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Adapting an ambient monitoring program to the challenge of managing emerging pollutants in the San Francisco Estuary

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Abstract

While over seven million organic and inorganic compounds that have been indexed by the American Chemical Society's Chemical Abstracts Service in their CAS Registry are commercially available, most pollution monitoring programs focus only on those chemical stressors for which regulatory benchmarks exist, and have been traditionally considered responsible for the most significant human and environmental health risks. Until the late 1990s, the San Francisco Estuary Regional Monitoring Program was no exception in that regard. After a thorough external review, the monitoring program responded to the need for developing a pro-active surveillance approach for emerging pollutants in recognition of the fact that the potential for the growing list of widely used chemical compounds to alter the integrity of water is high. We describe (1) the scientific and analytical bases underlying a new surveillance monitoring approach; (2) summarize approaches used and results obtained from a forensic retrospective; (3) present the growing data set on emerging pollutants from surveillance monitoring and related efforts in the San Francisco Bay Area to characterize newly targeted compounds in wastewater streams, sediment, storm water runoff, and biota; and (4) suggest next steps in monitoring program development and applied research that could move beyond traditional approaches of pollutant characterization. Based on the forensic analysis of archived chromatograms and chemical and toxicological properties of candidate compounds, we quantified a variety of synthetic organic compounds which had previously not been targeted for analysis. Flame retardant compounds, pesticides and insecticide synergists, insect repellents, pharmaceuticals, personal care product ingredients, plasticizers, non-ionic surfactants, and other manufacturing ingredients were detected in water, sediment, and/or biological tissue samples. Several of these compounds, especially polybrominated diphenyl ether flame retardants, exhibited concentrations of environmental concern. We also describe environmental management challenges associated with emerging pollutants and how pro-active surveillance monitoring might assist in implementing a more holistic approach to pollution prevention and control before emerging pollutants become a burden on future generations.

Keywords: Emerging pollutants; Surveillance monitoring; PBDEs; Bioaccumulation

1. Introduction

A growing number of organic compounds ranging from flame retardants, plasticizers, and water repellents to fragrances, health care, and personal care product ingredients, are being synthesized for a variety of uses. Therefore, the old assumption that the selective list of regulated chemicals is primarily responsible for the most significant human and environmental health risks needs to be re-examined. This need has been supported by numerous studies over the last decade that have (1) demonstrated increasing exposure and bioaccumulation trends for a variety of novel or emerging compounds that have not been traditionally monitored in the environment (e.g., Cadogan, 1999; Gatermann et al., 1998); (2) demonstrated pollutant-induced endocrine disruption in some species at environmentally relevant concentrations (e.g., White et al., 1994; Desbrow et al., 1998); and (3) identified compounds that have the potential to cause other adverse direct and indirect health effects in both humans and wildlife (e.g., Duty et al., 2003; Kuriyama et al., 2005; Luckenbach and Epel, 2005).

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We define "emerging pollutants" here as synthetic organic compounds or manufactured natural compounds where growing evidence suggests that adverse effects at environmentally relevant concentrations could occur but whose environmental releases are not regulated, and which are not routinely screened for their presence in water, sediment, or tissue. The term is also meant to include the wide range of compounds whose anticipated future risks or existing but so far unrecognized risks might justify precautionary management intervention despite a lack of existing statutory requirements.

The goals of this paper are to (1) describe the scientific and analytical basis underlying a new surveillance monitoring approach; (2) summarize approaches used and results obtained from a forensic "retrospective analysis"; (3) summarize the growing data set on emerging pollutants from surveillance monitoring conducted by the Regional Monitoring Program for Trace Substances (RMP) and related efforts to characterize newly targeted compounds in wastewater streams, sediment, storm water runoff, and biota; and (4) suggest next steps in monitoring program development that could move beyond traditional approaches of pollutant characterization.

As Daughton (2004) pointed out, nearly 23 million organic and inorganic compounds have been indexed by the American Chemical Society's Chemical Abstracts Service (CAS) in their Registry (CAS, 2004). Over seven million of these are commercially available, while the US Environmental Protection Agency (EPA) "Priority Pollutant List" contains a mere 126 compounds for which receiving-water benchmarks exist. Therefore, the potential for the growing list of compounds to alter the "integrity of water" (US EPA, 2002) is high. Examples of chemicals exhibiting acute or chronic adverse environmental and human health effects after they have been certified for widespread commercial use are numerous. Only after a fairly high threshold of evidence with respect to impairment of aquatic life, fishing, or recreational uses has been reached are regulatory actions triggered, such as adoption of "total maximum daily loads" (TMDLs), discharge limits, or product use or manufacturing restrictions. Often, the time lag between initial indications of harm and actual management action is considerable—more than 37 years in the case of PCBs (EEA, 2001). Clean-up and mitigation options are limited and expensive, especially for chemically stable synthetic compounds that can persist in the environment for decades. Therefore, a more pro-active monitoring approach is advisable if some of the costly mistakes of the past are to be avoided.

Ambient environmental monitoring programs are generally driven by regulatory requirements associated with a number of federal and state statutes. In this regard, the San Francisco Estuary is no exception. The reactive nature of the standards-based regulation of public trust resources results in most monitoring programs only collecting and evaluating those data that are linked to clear regulatory benchmarks such as receiving water quality objectives, clean-up targets, and fish tissue screening values.

The RMP began in 1993 by comparing a limited set of known pollutants against existing water quality standards. Water quality management efforts designed to protect human health and valued ecosystem components of the Estuary proper and its surrounding watersheds were initially focused on this list of known pollutants which, at the time, was considered responsible for the majority of adverse environmental impacts.

In 1998, the RMP, following an extensive external review, responded to the need for pro-active surveillance monitoring. After a forensic retrospective analysis using archived chromatograms, the Program added a series of new organic compounds to the traditional analyte list of 11 trace elements and a variety of organic compounds, which included EPA's "Priority Pollutant List" (US EPA, 2005; Oros et al., 2003). For 2 years, a small proportion of available resources (<2% of the annual budget of approximately $3 M) was applied toward answering questions about "unidentified" compounds. In particular, we focused on their identification, concentration, and spatial distribution in samples of the three matrices that are routinely monitored (water, sediment, and bivalve tissue), as well as their potential toxicity to aquatic biota, using EPA's Ecotox database (www.epa.gov/ecotox/) and literature citations therein.

