

# Sediment Chemistry





Southern California Bight 2003 Regional Monitoring Program Vol. II

# Southern California Bight 2003 Regional Monitoring Program: II. Sediment Chemistry

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# THE BIGHT '03 CHEMISTRY WORKING GROUP

Much of the success of the Southern California Bight Regional Monitoring Program is its concensus-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 2003 Southern California Bight Regional Monitoring Program (Bight '03) is part of an effort to provide an integrated assessment of the SCB through cooperative regional-scale monitoring. Bight '03 is a continuation of regional surveys conducted in 1994 and 1998, and represents the joint efforts of 58 organizations (Appendix A). Bight '03 is organized into three technical components: (1) Coastal Ecology, (2) Shoreline Microbiology, and (3) Water Quality. This report presents the results of the sediment chemistry portion of Bight '03, 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 the other Bight '03 guidance manuals, data, and reports are available for download at www.sccwrp.org.

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#### **Participating Analytical Laboratories**

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

## **EXECUTIVE SUMMARY**

More than \$30 million is expended annually on environmental monitoring in the Southern California Bight (SCB), yet only 5% is monitored on an ongoing basis. Therefore, environmental managers in the SCB decided to expand their monitoring programs and, starting in 1994, decided to conduct periodic regional assessments of ecosystem condition and assess the overall health of the SCB. Sixty-five different organizations collaborated in 2003 to create the third SCB Regional Monitoring Program (Bight '03). Bight '03 was designed to be an integrated regional monitoring program that encompassed regulatory, regulated, academic, and non-governmental agencies. 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 impairment vary among different habitats of interest?

Bight '03 had three components; coastal ecology, shoreline microbiology, and water quality. 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 (5-30 m, 30-120 m, 120-200 m), upper mainland slope (200-500 m), lower slope and basin (500-1000 m), embayments (marinas, ports/bays/harbors), estuaries (Los Angeles area estuaries, other SCB estuaries), large (>100 mgd) and small (<100 mgd) Publicly Owned Treatment Works (POTWs), and the Channel Islands National Marine Sanctuary (30-200 m surrounding Santa Barbara, Anacapa, Santa Rosa, Santa Cruz, and San Nicolas Islands).

A total of 359 samples were collected between July and October 2003, then analyzed for grain size, total organic carbon (TOC) and total nitrogen (TN), trace metals (Sb, As, Ba, 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 o,p' and p,p' isomers of dichlorodiphenyltrichloroethane and its degradation products), and total chlordane (alpha and gamma isomers).

The greatest accumulated mass of sediment constituents was located on the mainland slope and basins. Across all constituents, an average 76% of the mass (range 70-87%) was located in depths greater than 200m. Although these deep water habitats contain the greatest mass of sediment constituents, very little ongoing sediment monitoring occurs in this realm. Instead, the vast majority of monitoring occurs near POTWs where less than 3% of the SCB constituent mass is located.

Although the mass of most constituents was greatest in the deep ocean, it was embayments of the SCB that were perhaps subject to the greatest ecological risk from sediment contamination. The greatest sediment concentrations of trace metals and several organic constituents were observed in sediments sampled from marinas, estuaries draining urbanized watersheds, and industrialized port facilities. Finally, marinas, estuaries, and ports/harbors all had significantly elevated mass to area ratios indicating that they were predisposed to accumulating sediment contaminants.

Approximately 94% of the SCB was enriched in at least one sediment constituent. Eighty eight percent of the SCB was enriched by at least one trace metal constituent. Seventy one percent of the SCB was enriched by at least one organic constituent. Total DDT was the most widespread sediment contaminant enriching 71% of the SCB sediments. The highest total DDT concentrations were observed on the Palos Verdes shelf and extended northward, in the direction of net coastal currents. Trace metals and total PAHs, in contrast, were most concentrated in sediments from embayments such as marinas and urban estuaries. The lowest concentrations for metals were consistently observed in the Channel Islands and adjacent to small POTWs.

Despite the relatively widespread anthropogenic enrichment of SCB sediments, only 1% of the SCB was at a moderate to high risk of adverse biological effects based on the mean effects range median quotient (ERMQ > 0.5). The risk, however, was not evenly distributed throughout the SCB. The greatest risk was found in sediments of marinas, LA estuaries, and large POTWs; these were the only strata whose mean ERMQ exceeded 0.5. The least risk was observed at the Channel Islands and small POTWs where all sites were classified as a low risk of adverse biological effects.

Little change in the extent of sediment contamination has occurred over the last nine years. The areal extent of sediment contaminant risk in commonly sampled strata during regional surveys in 1994, 1998, and 2003 was nearly identical (86%, 87%, and 88%, respectively).

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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 \$9 billion into the economy (NRC 1990). 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 16.5 million people inhabit the five coastal counties that border the SCB, 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.

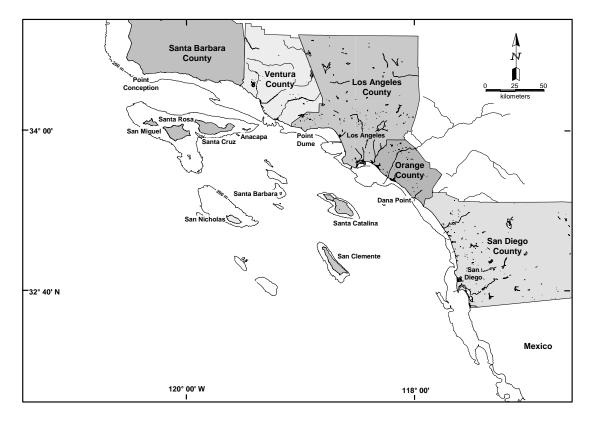


Figure I-1. A map of the Southern California Bight, which extends from Point Conception, California, to Ensenada, Mexico.

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 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). There were 264 sites sampled in 1994 and 404 sampled in 1998, reflecting an increase in habitats from the mainland continental shelf to several embayment habitats. Both surveys assessed the extent and magnitude of impacts for a number of indicators including sediment chemistry, benthic infauna, sediment toxicity, fish assemblages and bioaccumulation. Specifically for sediment contamination, both surveys found a large proportion of the SCB contaminated by anthropogenic pollutants with a disproportionate accumulation occurring near urban activities such as discharges from large publicly owned treatment works (POTWs) and ports, harbors, and marinas.

A large effort developing chemical analytical comparability was invested in the previous surveys (Gosset *et al.* 2003). Since both the Pilot Project and the Bight '98 program 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.

## **Objectives of the 2003 Regional Monitoring Program**

The purpose of the 2003 Southern California Bight Regional Monitoring Program (Bight '03) 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 impairment 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 '03 program was multi-faceted program. Bight '03 had three components; Coastal Ecology, Shoreline Microbiology, and Water Quality. The Coastal Ecology component measured sediment geochemistry 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).

## 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 (500-1000 m), embayments (marinas, other ports/bays/harbors), estuaries (Los Angeles (LA) area estuaries, other SCB estuaries), large (>100 mgd) and small (<100 mgd) POTWs, and the Channel Islands National Marine Sanctuary (30-120 m 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)	1065	7.0
Mid Shelf (30-120 m)	1782	11.8
Outer Shelf (120-200 m)	552	3.6
Upper Slope & Basin (200-500 m)	2952	19.5
Lower Slope & Basin (500-1000 m)	7318	48.3
Marinas	16	0.10
Estuaries	6.3	0.04
LA Estuaries	1.2	0.01
Ports/Bays/Harbors	77	0.51
Small POTW Outfalls	26	0.17
Large POTW Outfalls	166	1.1
Channel Islands (30-120 m)	1208	8.0
Entire Southern California Bight	15169	100.0

#### Table II-1. Area as a function of sampling strata for Bight '03.

#### 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 of a successful grab and were placed in appropriate containers for the subsequent analysis. All sample containers were purchased pre-cleaned, 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 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 '03 Field Operations Manual (Bight '03 Field Sampling and Logistics Committee 2003). All samples collected for the sediment chemistry portion of the Bight '03 survey were kept under

refrigeration (4°C), and samples for trace organic, metals, and total organic carbon (TOC) analysis were frozen within 24 hr. 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 '03 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 measurements 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 '03 Survey Quality Assurance Plan (QAP). See Section III for an assessment of these Bight '03 Chemistry Committee quality assurance activities.

#### **Target Analytes**

The target analytes for the Bight 2003 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 PAHsincludes 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 eight chlorinated pesticides selected as target analytes included the two isomers of dichlorodiphenyltrichloroethane (DDT) dichlorodiphenyldichloroethane and their respective metabolites. (DDD) and dichlorodiphenyldichloroethylene (DDE). Based upon previous studies, DDT and its metabolites are still the most ubiquitous organic contaminants in the SCB. Two isomers of chlordane were also added based on frequency of occurrence in previous surveys.

#### Sediment Grain Size Analysis

A total of 359 samples were analyzed for particle size distribution as part of the Bight '03 project. The City of Los Angeles Laboratory analyzed 112 samples using a Coulter LS230 instrument. The other 247 samples were analyzed by the City of San Diego Laboratory using an Horiba LA900 instrument. Both of these instruments are based upon light-scattering technology. The Horiba instrument can measure particles in the size range  $0.04-1019 \ \mu m$ . The Coulter instrument measures particles over the size range of  $0.04-2000 \ \mu m$ . Because the instruments have different measurement limitations for larger particles, all samples were screened through 1000  $\ \mu m$  and 2000  $\ \mu m$  sieves prior to analysis to ensure comparability of data among laboratories. The fraction of a sediment sample greater than 2000  $\ \mu m$  was designated as gravel.

Parameter	<b>CLAEMD</b> <sup>1</sup>		CSD <sup>1</sup>	LACSD <sup>1</sup>	OCSD <sup>1</sup>	SCCWRP <sup>1</sup>	Total No. Analyses <sup>1</sup>
Grain Size	112	0	247	0	0	0	359
Metals	45	114	138	27	35	0	359
PAH	45	144	108	27	35	0	359
PCBs/Pesticides	45	144	108	27	35	0	359
TOC/TN	0	0	141	0	0	218	359
Total No. Analyses per Lab	247	402	742	81	105	218	1795

Table II-2. The Distribution of Analyses and Number of Analyses Among Laboratories for the Bight '03 Sediment Chemistry Study.

<sup>1</sup>CLAEMD = City of Los Angeles; CRG = CRG Marine Laboratories; CSD = City of San Diego; LACSD = Sanitation Districts of Los Angeles County; OCSD = Orange County Sanitation District; SCCWRP = Southern California Coastal Water Research Project.

Frace Metals	PAHs	PCBs	Pesticides
Aluminum	Low Molecular Weight	PCB-18	4,4'-DDT
Antimony		PCB-28	2,4'-DDT
Arsenic	Acenaphthene	PCB-37	4,4'-DDD
Barium	Acenaphthylene	PCB-44	2,4'-DDD
Beryllium	Anthracene	PCB-49	4,4'-DDE
Cadmium	Biphenyl	PCB-52	2,4'-DDE
Chromium	Fluorene	PCB-66	alpha-Chlordane
Copper	2-Methylnapthalene	PCB-70	gamma-Chlordane
Iron	1-Methylphenanthrene	PCB-74	
Lead	Naphthalene	PCB-77	
Mercury	1-Methylnapthalene	PCB-81	
Nickel	2,6-Dimethylnaphthalene	PCB-87	
Selenium	1,6,7-Trimethyl-naphthalene	PCB-99	
Silver	Phenanthrene	PCB-101	
Zinc		PCB-105	
		PCB-110	
	High Molecular Weight	PCB-114	
		PCB-118	
	Benz[a]anthracene	PCB-119	
	Benzo[a]pyrene	PCB-123	
	Benzo[b]fluoranthene	PCB-126	Other Constituents
	Benzo[e]pyrene	PCB-128	Grain Size
	Benzo[g,h,i]perylene	PCB-138	TOC/TN
	Benzo[k]fluoranthene	PCB-149	
	Chrysene	PCB-151	
	Dibenz[a,h]anthracene	PCB-153	
	Fluoranthene	PCB-156	
	Indeno[1,2,3-c,d]pyrene	PCB-157	
	Perylene	PCB-158	
	Pyrene	PCB-167	
	, yrene	PCB-168	
		PCB-169	
		PCB-170	
		PCB-177	
		PCB-180	
		PCB-183	
		PCB-187	
		PCB-187	
		PCB-109 PCB-194	
		PCB-194 PCB-201	
		PCB-201 PCB-206	

Table II-3. Target analytes for the sediment chemistry component of the Bight '03 RegionalMonitoring Study.

#### Total Organic Carbon

All TOC and total nitrogen (TN) samples were performed by two laboratories, Southern California Coastal Water Research Project (SCCWRP) and the City of San Diego. The analyses were performed using a Carlo Erba 1108 CHN Elemental Analyzer. 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 the inorganic carbon. The acid-treated samples were again dried and weighed, and then crimped in a tin sample boat. Analytical grade acetanilide (99.95+%) was used for the external standard. Acetanilide and cyclohexanone-2,4-dinitrophenylhydrazone were used for periodic quality control (QC) checks. The PACS-1 marine sediment (National Research Council of Canada) was the certified reference material used for evaluating the 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 was 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), one reporting level spike, 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 roller table. 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.

#### Data Analysis

The sediment chemistry data from Bight '03 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 various sediment quality thresholds; and 3) comparison of sediment contamination extent to results from previous surveys. Several different thresholds were evaluated including an assessment of the fraction anthropogenically enriched, as well as empirically derived thresholds of potential biological impacts.

#### 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).

#### Estimating Sediment Contaminant Mass

The total mass of each constituent residing in the top 2 cm of sediment was calculated as follows:

$$Mass_{v} = AWM_{x} \times \delta \times A_{v} \times D \times CF$$

Where, AWM<sub>x</sub> is the area-weighted mean of constituent x in stratum y,  $\delta$  is the bulk density of the sediment (~1.5 g/cm<sup>3</sup>), A<sub>y</sub> is the area of stratum y, D is the depth of sample (2 cm), and CF is the cumulative unit conversion factor. The total mass for the SCB was calculated by summing the mass from all strata.

