San Francisco Estuary Regional Monitoring Program for Water Quality

# DRAFT Strategy for Addressing Emerging Contaminants in the RMP

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## TABLE OF CONTENTS

I. INTRODUCTION	3
A. Purpose and Goals of the Workgroup	3
B. Structure of the Regional Monitoring Program	
1. Status and Trends Monitoring	
2. Pilot and Special Studies	8
II. RMP Emerging Contaminant Monitoring To Date	
A. Identification and Evaluation of Previously Unknown and Unmonitored Organic	
Contaminants	
B. Concentrations of "New Analytes" in Status and Trends Monitoring in 2002 and	
2003	
C. Exposure and Effects Pilot Study/PRISM 2004: Pyrethroids	4
D. Development of a Conceptual Model for PBDEs 1	5
III. Developing a Comprehensive Strategy for Monitoring Emerging Contaminants in	
the RMP	
A. Strategy for Identifying Emerging Contaminants of Potential Concern in San	
Francisco Bay 1	6
1. Convene Workgroup	
2. Identify Groups Conducting Related Emerging Contaminant Work	7
3. Evaluate Published Literature for Emerging Contaminants	
B. Developing an Approach for Inclusion of New Analytes 1	
1. Potential Emerging Contaminants	
2. Methods for Ranking Emerging Contaminants	
C. Identifying Potential Pilot or Special Studies to Address Information Gaps 2	
IV. References	
List of Figures	

Figure 1	Location of Status and Trends Sampling Sites
Figure 2	Concentrations of total PBDEs in effluent and sludges

#### List of Tables

Table 1 Analytes by Matrices	
Table 2       Concentrations (ng/L) and distributions of contaminants	found in
San Francisco Estuary water samples	
Table 3Results of "New Analyte" Analysis 2002/2003	
Table 4Concentrations of Pyrethroids in Sediment (ng/g)	

## Appendices

Appendix A	Chemical Structure, Use and Properties of the "New Analytes"
Appendix B	2007 Pilot and Special Study Ideas – Emerging Contaminants

# I. INTRODUCTION

## A. PURPOSE AND GOALS OF THE WORKGROUP

The Regional Monitoring Program for Water Quality (RMP or Program) is an innovative collaborative monitoring and research program that was developed in 1993 by the following participants: the San Francisco Estuary Institute (SFEI); the San Francisco Bay Regional Water Quality Control Board (SFBRWQCB), and the NPDES permit holders that discharge to the San Francisco Bay. The Program is funded by the regulated dischargers, implemented by SFEI, and overseen by both the dischargers and the SFBRWQCB. One of the goals of the RMP is to develop an understanding of the impacts of contaminants on the beneficial uses of the San Francisco Bay (Estuary).

The foundation of the RMP is the following six objectives and related management questions (underlined management questions are particularly relevant to the Emerging Contaminants Workgroup):

# 1. Describe the distribution and trends of pollutant concentrations in the Estuary

- 1.1 Which pollutants should be monitored in the Estuary, in what media, and at what frequency?
- 1.2 Are pollutants of concern increasing, decreasing, or remaining the same in different media?
- 1.3 How are contaminant patterns and trends in the Estuary over time affected by remediation and source control or pollution prevention in the watersheds?
- 1.4 Do pollutant concentration distributions indicate particular areas of origin or regions of potential ecological concern?
- 1.5 What effects on beneficial uses or attainment of Water Quality Standards will occur due to large-scale habitat restoration in the Estuary in decades to come?

# 2. Project future contaminant status and trends using current understanding of ecosystem processes and human activities

- 2.1 Can reasonably accurate recovery forecasts be developed for major segments and the Estuary as a whole under various management scenarios?
- 2.2 Can potential impairment and degradation be better anticipated in the face of projected changes in land and water use and management, as well as product use and disposal?
- 2.3 Which pollutant categories are predicted to accumulate in the Estuary faster then they can be assimilated?
- 2.4 Do pollutant trends reflect historical changes in use patterns, transport and transformation processes, or control actions?
- 2.5 How will the importance of each pathway change through time under various management and development scenarios?
- 2.6 What is the projected future loading of pollutants of concern under various management and development scenarios?

- 2.7 What are the likely consequences of various management actions or risk reduction measures?
- 2.8 Do pollutants show existing distributions that fit our current understanding or models of their origin, loads, and transport?
- 2.9 What changes in loadings or ecosystem characteristics (e.g., extent of restored tidal marsh, Estuary circulation and flushing, food web shifts) would reduce or increase pollutant exposures and effects?
- 2.10 How are distributions and long-term trends in pollutants affected by current and predicted estuarine processes (e.g. sediment erosion, deposition, river inflows)?

#### 3. Describe sources, pathways, and loading of pollutants entering the Estuary

- 3.1 Where are/were the largest pollutant sources, in what context are/were these pollutants applied or used, and what are/were their ultimate points of release into the aquatic environment?
- 3.2 What are the circumstances and processes that cause the release of pollutants from both internal and external source areas?
- 3.3 Once released, how do pollutants travel from source areas to the Estuary, what are the temporal and spatial patterns of storage, and are they transformed along the way or after deposition?
- 3.4 What is the annual mass of each pollutant of concern entering the Bay from each pathway?
- 3.5 Can data with high temporal resolution from a few watersheds be projected to other watersheds and the Basin as a whole?
- 3.6 For each pollutant of concern, what forms are released from each pathway and what are the magnitude and temporal variation of concentrations and loadings?
- 3.7 How do loads change over time in relation to management activities?
- 3.8 What is the relative importance of pollutant loadings from different sources and pathways, including internal inputs, in terms of beneficial use impairment?

# 4. Measure pollution exposure and effects on selected parts of the Estuary ecosystem (including humans)

- 4.1 How are emerging problems reflected in exposure and effects measurements?
- 4.2 Which (co-)factors (e.g., food web structure) influence exposure and effects of specific pollutants on biota?
- 4.3 What ecological risks are caused by pollutants of concern?
- 4.4 What human exposure to pollutants of concern results from consumption of fish and game?
- 4.5 To what extent does exposure to multiple pollutants lead to effects?
- 4.6 Which forms of pollutants cause impairment?
- 4.7 To what extent do factors other than specific pollutants (invasive species, flow diversions, land use changes, toxic algal blooms) contribute to beneficial use impairment?

- 5. Compare monitoring information to relevant benchmarks, such as TMDL targets, tissue screening levels, water quality objectives, and sediment quality objectives
  - 5.1 What percentage of the Estuary is supporting beneficial uses?
  - 5.2 Which segments should be considered impaired and why, and how do segments compare in terms of recovery targets?
  - 5.3 How can specific source limitations, controls, and mitigation be best linked to appropriate beneficial use endpoints and recovery targets?
- 6. Effectively communicate information from a range of sources to present a more complete picture of the sources, distribution, fate, and effects of pollutants and beneficial use attainment or impairment in the Estuary ecosystem.

This objective applies to all of the questions listed under objectives 1-5.

The pollutants that the RMP monitors are primarily chemicals for which water quality objectives exist. However, in recent years, there has been much discussion about emerging contaminants and the potential impact these contaminants may have on the environment. Emerging contaminants are defined by the USGS as:

"Emerging contaminants" can be broadly defined as any synthetic or naturally occurring chemical or any microorganism that is not commonly monitored in the environment but has the potential to enter the environment and cause known or suspected adverse ecological and(or) human health effects. In some cases, release of emerging chemical or microbial contaminants to the environment has likely occurred for a long time, but may not have been recognized until new detection methods were developed. In other cases, synthesis of new chemicals or changes in use and disposal of existing chemicals can create new sources of emerging contaminants. (Source: www. http://toxics.usgs.gov/regional/emc/index.html)

The goals of the newly-formed Emerging Contaminants Workgroup (ECWG) are:

- 1. to develop a strategy for identifying emerging contaminants of potential concern in the Bay that should be screened in pilot studies;
- 2. to recommend pilot or special studies to identify emerging contaminants of potential concern;
- 3. to develop criteria for inclusion of emerging contaminants in long-term monitoring; and
- 4. to develop cost-effective strategies for long-term monitoring for emerging contaminants that are of sufficiently high concern.

The purpose of this document is to provide background information to the ECWG regarding the structure of the RMP and the RMP studies that have been conducted to date on emerging contaminants. In addition, this document outlines a strategy for identifying emerging contaminants, for developing an approach for inclusion of emerging contaminants into the RMP, and for identifying potential special studies to fill critical

gaps in our understanding of emerging contaminants. All of these issues will be discussed at the ECWG's first meeting on June 1, 2006.

### B. STRUCTURE OF THE REGIONAL MONITORING PROGRAM

The RMP is overseen by the Technical Review Committee (TRC), the Steering Committee (SC), and four workgroups. The TRC and SC are composed of representatives of Bay dischargers, and staff from the San Francisco Bay Regional Water Quality Control Board, US Environmental Protection Agency, and SFEI. The workgroups consist of interested members of the TRC, local stakeholders, and nationally or internationally recognized experts that are included to provide peer review in the planning, implementation, and reporting phases of RMP studies. Three RMP workgroups that have been in place for several years are: Sources, Pathways and Loadings Workgroup (estimating contaminant loads to the Estuary); Exposure and Effects Workgroup (developing biological indicators of effects of contaminants on biota); and Contaminant Fate Workgroup (fate and transport of contaminants). The TRC recommended in Fall of 2005 that a fourth workgroup be formed to address emerging contaminants, the Emerging Contaminants Workgroup (ECWG).

#### 1. Status and Trends Monitoring

A core program element of the RMP is the Status and Trends monitoring that occurs annually in August during the dry season. This monitoring is approximately one third of the annual operating budget of the RMP. Under the Status and Trends program, monitoring is conducting at 31 water stations, 47 sediment stations, and 11 bivalve stations in the Estuary (Figure 1). Sport fish are also collected and analyzed every three years as part of the Status and Trends program. The TRC is currently evaluating whether triennial monitoring of cormorant eggs at three locations in the Bay should also be included in Status and Trends.

Water and sediment samples are collected at stations selected using an EMAPstyle stratified random sampling design, and include a subset of fixed historical RMP stations (5 water and 7 sediment stations sampled since 1993). Bivalves, sport fish and cormorant eggs are collected at fixed sites.

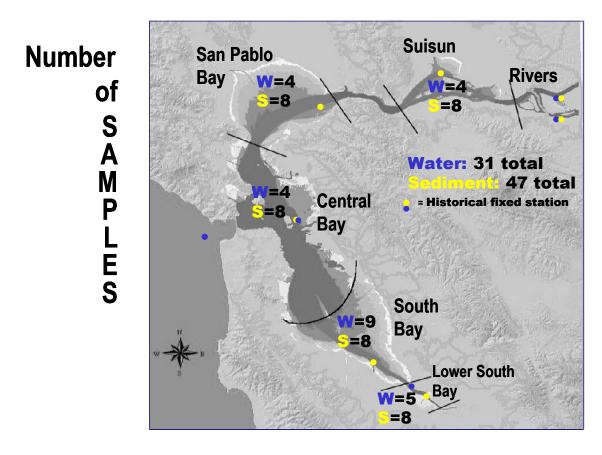


Figure 1. Allocation of Status and Trends sampling sites among the segments of the Bay.

Water and sediment are analyzed for trace organic and trace elements. At 27 of the sediment stations, additional sediment is collected for toxicity testing. Caged bivalves are deployed at nine locations and resident clams are collected at the two River stations (a total of 11 stations). Bivalve samples are analyzed for trace organics annually and trace elements approximately every five years. Popular sport fish species are collected every three years, including white croaker, striped bass, shiner surfperch, white sturgeon, anchovy, black surfperch, brown rockfish, Chinook salmon, and walleye surfperch. These fish are collected at five locations dispersed throughout the Bay (San Pablo Bay, San Francisco, Berkeley, Oakland Inner Harbor, and South Bay) and analyzed for mercury, PCBs, DDT, dieldrin, chlordane, PBDEs, and selenium. Cormorant eggs have been collected at three locations (north, central and south bay) for two years (2002 and 2004) for analysis of PCBs, PBDEs, dioxins, phthalates, dieldrin, DDT, mercury, selenium, musks, nonylphenol, and triphenylphosphate. Table 1 shows the analyte list by matrix.

Media	<b>Trace Elements</b>	Organics	Pesticides
Water	Al, As, Cd, Co, Cu, Fe, Pb, Mn, Hg, MeHg, Ni, Se, Ag, Zn	PAHs, PCBs, PBDEs, Phthalates <sup>1</sup> , Nonylphenol <sup>1</sup>	Cyclopentadienes (e.g., Dieldrin), chlordane, DDT, HCH, Chlorpyrifos, Dacthal, Diazinon, Endosulfans Hexachlorobenzene, Mirex, Oxadiazon
Sediment	Al, As, Cd, Co, Cu, Fe, Pb, Mn, Hg, MeHg, Ni, Se, Ag, Zn	PAHs, PCBs, PBDEs, Phthalates <sup>1</sup> , Nonylphenol <sup>1</sup>	Cyclopentadienes (e.g., Dieldrin), chlordane, DDT, HCH, Hexachlorobenzene Mirex
Bivalves		PAHs, PCBs, PBDEs, Phthalates <sup>1</sup> , Musks <sup>1</sup> , Nonylphenol <sup>1</sup> , Triphenylphosphate <sup>1</sup>	Cyclopentadienes (e.g., Dieldrin), chlordane, DDT, HCH, Hexachlorobenzene Mirex
Sport fish	Hg, Se	PCBs, PBDEs	Cyclopentadienes (e.g., Dieldrin), chlordane, DDT, HCH, Hexachlorobenzene Mirex
Small fish	Hg		
Cormorant eggs	Hg, Se	PCBs, PBDEs, Dioxins, Phthalates <sup>1</sup> , Musks <sup>1</sup> , Nonylphenol <sup>1</sup> , Triphenylphosphate <sup>1</sup>	Cyclopentadienes (e.g., Dieldrin), chlordane, DDT, HCH, Hexachlorobenzene Mirex

Table 1Analytes by Matrix

<sup>1</sup> Musks, phthalates, nonylphenol, and triphenylphosphate were analyzed in sediment, water, bivalve, and cormorant egg samples collected in 2002 and 2003.