2. Surveillance approaches and analytical challenges

As a first step in initiating a surveillance monitoring component, the RMP conducted a comprehensive assessment of the identities, concentrations, and distributions of previously unknown and unmonitored organic contaminants in the Bay. We subsequently reviewed the current literature to link newly identified contaminants to known or suspected adverse impacts on the ecosystem and human health and to evaluate their persistence and bioaccumulation potential. This retrospective analysis identified candidate pollutants that could be targeted for monitoring based on their general chemical characteristics of persistence, bioaccumulation potential, toxicity potential at environmentally relevant concentrations, and high-volume chemical usage (Oros and David, 2002; Oros, 2003). In the future, the RMP intends to continue to apply this approach within a conceptual framework based on mass budget models for selected priority pollutants in San Francisco Bay (Davis, 2004; Greenfield and Davis, 2005). The conceptual framework clearly outlines the types of parameters required with which to populate the mass budget model and identifies priorities for filling data gaps associated with emerging pollutants.

We evaluated a variety of emerging pollutants that exhibited similar chemical properties to PCBs, showed evidence of potential endocrine disruption, or were known to induce cytochrome *P*450 1A1 and 1A2, or elicit similar cellular stress responses. The forensic exercise was

accomplished by (1) evaluating ambient water and sediment samples from 1993/94 and 1998 effluent samples from a local wastewater treatment plant (North, 2004); and (2) evaluating more recent (1999–2001) data from San Francisco Bay water, sediment, and bivalve tissue samples collected by the RMP using gas chromatography–mass spectrometry (GC–MS) (Oros et al., 2003).

The GC–MS electronic data collected using full-scan mode chemical monitoring generally contained the signals of many organic compounds. The information provided in these electronic data was sufficient to characterize organic contaminants by compound classes and to provide other clues to their identification. The GC–MS data were screened using HP Chemstation Software with the National Institute of Standards and Technology NIST 98 mass spectral reference library. When organic compound identifications were not possible with the mass spectral reference libraries, identifications were made by comparison with literature mass spectra and by interpretation of mass spectrometric fragmentation patterns. Authentic standards were then used to confirm the identities of the most relevant contaminants when samples were available (Oros and David, 2002; Oros, 2003).

There are several limitations to using this approach: mass spectral libraries do not always contain mass spectra of emerging pollutants and their metabolites; GC–MS in full-scan mode is not a very sensitive method; mass spectral interpretation is very difficult and an uncommon skill among scientists; and chemical identifications need to be confirmed with authentic standards, which often are not available, especially for degradation products and metabolites.

As a result of the retrospective analysis and literature review, the RMP began monitoring the following organic contaminant groups in San Francisco Bay water, sediment, and bivalve tissue samples: polybrominated diphenyl ethers (PBDEs); phthalates (bis (2-ethylhexyl) phthalate (DEHP), butylbenzylphthalate (BBP), and di-*n*-butylphthalate (DBP)); *p*-nonylphenol (NP); triphenylphosphate (TPP); and musks (musk ketone, musk xylene, musk ambrette, musk moskene, Galaxolide, Tonalide, Versalide, and Celestolide). At the time when the surveillance component was added to the monitoring program, these compounds were not a focus of regulatory activity but were clearly drawing attention as potential threats to aquatic life in San Francisco Bay and elsewhere. Specifically, the PBDE flame retardants caught our attention, because of their similar degradation and bioaccumulation characteristics to PCBs, the growing literature on their adverse effects on experimental animals in laboratory tests (Carlson, 1980; Hallgren and Darnerud, 1998; Darnerud et al., 2001), their worldwide prevalence in environmental and animal tissue samples, and new data from the San Francisco Bay Area of high concentrations in marine mammals and human adipose tissue (She et al., 2002).

Advances in analytical capabilities are necessary to measure emerging chemical pollutants and their associated degradation products at the concentrations that are toxicologically significant to San Francisco Bay aquatic organisms. Once in the Bay, chemical contaminants are diluted to concentrations that are often below the detection limits of common methods, but are still above concentrations that might be harmful or toxic to aquatic organisms. For instance, measurement of pesticides such as the class of pyrethroid insecticides at the concentrations (low parts per trillion or less) that might be found in San Francisco Bay would be difficult and in most cases impossible if the chemical analysis were limited to the use of conventional pesticide collection and concentration methods combined with low-resolution GC–MS or liquid chromatography (LC) analyses. Important factors to consider when conducting emerging contaminant analysis of environmental samples include analyte molecular weight, volatility, and polarity; instrument sensitivity and linearity; sample matrix; sample preparation requirements; and analytical requirements by regulatory agencies. Mass spectrometry, especially GC–MS, LC-MS, high-resolution mass spectrometry (HRMS), negative-ion MS, chemical-ionization MS, and tandem MS methods, are currently the major analytical methods for chemical characterization and for field monitoring in environmental chemistry (Simoneit, 2004). GC–MS and LC instrumentation have been used for chemical analysis of pesticides and other contaminants by research and commercial laboratories for several decades. Unfortunately, in order to measure chemical contaminants at the very low concentrations (low parts per trillion) that might be found in the Bay with these methods, the analyst can only attempt to optimize recovery and measurement of the target analytes by improving on the sample preparation and handling steps (e.g., collection, clean-up, fractionation, concentration, extract transfer, derivatization, and storage of final extracts). Such optimization seldom improves sensitivity by more than one order of magnitude, nor does it eliminate all of the contaminant interferences that normally occur during the analyses. Furthermore, optimization methods are sometimes matrix- or even sample-specific and not easily transferred across analytical laboratories.

The occurrence of new or previously unmonitored contaminants such as pharmaceuticals, personal care product ingredients, flame retardants, pesticides, and other synthetic organics in the San Francisco Bay (Higgins et al., 2005; Oros et al., 2003, 2005) supports the need for developing new and optimizing existing methods of sample preparation and handling and using new types of analytical instruments that are sensitive enough to detect chemical contaminants at the very low ppt levels that are toxicologically relevant to marine and estuarine species.

The sampling and analytical methodologies employed by the RMP are described in detail in documents available on the San Francisco Estuary Institute's website (http://www.sfei.org/rmp/2003/05_2003_Methods%20chapter.pdf) and summarized in Oros et al. (2003). As a brief overview here, water samples were collected by using Amberlite

XAD-2 resin samplers. Field blanks were taken for both the resin columns and the glass fiber filters that collect the particulate fraction. The field blanks received the same analytical treatment in the laboratory as the field samples. Each sample was spiked with labeled quantification standards, Soxhlet extracted in solvent, with the resulting extract split into five portions for separate analyses of PAHs and phthalates, PCBs, diazinon and chlorpyrifos, PBDEs, organizchlorine pesticides, and nonylphenol. Analytical instruments used in extract quantification varied for the various fractions and included an Agilent 5873 MSD equipped with and Agilent 6890N GC, and Agilent 7683 autosampler, and an HP Chemstation; a Finnigan Incos 50 MS equipped with a Varian 3400 GC, or an Autospec Ultima high-resolution MS equipped with an HP 6890 gas chromatograph. In 2002, the RMP adopted a HRGC–HRMS methodology based on EPA Method 1668A for quantifying PCBs (US EPA, 1999) for analysis of several halogenated organic contaminant concentrations in San Francisco Bay water samples, including PBDE flame retardants and organochlorine pesticides, which are ubiquitous in the marine environment and food web.

Such sensitive methods would also be valuable for detecting ultra-trace levels of the targeted emerging pollutants, as well as for non-site-specific studies, such as evaluating sub-lethal toxic effects, assessing biological impacts of emerging contaminants at low levels, developing and evaluating immunoassay and other field detection methods, and characterizing chemical contaminant sources, reaction, transport pathways, and fate in the environment.

3. Results

While detailed results for some of the new pollutants recently included in the RMP's analyte list for monitoring in water and sediment have been published elsewhere (e.g., Oros et al., 2005), we are summarizing them here as a baseline record which can be compared to future exposure and effects research results, and as more information is assembled that demonstrate at which levels adverse environmental effects may occur. Results for all new analytes in water and sediment are reported in Tables 1 and 2, respectively. Results for bivalves monitored by the RMP in 2002 and 2003 include oysters *Crassostrea gigas* (Table 3), mussels *Mytilus californianus* (Table 4), and clams *Corbicula fluminea* (Table 5). In addition to data generated by the RMP, we are summarizing and reviewing data from other relevant efforts.

3.1. Polybrominated diphenyl ethers

Spatial distributions of PBDEs measured in water, sediment and bivalve tissue samples during 2002 and 2003 are illustrated in Figs. 1–3, respectively. The total PBDE (ΣPBDE) concentrations in San Francisco Bay

Table 1
Reportable concentrations (average blanks <30% of sample concentrations) of emerging pollutants in water from RMP 2002 and 2003 sampling years

Chemical name	Concentration (pg/L)			MDL (pg/L)	Blanks (pg/L)	Number of samples	Detection frequency (%)
	Median	Minimum	Maximum				
BDE 017	3.4	0.2	36.5	0.11–0.39	0.067–0.184	33	100
BDE 028	2.1	0.9	17.4	0.10–0.37	0.477–0.652	33	91
BDE 047	31.7	16.1	179.5	0.04–0.20	<MDL	33	91
BDE 066	1.6	0.8	7.9	0.07–0.38	<MDL	33	64
BDE 085	0.8	0.4	2.3	0.12–0.49	0.455–0.627	33	33
BDE 099	23.5	11.7	90.7	0.10–0.40	<MDL	33	58
BDE 100	6.0	2.7	20.7	0.06–0.24	0.811	33	79
BDE 138	0.5	0.2	1.4	0.13–0.47	0–0.118	33	55
BDE 153	2.9	2.2	10.3	0.12–0.45	0.632–0.632	33	42
BDE 154	2.2	1.2	9.3	0.06–0.23	0.504	33	58
BDE 183	1.5	0.8	26.9	0.06–0.30	0.435	33	27
BDE 190	0.4	0.3	1.1	0.15–0.45	<MDL	33	21
BDE 206	1.4	0.6	9.3	0.27–2.93	<MDL	33	36
BDE 207	1.7	0.8	13.5	0.27–2.93	<MDL	33	45
BDE 208	1.3	0.7	7.1	0.27–2.93	<MDL	33	33
BDE 209	30.7	12.2	191.0	1.52–38.5	<MDL	33	52
Sum of PBDEs	83.9	0.2	512.9	—	—	33	100
Bis(2-ethylhexyl)phthalate	301,000	62,600	459,000	63.0–510.9	12,660–29,000	63	100
Butylbenzylphthalate	13,580	13,580	13,580	129.5–479.0	1278–2420	63	100
Di-*n*-butylphthalate	7460	7460	7460	37.8–171.0	2870–4010	63	100
p-nonylphenol	22,600	5000	73,200	95.5–1570.0	~300	63	83

Concentrations represent sum of dissolved and particulate fractions. The detection frequency indicates the percentage of samples in which each contaminant was detectable.

Table 2
Reportable concentrations of emerging pollutants (average blanks <30% of sample concentrations) in sediment from RMP 2002 and 2003 sampling years

Chemical name	Concentration (ng/g)			MDL (ng/g)	Blanks (ng/g)	Number of samples	Detection frequency (%)
	Median	Minimum	Maximum				
BDE 047	3.8	1.1	100.0	0.5	<MDL	48	42
BDE 099	1.6	0.2	71.0	0.2–0.5	<MDL	48	77
BDE 183	0.2	0.2	0.2	0.1–0.5	<MDL	48	2
BDE 204	10.6	2.1	19.0	0.5	<MDL	48	4
BDE 205	21.8	21.8	21.8	0.5	<MDL	48	2
Sum of PBDEs	2.8	0.2	211.8	—	—	48	81
Bis(2-ethylhexyl)phthalate	242.0	208.0	605.0	0.32–0.58	13–240	95	100
Butylbenzylphthalate	49.4	12.7	323.0	0.32–0.58	4–51	95	100
Di-*n*-butylphthalate	27.3	21.4	93.8	0.32–0.58	3–15	95	100
p-nonylphenol	<5.0	<5.0	<5.0	0.32–0.58	<MDL	95	0

The detection frequency indicates the percentage of samples in which each contaminant was detectable.

Table 3
Reportable concentrations of emerging pollutants (average blanks <30% of sample concentrations) in oysters (*Crassostrea gigas*) from RMP 2002 and 2003 sampling years

Chemical name	Concentration (ng/g dry wt)			MDL (ng/g dry wt)	Number of samples	Detection frequency (%)
	Median	Minimum	Maximum			
Celestolide	16.7	8.2	57.0	20.0	5	60
Galaxolide	386.0	116.0	855.0	20.0	5	100
Tonalide	157.0	106.0	516.0	20.0	5	80
Versalide	22.7	20.3	25.1	20.0	5	40
Musk ambrette	3.4	1.9	6.0	20.0	5	60
Musk ketone	2.1	1.4	9.1	20.0	5	60
Musk moskene	ND	ND	ND	20.0	5	0
Musk xylene	3.6	2.6	7.1	20.0	5	80
BDE 017	ND	ND	ND	1.80–4.60	5	0
BDE 028	ND	ND	ND	1.90–4.90	5	0
BDE 047	25.2	9.1	43.0	2.50–6.40	5	100
BDE 066	ND	ND	ND	1.70–4.40	5	0
BDE 085	ND	ND	ND	1.70–4.50	5	0
BDE 099	9.6	4.7	13.3	2.50–6.50	5	80
BDE 100	6.2	3.8	7.4	2.00–5.20	5	60
BDE 138	ND	ND	ND	2.00–5.10	5	0
BDE 153	ND	ND	ND	1.90–4.80	5	0
BDE 154	ND	ND	ND	1.50–3.80	5	0
BDE 183	ND	ND	ND	2.20–5.70	5	0
BDE 190	ND	ND	ND	2.80–7.10	5	0
Sum of PBDEs	35.9	9.1	63.7	—	5	100
Triphenylphosphate	16.9	6.0	22.2	20.0	5	80
p-nonylphenol	21.5	21.5	21.5	20.0	5	20

The detection frequency indicates the percentage of samples in which each contaminant was detectable. All blanks were below method detection limits. ND: not detected or below detection limits.

water samples ranged from 0.2 to 513 pg/L. The Bay segment with the highest ΣPBDE concentrations in water was the Lower South Bay (range 56–513 pg/L, median 160 pg/L), with the next highest segment being the South Bay (range 42–124 pg/L, median 85 pg/L). The most abundant PBDE congeners detected in water samples were BDE-47, BDE-99, and BDE-209. In sediments, the ΣPBDE concentrations ranged from 0.2 to 212 ng/g dry wt with the highest ΣPBDE concentration found in the South Bay. Only five PBDE congeners were detected in the sediment samples; all others were below detection limits. BDE-47 (range 1–100 ng/g) was the most abundant

Table 4
Reportable concentrations of emerging pollutants (average blanks <30% of sample concentrations) in mussels (*Mytilus californianus*) from RMP 2002 and 2003 sampling years

Chemical name	Concentration (ng/g dry wt)			MDL (ng/g dry wt)	Number of samples	Detection frequency (%)
	Median	Minimum	Maximum			
Celestolide	31.9	7.1	93.4	20.0	7	43
Galaxolide	221.0	78.5	305.0	20.0	7	71
Tonalide	110.2	30.4	275.0	20.0	7	57
Versalide	ND	ND	ND	20.0	7	0
Musk ambrette	3.3	0.8	4.9	20.0	7	71
Musk ketone	3.8	1.3	4.8	20.0	7	71
Musk moskene	ND	ND	ND	20.0	7	0
Musk xylene	3.3	2.3	4.0	20.0	7	100
BDE 017	ND	ND	ND	1.70–2.86	15	0
BDE 028	ND	ND	ND	1.80–3.05	15	0
BDE 047	15.7	9.5	27.5	2.30–4.03	15	100
BDE 066	ND	ND	ND	1.60–2.77	15	0
BDE 085	ND	ND	ND	1.60–3.65	15	0
BDE 099	7.5	3.9	15.0	2.40–4.06	15	100
BDE 100	3.6	2.2	4.8	1.90–3.24	15	47
BDE 138	ND	ND	ND	1.90–4.13	15	0
BDE 153	ND	ND	ND	1.70–3.82	15	0
BDE 154	ND	ND	ND	1.40–3.39	15	0
BDE 183	ND	ND	ND	2.10–6.12	15	0
BDE 190	ND	ND	ND	2.60–9.00	15	0
Sum of PBDEs	23.4	13.4	46.9	—	15	100
Triphenylphosphate	18.9	1.1	378.0	20.0	7	86
p-nonylphenol	7.4	1.0	9.7	20.0	7	43

The detection frequency indicates the percentage of samples in which each contaminant was detectable. All blanks were below method detection limits. ND: not detected or below detection limits.

congener followed in decreasing order by BDE-99 (range 0.2–71 ng/g), BDE-204 (range 2–19 ng/g), BDE-205 (22 ng/g), and BDE-183 (0.2 ng/g). In bivalves, ΣPBDE concentrations ranged from 9 to 106 ng/g dry wt. Only four PBDE congeners were detected in bivalve tissue samples: BDE-47, BDE-99, BDE-100, and BDE-154; other congeners were below detection limits. For the individual bivalves, ΣPBDEs in oysters ranged from 9 to 64 ng/g dry wt (median 36 ng/g dry wt) with the highest ΣPBDE concentration found at Davis Point in San Pablo Bay. In mussels, the ΣPBDE concentrations ranged from 13 to 47 ng/g dry wt (median 23 ng/g dry wt) with the highest ΣPBDE concentration found in Central Bay. In clams, the ΣPBDE concentrations ranged from 85 to 106 ng/g dry wt (median 100 ng/g dry wt) with the highest ΣPBDE concentration found in the San Joaquin River. More extensive discussion of levels and spatial distributions of PBDEs in San Francisco Bay water, sediments, and bivalves is presented elsewhere (Oros et al., 2005).

PBDE concentrations in fish were measured in samples collected by the RMP in 1997 and the Environmental Working Group in 2002 (SFEI, 1999; Lunder and Sharp, 2003) (Fig. 4). ΣPBDE concentrations in six fish species ranged from 300 ng/g lipid in jacksmelt to 2000 ng/g lipid in Halibut. Striped bass and halibut each showed significant increases in ΣPBDE concentrations over the 5-year period between 1997 and 2002 (Holden et al., 2003; Lunder and Sharp, 2003).

She et al. (2004) examined PBDE levels in seabird eggs from San Francisco Bay (Fig. 5). PBDEs were measured in randomly collected eggs of Caspian Terns (14 eggs), and Forster's Terns (29 eggs). Six Least Tern eggs and four California Clapper Rail eggs that failed to hatch were also analyzed for PBDEs. Five PBDE congeners were found in all egg samples: BDE-47, BDE-99, BDE-100, BDE-153, and BDE-154. BDE-47 was the predominant congener generally making up 66% of ΣPBDE concentrations. Mean ΣPBDE concentrations in Caspian Tern eggs averaged 6.8 μg/g lipid weight (lw), Forster's Tern eggs 9.4 μg/g lw, Least Tern eggs 5.8 μg/g lw, and Clapper Rail eggs 0.39 μg/g lw. PBDE concentrations in tern eggs exceeded those of rail eggs by a factor of 20 or more. A maximum concentration of 63 μg/g lw was found in a Forster's Tern egg from South San Francisco Bay; the highest concentration ever recorded in the peer-reviewed literature. Sampling of Forster's Tern eggs from this same location in the following year yielded a similar maximum concentration (Terry Adelsbach, US Fish and Wildlife Service, Sacramento, CA, personal communication).

The sources, transport pathways, and fate of PBDEs in San Francisco Bay are not fully understood. In an effort to quantify contributions from suspected PBDE sources to

Table 5
Reportable concentrations of emerging pollutants (average blanks <30% of sample concentrations) in clams (*Corbicula fluminea*) from RMP 2002 and 2003 sampling years

Chemical name	Concentration (ng/g dry wt)			MDL (ng/g dry wt)	Number of samples	Detection frequency (%)
	Median	Minimum	Maximum			
Celestolide	24.1	22.6	25.5	20.0	2	100
Galaxolide	246.0	243.0	249.0	20.0	2	100
Tonalide	ND	ND	ND	20.0	2	0
Versalide	56.3	56.3	56.3	20.0	2	50
Musk ambrette	2.2	2.1	2.3	20.0	2	100
Musk ketone	13.6	10.6	16.5	20.0	2	100
Musk moskene	ND	ND	ND	20.0	2	0
Musk xylene	4.2	4.1	4.2	20.0	2	100
BDE 017	ND	ND	ND	3.27–4.88	4	0
BDE 028	ND	ND	ND	3.48–5.20	4	0
BDE 047	52.6	47.6	59.7	4.60–6.87	4	100
BDE 066	ND	ND	ND	3.16–4.73	4	0
BDE 085	ND	ND	ND	3.70–6.22	4	0
BDE 099	15.2	12.7	19.0	4.63–6.92	4	100
BDE 100	27.6	24.8	29.7	3.69–5.52	4	100
BDE 138	ND	ND	ND	4.20–7.03	4	0
BDE 153	ND	ND	ND	3.90–6.51	4	0
BDE 154	6.4	6.4	6.4	3.10–5.78	4	25
BDE 183	ND	ND	ND	4.70–10.40	4	0
BDE 190	ND	ND	ND	5.80–15.40	4	0
Sum of PBDEs	100.0	85.1	105.6	—	4	100
Triphenylphosphate	6.4	2.6	10.3	20.0	2	100
p-nonylphenol	ND	ND	ND	20.0	2	0

The detection frequency indicates the percentage of samples in which each contaminant was detectable. All blanks were below method detection limits. ND: not detected or below detection limits.

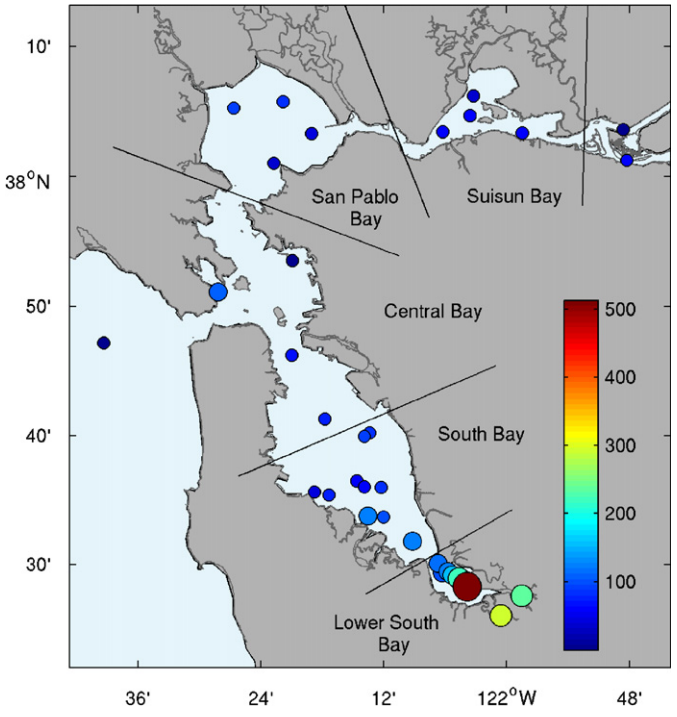

Fig. 1. Total PBDE concentrations (pg/L) in water from RMP 2002 and 2003 sampling years. Total PBDEs are the sum of all detected congeners (see Table 1 for list of congeners detected in water samples).

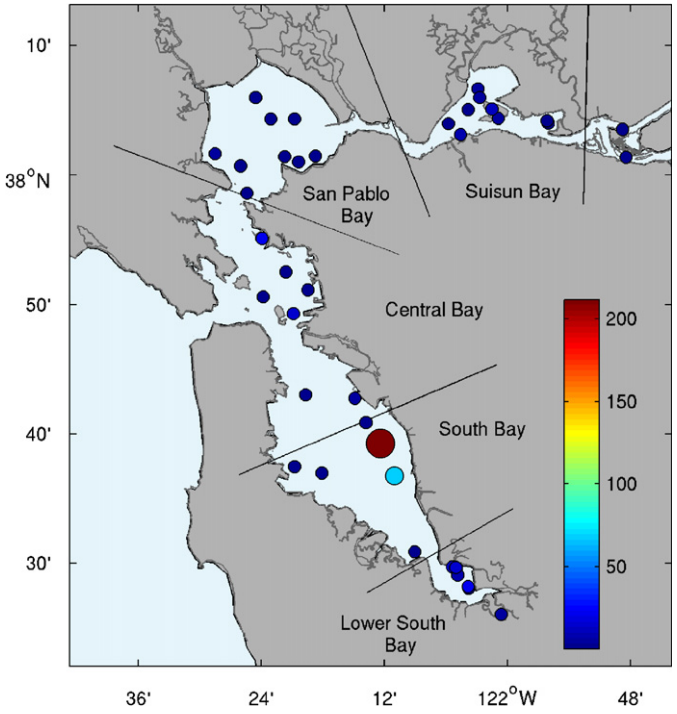

Fig. 2. Total PBDE concentrations (ng/g dry wt) in sediment from RMP 2002 and 2003 sampling years. Total PBDEs are the sum of all detected congeners (see Table 2 for list of congeners detected in sediment samples). Sediments are sampled from the top 5 cm.

