chapter. A summary of previous studies conducted by the RMP can be found by going to the Previous Pilot and Special Studies web page or by reading previous publications of the Annual Monitoring Results report. Specific details on the study development and selection processes can be accessed via the Selection Process web page.

The RMP synthesizes and distributes the results of our monitoring and studies 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, which are available on the web at RMP Documents and Reports. For more information on the RMP, refer to the RMP home page.

CHANGES TO THE STATUS AND TRENDS PROGRAM

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. Table 1.1 lists changes to the program during 2009 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 that conduct analyses, and significant changes in laboratory methods. A table of changes to the RMP since its inception in 1993 can be found in Appendix 9. Tables of reported analytes by matrix for the long-term Status and Trends monitoring of water, sediment, and bivalve tissue beginning in 1993 can be found in Appendices 6-8.

Table 1.1. Summary of Changes for the RMP Status and Trends Program, 2009

Action Codes: A= Analyte added or removed from sampling design; D= Data rejected or not available/data comparability issues; 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	2009	The RMP PCB list was expanded from 40 congeners to 209 congeners for all matrices.	The non-Aroclor PCB, PCB 11, was unexpectedly observed in air and effluent samples outside the Bay Area in significant concentrations, 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. Beginning in 2009, pesticides analyzed using the MRES method are considered the RMP's target analytes.
A	2009	Cyanide was analyzed in water.	New site specific objective was developed for cyanide in water in San Francisco Bay.
A	2009	Dioxins were analyzed for all 22 water stations, all 47 sediment stations, and in sport fish.	Data will fill the dearth of information that currently exists for dioxin. This is a 5 year special study that is not a part of the Status and Trends Component.
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. This is a special study.
A	2009	PFC samples were collected at a subset of water stations.	Special Study - Added because of concern over elevated concentrations found in Bay Area tissue samples as compared to reference samples from Tomales Bay.
A	2009	PFC analysis was added to bird samples.	Part of Exposure and Effects Pilot Study.
A	2009	PFC analysis was added to sport fish samples.	Part of Emerging Contaminants Special Study.
A	2009	Water PAHs were not analyzed.	Due to the Cosco Busan oil spill, PAHs were analyzed in 2008. Because no significant changes in the water column were identified, PAH sampling was skipped in 2009 and 2010. Water PAHs are scheduled to be sampled again in 2011.
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 include 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 detecting these PBDEs in water.
D	2009	2009 total cyanide water results are not reported.	The RMP's previous California Toxics Rule (CTR) work was based on the Weak Acid Dissociable (WAD) fraction. Total cyanide will most likely give an over-estimation of the bio-available fraction. Several of the 2009 total cyanide water results were above the cyanide trigger level (1.0 ug/L) for ambient monitoring as stated in the Basin Plan Amendment, which is based on the WAD fraction. Hence, at the request of the Water Board these samples were not reported to avoid confusion.
L	2009	Contra Costa County 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 sport fish samples.	The Dioxin Pilot Study is not part of the Status and Trends 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 rainy season sediment sampling which will occur every other year starting in 2010. Rainy season sediment sampling will occur at 20 random sites and 7 historic sites. Dry season sediment sampling will continue to occur at 40 random sites and 7 historic sites.
P	2009	Added Pesticides Fipronil, Fipronil desulfinyl, Fipronil sulfide, and Fipronil sulfone for sediment analysis	These pesticides are highly used in the Bay Area and are of emerging concern. Fipronil is widely-used in flea/tick applications. It is exceedingly toxic to insects/crustaceans. There is relatively little Bay Area data so it would be very helpful to report these data when available.

Changes to the Sampling Design for Water and Sediment

2009 was the eighth year of the 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 goals to collect data and communicate information about water quality in the San Francisco Estuary in support of management decisions. An important advantage of random station 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 water and sediment stations were retained from the original RMP monitoring design, established in 1993, to provide continuity in the long-term monitoring program.

The RMP water and sediment monitoring stations are located in six hydrographic regions of the Estuary. Random design stations are located in five of those regions: Suisun Bay, San Pablo Bay, Central Bay, South Bay, and Lower South Bay. Historic stations are also located in each of those five regions, and additionally 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 stations 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 stations were allocated into the hydrographic regions. Each year, a subset of the water stations are sampled in sequential order, increasing the spatial density of monitoring over time. For sediment, a station re-visit schedule was incorporated into the design to better evaluate trends over time.

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 sites and 7 historic sediment sites (a total of 31 water and 47 sediment sites). A second power analysis was conducted in 2006 using the random design data (Melwani et al. 2008). Based on those results for key contaminants of current concern 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 beginning in 2007, while the number of sediment sites was maintained at 47 sites per year.

In 2007/2008, a new redesign review was undertaken by the TRC. After a statistical review and consultation with the RMP participants, the RMP decided to add wet weather sediment sampling back into the Status and Trends program and recommended that wet weather sediment sampling be conducted biennially. The addition of wet weather sampling (typically done in February) will provide monitoring of contaminants that have higher ambient concentrations during the winter when runoff increases. Dry season sampling continues to include eight random sites per region (n = 40). Wet season sampling will include four random sites per region (n = 20). Sampling of the historic stations will not change and samples from these sites will continue to be collected during each sampling event (maintaining one station per region plus the two Rivers stations (n = 7)). This change was first implemented in August/September 2009 (a dry season sampling year). The change in design necessitated an update from a five-year repeat sampling cycle to a six-year repeat sampling cycle to allow for balanced alternating season sampling.

See the Memorandum on our web page for more details. Sites sampled in 2009 are listed in Appendix 3 and Appendix 4 for water and sediment, respectively.

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*.

Parameter Monitoring Changes

During 2008, the RMP began monitoring trace organic parameters in water biennially with the exception of PBDEs which will continue to be monitored annually. A table of analytes reported in water samples analyzed from 1993-2009 is available in Appendix 6.

The analyte list for sediment parameters remained the same as in 2008 with the addition of four pesticides fipronil, fipronil desulfinyl, fipronil sulfide, and fipronil sulfone. These parameters were added because they are commonly used in the Bay Area and are of emerging concern.

RMP WORK GROUPS

Five workgroups address the major technical subject areas covered by the RMP. Workgroups consist of scientists, regulators, stakeholders and nationally recognized experts who serve to advise the workgroups. 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 Work Group

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 to the Bay. The SPLWG ensures that RMP projects and products are relevant and help to answer developing management questions in the context of TMDLs and attainment of water quality standards. For further information, see the SPLWG web page.

Contaminant Fate Work Group

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. See the CFWG web page for further information.

Exposure and Effects Work Group

The Exposure and Effects Work Group (EEWG) developed a five-year biological effects pilot study (the Exposure and Effects Pilot Study (EEPS)) that would help address beneficial use management questions developed by the Regional Board. At the end of the study, EEWG 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 Work Group

The Emerging Contaminants Work Group (ECWG) evaluates the presence of emerging contaminants in the Estuary, defined as chemicals that are not currently regulated, but believed to potentially pose significant ecological or human health risks (e.g., pharmaceuticals, flame retardants, and perfluorinated compounds). For additional information see the ECWG web page.

Sport Fish Work Group

The Sport Fish Work Group (SFWG) guides the effort to collect and analyze select species of sport fish for target parameters of concern (e.g., mercury, PCBs and dioxins) in the San Francisco Estuary. The Sport Fish Study is a human health study and various thresholds are used to evaluate sport fish contaminant concentrations. For additional information visit the SFWG web page.

STRATEGY DEVELOPMENT

In addition to the work groups, teams from the workgroups and RMP stakeholders have been developing strategies for select issues that are of high priority to our stakeholders including a dioxin strategy, a modeling strategy, a mercury strategy, a PCB strategy and a small tributary loading strategy. A brief summary of strategies that have been completed are listed below. The crosswalk between the work plans and the strategies has been articulated in a five-year Master Plan for the RMP.

Dioxin Strategy

A dioxin strategy team was convened in September 2008 to discuss information gaps. At that time, a dioxin strategy plan was prepared including priority questions and a five-year plan. The following questions articulate the needs and priorities for obtaining information on dioxins in the Bay:

1) Are the beneficial uses of San Francisco Bay impaired by dioxins?
2) What is the spatial pattern of dioxin impairment?
3) What is the dioxin reservoir in Bay sediments and water?
4) Have dioxin loadings/concentrations changed over time?
5) What is the relative contribution of each loading pathway as a source of dioxin impairment in the Bay?
6) What future impairment is predicted for dioxins in the Bay?

Funds were allocated for dioxin analyses of surface sediment samples from the 2008 RMP Status and Trends collection effort and dioxin analyses of the 2006 sediment cores. In 2009, additional funds were allocated to fund analysis of sport fish, surface sediment (from RMP Cruise), surface water (from RMP Cruise), small tributaries, and atmospheric sampling. Funding will also be used for developing laboratory QA/QC protocols and intercomparisons. For additional information contact Susan Klosterhaus (Susan@SFEI.org) or Don Yee (Don@SFEI.org).

Mercury Strategy

The RMP Mercury Strategy was formed in 2008 to articulate key questions that scientists and managers need to answer for the best management of mercury in the Bay. The Mercury Strategy addresses five priority questions:

1) Where and when is mercury entering the food web?
2) What are the high leverage processes, sources, and pathways?
3) What are the best opportunities for management intervention?
4) What are the effects of management actions?
5) Will total mercury reductions result in reduced food web accumulation?

Based on the strategy, a request for proposals to address the first two key questions was sent out nationally to solicit studies to answer these questions. Of the number of meritorious proposals received, two were selected: a study of the use of mercury isotopes to identify potential sources; and the use of diffusive gradient in thin films (DGTs) to assess uptake of methylmercury into the foodweb. The Estuary Newsletter featured an article in the Winter 2010 newsletter highlighting some of the findings from the mercury isotope study entitled Tracking Mercury Signatures in Bay Sediments. These studies are discussed in more detail in the Special Studies section of this chapter. Additional information about these studies is on our web site. For more information on the RMP Mercury Strategy see this power point presentation.

Modeling Strategy

In 2009, the Modeling Strategy Team and the Contaminant Fate Workgroup identified the following priority questions:

1) What is the contribution of contaminated Bay margins to Bay impairment and what are the projected impacts of management actions to Bay recovery?

2) What patterns of exposure are forecast for major segments of the Bay under various management scenarios?
3) What are the projected impacts of management actions on loads or concentrations of pollutants of concern from high-leverage small tributaries?

Small Tributary Loading Strategy

In 2009, the Small Tributary Loading Strategy (STLS) Team (RMP stakeholders, SFEI staff, and RWQCB staff) developed a Small Tributary Loading Strategy to identify and prioritize the information that is most urgently needed by managers to reduce loads and impacts of pollutants of concern (POC) entering the Bay from small tributaries strategy. The STLS team worked to ensure that the strategy was integrated with the requirements in the Municipal Regional Stormwater Permit (MRP). The STLS team articulated the following high priority management questions:

1) Which are the "high-leverage" small tributaries that contribute or potentially contribute most to Bay impairment by pollutants of concern?
2) What are the loads or concentrations of pollutants of concern from small tributaries to the Bay?
3) How are loads or concentrations of pollutants of concern from small tributaries changing on a decadal scale?
4) What are the projected impacts of management actions on loads or concentrations of pollutants of concern from the high-leverage small tributaries and where should management actions be implemented in the region to have the greatest impact?

For additional information contact Lester McKee (lester@sfei.org).

PCB Strategy

PCBs are a pollutant of high concern in San Francisco Bay. This strategy has been developed to ensure that the RMP is providing the information most urgently needed by managers to find remedies to the Bay's PCB problem. The following management questions have been articulated to identify the information most urgently needed as a basis for the decisions listed above.

1) What are the rates of recovery of the Bay, its segments, and in-Bay contaminated sites from PCB contamination?
2) What are the present loads and long-term trends in loading from each of the major pathways?
3) What role do in-Bay contaminated sites play in segment-scale recovery rates?
4) What management actions have the greatest potential for accelerating recovery or reducing exposure?
5) What are appropriate guidelines for protection of beneficial uses?
6) What is the total maximum daily load of PCBs that can be discharged to the Bay without impairment of beneficial uses?
7) What potential for impacts on humans and aquatic life exists due to contaminants in the Estuary ecosystem?

RMP PILOT AND SPECIAL STUDIES

Pilot and Special Studies allow for adaptive management of the RMP by allowing for short-term projects based on the changing regulatory priorities, management of the Estuary, and scientific understanding of the Estuary. Summaries of the 2009 Pilot Study and Special Studies can be found on our web site.

Pilot Studies

Pilot studies augment Status and Trends monitoring by focusing on specific topics and providing 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).

Annual Small Fish Monitoring (2005 – 2010)

Contact: Ben Greenfield (ben@sfei.org)

Annual small fish monitoring has taken place since 2005 as part of the Exposure and Effects Pilot Study. Small fish are excellent indicators of biological uptake of contaminants, particularly mercury. 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? (2) Where are the highest mercury concentrations found in the nearshore portions of the system? The small fish study started a focused three-year intensive study in 2008 to determine hotspots of methylmercury bioavailability by monitoring mercury concentrations in small fish and sediments. The results of the three-year study will be summarized in a report in 2011.

Tributary Loading Studies (2002 – ongoing)

Contact: Lester McKee (Lester@sfei.org)

Tributary Loading Studies include monitoring small tributary loading (annual), large tributary loading (Mallard Island, triennial), and Guadalupe River loading (triennial). These studies will help us understand the sources of contaminants and the pathways by which they reach the Bay. During water year 2009/2010, samples were collected at a small tributary located in an industrialized area of Hayward (referred to as Zone 4 Line A), at two locations, on the Guadalupe River and at Mallard Island. A detailed look at the Tributary Loading Studies strategies and conclusions to date is available in the 2010 publication of The Pulse of the Estuary – Linking Watersheds and the Bay. For more information refer to the featured article "Advances in Understanding Pollutant Mass Loadings from Rivers and Local Tributaries" in the 2008 Pulse of the Estuary.

Special Studies

Special Studies help the RMP address either specific gaps in data 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 2009:

- CONTINUED DEVELOPMENT OF MERCURY TOXICITY THRESHOLDS FOR EGG HATCHABILITY IN FORSTER'S TERNS
- GUADALUPE RIVER WATERSHED MODEL – YEAR 2
- IDENTIFICATION OF SOURCES OF PERFLUORINATED COMPOUNDS TO SAN FRANCISCO BAY
- IMPACTS OF PAH-CONTAMINATED SEDIMENT ON EARLY LIFE HISTORY STAGES OF BENTHIC FISH, YEAR 2
- MERCURY STRATEGY STUDIES – YEAR 2
    - USE OF MERCURY ISOTOPES TO DETERMINE SOURCES
    - USE OF DIFFUSIVE GRADIENT IN THIN FILMS (DGTS) TO DETERMINE SOURCES OF BIOAVAILABLE METHYLMERCURY
- WHITE PAPER ON CONTAMINANTS OF CONCERN IN WASTEWATER EFFLUENT

Continued development of Mercury toxicity thresholds for egg hatchability in Forster's Terns

Contact: Jen Hunt (Jen@sfei.org)

The goal of this project is to develop egg thresholds for mercury. The USGS has developed a method in which a small amount of the individual egg albumen is sampled for mercury using micro-techniques. The amount of albumen is so small that the egg remains viable. The egg is then tracked to determine the success of the hatch and chick survival. The USGS began implementation of this technique in 2007 and will build upon the information collected to date. The USGS will donate in-kind services to complete this project. Results from this study were published in 2010 in the report Developing Impairment Thresholds for the Effects of Mercury on Forster's Tern Reproduction in the San Francisco Bay.

Guadalupe River Watershed Model – Year 2 (2008-2010)

Contact: Michelle Lent (michelle@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).

This multi-year project began in 2008. In 2008, a model was developed based on land use maps, precipitation, topography, and runoff. In 2009, continued testing of the model will occur and the model will be updated to include sediment transport. A draft report of the model will be prepared and distributed for review.

Identification of Sources of Perfluorinated Compounds to San Francisco Bay

Contact: Meg Sedlak (meg@sfei.org)

The preliminary results of the RMP pilot study evaluating perfluorinated compounds (PFCs) in Pacific Harbor Seals indicate that concentrations of these compounds are an order of magnitude higher in San Francisco Bay seals than those seals sampled at the reference site (Tomales Bay, approximately 45 miles to the north of San Francisco Bay). This study provides data on several of the pathways to the Bay in an attempt to understand the sources of significant concentrations observed in San Francisco Bay biota.

Water from the San Francisco Bay (2009) and small fish (2009) were sampled to determine the reservoir of PFCs in the Bay and concentrations in prey animals, respectively. In addition, small fish have high site fidelity and may indicate potential source areas. Wastewater effluent was also sampled as it is believed to be a potentially significant source to surface waters. Sediment from potential hotspots (e.g. former landfills, naval fleets and airports) was also analyzed. Lastly, this study will collaborate with the tributary loading studies to collect information on tributary loads of PFCs.

Impacts of PAH-contaminated Sediment on Early Life History Stages of Benthic Fish, Year 2

Contact: Meg Sedlak (meg@sfei.org)

This is the second year of funding for a two-year project evaluating the effects of PAH-contaminated sediments on the development of juvenile flatfish. The impacts of pyrogenic PAHs (like those detected in San Francisco Bay) on juvenile flatfish development are largely unknown. In the first year, the effects of pyrogenic (higher molecular weight) PAHs on a model fish such as zebra fish was evaluated.

After the identification of biological endpoints with a model fish species, in the second year, the study will examine a native species, California halibut. In addition, environmental sediment samples with a PAH signature similar to San Francisco Bay will be used. This work will continue into 2011. A manuscript on PAH effects to the model fish is currently in preparation.

Mercury Strategy Special Studies – Year 2

Contact: Ben Greenfield (Ben@sfei.org)

The following studies are being conducted in an effort to help answer the questions proposed by the Mercury Strategy team:

1. Where is mercury entering the food web?
2. Which processes, sources, and pathways contribute disproportionately to food web accumulation?