# 2. Pilot and Special Studies

In addition to the Status and Trends program, the RMP spends approximately 16 percent of its budget on Pilot and Special Studies (approximately \$500,000 annually). The Pilot and Special Studies (PS/SS) portion of the Program changes every year and has enabled the Program to adapt in response to changes in the regulatory landscape and advances in our understanding of the Estuary and the environment.

PS/SSs are solicited from committees and workgroups as well as the public at large. Once compiled, the ideas are evaluated in March by the TRC and requests are made for more detailed conceptual scope of works from select projects. These work

plans are presented to the TRC and SC for final evaluation, and decisions for inclusion in the following year's RMP are made by the committees in July.

In 2005, approximately \$200,000 of the PS/SS budget was allocated to an Exposure and Effects Pilot Study and \$100,00 was allocated to determining contaminant loads from the Delta (northern portion of the Bay) and the Guadalupe watersheds (southern portion of the Bay). Other studies in 2005 included monitoring of atmospheric deposition of mercury and development of a conceptual model for PBDEs.

To date, four studies relevant to emerging contaminants have been funded through the PS/SS process: two reviews of historical GC-MS chromatograms to identify previously unidentified contaminants (1993, 1994 and 1998; and 1999, 2000, and 2001), a study of PBDEs in the Bay, and a study of pyrethroids in urban tributaries to the Bay. A brief synopsis of each of these projects is presented in the next section.

# II. RMP EMERGING CONTAMINANT MONITORING TO DATE

The RMP has performed some studies of emerging contaminants. The initial impetus for evaluating emerging contaminants in the RMP came from Risebrough (1995), one of the original contractors in the Program. Risebrough called for "surveillance monitoring" to identify new chemicals of concern. In the 2001 and 2002, stemming from a proposal by Risebrough, historical chromatograms were reviewed to attempt to identify previously unidentified compounds. Based on the results of this study, the RMP added several "new analytes" to its annual Status and Trends monitoring list in 2002 and 2003. In the fall of 2004 the TRC decided to drop all "new analytes" with the exception of PBDEs. Funding in 2005 was allocated to the development of a conceptual model of PBDEs and an investigation into pyrethroids in urban streams. A discussion of these four studies is presented below.

# A. IDENTIFICATION AND EVALUATION OF PREVIOUSLY UNKNOWN AND UNMONITORED ORGANIC CONTAMINANTS

Two RMP Special Studies were conducted to determine the concentrations and distributions of previously unidentified and unmonitored organic compounds in the San Francisco Bay and to link these compounds to known or suspected adverse impacts. This was accomplished by analyzing the gas chromatography-mass spectrometry (GC-MS) electronic data from water, sediment, and tissue (bivalves) samples that were collected by the RMP. In the first study, samples that were analyzed included water from the Sacramento and San Joaquin Rivers (1993, 1994), water (1993, 1994) and sediments (1993) from the San Francisco Estuary and treated wastewater effluent (1998) from a publicly owned treatment works (POTW), located in the South Bay (Palo Alto, CA) (Oros and David 2002). In the second study, GC-MS chromatograms for water samples (1999, 2000), sediment (2000) and tissue samples (2001) were reviewed (Oros 2003).

Electronic outputs compiled by GC-MS are often used to measure organic contaminants in environmental and biological samples. These outputs of GC-MS full scan analysis contain signals of hundreds of unidentified contaminants. The information provided in these data is often sufficient to characterize contaminants by compound classes and to provide clues to their identification. By comparison to an electronic database, the environmental distributions of several previously unmonitored trace organic contaminants in the San Francisco Estuary were determined. This information, coupled with toxicological data, was then used to make preliminary assessments of the need to monitor for the newly identified contaminants.

These two studies identified the following chemicals present in Bay sediment, water, and tissue: polycyclic musks, nonylphenol, phosphorylated flame retardants, PBDEs, phthalates, and pesticides.

Very few chemicals were observed in sediment; the chemicals that were observed were primarily phthalates with high blank contamination (i.e., blank signal was more than 30 percent of the field signal). The only other chemicals identified were triallyisocyanurate (a vulcanizer in thermoplastics) and Galaxolide. Phthalates and Galaxolide (a musk fragrance) were also observed in tissue samples. Again, the concentrations in the blanks for these compounds were quite high. The only other chemicals identified were benziphenone (a fixative), Tonalide (fragrance), and PBDEs.

Table 2 presents the results of the compounds identified in water from the review of 1999 and 2000 water samples. Similar, compounds were observed in a review of the 1993 and 1994 water samples. For comparison, the lethal concentration (LC-50, fatal dose for 50 percent of the test population) is presented. Maximum concentrations are presented in bold.

# TABLE 2Concentrations (ng/L) and distributions of contaminants found in San Francisco Estuarywater samples.

Compound	Use	Delta	North	Central	South	Golden Gate <sup>1</sup>	$10^{10}$ (ug/l) <sup>2</sup>
Compound	Use	Della	Bay	Bay	Bay	Gale	LC <sub>50</sub> (µg/L) <sup>2</sup>
Acetaminophen	analgesic	102	182	14	390	1	814000 <sup>a</sup>
Atrazine	herbicide	81	Nd	nd	Nd	nd	5200 <sup>b</sup>
Benzophenone	fixative	Nd	91	nd	Nd	nd	9640 <sup>a</sup>
butylbenzyl phthalate	plasticizer	Nd	327	nd	Nd	nd	780 <sup>a</sup>
Dichlobenil	herbicide	Nd	Nd	1	9	nd	4 <sup>a</sup>
Galaxolide	fragrance	8	28	3	131	nd	-
Metolachlor	herbicide	89	35	nd	Nd	nd	5400 <sup>a</sup>
Molinate	herbicide	193	87	15	Nd	nd	21 <sup>a</sup>
N-butylbenzenesulfonamide	plasticizer insect	111	216	nd	454	nd	-
N,N-diethyltoluamide	repellant	76	49	8	188	nd	106000a
4-nonylphenol	surfactant	Nd	Nd	nd	4	nd	98 <sup>a</sup>
Octylmethoxy cinnamate	sunscreen insecticide	91	963	6	117	3	-
piperonyl butoxide	synergist	40	Nd	nd	Nd	nd	2830 <sup>b</sup>
Terbuthylazine	herbicide	Nd	nd	1	200	nd	21000 <sup>b</sup>
Thiobencarb	herbicide	47	36	nd	Nd	nd	1000 <sup>b</sup>
Tonalide	fragrance vulcanizatio	1	2	1	8	nd	-
Triallylisocyanurate	n agent	Nd	nd	nd	211	nd	-
Tributylphosphate	plasticizer	77	30	5	145	nd	1580 <sup>b</sup>
Triphenylphosphate tris(1,3-dichloro-2-	plasticizer flame	Nd	24	nd	56	nd	100 <sup>b</sup>
propyl)phosphate	retardant	47	35	5	76	nd	-

Concentrations are reported as the sum of the dissolved and particulate components (ng/L) and are blank corrected.

Bolded numbers indicate the maximum concentration.

 $LC_{50}$  (Lethal Concentration 50) = concentration of a chemical which kills 50% of a sample population.

LC<sub>50</sub> data from U.S. EPA Ecotoxicology database:

http://www.epa.gov/medecotx/quicksearch.htm (September 2002).

Abbreviations: nd, not detected.

<sup>1</sup>Golden Gate is the background site located 2 miles offshore.

<sup>2</sup>Lowest LC<sub>50</sub> for most sensitive freshwater indicator species.

<sup>a</sup>Fathead minnow (*Pimephales promelas*) - 96 h exposure LC<sub>50</sub>; <sup>b</sup>Water flea (*Daphnia magna*) - 48 h exposure LC<sub>50</sub>.

Method detection limit ~250 pg/L.

As shown on Table 2, for chemicals for which there is an LC-50, most of the contaminants are substantially below the LC-50. Exceptions include herbicides such as dichlobenlin and molinate.

Further details on this work can be found in the following reports:

- Oros, D.R. and N. David. 2002. Identification and Evaluation of Unidentified Organic Contaminants in the San Francisco Estuary. RMP Technical Report: SFEI Contribution 45. San Francisco Estuary Institute, Oakland, CA.
- Oros, Daniel (2003) Identification and evaluation of previously unknown organic contaminants in the San Francisco Estuary (1999-2001). RMP Technical Report: SFEI Contribution 75. San Francisco Estuary Institute, Oakland, CA.
- Oros, D.R., Jarman, W.M., Lowe, T., David, N., Lowe, S., Davis, J.A. (2003) Surveillance for previously unmonitored organic contaminants in the San Francisco Estuary. *Marine Pollution Bulletin*, 46:1102-1110.

# B. CONCENTRATIONS OF "NEW ANALYTES" IN STATUS AND TRENDS MONITORING IN 2002 AND 2003

Based on the review of historical chromatograms conducted by Oros and David (2002) and Oros (2003), the RMP expanded the Status and Trends chemical list in 2002/2003 to include the following chemicals, referred to as "new analytes": PBDEs, phthalates, nonylphenol, triphenylphosphate, and musks. Information on use and the structure of the compounds is included in Appendix A.

Results from the 2002/2003 analyses are presented in Table 3. PBDEs were detected in all matrices. Nonylphenol was not detected in sediment although it was detected in water and tissue. Concentrations of nonylphenol in water were substantially below the National Ambient Water Quality Criteria for saltwater of 1.7 ug/L (4-day average) (USEPA 2005). Nonylphenol and a metabolite of nonylphenol, nonylphenolethoxylate, were detected in tissue.

Phthalates were detected in all matrices; however, as a result of blank contamination, sediment and water results were rejected. Phthalates were detected in tissues. Triphenylphosphate and musks were detected in bivalves.

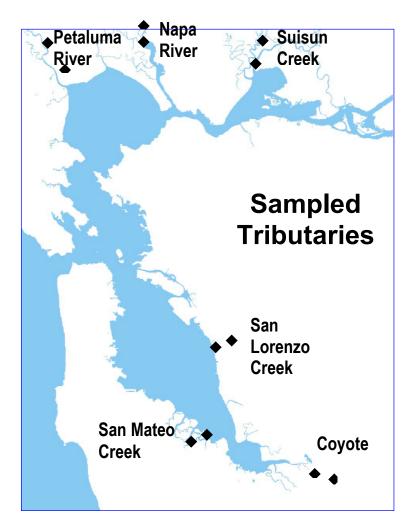
Based on the results from the two-year effort, the TRC decided in December 2004 to eliminate the "new analytes" from the Status and Trends program with the exception of PBDEs, which were retained for all matrices. The concentrations of most analytes were not considered to be a potential threat to aquatic life in the Bay.

Chemical	Major Health Concern/s		Occurrence	
		Water	Sediment	Bivalve
PBDEs (water, sediment, tissue)	Endocrine system disruption (targets thyroid), bioaccumulation, carcinogenic, persistent in the environment	Range of values observed: 38 -513 pg/L	Range of values observed: 0.23 – 12.6 ug/kg	Range of observed values: 9- 106 ug/kg
p-Nonylphenol (water, sediment, tissue)	Endocrine system disruption	Range of values observed: 5 – 72 ng/L	Not detected	Range of observed values (p-nonylphenol): 1 – 917 ug/kg Range of observed values – (nonylphenolethoxylate): 897 – 3,340 ug/kg
Nitro and Polycyclic Musks (tissue only)	Bioaccumulation, toxicity in aquatic biota (efflux pump inhibitors), estrogenic in fish	Not analyzed	Not analyzed	Galaxolide: 79 – 855 ug/kg Tonalide: 4 -516 ug/kg Versalide: 20 -56 ug/kg Musk ambrette: 1 -6 ug/kg Musk ketone 1 – 11 ug/kg Musk xylene: 2 -7 ug/kg Celestolide: 7- 93 ug/kg
Triphenylphosphate (tissue only)	Bioaccumulation, human toxicity, unknown toxicity to aquatic biota	Not analyzed	Not analyzed	Range of values observed: 0.55 – 378 ug/kg
Phthalates (water, sediment, tissue)	Endocrine system disruption, bioaccumulation, toxicity	Rejected due to blank contamination	Rejected data due to blank contamination	Bis(2- ethylhexyl)phthalate: 256-968 ug/kg Di-n-butylphthalate: 233- 2,620 ug/kg

#### Table 3Results of "New Analyte" Analysis 2002/2003

# C. EXPOSURE AND EFFECTS PILOT STUDY/PRISM 2004: PYRETHROIDS

The purpose of this project was to evaluate pyrethroids in sediments and their potential impact on benthic organisms. The project examined sediment concentrations in November 2004 (first rains) and April 2005 (after application of pesticides in the spring) to determine the concentrations of pyrethroids in the sediment and the toxicity of the sediments. Locations of the tributaries are presented below, followed by the observed pyrethroids concentrations.



Significant sediment toxicity was observed in Upper San Mateo Creek (November and April), San Lorenzo Creek (April and November) and Upper Coyote Creek (April). The highest concentrations of pyrethroids were observed in Upper San Mateo Creek. The range of pyrethroids is presented in Table 4. These values have not undergone rigorous data validation and should be considered preliminary results.

	November			April
	Min	Max	Min	Max
Bifenthrin	1.9	10.3	nd	2.4
Cyfluthrin	nd	8.62	nd	nd
Cypermethrin	nd	4.17	nd	nd
Esfenvalerate	nd	nd	nd	nd
Lambda- cyhalothrin	nd	nd	nd	nd
Permethrin	nd	20.5	nd	nd

#### Table 4Preliminary Concentrations of Pyrethroids in Sediment (ng/g)

### D. DEVELOPMENT OF A CONCEPTUAL MODEL FOR PBDES

SFEI is currently developing a conceptual model/impairment assessment (CM/IA) of PBDEs. The general objectives of the CM/IA reports are:

- Evaluate the current level of impairment of beneficial uses, including description of standards or screening indicators and relevant data.
- Develop a conceptual model that describes the current state of knowledge for the pollutant of concern, including sources, loads, and pathways into and out of the Bay and its water, sediment, and biota.
- Identify potential studies that might reduce uncertainties associated with the report's conclusions.

