

Sediment Chemistry

Period	1 IA 1A	2 IIA 2A											13 IIIA 3A	14 IVA 4A	15 VA 5A	16 VIA 6A	17 VIIA 7A	18 VIII 8A
1	1 <u>H</u> 1.008		<chem>Clc1ccc(cc1)C(Cl)(Cl)c2ccccc2Cl</chem>															2 <u>He</u> 4.003
2	3 <u>Li</u> 6.941	4 <u>Be</u> 9.012											5 <u>B</u> 10.81	6 <u>C</u> 12.01	7 <u>N</u> 14.01	8 <u>O</u> 16.00	9 <u>F</u> 19.00	10 <u>Ne</u> 20.18
3	11 <u>Na</u> 22.99	12 <u>Mg</u> 24.31	3 IIIB 3B	4 IVB 4B	5 VB 5B	6 VIB 6B	7 VIIB 7B	8 ----- VIII ----- 8	9 ----- VIII ----- 8	10 ----- VIII ----- 8	11 IB 1B	12 IIB 2B	13 <u>Al</u> 26.98	14 <u>Si</u> 28.09	15 <u>P</u> 30.97	16 <u>S</u> 32.07	17 <u>Cl</u> 35.45	18 <u>Ar</u> 39.95
4	19 <u>K</u> 39.10	20 <u>Ca</u> 40.08	21 <u>Sc</u> 44.96	22 <u>Ti</u> 47.88	23 <u>V</u> 50.94	24 <u>Cr</u> 52.00	25 <u>Mn</u> 54.94	26 <u>Fe</u> 55.85	27 <u>Co</u> 58.47	28 <u>Ni</u> 58.69	29 <u>Cu</u> 63.55	30 <u>Zn</u> 65.39	31 <u>Ga</u> 69.72	32 <u>Ge</u> 72.59	33 <u>As</u> 74.92	34 <u>Se</u> 78.96	35 <u>Br</u> 79.90	36 <u>Kr</u> 83.80
5	37 <u>Rb</u> 85.47	38 <u>Sr</u> 87.62	39 <u>Y</u> 88.91	40 <u>Zr</u> 91.22	41 <u>Nb</u> 92.91	42 <u>Mo</u> 95.94	43 <u>Tc</u> (98)	44 <u>Ru</u> 101.1	45 <u>Rh</u> 102.9	46 <u>Pd</u> 106.4	47 <u>Ag</u> 107.9	48 <u>Cd</u> 112.4	49 <u>In</u> 114.8	50 <u>Sn</u> 118.7	51 <u>Sb</u> 121.8	52 <u>Te</u> 127.6	53 <u>I</u> 126.9	54 <u>Xe</u> 131.3
6	55 <u>Cs</u> 132.9	56 <u>Ba</u> 137.3	57 <u>La*</u> 138.9	72 <u>Hf</u> 178.5	73 <u>Ta</u> 180.9	74 <u>W</u> 183.9	75 <u>Re</u> 186.2	76 <u>Os</u> 190.2	77 <u>Ir</u> 190.2	78 <u>Pt</u> 195.1	79 <u>Au</u> 197.0	80 <u>Hg</u> 200.5	81 <u>Tl</u> 204.4	82 <u>Pb</u> 207.2	83 <u>Bi</u> 209.0	84 <u>Po</u> (210)	85 <u>At</u> (210)	86 <u>Rn</u> (222)
7	87 <u>Fr</u> (223)	88 <u>Ra</u> (226)	89 <u>Ac~</u> (227)	104 <u>Rf</u> (257)	105 <u>Db</u> (260)	106 <u>Sg</u> (263)	107 <u>Bh</u> (262)	108 <u>Hs</u> (265)	109 <u>Mt</u> (266)	110 --- (0)	111 --- (0)	112 --- (0)		114 --- (0)		116 --- (0)		118 --- (0)



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SOUTHERN CALIFORNIA BIGHT 1998 REGIONAL MONITORING PROGRAM: VI. SEDIMENT CHEMISTRY

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FOREWORD

The Southern California Bight (SCB) is a 100,000-square-mile body of water and submerged continental shelf that extends from Point Conception, California, in the north to Cabo Colnett, Baja California, Mexico, in the south. The mild climate, combined with broad, sandy beaches and intermittent rocky shoreline, make this a unique and important ecological and economic resource for southern California. The SCB also includes diverse habitats that are home to a broad range of marine life including more than 500 species of fish and 1,500 species of invertebrates, as well as numerous species of marine mammals and birds.

However, the coastal areas adjacent to the SCB are some of the most populated in the country. The high population density and associated human activities place a variety of stresses on the coastal marine environment, including the introduction of pollutants from both point and nonpoint sources. As a result, over \$10 million is spent annually to monitor environmental quality in the SCB. These monitoring programs provide important information on a local scale concerning the impacts of specific waste discharges, but do not assess the condition of the SCB as a whole. An assessment of environmental quality on a more regional scale is needed to help environmental regulators and resource managers understand the impacts of pollution beyond the areas in proximity to the initial points of discharge.

In response to the need for a more regional perspective, the Southern California Bight 1998 Regional Monitoring Program (Bight'98 Survey) was conducted as a continuation and expansion of the efforts initiated with the 1994 Southern California Bight Pilot Project. The overall Bight'98 Survey was organized into three technical components: 1) Coastal Ecology, 2) Shoreline Microbiology, and 3) Water Quality. This report contains the results of the sediment chemistry portion of the Coastal Ecology component of the Bight'98 Survey. This report focuses on the nearshore areas of the SCB, including embayments, with water depths of less than 120 m. Copies of this report, as well as the other Bight'98 reports, are available for download from the SCCWRP website at: www.sccwrp.org.

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EXECUTIVE SUMMARY

As part of the Southern California Bight 1998 Regional Marine Monitoring Survey (Bight'98 Survey), sediment chemistry was measured at 290 sites between Point Conception, California, and the United States-Mexico international border in the summer of 1998. Sampling sites were selected using a stratified random sampling design. Five strata were located offshore (river mouths, large publicly owned treatment works, small publicly owned treatment works, remaining shallow areas, and remaining mid-depth areas); three were located within bays and harbors (marinas, port/industrial areas, and remaining harbor areas). An additional 71 sites were sampled between the U.S.-Mexico international border and Ensenada, Mexico. Stratification within Mexico was limited to north, central, and south.

Surficial sediment samples were collected using a 0.1 m Van Veen grab and were analyzed for grain size, total organic carbon (TOC), total nitrogen (TN), 15 major and trace elements (aluminum, antimony, arsenic, barium, beryllium, cadmium, chromium, copper, iron, lead, mercury, nickel, selenium, silver, and zinc), and five classes of organic compounds--total chlordanes (α and γ isomers), total DDTs (o, p- and p,p-isomers of DDT, DDD, and DDE), total PAHs (24 compounds), total PCBs (42 congeners), and linear alkylbenzenes (25 isomers). A subset of samples (108) was also analyzed for interstitial water metals and simultaneously extracted metals-acid volatile sulfide (SEM-AVS).

Seven laboratories participated in processing these samples. A performance-based approach was employed, with each laboratory permitted to use their own standard protocols as long as they could demonstrate their ability to achieve the required accuracy, precision, and sensitivity. Prior to sample analysis, an inter-laboratory calibration exercise was conducted to ensure that these laboratories produced data of comparable quality. Considerable differences among laboratories were encountered during initial inter-laboratory calibration runs, but corrective procedures reduced differences among laboratories to generally less than 40%. Quality control procedures conducted during processing of the study samples confirmed laboratory consistency.

Anthropogenic enrichment of sediment contaminant concentrations was estimated using elemental background threshold curves for metals and presence above the analytical detection limits for organic constituents. Eighty-six percent of the SCB was found to be anthropogenically enriched in at least one contaminant. Metals were enriched in 47% of the SCB, whereas 85% of the SCB was contaminated by at least one organic compound. These results are essentially the same as those obtained in a 1994 regional survey.

While anthropogenic contamination was present in 86% of the SCB, less than 1% of the Bight contained contaminants at concentrations having high risk for acute benthic organism toxicity (sufficient to cause severe biological harm or death soon after a single exposure or dose). Moreover, less than 20% of the Bight was at low to moderate risk for acute toxicity. These findings are consistent using either the National Oceanic &

Atmospheric Administration's (NOAA's) ERM-quotient sediment quality guidelines or the U.S. Environmental Protection Agency's (EPA's) equilibrium partitioning criteria. These results are also in agreement with the results of the Sediment Toxicity component of Bight'98, which found 19 and 2.7% of the SCB to be of potential and high concern for acute toxicity, respectively.

Total DDT was the most prevalent contaminant, found in 82% of the SCB and found as the only anthropogenically enriched contaminant in 14% of the Bight. Given its prevalence, eight different sediment quality guidelines were used to evaluate the potential for biological impacts associated with measured levels of DDT. While there was some disagreement among results from these different thresholds, the best available DDT-specific sediment quality guidelines indicated that less than 1% of the SCB sediments contained concentrations of total DDT expected to cause chronic or acute toxicity to benthic organisms.

The highest sediment concentrations for most target analytes were found in bays and harbors. Although bays and harbors constituted only about 6% of the area, they contained 22% of total Bight-wide contamination. The most elevated contaminants in bays and harbors were copper, lead, zinc, mercury, chlordanes, PAHs, and PCBs. Similarly, the areas near large POTW outfalls constituted about 4% of the area, but contained an estimated 11% of the Bight-wide contamination. Much of this is reflective of historically deposited DDT and PCB concentrations in areas near the Hyperion Wastewater Treatment Plant and Joint Water Pollution Control Plant outfalls.

In contrast, areas near river mouths and small POTW outfalls were not distinctively contaminated relative to other areas of the Bight. The areas affected by river discharges contained 1% of the Bight area and contributed an estimated 1.3% of the total contamination. Similarly, the areas near small POTW outfalls constituted 1.6% of the Bight and contained 1% of the total Bight-wide contamination. On a geographic basis, the central region of the SCB had significantly higher concentrations of most parameters in comparison to the northern (north of Point Dume) and southern regions (south of Dana Point).

Sediment extracts were also tested using the P450 Human Reporter Gene System (HRGS). This system is an indirect measure of exposure to organic chemicals using a biochemical response, and improves upon direct chemical measure by assessing the presence of unmeasured analytes. The P450 HRGS results were generally well correlated with total PAHs and/or total PCBs, but there were some high assay responses obtained for a few stations throughout the Bight that could not be explained by concentrations of the Bight'98 target analytes.

Historical contamination trends were evaluated at 13 reference sites common to previous surveys conducted in 1977, 1985, and 1990. Except for a single station just north of Santa Monica Bay, the results show that contaminant levels at the reference sites have been consistently low over the past 25 years. Thus, elevated levels of sediment contamination are remaining fairly localized in areas near the original sources. This also

implies that the rates of contaminant transport and dispersion in the Bight are offset by the rates of degradation and/or sequestration.

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I. INTRODUCTION

Overview

The Southern California Bight (SCB; Figure I1), an open embayment in the coast between Point Conception, California, and Cape 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. 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 Harbor is the largest commercial port in the United States, and San Diego Harbor is home to one of the largest U.S. Naval facilities in the country. More than 100 million people visit southern California beaches and coastal areas annually, bringing an estimated \$9 billion into the economy. Recreational activities include diving, swimming, surfing, and boating, with about 40,000 pleasure boats docked in 13 coastal marinas within the region (NRC 1990). Recreational fishing brings in more than \$500 million per year.

The coastal areas that form the SCB are some of the most densely populated regions in the country, which in turn creates a stress 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.

Each year, local, state, and federal agencies spend in excess of \$10 million to monitor the environmental quality of natural resources in the SCB (Bight '98 Steering Committee, 1998). Most of this monitoring is associated with National Pollutant Discharge Elimination System (NPDES) permits and is intended to assess compliance of waste discharge with the California Ocean Plan and the Federal Clean Water Act, which set water quality standards for effluent and receiving waters. Some of this information has played a significant role in management decisions in the SCB.

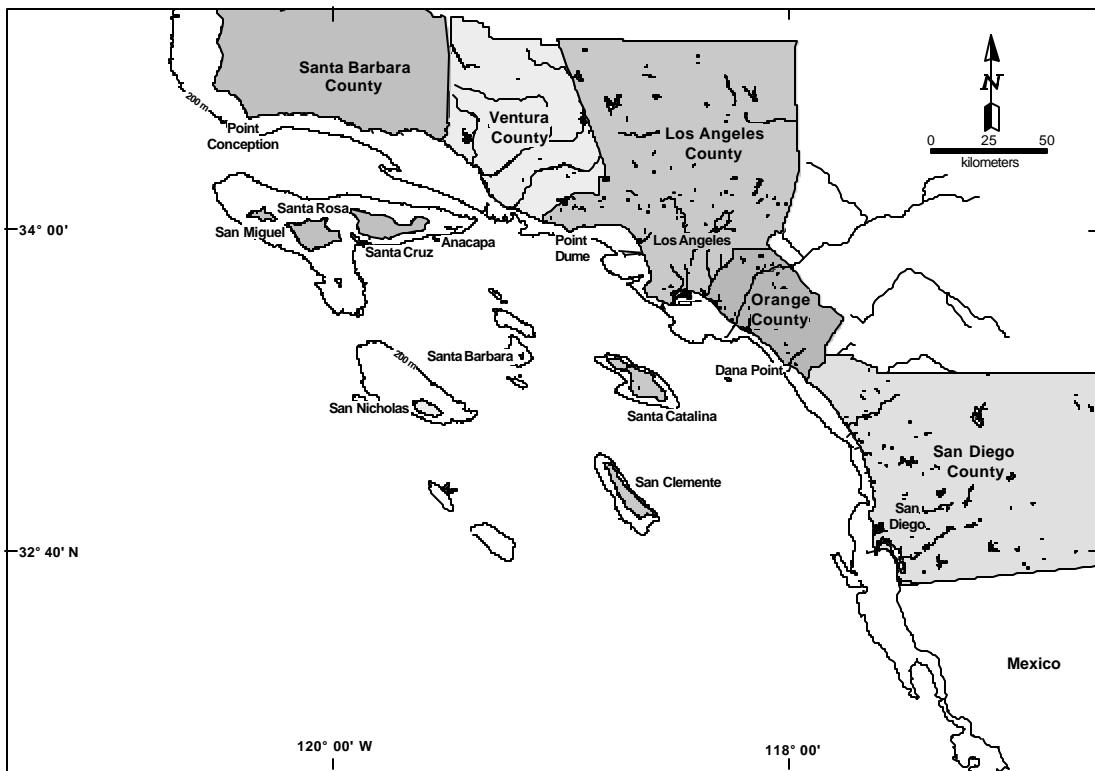


Figure I-1. A map showing the study area for the Southern California Bight 1998 Regional Monitoring Program which extends from Point Conception, California, to Ensenada, Mexico.

While these monitoring programs have important information, they were designed to evaluate impacts near individual discharges. Today, resource managers are being encouraged to develop management strategies for the entire SCB. To accomplish this task, they need regionally based information to assess cumulative impacts of contaminant inputs and to evaluate relative risk among different types of pollution sources and their associated stresses. It is difficult to use existing data to evaluate regional issues because the monitoring was limited to specific geographic areas, providing substantial data for some areas and little or no data for other areas. Beyond the spatial limitations, data from these programs are not easily merged to examine relative risk. The parameters measured often differ among programs. Even when the same parameters are measured, the methodologies used to collect the data often differ, and inter-laboratory quality assurance (QA) exercises to assess data comparability are rare.

The 1994 Regional Monitoring Pilot Project

In response to the need for a coherent, regionally based monitoring program, 12 agencies joined in a cooperative effort in 1994, called the Southern California Bight Pilot Project (SCBPP). Using consistent methodologies, the SCBPP sampled 261 sites along the continental shelf between Point Conception and the United States/Mexico international border. Assessments were made of water quality, sediment contamination, biological resources, species diversity, and marine debris. The SCBPP obtained the first “snapshot” of the state of the SCB.

Additional benefits derived from the SCBPP included the development of new useful technical tools that could only be developed with regional data sets and participation by multiple organizations. For example, the project produced iron-normalization curves for the SCB, allowing distinction between natural and anthropogenic contributions of metals in sediments (Schiff and Weisberg 1998). A benthic response index was developed that integrates complex benthic infaunal data into an easily interpreted form that describes the degree of perturbation at a site (Bergen *et al.* 1998). The project also produced a series of manuals containing standardized field, laboratory, and data management approaches that increased comparability of data among participants, even after the SCBPP was completed. Finally, the SCBPP sediment chemistry report produced a set of six recommendations for study design and quality assurance elements that should be incorporated into future surveys (Schiff and Gossett 1998). These recommendations are summarized as follows:

1. Assess the temporal changes in sediment contamination.
2. Improve techniques to associate sediment contamination with anthropogenic sources.
3. Use comparable methodology for sediment analyses and a performance-based approach to ensure data comparability.
4. Quantify a common list of target analytes, and include at least those analytes that have threshold values, ecotoxicological benchmarks, or serve as normalization tools.
5. Establish minimum reporting levels for all analytes, with specified levels of accuracy and precision.
6. The use of locally derived reference materials should be required of all participating laboratories for evaluation of initial and ongoing analytical performance.

The extent to which these recommendations have been incorporated into the Bight’98 program will become evident in the following sections.

The 1998 Regional Monitoring Program

The Southern California Bight 1998 Regional Monitoring Program (Bight'98) built upon the previous successes of the SCBPP and expanded on the 1994 survey by including more participants, sampling more habitats, and measuring more parameters. Sediment grab samples were collected at 343 sites in U.S. waters and 61 sites in Mexican waters, for a total of 404 stations. A subset of the samples (i.e., 290 U.S. stations and 61 Mexican stations), which excluded 53 Channel Islands stations, were analyzed for a full suite of chemical and physical parameters. In comparison to the 1994 SCBPP, the sediment sampling for the Bight'98 Survey had a distinct emphasis on the nearshore marine environment (inner shelf, 5-30 m; and middle shelf, 30-120 m), and embayments. This emphasis is readily apparent from the spatial distribution of the sediment chemistry sampling stations shown in Figure I-2. Also noteworthy is the increased sampling density near known sources of pollution.

The Bight'98 Survey was organized into three technical components: 1) Coastal Ecology, 2) Shoreline Microbiology, and 3) Water Quality. The overall goals of the Coastal Ecology component of the Bight'98 Survey are to assess the condition of the bottom environment and the health of the biological resources in the SCB. To this end, the Bight'98 Survey focused on four main objectives:

1. Estimate the extent and magnitude of ecological change in the SCB;
2. Compare condition among selected geographic regions of the SCB;
3. Assess the relationship between biological responses and contaminant exposure;
4. Describe temporal contamination trends at selected sites.

An accurate and comprehensive evaluation of sediment contamination in the SCB is an essential part of meeting the Coastal Ecology component objectives stated above. The methods employed and target analytes measured in the Bight'98 Survey were selected to achieve the four objectives stated above, and also to incorporate the recommendations made in the SCBPP Sediment Chemistry Report. With this in mind, the goals of the sediment chemistry portion of the Bight'98 Survey were to:

- Demonstrate comparable performance among the multiple analytical laboratories performing chemical analyses for the Bight'98 Survey.

A regional monitoring program on the scale of the Bight'98 Survey necessarily requires the contributions of many individuals and institutions. Therefore, it is of paramount importance that the data generated by the individual participating laboratories is of comparable quality so that all of the data obtained can be treated as a single entity for the purposes of subsequent evaluation and analyses. The extensive efforts undertaken to achieve comparable and consistent analytical results among the seven laboratories performing chemical analyses are the subject of the next chapter in this report.

- Determine the spatial distribution and magnitude of sediment contamination in the SCB.

Data on the chemical and physical parameters for each sediment sample were compared on a Bight-wide and local scale. All stations were statistically weighted according to the sampling design, and the area-weighted mean values for each subpopulation of interest were calculated. The resulting area-weighted mean values were then compared among the various subpopulations to identify trends in the spatial distribution and magnitude of the target parameters.

- Identify any relationships among contaminants that might facilitate evaluation of the relative importance of different pollution sources.

Two approaches were used in this study to evaluate the relative importance of different sources of contamination to the SCB. First, linear alkyl benzenes (LABs) were used as molecular markers for the extent and magnitude of the contaminant contribution from sewage treatment plant effluents (Zemg and Yu 1996). Second, principal component analysis (PCA) was used to identify any statistical relationships among target parameters. The PCA is a powerful multivariate statistical tool that can identify correlations among parameters in large, complex data sets that are not readily apparent (Phillips *et al.* 1997).

- Assess the potential for adverse biological impacts to benthic organisms due to the observed levels of sediment contamination.

Four approaches were used to assess the potential for biological impacts due to the measured levels of sediment contamination. First, the sediment quality guideline (SQG) quotient approach made use of empirically derived SQGs based upon previous integrated chemistry and toxicity studies. Second, the equilibrium partitioning (EqP) method used a more fundamental approach based upon the predicted *in situ* partitioning behavior and estimated bioavailable concentrations of individual chemicals, and the known or suspected mode of toxicity. Third, the potential for toxicity due to metals was evaluated using the acid volatile sulfide-simultaneously extracted metals (AVS-SEM) approach (Allen *et al.* 1993). This assessment tool is based upon the fact that as sediments become anoxic, bacteria begin to produce hydrogen sulfide and other reduced sulfur compounds as a result of their metabolic activity. Many toxic divalent transition metals (e.g., Cd^{2+} , Cu^{2+} , Hg^{2+} , Ni^{2+} , Pb^{2+} , and Zn^{2+}) form extremely insoluble sulfides. As a result, it was assumed that available sulfide would sequester an equimolar amount of these metals in the sediments. Therefore, a comparison of the amount of sulfide released from an acid-digested sediment to the amount of simultaneously extracted metals was used as a measure of the bioavailability, and hence the effective toxicity, of the metals. Lastly, a relatively new biochemical assay method called the P450 Human Reporter Gene System (P450 HRGS) (Anderson *et al.* 1995) was used to measure the carcinogenic potency of sediment extracts.

This method directly measures the ability of sediment extracts to induce a biochemical toxic response. The details of the technique and its implications are discussed in Chapter VI.

- Estimate the temporal changes in sediment contamination levels over the past 25 years at selected reference sites characterized in previous surveys.

The Southern California Coastal Water Research Project (SCCWRP) conducted three reference surveys in 1977, 1985, and 1990 (Word and Mearns 1979, Thompson *et al.* 1987 and 1993). The data at 13 historical sites from these previous surveys were compared with the data at the same sites from the present study to identify any temporal trends in sediment contamination over the past 25 years. The stations selected for this analysis were distant from known contaminant sources and were selected to allow a more integrated assessment of Bight-wide contamination changes over time, rather than assessing changes associated with any particular source.

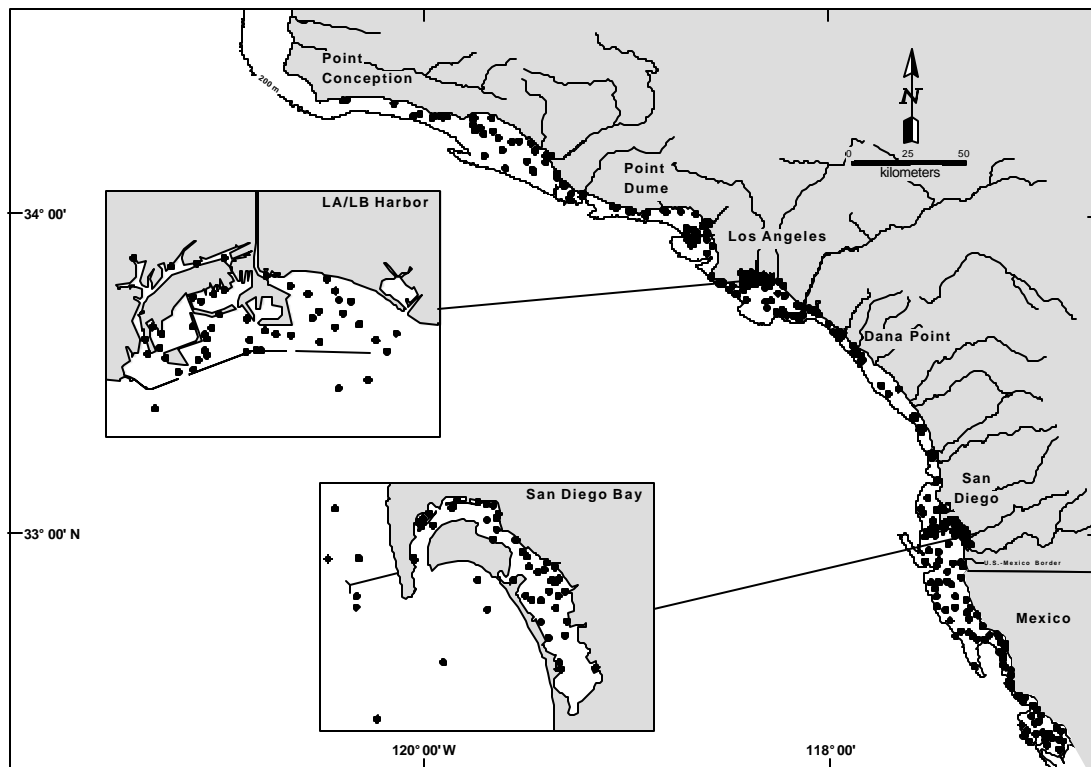


Figure I-2. Sampling locations for the sediment chemistry component of the Bight'98 Regional Monitoring program. Note the increased station density in embayments and near known pollution sources, and that all stations are within the 200 m contour.

II. METHODS

Sampling Design

Sampling locations were selected using a stratified random approach (Stevens 1997), with the strata corresponding to the subpopulations of interest shown in Table II-1. Stratification ensures that an appropriate number of samples are allocated to characterize each population of interest with adequate precision. The goal was to allocate at least 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 $p=0.2$). This level of desired precision was selected because differences in response of less than 10% among subpopulations are unlikely to yield different management decisions. A comparison between the number of samples in each stratum from the sampling design, and the actual samples obtained, is given in Table II-2.

Sites were selected randomly within strata, rather than by investigator pre-selection, to ensure that the sites were representative and could be extrapolated to the response of the entire stratum. Although sites were selected randomly, a systematic component was added to the selection process to minimize clustering of sample sites. The systematic element was accomplished by using an extension of the sampling design used in the 1994 SCBPP and in the U.S. Environmental Protection Agency's (EPA's) Environmental Monitoring and Assessment Program (EMAP) (Stevens 1997). A hexagonal grid was randomly placed over a map of the sampling area, a sub-sample of hexagons were chosen from this population, and one sample was obtained at a randomly selected site within each grid cell. The hexagonal grid structure ensures systematic separation of the sampling, while the random selection of sites within grid cells ensures an unbiased estimate of ecological condition.

While most sites in this study were selected randomly to address population parameter estimation objectives, 18 sites were pre-selected to address additional objectives. Thirteen sampling sites were assigned to locations that had been sampled in previous SCCWRP reference surveys. The purpose of these samples was to assess temporal trends in the condition of the SCB at far-field reference sites, as described in the stated objectives. Seven of these sites were located along a 60-m transect that had been sampled in 1977, 1985, and 1990. Six of the sites were located along a 30-m transect that was sampled in 1985 and 1990. An additional five sample points were assigned to river mouth areas to assess gradients in condition at varying distances from river mouths. Two of these sites were assigned to the Los Angeles River, and one each to Aliso Creek, the San Gabriel River, and the Santa Ana River.

Table II-1. Number of stations and percent of area as a function of sampling strata for the Southern California Bight and Baja California for the 1998 Regional Monitoring Project.

Strata	No. of Stations	Area (km ²)	% of Area
Region			
North	54	1,273	38.9
Central	133	1,172	35.7
South	103	834	25.4
Depth			
Shallow (0-30 m)	194	1,281	37.4
Middle (31-120 m)	94	1,996	62.5
Deep (121-200 m)	2	3	< 0.1
Bays and Harbors			
Santa Monica Bay	30	370	11.3
San Diego Bay	46	77	2.3
Ports	37	61	1.9
Marinas	39	116	3.5
Other Bay/Harbor	37	53	1.6
POTW			
Small	36	109	3.3
Large	30	187	5.7
Rivers	31	41	1.2
Historical	13	13	0.4
Total US Stations¹	290	3,279	---
Mexico²			
North	28	1,750	60.0
Central	20	426	14.6
South	23	742	25.4
Total Mexico Stations	71	2,918	100.0

¹ Individual stations fall in multiple strata, and stratum areas overlap. Therefore, stations do not sum to 290, and the areas do not sum to 100%.

² The area percentages in this section are for Mexico only.

Table II-2. A comparison of the targeted number of sediment chemistry samples to the actual number obtained for the various strata from the original 1998 Regional Monitoring Project Coastal Ecology Workplan.

Sampling Strata	Planned Number of Samples	Actual Number of Samples
Offshore		
River Mouths	44	31
Small POTW	36	36
Large POTW	30	30
Other Offshore		
5 - 30 m	30	33
30 - 120 m	30	34
Bays and Harbors		
Ports, Industrial	35	37
Marinas	39	39
Other Bay/Harbor	39	37
San Diego Bay*	(45)	(46)
Historical Samples		
30 m sites	6	6
60 m sites	7	7
Mexico		
North	30	28
Central	30	20
South	30	23
Totals	386	361

* San Diego Bay is a special subpopulation within the bay and harbor category and is already included in the other totals.

Sample Collection

Sediment samples were collected using a 0.1 m² modified VanVeen grab sampler (Stubbs *et al.* 1987). Grab samples were required to be within 100 m 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 EPA standards. Glass containers with Teflon®-lined closures (500 mL) were used for all samples except those for AVS-SEM, which were collected in polycarbonate centrifuge bottles (250 mL). All samples except those for AVS-SEM and grain size analysis were stored frozen (-20°C) until analyzed. Samples for grain size and AVS analyses were stored at 4°C until analyzed. Further details on the sample collection procedures used in this study can be found in the Bight'98 Field Operations Manual (Bight '98 Field Sampling and Logistics Committee 1998). All samples collected for the sediment chemistry portion of the Bight'98 survey were kept under refrigeration (4°C), and samples for trace organic, metals, and TOC analysis were frozen within 24 h. 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'98 chemistry component as a function of parameter and laboratory is given in Table II-3.

Analytical Materials and Methods

The Bight'98 Survey used a performance-based approach to chemical analysis. Analytical methods employed were at the discretion of the participating laboratories, contingent upon their ability to demonstrate acceptable analytical performance. As discussed previously, extensive inter-laboratory calibration studies were performed to ensure that all laboratories were able to achieve comparable results. Analytical performance criteria can be found in the Southern California Bight 1998 Regional Marine Monitoring Survey Quality Assurance Plan (Bight'98 Steering Committee 1998).

Target Analytes

The target analytes for the Bight'98 Survey are listed in Table II-4. The 15 metals analytes were compiled from the list of those metals normally monitored by the participating agencies. The list of 24 polynuclear aromatic hydrocarbons (PAHs) includes the 16 PAHs on the EPA's priority pollutant list, as well as 8 additional compounds, including 5 methylated PAHs.

For the Bight'98 Survey, the decision was made to measure polychlorinated biphenyls (PCBs) on a congener-specific basis. The justification for performing congener-specific PCB analysis is as follows: 1) Although PCB compounds have been introduced into the environment in the form of Aroclors (i.e., commercial mixtures), they undergo degradation and metabolism that varies for different congeners, and as a function of environmental conditions (Zell and Ballschmiter 1980, Brown *et al.* 1987, Lake *et al.*

1992). In most cases, the PCB congener pattern found in field samples differs substantially from that measured in the source materials. Therefore, quantitation of PCBs in field samples based on pattern-matching methods (using Aroclors as standards) is likely to result in significant errors. Secondly, the toxicity of PCB congeners has been shown to vary tremendously from compound to compound (McFarland and Clarke 1989, Safe 1984). The concentrations of some toxic and potentially toxic PCB congeners may be extremely low in Aroclor standards (Schultz *et al.* 1989) and field samples, while the more abundant PCB congeners may be less toxic. In this context, to define PCB toxicity based on total PCBs is misleading. Lastly, congener-specific analysis of PCBs has become much more feasible and commonplace in recent years. This is due primarily to improved chromatographic technology and declining prices for individual PCB congener standards. All 209 PCB congeners have been synthesized and their relative retention times obtained using gas chromatography/electron capture detectors (GC/ECD) and various capillary columns (Mullin *et al.* 1984, Schultz *et al.* 1989, Larsen 1995). Moreover, the sensitivity of gas chromatography/mass spectrometry (GC/MS) instruments has been improving continuously. In fact, ion trap GC/MS instruments can achieve detection limits comparable to those typically obtainable by GC/ECD. Hence, some co-eluting PCB congeners with different chlorine contents may be measured separately, yielding better quantitative results. The list of 41 PCB target analytes (Table II-4) was compiled by consideration of their potential toxicity (McFarland and Clarke 1989), and the occurrence of the congeners in the common Aroclors 1242, 1248, 1254, and 1260.

The eight chlorinated pesticides selected as target analytes included the two isomers of DDT and their respective metabolites, DDD and DDE. Based upon previous studies, DDT and its metabolites are still the most ubiquitous organic contaminants in the SCB. Two isomers of chlordane were added as target analytes because they were of special interest to some participating agencies. The 25 LAB target analytes are those most commonly found in the effluent from sewage treatment plants (Zeng and Yu 1996).

Sediment Grain Size Analysis

A total of 354 samples were analyzed for particle size distribution as part of the Bight'98 project. The City of Los Angeles Laboratory analyzed 211 samples using a Coulter LS230 instrument. The other 143 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 μm . The Coulter instrument measures particles over the size range of 0.04-2000 μm . Because the instruments have different measurement limitations for larger particles, all samples were screened through 1000 μm and 2000 μm sieves prior to analysis to ensure comparability of data among laboratories. The fraction of a sediment sample greater than 2000 μm was designated as gravel.

TABLE II-3. The distribution of analyses and number of samples among laboratories for the Bight'98 Sediment Chemistry Study.

Parameter	CRG	CAS	LAC	LACSD	OCSD	EPA	SCCWRP	CSD	UABC	Total Samples
Grain Size			211					143		354
LABs							290			290
Metals		89	45	20	50			86	71	361
PAH	90		44	20	50			86		290
PCBs/ Pesticides	90		44	20	50			86	71	361
IW Metals [†]						108				108
SEM/AVS						106				106
P450 HRGS		268								268
TN							290			290
TOC							290			290
Lab Totals	180	357	344	60	150	214	870	401	142	2,718

CRG = CRG Marine Laboratories; CAS = Columbia Analytical Services; LAC = City of Los Angeles, Environmental Monitoring Division; LACSD = Sanitation Districts of Los Angeles County; OCSD = Orange County Sanitation District; EPA = EPA Research & Development; SCCWRP = Southern California Coastal Water Research Authority; CSD = City of San Diego; UABC = Universidad Autonoma de Baja California- Instituto de Investigacione Oceanologicas.

[†] Sediment interstitial water trace metals analyses.

Table II-4. Target analytes for the sediment chemistry component of the Bight'98 Regional Monitoring Study.

Trace Metals	PAHs	PCBs	Pesticides	LABs
Aluminum	<u>Low Molecular Weight</u>	PCB-18	4,4'-DDT	5-phenyldecane
Antimony		PCB-28	2,4'-DDT	4-phenyldecane
Arsenic	Acenaphthene	PCB-37	4,4'-DDD	3-phenyldecane
Barium	Acenaphthylene	PCB-44	2,4'-DDD	2-phenyldecane
Beryllium	Anthracene	PCB-49	4,4'-DDE	6-phenylundecane
Cadmium	Biphenyl	PCB-52	2,4'-DDE	5-phenylundecane
Chromium	Fluorene	PCB-66	α -Chlordane	4-phenylundecane
Copper	2-Methylnaphthalene	PCB-70	γ -Chlordane	3-phenylundecane
Iron	1-Methylphenanthrene	PCB-74		2-phenylundecane
Lead	Naphthalene	PCB-77		6-phenyldodecane
Mercury	1-Methylnaphthalene	PCB-81		5-phenyldodecane
Nickel	2,6-Dimethylnaphthalene	PCB-87		4-phenyldodecane
Selenium	1,6,7-Trimethyl-	PCB-99		3-phenyldodecane
Silver	naphthalene	PCB-101		2-phenyldodecane
Zinc	Phenanthrene	PCB-105		7&6-phenyltridecane
		PCB-110		5-phenyltridecane
		PCB-114		4-phenyltridecane
	<u>High Molecular Weight</u>	PCB-118		3-phenyltridecane
		PCB-119		2-phenyltridecane
	Benz[a]anthracene	PCB-123		7-phenyltetradecane
	Benzo[a]pyrene	PCB-126		6-phenyltetradecane
	Benzo[b]fluoranthene	PCB-128		5-phenyltetradecane
	Benzo[e]pyrene	PCB-138		4-phenyltetradecane
	Benzo[g,h,i]perylene	PCB-149		3-phenyltetradecane
	Benzo[k]fluoranthene	PCB-151		2-phenyltetradecane
	Chrysene	PCB-153		
	Dibenz[a,h]anthracene	PCB-156		
	Fluoranthene	PCB-157		
	Indeno(1,2,3-c,d) pyrene	PCB-158		
	Perylene	PCB-167		
	Pyrene	PCB-168		
		PCB-169		
		PCB-170		
		PCB-177		
		PCB-180		
		PCB-183		
		PCB-187		
		PCB-189		
		PCB-194		
		PCB-201		
		PCB-206		

Total Organic Carbon and Total Nitrogen

All total organic carbon (TOC) and total nitrogen (TN) analyses were performed by a single laboratory (SCCWRP). 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 methods used for the trace metals analysis of the Bight'98 sediment samples are the same as those used for the inter-laboratory calibration study previously described. Briefly, the sediment samples being analyzed for all metal analytes except mercury were digested in strong acid according to one of 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 method detection limits (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 Metals in Interstitial Water

The sediment samples collected for AVS-SEM analysis were first processed to extract sediment interstitial water for trace metals analysis (Ozretich and Shults 1998). A total of 178 samples were received over the course of approximately six weeks from SCCWRP via overnight delivery. Samples were stored in cold-room conditions (~2°C) upon arrival. Processing of all samples was completed within 5 d of receipt at the EPA facility in Newport, OR. For 35 or fewer samples, the processing time was 1-2 d. For the batch of 92 samples, processing was completed within 5 d.

Any water overlying the sediment in the full bottles was aspirated and discarded. Using a Teflon®-coated spatula and under a stream of nitrogen, approximately 0.5 cm was removed from the top of the sediment and discarded. This was done as an additional precaution against any loss of sample integrity due to partial oxidation in the surface layer. A sub-sample for AVS/SEM determination was then taken from each sample in large chunks (to reduce oxidation) and placed in 2-oz jars and frozen.

As the sediment was being scooped out, its texture was evaluated as to its suitability for obtaining a significant volume of interstitial water (IW). If the sample was sandy, little IW would be obtained by centrifuging. Thus, only fine-grained samples were processed further by removing sediment to about 3 cm below the bottle shoulder to account for the tipping of the bottle in the angled rotor of the centrifuge. The resulting combined mass was noted, the bottle was placed in a nitrogen-filled glove bag and another was processed, taking care to match the mass of the preceding sample for rotor balancing. The bottles were capped in a nitrogen stream or bag, placed in the rotor (Sorvall GSA) and centrifuged for 30 min at 10,000 rpm (~11,000 x g) at 20-22°C.

The IW was harvested within 1 h of centrifugation following the method of Ozretich and Schults (1998) with direct aspiration of water into a 60-mL polyethylene bottle with no subsequent filtration. All samples were clear. When sufficient volume of IW was present, 10 mL was withdrawn using a plastic-tipped macro pipet, and placed in a vessel provided for subsequent MicroTox analysis. These samples were placed in a refrigerated room (1.5-1.8°C) until shipment on gel ice at the end of the sample collection period to southern California. The remaining IW was acidified with 50 μ L Ultrex nitric acid for metals analysis and also refrigerated. On a daily basis, MilliQ water was passed through the aspiration system and blank samples were collected to check for analyte carry-over. Also, water not passed through the system was not acidified, but analyzed for trace metals. The first 10 mL of passed water became a blank MicroTox sample; the rest of the water was acidified and analyzed for metals.

The IW samples were analyzed for cadmium, copper, lead, nickel, and zinc using EPA Method 1640. The method involves a preconcentration step by reductive precipitation of the metal analytes using sodium tetrahydroborate. After addition of reagents, the IW samples are allowed to precipitate for 15-20 h. Samples are then filtered through 0.45-micron polycarbonate filters, and the retained precipitate is re-dissolved in a small volume of hot concentrated nitric acid. After cooling, samples are diluted to 10 mL with reagent water and analyzed by inductively coupled plasma mass spectrometry.

Simultaneously Extracted Metals-Acid Volatile Sulfide (SEM-AVS)

The samples set aside for SEM-AVS were analyzed by the procedure described in the report EPA-821-R-91-100 (Allen *et al.* 1991) and also in Allen *et al.* (1993). Briefly, the sample is kept under nitrogen at all times during the analysis to prevent oxidation. The AVS in the sample is converted to hydrogen sulfide (H₂S) by acidification with hydrochloric acid. The H₂S is then swept by flowing nitrogen into another container,

where it is trapped in an aqueous solution containing a mixed diamine reagent. The H_2S reacts with the mixed diamine reagent to form methylene blue, which is then measured spectrophotometrically. After release of H_2S is complete, the sediment solution is membrane filtered and the filtrate is analyzed for the SEM by inductively coupled plasma-mass spectrometry (ICP-MS).

Trace Organic Analyses

The procedures used for extraction and analysis of the Bight'98 sediment samples the organic analytes in this study were the same as those described for the inter-laboratory calibration study. All samples were solvent extracted using one of the following methods: accelerated solvent extraction, sohxlet, roller table, or microwave-assisted extraction. The extracts obtained were subjected to each laboratory's own clean-up procedures and were analyzed by an appropriate gas chromatographic method. Halogenated organics 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.

The LABs were analyzed by the procedure described in Zeng and Yu (1996), except that the samples were extracted using microwave-assisted solvent extraction rather a roller table. Prior to clean-up, the microwave extracts were concentrated to 2.2 mL, and 200 μL was sent to Columbia Analytical Services, Inc., for P450 HRGS analysis. Cleanup was performed on the remaining 2 mL of extract prior to analysis by GC-MS. A commercial mixture of LABs was obtained from Condea Vista Chemical Company, and after verification of the relative concentrations of the individual LAB constituents, the mixture was used for instrument calibration and quality control.

P450 Human Gene Reporter System

The P450 human gene reporter system (HRGS) is a method that screens for the presence of compounds that induce the production of cytochrome P450 in a special line of human liver cells (Anderson et al. 1995). These special cells contain P450 enzyme with a modified gene that has been fused with the luciferase gene of a firefly. When this line of cells is exposed to an extract containing compounds that induce the production of cytochrome P450, the luminescent enzyme luciferase is produced in a 1:1 proportion. After the exposure period, luciferin is added to the sample, which in turn reacts with luciferase to produce light that is measured by a luminometer. The light produced is a function of the concentration and the induction potency of the chemicals present in the extract.

The analytical procedures for using the P450 HRGS system are detailed in EPA Method 4425. Briefly, sediment samples were extracted with hexane using microwave assisted solvent extraction. The 200 μL hexane extracts were solvent exchanged into methylene chloride prior to testing. A 2 μL aliquot of the extracts were applied to single or duplicate wells in six-well plates with each well containing 2 mL of culture media. The

cells were incubated for a 16-hr exposure period, after which they were washed, lysed, and centrifuged. A 50 µL aliquot of the supernatant was applied to one well in a 96-well plate, along with the luciferase assay reagents. The resulting luminescence was measured using a luminometer. Each batch of samples analyzed included an extraction method blank, and an extract of the Santa Monica Bay (E6) reference sample.

Data Analysis

The chemistry data from the Bight'98 Study were analyzed in several ways: 1) The mean values for each parameter were calculated for the whole Bight and for subpopulations of interest; 2) The background levels of metal contaminants in the sediments were determined using an iron-normalization approach; subsequently, the percent of the study area above the background levels (i.e., impacted by anthropogenic pollution) was determined; 3) The percentages of the total mass of each chemical constituent residing in selected source strata were calculated and contrasted; 4) The existence of spatial and multivariate relationships among stations, subpopulations, and contaminants were examined using geographic information system (GIS) tools and principal component analysis (PCA); and 5) the number of stations and percent of the study area exceeding sediment quality guidelines were determined, and the potential for acute and/or chronic biological impacts was assessed using both theoretical and empirically derived sediment quality guidelines.

Mean Parameter Values

The mean parameter values for each station group of interest were calculated using a ratio estimator (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:

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

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 preliminary examination of the data. The assumption is conservative, in that its violation would lead to overestimation of the confidence intervals (Stevens and Kincaid 1997).

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. Various approaches have been used to determine the background metals concentrations in environmental samples, including elemental-normalization and sediment cores. After consideration of several possible techniques, the iron-normalization approach described by Schiff and Weisberg (1998) was selected. This technique was developed from data for sediments in the SCB from the previous regional survey conducted in 1994. Briefly, stations were selected that were not in proximity to any known or suspected sources of contamination. From these stations, a background Metal:Fe regression relationship was established through an iterative statistical process for each of the target analytes. A comparison with background levels predicted from the 1994 data and the 1998 data produced comparable results (Appendix A). The 99% prediction intervals were calculated for the regression lines for each element. Trace metal sediment concentrations above the 99% prediction intervals for the background regression lines are assumed to be due to anthropogenic pollution.

Spatial Analysis

The total mass of each chemical constituent residing in the top 2 cm of sediment in the entire Bight, and in the major source strata, was calculated as follows:

$$\text{Mass of } x = \text{AWM}_x \times \rho \times A \times D \times \text{CF}$$

Where, AWM_x is the area-weighted mean of constituent x , ρ is the bulk density of the sediment ($\sim 1.5 \text{ g/cm}^3$) for these calculations, A is the area under consideration, D is the depth of sample (2 cm), and CF is the cumulative unit conversion factor. The percent mass of each individual constituent for any subpopulation was calculated by:

$$\% \text{ Mass of } x \text{ in stratum} = \frac{\text{Mass } x \text{ in stratum}}{\text{Mass } x \text{ in whole Bight}} \times 100$$

In addition, the average percent of the total mass across all constituents was calculated to facilitate comparison of the overall contamination load among the different source strata. The 95% confidence intervals for the average percent of constituent mass in the source strata were calculated by propagating the standard error associated with the individual parameter area-weighted mean values through the calculations using standard error propagation equations (Harris 1995), and multiplying the resulting cumulative error by 1.96.

The spatial distribution and variability of the sediment contamination at individual stations in the SCB was studied using *MapInfo Professional 6.0* GIS software. Maps of parameter concentration ranges, numbers of parameters above background, and numbers of sediment quality criteria exceeded at each station were produced for the entire Bight'98 study area.

The spatial patterns of sediment contamination in the SCB were further evaluated using the multivariate techniques of PCA and cluster analysis. These multivariate methods are particularly effective as exploratory tools for evaluating relationships in compositional patterns for large and complex data sets, and can identify relationships among contaminants that are not readily apparent. The PCA and cluster analyses were used to elucidate covariance among contaminants and identify regions of the SCB with similar contamination patterns. The PCA and cluster analyses were performed using JMP software (SAS Institute 2001). Further details on the specific procedures used for the PCA and cluster analyses are presented in Chapter VI.

Sediment Quality Assessment

Several approaches were used in evaluating the potential for adverse biological impacts stemming from the observed levels of sediment contamination. The first

approach is based on two sediment quality guidelines (SQGs) developed by Long and Morgan (1990) and revised by Long *et al.* (1995): the effects range low (ERL) and the effects range median (ERM). These SQGs were developed based on correlations between observed acute toxicity and the measured concentrations of selected sediment contaminants. The ERL and ERM values are the 10th and 50th percentiles of the measured sediment concentrations of the selected contaminants in samples with significant acute toxicity. The ERL and ERM values are based solely on coincidental occurrence and do not necessarily imply a cause-and-effect relationship between the observed toxicity and any individual contaminant. Inasmuch as the ERLs and ERMs were the primary criteria used to assess the potential for adverse biological impacts due to sediment contamination in the 1994 Southern California Bight Pilot Project (SCBPP, Schiff and Gossett 1998), these criteria were selected for use in this study to facilitate comparison with the data evaluations performed for the SCBPP. In addition, the ERL and ERM SQGs are widely recognized and applied by the environmental community for sediment quality assessment. The specific ERL and ERM values for each target analyte are given in Table II-5.

Long and MacDonald (1998) have made recommendations on the use of such empirically derived sediment quality guidelines for marine and estuarine ecosystems. In an effort to account for the possible additive toxic effects of chemical mixtures in sediments, the use of mean SQG quotients has been recommended. Specifically, numerical SQGs ranges based upon mean ERM quotient values have been developed (Long and MacDonald 1998, Fairey *et al.* 2001). The mean SQG quotient approach takes into account the number and magnitude of individual SQG exceedances. For example, the mean ERM quotient (MERMQ) is calculated as follows:

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

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 SQG quotients were calculated for all sediment samples and each station in the SCB was then assigned to one of several possible levels of concern for either acute or chronic toxicity.

The other approaches used for assessment of potential biological impacts are based on evaluation of the direct exposure of benthic organisms to the bioavailable fraction of the sediment-associated contaminants. It is a well-established concept in ecotoxicology that the freely dissolved (i.e., uncomplexed and non-sorbed) fraction of the total contaminant concentration in sediments is the most bioavailable (Hamelink *et al.* 1994). In this study, the freely dissolved concentrations of the sediment contaminants are calculated using equilibrium partitioning theory, simultaneous extracted metals relative to the acid volatile sulfide ($\Sigma\text{SEM-AVS}$), and by measuring interstitial water concentrations directly.

The essence of the EqP approach to assessing sediment-associated chemicals is the comparison of measured concentrations with those that are expected to cause biological effects of an acute or chronic nature. Concentrations of PAHs and DDTs associated with acutely toxic and chronic effects were computed from Swartz *et al.* (1995 and 1994), U.S. EPA (2000) and Swartz *et al.* (1994), respectively. The PCB and SEM-AVS concentrations of concern for chronic toxicity were computed using relationships from DiToro *et al.* (2000) and U.S. EPA (2000b), respectively. These computed organic carbon-normalized bulk sediment concentrations of PAHs and PCBs are considered to be 1.0 toxic unit (TU) or equilibrium partitioning sediment guideline (ESG) unit with respect to acute or chronic effects. The assessment of these two groups of compounds in a sample consisted of the summation of the ratios of the measured carbon-normalized concentrations to the computed threshold concentrations yielding fractional TUs and ESGs (TU_f and ESG_f). The probability of an expected biological response (Swartz *et al.* 1995) or the exceedance of a U.S. EPA guideline was determined by the magnitude of the $\acute{O}TU_f$ or $\acute{O}ESG_f$. Factors were applied to account for unmeasured or, in the case of using the Swartz *et al.* (1995) model, undetected PAH compounds. Carbon-normalized DDTs and SEM-AVS were compared to single-threshold concentrations of expected acute or chronic effects. The sediment interstitial water total dissolved metal concentrations were compared to the U.S. EPA Water Quality Criteria for freely dissolved metals (U.S. EPA 1999).

Quality Assurance and Quality Control

Quality assurance and quality control activities and procedures for the Bight'98 Study were carried out in accordance with the Bight'98 Quality Assurance Plan (QAP; Bight '98 Steering Committee 1998). The primary goal of the QAP was to ensure that the data generated for the Bight'98 Study were comparable among all participants. Many organizations participated in the collection and analysis of samples, and maintaining consistency throughout the field and laboratory operations to ensure data quality and comparability was critical to the success of the project.

The quality assurance program for Bight'98 addressed two distinct but related activities: quality assurance (QA) and quality control (QC). The QA portion included design, planning, and management activities conducted prior to implementation of the project to ensure that the appropriate kinds and quantities of data would be collected. The goals of QA were to ensure that: 1) appropriate collection, processing, and analysis techniques would be applied consistently and correctly; 2) the number of lost, damaged, and uncollected samples would be minimized; 3) the integrity of the data would be maintained and documented from sample collection to entry into the data record; 4) all data would be comparable; and 5) results could be reproduced.

Quality control (QC) activities were implemented during the data collection phase of the project, as prescribed by the QAP. The QC activities ensured that measurement error and bias were identified, quantified, and accounted for or eliminated, if practical.

The QC activities included both internal and external checks. Typical internal QC checks included repeated measurements, internal test samples, analysis of laboratory reagent blanks, use of independent methods to verify findings, and use of standard reference materials. Typical external QC checks included exchanging samples among laboratories for reprocessing to test comparability of results, independent performance audits, and periodic proficiency examinations. Data comparability for the sediment chemistry part of the Bight'98 project was achieved through a combination of method optimization and performance-based standards.

Many of the organizations participating in the Bight'98 Survey have well established monitoring programs. The QA activities for Bight'98 included developing a common field manual and documenting the comparability of methods and performance among participating field crews and laboratories. Training of field and laboratory personnel was focused on communicating the goals and objectives of the overall project as well any modifications in methods or procedures that have been made to ensure data comparability. The purpose of the training was to ensure that all participants were able to implement the agreed-upon procedures in a consistent manner with comparable proficiency. Quantitative measures of the overall effectiveness of QA/QC activities have been identified in the QAP in order to have a measure for the degree of success. These quantitative measures of QA/QC success are herein referred to as measurement quality objectives (MQOs).

Table II-5. The values of the sediment quality guidelines used for assessment of the potential for adverse biological impacts due to sediment contamination in this study (Long *et al.* 1995).

Contaminant	ERL (µg/g dry wt)	ERM (µg/g dry wt)	Other SQGs Used¹
Metals (µg/g dry wt)			
Arsenic	8.2	70	
Cadmium	1.2	9.6	4.21
Chromium	81	370	
Copper	34	270	
Lead	46.7	218	112.18
Mercury	0.15	0.71	
Nickel	20.9	51.6	
Silver	1.0	3.7	1.77
Zinc	150	410	
Organics (ng/g dry wt)			
Acenaphthene	16	500	
Acenaphthylene	44	640	
Anthracene	85.3	1,100	
Fluorene	19	540	
2-Methyl naphthalene	70	670	
Naphthalene	160	2,100	
Phenanthrene	240	1,500	
Benzo(a)anthracene	261	1,600	
Benzo(a)pyrene	430	1,600	
Chrysene	384	2,800	
Dibenzo(a,h)anthracene	63.4	260	
Fluoranthene	600	5,100	
Pyrene	665	2,600	
Total PAHs	4022	44,792	290, 1,800, 10,000
Total DDT	1.58	46.1	100, 300
Total PCBs	22.7	180	48, 470, 1,700

¹Metals: Probable effect level (PEL) values from MacDonald *et al.* (1996), and used in the SQG quotient approach developed by Fairey *et al.* (2001). Organics: SQGs for PAHs, and DDT. The units are µg/g-OC, and are from Swartz (1999) and Swartz (1994), respectively. The PCB SQGs are in ng/-dry-g from MacDonald *et al.* 2000.

