Central Coast Long-term Environmental Assessment Network

2006-2007 Annual Report

1.0 Program Background

The complexity of environmental issues affecting nearshore marine waters today have led to general agreement that their protection is only possible by implementing regional approaches to monitoring and resource management. Nearshore marine waters are affected by point-source discharges, storm runoff, rivers, discharges from ships, and aerial deposition. At the same time, many marine resources are diminishing under pressure from increasing usage. In the late 1990s, multiple agencies in the Monterey Bay area began working toward implementation of a regional approach to monitoring watersheds and marine waters.

The Central Coast Long-term Environmental Assessment Network (CCLEAN) is a long-term monitoring program that has been designed by program participants through a commitment to environmental stewardship in order to fulfill several regulatory objectives. CCLEAN is currently funded by the City of Santa Cruz, the City of Watsonville, Dynegy, Moss Landing, Monterey Regional Water Pollution Control Agency, and Carmel Area Wastewater District, under the direction of the California Regional Water Quality Control Board, Central Coast Region (RWQCB). CCLEAN fulfills a significant component of the subscribing agencies' compliance to their NPDES monitoring commitments, with an emphasis on receiving water monitoring. In addition, it represents a significant portion of their contributions to their communities' efforts at sustainability of their coastal environments. However, CCLEAN is also the current mechanism by which the RWQCB fulfills part of its obligations under a monitoring framework developed to provide an ecosystem-based Water Quality Protection Program for the Monterey Bay National Marine Sanctuary. The monitoring framework evolved to fulfill the RWQCB's obligations to the Management Plan for the Sanctuary. The Sanctuary's Management Plan includes a Memorandum of Agreement among eight federal, state, and regional agencies (including the Central Coast Regional Water Quality Control Board). The RWQCB's framework for partial fulfillment of this Water Quality Protection Program is the Central Coast Ambient Monitoring Program (CCAMP). This multidisciplinary program includes sampling in watersheds that flow into coastal regions, in estuarine coastal confluences, and at coastal sites. The goal of CCAMP is to "collect, assess, and disseminate scientifically based water quality information to aid decision-makers and the public in maintaining, restoring, and enhancing water quality and associated beneficial uses." CCLEAN provides the initial nearshore component of CCAMP. CCLEAN has been underway since 2001 and its QAPP is being revised to incorporate recent program changes, and to retain consistency with the RWQCB surface water ambient monitoring program (SWAMP) requirements for data compatibility.

Within the framework of CCAMP, the goal of the CCLEAN program is to assist stakeholders in maintaining, restoring, and enhancing nearshore water and sediment quality to support associated beneficial uses in the Central Coast Region, including recreation, wildlife and biological

communities. The program's objective is to use high-quality data to address the following questions and objectives:

- What are the major sources of contaminants to nearshore waters?
- What are the effects of wastewater discharges in nearshore waters?
- Do nearshore waters and sediments comply with California Ocean Plan?
- What are the status and long-term trends in the quality of nearshore waters, sediments, and associated beneficial uses?
- Develop a long-term database on trends in the quality of nearshore waters, sediments and associated beneficial uses.
- Ensure that the database is compatible with other regional monitoring efforts and regulatory requirements.
- Ensure that data are presented in ways that are understandable and relevant to the needs of stakeholders.

To answer these questions, CCLEAN uses various graphical and statistical approaches, as well as comparisons of data with numeric and narrative objectives, guidelines and alert levels from the California Ocean Plan (State Water Resources Control Board, 2005), Central Coast Basin Plan (RWQCB, 1997), California State Mussel Watch Program (California State Mussel Watch Program, 2003), California Office of Environmental Health Hazard Assessment (Office of Environmental Health Hazard Assessment, 2003), and the National Oceanic and Atmospheric Administration (Long *et al*., 1998; Long *et al*., 2000).

Program monitoring activities during 2006-2007and their relationship to program objectives are shown in Table 1. Sampling sites are shown in Figure 1.

2.0 Report Organization and Scope

The 2007-2008 program year involved numerous activities that were out of the ordinary CCLEAN scope and resulted in management resources that normally would be devoted to writing the 2006-2007 Annual Report being redirected to other activities. Those activities are discussed in sections 2.1 through 2.4. As a consequence of these out-of-scope activities in 2007-2008, this document constitutes an abbreviated 2006-2007 Annual Report. All data for the 2006-2007 program year will be submitted to the RWQCB, but the technical content of this report (Section 3) focuses only on initial measurements of a contaminant emerging of concern, polybrominated diphenyl ethers (PBDEs).

2.1 External Peer Review

In the 2006-2007 project year (July 1, 2006 – June 30, 2007), at the end of the first five-year phase of CCLEAN, an external peer review was undertaken. Dr. Brock Bernstein was retained to provide this review, which he based on conversations with program participants and other stakeholders and application of his experience in similar roles for other regional monitoring efforts, such as the Regional Monitoring Program for Trace Substances in San Francisco Bay.

Table 1. Sampling sites, parameters sampled, frequency of sampling, applicable water-quality stressors, and relevant program objectives for CCLEAN during the 2006–2007 program period.

Sampling Sites	Parameters Sampled at Each Site	Frequency of Sampling	Applicable Water-quality Stressors and Program Objectives
Water Sampling Four wastewater discharges (Santa Cruz, Watsonville, Monterey, Carmel) in effluent and four rivers (San Lorenzo, Pajaro, Salinas, Carmel)	30-day flow proportioned samples using automated pumping equipment, solid-phase-extraction techniques for persistent organic pollutants (POPs); screen effluent for reproductive endocrine disruption activity	Twice per year (wet season and dry season)	Sources, loads, trends, effects and permit compliance for: POPs Endocrine disrupting compounds
	Grabs of effluent for ammonia and nitrate, turbidity, temperature, conductivity, pH, urea, orthophosphate, dissolved silica and total suspended solids	Monthly	Sources, loads, trends and permit compliance for: Nutrients
	Evaluate satellite imagery for algal blooms	Periodically	Effects of: Nutrients
30-ft contour sites for Santa Cruz, Watsonville and MRWPCA	Grabs for total and fecal coliform, *enterococcus*	At least monthly	Sources, trends, effects and permit compliance for: Pathogen indicators
Two nearshore background sites	30-day time-integrated samples using automated pumping equipment and solid-phase-extraction techniques for: POPs, nitrate, ammonia, urea, orthophosphate and dissolved silica, total suspended solids, temperature, conductivity, pH, total and fecal coliform, *enterococcus*	Twice per year (wet season and dry season)	California Ocean Plan compliance for: POPs Nutrients Pathogen indicators
Sediment Sampling One depositional site and one background site along 80-m contour, four sites near sources	Single samples for benthic infauna, POPs, total organic carbon and grain size	Annually in the fall	Status, trends, effects and alert level comparisons for: POPs
Mussel Sampling Five rocky intertidal sites	One composite of 30-40 mussels for POPs, total and fecal coliform, and *enterococcus*	Annually in the wet season	Status, trends, effects and alert level comparisons for: POPs Pathogen indicators