The CM/IA will compile PBDE data collected from the analysis of municipal wastewater treatment plant effluent and sludge samples, RMP field data (water, sediment, and mussels), and from other non-RMP studies conducted in the San Francisco Bay. The published literature will also be evaluated to identify PBDE sources, estimated loading, transport pathways, and fate. It is anticipated that this project will be completed in the Fall of 2006. Figure 2 shows results of PBDE analysis of local wastewater treatment plant effluents and sludges.

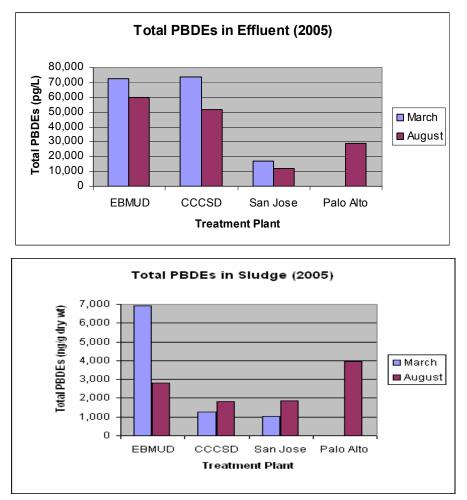


Figure 2. Concentrations of total PBDEs in effluent (top) and sludges (bottom). Palo Alto data are from North (2004).

# III. DEVELOPING A COMPREHENSIVE STRATEGY FOR MONITORING EMERGING CONTAMINANTS IN THE RMP

# A. STRATEGY FOR IDENTIFYING EMERGING CONTAMINANTS OF POTENTIAL CONCERN IN SAN FRANCISCO BAY

### 1. Convene Workgroup

The RMP will convene a Workgroup meeting on June 1, 2006 to solicit opinions from nationally-recognized experts in the field of emerging contaminant research. The goal of this meeting will be to develop a plan to address the general goals of the Workgroup (listed on page 5). Similar to other workgroups in the RMP, over the course

of the year, the panel will review RMP products, make recommendations, and periodically meet to discuss progress.

# 2. Identify Groups Conducting Related Emerging Contaminant Work

A substantial effort in the area of emerging contaminants has been undertaken by other environmental research and monitoring programs. The ECWG will seek to build off of these existing efforts. Potential programs to review include:

• US Geological Survey (USGS)

Under its Toxic Substance Hydrology Program, the USGS has developed an Emerging Contaminants in the Environment program. This program is dedicated to determining the occurrence, fate and risk posed by emerging contaminants. Under this program, in 1999 and 2000, the USGS conducted a survey of 139 streams in 30 states to determine the presence of emerging contaminants such as pharmaceuticals, pesticides, hormones and other organic contaminants (Koplin et al. 2002).

• San Francisco Bay Municipalities

Several of the San Francisco Bay municipalities have organized workgroups that are addressing emerging contaminants. These groups include: the Emerging Contaminants Workgroup of the Santa Clara Basin Watershed Management Initiative and East Bay Municipal District (EBMUD) pollution prevention program. The RMP will work in concert with these groups.

• Southern California Coastal Water Research Program (SCCWRP)

SCCWRP has several projects underway looking at the effect of endrocine disrupting compounds (EDC) such as contraceptives, detergents (nonylphenol), and pesticides on fish in the Southern California Bight. One project is developing assays for determining the impact of EDCs on hornyhead turbot and English sole; the research team has observed the feminization of male fish (e.g., vitellogenin induction) in the proximity of wastewater discharge outfalls. RMP staff will work with SCCWRP to obtain a list of chemicals that are of concern in the Southern California Bight and that may be relevant to the San Francisco Estuary. The lead fish biologist on this project Dr. Daniel Schlenk serves on the RMP's EEPS workgroup. In addition, Keith Mayra, a senior chemist at SCCWRP, has indicated his interest in ECWG.

• National Institute of Standards and Technology (NIST)

NIST is developing standards for emerging contaminants such as PBDEs, pharmaceuticals, and pesticides such as toxaphene. RMP staff

will discuss emerging contaminants with the Analytical Chemistry Division of NIST.

• Poseidon Project (EU)

In 2001, the European Union began a major directive to evaluate the presence of pharmaceuticals and personal care products (PPCPs) in European surface waters and strategies for the removal of these compounds from wastewater and drinking water (Ternes 2004). This project focused on the following compounds:

- Acidic drugs: diclofenac, ibuprofen (both antiphlogistics), bezafibrate (lipid regulator)
- Neutral drugs: diazepam (tranquilizer), carbamazepine (antiepileptic)
- Personal care products: tonalide and galaxolide (musk fragrances)
- Antibiotics: sulfamethoxazole and roxithromycin
- o Iodinated contrast media: iopromide
- ο Estrogens: 17α-ethinylestradiol, 17β-estradiol, estrone

Concentrations of all of these compounds were measured in wastewater influents, effluents, and surface waters in Germany, Austria, Poland, Spain, France and Switzerland. Treatment methods for the removal of these compounds were evaluated. RMP staff will work with select POSIEDON researchers to identify emerging contaminants.

• US Environmental Protection Agency (USEPA)

USEPA has several groups conducting research on emerging contaminants (see for example, the National Exposure Research Laboratory work on pharmaceuticals and personal care products). RMP staff will review the work currently being conducted by these groups.

• Industry Representatives

Several industry groups (e.g., Research Institute for Fragrance Materials) are pursuing research on emerging contaminants. These groups will be contacted.

### 3. Evaluate Published Literature for Emerging Contaminants

The published peer-reviewed scientific and grey literature will be evaluated where possible to identify emerging contaminants that might pose health risks to aquatic life in the Bay and potentially targeted for field monitoring. Furthermore, the methods used for evaluating or prioritizing emerging contaminants will be identified.

# B. DEVELOPING AN APPROACH FOR INCLUSION OF NEW ANALYTES

#### 1. Potential Emerging Contaminants

The ECWG will need to develop a list of emerging contaminants for potential inclusion in the Program. The list will be based upon the recommendations of the science advisory panel for ECWG, a review of other emerging contaminant programs, and a review of the literature. Compounds that may be relevant to monitoring San Francisco Bay include the following:

• Dechlorane Plus

Recently, Hoh et al. (2006) identified a chlorinated flame retardant, Dechlorane Plus in water, sediment, and fish samples from the Great Lakes. Dechlordane was introduced in the early 1960s as a substitute for Dechlorane (Mirex). It is still in use today as a coating for electronic cables, in plastics for computers and roofing materials. Production values since 1986 have varied between one and ten million pounds per year. Very little is known about its toxicity and fate. Dechlorane Plus has many of the physical/chemical properties of long-term legacy contaminants: high octanol-water partition coefficient and resistance to biological and photo degradation.