#### Estimation of Metal Background Concentrations

Metals occur naturally in sediments, and therefore total metals concentrations alone are not sufficient to determine the extent and degree of anthropogenic pollution. In order to determine the amount of anthropogenic metals pollution in the sediments, it is necessary to know the natural background concentrations of the target metal analytes in the samples. A reference element technique using iron facilitated the estimate of anthropogenic metal fraction (Schiff and Weisberg 1999). Iron is an extremely useful assessment tool on the mainland shelf where sediments are generally aerobic and iron mobilization is minimal. However, sediments in the deep ocean basins and in estuaries are frequently anaerobic resulting in reduction of iron, mobilization in pore waters and then oxidation at the sediment water interface where aerobic conditions return. This effectively concentrates iron in the surface sediment layers (i.e., top 2 cm) and invalidates the iron normalization technique. To account for this bias, we constrained our asessment of anthropogenic trace metal enrichment only to those sites with iron less than 6%, the limit of naturally abundant iron in previous regional surveys.

#### Comparison to Sediment Quality Guidelines

Two approaches were used in evaluating the potential for adverse biological impacts stemming from the observed levels of sediment contamination. The first approach, developed by Long *et al.* (1995), was used for assessing the areal extent of individual chemicals. The effects range low (ERL) and the effects range median (ERM) are empirically derived sediment quality guidelines based on relationships between observed biological responses and the measured concentrations of sediment contaminants (Table II-4). Based on a nationwide dataset, the ERL and ERM values correspond to the  $10^{th}$  and  $50^{th}$  percentiles of measured sediment concentrations in samples with significant biological response (i.e., toxicity). Concentrations below the ERL represent sediment quality that likely will not result in adverse biological effects. Concentrations above the ERM represent sediments that likely will result in adverse biological effects. However, the ERL and ERM values are based solely on coincidental occurrence, do not imply a cause-and-effect relationship between the observed toxicity and any individual contaminant, and are therefore subject to some level of prediction error (Long *et al.* 1995).

The second approach, developed by Long and MacDonald (1998), was used for assessing the areal extent of sediment contamination based on a composite of several constituents. In this approach, a sediment quality guideline (SQG) quotient is used where the mean quotient of sediment concentration and ERM is calculated (Table II-4). The use of mean SQG quotients accounts for the possible additive toxic effects of chemical mixtures in sediments and has been shown to improve predictive capability. The mean ERM quotient (ERMQ) was calculated as follows:

$$\mathbf{ERMQ} = \frac{1}{N} \sum_{x=1}^{N} \left( \frac{C_x}{\mathbf{ERM}_x} \right)$$

Where, N is the number of contaminants used in the evaluation, and  $C_x$  and  $ERM_x$  are the sediment concentration and ERM value for contaminant x, respectively. The mean ERM quotients were calculated for all sediment samples and each station in the SCB was then assigned to one of four possible levels of concern for either acute or chronic toxicity. Level I (ERMQ < 0.1) indicates a low risk of adverse biological impact. Level II (0.1 < ERMQ < 0.5) indicates a low to moderate risk of adverse biological impact. Level III (0.51 < ERMQ < 1.50) indicates a moderate to high risk of adverse biological impact. Level IV (1.51 < ERMQ) indicates a high risk of adverse biological impact.

Contaminant	ERL <sup>1</sup>	ERM <sup>1</sup>	ERMQ <sup>2</sup>
<u>Metals (mg/dry kg)</u>			
Arsenic	8.2	70	70
Cadmium	1.2	9.6	9.6
Chromium	81	370	370
Copper	34	270	270
Lead	46.7	218	218
Mercury	0.15	0.71	0.71
Nickel	20.9	51.6	51.6
Silver	1	3.7	3.7
Zinc	150	410	410
<u>Organics (μg/dry kg)</u>			
2-Methylnaphthalene	-	-	670
Acenaphthene	-	-	500
Acenaphthylene	-	-	640
Anthracene	-	-	1100
Benz(a)anthracene	-	-	1600
Benzo(a)pyrene	-	-	1600
Chrysene	-	-	2800
Dibenz(a,h)anthracene	-	-	260
Fluoranthene	-	-	5100
Fluorene	-	-	540
Naphthalene	-	-	2100
Phenanthrene	-	-	1500
Pyrene	-	-	2600
Total PAH	4022	44792	-
Total DDT	1.58	46.1	46.1
Total PCB	22.7	180	180
Total Chlordane	-	-	6

Table II-4. Sediment quality guideline values used for assessment of potential adverse biological impacts due to sediment contamination in this study.

<sup>1</sup> Long *et al.* 1995 <sup>2</sup> Long and MacDonald 1998

# 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 '03 QAP (Bight '03 Coastal Ecology Committee 2003).

#### **Reporting Limits**

To achieve study goals, minimum target reporting limits (RLs) for each analyte were set forth in the Bight '03 QAP (Table III-1). Overall, participant-specific minimum RLs were lower than the target RLs, indicating that the analyses performed provided adequate sensitivity. The few exceptions (ca. 3% of all analyses) were for high molecular weight PAH analytes reported by the City of San Diego (CSD). Even for these analyses, however, two-thirds were within 20% of the targeted RL. To ensure no data was lost or censured, all detectable concentrations falling between the method detection limit (ca. ten times lower than the RL) and RL for the CSD were reported.

#### 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

Three 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 '03 target list, there are certified values for 15 PAHs, 19 individual PCB congeners, and four chlorinated pesticides. For all of the SRM Bight '03 analytes, the laboratories were required to obtain concentrations within  $\pm$  40% of the certified or reference value for 3 out of 4 pesticides, 15 out of 19 PCB congeners, and 12 out of 15 PAHs. All five laboratories met this performance criterion for the analysis of SRM 1944 (Table III-2).

Two additional samples were collected off the coast of Southern California that were considered more realistic in terms of concentration ranges and potential for interefereces. The first 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

intercalibration exercise (Gossett *et al.* 2003). The second sample ("MRS032803") was collected very near the PV7C site in summer of 2003. Both reference samples were 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 and MRS032803 reference samples was  $\pm 40\%$  of the mean value for the participant group (n=5). This criterion was met for 27 of the possible 30 (90%) comparisons (Table III-3). All of the labs met the performance criteria for Total PAHs and PCBs for PV7C; only a single lab missed the target criteria and by less than 5% of its total concentration. This suggests that the QA/QC learned through the iterative intercalibration exercises in Bight '98 had now become standard laboratory practice at all of the agencies. What's more, when challenged with Total DDTanalysis from an entirely new sample (MRS032803), all of the laboratories met pre-ordained acceptability criteria for comparability.

#### Trace metals

A single certified reference material (CRM) consisting of dogfish (*Squalus acanthias*) muscle (DORM-2 from the National Research Council Canada) served as the intercalibration sample for trace metal analytes. 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 (Table III-4).

In addition, all participants were required to purchase two commercially available CRMs (CRM 16-050 Lot No. L516 and ERA 540). These CRMs were analyzed in conjunction with each sample batch by all participants during this study.

#### Performance-based QA/QC Goals and Success

The sample storage conditions and maximum hold time requirements and success achieved are summarized in Table III-5. Except for a very small percentage of samples (<5%) exceeding hold times for TOC and mercury, all participating labs performed their analyses within the specified holding times. Specifically for mercury, holding times were exceeded not because of any lack of quality, but simply because the wrong CRM was analyzed with the original batches so re-analysis was undertaken. A comparison of results was made for re-analysis of these samples made at 1 month, 7 months, and 20 months after collection (Figure III-1). Where detectable levels of mercury were measured, the results indicated that although the precision decreased with time, the relative percent difference (RPD) among the repeated analysis over 1 and one-half years was still within our duplicate sample criteria of  $\pm$  30%. Since none of these samples were measured more than 7 months after collection, these data were flagged in the study database, but were not eliminated from data analysis.

The remaining criteria and corresponding DQOs along with the degree of project success in attaining these goals are summarized in Table III-6. All 359 project samples delivered to the laboratories were analyzed and data reported (100% success) achieving our completeness DQO of 90%. The completeness of QA/QC data collection ranged from 93 to 100% for blanks, matrix spikes, and duplicate sample analysis of trace metals, PAHs, PCB congeners and pesticides. The

frequency of reporting level spikes was reduced to 28% (PAHs) and 72% (PCBs and pesticides) because some laboratories did not spike at these lower levels. Where these data were missing, data were flagged for QA/QC deviation, but not excluded from data analysis because no specific criteria for accuracy of RL spikes were prescribed in the QAP.

The success in achieving DQOs for accuracy of laboratory blanks ranged from 95% to 100% across all analyte classes. The corresponding success for accuracy of CRM analyses ranged from 94% to 100% across all analyte classes, whereas the success for accuracy and precision for trace metals in matrix spike samples were 94% and 97%, respectively. The success in achieving DQOs for precision of sample duplicate analysis for trace metals and PCB and pesticides were 95% and 93%, respectively. The success in achieving DQOs for precision of sample duplicate analysis for trace metals and PCB and pesticides were 95% and 93%, respectively. The success in achieving DQOs for precision of sample duplicate analysis for TOC was less than 90% (86%). The majority of samples that did not meet DQOs for precision of duplicate analysis were due to extremely low sample values that artificially inflated the RPD. If a minimum threshold for sample concentration were applied for evaluation of duplicate sample precision (i.e., five times the RL), then the frequency of success dramatically increased. Therefore, where the DQOs for precision of duplicate analysis were not met, data were flagged for QA/QC deviation, but not excluded from data analysis.

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.

In summary, the overall goal of the QA/QC effort to obtain a comparable and complete dataset was deemed successful, as indicated by the consistently high (> 90%) degree of success for each of the major QA/QC criteria (Table III-6). Thus, the collaborative, performance-based approach to QA/QC utilized for this study resulted in a sediment chemistry dataset of a similar high quality as that achieved several years earlier for the Bight '98 study (Noblet *et al.* 2002).

Analyte	CLA	CRG	CSD	LACSD	OCSD	Target RL
Metals (unit= mg/dry kg)						
Aluminum	200 - 50,000	5000	1150	10,000 - 100,000	27,000 - 270,000	
Antimony	20 - 1,000	100	130	300 - 30,000	ND - 100	10,000
Arsenic	10 - 500	100	330	250 - 25,000	170 - 1,700	1,600
Barium	10 - 500	100	1.8	1,000 - 10,000	ND - 600	
Beryllium	2 - 100	100	1.19	200 - 200	10 - 100	200
Cadmium	10 - 500	100	10.4	20 - 80,000	10 - 100	200
Chromium	10 - 500	100	16	3,000 - 3,000	130 - 5,200	16,000
Copper	10 - 500	100	27.8	3,000	150 - 6,000	7,000
Iron	100 - 250,000	5,000	750	200 - 200,000	10,000 - 100,000	
Lead	5 - 250	100	142	100 - 10,000	100 - 4,000	9,300
Mercury	20 - 20	25	3	30 - 60	2 - 90	30
Nickel	10 - 500	100	36.4	4,000	200 - 2,000	4,200
Selenium	20 - 1,000	100	240	250 - 25,000	140 - 1,400	1,000
Silver	10 - 500	100	12.9	25 - 50,000	10 - 100	200
Zinc	10 - 1,000	100	52.1	6,000	120 - 4,800	30,000
PAHs (unit= µg/dry kg)						
1,6,7-trimethylnaphthalene	50	5	21 - 21	50	2	50
1-methylnaphthalene	50	5	12 – 39	50	2	50
1-methylphenanthrene	50	5	40 – 41	50	2	50
2,6-dimethylnaphthalene	50	5	32 – 32	50	2	50
2-methylnaphthalene	50	5	12 – 12	50	2	50
Acenaphthene	50	5	28 – 28	50	2	50
Acenaphthylene	50	5	15 – 25	50	2	50
Anthracene	50	5	18 – 35	50	2	100

 Table III-1. Target reporting limits (RLs) by analyte and study participant.

Table III-1. (Cont.)

Analyte	CLA	CRG	CSD	LACSD	OCSD	Target RL <sup>1</sup>
PAHs continued (unit= µg/dry)	<u> </u>					
Benzo[a]anthracene	50	5	32 - 32	50	2	50
benzo[a]pyrene	50	5	55 – 55	50	2	50
benzo[b]fluoranthene	50	5	63 – 63	50	2	50
benzo[e]pyrene	50	5	57 – 57	50	2	100
benzo[ghi]perylene	100	5	56 – 56	100	2	50
benzo[k]fluoranthene	50	5	82 – 82	50	2	50
biphenyl	50	5	10 – 42	50	2	100
chrysene	50	5	36 – 36	50	2	50
dibenz[ah]anthracene	100	5	52 – 52	100	2	50
fluoranthene	50	5	24 – 24	50	2	50
fluorene	50	5	13 – 13	50	2	50
indoen(123-cd)pyrene	100	5	76 – 76	100	2	50
naphthalene	50	5	21 – 21	50	2	50
perylene	50	5	23 – 23	50	2	50
phenanthrene	50	5	21 – 37	50	2	50
pyrene	50	5	35 – 35	50	2	50
<u>CHCs (units = µg/dry kg)</u>						
PCB Congeners	7.5	5	0.03 – 3	7.5	0.1 – 1	7.5
2,4-DDD	1	5	0.10 – 6	1	0.1 – 1	1
2,4-DDE	1	5	0.10 – 6	1	0.1 – 1	1
2,4-DDT	1	5	0.10 – 4	1	0.01 - 0.1	1
4,4-DDD	1	5	0.08 - 4	1	0.1 – 1	1
4,4-DDE	1	5	0.11 - 4	1	0.1 – 1	1
4,4-DDT	1	5	0.20 – 11	1	0.1 – 1	1
alpha chlordane	1	5	0.14 - 6	1	0.1 – 1	1
gamma chlordane	1	5	0.20 - 4	1	0.1 – 1	1

<sup>1</sup> from B03 Quality Assurance Plan

Analyte	CSD	OCSD	CLA	LACSD	CRG	Certified	40%	40%
Anthracene	1380	1179	1190	1527	1377	1770	1062	2478
Benzo(a)anthracene	4680	4073	3570	4870	3410	4720	2832	6608
Benzo(a)pyrene	3570	3172	3000	4280	3523	4300	2580	6020
Benzo(b)fluoranthene	5470	3940	3800	6533	2170	3870	2322	5418
Benzo(e)pyrene	3250	3637	2130	4157	2433	3280	1968	4592
Benzo(g,h,i)perylene	3230	2441	1090	2883	2120	2840	1704	3976
Benzo(k)fluoranthene	2120	1345	3180	2480	1720	2300	1380	3220
Chrysene	5230	3798	4410	5520	4353	4860	2916	6804
Dibenz(a,h)anthracene	257	229	492	1037	584	424	254	594
Fluoranthene	7170	7384	6970	10180	7433	8920	5352	12488
Indeno(1,2,3-c,d)pyrene	2500	1984	1120	2393	2473	2780	1668	3892
Naphthalene	1420	1013	1100	1150	904	1650	990	2310
Perylene	1060	1065	742	910	844	1170	702	1638
Phenanthrene	5960	5257	4130	6400	4607	5270	3162	7378
Pyrene	12600	6984	6960	12233	7830	9700	5820	13580
Total PAH	59897	47501	43884	66553	45781	57854	34712	80996
# of analytes meeting DQO	14	13	13	13	13			
DQO Achieved for Total PAHs	yes	yes	yes	yes	yes			

Table III-2. Results of interlaboratory comparison exercise for PAH analytes (unit=  $\mu$ g/kg dry wt) in a marine sediment standard reference material (SRM 1944).

Data Quality Objective (DQO): 12 of 15 analytes within <u>+</u>40%

of certified values

Table III-3. Results of interlaboratory comparison exercise for total PAH, PCBs and chlorinated hydrocarbon (CHC) pesticides ( $\mu$ g/kg dry wt) in two reference sediment samples from the Palos Verdes Shelf (MRS032803 and PV7C).

Analyte	CSD	OCSD	CLA	LACSD	CRG	Mean	SD	с٧	40%	40%
Ref Sample								(%)	min	Max
Total PAHs										
MRS032803	999	1911	1385	1268	1194	1352	342.8	25.4	810.9	1892
PV7C	1048	1036	1926	1431	1726	1433	398.3	27.8	860.1	2007
Total PCBs										
MRS032803	677.5	959	1073	1432	876.9	1008	282.1	28.0	603.8	1409
PV7C	1015	920.4	1442	980.3	1197	1111	211.6	19.0	666.0	1555
Total DDTs										
MRS032803	8240	12689	13848	16774	11627	12636	3120	24.7	7581	17690
PV7C	7770	13393	14486	16662	15323	13527	3433	25.4	8116	18937

Analyte	CSD	OCSD	CLA	LACSD	CRG	Mean	Std	CV	30%	30%
							Dev	(%)	min	max
Ag	1.00	0.03	0.034		0.06	0.36	0.6	156.8	0.2	0.5
AI	22.40	5.17	ND		9.62	14	12.2	88.4	10	18
As	17.80	20.55	16.7	10.83	17.7	16.7	3.6	21.4	12	22
Ва	ND	ND	2.58	2.56	2.25	2.6	0.01	0.5	2	3
Ве	ND	ND	ND	ND	0.28	ND	ND	ND	ND	ND
Cd	0.02	0.05	0.03	0.05	ND	0.04	0.02	41.4	0.03	0.05
Cr	33.80	17.03	18.3	30.40	36.5	24.9	8.5	34.0	17	32
Cu	6.46	2.61	1.72	2.21	2.52	3.3	2.2	66.8	2	4
Fe	165	96.1	91.5	141	153	123	35.6	28.9	86	160
Hg	2.11	4.45	2.33	3.94	3.85	3.2	1.2	36.2	2.2	4.2
Ni	18.20	8.96	9.6	19.19	17.8	14.8	5.0	34.1	10	19
Pb	0.14	0.11	ND	ND	0.06	0.1	0.0	15.6	0	0
Sb	ND	ND	0.164	ND	0.2	0.2	na	na	0.1	0.2
Se	1.49	2.00	1.74	0.95	1.25	1.5	0.4	27.7	1.0	1.9
Zn	25.10	27.77	21.9	21.22	24.1	24.0	3.0	12.6	17	31
# of Analytes Meeting DQO	12	13	15	13	14	15				
DQO Achieved	yes	yes	yes	yes	yes	yes				

Table III-4. Results of interlaboratory comparison exercise for trace metals (mg/kg dry wt) in a dogfish muscle (*Squalus acanthias*) certified reference material (DORM-2). Laboratories needed to achieve the DQO for 12 of 15 metals are needed to pass the intercalibration. ND = not detected.

Table III-5. Achievement of sample storage conditions and holding time criteria.

Parameter	Storage Conditions	Maximum Hold Time <sup>1</sup>	Actual Hold Time (days)	Success
Grain Size	Cold (4°C)	6 months	17-131	100%
TOC/TN	Frozen (-20°C)	6 months	9-238	99%
Trace Metals	Frozen (-20°C)	1 year	10-348	100%
Hg		6 months	15-244	96%
Trace Organics	Frozen (-20°C)	1 year		
PAHs			4-338	100%
PCBs			0-324	100%
Pesticides			0-324	100%

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

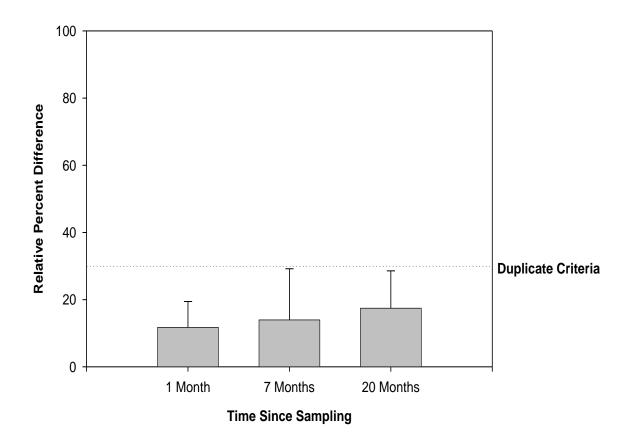


Figure III-1. Relative percent difference among duplicate analysis of total mercury from the same samples at one, seven and twenty months after sampling. The performance criterion for duplicate sample analysis of samples collected less than 6 months after sampling is 30% RPD.

	Metals		PAH	РАН		eners ides	тос	
Quality Control Parameter	DQO	Success	DQO	Success	DQO	Success	DQO	Success
<u>Completeness</u> <u>Blanks</u>	90%	100%	90%	100%	90%	100%	90%	100%
Frequency	1/batch	93%	1/batch	97%	1/batch	100%	1/batch	100%
Accuracy CRM <sup>1</sup>	< MDL OR < 5% of sample result	95%	< RL	99%	< RL	100%	< RL	100%
Frequency	1/batch	100%	1/batch	100%	1/batch	82%	1/batch	100%
Accuracy	within specified limits	94%	Within ± 40% of certified value for 80% of analytes	97%	Within ± 40% of certified value for 80% of analytes	96%	Within ± 20% of certified value	100%
<u>Matrix Spikes</u> Frequency	10% of total samples	93%	1/batch	97%	Not Required		Not Required	
Accuracy	Within ± 30% of true value	94%	N/A <sup>3</sup>		Not Required		Not Required	
Precision <sup>2</sup>	Within ± 30% RPD <sup>2</sup>	97%	N/A <sup>3</sup>		Not Required		Not Required	
<u>Reporting Level</u> Spikes								
Frequency	Not Required		1/batch	28%	1/batch	72%	Not Required	
Accuracy <u>Sample</u> Duplicates	Not Required		N/A <sup>3</sup>		N/A <sup>4</sup>		Not Required	
Frequency	10% of total samples <sup>2</sup>	93%	Not Required		1/batch	100%	1/batch	62%
Precision	Within ± 30% RPD	95%	Not Required		RPD < 30%	93%	RPD < 30%	86%

Table III-6. Summary of performance-based QC criteria and project success in performing within those criteria.

<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

# 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 (Appendix D). Grain size ranged from very fine (100% silt and clay) to very coarse (100% sand and gravel). On average, Bight '03 sediments were fined grained with approximately 75% silt and clay content. The TOC and TN measurements varied three orders of magnitude, from 0.004% to over 7% TOC. On average, Bight '03 sediments contained approximately 2% TOC with a 10:1 TOC/TN ratio. Six metals were detectable in 100% of the samples (Al, Ba, Cr, Cu, Fe, Zn). All but three of the metals (Sb, Se, Ag) were detectable at the 10<sup>th</sup> percentile. All of the trace metals ranged between one and three orders of magnitude with the largest relative range observed for lead. Area weighted average (+ standard deviation) concentrations among the different metals varied from a low of 0.11 + 0.02 mg/kg for mercury to a high of 26400 + 1780mg/kg for iron. Organic constituents were detectable in 8, 25, 46, and 56% of the samples for chlordane, total PCB, total DDT, and total PAH, respectively. Area weighted averages for the organic analyte classes ranged from a low of 0.03 + 0.03 ug/kg for chlordanes to a high of 343 + 72.6 ug/kg for PAHs. Total DDTs averaged 20+17 ug/kg while the area weighted mean for PCBs was an order of magnitude lower (2.5+2.7 mg/kg).

#### **Subpopulation Comparisons**

Area weighted mean (AWM) concentrations and their corresponding 95% confidence intervals (CI) for the 12 subpopulations of interest are presented in Table IV-2. Overall, the embayment (marinas, ports/bays/harbors) and LA estuary stratum exhibited the highest trace metal concentrations. The AWM concentrations were two to five times lower for non-LA estuaries as well as in the remaining non-embayment strata (Shelf, Slope & Basin, POTW outfalls and the Channel Islands). Sediments near large POTW outfalls remain the most contaminated with respect to DDT followed by the upper Slope & Basin, LA estuaries, middle Shelf, ports/bays/harbors and marinas. AWM concentrations for the Channel Islands were universally low in comparison, with the exception of PAHs.

For the Shelf and Slope & Basin strata, a clear enrichment in sediment fines and macronutrient content (TOC and TN) was evident along the depth gradient (Table IV-2). Mean sediment fine content increased from 31% at the shallowest depth zone (inner Shelf) to a maximum of 92% 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. In contrast, the chlorinated hydrocarbon analytes (DDTs, PCBs and chlordanes) did not show universal enrichment with sediment fines (and thus depth). Rather, DDT was most elevated in the upper Slope & Basin region (200-500 m) followed by the middle Shelf (30-120 m) region. PAHs, on the other hand, increased in mean concentration in concert with trace metals (i.e., with sediment fines and depth).

Marinas and LA estuaries consistently exhibited the highest mean concentrations for trace metal and organic analytes (Table IV-2). For example, copper was highest in marinas followed by ports/bays/harbors and LA estuaries. Mercury was eight fold higher on average in marinas than in non-LA estuaries. Other metals with a history of anthropogenic input (i.e., lead, silver and zinc) followed similar trends. Trace organics in sediments from LA estuaries were the highest on average, while those in non-LA estuaries were lowest. The relatively low values for non-LA estuaries held true for most, if not all, trace metal analytes also. These trends held true in the absence of obvious influences due to sediment texture and/or TOC/TN.

Trace metal and organic analytes were higher, on average, for large POTW outfall compared to small POTW sediments (Table IV-2). In some cases, the difference was large (e.g., a 260-fold difference in DDT), but for most trace metals the differences were much less (e.g., 2.8 times higher for mercury). Grain size was not substantially different among large and small POTW strata. However, TOC was higher for the large POTW compared to small POTW sediments ( $0.83\pm0.22\%$  vs.  $0.54\pm0.16\%$ ). Lastly, mean concentrations of trace metals and organics in Channel Island samples were lower and/or did not appear substantially different from other strata with the exception of total PAH ( $338\pm69.6 \mu g/kg$ ).

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

The geographic distribution and magnitude of the sediment analytical parameters in the SCB are presented in the series of maps in Appendix B. These maps show the location of each station and the associated concentration ranges for the principal target analytes measured for the Bight '03 Survey.

#### Grain Size, Total Organic Carbon, and Total Nitrogen

The geographical distribution for percent fines (<63 µm) is shown in Fig. IV-1; those for TOC and TN are shown in Appendix B. Percent fines increased with depth for the Shelf and Slope & Basin stations (Table IV-2), with an average of 92% ( $\pm$ 1.5%) fines for sediments in the deepest stratum (lower Slope & Basin). The embayment strata contained intermediate levels of fines, ranging from 41±11% for non-LA estuaries to 72±7.0% for marinas. POTW outfall, Channel Islands and inner Shelf sediments contained the lowest amount of sediment fines on average (32-41%). TOC and TN appear to follow the same pattern as percent fines with the exception of Channel Islands sediments (TOC=2.0±0.58%; TN=0.1±0.02%), which appear to be organically enriched relative to their mean grain size (32±6.3%).

#### Trace Metals

The geographical distribution for all trace metal analytes can be found in Appendix B. In general, the trace metals concentrations appear to correlate well with grain size as measured by percent fines; this is particularly evident for the Shelf and Slope & Basin strata (Table IV-2). For the embayment strata, metals appear to be enriched for LA estuaries, marinas and, to a lesser extent, for ports/bays/harbors. Mercury and copper in particular were highest in marinas. Trace metals were highest in large POTW sediments and with few exceptions (antimony, nickel) lowest in Channel Island sediments. As an example of these general trends for anthropogenically enriched metals (copper, lead, silver, zinc), the geographical distribution of

copper is shown in Fig. IV-2. In contrast, the relatively high levels of antimony and nickel in Channel Island sediments suggest their natural high abundance.

## Trace Organics

The results for the trace organic analytes are shown in Appendix B. Chlordanes were at or below RLs for 8 out of 359 stations analyzed. Where detectable, chlordanes appeared to be largely associated with the heavily industrialized/urbanized embayment strata (LA estuaries, marinas) and also with the large POTW outfalls. Total DDT were the predominant organic contaminants throughout the SCB in contrast to the rarely detectable chlordanes. Total DDTs were measured at 164 out of the 359 stations. Similar to that reported by Schiff (2000), the highest levels of DDTs remained clustered in the central coastal zone of the SCB, centered around the Palos Verdes Peninsula. Notably high levels of DDTs remained in sediments from LA/LB Harbor, but unlike for copper, elevated DDTs were generally not found in San Diego Bay (Fig. IV-4). It is also interesting to note that the upper Slope & Basin stratum (200-500 m) exhibited the highest mean DDTs ( $88\pm25 \mu g/kg$ ) for the deeper water subpopulations.