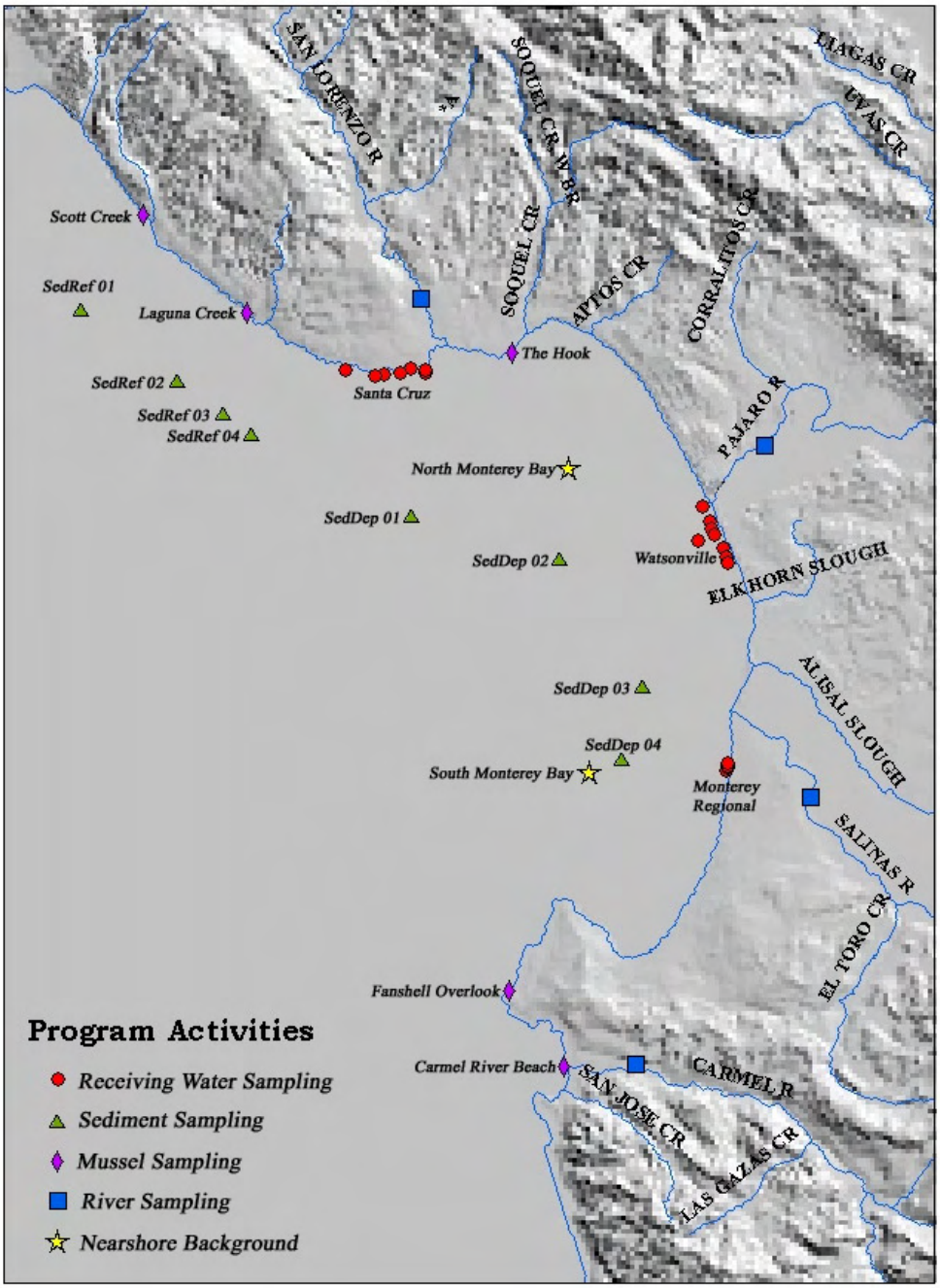

Figure 1. Locations of CCLEAN sampling sites for receiving water, sediment, mussels, and rivers.

Dr. Bernstein produced a report of his findings and recommendations (http://www.cclean.org/ftp/CCLEAN%20Peer%20Review.pdf). Dr. Bernstein's recommendations were as follows:

- Standardize data acquisition and management
- Link the QAPP's data quality objectives to core questions and related data analysis methods
- Expand the suite of data analysis methods
- Improve the efficiency of the monitoring design
- Define a reporting strategy that more effectively communicates results to key audiences
- Expand relationships with other monitoring and research programs and institutions.

Program participants spent considerable time in 2007-2008 discussing implementation of Dr. Bernstein's recommendations. In particular, the efficiency of the monitoring program was improved by reducing the frequency of mussel sampling to annually, in the wet season. This sampling timing and frequency is consistent with program findings that the mussels reflect inputs to the ocean of contaminants washing off the land during the wet season and that evaluation of long-term trends in such inputs should be based on analysis of the most relevant data. Moreover, an analysis of the first five years of sediment data was undertaken to determine whether this program element could be made more efficient and responsive to outstanding questions regarding the effects of sediment-associated contaminants being discharged by rivers into Monterey Bay. Based on this evaluation, the number of sediment sampling sites will be reduced in 2008-2009 from eight to six, with two of the original sites maintained for analysis of long-term trends and four sites moved closer to river discharges.

2.2 Use of CCLEAN Effluent Data for NPDES Permit Compliance

In 2007-2008, program participants also discussed ways to improve the applicability of CCLEAN data to their permit compliance needs, which accompanied actions by the RWQCB to include participation in CCLEAN and a requirement to perform high-volume water sampling in the NPDES permits of program participants. Through a desire to incorporate measurements of emerging contaminants of concern, program participants considered various methods for high-volume water sampling that might be amenable to measuring a wider range of contaminants in wastewater effluent than allowed by the current XAD-2 resin *in situ* solid-phase extraction sampling method. Ultimately, program participants decided to retain the existing sampling method, with the addition of dioxins and furans to the analyte list.

2.3 Expanded Measurements for Contaminants of Emerging Concern

In 2006-2007, CCLEAN began analyzing samples for the flame retardants polybrominated biphenyl ethers. In 2007-2008, it was decided to begin analyzing samples for perfluorinated compounds (PFCs). PFCs are polymers that are applied to numerous materials, such as paper food containers and carpeting, to make them repel liquid. They recently have been associated with sea otter mortality due to disease (Kannan *et al*., 2006).

2.3 Screen Effluent for Endocrine Disruption Activity

CCLEAN participants decided in 2007-2008 to implement assays for screening effluent for potential disruption of reproductive endocrine processes. Several assays were investigated, including fish assays developed by U.S. Environmental Protection Agency, those developed through collaboration between the City of Boulder, CO, University of Colorado and U.S. Geological Survey; and bench-top cellular assays. Quotes were obtained from several potential contractors for endocrine disruption assays and a workshop was conducted to further explore endocrine disruption assays and to help inform the CCLEAN Steering committee's choice of an assay. The workshop included Gary Ankley of USEAP and Brian Anderson of Granite Canyon laboratories. Discussions clarified technical concerns associated with a proposed static renewal approach versus flow-through assays for screening endocrine disruption, particularly with regard to confounding factors potentially associated with the use of static renewal tests for this purpose. Discussions during the workshop formed the basis for a revised approach to address technical concerns.

2.4 Update CCLEAN Quality Assurance Program Plan (QAPP)

The CCLEAN QAPP was revised to emphasize a hypothesis-testing approach for achieving program objectives, to provide greater discussion of sources of variability in data and how to address them, to include recommended analytical methods for POPs, to include analysis of perfluorinated compounds, dioxins and furans, and to include screening of effluent for reproductive endocrine disruption.

3.0 Initial Results for Sources, Loads and Effects of PBDEs

3.1 Introduction

Produced commercially since the 1970s for use as flame retardants, PBDEs are chemically similar to polychlorinated biphenyls (PCBs) (Figure 2). With PBDEs, the phenyl rings are separated by an oxygen atom and ring substitution is by bromine, rather than by chlorine. As with PCBs, there are potentially 209 compounds (congeners) that differ according to the number and placement of halogen atoms. PBDEs with the same number of bromine atoms are called homologues and, because the same number of bromine atoms can be distributed among different bonds on the phenyl rings, most homologues can include several different congeners. Commercial PBDE formulations are nominally based on the five-, eight- and 10-bromine homologues (penta-, octa- and deca-BDEs), although a recent study (La Guardia *et al*., 2006) reported all tested formulations contained a mixture of homologues (Figure 3). Total global market demand for PBDEs in 2001 was 67,390 metric tons, with 83% coming from deca-BDE, 11% from penta-BDEs and 6% from penta-BDEs.

Each of the three main formulations of PBDEs is used in slightly different ways. PBDEs are used as additive flame retardants in thermoplastics. The major use of deca-BDE is in high-impact polystyrene, but it is also used in a wide range of other plastics for electrical and electronic equipment. Penta-BDE is used primarily in the furniture industry, mostly as a flame retardant in polyurethane foam in mattresses and cushions. Nevertheless, only 7.5% of polyurethane foam

used for mattresses and cushions in the United States is treated with penta-BDE. The majority of treated foam products are sold in California, which is the only state with ignition resistance requirements for furniture. Octa-BDE is used primarily as a flame retardant in acrylonitrile butadiene styrene (ABS) computer and monitor cases.

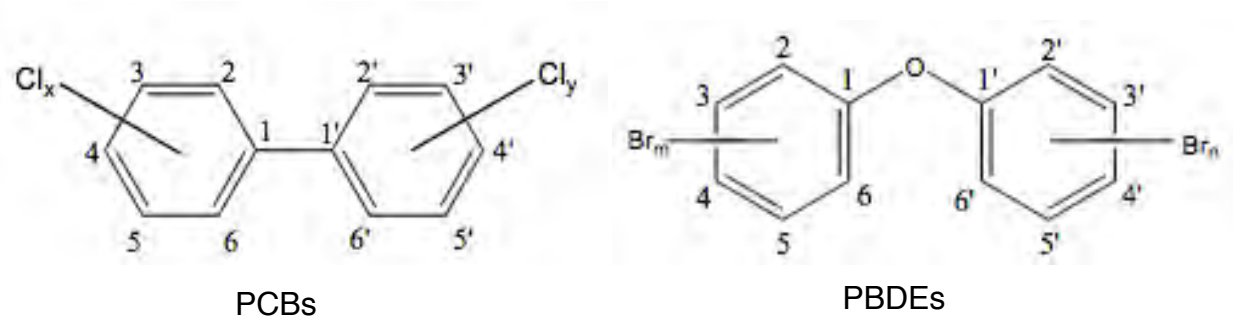

Figure 2. Chemical structures of PCBs and PBDEs.