III. INTER-LABORATORY PERFORMANCE AND CALIBRATION STUDIES

Organics

Background

Many environmental assessments require compilation of sediment chemistry data from multiple laboratories, either to extend temporal records for trend assessment or to extend geographic scale for spatial assessment. Such data compilations assume a degree of comparability among laboratories, even though analytical personnel, methods, and instrumentation may vary. Dissimilarity in sampling and subsampling techniques, sample preparation, clean-up procedures, detection capabilities, and instrumental techniques can lead to differences in analytical results.

The comparability of data among different laboratories is improved when state-certified laboratories using standardized methodologies perform the analyses. The certification process requires laboratories to demonstrate their ability to attain generic performance criteria, which only partially satisfies the presumption of data comparability in real-world environmental assessments. Reliance on *a priori* performance demonstration with standardized methods may be unsatisfactory when new compounds are added to the analytical list, when detection goals are set below the demonstrated method capability, when sample matrix components confound the standardized methods, and when methods must be modified or replaced with non-standard procedures in order to meet project-specific goals.

Standard reference materials (SRMs) are often used to help bridge such gaps and demonstrate performance capability among laboratories. However, SRMs typically fall short of the goal because certified values are typically given only for a subset of the target analytes, and may be influenced by the limitations of the methods used to generate the certified results in the first place. Moreover, substantial differences between the matrices of the samples and the SRM can significantly affect results. Although SRMs are an important component in any process to assess analytical performance, additional steps may be necessary.

To assess whether existing processes are effective for ensuring comparability when processing local samples with complex matrices, seven laboratories participated in an inter-laboratory performance assessment conducted as part of the Bight'98 Survey. All but one of the participating laboratories (SCCWRP) were certified by the State of California, and all had at least 10 years of experience. In the following sections, we present the results of the intercalibration efforts, identify reasons for observed differences, and discuss procedures important to increasing regional comparability when working with difficult samples and analytes.

Analytical Materials and Methods

Sediment for distribution among the laboratories was collected from two locations in southern California. The first was from the Palos Verdes Shelf (Los Angeles County Sanitation District Station 7C; Stull *et al.* 1986), which was selected because it typically contains concentrations of DDT and PCB at the upper range of southern California sediments. The second station was from Santa Monica Bay (City of Los Angeles Station E6; City of Los Angeles 2000), a station known to have high concentrations of PAHs. Both stations have complicated organic matrices as a result of decades of ocean disposal and benthic processes. After collection, the sediments were thoroughly homogenized and allowed to stabilize at 4°C for approximately one month. Thereafter, sediments were split into pre-cleaned glass jars with Teflon®-lined closures, and then kept frozen at –20°C until distributed to the participating laboratories.

The participating laboratories were allowed to use any method they would normally use to process such sediments. The extraction methods used are presented in Table III-1. Laboratories were also allowed to choose their own gas chromatographic (GC) detector as long as they could achieve the specified detection limits. The GC detectors used for this study included electron capture detectors, quadrupole mass spectrometers, or ion trap mass spectrometers. While laboratories were given considerable methodological freedom, several consensus-based restrictions were implemented to ensure consistent method detection limits and reporting limits among the laboratories. First, a minimum sample size of 10 grams dry weight was specified. Second, the gas chromatographic column was restricted to the equivalent of a J&W DB-XLB (Frame *et al.* 1996) for DDT/PCB and DB-5 for PAHs. For electron capture detection, DB-5 was recommended, but not required as the second column for verification purposes. Moreover, each laboratory had to demonstrate that its chromatographic approach separated 40 of the 41 congeners from the custom PCB calibration standard prepared for this study.

The Bight'98 Inter-laboratory Calibration Study included three components. The first was an initial intercalibration exercise to assess how the results of the laboratories compared using their existing procedures. The second phase involved a series of informal studies to identify the laboratory procedures that were contributing most to observed differences among the laboratories. These informal studies included aspects such as a single laboratory distributing its extract to other laboratories in order to determine the relative contributions of extraction procedures and final instrumental analyses to the overall analytical variation. The third phase involved redistribution of the original intercalibration samples to assess whether the methodological improvements adopted as a result of the informal studies were effective in improving laboratory comparability. To quantify the performance among laboratories, the mean, standard deviation (SD) and coefficient of variation (CV) of the results from all laboratories were calculated for each analyte. The CV, also known as the percent relative standard deviation, is the ratio of the standard deviation to the mean expressed as a percentage, and is a parameter commonly used as a measure of analytical precision.

Descriptive Results

For total detectable PAHs, the differences among laboratories in the first intercalibration were as much as an order of magnitude for both samples (Tables III-2 and III-3). Most of this difference was attributable to differences in detection limits. Lab 1 reported the lowest total detectable PAH concentration and detected measurable concentrations for less than 20% of the target compounds, whereas Lab 7 reported measurable concentrations for 100% of these compounds in both samples. However, detection limit differences did not explain all of the discrepancies, as exemplified by the order of magnitude difference for almost every compound between Labs 3 and 4.

By the second intercalibration test, the labs only differed from the mean PAH value by about 30% in both samples (Tables III-4 and III-5). The most notable changes were for Labs 1 and 4 that originally reported significantly lower values than the other labs in the first test, and Lab 3, which reported higher initial values. The greater comparability among labs was also apparent for individual compounds, as the median coefficient of variation for individual compounds was greater than 60% in the first test, but less than 30% in the latter test.

The pattern of performance results among the laboratories for total detectable PCBs and total detectable DDTs was similar to that observed for PAHs (Tables III-6 to III-9). In the initial test, there was about an order of magnitude difference among laboratories for both samples, but this difference was generally less than 40% between the highest and lowest laboratories in the second test. For DDT, the largest change was for the concentration of 4,4'-DDE. Each laboratory had different problems analyzing samples at the high concentrations in these samples. For example, one laboratory found that they were not diluting the sample extract sufficiently to get the peak size within the linear range of the detector. Another laboratory had to modify its extraction and clean-up procedures to account for the higher concentrations.

Discussion

This study was a precursor to the Bight'98 Survey. It was conducted to determine whether multiple laboratories using different methods could produce data of sufficient similarity, or if it was necessary to have a single laboratory conduct all analyses. While there were considerable differences prior to the intercalibration testing, it was ultimately possible to resolve these differences and achieve comparable results using a performance-based approach.

Resolving pre-existing differences among laboratories resulted from many factors, including adjustments to sample extraction methods, improvement of clean-up procedures, changing sample sizes, adjusting GC oven parameters for improved separation, and switching from older instrumentation to newer instrumentation with greater sensitivity. Another major factor affecting the results was interpretation of the chromatograms themselves. In some cases, a laboratory may have ignored a peak that other laboratories were identifying as a target analyte. In other cases, peaks were

switched or methods used to decide where to draw baselines for peak integration needed to be refined so that consistent techniques were used.

The specific analytical factors that were identified during this process are too numerous to describe here, but they are not critical to the discussion because another group of laboratories would probably encounter different issues. Of greater importance, the laboratories were given the opportunity to attain equivalent experience in handling extremely difficult matrices. Moreover, this type of study initiates a communication process that begins with a consensus on sample size, maximum MDL, and chromatographic separation. In the end, through an iterative approach, this consensus is extended to nearly every decision about sample processing alternatives. A good performance-based approach fosters communication among laboratories that would not normally occur in its absence. Another important factor in achieving success was the recognition among participants that a performance-based approach conducted with local samples was worth the commitment. For many of the laboratories involved, the work associated with achieving data comparability consumed more time and effort than processing the actual samples from the regional survey that this exercise was intended to support. In order for this approach to be pragmatic, the participants had to feel that the increased knowledge and staff education gained offset the extra costs incurred and the additional time invested.

To objectively determine whether all the laboratories had achieved comparability, performance criteria were established based on the National Institute of Standards and Technology (NIST) intercalibration exercises. To indicate acceptable performance, results from each laboratory needed to be within 40% of the mean for 80% of the sentinel compounds. We were able to achieve this goal, even with samples that were selected to be more complex and challenging than usual. Still, it is important to recognize that we did observe larger differences for some compounds and concluded that it is unrealistic to expect that all compounds will be measured within 40% of the mean even within the most rigorous performance-based exercise. Overall, this study has shown that performance-based chemistry can produce comparable results, even given a wide range of analytical methods and instrumentation.

Table III-1. Extraction method and instrumentation used by each laboratory.

Laboratory Number	Extraction Method	DDT/PCB Detector	PAH Detector
1	Accelerated Solvent Extraction	Electron Capture Detector and Ion Trap Mass Spectrometer	Mass Spectrometer
2	Roller Table	Electron Capture Detector	Mass Spectrometer
3	Accelerated Solvent Extraction	Electron Capture	Mass Spectrometer
4	Sohxlet Extraction	Electron Capture	Mass Spectrometer
5	Roller Table	Electron Capture	Mass Spectrometer
6	Microwave Assisted Extraction	Mass Spectrometer (SIM Mode)	Mass Spectrometer
7	Accelerated Solvent Extraction	Electron Capture Detector	Mass Spectrometer

Table III-2. The PAH results (ng/g-dry wt) for the first series of inter-laboratory calibration analyses of sediment from Station 7C.

COMPOUND	LAB1	LAB2	LAB3	LAB4	LAB5	LAB6	LAB7	Mean	SD	CV%
Naphthalene	ND	35	45	ND	31	58	42	42	10	25
2-Methylnaphthalene	ND	57	78	5	54	119	60	62	37	59
1-Methylnaphthalene	ND	23	32	ND	28	66	26	35	18	51
Biphenyl	ND	44	54	17	25	57	21	36	17	48
2,6-Dimethyl-naphthalene	28	30	62	ND	39	64	38	44	16	36
Acenaphthylene	25	6	36	11	32	40	28	25	13	50
Acenaphthene	ND	ND	ND	ND	ND	ND	39	ND	***	***
2,3,5-Trimethyl-naphthalene	ND	ND	ND	ND	ND	15	18	16	2	13
Fluorene	ND	7	9	ND	ND	20	6	10	6	63
Phenanthrene	ND	36	60	9	64	52	54	46	20	44
Anthracene	ND	ND	48	6	ND	49	34	34	20	58
1-Methyl phenanthrene	ND	42	ND	ND	21	ND	15	26	14	55
Fluoranthene	ND	ND	53	12	57	64	63	50	22	43
Pyrene	43	255	374	20	109	108	151	151	124	82
Benz[a]anthracene	ND	ND	79	9	47	49	47	46	25	53
Chrysene	ND	ND	67	9	53	25	63	43	25	58
Benzo[b]fluoranthene	ND	ND	292	14	160	61	168	139	108	77
Benzo[k]fluoranthene	ND	ND	104	10	55	64	83	63	35	56
Benzo[e]pyrene	ND	233	241	19	191	77	198	160	91	57
Benzo[a]pyrene	ND	ND	236	16	186	64	174	135	91	68
Perylene	41	359	312	20	165	138	101	162	129	80
Indeno[1,2,3-c,d]pyrene	ND	ND	26	ND	ND	53	93	57	34	59
Dibenz[a,h]anthracene	ND	ND	ND	ND	ND	ND	40	ND	***	***
Benzo[g,h,i]perylene	ND	ND	91	ND	112	37	144	96	45	47
Total PAHs	137	1,130	2,300	177	1,430	1,280	1,670	1,160	781	67

ND = Not detected.

*** = Data not reported.

Table III-3. The PAH results (ng/g-dry wt) for the first series of inter-laboratory calibration analyses of the sediment from Station E6.

COMPOUND	LAB1	LAB2	LAB3	LAB4	LAB5	LAB6	LAB7	Mean	SD	CV%
Naphthalene	54	171	279	27	139	259	211	163	97	59
2-Methylnaphthalene	129	485	721	59	405	615	653	438	258	59
1-Methylnaphthalene	61	172	272	23	181	222	226	165	91	55
Biphenyl	233	756	1140	97	606	770	650	607	350	58
2,6-Dimethyl-naphthalene	131	217	401	37	228	203	356	225	124	55
Acenaphthylene	ND	4	ND	ND	ND	ND	10	7	4	59
Acenaphthene	ND	15	46	ND	ND	ND	7	23	20	89
2,3,5-Trimethyl-naphthalene	ND	19	ND	4	15	ND	106	36	47	130
Fluorene	ND	38	75	2	24	69	26	39	28	72
Phenanthrene	ND	137	469	9	109	112	95	155	160	103
Anthracene	ND	ND	111	13	19	18	39	40	41	102
1-Methyl phenanthrene	ND	154	ND	ND	51	ND	31	79	66	84
Fluoranthene	76	ND	495	26	87	108	173	161	171	106
Pyrene	91	ND	1120	28	79	111	165	266	421	158
Benz[a]anthracene	ND	ND	284	30	65	38	100	103	105	101
Chrysene	60	ND	320	31	83	46	136	113	108	96
Benzo[b]fluoranthene	ND	ND	672	19	205	38	178	222	264	119
Benzo[k]fluoranthene	ND	ND	205	18	77	41	68	82	73	89
Benzo[e]pyrene	ND	ND	367	11	171	63	195	161	138	85
Benzo[a]pyrene	ND	ND	409	13	162	ND	189	193	163	85
Perylene	ND	249	183	5	72	32	59	100	95	95
Indeno[1,2,3-c,d]pyrene	ND	ND	ND	ND	69	23	155	82	67	81
Dibenz[a,h]anthracene	ND	ND	ND	ND	ND	38	42	40	3	8
Benzo[g,h,i]perylene	ND	ND	60	ND	109	30	163	90	58	64
Total PAHs	835	2,420	7,630	453	2,960	2,840	4,030	3,020	2,380	79

Table III-4. The PAH results (ng/g-dry wt) for the second series of inter-laboratory calibration analyses of the sediment from Station 7C.

COMPOUND	LAB1	LAB2	LAB3	LAB4	LAB5	LAB6	LAB7	Mean	SD	CV%
Naphthalene	***	32	28	34	27	11	11	27	9	35
2-Methylnaphthalene	45	54	63	56	51	54	***	54	6	11
1-Methylnaphthalene	***	19	29	20	29	ND	***	24	5	22
Biphenyl	49	26	39	47	27	33	***	37	10	26
2,6-Dimethyl-naphthalene	82	31	75	79	27	28	***	53	27	54
Acenaphthylene	***	15	42	87	43	12	***	40	30	76
Acenaphthene	***	ND	ND	7	ND	ND	***	ND	***	***
2,3,5-Trimethyl-naphthalene	***	ND	ND	19	ND	14	***	17	4	22
Fluorene	***	3	21	13	ND	ND	***	13	9	72
Phenanthrene	ND	71	53	58	69	66	***	63	8	12
Anthracene	***	20	39	44	24	21	***	29	11	38
1-Methylphenanthrene	***	25	ND	ND	ND	23	***	24	1	6
Fluoranthene	51	68	55	39	72	75	***	60	14	23
Pyrene	144	215	137	138	172	168	***	162	30	18
Benz[a]anthracene	48	46	61	56	30	60	***	50	12	24
Chrysene	36	58	63	78	74	63	***	62	15	24
Benzo[b]fluoranthene	***	163	267	103	53	95	***	136	83	61
Benzo[k]fluoranthene	***	49	80	63	50	95	***	67	20	29
Benzo[e]pyrene	97	124	193	131	62	113	***	120	43	36
Benzo[a]pyrene	76	141	203	109	67	52	***	108	57	52
Perylene	127	259	227	237	140	142	***	189	58	31
Indeno[1,2,3-c,d]pyrene	***	35	ND	ND	88	79	***	67	28	42
Dibenz[a,h]anthracene	***	18	ND	ND	ND	ND	***	ND	***	***
Benzo[g,h,i]perylene	28	99	75	ND	75	91	***	74	28	38
Total PAHs	***	1,570	1,750	1,420	1,180	1,300	***	1,440	224	15

ND = Not detected.

*** = Data not reported.

Table III-5. The PAH results (ng/g-dry wt) for the second series of inter-laboratory calibration analyses of the sediment from Station E6.

COMPOUND	LAB1	LAB2	LAB3	LAB4	LAB5	LAB6	LAB7	Mean	SD	CV%
Naphthalene	173	162	170	191	139	193	***	171	20	12
2-Methylnaphthalene	388	435	480	532	336	525	***	449	78	17
1-Methylnaphthalene	***	145	185	166	153	144	***	159	17	11
Biphenyl	650	644	850	800	535	796	***	712	121	17
2,6-Dimethyl-naphthalene	365	212	255	343	214	269	***	276	65	23
Acenaphthylene	***	8	ND	ND	ND	ND	***	ND	***	***
Acenaphthene	***	ND	25	15	ND	ND	***	20	7	35
2,3,5-Trimethyl-naphthalene	***	22	ND	119	47	ND	***	62	50	81
Fluorene	ND	25	49	40	39	52	***	41	11	26
Phenanthrene	114	131	145	130	142	141	***	134	11	7
Anthracene	***	33	34	58	41	29	***	39	11	29
1-Methyl phenanthrene	ND	62	27	68	73	128	***	71	36	51
Fluoranthene	183	280	150	135	146	183	***	179	53	30
Pyrene	211	196	155	230	125	185	***	184	38	21
Benz[a]anthracene	93	126	145	118	37	114	***	105	38	36
Chrysene	115	88	120	152	127	145	***	124	23	18
Benzo[b]fluoranthene	***	164	330	179	60	92	***	165	105	63
Benzo[k]fluoranthene	***	63	103	167	60	90	***	97	43	45
Benzo[e]pyrene	117	115	155	183	51	115	***	123	44	36
Benzo[a]pyrene	94	109	195	191	52	65	***	118	62	52
Perylene	ND	91	78	110	70	26	***	75	31	42
Indeno[1,2,3-c,d]pyrene	***	44	ND	ND	88	66	***	66	22	33
Dibenz[a,h]anthracene	***	26	ND	ND	ND	ND	***	ND	***	***
Benzo[g,h,i]perylene	34	100	ND	ND	80	97	***	78	30	39
Total PAHs	***	3,280	3,650	3,930	2,610	3,450	***	3,390	494	15

ND = Not detected.

*** = Data not reported.

Table III-6. The DDT and PCB results (ng/g-dry wt) for the first series of inter-laboratory calibration analyses for Station 7C

COMPOUND	LAB1	LAB2	LAB3	LAB4	LAB5	LAB6	LAB7	Mean	SD	CV%
4,4'-DDE	6,570	12,900	***	17,100	16,300	5,930	4,830	10,600	5,500	52
4,4'-DDD	410	886	***	1,090	8	384	285	510	401	79
4,4'-DDT	547	683	***	1,490	480	185	483	645	447	69
2,4'-DDE	820	1870	***	2,060	769	769	801	1180	610	52
2,4'-DDD	113	413	***	363	328	73	143	239	146	51
2,4'-DDT	7	26	***	ND	352	12	23	84	150	179
Total DDTs	8,460	16,800	***	21,900	19,500	7,350	6,560	13,400	6,760	50
PCB 18	ND	18	***	23	12	10	13	15	5	34
PCB 28	25	49	***	45	33	12	42	35	14	41
PCB 52	46	91	***	98	61	55	88	73	22	30
PCB 49	30	65	***	64	39	17	60	46	20	44
PCB 44	56	80	***	70	46	31	60	57	17	30
PCB 37	ND	230	***	ND	163	10	3	102	113	111
PCB 74	29	57	***	54	34	35	58	44	13	30
PCB 70	78	150	***	104	71	52	137	99	39	39
PCB 66	61	129	***	73	79	25	90	76	34	45
PCB 101	12	95	***	73	302	50	73	101	102	102
PCB 99	24	58	***	49	22	31	52	39	15	39
PCB 119	ND	ND	***	ND	ND	ND	2	ND	***	***
PCB 87	18	ND	***	28	440	24	44	111	184	166
PCB 110	24	335	***	ND	90	46	85	116	125	108
PCB 81	ND	ND	***	ND	ND	10	38	24	20	83
PCB 151	ND	ND	***	30	20	12	14	19	8	43
PCB 77	ND	ND	***	8	24	8	2	10	10	91
PCB 149	24	54	***	50	12	28	40	35	16	47
PCB 123	ND	ND	***	9	3	11	ND	8	4	58
PCB 118	60	102	***	94	10	48	87	67	35	52
PCB 114	ND	ND	***	ND	ND	9	***	ND	***	***
PCB 168/153	23	97	***	83	37	34	99	62	35	55
PCB 105	ND	85	***	62	21	32	49	50	25	50
PCB 138	ND	117	***	ND	314	26	975	358	429	120
PCB 158	ND	ND	***	ND	7	21	6	11	8	74
PCB 187	9	22	***	17	9	14	22	15	6	38
PCB 183	ND	10	***	8	6	8	11	8	2	21
PCB 126	ND	ND	***	ND	ND	8	ND	ND	***	138
PCB 128	ND	20	***	14	7	12	16	14	5	34
PCB 167	ND	ND	***	5	ND	6	3	5	1	29
PCB 177	ND	12	***	ND	4	9	10	9	3	37
PCB 200	ND	3	***	18	ND	5	***	8	8	94
PCB 156	ND	ND	***	7	ND	13	15	12	4	36
PCB 157	ND	ND	***	ND	ND	7	1	4	4	97
PCB 180	11	40	***	1	18	19	48	23	18	78
PCB 170	ND	19	***	ND	13	14	21	17	4	24
PCB 169	ND	ND	***	ND	13	9	ND	7	6	88
PCB 189	ND	5	***	3	ND	6	2	4	2	50
PCB 194	ND	9	***	4	6	12	2	7	4	57
PCB 206	ND	ND	***	6	4	6	21	9	8	81
Total PCBs	529	1,950	***	1,100	1,920	785	1,390	1,280	586	46

ND = Not detected.

*** = Data not reported.

Table III-7. DDT and PCB results (ng/g-dry wt) for the first series of inter-laboratory calibration analyses for Station E6.

COMPOUND	LAB1	LAB2	LAB3	LAB4	LAB5	LAB6	LAB7	Mean	SD	CV%
4,4'-DDE	207	316	***	474	123	188	151	254	123	48
4,4'-DDD	17	26	***	35	21	10	26	24	8	36
4,4'-DDT	2	67	***	79	42	17	10	34	30	89
2,4'-DDE	25	54	***	30	23	13	21	27	14	51
2,4'-DDD	26	56	***	107	67	5	14	46	38	84
2,4'-DDT	1	ND	***	ND	6	16	4	7	6	97
Total DDTs	277	519	***	725	283	249	226	378	182	48
PCB 18	ND	7	***	12	6	11	8	9	2	26
PCB 28	18	17	***	22	20	ND	27	21	4	18
PCB 52	26	24	***	39	29	31	40	30	7	22
PCB 49	15	18	***	25	17	3	24	17	7	42
PCB 44	45	26	***	27	19	14	34	26	11	42
PCB 37	ND	29	***	21	15	22	ND	22	5	25
PCB 74	ND	16	***	17	12	13	25	17	5	27
PCB 70	24	29	***	37	30	15	52	31	12	37
PCB 66	35	42	***	40	32	9	39	33	12	37
PCB 101	50	52	***	44	84	29	64	53	17	33
PCB 99	19	16	***	15	14	13	35	20	8	41
PCB 119	ND	ND	***	ND	ND	ND	2	ND	***	***
PCB 87	16	26	***	26	22	23	33	24	5	22
PCB 110	18	63	***	7	35	33	66	38	22	58
PCB 81	ND	ND	***	ND	ND	14	23	19	7	35
PCB 151	ND	ND	***	17	15	9	13	13	3	25
PCB 77	ND	ND	***	8	ND	7	2	6	4	64
PCB 149	25	31	***	40	14	25	37	29	9	30
PCB 123	ND	ND	***	6	4	12	ND	7	4	61
PCB 118	48	50	***	56	8	32	74	45	21	46
PCB 114	ND	ND	***	ND	ND	11	***	ND	***	***
PCB 168/153	27	62	***	61	21	32	100	50	27	55
PCB 105	ND	36	***	35	15	21	29	27	8	30
PCB 138	36	50	***	49	8	33	80	45	23	51
PCB 158	ND	6	***	ND	5	11	67	22	30	135
PCB 187	ND	16	***	15	5	15	22	15	6	37
PCB 183	ND	9	***	7	4	9	11	8	2	29
PCB 126	ND	ND	***	ND	ND	19	1	10	13	134
PCB 128	ND	17	***	15	7	12	16	13	4	29
PCB 167	ND	ND	***	3	ND	8	3	4	3	61
PCB 177	ND	9	***	8	5	8	12	8	2	25
PCB 200	ND	4	***	21	ND	6	***	10	9	90
PCB 156	ND	ND	***	5	ND	14	12	9	4	44
PCB 157	ND	ND	***	ND	ND	10	1	4	5	121
PCB 180	10	32	***	1	43	18	43	25	16	65
PCB 170	ND	22	***	24	5	17	22	17	7	41
PCB 169	ND	ND	***	ND	ND	11	ND	ND	***	***
PCB 189	ND	4	***	1	ND	8	2	3	3	86
PCB 194	ND	13	***	7	7	11	3	8	3	42
PCB 206	ND	14	***	4	ND	6	9	8	4	53
Total PCBs	411	739	***	713	502	595	1,030	657	200	30

ND = Not detected.

*** = Data not reported.

TableIII-8. The DDT and PCB results (ng/g-dry wt) for the second round of inter-laboratory calibration analyses for Station 7C.

COMPOUND	LAB1	LAB2	LAB3	LAB4	LAB5	LAB6	LAB7	Mean	SD	CV%
4,4'-DDE	***	11,800	14,800	11,800	6,680	8,610	***	10,700	3,150	29
4,4'-DDD	***	791	994	693	382	398	***	652	262	40
4,4'-DDT	***	879	562	334	326	434	***	507	229	45
2,4'-DDE	***	1,720	2,780	1,210	908	1,230	***	1,570	736	47
2,4'-DDD	***	300	383	317	102	264	***	273	105	38
2,4'-DDT	***	13	ND	ND	6.0	11	***	10	4	35
Total DDTs	***	15,500	19,500	14,400	8,410	10,900	***	13,800	4,280	31
PCB 18	***	13	18	17	10	12	***	14	3	24
PCB 28	***	35	54	34	24	29	***	35	11	32
PCB 52	***	72	91	73	47	71	***	71	16	22
PCB 49	***	49	53	46	33	43	***	45	8	17
PCB 44	***	54	66	53	37	47	***	51	11	21
PCB 37	***	156	36	9	11	14	***	45	63	139
PCB 74	***	47	73	38	40	47	***	49	14	28
PCB 70	***	93	83	74	65	82	***	79	11	13
PCB 66	***	95	98	72	57	60	***	76	19	25
PCB 101	***	101	77	63	51	78	***	74	19	25
PCB 99	***	54	68	49	33	34	***	48	15	31
PCB 119	***	ND	ND	ND	ND	ND	***	ND	***	***
PCB 87	***	29	63	35	32	34	***	39	14	36
PCB 110	***	40	269	220	61	64	***	131	106	81
PCB 81	***	ND	ND	ND	ND	ND	***	ND	***	***
PCB 151	***	ND	22	23	8	16	***	17	7	41
PCB 77	***	ND	ND	ND	5	6	***	6	1	24
PCB 149	***	45	49	34	31	39	***	40	8	19
PCB 123	***	ND	9	6	8	7	***	7	1	19
PCB 118	***	94	85	67	60	77	***	77	14	18
PCB 114	***	ND	ND	ND	19	ND	***	19	***	***
PCB 168/153	***	71	71	59	56	54	***	62	8	13
PCB 105	***	53	44	46	51	50	***	49	4	8
PCB 138	***	126	22	ND	62	66	***	69	43	62
PCB 158	***	10	ND	ND	6	4	***	6	3	49
PCB 187	***	15	21	12	15	18	***	16	3	21
PCB 183	***	8	10	5	7	9	***	8	2	23
PCB 126	***	ND	ND	ND	ND	ND	***	ND	***	***
PCB 128	***	18	19	12	9	20	***	15	5	31
PCB 167	***	ND	ND	2	8	8	***	6	3	58
PCB 177	***	ND	11	9	8	8	***	9	1	16
PCB 200	***	ND	ND	4	ND	4	***	4	0.4	10
PCB 156	***	ND	11	10	ND	21	***	14	6	44
PCB 157	***	ND	ND	1	ND	ND	***	ND	***	***
PCB 180	***	28	35	16	31	33	***	28	8	27
PCB 170	***	15	21	10	11	15	***	14	4	29
PCB 169	***	ND	ND	ND	ND	ND	***	ND	***	***
PCB 189	***	2	ND	ND	ND	ND	***	ND	***	***
PCB 194	***	4	18	ND	7	10	***	10	6	62
PCB 206	***	ND	ND	ND	4	5	***	5	0.4	9
Total PCBs	***	1,330	1,500	1,100	901	1,080	***	1,180	232	20

ND = Not detected.

*** = Data not reported.

TableIII-9. DDT and PCB results (ng/g-dry wt) for the second series of inter-laboratory calibration analyses for Station E6.

COMPOUND	LAB1	LAB2	LAB3	LAB4	LAB5	LAB6	LAB7	Mean	SD	CV%
4,4'-DDE	***	390	332	345	164	219	***	290	94	33
4,4'-DDD	***	24	24	28	3	18	***	19	10	51
4,4'-DDT	***	49	69	70	45	25	***	52	19	36
2,4'-DDE	***	57	32	20	17	17	***	29	17	60
2,4'-DDD	***	55	64	78	49	14	***	52	24	46
2,4'-DDT	***	3	ND	ND	19	6	***	9	9	92
Total DDTs	***	579	521	541	297	299	***	447	138	31
PCB 18	***	12	11	8	9	9	***	10	2	15
PCB 28	***	17	24	19	19	18	***	19	3	13
PCB 52	***	29	46	33	28	31	***	34	7	21
PCB 49	***	18	20	20	15	16	***	18	2	13
PCB 44	***	23	26	23	18	18	***	22	4	17
PCB 37	***	35	16	6	20	20	***	19	11	55
PCB 74	***	15	15	18	12	16	***	15	2	14
PCB 70	***	32	30	34	27	28	***	30	3	10
PCB 66	***	33	33	35	28	23	***	30	5	16
PCB 101	***	59	88	40	87	46	***	64	22	35
PCB 99	***	31	69	23	15	15	***	31	22	73
PCB 119	***	ND	ND	ND	ND	ND	***	ND	***	***
PCB 87	***	19	26	24	24	19	***	22	3	14
PCB 110	***	15	56	64	23	38	***	39	21	53
PCB 81	***	ND	ND	ND	ND	ND	***	ND	***	***
PCB 151	***	16	ND	16	4	10	***	11	5	48
PCB 77	***	ND	ND	ND	ND	ND	***	ND	***	***
PCB 149	***	29	34	32	7	23	***	25	11	44
PCB 123	***	ND	5	5	4	8	***	5	2	28
PCB 118	***	46	46	51	10	40	***	39	17	43
PCB 114	***	ND	ND	ND	ND	ND	***	ND	***	***
PCB 168/153	***	47	50	53	39	29	***	44	10	22
PCB 105	***	27	24	33	28	22	***	27	4	16
PCB 138	***	41	14	47	33	40	***	35	13	36
PCB 158	***	6	ND	ND	8	8	***	8	1	16
PCB 187	***	14	16	14	11	15	***	14	2	12
PCB 183	***	11	7	7	7	12	***	9	3	30
PCB 126	***	ND	ND	ND	ND	ND	***	ND	***	***
PCB 128	***	23	17	14	6	9	***	14	7	50
PCB 167	***	ND	ND	3	ND	4	***	4	1	38
PCB 177	***	7	7	7	4	8	***	7	2	23
PCB 200	***	ND	ND	6	ND	ND	***	6	***	***
PCB 156	***	ND	6	7	ND	3	***	5	2	39
PCB 157	***	ND	ND	1	ND	ND	***	ND	***	***
PCB 180	***	24	22	ND	16	17	***	20	4	20
PCB 170	***	15	14	15	6	18	***	14	4	32
PCB 169	***	ND	ND	ND	***	ND	***	ND	***	***
PCB 189	***	ND	ND	ND	ND	ND	***	ND	***	***
PCB 194	***	10	9	8	4	7	***	8	2	29
PCB 206	***	7	ND	11	ND	5	***	8	3	33
Total PCBs	***	678	732	688	513	562	***	635	93	15

ND = Not detected.

*** = Data not reported.

Trace Metals

Background

A similar inter-laboratory calibration and performance study was undertaken to assess the ability of the participating laboratories to produce comparable data for trace metal analytes. Again, a performance-based approach was used whereby each laboratory could use their standard analytical methods provided they demonstrated acceptable results. Six laboratories participated in this effort, five from the United States and one from Mexico.

Materials and Methods

All laboratories were required to purchase two commercial certified reference materials (CRMs) for demonstration of performance. In addition, the five U.S. laboratories were required to demonstrate acceptable and comparable analytical performance on the southern California marine sediment, Palos Verdes Station 7C, which was also used for the organic inter-laboratory calibration effort. Two CRMs were required because no single CRM available contained all of the analytes at the desired concentrations. The two commercial materials were soils CRM 16-050 Lot No. L516 (Resource Technology Corporation, Laramie, WY) and PPS-46 Lot No. 237 (Environmental Resource Associates, Arvada, CO). The third reference material, from Palos Verdes Station 7C, is a local marine sediment with a complex matrix more representative of the marine sediments analyzed in the Bight'98 Survey. The use of a local reference material similar to the samples to be analyzed helps to alleviate concerns about differences between the CRMs and the actual study samples.

The specific analytical methods used by each participating laboratory are summarized in Table III-10. All laboratories digested the sediment samples using EPA Methods 3055, 3050A, and/or 3050B, which for the purposes of this report can be considered functionally equivalent. These procedures are suitable for the measurement of all the metal analytes except mercury. All of these methods are strong acid digestions using some combination of hydrochloric acid, nitric acid, or hydrogen peroxide and heat. These strong acid methods are capable of quantitatively extracting the target metal analytes, but do not completely dissolve the sample. The possible variations in digestion methods are dependent upon the type of analytical instrument used for the final analysis. After digestion, samples are filtered and diluted to a specified volume with de-ionized reagent water. The digestates were then analyzed using one or more of the following instrumental techniques: flame atomic absorption spectroscopy, graphite furnace atomic absorption spectroscopy, inductively coupled plasma emission spectroscopy, and inductively coupled plasma mass spectrometry. One laboratory opted to analyze arsenic and selenium by hydride generation atomic absorption spectroscopy, EPA Methods 7061a and 7741, respectively. All of the laboratories that analyzed for mercury used cold vapor atomic absorption spectroscopy as described in EPA Methods 7471A and 245.5.

Table III-10. Bight'98 sample preparation and instrumental methods used for metals analysis as a function of laboratory and analyte.

Laboratory Number	Metal Analyte ¹	EPA Approved Preparation Method ²	Instrumental Method ³
1	Ag, Al, Ba, Be, Cd, Cr, Cu, Fe, Ni,	3055 or 3050A	ICPAES
	Sb, Zn		
	Ag, Cd	3055	GFAA
	As, Se	7061A, 7741A	HAA
	Pb	3055	FAA
	Hg	7471A	CVAA
2	Al, Ba, Cd, Cr, Cu, Fe, Ni, Sb, Zn	3055	ICPAES
	Ag, As, Be, Cd, Ni, Sb, Se		
	Ag, Pb	3055	GFAA
	Hg	3055	FAA
		245.5	CVAA
3	Ag, Al, As, Ba, Be, Cd, Cr, Cu, Fe,	3055	ICPAES
	Ni, Pb, Sb, Se, Zn		
	Ag, As, Pb, Sb, Se, Zn	3055	GFAA
	Hg	7471A	CVAA
4	Ag, Al, As, Ba, Be, Cd, Cr, Cu, Fe,	3055	ICPMS
	Ni, Pb, Sb, Zn		
	Se	3050A	GFAA
	Hg	245.5	CVAA
5	Al, Ba, Cr, Cu, Fe, Ni, Zn	3050B	ICPAES
	Ag, As, Be, Cd, Pb, Sb, Se	3050B	ICPMS
	Hg	7471A	CVAA
6	Ag, Cd, Cr, Cu, Fe, Ni, Pb, Zn	3050A	GFAA

¹For some laboratories, if the initial results for certain metals were near or below the detection limit, the samples were re-analyzed using a more sensitive method.

² Method 3055 is not an EPA method. It was a draft analytical procedure issued by the California Department of Health Services, Division of Laboratory Science, Environmental Laboratory Accreditation Program (ELAP). The procedures of 3055 were incorporated into the EPA 3050 series, and for the purposes of this report Methods 3055, 3050A, and 3050B can be considered equivalent.

³ ICPAES = Inductively-coupled plasma atomic emission spectroscopy; ICPMS = Inductively-Coupled plasma mass spectrometry; GFAA = Graphite furnace atomic absorption spectroscopy; FAA = Flame atomic absorption spectroscopy; HAA = Hydride atomic absorption spectroscopy; CVAA = Cold vapor atomic absorption spectroscopy.

Laboratories performed at least seven replicate measurements so that meaningful means, standard deviations (SDs) and coefficient of variations (CVs) could be calculated.

Results and Discussion

The results from the trace metals inter-laboratory calibration study are presented in Tables III-11 and III-12. Specifically, Table III-11 presents the results from the analyses of the two commercial CRMs as a function of analyte and laboratory. The results from all of the laboratories were within the performance acceptance limits specified by the supplier. Each CRM supplier determines the analytical acceptance ranges through their own inter-laboratory performance study. Acceptance ranges are generally determined by calculating the 95% confidence limits for the analytical results from the number of selected laboratories employing commonly used EPA-approved methods. Some suppliers even provide different acceptance ranges based on different analytical methods. However, since analytical results among laboratories can differ significantly, the absolute variability in data values that qualify as acceptable is often large (e.g., 50-100% relative percent difference). Thus, a more important measure of data quality from the standpoint of comparability among laboratories is the precision of analytical results. As previously stated, a commonly used measure of precision is the CV.

In general, the CV values for the CRMs were high (>20%) for analytes that were present at low concentrations. Antimony, the one exception, is problematic in that the analytical results are extremely sensitive to the digestion methods used. Low recoveries and variable results are common for antimony when not using modifications detailed in EPA Method 3050B. The results for the local reference sample, Station 7C, are presented in Table III-12. A comparison of the results for the local reference sediment from Station 7C and those for the two CRMs clearly highlight the effect that a different matrix can have on analytical results. For most analytes, the results were better for the local reference sediment relative to the CRMs. In contrast, the CVs for antimony and selenium increased. Since these elements are not critical parameters for the purposes of the Bight program, these results were considered acceptable.

Overall, the outcomes from this study are significant in that multiple laboratories were able to produce analytical results comparable to those that could be produced from a single highly qualified laboratory. The performance of the participating laboratories is even more significant when considering the complexity of the samples being analyzed, and the diversity of the analytical methods employed. The results from this study show that it is feasible to use a performance-based approach to obtain comparable quality data for trace metals from multiple laboratories. This approach, which obviates the need for laboratories to conform to common analytical methods, contributes to enhanced participation and the potential for significant cost savings.

Table III-11. Results from the trace metals analyses (mg/g-dry wt) of the certified reference materials (CRMs) for the Bight'98 Inter-laboratory Calibration Study.

METAL	LAB1	LAB2	LAB3	LAB4	LAB5	LAB6	Mean	SD	%CV
Aluminum	18,300	15,700	18,200	20,800	14,100	***	17,420.0	2,587.9	14.9
Antimony [†]	41.0	96.2	***	78.9	94.0	***	77.5	25.5	32.9
Arsenic	7.62	7.13	12.0	4.60	6.53	***	7.6	2.7	36.0
Barium [†]	84.5	85.1	***	96.3	93.1	***	89.8	5.9	6.5
Beryllium	0.48	0.52	0.917	0.22	0.53	***	0.5	0.2	46.7
Cadmium	0.697	0.270	0.39	0.25	0.41	0.31	0.4	0.2	42.4
Chromium	21.6	22.7	21.0	17.4	22.0	21.5	21.0	1.9	8.9
Copper	18.1	16.1	14.0	13.7	16.1	16.5	15.8	1.6	10.5
Iron	18,800	20,400	18,200	20,900	17,200	18,600	19,016.7	1,389.1	7.3
Lead	12.9	18.2	13.6	16.2	17.0	12.1	15.0	2.5	16.5
Mercury	0.11	0.104	0.171	0.124	0.13	***	0.13	0.03	20.6
Nickel	14.1	18.2	18.3	18.4	19.4	16.0	17.4	2.0	11.3
Selenium [†]	63.5	59.4	***	49.9	57.7	***	57.6	5.7	9.9
Silver [†]	73.4	78.6	***	63.2	68.1	***	70.8	6.6	9.4
Zinc	73.9	71.9	71.8	72.2	70.0	71.9	72.0	1.2	1.7

[†]The data for these analytes were obtained using the ERA PPS-46 CRM; all other metals were measured on the RTC CRM 16-050. See text for explanation.

*** = Not reported.

Table III-12. Results from the trace metals analyses of local reference sediment at Station 7C (mg/g-dry wt) for the Bight'98 Inter-laboratory Calibration Study.

METAL	LAB1	LAB2	LAB3	LAB4	LAB5	Mean	SD	%CV
Aluminum	22,000	23,000	20,500	21,700	23,200	22,080.0	1,089.5	4.9
Antimony	7.2	1.97	11.1	1.61	1.64	4.7	4.3	91.2
Arsenic	16.5	16.3	14.5	15.3	16.1	15.7	0.8	5.3
Barium	223	277	276	327	***	275.8	42.5	15.4
Beryllium	0.54	0.90	0.84	***	0.46	0.7	0.2	31.7
Cadmium	12.3	11.2	13.9	12.6	13.7	12.7	1.1	8.6
Chromium	244	216	276	250	313	259.8	36.6	14.1
Copper	165	157	174	157	191	168.8	14.3	8.4
Iron	26,800	29,700	25,800	27,600	29,800	27,940.0	1,771.4	6.3
Lead	95.8	105	136	99.8	119	111.1	16.4	14.8
Mercury	1.03	1.28	1.34	0.643	1.18	1.1	0.3	25.4
Nickel	37.4	30.4	38.0	32.9	34.2	34.6	3.2	9.2
Selenium	1.82	1.56	2.26	0.93	4.0	2.1	1.2	54.8
Silver	8.2	5.7	6.5	4.71	5.31	6.1	1.3	22.2
Zinc	423	479	484	435	535	471.2	44.5	9.4

IV. QUALITY CONTROL RESULTS

Sample Collection

All of the collection of sediment samples for chemical and physical analyses was performed in accordance with the procedures detailed in the Southern California Bight 1998 Regional Marine Monitoring Survey Field Operations Manual (B98FOM; Bight'98 Field Sampling and Logistics Committee 1998). Specific criteria are given in the B98FOM for acceptable sediment grab with respect to location, depth, and sample condition. In short, samples were required to be within 100 m of the specified design coordinates, and within $\pm 10\%$ of the nominal depth. Samples were required to meet certain conditions in order to ensure that a given grab would yield relatively undisturbed and representative surficial sediments. Grab samples were inspected upon retrieval for evidence of surface disturbance, leakage, canting, washing, and acceptable surface penetration. Special care was taken in removing any overlying water so as to minimize any disturbance to surface sediments. In addition, field personnel were trained to recognize and avoid potential sources of contamination. The required amount of sample, acceptable utensils and containers, and the required transport and storage conditions are specified in the B98FOM for each type of analytical sample.

Storage Conditions and Holding Time

The sample storage conditions and holding times for the sediment samples collected for the Bight'98 Study are summarized in Table IV-1. The Bight'98 QAP initially sets the storage conditions and holding time for sediments at six months, frozen at a nominal temperature of -20°C in glass containers for TOC, trace organics, and metals (except mercury). A 28-d holding time was initially suggested for mercury, based on U.S. EPA requirements for water samples. Storage of samples for grain size and AVS-SEM was designated as 4°C , for 28 d and 6 months, respectively. These times refer strictly to the holding time prior to analysis but, in a practical sense, were set to insure data reporting within this time frame. Subsequent to the Bight'98 sample collection campaign, storage times for grain size and mercury were changed to 6 months, consistent with the other sediment analytes.

Some discussion of the basis for holding times is warranted because few technically based criteria have been established. The Bight'98 Chemistry Committee members recognized that the various holding times for water sample tests for trace analytes, where they existed, were largely derived from contractual reporting requirements of the respective agency that promulgated or approved the methods. In addition, the Chemistry Committee recognized the following:

- Trace constituents in marine sediments have likely been in the environment for decades, and should be considered stabilized.

- Frozen storage at ca. -20°C would virtually eliminate biological or physical-chemical changes that might otherwise affect the planned tests.
- Standard reference materials for trace constituents in sediment are considered stable, and these materials are used for several years on that basis.
- Some Chemistry Committee members have re-tested freezer-archived samples after many years and obtained equivalent results.
- Published references demonstrated that archived sediment samples were stable with respect to trace metals and trace organics for a decade or more.¹⁻³

Given this information, the Chemistry Committee agreed that sediment analysis realistically could be accomplished within a six-month period. Revision of the holding time criterion for total mercury was based on this same practicality, recognizing that the test was for total mercury rather than speciation of organic and inorganic mercury, which could have then required a more stringent holding time. The original holding time for grain size was entirely arbitrary, and was a carryover from the 1994 SCBPP. There was no technical concern about extending this to a more practical holding time of six months.

It should be noted that the holding times discussed above are from the time of collection until the initial sample processing. The time span between sample preparation and final analysis is another potential hiatus in the analytical process not addressed by the Bight'98 QAP. However, it was generally agreed by the Chemistry Committee that once samples were prepared for analysis (e.g., extraction or acid-digestion), instrumental analysis should proceed thereafter in a timely manner, consistent with current analytical methodology. This would mean, for example, that solvent extracts for trace organics would typically be analyzed with 42 d of extraction. Again, although this timeframe lacks a technical basis, it was considered to be sound laboratory practice to follow through with the analysis of solvent extracts and/or digestates in an expedient manner.

Even with the modifications to holding times made by the Bight'98 Chemistry Committee, all or part of the samples for certain analytes were still not processed within the specified timeframes. In the case of silver and cadmium, 23% of the samples exceeded the specified hold times. Because silver and cadmium are typically present at very low concentrations in sediments, a significant number of samples originally analyzed by inductively coupled plasma emission spectroscopy were below the detection limits for these analytes. These samples were subsequently re-analyzed by graphite furnace atomic absorption spectroscopy to lower the detection limits and obtain measured values for these analytes, which in turn extended holding times beyond the criteria for some samples.

The AVS-SEM samples were all analyzed between 10 and 11 months from the date of collection. Therefore, all AVS-SEM samples exceeded the stated maximum hold time of six months. Since the samples were stored frozen (-20°C), the long hold time is not expected to have a significant effect on the simultaneously extracted metals (SEM). In order to estimate the impact of the hold time for the AVS values, a comparison can be made to previous studies. Allen *et al.* (1993) investigated the effect of sample storage on

AVS values for three lake sediments. After five months of frozen storage, they found that the measured AVS was about 90% of its initial value. Therefore, by extrapolation of their results, the samples in this study may reasonably be expected to retain at least 80% of their original AVS despite the long storage time.

The samples that were evaluated using the P450 HRGS also did not meet the specified hold time criteria. The extracts used for these analyses were a fraction of the extracts obtained from the LAB analysis. The majority of the holding time is therefore from time of collection until the initial LAB extraction. Given that the samples were stored frozen (-20°C) prior to extraction, and given the kind of compounds that induce a response with the P450 HRGS system (i.e., PAHs, PCBs, and dioxins), it is the opinion of the Bight'98 Chemistry Committee that the results of the analysis were not profoundly affected by the longer storage time.

The last group of compounds that did not meet the original holding time specified in the Bight'98 QAP are the LABs. During the analysis of the data, it was discovered that the relative ratios of the LAB isomers were inconsistent with those measured in previous studies and from known sources of LABs to the SCB. These problems were exacerbated by high background levels and inconsistent results observed for some QC samples. Thus, in order to ensure data of the highest possible quality, the decision was made to reanalyze the entire suite of samples from the Bight'98 Survey for LABs. The decision to reanalyze the LAB samples was weighed against the increased storage time required to complete this task. In the end, the Bight'98 Chemistry Committee concluded that reanalyzing the samples was worthwhile in that increased confidence in the quality of the LAB data would outweigh concerns about the holding time. The source of the problems with the LAB results is not known, but it is suspected that the problems stemmed primarily from a sample mass that was too small given the concentration of LABs in most of the SCB. This conclusion was supported by the fact that reanalysis of all the samples from the Bight'98 Survey produced very similar results. Moreover, the results were not improved even though the method detection limit for the reanalysis was decreased to approximately ~20 ng/g-dry wt, less than half the reporting limit (50 ng/g-dry wt) specified in the Bight'98 QAP.

Quality Control

The MQOs used for quality control during the Bight'98 project are explicitly stated for each analyte group in the Bight'98 QAP. The results from the Bight'98 for metals and organic analytes relative to specified MQOs are summarized in Table IV-2. The MQOs used for the Bight'98 project included performance criteria with respect to completeness, blanks, certified reference materials, matrix spikes, and sample duplicates. The overall target success rate for attainment of MQOs was specified as 90% in the Bight'98 QAP. Therefore, the participating laboratories achieved complete success with respect to the MQOs, with one exception. The precision for the analyses of halogenated organics was 4% below the MQO. However, of the 14% of duplicate analyses for trace organics that were > 30% relative percent difference (RPD), all were 50% RPD.

The succinct method of QC evaluation used in Table IV-2 does not fully describe the overall analytical performance for the chemistry part of the Bight'98 Survey. The data in Table IV-2 show what percentage of samples were within the stated MQOs, and convey nothing with respect to the magnitude by which the QC results attained or exceeded the stated MQOs. Moreover, the level of precision and accuracy in analytical measurements varies as a function of concentration. Even under optimum conditions, accuracy and precision will decrease with lower concentrations of analytes. In order to better evaluate and depict the analytical performance for the Bight'98 Survey, a series of quality control charts have been prepared which plot the primary measurement quality parameters versus concentration as a function of analyte concentration. These plots are presented in Appendix B. In brief, the quality control charts show that accuracy and precision for all analytes are lowest when the analyte concentrations are near the method detection limits, and rapidly improve with increasing concentration. This is exactly the behavior that would be expected if all of the analytical components were operating correctly. Therefore, it can be concluded from the QC data that the overall analytical results were consistent with properly functioning analytical laboratories and, with a few minor exceptions, met the MQOs stated in the Bight'98 QAP.

Table IV-1. A summary of the sample storage conditions and holding times relative to the criteria specified in the Bight'98 Quality Assurance Plan.

Parameter	Storage Conditions	Maximum Hold Time ¹	Actual Hold Time (days)	Success
Grain Size	Cold (4°C)	28 days ²	1 -171	8.8 %
TOC/TN	Frozen (-20°C)	6 months	72 - 130	100.0 %
<u>Trace Metals</u>	Frozen (-20°C)	All 6 months		
Hg ³			11 - 141	100.0 %
As, Se			17 - 231	99.0 %
Ag, Cd			33 - 243	77.0 %
All others			51 - 191	94.0 %
AVS-SEM	Frozen (-20°C)	6 months	298 - 333	0.0 %
Interstitial Water Metals	Cold (1.5 – 2.0°C)	6 months ⁴	117 - 201	74.5 %
P450 HRGS	Frozen (-20°C)	6 months	225 -316	0.0 %
<u>Trace Organics</u>	Frozen (-20°C)	All 6 months		
PAHs			1 - 176	100.0 %
PCBs			2 - 176	100.0 %
Pesticides			2 - 176	100.0 %
LABs			>1200 ⁵	0.0 %

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

²This is the holding time specified in the Bight'98 QAP. However, the need for any specific holding time has subsequently been questioned by the Bight'98 Chemistry Committee.

³The original holding time for Hg of 28 days stated in the Bight'98 QAP was changed to 6 months by agreement of the Chemistry Committee.

⁴No holding time was specified in the Bight'98 QAP; this holding time is from EPA Method 1640.

⁵After thorough analysis, the quality of data from the original LAB analyses were found to be questionable. As a result, the entire set of Bight'98 samples was re-analyzed.

Table IV-2. Summary of results relative to the measurement quality objectives (MQOs) stated in the Southern California Bight 1998 Regional Monitoring Quality Assurance Plan.

Quality Control Parameter	Organics		Metals	
	MQO	Success	MQO	Success
Completeness	90%	100%	90%	100%
Blank Frequency	1/batch	100%	1/batch	100%
Blank Accuracy	All analytes < RL ¹	100%	All metals <MDL ¹	100%
CRM Frequency	1/batch	100%	1/batch	100%
CRM Accuracy	±30% for 80% of target analytes	90%	Within specified ranges ²	100%
<u>Matrix Spikes</u>				
Frequency	1/batch	100%	1/batch	100%
Accuracy	N/A ³	---	±25% of true value	93%
Precision	N/A	---	< 20 RPD	100%
<u>Sample Duplicates</u>				
Frequency	10% of total samples	100%	10% of total samples	100%
Precision	< 30% RPD ⁴	86%	Specified ranges ⁵	100%

¹ RL = Reporting level; MDL = Method detection limit; RPD = Relative percent of difference.

² Acceptable result ranges are specified by the certifying agency.

³ No MQO specified; data used for monitoring performance only.

⁴ MQO specified for chlorinated organics only (i.e., pesticides and PCBs); however 95% of results are < 30% RPD when PAHs are included.

⁵ Statistical process control specified as < 3 standard deviations for each analyte; for comparison, 95% of the results were < 25% RPD.

V. ANALYTICAL RESULTS

Bight-Wide Results

An overview of the sediment chemistry analytical results for the Bight'98 Study is presented in Table V-1. The range of results for each analyte is presented relative to method detection limits, reporting levels, and the ERL values. The ERLs were the most sensitive sediment quality criteria (i.e., lowest threshold concentrations) used for biological impact assessment in this study. The Bight'98 QAP specified that the maximum method detection limits and/or reporting limits would be one-fifth of the ERL values for those metals for which an ERL had been established. The reporting limits for the remainder of the analytes were as agreed upon by the Bight'98 Chemistry Committee and specified in the QAP. Note that some laboratories did not meet the specified reporting limit for cadmium, mercury, nickel, and silver. However, except for mercury, the reporting limits were all still less than half of the corresponding ERL values.

The sediment chemistry results for mercury are problematic. One laboratory had an MDL that was significantly (4-20 times) higher than the other laboratories. The particular laboratory analyzed a total of 89 samples, of which 78 were below its stated MDL of 0.2 $\mu\text{g/g}$ -dry weight. Out of the 201 remaining stations, only 18 were below the MDLs (0.01-0.05 $\mu\text{g/g}$ -dry weight) for all the other laboratories. Therefore, 81% (78/96) of the non-detectable values reported for all 290 stations were from the laboratory with the highest MDL. Because of the significant difference in the MDLs among laboratories, it is difficult to make comparisons among different areas of the Bight. The problems with the mercury data are exacerbated by the fact that the sediment mercury concentrations throughout the study area were low; only 74 stations (26%) had mercury concentrations above 0.2 $\mu\text{g/g}$ (i.e., the highest MDL). Therefore, to simply evaluate all the mercury data relative to the highest MDL would eliminate 76% of the data, many of which are valid with respect to the analyzing laboratory's MDL. As a result, the area-weighted mean concentrations for mercury were calculated using all available data, recognizing that a significant negative bias may be associated with results below 0.2 $\mu\text{g/g}$. Further implications of the problems with the mercury data are discussed in following sections. For the other trace metals, only arsenic, barium, and zinc had detectable sediment concentrations at all 290 stations. Chromium had only a single station below the detection limit.