The highest concentrations of PAHs were overwhelmingly associated with the embayment strata (e.g., LA estuaries > ports/bays/harbors > marinas > non-LA estuaries). Lesser, but detectable concentrations of PAHs were found in most of the Shelf and Slope & Basin stations, as well as in both small and large POTW outfalls. Of particular interest was the relatively high AWM total PAHs observed for the Channel Islands (338+69.6 µg/kg) and lower Slope & Basin (580+113 µg/kg) strata. Previous investigators have utilized specific diagnostic ratios of PAH compounds to determine the degree of petrogenic vs. pyrogenic influence in a given bedded sediment sample. For example, the relative ratio of the alkylated compound 1-methylphenanthrene to its parent homolog phenanthrene is indicative of their origin and/or state of weathering (Blumer & Youngblood, 1975). Moreover, the relative distribution of low vs. high molecular weight PAH homologs (see Table IV-3) also is suggestive of petroleum vs. combustion signatures in environmental PAH residues (Prahl and Carpenter 1983; Farrington et al. 1983). When tabulated by stratum, it appears that the Channel Islands and lower Slope & Basin strata both demonstrate more petroleum and/or less weathering influence compared with the more combustion like signatures found in strata such as the Large POTWs, marinas, and estuaries (1-MP/PHEN and LPAH/HPAH < 1; Table IV-3). The occurrence of petrogenic-like PAH signatures for strata such as the Channel Islands may be due, in part, to the proximity of offshore crude oil production platforms in the Santa Barbara Channel and the colder, deep water environment, which is likely to be less conducive to PAH weathering (degradation and selective dissolution).

The highest sediment concentrations of total PCBs were found in the LA estuaries  $(66\pm3.75 \ \mu g/kg)$  followed by large POTW outfall sediments. Within these strata, the highest levels of PCBs were found on the Palos Verdes Shelf and in LA/LB Harbor. Levels in Shelf and Slope & Basin sediments were not particularly elevated, but did increase with depth in a fashion similar to that for percent fines, TOC, PAHs, and most metals. Average total PCB concentrations for the small POTW outfalls, Channel Islands, inner shelf and lower basin strata were at/near detection limits (0.13-0.28  $\mu g/kg$ ).

Chemical Group (units in dry wt)	Area Weighted Mean	95% CI	Min	10th Percentile	Median	90th Percentile	Max
Fines %	73	4.3	0.00	23	86	96	100
TOC %	2.3	0.16	0.004	0.42	2.3	4.2	7.6
TN%	0.23	0.03	0.004	0.03	0.2	0.4	2.1
Aluminum (mg/kg)	17224	886	809	6373	18500	24600	54900
Anitmony (mg/kg)	0.62	0.11	<rl< td=""><td><rl< td=""><td>0.24</td><td>0.97</td><td>4.8</td></rl<></td></rl<>	<rl< td=""><td>0.24</td><td>0.97</td><td>4.8</td></rl<>	0.24	0.97	4.8
Arsenic (mg/kg)	5.7	0.61	<rl< td=""><td>2.3</td><td>4.8</td><td>9.8</td><td>33</td></rl<>	2.3	4.8	9.8	33
Barium (mg/kg)	220	22	1.7	48	182	433	3630
Beryllium (mg/kg)	0.71	0.13	<rl< td=""><td>0.14</td><td>0.61</td><td>0.91</td><td>8.8</td></rl<>	0.14	0.61	0.91	8.8
Cadmium (mg/kg)	1.1	0.13	<rl< td=""><td>0.20</td><td>0.97</td><td>2.0</td><td>6.6</td></rl<>	0.20	0.97	2.0	6.6
Chromium (mg/kg)	62	11	2.8	21	55	94	410
Copper (mg/kg)	24	1.5	0.42	5.5	24	42	362
lron (mg/kg)	26436	1775	2440	11000	28500	33100	13100
Lead (mg/kg)	11	1.0	<rl< td=""><td>3.9</td><td>9.9</td><td>22</td><td>720</td></rl<>	3.9	9.9	22	720
Mercury (mg/kg)	0.11	0.02	<rl< td=""><td>0.02</td><td>0.07</td><td>0.28</td><td>2.1</td></rl<>	0.02	0.07	0.28	2.1
Nickel (mg/kg)	31	2.1	<rl< td=""><td>8.7</td><td>32</td><td>52</td><td>75.1</td></rl<>	8.7	32	52	75.1
Selenium (mg/kg)	2.1	0.22	<rl< td=""><td><rl< td=""><td>1.6</td><td>4.0</td><td>8.1</td></rl<></td></rl<>	<rl< td=""><td>1.6</td><td>4.0</td><td>8.1</td></rl<>	1.6	4.0	8.1
Silver (mg/kg)	0.38	0.07	<rl< td=""><td><rl< td=""><td>0.16</td><td>0.82</td><td>7.4</td></rl<></td></rl<>	<rl< td=""><td>0.16</td><td>0.82</td><td>7.4</td></rl<>	0.16	0.82	7.4
Zinc (mg/kg)	81	3.2	2.6	29	89	119	822
Total DDT (μg/kg)	20	17	<rl< td=""><td><rl< td=""><td>2.4</td><td>45</td><td>3955</td></rl<></td></rl<>	<rl< td=""><td>2.4</td><td>45</td><td>3955</td></rl<>	2.4	45	3955
Total PCB (μg/kg)	2.5	2.7	<rl< td=""><td><rl< td=""><td><rl< td=""><td>1.1</td><td>713</td></rl<></td></rl<></td></rl<>	<rl< td=""><td><rl< td=""><td>1.1</td><td>713</td></rl<></td></rl<>	<rl< td=""><td>1.1</td><td>713</td></rl<>	1.1	713
Chlordanes (µg/kg)	0.03	0.03	<rl< td=""><td><rl< td=""><td><rl< td=""><td><rl< td=""><td>153</td></rl<></td></rl<></td></rl<></td></rl<>	<rl< td=""><td><rl< td=""><td><rl< td=""><td>153</td></rl<></td></rl<></td></rl<>	<rl< td=""><td><rl< td=""><td>153</td></rl<></td></rl<>	<rl< td=""><td>153</td></rl<>	153
Total PAH (μg/kg)	342.9	72.6	<rl< td=""><td>3.5</td><td>240</td><td>799</td><td>10333</td></rl<>	3.5	240	799	10333

Table IV-1. Area weighted means and selected ranges of the sediment chemistry data for the entire Southern California Bight in the summer of 2003.

			SH		SLOPE (	& BASIN				
	Inner (	5-30 m)	Mid (30	)-120 m)		iter 200 m)		per 500 m)		wer 000 m)
Parameter	Mean	95%CI	Mean	95%Cl	Mean	95%CI	Mean	95%Cl	Mean	, 95%C
Fines %	31	9.2	45	8.4	59	6.4	79	6.9	92	1.5
TOC %	0.27	0.08	0.75	0.19	1.0	0.19	1.9	0.29	3.3	0.30
TN %	0.03	0.01	0.05	0.01	0.1	0.02	0.2	0.04	0.35	0.03
Aluminum (mg/kg)	9212	2233	13165	3651	11693	2072	17359	2168	21770	1293
Antimony (mg/kg)	0.14	0.04	0.10	0.05	0.08	0.04	0.20	0.10	0.68	0.23
Arsenic (mg/kg)	4.2	1.2	4.1	1.1	6.1	2.2	6.1	1.3	6.5	1.1
Barium (mg/kg)	99	26	153	70	113	18.1	168	30	306	39
Beryllium (mg/kg)	0.47	0.22	0.62	0.44	0.58	0.20	1.1	0.58	0.66	0.06
Cadmium (mg/kg)	0.20	0.06	0.36	0.11	0.54	0.11	1.4	0.49	1.3	0.18
Chromium (mg/kg)	27	6.8	36	8.0	38	8.1	61	15	82	21
Copper (mg/kg)	6.6	1.8	12	2.1	15	5.8	19	2.5	34	2.8
lron (mg/kg)	12952	2784	19511	4219	27590	8546	28760	2885	31782	3238
Lead (mg/kg)	4.7	1.1	7.4	1.5	8.3	1.2	11	1.6	15	2.0
Mercury (mg/kg)	0.03	0.01	0.10	0.03	0.10	0.07	0.09	0.03	0.13	0.03
Nickel (mg/kg)	13	3.8	14	3.7	18	2.4	29	4.2	44	3.9
Selenium (mg/kg)	0.69	0.22	1.2	0.43	0.82	0.37	1.3	0.31	2.8	0.43
Silver (mg/kg)	0.13	0.06	0.11	0.06	0.35	0.31	0.24	0.13	0.46	0.13
Zinc (mg/kg)	34	7.8	47	8.4	55	5.7	82	9.3	107	4.8
Total DDT (μg/kg)	2.3	0.40	36	6.3	11	2.3	88	25	19	2.5
Total PCB (μg/kg)	0.24	0.01	2.4	0.13	4.6	0.27	7.6	0.44	0.28	0.02
Total PAH (μg/kg) Total	51.2	44.9	60.3	43.3	68.6	40.6	75.3	56.2	579.5	112.9
Chlordane(µg/kg)	0.01	0.01	0.02	0.03	0.0	0.0	0.08	0.13	0.0	0.0

Table IV-2. Area-weighted means and associated 95% confidence intervals (CIs) for selected geographic subpopulations of the sediment chemistry data from the Bight '03 Study.

#### Table IV-2 (cont.)

	Mar	inas	Estu	aries	LA Est	tuaries	Ports/Ba	ys/Harbo
Parameter	Mean	95%CI	Mean	95%CI	Mean	95%CI	Mean	95%C
Fines %	72	7.0	53	12	41	11	68	9.0
TOC %	1.6	0.36	1.1	0.40	1.6	0.58	1.3	0.24
TN %	0.2	0.5	0.02	0.06	0.1	0.04	0.1	0.02
Aluminum (mg/kg)	22203	3083	23182	5450	11473	3149	23761	3273
Antimony (mg/kg)	0.38	0.09	0.28	0.06	0.94	0.34	0.11	0.14
Arsenic (mg/kg)	7.3	1.13	5.8	1.4	5.0	1.4	4.3	1.2
Barium (mg/kg)	111	22	95	21	84	23	109	21
Beryllium (mg/kg)	0.64	0.13	0.67	0.16	0.40	0.12	0.21	0.08
Cadmium (mg/kg)	0.65	0.18	0.57	0.23	0.92	0.37	0.86	0.32
Chromium (mg/kg)	48	8.7	33	7.0	47	21	39	5.8
Copper (mg/kg)	116	30	28	7.7	55	21	70	19
lron (mg/kg)	27761	3449	22150	4707	17034	3830	30254	4063
Lead (mg/kg)	43	12	19	8.1	68	37	29	8.5
Mercury (mg/kg)	0.42	0.17	0.05	0.02	0.14	0.05	0.28	0.10
Nickel (mg/kg)	20	3.9	14	3.0	19	5.0	18	3.7
Selenium (mg/kg)	1.3	0.58	1.5	0.45	0.77	0.25	2.7	0.98
Silver (mg/kg)	0.73	0.55	0.33	0.08	0.78	0.33	0.20	0.27
Zinc (mg/kg)	183	29	94	26	190	69	128	24
Total DDT (μg/kg)	21	3.1	8.8	1.7	78	12	25	3.8
Total PCB (μg/kg)	11	0.57	2.7	0.20	66	3.75	7.7	0.44
Total PAH (μg/kg)	796.0	428.9	192.5	91.4	2168.3	971.7	1229.4	653.0
TotalChlordane(µg/kg)	1.2	0.98	0.08	0.14	11	7.9	0.14	0.26

#### Table IV-2 (cont.)

	Small POT	W Outfalls	Large POT	W Outfalls	Channel Islan	ds (30-120 m)
Parameter	Mean	95%CI	Mean	95%CI	Mean	95%CI
Fines %	40	9.2	38	6.5	32	6.3
TOC %	0.54	0.16	0.83	0.22	2.0	0.58
TN %	0.05	0.02	0.08	0.04	0.1	0.02
Aluminum (mg/kg)	13244	3585	10519	1662	5439	730
Antimony (mg/kg)	0.15	0.02	0.03	0.02	0.27	0.06
Arsenic (mg/kg)	4.6	0.67	3.2	0.69	3.2	.34
Barium (mg/kg)	84	15	351	235	75	20
Beryllium (mg/kg)	0.35	0.07	0.64	0.38	0.22	0.03
Cadmium (mg/kg)	0.22	0.05	0.76	0.32	0.76	0.14
Chromium (mg/kg)	27	5.6	37	9.3	27	4.4
Copper (mg/kg)	9.0	2.5	20	4.9	6.6	0.97
Iron (mg/kg)	16255	3655	15228	1767	11473	1482
Lead (mg/kg)	4.9	0.81	9.2	2.0	4.8	0.62
Mercury (mg/kg)	0.05	0.03	0.14	0.05	0.02	0.003
Nickel (mg/kg)	11	2.0	10	2.1	13	1.7
Selenium (mg/kg)	0.55	0.12	0.98	0.37	0.45	0.13
Silver (mg/kg)	0.14	0.06	0.39	0.21	0.06	0.03
Zinc (mg/kg)	40	8.0	51	11	30	3.4
Total DDT (μg/kg)	1.2	0.18	316	52	1.6	0.23
Total PCB (μg/kg)	0.13	.01	29	1.5	0.24	0.02
Total PAH (μg/kg)	24.9	8.7	117.7	51.5	337.8	69.6
TotalChlordane(µg/kg)	0.0	0.0	0.50	0.61	0.0	0.0



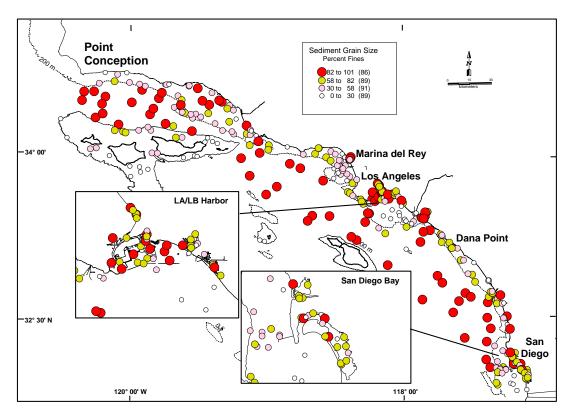


Figure IV-1. Geographical distribution of sediment grain size (as percent fines < 63  $\mu$ m) during the 2003 Southern California Bight regional monitoring survey.



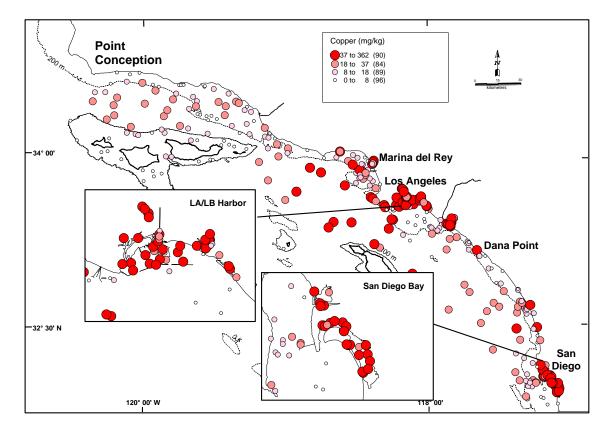


Figure IV-2. Geographical distribution of copper concentrations in sediment during the 2003 Southern California Bight regional monitoring survey.