- Hexabromocyclodecane and Tetrabromobisphenol A Hexabromocyclodecane and Tetrabromobisphenol A are brominated flame retardants. With the phasing out of the octa and penta mixes of PBDEs in the European Union, these chemicals have become more prevalent in use and subsequent detection in environmental matrices (Law et al. 2006). For example, concentrations of this compound in Swedish bird eggs increased substantial from the 1970s until the 1990s. It has been relatively constant in the last ten years (Sellstrom et al. 2003). Little is know about its toxicity; however, there is some indication that it may increase the recombination frequency, suggesting it may be carcinogenic.
- Triclosan

Triclosan is a commonly-used bactericide and preservative found in many household and personal care products (e.g., soaps, toothpaste, deodorants, and laundry detergent). Triclosan and a metabolite of Triclosan (methyl-triclosan) were detected in San Francisco water as part of the retrospective study conducted by Oros and David (2002). Few studies have been conducted on the toxicity of Triclosan; however, the studies that have been conducted to date on aquatic organisms suggest it is very toxic (Wilson et al. 2003). In addition and perhaps even more importantly, it has been demonstrated that Triclosan can under certain circumstances photodegrade to dioxin (Latch et al. 2005). A PS/SS for 2007 proposed evaluating the presence of pharmaceuticals in the Bay included Triclosan in a list of compounds to analyze (see Appendix B).

- Perfluorinated compounds The TRC has expressed a strong interest in pursuing monitoring the perfluorinated compounds. A PS/SS for 2007 was submitted on this topic (see Appendix B).
- Octylmethoxy cinnamate/Oxybenzone Octylmethoxy cinnamate and Oxybenzone are ultra-violet filters used in sunscreen and are believed have endrocrine disrupting effects on fish.
- Musks

Synthetic musks are in frequent use in personal care products. Galaxolide and Tonalide are some of the most widely used musk fragrances and, as shown on Table 3, were detected in the limited monitoring that was conducted on bivalves in 2002/2003. Research undertaken by Dr. David Epel laboratory at the Hopkins Marine Laboratories in Monterey Bay suggests that the presence of musks may reduce bivalve's ability to inhibit the introduction of xenobiotics into the cell (Luckenbach and Epel 2005).

• Atrazine

Atrazine is widely-used herbicide. Low levels have been reported in the Estuary; however, significant toxicological effects have been observed in amphibians.

• Nonylphenol

Nonylphenol is an intermediate in the production of nonylphenol ethoxylates and alkylphenyl ethoxylates, which are components of household detergents, lubricants, emulsifiers for agrichemicals and oil additives. Alkylphenol ethoxylates can degrade to nonylphenol. Nonylphenol wAS detected in water as part of the 2002/2003 monitoring effort; concentrations were below the ambient water quality criteria. Nonetheless, because nonylphenols can bioaccumulate, it may be prudent to consider them for inclusion in an emerging contaminant monitoring program.

This list is by no means inclusive. Its purpose is to begin the discussion of appropriate emerging contaminants for the RMP to consider.

# 2. Methods for Ranking Emerging Contaminants

Once a list of emerging contaminants is developed, it will need to be prioritized to determine which chemicals will be included in the program. The chemicals can be ranked based as such factors as production, use, chemical/physical properties, persistence, potential for bioaccumulation, toxicity, and risk. Several research groups

have developed methods for prioritizing chemicals (see for example Roth et al. 2005). The ECWG will need to recommend a process.

### C. IDENTIFYING POTENTIAL PILOT OR SPECIAL STUDIES TO ADDRESS INFORMATION GAPS

An important discussion point at the June 1<sup>st</sup> meeting will be critical studies necessary to fill data gaps in our understanding of emerging contaminants in the Estuary. The following issues will be topics for discussion:

- What are the current information gaps and what types of studies are necessary to fill them?
- What types of matrices should the RMP be monitoring for emerging contaminants?
  - Effluent?
  - Sludge (largely upland disposal and therefore not an issue for the Bay)?
  - Semi-permeable membranes?
  - Water?
  - Sediment?
  - o Biota?
  - Targeted sampling of select sites (e.g., effluent outfall for dissolved-phase pharmaceuticals)
- Should the RMP use biological assays to determine effects and then pursue chemical analyses (e.g., should the program use broad-screening tools to identify potential issues)?

As part of the PS/SS, study ideas for the following year are solicited in March. This year, the RMP received three study ideas that are related to emerging contaminants: pharmaceuticals; pyrethroids, and perfluorinated compounds. It was suggested that these ideas be reviewed by the ECWG. Copies of these proposals are attached in Appendix B.

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#### APPENDIX A Chemical Structure, Use and Properties of the "New Analytes"

#### **Polybrominated Diphenylethers**

Compound Name	Chemical Structure	Use	Properties
2,2',4,4'-Tetrabromo diphenyl ether CAS#: Formula: C <sub>12</sub> H <sub>6</sub> Br <sub>4</sub> O MW: 486	Br Br Br Br	Flame retardant in plastic products, polymers, resins and components of electronic devices, building materials and textiles.	Accumulates and magnifies in biological tissues; disrupts hormonal systems.
2,2',3,3',4- Pentabromo diphenyl ether CAS#: Formula: C <sub>12</sub> H <sub>5</sub> Br <sub>5</sub> O MW: 565	Br Br Br Br Br O G Br	Flame retardant in plastic products, polymers, resins and components of electronic devices, building materials and textiles.	Accumulates and magnifies in biological tissues; disrupts hormonal systems.
2,2',3,3',4,4'- Hexabromo diphenyl ether CAS#: Formula: C <sub>12</sub> H <sub>4</sub> Br <sub>6</sub> O MW: 644	Br Br Br Br Br O G Br	Flame retardant in plastic products, polymers, resins and components of electronic devices, building materials and textiles.	Accumulates and magnifies in biological tissues; disrupts hormonal systems.
2,2',3,4,4',5',6- Heptabromo diphenyl ether CAS#: Formula: C <sub>12</sub> H <sub>3</sub> Br <sub>7</sub> O MW: 723	Br Br Br Br Br Br Br Br Br Br	Flame retardant in plastic products, polymers, resins and components of electronic devices, building materials and textiles.	Accumulates and magnifies in biological tissues; disrupts hormonal systems.

#### **Phthalate Esters**

Compound Name	Chemical Structure	Use	Properties
Di-N-butyl phthalate CAS#: 84-74-2 Formula: $C_{16}H_{22}O_4$ MW: 278		Plasticizer added to polyvinyl chloride to increase flexibility, adhesives, and coatings. Lubricant for aerosol valves, antifoaming agent, skin emollient, plasticizer in personal care products and cosmetics.	Disrupts human hormonal systems and reproductive development.
Butyl benzyl phthalate CAS#: Formula: 117-81-7 $C_{19}H_{20}O_4$ MW: 312		Plasticizer added to polyvinyl chloride to increase flexibility, adhesives, and coatings.	Suspected carcinogen and neural toxicant; disrupts human hormonal systems and reproductive development.
Bis(2-ethylhexyl) phthalate CAS#: 117-81-7 Formula: C <sub>24</sub> H <sub>38</sub> O <sub>4</sub> MW: 390		Plasticizer in flexible vinyl products, replacement for PCBs in dielectric fluids for electric capacitors.	Disrupts human hormonal systems and reproductive development.