USES OF MERCURY ISOTOPES TO DETERMINE SOURCES

The University of Michigan group led by Dr. Joel Blum evaluated whether mercury isotopes can be used to identify sources of mercury to the aquatic food web. Working in conjunction with the Diffusive Gradient in Thin Film project discussed below and the small fish mercury project, these researchers will collect sediment, water, small fish and atmospheric samples from a number of Bay Area locations to evaluate whether certain sources are contributing more to the uptake of methylmercury in biota. A summary of this work is presented in the 2010 Estuary Newsletter, Tracking Mercury Signatures in Bay Sediments. Findings from this study were reported in two journal articles Mercury Isotopes Link Mercury in San Francisco Bay Forage Fish to Surface Sediments and Sources of Mercury to San Francisco Bay Surface Sediment as Revealed by Mercury Stable Isotopes.

USE OF DIFFUSIVE GRADIENT IN THIN FILMS (DGTS) TO DETERMINE SOURCES OF BIOAVAILABLE METHYLMERCURY

The Trent University group led by Dr. Holger Hintelmann worked with the University of Michigan group and the RMP small fish project to assess the uptake of methylmercury using diffusive gradient in thin films (DGTs). A draft report summarizing these results has been prepared, "DGT (Diffusive Gradient Thin-film) as a Tool to Assess Sources of Bioavailable Methyl Mercury to San Francisco Bay". It is currently undergoing workgroup review.

Profiles on Contaminants of Concern in Wastewater Effluent

Contact: Susan Klosterhaus (Susan@sfei.org)

This special study evaluated three emerging contaminants (triclosan, carbamazepine and alkylphenol ethoxylates) from wastewater treatment facilities. The profiles of the contaminants reviewed literature to obtain ranges of concentrations likely to be observed in effluents, and evaluate these data in the context of literature values and effects thresholds. These three profiles are undergoing review by the Emerging Comtaminants Work Group (ECWG).

ANNUAL MONITORING ONLINE GRAPHICS AND DATA ACCESS TOOLS

Web Query Tool

The 2009 data are now available online using a dynamic mapping and graphing tool. The online Web Query Tool allows water, sediment, and tissue monitoring results from 1993 to 2009 to be summarized graphically for many trace contaminants and important ancillary measures. The Web Query Tool displays the data graphically on maps and in cumulative distribution function (CDF) plots (Figure 1.1).

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.

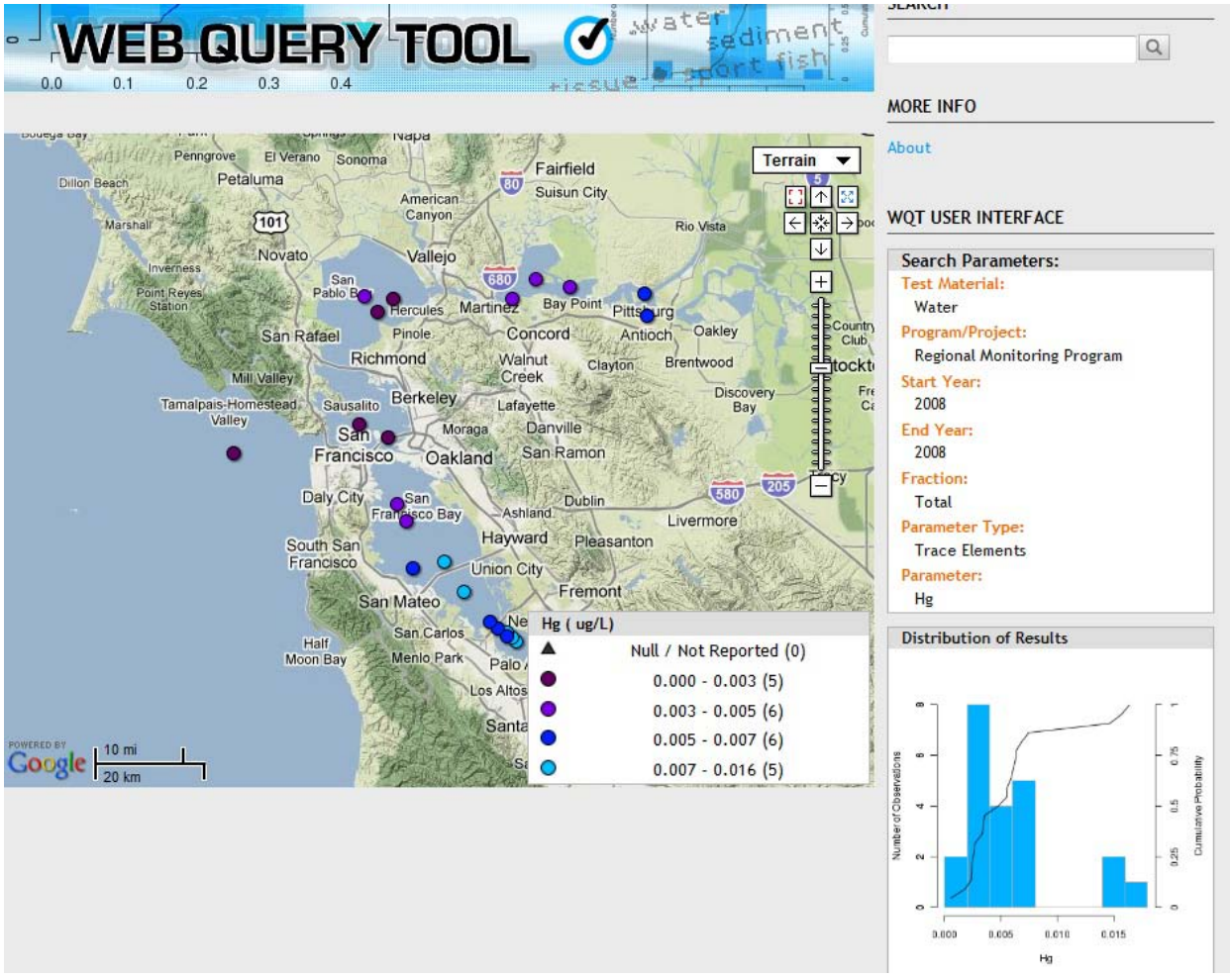

Figure 1.1 Web Query Tool Map Interface

All RMP results, from 1993-2009, can be downloaded 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 below the method detection limit (MDL) are estimated to be ½ of the MDL in all calculations and graphics. Some organic compounds are summed based on the target list of RMP congeners (*Appendix 5*) for that specific compound group (e.g., PBDEs, PAHs, and PCBs). When laboratory or field replicate data are available, the average of all the replicate concentrations is provided.

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2
WATER MONITORING

2. WATER MONITORING

BACKGROUND

Trace contaminants are introduced into 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 *Shana Rae* between August 23 and September 3, 2009.

CHANGES IN WATER SAMPLING

The Status and Trends program for water and sediment was revised in 2002 to include a randomized sampling design. From 2002 to 2006, five historic stations and 26 randomly allocated stations in each Bay segment were monitored for contaminants in water. 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. The five historic sites continue to be sampled.

During the first four years (1993-1996) 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 Analytical Services 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.

As of 2008, water samples are analyzed annually for PBDEs and biennially for PCBs, PAHs, and legacy pesticides. This reduction in sampling frequency for PCBs, PAHs, and legacy pesticides was based on recommendations from the redesign process and is discussed in detail in the report Power Analysis and Optimization of the RMP Status and Trends Program. In 2008, an exception was made to analyze water for PAHs as a result of the recent Cosco Busan oil spill that occurred in November 2007. 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 2011. See *Appendix* 5 for the 2009 target analyte list and *Appendix* 6 for a table of analytes reported by the RMP in water from 1993-2009.

SAMPLING SITES

For 2009, RMP Status and Trends Program continued with implementation of the stratified, random sampling design started in 2002 and revised in 2007. Water sampling for the Status and Trends Program is currently only conducted during the dry season, specifically in late summer.

In 2009, 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. Sampling of the 22 sites was successfully completed, with the following changes made to the sampling plan. Site SU032W was abandoned during the planning process, as it was located inside the restricted zone surrounding the Concord Naval Weapons Station. The first oversample site in the region, SU033W, was located in approximately 4 feet of water depth relative to mean lower low water, and so SU032W was instead replaced with the next oversample site, SU034W. Site LSB041W was inaccessible due to shallow water and was replaced with LSB043W. The actual sampling site for LSB043W was shifted by approximately 150m due to underground pipes. Site SB056W was inaccessible due to shallow water and was replaced by SB057W. All other stations were sampled according to the proposed water cruise plan.

Station names, codes, location, and sampling dates for 2009 are listed in Appendix 3. A map of the station locations is shown in Figure 2.1.

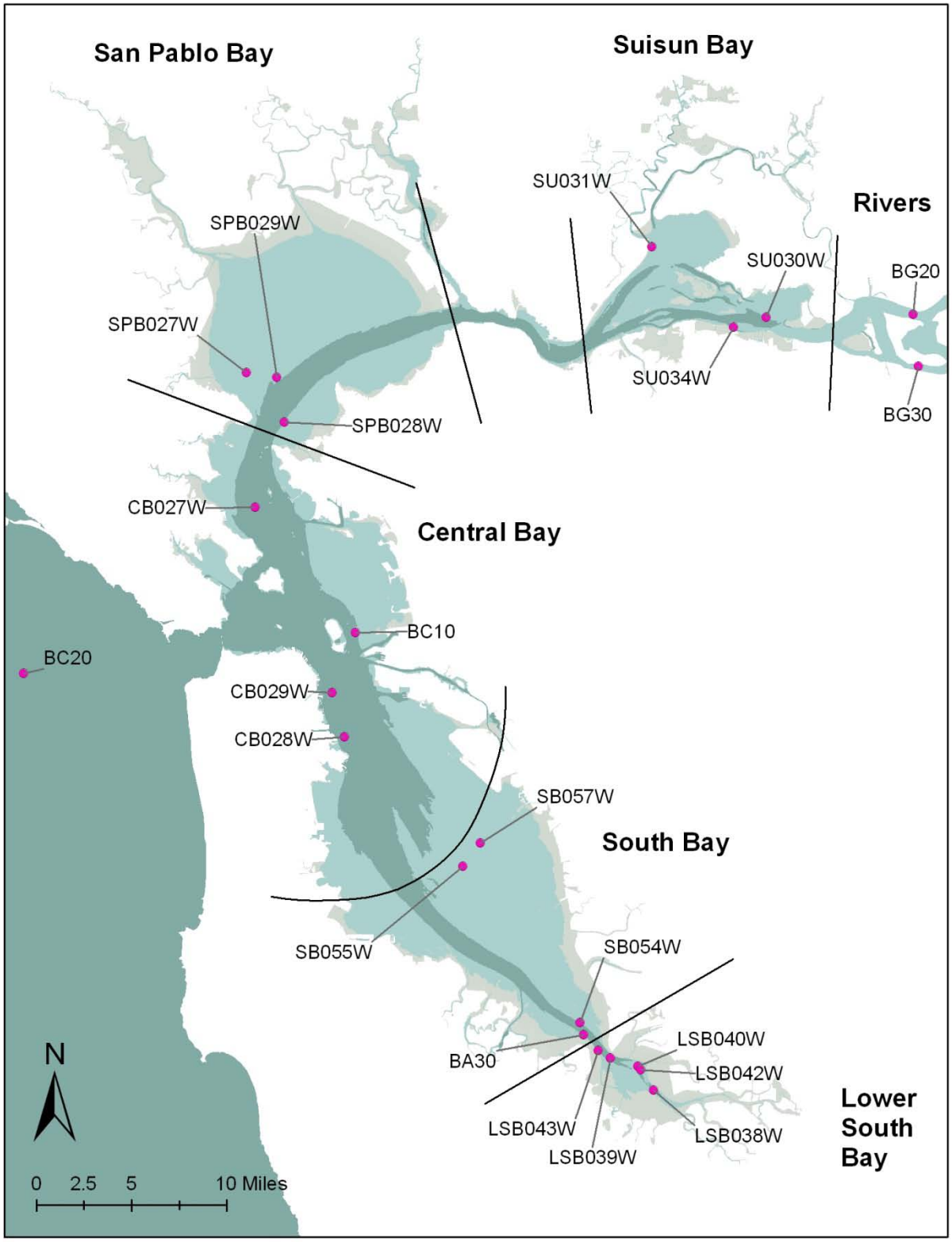

Figure 2.1 Map showing location of 2009 Water Stations

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 Applied 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 the AXYS Infiltrex system. Whole water samples were collected to evaluate the adsorption capacity of the Infiltrex filter system.

Collection of Samples for Trace Organics

Water for analysis of trace organics was collected one meter 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 retention of 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 was passed 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.

In 2009, pesticide samples were inadvertently not collected at site LSB038W.

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 using “clean hands, dirty hands” techniques. 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 sampling.

For 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 Data and 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).

Conductivity, temperature and depth (CTD) casts were taken at all stations to document their water column profiles. CTD casts were taken by AMS 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).

In 2009, CTD data were captured only for an at-depth cast at site BA30, and for only a partial cast at site LSB034W.

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 intervals 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 2009. The next aquatic bioassay sampling will occur in 2012.

LABORATORY METHODS FOR WATER ANALYSIS

SFEI contracts with a number of laboratories that provide high quality analytical services. Qualifications for our labs include ISO registration, NELAP accreditation and certification by the California Department of Public Health. SFEI maintains copies of SOPs for all laboratory analyses. Please contact SFEI (Cristina@sfei.org) for more details.

Laboratory Methods for Water Quality Parameters

In 2009, 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 in 2008. In 2009, CAS determined particulate organic carbon concentration using EPA Method 9060M, using a carbonaceous analyzer.

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. In the past Ammonium as N has been analyzed using EPA method 350.1 by flow injection analysis. In 2009, it was measured using a method based on the indophenol reaction with o-phenylphenol (OPP) (Solorzano, L., 1969). 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(s) SM 10200 H-2aM and SM 10200 H-2bM, respectively, using spectrophotometric determination. Suspended sediment concentration was measured using Standard Method SM 2540DM in 2008 and ASTM D3977 in 2009. 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).

Laboratory Methods for Trace Elements

Water samples for Trace Elements (Ag, As, Cd, Co, Cu, Fe, Ni, Hg, MeHg, Pb, Se, and Zn) were analyzed by Brooks Rand Labs LLC (BR). All results will be reported for 2009

Upon receipt by the lab, all samples to be 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).

BR determined concentrations of Ag, As, Cd, Co, Cu, Ni, Pb, and Zn by reductive precipitation, followed by filtration, and measured using inductively coupled plasma-mass spectrometry (ICP-MS) by EPA Method 1640. Mn and Fe concentrations were 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, BR, and the column chelating method used by the City of San Jose (CSJ) and UCSC. In 2008 and 2009, a laboratory inter-comparison exercise was conducted for analyses of copper and nickel using the two different methods by CSJ and BR. The results showed good agreement between the reductive precipitation method and the column chelating methods. Both labs followed procedures outlined in EPA Method 1640.

BR results for iron in the total water fraction were much lower than previous years (2002-2006) and those data were not reported in 2008 based on professional judgment. In 2009, water samples were analyzed and reported by BR using Inductively Couple Plasma - Mass Spectrometry (ICP-MS) in accordance with the modified EPA Method 1638. Selenium analysis was also conducted by BR using preconcentrations and ICP-MS in accordance with EPA Method 1640.

Total Mercury Analysis in Water Samples

In 2009, total mercury analysis of water samples was conducted by BR. 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. BR 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 2009, total methylmercury analysis of water samples was conducted by BR. 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.

BR 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 2009, trace organic water analyses were conducted for PCBs, pesticides, PBDEs, Dioxins and Furans. Appendix 5 contains a list of individual parameters reported by the RMP in 2009 and *Appendix* 6 contains a table of analytes reported by the RMP in water from 1993-2009.

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. Please contact SFEI (Cristina@sfei.org) for more details. Pesticides (AXYS MLA-035), PBDEs (AXYs MLA-033) PCBs (AXYS MLA-010) and Dioxins (AXYS MLA-017) were analyzed by AXYS Analytical Services Ltd. (AXYS).

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.

PBDEs were analyzed using a modified version of EPA 1614. 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).

Starting in 2008, AXYS has analyzed water samples for Dioxins and Furans using a procedure that in is general accordance with USEPA Method 1613, Revision B. Extracts were spiked and cleaned up using acid/base silica, Florisil and Alumina chromatographic columns prior to instrumental analysis. Analysis was then performed using a high-resolution mass spectrometer coupled to a high-resolution gas chromatograph equipped with a DB-5 capillary chromatographic column. A second column was used for confirmation of specific congener identification.

Prior to 2008, AXYS used gas chromatography coupled to low resolution mass spectrometry (GC/LRMS) to determine pesticides in water. In 2008, AXYS developed a new method for detecting pesticides in whole water samples.. The new method uses high resolution gas chromatography coupled to high resolution mass spectrometry (HRGC/HRMS, multi-residue pesticides referred to as MRES), in accordance with AXYS MLA-035. In 2008, an Intercomparison study was conducted between the old method and the new MRES method. 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 samples for the standard suite of RMP pesticide parameters, diazinon and chlorpyriphos. Pesticide results reported for 2008 and 2009 sampels were determined using the new MRES method.. .

Table 2.1. Target Analytes: A summary table of the 2009 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 Labs LLC
Methylmercury	Preserved with sulfuric acid, cooled with wet ice and refrigerated	Brooks Rand Labs LLC
Total Mercury	Cooled with wet ice and refrigerated	Brooks Rand Labs LLC
Copper and Nickel	Cooled with wet ice and refrigerated	City and County of San Jose
Cyanide	Preserved with NaOH to a pH ≥ 12	Contra Costa County Sanity District
Trace Organics (PBDEs, PCBs, Dioxins/Furans)	Cooled with wet ice and refrigerated	AXYS Analytical Services Ltd.
Pesticides	Preserved with Dichloromethane	AXYS Analytical Services Ltd.
DOC	Field filtered, preserved with 1-2 ml Sulfuric acid, cooled with wet ice and refrigerated	Columbia Analytical Services
POC	Field filtered, field frozen on dry ice	Columbia Analytical Services

Analyte	Special Field Handling Requirements	Analytical Lab
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	Preserved with sulfuric acid, cooled with wet ice and refrigerated	East Bay Municipal Utility District
Phosphate, 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 samples collected between 1997 and 2002 were toxic, 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*.

QUALITY ASSURANCE/ QUALITY CONTROL (QA/QC)

All samples results reported by SFEI have undergone a rigorous Quality Assurance/Quality Control (QA/QC) process by trained SFEI staff. Highlights for the 2009 water samples are summarized below.

Ancillary Parameters

QA/QC for Dissolved Organic Carbon and Particulate Organic Carbon analyzed by Columbia Analytical Services (CAS)

Detection limits for dissolved organic carbon (DOC) and particulate organic carbon (POC) were sufficient to report concentrations for all samples. DOC and POC in blanks were below detection limits. Lab-replicates for DOC analyses had an average relative standard deviation (RSD) just above the target 5% , so DOC results were flagged but not censored. POC replicates averaged within their 10% RSD target. Average errors on recoveries for spiked samples were within targets of 5% and 10% for DOC and POC respectively. Concentrations were generally in a similar range as in previous years.

QA/QC for Cognates analyzed by East Bay Municipal Utility District Laboratory (EBMUD)

Cognates analyzed for the RMP Status and Trends monitoring effort include ammonium as N, chlorophyll a, hardness as CaCO3, nitrate as N, nitrite as N, pheophytin a, phosphate as P, salinity, silica, and suspended sediment concentration. Detection limits were sufficient for most analytes, except nitrite, which was non-detect in half of the samples. Only ammonia was detected in blanks, and flagged but not censored for one batch. Precision was generally within targets (10% for chl-a, phaeophytin, SSC, 15% for N nutrients, 5% for salinity, hardness, phosphate, silicate), except phosphate which was slightly higher and flagged, and phaeophytin, which at 21% was slightly over (2x outside the target range) and censored. Average recovery errors were also mostly within target, but flagged for phosphate and silica for being over their targets of 5%. No recovery samples were available for chl-a, phaeophytin, or SSC. Concentrations were similar to past results, except nitrate and nitrate were <25% and silica was near double long-term RMP historical averages, although these analytes were reported in 2008 at similar concentrations, possibly reflecting a laboratory bias.

QA/QC for Trace Metals by Brooks Rand Labs LLC (BR)

For analysis of trace elements in water samples, MDLs were sufficient for most analytes, except silver which had many results near or below the detection limit. Results were all reported as blank corrected, but because variability (standard deviation) in lab blanks was larger than detection limits, lower concentration sample results could be affected by blank concentrations. Copper results were generally sufficiently above blank levels and only flagged, but about half the dissolved silver results were <3x stdev of blanks and censored. Precision on lab and field replicates was good, with 25% or better RSD except for dissolved silver, which was flagged for marginal precision as a result. Recoveries on SRMs and matrix spikes were within target average recovery errors of 25% or better. Dissolved concentrations of elements were all less than or the same as total concentrations (within analytical error). Concentrations were on average lower than historical RMP averages, except for dissolved copper

and iron. Copper was only slightly higher, but iron was much higher than its historical average concentrations. Iron results are therefore not reported for 2009 pending further investigation of analytical artifacts with the lab and possible reanalysis. Split water samples were analyzed for copper and nickel by the City of San Jose Environmental Services Division to confirm the comparability of RMP results.

Organic Parameters

QA/QC for Trace Organics by AXYS Analytical Services Ltd. (AXYS)

Many dioxin and furan congeners were not detected in most samples, with only octa- and a few hepta- congeners detected in most samples. TCDF, PeCDF, a few HxCDFs, and HpCDD were detected in blanks at concentrations over 1/3 of the concentrations in some field samples, with those samples censored for being largely blank contamination. Precision for analytes in a quantitative range (at least 3xMDL) averaged within the target 35% RSD. Recoveries on blank spike samples had average errors <20%, well within the target 35%. Dissolved to particulate phase ratios fit expected patterns with larger dissolved fractions (~30% of total concentrations) for lower substituted congeners, and less (~10% of total) for higher congeners like HpCDD/F and OCDD/F. Concentrations averaged about 50% higher than previous Bay sampling (CTR study in 2002-2003). This was perhaps expected, due to inclusion of more shallow water sites in 2009, compared to 2002-2003, which only included three deeper water main channel sites.

Pesticides were analyzed in 2009 by a new method using (4-liter) whole water samples to include more current use pesticides. Given the smaller sample size, MDLs reported were higher than in past RMP sampling using XAD solid phase extraction, and 13 of the 29 reported analytes were not detected in >50% of the samples. Five of the reported analytes had some samples that were censored due to blank concentrations >1/3 of field sample concentrations. Precision evaluated on field replicates was good, with average RSDs <35% except for Chlorpyrifos and Heptachlor, which were qualified but not censored. Recoveries on blank spike samples were within the target 35% average error except for Chlorpyriphos oxon, which was qualified but not censored. Because of the differences in collection methods and detection limits (and thus the frequency of non-detects) the results from the new sampling analytical methods are not directly comparable to results from the method (100-liter solid phase extraction) previously employed by the RMP S&T program. For analytes still detected despite higher MDLs, a whole water method generally yields more complete recovery and thus provides higher but more accurate estimates of ambient concentrations. For less abundant compounds the increased frequency of non-detects also makes it inadvisable to use direct combinations of data from the new and old methods in regressions and other inter-annual trend comparisons.

MDLs were sufficient for detection of most target PBDE analytes in water samples, with only a few analytes non-detect in most samples. Most analytes including the most abundant congeners were found in blank samples for solid phase extracted samples, but concentrations were less than 1/3 those in field samples for the major congeners and thus qualified but not censored. Recovery on blank spikes was acceptable, well within the target average 35% error for all analytes. Precision on field replicates was outside of the 35% average RSD target and qualified but not censored for total phase PBDEs in solid phase extracted samples. Most of the issues were with less abundant and less quantitative congener results. Average concentrations for 2009 were generally in the same range as previous years for most congeners, but highly variable (many higher or lower by a factor of 2 or 3).

Detection limits were sufficient to report concentration for most PCB congeners in water. Some (mostly less abundant congeners) were detected in blank samples, with 14 of those less abundant PCBs censored in one or

more samples due to concentrations <3x those found in blanks. Field replicate samples were evaluated for measurement precision, with average RSDs of ~10% for all analytes, well within the target 35%. Recoveries on blank spike samples were also within the target average 35% error for all reported compounds in a quantitative range (results >3xMDL). Average PCB concentrations in 2009 were similar to those in previous years.

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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 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 concentration. Information about sediments addresses several of the RMP questions listed in the *Introduction*. All sediment samples were collected aboard the R/V *Questuary* operated by Romburg Tiburon Center (RTC) during September 15 – September 23, 2009.

SITES

In 2009, 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 (September) 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 samples were collected at the same 27 sites. Station names, codes, coordinates, and sampling dates for the 2009 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 (annual) 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 selected 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 target coordinates in the field. 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 obtaining acceptable grabs. The area was then subject to active dredging which changed the bottom profile significantly.

In 2009, sampling was not possible at one target site, SU058S, and was replaced with the first oversample site from the region, SU042S. Difficulties arose at SU058S due to sand and peat substrate that prevented grab closure and collection of an acceptable sample.

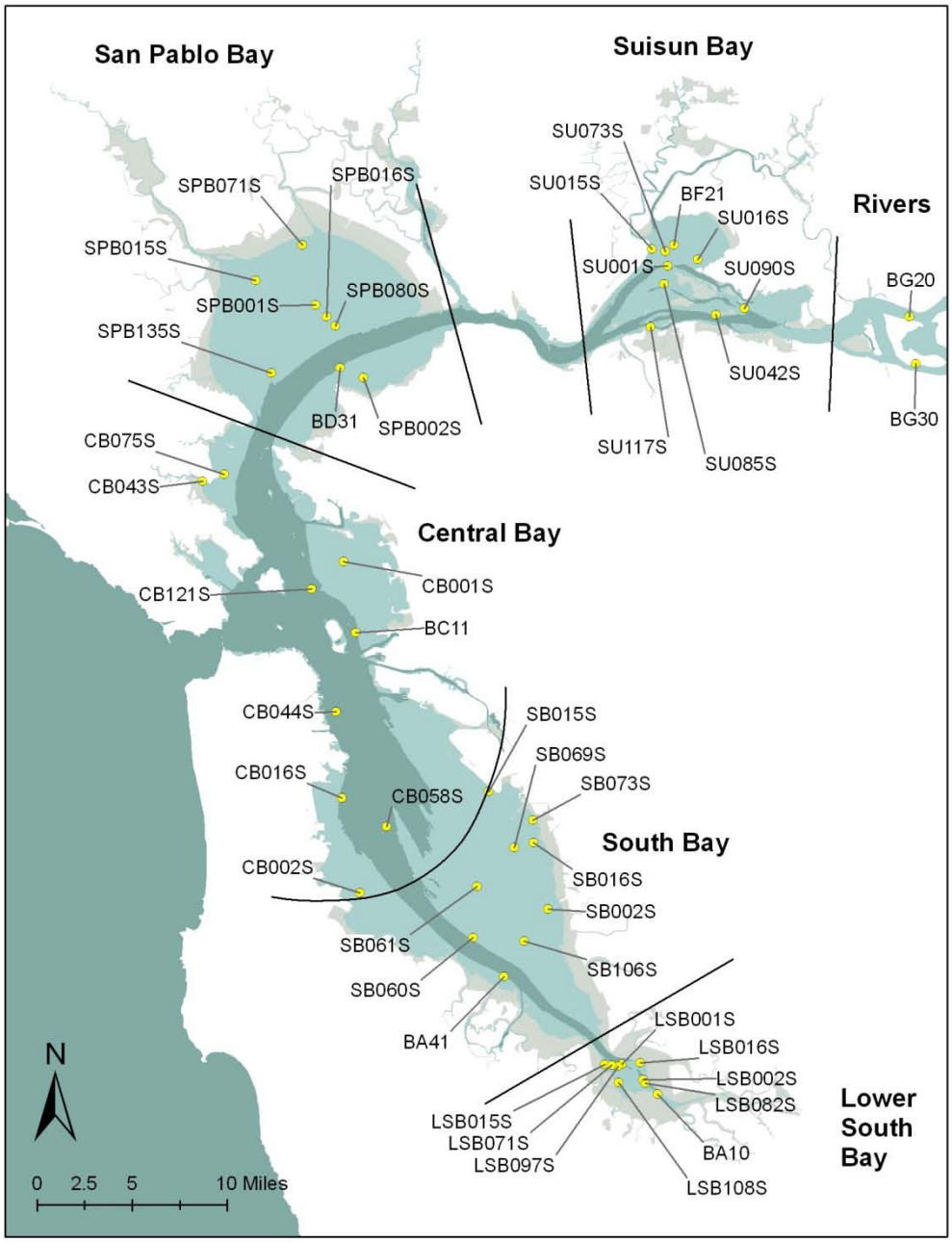

Figure 3.1. Map showing locations of 2009 Sediment Stations

FIELD METHODS

Shipboard Measurements

Conductivity, Temperature, and Depth (CTD) casts were taken by Applied Marine Sciences (AMS-CA) at each site, with the exception of BA10, where only a partial CTD cast was retrievable, and SPB022, where no CTD data was retrievable. 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 were taken by SFEI staff at each site. Two measurements of *in situ* pH were recorded onboard the sampling vessel by submerging a Hach™ pH probe directly into the sediment sample to approximately 1" in depth after the sediment grab was brought on deck. A total of four measurements (two from each grab) were recorded at each station. Measurement of sediment ORP was began in 2003. ORP is measured in a cored sub-sample of the sediment grab by a probe (WTW Sentix ORP, KCl electrolyte) inserted 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 ancillary, 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 wore gloves and employed 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. At 27 of the stations, Surface Water Interface Core (SWIC) samples were collected for toxicity testing using estuarine species. At 7 of these sites additional SWICs were collected for toxicity testing using freshwater crustaceans. Due to the area requirements associated with the collection of SWICs, no sediment for chemical analysis could be collected from these grabs. The top 5 cm of sediment was scooped from each of the grabs (avoiding portions cored or probed) 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 analysis of sediment quality, trace metals, trace organics, and toxicity analyses. Samples were also collected for trace metals archive and trace organics archive. Cruise Reports documenting RMP sampling events are available on our website.

Collection of Ancillary Parameters

The RMP analyzed sediments collected at 47 sites within the San Francisco Estuary for grainsize, percent solids, total organic carbon (TOC), and total nitrogen (TN). Moss Landing Marine Laboratories (MLM) conducted the grainsize analysis. Sediments for grainsize analysis were collected in Whirl-pak bags and were stored without refrigeration. Sediment samples collected for TOC, % solids and TN were analyzed by Columbia Analytical Services (CAS). Sediments for these analyses were collected in 60 ml glass jars and frozen at the end of the day.

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), 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 Labs LLC. (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 were kept frozen until analysis.

Sediment was collected for the analysis of dioxins at 47 sites by AXYS Analytical Services Ltd. (AXYS). All samples were placed into factory cleaned 250 ml amber 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

Two types of samples were taken for analysis of sediment toxicity by the UC Davis Marine Pollution Studies Laboratory at Granite Canyon (UCD-GC). Whole sediments samples were taken from 27 of 47 stations for analysis of toxicity to *Eohaustorius estuarius*. Samples from 7 of the sites in the north east part of the estuary were additionally tested for toxicity using two freshwater species *Hyalella azteca* and *Chironomus dilutus*. In 2008, the RMP reinstated collection of surface water interface cores (SWICs). This year, SWICs were collected at 27 stations for development tests using the bivalve Mytilus galloprovincialis. Additional SWICs were collected at 7 of the north east estuary stations for tests using freshwater species *Ceriodaphnia dubia*.

One liter plastic containers were provided by UCD-GC for the collection of homogenized sediment for the amphipod toxicity tests. 3-inch cores were used to collect intact cores (~1.5 inches deep) for the SWIC toxicity tests. Each core were capped with a lid that contained air holes and sealed around the edges using parafilm. The cores 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

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 onboard ship. The material retained on the screen was placed in sample jars, and a solution of magnesium chloride was added to the jar as a relaxant. 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. Taxonomic identification of benthic organisms will be led by City and County of San Francisco – Oceanside Biology Laboratory (CCSF-OBL) with additional assistance from James Oakden (Moss Landing Marine Lab), and Susan McCormick.

Laboratory Methods for Sediment Analysis

SFEI contracts with a number of laboratories that provide high quality analytical services. Qualifications for our labs include ISO registration, NELAP accreditation and certification by the California Department of Public Health. A brief overview of the laboratory methods used for RMP 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

Each lab determines percent solids in order to report the chemical analysis by a uniform measurement of dry weights. Percent solids are the percent content by weight of solid material in a sediment sample.

Brooks Rand Labs LLC (BR) measured percent solids in sediment using Method SM 2540G. For this method, a solid sample was homogenized, then portioned, measured, dried, and measured and the percent of dried solid material was calculated.

Columbia Analytical Services (CAS) measured percent solids in sediment using EPA Method 1684. In this method, aliquots of 25-50 g in size are dried at 103° C to 105° C. The sample is then cooled, weighed, and dried again at 550° C. Percent solids are determined by comparing the mass of the sample before and after each drying step.

City and County of San Francisco (CCSF) analyzed percent solids as part of their analysis of trace metals using a modification of EPA method 6020A. 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 by a modification of EPA Method 8081B, 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.

East Bay Municipal Utility District (EBMUD) measured percent solids in sediment using EPA Method 160.3. Samples are dried at 103° C to 105° C and weighed before and after to determine percent solids.

AXYS Analytical Services Ltd. (AXYS) analyzed percent solids using proprietary method MLA-017 in combination with the analysis of dioxins and furans. EBMUD analyzed percent solids using EPA Method 160.3 as part of the analysis of trace organics and CAS analyzed percent solids using EPA Method 1684 on combination with TOC and TN.Grainsize

Grainsize

Grainsize analysis prior to 2008 was conducted by the University of California Santa Cruz – Department of Environmental Toxicology (USCS-DET). In 2008 and 2009 grainsize determination changed to an opical method and was analyzed by Moss Landing Marine Lab - Geological Oceanography (MLML-GeoOc) using a Beckman-Coulter laser particle size analyzer after digestion with hydrogen peroxide according to Aiello and Kellett (2006). In addition to silt (0.0039 to <0.0625 mm) and sand (0.0625 to <2.0 mm), granule and pebble (2.0 to <64 mm) and clay particles (<0.0039 mm) were also analyzed with the LS 13 320 laser particle sizer in 2009.

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

Analysis of TOC and TN was performed by Columbia Analytical Services (CAS) using EPA 440. The samples were prepared for analysis by air drying followed by grinding in a mini ball mill. All samples were then analyzed for TOC and TN on HCL acidified samples using combustion at 950°C with thermoconductivity detection.

Analysis of Sediment Trace Metals

Trace metals in sediment were analyzed by the City and County of San Francisco (CCSF) and Brooks Rand Labs LLC. (BR).

Total trace metals analyzed by CCSF consisted of aluminum (Al), cadmium (Cd), copper (Cu), iron (Fe), lead (Pb), manganese (Mn), nickel (Ni), silver (Ag) and zinc (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).

Sediments were analyzed for mercury by BR using a modified version of 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.

Arsenic and selenium concentrations were measured in sediments using proprietary method BR-0020 Rev 007 by BR. Samples were first oxidized by heating with specific reagents. For the analysis of arsenic, sample concentrations were determined by hydride generation – cryogenic trapping – atomic absorption spectrometry (HG-CT-AAS). For the determination of selenium, samples were reduced in HCl with addition of hydroxylamine hydrochloride (NH_2OH HCl) and heating, converting all selenium to Se(IV). After that HG-CT-AAS was performed.

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. In 2009 analysis was again conducted by California Department of Fish and Game Water Pollution Control Laboratory (CDFG-WPCL). Samples were prepared using an automated extraction system and analyzed using a modified version of EPA 8081B by dual column gas chromatography with dual electron capture detectors (GC-ECD) and/or gas chromatography with triple quadrupole mass spectrometry (GC-MSMS).

Sediment organics were analyzed by EBMUD. 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).

EBMUD used the following extraction and concentration procedure for all sediment trace organic compounds of interest. 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).

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.

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.

Starting in 2008, sediment samples were also analyzed for polychlorinated dibenzodioxins and furans. The analysis was conducted by AXYS Analytical Services Ltd. (AXYS) using AXYS MLA-017 Rev 16. Extraction and analysis procedures were in general in accordance with USEPA Method 1613, Revision B using isotope dilution and a high-resolution mass spectrometer (HRMS) coupled with a high-resolution gas chromatograph (HRGC) equipped with a DB-5 capillary chromatography column. A second column was used for confirmation of specific congener identification.

Table 3.1. Target Analytes: A summary table of the 2009 target analytes, analytical laboratories, reporting units, and method codes.

Parameter	Lab(s)	Reporting Unit	Method Code(s)
Depth	AMS-CA	m	NA
pH (porewater, interstitial sediment)	AMS-CA	pH	NA
Dioxins/Furans	AXYS	Pg/g	EPA 1613B Mod.
Arsenic (As)	BR/CCSF	mg/Kg	EPA 1638 Mod./ EPA 6020A Mod.
Mercury (Hg)	BR/CCSF	mg/Kg	EPA 1631/ EPA 6020A Mod.
% solids	BR/CCSF/CDFG/MLML	%	Various

Parameter	Lab(s)	Reporting Unit	Method Code(s)
Selenium (Se)	BR/CCSF	mg/Kg	EPA 1638 Mod/ EPA 6020A Mod.
Mercury, Methyl (MeHg)	BR	µg/Kg	EPA 1630 Mod.
Total Organic Carbon	CAS	%	EPA 440
Total Nitrogen	CAS	%	EPA 440
Aluminum (Al)	CCSF	mg/Kg	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.
Nickel (Ni)	CCSF	mg/Kg	EPA 6020A Mod.
Silver (Ag)	CCSF	mg/Kg	EPA 6020A Mod.
Zinc (Zn)	CCSF	mg/Kg	EPA 6020A Mod.
Pyrethroids	CDFG-WPCL	µg/Kg	EPA 8081B 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.
Grainsize	MLML-GeoOc	%	Beckman-Coulter Laser Particle Size Analyzer
Sediment Toxicity – (Amphipod) Mean % Survival	UCD-GC	%	EPA 600/R-94-025
Sediment Toxicity – (Bivalve) Mean % Normal Alive	UCD-GC	%	EPA 600/R-95-136M
Sediment Toxicity – Fresh Water *H. azteca*	UCD-GC	%	EPA 600/R-99-064
Sediment Toxicity – Fresh Water *C. dubia*	UCD-GC	%	EPA 821/R-02-012M
Sediment Toxicity – Fresh Water *C. dilutus*	UCD-GC	%	EPA 600/R-99-064

Quality Assurance/ Quality Control (QA/QC)Ancillary Parameters

QA/QC of Percent Solids

Percent solids were measured individually along with analyzed samples by all chemical analytical labs in order to determine chemical concentrations on a dry weight basis. Variations of a few percent among subsamples between labs (and within labs for replicates) frequently result due to slight heterogeneity within samples.

QA/QC of Grain Size by Moss Landing Marine laboratory

Starting in 2008, grain size for particles <2mm was determined by an optical (laser scattering) method, which measures particle size distribution as a percentage of volume (rather than mass from sieving and weighing methods). In 2009, the fraction >2mm (larger than sand, typically bivalve shells and shell fragments) was determined as a percentage of bulk sediment mass, with the size distribution of the remaining (<2mm) fraction determined by the optical method. Comparisons of optical and sieving particle size distribution determinations in the literature have shown good agreement for deep marine sediments. Although split samples measured for RMP in 2008 generally showed reasonable agreement between methods (% fines within 10% for most samples), the dry sieving method in 2009 showed sensitivity to artifacts, in particular dried aggregates of smaller particles increasing the apparent proportion of larger size fractions. The laboratory is currently testing a wet sieving method for comparison of split samples to the optical method, which should be less subject to aggregation artifacts. For the optical method, reproducibility with splits from a single sample were generally good, averaging ~5% difference among replicate measurements of subsamples from collected sediments.

QA/QC of Total Organic Carbon and Totoal Nitrogen by Columbia Analytical Services (CAS)

Measurements of sediment total organic carbon (TOC) and total nitrogen (TN) showed no major issues. All TOC results were above the method detection limit of 0.01% (similar to previous years). Detection limits for TN were slightly higher than in previous years (0.01% vs 0.001 % in 2008) but only ~5% of samples were not detected. Minor TOC contamination was found in some blanks, but was small compared to sample amounts (no results censored). Accuracy and precision of QC sample measurements were within the average recovery error and RSD targets of 15% for TN and 5% for TOC. Several different laboratories have analyzed sediment ancillary measures for RMP in the past several years, results were generally within similar concentration ranges as previous years, so any analytical bias of changing labs would likely be fairly small.

QA/QC of Trace Metals

For trace elements (aside from As, Hg, Se) measured by City and County of San Francisco Laboratory (CCSF), concentrations were above detection limits in sediment samples. Although one batch was missing a blank (containing an extra blank spike instead) there were no target analytes aside from Zn detected in blank samples. Blank concentrations of Zn were low compared to those in samples. Precision on replicates was good, with RPDs or RSDs <25% for all target analytes. Recoveries on reference material samples were good for the target analytes, with only Al outside the average error target of 25% (at 56%), so Al results were censored and not reported. Because the laboratory uses a near total rather than “true” total metals (HF acid) digestion, resistant mineral phase elements such as Al are often not fully recovered. Average concentrations of these elements were 80-120% of previous years’ RMP averages.

Trace elements As, Hg, MeHg, and Se, measured by Brooks Rand Labs LLC (BR), had good data quality, with few non-detects (only 7% of Se results). No target analytes were detected in blanks. Precision on replicate analyses were good (average RSDs <25%), and SRM recoveries averaging within 25% of target values. Concentrations of analytes were generally similar to previous years’, with the 2009 averages within 25% of historical averages except for selenium, which was about half the historical average. The non-detects in selenium data may have contributed to the lower average, along with a lower maximum concentration. However, given that 2006 data had similar maximum and average concentrations (but no NDs), so it appears the 2009 results may still be within a reasonable range, even if a bit lower than typical.

QA/QC of Trace Organics

Sediments were tested for pyrethroids by California Department of Fish and Game Laboratory (CDFG). Sediment pyrethroid data usability was better than in past years due to fewer non-detects, although half the analytes were not detected in all samples. Detection limits were in the range that toxicity is sometimes seen in lab test organisms suggesting that despite many NDs these detection limits may be sufficient to evaluate risk (pyrethroid risk is mostly toxicity not bioaccumulation). Bifenthrin, permethrin, and cyhalothrin were measured in blanks, requiring censoring of many low concentration results. Precision on replicate field samples (where at least 3xdetection limit) and matrix spikes was good (<35% RSD). Recovery on matrix and blank spikes was generally good, <35% average error, except resmethrin which was slightly above the target range at 41% and flagged for marginal recovery but not censored. In previous years pyrethroids were nearly all NDs, so comparisons to past years' means are not possible, but maximum concentrations near ~1ug/kg for a few analytes were similar to those for 2008. However, phenothrin, which was found as high as 4.8ug/kg in 2008 was not measured in any 2009 samples.

Sediments were tested for PAHs, PCBs, PBDEs and OC Pesticides by the East Bay Municipal Utility District Laboratory (EBMUD). Non-detects were found for <10% of the samples for most of the PAHs, but for alkylated PAHs about half the analytes were non-detects in all samples. PAHs were not detected for most blank samples, with exception of various naphthalenes in one batch, requiring individual results censored for being <3x blank. Precision on replicates was good, except for two alkylated PAH groups, which were censored and not reported. Recoveries on SRMs and matrix spikes were generally good, averaging < 35% error, except for acenaphthylene and fluoranthene, which were flagged but not censored. Alkylated PAHs (reported as groups of related compounds) have no certified recovery standards and thus are estimates. A few analytes had maximum concentrations much (5x to 10x) higher than in previous years: acenaphthene, acenaphthylene, dibenzothiophene, and 2,3,5-trimethylnaphthalene. Although QC samples did not indicate analytical problems, these analytes may require more careful examination for anomalous patterns. Most other analytes were on average less than 2x previous averages.

For the major PBDE congeners, detection limits were generally sufficient, with no/few non-detects, although 9 less abundant PBDEs were NDs in over half the samples. Major congeners and some minor ones were found in blanks, with 190, 196, and 204 blanks >1/3 of field sample concentrations and censored in most of their results. For some less abundant congeners, replicates were variable, with BDE 79 and 119 too variable to report and censored, and 8 other congeners flagged for marginal precision (RSDs > 35%). Recoveries on matrix spikes were generally good, except BDE 27, 196, and 203 having average recovery errors >35%, flagged but not censored. Average concentrations were similar to previous years' averages, with only a handful noticeably higher or lower than in previous years.

PCB quality control data were generally acceptable. Minor congeners had non-detects for over half the samples. Many PCB congeners were found in blanks, with 15 of the 209 congeners censored for blank contamination similar to (>1/3 of) field sample concentrations. Lab replicates from field samples had RSDs averaging <35% target, except PCB 54, which was flagged, and PCB 24, well above the target range and censored. Recoveries on SRMs or matrix spikes averaged within 35% of targets except for PCBs 87 and 151, flagged but not censored. Concentrations were on average 94% of previous years results, ranging ~0.5x to 1.2x the RMP S&T average concentrations from the previous five years.

For pesticides, detection limits were sufficient for most analytes, with only fipronil non-detect in over half the samples. Nearly all analytes were found in the blanks of one or more batches, with some results censored for

blanks >1/3 sample concentrations; delta HCH, Fipronil, and Endrin were most impacted. Replicates were generally within the target range for precision (average <35% RSD), except Fipronil, Fipronil sulfone, DDT(p,p'), Aldrin, and Endrin which were flagged. Recoveries on SRMs/Matrix spikes were somewhat above the 35% target average error for Fipronil desulfinyl, trans-Nonachlor, and alpha HCH, but not censored. Average recoveries for trans-Chlordane, Fipronil, and Fipronil sulfone were poor, with those analytes censored and not reported. Averages of most pesticides were within 2x previous average concentrations (most slightly higher), but (p,p') DDT and Endrin, both averaged over 2x higher than previous averages, largely driven by >10x higher maximum concentrations.

QA/QC for Sediment Toxicity

Sediments were tested for toxicity at University of California at Granite Canyon laboratory (UCD-GC). A number of samples used for sediment toxicity tests exceeded the lab recommended holding time limit of 14 days (flagged in the results), as test organisms received from the supplier were not viable and needed to be re-ordered. The lab did not believe the longer hold times had a significant impact on the toxicity testing results. Some water quality measures that were outside the recommended organism tolerance range as outlined by the test protocol were qualified; the criterion that failed most often was conductivity/salinity. Not all tests with water quality range exceedances showed apparent toxic effects, but some of the tests with significant toxic effects included deviations in test water quality. The lab however generally thought these deviations alone were not large enough to cause the observed toxicity.

SEDIMENT TOXICITY

Two types of sediment bioassays were conducted at 27 of the RMP stations in 2009 (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 jars 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 was 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 *E. estuarius* 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 cores (SWIC) were tested using the bivalve *Mytilus galloprovincialis* in a 48-hour static embryo-larval development toxicity tests (EPA 600/R-95-136M). SWICs 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 tubes and rinsing the larvae into 20 ml scintillation vials. 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 SWICs 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 90th 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 a 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 90th 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 90th percentile MSD is 15.2% (Phillips *et al*., 2001). The control responses in the three amphipod tests ranged from 94% to 95%, and the toxicity thresholds from 75.2% to 76.2%. Control responses in the bivalve larvae tests ranged from 70.1% to 84.4% and the toxicity thresholds ranged from 54.9% to 69.2%.

Figure 3.2 shows the results of the 2009 sediment bioassays. Sediments were not toxic to amphipod, *Eohaustorius estuarius*, or mussel, *Mytilus galloprovincialis*, larvae at 9 out of 27 stations. Amphipod toxicity was observed at fourteen stations: Suisun Bay (Grizzly Bay (BF21), SU016S, and SU073S), San Pablo Bay (SPB080S, and SPB135S), South Bay (SB002S, SB016S, SB060S, and SB106S), and Lower South Bay (Coyote Creek (BA10), LSB002S, LSB016S, LSB082S, and LSB108S). Sediment samples from ten stations were toxic to larval mussels: Sacramento River (BG20), San Joaquin River (BG30), Suisun Bay (Grizzly Bay (BF21), SU016S, and SU073S), San Pablo Bay (SPB002S, and SPB080S), South Bay (Redwood Creek (BA41)), and Lower South Bay (LSB016S, and LSB108S). 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 2009. 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 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.

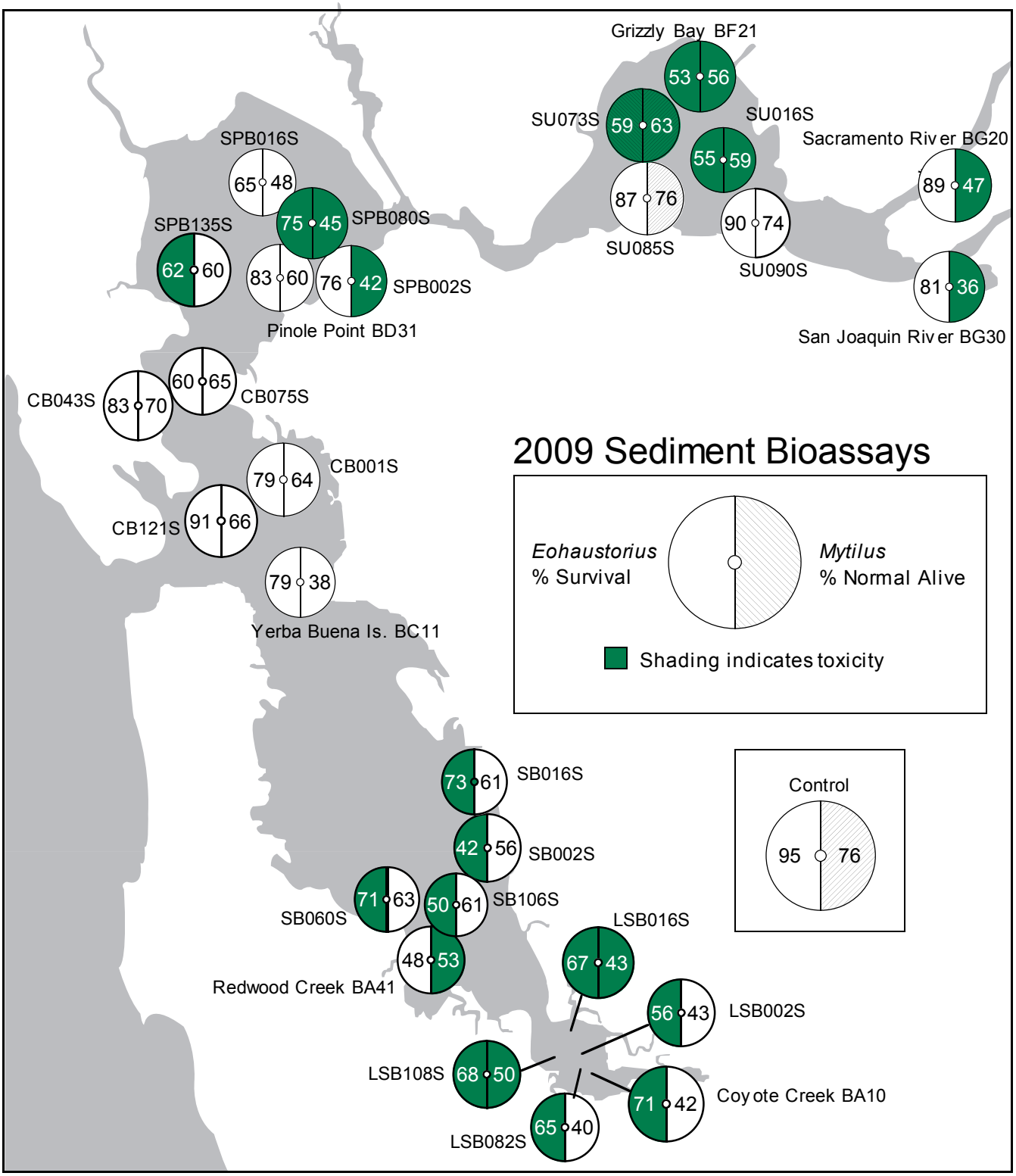

Figure 3.2. Sediment bioassay results for 2009. Sediments were not toxic (see Section 3.4 Sediment Toxicity) to both amphipods, *Eohaustorius estuarius*, and mussel, *Mytilus galloprovincialis*, larvae at 8 out of 27 stations. Amphipod toxicity was observed at fourteen stations: Suisun Bay (Grizzly Bay (BF21), SU016S, and SU073S), San Pablo Bay (SPB080S, and SPB135S), South Bay (SB002S, SB016S, SB060S, and SB106S), and Lower South Bay (Coyote Creek (BA10), LSB002S, LSB016S, LSB082S, and LSB108S). Sediment samples from ten stations were toxic to larval mussels: Sacramento River (BG20), San Joaquin River (BG30), Suisun Bay (Grizzly Bay (BF21), SU016S, and SU073S), San Pablo Bay (SPB002S, and SPB080S), South Bay (Redwood Creek (BA41)), and Lower South Bay (LSB016S, and LSB108S)..

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 2009 Regional Monitoring Program samples (Table 3.3). 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 2009 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 2009 mERMqs were calculated using 24 parameters as indicated in Table 3.2 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 2009 sediment samples had at least 21 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 2009 RMP sediment samples for potential adverse ecological effects. Three stations had a mERMq value greater than 0.15 (CB016S, CB044S, SB073S) and at least 21 results above the ASC guidelines (Table 3.2).

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 2009, five stations were considered potentially toxic by the RMP (CB002S, CB016S, CB044S, CB121S, and SB073S) because nine or more contaminant concentrations were above the ERL guidelines. One station sampled in 2009 (CB044S) had thirteen contaminant concentrations above the ERM guidelines and another station (SB073S) had four contaminant concentrations above ERM guidelines (Table 3.3).

Table2.3. Summary of sediment quality for the RMP in 2009

• indicates not tested, * indicates number of exceedances above ASC guidelines for sandy samples.