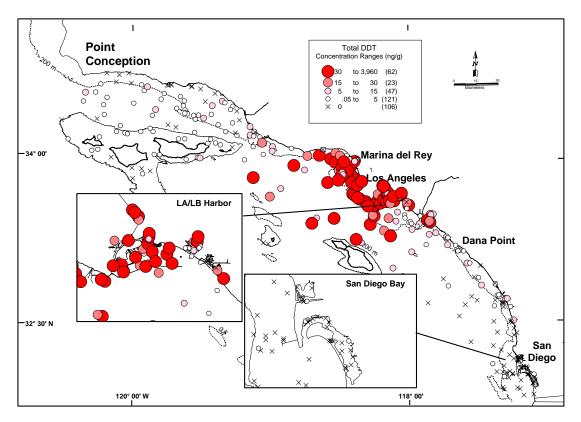


Figure IV-3. Geographical distribution of total DDT concentrations in sediment during the 2003 Southern California Bight regional monitoring.

Stratum	n	∑PAH	1-MP/PHEN	LPAH/HPAH
Inner Shelf	7	51.2 <u>+</u> 44.9	2.34 <u>+</u> 0.18	6.84 <u>+</u> 9.39
Mid Shelf	17	60.3 <u>+</u> 43.3	1.00 <u>+</u> 0.62	1.56 <u>+</u> 2.76
Outer Shelf	8	68.6 <u>+</u> 40.6	1.52 <u>+</u> 0.24	2.55 <u>+</u> 3.17
Upper Slope	7	75.3 <u>+</u> 56.2	1.05 <u>+</u> 1.25	1.99 <u>+</u> 2.13
Lower Slope & Basin	31	580 <u>+</u> 113	2.05 <u>+</u> 0.82	6.93 <u>+</u> 4.89
Ports/Bays/Harbors	28	1230 <u>+</u> 653	1.27 <u>+</u> 0.69	0.81 <u>+</u> 2.05
Marinas	22	796 <u>+</u> 429	0.63 <u>+</u> 0.65	0.59 <u>+</u> 0.95
LA Estuaries	12	2170 <u>+</u> 972	1.00 <u>+</u> 0.90	2.41 <u>+</u> 3.25
Large POTWs	27	118 <u>+</u> 51.5	0.93 <u>+</u> 1.10	0.80 <u>+</u> 1.18
Small POTWs	8	24.9 <u>+</u> 8.7	0.06 <u>+</u> 0.00	0.32 <u>+</u> 0.12
Channel Islands	30	338 <u>+</u> 69.6	2.37 <u>+</u> 1.28	8.65 <u>+</u> 6.12

### Table IV-3. PAH diagnostic ratios<sup>1</sup> by stratum (mean<u>+</u>sd).

 $^{1}\Sigma$ PAH = area weighted mean concentration of total PAHs (µg/kg dry wt). 1-MP/PHEN = ratio of AWM concentrations for 1-methylphenanthrene (1-MP) and phenanthrene (PHEN).

LPAH/HPAH = ratio of AWM concentrations for low molecular weight PAH (sum of 12 compounds with < 4 rings; Table II-3) and high molecular weight PAH (sum of 12 compounds with > 4 rings; Table II-3)

### V. ASSESSMENT RESULTS

#### **Relative Distribution of Contaminant Mass**

The proportion of the total area and the total mass for each constituent in each stratum are shown in Table V-1. The greatest mass of sediment constituents was observed in the deep ocean stratum of the upper Slope and lower Slope & Basin. On average, 77% of the total constituent mass in the surficial sediments of the SCB was found in these two strata that occur depths greater than 200m. The amount of mass in the upper Slope and lower Slope & Basin strata varied from 71% (Al) to 86% (Cd, Ni, Ag, total PAH). Generally, there was a greater mass in the lower Slope & Basin (500-1000 m depth) than in the upper slope (200-500 m depth). However, the upper Slope did have a greater mass of total DDT, total PCB, and chlordanes than the lower Slope & Basin stratum.

Wherever the percent of mass of a given constituent exceeds the percent of area for a given stratum, there was a disproportionate amount of that constituent in that stratum (Table V-1). In general, trace metals were disproportionately concentrated within the lower Slope & Basin. For certain metals (e.g., copper, lead and mercury), disproportionately high mass was observed for marinas and ports/bays/harbors.

Total mass for each of the four trace organic analyte classes was disproportionally found in LA estuaries. Large POTWs, marinas, ports/bays/harbors and the upper Slope & Basin strata had disproportionately high masses for three of the four organic analyte classes. It is noteworthy that total DDT and chlordanes were highly enriched in terms of mass/area for the large POTW stratum. Although these outfalls were evaluated together, the vast majority of the contamination was associated with the City of Los Angeles Hyperion and the County of Los Angeles Joint Water Pollution Control Plant outfalls. Moreover, the high levels of contaminants measured near the outfalls are of historical origin and do not reflect recent inputs (Zeng *et al.* 2001).

Total mass to area ratios for all four classes of trace organic analytes and all 15 trace metals was approximately 1:1, or less, in the small POTW, inner Shelf and the Channel Islands strata. This ratio indicates that pollutants were not disproportionately accumulating in these strata.

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

A summary of SCB percent area exceeding four thresholds of increasing concern is presented in Table V-2. The four thresholds for selected individual sediment parameters include analytical detection limits, anthropogenic enrichment, ERL, and ERM. Anthropogenic enrichment for trace metals was assessed utilizing an iron-normalization approach, while any detectable concentration of pesticides (which are manmade) represented enrichment. There is no tool for assessing anthropogenic PAH enrichment. Sediment concentrations below the ERL indicate levels where adverse biological impacts are unlikely and concentrations above the ERM indicate levels where adverse biological impacts are likely.

Approximately 94% of the areal extent in SCB sediments was enriched by at least one sediment contaminant (Table V-2). Eighty eight percent of the SCB was enriched by at least one

trace metal. Twenty percent or less of the SCB was enriched by arsenic, nickel, or lead. Twenty to 50% of the SCB was enriched by chromium, copper, silver, or zinc. Cadmium was the metal with the greatest bightwide enrichment at 82%. Seventy one percent of the SCB was enriched by at least one organic constituent. Total DDT was the most widespread organic constituent enriching SCB sediment; all sites that had organic enrichment were enriched with total DDT. Total PCB and chlordanes were enriched in 13% and 4% of SCB sediments, respectively.

Another approach to the evaluation of the sediment chemistry data is to determine the degree of anthropogenic contamination at each station in the study area. Pollutants are usually emitted from the various anthropogenic sources as complex mixtures containing multiple chemical species. Therefore, the degree of anthropogenic contamination at a given site can be determined by the number of organic and inorganic pollutants that are co-occurring. Such an analysis was performed and the results are presented in Figure V-1. For this analysis, consideration was limited to the eight metals for which iron-normalized background regression curves were developed, and three groups of organic target analytes (total chlordanes, total DDT, and total PCB), for a total of 11 possible "contaminants." The number of anthropogenically enriched parameters per station ranged from zero to 11. The sites with the greatest number of enriched contaminants occurred near Los Angeles with the maximum number of enriched contaminants occurring predominantly in LA Estuaries.

An estimated 87% of the SCB sediments exceeded the ERL for at least one constituent (Table V-2). Seventy six percent of the SCB exceeded the ERL for at least one trace metal. Sixty percent of the SCB exceeded the ERL for at least one organic constituent. Relative to the ERL, nickel and total DDT were the most widespread trace metal and organic contaminants with more than 60% of the Bight above their respective ERL. More than 10% of the SCB sediment was above the ERL for cadmium, copper, mercury, nickel, and total DDTs.

Approximately 20% of the SCB sediments exceeded the ERM for at least one consitutent (Table V-2). Thirteen percent of the SCB exceeded the ERM for at least one trace metal. Nine percent of the SCB exceeded the ERM for at least one organic constituent. Most of the trace metal exceedence was due to nickel (12%) followed by chromium (2%). Virtually all of the organic exceedence of the ERM was due to total DDT (9%).

#### **Subpopulation Comparisons**

Estimates of areal exceedances of ERLs and ERMs by stratum were assessed for metals, organics and both together, respectively. ERM exceedances for metals were highest (~20%) for the lower Slope & Basin and marinas; the corresponding values for LA estuaries and ports/bays/harbors was ~10% (Fig. V-2). ERM exceedances for organics were more geographically widespread but of the same order of magnitude (10-20%) (Fig. V-3). The highest percent area for ERM exceedance was for large POTW outfalls. Taken together, ERM exceedances approached 40% for large outfalls and marinas; with other embayment strata (LA estuaries, ports/bays/harbors) and the lower Slope & Basin ranging between 20-35% (Fig. V-4). More than half of the area for the inner Shelf, small POTW outfalls and Channel Islands strata did not exceed either ERL or ERM.

Comparisons of the percent of area exceeding ERL and ERM values for individual parameters among the various Bight '98 station subpopulations are presented in Table V-3. The results of the subpopulation comparisons are consistent with the results of the other analyses. Overall, the general trend in the Bight by stratum for ERM areal exceedances was large POTW outfalls (39%) > Marinas (38%) > lower Slope & Basin (33%) > ports/bays/harbors (29%) > LA estuaries (23%) > mid-Shelf (16%) > non-LA estuaries (7.9%) > outer Shelf (7.4%) > upper Slope & Basin (3.6%). None of the area associated with the remaining three strata - small POTW outfalls, Channel Islands and inner Shelf - exceeded ERM values for the 12 classes of contaminants assessed (Table V-3). The majority of ERM exceedances by area were due to DDTs, with the exception of the lower Slope & Basin (nickel accounted for 24%); and Marinas (mercury accounted for 22%). In addition to nickel and mercury, copper, silver and zinc also contributed to areal ERM exceedances in Marina, LA estuaries, ports/bays/harbors and the outer Shelf subpopulations. Other than DDT, PCBs were the only other class of organics that contributed to ERM areal exceedances (LA estuaries, large POTW outfalls and upper Slope & Basin). Of the new strata evaluated in 2003, the ERM areal exceedance for DDTs of 12% for the lower Slope & Basin was unexpectedly high (Table V-3), whereas the elevated nickel may signifiv a naturally occurring condition for these fine-grained sediments.

The areal extent of the SCB that exceeded the ERL ranged between 37 and 100 percent for the inner Shelf and the two Slope & Basin strata, respectively. The 100 percent exceedance for the latter strata was due to DDTs, nickel and cadmium (both naturally occurring metals). Copper was a significant areal contributor to ERL exceedance for the lower Slope & Basin, suggesting an anthropogenic influence in these sediments. In the embayment category (marinas, LA estuaries, ports/bays/harbors), mercury, lead and zinc had >50% areal ERL exceedances. DDTs (79%) and mercury (36%) were the contaminants with the highest percent area exceedance for the large POTWs. The data presented in Table V-3 show that anthropogenic contamination is widespread and in some cases relatively severe in the nearshore embayments, particularly in marinas, ports/bays/harbors and LA estuaries. Conversely, contaminants around small POTW outfalls, the Channel Island, and throughout the three Shelf strata (inner, mid and outer) are less widespread and at levels lower in comparison. As with the ERM analysis, total DDT and some metal contaminants are surprisingly widespread throughout the Slope & Basin stratum.

#### **Multiple Parameter Assessment**

It is well established that the exceedance of sediment quality guidelines by multiple parameters in a sample is a better predictor of the potential for biological impacts than are single parameter exceedances (Long and MacDonald 1998, Long *et al.* 2000). Therefore, the number of ERL and ERM exceedances per station were calculated and are presented in Figures V-5 and V-6, respectively. There were 269 ERL exceedances out of a possible 359 (75%) (Fig. V-5). For ERM, there were 61 out of a possible 359 exceedances (17%) (Fig. V-6). Of the ERM exceedances, only 16 of 61 (26%) were due to two or more analytes. ERL/ERM exceedances for copper revealed that only 2 stations were above the ERM with an additional 98 above the ERL (Fig. V-7). Of these exceedances, the vast majority were located in the vicinity of LA/LB Harbor and San Diego Bay (Fig. V-7). In contrast, 43 stations exceeded the ERM for DDT with

an additional 162 stations exceeding the ERL (Fig. V-8), representing a sum total of 57% of the stations exceeding the ERL for DDT. It is clear that the vast majority of DDT ERM exceedances occurred at stations clustered around the nearshore LA county area, near the Palos Verdes peninsula (Fig. V-8), whereas stations that exceeded the ERL for DDT were spread throughout the entire SCB.

A second approach to multi-parameter assessment s the use of the ERMQ (Table V-4). Approximately 1% of the SCB exceeded an ERMQ of 1.5, a level associated with a high risk of adverse biological effects. However, approximately 65% of the SCB was less than an ERMQ of 0.1, a level associated with a low risk of adverse biological effects.

Based upon the mean ERMQ, the majority (>98%) of area within all strata was classified as low or low-moderate risk (mean ERMQ < 0.5). Large POTW outfalls, LA estuaries and marinas contained measurable, but relatively small percentages (3-18%) of areas that could be considered high risk adverse biological effects. Similarly, 4% of sediments in the upper Slope & Basin were classified as having high risk of adverse biological effects. Fifty eight percent of the lower Slope & Basin area were considered a low to moderate risk (0.1 <mean ERMQ < 0.5).

All Bight '03 stations and their associated mean ERMQ are plotted in Figure V-9. The stations with the greatest mean ERMQ (moderate and high risk of adverse biological effects) were observed in the LA/LB Harbor and on the Palos Verdes Shelf. An abundance of sites with low to moderate risk of adverse biological effects were observed on the mainland shelf, slope and basins of the LA margin. This same level of enhanced risk was observed in San Diego Bay. The smallest risk was observed at the Channel Islands and along the mainland shelf and slope either in the Santa Barbara Channel or south of Newport.

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

Detailed comparisons between this study and the results from the 1994 SCBPP and Bight '98 were hindered because of the differences in the study frame. Therefore, the comparisons made were only for those areas all three surveys had in common. These areas included the mainland shelf (<120 m) and Large POTWs strata.