The results for the trace organics show that some stations were below the MDLs for all analytes. Most notable were PCBs and chlordanes, for which only 58 and 35% of the stations were above the MDLs, respectively. As agreed upon by the Bight'98 Chemistry Committee, participating laboratories were free to report data below the nominal reporting limits or method detection limits provided they could demonstrate increased sensitivity for a given target analyte in a given sample, and could make a reasonable estimate of its concentration.

Table V-1. Data ranges for the Bight'98 sediment chemistry analytes relative to the lowest sediment quality criteria, reporting levels, and method detection limits.

Parameters	Data Range ¹ (Min. – Max.)	ERL ²	Reporting Level or Range ³	No. of Samples > mdl	% of Samples > mdl
Percent (%) Dry Weight					
Fines (≤ 63µm)	0.00 - 99.00		N/A	342	100
Total Organic Carbon	0.05 - 3.64		0.28	290	100
Total Nitrogen	0.020 - 0.330		0.04	290	100
Aluminum	0.06 - 5.87		1.0 - 30	290	100
Iron	0.12 - 5.46		1.0 - 10	290	100
mg/g (ppm) Dry Weight					
Antimony	<mdl - 38.00		0.05 - 10	164	57
Arsenic	0.80 - 43.00	8.2	0.08 - 1.6	290	100
Barium	3.00 - 1,800		0.04 - 50	289	100
Beryllium	<mdl - 4.93		0.02 - 0.2	265	91
Cadmium	<mdl - 8.90	<u>1.2</u>	0.01 - 0.5	262	92
Chromium	<mdl - 238.00	81	0.05 - 16	290	100
Copper	<mdl - 340.00	34	0.15 - 7.0	274	94
Lead	<mdl - 193.00	46.7	0.02 - 9.3	258	89
Mercury	<mdl - 1.685	<u>0.15</u>	0.01 - 0.2	193	67
Nickel	<mdl - 168.50	<u>20.9</u>	0.31 - 10	258	89
Selenium	<mdl - 6.00		0.11 - 1	199	69
Silver	<mdl - 7.50	<u>1.0</u>	0.01 - 0.5	228	79
Zinc	2.00 - 420.00	150	0.10 - 30	290	100
Interstitial Water (mg/L)					
Cadmium	<mdl - 0.65		0.01	107	99
Copper	0.81 - 65.91		0.02	108	100
Lead	0.11 - 4.52		0.01	108	100
Nickel	1.31 - 86.29		0.02	108	100
Zinc	2.50 - 19.67		0.02	108	100
AVS/SEM (mmole/g)					
AVS	<mdl - 42.29			103	97
Cadmium	<mdl - 0.03		0.001	90	85
Copper	0.03 - 1.93		0.001	106	100
Lead	0.03 - 0.66		0.001	106	100
Nickel	0.01 - 0.20		0.006	106	100
Zinc	0.10 - 4.08		0.02	106	100
ng/g (ppb) Dry Weight					
Total DDT	<mdl - 5,728	1.58	0.02 - 3.8	223	77
Total PCB	<mdl - 411.8	22.7	0.04 - 9.6	169	58
Total PAH	<mdl - 12,778	4022	7.5 - 100	212	73
Chlordane (α + γ)	<mdl - 21.5		0.5 - 14	101	35

¹ mdl = Method detection limit.

² ERL = Effects range low; underlined values indicate that some laboratories did not meet the Bight'98 QAP criteria of RL = 0.2 ERL for trace metal analyses.

³ N/A = Not applicable; reporting limits for aluminum and iron are in ppm or µg/g dry weight.

Table V-2. Selected statistical ranges of the sediment chemistry data for the entire Southern California Bight.

Parameters	Area-Weighted Mean	95% Conf. Interval	Min.	10 th Percentile	Median	90 th Percentile	Max.
Percent Dry Wt.							
Fines ($\leq 63\mu\text{m}$)	30.74	5.06	0.0	1.0	24.0	71.0	99.0
TOC	0.76	0.12	0.04	0.16	0.67	1.52	3.64
TN	0.080	0.009	0.017	0.035	0.072	0.139	0.328
Aluminum	1.10	0.11	0.06	0.39	0.94	1.73	5.87
Iron	1.87	0.21	0.12	0.78	1.70	3.18	5.46
mg/g (ppm) Dry Wt.							
Antimony	0.91	0.70	<mdl	<mdl	0.10	1.50	38.0
Arsenic	5.46	0.60	0.80	2.40	4.77	9.05	43.0
Barium	131.13	31.64	3.00	29.50	89.90	249.50	1800
Beryllium	0.47	0.11	<mdl	0.12	0.36	0.75	4.93
Cadmium	0.35	0.08	<mdl	0.03	0.22	0.80	8.90
Chromium	27.57	2.92	<mdl	10.20	23.20	48.00	238.0
Copper	14.94	2.14	<mdl	2.30	9.00	26.00	340.0
Lead	12.85	3.14	<mdl	<mdl	7.90	32.38	193.0
Mercury	0.054	0.016	<mdl	<mdl	0.007	0.15	1.69
Nickel	20.12	5.59	<mdl	1.50	14.00	37.00	168.5
Selenium	0.65	0.17	<mdl	<mdl	0.36	2.00	6.00
Silver	0.33	0.18	<mdl	<mdl	0.11	0.91	7.50
Zinc	56.78	6.49	2.00	16.50	47.00	99.5	420.0
ng/g (ppb) Dry Wt.							
Chlordane ($\alpha + \gamma$)	0.21	0.05	<mdl	<mdl	<mdl	0.37	21.5
Total DDT	46.79	25.20	<mdl	<mdl	6.20	65.95	5728
Total PAH	134.10	35.88	<mdl	<mdl	35.60	289.21	12778
Total PCB	7.06	2.79	<mdl	<mdl	0.24	41.00	411.8

It was the opinion of the Bight'98 Chemistry Committee that a reasonable estimate of the concentration for a given target analyte present above the background noise was a better option than designating it as not detected simply because it was below the nominal MDL. Similar to the situation for mercury, one laboratory had a nominal reporting level DDT that was above the ERL. In calculating the area-weighted mean concentrations, all reported data were used while recognizing that the effective minimum detection limits for specific analytes varied among the different laboratories. The area-weighted mean concentrations of the target analytes for the entire SCB are given in Table V-2. Also shown are the sediment concentrations associated with selected regions of a cumulative distribution function plot for each of the target analytes, including the minimum values; 10th, 50th, 90th percentiles; and maximum values.

Subpopulation Comparisons

Comparisons of selected station subpopulations were made to evaluate the distribution of sediment chemical contamination in the SCB. Five subpopulation comparisons were made based on both geographic and pollution source considerations. The first comparison was made to evaluate the geographic variability in the sediment chemistry from north to south. To this end, the SCB was divided into three regions - a northern region from Point Conception to Point Dume; a central region from Point Dume to Dana Point; and a southern region from Dana Point to the U.S. Mexico International border. A fourth region, consisting of all the Mexico stations, was also used in the comparison.

The second subpopulation comparison group was selected to evaluate the variations in sediment contamination along a geographic and depth gradient from east to west. The three subpopulation groups compared consisted of bay and harbor stations, shallow coastal stations (5-30 m), and mid-depth coastal stations (30-120 m).

The third comparison of subpopulations was intended to evaluate differences among three groups of stations within the coastal embayments designated as ports, marinas, or "other bay and harbor." The port and marina stations were identified by their proximity to the areas of embayments associated with these specific uses. The other bay and harbor stations were those stations within the embayments but beyond the areas believed to be influenced by industrial port and marina operations.

The fourth comparison is among three different types of shallow coastal zone environments. For this comparison, the shallow coastal stations (excluding embayments) are divided into three categories: those near river mouths, those near small publicly owned treatment work (SPOTW) outfalls, and the remainder of the stations designated as "other shallow." This comparison evaluates the target analyte sediment concentrations associated with river mouths and SPOTW outfalls relative to the sediment concentrations in the shallow coastal marine environment as a whole.

The fifth comparison was selected to evaluate differences among three groups of stations in the mid-depth coastal marine environment. For this comparison, the mid-depth stations were assigned to one of three groups, those associated with SPOTWs, large publicly owned wastewater treatment works (LPOTWs), or “other mid-depth.” This grouping of stations contrasts sediment concentrations associated with two known point sources of contaminants with the remainder of the mid-depth stations throughout the Bight.

The five station subpopulation comparisons discussed above are presented in Tables V-3 through V-7. The area-weighted means (AWM) and the corresponding 95% confidence intervals (CI) are calculated as previously described. The values in these tables are conservative in that all results below the MDLs were treated as zero for the purposes of calculating the area-weighted means.

Several general trends are evident in the tabulated data. For the U.S. stations, the central region of the SCB has the highest mean concentrations for most analytes, followed by the southern and northern regions, respectively. Mexico has the lowest mean concentrations for its reduced set of target analytes. The northern region of the SCB has a higher proportion of fine-grained sediments, and the highest mean concentrations for TOC, TN, barium, and selenium. The southern region of the SCB has comparable mean copper concentrations to those observed in the central SCB, driven by the relatively high copper concentrations in many San Diego Bay stations. The central region of the SCB had significantly higher sediment concentrations of all other target analytes.

The bay and harbor areas as a whole have significantly higher mean concentrations of most target analytes (except Ba, Ni, Se) relative to the shallow coastal or mid-depth areas. However, as will be shown in Chapter VI on PCA, many but not all of the higher analyte concentrations associated with bay and harbor stations can be attributed to the significantly higher percentage of fine-grained sediments. Within the embayments, the port areas have somewhat higher concentrations than either the marinas or other bay/harbor areas. In the shallow coastal areas, the sediment concentrations of the target analytes are similar among the three station groups compared. However, some minor differences can be identified. Slightly higher concentrations of most metals are associated with the areas in proximity shallow SPOTWs. Also, the areas near river mouths appear enriched in chlordanes, PAHs, and PCBs relative to the other shallow station groups. Lastly, with the exception of Ni and Se, the highest concentrations of target analytes for stations in the mid-depth coastal zone are for those near LPOTW outfalls. Interestingly, except for PAHs, the sediments in proximity to mid-depth SPOTW outfalls are typically similar to or less than the other mid-depth stations.

Table V-3. Area-weighted means (AWMs) and associated 95% confidence intervals (CIs) for selected geographic subpopulations of the sediment chemistry data from the Southern California Bight 1998 Regional Marine Monitoring Study.

Parameter	North		Central		South		Mexico	
	AWM	CI	AWM	CI	AWM	CI	AWM	CI
Number of Stations	54		133		103		71	
Percent (%) Dry Wt.								
Fines ($\leq 63\mu\text{m}$)	47.6	11.7	35.0	7.2	37.4	8.5	17.6	4.9
TOC	0.904	0.251	0.72	0.13	0.61	0.13	-	-
TN	0.091	0.017	0.073	0.011	0.071	0.008	-	-
mg/g (ppm) Dry Wt.								
Antimony	0.10	0.03	1.71	1.82	1.03	0.86	-	-
Arsenic	6.39	0.62	5.83	0.90	3.54	0.40	-	-
Barium	177.10	58.75	133.16	50.72	58.02	12.39	-	-
Cadmium	0.36	0.08	0.58	0.17	0.09	0.03	0.09	0.03
Chromium	26.02	3.99	34.92	5.70	19.61	3.73	15.57	2.08
Copper	11.14	3.13	16.98	3.94	17.49	5.14	6.22	1.05
Lead	8.03	1.56	22.61	7.30	6.47	2.32	1.87	0.41
Mercury ¹	<0.005	<0.005	0.106	0.033	0.057	0.03	-	-
Nickel	23.34	5.56	25.02	13.28	7.13	1.75	12.23	2.12
Selenium	1.08	0.32	0.57	0.16	0.14	0.06	-	-
Silver	0.08	0.02	0.83	0.45	0.37	0.48	0.027	0.004
Zinc	59.11	12.58	62.92	8.93	44.66	8.64	23.04	3.43
ng/g (ppb) Dry Wt.								
Chlordane ($\alpha + \gamma$)	0.21	0.15	0.37	0.17	0.007	0.010	0.01	0.01
Total DDT	12.29	5.90	115.29	69.28	1.41	0.97	0.73	0.24
Low MW PAH	21.90	14.15	28.44	11.71	24.28	12.06	9.10	8.84
High MW PAH	54.43	26.17	156.44	64.52	126.62	82.98	47.06	52.26
Total PAH	76.33	32.78	184.88	73.38	150.90	91.11	56.16	59.71
Total PCB	0.69	0.57	18.32	7.17	0.95	0.76	0.83	0.57

¹ In the northern region of the SCB, 40 of the 54 stations were below the method detection limits for Hg; hence, the very low area mean concentration.

Table V-4. Area-weighted means (AWMs) and associated 95% confidence intervals (CIs) for depth gradient subpopulations of the sediment chemistry data from the Southern California Bight 1998 Regional Marine Monitoring Study.

Parameter	Bays/Harbors		Shallow		Mid-Depth	
	AWM	CI	AWM	CI	AWM	CI
Number of Stations	113		81		96	
Percent (%) Dry Wt.						
Fines ($\leq 63\mu\text{m}$)	63.3	8.5	22.8	6.31	32.0	7.0
TOC	1.30	0.13	0.42	0.12	0.89	0.17
TN	0.119	0.011	0.057	0.007	0.088	0.01
mg/g (ppm) Dry Wt.						
Antimony	2.20	0.83	1.44	1.98	0.499	0.37
Arsenic	8.40	0.75	4.65	0.82	5.62	0.87
Barium	123.30	14.46	108.08	52.99	144.38	43.01
Cadmium	0.49	0.10	0.35	0.14	0.37	0.10
Chromium	44.71	3.47	19.22	3.27	30.35	4.18
Copper	80.48	12.21	6.75	2.10	12.71	2.23
Lead	36.64	5.70	10.18	3.82	11.88	4.56
Mercury	0.31	0.07	0.03	0.02	0.04	0.02
Nickel	20.50	2.19	14.58	8.70	22.59	7.59
Selenium	0.59	0.13	0.51	0.26	0.75	0.23
Silver	0.70	0.19	0.18	0.14	0.50	0.36
Zinc	153.55	13.97	35.62	7.23	58.09	8.79
ng/g (ppb) Dry Wt.						
Chlordane ($\alpha + \gamma$)	1.97	0.73	0.08	0.06	0.11	0.08
Total DDT	41.16	13.23	33.48	33.30	53.83	37.64
Low MW PAH	122.92	46.26	21.57	8.44	16.90	9.56
High MW PAH	983.25	321.15	56.41	41.41	50.37	20.40
Total PAH	1,106.18	361.68	77.98	43.36	67.28	25.20
Total PCB	25.57	8.92	4.74	3.43	6.46	4.00

Table V-5. Area-weighted means (AWMs) and associated 95% confidence intervals (CIs) for embayment-associated subpopulations of the sediment chemistry data from Southern California Bight 1998 Regional Marine Monitoring Study.

Parameter	Ports		Marinas		Other Bays/Harbors	
	AWM	CI	AWM	CI	AWM	CI
Number of Stations	37		39		37	
Percent (%) Dry Wt.						
Fines ($\leq 63\mu\text{m}$)	64.0	6.7	67.0	6.6	56.6	7.8
TOC	1.36	0.20	1.39	0.23	1.08	0.20
TN	0.016	0.016	0.135	0.02	0.10	0.01
mg/g (ppm) Dry Wt.						
Antimony	2.04	1.59	2.37	1.28	2.11	1.44
Arsenic	10.07	1.43	7.53	0.89	7.91	1.71
Barium	144.37	34.89	109.82	15.11	121.15	27.03
Cadmium	0.40	0.15	0.61	0.17	0.39	0.13
Chromium	51.76	6.93	42.86	5.23	39.73	5.37
Copper	106.86	20.02	83.35	21.77	45.58	7.85
Lead	44.94	11.33	34.72	8.83	30.39	8.38
Mercury	0.39	0.09	0.33	0.144	0.19	0.04
Nickel	21.50	4.34	20.34	3.30	19.62	3.92
Selenium	0.56	0.24	0.78	0.20	0.30	0.18
Silver	1.10	0.069	0.47	0.24	0.62	0.36
Zinc	179.51	27.98	159.32	28.79	127.63	13.21
ng/g (ppb) Dry Wt.						
Chlordane ($\alpha + \gamma$)	0.67	0.98	3.19	1.22	1.48	1.38
Total DDT	30.77	19.17	52.17	25.60	35.13	13.39
Low MW PAH	276.54	133.28	55.53	29.25	57.03	23.23
High MW PAH	1,993.87	889.39	648.62	278.13	373.00	107.47
Total PAH	2,270.41	1,006.29	704.15	300.69	430.03	126.17
Total PCB	38.28	22.63	22.60	11.55	15.77	9.31

Table V-6. Area-weighted means (AWMs) and associated 95% confidence intervals (CIs) for shallow subpopulations of the sediment chemistry data from the Southern California Bight 1998 Regional Marine Monitoring Study.

Parameter	Rivers		Shallow SPOTW		Other Shallow	
	AWM	CI	AWM	CI	AWM	CI
Number of Stations	31		17		33	
Percent (%) Dry Wt.						
Fines ($\leq 63\mu\text{m}$)	32.0	13.0	32.0	10.0	22.5	7.0
TOC	0.56	0.24	0.55	0.25	0.42	0.14
TN	0.057	0.015	0.057	0.015	0.058	0.008
mg/g (ppm) Dry Wt.						
Antimony	0.34	0.34	1.09	0.06	1.59	2.21
Arsenic	5.08	0.83	7.67	4.34	4.39	0.83
Barium	91.32	18.15	114.19	43.64	105.71	58.78
Cadmium	0.37	0.15	0.28	0.123	0.36	0.16
Chromium	21.52	3.96	24.72	9.53	19.02	3.63
Copper	12.04	4.61	17.41	10.78	6.82	2.39
Lead	15.44	6.57	15.92	12.53	10.14	4.20
Mercury	0.032	0.014	0.050	0.047	0.036	0.018
Nickel	14.22	3.57	13.85	6.15	15.50	9.56
Selenium	0.43	0.16	0.97	0.74	0.47	0.29
Silver	0.20	0.26	0.12	0.09	0.19	0.16
Zinc	56.35	18.40	52.14	23.42	33.59	7.77
ng/g (ppb) Dry Wt.						
Chlordane ($\alpha + \gamma$)	1.55	1.34	0.06	0.09	0.03	0.05
Total DDT	9.47	4.91	20.20	18.39	36.35	36.96
Low MW PAH	48.40	33.93	35.40	16.39	20.44	8.83
High MW PAH	149.02	111.73	82.95	61.56	52.74	43.58
Total PAH	197.43	144.23	118.35	75.29	73.18	45.51
Total PCB	10.11	7.41	4.41	5.13	4.80	3.78

Table V-7. Area-weighted means (AWMs) and associated 95% confidence intervals (CIs) for the mid-depth subpopulations of the sediment chemistry data from the Southern California Bight 1998 Regional Marine Monitoring Study.

Parameter	Mid-Depth SPOTW		LPOTW		Other Mid-Depth	
	AWM	CI	AWM	CI	AWM	CI
Number of Stations	19		30		34	
Percent (%) Dry Wt.						
Fines ($\leq 63\mu\text{m}$)	51.0	7.8	35.2	5.8	47.8	8.8
TOC	0.78	0.21	1.00	0.24	0.87	0.18
TN	0.086	0.020	0.077	0.013	0.088	0.013
mg/g (ppm) Dry Wt.						
Antimony	0.06	0.02	0.95	0.63	0.46	0.39
Arsenic	4.00	0.62	5.91	1.08	5.68	0.93
Barium	92.33	12.19	197.67	128.78	142.34	44.79
Cadmium	0.23	0.09	1.04	0.62	0.32	0.09
Chromium	24.47	3.81	50.88	15.79	28.78	4.28
Copper	12.71	2.55	26.67	9.77	11.46	2.27
Lead	6.55	1.41	22.00	7.04	11.11	4.82
Mercury	< mdl	-	0.16	0.06	0.03	0.02
Nickel	8.13	4.10	14.84	2.66	22.76	8.16
Selenium	0.59	0.36	0.60	0.39	0.77	0.24
Silver	0.07	0.14	1.34	0.63	0.43	0.38
Zinc	48.81	7.87	68.62	17.4	58.17	9.31
ng/g (ppb) Dry Wt.						
Chlordane ($\alpha + \gamma$)	0.22	0.21	0.15	0.12	0.10	0.09
Total DDT	5.70	3.28	539.47	482.40	19.35	13.49
Low MW PAH	46.30	7.22	50.55	28.41	13.97	10.17
High MW PAH	62.58	18.91	137.74	78.58	44.07	21.37
Total PAH	108.88	23.90	188.29	101.40	58.05	26.24
Total PCB	0.56	0.71	48.81	32.03	3.45	3.32

mdl = Below method detection limit.

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 shown in Figures 318. These maps show the location of each station and the associated concentration ranges for the principal target analytes measured for the Bight'98 Survey. Mexico stations are included for those analytes measured in samples from Mexico. The total stations analyzed for each parameter are divided into four groups based upon the measured concentration range: the lowest 10%, 11 to 50%, 51 to 90%, and the top 10%.

Grain Size, Total Organic Carbon, and Total Nitrogen

The results for percent fines (<63 μm), total organic carbon (TOC), and total nitrogen (TN) are shown in Figures V-1, V-2, and V-3, respectively. Sediments with higher percent fines (e.g., >40%) are generally found in the bay and harbor areas, and near POTW outfalls. There is also a conspicuous area with stations having some of the highest sediment percent fines (>80%) in the eastern part of the Santa Barbara Channel, just northwest of the mouth of the Santa Clara River. Another interesting result is the number of stations with coarse-grained sediments (<5% fines) in the area around the U.S.–Mexico international border. The results for TOC and TN appear to follow the same pattern as the percent fines, with the higher values being associated with POTW outfalls and embayments.

Trace Metals

The results for the trace metals are shown in Figures V-4 through V-12. In general, the trace metals concentrations appear to correlate with the grain size data. The higher concentrations of the trace metals analytes are typically associated with sediments containing higher percent fines. One exception to this trend is the mercury data for stations in the northern part of the Bight. The laboratory that had the highest detection limit for mercury analyzed most of the stations in the northern section of the Bight. Therefore, the lack of correlation between the mercury data and the percent fines in the northern SCB is a result of analytical limitations and does not constitute a true deviation from the general relationship between metals concentrations and grain size. The trace metal data are difficult to interpret because all of the metals occur naturally; therefore, it is necessary to differentiate between the natural and anthropogenic contributions to the total sediment concentration. Both the relationship with grain size and the natural background levels of the metals will be addressed in subsequent chapters of this report.

Trace Organics

The results for the trace organic analytes are shown in Figures V-13 through V-16. Chlordanes were below detection limits for 273 out of 361 stations analyzed. Where detectable, chlordanes appeared to be mostly associated with river discharges and certain bay and harbor areas.

The contaminant DDT and its metabolites were the most ubiquitous organic contaminants in the Bight. Detectable amounts of total DDTs were measured at 269 out of the 361 stations, with the vast majority of non-detectable values occurring for stations from near San Diego and in Mexico. The highest levels of DDTs were found in stations near the Palos Verdes Peninsula, an area that has historically been known to have high levels of contaminants. Notably high levels of DDTs were also found in Los Angeles/Long Beach Harbor.

For PAHs, the highest concentrations were overwhelmingly associated with bay and harbor areas. Lesser but detectable concentrations of PAHs were found in nearshore stations throughout the Bight and in Mexico. However, two conspicuous clusters of stations with no detectable levels of PAHs were located between Los Angeles/Long Beach Harbor and Newport Harbor, and between San Diego and the U.S.-Mexico international border.

The highest concentrations of PCBs were found in the central region of the SCB, associated with POTW outfalls and bay/harbor areas. The highest levels of PCBs were found on the Palos Verdes Shelf and in Los Angeles/Long Beach Harbor. In contrast, most of the stations in San Diego Bay were below detection limits for PCBs. Detectable PCBs were also found intermittently in some Mexico stations from the U.S.-Mexico international border south to Ensenada Bay.

The results for the LAB samples are shown in Figure V-17. The LABs were found at levels above the reporting limit (20 ng/g-dry weight) in only 7 out of 284 stations analyzed. This reporting level is lower than the 50 ng/g-dry weight specified in the Bight'98 QAP. Although some LABs were detected at lower concentrations, quantitation below 20 ppb was found to be unreliable.

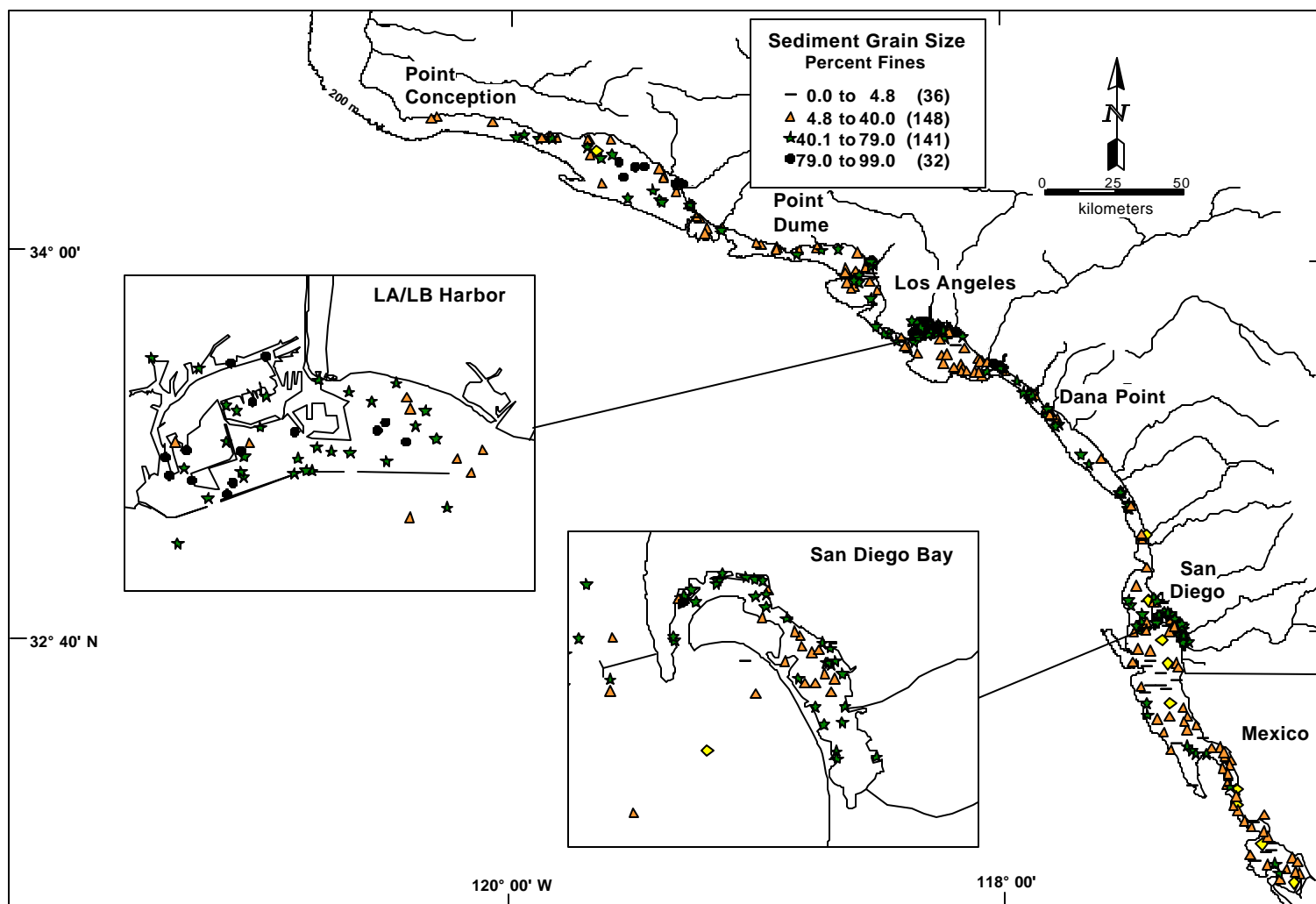


Figure V-1. Map of sediment grain size distribution (% fines) for the SCB (number of stations in each range shown in parentheses).

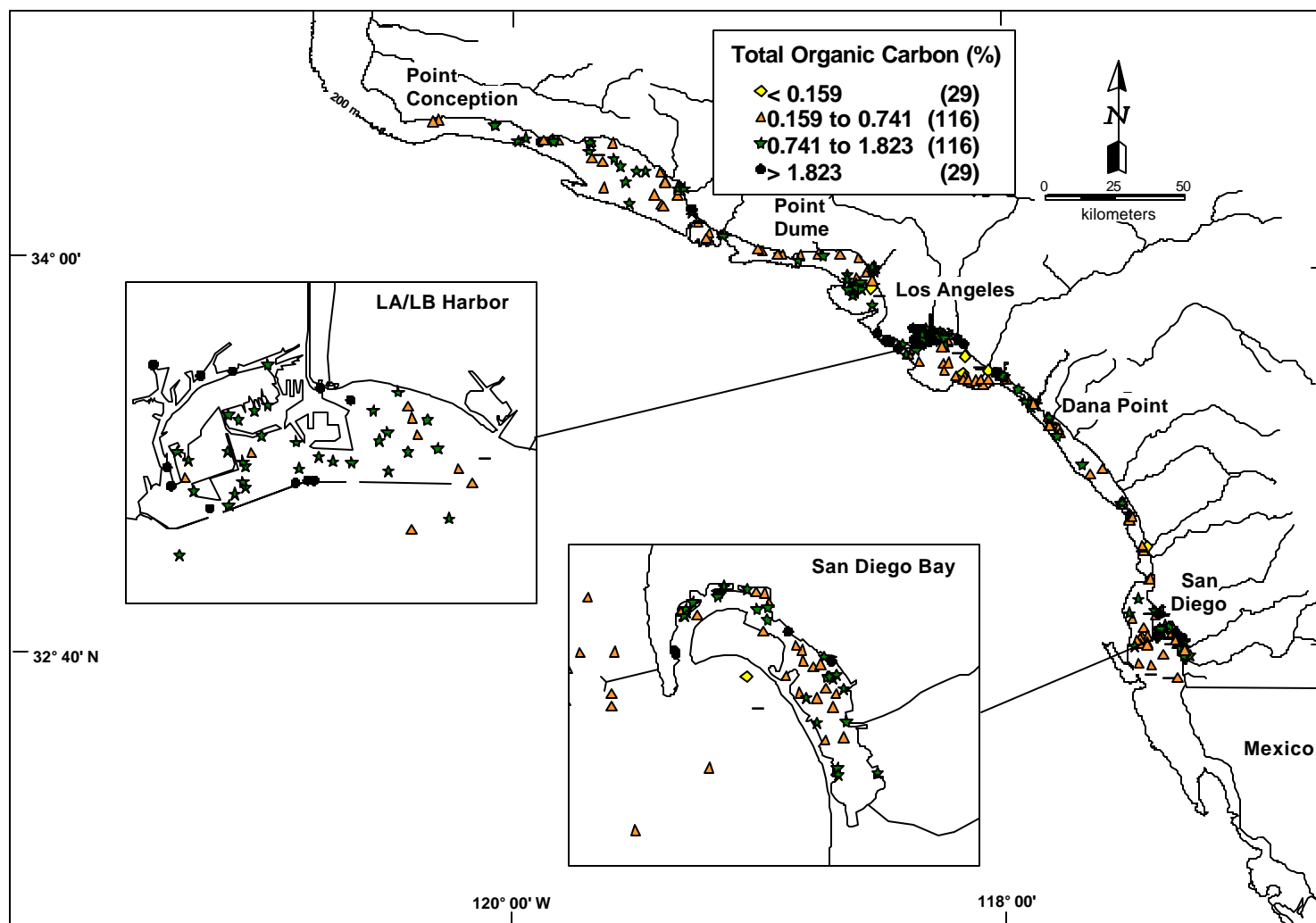


Figure V-2. Map of sediment total organic carbon (TOC) concentrations for the SCB (number of stations in each range shown in parentheses).

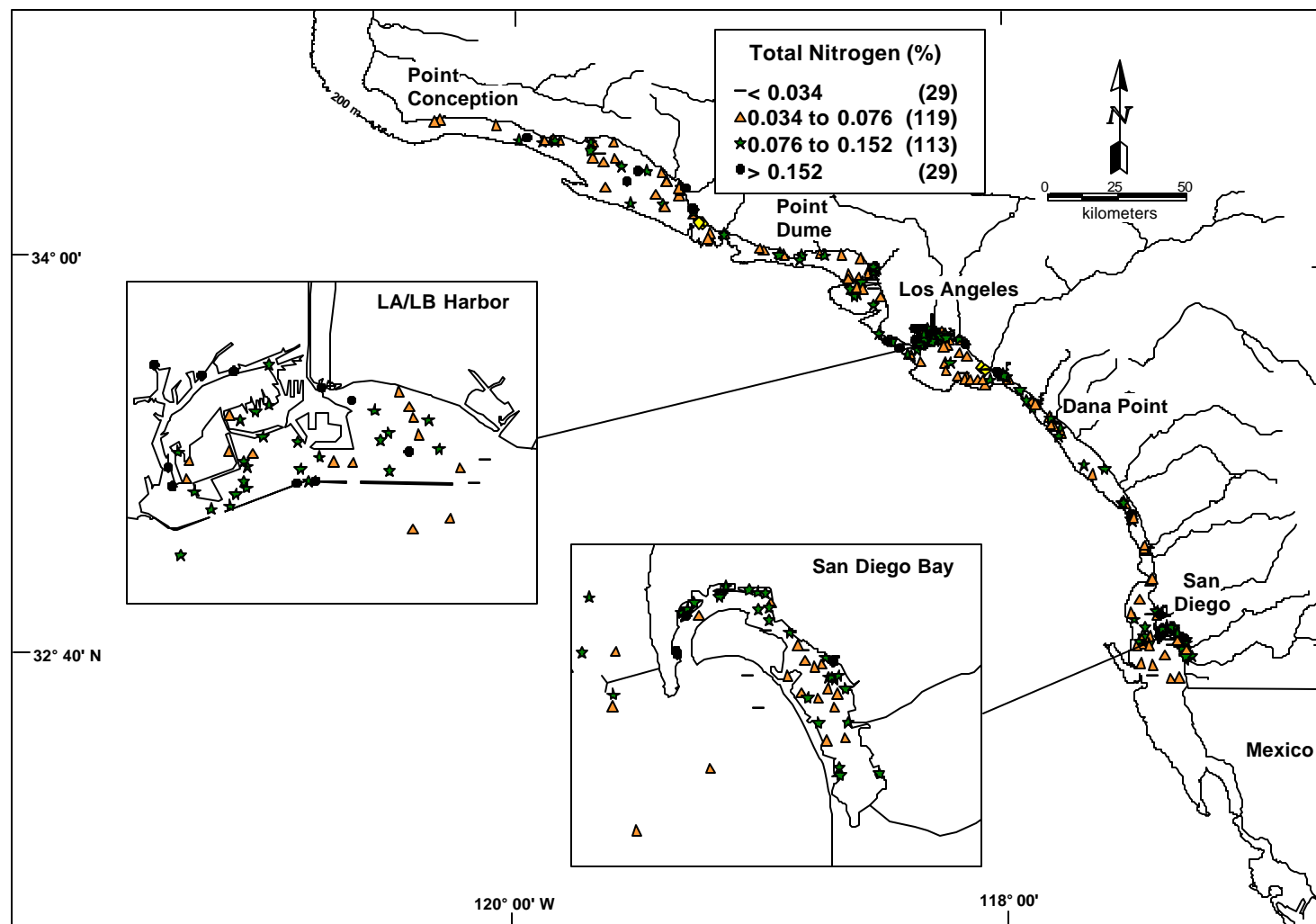


Figure V-3. Map of sediment total nitrogen (TN) concentrations for the SCB (number of stations in each range is shown in parentheses).

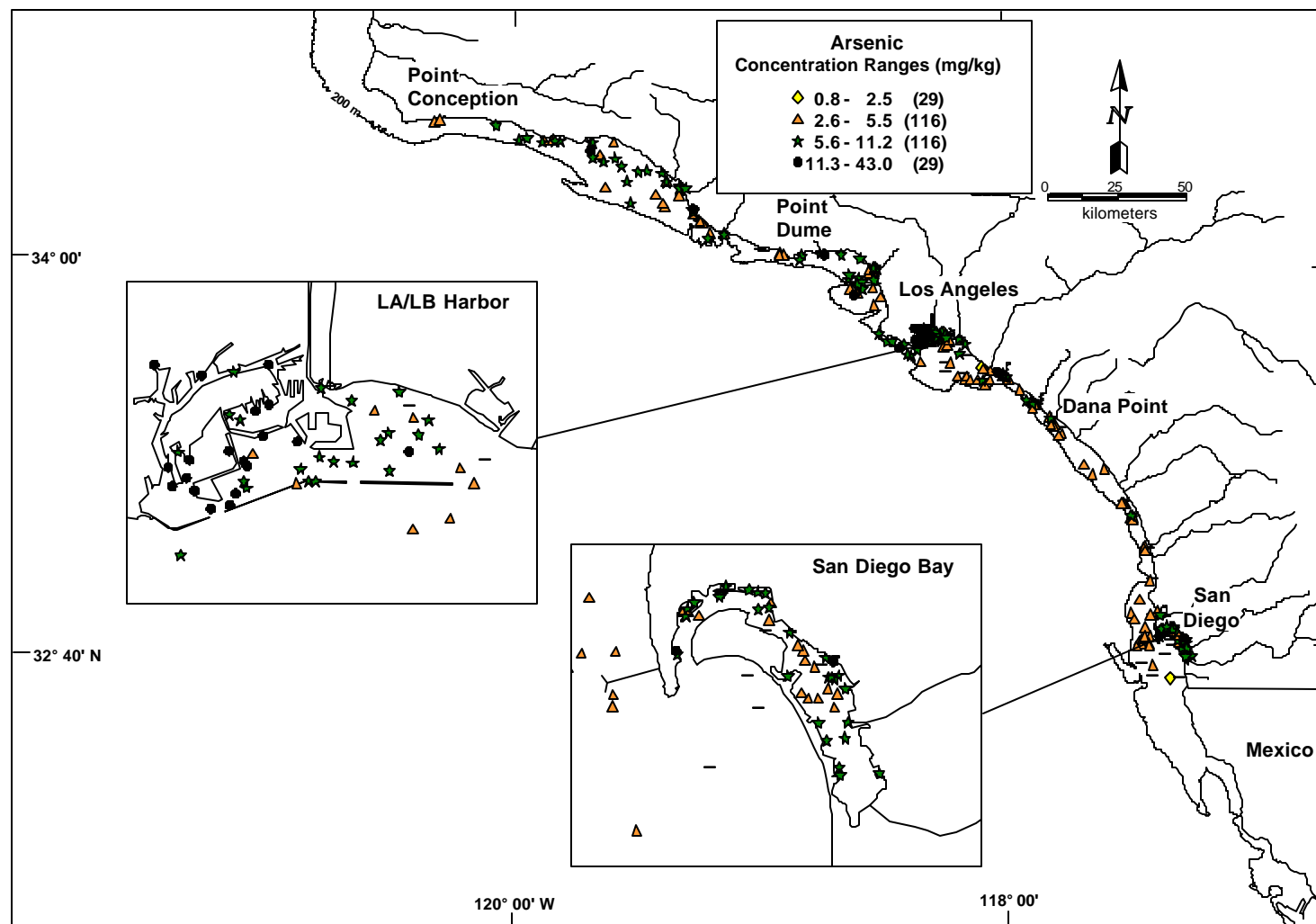


Figure V-4. Map of sediment arsenic concentrations for the SCB (number of stations in each range shown in parentheses).

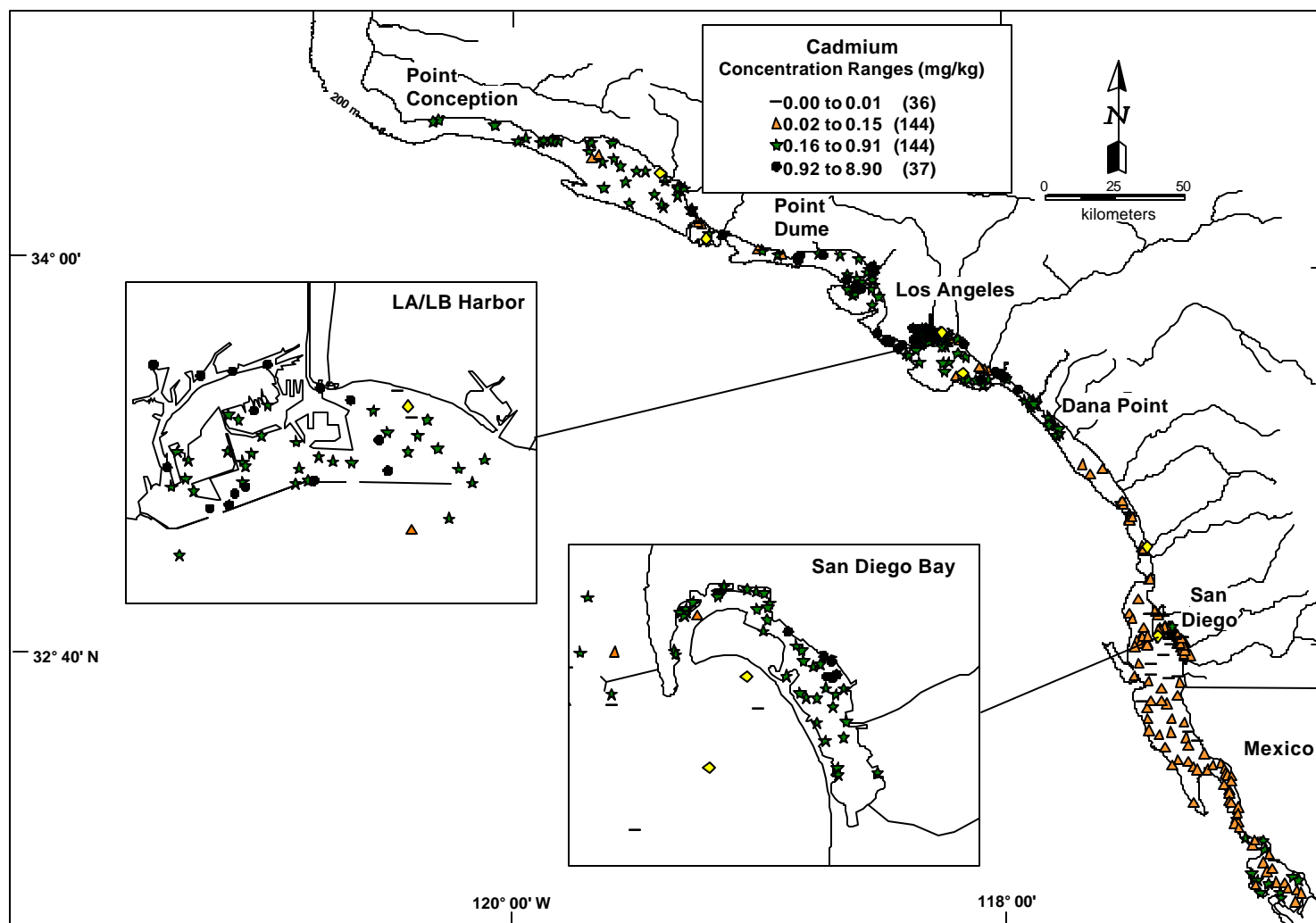


Figure V-5. Map of sediment cadmium concentrations for the SCB (number of stations in each range shown in parentheses).

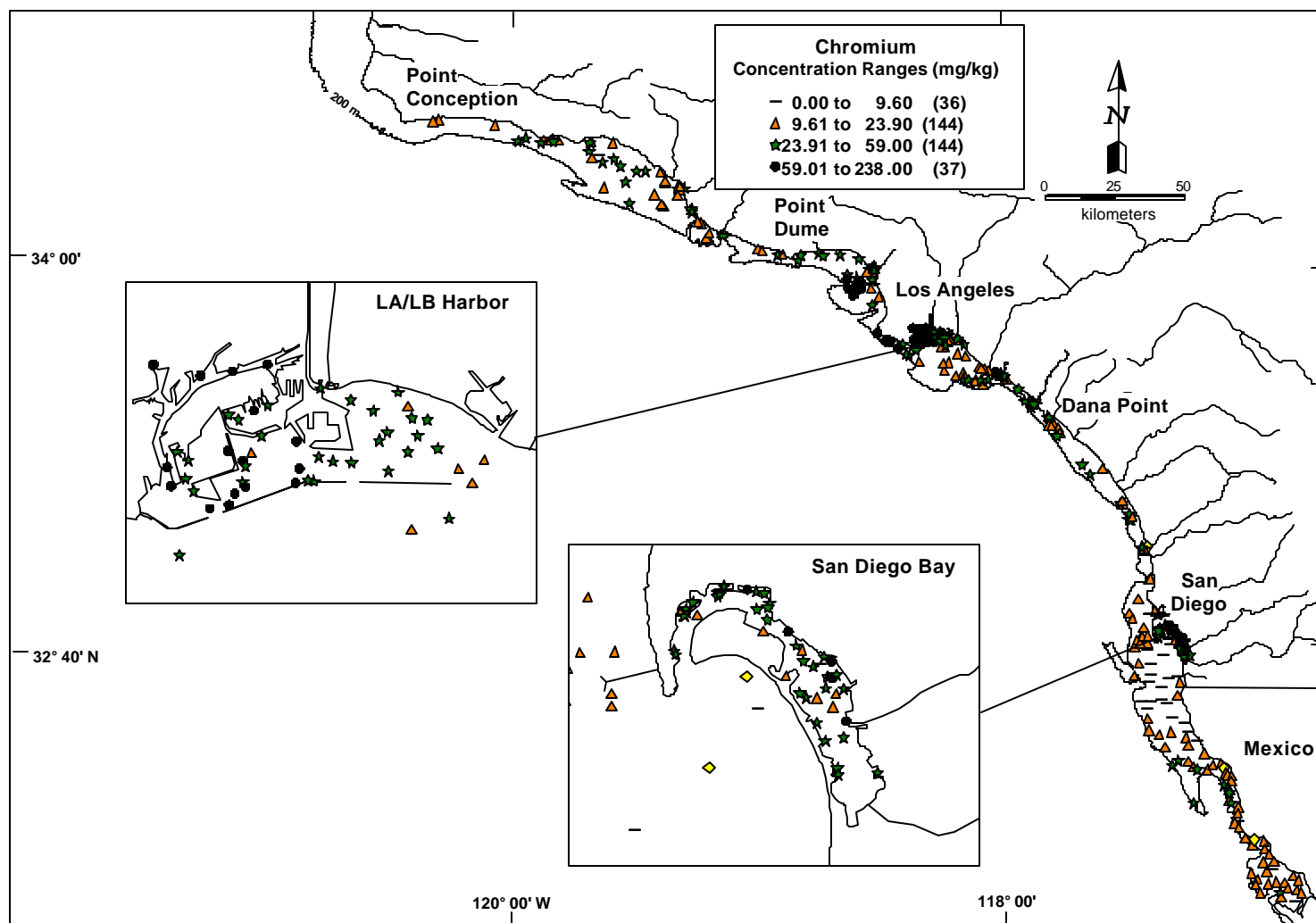


Figure V-6. Map of sediment chromium concentrations for the SCB (number of stations in each range shown in parentheses).

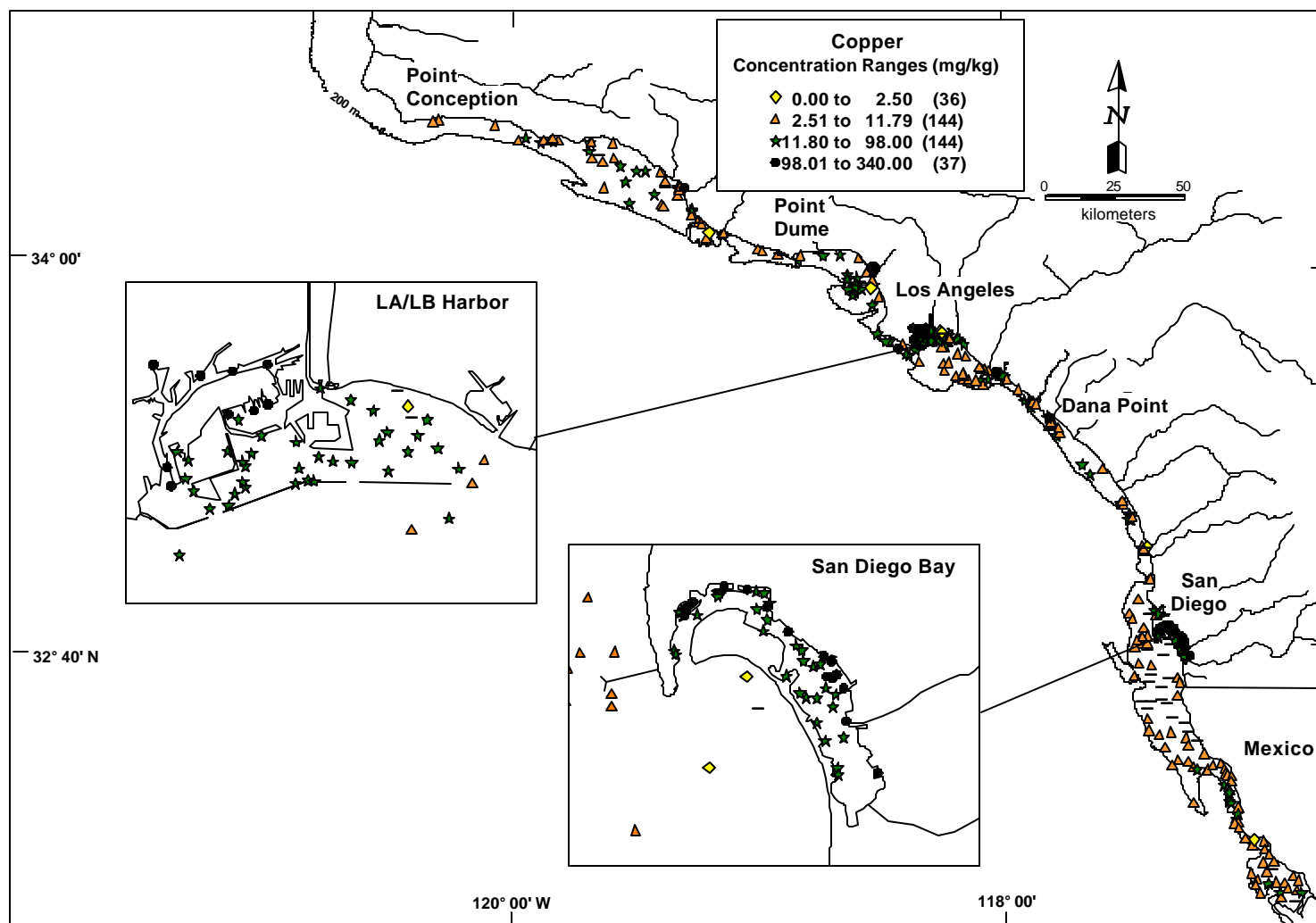


Figure V-7. Map of sediment copper concentrations for the SCB (number of stations in each range shown in parentheses).

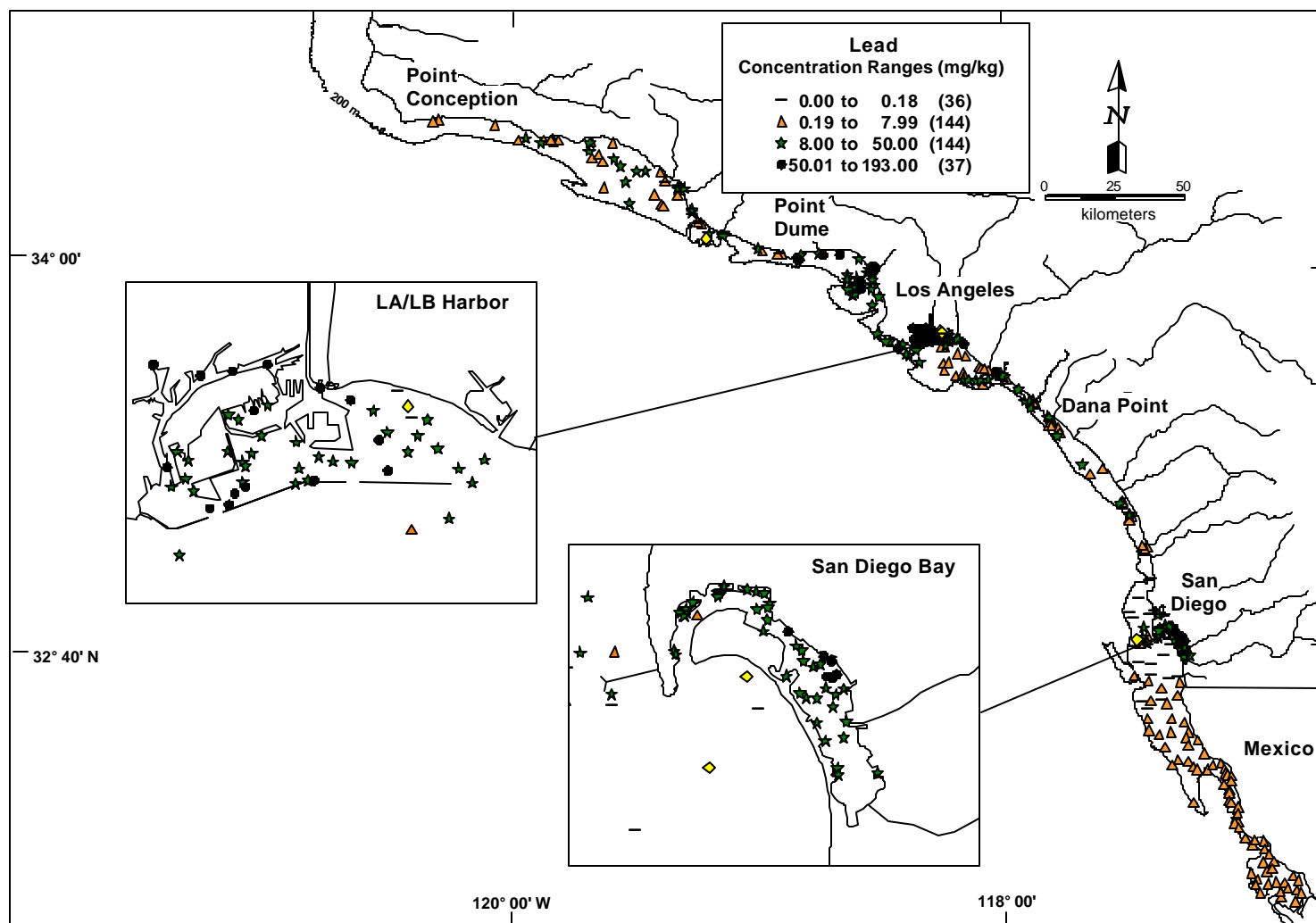


Figure V-8. Map of sediment lead concentrations for the SCB (number of stations in each range shown in parentheses).

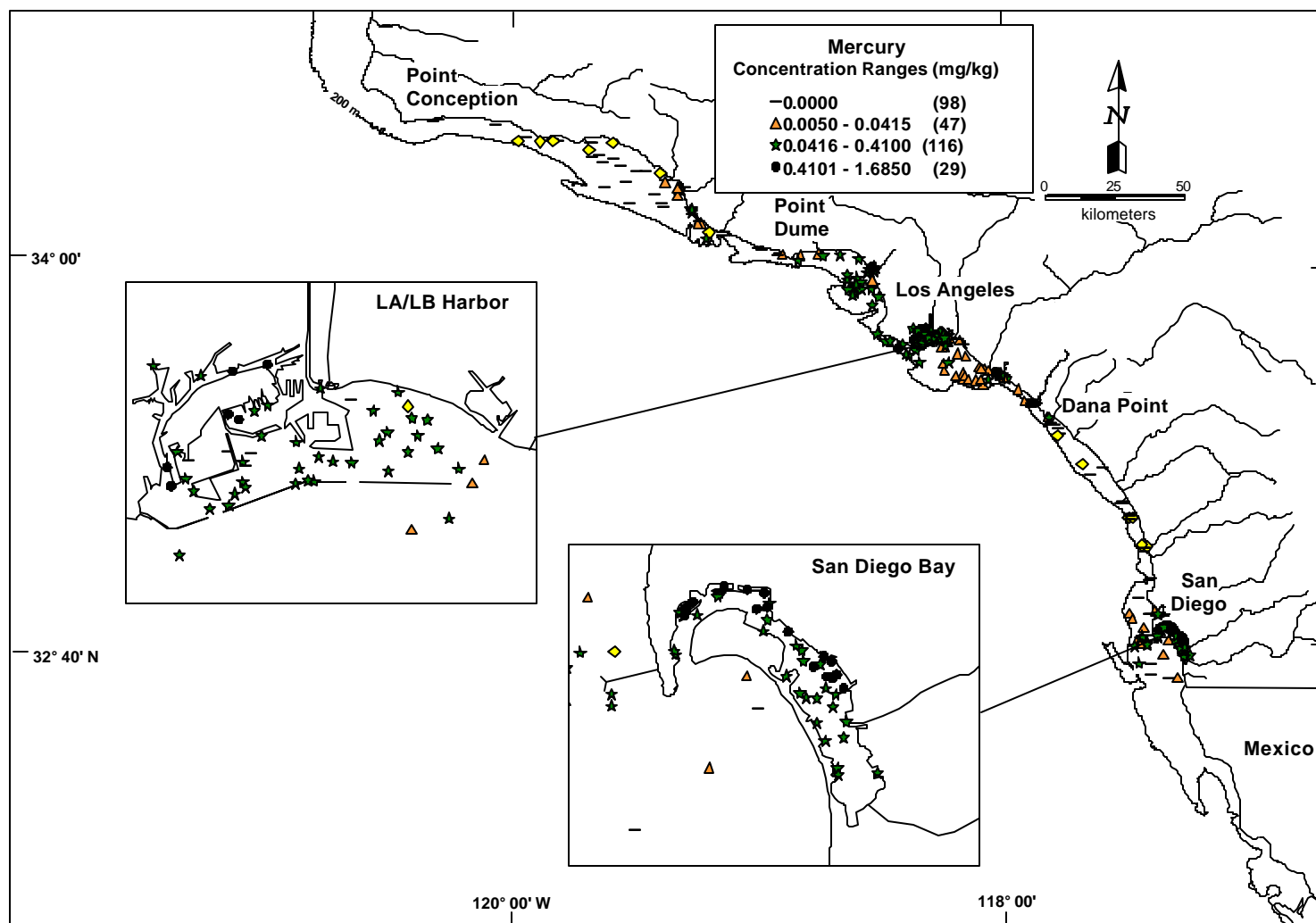


Figure V-9. Map of sediment mercury concentrations for the SCB (number of stations in each range shown in parentheses).

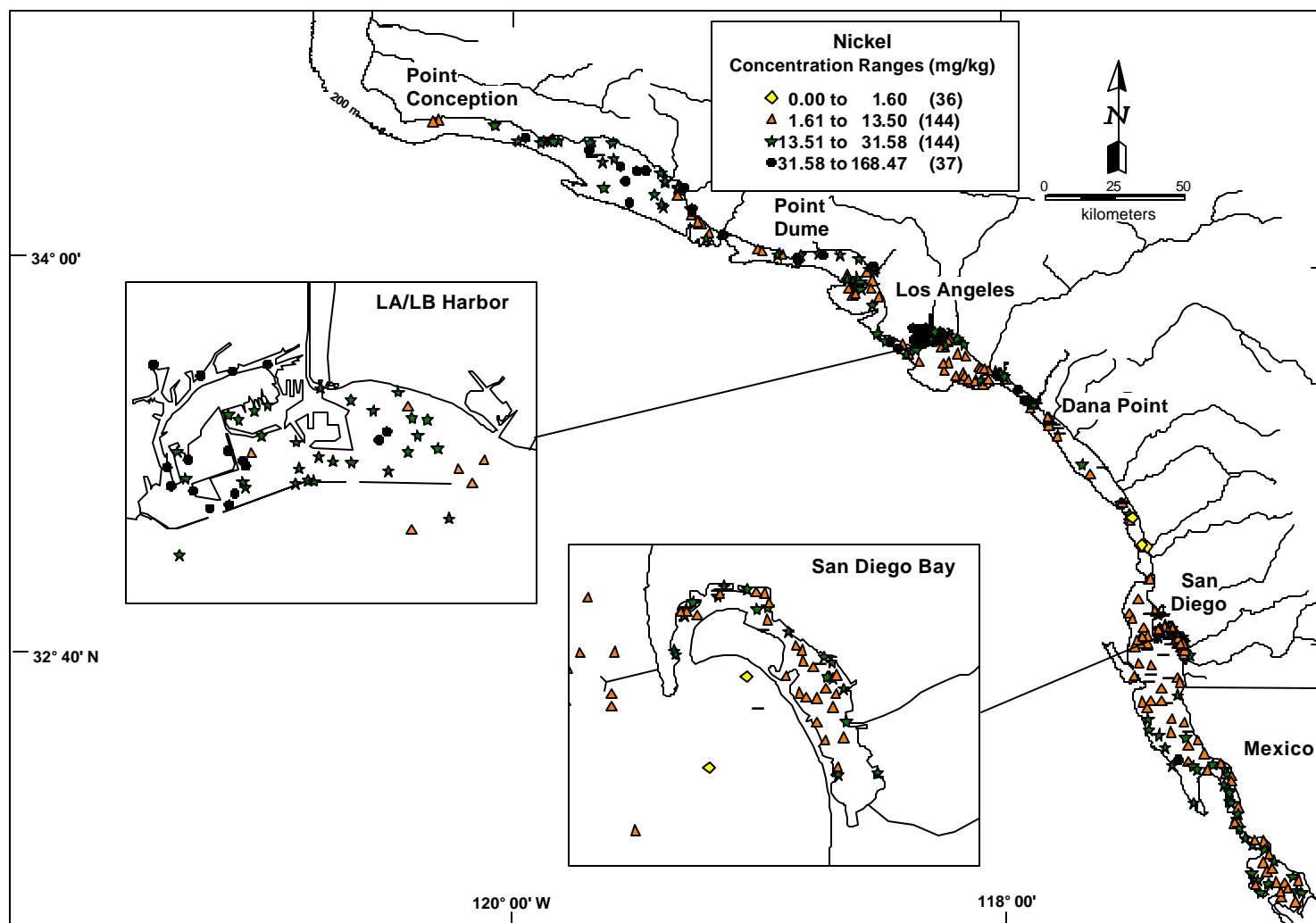


Figure V-10. Map of sediment nickel concentrations for the SCB (number of stations in each range shown in parentheses).

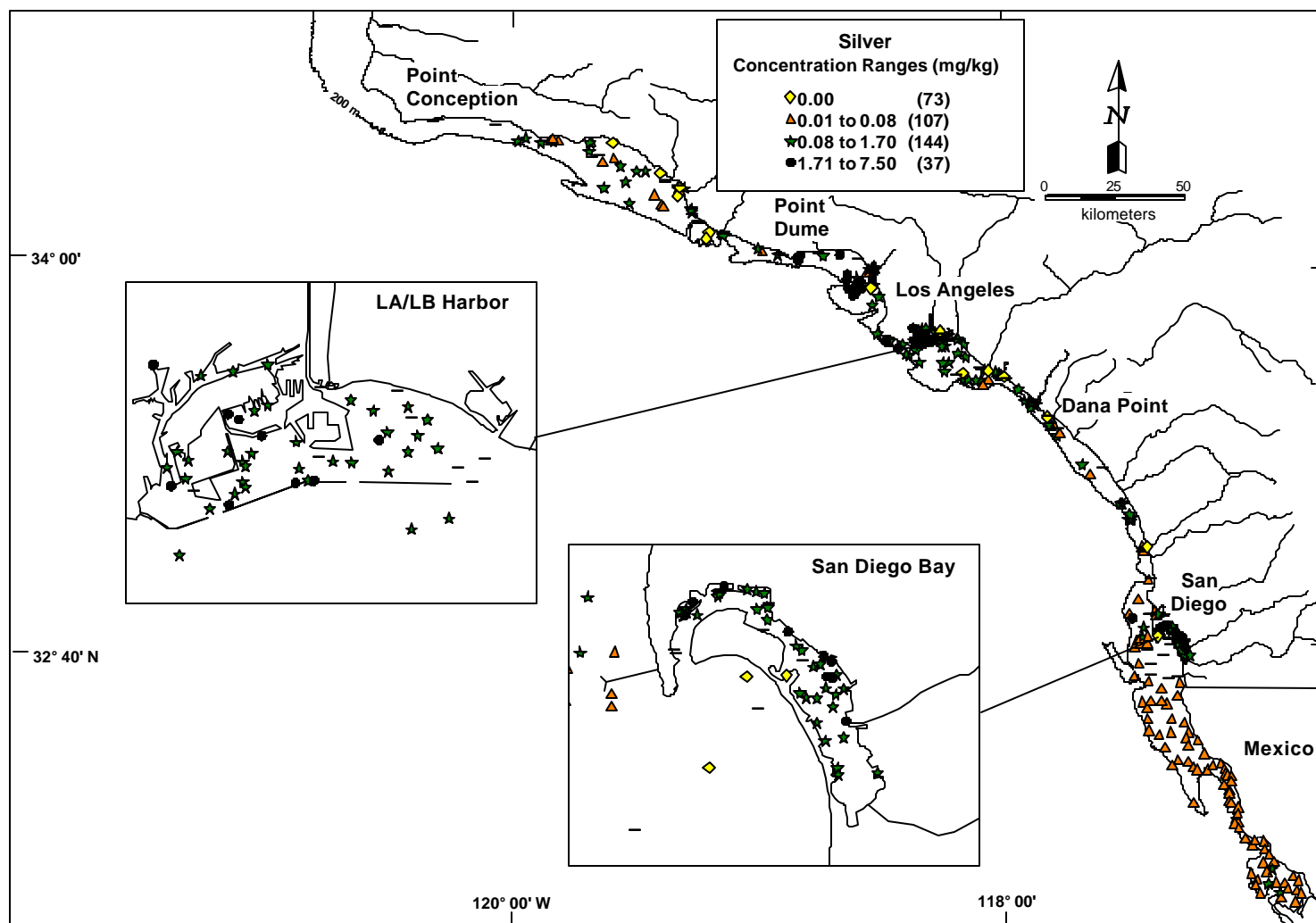


Figure V-11. Map of sediment silver concentrations for the SCB (number of stations in each range shown in parentheses).

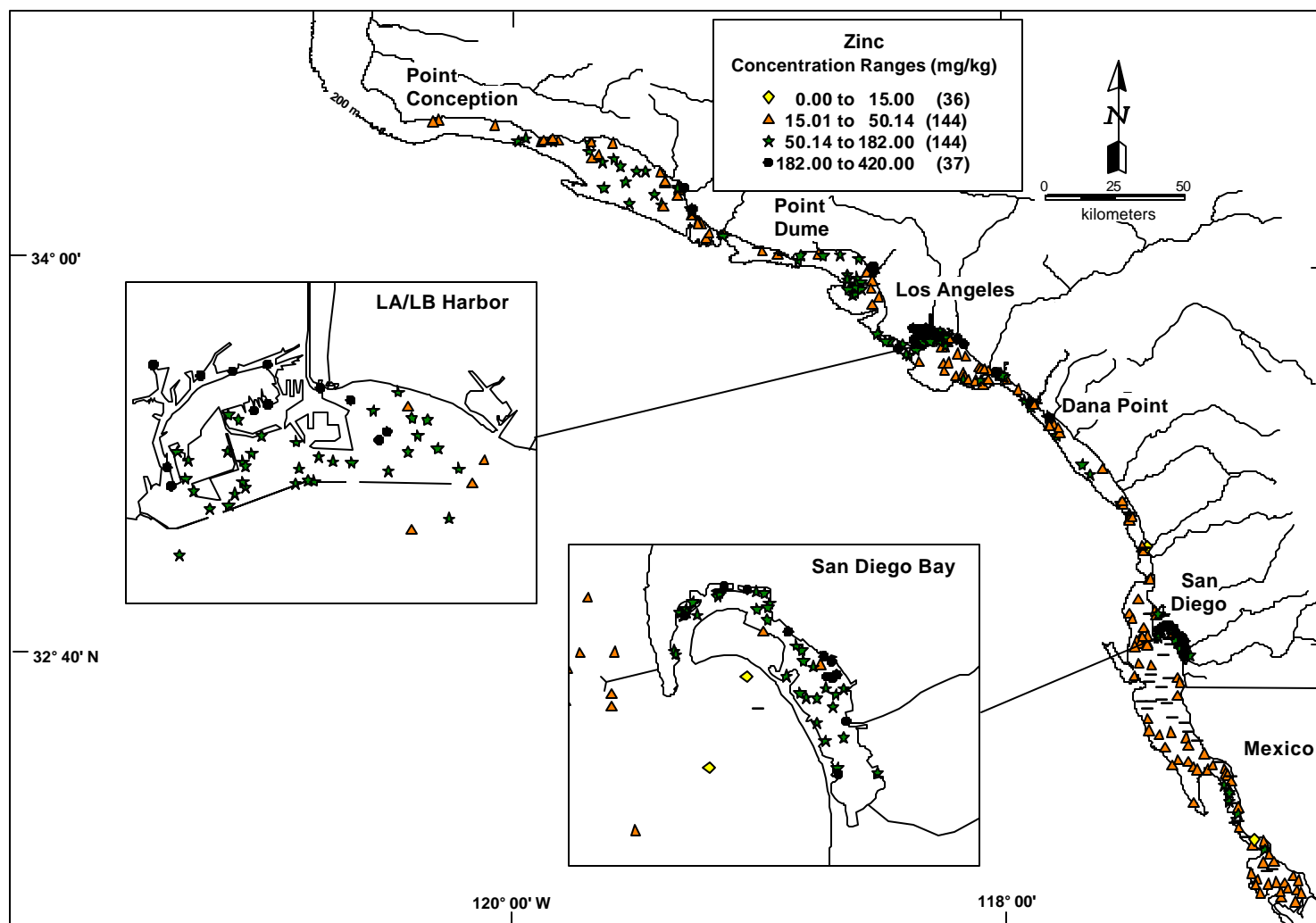


Figure V-12. Map of sediment zinc concentrations for the SCB (number of stations in each range shown in parentheses).

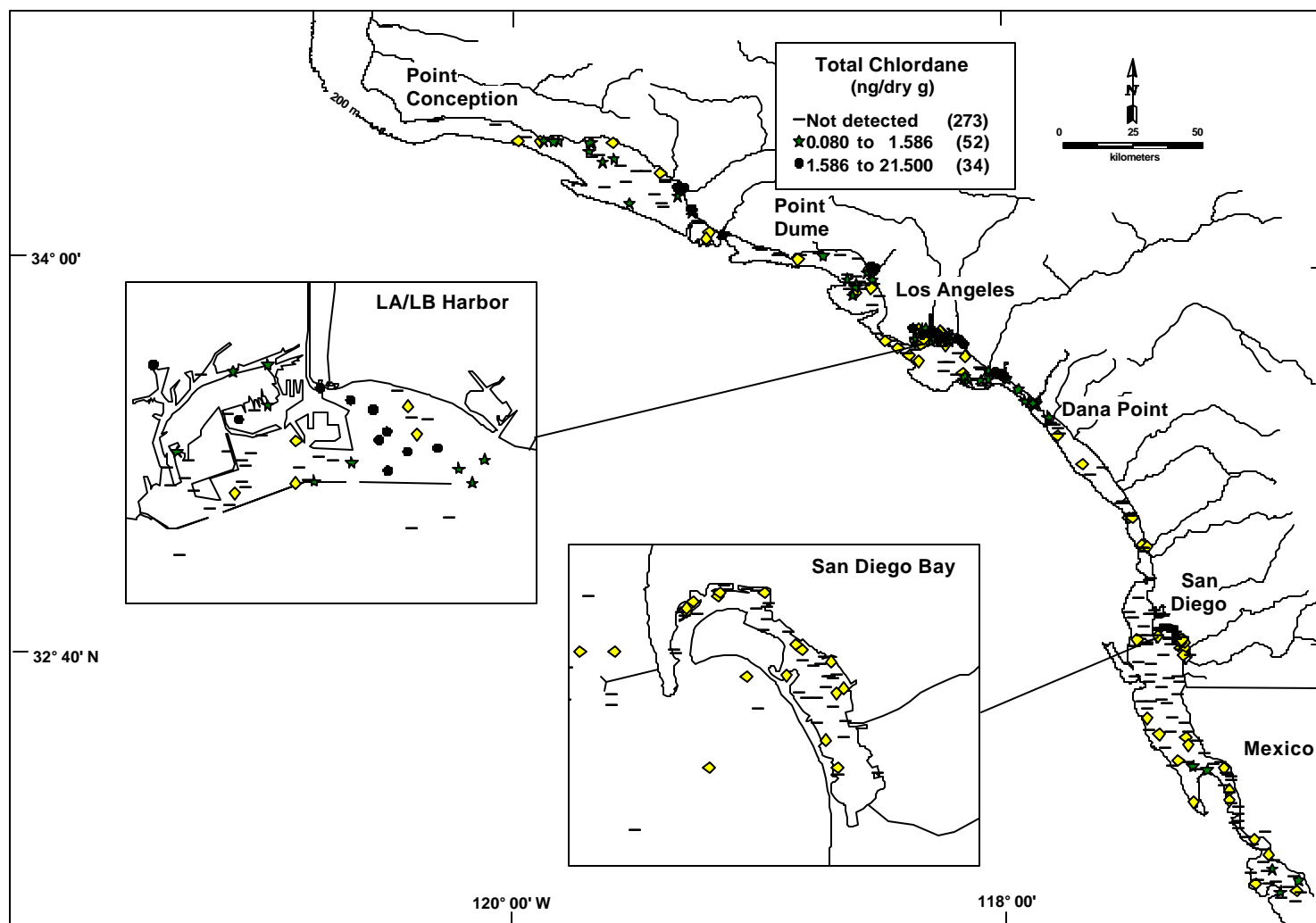


Figure V-13. Map of sediment total chlordane concentrations for the SCB (number of stations in each range shown in parentheses).

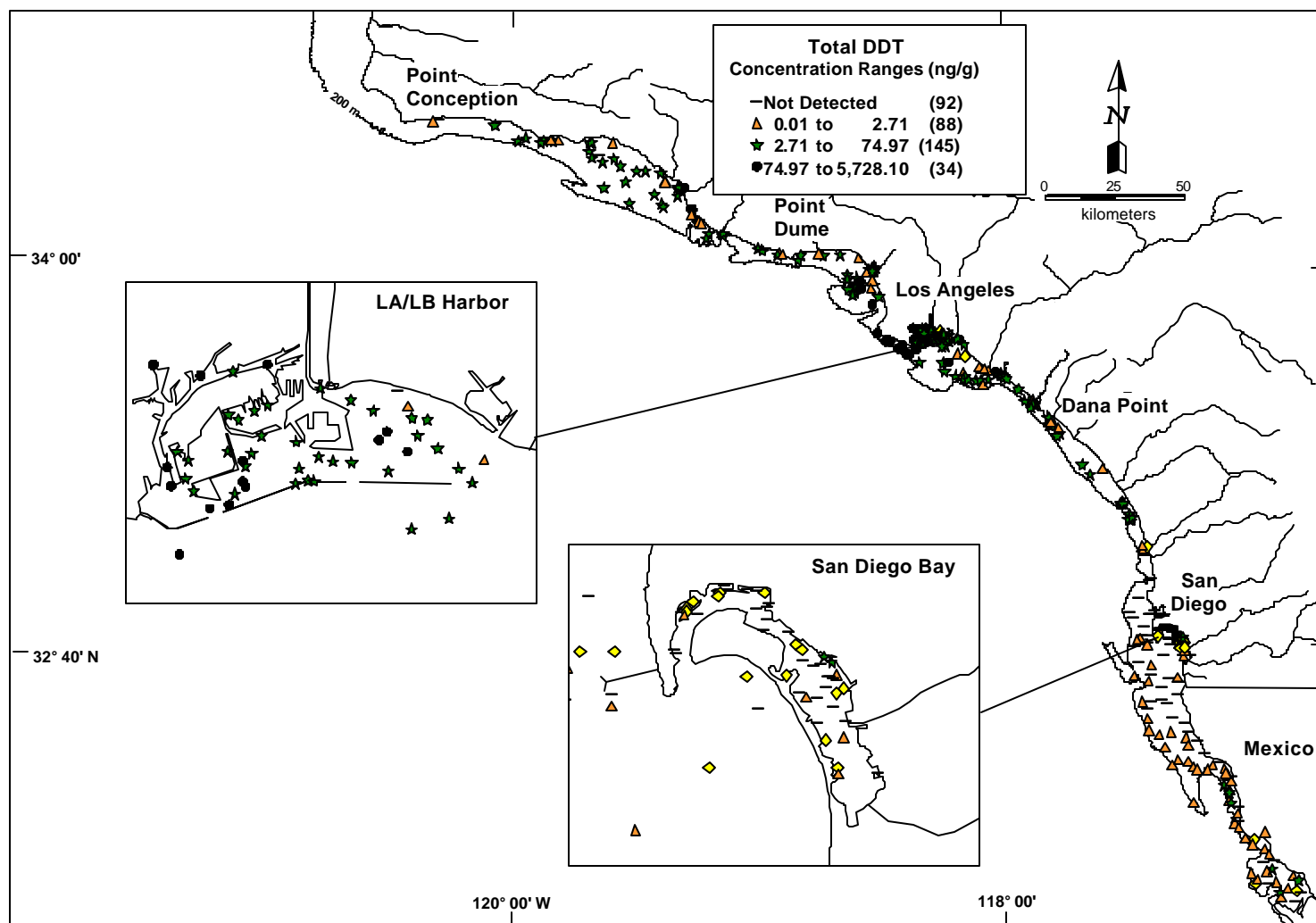


Figure V-14. Map of sediment total DDT concentrations for the SCB (number of stations in each range shown in parentheses).

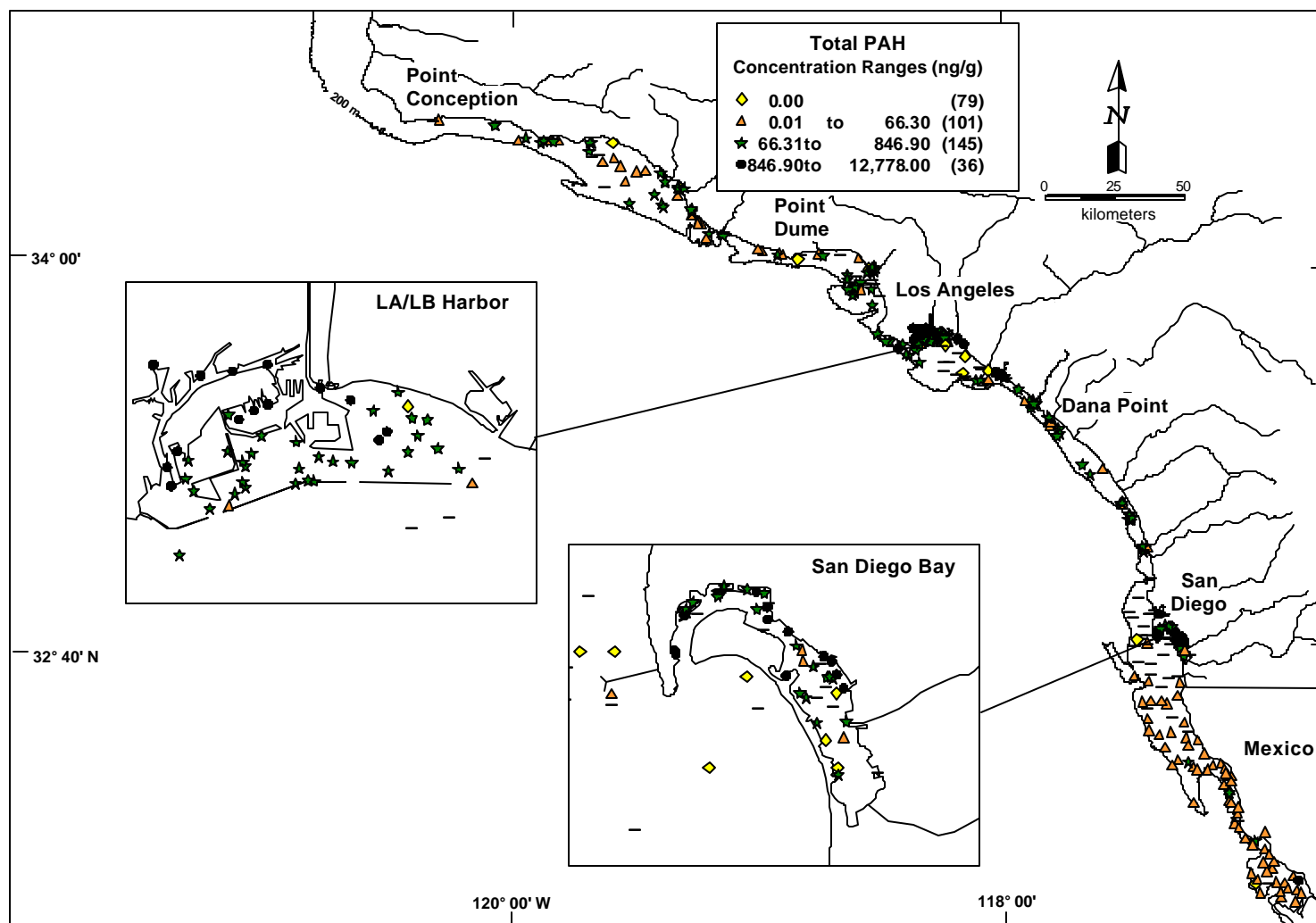


Figure V-15. Map of sediment total PAH concentrations for the SCB (number of stations in each range shown in parentheses).

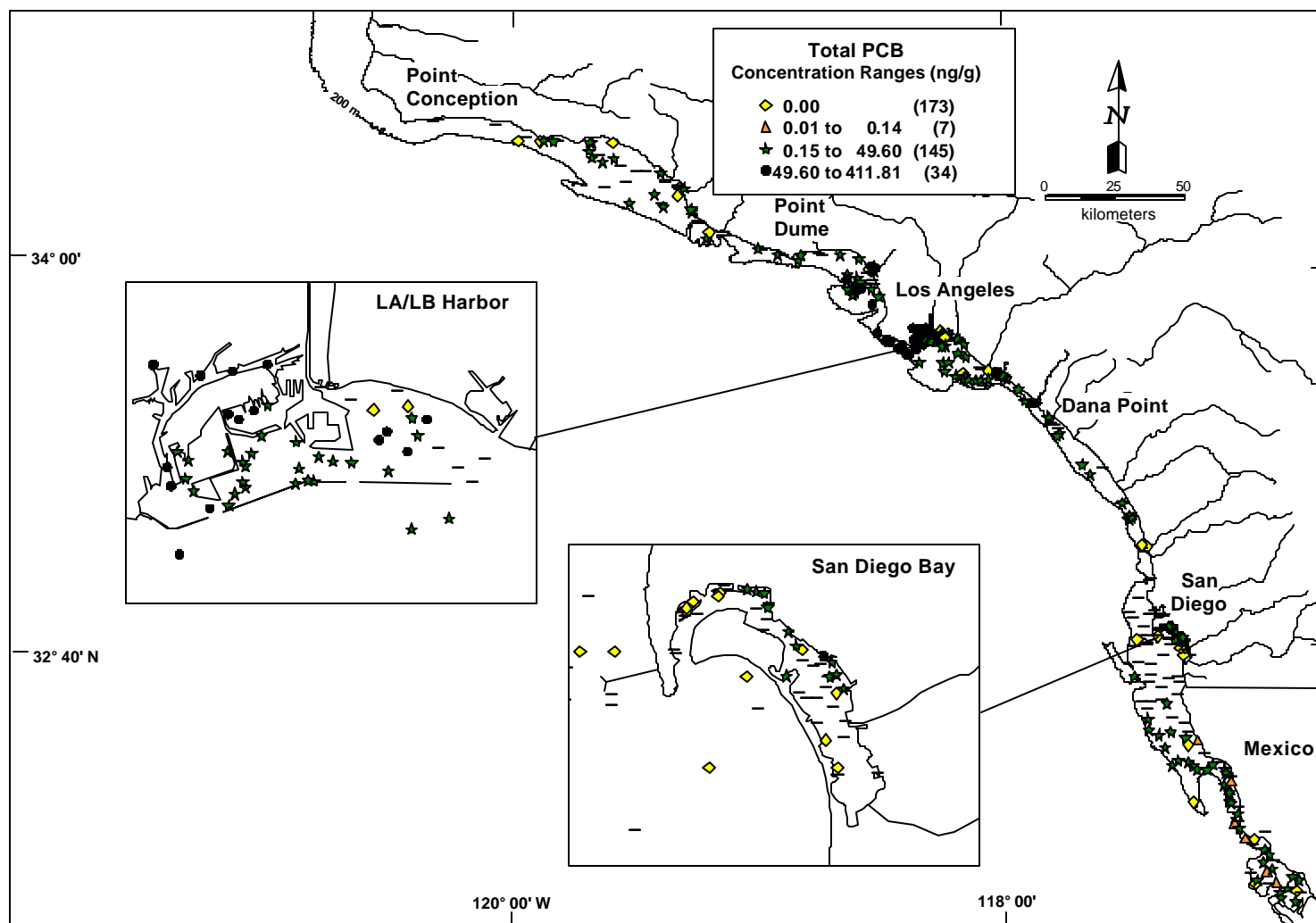


Figure V-16. Map of sediment total PCB concentrations for the SCB (number of stations in each range shown in parentheses).

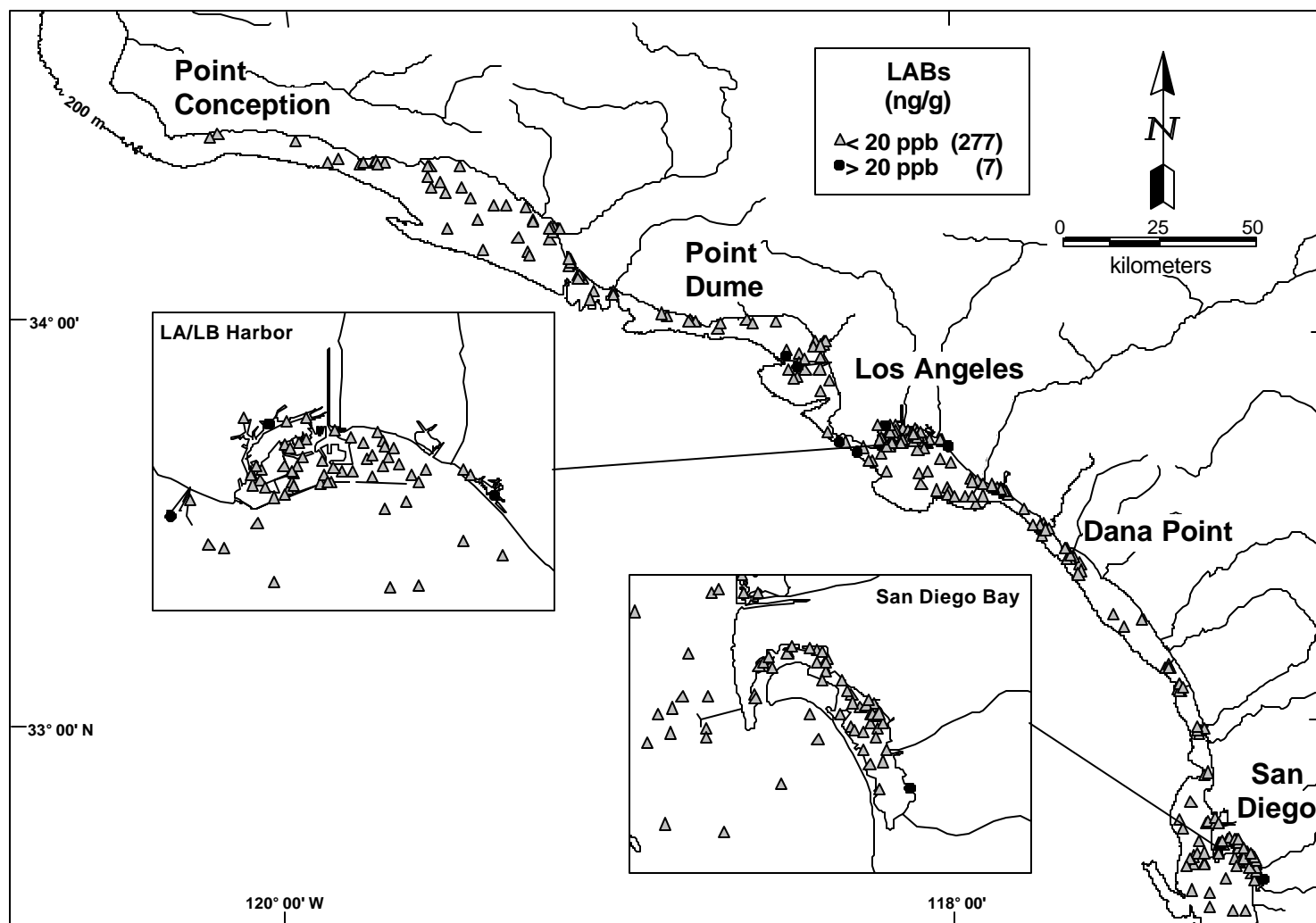


Figure V-17. Map of sediment total LAB concentrations for the SCB (number of stations in each range shown in parentheses).

VI. ASSESSMENT RESULTS

Proportional Distribution of Sediment Parameters

An evaluation was performed to determine the percentage of the total mass of each target analyte in the SCB associated with the various strata defined in this study. Estimates of the total mass of each parameter in the whole SCB, and in each source/sink stratum, was calculated using the respective area-weighted mean values and the sum of the station area-weights for the stratum under consideration. The strata chosen for this evaluation were bays and harbors (Los Angeles/Long Beach Harbor, San Diego Bay, and “other bays and harbors”), large POTWs, small POTWs, and river mouths. Substrata within bays and harbors related to specific human use and activities were also evaluated. The results from these analyses are presented in Tables VI-1a and VI-1b, respectively. The proportion of the total area and the total mass of all constituents in each of the strata areas are shown. The average percentage of the total SCB mass of all constituents for each subpopulation with the estimated 95% confidence intervals relative to the corresponding area percentage are shown in Figure VI-1. Wherever the percent of mass of a given constituent exceeds the percent of area for a given stratum, there is a disproportionate amount of that constituent in that stratum.

It is evident from the data in Table VI-1a that both trace element and trace organic analytes are disproportionately concentrated within the bay and harbor areas (9.5 average percent of mass), and near large POTW outfalls (12.0 average percent of mass). However, variations in the profiles of the target analytes among the different bays and harbors are readily apparent. Los Angeles/Long Beach Harbor shows a fairly homogeneous enrichment in trace metals and chlordanes; total DDT has a percent of mass nearly at proportional levels (2.2), whereas total PCB (10.7) and total PAH (17.7) are significantly elevated. In contrast, San Diego Bay has much higher percentages of mass for copper (16.2), mercury (20.3), and total PAH (21.4) than the other constituents. The remaining smaller bays and harbors throughout the Bight were treated as a single group for the purposes of this comparison. These remaining areas had high percentages of mass for cadmium (5.0), copper (10.1), lead (6.0), mercury (6.0), zinc (6.2), total PAH (11.3), and an extremely disproportionate amount of total chlordanes (51.2). The smaller bays and harbors accounted for more than 50% of the total chlordanes detected in the SCB. The evaluation of sub-areas within bays and harbors is shown in Table VI-1b. The trace metals masses are comparable for the ports and marinas (8.0 and 9.9 average percent of mass, respectively), but the ports occupy about 30% less area. Noteworthy differences are the high percentage of mass for chlordanes (39.8) in the marinas areas, and the high percentage of mass for total PAH (31.2) in the port areas. In general, the other areas in the bays have lower masses (3.9 average) of the target parameters relative to the port and marinas areas. The one exception is the high percentage of mass for chlordanes found in the other bay and harbor areas (11.4), which may be due to spillover from the marina areas.

Table VI-1a. The percent of total Bight-wide mass for each constituent residing within various source 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.

Parameters	LA/LB Harbor	San Diego Bay	All Other Bays/Harbors	LPOTWs	SPOTWs	River Mouths	Total
% of Area	1.5	2.3	2.3	4.0	1.6	1.0	12.7
% of Mass							
Arsenic	3.7	2.9	3.4	4.3	1.6	0.9	16.9
Cadmium	2.6	0.9	5.0	11.9	1.1	1.1	22.5
Chromium	3.2	3.4	3.6	7.4	1.4	0.8	19.7
Copper	7.3	16.2	10.1	7.1	1.6	0.8	43.2
Lead	5.2	6.6	6.0	6.8	1.3	1.2	27.1
Mercury	7.8	20.3	7.6	11.9	0.7	0.6	48.9
Nickel	2.5	1.4	2.6	2.9	0.8	0.7	11.0
Silver	5.3	5.4	2.5	16.2	0.5	0.6	30.6
Zinc	4.2	6.3	6.2	4.8	1.4	1.0	24.0
Chlordanes	6.1	0.0	51.2	2.9	1.1	7.4	68.7
ΣDDTs	2.2	0.0	4.4	46.1	0.4	0.2	53.3
ΣPAHs	17.7	21.4	11.3	5.6	1.3	1.5	58.9
ΣPCBs	10.7	2.3	9.4	27.6	0.5	1.4	52.0
Average % of Mass	6.0	6.7	9.5	12.0	1.1	1.4	36.7

LPOTW = Large publicly owned treatment works; SPOTW = Small publicly owned treatment works; i.e., wastewater treatment plants.

Table VI-1b. The percent of total Bight-wide mass for each constituent residing within the bay and harbor substrata relative to the percent of total Bight area.

Parameters	Ports & Industrial	Marinas	Other Bay & Harbor Areas
% of Area	1.9	2.6	1.6
% of Mass			
Arsenic	3.4	3.6	2.3
Cadmium	2.1	4.6	1.8
Chromium	3.5	4.1	2.3
Copper	13.2	14.6	4.9
Lead	6.4	7.0	3.8
Mercury	13.3	16.0	5.7
Nickel	2.0	2.6	1.6
Silver	6.1	3.7	3.0
Zinc	5.8	7.4	3.6
Total Chlordanes	5.9	39.8	11.4
Total DDT	1.2	2.9	1.2
Total PAH	31.2	13.8	5.2
Total PCB	10.0	8.4	3.6
Average	8.0	9.9	3.9
% of Mass			

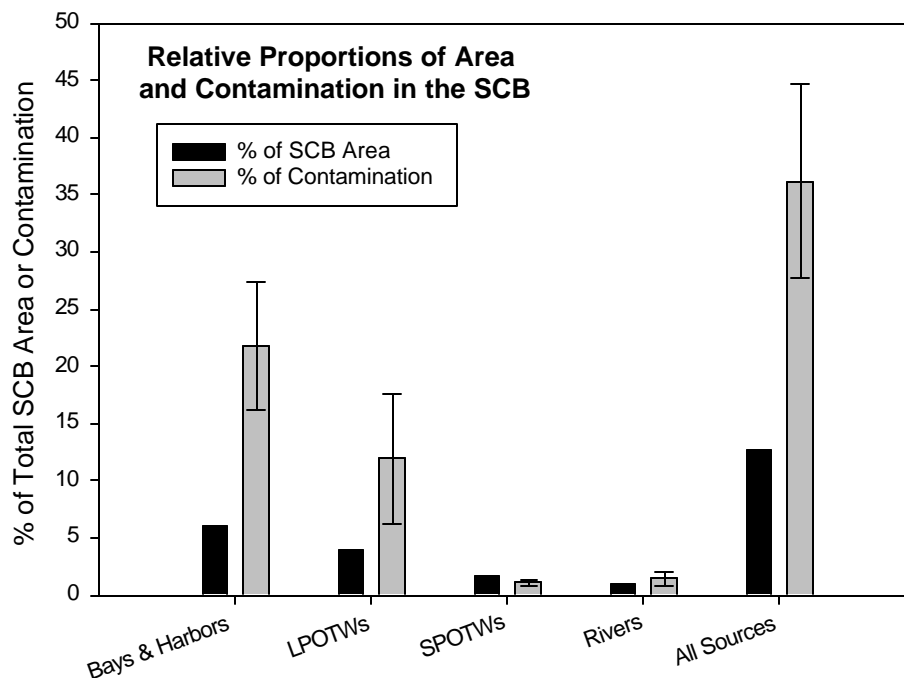


Figure VI-1. Relative proportions of area and contaminant mass for the SCB source strata. The error bars are the calculated 95% confidence intervals.

Similarly, although all LPOTWs were evaluated together, the vast majority of the contamination was associated with the Hyperion (City of Los Angeles) and JWPCP (County of Los Angeles) 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)

In contrast, the proportion of the total mass for most parameters in areas near small POTWs (1.1) and river mouths (1.4) are consistent with the percent of the total area (1.6 and 1.0, respectively) occupied by these strata. The single exception is the proportion of chlordanes (7.4) found in the river strata, which is approximately seven times higher than the corresponding proportion of the total area (1.0). Also presented are data on the summed proportion of the mass found in all of these strata. Only for nickel is the proportion of the total mass consistently below the percent of area for each of the strata under consideration.

Extent of Anthropogenic Sediment Contamination

Individual Parameter Analysis

The initial step in the assessment of the sediment chemistry data was to determine what proportion of the total sediment concentration of the target analytes is due to human activities. Assessing the anthropogenic contribution to the sediment concentration is straightforward for synthetic organic compounds, such as chlordanes, DDTs, and PCBs. Since these compounds do not occur naturally, their presence at any detectable level is indicative of anthropogenic pollution. In contrast, other organic compounds such as PAHs can result from both natural and anthropogenic sources. PAHs are natural components of petroleum and are synthesized by some plants and bacteria (Libes 1992). However, after consideration of the biogenic and seepage fluxes of hydrocarbons into the SCB, Eganhouse and Venkatesan (1993) concluded that the “vast majority” of hydrocarbon pollution in the SCB is of anthropogenic origin. Therefore, for the purposes of this study and the following evaluations, all PAHs were assumed to be of anthropogenic origin. The extent and distribution of anthropogenic contamination from organic compounds can be ascertained directly from the concentration data in the preceding section (Figures V-13 to V-16).

Determination of the anthropogenic contribution of trace metals to marine sediments can be particularly problematic. All of the metal analytes in this study are naturally occurring elements. Several approaches have been developed to estimate the natural background concentrations for the metals of environmental concern. As previously stated, the iron-normalization method described by Schiff and Weisberg (1999) was used in this study to estimate the natural sediment background concentrations of the trace metal analytes. Details of the method used to evaluate the Bight’98 sediment metals data are given in Appendix A. All of the U.S. stations were evaluated for nine of the trace metal analytes using this approach, and stations were designated as either above or below background levels. Stations designated as above background are assumed to be contaminated by metals from anthropogenic sources. The results from this analysis are shown in Figures VI-2 to VI-10.

The efficacy of using an approach such as iron-normalization to differentiate between background and contaminated sites is readily apparent from the resulting maps. The association of anthropogenic trace metal contamination with specific areas such as harbors, LPOTW outfalls, and river mouths is greatly emphasized. Several patterns in the metals contamination are apparent. Arsenic, mercury, and silver were enriched near POTW outfalls and industrial port areas. Interestingly, only three stations in San Diego Bay were enriched in arsenic. Also, the four shoreline stations between Ballona Creek and Malibu Lagoon in the northern part of the Santa Monica Bay were enriched in arsenic. Cadmium was enriched in many stations in the northern and central regions of the SCB, but cadmium-enriched stations were conspicuously absent south of Dana Point. Cadmium contamination was primarily associated with rivers and POTW outfalls, although many enriched stations were found in the port areas of Los Angeles/Long Beach Harbor. Chromium was above background levels at only 24 stations in the entire Bight. Anthropogenic chromium contamination was limited to the large POTW outfalls in the central Bight (Hyperion and JWPCP) and port areas (five in LA/LB and two in San Diego Bay). Copper, lead, and zinc showed similar patterns of contamination. All three metals appeared to be equally associated with rivers and POTW outfalls. The majority of the enriched stations occurred in the central region of the Bight and in San Diego Bay. All but one station in San Diego Bay was enriched in copper, lead, and zinc. In Santa Monica Bay, copper and zinc contamination occurred in sediments around Ballona Creek/Marina Del Rey, and in proximity to the Hyperion outfall. In contrast, all but one station in Santa Monica Bay appeared to be contaminated by anthropogenic lead. Although nickel was found to be at detectable levels for most stations throughout the SCB, it only appeared to be above background levels at four sites.

Multiple Parameter Analysis

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 VI-11. For this analysis, consideration was limited to the nine metals for which iron-normalized background regression curves were developed, and the four groups of organic target analytes: total chlordanes, DDTs, PAHs, and PCBs, for a total of 13 possible "contaminants." The number of anthropogenically enriched parameters per station ranged from zero to 12, with nickel being the only parameter not above background at the most polluted sites.

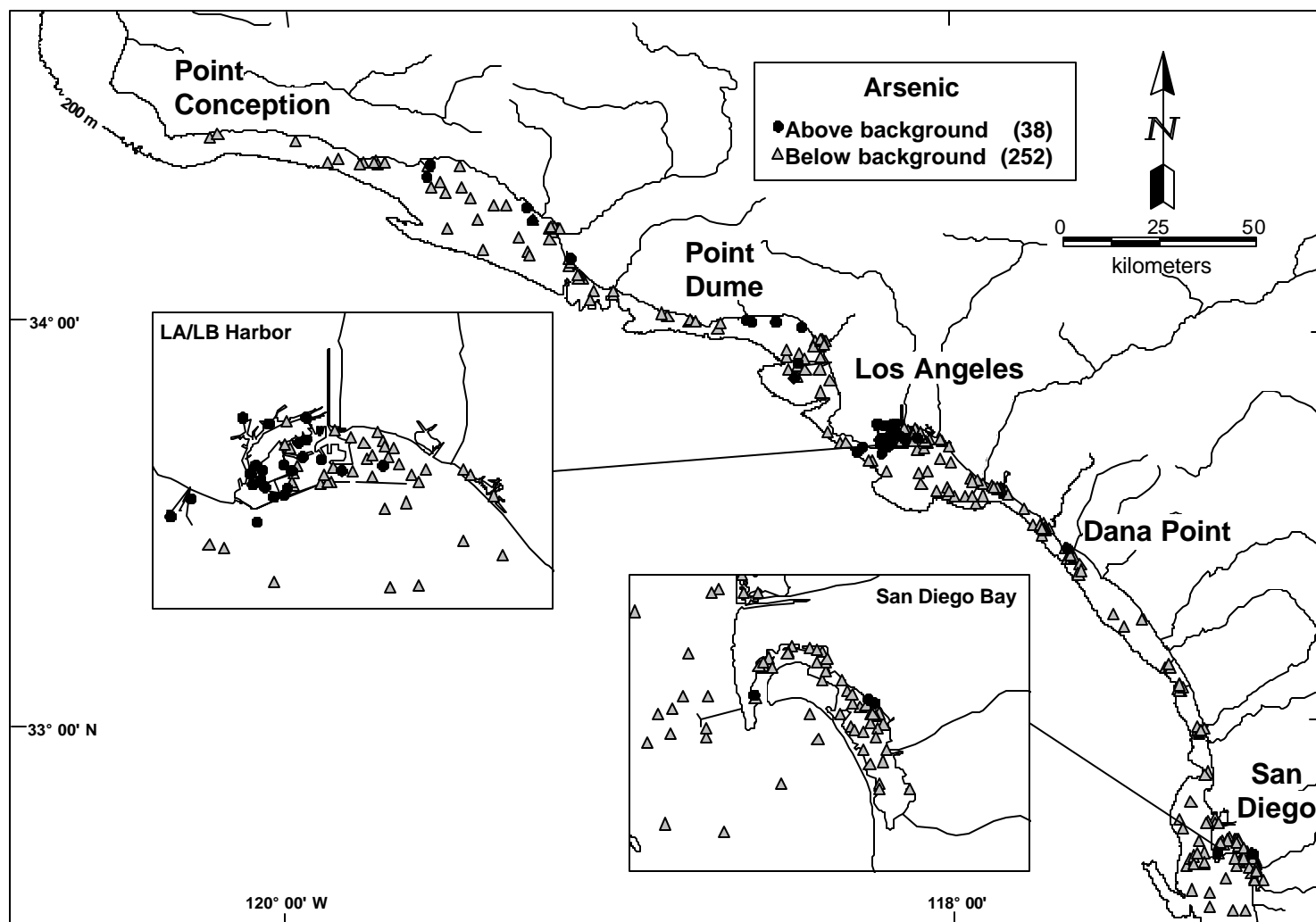


Figure VI-2. Bight'98 stations above and below estimated natural sediment background concentrations for arsenic.

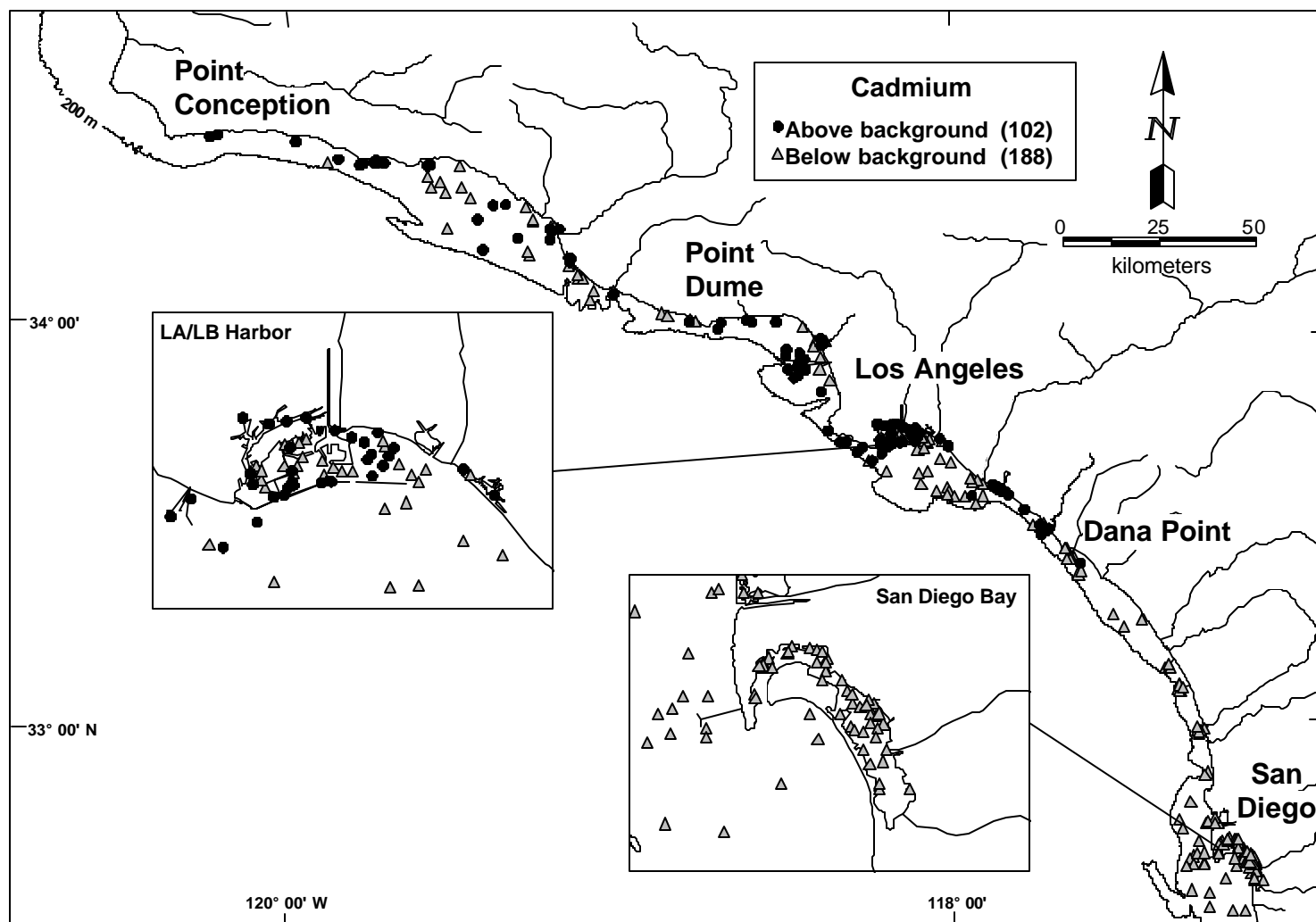


Figure VI-3. Bight'98 stations above and below estimated natural sediment background concentrations for cadmium.

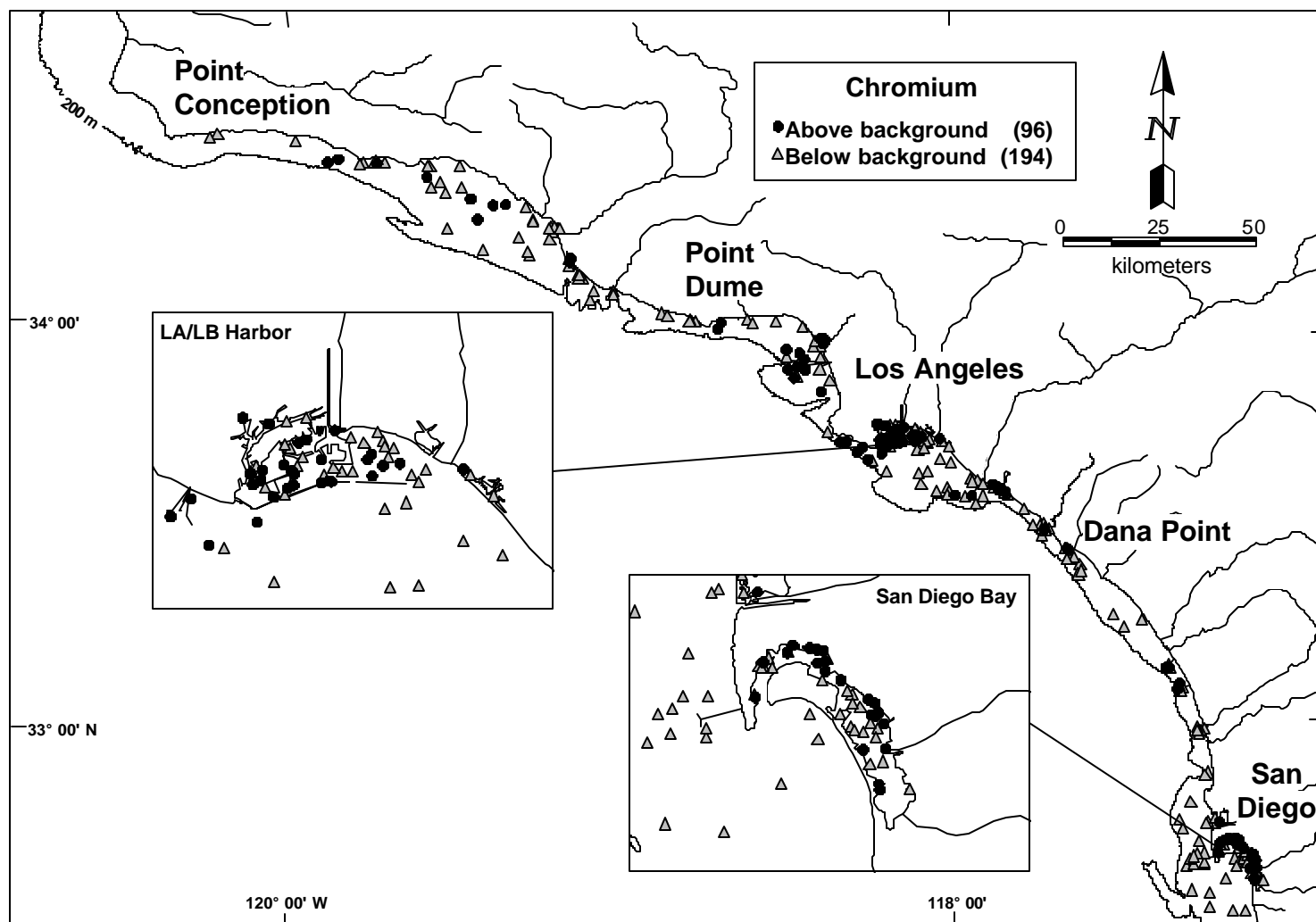


Figure VI-4. Bight'98 sediment stations above and below estimated natural background concentrations for chromium.

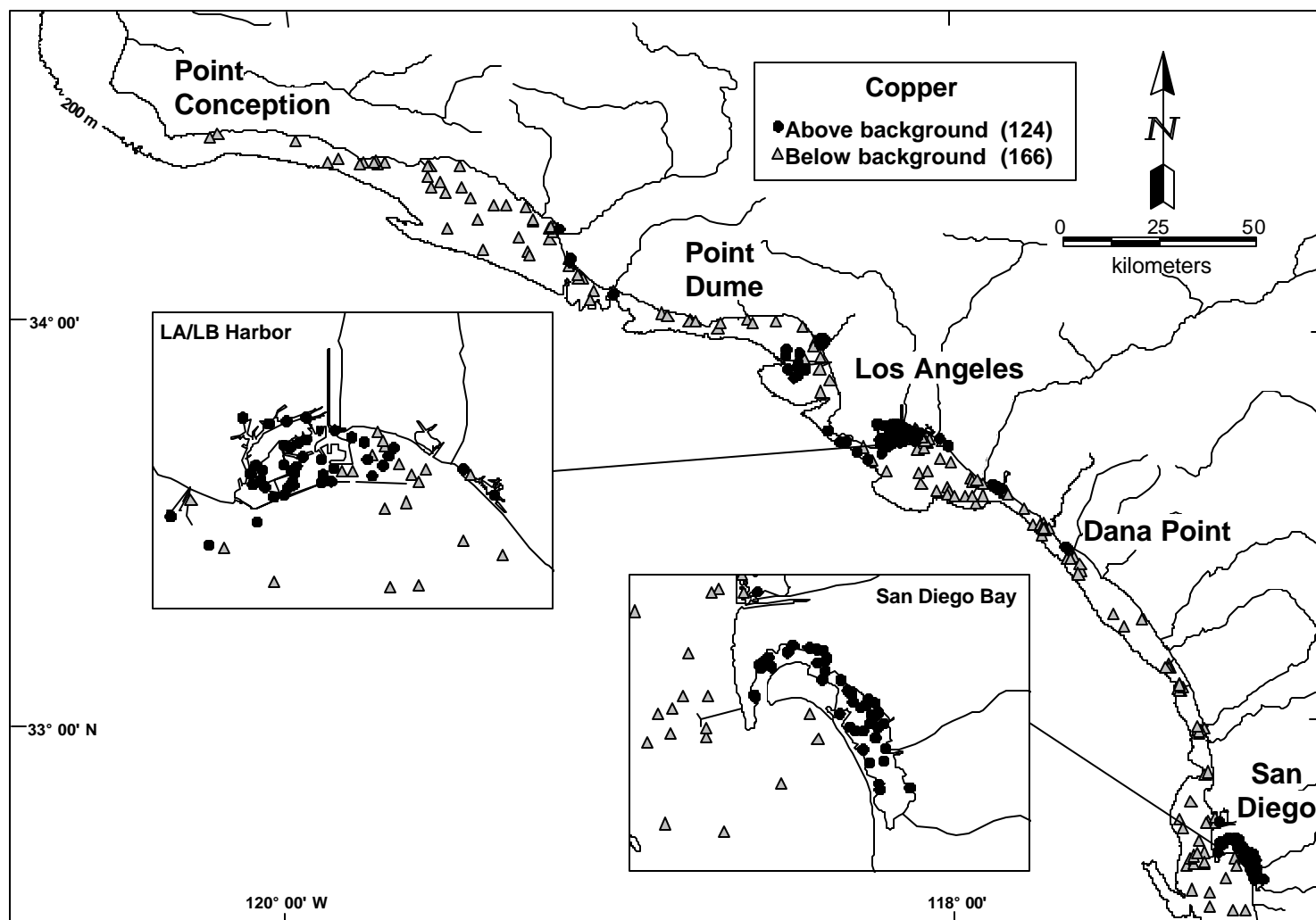


Figure VI-5. Bight'98 sediment stations above and below estimated natural background concentrations for copper.

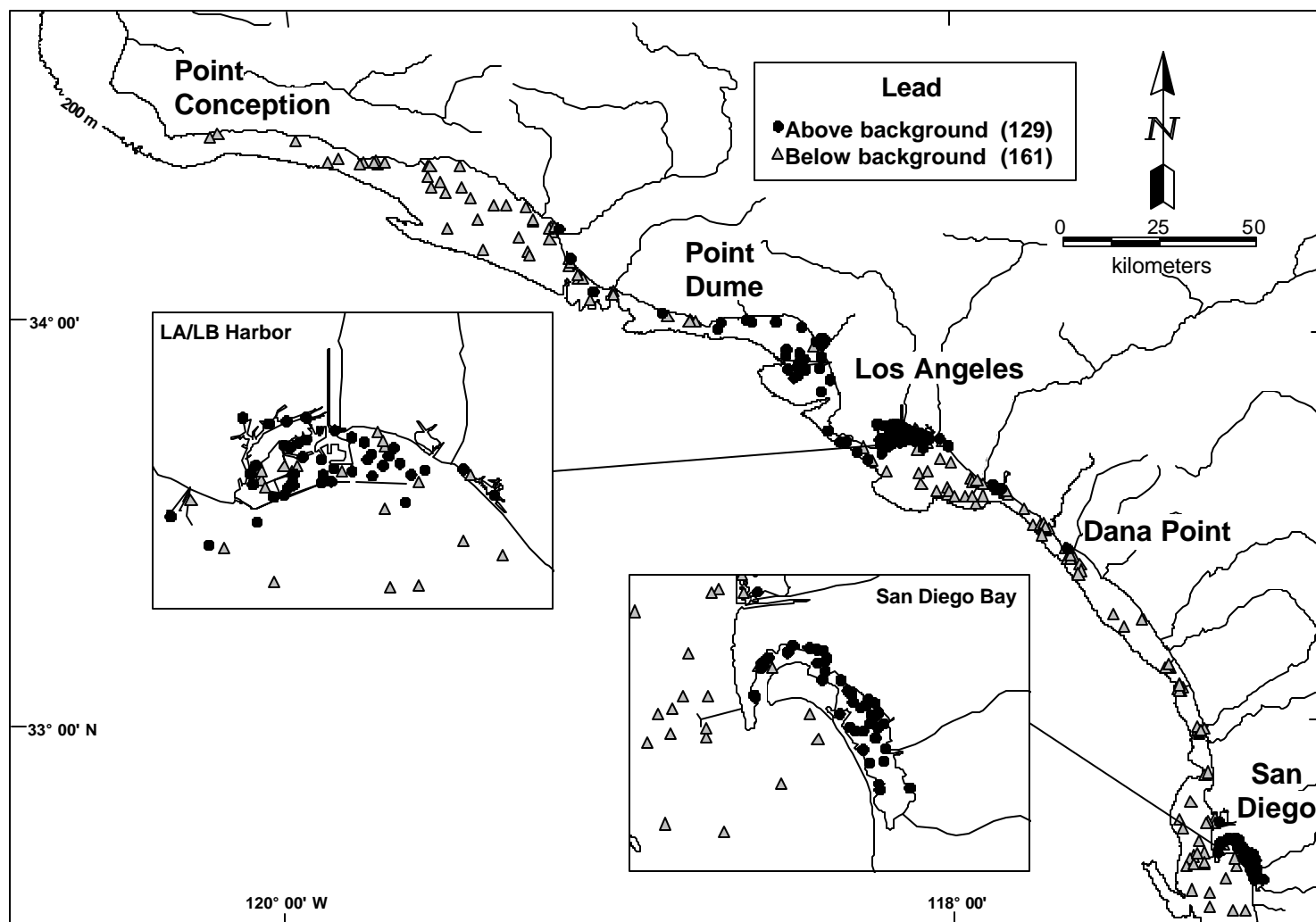


Figure VI-6. Bight'98 sediment stations above and below estimated natural background concentrations for lead.

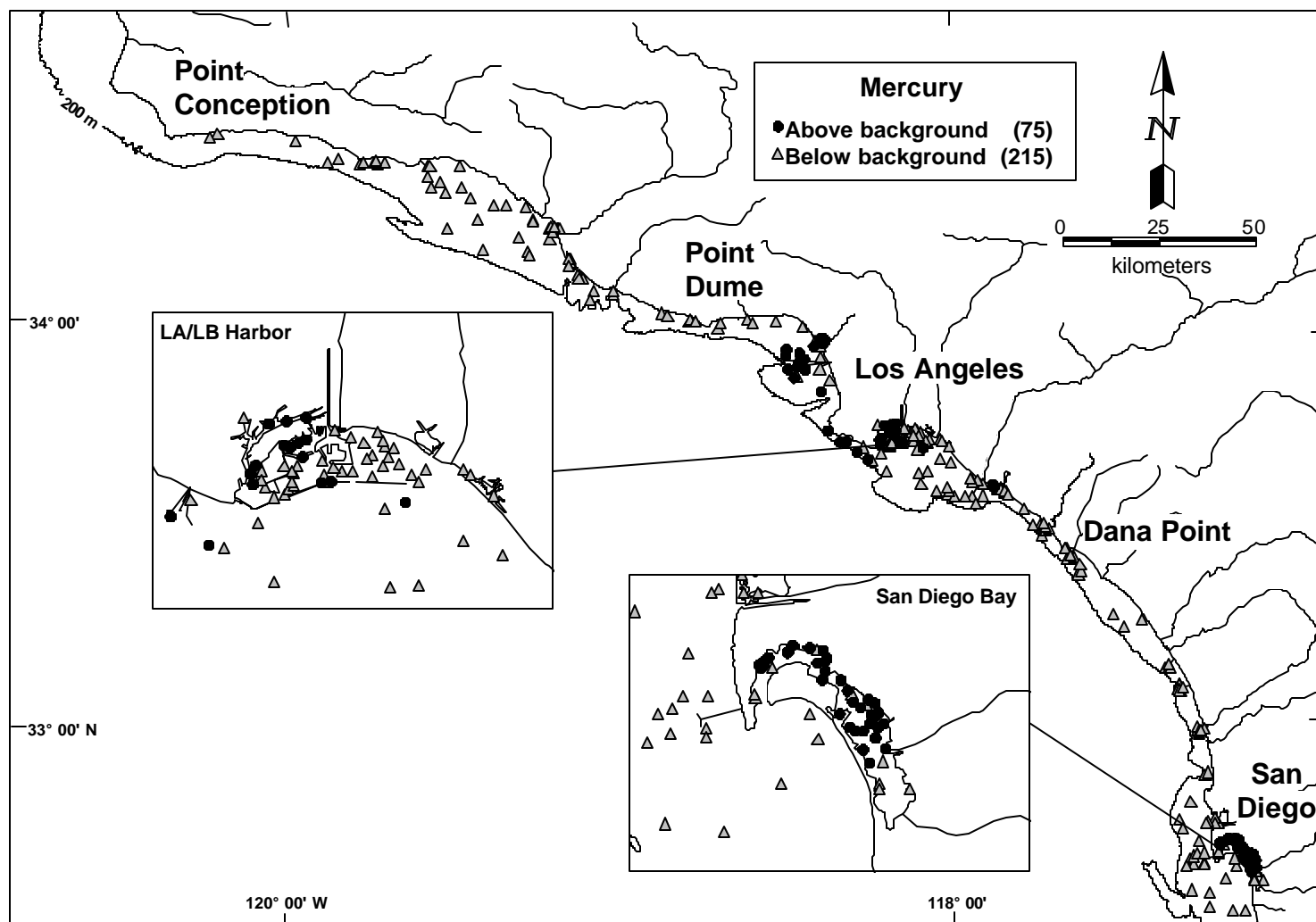


Figure VI-7. Bight'98 sediment stations above and below estimated natural background concentrations for mercury.

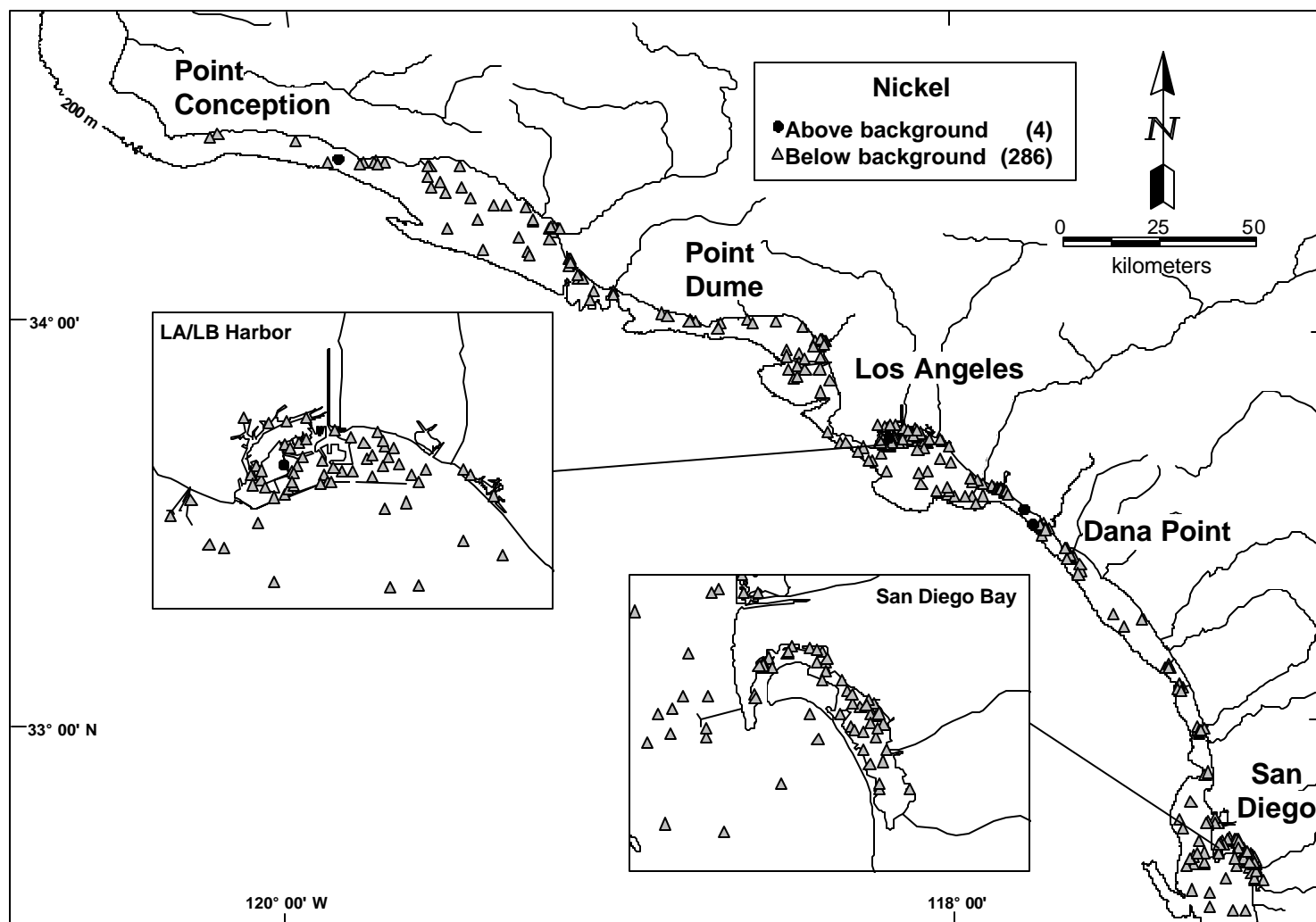


Figure VI-8. Bight'98 sediment stations above and below estimated natural background concentrations for nickel.

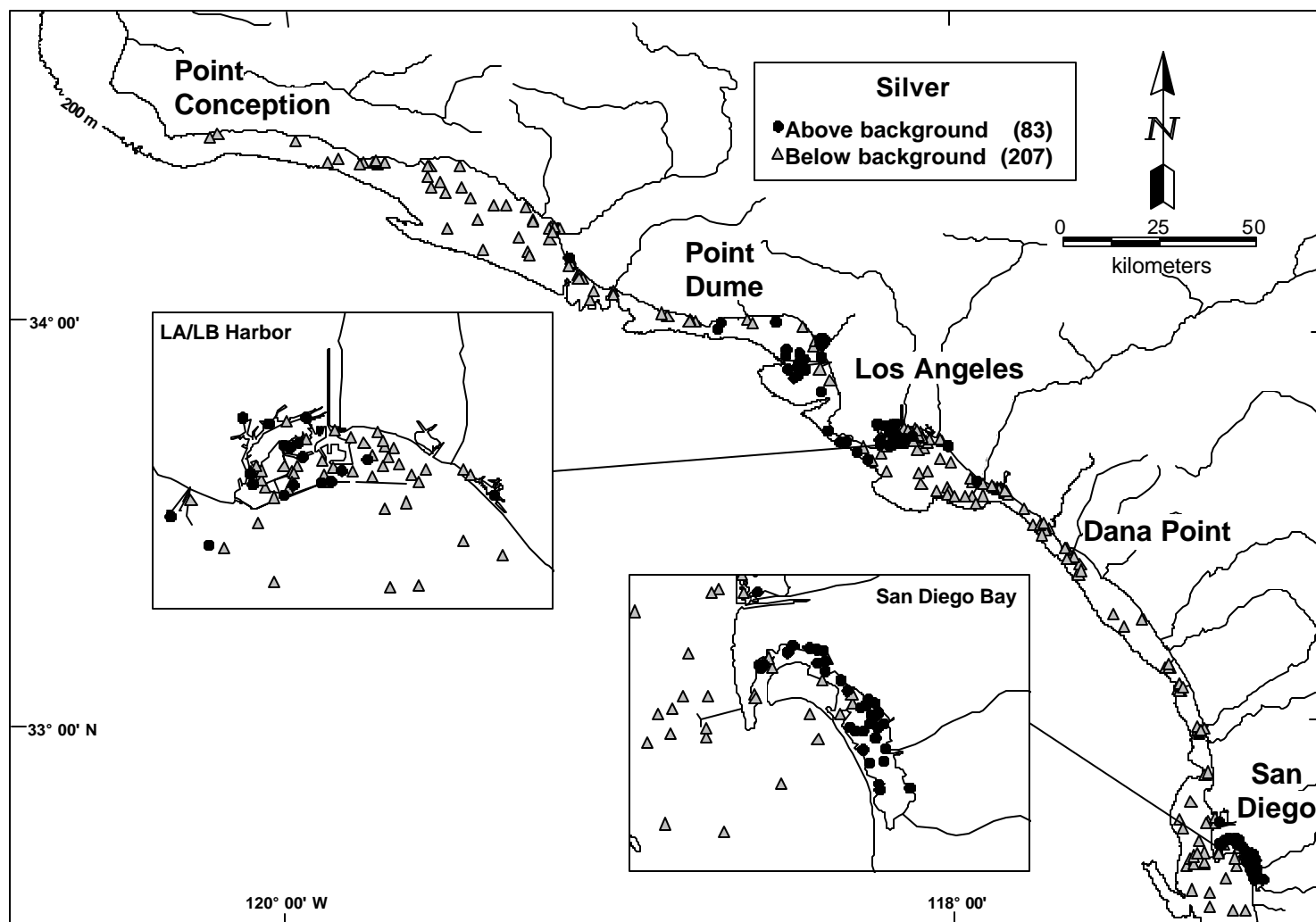


Figure VI-9. Bight'98 sediment stations above and below estimated natural background concentrations for silver.

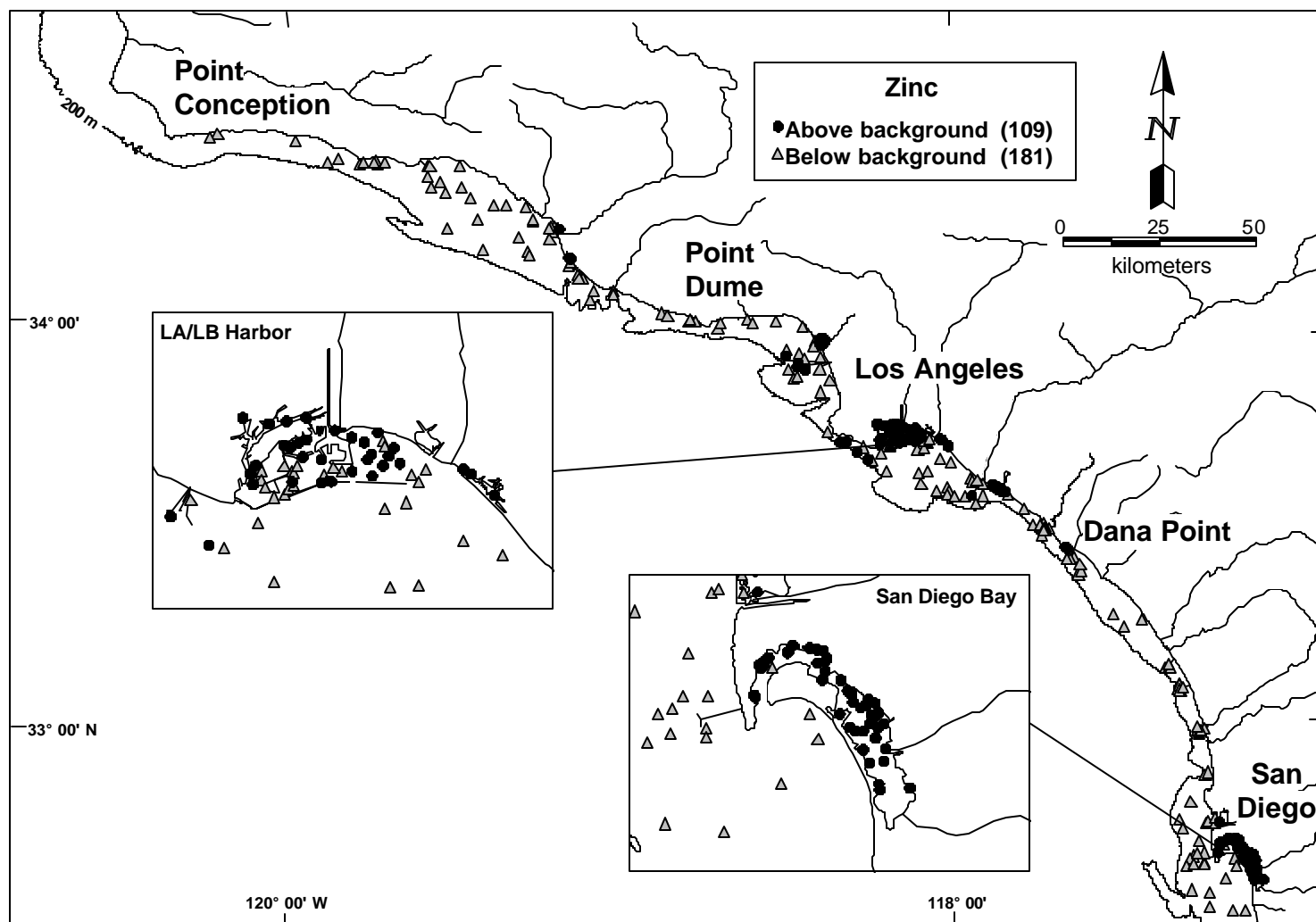


Figure VI-10. Bight'98 sediment stations above and below estimated natural background concentrations for zinc.

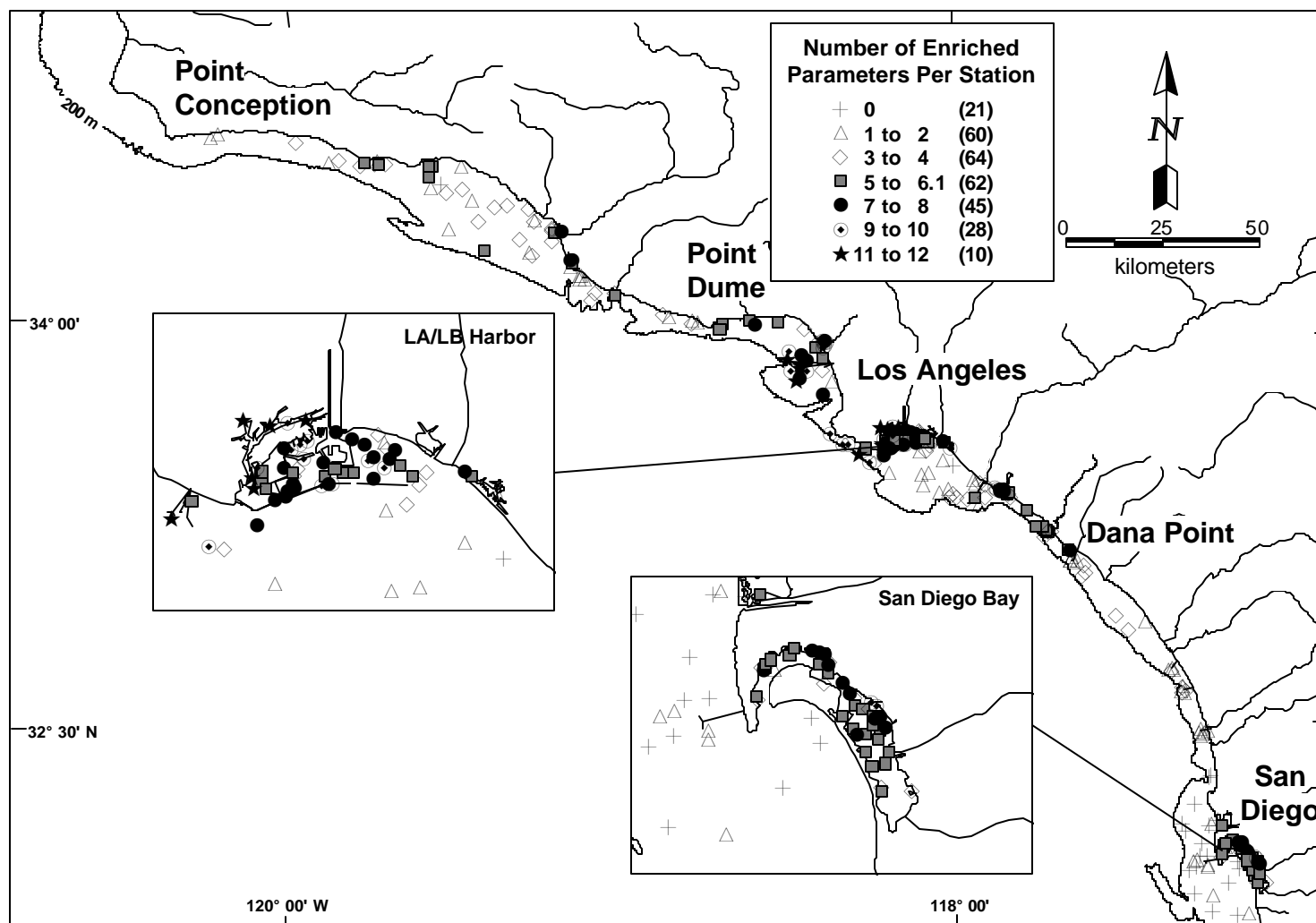


Figure VI-11. Number of anthropogenically enriched target analytes (metals and organics) per station for the Southern California Bight.

Principal Components and Cluster Analysis

The patterns in sediment metal, PAH, chlorinated pesticide, and PCB concentrations at 290 sites within coastal, port, harbor, and marina areas of the SCB were evaluated using the multivariate techniques cluster analysis and principal components analysis (PCA). A detailed presentation of these analyses is presented in Appendix C.

Cluster analysis identified five primary site groups, with two large groups representing 96% of the total area of the SCB. One of these two groups contained many of the open coastal sites, characterized by relatively coarse-grained sediments (~20% fines), low organic carbon, and low contaminant concentrations. The second large cluster group included a higher proportion of the bay and harbor sites, with finer-grained sediments and proportionately higher mean concentrations of most metals and trace organics. Both site groups were considered representative of SCB background conditions with minimal contaminant inputs.

The remaining three smaller station groups exhibited elevated concentrations of one or more contaminants, but accounted for only 4% of the total SCB area. In particular, two small cluster groups consisted mainly of port, harbor, and marina stations with elevated mean concentrations of certain metals (e.g., copper, lead, antimony, and zinc), as well as elevated chlordane, PAH, and PCB concentrations for one of the two site clusters. The fifth cluster group consisted of Palos Verdes Shelf sites that were characterized by high sediment DDT, PCB, Cd, and Ba concentrations. These stations were clearly different from other open coastal sites in the SCB.

The PCA identified four principal components that explained 67% of the variance in the data set. The first two components (PC1 and PC2) accounted for 52% of the total variance. PC1 was highly loaded with a suite of metals (Cu, Pb, Hg, Zn, Al, and Fe), with high scores primarily for industrialized port and harbor sites. PC2 had high loadings for DDTs, PCBs, and Cd, with highest scores for sites on the Palos Verdes Shelf. PC3 and PC4 each accounted for less than 10% of the total variance, with high loadings for low- and high-molecular-weight PAHs and for a subset of metals (Ba, Ni, and Se) and fines, respectively.

Although contaminant sources were not analyzed for this study, PC1 and, to a lesser extent, PC3 likely reflected recent industrial inputs to ports, commercial shipping and boatyard operations, and small marina activities. In contrast, PC2 reflected historical, wastewater-derived inputs to the Palos Verdes Shelf. Distinct sediment contaminant patterns were not evident for other large and small wastewater or riverine discharges.

Evaluation of Potential Biological Impacts

Empirical Sediment Quality Guidelines

The use of empirically derived sediment quality guidelines (SQGs) is one of the most commonly used approaches in evaluating marine sediments for potential toxicity to benthic organisms. Empirical SQGs were developed by deriving correlative relationships between observed adverse biological effects and the concentrations of potentially toxic substances in aquatic sediments. Two commonly used SQGs are the effects range low (ERL) and the effects range median (ERM), originally developed by Long and Morgan (1990) and revised by Long *et al.* (1995) for evaluation of sediments tested as part of the NOAA National Status and Trends Program. The ERL and ERM SQGs were selected because of their widespread use and to facilitate comparisons with the results from the 1994 SCBPP.

To review, the ERL and ERM are the 10th and 50th percentile concentrations, respectively, of 25 toxic metals and organic compounds measured in sediment samples that were found to be acutely toxic to benthic organisms. It must be emphasized that these SQGs are based solely on coincidental occurrence and the no cause-and-effect relationship between the observed toxicity and any individual contaminant is implied.

The ERL and ERM thresholds establish three concentration ranges into which a particular sediment contaminant may fall. The concentrations below the ERL value represent a range where effects are rarely observed. Concentrations above the ERL but below the ERM represent a region where occasional effects are possible. The concentrations above the ERM value fall into a probable effects range within which effects would be expected to occur frequently.

A summary of the percent of area of the SCB exceeding several thresholds, including analytical detection limits, estimated background levels, and ERL and ERM values for selected individual sediment parameters, is presented in Table VI-2. The estimated background levels are provided from two sources for comparison: The iron-normalization approach used in this study, and the NOAA proposed sediment elemental background concentrations for the SCB determined from sediment cores taken in the Santa Monica Bay. It is evident that a significant portion of the Bight (=10%) is above the ERL values for mercury, nickel, DDTs, and PCBs. Relative to these SQGs, DDT is the most widespread contaminant with more than 70% of the Bight above the ERL. In addition, DDT is the only compound group found above the ERM for a significant portion of the Bight area.

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

Parameter	% of Area Above Detection Limit	% of Area Above Background Levels (NOAA) ¹	% of Area Above Background Levels (iron-normalized) ²	% of Area > ERL ³	% of Area > ERM
<i>Metals</i>					
Arsenic	100.0	43.3	8.0	15.9	0.0
Cadmium	92.0	6.7	33.8	4.4	0.0
Chromium	100.0	0.3	5.7	<u>0.6</u>	0.0
Copper	94.3	5.9	9.4	<u>6.1</u>	0.03
Lead	88.3	34.1	20.2	6.6	0.0
Mercury	48.7	21.6	9.0	<u>10.0</u>	0.8
Nickel	90.3	2.6	4.3	<u>30.4</u>	2.6
Silver	74.9	13.4	11.9	9.8	2.7
Zinc	99.2	8.3	7.4	3.0	0.06
<i>Organics</i>					
Total DDT	82.3	-	-	71.4	11.6
Total PCB	52.3	-	-	20.8	0.4
Total PAH	62.4	-	-	0.5	0.0
Chlordane ($\alpha + \gamma$)	17.9	-	-	-	-

¹ NOAA proposed background trace element concentrations (pre-ca.1850) measured in sediment cores from Santa Monica Bay by Huh and Venkatesan (1998).

² Natural background levels for metals determined using the iron-normalization approach described by Schiff and Weisberg (1999).

³ The underlined values are greater than the percent of area above background because the ERL is below one or both of the estimated background levels.

Subpopulation Comparisons

Comparisons of the percent of area exceeding ERL and ERM values for individual parameters among the various Bight'98 station subpopulations are presented in Tables VI-3 through VI-7. The results of the subpopulation comparisons are consistent with the results of the other analyses. Geographically by region, the general trend in the Bight for overall parameter exceedances is central > southern > northern > Mexico. One prominent exception to this trend is DDT, which affects almost three times the area in the northern region relative to the southern region. Bay and harbor areas had higher levels for most of the target analytes relative to shallow and mid-depth coastal areas. In this comparison, DDTs and PCBs are the exceptions, affecting a greater percent of area in both coastal zones than in the harbors. Within the embayments, a significant percentage of all three substrata exceeded the ERL values. Again, DDT exceeded the ERM values for a significant percentage of the area in all three substrata. It was noteworthy that elevated levels of mercury were associated with marinas. Approximately 17% of the total marina area in the Bight exceeded the ERM for mercury. However, this represents only 17% of a subpopulation that comprises approximately 6% of the entire study area. Among the shallow strata, the assessment results are comparable, with those stations in proximity to SPOTWs being slightly more impacted. Finally, among the mid-depth strata, LPOTWs have a clearly greater impact on the mid-depth areas relative to SPOTWs. Interestingly, the other mid-depth areas appear more impacted by several parameters, particularly nickel, than the areas near SPOTWs. This may be due to historical inputs of those parameters from LPOTWs.

A significant percentage of some subpopulations exceeded the ERLs. However, with the exception of DDT, only a very small percentage of the total Bight area exceeded the ERM for any constituent. The data presented in Tables VI-3 through VI-7 show that although anthropogenic contamination in the SCB is widespread, the majority of the area is at concentrations that would not be expected to impart significant adverse biological impacts (<ERL), and the remainder of the area is at concentrations where effects are expected to occur occasionally (>ERL and <ERM).

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 VI-12 and VI-13. The results are consistent with the previous results. There were 238 of the 290 stations that exceeded the ERL for a least one parameter. However, only 75 stations exceeded the ERM for at least one parameter. Of these, 58 stations exceeded the ERM for only one parameter, 52 of which were due solely to DDT.

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

Region	Northern SCB		Central SCB		Southern SCB		Mexico	
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
mg/g (ppm) Dry Wt.								
Arsenic	13.8	0.0	23.0	0.0	2.1	0.0	-	-
Cadmium	0.1	0.0	16.9	0.0	0.0	0.0	0.0	0.0
Chromium	0.0	0.0	1.7	0.0	0.0	0.0	0.0	0.0
Copper	0.4	0.0	9.9	0.1	8.8	0.0	0.0	0.0
Lead	0.0	0.0	16.6	0.0	1.6	0.0	0.0	0.0
Mercury	0.0	0.0	24.0	0.7	8.1	1.1	-	-
Nickel	44.7	0.0	33.6	7.3	0.0	0.0	15.1	0.0
Silver	0.0	0.0	21.0	7.2	6.2	4.2	0.1	0.0
Zinc	0.4	0.0	4.7	0.0	4.1	0.2	0.0	0.0
ng/g (ppb) Dry Wt.								
Total DDT	79.5	5.0	96.3	25.6	24.0	0.0	13.7	0.0
Total PAH	0.0	0.0	0.3	0.0	0.9	0.0	0.0	0.0
Total PCB	0.0	0.0	57.3	1.0	0.9	0.0	0.0	0.0

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

Table VI-4. Percent of area exceeding sediment quality guidelines (ERLs and ERMs)¹ for selected subpopulations of the sediment chemistry data from the 1998 Southern California Bight Regional Marine Monitoring Study.

Strata	Bays/Harbors		Shallow		Mid-Depth	
Parameter	% of Area >ERL	% of Area >ERM	% of Area >ERL	% of Area >ERM	% of Area >ERL	% of Area >ERM
mg/g (ppm) Dry Wt.						
Arsenic	45.7	0.0	7.4	0.0	15.1	0.0
Cadmium	9.5	0.0	8.2	0.0	1.8	0.0
Chromium	1.4	0.0	0.0	0.0	0.7	0.0
Copper	77.8	0.5	2.6	0.0	1.5	0.0
Lead	26.1	0.0	4.1	0.0	6.0	0.0
Mercury	57.7	9.0	9.6	0.0	5.8	0.1
Nickel	41.7	0.7	14.0	2.0	37.4	2.8
Silver	18.9	3.1	5.0	0.5	9.4	5.6
Zinc	44.0	0.5	0.8	0.0	0.2	0.0
ng/g (ppb) Dry Wt.						
Total DDT	59.5	31.0	66.6	10.0	75.4	11.0
Total PAH	6.4	0.0	0.0	0.0	0.0	0.0
Total PCB	13.9	1.4	28.1	0.0	16.5	0.4

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

Table VI-5. Percent of area exceeding sediment quality guidelines (ERLs and ERMs)¹ for selected subpopulations of the sediment chemistry data from the 1998 Southern California Bight Regional Marine Monitoring Study.

Strata	Ports		Marinas		Other Bay/Harbor	
Parameter	% of Area >ERL	% of Area >ERM	% of Area >ERL	% of Area >ERM	% of Area >ERL	% of Area >ERM
mg/g (ppm) Dry Wt.						
Arsenic	59.0	0.0	41.9	0.0	29.1	0.0
Cadmium	8.3	0.0	13.7	0.0	3.5	0.0
Chromium	4.7	0.0	0.0	0.0	0.0	0.0
Copper	88.8	0.0	72.7	1.3	71.3	0.0
Lead	35.7	0.0	21.4	0.0	17.0	0.0
Mercury	79.8	8.5	39.5	16.9	62.1	0.0
Nickel	35.1	2.0	44.8	0.0	40.6	0.0
Silver	34.2	3.9	11.2	0.0	9.9	7.4
Zinc	55.1	0.1	50.6	0.0	24.1	0.0
ng/g (ppb) Dry Wt.						
Total DDT	50.6	11.7	65.6	40.8	55.2	36.0
Total PAH	14.0	0.0	2.7	0.0	0.0	0.0
Total PCB	29.6	3.5	21.9	0.0	17.0	0.0

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

Table VI-6. Percent of area exceeding sediment quality guidelines (ERLs and ERMs)¹ for selected subpopulations of the sediment chemistry data from the 1998 Southern California Bight Regional Marine Monitoring Study.

Strata	Rivers		Shallow SPOTW		Other Shallow	
Parameter	% of Area >ERL	% of Area >ERM	% of Area >ERL	% of Area >ERM	% of Area >ERL	% of Area >ERM
mg/g (ppm)						
Dry Wt.						
Arsenic	9.8	0.0	11.6	0.0	6.1	0.0
Cadmium	6.5	0.0	0.0	0.0	7.0	0.0
Chromium	0.0	0.0	0.0	0.0	0.0	0.0
Copper	6.0	0.0	20.5	0.0	0.0	0.0
Lead	9.5	0.0	8.7	0.0	1.5	0.0
Mercury	0.0	0.0	23.7	0.0	8.8	0.0
Nickel	22.6	0.0	23.1	0.0	15.2	2.5
Silver	3.0	3.0	0.0	0.0	2.8	0.0
Zinc	4.8	0.0	2.7	0.0	0.0	0.0
ng/g (ppb)						
Dry Wt.						
Total DDT	67.7	3.3	72.7	13.1	60.6	9.1
Total PAH	0.0	0.0	0.0	0.0	0.0	0.0
Total PCB	12.5	0.0	11.5	0.0	27.6	0.0

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

Table VI-7. Percent of area exceeding sediment quality guidelines (ERLs and ERMs)¹ for selected subpopulations of the sediment chemistry data from the 1998 Southern California Bight Regional Marine Monitoring Study.

Strata	LPOTW		Mid-Depth SPOTW		Other Mid-Depth	
Parameter	% of Area >ERL	% of Area >ERM	% of Area >ERL	% of Area >ERM	% of Area >ERL	% of Area >ERM
mg/g (ppm) Dry Wt.						
Arsenic	18.0	0.0	0.0	0.0	14.7	0.0
Cadmium	23.3	0.0	0.0	0.0	0.0	0.0
Chromium	10.0	0.0	0.0	0.0	0.0	0.0
Copper	13.3	0.0	0.0	0.0	0.0	0.0
Lead	6.7	0.0	0.0	0.0	3.9	0.0
Mercury	43.7	0.6	0.0	0.0	3.0	0.0
Nickel	20.0	0.0	4.9	0.0	38.2	2.9
Silver	35.2	10.8	0.0	0.0	7.5	2.5
Zinc	2.4	0.0	0.0	0.0	0.0	0.0
ng/g (ppb) Dry Wt.						
Total DDT	73.2	41.0	80.6	0.0	73.5	8.8
Total PAH	0.0	0.0	0.0	0.0	0.0	0.0
Total PCB	39.0	6.0	0.0	0.0	11.8	0.0

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

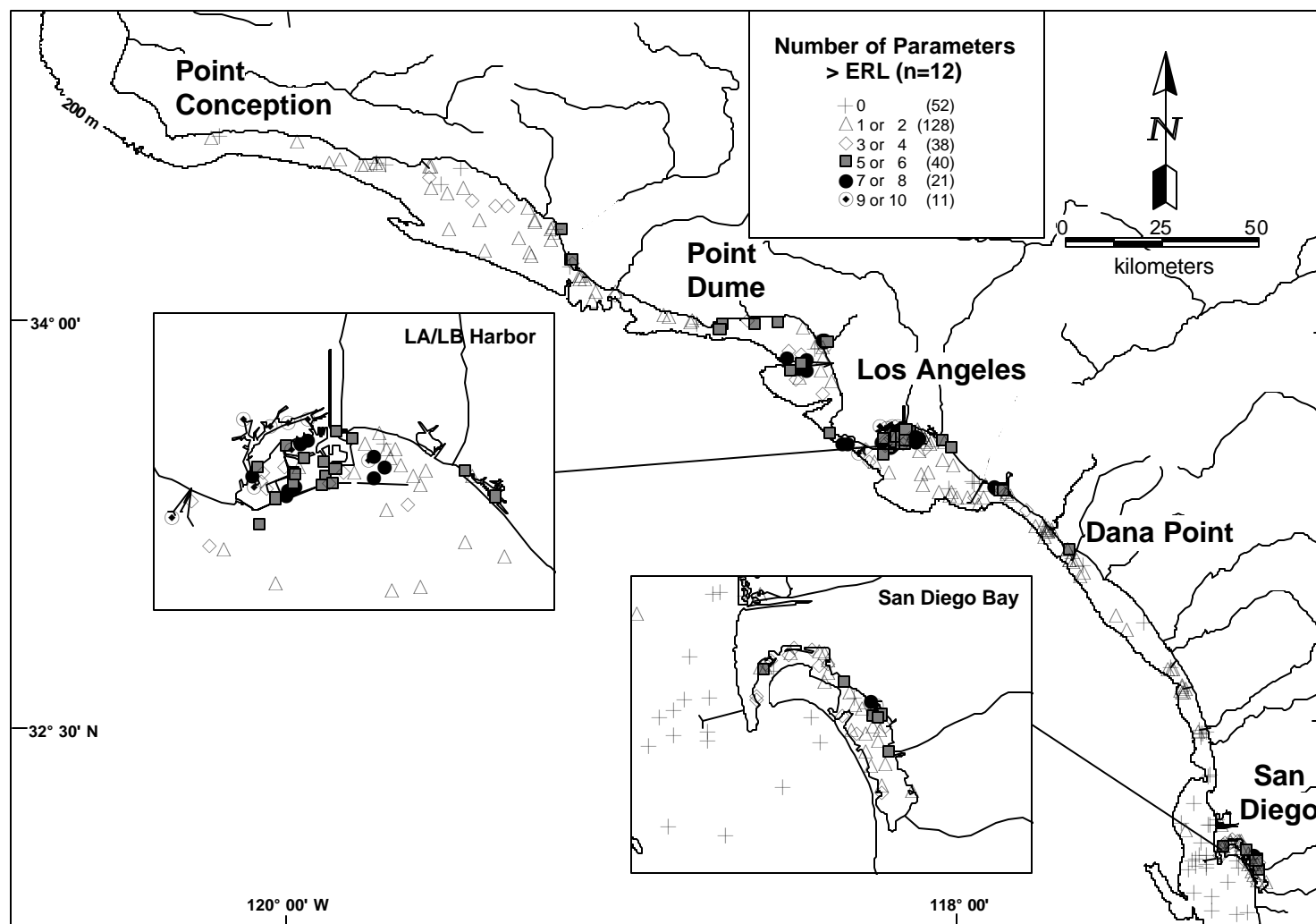


Figure VI-12. Number of parameters above the corresponding ERL values at all of the Bight'98 sediment chemistry stations.

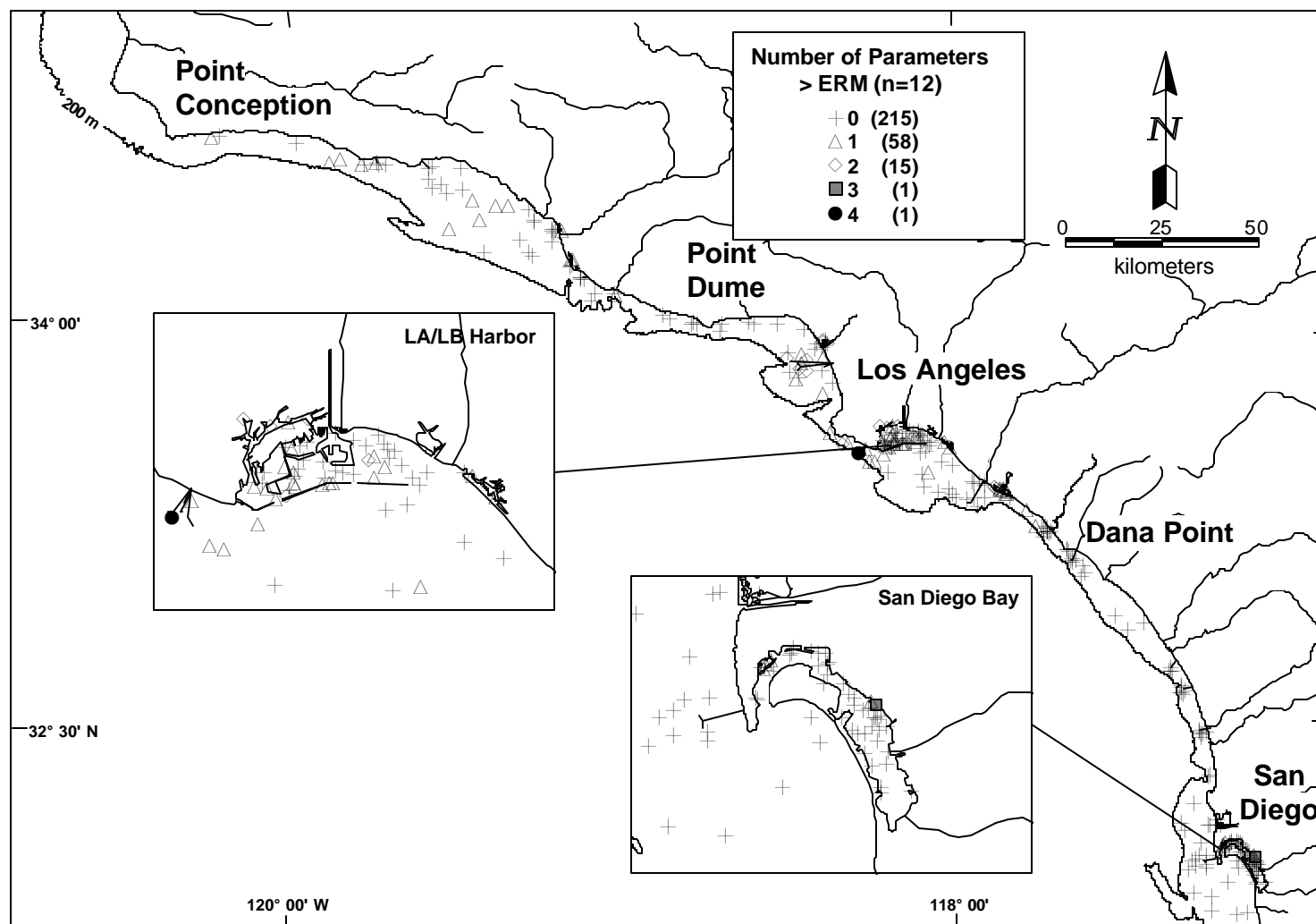


Figure VI-13. Number of parameters above the corresponding ERM values at all of the Bight'98 sediment chemistry stations.

Comparison to the 1994 Southern California Bight Pilot Project Results

It is difficult to make a detailed comparison between this study and the results from the 1994 SCBPP because of the differences in the study design. However, a Bight-wide general comparison can be easily made because the total area is nearly the same (3,520 versus 3,279 km² in 1994 and 1998, respectively). One of the assessments performed in the 1994 SCBPP Report (Schiff and Gossett 1998) was to calculate the percent of area of the Bight above background, and above the ERLs and ERMs for any metal, for any organic, and for any contaminant (either metal or organic). The same assessment was made for the 1998 survey data, and the results are compared in Table VI-8. Since no samples were taken from harbor areas in the 1994 SCBPP, the assessment has been performed both with and without the data for the harbor areas for the 1998 data to facilitate a more appropriate comparison between the two studies.

In general, the results of this assessment were very comparable between the 1994 and the 1998 regional surveys. The effect of removing the harbor sites from the assessment of the 1998 results had only a minimal effect. Although these areas typically have some of the highest sediment parameter concentrations in the Bight, the harbors account for only 6.1% of the total Bight area. The only significant difference between the 1994 and 1998 projects for this assessment were for the percent of area above the ERLs for trace metals. However, this difference can be explained by differences in the study designs. All of the stations for the 1998 survey were shallow and mid-depth, with 6.1, 31.3, 62.6, and 0% of the study area being in bay/harbor, shallow, mid-depth, and deep areas, respectively. In contrast, the depth breakdown for the 1994 survey was 0, 19.7, 56.8, and 23.5% of the study area in bays/harbors, shallow, mid-depth, and deep areas, respectively. Average sediment concentrations increased somewhat as the study area shifted closer to the shore, and hence closer to known sources of trace metal contamination.

There was also good agreement among other comparable data assessments made for the 1994 and 1998 surveys, namely the number of parameters above background, above ERLs and above ERMs. The results of these analyses from the 1998 survey are shown in Figures VI-11, VI-12, and VI-13, respectively. The general pattern of contamination is the same for both the 1994 and 1998 studies. The differences in the number of stations falling into each category can again be explained by the differences in study design. There were 49 more stations in the 1998 study, and all stations were within mid-depth and shallow waters (=120 m).

Table VI-8. Percent of area of the Southern California Bight exceeding the specified contaminant thresholds as function of parameter group for the 1994 and 1998 regional marine monitoring surveys.

Parameter	>Background	>ERL	>ERM
<u>Any Metal</u>			
1994	50.1	13.7	2.8
1998	46.5	36.2	5.8
1998 (no harbors)	43.4	32.9	5.3
<u>Any Organic</u>			
1994	82.1	63.7	10.4
1998	85.0	69.8	11.6
1998 (no harbors)	84.7	70.3	10.3
<u>Any Contaminant</u>			
1994	89.0	66.8	12.3
1998	85.6	71.8	14.7
(1998 no harbors)	84.8	70.4	13.0

Mean ERM Quotient Assessment

The data from this study were further evaluated using the mean ERM quotient approach (ERMQ). The ERMQs for each station were calculated with and without including total DDT as one of the parameters to ascertain the effect of this pervasive pollutant on the outcome of the assessment. The data were evaluated for potential acute toxicity using the four ERMQ ranges identified by Long *et al.* (1998). The four ranges are referred to herein as Levels I to IV, corresponding to ERMQs of <0.1, 0.11-0.5, 0.51-1.50, and >1.50, respectively. These ranges are given qualitative descriptions of low, low-moderate, moderate-high, and high potential for acute toxicity to benthic organisms, respectively. The ranges have also been classified quantitatively by the percent of samples within each range expected to be acutely toxic based upon the results of over 1,000 matched chemistry-toxicity studies nationwide (Long *et al.* 1998). The percent of stations predicted to be toxic within Levels I to IV are 11, 30, 46, and 75%, respectively.

The results of the mean ERMQ evaluations are given in Table VI-9. The results show that 81 and 19% of the SCB fall within the ERMQ ranges of Level I and Level II, respectively. These results suggest that the vast majority of the Bight is at a low to moderate risk for acute toxicity. Applying the predictive ability associated with these ranges, the number of stations predicted to be toxic by the mean ERMQ approach were in approximate agreement with the results of the Bight'98 Sediment Toxicity Study (see Appendix D). All 290 U.S. stations and their associated mean ERMQ values calculated without and with total DDT are plotted on the map in Figures VI-14 and VI-15, respectively.

It must be emphasized that the results of the preceding assessment define the potential for *acute* toxicity to benthic biota, specifically *amphipods*, with the endpoint being mortality. This does not necessarily imply that there are no potential adverse biological impacts stemming from the measured levels of sediment contamination. However, assessment of the potential for sublethal impacts to benthic organisms was not possible because studies relating empirical SQGs to sublethal or chronic effects are almost nonexistent. After a thorough literature search, only a single study was identified that related mean ERMQ values to benthic community degradation (Hyland *et al.* 1999). In that study, the researchers identified three ERMQ ranges corresponding to =0.02, 0.02-0.058, and >0.058. These ranges were assigned the qualitative designations of low, moderate, and high risk of benthic community impacts, respectively. These SQGs for sublethal effects were approximately an order of magnitude lower than the analogous ranges for acute toxicity.

In contrast to the results of the MERMQ evaluation for acute toxicity, the SQG ranges defined by Hyland *et al.* (1999) suggest that a significant percentage of the SCB may be at a moderate to high risk for benthic community degradation. Again, these SQGs are based upon only a single study, and the relationships were based upon benthic communities on the east coast of the United States. Moreover, the results from the 1994 SCB Pilot Project (Bergen *et al.* 1998) do not support this finding as approximately 90%

of the SCB was found to have undisturbed benthic communities. Nevertheless, even with these caveats, these alternative SQGs imply that benthic community degradation, or even more sensitive measures such as bioaccumulation, may be more relevant criteria for future sediment quality evaluation in the SCB.

Table VI-9. Percent of area of the Southern California Bight within different sediment quality guideline ranges in 1998 using the mean ERM quotient approach. The numbers in parentheses are the mean ERM quotient range for each category.

Acute Toxicity¹	Level I (< 0.1)	Level II (0.11-0.5)	Level III (0.51-1.5)	Level IV (>1.5)
All Contaminants				
With DDT	80.6	18.7	0.3	0.4
Without DDT	88.3	11.7	0.0	0.0

¹ Potential acute toxicity categories: Level I = Low; Level II = Low-moderate; Level III = Moderate to high; Level IV = High; for amphipod mortality (Long *et al.* 1998).

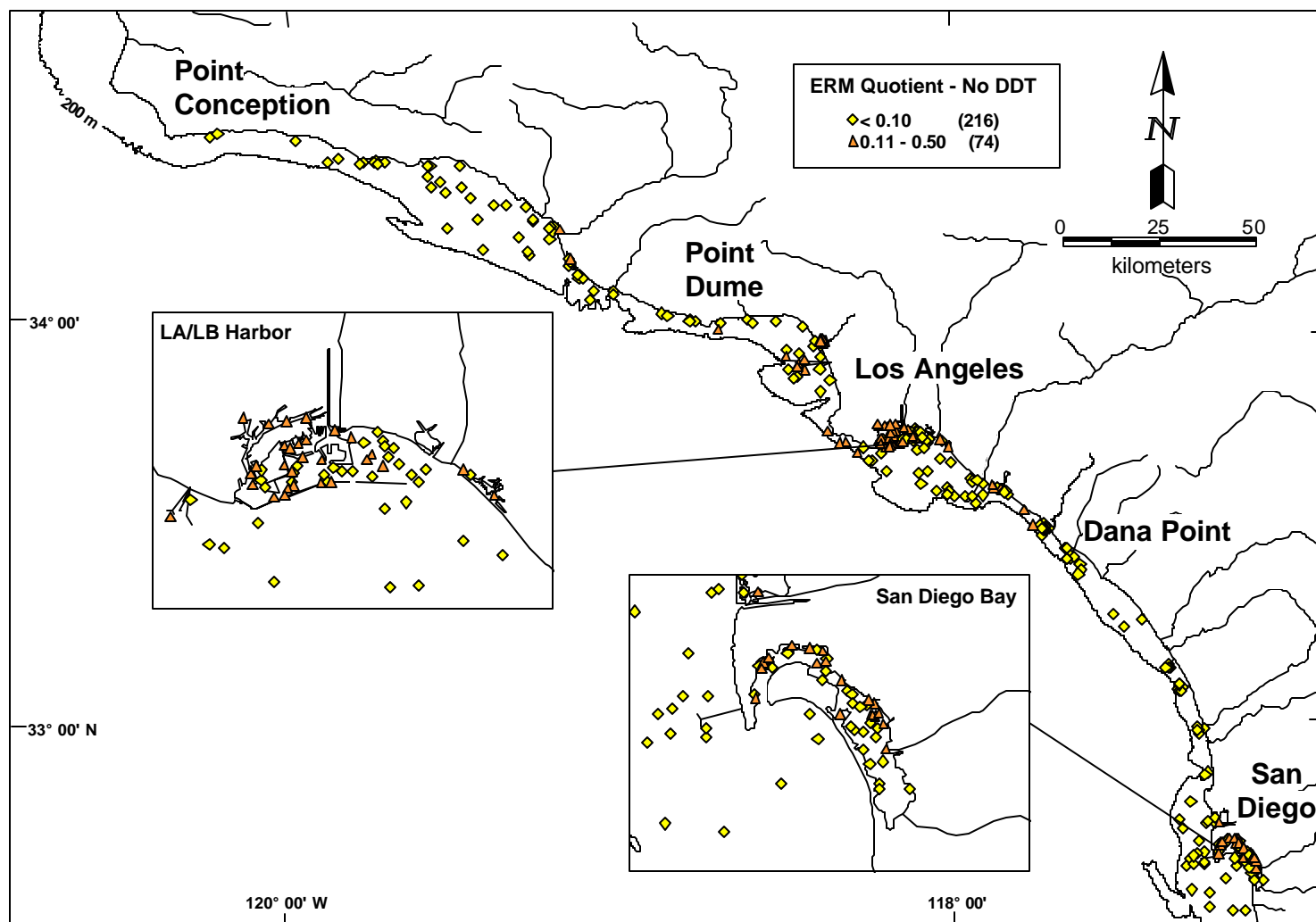


Figure VI-14. The calculated mean ERM quotient values (excluding DDT) for the Bight'98 U.S. sediment chemistry stations.

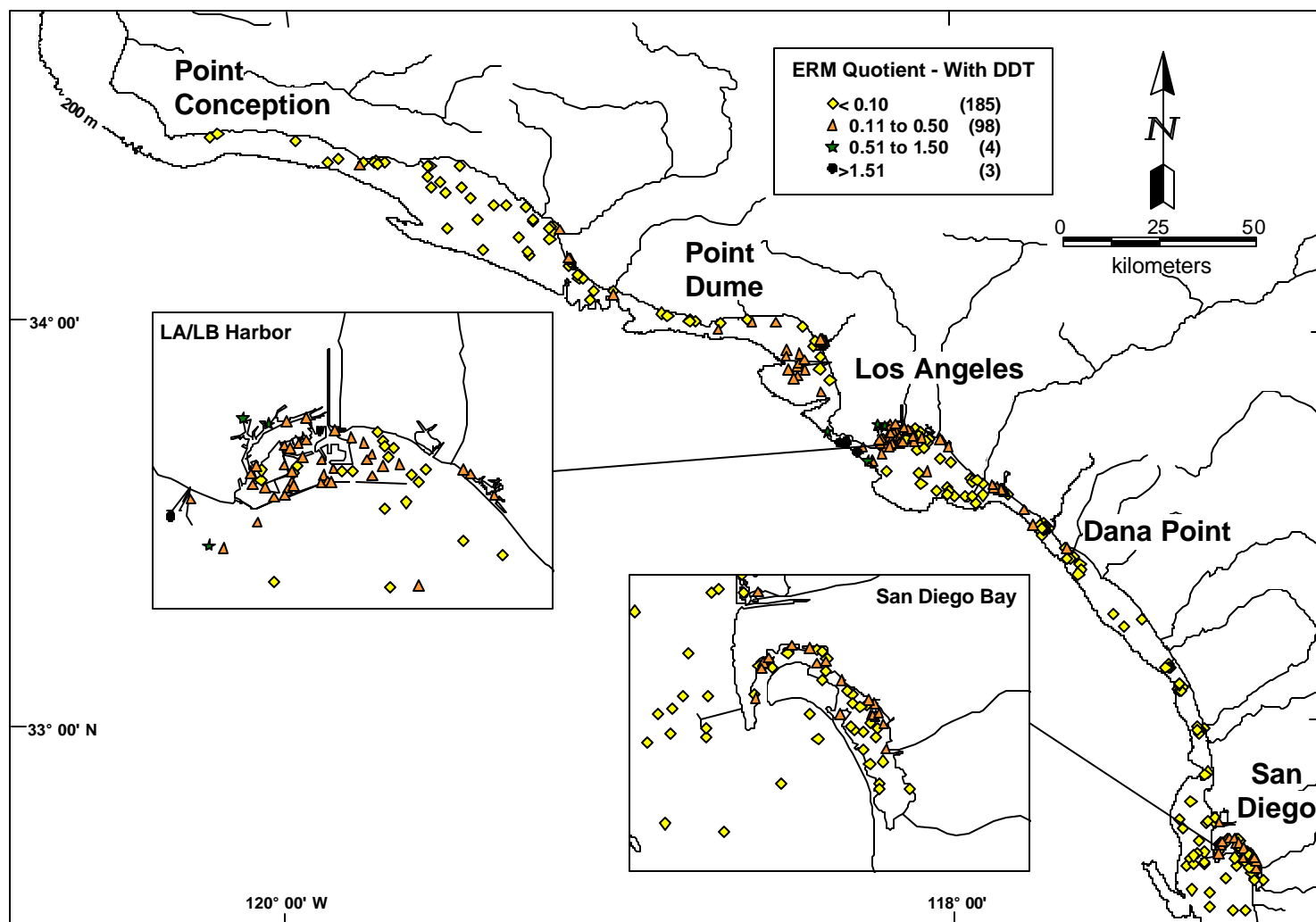


Figure VI-15. The calculated mean ERM Quotient values (including DDT) for the Bight'98 U.S. sediment chemistry stations.

Equilibrium Partitioning Assessment

The data from this study were also evaluated using the EqP approach. The details of this analysis are presented in Appendix E. Briefly, the sediment quality was assessed by calculating the freely dissolved porewater concentrations of total PAHs and total PCBs that would be expected from the measured sediment concentrations of these chemicals. Also, the sediment interstitial water concentrations of cadmium, copper, lead, nickel, and zinc were directly measured and evaluated relative to national water quality criteria for freely dissolved metal pollutants. Finally, sediment quality was assessed by the SEM-AVS method.

The results of the EqP evaluation of PAHs and PCBs was that 10 stations out of the 290, corresponding to about 0.5% of the Bight area, exceeded sediment quality guidelines for these constituents. Copper and nickel were the only metals found to exceed water quality criteria in the interstitial water. These exceedances were found to represent about 18 and 1% of the SCB for copper and nickel, respectively. Although an estimated 57% of the study area (57 stations) had SEM-AVS>0, only 0.3% of the area (8 stations) exceeded the U.S. EPA-proposed sediment quality guideline of 130 $\mu\text{mole/g-OC}$.

Compound Specific Assessments

Several other assessments were performed for the Bight'98 Chemistry Study based upon available sediment quality guidelines in the literature. The potential impacts stemming from total PAHs and total PCBs were assessed using consensus-based sediment quality guidelines (Swartz *et al.* 1999 and MacDonald *et al.* 2000). Both of the consensus-based SQGs identify three possible thresholds of concern, a threshold effects concentration (TEC), a median effects concentration (MEC), and an extreme effects concentration (EEC). The TEC is the concentration below which adverse biological effects are unlikely to occur. The MEC is the concentration above which adverse effect frequently occur. The EEC is the concentration above which adverse effects usually or always occur. The results of the evaluations are given in Table VI-10. The evaluation shows that only an estimated 5.5 and 0.4% of the SCB area is above the TEC for PCBs and PAHs, respectively.

A separate assessment was performed for total DDT since it is the most widespread contaminant in the SCB. Total DDT data was evaluated relative to the six DDT-specific sediment quality guidelines and contrasted with the evaluations using the ERL and ERM values. The results from these evaluations are presented in Table VI-11. While a significant percentage of the Bight is above the ERL and ERM values, zero percent of the Bight is above any of the other thresholds for acute toxicity. Also, only 0.6% of the Bight was above the single threshold for the onset of chronic effects.

P450 HRGS Assessment

A final assessment of potential biological impacts was performed using the P450 HRGS assay. This method evaluates a sample for the presence of organic compounds which induce the production of a specific family of cytochrome P450 enzymes (CYP1A1). Compounds that are known to induce such a response are PAHs, dioxins, furans, and co-planar PCBs (Anderson *et al.* 1995). The results from the P450 HRGS analyses are presented in Appendix F. The results show a general correlation between the P450 HRGS response and total PAH concentrations over about 1.0 µg/g-dry weight. This assay appears to be useful for identifying areas of high PAH contamination. The correlations of the P-450 HRGS response to total PCBs were more variable, and both the lowest and highest degrees of correlation were obtained for total PCBs. Most noteworthy was the exceptionally high degree of correlation for the P450 HRGS assay with total PCBs for the LPOTW stratum ($r^2 = 0.92$).

Some of the most interesting results of these analyses were the high assay responses obtained for several stations where none of the target analytes were at high concentrations. For one station in the northern region of the Bight that had an extremely high assay response, the samples were re-analyzed to make sure that the results were not an aberration. Nearly identical results were obtained upon re-analysis even though the extracts had been in frozen storage for more than two years. The results observed could not be explained by the measured concentrations for any of the target analytes in this study. The sample extract was also re-analyzed by GC-MS to confirm there was no error in the analytical chemistry results. When a second analysis by the same laboratory returned the same low levels of target analytes, the sample extract was sent to an outside laboratory for analysis. In all cases, the sample contained low levels of the target analytes for this study.

Recent studies have identified unknown toxins associated with crude oil seepage (Rowland *et al.* 2001). This is consistent with the prevalence of petroleum operations in the northern SCB. In order to gain insight into the fraction responsible for the observed responses, the sediment extract that gave the highest response was subjected to a typical alumina and silica gel cleanup designed to remove a significant portion of the so-called unresolved complex mixture or hydrocarbon “hump.” The cleaned extract was re-analyzed and was found to have lost approximately half of the response. Therefore, at least some of the response is due to the presence of unknown toxins in the aliphatic fraction of the extracted compounds. More research is needed to identify the exact compounds responsible for the observed responses.

Table VI-10. Percent of the Southern California Bight (SCB) study area exceeding consensus-based sediment quality guidelines in 1998.

Parameter	TEC ¹	MEC	EEC
SPA²			
Threshold	290 µg/g-OC	1,800 µg/g-OC	10,000 µg/g-OC
% of SCB above	0.3	0.1	0.0
SPCB³			
Threshold	0.048 µg/dry-g	0.47 µg/dry-g	1.70 µg/dry-g
% of SCB above	5.3	0.2	0.0

¹ TEC = Threshold effects concentration; MEC = Median effects concentration; EEC = Extreme effects concentration.

² Consensus-based PAH SQGs (Swartz *et al.* 1999)

³ Consensus-based PCB SQGs (MacDonald *et al.* 2000)

Table VI-11. Areal extent of total DDT sediment contamination in the Southern California Bight (SCB) relative to different sediment quality criteria.

Source	Units ¹	Total DDT Threshold	Percent of SCB Exceeding Threshold
NOAA ²			
ERL	ng/dry-g	1.58	71.4
ERM	ng/dry-g	46.1	11.6
MacDonald 1994			
SEC ³	µg/dry-g	7.12	0.0
	µg/g-OC	199.0	0.0
Chapman 1996			
NOEC ⁴	µg/dry-g	8.51	0.0
	µg/g-OC	269.0	0.0
Swartz <i>et al.</i> 1994			
Chronic Toxicity	µg/g-OC	100.0	0.6
Acute Toxicity	µg/g-OC	300.0	0.0

¹ µg/g-OC = µg/g divided by the mass fraction of organic carbon in the sediment sample.

² NOAA Sediment Quality Guidelines – ERL = Effects range low; ERM = Effects range median.

³ SEC = Sediment effects concentration.

⁴ NOEC = No observable effects concentration.

VII. SEDIMENT CONTAMINATION LEVELS AT COASTAL REFERENCE STATIONS 1977 - 1998

Introduction

In 1977 SCCWRP conducted a regional monitoring survey in the SCB with the goal of identifying possible reference or "control" stations that would represent typical natural background conditions of the benthic environment that would exist in the absence of anthropogenic pollution. Such reference stations were needed for comparison with municipal wastewater outfall sites and were of critical importance for evaluating the effects of such discharges. To this end, SCCWRP collected samples from 71 sites along the 60-m depth contour from Point Conception to the U.S.-Mexico international border. Among the parameters measured at the potential reference sites were the sediment concentrations of seven trace metals (cadmium, chromium, copper, lead, nickel, silver, and zinc), total DDT and total PCBs. As a result of this survey, SCCWRP identified 29 stations that could potentially be considered as reference sites for the 60-m depth zone. The survey was limited to the single depth because that was the depth of discharge from the largest municipal wastewater treatment plants along the coast, and because discharged materials tended to drift along depth contours (Word and Mearns 1979).

In 1985, a second reference site survey was conducted by SCCWRP to update and complement the 1977 survey. Based upon the results from the previous survey, including a separate multivariate analysis of the benthic infaunal data, 13 of the 60-m stations from the 1977 survey were designated as suitable "control" sites and were selected for re-sampling (Thompson *et al.* 1987). Additional samples were collected at the same locations at 30 and 150 m, creating cross-shelf transects to identify variability of the reference station properties with depth. Among the parameters measured for the 1985 survey were the same seven trace metals, total DDT, and total PCB. Analysis for total PAHs was added to the target analytes for the 1985 survey. The results from the 1985 survey were consistent with those from the 1977 survey and showed that, in general, sediment contamination increased with increasing shelf depth and proximity to Santa Monica Bay.

In 1990, SCCWRP conducted a third reference site survey (Thompson *et al.* 1993). Seven of the original 1977 60-m survey stations were selected for re-sampling, a decrease from the 13 sampled in the 1985 survey. Again, additional samples were taken at 30 and 150 m at the same locations. One of the 30-m stations near La Jolla was abandoned due to kelp (adjacent to Station 2351, Figure VII-1). The chemical parameters measured in the 1990 survey were essentially the same as those for the previous surveys except for minor changes to the individual target analyte lists. Except for silver, the contaminant concentrations measured in the 1990 survey were consistent with the previous surveys. Silver was about an order of magnitude higher in 1985 relative to 1977 and 1990. The concentrations of all contaminants at all locations were generally very low, with the highest levels observed off Zuma Beach, the nearest stations to Santa Monica Bay.

In 1998, the same seven 60-m stations and the adjacent six 30-m stations sampled in the 1990 reference survey were re-sampled as part of the Bight'98 Survey. This resulted in six 30-m reference stations with data from three surveys from 1985 to 1998, and seven 60-m reference stations with data from four surveys from 1977 to 1998. The locations of 13 reference stations are shown in Figure VII-1.

The objectives of this study were two-fold. The primary objective was to ascertain whether there have been any significant changes in contaminant concentrations at these historical reference stations over the eight years since the 1990 survey. It was envisioned at the onset of the Bight'98 Survey that measuring concentration trends over time at stations distant from known sources would allow for a more integrated assessment of contamination trends, rather than assessing changes from particular sources. In addition, it might be possible to infer from these data whether contamination is becoming more widely dispersed in Bight, or if it remains mostly localized in areas around known sources. A secondary objective of this study was to compare the concentrations of trace metals at these designated reference sites to background levels predicted for the 1994 and 1998 regional surveys using an independent iron-normalization and regression approach. As part of the 1994 SCBBP, trace metal background concentrations for the Bight were determined using an iron-normalization and regression approach (Schiff and Weisberg 1999). The trace element-iron relationships determined from the 1994 data have been further validated by the results of the present study, and by comparison to sediment core data from other regional studies (Appendix A).

In this chapter, the background trace metal concentrations for the Bight are predicted using the iron-normalization and regression approach and compared to the results from the coastal sites used as reference or "control" stations over the past 25 years. This comparison serves as an independent assessment of the validity of using these sites as "controls" for pollution monitoring studies in the SCB prior to 1994.

In contrast to the trace metals, DDT and its metabolites and PCBs do not occur naturally, so any detectable amount of these compounds is evidence of anthropogenic pollution. Only the PAHs may have a small natural background concentration in marine sediments. Thus, with respect to organics, the reference stations serve to indicate the extent to which pollution has been transported away from the discharge areas. Moreover, these stations can be used to identify any temporal trends in sediment organic contamination at stations distant from known point sources.

Methods

Trace Metals

The digestion technique used for analysis of trace metals in marine sediments and tissues has not changed significantly over the period covered by these surveys. For all four surveys, samples were digested by the addition of a mixture of nitric and hydrochloric acids followed by heating and reflux period. Heating is typically accomplished by either of two methods - hot plate or microwave. This technique is known generically as the "strong acid digestion" technique and will digest much of sample matrix, but leaves the more resistant components such as silica and some aluminosilicate mineral phases.

In contrast to the digestion techniques, the analytical instrumentation used for trace metal analyses has changed over time. Samples from the 1977, 1985, and 1990 reference surveys samples were analyzed in the trace metals laboratory at SCCWRP using the same instrument, a Varian Techtron atomic absorption spectrophotometer, with either flame or graphite furnace atomization. Five different laboratories using multiple techniques depending on the metals and the concentration ranges analyzed the 1998 samples. Techniques used for Bight'98 metals analyses included graphite furnace (GFAA) and flame atomic absorption spectroscopy (FLAA), inductively coupled plasma atomic emission spectroscopy (ICP-AE), and inductively coupled plasma mass spectrometry (ICP-MS). However, inter-laboratory calibration exercises conducted during the Bight'98 Survey indicated very good consistency among the different instruments and the different laboratories, suggesting that the results from these four surveys can be considered comparable.

Trace Organics

The 1977 Reference Survey - Sediments were analyzed for total DDT (6 compounds), and total PCB as the sum of Aroclors (1242 and 1254). Sediments were dried at 60°C and then extracted by Soxhlet using Hexane. All sample extracts were cleaned up using activated Florisil and analyzed by packed column gas chromatography using a Tracor GC equipped with an ECD. It was later discovered that drying the sediments at 60°C caused an unknown loss of up to 50% of the DDTs and PCBs from the sediment samples, so these results are biased low.

The 1985 Reference Survey - Sediments were analyzed for total DDT (6 compounds), total PCB as the sum of Aroclors (1242 and 1254), and total PAH (28 individual compounds). Sediment samples were extracted by homogenization with a mixture of methanol, chloroform, and water. The chloroform was then exchanged into hexane and cleaned up using activated Florisil for the DDTs and PCBs and using silica gel for the PAHs. Sample analysis for DDTs and PCBs was performed using a Varian Vista 44 GC-ECD equipped with a 30 m, DB-5 capillary column. An analysis for PAHs was

performed using a Hewlett Packard 5970B GC-MS also equipped with a DB-5 capillary column.

The 1990 Reference Survey - Sediments were analyzed for total DDT (5 compounds; o,p-DDD was not measured), total PCB by sum Aroclors (1242 and 1254), and total PAH (30 individual compounds). Sediment samples were mixed with anhydrous sodium sulfate and extracted with methylene chloride using a roller table. The extracts were cleaned up using alumina and silica gel. Sample analysis for DDTs and PCBs was performed using a Varian Vista 44 GC-ECD equipped with a 30 m, DB-5 capillary column. An analysis for PAHs was performed using a Hewlett Packard 5970B GC-MS, also equipped with a DB-5 capillary column.

The 1998 Regional Monitoring Survey - The sediments from the 13 reference stations for the Bight'98 Survey were analyzed for total DDT (sum of 6 compounds), total PCBs (sum of 41 congeners), and total PAHs (sum of 24 compounds). Two different laboratories analyzed the samples. One laboratory used microwave assisted solvent extraction (MASE) and capillary GC-MS. The other laboratory used accelerated solvent extraction (ASE) and capillary GC-ECD, respectively. The Bight'98 Survey used a performance-based approach whereby laboratories could use whatever methods they chose provided they could demonstrate comparable analytical performance.

Natural Background Trace Metal Concentrations in Sediments

The natural background concentrations for trace metals in sediments of the SCB were calculated using the iron-normalization and regression method described by Schiff and Weisberg (1999), and further evaluated in Appendix A. For all trace metals except nickel, the background concentrations were calculated for each station using the Bight'98 iron concentrations and the 1994 baseline metal-iron relationships. For nickel, the 99% prediction intervals for the 1994 regression line were very large. Therefore, the regression line and the associated 99% prediction intervals from the Bight'98 Survey were used for comparison with the reference sites. This was valid because the nickel background regression lines for the 1994 and 1998 data sets are very similar but the 99% prediction intervals were significantly smaller for the 1998 regression line (i.e., ± 9 versus ± 19 ppm). Therefore, the 1998 regression relationship was used as a more conservative estimate of the background nickel concentrations associated with the reference sites.

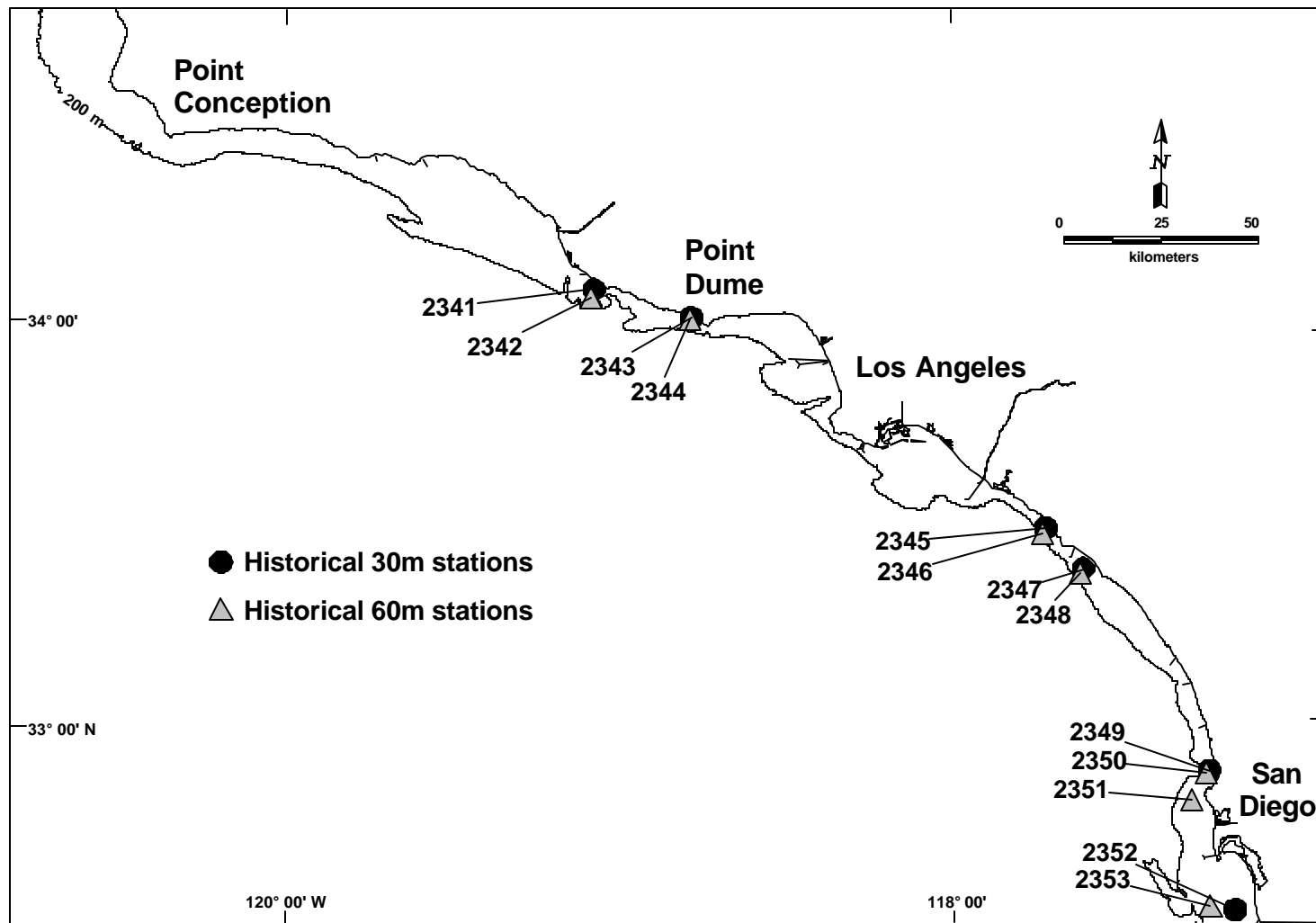
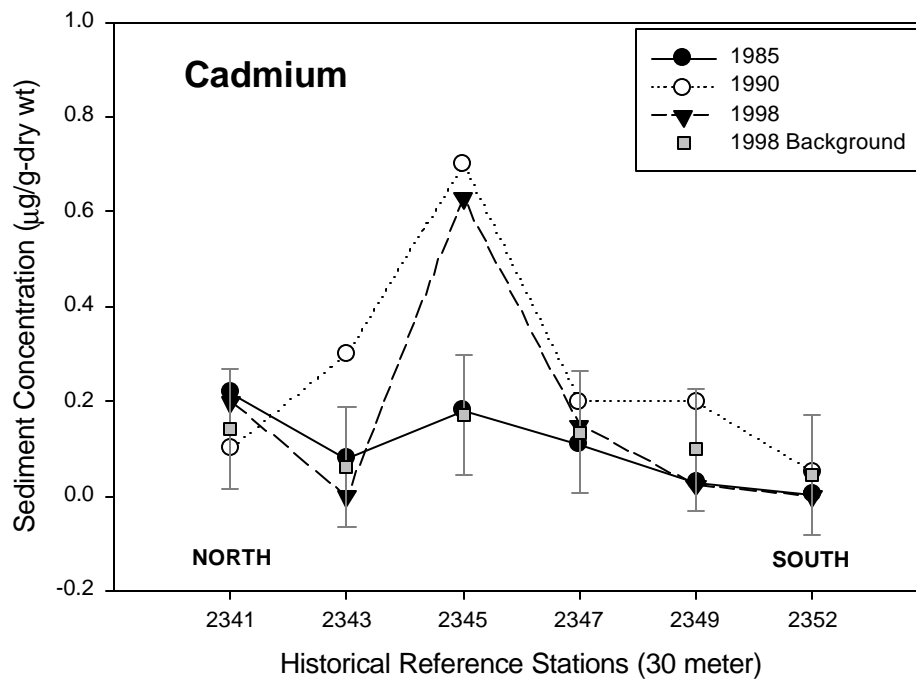
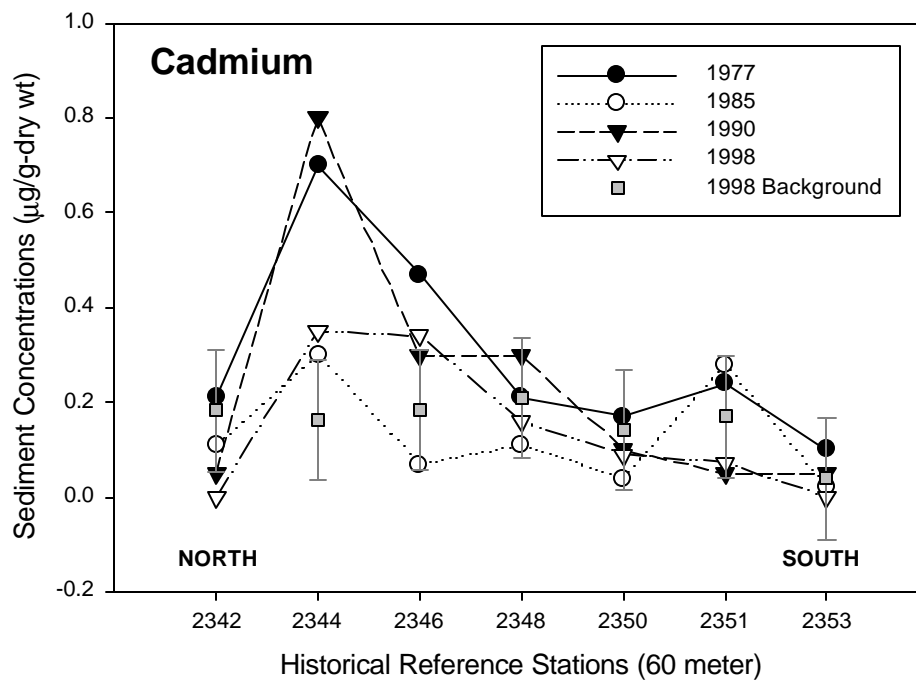


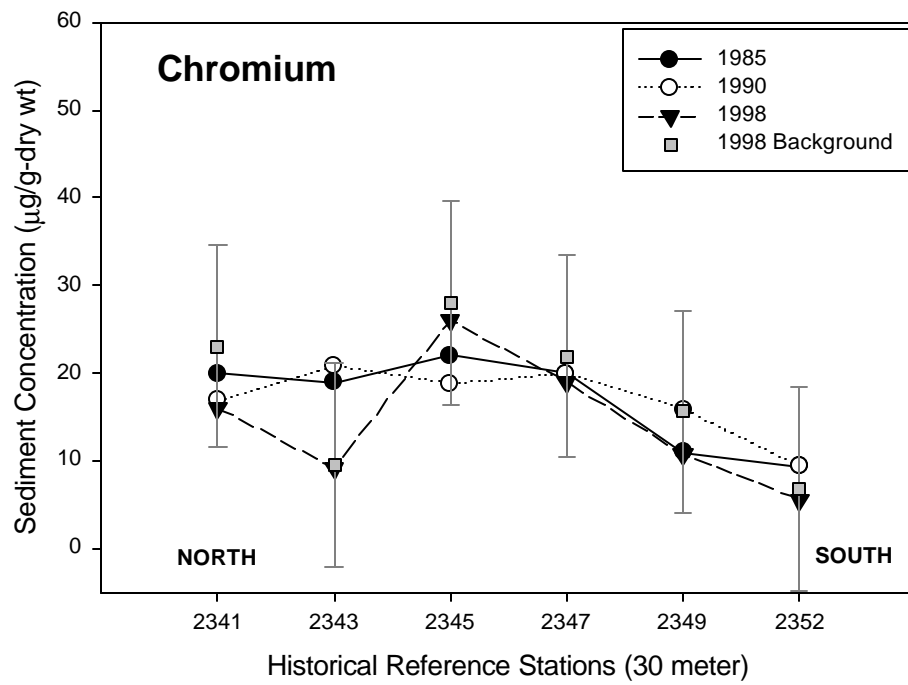
Figure VII-1. Location of the 13 reference stations common to surveys conducted by SCCWRP in the Southern California Bight from 1977 through 1998. The station numbers shown are the station ID's from the 1998 Southern California Bight Regional Marine Monitoring Survey.



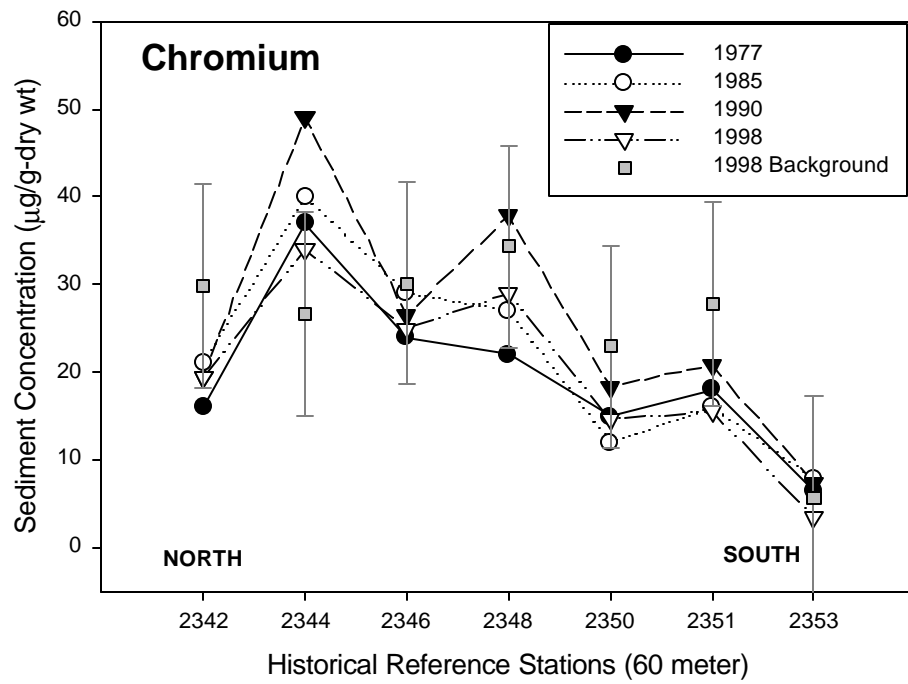
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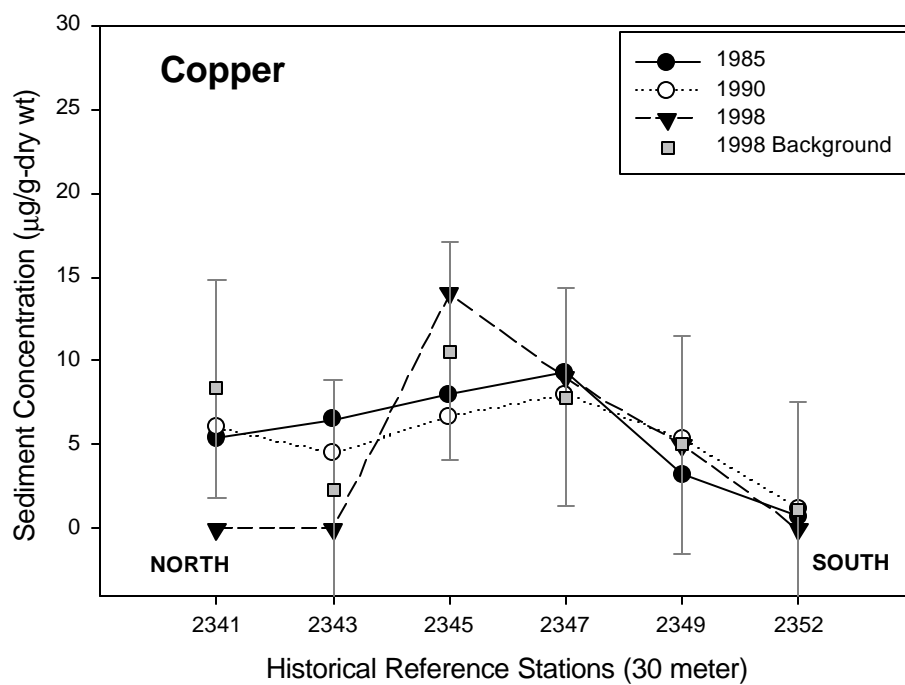
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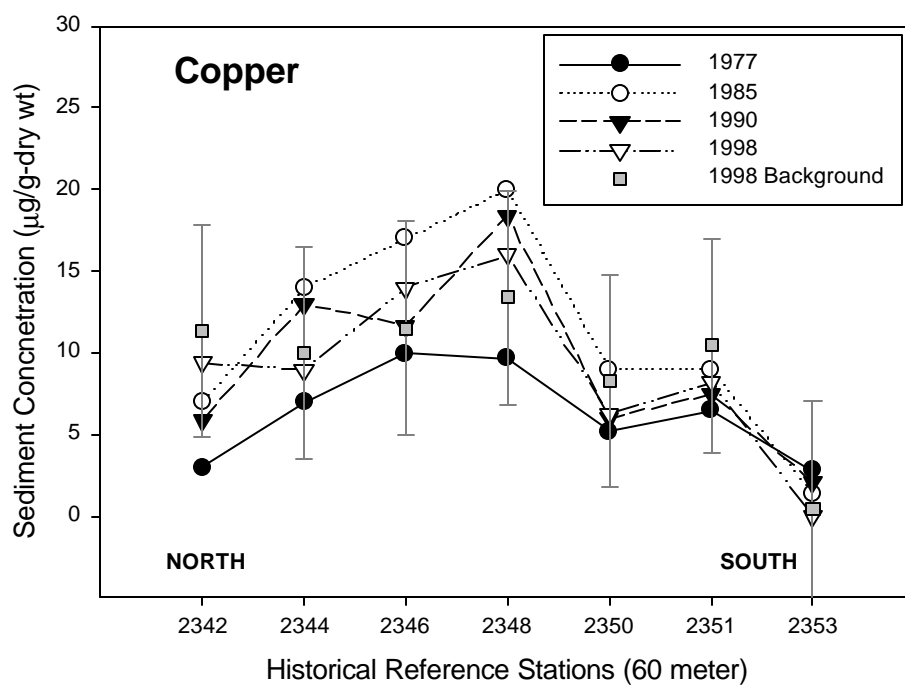
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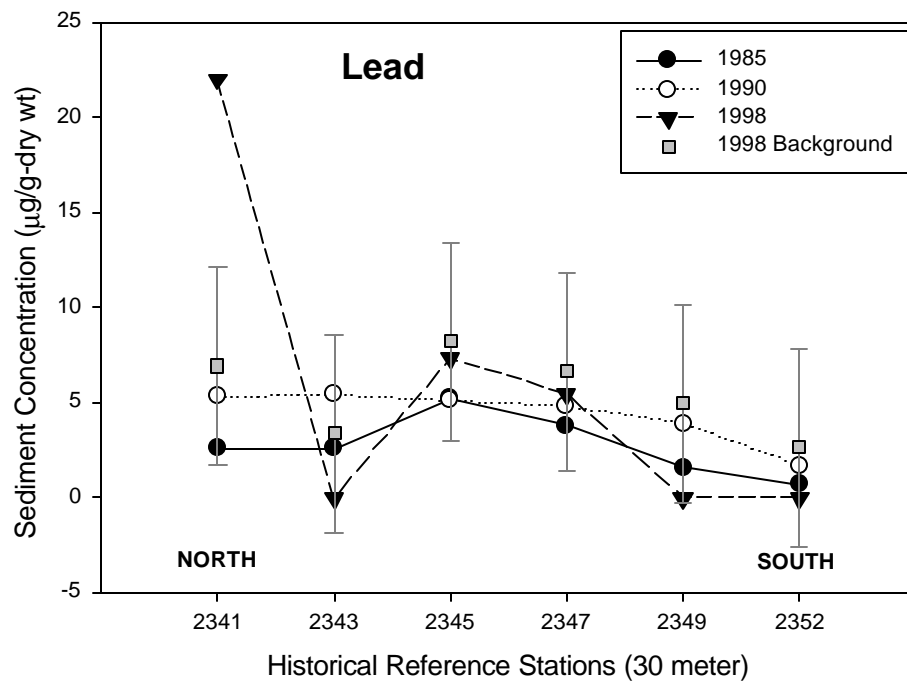
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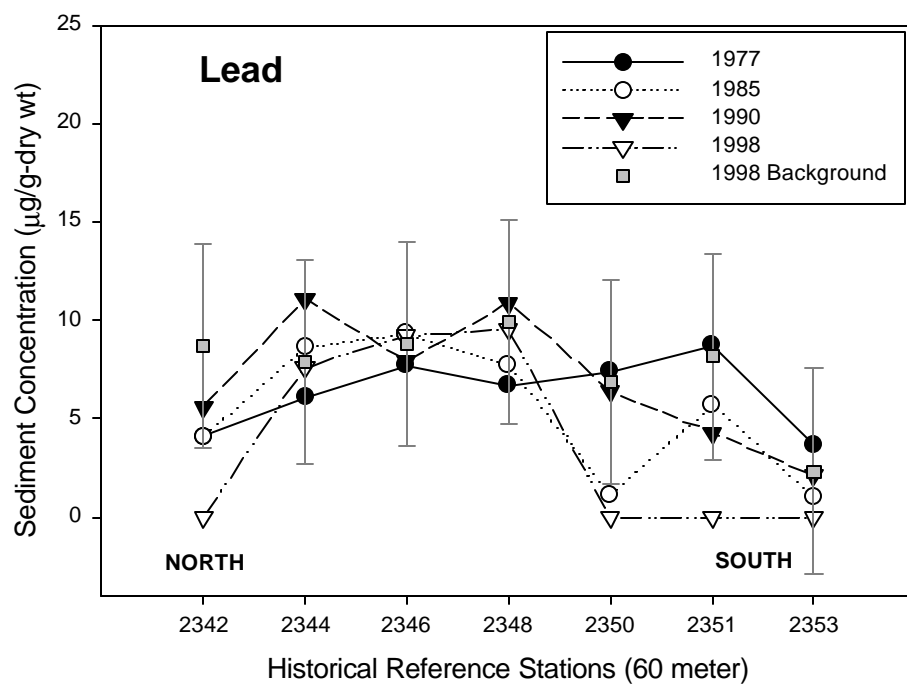
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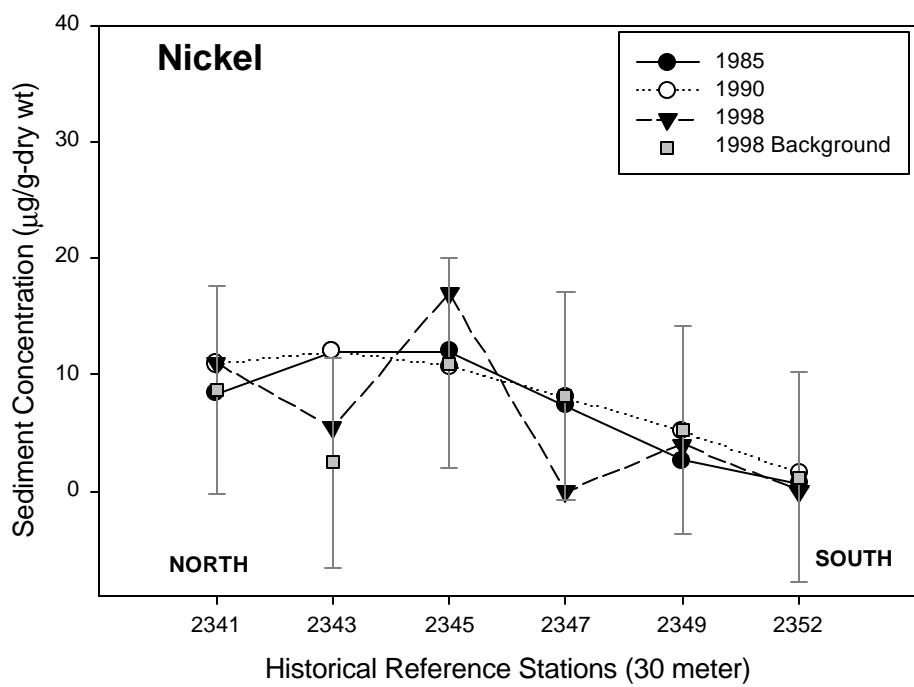
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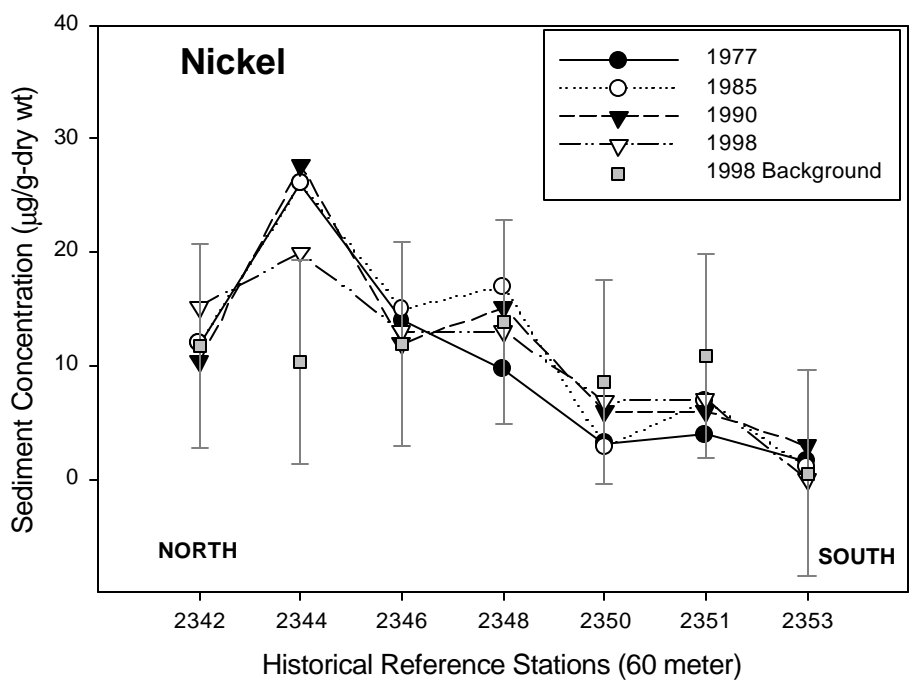
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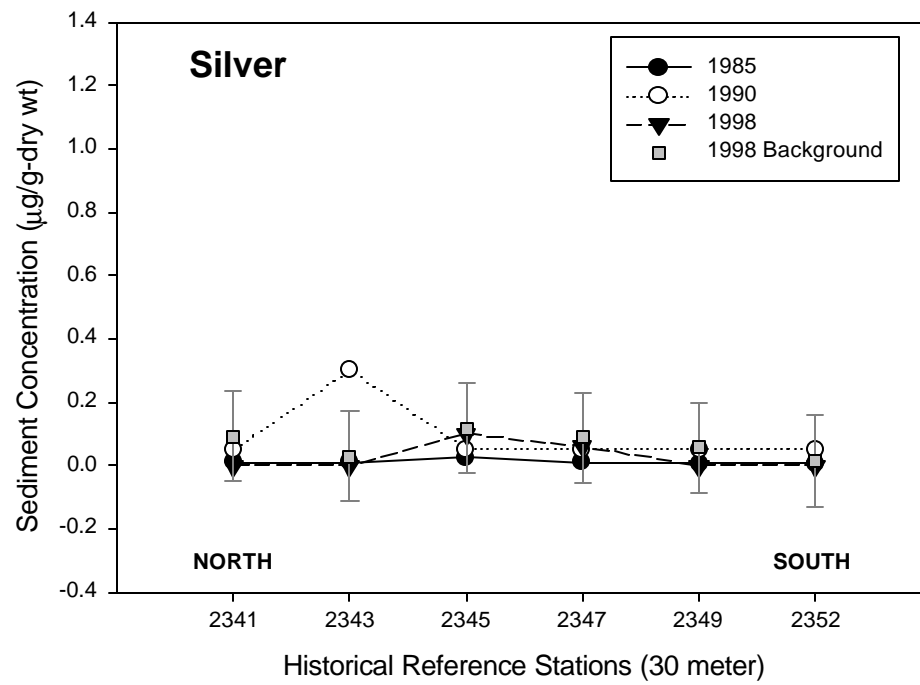
(h)



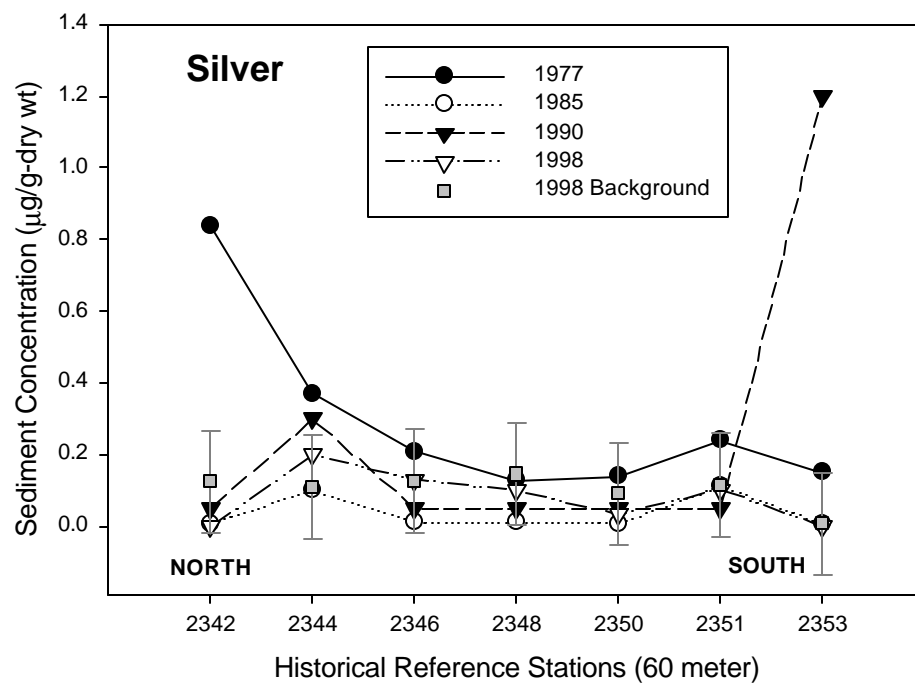
(i)



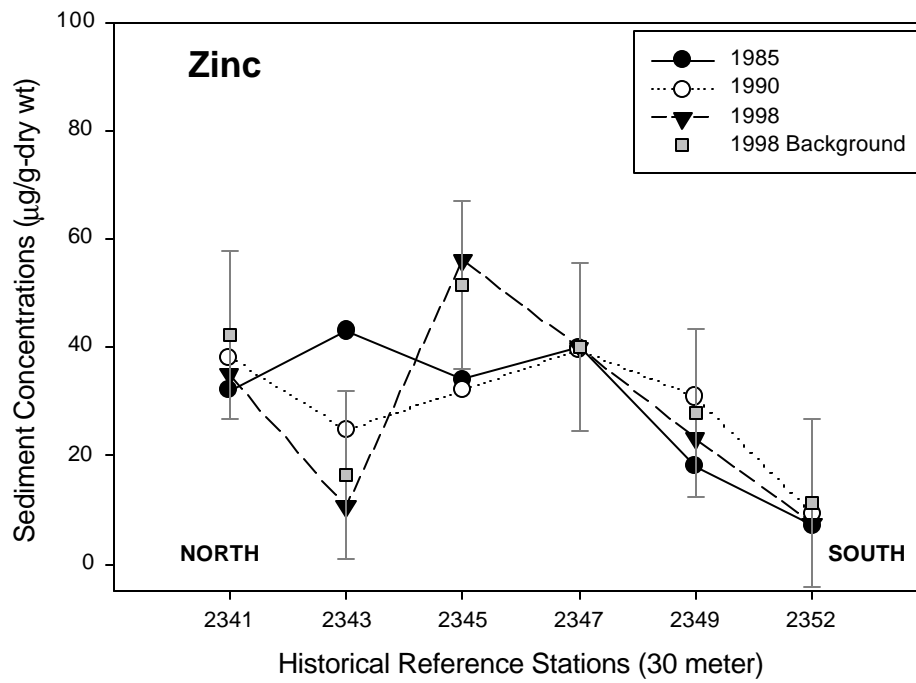
(j)



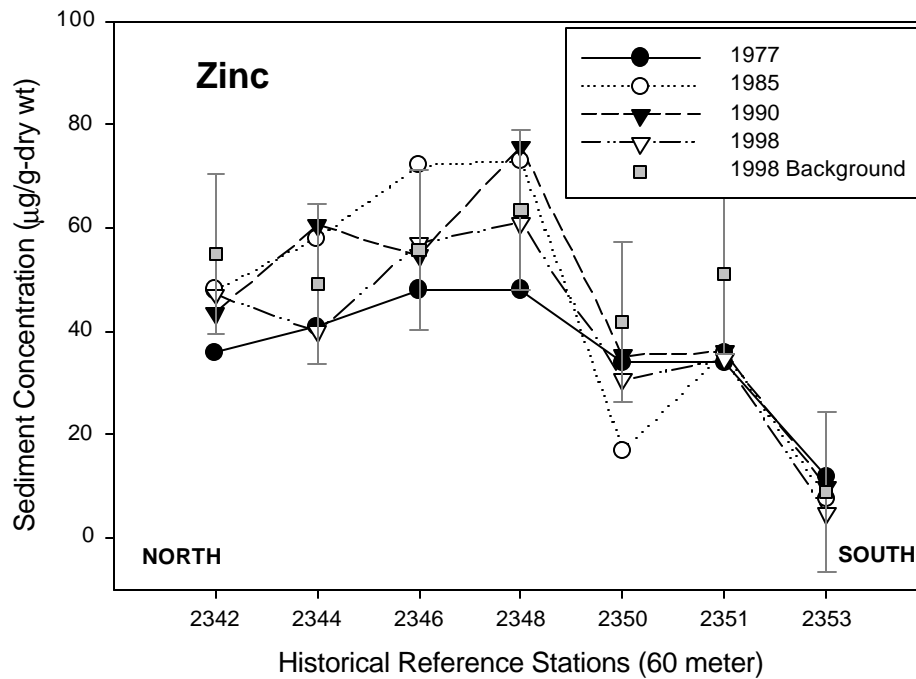
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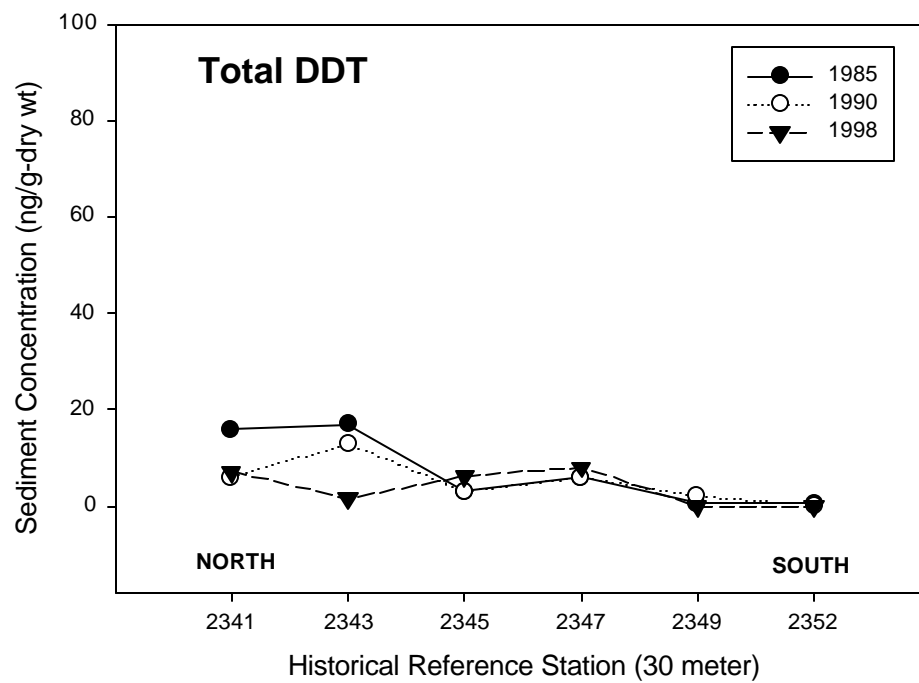
(l)



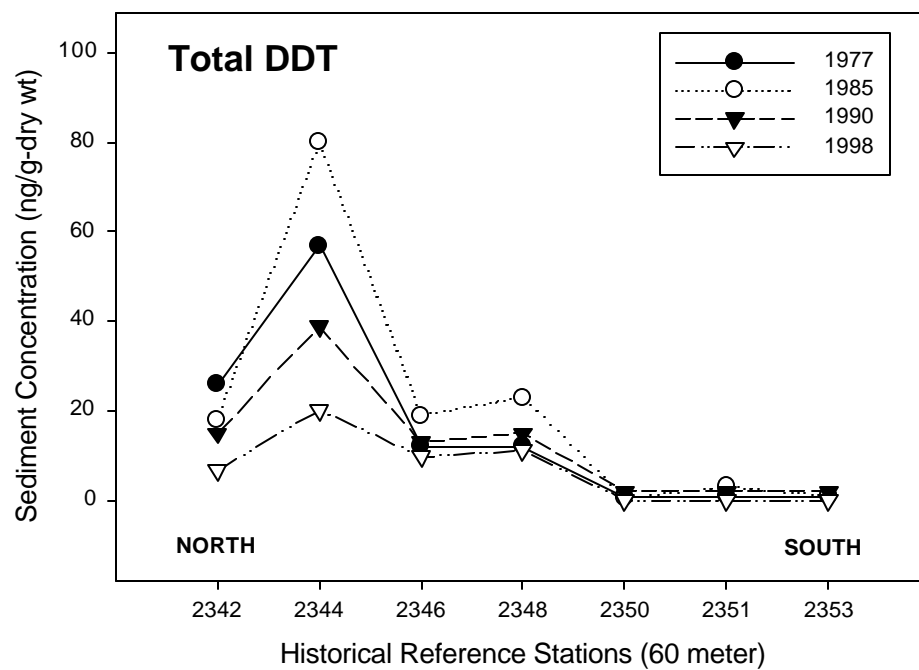
(m)



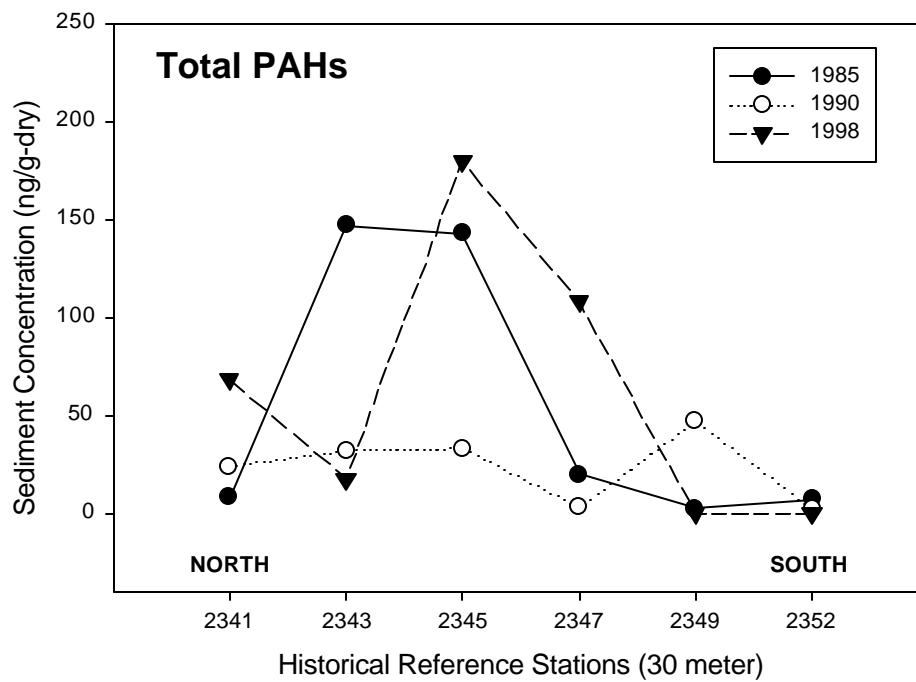
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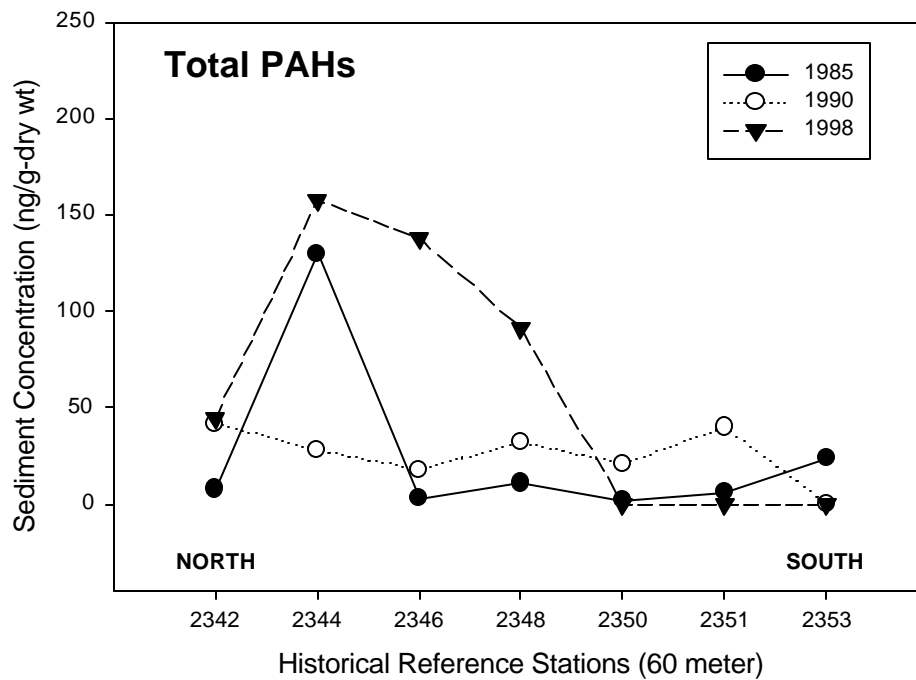
(o)



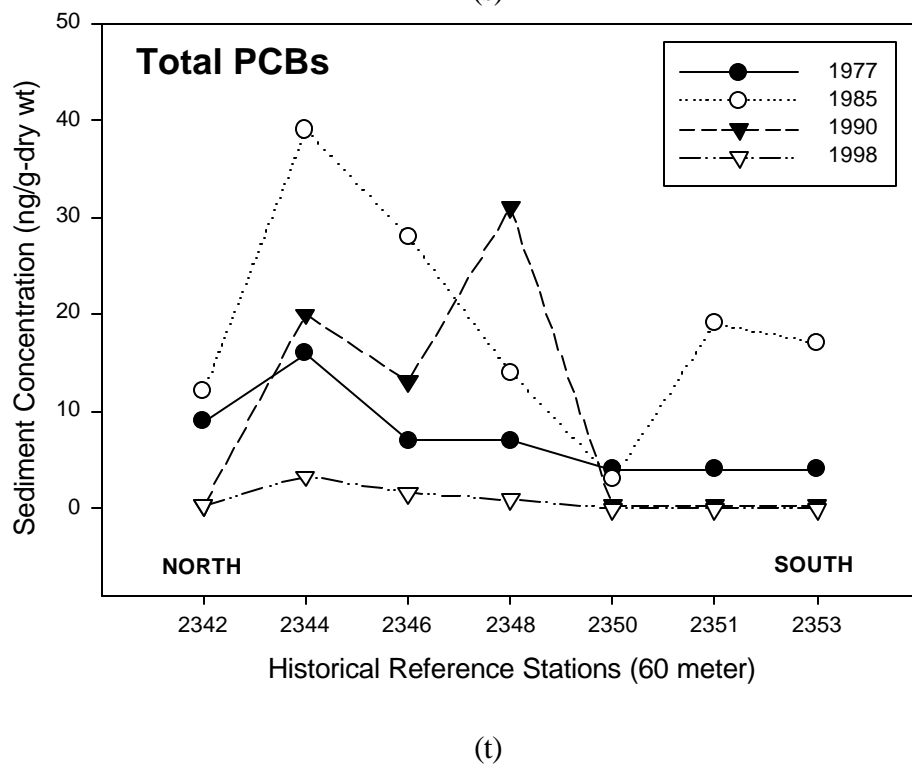
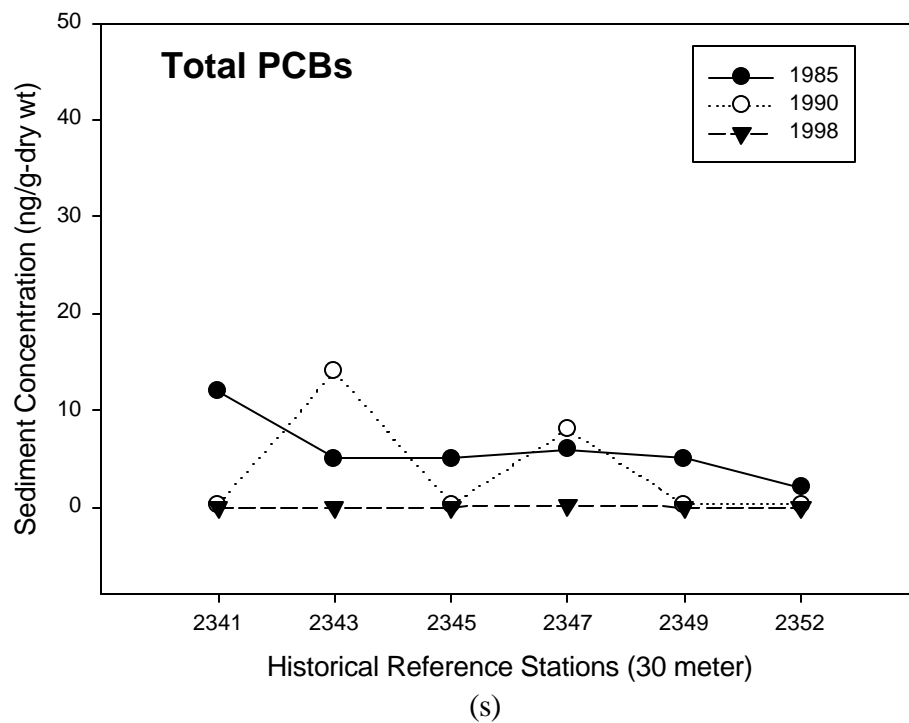
(p)



(q)



(r)



Figures VII - 2 (a) – (t). Concentrations of the indicated contaminants at 13 coastal reference stations in the Southern California Bight from 1977 through 1998. The 1998 background concentrations for the trace metals were derived from iron-normalization and regression relationships applied to the iron data from the Bight'98 regional survey. The error bars on the background values are the 99% prediction intervals.

Results And Discussion

Trace Metals

The plots of the trace metals concentration data at the reference sites from 1977 through 1998 are shown in Figure VII-2 (a) through (n). Also shown are the background concentrations and the 99% prediction intervals for the specified metal at each station predicted from the Bight'98 iron data. The trace metal results from the present study were consistent with those from the three previous reference surveys. The sediment concentrations were low for all metals measured, and most of the stations fell within the predicted background intervals.

Several other trends are consistent with the previous surveys. First, trace metal concentrations were frequently somewhat higher at the 60-m stations relative to the 30-m stations. Second, concentrations above background were observed for cadmium, chromium, nickel, and silver at the 30-m and/or 60-m stations off of Zuma Beach (Stations 2343, 2344). Cadmium was also above background levels at Stations 2345 and 2346, which are in the general area of Laguna Beach and near the mouth of Aliso Creek. Lastly, trace metals concentrations trended lower in the southern part of the Bight. However, other than a few outlier values for lead and silver, the results are all within the predicted natural background levels and show the trend toward lower concentrations in the southern Bight. Therefore, this trend is probably due as much to natural sediment geochemistry as it is to lower contaminant inputs in the southern section of the SCB.

Trace Organics

The chlorinated organic compounds measured in these surveys, DDTs and PCBs, do not occur naturally; therefore, detectable levels of DDT or PCBs are indicative of anthropogenic pollution. However, PAH concentrations occur naturally as a result of petroleum seepage and erosion of oil shales. The natural contribution to the total PAH levels in marine sediments can be estimated from sediment core data. As part of NOAA's National Status and Trends Program, PAH levels were measured in sections of sediment cores from the Santa Monica Basin dating back to circa 1900. In these sediment cores, PAH concentrations of 10-500 ppb were found in pre-industrial age sediments, and appear to represent the natural range of total PAH concentrations in sediments of the SCB (Huh and Venkatesan 1998). Also, this background range is consistent with the PAH results from the 1994 SCBPP, which were all below the project reporting limits of 300-500 ppb.

Data Comparability Issues

Direct comparison of the results for trace organic analyses from the four surveys is problematic. In contrast to trace metals, the extraction methods and/or the instrumental methods were different for each survey. These analytical differences among surveys account for some, but not all of the variability in the results over time.

The trace organic analyses for the 1977 survey were performed on a packed-column GC. Packed columns produce much lower resolution of the target compounds than do modern capillary columns. Because of the poor resolution, especially for groups of similar, closely eluting compounds such as commercial PCB mixtures (e.g., Aroclors), identification was often based on peak-pattern recognition. Quantitation was then based on a few selected peaks, and assumptions were made regarding the presence of other compounds in the sample based upon composition of analytical standards. In addition, the poor resolution from packed columns produced broad peaks that could hide the presence of non-target co-eluting compounds, as well as hide the absence of target compounds. Thus, either positive or negative errors are possible where packed-column GC are used to analyze complex environmental samples.

The potential problems associated with packed-column GC analyses were alleviated in future surveys because by 1985 SCCWRP was using capillary-column GC for trace organic analyses. The higher resolution provided more accurate analysis of DDT and its metabolites and PAHs. However, although it was now possible to measure individual PCB congeners, total PCBs were still calculated as the sum of the two Aroclors (1242 and 1254) for the 1985 and 1990 reference surveys. This is problematic because quantitation was still being performed using Aroclor standards and assumptions must be made regarding the relative concentrations of the constituent congeners.

The potential problem with reporting total PCBs in the marine environment as the sum of Aroclors was demonstrated in a collaborative study by Palmork *et al.* (1982). In ocean water samples, they found that the relative concentrations of the individual congeners of Aroclor 1254 could vary by as much as a factor of 25 from the original nominal values. This represents a severe deviation from the presumed Aroclor pattern, which is the result of differential transport and degradation in the environment. As a result of their study, Palmork *et al.* (1982) concluded that the only acceptable way of reporting PCBs in the marine environment is on a congener-specific basis.

The conversion between Aroclor and congener-specific PCB data to facilitate comparison of past, present, and future studies has been the subject of several recent papers (Sather *et al.* 2001, Newman *et al.* 1998, and Butcher *et al.* 1997). The conversion of congener-specific data to Aroclors and vice versa is rather involved and requires detailed information on how the quantitation and calibration were performed in each study. Therefore, no attempt was made to convert the data herein.

Even given these issues, it is still possible to make an approximate comparison of Bight'98 total PCB data with the total PCB from three previous surveys. The Bight'98 Survey measured 41 individual PCB congeners. The 1977, 1985, and 1990 reference surveys reported total PCB as the sum of Aroclors 1242 and 1254. A mixture of these two Aroclors would have approximately 70-80 individual congeners, although not all at the same concentration (Erickson 1990). Therefore, in the worst case, the sum of 41 PCB congeners would be lower by a factor of about two relative to the sum of the Aroclors.

Temporal Trends in Organic Contamination

The plots of the reference data from 1977 through 1998 for total DDT, total PAH, and total PCB are shown in Figure VII-2 (o) - (t). For total DDT, only the Zuma Beach 60-m station (Station 2344) was found to show any change in concentration over time. The location of this station is consistent with the observed northward transport of DDT from the known source area on the Palos Verdes Shelf. Given the very orderly temporal trend, and the agreement of the other stations, this is probably a true change in DDT levels over the past 25 years and not an artifact of the analytical methods.

For total PAH, no temporal trend was evident. Total PAH levels of up to ~200 ppb were measured at a few stations in the central Bight in 1985 and 1998, whereas stations at the northern and southern ends of the Bight were near detection limits. In contrast, total PAHs were uniformly low at all sites for the 1990 survey. The low values in 1990 are probably related to analytical methods, as it is hard to envision an environmental process that would account for such a variation in the data between surveys. If the 1990 results are ignored, PAH concentrations appear to have been similar between 1985 and 1998. Moreover, all total PAH values for the reference sites are within the natural range of PAH concentrations inferred from sediment core historical profiles (i.e., < 500 ppb; Huh and Venkatesan 1998).

The total PCB data for the reference sites show a similar pattern to that for DDT. The PCB levels at the 30-m reference stations are consistently very low. Three 60-m stations (Stations 2344, 2346, and 2348) show elevated levels in previous surveys but drop to very low levels in 1998. While some of this variation can be attributed to differences in analytical methods, the majority probably reflects actual changes in PCB concentrations over time.

Conclusions

The results presented in this chapter support the historical designation of the 13 stations discussed herein as reference sites approximating natural background conditions for the SCB coastal shelf. With few exceptions, trace metal concentrations at the reference sites were found to fall within estimated background ranges predicted by an independent regression method. Moreover, the concentrations of trace metals appear to have been fairly constant over the past 25 years. Although comparison of trace organic data among surveys is made problematic by differences in analytical methods, there does seem to be a trend towards decreasing levels of DDTs and PCBs at selected reference sites. The levels of PAHs measured in sediments at the reference sites are essentially the same as those measured in 1985. Also, the levels of PAHs at these reference sites are probably due largely to natural sources as evidenced by PAH concentrations measured in sediment cores.

In any case, the levels of all contaminants measured at these 13 reference sites were low enough to validate their past, present, and even future use as control stations for monitoring in the SCB. Because the concentrations of contaminants at these stations have always been so low, it is difficult to make any definitive conclusions regarding temporal trends. However, it can be said with certainty that contamination in the Bight does not appear to be getting any worse. Furthermore, the fact that contaminant concentrations at these sites have not changed significantly over a 25-year period implies that extensive, Bight-wide transport and redistribution of pollutants is not occurring, or that the rate of dispersion is slow compared to the rates of sequestration and/or degradation. Whatever the operative mechanisms, these data suggest that elevated levels of both trace metal and organic contaminants appear to remain fairly localized and associated with depositional zones in relative proximity to the original sources.

VIII. DISCUSSION

The sediment chemistry component of the Bight'98 Survey was successful in accomplishing all five of the objectives stated at the beginning of the study. These objectives were to: 1) Demonstrate comparable performance among the multiple participating analytical laboratories, 2) Determine the spatial distribution and magnitude of sediment contamination in the Bight, 3) Identify any relationships among sediment parameters that might aid in evaluating the relative importance of different pollution sources, 4) Assess the potential for adverse impacts to benthic organisms due to the measured levels of sediment contamination, and 5) Identify temporal changes in contamination at selected reference stations over the past 25 years.

The inter-laboratory calibration efforts undertaken prior to sample analysis for the Bight'98 project were successful in identifying analytical inconsistencies, and taking appropriate corrective measures. Through an iterative approach of analysis, performance evaluation, and method modification, the inter-laboratory calibration efforts resulted in greatly improved agreement among the contributing laboratories. One of the unique and important aspects of these calibration exercises was that laboratories were required to demonstrate acceptable analytical performance on both commercial certified reference materials and selected local marine reference sediments. The use of local marine sediments provided an additional level of quality assurance in that analytical performance was evaluated using samples similar to those that would be analyzed during the course of the study. In addition, specific on-going quality control measures were employed to ensure that the analytical performance was maintained during the course of the study.

The Bight'98 Survey adopted a performance-based approach to the analysis of the sediment chemical and physical parameters, whereby laboratories were allowed to use any analytical methods, provided that acceptable performance could be demonstrated. However, in order to achieve acceptable results certain methods had to be standardized among laboratories. For example, the quality of results for trace metal analyses was found to be mostly a function of digestion methods. Therefore, all laboratories adopted a common strong acid digestion method (EPA Method 3050B) in order to achieve comparable results. In contrast, the laboratories performing trace organic analyses were ultimately able to produce comparable results using a variety of methodologies.

Although the inter-laboratory calibration study was successful, some problems were encountered in achieving comparable detection limits among laboratories. This was particularly true for mercury and PCBs. In each case, the results of a single laboratory were significantly different from those of other laboratories. In the case of mercury, data from one laboratory did not meet the quality control criteria stated in the QA Plan. By the time the problem was identified, it was too late to re-analyze the samples. This problem was exacerbated by the fact that, for pragmatic reasons associated with sample collection and distribution, each laboratory typically analyzed samples from a separate region of the Bight. In such cases, differences in detection limits hindered the ability to make meaningful sub-regional comparisons.

The method detection limits in the Sediment Chemistry Study were set relative to the lowest anticipated sediment quality criterion, in this case the NOAA ERL values (Long *et al.* 1995). However, the large number of non-detectable values for certain analytes made some evaluations difficult. Inserting an arbitrary number, such as half of the detection limit, can be a problem for compound groups with many target analytes (e.g., PCBs and PAHs) and may lead to erroneous interpretations. Given the biological impact assessment results, it is likely that sediment quality thresholds used in future monitoring projects will be for sub-lethal effects, and therefore threshold concentrations will be significantly lower. Requiring the participating laboratories to lower method detection limits may be one way of addressing these issues. Lowering detection limits would also make the data more generally useful beyond the scope of the current study. However, achieving lower detection limits in practice for the entire suite of analytes could be quite costly, and a comprehensive cost-benefit analysis should be performed to evaluate the efficacy of this approach.

Sediment trace element enrichment above natural conditions due to anthropogenic inputs was estimated using the iron-normalization and regression background lines developed as part of the 1994 Southern California Bight Pilot Project (SCBPP) (Schiff and Weisberg, 1999). For mercury, a new regression line was developed from the 1998 data because no regression line was obtained from the 1994 SCBPP. The decision was made to use the trace metal background regression lines produced during the 1994 Pilot Project because the results were based upon a greater number of offshore sites, and because the results were confirmed by developing similar regression lines using the Bight '98 data. The resulting trace element:iron background relationships were further evaluated and validated using sediment core data from two independent studies conducted in the Southern California Bight (see Appendix A). For trace organic contaminants, any amount present in the sediments above the analytical detection limits was assumed to be of anthropogenic origin.

Using these criteria, sediments over an estimated 86% of the Southern California Bight area was contaminated by at least one anthropogenic pollutant in 1998. More specifically, an estimated 47% of the SCB area was contaminated by at least one trace metal. An estimated 85% of the SCB was contaminated by at least one organic compound, of 14% was due solely to total DDTs. These results are nearly identical to those obtained for the 1994 SCBPP (Schiff and Gossett, 1998). No bay and harbor stations were analyzed in 1994, and therefore comparisons to 1998 results were made with and without inclusion of the embayment stations. The removal of the embayment stations in the Bight '98 data, however, had very little impact on bight-wide evaluations because they accounted for only about 6% of the total area.

Comparisons of sediment contamination among different sections of the Bight showed that the highest sediment concentrations for most of the target analytes were associated with bays and harbors, and areas in proximity to large POTW outfalls. The bay and harbor areas were further subdivided into industrial ports, marinas and "other" bay and harbor areas, which were areas within the embayments believed to be beyond the immediate influence of port and marina activities. Sediment contamination in bays and

harbors was found to exhibit the general trend of ports > marinas > other bay and harbor areas.

However, all bay and harbor areas were not the same. Differences in contaminant profiles were observed among the different embayments. For example, San Diego Bay contained significantly higher levels of copper, mercury, and PAHs relative to the other embayments, but lower PCBs and virtually no DDT. Also, the proportion of chlordanes was much higher in the smaller bays and harbors throughout the Bight relative to Los Angeles/Long Beach Harbor and San Diego Bay.

Similar variability was observed among the LPOTWs. The sediment contamination in areas adjacent to the Hyperion Wastewater Treatment Plant (Hyperion) and Joint Water Pollution Control Plant (JWPCP) outfalls was significantly greater in terms of both concentrations and number of elevated contaminants relative to the Orange County Sanitation District or City of San Diego LPOTW outfalls. The high levels of sediment contamination in proximity to the Hyperion and JWPCP outfalls is of historical origin, and does not reflect the levels of contaminants associated with recent discharges (Zeng *et al.* 2001).

A comparison of the percent of total Bight-wide mass for the measured chemical constituents in the source strata (i.e., bays and harbors, LPOTWs, SPOTWs, and rivers) versus the percent of the SCB area occupied by the same strata produced some telling results (see Table VI-1 and Figure VI-1). All of the source strata combined account for on average nearly 37% of the total mass of all constituents in the Bight, but occupy only about 13% of the area. Conversely, this necessarily implies that the remaining 87% of the Bight contains on average about 63% of the total mass of all constituents. Of the source strata, the vast majority of the contamination is associated with the LPOTWs and bays and harbors, which account for about 34% of the constituent mass, and about 10% of the area.

Interestingly, SPOTWs and river mouths did not contain a disproportionate amount of the contaminant mass relative to their aerial extent. With the exception of chlordanes in the river mouth stratum, these areas contained an average percent of the total mass for each of the contaminants that were less than or equal to their proportion of the total area of the Bight. This does not necessarily mean that SPOTWs and rivers are not significant sources of contamination to the Bight, but it could mean that the contaminants discharged by these sources are not accumulating in the surrounding sediments. Initially, we speculated that the dynamic and energetic nature of these discharge zones may contribute to the transport of contaminants away from these areas. However, sediment contaminant levels are similar for SPOTWs that discharge into shallow and mid-depth environments, which would tend to refute this contention.

In the case of rivers, studies of discharges during storm events have shown that salinity stratification is prevalent, and that fresh water plumes with entrained fines particles can travel significant distances offshore before mixing and deposition occurs. This process most likely contributes to the dispersion of river-derived contaminants over

a wide area, and minimizes deposition near the river mouths (Bay *et al.* 1999). Also, the intermittent nature of contamination near river mouths has been observed. Bay *et al.* (1997) found that initial elevated contaminant levels near the mouth of Ballona Creek were dissipated within two weeks. Moreover, they found a generally increasing trend in sediment contamination from the mouth of Ballona Creek to 2 km offshore (10-26 m depth).

The methods used in this study to delineate the relative importance of different contaminant sources were mostly ineffective for this purpose. The chemical marker compounds selected for tracking the extent of sewage pollution, LABs, were below detection limits for all but seven stations throughout the Bight. The lowering of detection limits for LABs would require the use of samples sizes that would be impractical for a monitoring project of the Bight'98 scale. Based upon these results, LABs are probably not useful for monitoring the spatial influence of wastewater discharges on a regional scale. The second method employed to potentially identify the influence of different contamination sources was the multivariate statistical technique of PCA. This approach was able to identify unique contaminant patterns, which were consistent with other data evaluations used in this study, as well as the contaminant patterns observed in previous studies. . In particular, two groups of stations were identified using cluster analysis, which accounted for 96% of the total Bight area. Unfortunately, the primary parameter distinguishing these two groups appeared to be grain-size, and not a unique assemblage of chemical constituents. It is clear that better, more sensitive tools need to be identified for discriminating among, and assessing the relative importance of, different sources of pollution to the SCB.

The Bight '98 Survey provided a data set for characterizing sediment quality in terms of bulk sediment concentrations and spatial distributions. As of the writing of this report, there are still no regulatory sediment quality criteria promulgated by either the U.S. Environmental Protection Agency, or the State of California, with which to evaluate the Bight'98 sediment chemistry data. Pursuant to a recent court decision (*San Francisco BayKeeper, Inc. v. State Water Resources Control Board, August 2001*), the State Water Resources Control Board is required to develop sediment quality objectives (SQOs) for enclosed bays and estuaries by March, 2007 (Beegan 2002). However, development of SQOs for the coastal shelf is not anticipated to be on the state regulatory agenda for the foreseeable future. Therefore, sediment contaminant concentrations were evaluated for the potential to impart adverse biological impacts using several empirical, theoretical, and consensus-based sediment quality guidelines (SQGs). The evaluations using empirical SQGs were based on the NOAA ERL and ERM parameters (Long *et al.* 1995). These SQGs were developed based on statistical analyses of empirical data, and have been applied with varying success at a number of water bodies throughout the U.S. However, guidelines are not available for the entire list of Bight '98 target analytes, and the confidence of specific guidelines varies for individual analytes. Employing the available guidelines to the entire Bight, an estimated 72 and 15% of the area exceeded the ERL and ERM, respectively, for any contaminant. Approximately 70 and 12% of the area exceeded the ERL and ERM, respectively, for any organic chemical. For trace metals, about 36 and 6% of the area exceeded the ERL and ERM, respectively. These

comparisons were made in order to facilitate direct comparison with the 1994 survey results. However, these evaluations are somewhat misleading in that it is now widely recognized by ecotoxicologists that a single, or even a few ERM exceedances is not a good predictor of the potential for adverse biological effects (Long and MacDonald 1998, Bay 2001).

A more detailed evaluation of the data with respect to ERM values is important for putting the previous Bight-wide assessments into the appropriate context. Out of the 290 U.S. stations, 24 exceeded the ERM value for at least one metal, and 54 stations exceeded the ERM for at least one organic contaminant, or a total of 66 stations above the ERM for either a metal, organic, or both. However, the vast majority of the ERM exceedances were for a single parameter. For example, only 3 of the 24 stations above the ERM for any metal had more than one exceedance. Similarly, only 4 of the 54 stations above the ERM for any organic compound had two parameters above the ERM. Only one station in the study had four parameters above the ERM, and all other stations had either one or two parameters above the ERM. Also, of the 54 stations above the ERM for any organic, 52 were due solely to total DDT, and the other two were for total PCBs. Of the 24 stations above the ERM for any metal, 22 were due either to silver or mercury (11 stations each).

On a percent of area basis, for the 5.8% of the SCB that had at least one metal above the ERM, only 0.2% was above the ERM values for two trace metals. In addition, of the 11.6% of the Bight above the ERM for any organic compound, only 0.4% was above the ERM for two organic constituents. None of the Bight area was above the ERM values for more than two metals or two organics. Considering all contaminants together, 14.7% of the Bight was above the ERM for any contaminant, of which 11.7% exceeded the ERM for just a single parameter.

In an effort to obtain a more reliable assessment of the potential for acute toxicity to benthic organisms, the sediment chemistry was assessed using the multi-parameter mean ERMQ approach (Long *et al.* 1998). All of the stations in the Bight'98 Survey were within the lowest two risk categories for acute toxicity to benthic organisms (amphipods). These categories correspond to a predicted incidence of acute toxicity of 11 and 30% of the samples in ERMQ ranges I and II, respectively. Therefore, it is not surprising that ERMQ values showed a poor correlation with the results of the Bight'98 amphipod toxicity testing (Bay *et al.* 2000), and that these SQGs cannot reliably predict toxicity on a site-by-site basis. However, the mean ERMQ approach can, and did, correctly predict the incidence of toxicity observed for Bight'98 samples within the specified ERMQ ranges.

In addition to the empirical SQGs, a comparative evaluation of sediment quality was performed using multiple EqP-based assessment tools (Appendix E). The potential for acute toxicity stemming from PAHs was assessed using the Σ PAH model (Swartz *et al.* 1995). In addition, the potential for acute and chronic toxicity associated with trace metals in the sediments and interstitial water were assessed relative to EPA water quality criteria. Sediment trace metal contamination was evaluated using the SEM-AVS

approach. Finally, so-called consensus-based SQGs, which are a hybrid of the empirical and theoretical SQGs, were used to evaluate the PAH and PCB contamination (Swartz *et al.* 1999, MacDonald *et al.* 2000). The results from the theoretical assessments are in general agreement with the results from the empirical SQG assessment. Both approaches predict that only a very small percentage of the Bight is at risk for acute toxicity. Moreover, both approaches do a poor job of predicting toxicity for any specific station, but correctly predict the incidence of toxicity among stations within specified contamination ranges.

As the most widespread contaminant in the SCB, DDT was given special consideration. Eight different SQGs were used to evaluate the potential for biological impacts associated with measured levels of total DDT. Total DDT exceeded the ERL and ERM values for an estimated 71 and 12% of the SCB area, respectively. In contrast, other SQGs developed specifically for DDT are about roughly two orders of magnitude higher than the NOAA SQGs (MacDonald 1994, Swartz *et al.* 1994, Chapman 1996). As such, the latter SQGs predict that zero percent of the SCB is at risk for acute toxicity from total DDT. These results are in apparent contrast to the assessment results presented in the 1994 SCBPP report using the same SQGs. However, a unit error was discovered in the 1994 report, which led to an incorrect assessment of the total DDT data. When the unit error was corrected, the 1994 and 1998 assessments were in complete agreement.

Sediment extracts were also screened using the P450 HRGS for the ability to induce a toxic biochemical response. The results showed a consistently good correlation with total PAHs, while the correlations with total PCBs were more variable. The one exception was an exceptionally good correlation ($r^2=0.92$) observed for PCBs in samples from the LPOTW stratum. Also noteworthy were some high responses throughout the Bight that could not be explained based on the concentration of the Bight'98 target analytes. These results indicate that there were carcinogenic compounds in some SCB sediments capable of inducing a P450 response in human liver cells that were not on the Bight'98 target analyte list. Overall, the P450 HRGS assay appears to be a rapid, effective assessment tool for screening sediments for contamination and potential toxicity.

The overall results of the various assessments indicate that while over 85% of the SCB showed some evidence of being affected by anthropogenic pollution, only a small portion of the total Bight area (<15%) was found to have contaminant concentrations of any concern for acute toxicity. Moreover, less than 1% of the Bight was at concentrations that indicate a high potential for acute toxicity. These results are in general agreement with the results of the sediment toxicity component of the Bight'98 project, which found that an estimated 19 and 2.7% of the SCB was of potential and high concern for acute toxicity, respectively.

The assessment results from this study are in agreement with those from the State of California Bay Protection and Toxic Cleanup Program (BPTCP) (Anderson *et al.* 1998, Phillips *et al.* 1998, Faurey *et al.* 1996). While the BPTCP studies found that anthropogenic contamination in the bays, harbors, marinas, and lagoons was ubiquitous, a

significant majority of the stations were in the lowest two categories of concern for acute toxicity based upon mean ERM quotient values, in agreement with the present study. Also, the chemicals found to be disproportionately elevated in the bay and harbor strata for the Bight'98 Survey were the same as those identified as "chemicals of concern" in the BPTCP; namely, copper, lead, mercury, zinc, chlordanes, total PAH, and total PCB. Due to the low to moderate levels of contamination at most sites, the BPTCP also found a poor correlation between mean ERM quotient values and amphipod toxicity on a station-by-station basis. Finally, the BPTCP found that within the bay and harbor areas, the highest contamination was consistently found in the industrial port areas (e.g., consolidated slip), also in agreement with the findings herein.

It is important to emphasize that while the vast majority of the SCB was below the SQGs for acute toxicity, this does not imply that there are no potential biological impacts stemming from the observed sediment contamination. The commonly used SQGs are all based on an endpoint of mortality, and thus sublethal effects are not assessed. Only a single study was found in which ERMQ values were correlated with sublethal impacts to benthic communities (Hyland *et al.* 1999). This study correlated effects on the abundance and diversity of benthic organisms to ERMQ ranges for sediments in the southeastern United States. Based upon the criteria developed therein, the ERMQ values in the SCB suggest a significant percentage of the Bight (~77%) is at a moderate to high potential for sublethal benthic degradation. Interestingly, this is in agreement with the results predicted from the cumulative concentrations of trace metals found in the interstitial water of SCB sediments. As part of the theoretical assessments described above, the sum of the interstitial water trace metal concentrations (mostly copper and nickel) suggested that approximately 70% of the Bight is potentially at risk for sublethal effects to benthic organisms.

These assessment results, however, are not supported by the results of the 1994 SCBPP Benthic Infauna Survey (Bergen *et al.* 1998), which found that 91% of the SCB area consisted of healthy benthic communities. The contrast between the predictions based on previous studies, and the findings of the 1994 Benthic Survey, underscore the need for the development of sublethal SQGs specifically for the SCB. Although the sublethal empirical SQG assessment mentioned here is based on only one study, performed in a different part of the country, the results do suggest a need for more sensitive measures of potential biological impacts. Follow-up efforts should be made to integrate the data from the Bight'98 chemistry, benthic ecology, and demersal fish (i.e., bioaccumulation) components to identify new and more sensitive SQGs for defining the health of the SCB relative to sediment contamination.

The final objective of the Bight'98 Sediment Chemistry Study was to identify temporal trends at selected reference stations in the SCB. To this end, the sediment chemistry data from four regional surveys conducted over the past 25 years were compared at 13 common reference sites. Data for this temporal evaluation of sediment contamination were derived from the 1977, 1985, 1990, and 1998 regional surveys conducted by SCCWRP (Word and Means 1979, Thompson *et al.* 1987, Thompson *et al.* 1993). A straightforward comparison of results was somewhat complicated by changes

in analytical methods among the surveys. However, methods for most analytes were similar enough to allow for a reasonable evaluation of temporal changes. The trace metals data were also compared to the predicted background levels derived from the iron-normalization and regression relationships used in 1994 and 1998.

The results of these analyses showed that sediment contamination at the 13 reference stations did not change significantly over the period from 1977 to 1998. The one possible exception is DDT, where an apparent decrease in concentration was evident at a single station just north of Santa Monica Bay. Because the 13 stations evaluated are distant from known contaminant sources, these results suggest that large-scale transport and redistribution of contaminants in SCB is not occurring, and that elevated levels of pollution remains fairly localized within areas near the point of discharge. This assessment is consistent with the comparison of 1994 and 1998 sediment chemistry results. As previously stated, the sediment chemistry results for the Bight'98 Survey were essentially identical to those from the 1994 SCBPP. However, some transport of contaminants is certainly occurring on a sub-regional scale, as evidenced from the consistent levels of contamination found throughout Santa Monica Bay, and trends in DDT contamination from Palos Verdes northward (Zeng *et al.* 2001, Lee 1994).

Despite the notable accomplishments of the sediment chemistry component of the Bight '98 Survey, some important issues remain unresolved. Remaining challenges include improving, or explaining the lack of, predictability of acute toxicity based on bulk contaminant concentrations. In addition, more sensitive, source-specific markers are needed to identify key contaminant sources, and for source apportionment. Finally, the relationship between sediment contamination and bioaccumulation needs to be fully understood and evaluated.

IX. CONCLUSIONS

The 1998 Regional Marine Monitoring Survey was the second and most comprehensive survey of environmental quality in the SCB. The Bight'98 Sediment Chemistry Study was an important component of the overall Bight'98 Survey, and has been a successful follow-up to the 1994 SCBPP Sediment Chemistry Study. Where the two studies could be directly compared, the results of the present study support the conclusions of the 1994 survey. However, where the 1998 and 1994 surveys differed (namely in sampling bays and harbors), new information was obtained regarding the spatial distribution and magnitude of sediment contamination in the SCB. In preparing this report, the Bight'98 Chemistry Committee has identified the following as the major findings of this study:

1. Anthropogenic sediment contamination was widespread in the SCB.

- Almost 50% of the SCB is contaminated by at least one trace metal.
- Approximately 85% of the SCB is contaminated by at least one organic compound.
- Approximately 86% of the SCB is affected by any anthropogenic contaminant.
- These findings are nearly identical to the results from the 1994 SCBPP.

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

- Based on both ERM quotient and equilibrium partitioning sediment quality guidelines, less than 20% of the Bight was at a low to moderate risk, and less than 1% of the Bight was at high risk for acute toxicity to benthic organisms.
- These results are in general agreement with the results from the Bight'98 Sediment Toxicity Study.

3. Total DDT was the most widespread contaminant group in the SCB.

- An estimated 82% of the SCB area had detectable levels of total DDT in sediments.
- Based on the best available DDT-specific sediment quality guidelines, less than 1% of the SCB sediments contain concentrations of total DDT expected to cause chronic or acute toxicity to benthic organisms.

4. The highest concentrations and largest proportion of measured contaminants were associated with bays and harbors, and with areas in proximity to large POTW outfalls.

- Although bays and harbors constitute only about 6% of the area, they contain on average about 22% of the total Bight-wide contaminant mass.
- Similarly, the areas near LPOTW outfalls constitute about 4% of the area, but contain an estimated 11% of the total Bight-wide contaminant mass.
- While these two strata combined occupy about 10% of the area, they are estimated to contain nearly 37% of the total contamination in the SCB.

5. The areas near river mouths and small POTW outfalls were not significantly contaminated relative to other areas of the Bight.

- While areas near small POTW outfalls constitute 1.6% of the Bight, they contain an estimated 1% of the total Bight-wide contamination
- The areas affected by river discharges make up about 1% of the Bight, but contribute an estimated 1.3% of the total contamination.
- In the river discharge zones, only the mass contributions of lead (1.2%), chlordanes (7.4%) and PAHs (1.5%) were in excess of their proportional area contributions to the Bight.

6. Concentrations of the target contaminants at 13 historical reference sites appear to have been low and fairly stable over the last 25 years.

- The one exception is for a station just north of Santa Monica Bay, where subtle decreasing trends were observed for cadmium, chromium, and DDT.
- Except for a few apparent outlier values, the sediment trace metals concentrations at the 13 reference sites fell within 1998 predicted background concentrations.
- The data for PAHs and PCBs were variable, probably due to analytical differences, but the concentrations have been consistent low since 1977.
- These results suggest that contamination is not being widely dispersed throughout the Bight, and that contamination levels in the SCB appear to be stable or decreasing since 1985.

X. RECOMMENDATIONS

- **The inter-laboratory calibration studies performed as part of the Bight'98 Quality Assurance and Quality Control Program should be refined, repeated, and expanded to include other laboratories.**

All but one of the laboratories (i.e., SCCWRP) that participated in Bight'98 were California Department of Health Services, Environmental Laboratory Accreditation Program (ELAP) certified, and among the largest, most well-equipped, and well-staffed laboratories in southern California. Yet, large differences in the data reported for identical samples were originally observed among the participating laboratories. Through an iterative process of analysis, evaluation, and adaptation, the consistency of analytical results among the participating laboratories was greatly improved. Presumably, this problem is not an isolated one, and comparability of results is a pervasive problem among laboratories generating environmental chemistry data. It is evident that the ELAP certification process is not adequate for ensuring data quality for specific projects, and for specific environmental matrices. The results of this study show that it is possible to greatly improve the comparability of data produced by different laboratories using a concerted performance-based approach. These matrix-specific, inter-laboratory calibration studies should be performed on a regular basis, in addition to the normal ELAP certification, by all laboratories generating environmental data.

- **Identify better methods and/or chemical markers for the association of known or suspected sources with the observed anthropogenic pollution.**

Two source tracking methods, linear alkylbenzenes and principal components analysis, were used in this study to identify sources of pollution at high contaminant concentration sites; neither was successful. Effective management requires not only condition assessment, but source attribution as well. There is a need for new tools and methodologies for associating individual constituents or groups of contaminants with specific point and nonpoint sources. The new tools may include applying newer technologies such as enantiospecific and isotopic analysis to generate new types of data, or new methods for evaluating the currently available data.

- **Develop or identify new sediment quality guidelines, if possible, for the Southern California Bight relating the observed sediment contamination levels to the potential for relevant biological impacts.**

Currently available sediment quality guidelines (SQGs) are based primarily on the endpoint of acute toxicity to benthic organisms. While good agreement was obtained between the percent of the SCB area at risk for acute toxicity as predicted from these guidelines, and the percent of the SCB area at risk resulting from actual toxicity tests, there was poor correspondence on a site-by-site basis. This is because the concentrations of contaminants in

the SCB are typically near the low end of the range for these SQGs, where there is a low probability for toxicity. All of the stations in the SCB were in the contamination ranges wherein the predicted incidence of acute toxicity to amphipods was 30% or less. Clearly, better tools for understanding and predicting sediment toxicity need to be identified. Alternatively, it may be preferable to adopt new SQGs that evaluate sediment quality with respect to sub-lethal biological effects, or potential risk to organisms at higher trophic levels. While it is clear from the results of this study that the majority of the Bight is not predicted to be at risk for acute toxicity, the assessment results from the available sub-lethal empirical and theoretical SQGs suggest that a significant portion of the SCB may be at risk for benthic degradation. New SQGs should be developed and applied to the results of this study as they become available to reassess the observed sediment contamination in terms of other possible biological impacts.

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APPENDIX A

A Comparison of Iron-Normalization and Regression versus
Sediment Core Data for Determining Natural Trace Metal
Background Concentrations in Sediments of
the Southern California Bight

INTRODUCTION

Trace metals occur in marine sediments as a result of both natural geologic processes and human activities. Therefore, in order to evaluate the extent of trace metal pollution associated with sediments, it is necessary to estimate the fraction of the total metal concentration in excess of that which would be present naturally. Two approaches have been commonly used to estimate the natural metal concentrations in sediments: 1) Reference element normalization and regression, and 2) sediment core historical profiles. The objectives of this study are two-fold: first, to compare the results from these two approaches for determining background level of trace metals in sediments from the Southern California Bight; and second, to validate the iron-normalization-regression relationships developed by Schiff and Weisberg from the 1994 Southern California Bight Pilot Project data.

Many different reference elements and parameters have been used for normalization, including Fe, Al, Sc, Eu, Rb, Cs, Th, Li, organic carbon, and grain size (Daskalakis and O'Connor 1995, Luoma 1990). Although there is no consensus on the most appropriate sediment constituent to be used for normalization, aluminum has been used most frequently (e.g., Windom *et al.* 1989). To be useful as a reference element, several assumptions must be met (Schiff and Weisberg 1999): 1) the reference element must covary in proportion to the naturally occurring concentrations of the metals of interest, 2) it must be unaffected by inputs from anthropogenic sources, and 3) it must be stable and relatively unaffected by diagenetic processes that may alter the concentration after deposition.

Iron was selected as the reference element for the 1994 and 1998 Regional Marine Monitoring Survey sediment chemistry evaluations for several reasons. First, most environmental laboratories use a strong acid digestion for trace metals analysis; i.e., some variant of EPA Method 3050B (nitric acid with hydrogen peroxide and/or hydrochloric acid). Strong acid digestions typically achieve good recoveries for iron (> 70%), but low or variable recoveries for aluminum (~20%; Schiff and Weisberg 1999; Trimm *et al.* 1998). Second, Schiff and Weisberg (1999) found that iron produced correlations as good or better than aluminum or grain size for all of the trace metal analytes. This finding is supported by the results of other studies on sediments from the western U.S. coastal shelf. Daskalakis and O'Connor (1995) also found that these sediments showed a much better correlation with iron (Fe) as compared to aluminum (Al). Furthermore, Lauenstein *et al.* (2000) found that it was not possible to normalize U.S. West Coast sediment trace metal concentrations using Al, because simple linear or log-linear relationships did not exist. Third, strong acid digestion has been the method most commonly employed for metals analysis in environmental monitoring programs in the Southern California Bight (SCB) for the past 25 years. Finally, sound scientific evidence supports the vital role played by various iron mineral phases in the biogeochemical cycling of trace metals in marine sediments. Thus, the concentration of trace metals from both natural and anthropogenic sources may be expected to vary as a function of iron content (Cooper and Morse 1998, Stumm 1992).

Sediment cores have been used primarily to study historical contamination trends from pre-industrial times to the present (Valette-Silver 1992, Huh and Venkatesan 1998). However, it has recently been suggested that sediment cores can also be used to determine the natural background concentrations of metals that prevailed prior to modern industrialization and the associated pollution (Lauenstein *et al.* 2000). If the trace metals in the sediments have not undergone significant post-deposition diagenetic redistribution or bioturbation, then pre-1900 sediment strata should be minimally impacted by human activity, and therefore exhibit the natural background concentrations of the constituent elements. The layers of the sediment cores are dated using radioactive tracer elements, most commonly ^{228}Th , ^{210}Pb , and ^{137}Cs (Valette-Silver 1992).

Herein, we compare natural trace metal background concentrations derived using iron-normalized regression data from two independent large-scale regional monitoring surveys to those measured sediment cores for pre-1900 strata from two additional studies.

METHODS

Sample Collection

Sediment cores were collected as part of the U.S. Department of Energy (DOE) sponsored California Basin Study (CaBS), and the National Oceanic and Atmospheric Administration (NOAA) National Status and Trends Program (NS&T) from eight locations in the Santa Monica Basin between Santa Monica Bay/Palos Verdes Peninsula and Santa Catalina Island. Two of the eight samples (CaBS) were collected in January 1990, and the remaining six cores (NS&T) were collected in September of 1991. Samples were collected at depths ranging from 200 to 500 m. The cores were collected using a Soutar box corer, and the CaBS cores were sectioned onboard ship immediately after collection. The six NOAA NS&T cores were frozen aboard ship and sectioned later in the laboratory.

The sediment cores for the U.S. Geological Survey (USGS)-SCCWRP study were collected in June of 1997 at twenty-five sites within Santa Monica Bay, at depths ranging from 10 to 200 m. Sediment cores were collected using a NEL Box corer, and separate subcores were collected for chemistry and chronology. The subcores for chronology were sent directly to the lab for analysis. The subcores for chemical analyses were kept frozen until the dating was complete (Zeng *et al.* 2001).

The samples from the two regional surveys were collected using a modified Van Veen grab sampler, of which the top 2 cm were taken for chemical analysis. For the 1994 Survey, samples were collected from 248 sites, at depths ranging from 10-200 m. For the 1998 survey, samples were collected from 290 sites, at depth ranging from 5 to 120 m. The sites for the NOAA NS&T cores were selected deliberately to enhance spatial coverage and fill existing data gaps. The sampling sites for the USGS-SCCWRP study and the two regional surveys were selected using a stratified random sampling design.

Sample Preparation and Analysis

Samples from the NOAA NS&T-DOE CaBS Cores were dated using ^{210}Pb following the method described by Huh *et al.* 1987. The USGS-SCCWRP sediment cores were dated using both ^{210}Pb and ^{137}Cs , following the method described by Alexander *et al.* (1993).

Samples from the NOAA NS&T-DOE CaBS cores were digested using a 1:1 mixture of nitric acid and hydrofluoric acid. Samples were digested in a 70°C oven overnight. Samples from the USGS-SCCWRP cores, and from the 1994 and 1995 regional surveys, were digested in a strong acid mixture of 4:1 mixture of nitric acid:hydrochloric acid (i.e., aqua regia), with refluxing on a hot plate for several hours.

The NOAA NS&T-DOE CaBS samples digestates were analyzed by either inductively coupled plasma-mass spectrometry (ICP-MS) or graphite furnace atomic absorption spectroscopy (GFAA), depending on the metal. Mercury was measured using neutron activation analysis. The digestates from the USGS-SCCWRP cores, and the samples from the 1994 and 1998 surveys, were analyzed by either ICP-atomic emission spectroscopy (EPA Method 6010), ICP-MS, or GFAA (EPA Methods 7010), depending on the concentration and nature of the analytes. Mercury was measured using cold vapor AA (EPA Method 7471).

The samples from the sediment cores and the 1994 Southern California Bight Pilot Program (SCBPP) were all analyzed by a single laboratory.. In contrast, the samples from the Southern California Bight 1998 Regional Survey (Bight'98) were analyzed by five different laboratories, none of which was the same lab used in 1994.

Data Analysis

The data from the 1994 and 1998 regional surveys were analyzed using the iron-normalization and regression approach of Schiff and Weisberg (1999) to determine the background concentrations of the target metal analytes in the Bight sediments. Briefly, sites were initially removed from consideration for background determination based upon their proximity to known contaminant sources, e.g., river mouths, POTW outfalls, and bays and harbors. This initial screening resulted in a reduced set of 115 possible stations for the 1994 survey, and 105 possible stations for the 1998 survey. Next, all values in the non-detectable range were removed from consideration. The resulting data sets for each metal were plotted with their respective iron concentrations, and a linear regression was performed. The distribution of the metal:iron ratios about the regression line were tested for normality using the Kolmogorov-Smirnov test. If the remaining sites were not normally distributed, any station with a residual greater than two standard deviations was designated an outlier and removed from consideration. The regression was then performed again, and the distribution of the remaining stations was tested for normality. This process of regression, elimination of outliers, and regression was repeated until a normal distribution of stations about the regression line was achieved.

RESULTS AND DISCUSSION

A detailed comparison of the iron-normalization and regression analysis results from the 1994 and 1998 monitoring surveys is presented in Table A1. The number of stations upon which the results are based is generally smaller for the 1998 survey relative to the 1994 survey. This is due to the fact that the stations from the 1998 survey were confined to an area closer to shore (i.e., all stations were shallow or mid-depth, <120 m); therefore more stations were impacted by anthropogenic pollution, were identified as outliers, and subsequently removed from the regression analysis. The one exception was chromium, where the number of stations upon which the baseline relationship is based was greater for the 1998 data set.

Comparisons of the results from these four independent studies are shown in Figures A-1 (a) through (i). The iron-normalization and regression line and the 99% prediction intervals obtained from the 1994 data are plotted for each of the nine trace metal analytes. The one exception is mercury, where no baseline relationship was produced from 1994 data; therefore, the 1998 iron-normalization and regression lines are used. The background stations obtained from the Bight'98 data, as well as the pre-1900 data from the sediment core stations, are overlain on the same plots for comparison. The number of stations identified as representing background levels varied by analyte, and ranged from 96 for chromium to 39 for mercury.

Most of the stations identified as background levels from the Bight'98 project plotted within the 99% percent prediction intervals for the regression relationships developed from the 1994 data. Copper is a noteworthy exception to this trend. After the iterative regression analysis had reduced the data set to 74 stations with a normal distribution about the regression line, there were 22 stations that plotted above the 1994 99% prediction interval. Although a normal distribution of stations had been achieved, there were still a significant number of outlier stations (residuals $> 2 \sigma$ away from the regression line). As a result, the iterative process was repeated until no outliers remained in the data set. This process reduced the number of stations to 50, all of which fell within the 1994 99% prediction intervals. This requirement of no outlier stations was not enforced for the other trace metals, although in most cases few outliers remained once a normal distribution of residuals was achieved.

There is remarkable agreement between the background concentration data obtained from the four different studies, especially when considering the differences in sampling locations, number of laboratories involved, and analytical methodologies. The degree of agreement among these independent data sets supports the validity of the background metal concentrations obtained via the different approaches. The validity and utility of the baseline metals relationships developed by Schiff and Weisberg (1999) have been borne out by other independent studies conducted in Santa Monica Bay (e.g., Noblet *et al.* 2001).

Based upon these results, a decision was made to use the regression equations from Schiff and Weisberg (1999) developed from the 1994 data for evaluation of the sediment chemistry results from the Bight'98 Survey. Of necessity, mercury was evaluated using the regression equation developed from the Bight'98 data.

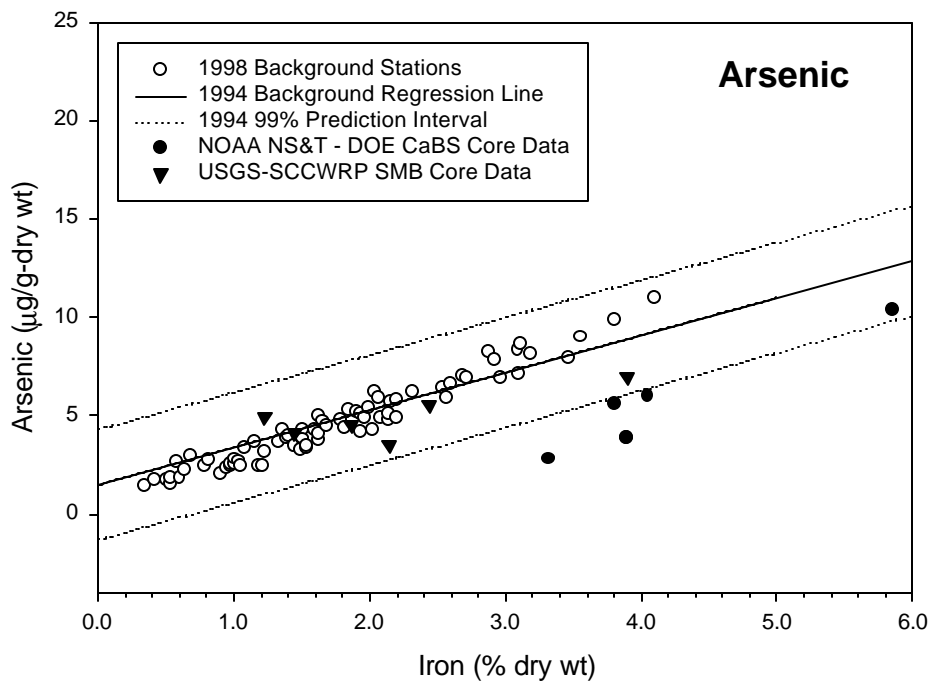
CONCLUSIONS

The iterative iron-normalization and regression approach for determining metals background concentrations appears to work very well for sediments from the SCB. This conclusion is consistent with the results of other studies, which found that iron works better than other reference elements for normalizing sediments of the U.S. western coast. This use of this approach avoids the potential problems associated with sediment core data, such as diagenetic mobilization of metals after deposition. Also, the iterative statistical approach allows for the identification and removal of data outliers. Lastly, normalization and regression has the advantage of not requiring multiple separate radioisotopic analyses to establish chronology.

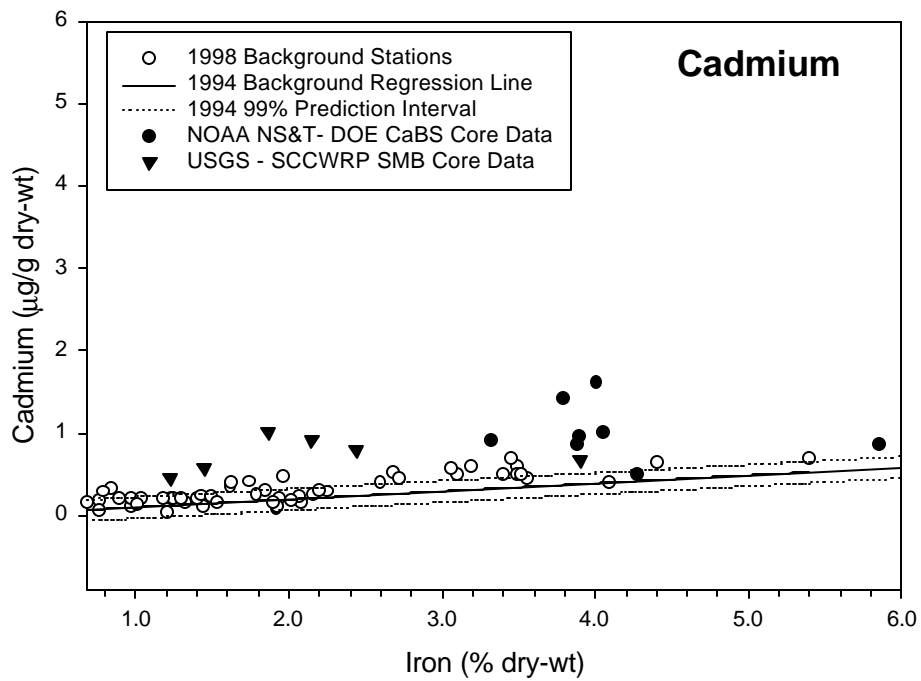
Table A-1. A comparison of the trace element: % iron linear regression and correlation data from the 1994 SCBPP (94) and the Bight '98 Regional Survey (98).

Parameter (ppm-dry : %Iron)	Sample Size	r²	Slope (m)	Intercept (b)	±99% Prediction Interval
Arsenic 94	110	0.752	1.90	1.490	2.80
Arsenic 98	74	0.950	2.413	0.343	1.31
Cadmium 94	83	0.734	0.0978	0.006	0.127
Cadmium 98	52	0.674	0.134	0.031	0.275
Chromium 94	88	0.882	16.50	-0.021	11.56
Chromium 98	96	0.903	12.46	1.947	11.73
Copper 94	96	0.833	7.40	-2.010	6.50
Copper 98	50	0.894	8.839	-3.911	5.15
Lead 94	103	0.738	4.35	0.836	5.20
Lead 98	47	0.868	3.965	0.396	3.57
Mercury 94 ¹	n/a	n/a	n/a	n/a	n/a
Mercury 98	39	0.802	0.0508	-0.0286	0.089
Nickel 94	110	0.533	9.85	-0.407	19.60
Nickel 98	71	0.857	7.654	-2.303	9.00
Silver 94	99	0.581	0.0795	-0.018	0.143
Silver 98	53	0.530	0.0809	-0.0327	0.183
Zinc 94	88	0.967	31.50	-1.95	15.45
Zinc 98	73	0.963	34.97	-10.17	17.72

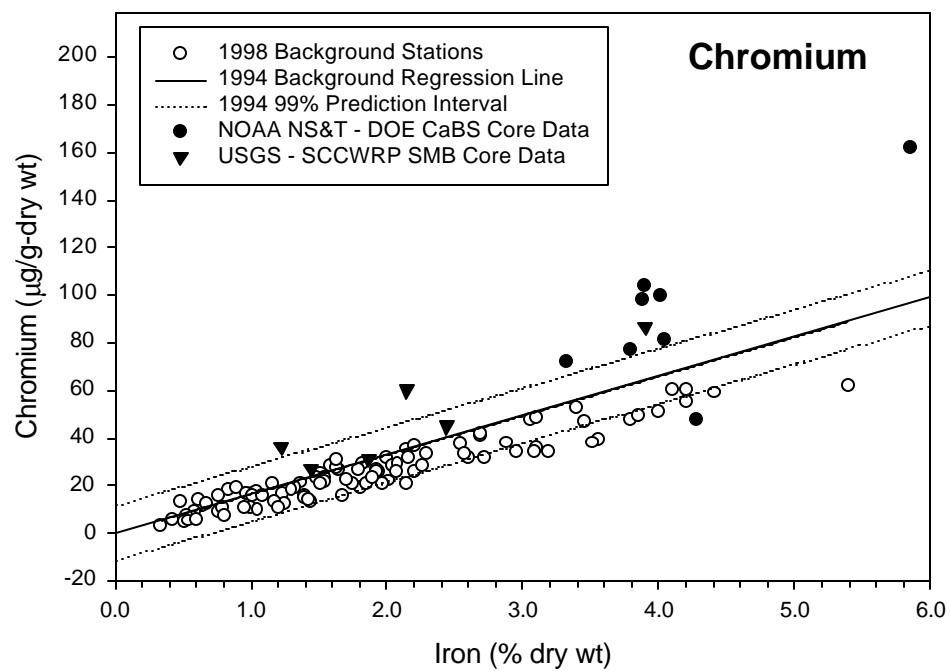
¹ No background regression line could be determined for mercury from the 1994 data.



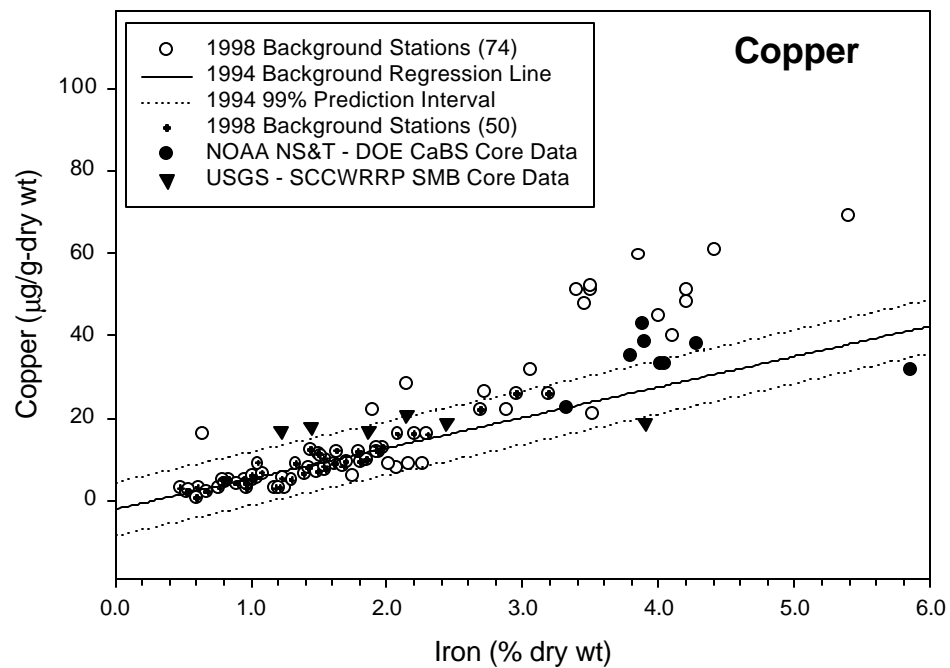
(a)



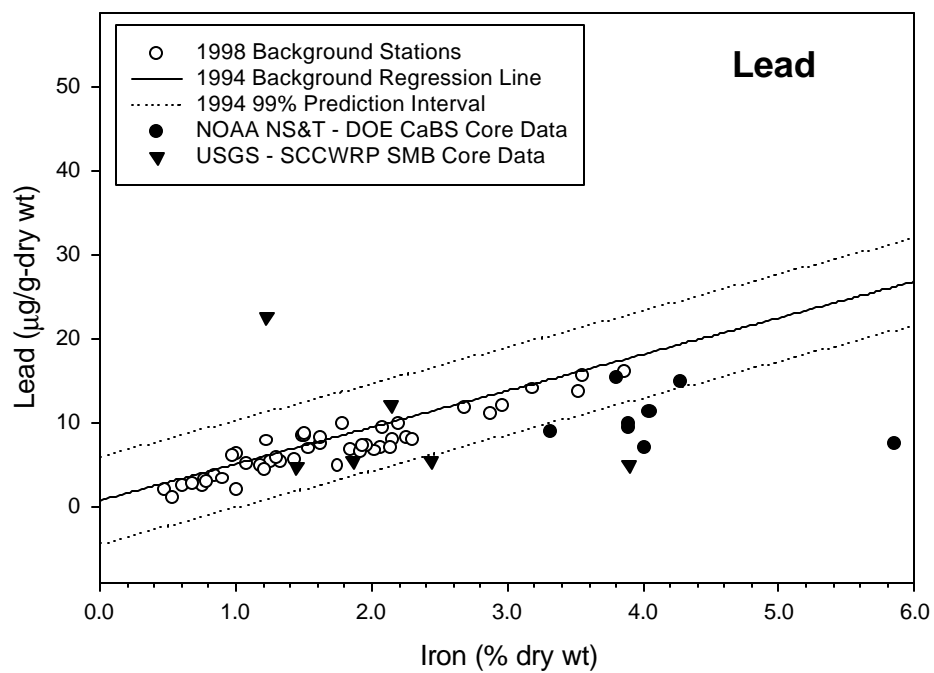
(b)



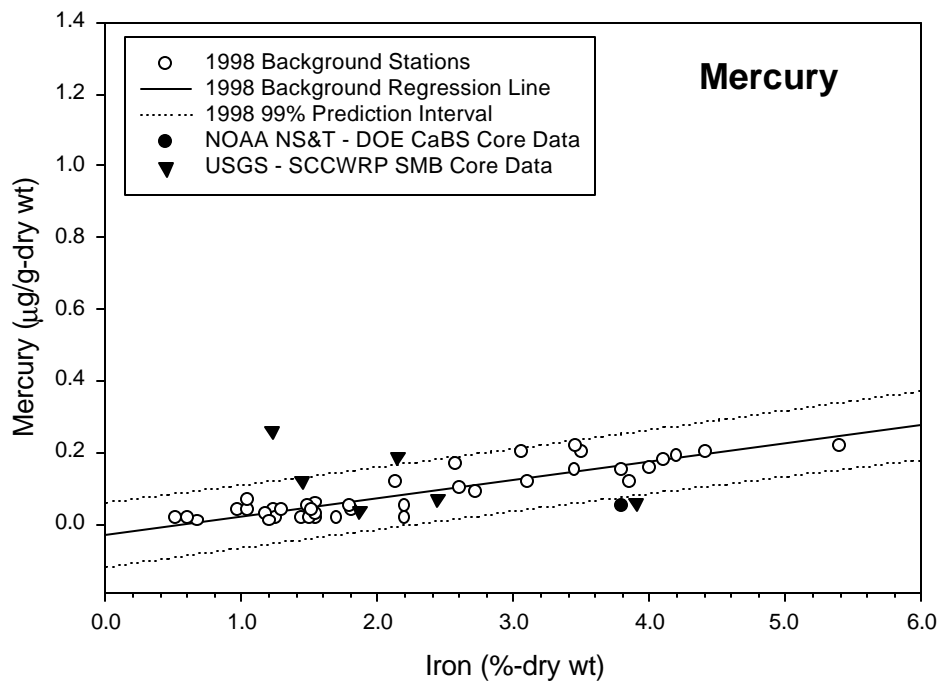
(c)



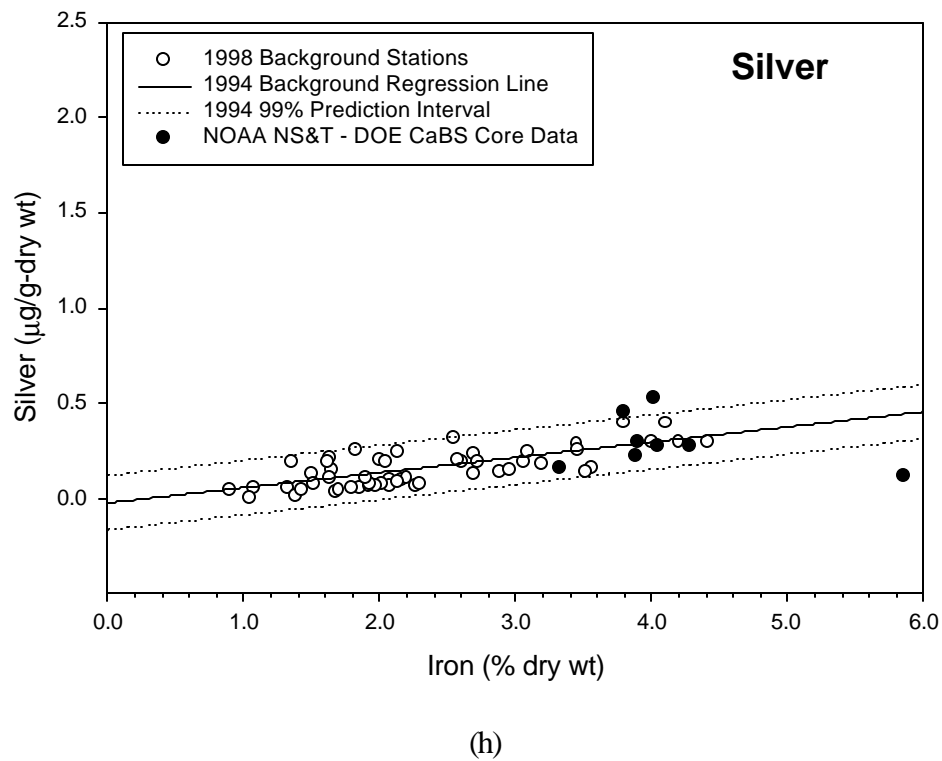
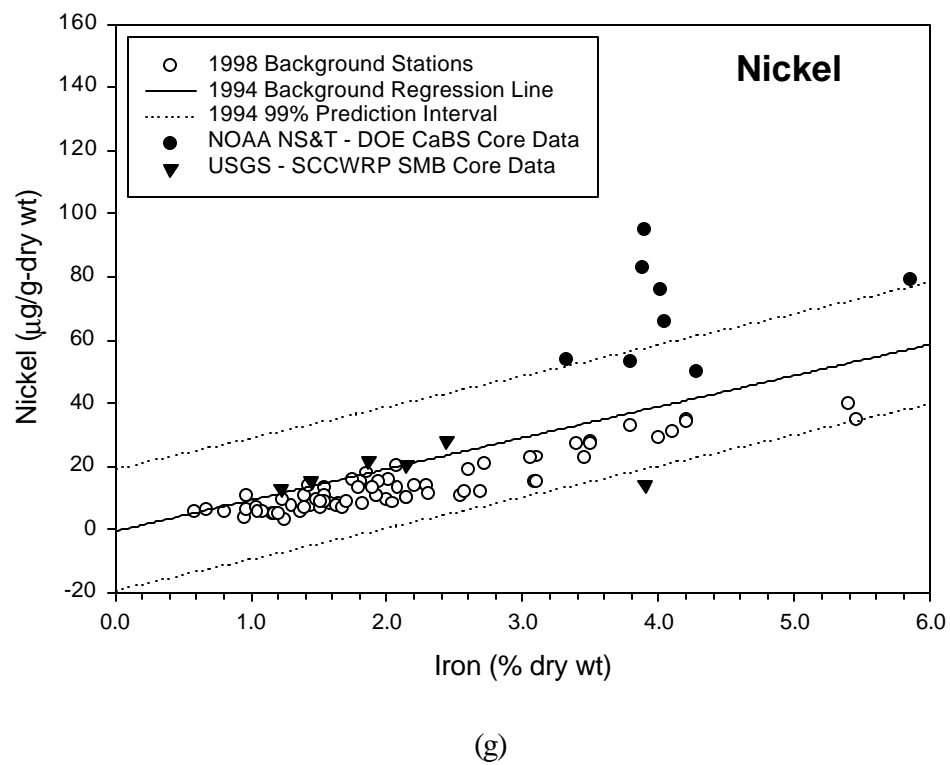
(d)

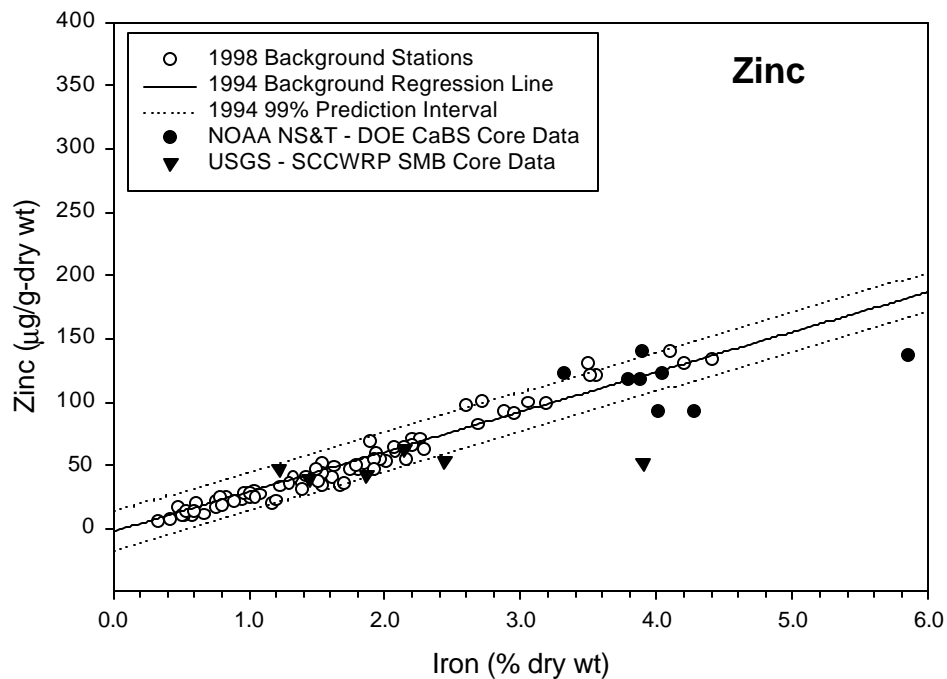


(e)



(f)





(i)

Figure A1- (a) - (i) The background stations determined for the 1998 Southern California Bight Regional Marine Monitoring Survey superimposed on the background regression lines and 99% prediction intervals from the 1994 Southern California Bight Pilot Project for the indicated element. The background iron normalization-regression results were derived using the approach of Schiff and Weisberg (1999). Also shown are two sets of sediment core data (dated pre-1900) from the same general area obtained by the NOAA National Status and Trends Program (NS&T) and the DOE California Basin Study (CaBS), and data from a joint United States Geological Survey (USGS)-SCCWRP study in Santa Monica Bay (SMB). Note that for mercury, all regression data are from the Bight'98 Survey, as no adequate background regression line could be obtained from the 1994 data. Also, the sediment core results for silver reported by the USGS-SCCWRP Study were all below detection limits.

APPENDIX B

Quality Control Charts for the Bight'98 Sediment Chemistry Analyses

INTRODUCTION

Quality control charts showing certified or laboratory control materials versus actual results were prepared to better understand and evaluate the analytical performance for the Bight'98 sediment chemistry analyses as a function of analyte and concentration. Laboratory blanks were used to monitor laboratory procedures and check for potential sources of contamination. Accuracy was assessed using a combination of certified reference materials and laboratory control materials. The local reference samples were selected to represent the type of sample matrices and analyte concentrations characteristic of the study area. Precision was assessed by analyzing approximately 10% of the samples in duplicate, requiring at least one duplicate analysis for every sample batch. The effect of different sample matrices was addressed through the use of spiked samples. Specific measurement quality objectives (MQOs) were defined for metals matrix-spiked samples, whereas organic analytes matrix-spiked samples had no specific MQOs and were used only for monitoring analytical performance.

REFERENCE MATERIALS

Reference sediment samples were used to assess accuracy for the Bight'98 chemistry analyses as prescribed in the Quality Assurance Plan (QAP). Laboratories were allowed to use either certified reference materials (CRMs) or laboratory control materials (LCMs). The CRMs and LCMs used for the Bight'98 study are given in Table B-1. The LCMs used for the Bight'98 project were two local sediments, Santa Monica Bay (SMB E6) and a sediment sample from the Palos Verdes Peninsula area (PV-7C). No CRM or LCM was used for total nitrogen analysis; however, accuracy was checked using two neat organic compounds, acetanilide and cyclohexanone-2,4-dinitrophenylhydrazine. The percent of difference from the mean certified or consensus value for each analyte was calculated as follows:

$$\% \text{ Difference from Certified Value} = \frac{(C_{\text{sample}} - C_{\text{reference}})}{C_{\text{reference}}} \times 100$$

The percent of difference from the CRM or LCM values for all analytes were plotted versus concentration to evaluate analytical accuracy. These quality control charts are presented in Figures B-1 through B4. For the organic compounds, not all the Bight'98 target analytes had certified values in the CRMs used. Therefore, the points plotted in the QC charts are only for compounds that had certified values in the CRM or LCM used. All target trace metal analytes had certified values in one of the two commercial CRMs used.

Table B-1. The certified reference materials (CRMs) and laboratory control materials (LCMs) used for quality control during the Bight'98 Survey.

Analytes	CRMs	Certifying Agency/Supplier ¹	LCMs
Trace Organics	SRM 1941a	NIST	PV-7C SMB E6
Trace Metals	CRM 16-050 Lot L516 EPA PPS-46 Lot 237	RTC ERA	PV-7C
TOC	PACS-1	NRC	N/A

¹NIST – National Institute of Standards and Technology (US Dept. of Commerce); RTC-Resource Technology Corporation (Laramie, WY); ERA- Environmental Resource Associates (Arvada, CO); NRC – National Research Council of Canada.

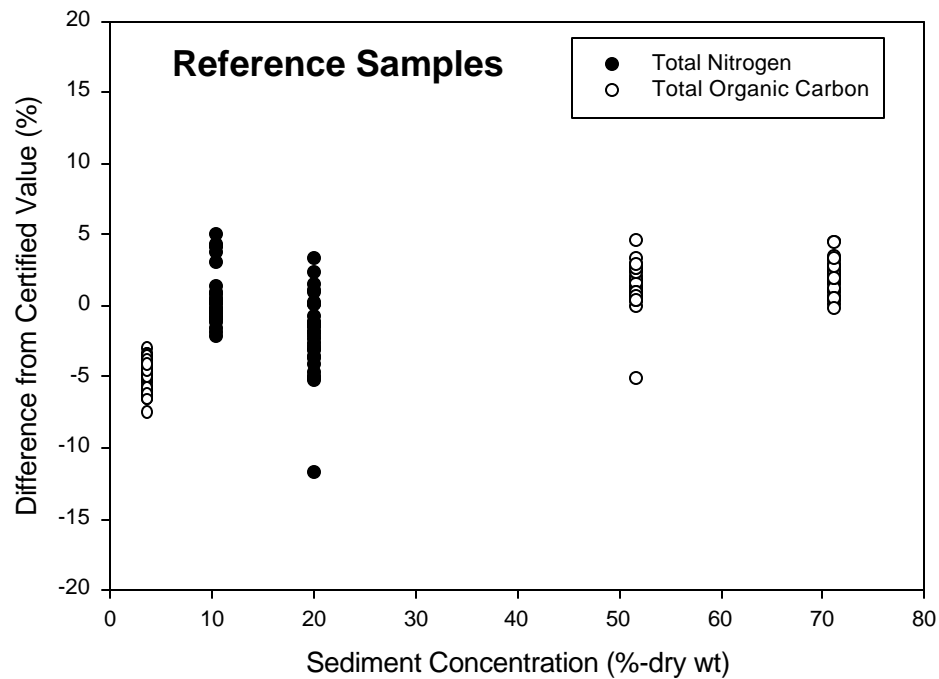


Figure B1. Quality control chart showing the results from the analyses of QC reference samples performed during the Bight'98 Survey for total nitrogen and total organic carbon.

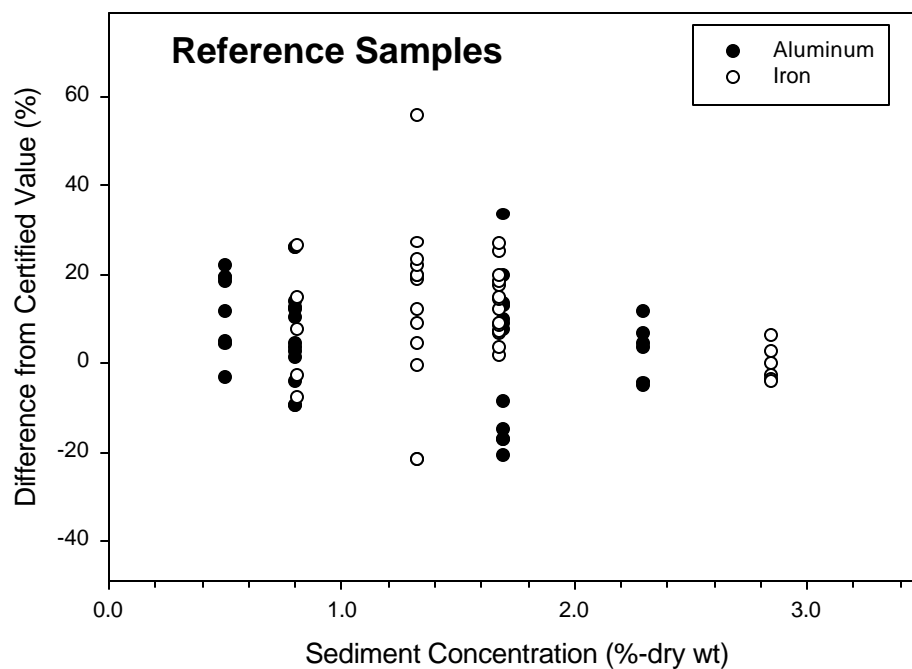


Figure B2. Quality control chart showing the results from the analyses of QC reference samples performed during the Bight'98 Survey for aluminum and iron.

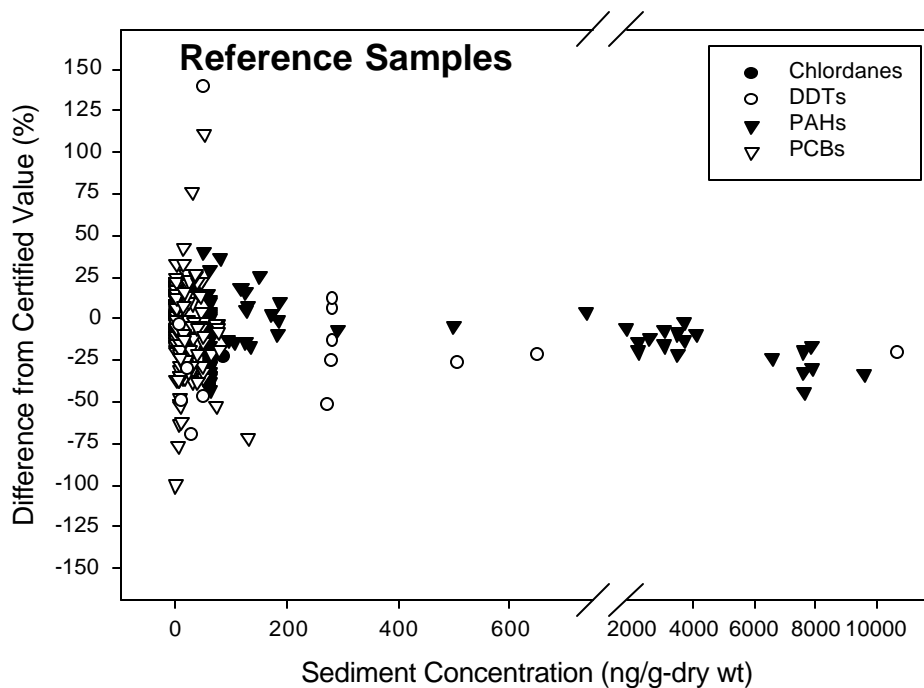


Figure B3. Quality control chart showing the results from the analyses of QC reference samples performed during the Bight'98 Survey for trace organic analytes.

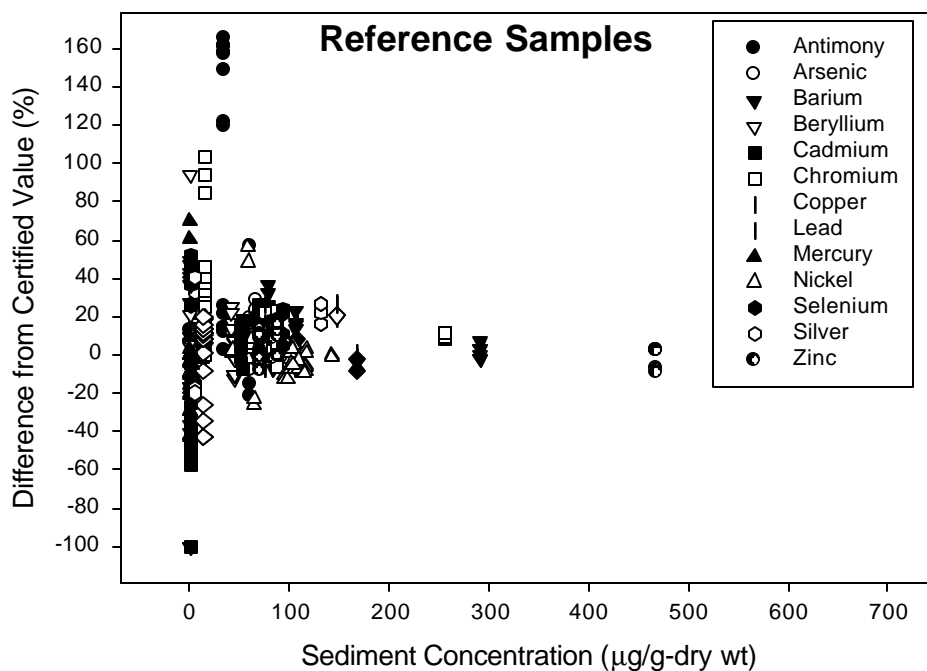


Figure B-4. Quality control chart showing the results from the QC analyses of reference samples performed during the Bight '98 study for trace metal analytes.

As shown in Figures B-1 through B-4, the greater deviations from the certified values occur only at very low concentrations and accuracy increases dramatically with increasing concentrations. This result is consistent with the performance expected for any analytical method under optimum conditions. Moreover, the analytical results observed for most analytes were within the acceptable ranges specified in the CRMs. Typically, CRMs are accompanied by documents that specify the mean concentration for each analyte, as well as a range of values that are considered acceptable. The CRM may have multiple certified values associated with different analytical methodologies. Also, the range of acceptable values can vary substantially from one analyte to another. Therefore, although most of the results meet the criteria specified in the Bight'98 QAP, the single MQOs specified therein for groups of analytes, i.e., metals and organics, is somewhat unrealistic.

DUPLICATE ANALYSES

Analytical precision was assessed by analyzing duplicate samples for approximately 10% of the sediment samples in the Bight'98 Survey (~ 30 samples). The agreement between two measurements was quantified by calculating the relative percent difference (RPD) as follows:

$$RPD = \frac{(C_1 - C_2)}{(C_1 + C_2)/2} \times 100$$

Where C_1 and C_2 are the measured concentrations in the sample for the duplicate analyses, and also $C_1 = C_2$. The RPDs for all analytes were plotted versus concentration for all analytes, and the results are shown in Figures B-5 through B-7. Most of the samples were within the acceptable ranges for precision; i.e., < 30% RPD for trace organics and < 25% for trace metals specified in the Bight'98 QAP. The few samples that exceeded the precision criteria were all below 50% RPD. Moreover, a general increase in precision was evident with increasing concentration for metals and trace organics, consistent with the trend observed for the reference materials.

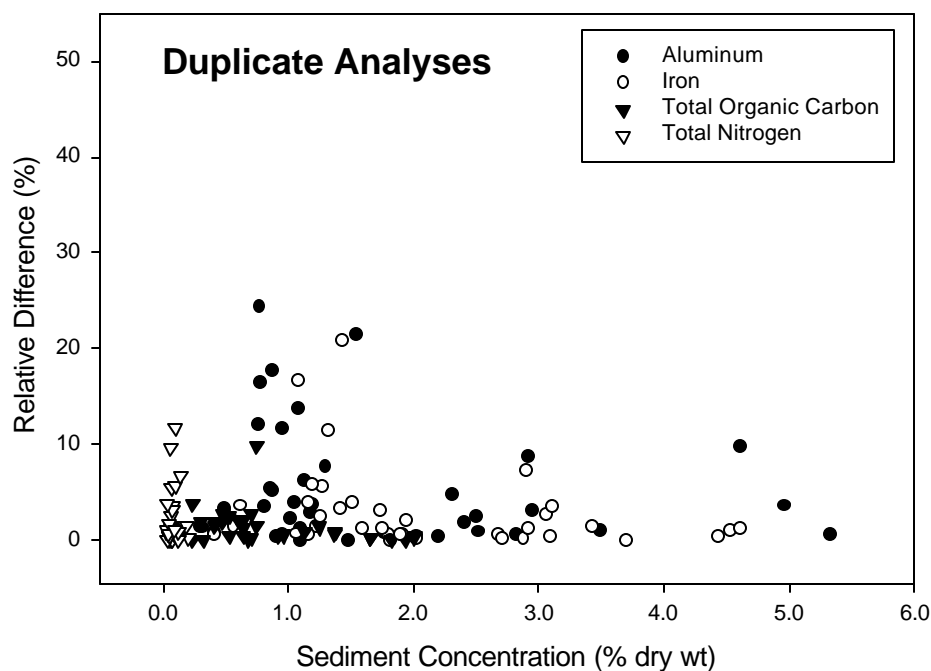


Figure B-5. Quality control chart showing the results from the duplicate QC sample analyses performed during the Bight'98 study for aluminum, iron, total nitrogen, and total organic carbon.

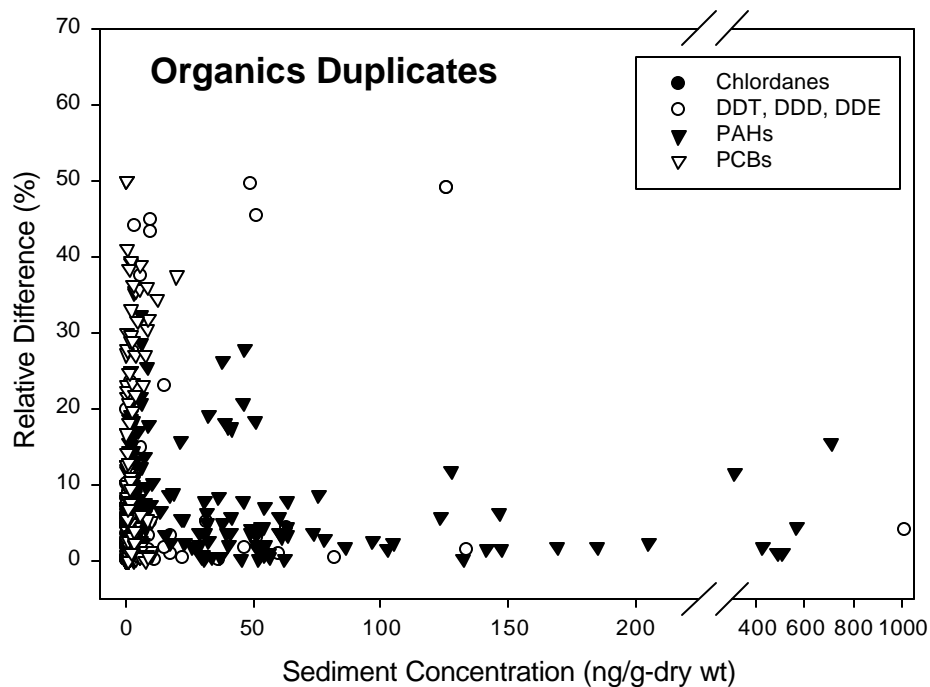


Figure B-6. Quality control chart showing the results from the duplicate QC sample analyses performed during the Bight '98 study for trace organic analytes.

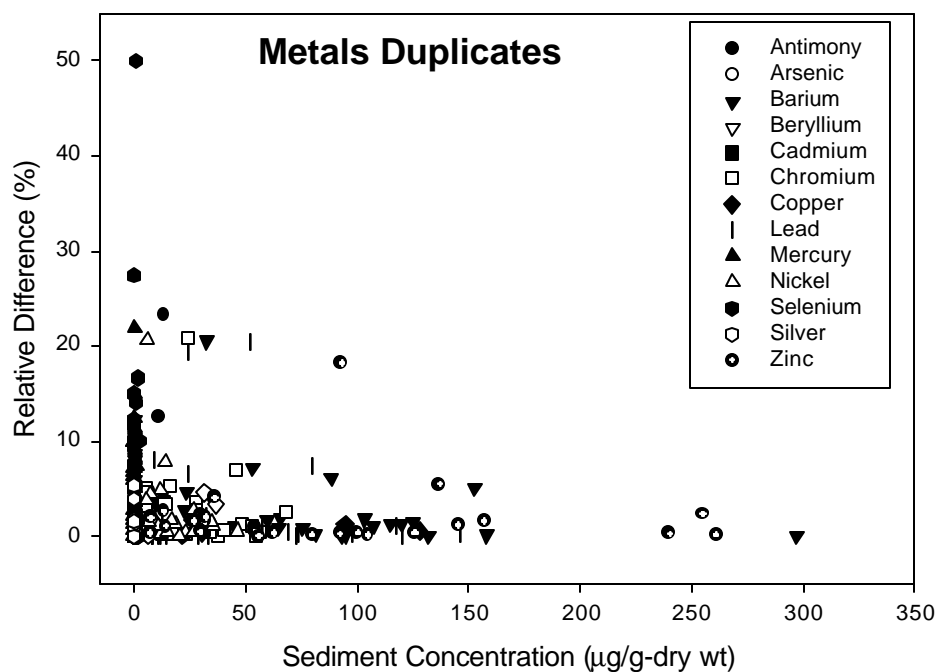


Figure B-7. Quality control chart showing the results from the duplicate QC sample analyses performed during the Bight '98 study for trace metal analytes.

MATRIX SPIKED SAMPLES

Separate aliquots from selected sediment samples (one per analytical batch) were spiked with target analytes and re-analyzed to assess effects due to matrix differences between the SCB samples and the CRMs., and also among samples from within the study area. Specific MQOs were given for metals analytes in the Bight'98 QAP, but no specific MQOs were identified for trace organics. Instead, the results from the samples spiked with organic analytes were used for ongoing assessment and monitoring of analytical performance. The difference between the calculated and measured values for the spiked sediment samples was expressed as the percent of difference from the calculated value, which was calculated as follows:

$$\% \text{ Difference from the Calculated Value} = \frac{[C_{\text{measured}} - (C_{\text{original}} + C_{\text{spike}})]}{(C_{\text{original}} + C_{\text{spike}})} \times 100$$

Where C_{measured} is the measured concentration of an analyte in the spiked sample, C_{original} is the original measured concentration of the analyte in the sample before spiking, and C_{spike} is the contribution to the sample analyte concentration due to spiking. The plots of percent of difference versus concentration for all the analytes are shown in Figures B-7 through B-9. The plots for aluminum, iron, and trace organics do not follow the trend exhibited by the previous QC plots toward increasing accuracy with increased analyte concentration. This is expected in the case of iron and aluminum, because even the lowest concentrations for these analytes are 0.4 % (i.e., 4,000 $\mu\text{g/g}$). Therefore, all samples are far above the method detection limits for these analytes, and the increased measurement error associated with the lower concentrations is not observed. The constant variability over a wide concentration range observed for the trace organic analytes is not as easily explained. In contrast, the plot for the trace metal QC analyses shows a clear trend toward decreasing variability with increasing concentration.

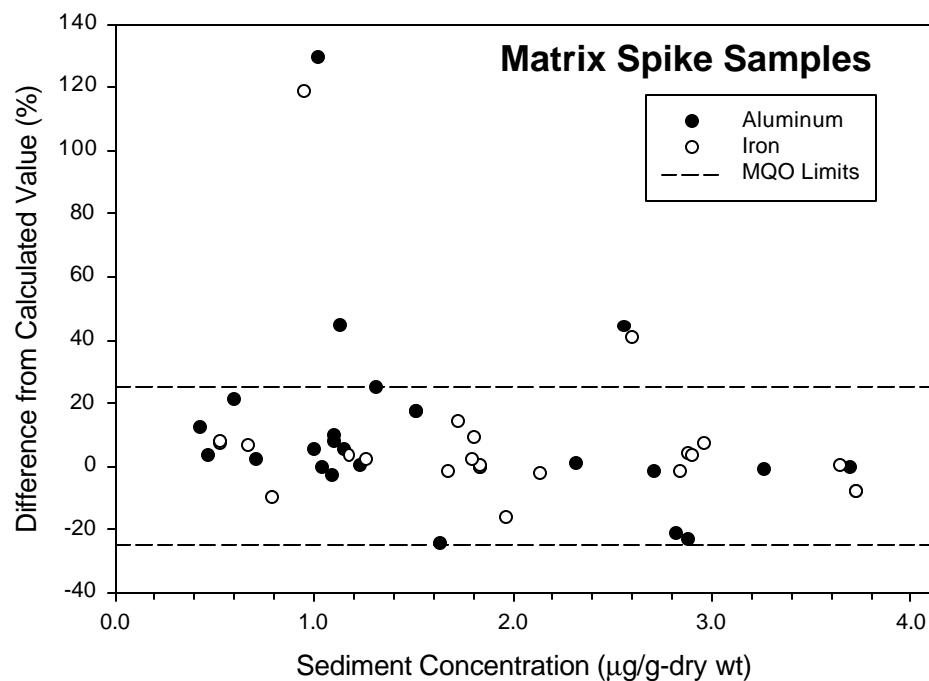


Figure B8. Quality control chart showing the results from the matrix spike QC sample analyses performed during the Bight '98 Survey for aluminum and iron.

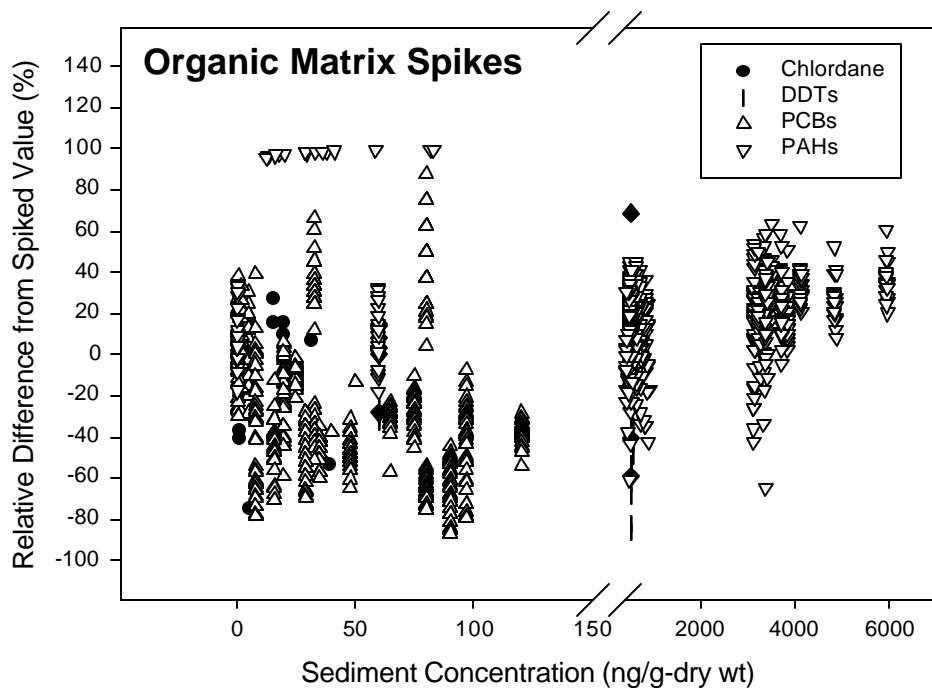


Figure B9. Quality control chart showing the results from the matrix spike QC sample analyses for trace organics performed during the Bight '98 Survey.

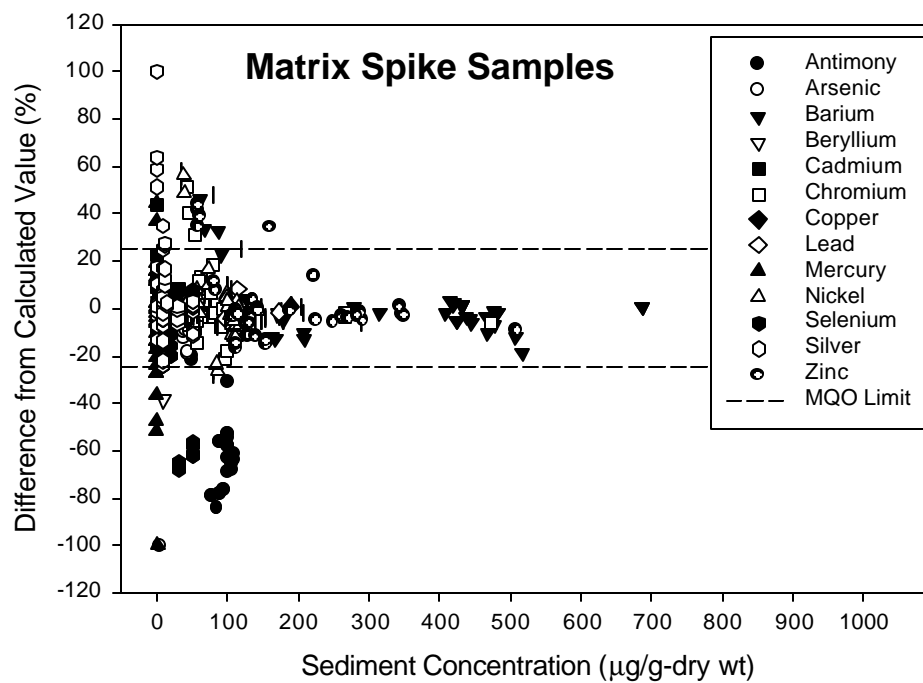


Figure B-10. Quality control chart showing the results from the matrix spike QC sample analyses for trace metals performed during the Bight '98 Survey.

APPENDIX C

Principal Components and Cluster Analysis

Sediment Contaminant Patterns Within Coastal Areas of the Southern California Bight: Multivariate Analyses of Bight'98 Regional Monitoring Survey Data

Charles R. Phillips, Science Applications International Corporation

ABSTRACT

Patterns in sediment metal, polycyclic aromatic hydrocarbon (PAH), chlorinated pesticide, and polychlorinated biphenyl (PCB) concentrations at 290 sites within coastal, port, harbor, and marina areas of the Southern California Bight (SCB) were evaluated using the multivariate techniques cluster analysis and principal components analysis (PCA). Cluster analysis identified five primary site groups, with two large groups representing 96% of the total area of the SCB. One of these two groups contained many of the open coastal sites, characterized by relatively coarse-grained sediments (~20% fines), low organic carbon, and low contaminant concentrations. The second large cluster group included a higher proportion of the embayment, marina, and harbor sites, with finer-grained sediments and proportionately higher mean concentrations of most metals and trace organics. Both site groups were considered representative of SCB background conditions with minimal contaminant inputs. The other three site groups exhibited elevated concentrations of one or more contaminants, but accounted for only 4% of the total area of the SCB. In particular, two small cluster groups consisted mainly of port, harbor, and marina sites with elevated mean concentrations of certain metals (e.g., Cu, Pb, Sb, and Zn), as well as elevated chlordane, PAH, and PCB concentrations for one of the two site clusters. The fifth cluster group consisted of Palos Verdes Shelf sites that were characterized by high sediment DDT, PCB, Cd, and Ba concentrations, and were clearly different from other open coastal sites in the SCB. PCA identified four principal components that explained 67% of the variance in the data set. The first two components (PC1 and PC2) accounted for 52% of the total variance. PC1 was highly loaded with a suite of metals (Cu, Pb, Hg, Zn, Al, and Fe), with high scores primarily for industrialized port and harbor sites. PC2 had high loadings for DDTs, PCBs, and Cd, with highest scores for sites on the Palos Verdes Shelf. PC3 and PC4 each accounted for less than 10% of the total variance, with high loadings for low- and high-molecular-weight PAHs and for a subset of metals (Ba, Ni, and Se) and fines, respectively. Although contaminant sources were not analyzed for this study, PC1 and, to a lesser extent, PC3 likely reflected recent industrial inputs to ports, commercial shipping, and boatyard operations, and small marina activities. In contrast, PC2 reflected historical, wastewater-derived inputs to the Palos Verdes Shelf. Distinct sediment contaminant patterns were not evident for other large and small wastewater or riverine discharges.

INTRODUCTION

Nearshore portions of the Southern California Bight (SCB) are affected to varying degrees by chemical contaminants from multiple sources (Schiff *et al.* 2000; Eganhouse and Venkatesan 1993). Contaminant sources include wastewater and industrial discharges, runoff from urbanized and agricultural areas, commercial and recreational vessel activities, oil and gas operations, and dredged material disposal, as well as atmospheric deposition and natural oil seeps (Anderson *et al.* 1993). Bottom sediments in coastal environments represent a potential sink for chemical contaminants, including many trace metals, organochlorines (e.g., DDTs and PCBs), and polycyclic aromatic hydrocarbons (PAHs), which typically have strong affinities for particles. Consequently, contaminant patterns in bottom sediments are expected to manifest the chemical characteristics as well as the magnitude and proximity to these inputs.

The Bight'98 Regional Monitoring Program collected sediment samples at 290 sites throughout coastal portions of the SCB including commercial ports, harbors, and marina areas (Bight'98 Steering Committee 1998). Concentrations of suites of metals, organochlorines, and PAHs were analyzed using comparable, performance-based methods. Previous studies of sediment contaminants focused primarily on specific sites or portions of the SCB, such as Palos Verdes Shelf (Lee 1994, Eganhouse *et al.* 2000), Port of Los Angeles (Malins *et al.* 1987), and San Diego Bay (McCain *et al.* 1992, Fairey *et al.* 1998), which represent only a small fraction of the total nearshore area of the SCB. The 1994 Southern California Bight Pilot Project (SCBPP; