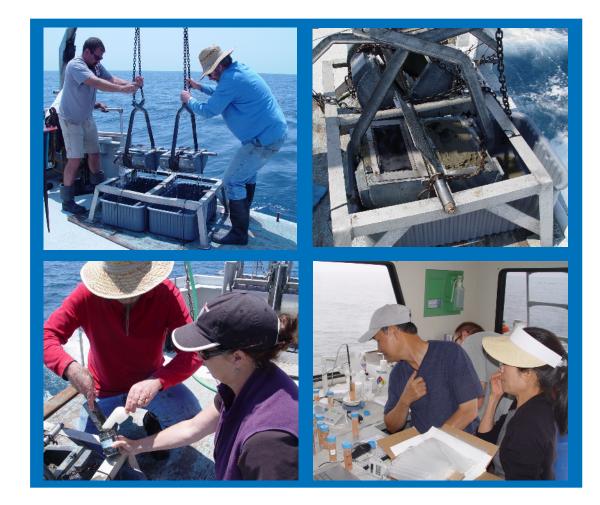


# Sediment Chemistry



Southern California Bight 2008 Regional Monitoring Program Vol. III

L C E T

# SOUTHERN CALIFORNIA BIGHT 2008 REGIONAL MONITORING PROGRAM: III. SEDIMENT CHEMISTRY

July 2011

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# The Bight '08 Chemistry Working Group

Much of the success of the Southern California Bight Regional Monitoring Program is its consensus-based management structure. A Project Steering Committee comprised of environmental managers from each of the participating agencies provides design, oversight, and approval, while most of the technical work is accomplished through individual Working Groups. In this case, the Sediment Chemistry Working Group was charged with implementing much of the work contained in this report. The members of the Sediment Chemistry Working Group include:

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# Foreword

The 2008 Southern California Bight Regional Monitoring Program (Bight '08) is part of an effort to provide an integrated assessment of the SCB through cooperative regional-scale monitoring. Bight '08 is a continuation of regional surveys conducted in 1994, 1998, and 2003 that represents the joint efforts of more than 90 organizations (Appendix A). Bight '08 is organized into six technical components: (1) Coastal Ecology; (2) Shoreline Microbiology; (3) Water Quality; (4) Areas of Special Biological Significance; (5) Rocky Reefs; and (6) Wetlands. This report presents the results of the sediment chemistry portion of Bight '08, which is a part of the Coastal Ecology component. Other Coastal Ecology components include sediment toxicity, benthic macrofauna, and demersal fish and megabenthic invertebrates. Copies of this and other Bight'08 guidance manuals, data, and reports are available for download at www.sccwrp.org.

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# Acknowledgements

This report is the product of the dedication and hard work of many individuals who share a common goal of improving our understanding of the environmental quality of the Southern California Bight. The authors wish to thank the members of the Bight '08 Coastal Ecology Planning Committee for supporting the application of sediment chemistry in regional monitoring. This study would not have been possible without the exceptional skill of the field sampling personnel from the following organizations: City of San Diego, Weston Solutions, Orange County Sanitation District, Sanitation Districts of Los Angeles County, City of Los Angeles, Southern California Coastal Water Research Project, Aquatic Bioassay and Consulting Laboratories, Channel Islands National Marine Sanctuary, and Moss Landing Marine Laboratories. Most of all, this study is indebted to the talent and commitment of the laboratories and personnel that contributed to the success of the sediment chemistry portion of Bight '08.

#### **Participating Analytical Laboratories**

B&B Laboratories, Inc. City of Los Angeles City of San Diego CRG Marine Laboratories, Inc. Sanitation Districts of Los Angeles County Orange County Sanitation District Southern California Coastal Water Research Project

# **Executive Summary**

Regional monitoring has become an important component of assessing the status of our coastal resources in the Southern California Bight (SCB). The 2008 Regional Marine Monitoring Program (Bight'08) is the fourth in a series of regional marine monitoring efforts beginning in 1994 and repeated again in 1998 and 2003. More than 90 different organizations encompassing regulatory, regulated, academic, and non-governmental agencies collaborated to create Bight '08. Collectively, these organizations asked two primary questions:

- 1) What is the extent and magnitude of impact in the SCB?
- 2) Does the extent and magnitude of impact vary among different habitats of interest?

Bight '08 had six components; coastal ecology, shoreline microbiology, water quality, wetland eutrophication, rocky subtidal, and areas of special biological significance. The Coastal Ecology component measured sediment chemistry, sediment toxicity, benthic infauna, fish assemblages and bioaccumulation. The focus of this report is on sediment chemistry.

A stratified random design was selected to ensure an unbiased sampling approach to provide areal assessments of environmental condition. There were 12 strata selected including three mainland shelf (5-30m, 30-120m, 120-200m), upper mainland slope (200-500m), lower slope and basin (500-1000m), marinas, ports, bays, estuaries, and the Channel Islands National Marine Sanctuary (30-200m surrounding Santa Barbara, Anacapa, Santa Rosa, Santa Cruz, and San Nicolas Islands).

A total of 383 sites were sampled between July and September 2008, then analyzed for grain size, total organic carbon (TOC) and total nitrogen (TN), trace metals (As, Cd, Cr, Cu, Pb, Ni, Ag, Se, and Zn), total PAH (sum of 24 individual polynuclear aromatic hydrocarbons), total PCB (sum of 41 different polychlorinated biphenyl congeners), total DDT (sum of 2,4' and 4,4' isomers of dichlorodiphenyltrichloroethane and its degradation products DDE, DDD, and DDMU), total chlordane (alpha and gamma isomers). The following constituents of emerging concern were measured in a subset of sites in a special study: polybrominated diphenyl ethers (51 PBDE congeners), and pyrethroid pesticides (8 different pyrethroids).

The distribution of many sediment contaminants in the SCB was a function of their source inputs. For example, the greatest concentrations of total DDT were located on the continental shelf where submarine outfalls at depths of 60m discharged hundreds of metric tons more than 40 years ago. These legacy contaminants remain on the continental shelf to this day. In contrast, the largest discharges of other contaminants such as copper, zinc, and total PAHs come from vessel antifouling paints and land-based runoff. As a result, the greatest concentrations of these contaminants are found in embayment strata such as marinas and estuaries.

The newest feature of the B'08 sediment chemistry program was the application of recently developed sediment chemistry assessment tool. This assessment tool was developed for the State of California in order to promulgate sediment quality objectives (SQO) for bays, harbors, and estuaries (SWRCB 2009; Bay and Weisberg 2008). This tool, and the regulatory framework that goes with it, was not available during previous surveys. Although the sediment chemistry

assessment tool does not apply to coastal shelf, slope, and basin sediments, we used it for consistency across habitats and because we consider it to be the best currently available. When we apply this new assessment tool, roughly three-quarters of the SCB sediments were in acceptable condition based on exposure to sediment contamination. The remaining one-quarter of the SCB in unacceptable condition was not evenly distributed throughout the SCB. The potential for environmental risk due to sediment contamination was dramatically higher in marinas and estuaries. Ports were also disproportionately impacted. In contrast, much of the continental shelf and Channel Islands were in uniformly acceptable condition for sediment contamination.

Trends in sediment contamination were mixed over the last 10 years. While sediment condition has generally improved in the SCB as a whole, this trend did not hold true for individual strata. The most notable improvements in sediment condition were observed on the mainland continental shelf, Channel Islands, and ports/bays/harbors. For example, acceptable sediment condition based on sediment contamination has increased from 46% to 62% of the port/bay/harbor stratum composite. However, acceptable sediment condition decreased in estuaries from 86% to 62% of the area in just the last five years.

Special studies measuring contaminants of emerging concern have identified potential new environmental issues. Pyrethroid pesticides, a relatively new class of chemicals not routinely analyzed in existing ocean monitoring programs, was detected in 35% of the SCB embayment area, and found at levels great enough to induce toxicity in the laboratory. PBDEs, a flameretardant, were widespread in sediments throughout the SCB. Sediment-associated PBDEs appear to be one pathway to bioaccumulation in higher order marine organisms such as mussels and marine mammals. Both of these emerging contaminants were found in greatest concentration in embayments that receive land-based runoff.

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# I. Introduction

#### Overview

The Southern California Bight (SCB; Figure I-1), an open embayment in the coast between Point Conception, California, and Cabo Colnett (south of Ensenada), Baja California, is an important and unique ecological resource. The SCB is a transitional area that is influenced by currents from cold, temperate ocean waters from the north and warm, tropical waters from the south. In addition, the SCB has a complex topography with offshore islands, submarine canyons, ridges, and basins, which provide a variety of habitats. The mixing of currents and the diverse habitats in the SCB allow for the coexistence of a broad spectrum of species, including more than 500 species of fish and 1,500 species of invertebrates (Dailey *et al.* 1993). The SCB is also a major migration route, with marine bird and mammal populations ranking among the most diverse in north temperate waters.

The coastal zone of the SCB is a substantial economic resource. Los Angeles/Long Beach (LA/LB) Harbor is the largest commercial port in the United States and San Diego Harbor is home to one of the largest US Naval facilities in the country. There are more than 175 million beach-goer days at southern California beaches and coastal areas annually (Schiff *et al.* 2000), bringing an estimated \$24 billion and 374,000 jobs into the regional economy (Kildow and Colgan 2005). Recreational activities include diving, swimming, surfing, and boating, with about 40,000 pleasure boats docked in 13 coastal marinas within the region. Commercial fishery landings in the SCB generated an estimated \$45 billion in 2002 and recreational fishing generated more than \$500 million that same year (Kildow and colgan 2005).

The coastal areas that form the SCB are some of the most densely populated regions in the country, which in turn creates stresses upon the adjacent marine environment. The most recent census data show that approximately 17 million people inhabit the five coastal counties that border the SCB (US Census Bureau 2010), a number that is projected to increase to over 20 million by 2020 (State of California 2001). Population growth generally results in conversion of open land into non-permeable surfaces. More than 75% of southern Californian bays and estuaries have already been dredged and filled for conversion into harbors and marinas (Horn and Allen 1985). This "hardening of the coast" increases the rate of runoff and can impact water quality through the addition of sediment, toxic chemicals, pathogens, and nutrients to the ocean. Besides the impacts of land conversion, the SCB is already home to 15 municipal wastewater treatment facilities, 8 power-generating stations, 10 industrial treatment facilities, and 18 oil platforms that discharge to the open coast (Schiff *et al.* 2001).

Each year, local, state, and federal agencies spend in excess of \$31 million to monitor the environmental quality of natural resources in the SCB (Schiff *et al.* 2002). Three-quarters of this monitoring is associated with National Pollutant Discharge Elimination System (NPDES) permits and is primarily intended to assess regulatory compliance. While these monitoring programs have answered important questions regarding the health of coastal waters, they were specifically designed to evaluate impacts of individual discharges. So despite the enormous resources spent on monitoring, information from NPDES monitoring only covers approximately 5% of the total SCB area.

Today, resource managers are developing management strategies for the entire SCB. To accomplish this task, a regionally-based monitoring program has been initiated to gather information for assessing cumulative impacts of multiple and often diffuse sources of contaminant inputs and to evaluate relative risk among these different sources and their associated stresses. Regional monitoring also provides an opportunity to assess large-scale reference conditions that cover the entire range of natural variability observed in the SCB, in contrast to comparing an individual discharge to a small number of local reference sites.

## **Previous Regional Monitoring Studies**

The first regional sediment chemistry monitoring program occurred in 1994 (Pilot Project) and consisted of 12 collaborating agencies (Schiff and Gossett 1998). The second occurred in 1998 (Bight '98) and consisted of more than 60 collaborating agencies (Noblet *et al.* 2002). The third occurred in 2003 (Bight'03) and also consisted of more than 60 agencies. There were 264 sites sampled in 1994, 404 sampled in 1998, and 359 sampled in 2003. Each reflects a focus on differing habitats from the mainland continental shelf, offshore Channel Islands, and several types of embayment habitats (open bays, enclosed estuaries, ports, etc.). Every survey assessed the extent and magnitude of impacts for a number of indicators including sediment chemistry, benthic infauna, sediment toxicity, fish assemblages and bioaccumulation.

A large effort developing chemical analytical comparability was invested in the previous surveys (Gossett *et al.* 2003). Since all of the regional programs were conducted in a collaborative fashion with multiple analytical laboratories participating, intercalibration studies were a focal point for trace metal and trace organic constituents. Despite all of the laboratories being certified by the State of California, there was significant discrepancy at times for specific constituents (i.e., polynuclear aromatic hydrocarbons or PAHs). Therefore, iterative intercomparison and intercalibration exercises were done until all of the laboratories could meet stated data quality objectives for interlaboratory precision. These intercalibrations remain one of the foundational elements of the regional monitoring quality assurance/quality control program.

# **Objectives of the 2008 Regional Monitoring Program**

The purpose of the 2008 Southern California Bight Regional Monitoring Program (Bight '08) is to address two specific management questions:

- 1) What is the extent and magnitude of impact in the SCB?
- 2) Does the extent and magnitude of impact vary among different habitats of interest?

Answering these questions addresses the management needs for assessing the overall environmental health of the SCB, describing regional reference conditions, and developing regional assessment tools. Like the earlier regional monitoring surveys, the Bight '08 program was a multi-faceted program. Bight '08 had six components; Coastal Ecology, Shoreline Microbiology, Water Quality, Areas of Special Biological Significance, Rocky Reefs, and Wetlands. The Coastal Ecology component measured sediment chemistry and toxicity, benthic infauna, fish assemblages, and bioaccumulation. The focus of this report is sediment chemistry and includes sections on materials and methods (Section II), quality assurance and quality control activities (Section III), descriptive results (Section IV), assessment results (Section V), discussion (Section IV), conclusions and recommendations (Sections VII and VIII).

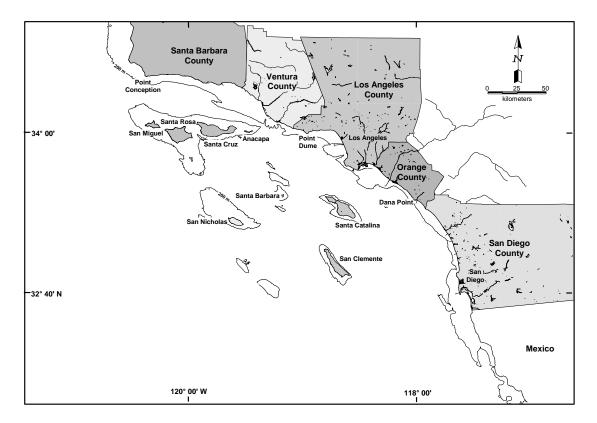


Figure I-1. A map of the Southern California Bight, which extends from Point Conception, California, to Ensenada, Mexico.

# II. Methods

# Sampling Design

A stratified random design was selected to ensure an unbiased sampling approach to provide areal assessments of environmental condition (Stevens 1997). There were 12 strata selected for this study including three mainland shelf (5-30 m, 30-120 m, 120-200 m), upper mainland slope (200-500 m), lower slope and basin (500-1000m), embayments (marinas, ports, open bays and harbors), estuaries, and the Channel Islands National Marine Sanctuary (30-120m surrounding Santa Barbara, Anacapa, Santa Cruz, Santa Rosa, and San Nicolas Islands) (Table II-1). Stratification ensures that an appropriate number of samples are allocated to characterize stratum with adequate precision. The goal was to allocate approximately 30 sites to each stratum because this yields a 90% confidence interval of about  $\pm$  10% around estimates of areal extent (assuming a binomial probability distribution and p=0.2).

	Stratum	Area (km²)	% Of Bight Total
	Inner Shelf (5-30 m)	1,171	7.0
Mainland Continental Shelf	Mid Shelf (30-120 m)	2,019	12.0
	Outer Shelf (120-200 m)	605	3.6
Slope	Upper Slope (200-500 m)	7,535	44.9
Basin	Lower Slope & Basin (500-1000 m)	3,130	18.7
	Marinas	17.5	0.1
	Estuaries	11.9	0.1
Embayments	Ports	29.3	0.2
	Bays and Harbors	70.0	0.4
Channel Islands	Channel Islands (30-120 m)	2,193	13.1
	Entire Southern California Bight	15,782	100.0

#### Table II-1. Area as a function of sampling strata for Bight '08.

### Sample Collection

Sediment samples were collected using a  $0.1 \text{ m}^2$  modified VanVeen grab sampler (Stubbs *et al.* 1987). Grab samples were required to be within 100 m and 10% of water depth of the location specified by the sampling design. Sediment samples were taken from the top 2 cm in coastal shelf, slope and basin strata, and the top 5 cm from embayment strata and placed in appropriate containers for the subsequent analysis. All sample containers were purchased precleaned, and were certified to meet Environmental Protection Agency (EPA) standards. Glass containers with Teflon<sup>®</sup>-lined closures (500 mL) were used for all samples. All samples except those for grain size analysis were stored frozen (-20°C) until analyzed. Samples for grain size were stored at 4°C until analyzed. Further details on the sample collection procedures used in this study can be found in the Bight '08 Field Operations Manual (Bight '08 Coastal Ecology Committee 2008). As soon as possible after collection, samples were distributed to the appropriate laboratories for analysis. A summary of the division of effort for the Bight '08 chemistry component as a function of parameter and laboratory is given in Table II-2.

# **Analytical Methods**

Analytical methods employed were at the discretion of the participating laboratories, contingent upon their ability to demonstrate acceptable analytical performance. Acceptable analytical performance required strict adherence to common quality assurance/quality control (QA/QC) practices, routine analysis of certified standard reference materials (SRMs) and participation in an inter-laboratory calibration study. Each laboratory was required to demonstrate its capability to meet the stated measurement quality objectives (MQOs) for each of the target analytes. Initially, each laboratory established a method detection limit (MDL) for each target analyte following the MDL protocol cited in EPA 40 CFR Part 136. Laboratories participated in an inter-calibration exercise and were required to meet specified performance criteria prior to any analysis of the survey samples. Analytical performance criteria can be found in the Bight '08 Survey Quality Assurance Plan (QAP). See Section III for an assessment of these Bight '08 Chemistry Committee quality assurance activities.

# **Target Analytes**

The target analytes for the Bight '08 Survey are listed in Table II-3. The 15 metals analytes were compiled from the list of those metals normally monitored by the participating agencies. The list of 24 PAHs includes the 16 PAHs on the EPA's priority pollutant list, as well as 8 additional compounds, including 5 methylated PAHs. The list of 41 polychlorinated biphenyl congeners (PCBs) was compiled by consideration of their potential toxicity (McFarland and Clarke 1989), and the occurrence of the congeners in the commonly used (and subsequently discharged) Aroclors 1242, 1248, 1254, and 1260. The 9 chlorinated pesticides selected as target analytes included the 4,4'- and 2,4' isomers of dichlorodiphenyltrichloroethane their respective metabolites, dichlorodiphenyldichloroethane (DDT) and (DDD), dichlorodiphenyldichloroethylene (DDE), and di(*p*-chlorophenyl)-2-chloroethylene (DDMU). Based upon previous regional monitoring studies, DDT and its metabolites are still the most ubiquitous organic contaminants in the SCB. Two isomers of chlordane (*alpha* and *gamma*) were also added based on frequency of occurrence in previous surveys. Three groups of emerging contaminants were targeted in Bight '08, not previously measured in any Bight regional monitoring program. These included pyrethroid pesticides (bifenthrin, cyfluthrin, cypermethrin, deltamethrin, esfenvalerate, fenpropathrin,  $\lambda$ -cyhalothrin, and permethrin), the polybrominated diphenyl ether flame retardant (51 congeners), and a co-biocide used in vessel bottom paint called Irgarol.

# Sediment Grain Size Analysis

A total of 383 samples were analyzed for particle size distribution as part of the Bight '08 program. All of the samples were analyzed using a Horiba LA920 instrument. This instrument utilizes light-scattering technology to measure particles in 85 size categories ranging from 0.04-1019  $\mu$ m. All samples were screened through 1000 and 2000  $\mu$ m sieve prior to analysis to remove methodological interferences and bias. The sample fraction greater than 2000  $\mu$ m was designated as gravel. All categories <63  $\mu$ m were considered fine-grained material (silts + clays). Table II-2. The Distribution of Analyses and Number of Analyses Among Laboratories for the Bight '08 Sediment Chemistry Study.

Parameter		CRG <sup>1</sup>	CSD <sup>1</sup>		NOAA <sup>1</sup>	OCSD <sup>1</sup>	Total No Analyses
Grain Size	0	0	383	0	0	0	383
Metals	18	173	137	29	0	26	383
PCB Congeners	28	173	127	29	0	26	383
Polycyclic Aromatic Hydrocarbons (PAH)	28	173	127	29	0	26	383
Chlorinated Hydrocarbons (CHC)	28	173	127	29	0	26	383
Pyrethroid Pesticides	0	169	0	0	0	0	169
Polybrominated Diphenyl Ethers (PBDEs)	0	0	0	0	130	0	130
Total Organic Carbon (TOC)	18	173	166	0	0	26	383
Total Nitrogen	0	167	166	0	0	0	333
Total No. Analyses per Lab	120	1201	1233	116	130	130	2930

<sup>1</sup>CLAEMD = City of Los Angeles; CRG = CRG Marine Laboratories; CSD = City of San Diego; LACSD = Sanitation Districts of Los Angeles County; NOAA = National Oceanic Atmospheric Administration; OCSD = Orange County Sanitation District.

Trace Metals	PAHs	PCBs	Pesticides	PBDEs
Aluminum	Low Molecular Weight	PCB-18	Chlorinated	BDE001
Antimony		PCB-28	Pesticides	BDE002
Arsenic	Acenaphthene	PCB-37	4,4'-DDT	BDE003
Barium	Acenaphthylene	PCB-44	2,4'-DDT	BDE007
Beryllium	Anthracene	PCB-49	4,4'-DDD	BDE008
Cadmium	Biphenyl	PCB-52	2,4'-DDD	BDE010
Chromium	Fluorene	PCB-66	4,4'-DDE	BDE011
Copper	2-Methylnapthalene	PCB-70	2,4'-DDE	BDE012
Iron	1-Methylphenanthrene	PCB-74	4,4'-DDMU	BDE012 BDE013
Lead	Naphthalene	PCB-77	alpha-Chlordane	BDE015
Mercury	1-Methylnapthalene	PCB-81	gamma-	BDE013
Nickel	2,6-	PCB-87	Chlordane	BDE017 BDE025
Selenium	Dimethylnaphthalene	PCB-99	Oniordarie	BDE028
Silver	1,6,7-Trimethyl-	PCB-101	Pyrethroid	BDE020 BDE030
Zinc	naphthalene	PCB-105	Pesticides	BDE030 BDE032
	Phenanthrene	PCB-105 PCB-110	Bifenthrin	BDE032 BDE033
	i nenantinene	PCB-114	Cyfluthrin	BDE035 BDE035
	High Molecular Weight	PCB-114 PCB-118	Cypermethrin	BDE035 BDE037
General		PCB-119	Deltamethrin	BDE037 BDE047
<u>Constituents</u>	Benz[a]anthracene	PCB-123	Esfenvalerate	BDE047 BDE049/071
Grain Size	Benzo[a]pyrene	PCB-123	Fenpropathrin	BDE049/07 1 BDE066
	Benzo[b]fluoranthene	PCB-120		BDE000 BDE075
Total Organic Carbon		PCB-120 PCB-138	λ-cyhalothrin Permethrin	BDE075 BDE077
	Benzo[e]pyrene Benzo[g,h,i]perylene	PCB-130 PCB-149	Ferneunn	BDE077 BDE085
Total Nitrogen		PCB-149 PCB-151		BDE005 BDE099
	Benzo[k]fluoranthene			
	Chrysene	PCB-153		BDE100
	Dibenz[a,h]anthracene	PCB-156		BDE116
	Fluoranthene	PCB-157		BDE118
	Indeno[1,2,3-	PCB-158		BDE119
	c,d]pyrene	PCB-167		BDE126
	Perylene	PCB-168		BDE138
	Pyrene	PCB-169		BDE153
		PCB-170		BDE154
		PCB-177		BDE155
		PCB-180		BDE166
		PCB-183		BDE181
		PCB-187		BDE183
		PCB-189		BDE190
		PCB-194		BDE194
		PCB-201		BDE195
		PCB-206		BDE196
				BDE197
				BDE198
				BDE201
				BDE202
				BDE204
				BDE205
				BDE206
				BDE207
				BDE208
				BDE 209

 Table II-3. Target analytes for the sediment chemistry component of the Bight '08 Regional Monitoring Study.

# Total Organic Carbon

All total organic carbon (TOC) and total nitrogen (TN) analyses were performed using an Elemental Analyzer, in which samples are combusted at high temperature (>1000°C) and separated by gas chromatography. Frozen sediments were thawed to room temperature and homogenized before being dried in an air oven at 60°C overnight. The dried samples were then exposed to concentrated hydrochloric acid vapors in a closed container to remove inorganic carbon. The acid-treated samples were again dried and weighed, and crimped in a tin or silver capsule prior to analysis. Sample duplicates as well as a calibration verification sample were included in each batch for assessment of precision and accuracy. SRM 1944 and/or the PACS-2 marine sediment (National Research Council of Canada) were the certified reference materials used for evaluating analytical performance.

# Trace Metals in Sediments

The sediment samples analyzed for all metal analytes except mercury were digested in strong acid according to the procedures described in EPA Method 3050B (formerly 3055). The resulting digestates were diluted to a specific volume with de-ionized water and subsequently analyzed by one or more of the following instrumental methods, depending on the laboratory: inductively coupled plasma mass spectrometry, inductively coupled plasma emission spectroscopy, flame atomic absorption, or graphite furnace atomic absorption. Some laboratories analyzed arsenic and selenium by hydride generation atomic absorption spectroscopy. All laboratories analyzed mercury using cold vapor atomic absorption spectroscopy. Again, participating laboratories were allowed to use their own analytical methods as long as they met minimum MDLs and produced consistent results. The required trace metals MDLs for this study were specified as one-fifth the effects range low (ERL) sediment quality guideline (Long *et al.* 1995). For quality control purposes, at least one blank, one matrix spike, and a certified reference material were analyzed with each batch of samples.

# Trace Organic Analyses

Participating laboratories were allowed to use their own analytical methods as long as they met minimum reporting level objectives and produced consistent results through quality assurance samples. The required reporting level objectives for the sediment PAHs were 50 to 100  $\mu$ g/kg, PCB congeners at 7.5  $\mu$ g/kg, and pesticides at 1  $\mu$ g/kg dry. For quality assurance purposes, at least one blank, one set of duplicates, one matrix spike set (for PAHs only), and a certified reference material were analyzed with each batch of 20 samples. All samples requiring organic chemistry analysis were solvent extracted using one of the following methods: accelerated solvent extraction, sohxlet, or sonication. The extracts obtained were subjected to each laboratory's own clean-up procedures and were analyzed by an appropriate gas chromatographic method. PCB congeners and organochlorine pesticides were analyzed using either dual-column GC-ECD or GC-MS in the selected ion monitoring (SIM) mode. All laboratories analyzed PAHs by GC-MS.

Eight pyrethroid pesticides (bifenthrin, cyfluthrin, cypermethrin, deltamethrin, esfenvalerate, fenpropathrin,  $\lambda$ -cyhalothrin and permethrin) were targeted for analysis in this study. Sediment samples were extracted by methylene chloride using a microwave extraction system according to Environmental Protection Agency (EPA) method 3546. The extracts were cleaned up using silica gel/alumina combination columns. Sediment extracts were analyzed using

GC-MS operated in negative chemical ionization (NCI) mode. Fifty-one PBDE congeners were measured using pressurized liquid extraction followed by GC-MS analysis in NCI and SIM modes.

#### Data Analysis

The sediment chemistry data from Bight '08 were analyzed to determine descriptive statistics of sediment contamination and to assess the extent and magnitude of sediment contamination. Descriptive statistics focused on two types of analyses: 1) distributions and central tendencies of parameter values including the area-weighted mean and confidence interval for each of the strata of interest and the SCB as a whole; and 2) geographical distributions including thematic maps of sediment concentrations by parameter. Assessment of extent and magnitude focused on three types of analyses: 1) estimating the proportion of contaminant mass for each constituent relative to the amount of area occupied for individual strata; 2) comparison of sediment concentrations to sediment quality thresholds; and 3) comparison of sediment contamination extent to results from previous surveys. The threshold of choice was the newly promulgated sediment quality objectives by the State of California (SWRCB 2009). Data below the method detection limit were treated as zero for all calculations. The only exception was for thematic mapping in Sections IV and V where data below detection limits were treated as one-half the detection limit to visualize spatial gradients.

## Calculation of Area-Weighted Means and Confidence Intervals

The area-weighted mean for each stratum was calculated using a ratio estimator approach following Thompson (1992):

$$m = \frac{\sum_{i=1}^{n} (p_i * w_i)}{\sum_{i=1}^{n} w_i}$$

m = Area-weighted mean concentration for population j.

 $p_i$  = Parameter value (e.g., concentration) at station *i*.

 $w_i$  = Area weight for station *i*.

n = Number of stations in population *j*.

The ratio estimator was used in lieu of a stratified mean because an unknown portion of each stratum is sampleable (e.g., hard bottom). As a result, the estimated area, a random variable, is used in the denominator rather than the unknown true area. The standard error of the mean is calculated using the following equation:

Standard Error = 
$$\sqrt{\frac{\sum_{i=1}^{n} ((p_i - m) * w_i)^2}{\left(\sum_{i=1}^{n} w_i\right)^2}}$$

The 95% confidence intervals about the mean were calculated as 1.96 times the standard error. Use of the ratio estimator for the standard error approximates joint inclusion probabilities among samples and assumes a negligible spatial covariance, an assumption that appears to be valid based upon examination of the data. The assumption is conservative, in that its violation would lead to overestimation of the confidence intervals (Stevens and Kincaid 1997).

#### Comparison to Sediment Quality Objectives

California recently promulgated sediment quality objectives (SQO) for bays and estuaries of the state (SWRCB 2009). The objective for benthic ommunity protection requires three lines of evidence for evaluation; benthic infauna, sediment toxicity, and sediment chemistry. For each line of evidence, an assessment of condition is made, then the three lines of evidence are combined for a final site assessment. In the case of sediment chemistry, concentrations for constituents were combined into a single index scaled from one to four. Four graduated thresholds are then applied equating to:

- **Minimal Exposure** Sediment-associated contamination may be present, but exposure is unlikely to result in effects.
- Low Exposure Small increase in contaminant exposure that may be associated with increased effects, but magnitude or frequency of occurrence of biological impacts is low.
- **Moderate Exposure** Clear evidence of sediment contaminant exposure at concentrations that are likely to result in biological effects.
- **High Exposure** Contaminant exposure is highly likely to result in substantial biological effects.

The list of constituents and their respective thresholds are shown in Table II-4. The threshold for determining if a site is "acceptable" or "impacted" lies between low and moderate exposure.

We make two large assumptions in using this guideline for this study. First, we only apply the sediment chemistry line of evidence because sediment toxicity and benthic infaunal data are not yet available. In order to comply with the evaluation, these two remaining lines of evidence must be applied. Our second assumption was applying the SQO chemistry index to sediments on the continental shelf, slope and basin. The SQO sediment chemistry index was developed specifically for bays and estuaries of the state and this is the only habitat in which the regulatory application is appropriate. However, no other California-specific sediment chemistry assessment tool currently exists for these offshore habitats.

Chemical Name	Chemical Group	Chemical Name	Chemical Group
Total Organic Carbon	General	Alpha Chlordane	Pesticide
Percent Fines	General	Gamma Chlordane	Pesticide
		Trans Nonachlor	Pesticide
Cadmium	Metal	Dieldrin	Pesticide
Copper	Metal	2,4'-DDE	Pesticide
Lead	Metal	2,4'-DDD	Pesticide
Mercury	Metal	2,4'-DDT	Pesticide
Zinc	Metal	4,4'-DDD	Pesticide
		4,4'-DDE	Pesticide
		4,4'-DDT	Pesticide
Acenaphthene	PAH	2,4'-Dichlorobiphenyl	PCB congener
Anthracene	PAH	2,2',5-Trichlorobiphenyl	PCB congener
Biphenyl	PAH	2,4,4'-Trichlorobiphenyl	PCB congener
Naphthalene	PAH	2,2',3,5'-Tetrachlorobiphenyl	PCB congener
2,6-dimethylnaphthalene	PAH	2,2',5,5'-Tetrachlorobiphenyl	PCB congener
Fluorene	PAH	2,3',4,4'-Tetrachlorobiphenyl	PCB congener
1-methylnaphthalene	PAH	2,2',4,5,5'-Pentachlorobiphenyl	PCB congener
2-methylnaphthalene	PAH	2,3,3',4,4'-Pentachlorobiphenyl	PCB congener
1-methylphenanthrene	PAH	2,3',4,4',5-Pentachlorobiphenyl	PCB congener
Phenanthrene	PAH	2,2',3,3',4,4'-Hexachlorobiphenyl	PCB congener
Benzo(a)anthracene	PAH	2,2',3,4,4',5'-Hexachlorobiphenyl	PCB congener
Benzo(a)pyrene	PAH	2,2',4,4',5,5'-Hexachlorobiphenyl	PCB congener
Benzo(e)pyrene	PAH	2,2',3,3',4,4',5-Heptachlorobiphenyl	PCB congener
Chrysene	PAH	2,2',3,4,4',5,5'-Heptachlorobiphenyl	PCB congener
Dibenz(a,h)anthracene	PAH	2,2',3,4',5,5',6-Heptachlorobiphenyl	PCB congener
Fluoranthene	PAH	2,2',3,3',4,4',5,6-Octachlorobiphenyl	PCB congener
Perylene	PAH	2,2',3,3',4,4',5,5',6-Nonachlorobiphenyl	PCB congener
Pyrene	PAH	Decachlorobiphenyl	PCB congener

Table II-4. Parameters used for the new Sediment Quality Objectives chemical assessment tool.The new tool does not have chemical specific thresholds, but has a composite chemical score.

# III. Quality Assurance/Quality Control (QA/QC)

The primary goal of the quality assurance/quality control (QA/QC) effort was to ensure that the sediment chemistry data generated among the many study participants were comparable and complete. Therefore, a performance-based approach to QA/QC was adopted, allowing each participating lab the flexibility to utilize their own protocols, while meeting common data quality objectives (DQOs) for criteria pertaining to sensitivity, accuracy, and precision. This is the same approach used in previous regional surveys (Gossett *et al.* 2003), and was carried out in accordance with the Bight '08 QAP (Bight '08 Coastal Ecology Committee 2008b).

# **Reporting Limits**

To achieve study goals, minimum target reporting limits (RLs) for each analyte were set forth in the Bight '08 QAP (Appendix E). These RLs were set to achieve the SQO assessment thresholds. Overall, participant-specific minimum RLs were lower than the target RLs, indicating that the analyses performed provided adequate sensitivity. There were two types of exceptions. The first was where laboratory RLs did not achieve the target; these were few and isolated such as cadmium or silver. The frequency of QA discrepency was very low, approximately 1% of all trace metal analyses. A more frequent occurrence was for pyrethroid pesticides where the majority of analyses were four times the target RL. This deviation did not have an impact on SQO assessment, however, since pyrethroid pesticides are not a component of SQO (Table II-4).

# Interlaboratory Comparison Exercise

Prior to analysis of actual study samples, reference sediment samples were selected, prepared, and analyzed by all five participating labs to assess interlaboratory comparability of analytical results. Because of the need to identify reference sediments representing a regionally relevant range of expected target analyte concentrations and matrices, a separate set of reference samples for organics and trace metals were analyzed.

### Organics

Two sediment samples were selected for analysis of organic constituents prior to field sampling. The primary sample used for evaluation of interlaboratory comparability was Standard Reference Material 1944 (NIST, Gaithersburg, MD, USA), a mixed marine sediment from urbanized areas containing elevated levels of organic analytes representing the three compound classes of interest. Within the Bight '08 target list, there are certified values for 15 PAHs, 19 individual PCB congeners, and four chlorinated pesticides. For all of the SRM Bight '08 analytes, the laboratories were required to obtain concentrations within  $\pm$  40% of the certified or reference value for 6 out of 8 pesticides, 21 out of 29 PCB congeners, and 12 out of 15 PAHs (Table III-1, Appendix E). Four of five laboratories met this performance criterion for analysis of pesticides. Five of five laboratories met this performance criterion for analysis of PAHs. Three of five laboratories met this performance criterion for analysis of PCBs.

An additional sample was collected off the coast of Southern California that was considered more realistic in terms of concentration ranges and potential for interferences. The sample ("PV7C") was collected from the 60 m isobath of the Palos Verdes Shelf in 1998 and has

been characterized as containing elevated organic contaminants including total DDTs and total PCBs (Stull *et. al.* 1986). This was the same sample used in the Bight '98 and Bight'03 intercalibration exercises (Gossett *et al.* 2003). The reference sample was homogenized and split into pre-cleaned glass jars with Teflon<sup>®</sup>-lined closures, which were then kept frozen at  $-20^{\circ}$ C until distributed to each of the participating laboratories.

The DQO for total PAH, PCB and chlorinated hydrocarbon (CHC) pesticide concentrations in the PV7C reference sample was  $\pm 40\%$  of the mean value for the participant group (Table III-1, Appendix E). All of the participating labs met the performance criteria for total PAHs, total PCBs, and total DDTs. One lab did not measure total DDTs and total PCBs.

One valuable evaluation of performance-based quality is the comparability achieved by participating laboratories over time (Table III-2). The same sediment sample has been used for multiple intercalibrations since 1998. In 1998, two iterations of intercalibrations were required in order to achieve the comparability necessary for the Bight regional monitoring program. In the first 1998 iteration, coefficients of variations (CV) ranged from 46-67% for the three trace organic constituent groups (total DDT, total PCB, total PAH). This CV was reduced to 15-31% after the second iteration. In 2003, only one iteration was required; CVs ranged from 19-27%. Ten years later, the CV remains comparable, ranging from 10-21% among labs for the three trace organic constituent groups. This impressive longevity indicates that quality work likely occurs between regional surveys at each of the participating laboratories.

### Trace metals

A single certified reference material (CRM) from Environmental Resources Associates (ERA540, lot D056-540) was analyzed by all participating trace metal laboratories. The participating laboratories were required to obtain concentrations within  $\pm$  30% of the certified value for 12 of 15 analytes. All five laboratories met this performance criterion (Appendix E). CVs among laboratories ranged from 3-59%, averaging 12% for all elements.

## Performance-based QA/QC Goals and Success

The sample storage conditions and maximum hold time requirements and success achieved are summarized in Table III-3. Except for four grain size samples, all participating labs performed their analyses within the specified holding times.

The remaining criteria and corresponding DQOs, along with the degree of project success in attaining these goals, are summarized in Table III-2. Of the 383 samples delivered to the laboratories, over 97% of the samples were analyzed and data reported attaining our completeness DQO of 90%. Of the 11,455 laboratory analyses run for chemical contamination, approximately 99% had no detectable chemical measurements in blank samples. Of the remaining samples with detectable blanks values, no batch had a value more than three times the detection limit. Laboratories also attained success in accuracy DQOs for blank spiked samples (99.8% for trace metals), matrix spiked samples (99.5% for trace metals), and CRMs (96% for trace metals, 97% for PAH, 93% for CHCs, 100% for TOC). Finally, laboratories attained success in precision DQOs for laboratory duplicate samples (98% for trace metals, 99% for CHCs, 100% for PBDEs and pyrethroids, and 100% for TOC) and matrix spike duplicate samples (97% for trace metals).

The primary deviation during the Bight '08 sediment chemistry laboratory analysis was completeness of QA/QC samples. One laboratory did not run spiked blank or matrix spiked samples with any batch. Unfortunately, this laboratory also ran a lot of batches resulting in only 66% and 50% QA completeness over the entire survey for spiked blank and matrix spiked samples, respectively. Fortunately, this same laboratory did run CRMs with each batch, so at least one assessment of accuracy is available for judging QA; this laboratory passed virtually all of its CRM analyses. Therefore, this deviation was not considered to affect the overall study and trace metal results were flagged, but not removed from the project database.

The second deviation for missing QA/QC samples was assessing accuracy for trace organic constituents. Once again, one laboratory with many batches did not run CRMs for PAHs or CHCs. As a result, 56% of the PAH and 53% of the CHC batches over the entire survey do not have CRM assessment information. Matrix spikes from this laboratory were run for PAH and the laboratory met all accuracy DQOs. However, no matrix spikes were run for CHCs. While we have no CRM or matrix spike information for approximately 90% of the CHC analyses from this laboratory, the subset of samples from this laboratory that did have CRM analysis met the DQO established in the QA Plan. Therefore, this deviation was not considered to affect the overall study and the CHC results from this laboratory were flagged, but not removed from the project database.

Overall, the vast majority of QA/QC criteria were met with greater than 90% success. For those few instances where specific criteria were not met, deviations did not impart additional uncertainty in the measurements and therefore did not warrant removal or exclusion of any data from the study database. All of these deviations, however, were noted in the study database for individual users to make their own decisions regarding data quality.

Table III-1. Summary of interlaboratory comparison exercise for Total DDTs, Total PCBs, and Total PAHs in the Certified Standard Reference Material from the National Institute of Standards and Technology (SRM1944) and Laboratory Control Material from the Palos Verdes Shelf (PV7C). See Appendix E for individual target analytes.

	OCSD	City of San Diego	LACSD	City of Los Angeles	CRG	Expected Value	Acceptance Range (-40%)	Acceptance Range (+40%)
SRM 1944 <sup>a</sup>								
Total PAH	47718	67961	61201	59985	52192	62764	37658	87870
Total PCB	637	472	719	737	680	683	410	955
Total DDT	373	285	480	563	359	405	286	523
PV7C <sup>b</sup>								
Total PAH	1306	1982	1888	1251	1525	1651	991	2311
Total PCB	No Data	727	1058	1022	947	939	563	1314
Total DDT	No Data	12723	15069	15985	14898	14669	8801	20536

<sup>a</sup> Expected value = sum of certified values <sup>b</sup> Expected value = mean of participating laboratories

	Bight Study	Intercalibration Effort	Concentration Range Between Labs (ug/kg)	Coefficient of Variation
Ŧ	1998	First	135 - 2,300	67%
PAF	1998	Second	1,180 - 1,750	15%
Total PAH	2003	First	1,035 - 1,936	27%
F	2008	First	1,250 - 1,980	21%
г	1998	First	6,560 - 21,900	50%
D D	1998	Second	8,410 - 19,500	31%
Total DDT	2003	First	7,770 - 16,662	25%
F	2008	First	11,370 - 14,310	10%
m	1998	First	530 - 1,950	46%
PCI	1998	Second	900 - 1,500	20%
Total PCB	2003	First	920 - 1,440	19%
F	2008	First	730 - 1,060	16%

 Table III-2.
 Comparison of PV-7 split sample analysis among regional surveys.

Parameter	Storage Conditions	Maximum Hold Time <sup>1</sup>	Actual Hold Time (days)	Percent Success
Grain Size	Cold (4°C)	6 months	1-427	94%
TOC/TN	Frozen (-20°C)	1 year	7-301	100%
Trace Metals	Frozen (-20°C)	1 year	16-304	100%
Hg	Frozen (-20°C)	6 months	15-168	100%
Trace Organics	Frozen (-20°C)	1 year		
CHCs			16-337	100%
PAHs			12-273	100%
PCBs			16-337	100%
Pyrethroids			27-153	100%
PBDEs			140-325	100%

 Table III-3. Achievement of sample storage conditions and holding time criteria.

<sup>1</sup>Hold time is defined herein as the time from sample collection to extraction, digestion, or other initial processing.

	Metals	PAH		CHC & I		Pyrethroid	s & PBDE	TOC		
Quality Control Parameter	DQO	Success	DQO	Succe ss	DQO	Succe ss	DQO	Success	DQO	Succe ss
<u>Completeness</u>	83.0%	98.0%	97.0%	86.0%	81.0%	94.9%	94.5%	100.0%	94.0%	100.0 %
<u>Blanks</u>										
Frequency	1/batch	97%	1/batch	100%	1/batch	100%	1/batch	100%	1/batch	95%
Accuracy	< MDL OR < 5% of sample result	96.9%	< 10X MDL/RL	99.6%	< 10X MDL/RL	98.8%	< 10X MDL/RL	100%	< 10X MDL/RL	100%
<u>Spiked Blanks</u>					•• •				•• •	
Frequency	1/batch	66%	Not Required		Not Required		Not Required		Not Required	
Accuracy	± 15-25% of true value	99.8%	Not Required		Not Required		Not Required		Not Required	
<u>CRM<sup>1</sup></u>										
Frequency	1/batch	100%	1/batch	44%	1/batch	47%	1/batch	100% PBDE	1/batch	93%
Accuracy	within specified limits	96%	Within ± 40% of certified value for >80% of analytes	96.7%	Within ± 40% of certified value for >70% of selected analytes	92.5%	Within ± 40% of certified value for >70% of selected analytes	No true value	Within ± 20% of certified value	100%
<u>Matrix Spikes</u> Frequency	10% of total samples	50%	1/batch	100%	Not Required		1 set/batch	89%	Not Required	
Accuracy	Within ± 30% of true	99.5%	N/A <sup>3</sup>		Not		70-130% recovery of spiked		Not	
Accuracy	value	99.070	IN/ <i>I</i> A		Required		mass for >70% of analytes		Required	

Table III-4. Summary of performance-based QC criteria and project success in performing within those criteria.

	Metals		PAH		CHC & P	CBs	Pyrethroids	s & PBDE	тос	
Quality Control Parameter	DQO	Success	DQO	Succe ss	DQO	Succe ss	DQO	Success	DQO	Succe ss
							w/in each class			
Precision <sup>2</sup>	Within $\pm 30\% \text{ RPD}^2$	97.4%	N/A <sup>3</sup>		Not Required		Not Required		Not Required	
Sample Duplicates										
Frequency	10% of total samples <sup>2</sup>	99%	Not Required		1/batch	89%	1/batch	95%	1/batch	95%
Precision	Within ± 30% RPD	97.7%	Not Required		RPD < 30%	99.4%	RPD < 30%	100%	RPD < 30%	100%

<sup>1</sup>For metals, accuracy success calculated based on the sum of all analytes that passed across all labs. For Organics, accuracy based on the number of batches that passed the DQO out of the total number of batches, where one batch = <20 samples per batch. <sup>2</sup>Sample duplicate or Matrix Spike Duplicate was

required, not both.