Code	Site Name	Date	% Fines	mERMq	No. of ASC above Guidelines	No. of ERL above Guidelines	No. of ERM above Guidelines	Toxic to Amphipods Eohaustorius?	Toxic to Bivalves Mytilus?
BG20	Sacramento River	09/23/2009	21	0.0225	0*	3	1	N	Y
BG30	San Joaquin River	09/23/2009	61	0.0595	2	4	1	N	Y
BF21	Grizzly Bay	09/22/2009	92	0.0764	0	7	1	Y	Y
SU001S	Suisun Bay	09/22/2009	21	0.0295	2*	3	1	.	.
SU015S	Suisun Bay	09/22/2009	94	0.0994	2	6	1	.	.
SU016S	Suisun Bay	09/22/2009	86	0.0678	2	7	1	Y	Y
SU042S	Suisun Bay	09/22/2009	6	0.0143	1*	1	1	.	.
SU073S	Suisun Bay	09/22/2009	77	0.0739	2	6	1	Y	Y
SU085S	Suisun Bay	09/23/2009	20	0.0278	0*	1	1	N	N
SU090S	Suisun Bay	09/23/2009	18	0.0371	11*	4	1	N	N
SU117S	Suisun Bay	09/22/2009	82	0.1045	4	6	1	.	.
BD31	Pinole Point	09/18/2009	55	0.0733	0	7	1	N	N
SPB001S	San Pablo Bay	09/21/2009	80	0.0774	2	6	1	.	.
SPB002S	San Pablo Bay	09/18/2009	86	0.0671	1	5	1	N	Y
SPB015S	San Pablo Bay	09/21/2009	99	0.0899	0	7	1	.	.
SPB016S	San Pablo Bay	09/21/2009	98	0.0791	2	6	1	N	N
SPB071S	San Pablo Bay	09/21/2009	87	0.0741	0	6	1	.	.
SPB080S	San Pablo Bay	09/21/2009	94	0.0826	2	6	1	Y	Y
SPB135S	San Pablo Bay	09/18/2009	65	0.0850	1	6	1	Y	N
SPB136S	San Pablo Bay	09/21/2009	54	0.0584	0	6	1	.	.
BC11	Yerba Buena Island	09/17/2009	75	0.0892	1	7	1	N	N
CB001S	Central Bay	09/18/2009	53	0.1118	1	8	1	N	N
CB002S	Central Bay	09/16/2009	93	0.1138	10	9	1	.	.
CB016S	Central Bay	09/16/2009	63	0.1876	23	19	1	.	.
CB043S	Central Bay	09/18/2009	92	0.0817	1	6	1	N	N
CB044S	Central Bay	09/17/2009	23	0.8647	30*	21	13	.	.
CB058S	Central Bay	09/16/2009	36	0.0563	23*	4	1	.	.
CB075S	Central Bay	09/18/2009	79	0.0921	0	7	1	N	N
CB121S	Central Bay	09/18/2009	41	0.1107	12	13	1	N	N
BA41	Redwood Creek	09/16/2009	70	0.0785	0	5	1	N	Y
SB002S	South Bay	09/16/2009	85	0.0794	0	6	1	Y	N
SB015S	South Bay	09/17/2009	25	0.0318	18*	2	0	.	.
SB016S	South Bay	09/17/2009	68	0.0635	0	3	1	Y	N
SB060S	South Bay	09/16/2009	45	0.0853	5	5	1	Y	N
SB061S	South Bay	09/16/2009	45	0.0522	0	3	1	.	.
SB069S	South Bay	09/17/2009	23	0.0533	21*	2	0	.	.
SB073S	South Bay	09/17/2009	65	0.3185	22	18	4	.	.
SB106S	South Bay	09/16/2009	82	0.1024	4	7	1	Y	N
BA10	Coyote Creek	09/15/2009	71	0.0858	1	6	1	Y	N
LSB001S	Lower South Bay	09/15/2009	55	0.0710	0	5	1	.	.
LSB002S	Lower South Bay	09/15/2009	95	0.0869	0	6	1	Y	N
LSB015S	Lower South Bay	09/15/2009	90	0.0844	0	5	1	.	.
LSB016S	Lower South Bay	09/15/2009	93	0.0856	0	6	1	Y	Y
LSB071S	Lower South Bay	09/15/2009	90	0.0852	0	6	1	.	.
LSB082S	Lower South Bay	09/15/2009	84	0.0810	0	6	1	Y	N

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

Estuary sediments and the importance of performing future studies to reconcile and understand the observed contradictions.

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4
APPENDIX TABLES

4. APPENDIX TABLES

APPENDIX 1 RMP PROGRAM PARTICIPANTS IN 2009

Municipal Dischargers	**Industrial Dischargers**
Burlingame Waste Water Treatment Plant	C & H Sugar Company
Central Contra Costa Sanitary District	Chevron Products Company
Central Marin Sanitation Agency	Crockett Cogeneration
City of Benicia	Dow Chemical Company
City of Calistoga	General Chemical Corporation
City of Palo Alto	Martinez Refining Company
City of Petaluma	Rhodia, Inc.
City of Pinole/Hercules	Tesoro Golden Eagle Refinery
City of Saint Helena	Tosco - Rodeo Refinery
City and County of San Francisco	USS – POSCO Industries
City of San Jose/Santa Clara	Valero Refining Company
City of San Mateo	
City of South San Francisco/San Bruno	**Dredgers**
City of Sunnyvale	Aeolian Yacht Club
Delta Diablo Sanitation District	Belvedere Cove Access Channel
East Bay Dischargers Authority	Chevron Richmond Long Wharf
East Bay Municipal Utility District (SD#1)	City of Benicia
Fairfield-Suisun Sewer District	Clipper Yacht Harbor
Las Gallinas Valley Sanitation District	Conoco Phillips Company
Marin County Sanitary District #5, Tiburon	Corinthian Yacht Club
Millbrae Waste Water Treatment Plant	Marin Rowing Association
Mountain View Sanitary District	Marin Yacht Club
Napa Sanitation District	Marina Vista Homeowners Association
Novato Sanitation District	Oyster Point Marina
Rodeo Sanitary District	Paradise Cay Yacht Harbor
San Francisco International Airport	Port of Oakland
Sausalito Sanitation District	Port of San Francisco
Sewer Agency of Southern Marin	San Rafael Yacht Harbor
Sonoma County Water Agency	Strawberry Channel

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

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

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

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

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
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 2009

Logistical Coordinator; Shipboard Conductivity, Temperature, and Depth (CTD) Readings	Mr. Paul Salop Applied Marine Sciences (AMS), Livermore, CA
Ship Captain - Sediment Cruise	Mr. David Morgan Captain, *RV Questuary* Romburg Tiburon Center
Ship Captain – Water Cruise	Mr. Jim Christmann Captain, *RV Shana Rae* Monterey Canyon Research Vessels, Inc.
Water Trace Element Chemistry	Ms. Tiffany Stilwater Brooks-Rand Ltd. (BR), Seattle, WA
Water Trace Organic Chemistry	Ms. Candice Navaroli AXYS Analytical Services Ltd. (AXYS), Sidney, BC
Water Ancillary Measurements	Water Cognates: Ms. Nirmela Arsem and Mr. Ken Gerstman East Bay Municipal Utility District (EBMUD), Oakland, CA
	Water DOC and POC: Mr. Pradeep Divvela and Mike Shelton Columbia Analytical Services (CAS), Kelso, WA
Sediment Trace Element Chemistry	Sediment As, Se, Hg, and Methyl Mercury 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	Mr. François Rodigari and Ms. Saskia van Bergen

Chemistry	East Bay Municipal Utility District (EBMUD), Oakland, CA
Sediment Toxicity Testing	Dr. John Hunt, Dr. Brian Anderson, and Dr. Bryn Phillips Marine Pollution Studies Lab (MPSL), Granite Canyon, CA
Sediment Ancillary Measurements (Grainsize, TOC, TN)	Sediment TOC, TN and % Solids Mr. Pradeep Divvela and Mr. Mike Shelton Columbia Analytical Services (CAS), Kelso, WA
	Sediment Grainsize Dr. Ivano Aiello and Ms. Autumn Bonnema Geological Oceanography Lab at Moss Landing, 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 2009 RMP WATER SAMPLING STATIONS

Region	Site Code	Historic Site	Collection Date	Latitude	Longitude	Site Depth (m)
Rivers	BG20	X	9/3/2009	38.05972	-121.81108	9
Rivers	BG30	X	9/3/2009	38.02050	-121.80633	7
Suisun Bay	SU030W		9/2/2009	38.05898	-121.95238	6
Suisun Bay	SU031W		9/2/2009	38.11355	-122.06210	2
Suisun Bay	SU034W		9/2/2009	38.05167	-121.98387	7
South Bay	SB027W		9/1/2009	38.02003	-122.45320	4
South Bay	SB028W		9/1/2009	37.98238	-122.41667	4
South Bay	SB029W		9/1/2009	38.01667	-122.42397	7
Central Yerba Buena Island	BC10	X	8/31/2009	37.82162	-122.34955	7
Central Bay/Golden Gate	BC20	X	8/28/2009	37.79197	-122.66822	29
Central Bay	CB027W		8/31/2009	37.91763	-122.44523	13
Central Bay	CB028W		8/27/2009	37.74218	-122.36108	15
Central Bay	CB029W		8/28/2009	37.77597	-122.37275	16
South Bay/Dumbarton Bridge	BA30	X	8/26/2009	37.51380	-122.13462	5
South Bay	SB054W		8/26/2009	37.52315	-122.13783	4
South Bay	SB055W		8/27/2009	37.64285	-122.24867	4
South Bay	SB057W		8/27/2009	37.66070	-122.23180	3
Lower South Bay	LSB038W		8/24/2009	37.47117	-122.06802	2
Lower South Bay	LSB039W		8/25/2009	37.49597	-122.10910	13
Lower South Bay	LSB040W		8/25/2009	37.48960	-122.08327	8
Lower South Bay	LSB042W		8/25/2009	37.48712	-122.08058	4
Lower South Bay	LSB043W		8/24/2009	37.50120	-122.12065	8

APPENDIX 4 SUMMARY OF 2009 RMP SEDIMENT SAMPLING STATIONS

Region	Site Code	Historic Site	Collection Date	Latitude	Longitude	Site Depth (m)
Central Bay/Yerba Buena Island	BC11	X	9/17/2009	37.82218	-122.34962	7.1
Central Bay	CB001S		9/18/2009	37.87633	-122.36092	2.9
Central Bay	CB002S		9/16/2009	37.62385	-122.34775	5.3
Central Bay	CB016S		9/16/2009	37.69607	-122.36455	7.3
Central Bay	CB043S		9/18/2009	37.93813	-122.49622	4.3
Central Bay	CB044S		9/17/2009	37.76197	-122.36913	15.1
Central Bay	CB058S		9/16/2009	37.67405	-122.32158	8.9
Central Bay	CB075S		9/18/2009	37.94355	-122.47525	3.7
Central Bay	CB121S		9/18/2009	37.85542	-122.39193	8.9
Lower South Bay/Coyote Creek	BA10	X	9/15/2009	37.46807	-122.06448	1.5
Lower South Bay	LSB001S		9/15/2009	37.49147	-122.09798	6
Lower South Bay	LSB002S		9/15/2009	37.47932	-122.07792	7.5
Lower South Bay	LSB015S		9/15/2009	37.49122	-122.1148	1.8
Lower South Bay	LSB016S		9/15/2009	37.49235	-122.08052	2.1
Lower South Bay	LSB071S		9/15/2009	37.49075	-122.10787	2.2
Lower South Bay	LSB082S		9/15/2009	37.47653	-122.07608	6.8
Lower South Bay	LSB097S		9/15/2009	37.48990	-122.10187	3.7
Lower South Bay	LSB108S		9/15/2009	37.47733	-122.10147	2.1
Rivers/Sacramento River	BG20	X	9/23/2009	38.05893	-121.81452	9.3
Rivers/San Joaquin River	BG30	X	9/23/2009	38.02283	-121.8088	7.9
San Pablo Bay/Pinole Point	BD31	X	9/18/2009	38.02427	-122.36318	7.6
San Pablo Bay	SPB001S		9/21/2009	38.07218	-122.38647	3
San Pablo Bay	SPB002S		9/18/2009	38.01637	-122.34098	3.6
San Pablo Bay	SPB015S		9/21/2009	38.09135	-122.44413	4.8

Region	Site Code	Historic Site	Collection Date	Latitude	Longitude	Site Depth (m)
San Pablo Bay	SPB016S		9/21/2009	38.06337	-122.37570	3.2
San Pablo Bay	SPB071S		9/21/2009	38.11800	-122.39910	1.2
San Pablo Bay	SPB080S		9/21/2009	38.05618	-122.36747	3.1
San Pablo Bay	SPB135S		9/18/2009	38.02067	-122.42947	7.3
San Pablo Bay	SPB136S		9/21/2009	38.03713	-122.30427	2.9
South Bay	BA41	X	9/16/2009	37.55890	-122.21053	1.8
South Bay	SB002S		9/16/2009	37.61017	-122.16725	2.3
South Bay	SB015S		9/17/2009	37.70008	-122.22333	3
South Bay	SB016S		9/17/2009	37.66077	-122.18098	1.7
South Bay	SB060S		9/16/2009	37.58870	-122.23985	3
South Bay	SB061S		9/16/2009	37.62780	-122.23545	4.6
South Bay	SB069S		9/17/2009	37.65723	-122.19957	1.7
South Bay	SB073S		9/17/2009	37.67792	-122.18120	1.9
South Bay	SB106S		9/16/2009	37.58595	-122.19055	3.3
Suisun Bay	BF21	X	9/22/2009	38.11543	-122.04048	1.9
Suisun Bay	SU001S		9/22/2009	38.09968	-122.04670	6.3
Suisun Bay	SU015S		9/22/2009	38.11270	-122.06173	1.9
Suisun Bay	SU016S		9/22/2009	38.10427	-122.01755	1.9
Suisun Bay	SU042S		9/22/2009	38.06208	-122.00082	5.8
Suisun Bay	SU073S		9/22/2009	38.11068	-122.04890	1.9
Suisun Bay	SU085S		9/23/2009	38.08595	-122.05017	3.2
Suisun Bay	SU090S		9/23/2009	38.06650	-121.97292	5.9
Suisun Bay	SU117S		9/22/2009	38.05327	-122.06367	2.3

APPENDIX 5 RMP TARGET PARAMETER LIST IN 2009

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

[Basis codes: dw=dry weight, ww=wet weight]

Conventional Water Quality Parameters	**Reporting Units**	**Basis**
Ammonium as N	mg/L	ww
Chlorophyll a	mg/m3	ww
Dissolved Organic Carbon	ug/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	ug/L	ww
pH	pH	ww
Pheophytin a	mg/m3	ww
Phosphate as P	mg/L	ww
Salinity	psu	ww
Silica as SiO2	mg/L	ww
SpecificConductivity	umho	ww
Suspended Sediment Concentration	mg/L	ww
Temperature	Deg C	ww
Sediment Quality Parameters		
% Solids	%	dw
CollectionDepth	m	
Nitrogen, Total	%	dw
Total Organic Carbon	%	dw
Grainsize Parameters [**Sum of Clay and Silt]		
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		
Mean % Survival; SD - Mean % Survival	%	dw
Sediment Toxicity Parameters - Surface Water Interface for MCAL		
Mean % Normal Alive; SD - Mean % Normal Alive	%	dw
Bivalve Tissue Parameters 1. Reported with Trace Metals 2. Reported with Trace Organics		
% 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
Fish Tissue Parameters		
Lipid	%	ww or dw
Moisture	%	ww or dw
Length	cm	

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

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

Trace organic parameters (reporting units) analyzed in water (pg/L), sediment (ug/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 ug/Kg, tissue – 5 ng/g)
[1]Sum of LPAHs and HPAHs
[2]Reported in sediment only
[3]Reported in water only

Low molecular weight PAHs	**High molecular weight PAHs**	**Alkylated PAHs**
Acenaphthene	Benz(*a*)anthracene	Benz(a)anthracenes/Chrysenes, C1-[3]
Acenaphthylene	Benzo(*a*)pyrene	Benz(a)anthracenes/Chrysenes, C2-[3]
Anthracene	Benzo(*b*)fluoranthene	Benz(a)anthracenes/Chrysenes, C3-[3]
Biphenyl	Benzo(*e*)pyrene	Benz(a)anthracenes/Chrysenes, C4-[3]
Dibenzothiophene	Benzo(g,h,i)perylene	Chrysenes, C1-[2]
Dimethylnaphthalene, 2,6-	Benzo(*k*)fluoranthene	Chrysenes, C2-[2]
Fluorene	Chrysene	Chrysenes, C3-[2]
Methylnaphthalene, 1-	Dibenz(*a,h*)anthracene	Chrysenes, C4-[2]
Methylnaphthalene, 2-	Fluoranthene	Dibenzothiophenes, C1-
Methylphenanthrene, 1-	Indeno(1,2,3-c,d)pyrene	Dibenzothiophenes, C2-
Naphthalene	Perylene	Dibenzothiophenes, C3-
Phenanthrene	Pyrene	Fluoranthene/Pyrenes, C1-
Trimethylnaphthalene, 2,3,5-	Sum of HPAHs (SFEI)	Fluorenes, C1-
Sum of LPAHs (SFEI)	Sum of PAHs (SFEI)[1]	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 ug/Kg, tissue – 1 ng/g)
[1] Parameter reported for water matrix only.
[2]Parameter reported for sediment matrix only.
Sums calculated by SFEI.

Cyclopentadienes	**Chlordanes**	**DDTs**	**HCH**	**Other Synthetic Biocides**
Aldrin	Chlordane, cis-	DDD(o,p')	HCH, alpha	Chlorpyrifos[1]
Dieldrin	Chlordane, trans-	DDD(p,p')	HCH, beta	Dacthal[1]
Endrin	Heptachlor	DDE(o,p')	HCH, delta	Diazinon[1]
	Heptachlor Epoxide	DDE(p,p')	HCH, gamma	Endosulfan I[1]
	Nonachlor, cis-	DDT(o,p')	Sum of HCHs (SFEI)	Endosulfan II[1]
	Nonachlor, trans-	DDT(p,p')		Endosulfan sulfate[1]
	Oxychlordane	Sum of DDTs (SFEI)		Fipronil desulfinyl[2]
	Sum of Chlordanes (SFEI)			Fipronil sulfide[2]
				Fipronil sulfone[2]
				Fipronil[2]
				Hexachlorobenzene
				Mirex

OTHER SYNTHETIC COMPOUNDS

Polychlorinated Biphenyls (PCBs)
(Target MDLs: water – 2 pg/L, sediment - 1 ug/Kg , tissue – 1 ng/g)
IUPAC numbers listed. Sums calculated by SFEI.
*Congeners included in the Sum of 40 PCBs (SFEI).