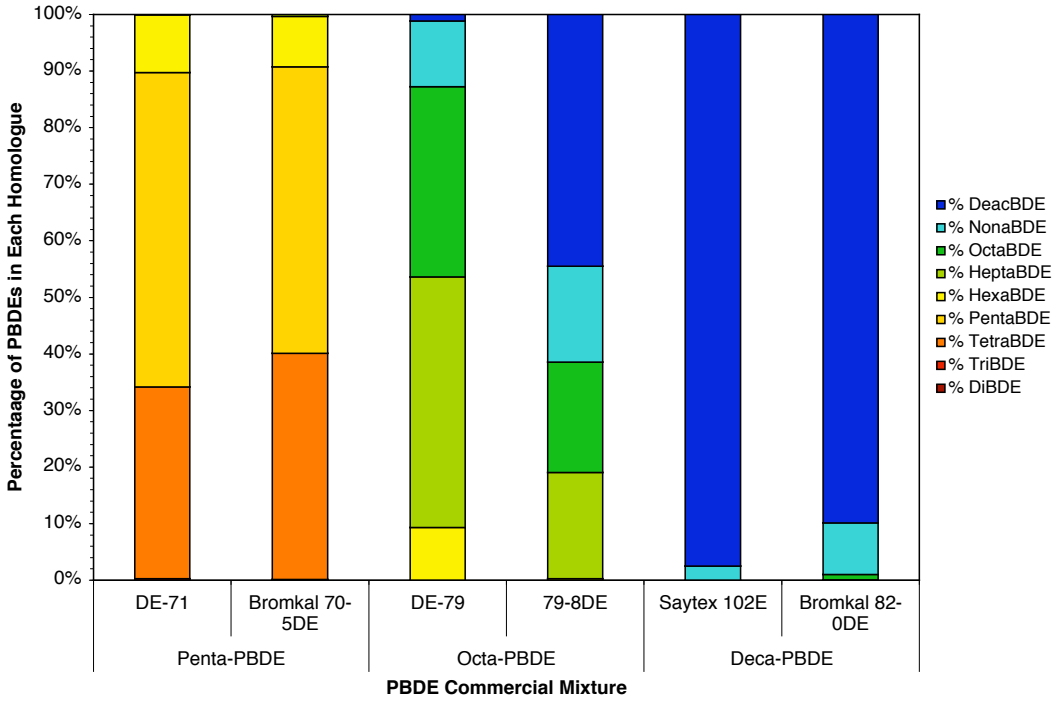

Figure 3. Homologue composition of commercial PBDE mixtures. Data from La Guardia et al, (2006).

Tests have shown that some PBDEs, mostly those with lower numbers of bromine atoms, are toxic. Exposure of test animals to lower brominated PBDEs resulted in thyroid effects and possible immune suppression (Agency for Toxic Substances and Disease Registry, 2004). Studies also have shown very high concentrations of PBDEs in women's breasts in the San Francisco Bay area, with an inverse relationship between age and concentration that suggests

recent exposures (Petreas *et al*., 2003; She *et al*., 2002). Consequently, the use of some PBDE formulations has been limited due to their persistence, toxicity and apparent propensity to bioaccumulate. In 2004, the European Union banned products with greater than 0.1% penta- and octa-BDE. In 2003, the California legislature also passed legislation (AB 302) that states "a person may not manufacture, process, or distribute in commerce a product, or a flame-retarded part of a product, containing more than one-tenth of 1 percent of pentaBDE or octaBDE, by mass." This ban went into effect in January 2008.

3.2 Sampling Methods

PBDEs were measured in wastewater effluent from the City of Santa Cruz, City of Watsonville, Monterey Regional Water Pollution Control Agency and Carmel Area Wastewater District and in discharges from the San Lorenzo, Pajaro, Salinas and Carmel rivers. Flow-proportioned samples were collected over approximately a 30-day period in the wet season and the dry season. ISCO® samplers were configured as shown in Figure 3. Signals from the treatment plant flow meters or depth sensors in the rivers were used to trigger sample collection so that approximately 200 liters of water would be sampled over the 30-day period. Water was first pumped through a glass-fiber filter to retain suspended particles nominally greater than one micron, then through a Teflon column packed with XAD-2 resin beads, to which dissolved nonpolar compounds are adsorbed. The particle filter and XAD-2 resin are extracted in the laboratory and analyzed for the CCLEAN list of analytes (Appendix 1). The dates and volumes for 2006-2007 effluent and river samples are shown in Table 2. Annual loads of PBDEs were estimated as follows:

Annual Load = [Average of (flow-proportioned concentration x average daily flow for wet season and dry season)] x 365.

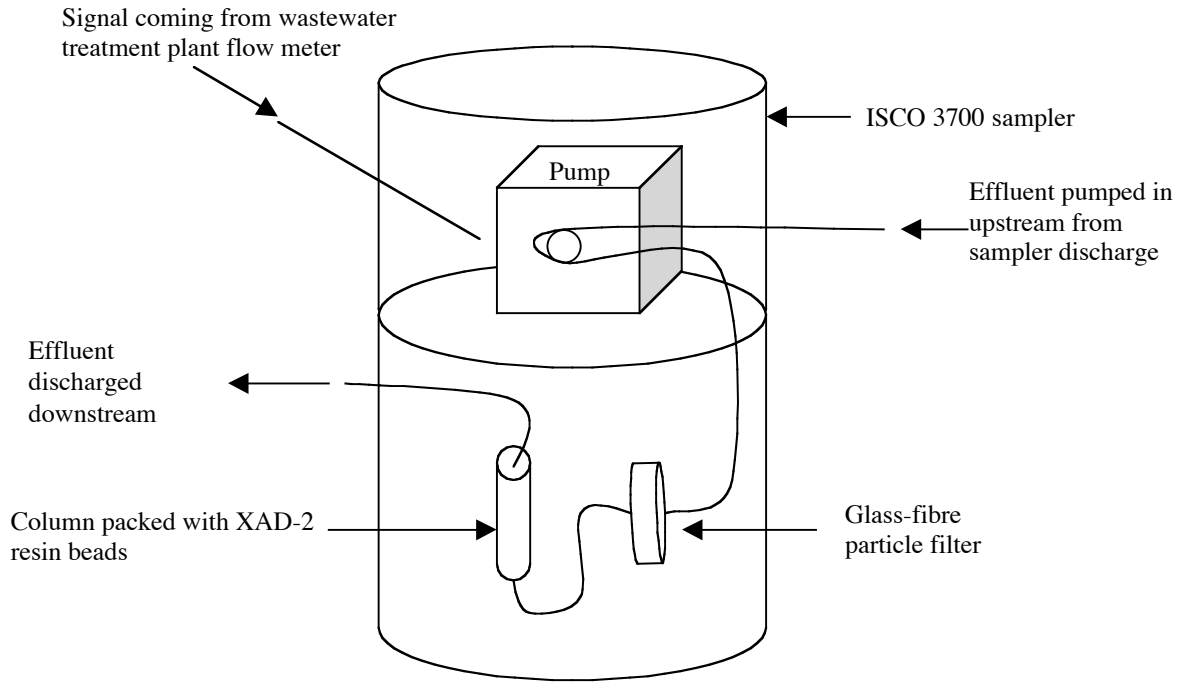

Figure 3. Configuration of ISCO samplers for CCLEAN effluent and river sampling.

Table 2. Dates and volumes of effluent and river samples, 2006–2007.

Season	Source	Start Date	End Date	Number of Liters Sampled
Dry	Santa Cruz effluent	September 7, 2006	October 17, 2006	150
	Watsonville effluent	September 6, 2006	October 10, 2006	213
	Monterey Regional effluent	September 6, 2006	October 6, 2006	207
	Carmel Area effluent	September 6, 2006	October 16, 2006	218
	San Lorenzo River	September 8, 2006	October 11, 2006	212
	Pajaro River	September 8, 2006	October 12, 2006	203
	Salinas River	September 7, 2006	October 16, 2006	194
	Carmel River	No Flow	No flow	NS
Wet	Santa Cruz effluent	February 14, 2007	March 19, 2007	210
	Watsonville effluent	February 14, 2007	March 16, 2007	203
	Monterey Regional effluent	February 14, 2007	March 16, 2007	206
	Carmel Area effluent	February 14, 2007	March 16, 2007	210
	San Lorenzo River	February 16, 2007	April 11, 2007	214
	Pajaro River	February 14, 2007	March 21, 2007	198
	Salinas River	Insufficient Flow	Insufficient Flow	NS
	Carmel River	February 13, 2007	April 11, 2007	205

PBDEs also were analyzed in samples collected from the two Monterey Bay nearshore background sites, each of the five mussel sites and from each of the eight sediment sites shown in Figure 1. Sampling dates are shown in Table 3 and Table 4. Water samples from the nearshore background sites were collected on a time-integrated basis with moored buoys using the same solid-phase extraction methods as used for effluent and river samples (Figure 4). The North Monterey Bay buoy came off its mooring three days after being deployed and was redeployed on September 18. It was estimated that 5–10 samples were collected during the time the buoy drifted free. The North Monterey Bay buoy also was separated from its mooring during the wet-season sampling, when it was run over by a crab fishing vessel on March 1. The surface buoy was recovered from the beach adjacent to Monterey Bay Academy on March 6, 2007. A slight leak in the sampling equipment shorted out the battery so that it is unlikely that any samples were collected during the time the buoy was drifting free of its mooring.

Table 3. Dates and volumes of nearshore background samples, 2006–2007.

Season	Site	Start Date	End Date	Number of Liters Sampled
Dry	North Monterey Bay	September 10, 2006	October 10, 2006	200
	South Monterey Bay	September 10, 2006	October 10, 2006	200
Wet	North Monterey Bay	February 1, 2007	March 6, 2007	164

	South Monterey Bay	February 1, 2007	March 7, 2007	170

Table 4. Dates of mussel and sediment samples, 2006-2007.

Season	Matrix	Site	Sampling Date
Dry	Mussels	Scott Creek	October 8, 2006
		Laguna Creek	October 8, 2006
		The Hook	October 8, 2006
		Fanshell Overlook	October 8, 2006
		Carmel River Beach	October 8, 2006
	Sediment	SedRef 01	October 25, 2006
		SedRef 02	October 25, 2006
		SedRef 03	October 25, 2006
		SedRef 04	October 25, 2006
		SedDep 01	October 25, 2006
		SedDep 02	October 25, 2006
		SedDep 03	October 25, 2006
		SedDep 04	October 25, 2006
Wet	Mussels	Scott Creek	March 18, 2007
		Laguna Creek	March 18, 2007
		The Hook	March 18, 2007
		Fanshell Overlook	March 18, 2007
		Carmel River Beach	March 18, 2007

CCLEAN samples were analyzed for 46 PBDE congeners, several of which co-elute during analysis and cannot be distinguished, in nine homologues (Table 5). Congeners 10, 30, 79, 105, 116 and 126 were not detected in any matrix. When "sum of PBDEs" is reported in following sections, it refers to the cumulative concentrations or loads of all detected PBDE congeners.

3.3 Sources of PBDEs Discharged to Monterey Bay

PBDEs were detected in all river and effluent samples, with very low concentrations found in equipment and lab blanks (Table 6), and effluent samples had approximately ten times higher concentrations of PBDEs than were found in river samples. The composition of the PBDEs also differed between effluent and rivers, with less brominated PBDEs (tetra- and penta-BDEs) dominating effluent, which also consistently contained tri-BDEs, whereas river samples were dominated by more brominated PBDEs (nona- and deca-BDEs) with lower proportions of tri-BDEs than wastewater (Figure 5). Monterey Regional and Carmel Area Wastewater District effluent tended to have slightly greater proportions of nona- and deca-BDE, with correspondingly lower proportions of tetra- and penta-BDE than did Santa Cruz or Watsonville, with no apparent differences in homologue proportions between dry-season and wet-season samples. The San Lorenzo River tended to have greater proportions of deca-BDE and lower proportions of tetra- and penta-BDE than the other rivers and the San Lorenzo and Pajaro rivers had slightly lower proportions of deca-BDE and higher proportions of tetra- and penta-BDE in the wet season than in the dry season.

Across all samples, the three most abundant congeners in effluent were PBDE-47 (a tetra-BDE) and PBDE-99 (a penta-BDE) and PBDE-209 (deca-BDE), with average concentrations of 3,871 ng/L, 3,191 ng/L and 2,701 ng/L, respectively. These three congeners accounted for 31%, 25% and 21% of wastewater loads, respectively. In rivers, the three most abundant congeners also were PBDE-209, PBDE-99 and PBDE-47, with average concentrations of 529 ng/L, 90 ng/L and 70 ng/L, respectively. These three congeners accounted for 61%, 10% and 8% of river loads, respectively.

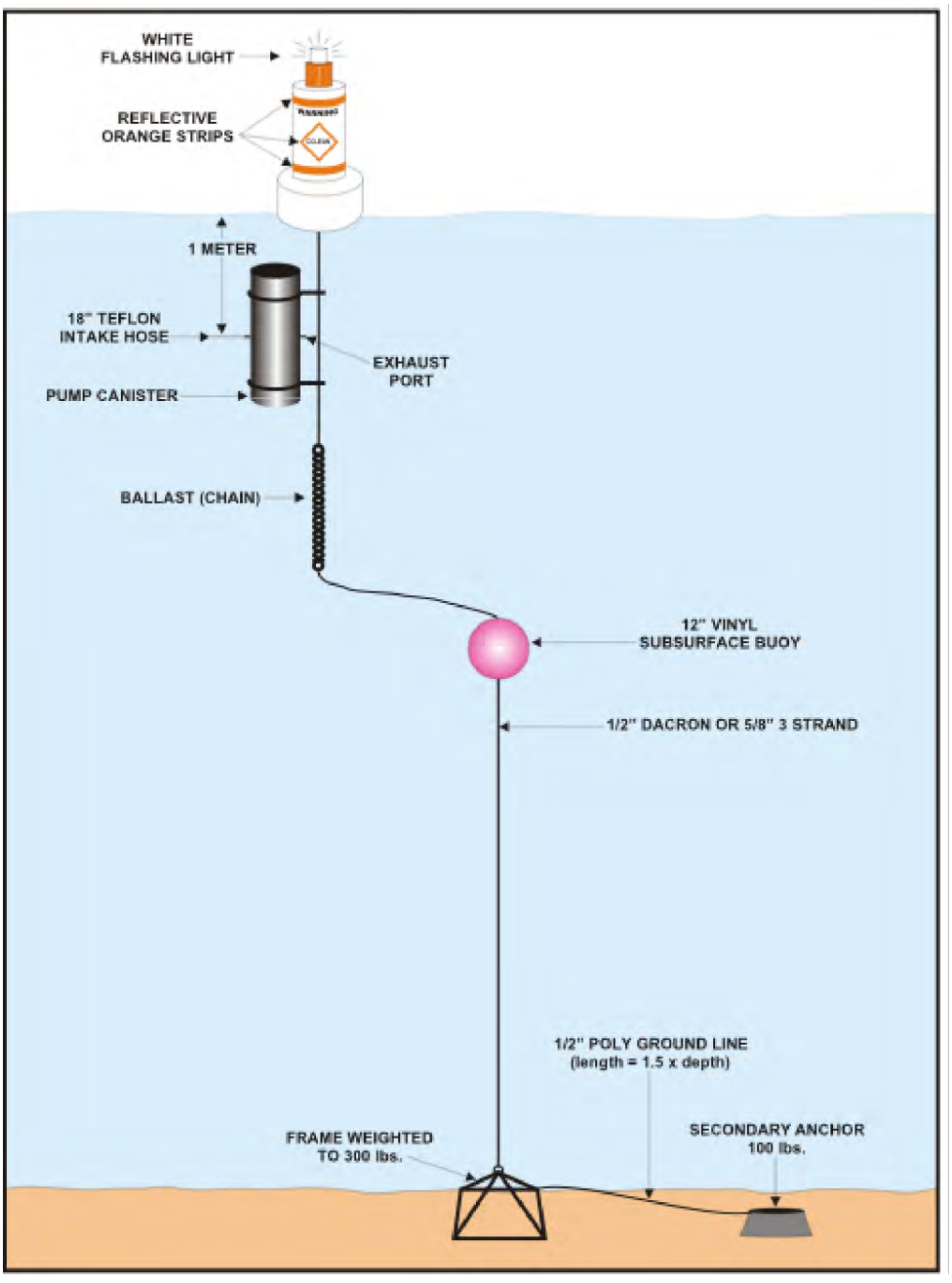

Figure 4. Moorings deployed to measure nearshore background water quality

Table 5. PBDE congeners and homologues measured by CCLEAN and matrices in which each was detected.

PBDE Congener	Homologue	Matrix[1]
PBDE-7	DiBDE	E R M S
PBDE-8/11	DiBDE	E R M S
PBDE-10	DiBDE	
PBDE-12/13[2]	DiBDE	E R M S
PBDE-15	DiBDE	E R M S
PBDE-17/25	TriBDE	E R M S
PBDE-25	TriBDE	E R
PBDE-28/33	TriBDE	E R M S
PBDE-30	TriBDE	
PBDE-32	TriBDE	E R M
PBDE-35	TriBDE	E R M S
PBDE-37	TriBDE	E R M S
PBDE-47	TetraBDE	E R M S
PBDE-49	TetraBDE	E R M S
PBDE-51	TetraBDE	E R M S
PBDE-66	TetraBDE	E R M S
PBDE-71	TetraBDE	E R M S
PBDE-75	TetraBDE	E R M S
PBDE-77	TetraBDE	R M
PBDE-79	TetraBDE	
PBDE-85	PentaBDE	E R M S
PBDE-99	PentaBDE	E R M S
PBDE-100	PentaBDE	E R M S
PBDE-105	PentaBDE	
PBDE-116	PentaBDE	
PBDE-119/120	PentaBDE	E R M S
PBDE-126	PentaBDE	
PBDE-128	HexaBDE	E R
PBDE-138/155	HexaBDE	E R M
PBDE-140	HexaBDE	E R M
PBDE-153	HexaBDE	E R M S
PBDE-154	HexaBDE	E R M S
PBDE-166	HexaBDE	E R M
PBDE-181	HeptaBDE	R
PBDE-183	HeptaBDE	E R M S
PBDE-190	HeptaBDE	E R M
PBDE-203	OctaBDE	E R M S
PBDE-206	NonaBDE	E R M S
PBDE-207	NonaBDE	E R M S
PBDE-208	NonaBDE	E R M S
PBDE-209	DecaBDE	E R M S

[1] = E, effluent; R, rivers; M, mussels; S, sediment.

[2] = The two indicated congeners co-elute during analysis and cannot be distinguished.

Contrary to the patterns for other POPs (CCLEAN, 2007), the loads of PBDEs discharged in effluent were much higher than those discharged by rivers (Figure 6), consistent with higher concentrations in effluent than in rivers. At least some of the difference in loads between wastewater and rivers could be due to incomplete sampling for the Salinas and Carmel Rivers, where wet-season and dry-season samples, respectively, were not collected due top insufficient river flow (see Table 2).

The differences between effluent and rivers in the composition of PBDEs suggest either different sources or the effects of environmental debromination. Several recent studies have shown that debromination of PBDEs can occur through a variety of processes, including photolysis (Eriksson *et al*., 2004; Soderstrom *et al*., 2004), microbial activity under anaerobic conditions, including wastewater treatment plants (Gerecke *et al*., 2005; Tokarz *et al*., 2008) and metabolism in vertebrates (Stapleton *et al*., 2004).

Table 6. Concentrations of PBDEs in effluent, rivers, equipment blanks and lab blanks during the 2006-2007 program year.