<sup>3</sup>N/A=no DQO set, data are for evaluation purposes only as part of ongoing QA/AC efforts

# **IV. Descriptive Results**

## **Bight-Wide Results**

The area weighted mean (and 95% confidence interval), along with minimum, median, maximum and 10<sup>th</sup> and 90<sup>th</sup> percentile concentrations for each analyte is summarized in Table IV-1. Grain size ranged from very fine (100% silt and clay) to very coarse (86% sand and gravel). On average, Bight '08 sediments were fined grained with approximately 69% silt and clay content. The TOC and TN measurements varied three orders of magnitude, from 0.01% to 11% TOC. On average, Bight '08 sediments contained approximately 3% TOC with a 15:1 TOC/TN ratio. Twelve of 14 trace metals were detectable in 100% of the samples (Al, As, Ba, Be, Cd, Cr, Cu, Fe, Pb, Hg, Ni, Se, Zn). All of the trace metals ranged between two and five orders of magnitude with the largest relative range observed for mercury, partly because it had the lowest RL. Area weighted average (+ 95% CI) concentrations (dry weight basis) among the different metals varied from a low of 0.28 + 0.04 mg/kg for antimony to a high of 26,218 + 3125mg/kg for iron. Organic constituents were detectable in 14, 26, 33, and 42% of the samples for total PCB, total chlordane, total DDT, and total PAH, respectively. Area weighted averages for the organic analyte classes ranged from a low of 1.6 + 0.8 ug/kg for chlordanes to a high of 286 + 39 ug/kg for PAHs. Total DDTs averaged 126 + 97 ug/kg while the area weighted mean for PCBs was an order of magnitude lower (17 + 7 ug/kg). The area weighted mean for PBDEs (sum of all congeners) was  $4.1 \pm 1.9$  ug/kg. Area weighted mean concentration for pyrethroid pesticides was 5.15 + 3.09 ug/kg).

### **Subpopulation Comparisons**

Area weighted mean (AWM) concentrations and their corresponding 95% confidence intervals (CI) for the 10 subpopulations of interest are presented in Table IV-2. The embayment (marinas, ports, bays, estuaries) strata exhibited the highest concentrations for nine of the 15 trace metals measured. For example, the highest area-weighted mean concentrations for copper occurred in the marina stratum, double the concentration observed in the estuary stratum, but an order of magnitude greater than the average concentration on the middle shelf. Similar comparisons were observed for zinc, lead, or mercury. Ports had the greatest area-weighted mean concentrations for total PAH (2,500 ug/kg), double the concentration observed in marinas, but once again an order of magnitude greater than the middle continental shelf (179 ug/kg). Sediments in the deepest regions of the SCB, those from the continental shelf and slope had the greatest concentrations of total DDT (167-235 ug/kg). In contrast, sediments from the Channel Islands consistently had the lowest concentrations of most trace metals and trace organics constituents. Sediments in the Channel Islands had the greatest concentrations of TOC.

A clear enrichment in sediment fines and macronutrient content (TOC and TN) was evident along the depth gradient from the shelf, slope and basin strata (Table IV-2). Mean fine sediment content increased from 22% at the shallowest depth zone (inner Shelf) to a maximum of 90% for the lower Slope & Basin zone, with concomitant increases in both TOC and TN. Not surprisingly, average trace metal concentrations generally increased along this depth gradient also, in proportion to the increase with sediment fines. Thus, trace metal concentrations were higher on average in the deeper regions of the SCB. A similar trend of increasing concentration with depth was observed for a subset of the trace organic constituents including total PAH. In

contrast, the chlorinated hydrocarbon analytes (DDTs, PCBs and chlordanes) did not show universal enrichment with sediment fines (and thus depth). Rather, the chlorinated hydrocarbon concentration maxima were most elevated in the upper Slope stratum (200-500 m).

The concentration of 4,4'-DDMU, a new constituent measured in the Bight '08 survey, was highly correlated to 4,4'-DDE concentration ( $r^2 = 0.80$ , p<0.01; Figure IV-1). The slope of this relationship was very near unity (m=0.95), but offset by approximately one order of magnitude. On average across all samples in the SCB, DDMU comprised approximately 5% of the total DDT concentration in sediment. Therefore, it is assumed that previous surveys were not overly biased without this measurement. The one notable exception was located on the upper slope (232m) just offshore the LACSD outfall (Figures IV-1 and IV-2). At this station, where total DDT concentration was 6,460 ug/kg, 4'4-DDMU exceeded 4,4'DDE concentration and comprised nearly 50% of the total DDT measured.

#### **Geographic Distribution of Sediment Parameters**

The geographic distribution and magnitude of sediment concentrations in Bight '08 illustrate that not all constituents have the same source and may differ in their ultimate fate within the SCB (Figure IV-1 through IV-6, Maps of all parameters can be found in Appendix B).

The spatial distribution of total DDT sediment concentrations were greatest near Palos Verdes and Los Angeles Harbor, then declined moving northward through Santa Monica Bay and the Santa Barbara Channel in the net current direction (Hickey 1993) (Figure IV-2). Sediment concentrations to the south stayed uniformly low. This pattern, observed during previous regional surveys, is consistent with the large inputs of total DDT from the Montrose Chemical Corporation between 1950-1972 via the Los Angeles County Sanitation District's ocean outfall and the Dominguez Channel to inner Los Angeles Harbor (Schiff 2000). Total DDT has a long half-life and these spatial patterns are unlikely to change at a rapid pace.

The spatial pattern of copper sediment concentrations differed from total DDT (Figure IV-3). Copper sediment concentrations were generally greater in embayments than offshore, with many of the sites with the highest concentrations occurring in marinas and, to a lesser extent, estuaries. This pattern was also observed during previous regional surveys (Maruya and Schiff 2009) and is consistent with the large inputs of copper to marinas from anti-fouling paints used on the bottom of recreational and commercial vessels. Copper, which acts as a biocide, may be added in large doses (up to 76%) to bottom paints specifically to retard the growth of algae and encrusting marine organisms (Schiff *et al.* 2004). Copper is also a well-known constituent in urban runoff during storm events (Tiefenthaler *et al.* 2008). Copper is added to brake pads in automobiles and contributes greatly to urban dusts and particles, only to be washed from land surfaces when it rains (Sabin, *et al.* 2006, 2005). Virtually all of the large urban watersheds in the SCB drain to an estuary sampled during this survey.

The spatial pattern of silver sediment concentrations differed from both total DDT and copper (Figure IV-4). Silver sediment concentrations are generally greater offshore, decreasing moving south to north. The greatest sediment concentrations occurred in slope and basin habitats offshore San Diego while the lowest sediment concentrations were observed in slope

and basin habitats offshore Santa Barbara and the northern Channel Islands. There was only a moderate increase in silver sediment concentrations in the slope and basin habitats offshore Los Angeles and Santa Monica Bay.

PBDEs are used as flame-retardants in a variety of products including furniture, textiles, and electronics. Bight '08 was the first known survey of PBDEs in southern California marine sediments (Appendix C). PBDEs were widely distributed in the Bight, with the highest concentrations occurring in embayments (Figure IV-5). Their concentrations are on the high end of marine sediment concentrations reported world-wide (Mai *et al.* 2005), but this is not unexpected given the level of urbanization in southern California. The abundance of the various congeners also matched that reported in the literature, with BDE-209 (containing 10 bromines) dominating, followed by BDE-47 (4 bromines) and BDE-99 (5 bromines). This pattern results from the make-up and production levels of the PBDE technical mixtures (La Guardia *et al.* 2006). The highest PBDE concentrations occurred at the mouths of urban rivers; a pattern that is consistent with terrestrial sources. PBDEs can enter the environment from the manufacturing and disposal of products in which they were used. During storm events, PBDEs are likely transported to urban rivers and flushed out of the watersheds. Thus, PBDEs have a similar spatial pattern to copper, for which stormwater is also a major source.

The spatial pattern of pyrethroid pesticide sediment concentrations is limited relative to other constituents measured in this study since only embayment samples inclusive of estuaries, marinas, open bays, and ports were measured (Figure IV-6, Appendix D). Total pyrethroid concentrations ranged from less than 0.5 to 230  $\mu$ g/kg dry weight (area-weighted mean = 5.15 ± 3.09) and were detected in 35% of the SCB embayment area. Estuaries and marinas had the greatest area-weighted-mean concentrations (up to 22.1  $\mu$ g/kg) and extent (up to 65% of area) with detectable concentrations. Bifenthrin and cyfluthrin were detected in 32% and 15% of samples, respectively, whereas the other six pyrethroid pesticides were detected in  $\leq$  5% of samples.

Chemical Group	Area Weighted	95% CI	Min	10th	Median	90th	Max
(units in dry wt)	Mean			Percentile		Percentile	
Fines%	69.1	4.60	0.00	14.5	64.4	92	100
TOC%	3.0	0.30	0.01	0.3	1.2	3.9	11
TN%	0.21	0.03	0.003	0.02	0.08	0.25	0.66
Aluminum (mg/kg)	15372	1594	1040	4576	14315	25268	53700
Antimony (mg/kg)	0.28	0.04	<rl< td=""><td>0.10</td><td>0.16</td><td>0.58</td><td>1.4</td></rl<>	0.10	0.16	0.58	1.4
Arsenic (mg/kg)	6.7	1.2	0.005	2.36	5.6	11	39
Barium (mg/kg)	234	46	4.4	30	103	267	4346
Beryllium (mg/kg)	0.29	0.06	0.005	0.009	0.22	0.63	1.9
Cadmium (mg/kg)	0.88	0.12	0.001	0.1	0.34	1.1	3.9
Chromium (mg/kg)	56	9.9	1.4	12	34	68	347
Copper (mg/kg)	23	5.8	0.10	4.0	24	137	458
lron (mg/kg)	26218	3125	990	7555	22805	37296	132700
Lead (mg/kg)	12	1.4	0.584	3.0	12	42	138
Mercury (mg/kg)	1.6	2.8	0.002	0.01	0.0575	0.42	32
Nickel (mg/kg)	27	2.8	0.431	5.0	13	35.6	60
Selenium (mg/kg)	3.5	2.6	0.013	0.12	0.39	2.49	32
Silver (mg/kg)	0.91	0.4	<rl< td=""><td>0.02</td><td>0.18</td><td>0.93</td><td>7.0</td></rl<>	0.02	0.18	0.93	7.0
Zinc (mg/kg)	71	5.9	3.2	12	75	69.25	435
Total DDT (ug/kg)	126	97	<rl< td=""><td>2.1</td><td>5.2</td><td>57</td><td>6460</td></rl<>	2.1	5.2	57	6460
Total PCB (ug/kg)	17	6.7	<rl< td=""><td>4.8</td><td>20</td><td>51</td><td>1418</td></rl<>	4.8	20	51	1418
Total Chlordanes (ug/kg)	1.6	0.77	<rl< td=""><td><rl< td=""><td>1</td><td>3.32</td><td>48.8</td></rl<></td></rl<>	<rl< td=""><td>1</td><td>3.32</td><td>48.8</td></rl<>	1	3.32	48.8
Total Pyrethroid Pesticides (ug/kg)	5.15	3.09	<rl< td=""><td><rl< td=""><td><rl< td=""><td><rl< td=""><td>230</td></rl<></td></rl<></td></rl<></td></rl<>	<rl< td=""><td><rl< td=""><td><rl< td=""><td>230</td></rl<></td></rl<></td></rl<>	<rl< td=""><td><rl< td=""><td>230</td></rl<></td></rl<>	<rl< td=""><td>230</td></rl<>	230
Total PAH (ug/kg)	286	39	<rl< td=""><td>4.0</td><td>275</td><td>1443</td><td>14065</td></rl<>	4.0	275	1443	14065
Total PBDEs (ug/kg)	4.1	1.9	<rl< td=""><td>0.30</td><td>1.1</td><td>10</td><td>560</td></rl<>	0.30	1.1	10	560
Irgarol (ug/kg)	2.8	1.1	<rl< td=""><td><rl< td=""><td>1.2</td><td>8.3</td><td>13</td></rl<></td></rl<>	<rl< td=""><td>1.2</td><td>8.3</td><td>13</td></rl<>	1.2	8.3	13

Table IV-1. Area weighted means and selected ranges of the sediment chemistry data for the entire Southern California Bight in the summer of 2008.