PCB 001	**PCB 031***	PCB 061	PCB 091	PCB 121	**PCB 151***	PCB 181
PCB 002	PCB 032	PCB 062	PCB 092	PCB 122	PCB 152	PCB 182
PCB 003	**PCB 033***	PCB 063	PCB 093	PCB 123	**PCB 153***	**PCB 183***
PCB 004	PCB 034	PCB 064	PCB 094	PCB 124	PCB 154	PCB 184
PCB 005	PCB 035	PCB 065	**PCB 095***	PCB 125	PCB 155	PCB 185
PCB 006	PCB 036	**PCB 066***	PCB 096	PCB 126	**PCB 156***	PCB 186
PCB 007	PCB 037	PCB 067	**PCB 097***	PCB 127	PCB 157	**PCB 187***
PCB 008*	PCB 038	PCB 068	PCB 098	**PCB 128***	**PCB 158***	PCB 188
PCB 009	PCB 039	PCB 069	**PCB 099***	PCB 129	PCB 159	PCB 189
PCB 010	PCB 040	**PCB 070***	PCB 100	PCB 130	PCB 160	PCB 190
PCB 011	PCB 041	PCB 071	**PCB 101***	PCB 131	PCB 161	PCB 191
PCB 012	PCB 042	PCB 072	PCB 102	**PCB 132***	PCB 162	PCB 192
PCB 013	PCB 043	PCB 073	PCB 103	PCB 133	PCB 163	PCB 193
PCB 014	**PCB 044***	**PCB 074***	PCB 104	PCB 134	PCB 164	**PCB 194***
PCB 015	PCB 045	PCB 075	**PCB 105***	PCB 135	PCB 165	**PCB 195***
PCB 016	PCB 046	PCB 076	PCB 106	PCB 136	PCB 166	PCB 196
PCB 017	PCB 047	PCB 077	PCB 107	PCB 137	PCB 167	PCB 197
PCB 018*	PCB 048	PCB 078	PCB 108	**PCB 138***	PCB 168	PCB 198
PCB 019	**PCB 049***	PCB 079	PCB 109	PCB 139	PCB 169	PCB 199
PCB 020	PCB 050	PCB 080	**PCB 110***	PCB 140	**PCB 170***	PCB 200
PCB 021	PCB 051	PCB 081	PCB 111	**PCB 141***	PCB 171	**PCB 201***
PCB 022	**PCB 052***	PCB 082	PCB 112	PCB 142	PCB 172	PCB 202
PCB 023	PCB 053	PCB 083	PCB 113	PCB 143	PCB 173	**PCB 203***
PCB 024	PCB 054	PCB 084	PCB 114	PCB 144	**PCB 174***	PCB 204
PCB 025	PCB 055	PCB 085	PCB 115	PCB 145	PCB 175	PCB 205
PCB 026	**PCB 056***	PCB 086	PCB 116	PCB 146	PCB 176	PCB 206
PCB 027	PCB 057	**PCB 087***	PCB 117	PCB 147	**PCB 177***	PCB 207

Polybrominated Diphenyl Ethers (PBDEs)
(Target MDLs: water – 1 pg/L, sediment – 1 ug/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	

Special Study Parameters
Not measured regularly by the Status and Trends Program

Dioxins and Furans (PCDD/F)
(sediment and tissue – pg/g; water – pg/L)

Dioxins	**Furans**
HpCDD, 1,2,3,4,6,7,8-	HpCDF, 1,2,3,4,6,7,8-
HxCDD, 1,2,3,4,7,8-	HpCDF, 1,2,3,4,7,8,9-
HxCDD, 1,2,3,6,7,8-	HxCDF, 1,2,3,4,7,8-
HxCDD, 1,2,3,7,8,9-	HxCDF, 1,2,3,6,7,8-
OCDD, 1,2,3,4,6,7,8,9-	HxCDF, 1,2,3,7,8,9-
PeCDD, 1,2,3,7,8-	HxCDF, 2,3,4,6,7,8-
TCDD, 2,3,7,8-	OCDF, 1,2,3,4,6,7,8,9-
	PeCDF, 1,2,3,7,8-
	PeCDF, 2,3,4,7,8-
	TCDF, 2,3,7,8-

Pyrethroids
(Target RDLs: sediment – 1 to 10 ug/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, cis-	Tetramethrin
Cypermethrin, total*	Permethrin, trans-	Tralomethrin
		Sum of Pyrethroids (SFEI)

Perfluorinated Compounds (PFC)
(Target RDLs: water – 1 ng/L or * 2 ng/L; tissue – ng/g; water – ng/L; sediment ug/kg)

Carboxylic Acids	**Sulphonic Acids**
Perfluorobutanoate	Perfluorobutanesulfonate*
Perfluorodecanoate	Perfluorohexanesulfonate*
Perfluorododecanoate	Perfluorooctanesulfonamide
Perfluoroheptanoate	Perfluorooctanesulfonate*
Perfluorohexanoate	
Perfluorononanoate	

APPENDIX 6 ANALYTES REPORTED IN WATER SAMPLES (1993-2009)

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
* Data available upon request

Reportable Water Parameter	Type	1993	1994	1995	1996	1997	1998	1999	2000	2001	2002	2003	2004	2005	2006	2007	2008	2009
Ammonium as N	ANC	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■
Chlorophyll a	ANC	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■
CTD*	ANC		■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■
Dissolved Organic Carbon	ANC	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■
Hardness as CaCO3	ANC	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■
Nitrate as N	ANC	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■
Nitrite as N	ANC	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■
Oxygen, Dissolved	ANC	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■
Particulate Organic Carbon	ANC												■	■	■	■	■	■
pH	ANC	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■
Pheophytin a	ANC	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■
Phosphate as P	ANC	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■
Salinity (by salinometer)	ANC	■		■	■	■	■	■	■	■	■	■	■	■	■			
Salinity (by SCT)	ANC	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■
Salinity (by Solomat)	ANC					■												
Silica	ANC	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■
SpecificConductivity	ANC	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■
Suspended Sediment Concentration	ANC										■	■	■	■	■	■	■	■
Temperature	ANC	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■
Total Suspended Solids	ANC	■	■	■	■	■	■	■	■	■				■	■	■		
Alkanes (C10-C34)	ORGS	■	■	■														
Dioxins/Furans	ORGS																	■
PAHs (biennially beginning 2008)	ORGS	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	
PAHs Alkylated (biennially beginning 2008)	ORGS						■	■	■	■	■	■	■	■	■	■	■	
PBDEs (annually)	ORGS										■	■	■	■	■	■	■	■
PCBs 209 (biennially beginning 2008)	ORGS																	■
PCBs 40 (biennially beginning 2008)	ORGS	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■		■
Pharmaceuticals	ORGS														■			

Reportable Water Parameter	Type	1993	1994	1995	1996	1997	1998	1999	2000	2001	2002	2003	2004	2005	2006	2007	2008	2009
Phthalates	ORGS																	
Chlordanes	PESTs																	
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																	
Chromium	TE																	
Cobalt	TE																	
Copper	TE																	
Cyanide	TE																	
Iron	TE																	
Lead	TE																	
Manganese	TE																	
Mercury	TE																	
Mercury, Methyl	TE																	
Nickel	TE																	
Selenium	TE																	
Silver	TE																	
Zinc	TE																	
Cell Count	WaterTox																	
Mean % Normal Development	WaterTox																	

Reportable Water Parameter	Type	1993	1994	1995	1996	1997	1998	1999	2000	2001	2002	2003	2004	2005	2006	2007	2008	2009
Mean % Survival	WaterTox																	
SWI Mean % Normal Alive	WaterTox																	

APPENDIX 7 ANALYTES REPORTED IN SEDIMENT SAMPLES (1993-2009)

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
* Data available upon request

Reportable Sediment Parameter	Type	1993	1994	1995	1996	1997	1998	1999	2000	2001	2002	2003	2004	2005	2006	2007	2008	2009
% Solids	ANC																	
Ammonia	ANC																	
Clay <0.0039 mm	ANC																	
Clay <0.005 mm	ANC																	
CTD*	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																	
Dioxins/Furans	ORGS																	
PAHs	ORGS																	
PAHs Alkylated	ORGS																	
PBDEs	ORGS																	
PCBs 209	ORGS																	
PCBs 40	ORGS																	
Phthalates	ORGS																	
Chlordanes	PESTs																	

Reportable Sediment Parameter	Type	1993	1994	1995	1996	1997	1998	1999	2000	2001	2002	2003	2004	2005	2006	2007	2008	2009
Cyclopentadienes	PESTs																	
DDTs	PESTs																	
Fipronil	PESTs																	
HCHs	PESTs																	
Hexachlorobenzene	PESTs																	
Mirex	PESTs																	
Pyrethroids	PESTs																	
Mean % Normal Alive	SedTox																	
Mean % Survival	SedTox																	
p-Nonylphenol	SYN																	
Aluminum	TE																	
Arsenic	TE																	
Cadmium	TE																	
Copper	TE																	
Chromium	TE																	
Iron	TE																	
Lead	TE																	
Manganese	TE																	
Mercury	TE																	
Mercury, Methyl	TE																	
Nickel	TE																	
Selenium	TE																	
Silver	TE																	
Zinc	TE																	

APPENDIX 8 ANALYTES REPORTED IN BIVALVE TISSUE SAMPLES (1993-2009)

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

Reportable Bivalve Tissue Parameter	Parameter Type	1993	1994	1995	1996	1997	1998	1999	2000	2001	2002	2003	2004	2005	2006	2007[1]	2008	2009[1]
% Moisture	ANC																	
% Solids	ANC																	
% Survival per Species	ANC																	
% Survival per Species (caged)	ANC																	
Condition Index Mean	ANC																	
CTD	ANC																	
Dry Weight	ANC																	
Gonad Index CI Mean	ANC																	
Growth Mean	ANC																	
209 PCBs	ORGS																	
40 PCBs	ORGS																	
Alkanes (C10-C34)	ORGS																	
Musk	ORGS																	
PAHs	ORGS																	
PAHs Alkylated	ORGS																	
PBDEs	ORGS																	
Phthalates	ORGS																	
Chlordanes	PESTs																	
Cyclopentadienes	PESTs																	
DDTs	PESTs																	
HCHs	PESTs																	
Hexachlorobenzene	PESTs																	
Mirex	PESTs																	
p-Nonylphenol	SYN																	
Triphenylphosphate	SYN																	

Reportable Bivalve Tissue Parameter	Parameter Type	1993	1994	1995	1996	1997	1998	1999	2000	2001	2002	2003	2004	2005	2006	2007[1]	2008	2009[1]
Aluminum	TE																	
Arsenic	TE																	
Cadmium	TE																	
Copper	TE																	
Cromium	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																	

APPENDIX 9 – CHANGES TO THE RMP PROGRAM 1993-2009

Action Codes: A= Analyte added or removed from sampling design; D= Data rejected or not available/data comparability issues; 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	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.	Since this was part of a pilot study, the results are not displayed via the WQT. 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 rainy 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 rainy 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 rainy 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	Original RMP sampling design.

Action Codes: A= Analyte added or removed from sampling design; D= Data rejected or not available/data comparability issues; 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**
		sediment; toxicity was measured at 8 of these stations for each matrix. Bivalves were deployed at 11 of the stations.	
S	1994	Added 6 stations for water and sediment sampling (previously 16): San Bruno Shoal (BB15), Alameda (BB70), Red Rock (BC60), Honker Bay (BF40), Petaluma River mouth (BD15), Coyote Creek mouth (BA10)	Sites selected to fill large areas in Estuary where no samples were taken and to better monitor areas around tributaries. Total water stations = 22.
S	1994	Added 2 stations for water and sediment sampling (previously 22) as part of the Local Effects Monitoring Program (LEMP): C-1-3 (Sunnyvale) and C-3-0 (San Jose)	Sites located by water pollution control plants. Added on a trial basis by Water Board. Sites were 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 rainy 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,	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.

Action Codes: A= Analyte added or removed from sampling design; D= Data rejected or not available/data comparability issues; 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**
		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	
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).
A	1998	T-1 samples analyzed for trace organics and trace elements	While T-0 samples have bee consistently analyzed throughout the years, T-1 samples were analyzed for only two cruises: 1998-04 and 2001-09. The decision to analyze was because a lot of the 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

Action Codes: A= Analyte added or removed from sampling design; D= Data rejected or not available/data comparability issues; 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**
			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 rainy 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.
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.
D	2001	PBDE Tissue Data not reported	A minimum amount of QA/QC was conducted. Dataset was missing replicates and SRMs. Data was treated as a special study and not added to S&T db.
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.

Action Codes: A= Analyte added or removed from sampling design; D= Data rejected or not available/data comparability issues; 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	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)

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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	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.

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		each site	
S	2003	Removed water sampling from one random site in the South Bay segment and one random site in the Lower South Bay segment in order to add water sampling at historic sites BA30 (Dumbarton Bridge) in the South Bay and BC10 (Yerba Buena Island) in the Central Bay	Dropping these two random sites enabled the two historic sites to be added back into the sampling design at no additional cost to the program. These sites, along with BG20 (Sacramento River) are used by the Water Board for NPDES permit processing
S	2003	Removed two water and sediment stations (previously 24) C-1-3 (Sunnyvale) and C-3-0 (San Jose), part of the Local Effects Monitoring Program (LEMP)	Funding ended for monitoring of trace organics in water and sediment which began in 1996 at these stations as part of the NPDES. Stations = 24.
S	2003	Removed three stations (previously 14) BD50 (Napa River), BD15 (Petaluma River in San Pablo Bay), and BC21 (Horseshoe Bay in Central Bay) for bivalve tissue monitoring	Findings indicated that only 2-3 stations were required to track long term changes in contaminant concentrations in bivalves. Stations = 11.
A	2004	Added Particulate Organic Carbon (POC) analysis in water samples	Began analyzing for POC in order to be able to calculate Total Organic Carbon values (DOC+POC).
A	2004	Removed phthalates and p-nonylphenol analysis in water and sediment samples	These analytes posed low levels of concern for the San Francisco Bay Region based on current literature.
A	2004	Removed PBDEs, phthalates, p-nonylphenol, 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	Poor recovery and high detection limits created “too many holes in the dataset”. Samples will be archived but not re-analyzed.
D	2004	Bivalve Organics data are not available for pesticides, PAHs, PCBs, and PBDEs	Poor recovery and high detection limits created “too many holes in the dataset”. Samples will be archived but not re-analyzed.
A	2005	Removed Toxicity Identification Evaluations	Method development is needed to aid in understanding the toxicity found in the bay

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		(TIEs) from sediment toxicity analysis	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.
D	2005	2005 Bivalve samples were analyzed for orgaincs by CDFG. PAHs were rejected. PBDEs, PCBs and PESTS were approved.	About half the analytes in each group were NDs.
D	2005	7 archived bivalve samples (T-0,BA10,BA40,BC10,BD20,BD30,BG30) were reanalyzed in 2007 by AXYS for PBDES, PCBs, Pests and PAHs. 3 samples (BA40, BD20, BD30) were reanalyzed for PAHs using Base Extraction Method as a demonstration of appropriate lab method. Results were approved. Samples not reanalyzed included BB71, BC61, BG20, BD40, BA30. Due to lack of archived material not all samples were re-analyzed.	Reanalyzed in 2007 by AXYS as part of Intercomparison study with CDFG. The data available on the WQT include the 7 reanalyzed samples from AXYS and 5 samples analyzed in 2005 by CDFG.
L	2005	2005-09 archived bivalve tissue samples reanalyzed for organics by AXYS and CDFG in 2007	Data analyzed by two different labs: 5 samples were analyzed by CDFG and 7 samples reanalyzed by AXYS.
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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		(BD20)	
D	2006	Tissue data are unavailable for Coyote Creek (BA10)	Nearly full mortality (1% survival) due to heavy biofouling and sedimentation
D	2006	Analyses of 2006 bivalves for trace organics data were delayed until 2008.	Analysis was delayed pending a decision regarding a demonstration of lab capabilities.
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 and chlorpyrifos analysis from CDFG to AXYS	Changed labs based on new method development for this analysis and difficulties with prior method for analyzing these compounds.
P	2006	Stopped analyzing the dissolved water fraction for organics 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. At three stations, the RMP will report our dissolved and particulate fractions separately for comparative purposes.
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	Annual Bivalve Maintenance Cruise discontinued and biannual cruise implemented	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.

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Action Code	**Year**	**Action**	**Detail/Rationale**
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	No bivalves data for 2007	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 analyses were conducted by AXYS. A subset of 2005 archive bivalves were reanalyzed by AXYS in 2007 and results much improved.
L	2007	Intercomparison study with UCSC and BR for trace metals in water samples	UCSC sampled 9 of the 22 sites, BR 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	RMP S&T aquatic toxicity monitoring in the Estuary has shown no toxicity over the past several years. Next scheduled sampling will occur in 2012.

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		screening effort approximately every five years	
P	2007	The S&T monitoring program was expanded to triennial bird egg monitoring (cormorant and tern).	Part of the redesign process implemented in 2006.
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 (CDFG)	To investigate the potential toxicity of pyrethroids in the Bay.
A	2008	Added selenium analysis in tissue (BR)	Added to provide information for the Selenium TMDL
A	2008	Added benthos analysis (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 to validate the detection level for AXYS Analytical'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 because 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	Granule fraction was not analyzed. In 2008, RMP switched labs from UCSC-DET to

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		available	MLML-Aiello. MLML did not analyze larger grainsize fractions, and only fractions <2mm are available.
D	2008	Grainsize determination changed to an optical method.	In 2008, RMP switched grainsize labs from UCSC-DET to MLML-Aiello where they employ a different method.
D	2008	Water MRES pesticide data	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 BR and changed principle lab for trace metals in tissue from UCSC to BR (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 BR'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. BR used reductive precipitation according to EPA Method 1640.
L	2008	Intercomparison study with BR and City and County of San Jose for Copper and Nickel in water	Samples were analyzed by 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 UCSC to EBMUD	Changed labs based on an evaluation of turn around time, cost, and analytical capabilities.