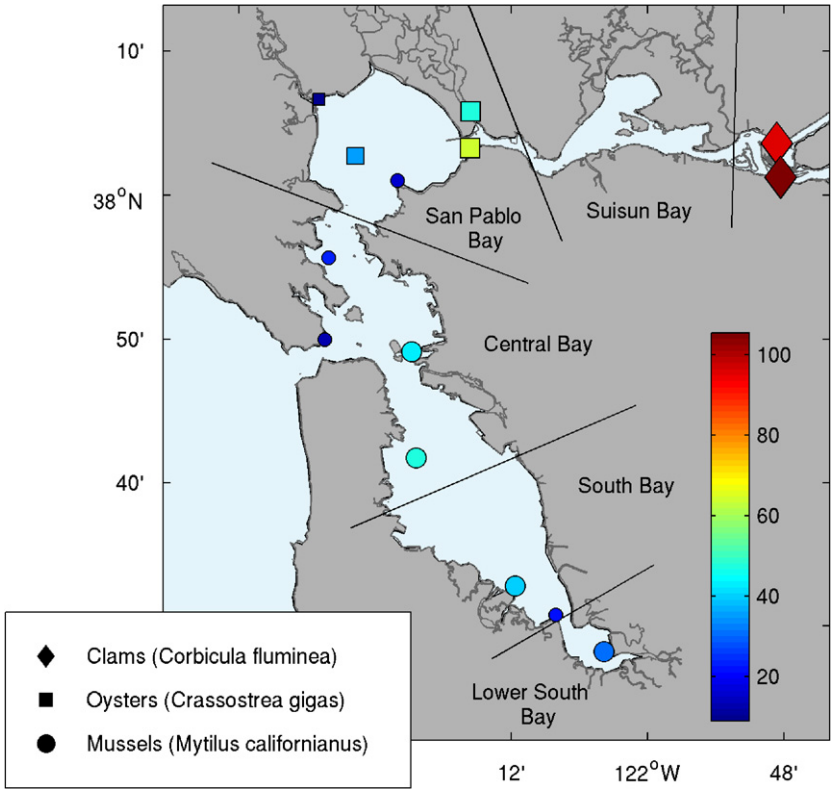

Fig. 3. Total PBDE concentrations (ng/g lipid wt) in bivalve tissue from RMP 2002 and 2003 sampling years. Total PBDEs are the sum of all congeners detected in a given bivalve (see Tables 3–5 for lists of congeners detected in oysters, mussels, and clams, respectively).

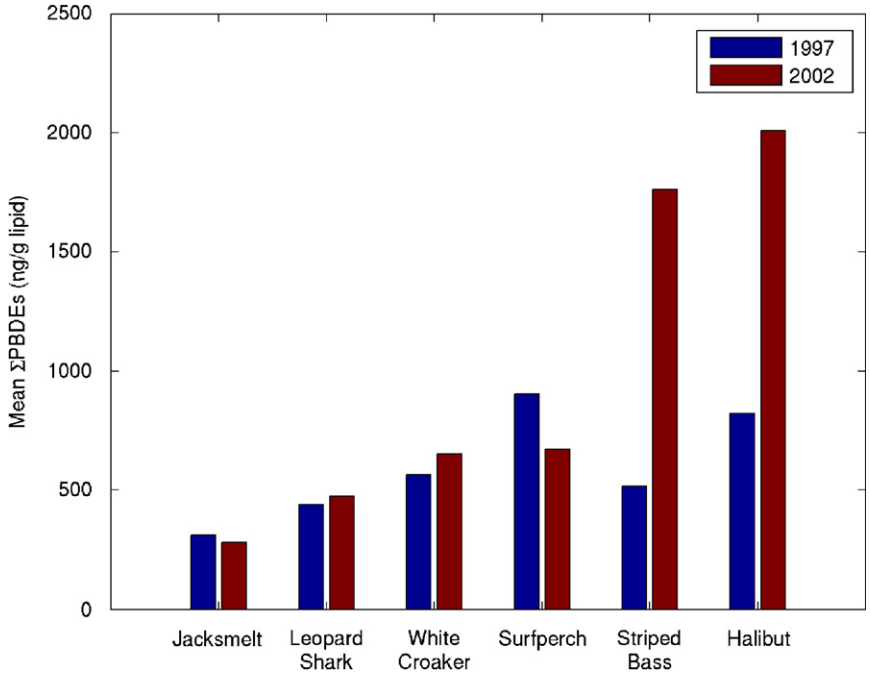

Fig. 4. Mean total PBDE concentrations in San Francisco Bay fish (*source*: Holden et al., 2003; SFEI, 1999). Striped bass and halibut each showed significant increases in their total PBDE tissue concentrations between 1997 and 2002.

the Bay, PBDE levels were examined in effluent from a wastewater treatment plant (North, 2004) and in storm-water runoff from a local tributary, Guadalupe River, which drains an area of approximately 440 km^2 of which roughly half is comprised of urban land uses. ΣPBDE concentrations in treated wastewater effluent ranged from

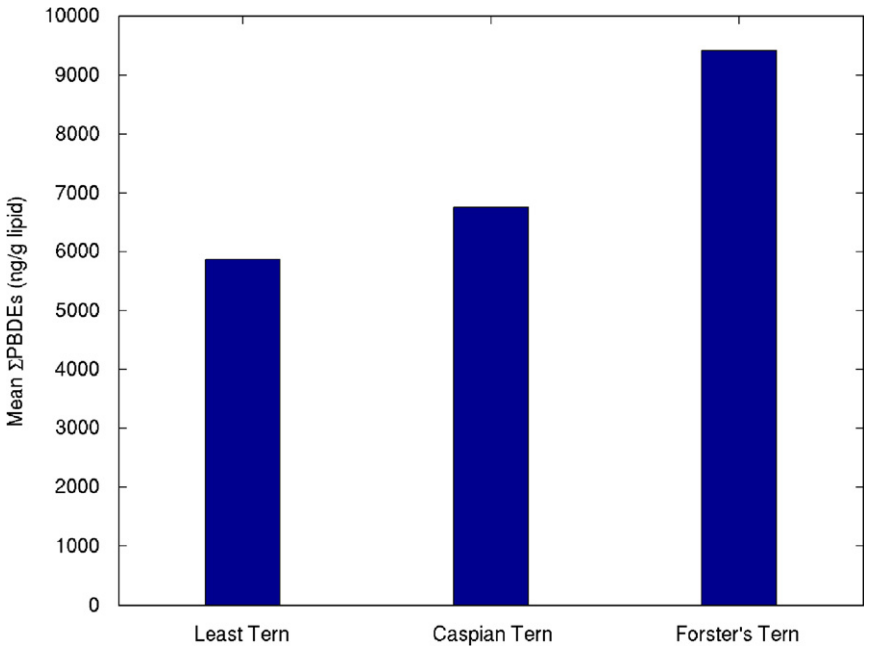

Fig. 5. Mean total PBDE concentrations in San Francisco Bay Tern Eggs (*source*: She et al., 2004). The highest concentrations of total PBDEs ever reported in wildlife were found in San Francisco Bay Forster's tern eggs (63 ppm).

4 to 29,000 pg/L. Congeners of highest abundance were BDE-47, BDE-99, and BDE-209. ΣPBDE levels from a scan of three Guadalupe River samples ranged from 40 to 140 ng/L—considerably higher than total PCB concentrations from this tributary (Leatherbarrow et al., 2002). It is likely that use patterns and product application of PBDEs will result in widely dispersed sources throughout urban watersheds that may be difficult to control (de Wit, 2002).

3.2. Phthalates

Phthalates are a class of widely used industrial compounds that are generally applied as plasticizers in industrial products such as nitrocellulose, polyvinyl acetate, polyvinyl chloride, adhesives, and coatings. They add flexibility to synthetic organic polymers. Furthermore, these compounds are found in personal care products such as hairspray, fingernail polish, and cosmetics. They are ubiquitous in environmental samples due to their release during manufacture, use, and disposal of industrial and consumer products. Phthalates have been reported to cause endocrine system disruption and cancer in humans and animals (Cadogan, 1999). The phthalates that were analyzed in San Francisco Bay water, sediments, and bivalves include DEHP, BBP, and DBP. The reportable concentrations and concentration ranges in RMP water samples from 2002 and 2003 were the following: DEHP = 63–459 ng/L; BBP = 13 ng/L; and DBP = 7 ng/L. In sediments, the reportable phthalate concentration ranges were the following: DEHP = 208–605 ng/g dry wt; BBP = 13–323 ng/g dry wt; and DBP = 22–94 ng/g dry wt. Bivalve concentrations were not reportable due to significant laboratory blank contamination. (If average concentrations in analytical blanks exceed the method detection limits, results are flagged. If the average found in blanks is greater than 30% of the reported concentration in any sample, in addition to being flagged, that sample result is not reported.)

3.3. p-nonylphenol (NP)

NP is primarily used as a precursor in the manufacture of non-ionic surfactants. It is also a degradation product of the alkylphenol ethoxylate surfactants that are used in household detergents and pesticide formulations. The capacity of NP to bioaccumulate and its potential to disrupt normal endocrine system functions further increase concern over its occurrence in the aquatic environment (Giesy et al., 2000; Harris et al., 2001). NP was analyzed in San Francisco Bay water, sediments, and bivalves in 2002 and 2003. It was detected in water and bivalve tissue, but was below detection limits (< 5 ng/g) in sediments. In water the NP concentration ranged from 5 to 73 ng/L, with the highest concentration found in Central Bay. Overall, NP levels in the Bay were far below the National Toxics Rule saltwater national aquatic life criterion of 12.4 μg/L. NP concentrations and concentration ranges in bivalves were the following: clams (2.6–10.3 ng/g dry wt); oysters (21.5 ng/g dry wt); and mussels (1–9.7 ng/g dry wt).

3.4. Triphenylphosphate (TPP)

TPP is a widely used flame retardant in video monitors and a plasticizer in some pesticide formulations, gasoline additives, synthetic motor oils, and in roofing paper. It has been demonstrated that major transport pathways of TPP

into the aquatic environment are primarily urban runoff from hydraulic fluid leakage, leaching from vinyl plastics, and manufacturing processes. TPP can bioaccumulate and biomagnify in biological tissues and also has the potential to disrupt normal endocrine system functions (IPCS, 1998). TPP was analyzed in San Francisco Bay bivalve tissue only and not in water or sediment samples. Its concentration in mussels ranged from 1 to 378 ng/g dry wt with the highest concentration found at a San Pablo Bay site. In oysters, TPP ranged from 6 to 22 ng/g dry wt with the highest concentration found at a Lower South Bay site. TPP in clams ranged from 2.5 to 10.3 ng/g dry wt with the highest concentration found in the Sacramento River.

3.5. Nitro and polycyclic musks

The nitro and polycyclic musks are used as fragrances in laundry detergents, cosmetics, perfumes, and personal care products. The major source of the musk compounds is municipal wastewater effluent that is discharged directly into receiving waters. The capacity of these compounds to bioaccumulate and induce indirect toxicity raises concern over their occurrence in the environment (Luckenbach et al., 2004; Schreurs et al., 2004; Luckenbach and Epel, 2005). Nitro and polycyclic musks were analyzed in San Francisco Bay bivalve tissue samples only and not in water or sediment, primarily because of resource limitations. The concentrations of nitro and polycyclic musks in bivalve tissue samples are reported in Tables 3–5. Galaxolide was the most abundant musk compound found in bivalves. Its highest concentrations were found in oysters from Davis Point in San Pablo Bay (855 ng/g dry wt), in mussels from a Central Bay site (305 ng/g dry wt), and in clams from the San Joaquin River (249 ng/g dry wt).

4. Discussion

The RMP and its analytical laboratories put much effort into developing new chemical methods for detecting new target analytes in each of the monitored matrices. In 2004, the RMP decided to continue monitoring for PBDEs in the Bay and to discontinue monitoring of TPP, musks, phthalates, and NP due to budget constraints and, for some of the newly characterized compounds, the very low concentrations that were found in the monitored matrices based on 2 years of data collection. Results from these 2 years formed a baseline that will serve as a reference in the future to evaluate both changes in the chemical profile of sediment, water, or tissue samples and concentration trends. This baseline will be useful in the future for prioritization of additional pollution prevention and management adjustments at the local or regional level, or when more or less comprehensive adjustments to the existing regulatory system are considered at the state or federal level.

No comprehensive framework exists in the US to encourage risk reduction before full proof of harm is available, or when impacts, not yet manifest, could become serious or irreversible. At this point, no accepted process is in place for determining when the costs of actions designed to prevent hazards to human or wildlife health outweigh the benefits that chemical compounds were designed to achieve. The benefits of those compounds that have reached a stage where they are marketed and used in a wide variety of industrial, agricultural, health care, or domestic applications tend to be much more obvious than their risks. Therefore, the burden of proof with regard to demonstrating environmental or human health risks becomes high.

A recent example of the level of proof required to prompt regulatory action are the PBDEs which are widely used as flame retardants in a variety of manufacturing applications. New findings by She et al. (2002) on PBDE concentrations in harbor seal blubber and human adipose tissue from Bay Area women, and the RMP review of archived chromatograms from a variety of San Francisco Bay water, sediment, and wastewater effluent samples confirmed findings from other regions in the US and Europe about the ubiquitous nature of these compounds. These recent data revealed some of the highest body burdens recorded for PBDEs. Harbor seal data from the Bay suggested that PBDE concentrations were doubling every 1.8 years (She et al., 2002). Shortly after these results received public attention, the California Legislature followed the European example and slated Penta-mix and Octa-mix PBDE commercial mixtures for phase out. However, the Deca-mix, which is the most commonly used in the US, is not affected by the phase-out. Bezares-Cruz et al. (2004) showed that BDE-209, which is the primary congener in the Deca-mix, can degrade in the presence of sunlight to lower-molecular-weight congeners that are more readily bioavailable. Gerecke et al. (2005) studied BDE-209 degradation rates under anaerobic conditions, such as those found in submerged sediments, and documented degradation to lower-molecular-weight congeners. All indications therefore point toward continued presence of PBDEs in the estuarine food web, as long as the Deca-mix remains commercially available. Further monitoring is required to evaluate degradation rates, fate, and transport of the Deca-mix (BDE-209) in San Francisco Bay and the effectiveness of the ban on other non-BDE-209-containing mixes.

Similarly, recent identification and quantification of perfluorochemicals in San Francisco Bay sediments and domestic sludge samples (Higgins et al., 2005), coupled with their resistance to degradation, potential particle affinity, and bioaccumulative and toxicological properties, indicates that this group of compounds should be targeted for future monitoring. Another group of emerging pollutants that should be targeted for further tracking is in the fragrance compound category, including musk ketone, Celestolide, Galaxolide, Tonalide, and Traseolide. Luckenbach and Epel (2005) showed that these musk compounds may act as chemosensitizers that allow other

toxicants, which would normally be excluded by multi-xenobiotic resistance efflux transporters, to enter the cell. Their direct toxicity and environmental risks have been generally regarded as low. However, their newly demonstrated indirect effects, the unexpectedly long periods of efflux transporter inhibition after removal of musk compound exposure, and the additive effects of these kinds of inhibitors indicate that periodic screening of musk compounds and other pollutants that contribute to chemosensitizing effects in the Bay may be advisable.

Compared to the slow regulatory response time to emerging pollutants in the past (EEA, 2001), the State Water Resources Control Board acted rapidly on new monitoring information and placed PBDEs on a non-regulatory "watch list" of pollutants that are potential threats to beneficial uses. Pollutants on the "watch list" become slated for increased monitoring and assessment activities. The relatively rapid response of the regulatory system with regard to PBDEs after region-specific data became available within the context of the toxicological literature, and the evolving shift in the RMP informing regulatory priorities are hopeful signs of a tighter feedback loop between science and environmental management.

While the management response time to emerging information may have improved compared to past examples listed above, other aspects of the management system could benefit from more holistic exposure assessments that include interactions among multiple stressors and evaluate cumulative and synergistic effects. For example, while the use of biomarkers as indicators of exposure to the total numbers and quantities of stressors is increasing as a monitoring tool, the environmental management system is currently not well equipped to use such information as a trigger for action. Exposure to various stressors is only relevant if it exceeds the organism's ability to respond to it, and biomarkers as toxic exposure indicators do not always tell regulators where that ability is exceeded or what kind of intervention might be most effective. However, physiological biomarkers are capable of reducing the confounding effects of a variety of effects bioassays, such as exposing various kinds of benthic organisms to sediment samples whose physical characteristics can influence the survival of test organisms (Gunther et al., 1997; Werner et al., 1998). The expanded use of biomarkers could therefore contribute significantly to the traditional "tool chest" of environmental managers to determine when management action might be warranted.

Our current limitations concerning more holistic assessment approaches contribute to our inability to effectively deal with the wide variety of chemicals entering the market place, especially with pharmaceuticals, personal care products, and more recently, manufactured nanomaterials. A strong need exists, therefore, to further evaluate the use of biomarkers as management tools and incorporating them into potential benchmarks for anticipating effects.

Improvements can also be made in the application of a variety of screening tools that are available for the design of chemical products and processes that reduce or eliminate the use and generation of hazardous substances (Green Chemistry Program, http://www.epa.gov/greenchemistry/). At this point, only compounds for which manufacturers are required to submit pre-manufacture notification reports are routinely screened, and implementation of recommendations following an evaluation is entirely voluntary on the part of the manufacturers. Drugs, cosmetics, and food additives, among other chemicals, do not fall under pre-manufacture notification requirements.

While the RMP has not yet become a monitoring program with the ability to forecast recovery scenarios, it is beginning to move in that direction as a result of expanded monitoring objectives endorsed by its participants in early 2005. A new category of assessment questions is prompting the partners governing the RMP to consider strengthening a modeling component that could predict recovery rates from past and current pollutant inputs, to evaluate to what extent emerging pollutant inputs are exceeding loss rates, and to anticipate risks associated with chronic pollutant inputs.

Next steps in the evolution of the monitoring program might also include a focus on chemical fingerprinting. The new baseline generated from archived chromatograms and newly screened emerging pollutants will be useful for future comparisons to chemical distribution and occurrence patterns in the Estuary which could then trigger detailed follow-up investigations and possible management action (Daughton, 2004). The effort will likely require development and application of appropriate field and laboratory methods to characterize the compounds in the sample matrices.

The RMP is also exploring a wider application of effects and exposure indicators that could ultimately be used in ways that are similar to the current TMDL approach to pollution abatement. Appropriate indicators of chronic toxicity and exposure that integrate the mixtures of stressors present in the water column or sediment could be used to meet one of the ultimate intents of the Clean Water Act, namely protection of aquatic life and human health, by apportioning maximum allowable toxicity or exposure units to their sources.

The RMP is moving in a direction that promises to meet the new challenges associated with emerging pollutants. A continued concerted effort will be required to maintain a pro-active monitoring approach. The appropriate mix of monitoring, evaluating sources and fate, methodological improvements, and modeling will likely generate a payoff of potentially tremendous cost savings in future clean-up and mitigation.

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