#### Others

Compound Name	<b>Chemical Structure</b>	Use	Properties
Triphenyl phosphate CAS#: 115-86-6 Formula: C <sub>18</sub> H <sub>15</sub> O <sub>4</sub> P MW: 326		Flame retardant in plastic of video monitors. Plasticizer in some pesticides, gasoline additives, synthetic motor oils, and nerve gas.	Accumulates and magnifies in biological tissues, disrupts hormonal systems; toxic to aquatic green algae
Nonylphenol CAS#: 25154-52-33 Formula: C <sub>15</sub> H <sub>24</sub> O MW: 220	но	Preparation of lubricating oil additives, resins, plasticizers, pesticides, anionic detergents, surface-active agents, and toiletries.	Moderate potential for bioaccumulation in aquatic organisms; disrupts hormonal systems and reproductive development.

Compound Name	Chemical Structure	Use	Properties
Musk ambrette CAS#: 83-66-9 Formula: $C_{12}H_{16}N_2O_5$ MW: 268		Fragrances and personal care products. Banned in the European Union	Neurotoxic; bioaccumulates in aquatic species and humans
Musk xylene CAS#: $81-15-2$ Formula: C <sub>12</sub> H <sub>15</sub> N <sub>3</sub> O <sub>6</sub> MW: 297		Fragrances and personal care products.	Induces detoxifying liver enzymes and is genotoxic; bioaccumulates in aquatic species and humans
4-Amino-musk xylene CAS#: 107342-55-2 Formula: $C_{12}H_{17}N_3O_4$ MW: 267		Fragrances and personal care products.	Genotoxic; biodegradation product; bioaccumulates in aquatic species and humans
Musk ketone CAS#: $81-14-1$ Formula: C <sub>14</sub> H <sub>18</sub> N <sub>2</sub> O <sub>5</sub> MW: 294		Fragrances and personal care products.	Induces detoxifying liver enzymes; bioaccumulates in aquatic species and humans
Galaxolide CAS#: 88-29-9 Formula: C <sub>18</sub> H <sub>26</sub> O MW: 258	XCC	Fragrances and personal care products.	Bioaccumulates in aquatic species and humans
Tonalide CAS#: Formula: C <sub>18</sub> H <sub>26</sub> O MW: 258		Fragrances and personal care products.	Bioaccumulates in aquatic species and humans
Versalide CAS#: 88-29-9 Formula: $C_{18}H_{26}O$ MW: 258		Fragrances and personal care products.	Bioaccumulates in aquatic species and humans

#### Nitro and Polycyclic Musks

Appendix B 2007 Pilot and Special Study Ideas – Emerging Contaminants

#### Topic: Evaluation of Pharmaceuticals in the San Francisco Estuary Proposed by: Daniel R. Oros (SFEI) and Million Woudneh (AXYS Analytical Services)

**Description**: Pharmaceuticals such as antibiotics (e.g., erythromycin and trimethoprim), analgesics (e.g., ibuprofen and acetaminophen), antiinflammatories (e.g., diclofenac and naproxen), antidepressants (e.g., Prozac and lofepramine), antihypertensives (e.g., atenolol and propranolol), anticancers (e.g., paclitaxel and tamoxifen), and sexual performance enhancers (e.g., Viagra and Levitra), among other drugs, are used to treat illness, disease, and medical conditions in humans and animals. They enter the environment from consumer use and actions and, in the case of industrial confined animal feedlots where antibiotics are used, from waste effluents. The primary pathway is ingestion followed by subsequent excretion into the municipal sewage system, while the secondary pathway is disposal of unused and outdated medications directly into the sewage system. These biologically active compounds and their metabolites are not completely removed by current wastewater treatment technologies and are often found in treated effluents and receiving waters. For example, the analgesic, acetaminophen, was previously found in the San Francisco Bay at a maximum estimated concentration of 390 ng/L [Oros et al., Marine Pollution Bulletin, 2003, 46, 1102-1110]. Because wastewater treatment plants discharge ~230 billion gallons of treated effluents into the Bay each year, this could represent a significant loading of pharmaceutically active drugs and other personal care products into the Bay. Discharged pharmaceuticals are diluted and even mixed with other pharmaceuticals from multiple discharge sites in the Bay. Concentration levels are expected to peak during the dry season when freshwater flow into the Bay is at its lowest. The RMP does not currently monitor for pharmaceuticals in the Bay, so it is not known which pharmaceuticals are actually present and at what concentrations but there is heightened concern now given that pharmaceutically active drugs and other personal care products have been found to occur in most U.S. water bodies. Several key questions that could be addressed in this proposed special study include: What pharmaceuticals and drug metabolites are present in the Bay? Are they present at concentrations that could potentially cause toxicity or endocrine system disruption to critical aquatic species? What are their major sources and levels of loading from those sources? The deliverable will be a RMP Technical Report and a paper to be submitted for potential publication in a peer reviewed scientific journal.

# **RMP Objectives and Management Question Addressed:** 1c, 1d, 2a, 2b, 2c, 3c, 4a, and 5a-c.

Time Sensitivity: This project will not exceed 2 years.

Estimated Cost: \$50,000 for field sampling, data handling, and project management. AXYS will provide instrumental analysis at a match that is equivalent to 25% of the total budget; Efforts will also be made to collaborate with BACWA, which could further expand this proposed scope of work.

Proposed Timing: 2007-2008

Pharmaceuticals and Personal Care Products (PPCP) that will be analyzed by AXYS Analytical Services in this study Acetaminophen Albuterol Caffeine Carbadox Chlorotetracycline Cimetidine Ciprofloxacin Cotinine Digoxigenin Digoxin Digoxin Diltiazem Doxycycline 1,7 DimethylXanthine Enrofloxacin Erythromycin-H2O Fluoxetine Gemfibrozil Ibuprophen Lincomycin Metformin Norfloxacin Oxytetracyclin Ranitidine Roxithromycin Sarafloxacin Sulfachloropyridazine Sulfadimethoxine Sulfamerazine Sulfamethazine Sulfamethizole Sulfamethoxazole Sulfathiazole Tetracycline Triclosan Trimethoprim Tylosin Virginiamycin Warfarin

#### Topic: Evaluation of Pyrethroid Insecticides in San Francisco Bay Tributaries Proposed by: Daniel R. Oros (SFEI) and Million Woudneh (AXYS Analytical Services)