Considering the percent of area above ERMs, there was almost no change over the last 10 years regardless of contaminant (Table V-5). There were few observable differences in the extent of ERL exceedences across the three surveys. Perhaps the only noteworthy change was the reduction in percent area ERL exceedances for total PCB from 15% in 1994 to just 1.6% in 2003. The percent of SCB that exceeded either the ERL or ERM for total DDT, the most widespread contaminant, did not appear to change over time. Apparent trends in area extent for the other analytes were largely inconclusive.

A second comparison over time was examining mass in the surface sediments of these same strata (Table V-6). There were very few monotonic trends. There was a monotonically decreasing trend in the mass of total PCB in SCB surface sediments. An estimated 13 mt was observed in 1994 compared to 1 mt in 2003. There was a monotonically increasing trend in the mass of selenium in SCB surface sediment. An estimated 0.2 mt was found in 1994 compared

to 0.9 mt in 2003. The mass of total DDT remained relatively steady (36 to 43 mt) between 1994 and 2003.

We focused on the large POTW stratum to assess changes in sediment concentrations between 1994 and 2003 (Table V-7). We did not observe any monotonically increasing or decreasing trends in average sediment concentrations across the three surveys for this stratum. The highest concentrations were consistently observed in 1998. However, these concentrations were not significantly higher than the concentrations observed in either the 1994 and/or 2003 surveys.

Table V-1. The percent of total Bight-wide mass for each constituent residing within study strata relative to the percent of total Bight area. Those strata where the percent of mass of a given contaminant exceeds the corresponding percent of area contain a disproportionate amount of the total mass for that contaminant.

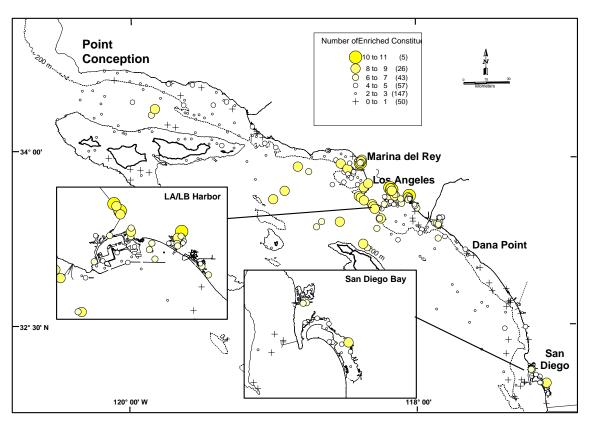
	% Area							% Mass								
Stratum		AI	Sb	As	Ba	Be	Cd	Cr	Cu	Fe	Hg	Ni	Pb	Se	Ag	Zn
Inner Shelf (5-30 m)	7.0	3.8	2.4	5.2	3.2	4.8	1.3	3.1	1.97	3.49	2.0	2.9	2.9	2.7	2.2	2.9
Mid-Shelf (30-120 m)	11.8	8.8	2.8	8.5	8.2	10.6	4.0	6.8	5.8	8.7	11.4	5.3	7.6	7.7	3.6	6.8
Outer Shelf (120-200 m)	3.6	2.5	0.7	3.9	1.9	3.1	1.9	2.2	2.3	3.8	3.5	2.1	2.6	1.6	4.5	2.5
Upper Slope (200-500 m)	19.5	19.6	9.39	21.0	14.9	31.2	25.9	19.2	15.4	21.2	17.0	18.2	18.9	13.8	12.0	19.8
Lower Slope & Basin (500-1000 m)	48.3	61	79.1	55.5	67.1	46.4	59.7	64.0	69.2	58.0	61.0	67.3	61.9	70.9	74.3	63.3
Ports/Bays/Harbors	0.51	0.7	0.1	0.4	0.3	0.15	0.4	0.3	1.5	0.6	1.4	0.3	1.3	0.7	0.3	0.8
Marinas	0.10	0.1	0.09	0.1	0.05	0.10	0.06	0.08	0.51	0.1	0.42	0.07	0.4	0.07	0.2	0.2
Estuaries	0.04	0.05	0.03	0.04	0.02	0.04	0.02	0.02	0.04	0.03	0.02	0.01	0.07	0.03	0.04	0.05
LA Estuaries	0.01	0.01	0.02	0.01	0.003	0.005	0.007	0.006	0.02	0.01	0.01	0.004	0.05	0.003	0.02	0.02
Large POTW Outfall	1.1	0.7	0.08	0.6	1.7	1.0	0.79	0.65	0.92	0.6	1.5	0.4	0.9	0.6	1.3	0.7
Small POTW Outfall	0.17	0.1	0.06	0.1	0.07	0.09	0.04	0.08	0.07	0.1	0.08	0.06	0.07	0.06	0.05	0.08
Channel Islands (30-120 m)	8.0	2.5	5.2	4.5	2.7	2.6	5.8	3.5	2.2	3.5	1.5	3.4	3.3	1.9	1.5	2.8

	% Area		%	Mass	
Stratum		Total DDT	Total PAH	Total PCB	Total Chlordane
Inner Shelf (5-30 m)	7.0	0.5	1.0	0.8	2.6
Mid-Shelf (30-120 m)	11.8	12.1	2.1	13.1	8.7
Outer Shelf (120-200 m)	3.6	1.1	0.7	7.8	0.0
Upper Slope (200-500 m)	19.5	49.2	4.3	68.5	57.8
Lower Slope & Basin (500-1000 m)	48.3	26.3	81.5	6.3	0.0
Ports/Bays/Harbors	0.51	0.4	1.8	1.8	2.6
Marinas	0.10	0.06	0.2	0.5	4.6
Estuaries	0.04	0.01	0.02	0.05	0.1
LA Estuaries	0.01	0.02	0.05	0.2	3.2
Large POTW Outfall	1.1	9.9	0.4	0.1	20.2
Small POTW Outfall	0.17	0.006	0.01	0.0	0.0
Channel Islands (30-120 m)	8.0	0.4	7.8	0.9	0.0

#### Table V-1 (cont.)

Table V-2. Percent of the Southern California Bight sediments with contamination above analytical detection limits, estimated background levels, and empirical sediment quality guidelines (ERLs and ERMs).

Parameter	% of Area Above Detection Limit	% of Area Above Background Levels	% of Area > ERL	% of Area > ERM
Metals				
Arsenic	99.0	8.2	15.2	0.0
Cadmium	97.8	82.4	33.3	0.0
Chromium	100.0	42.4	18.5	1.5
Copper	100.0	46.4	28.6	0.0
Lead	100.0	17.9	0.1	0.0
Mercury	98.4	-	21.5	0.2
Nickel	99.3	16.1	69.7	11.7
Silver	83.3	31.2	6.9	0.2
Zinc	100.0	23.3	1.0	0.0
Organics				
Total DDT	71.4	71.4	60.3	9.2
Total PCB	12.8	12.8	1.6	0.7
Total PAH	91.4	-	0.1	0.0
Chlordane	4.1	4.1	-	-
Any Metal	100	88.3	76.4	13.4
Any Organic	71.4	71.4	60.3	9.2
Any Contaminant	100	94.4	86.5	19.5



#### **Number of Enriched Constituents**

Figure V-1. Map of the number of enriched contaminants by station.

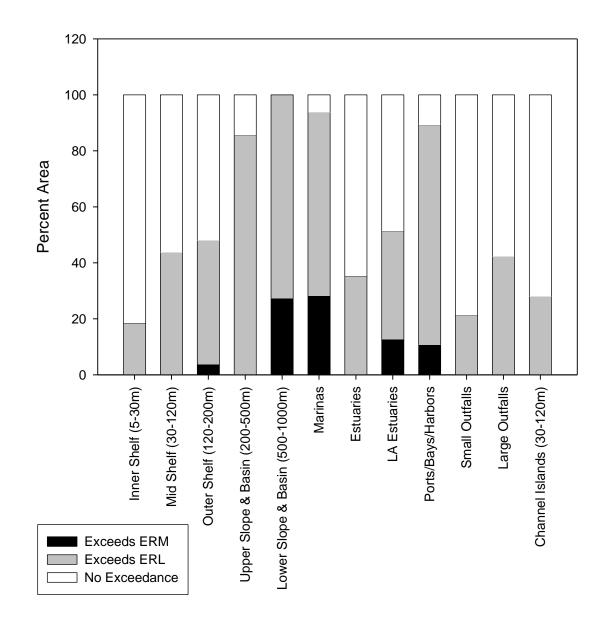


Figure V-2. Percent area exceeding Effects Range Low (ERL) and Effects Range Median (ERM) sediment quality guidelines for any metal analyte.

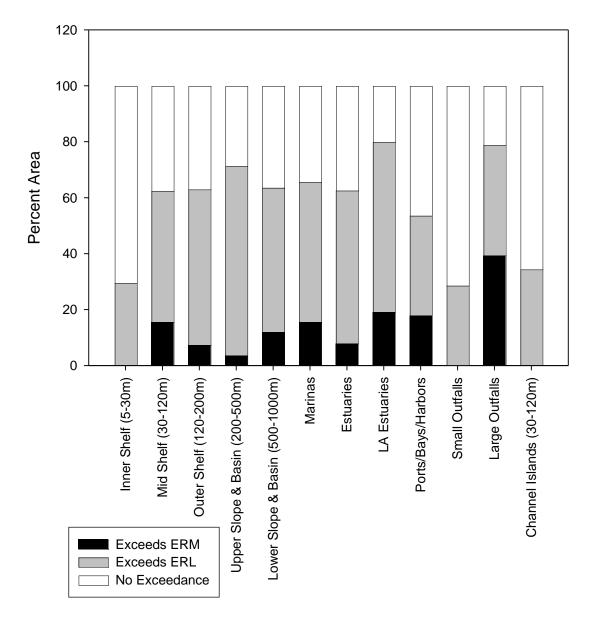
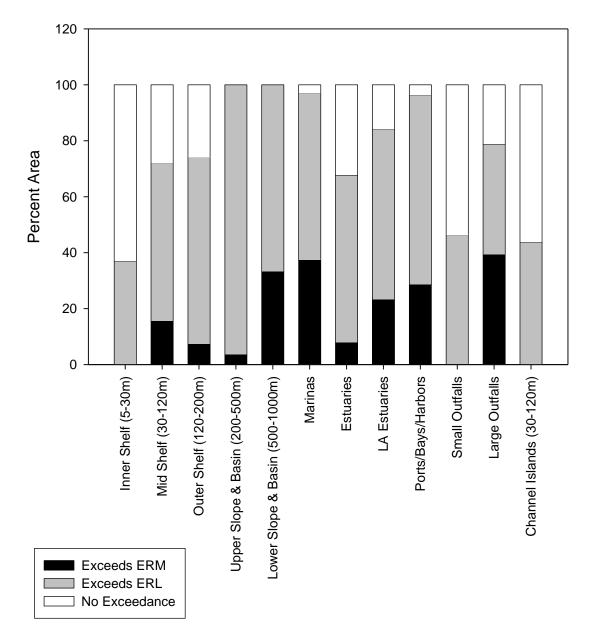


Figure V-3. Percent area exceeding Effects Range Low (ERL) and Effects Range Median (ERM) sediment quality guidelines for any organic analyte.



FigureV-4. Percent area exceeding Effects Range Low (ERL) and Effects Range Median (ERM) sediment quality guidelines for any analyte.

			Sh		Slope	& Basin				
	Inner (5-30 m)		Mid (30-120 m)		Outer (120-200 m)		Upper (20	00-500 m)	Lower (50	0-1000 m)
Parameter	% of Area > ERL	% of Area >ERM	% of Area > ERL	% of Area >ERM	% of Area > ERL	% of Area >ERM	% of Area > ERL	% of Area >ERM	% of Area > ERL	% of Area >ERM
Metals										
Arsenic	11.1	0.0	18.8	0.0	11.1	0.0	7.14	0.0	21.2	0.0
Cadmium	0.0	0.0	0.03	0.0	0.07	0.0	53.6	0.0	42.4	0.0
Chromium	0.0	0.0	6.3	0.0	3.7	0.0	7.1	0.0	33.3	3.0
Copper	0.0	0.0	0.0	0.0	3.7	0.0	0.0	0.0	57.6	0.0
Lead	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Mercury	3.7	0.0	21.9	0.0	11.1	3.7	7.1	0.0	36.4	0.0
Nickel	14.8	0.0	18.8	0.0	29.6	0.0	82.1	0.0	100	24.2
Silver	0.0	0.0	0.0	0.0	7.4	3.7	3.6	0.0	12.1	0.0
Zinc	0.0	0.0	0.0	0.0	0.0	0.0	3.6	0.0	0.0	0.0
Organics										
Total DDT	29.6	0.0	62.5	15.6	63.0	7.4	71.4	3.6	63.6	12.1
Total PCB	0.0	0.0	3.1	0.0	3.7	0.0	3.6	3.6	0.0	0.0
Total PAH	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Any Metal	18.5	0.0	43.8	0.0	48.1	3.7	85.7	0.0	100.0	27.3
Any Organic	29.6	0.0	62.5	15.6	63.0	7.4	71.4	3.6	63.6	12.1
Any Parameter	37.0	0.0	71.9	15.6	74.1	7.4	100.0	3.6	100.0	33.3

 Table V-3. Percent of area exceeding sediment quality guidelines (ERLs and ERMs)<sup>1</sup> for selected subpopulations of the sediment chemistry data from the 1998 Southern California Bight Regional Marine Monitoring Study.