	SHELF							SLOPE	& BASIN	Lower			
	Inner (5-30 m)		N	Mid		Outer		Upper		Lower			
			(30-120 m)		(120-200 m)		(200-500 m)		(500-1000 m)				
Parameter	Mean	95% CI	Mean	95% CI	Mean	95% CI	Mean	95% CI	Mean	95% CI			
Fines%	22.2	6.6	46.8	6.9	60.0	6.5	81.3	5.5	90.4	3.0			
TOC%	0.66	0.41	1.0	0.28	1.5	0.30	2.6	0.43	4.0	0.39			
TN%	0.03	0.01	0.07	0.01	0.10	0.01	0.25	0.05	0.33	0.04			
Aluminum (mg/kg)	5256	726	10035	1512	11473	2043	17536	2231	20760	1198			
Antimony (mg/kg)	0.12	0.02	0.18	0.05	0.22	0.06	0.24	0.08	0.36	0.13			
Arsenic (mg/kg)	4.3	1.2	6.1	2.2	6.1	1.3	8.8	1.2	7.3	1.1			
Barium (mg/kg)	85	20	289	33	151	64	174	70	330	39			
Beryllium (mg/kg)	0.12	0.02	0.30	0.09	0.19	0.08	0.29	0.13	0.39	0.11			
Cadmium (mg/kg)	0.23	0.03	0.32	0.04	0.47	0.06	1.4	0.4	1.0	0.28			
Chromium (mg/kg)	16	3.8	31	4.2	36	3.5	68	15	78	21			
Copper (mg/kg)	4.4	0.83	10.7	1.7	12.3	2.6	22.8	3.5	34.5	3.3			
lron (mg/kg)	10239	2233	20724	4826	23988	3196	33427	2916	31967	3378			
Lead (mg/kg)	5.0	1.3	7.8	1.8	9.1	0.076	15	1.3	16	1.6			
Mercury (mg/kg)	0.02	0.01	0.05	0.02	0.05	0.01	0.09	0.02	0.12	0.03			
Nickel (mg/kg)	8.6	1.7	12	3.4	17	2.2	29	3.8	39	4.1			
Selenium (mg/kg)	0.44	0.11	0.72	0.26	0.54	0.15	1.6	0.31	3.8	0.38			
Silver (mg/kg)	0.12	0.06	0.24	0.12	0.25	0.14	0.29	0.16	1.9	0.29			
Zinc (mg/kg)	25	6.8	46	7.9	52	4.9	79	8.8	96	4.3			
Total DDT (ug/kg)	20	22	16	6.4	56	82	238	432	165	92			
Total PCB (ug/kg)	10	2.1	13	3.3	19	8.2	36	31	11	3.5			
Total PAH (ug/kg)	199	43	179	40	231	37	234	47	358	81			
Total Chlordanes (ug/kg)	0.48	0.13	0.61	0.18	0.62	0.28	2.6	3.3	2.1	0.84			
Total Pyrethroid Pesticides (ug/kg)	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA			
Total PBDE (ug/kg)	0.22	0.15	2.2	0.83	2.0	2.0	4.3	5.1	4.9	2.8			
Irgarol (ug/kg)	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA			

Table IV-2. Area-weighted means and associated 95% confidence intervals (CIs) for selected geographic subpopulations of the sediment chemistry data from the Bight '08 Study. Units in ug/kg dry weight.

# Table IV-2 (cont.)

		EMBAYMENT AREA								OFFSHORE ARE Channel Islands	
	Ма	rinas	Estu	iaries	Po	orts	B	ays	(30-	120 m)	
Parameter	Mean	95% CI	Mean	95% CI	Mean	95% CI	Mean	95% CI	Mean	95% CI	
Fines%	78.1	7.8	60.6	3.1	69.9	5.5	61.3	5.0	28.1	6.0	
TOC%	1.5	0.31	1.6	0.5	0.9	0.35	1.1	0.3	4.1	0.9	
TN%	0.10	0.02	0.13	0.04	0.07	0.01	0.08	0.02	0.07	0.01	
Aluminum (mg/kg)	20831	2646	16062	2168	17835	1932	18854	2168	5375	715	
Antimony (mg/kg)	0.34	0.06	0.32	0.05	0.51	0.09	0.39	0.07	0.29	0.04	
Arsenic (mg/kg)	9.7	1.2	6.1	1.5	9.8	1.3	8.0	1.4	3.0	0.28	
Barium (mg/kg)	123	25	80	19	162	31	138	26	63	14	
Beryllium (mg/kg)	0.53	0.12	0.24	0.08	0.44	0.12	0.36	0.18	0.01	0.00	
Cadmium (mg/kg)	0.57	0.23	0.60	0.13	0.30	0.18	0.52	0.14	0.61	0.17	
Chromium (mg/kg)	51	8.8	27	7.5	42	16	38	21	21	3.5	
Copper (mg/kg)	160	45	34	10	68	12	48	7.3	5.4	0.85	
Iron (mg/kg)	30630	3568	22363	4762	27942	3456	26822	3397	9693	1282	
Lead (mg/kg)	51	29	20	8.2	27	9.0	28	9.4	3.2	0.49	
Mercury (mg/kg)	0.51	0.19	0.05	0.008	0.23	0.13	0.18	0.10	0.02	0.003	
Nickel (mg/kg)	23	4.1	16	3.4	22	5.6	17	3.8	10	1.4	
Selenium (mg/kg)	0.60	0.21	0.45	0.14	0.37	0.10	1.63	0.86	0.37	0.12	
Silver (mg/kg)	0.79	0.58	0.55	0.17	0.33	0.08	0.37	0.08	0.02	0.001	
Zinc (mg/kg)	218	34	108	29	127	24	126	26	23	2.6	
Total DDT (ug/kg)	45	19	33	34	49	20	22	11	4.6	1.6	
Total PCB (ug/kg)	58	22	17	5.4	43	19	27	6.5	10.74	1.32	
Total PAH (ug/kg)	1086	477	417	157	2549	1493	503	128	251	32	
Total Chlordanes (ug/kg) Total Pyrethroid	4.8	3.4	3.2	1.8	1.1	0.15	1.6	0.63	0.29	0.09	
Pesticides (ug/kg)	20	18	22	26	0.23	0.18	2.8	3.3	NA	NA	
Total PBDE (ug/kg)	52	41	57	38	31	38	19	4.5	NA	NA	
Irgarol (ug/kg)	2.8	1.1	NA	NA	NA	NA	NA	NA	NA	NA	

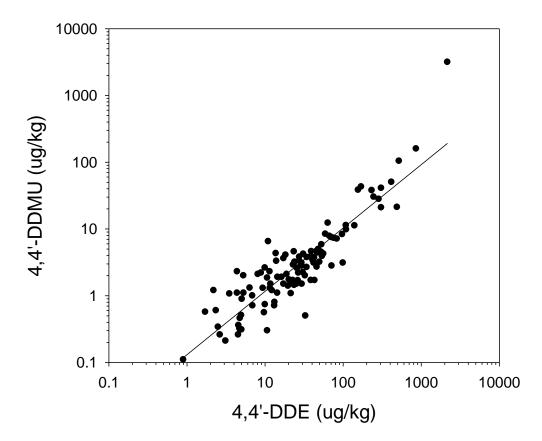


Figure IV-1. Relationship between 4,4'-DDE, the predominant component of Total DDT, and DDMU, a new parameter measured in Bight '08.

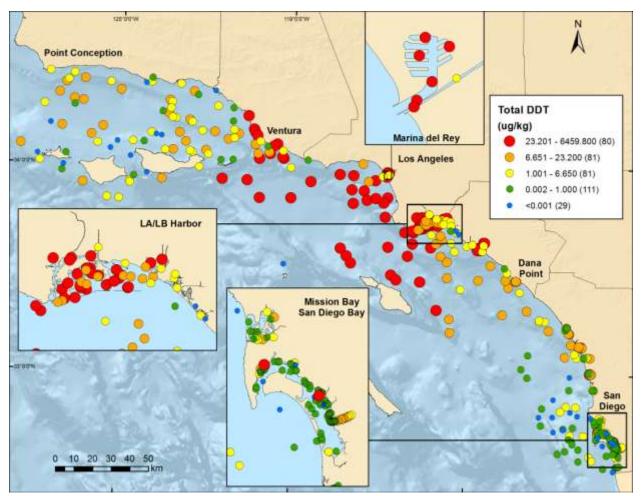


Figure IV-2. Geographical distribution of total DDT sediment concentrations (µg/kg dry wt) during the 2008 Southern California Bight regional monitoring survey.

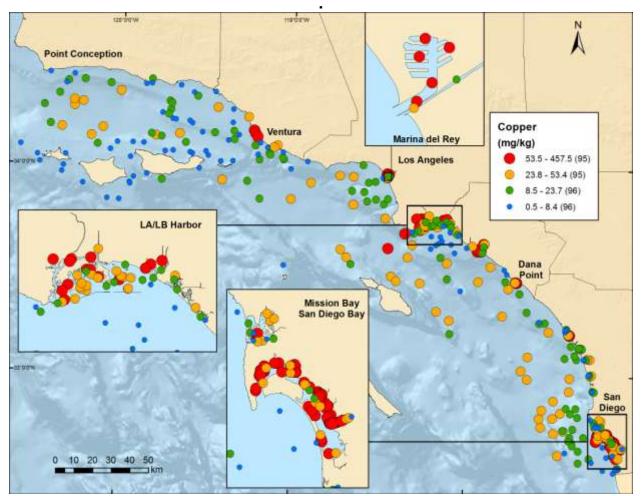


Figure IV-3. Geographical distribution of copper concentrations (mg/kg dry wt) in sediment during the 2008 Southern California Bight regional monitoring survey.

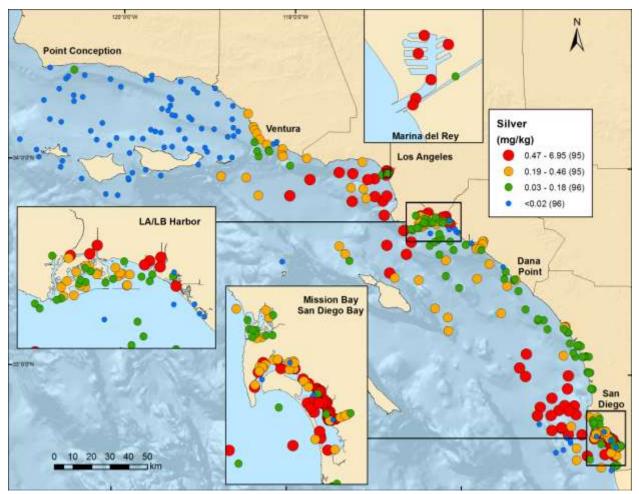


Figure IV-4. Geographical distribution of silver concentrations (mg/kg dry wt) in sediment during the 2008 Southern California Bight regional monitoring.

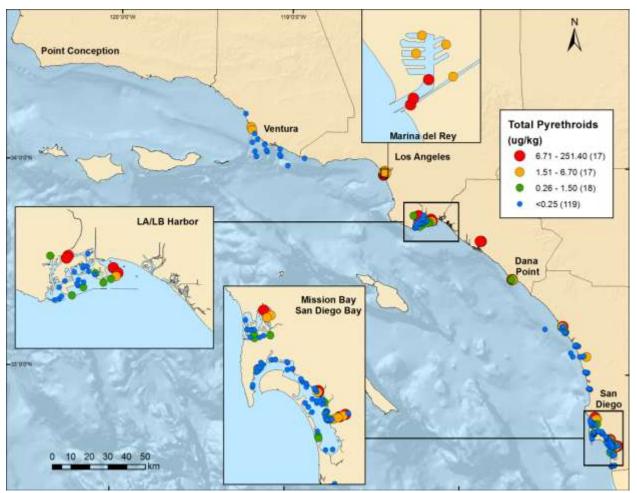


Figure IV-5. Geographical distribution of total pyrethroid concentrations (ug/kg dry wt) in sediment during the 2008 Southern California Bight regional monitoring.

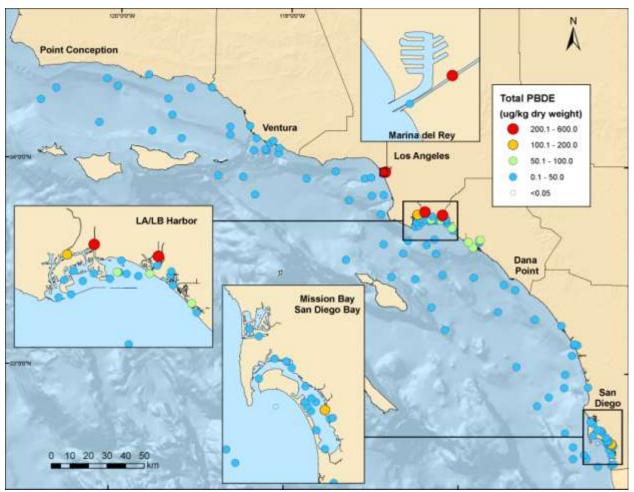


Figure IV-6. Geographical distribution of total PBDE concentrations (ug/kg dry wt) in sediment during the 2008 Southern California Bight regional monitoring.

### V. Assessment Results

#### **Comparison To Sediment Quality Thresholds**

A summary of SCB percent area exceeding four sediment chemistry thresholds of increasing concern is presented in Figure V-1. The four thresholds are derived from the State's sediment quality objectives framework (SWRCB 2009; Bay and Weisberg 2008): Category 1 minimal exposure; Category 2 is low exposure; Category 3 is moderate exposure; and Category 4 is high exposure. Categories 1 and 2 are considered acceptable condition by the State. Three important aspects of this assessment are that: 1) this assessment is based on a composite scoring index that aggregates many chemicals so that individual chemical assessments are unknown; 2) the regulatory assessment relies on biological and toxicological lines of evidence and cannot be scored on a single chemistry line of evidence alone; and 3) the regulatory framework only applies to marine embayments, but we use the tool for offshore habitats including shelf, slope, basin, and island sediments.

Approximately 77% ( $\pm$  6%) of SCB sediments were in acceptable condition based on sediment contamination (Figure V-1). Approximately 21% ( $\pm$  14%) of SCB sediments had moderate exposure to sediment contamination. The remaining 2% ( $\pm$  2%) of the SCB had high exposure to sediment contamination.

The areal extent of acceptable condition among strata based on sediment contamination varied from 25% to 100% depending upon the stratum (Figure V-2). The three most impacted strata were located in the SCB marinas, ports, and estuaries (26%, 46%, and 59% of area with acceptable sediment contamination, respectively). The two least impacted strata were the inner and mid-shelf habitats, where 100% of the area exhibited acceptable condition based on sediment contamination. The outer shelf and Channel Islands strata were similarly unimpacted (96% and 97% of area with acceptable sediment contamination, respectively). The upper slope, lower slope and basin, and bay strata exhibited an intermediate extent of impact (62%, 66%, and 68% of area with acceptable sediment contamination, respectively).

#### **Comparison to Previous Southern California Bight Project Results**

Detailed comparisons between this study and the results from previous Bight studies in 1998 and 2003 were hindered because of the differences in the study frame. Therefore, the temporal comparisons made in this section pertain only to those habitats that all three surveys had in common. These habitats included embayments (inclusive of ports, bays, marinas, and harbors), estuaries, mainland continental shelf (<200 m inclusive of large and small POTW strata), and the continental slope and basin, and the Channel Islands.

The areal extent of acceptable condition in the SCB based on sediment contamination decreased from 91% ( $\pm$  8%) in 1998 to 75% ( $\pm$ 6%) in 2008 (Figure V-3). The areal extent of acceptable condition in 2003 (65  $\pm$  6%) was similar to 2008. While the areal extent of unacceptable sediment contamination increased between 1998 and 2008, the areal extent of high

exposure to sediment contamination (the worst condition category) was small regardless of survey year (between 0.1 and 2.0% of SCB area).

The change in extent of acceptable sediment condition from Bight '08 relative to previous surveys was inconsistent between the five strata examined in the SCB (Figure V-4). Based on sediment contamination, the greatest increase in the areal extent of acceptable sediment condition occurred in the ports/bays/harbors stratum; 40% ( $\pm$ 5%) of the area was acceptable in 1998 compared to 62% ( $\pm$ 5%) in 2008 for this stratum composite. Increases of less than 10% in the extent of acceptable sediment condition between surveys occurred in the Channel Islands and slope/basin strata. The areal extent of acceptable sediment condition on the mainland shelf was relatively static, changing less than 5% from 1998 to 2008. In contrast, the areal extent of acceptable in 2003 compared to 62% ( $\pm$ 8%)in 2008 for this stratum; 86% ( $\pm$ 7%)of the area was acceptable in 2003 compared to 62% ( $\pm$ 8%)in 2008 for this stratum.

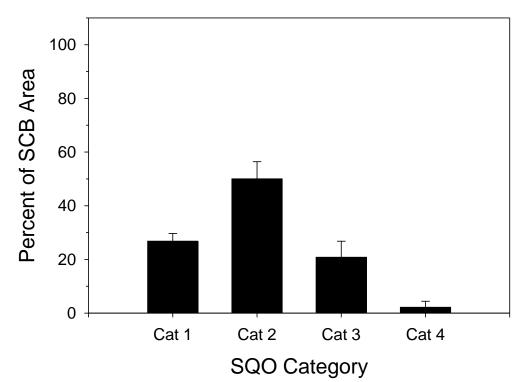


Figure V-1. Areal extent of SCB sediments in varying categories of exposure to sediment contamination. Category 1 is minimal exposure; Category 2 is low exposure; Category 3 is moderate exposure; and Category 4 is high exposure.

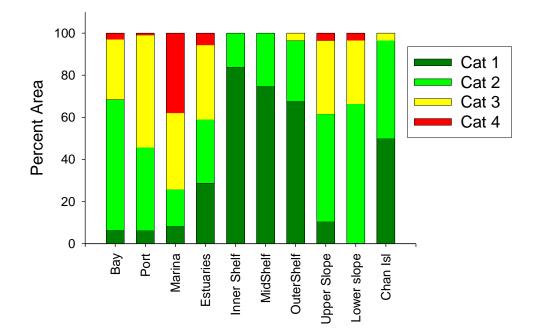


Figure V-2. Areal extent of SCB sediments by stratum in varying categories of exposure to sediment contamination. Category 1 is minimal exposure; Category 2 is low exposure; Category 3 is moderate exposure; and Category 4 is high exposure.

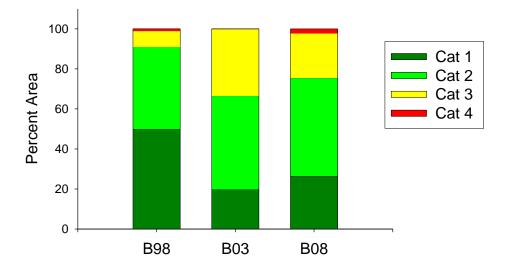
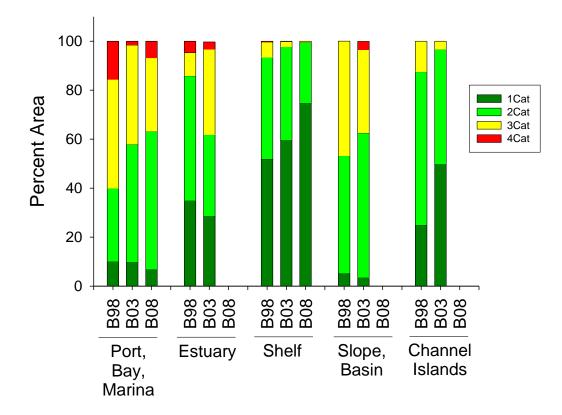


Figure V-3. Areal extent of SCB sediments by survey year in varying categories of exposure to sediment contamination. Category 1 is minimal exposure; Category 2 is low exposure; Category 3 is moderate exposure; and Category 4 is high exposure.



FigureV-4. Areal extent of SCB sediments by stratum and survey year in varying categories of exposure to sediment contamination. Category 1 is minimal exposure; Category 2 is low exposure; Category 3 is moderate exposure; and Category 4 is high exposure. Missing bars represent no data.

### **VI.** Discussion

The newest feature of the Bight '08 sediment chemistry program was the application of recently developed assessment tools. This assessment tool was developed for the State of California in order to promulgate sediment quality objectives (SQO) for bays, harbors, and estuaries (Bay and Weisberg 2008). This tool, and the regulatory framework that goes with it, was not available during previous surveys. When we apply this new assessment tool, roughly three-quarters of the SCB sediments were in acceptable condition based on exposure to sediment contamination. The remaining one-quarter of the SCB in unacceptable condition was not evenly distributed. The potential for environmental risk due to sediment contamination was dramatically higher in marinas. Estuaries and ports were also disproportionately impacted. In contrast, much of the mainland continental shelf and Channel Islands were in uniformly acceptable condition for sediment contamination.

We assessed the same Bight '08 sediment chemistry results using both the new SQO chemical approach and the approach used in previous surveys in order to determine potential bias in past reports. The previous assessment tool, the effects range median quotient (ERMQ), is similar in many ways to the SQO chemical tool (Fairey *et al.* 2001). The ERMQ compiles the concentrations of many contaminants into a single measure and has multiple thresholds based on confidence in our expectation of biological response. There are also many differences between the two tools. For example, the SQO chemistry tool has a large focus on estimating responses from biological communities such as benthic infauna while the ERMQ has a much greater emphasis on estimating responses based on laboratory toxicity tests. Another large difference is that the SQO chemistry tool was derived strictly from California data whereas the ERMQ was developed from data nationwide. It was these differences that led us to focus on the SQO chemistry tool as our primary assessment mechanism.

The difference in areal extent of impact marginally differed using either assessment tool (Figure VI-1). The SQO estimated 77% ( $\pm$  6%) of the SCB was in acceptable condition based on sediment contamination compared to 92% ( $\pm$  7%) using the ERMQ. The SQO estimated 2% ( $\pm$  2%) of the SCB exhibited high exposure from sediment contamination compared to 1% ( $\pm$  1%) using the ERMQ. Both assessment tools, the SQO and ERMQ, lack certain attributes that are necessary for a full evaluation of sediment quality. These attributes include having biological response data, such as benthic infaunal community or sediment toxicity measures, as additional lines of evidence. Also, it will be necessary to identify the specific contaminant(s) that are responsible for causing the biological effects when toxicity or impacted benthic communities are encountered concomitant with high exposure to chemical contamination. This is often difficult because contaminants rarely occur in isolation and are most frequently encountered as a complex mixture. The SQO accounts for this forensic work by stipulating the need for a sediment-based stressor identification such as toxicity identification evaluations (SWRCB 2009).