- **Description**: The objective is to determine the potential sources, concentrations, and distributions of pyrethroids in San Francisco Bay tributaries. The results of SFEI's recent PRISM Grant, which focused on developing new chemical methods for measuring pyrethroids in surface water and sediment samples, showed that pyrethroids including allethrin, bifenthrin, deltamethrin, fenvalerate, flucythrinate, L-cyhalothrin, and permethrin and their synergist, piperonyl butoxide (PBO), were detectable in water and sediments from San Francisco Bay urban tributaries including Coyote Creek, Petaluma River, San Mateo Creek, San Lorenzo Creek and Suisun Creek. Pyrethroid occurrence is evidence that more work can be done to identify the sources, critical temporal periods (wet and dry season application periods) and spatial areas (e.g., critical fish spawning habitat) of the Bay where concentrations could potentially reach levels that are high enough to cause toxicity to sensitive aquatic species including fish and benthic invertebrates. Both water and sediment samples will be collected and tested for pyrethroids. In addition, sediment samples will be tested for toxicity using the benthic freshwater amphipod Hvallela azteca. Field sample collection and toxicity testing can be coordinated with the RMP's Episodic Toxicity Monitoring efforts. Water samples will be collected in the wet season during the period of first flush events in at least five major urban tributaries of the San Francisco Bay. The attached table lists the 20 pyrethroids and their synergist PBO that are targeted for analysis. These were selected based on their recommended uses (e.g., structural pest care, lawn and garden care, public health), use amounts (mass), and consumer product availability. Pyrethroids will be collected from 100 L water samples using XAD solid phase extraction. Water and sediment extracts will be analyzed by high resolution gas chromatography-high resolution mass spectrometry (HRGC-HRMS). This instrument provides high selectivity and mass resolution to reduce potential interferences and when combined with large volume sampling enables the method to routinely achieve very low levels of chemical detection (water at ppg-ppt range). The project deliverables will be a RMP Technical Report and a paper that will be submitted for potential publication in a peer-reviewed scientific journal.
- **RMP Objectives and Management Question Addressed:** 1c, 1d, 2a, 2b, 2c, 3c, 4a, and 5a-c.

**Time Sensitivity:** This project will not exceed 2 years.

**Estimated Cost:** \$50,000 for field sampling, data handling, toxicity testing, and project management; AXYS will provide instrumental analysis at a match that is 25% of the total budget. Efforts will also be made to collaborate with BASMAA, which could further expand this proposed scope of work.

Proposed Timing: 2007-2008

in this study Allethrin-A Allethrin-B
Prallethrin-A
Prallethrin-B
Cinerin-I
Jasmolin-I
Pyrethrin-I
Resmethrin-A
Bioresmethrin
Piperonyl-butoxide
Tetramethrin-A
Tetramethrin-B
Bifenthrin
Phenopropathrin
Phenothrin-A
Phenothrin-B
Permethrin-A
Permethrin-B
L-Cyhalothrin-A
L-Cyhalothrin-B
Cyfluthrin-A
Cyfluthrin-B
Cyfluthrin-C
Cyfluthrin-D
Cypermethrin-A
Cypermethrin-B
Cypermethrin-C
Cypermethrin-D
Cyper-flucy-calc
Flucythrinate-A
Flucythrinate-B
Fenvalerate-A
Fenvalerate-B
Delta/Tralomethrin-A
Delta/Tralomethrin-B

Pyrethroids that will be analyzed by	AXYS Analytical Services
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#### Perfluorinated Compounds in San Francisco Bay

Author: Meg Sedlak, SFEI

**Description:** In the last 50 years, fluorinated alkyl substances have been used extensively in a variety of commercially available products including fire-fighting foams, refrigerants, stain repellants in textiles, and coatings for paper used in contact with food products. Their popularity in commercial and industrial applications in part results from their unique ability to be both hydrophobic and oleophobic, that is able repel both water and oil.

Fluorinated alkyl substances are synthesized from perfluornated sulfonyl fluoride and carbonyl fluoride intermediates by electrochemical fluorination process (ECF) or telomerization fluorination processes. Because these processes are not selective, numerous by-products are produced in the manufacture of these intermediates such as perfluorooctane sulfonate (PFOS) and perfluorooctanoic acid (PFOA).

As a result of their chemical stability and widespread use, fluorinated alkyl substances such as PFOS and PFOA have been detected in marine mammals and aquatic organisms throughout the world including relatively pristine environments such as the Artic. PFOS and related perfluorinated compounds have been associated with a variety of toxic effects including mortality, carcinogenity, and adverse development. Their widespread dispersal throughout the global and their potential toxicity has caused increasing concern among scientists and regulators. In response to this concern, the US Environmental Protection Agency banned the use of PFOS and 3M Corporation initiated a voluntary phase out of the carboxylated and sulfonyl-based perfluorinated chemicals; however, PFOA and perfluorinaed carboxylic acids (PFCAs) continue to be produced in the manufacture of fluoropolymers. It is thought that these compounds degrade to form PFOS.

The objective of this study will be to determine concentrations of PFOS and related compounds in San Francisco Bay. At present, little information is available regarding the presence of PFOS and perfluorinated compounds in the Estuary. A research group at Stanford University has recently analyzed South Bay sediment and wastewater sludge for PFOS and its precursors (Higgins *et al.* 2005). PFOS observed in San Francisco Bay sediment is reported to range from 0.124 ng/g to 4.65 ng/g. The range of concentrations in wastewater sludge was approximately two orders of magnitude higher. Of particular interest was the elevated concentrations of PFOS precursors (i.e., 2-(N-methylperfluorooctanesulfonamido) acetate and 2-(N-

ethylperfluorooctanesulfonamido) acetate) suggesting that it is important to monitor the precursors which may degrade to PFOS.

To date, no biological samples have been analyzed for perfluorinated compounds in the San Francisco Estuary. The RMP has a number of fish monitoring studies scheduled for 2006 including the triennial sportfish event and the mercury small fish study. The scope of works for these projects were developed in 2005 and funding for additional analyses of perfluorinated compounds are not possible within the currently allocated budgets. We propose to piggyback off these existing collection efforts and to analyze select fish samples for perfluorinated compounds. In addition, we have contacted the Marine Mammal Center which will be sampling ten young of the year pups in the summer of 2006. The Marine Mammal Center is interested in collecting blood and blubber samples for us that could be analyzed for perfluorinated compounds. In addition to the biological samples, we would propose collecting water and sediment samples from select locations for perfluorinated analyses. These samples would be collected as part of the existing 2006 Status and Trends sampling event to again be most cost-efficient. These samples would be used to evaluate concentrations relative to other estuaries and to determine the potential for these compounds to bioaccumulate in San Francisco Estuary.

Although the funding for Pilot and Special studies is allocated for 2007, because 2006 presents a unique year for collection of tissue samples, we would collect the samples in the summer of 2006 and archive the samples for analyses until 2007 (assuming that this study is funded).

The results of this study will be summarized in a technical report and a journal manuscript.

#### RMP Management Objectives Addressed by this Study:

- 1. Describe the distribution and trends of pollutants concentrations in the Estuary.
  - This study will provide some of the first data to determine the distribution of concentrations of perfluorinated compounds in the Estuary and to place these concentrations in context with concentrations observed in other estuaries.
- 2. Project future contaminant status and trends using current understanding of ecosystem processes and human activities.
- 4. Measure pollution exposure and effects on selected parts of the Estuary ecosystem (including humans).
  - 4.1. Perfluorinated compounds are considered an emerging contaminant. As such, it is important that we determine their concentrations in biota to evaluate whether management actions are needed
  - 4.4 Determining the concentrations of perfluorinated compounds in the upper trophic level is important for assessing both ecological and human health risks.
- 5. Compare monitoring information to relevant benchmarks, such as TMDL targets, tissue screening levels, water quality objectives, and sediment quality objects
  - The concentrations detected in this study would be compared to known threshold effect levels, where possible.

#### **Estimated Cost:** \$60,000 **Proposed start date:** 2006

References:

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