	Mar	inas	Estu	aries	LA Es	tuaries	Ports/Bay	s/Harbors
Parameter	% of Area >ERL	% of Area >ERM						
Metals								
Arsenic	34.4	0.0	22.0	0.0	16.7	0.0	14.3	0.0
Cadmium	21.9	0.0	12.1	0.0	19.0	0.0	10.7	0.0
Chromium	9.4	0.0	0.0	0.0	12.6	0.0	3.6	0.0
Copper	90.6	6.3	30.7	0.0	39.3	0.0	89.3	0.0
Lead	28.1	0.0	9.2	0.0	36.8	6.4	21.4	0.0
Mercury	65.6	21.9	0.0	0.0	31.2	0.0	71.4	10.7
Nickel	53.1	0.0	12.2	0.0	43.0	2.1	35.7	0.0
Silver	12.5	6.3	0.0	0.0	20.0	4.3	3.6	3.6
Zinc	65.6	0.0	17.3	0.0	43.9	12.6	28.6	0.0
Organics								
Total DDT	65.6	15.6	62.6	7.9	79.9	19.2	53.6	17.9
Total PCB	9.4	0.0	4.0	0.0	15.1	13.0	17.9	0.0
Total PAH	3.1	0.0	0.0	0.0	21.3	0.0	10.7	0.0
Any Metal	93.8	28.1	35.3	0.0	51.4	12.6	89.3	10.7
Any Organic	65.6	15.6	62.6	7.9	79.9	19.2	53.6	17.9
Any Contaminant	96.9	37.5	67.7	7.9	84.0	23.3	96.4	28.6

### Table V-3 (cont.)

	Small PO	TW Outfalls	Large POT	W Outfalls	Channel Islar	nds (30-120 m)
Parameter	% of Area >ERL	% of Area >ERM	% of Area >ERL	% of Area >ERM	% of Area >ERL	% of Area >ERM
Metals						
Arsenic	7.1	0.0	3.0	0.0	0.0	0.0
Cadmium	0.0	0.0	15.2	0.0	18.8	0.0
Chromium	0.0	0.0	12.1	0.0	0.0	0.0
Copper	0.0	0.0	15.2	0.0	0.0	0.0
Lead	0.0	0.0	0.0	0.0	0.0	0.0
Mercury	7.1	0.0	36.4	0.0	0.0	0.0
Nickel	7.1	0.0	9.1	0.0	9.4	0.0
Silver	0.0	0.0	12.1	0.0	0.0	0.0
Zinc	0.0	0.0	0.03	0.0	0.0	0.0
Organics						
Total DDT	28.6	0.0	78.8	39.4	34.4	0.0
Total PCB	0.0	0.0	24.2	3.0	0.0	0.0
Total PAH	0.0	0.0	0.0	0.0	0.0	0.0
Any Metal	21.4	0.0	42.4	0.0	28.1	0.0
Any Organic	28.6	0.0	78.8	39.4	34.4	0.0
Any Contaminant	46.4	0.0	78.8	39.4	43.8	0.0

<sup>1</sup>ERL = Effects range low (10<sup>th</sup> percentile); ERM= Effects range median (50<sup>th</sup> percentile); from Long *et al.* 1995.

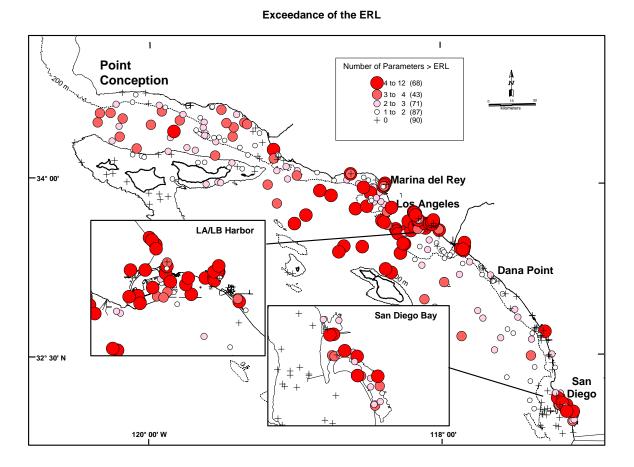
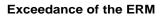


Figure V-5. Exceedances of the Effects Range Low (ERL).



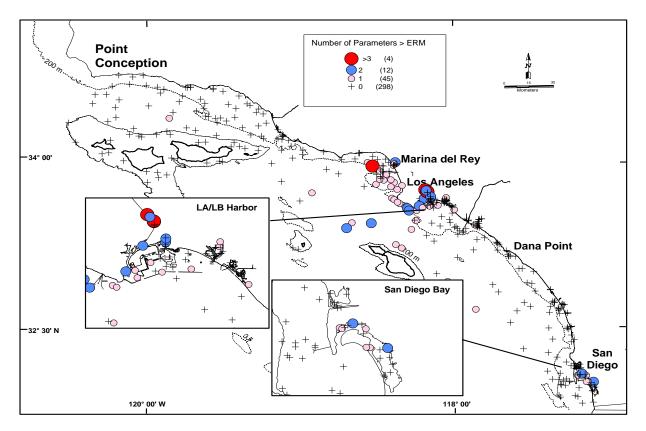


Figure V-6. Exceedances of the Effects Range Median (ERM).

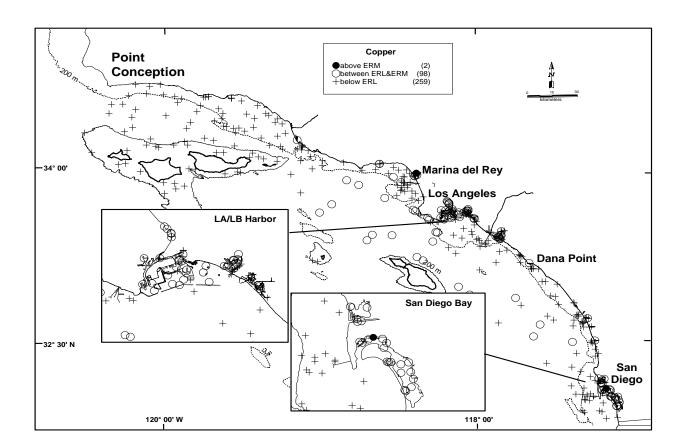


Figure V-7. Effects Range Low (ERL) and Effects Range Median (ERM) exceedances by station for copper.

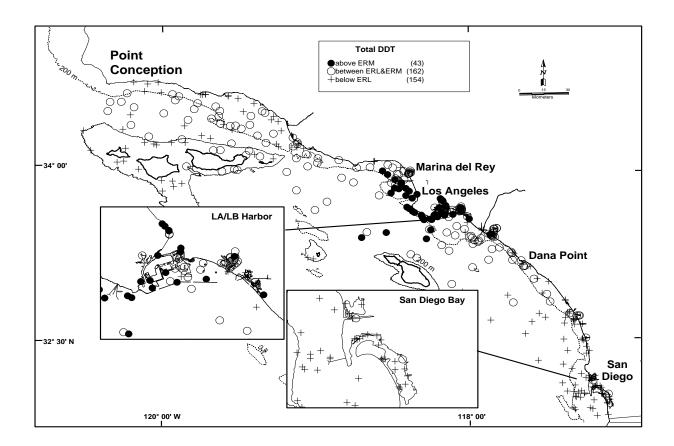


Figure V-8. Effects Range Low (ERL) and Effects Range Median (ERM) by station for total DDT.

Stratum	Low (ERMq < 0.1)	Low to Moderate (0.11< ERMq < 0.5)	Moderate to High (0.51 < ERMq <1.5)	High (ERMq > 1.5)
Entire SCB	64.8	34.3	0.1	0.8
Ports/Bays/Harbors	32.1	67.9	0.0	0.0
Marinas	34.4	62.5	3.1	0.0
Estuaries	88.0	12.0	0.0	0.0
LA Estuaries	57.3	29.7	8.7	4.3
Inner Shelf (5-30m)	88.9	11.1	0.0	0.0
Mid Shelf (30-120m)	65.6	34.4	0.0	0.0
Outer Shelf (120-200m)	92.6	7.4	0.0	0.0
Upper Slope & Basin (200-500m)	92.9	3.6	0.0	3.6
Lower Slope & Basin (500-1000m)	42.4	57.6	0.0	0.0
Small POTW	100.0	0.0	0.0	0.0
Large POTW	51.5	30.3	12.1	6.1
Channel Islands (30-120m)	100.0	0.0	0.0	0.0

 Table V-4. Percent area of the Southern California Bight within the Effects Range Median quotient (ERMq) sediment quality guidelines for potential sediment toxicity by stratum.

#### **NOAA ERM Quotient**

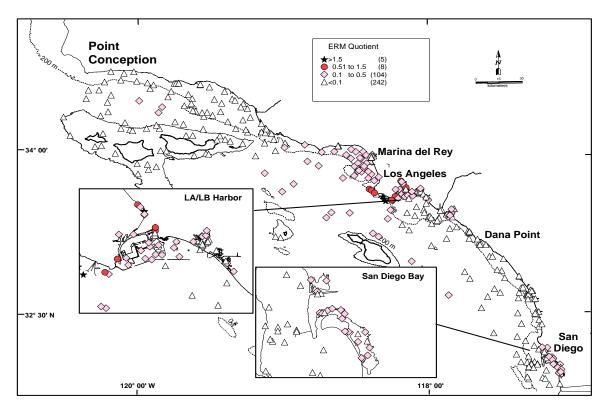


Figure V-8. Mean Effects Range Median Quotient (ERMq) classification of all Bight '03 sediment chemistry stations.

	<u>1994</u>		1998		2003	
Parameter	% of Area >ERL	% of Area >ERM	% of Area >ERL	% of Area >ERM	% of Area >ERL	% of Area >ERM
Metals						
Arsenic	1.5	0.0	12.1	0.0	14.5	0.0
Cadmium	2.1	0.0	3.8	0.0	3.4	0.0
Chromium	7.3	0.0	0.6	0.0	4.2	0.0
Copper	6.8	0.0	1.1	0.0	1.3	0.0
Lead	0.5	0.0	5.1	0.0	0.0	0.0
Mercury	6.3	0.0	6.9	0.1	15.4	0.6
Nickel	3.2	1.8	20.2	1.0	18.7	0.0
Silver	7.3	1.0	7.4	2.6	1.7	0.6
Zinc	2.7	0.0	0.2	0.0	0.1	0.0
Organics						
Total DDT	63.7	10.4	70.4	10.3	68.0	11.4
Total PCB	15.3	0.7	9.4	0.3	3.2	1.7
Total PAH	-	-	0.5	0.0	0.0	0.0

 Table V-5. Comparison of Effects Range Low (ERL) and Effects Range Median (ERM) threshold

 exceedences between Reginal Monitoring surveys across similar strata.

 Table V-6.
 Comparison of mass estimates (95% Confidence Intervals) in surface sediments

 between Reginal Monitoring surveys across similar strata.

	1994		1998		2003	
Parameter	Mass	95% CI	Mass	95% CI	Mass	95% CI
Metals (mt x 10 <sup>3</sup> )						
Antimony	0.17	0.02	0.53	0.88	0.10	0.04
Arsenic	4.3	0.5	4.7	0.8	3.7	1.0
Cadmium	277	65	309	124	249	92
Chromium	31.6	5.1	23.8	4.1	29.7	6.9
Copper	11.5	2.0	9.0	2.4	9.3	1.9
Lead	9.1	1.4	10.0	4.2	5.9	1.2
Mercury	0.040	0.007	0.035	0.020	0.070	0.020
Nickel	15.2	2.5	17.9	7.5	12.2	3.3
Selenium	0.23	0.03	0.51	0.24	0.91	0.32
Silver	0.28	0.09	0.28	0.24	0.11	0.06
Zinc	48.0	6.6	44.5	8.3	38.7	7.5
Organics (mt)						
Total DDT	38.4	19.9	42.8	37.5	35.7	30.0
Total PCB	12.7	5.4	5.1	4.1	1.4	3.8
Total PAH	-	-	62.9	33.1	54.4	40.0
Total Chlordane	-	-	0.074	0.070	0.039	0.053

 Table V-7. Comparison of Area Weighted Mean (AWM) concentrations (95% Confidence Intervals)

 in surface sediments between Reginal Monitoring surveys in the Large POTW stratum.

Parameters	19	1994		1998		2003	
	AWM	95% CI	AWM	95%CI	AWM	95%CI	
Metals (mg/dry kg)							
Arsenic	4.5	0.4	5.9	1.1	3.2	0.7	
Cadmium	0.43	0.13	1.04	0.62	0.76	0.3	
Chromium	48	9	51	16	37	9.3	
Copper	21	4	27	9.8	20	4.9	
Lead	14	2	22	7.0	9.2	2.0	
Mercury	0.100	0.023	0.16	0.06	0.14	0.04	
Nickel	14	2	15	2.7	10	2.1	
Silver	0.90	0.28	1.34	0.63	0.39	0.2	
Zinc	60	7	69	17	51	11	
Organics (µg/dry kg)							
Total DDT	146.8	96.3	539.5	482.4	316	264	
Total PCB	43.0	16.2	48.8	32.0	29	37	
Total PAH	-	-	188.3	101.4	117.7	51.5	
Total Chlordanes	-	-	0.15	0.12	0.5	0.6	

#### **VI. DISCUSSION**

Sediment contamination during the summer of 2003 was relatively widespread. Approximately 94% of the SCB area was enriched by at least one constituent. This overall extent of contamination was similar to the extent measured in previous surveys of the SCB. Approximately 85% and 86% of the SCB was enriched in at least one constituent in 1994 and 1998, respectively.

The majority of accumulated contaminants in the SCB were found in the deep ocean of the mainland slope and basins. Nearly all of the deep ocean was enriched in at least one constituent and, for all of the individual constituents measured, between 58% and 86% of the contaminant mass in the top 2 cm was found in depths greater than 200 m. The significance of this accumulation is attributed to the fact that little to no ongoing monitoring occurs in these strata. Except for total DDT, less than 2% of the of the sediment contaminant mass was found in the POTW strata where the vast majority of monitoring occurs. Other investigators have observed the potential for pollutants to be transported downslope. Zeng and Venkatesan (1999) have observed total DDT accumulating in the surface sediments of cores collected from the San Pedro Basin. Likewise, Finney and Huh (1989) observed an accumulation of anthropogenic trace metals in another set of sediment cores from the San Pedro Basin. While the sediment cores provide invaluable insight into the temporal accumulation of sediment contaminants, none of the previous investigators were able to assess the spatial extent of this accumulation. This survey was the first to recognize the truly widespread distribution of anthropogenic enrichment in these largely unexplored areas of the SCB.

There are several potential sources of anthropogenic contaminants that can be transported to the deep ocean. Large POTW discharges, located between 60 and 100m in the SCB, are often located near submarine canyons that form a conduit to the deep ocean. Runoff plumes from urban and agricultural watersheds can extend to the mainland slope and basin (Nezlin *et al.* 2005), not to mention the secondary transport of settled particulates from the plume (Kolpack and Drake 1985, Schiff and Bay 2003). All three of the currently designated dredge material disposal sites are located in depths greater than 200 m (Steinberger *et al.* 2003). As many as 14 ocean disposal sites have been used historically, including one in the San Pedro Basin exclusively for DDT manufacturing waste. Once accumulated in the deep oceans, anthropogenic contaminants are unlikely to be advected because most basins lack significant mixing and dispersion. In fact, the Santa Barbara Basin rarely exchanges with surface water (Dailey *et al.* 1993).