	Sum of PBDEs, ng/L	
Sample	**Dry Season**	**Wet Season**
Santa Cruz effluent, 140[1]	10.97	6.35
Watsonville effluent, 84[1]	10.36	20.64
Monterey Regional effluent, 145[1]	18.91	14.83
Carmel Area effluent, 121[1]	7.56	11.90
San Lorenzo River	1.11	0.98
Pajaro River	1.24	1.59
Salinas River	0.13	NS
Carmel River	NS	0.16
Equipment Blank	0.03	0.04
Lab blank	0.04	0.06

[1] = Dilution factors based upon outfall diffuser performance are indicated for each wastewater discharger.

While wastewater effluent is the major source of PBDEs measured by CCLEAN, the concentrations of PBDEs in effluent from wastewater treatment plants in the Monterey Bay area are lower than have been reported elsewhere. Comparison of data collected in different years from San Francisco Bay area and Monterey Bay area wastewater treatment plants suggests the concentrations of PBDEs in effluent from several San Francisco Bay area wastewater treatment plants are generally higher than those reported from Monterey Bay area wastewater treatment plants (Table 8). Because of lower annual flows, the Monterey Bay area treatment plants also discharged much lower loads of PBDEs than did the San Francisco Bay area treatment plants. It should be noted that these results are based on a single year of data and may not represent long-term conditions. It is possible that the relative contributions to PBDE loads by different sources will vary among years.

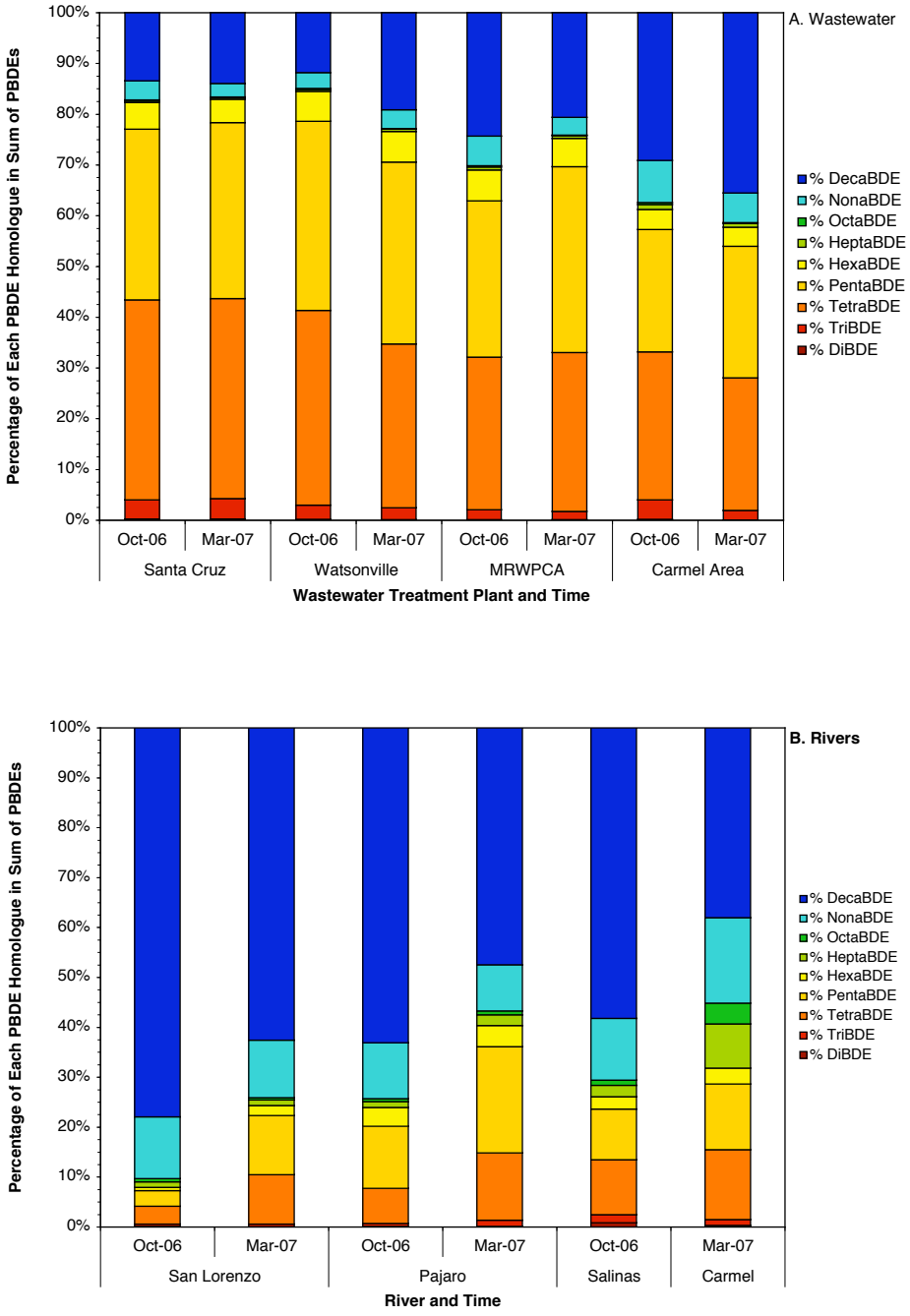

Figure 5. Percentage of each PBDE homologue in the sum of PBDEs for wastewater effluent (A) and rivers (B).

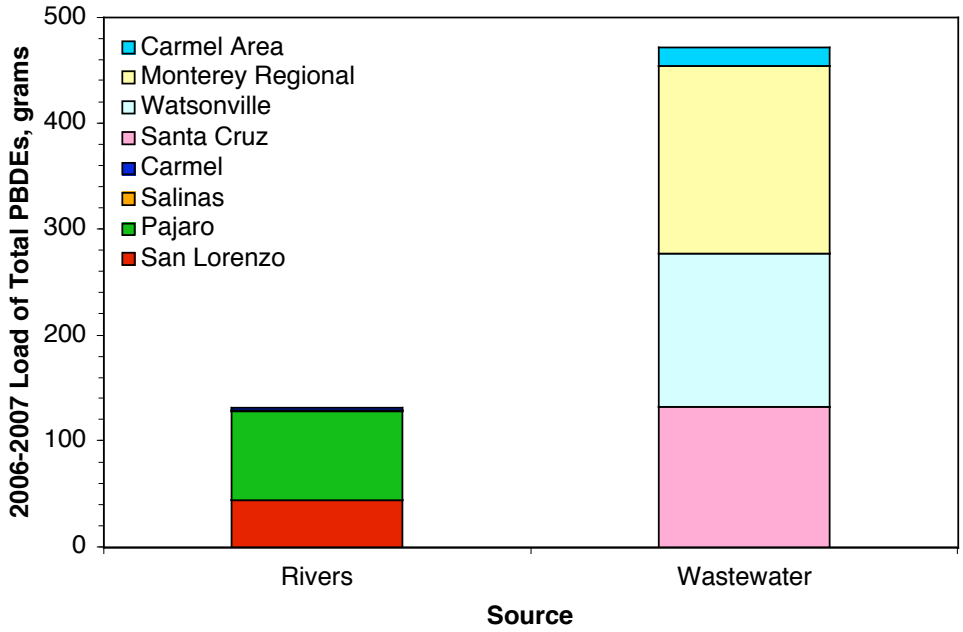

Figure 6. Loads of total PBDEs from rivers and wastewater effluent in 2006-2007.

Table 8. Comparison of PBDE concentrations in wastewater effluent treatment plants in the Monterey Bay and San Francisco Bay areas.

Treatment Plant	Mean Flow, MGD	Mean Effluent PBDE Concentration, ng/L	Estimated Effluent PBDE Load, kg/year
Plant 1, SF Bay Area[1]	80	66	7.3
Plant 2, SF Bay Area[1]	46	63	4
Plant 3, SF Bay Area[1]	120	14	2.4
Palo Alto[2]	19	29	0.9
Santa Cruz	12.3	8.7	.13
Watsonville	7.6	15.5	.14
Monterey Regional	8.4	16.9	.18
Carmel Area	1.3	9.7	.018

[1] = 2005 data from (Petreas & D. Oros, 2006).
[2] = Data from North (2004).

3.3 Effects of PBDEs Entering Monterey Bay Waters

There currently are no water quality objectives or tissue or sediment alert levels for PBDEs. Consequently, effects of PBDEs cannot necessarily be inferred from the concentrations measured in CCLEAN samples. Nevertheless spatial and temporal patterns of PBDEs in Monterey Bay, mussels and sediments can be compared to other areas to provide context for evaluating the concentrations found here.

Total concentrations of PBDEs in Monterey Bay waters were comparable to those in San Francisco Bay. Total PBDEs in three out of four samples from Monterey Bay exceeded average concentrations found during 2006 in San Francisco Bay between San Pablo Bay and southern San Francisco Bay (Figure 7). Moreover, the October 2006 sample for the North Monterey Bay site exceeded the maximum concentration of total PBDEs measured in San Francisco Bay in 2006, due to high concentrations of nona- and deca-BDEs. Except for October 2006, PBDE concentrations were generally similar between the South Monterey Bay and North Monterey Bay sites. The composition of PBDES in Monterey Bay waters were generally more similar to rivers that to effluent, as they were dominated by nona- and deca-BDEs (compare Figure 5 with Figure 7).

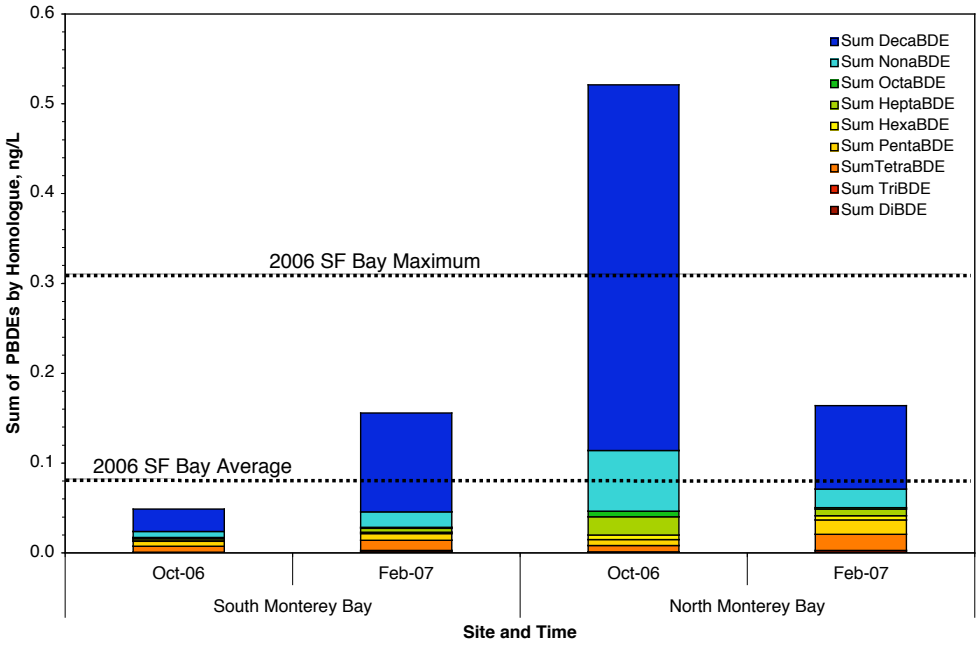

Figure 7. Concentrations of total PBDEs in Monterey Bay waters in 2006-2007.

As has been consistently reported for other POPs in mussels (CCLEAN, 2007), total PBDEs at CCLEAN sites during 2006-2007 were highest at The Hook (Figure 8). All sites had higher concentrations of PBDEs in the wet season than in the dry season and mussels from The Hook had greater proportions of tetra- and penta-BDEs and lower proportions of deca-BDE than mussels from the other sites. Higher wet-season concentrations at The Hook were due to increases in tetra-, penta- and decaBDEs, whereas at the other sites they were due mostly to increases in deca-BDE. The relative proportions of PBDE homologues in mussels were more similar to those in wastewater than to those in rivers (compare Figure 5 with Figure 8).

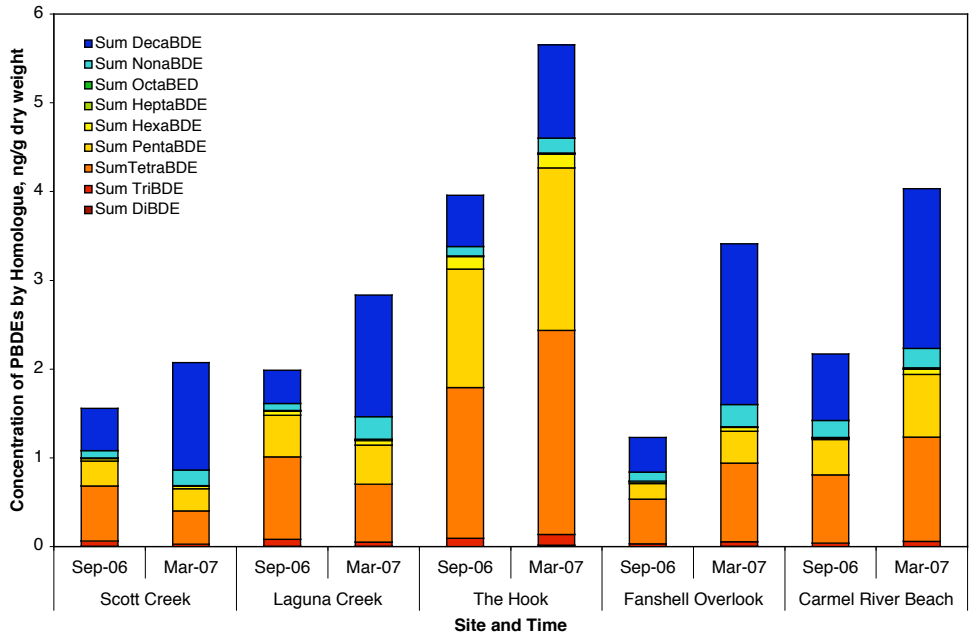

Figure 8. Concentrations of total PBDEs in mussels from CCLEAN sites in 2006-2007.

Sediments from site SedRef 04 had the highest concentrations of total PBDEs among CCLEAN sites, which was due to the presence of nona- and deca-BDEs at SedRef 04 (Figure 9). These two homologues were absent from the other sites. The other sites had generally similar proportions of homologues, with slightly higher overall concentrations at SedRef 01, SedRef 02, SedRef 03 and SedDep 01 than at SedDep 02, SedDep 03 and SedDep 04. There were no differences in sediment grain size or total organic carbon that would account for the differences between SedRef 04 and the other sites (Figures 10 and 11). While we cannot explain the difference in homologues between SedRef 04 and the other sites, the proportion of deca-BDE at SedRef 04 is similar to what was reported for sites in central San Francisco Bay in 2006 (http://www.sfei.org/RMP/report), where the proportion of deca-BDE in sediments ranged from 41% to 69% and averaged 53%. With the dominance of tri- tetra- and penta-BDEs in sediment samples, they more closely resemble wastewater than rivers.

In a recent CCLEAN study of the relationships between POPs and sea otter mortality, which was funded by a Prop 13 grant (Miller *et al*., 2007), total PBDEs in sea otter livers were not found to be a significant risk factor for sea otters dying from disease. Nevertheless, one congener, PBDE-28, which is a tri-BDE, was found to be a significant risk factor for otters dying from protozoal infection. For this analysis, each otter's exposure to wastewater also was estimated by comparing its stranding location to the estimated concentrations of wastewater effluent at that location, based upon a simple exponential dilution from the point of discharge; no attempt was made to correct for temporal variations in the volume of wastewater discharged at each site or local effects attributable to wind, marine currents or coastal geography. Statistical analysis revealed that stranding in an area characterized by medium exposure to municipal wastewater (no otters stranded in areas characterized by high exposure to wastewater) was determined to be a

significant risk factor in having high liver concentrations of PBDE-28, compared to stranding in an area with a low exposure to wastewater.

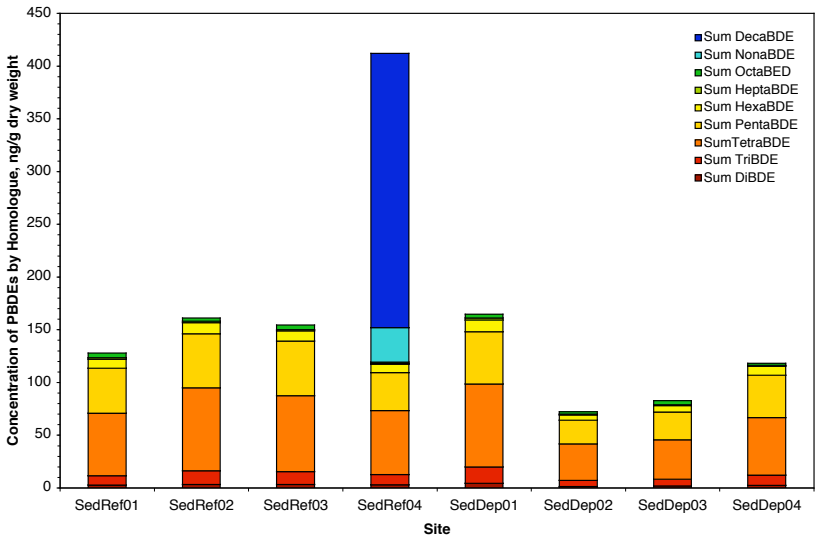

Figure 9. Concentrations of total PBDEs in sediments from CCLEAN sites in Monterey Bay in 2006.

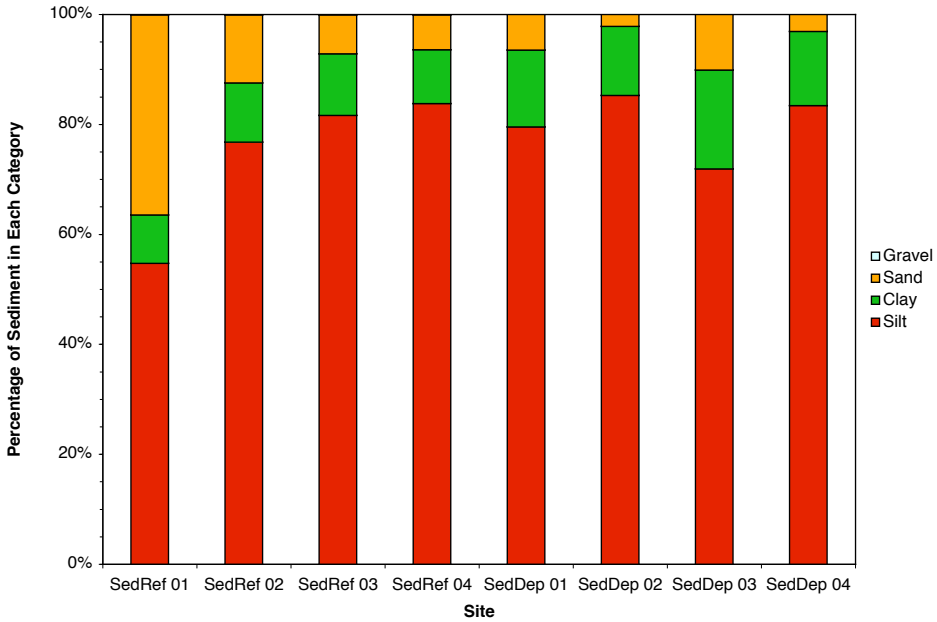

Figure 10. Percent gravel, sand, silt and clay in sediments from CCLEAN sites in 2006.

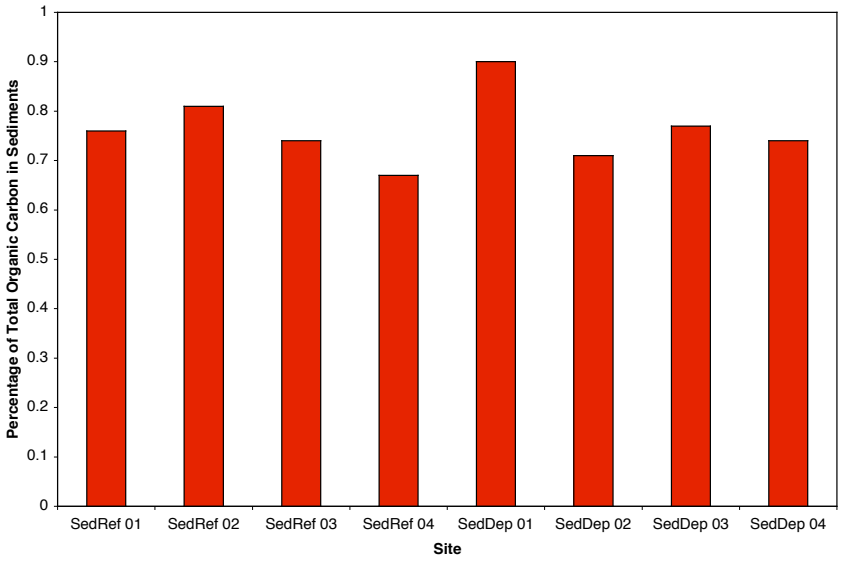

Figure 11. Percentage of total organic carbon in sediments from CCLEAN sites in 2006.

Although the proportions of PBDE-28 in total loads of PBDEs from rivers and wastewater were small (i.e., 0.27% - 2.55%; Figure 12), wastewater is the major source accounting for roughly 86%of the total load. All wastewater and river sources for which both dry-season and wet-season samples were available, except for Santa Cruz wastewater, discharged higher daily loads during the wet season than during the dry season.

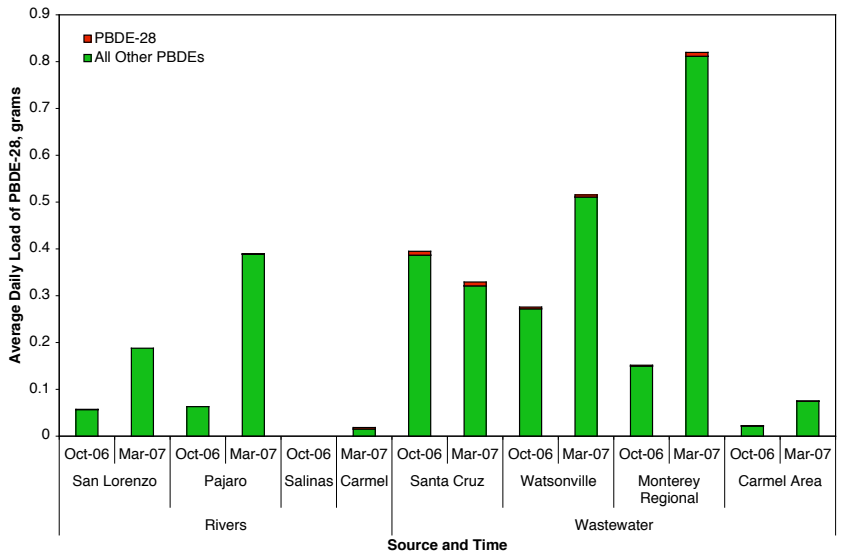

Figure 12. Annual loads of PBDE-28 from rivers and wastewater effluent in the Monterey Bay area compared to total loads of PBDEs.

Concentrations of PBDE-28 in Monterey Bay waters were very low, less than 0.0012 ng/L (<1.2 pg/L). This concentration was below the average concentration in San Francisco Bay, but within the range of concentrations measured in San Francisco Bay (http://www.sfei.org/RMP/report) (Figure 13). Both Monterey Bay sites had higher concentrations of PBDE-28 in the wet season than in the dry season.

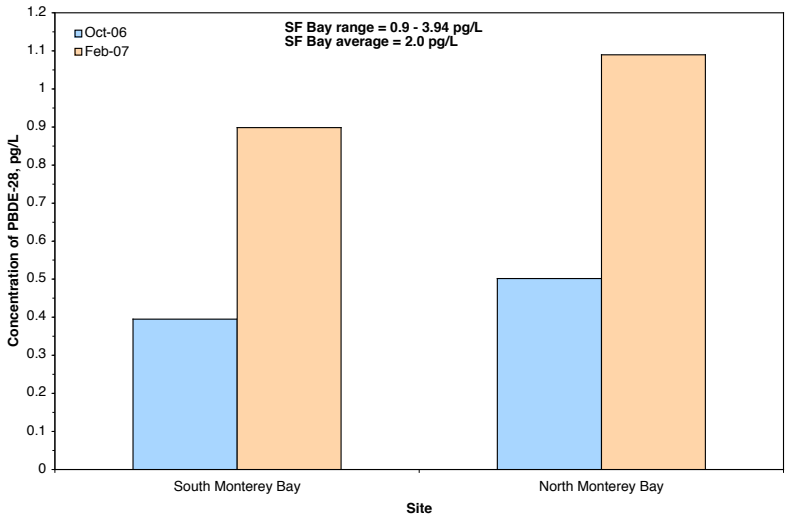

Figure 13. Concentrations of PBDE-28 in Monterey Bay waters in 2006-2007.

PBDE-28 concentrations in mussels displayed inconsistent temporal patterns among sites. The Hook, Fanshell Overlook and Carmel River Beach each had higher concentrations of PBDE-28 in the wet season than in the dry season, consistent with seasonal patterns exhibited by most reivers and wastewater discharges, whereas Scott Creek and Laguna Creek had lower wet-season concentrations (Figure 14). Surprisingly, PBDE 028 was not detected in San Francisco Bay mussels in 2005, although these analyses were performed by a different laboratory from that used by CCLEAN and subtle differences in analytical methods could account for this difference.

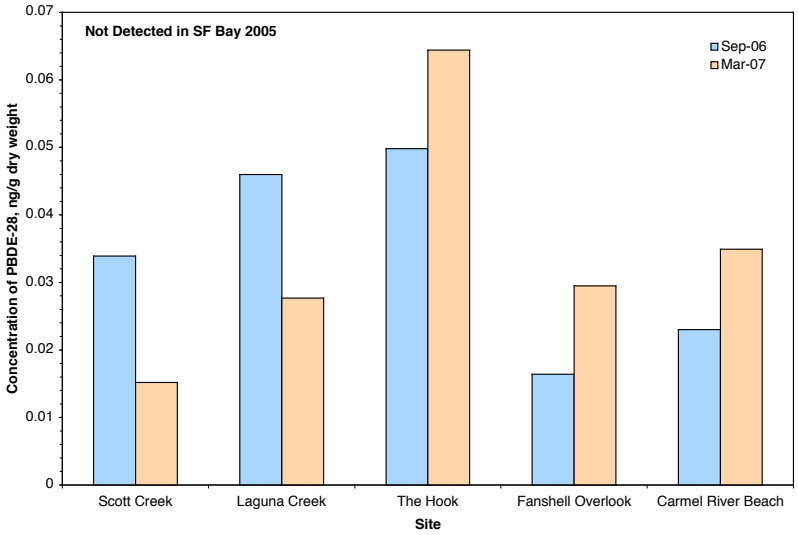

Figure 14. Concentrations of PBDE-28 in mussels from CCLEAN sites in 2006-2007.

In contrast to mussels, PBDE-28 was detected in San Francisco Bay sediments, and occurred in much higher concentrations than found at CCLEAN sediment sites (Figure 16). Slight differences among sites in sediment concentrations of PBDE-28 were similar to those for total PBDEs minus the nona- and deca-BDEs measured at SedRef 04 (compare Figure 9 and Figure 15).

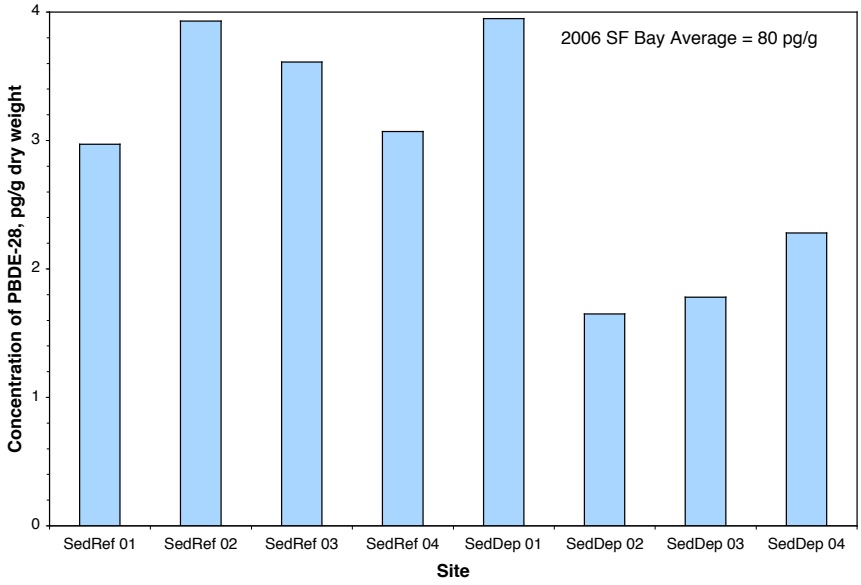

Figure 15. Concentrations of PBDE-28 in sediments from CCLEAN sites in Monterey Bay during October 2006.

Consequently, while PBDE-28 is a significant risk factor for sea otters dying from protozoal infection (Miller *et al*., 2007) concentrations of this congener in ocean water, mussels and sediments are low in the Monterey Bay area and water and sediment concentrations are much lower in Monterey Bay than in San Francisco Bay.

4.0 Conclusions

Data from a single year suggest that wastewater treatment plants discharge greater loads of PBDEs into the waters of Monterey Bay than do rivers, a result that must be qualified by incomplete data from Salinas River and Carmel River. Proportions of homologues in ocean waters were more similar to rivers than to wastewater, but mussels and sediment werfe more similar to wastewater. Nevertheless, definitively fingerprinting PBDEs in order to estimate contributions from different anthropogenic sources is problematic due to the numerous debromination processes at work in the environment.

The toxic effects of PBDEs (Agency for Toxic Substances and Disease Registry, 2004; Miller *et al*., 2007) warrant efforts to limit their use. Recent California legislation (AB 302) is one such effort that seeks to ban the commercial use of penta- and octa-BDEs due to their toxicity and because they apparently bioaccumulate more easily than deca-BDE. The relatively high proportion of penta-BDEs in wastewater reported here might suggest implementation of source control as a way of reducing wastewater loads of this homologue. Nevertheless, recent studies

describing numerous natural debromination processes suggest that at least some of the distribution and bioaccumulation or penta- and octa-BDEs may be due to biotransformation of higher brominated homologues. For example, the wastewater treatment process, itself, has been shown to debrominate higher brominated homologues into lower brominated homologues (Gerecke *et al*., 2005; Tokarz *et al*., 2008) thus potentially producing penta- and octa-BDEs from deca-BDE. Moreover, there is evidence that animals debrominate PBDEs during metabolism (Stapleton *et al*., 2004). These findings indicate that regulation of deca-BDE could be necessary to effectively reduce environmental concentrations of toxic and bioaccumulative PBDE homologues.

Without either reductions in the amounts of PBDEs coming into wastewater treatment plants or more complete knowledge of the effects of the wastewater treatment process on PBDE debromination, any measures aimed at decreasing the discharge of the most toxic PBDE homologues in wastewater will have uncertain benefits. A fuller exploration of the effects of wastewater treatment on debromination would require analysis of influent and sludge, as well as effluent, in order to develop a mass-balance model for homologues in the wastewater treatment process.

5.0 Future directions

A five-year study plan has been developed for CCLEAN that will broadly guide its activities in the near future. This plan includes implementation of effluent screening for endocrine disruption activity and analysis of samples for analytes currently included in the Quality Assurance Program Plan. These include the contaminants of emerging concern PBDEs and perfluorinated compounds. The program will continue to be adaptively managed so that revisions will be made based upon information gathered. Implementation of new program efficiencies will be based on a continuing analysis of data to discern the optimum site distribution and sampling frequencies to achieve program objectives.

In order to ensure continuing respect for program results, a quality assurance audit will be performed and reported to the CCLEAN Steering Committee and the RWQCB on an annual basis. The Quality Assurance Program Plan also will be revised annually, as necessary, and submitted to the Steering Committee and the RWQCB.

6.0 References Cited

AGENCY FOR TOXIC SUBSTANCES AND DISEASE REGISTRY. (2004). Toxicological Profile for Polybrominated Biphenyls and Polybrominated Diphenyl Ethers, pp. 619. U.S. Department of Health and Human Services Public Health Service, Atlanta, GA.

CALIFORNIA STATE MUSSEL WATCH PROGRAM. (2003). SMW Program Data 1977-2000. 2003. http://www.waterboards.ca.gov/programs/smw/.

CCLEAN. (2007). 2001–2006 Program Overview. Central Coast Long-term Environmental Assessment Network, Santa Cruz, CA.

ERIKSSON, J., N. GREEN, G. MARSH & A. BERGMAN. (2004). Photochemical Decomposition of 15 Polybrominated Diphenyl Ether Congeners in Methanol/Water. *Envirnomental Science and Technology* **38,** 3119-3125.

GERECKE, A. C., P.C. HARTMANN, N.V. HEEB, H.E KOHLER, W. GIGER, P. SCHMID, M. ZENNEGG & M. KOHLER. (2005). Anaerobic Degradation of Decabromodiphenyl Ether. *Envirnomental Science and Technology* **39,** 1078-1083.

KANNAN, K., PERROTTA, E. & THOMAS, N. J. (2006). Association between Perfluorinated Compounds and Pathological Conditions in Southern Sea Otters. *Environmental Science & Technology [Environ. Sci. Technol.]* **40,** 4943-4948.

LA GUARDIA, M. J., R.C. HALE & E. HARVEY. (2006). Detailed Polybrominated Diphenyl Ether (PBDE) Congener Composition of the Widely Used Penta-, Octa-, and Deca-PBDE Technical Flame-retardant Mixtures. *Envirnomental Science and Technology* **40,** 6247-6254.

LONG, E. R., FIELD, L. J. & MACDONALD, D. D. (1998). Predicting toxicity in marine sediments with numerical sediment quality guidelines. *Environmental Toxicology and Chemistry [Environ. Toxicol. Chem.].* **17,** 714-727.

LONG, E. R., MACDONALD, D. D., SEVERN, C. G. & HONG, C. B. (2000). Classifying probabilities of acute toxicity in marine sediments with empirically derived sediment quality guidelines. *Environmental Toxicology and Chemistry [Environ. Toxicol. Chem.].* **19,** 2598-2601.

MILLER, M., E. DODD, M. ZICCARDI, D. JESSUP, D. CRANE, C. DOMINIK, R. SPIES & HARDIN, D. (2007). Persistent organic pollutant concentraitons in southern sea otters (Enhydra lutris nereis): Patterns with respect to envirnmental risk factors and major cuases of mortality, pp. 108. Central Coast Long-term Environmental Assessment Network, Santa Cruz.

OFFICE OF ENVIRONMENTAL HEALTH HAZARD ASSESSMENT. (2003). Summary of the Chemicals of Concern Found in Fish: San Francisco Bay Pilot Study, 1994. http://www.oehha.org/fish/nor_cal/sfpilot.html.

PETREAS, M. & D. OROS. (2006). PBDEs in California Waste Streams. *Organohalogen Compounds* **68,** 499-502.

PETREAS, M., SHE, J. W., BROWN, F. R., WINKLER, J., WINDHAM, G., ROGERS, E., ZHAO, G. M., BHATIA, R. & CHARLES, M. J. (2003). High body burdens of 2,2 ',4,4 '-tetrabromodiphenyl ether (BDE-47) in California women. *Environmental Health Perspectives* **111,** 1175-1179.

RWQCB. (1997). Water Quality Control Plan (Basin Plan), pp. 197. California Regional Water Quality Control Board, Central Coast Region.

SHE, J. W., PETREAS, M., WINKLER, J., VISITA, P., MCKINNEY, M. & KOPEC, D. (2002). PBDEs in the San Francisco Bay Area: measurements in harbor seal blubber and human breast adipose tissue. *Chemosphere* **46,** 697-707.

SODERSTROM, G., U.SELLSTROM, C.A. DE WIT & M. TYSKLING. (2004). Photolytic Debromination of Decabromodiphenyl Ether (BDE 209). *Envirnomental Science and Technology* **38,** 127-132.

STAPLETON, H. M., M. ALAEE, R.J. LETCHER & J.E. BAKER. (2004). Debromination of the Flame Retardant Decabromodiphenyl Ether by Juvenile Carp (Cyprinus carpio) following Dietary Exposure. *Envirnomental Science and Technology* **38,** 112-119.

STATE WATER RESOURCES CONTROL BOARD. (2005). California Ocean Plan, pp. 57. California Environmental Protection Agency, Sacramento, CA.

TOKARZ, J. A., M-Y. AHN, J. LENG, T.R. FILLEY & NIES, L. (2008). Reductive Debromination of Polybrominated Diphenyl Ethers in Anaerobic Sediment and a Biomimetic System. *Envirnomental Science and Technology* **42,** 1157-1164.