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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	Added sediment-water interface cores exposure (SWIC) toxicity testing method for bivalve larval (*Mytilus galloprovincialis*) SWIC will be analyzed for toxicity by UCD-GC.	The Sediment Quality Objectives recommend using sediment–water interface core exposure (SWIC) for bivalve larva toxicity instead of elutriate testing for toxicity. Toxicity testing for amphipods will continue to be conducted using the elutriate method. TIEs will be conducted in samples that show significant toxicity.
L	2008	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).
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 for all matrices.	The non-Aroclor PCB, PCB 11, was unexpectedly observed in air and effluent samples outside the Bay Area in significant concentrations, 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. Beginning in 2009, pesticides analyzed using the MRES method are considered the RMP's target analytes.
A	2009	Cyanide was analyzed in water.	New site specific objective was developed for cyanide in water in San Francisco Bay.

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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. This is a 5 year special study that is not a part of the Status and Trends Component.
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. This is a special study.
A	2009	PFC samples were collected at a subset of water stations.	Special Study - Added because of concern over elevated concentrations found in Bay Area tissue samples as compared to reference samples from Tomales Bay.
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 Special Study.
A	2009	Water PAHs were not analyzed.	Due to the Cosco Busan oil spill, PAHs were analyzed in 2008. Because no significant changes in the water column were identified, PAH sampling was skipped in 2009 and 2010. Water PAHs are scheduled to be sampled again in 2011.
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 include 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 detecting these PBDEs in water.
D	2009	2009 total cyanide water results are not reported.	The RMP's previous California Toxics Rule (CTR) work was based on the Weak Acid Dissociable (WAD) fraction. Total cyanide will most likely give an over-estimation of the bio-available fraction. Several of the 2009 total cyanide water results were above the cyanide trigger level (1.0 ug/L) for ambient monitoring as stated in the Basin Plan Amendment, which is based on the WAD fraction. Hence, at the request of the Water Board these samples were not reported to avoid confusion.
L	2009	Contra Costa County 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	The Dioxin Pilot Study is not part of the Status and Trends component, but samples were collected during regular RMP sampling events.

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		loading, and sportfish samples.	
P	2009	Changed the statistical design for sediment sampling from five-year panels to six-year panels	Changed to incorporate rainy season sediment sampling which will occur every other year starting in 2010. Rainy season sediment sampling will occur at 20 random sites and 7 historic sites. Dry season sediment sampling will continue to occur at 40 random sites and 7 historic sites.
P	2009	Added Pesticides Fipronil, Fipronil desulfinyl, Fipronil sulfide, and Fipronil sulfone for sediment analysis	These pesticides are highly used in the Bay Area and are of emerging concern. Fipronil is widely-used in flea/tick applications. It is exceedingly toxic to insects/crustaceans. There is relatively little Bay Area data so it would be very helpful to report these data when available.

5

STATISTICAL ANALYSIS OF CENSORED DATA

5. STATISTICAL ANALYSIS OF CENSORED DATA

A supplemental chapter to the RMP's Annual Monitoring Results

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Censored data are measurements whose values are known only to fall above or below a certain threshold. Left-censored data are commonly encountered in environmental studies as values below a detection limit, "non-detects". The most common approach used for dealing with such data is to substitute an arbitrary value such as one-half the method detection limit (MDL). Substitution, however, can produce an invasive pattern alien to the concentrations actually in the samples, resulting in generally poor estimates and incorrect statistical tests (Helsel, 2005; Helsel 2009).

The reason for this poor performance is that method detection limits can be a function of the concentration chosen for method calibration, dilution or other lab preparation, or of matrix interference from other analytes. When these conditions change, using a fraction of the MDL can add a pattern to the data that was not in the samples themselves. Instead, the resulting pattern reflects lab method and choices that obscure or dominate the original values (Helsel, 2005; Helsel 2009).

This does not have to be the case. Methods developed in the social, economic, medical and industrial sciences allow for the incorporation of censored data into the computation of summary statistics, regression, and hypothesis tests. Unfortunately, these methods have rarely been used in environmental studies (Helsel, 2005).

The aim of this work is to investigate and compare approaches for extracting information from an environmental dataset, San Francisco estuary sediment DDT and its metabolites, which include left-censored data. DDT and its metabolites have been routinely monitored at stations throughout the estuary by the Regional Monitoring Program for Water Quality (RMP) since 1993.

Methods

This evaluation was conducted by comparing the statistical results obtained using two substitution methods, replacing non-detects by 0 or one-half the method detection limit, with the results from analytical approaches that incorporate censored data without the need to assign fabricated values.

Regional comparisons

Comparisons between estuary segments were conducted for surface sediment (top 5 cm) DDT concentrations and its metabolites using the nonparametric Kruskal–Wallis test for the period 2002 to 2008, no data being available for 2003. In addition, the Wilcoxon score test was used for the censored data, because when data have multiple detection limits, a score test will have more power than the Kruskal–Wallis test (Helsel, 2005).

Multiple pairwise comparisons were conducted when the null hypothesis of no difference was rejected, and the p-values compared to the Bonferroni individual comparison level at an overall (family) error rate set at an alpha of 0.05.

Temporal trends

Temporal trends were examined for seven historical stations (1993-2008) by performing an Ordinary Least Squares (OLS) regression analysis for the two substitution methods, with lognormal transformed ln(x+1) concentrations used as the dependent variable, and sampling date as the independent variable. Censored data (no substitution of non-detects) were investigated using Maximum Likelihood Estimation (MLE) Regression assuming a lognormal distribution. A significantly positive slope (p<0.05) was assumed to indicate an increase in the concentration of the contaminant at the station over time. Similarly, a significant negative slope assumes a decrease over time, while a lack of significance indicates no change in sediment concentration.

Results

Regional comparisons

The regional distribution of DDT and its metabolites are documented in side-by-side censored boxplots (Figure 1), with a line shown at the highest method detection limit, and the values of percentiles below the line estimated using the robust regression on order statistics (ROS) method of Helsel and Cohn (1988).

Table 1. Percent of non-detects for DDT metabolites by San Francisco estuary region.

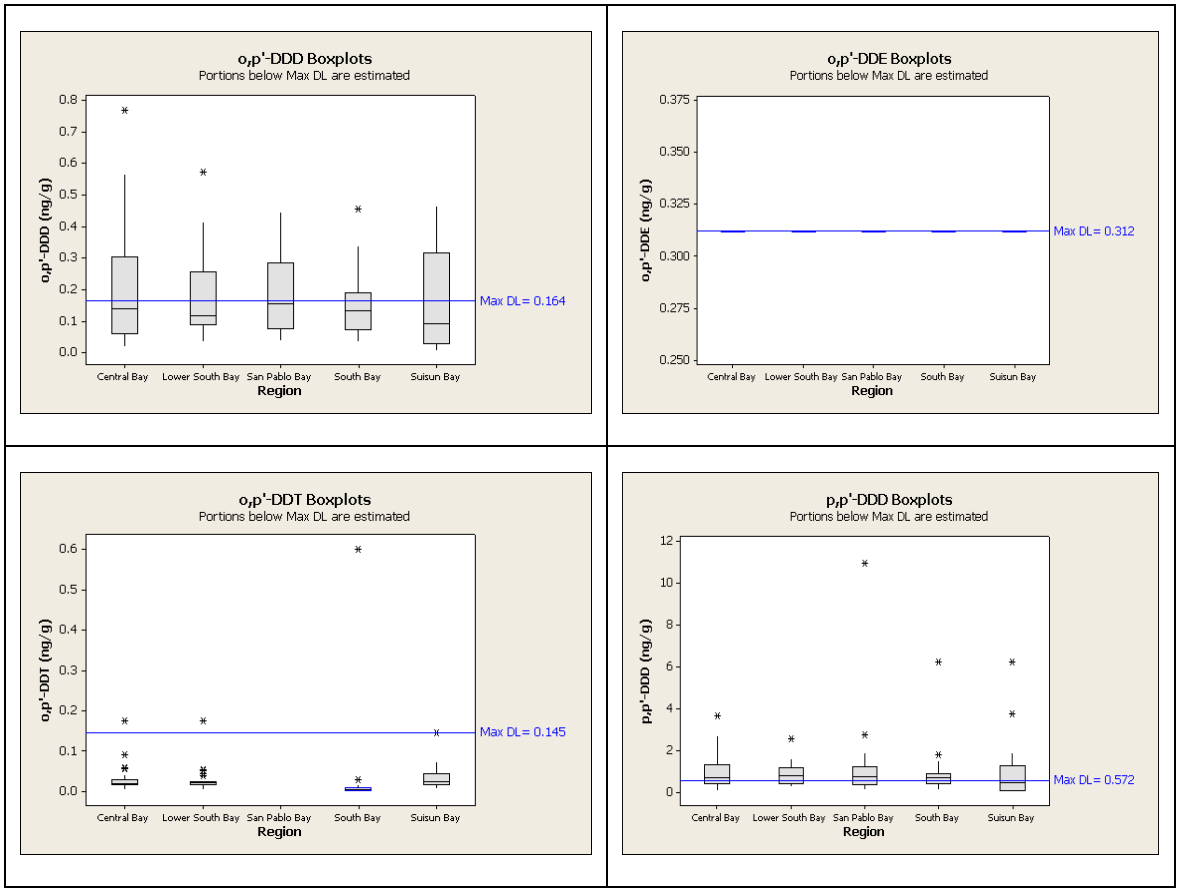
Region	o,p-'DDD	o,p-'DDE	o,p-'DDT	p,p-'DDD	p,p-'DDE	p,p-'DDT
Suisun Bay	26	19	33	17	9	0
San Pablo Bay	17	19	45	13	2	0
Central Bay	17	17	34	6	10	9
South Bay	17	17	60	4	6	15
Lower South Bay	17	21	43	0	0	18

o,p'-DDD

Non-detects for o,p-'DDD ranged from 26% in Suisun Bay to 17% in the other Bay regions (Table 1). No significant differences were documented between the five estuary regions (Figure 1).

o,p'-DDE

Non-detects for o,p-'DDE ranged from 17% in the Central and South Bay to 21% in the Lower South Bay (Table 1). No significant differences were documented between the five estuary regions (Figure 1, Table 2).



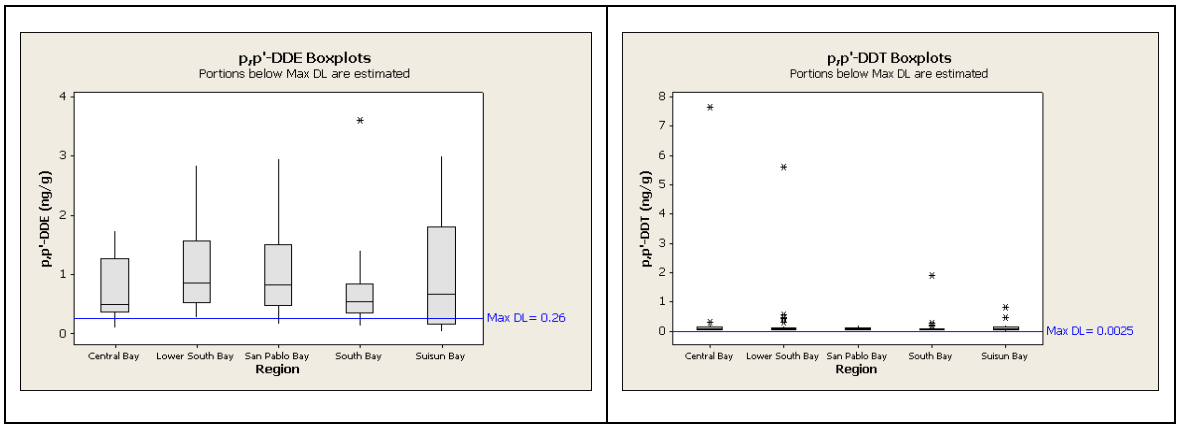


Figure 1. Censored boxplots showing the distribution of DDT and its metabolites by San Francisco estuary region.

o,p'-DDT

Non-detects for o,p-'DDT ranged from 33% in Suisun Bay to 60% in the South Bay (Table 1). Regions were significantly different in concentrations of o,p'-DDT using both methods of substituting for non-detects (ND=0; H=11.31, *df*=4, *p*=0.023 and ND=1/2 MDL; H=10.51, *df*=4, *p*=0.033) (Figure 1, Table 2). Suisun Bay sediments were found to be significantly greater in o,p'-DDT than the South Bay when non-detects were replaced with zero (Z=3.054, critical value=2.807, *p*=0.002), but no

Table 2. Coefficients for tests of significance between estuary regions.

	Kruskal-Wallis adjusted for ties (ND = 0)	Kruskal-Wallis adjusted for ties (ND = 1/2 MDL)
o,p'-DDD	H = 2.89, df = 4, p = 0.577	H = 4.45, df = 4, p = 0.349
o,p'-DDE	H = 5.09, df = 4, p = 0.279	H = 8.32, df = 4, p = 0.080
o,p'-DDT	**H = 11.31, df = 4, p = 0.023**	**H = 10.51, df = 4, p = 0.033**
	Suisun Bay > South Bay	no significant regional differences
	Z = 3.05444, Critical value = 2.807, p = 0.0023	

p,p'-DDD	H = 4.68, df = 4, p = 0.321	H = 5.40, df = 4, p = 0.249
p,p'-DDE	**H = 16.10, df = 4, p = 0.003** Lower South Bay > South Bay **Z = 3.34762, Critical value = 2.807, p = 0.0008**	**H = 16.10, df = 4, p = 0.003** Lower South Bay > South Bay **Z = 3.35030, Critical value = 2.807, p = 0.0008** San Pablo Bay > South Bay **Z = 2.81812, Critical value = 2.807, p = 0.0048**
p,p'-DDT	H = 6.73, df = 4, p = 0.151	H = 7.14, df = 4, p = 0.129

significant pairwise comparisons were found when non-detects were replaced with one-half their MDL. The Kruskal-Wallis test for censored data found no significant differences between the regions, but the more powerful Wilcoxon score test was highly significant (Chi-square=14.48, *df*=4, *p*=0.006). Multiple pairwise comparisons after the Wilcoxon score test showed sediment o,p'-DDT concentrations in the South Bay were significantly lower than in Suisun Bay (Chi-square=8.11, *df*=1, *p*=0.004), and the Central Bay (Chi-square=8.10, *df*=1, *p*=0.004).

p,p'-DDD

Non-detects for o,p-'DDE ranged from 0% in the Lower South Bay to 17% in the Suisun Bay (Table 1). No significant differences were documented between the five estuary regions (Figure 1, Table 2).

p,p'-DDE

Non-detects for p,p-'DDE ranged 0% in the Lower South Bay to 10% in the Central Bay (Table 1). The regions were significantly different in concentrations of p,p'-DDE using both methods of substitution (ND=0; H=16.10, *df*=4, *p*=0.003 and ND=1/2 MDL; H=16.10, *df*=4, *p*=0.003) (Figure 1, Table 2). Lower

Table 2 (cont). Coefficients for tests of significance between estaury regions.

	Kruskal-Wallis for censored data (no substitution)	Wilcoxon score test (no substitution)
o,p'-DDD	H = 2.58, df = 4, p = 0.630	Chi-square = 3.5283, df = 4, p = 0.474
o,p'-DDE	H = 0.00, df = 4, p = 1.000	Chi-square = 8.73571, df = 4, p = 0.068
o,p'-DDT	H = 1.14, df = 4, p = 0.888	**Chi-square = 14.4777, df = 4, p = 0.006** Suisun Bay > South Bay **Chi-square = 8.11, df = 1, p = 0.004** Central Bay > South Bay **Chi-square = 8.10, df = 1, p = 0.004**
p,p'-DDD	H = 2.58, df = 4, p = 0.629	Chi-square = 4.6586, df = 4, p = 0.324
p,p'-DDE	**H = 16.16, df = 4, p = 0.003** Lower South Bay > South Bay **Z = 3.37909, p = 0.0007** San Pablo Bay > South Bay **Z = 2.82859, p = 0.0047**	**Chi-square = 16.0984, df = 4, p = 0.003** Lower South Bay > South Bay **Chi-square = 14.15, df = 1, p < 0.0005** San Pablo Bay > South Bay **Chi-square = 9.02, df = 1, p = 0.003** Lower South Bay > Central Bay **Chi-square = 8.52, df = 1, p = 0.004**
p,p'-DDT	H = 6.73, df = 4, p = 0.151	Chi-square = 6.18762, df = 4, p = 0.186

South Bay sediments were found to be significantly greater in the concentration of p,p'-DDE than the South Bay (ND=0; Z=3.348, critical value=2.807, *p*=0.001), and South Bay sediments significantly lower than Lower South Bay (ND=1/2 MDL; Z=3.350, critical value=2.807, *p*=0.001), and San Pablo Bay (ND=1/2 MDL; Z=2.818, critical value=2.807, *p*=0.005).

Statistically significant differences were found between regional sediment concentrations using the two approaches for analyzing censored data (Kruskal-Wallis, H=16.16, *df*=4, *p*=0.003 and Wilcoxon, Chi-square=16.10, *df*=4, *p*=0.003). Multiple pairwise comparisons after the Kruskal-Wallis test on censored data found sediment p,p'-DDE concentrations in the South Bay were lower than in the Lower South Bay (Z=3.379, critical value=2.807, *p*=0.001) and San Pablo Bay (Z=2.829, critical value=2.807, *p*=0.005).The multiple pairwise comparisons, after the Wilcoxon score test, show sediment concentrations in the South Bay were significantly lower than in the Lower South Bay (Chi-square=14.15, *df*=1, *p*<0.0005), and San Pablo Bay (Chi-square=9.02, *df*=1, *p*=0.003), similar to results for the substitution methods. Additionally, Lower South Bay p,p-DDE concentrations were found to be significantly higher than in the Central Bay (Chi-square=8.52, *df*=1, *p*=0.004).

Table 3. Percent of non-detects for DDT and its metabolites by San Francisco sediment station.

Station	o,p-'DDD	o,p-'DDE	o,p-'DDT	p,p-'DDD	p,p-'DDE	p,p-'DDT
BA10	56	72	65	0	0	20
BA41	64	76	89	9	0	42
BC11	48	68	80	14	5	42
BD31	50	73	80	9	5	17
BF21	55	71	71	9	0	16

BG20	73	76	85	27	9	58
BG30	81	77	95	57	30	65

p,p'-DDT

Non-detects for p,p-'DDT ranged from 0% in Suisun and San Pablo Bay to 18% in the Lower South Bay (Table 1). No significant differences were documented between the five estuary regions (Figure 1, Table 2).