The new assessment tool was applied to past surveys to determine trends in sediment condition and the results were mixed. Considering the SCB as a whole, little noticeable change was apparent between 1998 and 2008. When considering strata individually, however, several observed generally improving sediment contamination over the last 10 years. The most notable

improvement has been observed on the mainland continental shelf in depths of 5 to 200m; acceptable sediment condition relative to sediment contamination now dominates (75%) the shelf area. The exception to this improving trend was observed in estuaries where one-third of the area is now in unacceptable sediment condition. This is over double the area observed just five years ago during Bight '03. The improvements since 1998 bode well for the actions taken by managers, but the increases in sediment contamination from embayments indicates further work lies ahead.

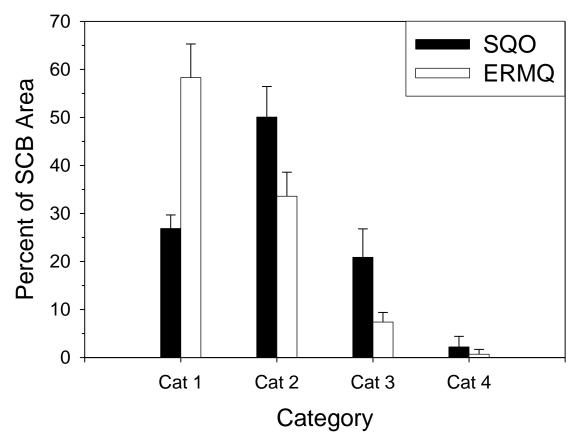
The Bight platform provided a venue for additional benefits not typically observed in ongoing regulatory monitoring programs. For example, the analysis of emerging contaminants of concern (CECs) illustrated that these constituents are widespread in SCB sediments and are greatest near sources of discharge. Two groups of constituents were analyzed in Bight '08; pyrethroid pesticides and PBDEs (See Appendices C and D for details). Pyrethroid pesticides are relatively well-known urban and agricultural pesticides commonly found in stormwater runoff (Weston and Lydy 2010), but had never been measured in bightwide surveys of sediment condition. The areal extent and area-weighted mean concentrations of pyrethroid pesticides were greatest in estuaries and marinas, particularly those estuaries and marinas that received inputs from urbanized watersheds. The collection sites with the greatest pyrethroid concentrations were located adjacent to runoff from urban watersheds, suggesting runoff is most likely a primary source of pyrethroid pesticides to SCB embayment. A large fraction of pyrethroid pesticides likely reside in freshwater sediments upstream of SCB embayments. This is consistent with the higher concentrations found in freshwater than marine sediments noted in previous studies (Brown et al. 2010). Erosion of these freshwater sediments may provide an ongoing source of contamination to estuaries. Quantifying pyrethroid emissions from SCB watersheds will help quantify ongoing and future risks to estuaries, especially relative to upcoming management actions for this highly toxic pesticide.

PBDEs are already known to bioaccumulate through the food chain, and some of the highest tissue concentrations in the coastal United States are observed within the SCB (Meng *et al.* 2009, Kimbrough *et al.* 2008). Like pyrethroid pesticides, the greatest concentrations of PBDEs were observed in embayments, particularly in urban estuaries that receive drainage from highly developed watersheds. Unlike pyrethroid pesticides, the risk of PBDEs is still largely unknown. Now that it is clear widespread distribution of PBDEs occurs in SCB sediments, and that these PBDE concentrations are high enough to bioaccumulate through the food chain, future work on biological effects is warranted. In particular, human health thresholds for seafood consumption have recently been promulgated by the State Department of Environmental Health and Hazard Assessment (Klasing and Brodberg 2011). The Bight program may be an optimal platform to assess the risk of this CEC to seafood consumers.

A third new target analyte was measured in Bight '08, and is not routinely measured in most existing monitoring programs or in previous Bight surveys, was 4,4'-DDMU. 4,4'-DDMU is thought to be one additional step along the major dechlorination pathway for DDT after DDE and DDD (Eganhouse and Pontolillo 2008). On average across the entire SCB, 4,4'-DDMU was approximately one-twentieth (5%) the concentration of total DDT. Because 4,4'-DDMU appears to comprise such a small proportion of total DDT, we assume that previous estimates of total DDT are not heavily biased. One notable exception was a sample near the Palos Verdes margin,

which contained the greatest total DDT concentration in Bight '08 at nearly 6,500 ug/kg. The 4,4'-DDMU composition at this site was nearly 50%. Thus, DDMU may comprise larger fractions of total DDT in specific locations, particularly where large quantities of total DDT exist and may be undergoing reductive dechlorination.

This report only evaluated sediment chemistry when assessing the status of the SCB in 2008. However, the assessment tool used for making final conclusions about the status of sediment condition requires multiple lines of evidence (Bay and Weisberg 2008). These additional lines of evidence include sediment toxicity and benthic infaunal community composition. These additional lines of evidence are important since chemistry alone may provide incomplete or inaccurate information such as variability in bioavailability of sediment-bound contaminants. Likewise, sediment toxicity and benthic infaunal community composition have their limitations. Only in combination do the three lines of evidence illustrate both exposure and response to sediment contamination. The integration of sediment chemistry, sediment toxicity, and benthic infaunal community composition will be an important step in making final conclusions about the status of SCB sediment condition.



FigureV1-1. Areal extent of SCB sediments in varying categories of condition by Assessment tool. The two tools include the sediment quality objectives (SQO) and the effects range median quotient (ERMQ). Category 1 is minimal exposure; Category 2 is low exposure; Category 3 is moderate exposure; and Category 4 is high exposure.

### VII. Conclusions

# • Approximately three-quarters of the SCB has acceptable condition for sediment contamination.

Based on our newest sediment chemistry assessment tool, 77% of the SCB sediments have minimal or low exposure to sediment contamination. Approximately 2% of the SCB sediments have high exposure to sediment contamination, the worst category of contamination in the new chemistry assessment toolbox. This new assessment tool uses an integrative approach to sediment chemistry so that we cannot determine the contaminant of greatest concern from chemistry alone.

#### • The relative extent of sediment contamination was greater in embyaments than offshore

The new sediment chemistry assessment tool used for Bight '08 was calibrated and validated for embayments such as estuaries, bays, ports and harbors. The tool was not calibrated or validated in offshore sediments from the mainland shelf or slope. However, the new assessment tool is the best we have for the offshore environment and it provided some continuity for comparisons to the embayment strata. As such, between one-quarter and nearly one-half of area in embayment strata such as marinas, ports and estuaries had acceptable sediment contamination. In contrast, more than 90% of the offshore strata such as the mainland shelf and Channel Islands had acceptable sediment contamination.

#### • The distribution of many sediment contaminants was a function of their source inputs.

The greatest concentrations of total DDT were located on the continental shelf where submarine outfalls at depths of 60m discharged hundreds of metric tons more than 40 years ago. These legacy contaminants remain on the continental shelf to this day. In contrast, the largest discharges of other contaminants such as copper, zinc, and total PAHs come from vessel antifouling paints and land-based runoff. As a result, the greatest concentrations of these contaminants are found in embayment strata such as marinas and estuaries.

#### • Trends in sediment contamination were mixed.

While sediment condition has generally improved in the SCB as a whole, this trend did not hold true for individual strata. The most notable improvements in sediment condition were observed on the mainland continental shelf, Channel Islands, and ports/bays/harbors. For example, acceptable sediment condition based on sediment contamination has increased from 46% to 62% of the port/bay/harbor stratum composite. However, acceptable sediment condition decreased in estuaries from 86% to 62% of the area in just the last five years.

# • Special studies measuring contaminants of emerging concern have identified potential new environmental issues.

Pyrethroid pesticides, a relatively new class of chemicals not routinely analyzed in existing ocean monitoring programs, was found at levels predicted to induce toxicity in the laboratory. PBDEs, a flame-retardant found in many household items, were widespread in sediments throughout the SCB. Sediment-associated PBDEs appear to be one pathway to

bioaccumulation in higher order marine organisms such as mussels and marine mammals. Both of these emerging contaminants were found in greatest concentration from embayments that receive land-based runoff.

### VIII. Recommendations

# • Integrate sediment chemistry with other measurements of environmental condition to assess impacts.

The State Water Board's newest regulatory tools were used to make assessments of sediment chemistry for this report. However, the regulatory guidelines call for a weight of evidence approach, whereby sediment chemistry is combined with sediment toxicity and benthic infauna to make a final assessment of sediment impacts. The good news is that the additional lines of evidence not utilized in this report were collected and are being evaluated in other reports for Bight'08. Integrating the three lines of evidence will be crucial for a complete and accurate assessment of overall sediment condition.

# • A calibrated and validated assessment tool for sediment chemistry is needed for offshore sediments

The sediment chemistry assessment was calibrated and validated for embayment sediments and, while it was applied it to offshore sediments for this report, there are important limitations to this assumption. The best alternative is to calibrate and validate a sediment chemistry assessment tool for offshore sediments. The data to begin this process was collected as part of Bight '08, including numerous chemical constituents and various measures of chemical exposure and biological responses.

### • Follow-up on the results from special studies conducted as part of Bight'08.

Measuring PBDEs and pyrethroid pesticides indicated that these constituents of emerging concern are relatively widespread and might be at concentrations of ecological relevance. Additional studies should be conducted to help determine if these constituents are resulting in environmental degradation. Such studies could include biological effects and source attribution, including mass emissions to the coastal ecosystem.

### • Begin defining special studies for Bight'13.

The Bight program provides a unique platform for examining new issues. In the case of Bight'08, measuring contaminants of emerging concern was a valuable special study addition for three reasons. First, the results are put into a context relative to our traditional measures as a point of comparison. Second, it's a cost-effective way to get new measures since many of the analyses were provided as in-kind services from specialty laboratories. As a corollary, the specialized expertise that accompanies the new measurements helps improve the knowledge of Bight participants. Third, answers to nagging environmental questions can be achieved without having to modify monitoring permits. Oftentimes, regulatory permit modifications are a long process, but special studies as part of the Bight program provide the opportunity for adaptability and timeliness.

# • There is a need for additional effort in sediments found further offshore and in deeper water

Sediments are rarely monitored on the mainland slope and basin. This is, in part, because sampling in these deep waters (>200m depth) is difficult and costly. However, results from Bight '08 indicated that sediments from the mainland slope and basin had greater sediment

concentrations and a propensity towards increased threshold exceedences than sediments on the mainland shelf where most discharges and related monitoring occurs. It is possible that much of the pollutants discharged on the mainland shelf find their way to the slope and basin as they travel down elevational gradients. Therefore, further chemical characterization and other measures of exposure and biological response such as toxicity and benthic infauna should be conducted in these deep water habitats during future surveys.

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### APPENDIX A: Participants in the Bight'08 Regional Monitoring Program

ftp://ftp.sccwrp.org/pub/download/DOCUMENTS/TechnicalReports/661\_B08\_SedChem\_Appendix\_A.pdf

## **APPENDIX B: Geographic Distribution and Magnitude of Analytes**

ftp://ftp.sccwrp.org/pub/download/DOCUMENTS/TechnicalReports/661\_B08\_SedChem\_Appendix\_B.pdf

### **APPENDIX C: PBDE Sources and Distribution in the SCB**

ftp://ftp.sccwrp.org/pub/download/DOCUMENTS/TechnicalReports/661\_B08\_SedChem\_Appendix\_C.pdf

## **APPENDIX D: Pyrethroids in Southern California Coastal Sediments**

ftp://ftp.sccwrp.org/pub/download/DOCUMENTS/TechnicalReports/661\_B08\_SedChem\_Appendix\_D.pdf

## **APPENDIX E: Laboratory Quality Assurance Information**

ftp://ftp.sccwrp.org/pub/download/DOCUMENTS/TechnicalReports/661\_B08\_SedChem\_Appendix\_E.pdf