Although the mass of most constituents was greatest in the deep ocean, it was the shallowest areas of the SCB that were perhaps subject to the greatest ecological risk from sediment contamination. Embayments of the SCB had the greatest relative areal extent of ERMQ exceedence; more than a third of the embayment area was predicted to have a moderate to high risk of adverse biological effect. The greatest sediment concentrations of trace metals and several organic constituents were observed in sediments sampled from marinas, estuaries draining urbanized watersheds, and industrialized port facilities. Finally, marinas, estuaries, and ports/harbors all had significantly elevated mass to area ratios indicating that they were predisposed to accumulating sediment contaminants. This information is supported by the

relatively high concentrations of metals and organics measured in these areas by others (Fairey *et al.* 2001; Anderson *et al.* 1988). Additionally, marinas, estuaries, and ports/harbors (in that order) had the greatest frequency of sediment toxicity during Bight '03 (Bay *et al.* 2005).

LA estuaries appeared to have greater sediment contamination than other estuaries of the SCB. This may be due, in part, to two overriding factors. First, these estuaries drain some of the largest, most urbanized watersheds in the SCB. For example, four of the five watersheds in the LA estuary stratum are more than 50% developed, with two (Ballona Creek and Dominguez Channel) exceeding 85% urban land uses. In contrast, the watersheds of the remaining six estuaries in the SCB have much lower levels of urbanization with the majority less than 50% developed. The second factor that may have contributed to the notably increased sediment contamination of the LA estuary stratum was estuarine morphology. LA estuaries were distinct in that most were characterized by long, parallel rocky levees extending through the surfzone. While this morphology is extremely efficient for hydrodynamic transport and reduced flooding, they lack almost completely any of the estuarine processes associated with brackish water/mudflat fauna and flora. Only a single LA estuary exhibited this morphology (Malibu Lagoon) and it contained the lowest sediment concentrations of all LA estuaries. In contrast, nearly all of the remaining estuaries, at least to some degree, exhibited the more typical brackish water/mudflat morphology.

Total DDT was the most widespread contaminant in the SCB. Seventy one percent of the SCB was enriched in this legacy pesticide that was manufactured by Montrose Chemical Corporation in Torrance, CA from 1943 to 1971 (Chartrand 1988, Stull 1995, Lee and Wiberg 2002). The spatial distribution of total DDT in sediments follows an expected pattern emanating from the Los Angeles County Sanitation District outfall at White Point (Palos Verdes), the sewage treatment plant that received much of the manufacturing waste, northwestward in the direction of the predominant ocean current (Hickey 1993). This is the same pattern observed in earlier regional surveys (Schiff 2000).

The ongoing risk of sediments contaminated by total DDT is still unknown. We used the sediment quality guidelines developed by NOAA (i.e., ERL/ERM)(Long *et al.* 1995) and 20% of the SCB was expected to have high likelihood of adverse biological impacts, nearly half of which was a result of total DDT. However, the ERM is known to have low precision for predicting biological impacts, so additional DDT-specific thresholds were applied and the areal extent of potential impact significantly decreased (Table VI-1). Using these additional sediment quality guidelines, <0.1% of the SCB is at risk from DDT or its metabolites. While these additional guidelines provide alternative predictions for the acute or chronic impact to marine life, there are no guidelines that currently exist for impacts due to bioaccumulation. Earlier regional surveys identified bioaccumulation of total DDT in nearly 100% of the flatfish in the SCB (Schiff and Allen 2000). This widespread bioaccumulation was significantly correlated with sediment concentrations near where the fish were collected. Furthermore, no regional survey of total DDT bioaccumulation in pelagic fish or recreationally caught fish has been published. However, there are site specific warnings for fish consumption and food chain biomagnification of total DDT is still observed in specific locations (Allen *et al.* 2004).

There were several valuable features of regional monitoring that extended beyond the regionwide assessment results. One such feature is the ongoing interaction among some of the best analytical laboratories in the SCB. Significant effort was expended in 1998 to ensure comparability among the constituents measured routinely by participating laboratories (Gossett *et al.* 2003). Most of the comparability achieved during the intercalibration effort in 1998 was retained five years later since all five laboratories were able to achieve the data quality objectives established during Bight '98. Moreover, a similar level of interlaboratory variability was achieved using a newly collected sample specifically for Bight '03. This same process of iterative intercalibrations could be used to refine techniques for constituents not routinely measured, but are constituents that may have detrimental impact in the SCB. Several examples exist including current use pesticides (i.e., pyrethroids) or emerging chemical of concern (i.e., pharmaceuticals).

While there may be many numerous assets of regional monitoring, there are also several hurdles that need to be addressed. The first issue is assessing trace metal anthropogenic enrichment using iron. In this regional survey, a reference element technique using iron facilitated the estimate of anthropogenic metal fraction (Schiff and Weisberg 1999). Iron is an extremely useful assessment tool on the mainland shelf where sediments are generally aerobic and iron mobilization is minimal. However, sediments in the deep ocean basins and in estuaries can be anaerobic resulting in reduction of iron, mobilization in pore waters, and then oxidation at the sediment water interface where aerobic conditions return. This effectively concentrates iron in the surface sediment layers (i.e., top 2 cm) and invalidates the iron normalization technique. Two options were available for dealing with this potential bias: 1) utilize another reference element; or 2) do not make assessment for anaerobic sediments. The use of aluminum as a reference element was attempted in this survey because aluminum is not subject to digenesis like iron and, therefore, should operate in both aerobic and anaerobic sediments. Aluminum has been used as a reference element in other locations (Windhom et al. 1989). In the end, however, aluminum normalization had far too much positive bias in fine grained sediments, which generally covaried with depth. The bias was most likely due to the incomplete sediment digestion method used in this regional survey, a method adopted by every NPDES monitoring laboratory in southern California for the last 35 years. Windom et al. (1989) used a total dissolution digestion that will retrieve all of the aluminum regardless of grain size thereby negating any potential bias.

Source	Units <sup>1</sup>	Total DDT Threshold	Percent of SCB Exceeding Threshold
MacDonald 1994	μg/dry-g	7.12	0.0
SEC <sup>2</sup>	μg/g-OC	199.0	0.0
Chapman 1996	μg/dry-g	8.51	0.0
NOEC <sup>3</sup>	μg/g-OC	269.0	0.0
Swartz <i>et al.</i> 1994 Chronic Toxicity Acute Toxicity	μg/g-OC μg/g-OC	100.0 300.0	0.1 0.0

Table VI-1. Areal extent of total DDT sediment contamination in the Southern California Bight (SCB) relative to different sediment quality criteria.

 $^{1}$  µg/g-OC = µg/g divided by the mass fraction of organic carbon in the sediment sample.  $^{2}$  SEC = Sediment effects concentration.  $^{3}$  NOEC = No observable effects concentration.

### VII. CONCLUSIONS

#### • Anthropogenic sediment contamination was widespread in the SCB.

Approximately 94% of the SCB in 2003 was enriched by at least one sediment contaminant measured during this study. Seventy one percent of the SCB area was enriched by at least one organic constituent. Eighty eight percent of the SCB was enriched by at least one trace metal.

# • Although sediment contamination was widespread, most of the Bight was below concentrations of concern for acute toxicity to benthic organisms.

Less than 20% of the SCB was above the Effects range median (ERM), a national sediment quality guideline designed to estimate the likelihood of adverse biological effects for individual constituents. Application of the mean ERM quotient, another national sediment quality guideline that evaluates complex mistures of sediment contaminants, showed that only 1% of the SCB was at a moderate to high risk of adverse biological effects.

#### • Total DDT was amongst the most widespread contaminant in the SCB.

An estimated 71% of the SCB area had detectable levels of total DDT in sediments. Therefore, we applied the best available DDT-specific sediment quality guidelines, which suggested 0.1% or less of the SCB sediments contained concentrations of total DDT expected to cause adverse biological effects. However, these guidelines to do not account for bioaccumulative effects.

# • The greatest mass accumulation of sediment constituents was observed on the mainland slope and basins of the SCB.

More than 80% of the contaminant mass measured in the top 2 cm of sediments bightwide was found at depths from 200 to 1,000m. These habitats likely accumulate anthropogenic inputs from shallower depths and have little to no capability for advection to remove them. These depths are rarely, if ever, monitored.

# • The highest average concentrations, disproportionately large accumulations of contaminant mass, and greatest frequency of sediment quality guideline exceedences were associated with embayments and areas in proximity to large POTW outfalls.

Although bays, harbors, and estuaries constituted approximately 1% of the area, they contained concentration maxima for copper, zinc and lead. For example, 85% of their areas exceeded ERL guidelines for copper and mass to area ratios ranged from two to five. Large POTW areas contained the concentration maxima, exceeded ERL guidelines in 79% of its area, and had a mass to area ratio of nine for total DDT.

• The lowest average concentrations, disproportionately small accumulations of contaminant mass, and lack of sediment quality guideline exceedences were associated with the Channel Islands and areas in proximity to small POTW outfalls.

Concentration minima for both trace metals and organic constituents were consistently associated with the Channel Islands and Small POTW strata. ERM guidelines were never exceeded and mass to area ratios were less than unity for all constituents in these two habitats.

#### VIII. RECOMMENDATIONS

#### • Explore the use of new sediment quality objectives.

The assessments of extent in Bight '03 were wholly dependent upon the accuracy and precision of the sediment quality guidelines we used. Sometimes these guidelines are predictive, but sometimes they are not. Specifically, the ERM for total DDT is imprecise and prone to false positives (i.e., predicts adverse biological effects when there is none). This is problematic because total DDT is one of the most widespread sediment contaminants in the SCB. The State of California is developing sediment quality objectives for bays and estuaries of which revised sediment quality guidelines will undoubtedly play a role. We recommend using these newly developed California-based sediment quality guidelines when they become available.

If new California-based sediment quality guidelines for bays and estuaries become available, then several issues may arise for sediment chemistry in future surveys. The first is application of these guidelines in deeper waters where they have not been validated. The second issue is reviewing and revising the list of target analytes and re-evaluating the targeted reporting levels to ensure the proper data are collected to compare sediment sample results to guidelines. Third, the differences introduced by changing analyte lists and reporting levels may impact our ability to track trends.

# • The next regional survey should continue to assess the new habitats measured in Bight '03 and examine other habitats that might accumulate potential contaminants.

It was clear from Bight '03 that sediment contaminants can and do accumulate in locations that are typically out of our ongoing monitoring purview. One example was the deeper slope and basins (> 200 m) and a second was estuaries. We recommend continuing to measure these habitats in future surveys. Further, we recommend focusing some effort in areas of known accumulation to refine our understanding of contaminant accumulation and potential risk to marine life. New habitats that could be explored in the next regional survey include dredged material disposal sites and submarine canyons. Both of these habitats are likely focal points of contaminant transport into waters deeper than 200 m.

#### • The next regional survey should address new constituents of concern.

The list of constituents from Bight '03 has been refined over the last 10 years from the list of standard monitoring analytes in most NPDES permits. However, there are some constituents that represent potential risk to marine life that could to be explored. These include dieldrin, DDMU, tributyl tin (TBT), current use pesticides (i.e., pyrethroids), and pharmaceutical compounds. While dieldrin was measured in the 1994 pilot project and little was found on the mainland shelf, we are examining new habitats where these legacy pesticides may accumulate. DDMU, which is a degradation product of DDT, should be measured since total DDT was the most widespread sediment contaminant in the SCB. Bight '03 identified marina sediments as one of the most significantly contaminated habitats in the SCB for copper, most likely from the use of antifouling paints. Like copper, TBT was once used as a biocide in antifouling paint and the areal extent of this potentially long-lived

contaminant is unknown. The extent and magnitude of many legacy pesticides was observed in estuaries during Bight '03, but the extent of current use pesticides is unknown. Estuaries, in particular, are the immediate receiving water for the application of current use pesticides in our urban and agricultural dominated watersheds. Pharmaceutical compounds are receiving notoriety as potential environmental contaminants. Some recent work has shown that some of these compounds may affect fish in the SCB. Despite the presence of these compounds in some POTW discharges, the extent and magnitude of these contaminants in sediments, which may be a sink and long-term exposure route of these constituents remains unknown.

Dieldrin and DDMU can be readily measured using existing techniques, while TBT, pyrethroid, and pharmaceuticals are not routinely measured by Bight '03 participating laboratories. Developing these methods will require significant resources. Therefore, measurement of these compounds may best be undertaken as a research element in the next survey.

#### • Additional assessment tools for anthropogenic enrichment need to be explored.

In Bight '03, and in previous surveys, iron was used as a reference element to assess anthropogenic enrichment of trace metals. After moving to new habitats in Bight '03, the limitation of using iron in anaerobic sediments has been revealed. While other reference elements could be used (i.e., aluminum), we had insufficient data in this study to create this new assessment tool. We recommend conducting dedicated sampling to collect the necessary data to create this new assessment tool prior to, or in conjunction with, the next survey.

# • The next Regional Monitoring survey should be re-evaluated to maintain and improve trend detection.

Previous regional monitoring surveys were specifically designed to address questions about extent and magnitude. Implicit within this study design is that trend evaluation can occur after multiple surveys are conducted. Bight '03 represented the first opportunity to examine potential trends in spatial extent over the last 10 years. However, this analysis was met with some difficulty. Some temporal comparisons were stymied by differences chemical methods, but most of these difficulties have been remedied. A second hurdle was dissimilarity in sample frame. Since 1994, the Regional Monitoring Program has moved into both shallower and deeper water, increasing its areal extent by a factor of three and often into unexplored habitats. Even more habitats are being recommended in future surveys. However, some consistency in areal extent is required to ensure that temporal trends can be conducted. Therefore, the study design for future Regional Monitoring surveys needs to be re-evaluated and configured to ensure that information to address questions about trends are occurring over similar spatial scales and habitats.

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# APPENDIX A: PARTICIPANTS IN THE BIGHT'03 REGIONAL MONITORING PROGRAM

ftp://ftp.sccwrp.org/pub/download/DOCUMENTS/TechnicalReports/492\_AppendixA\_participants.pdf

# APPENDIX B: GEOGRAPHIC DISTRIBUTION AND MAGNITUDE OF ANALYTES

ftp://ftp.sccwrp.org/pub/download/DOCUMENTS/TechnicalReports/492\_AppendixB\_concentrations.pdf

# APPENDIX C: ERL/ERM EXCEEDANCE

ftp://ftp.sccwrp.org/pub/download/DOCUMENTS/TechnicalReports/492\_AppendixC\_ERLERM.pdf

# APPENDIX D: CUMULATIVE DISTRIBUTION FREQUENCY GRAPHS

ftp://ftp.sccwrp.org/pub/download/DOCUMENTS/TechnicalReports/492\_AppendixD\_CDFgraphs.pdf