Temporal trends

o,p'-DDD

Non-detects for o,p-'DDD ranged from a low of 48% at Yerba Buena Island (BC11) to a high of 81% at the San Joaquin River (BG30) station (Table 3). Only one significant positive trend was documented in o,p-'DDD concentrations (BG20 Sacramento River: OLS Regression, ND=0, p=0.009) (Table 4).

o,p'-DDE

Non-detects for o,p-'DDE ranged from a low of 68% at Yerba Buena Island (BC11) to a high of 77% at the San Joaquin River (BG30) station (Table 3). Significant trends in o,p-'DDE concentrations were found for at least one of the three regression methods at 71% (5 of 7) of the stations (Table 4).

Table 4. Station trends from 1993 to 2008 for DDT and its metabolites, values shown are alpha values. Slope indicates the direction of trend (- or +) , OLS(0) indicates ordinary least squares regression after substitution of ND with value of zero, OLS(1/2 MDL) indicates ordinary least squares regression after substitution of ND with value of one-half its method detection limit, and MLE indicates maximum likelihood estimation regression for censored data.

Station	Method	Slope	o,p-'DDD	Slope	o,p-'DDE	Slope	o,p-'DDT	Slope	p,p-'DDD	Slope	p,p-'DDE	Slope	p,p-'DDT
BA10	OLS(0)	**-**	0.509	**+**	**0.000**	**-**	0.379	**-**	0.073	**-**	0.066	**-**	0.303
	OLS(1/2 MDL)	-	0.294	-	**0.007**	-	0.233	-	0.073	-	0.066	-	0.202
	MLE	+	0.882	+	0.834	-	0.386	-	0.054	-	**0.039**	-	0.136
BA41	OLS(0)	+	0.968	-	0.288	+	**0.001**	-	0.057	-	0.124	+	0.809
	OLS(1/2 MDL)	-	0.712	-	0.367	+	0.951	-	0.117	-	0.124	+	0.985
	MLE	-	0.823	-	0.145	+	0.401	-	0.310	-	0.059	-	0.899
BC11	OLS(0)	-	0.837	-	0.715	+	0.933	-	0.309	-	0.580	-	0.530
	OLS(1/2 MDL)	-	0.680	-	**0.007**	-	0.507	-	0.225	-	0.591	-	0.412
	MLE	-	0.800	-	0.050	+	0.380	-	0.228	-	0.390	-	0.655
BD31	OLS(0)	-	0.749	-	**0.017**	+	0.608	-	0.249	-	0.441	-	0.597
	OLS(1/2 MDL)	-	0.354	-	0.265	-	0.253	-	0.174	-	0.433	-	0.489
	MLE	-	0.650	+	1.000	+	0.375	-	0.206	-	0.446	-	0.390
BF21	OLS(0)	+	0.849	+	0.940	+	0.736	-	0.295	-	0.516	-	0.295
	OLS(1/2 MDL)	-	0.679	-	0.210	-	0.250	-	0.207	-	0.516	-	0.220

	MLE	+	0.929	-	0.613	+	0.441	-	0.211	-	0.522	-	0.114
BG20	OLS(0)	+	**0.009**	+	**0.002**	+	**0.000**	+	0.574	+	0.195	+	0.604
	OLS(1/2 MDL)	+	0.083	+	0.609	-	**0.018**	+	0.529	+	0.180	+	0.859
	MLE	+	0.102	+	0.038	+	**0.002**	+	0.800	+	0.573	+	0.458
BG30	OLS(0)	-	0.772	-	0.622	+	0.053	-	0.327	-	0.523	-	0.858
	OLS(1/2 MDL)	-	0.175	-	**0.035**	-	**0.011**	-	0.184	-	0.352	-	0.675
	MLE	-	0.658	-	**0.033**	-	1.000	-	0.192	-	0.300	-	0.322

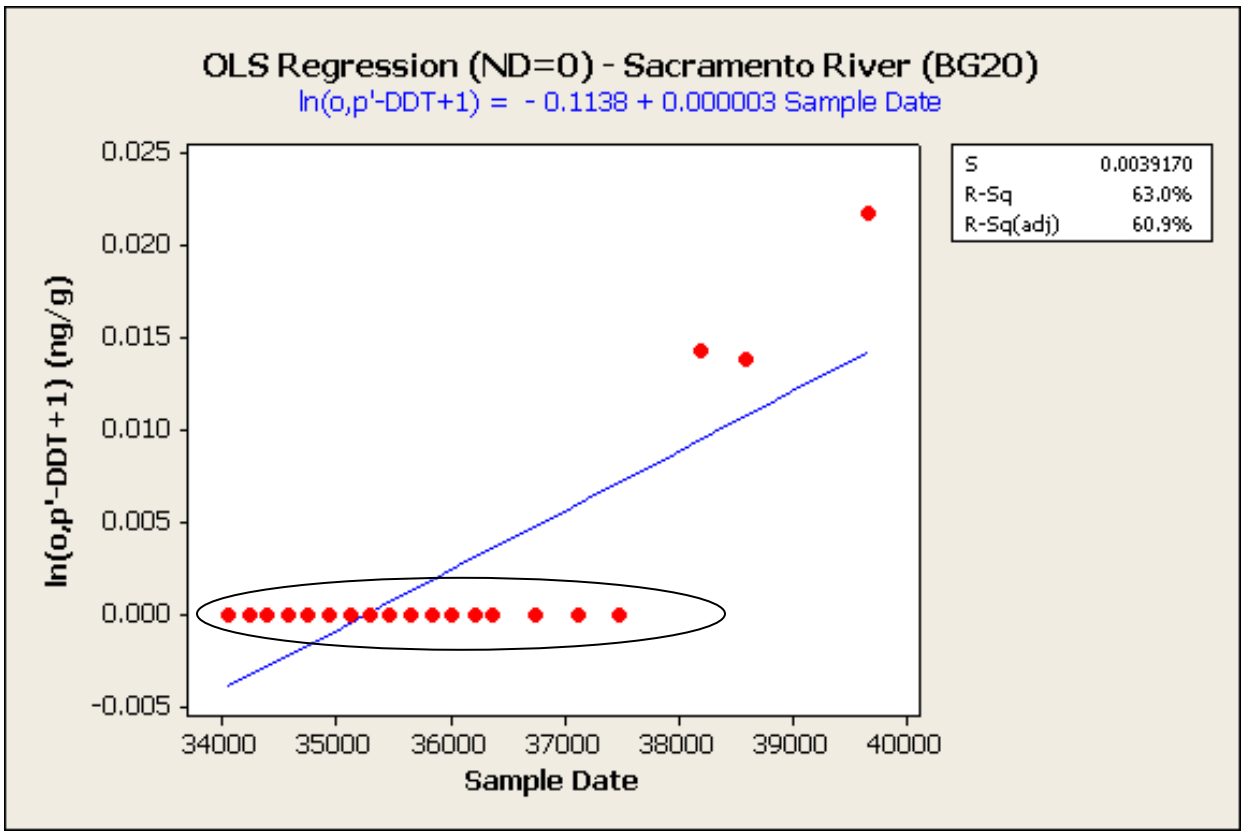


Figure 2. Ordinary Least Squares (OLS) regression showing trend in o,p-'DDT at the Sacramento River station, after non-detects were replaced with an arbitrary value of zero. Substitute values lie inside the oval.

o,p'-DDT

Non-detects for o,p-'DDT ranged from a low of 65% at Dumbarton Bridge (BA10) to a high of 95% at the San Joaquin River (BG30) station (Table 3). Significant trends were found at three stations: BA41 Point Isabel (OLS Regression, ND=0, p=0.001), BG30 San Joaquin River (OLS Regression, ND=1/2 MDL, p=0.011), and BG20 Sacramento River (OLS Regression, ND=0, p<0.0005; OLS Regression, ND=1/2 MDL, p=0.018; MLE Regression, no substitution, p=0.002) (Table 4). The three significant Sacramento River (BG20) trends are shown in Figures 2, 3, and 4.

p,p'-DDD

Non-detects for p,p-'DDD ranged from a low of 0% at Dumbarton Bridge (BA10) to a high of 57% at the San Joaquin River (BG30) station (Table 3). No significant trends were found in p,p-'DDD at any of the seven stations (Table 4).

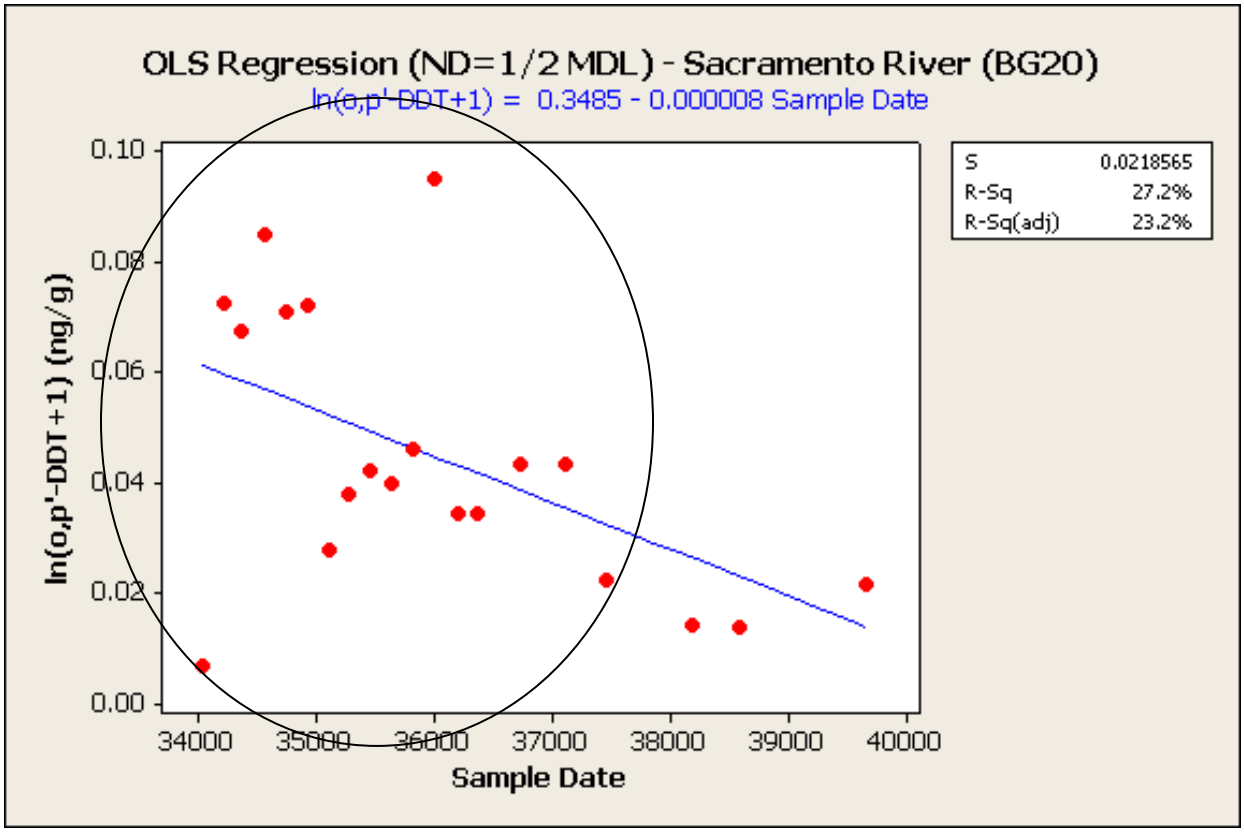


Figure 3. Ordinary Least Squares (OLS) regression showing trend in o,p-'DDT, after non-detects were replaced with an arbitrary value of one-half the method detection limit, at the Sacramento River station. Substitute values are enclosed within the circle.

p,p'-DDE

Non-detects for p,p-'DDE ranged from a low of 0% at several stations (BA10, BA41, and BF21) to a high of 30% at the San Joaquin River (BG30) station (Table 3). No significant trends in p,p-'DDE were found (Table 4).

p,p'-DDT

Non-detects for p,p-'DDT ranged from a low of 16% at Grizzly Bay (BF21) to a high of 65% at the San Joaquin River (BG30) station (Table 3). No significant trends were found for p,p-'DDT (Table 4).

Discussion

Regional results were the same for the majority of comparisons, regardless of the approach, with no significant differences found between San Francisco estuary regions in the sediment concentrations of o,p-'DDD, o,p-'DDE, p,p -'DDD, and p,p-'DDT concentrations. Significant regional differences in the

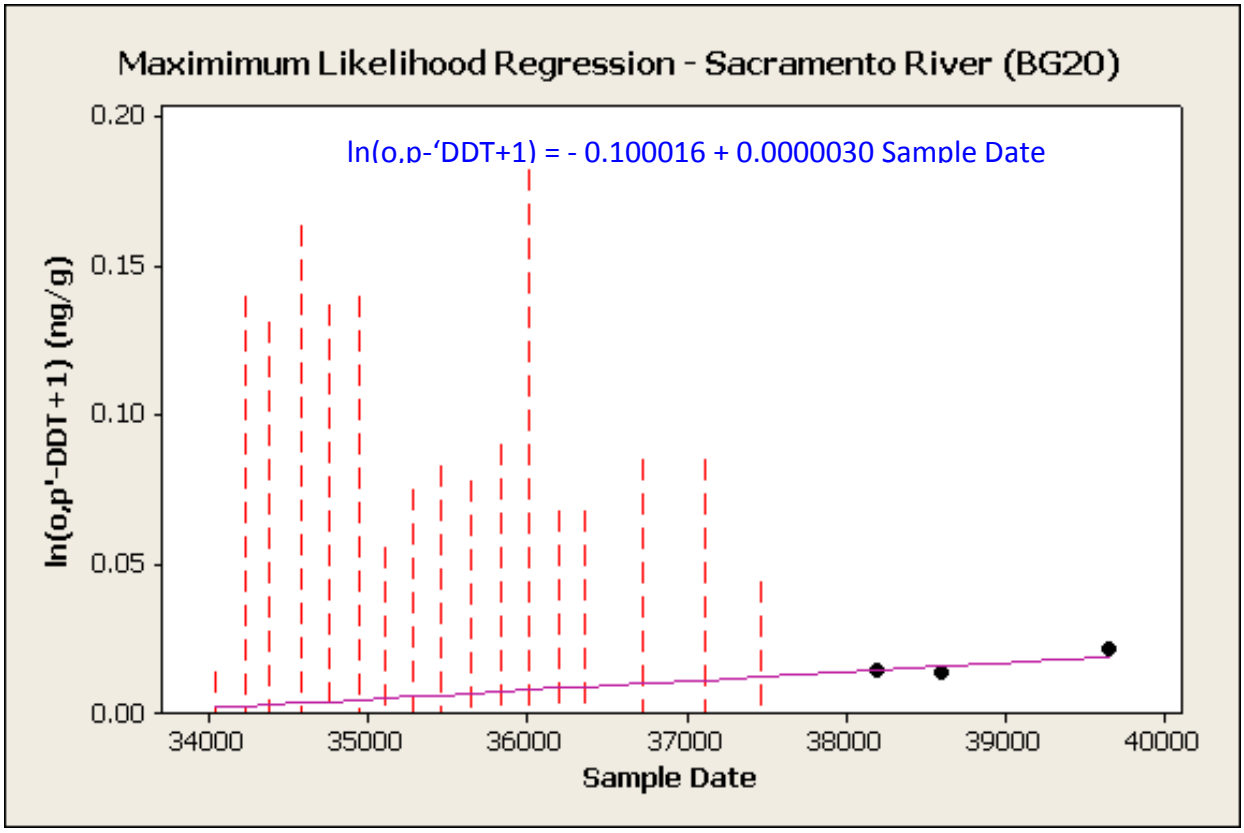


Figure 4. Maximum Likelihood Estimation (MLE) regression on censored data showing trend in o,p-'DDT at the Sacramento River station. Non-detects are shown as interval-censored data, drawn as dotted lines from 0 up to their method detection limit.

concentrations of o,p-'DDT, and p,p-'DDE were documented. The multiple pairwise comparisons found that the concentration of o,p-'DDT in Suisun Bay sediments was greater than in sediments collected in the South Bay; when non-detects were replaced with the arbitrary value of zero.

When non-detects were replaced with one-half the MDL no significant multiple pairwise differences were found in o,p-'DDT sediment concentrations between the five regions. The pairwise comparisons done after the Wilcoxon score test, however, showed sediment o,p-'DDT concentrations in the South Bay were lower than in the Suisun and Central Bay.

Sediment p,p-'DDE concentrations in the Lower South Bay were greater than in the South Bay, irrespective of the approach, and San Pablo Bay p,p-'DDE concentrations were greater than in the South Bay for all approaches, except for the substitution of non-detects with a value of zero. Pairwise multiple comparisons done after the Wilcoxon score test showed p,p'-DDE concentrations were significantly higher in the Lower South Bay compared to the Central Bay (Chi-square=8.52, *df*=1, *p*=0.004).

Trends in DDT and its metabolites were generally identical, regardless of which method was used to treat non-detects, and analyze the data. There were several cases where zero substitution resulted in a significant increasing trend (Table 4), including the Sacramento River Station (BG20). The Sacramento River station was the only instance where all three methods resulted in significant trends (o,p-'DDT, Table 4). The direction of the trend, however, was different increasing for substitution of ND with 0 (Figure 2), but decreasing when non-detects were replaced with one-half the method detection limit (Figure 3).

The trend reversal for o,p-'DDT at the Sacramento River station (Figure 3) indicates how invasive patterns can be introduced into the data that was not in the samples themselves. In fact, the trend in o,p-'DDT does not represent a decrease in sediment concentrations, but the lowering of detection limits due to more sensitive methods. The MLE regression for censored data reveals a significant increase in o,p-'DDT at the Sacramento River station (Figure 4). It should be noted, however, that MLE regression works best when the data are close to the assumed distribution (Helsel, 2005; Helsel 2009), in this case lognormal, and that all methods for analyzing censored data have lower errors when there is more data (Helsel 2009).

Recommendations

Erroneous statistical conclusions can be extremely costly in time and money, especially if they result in inappropriate management or regulatory actions. Therefore, whenever feasible, appropriate methods for incorporating censored data should be used for statistical analysis and substitution should be avoided. Substitution is not imputation, but fabrication (Helsel 2009). The use of appropriate methods will result in generally better estimates and correct statistical tests, even though the statistical conclusions may not change.

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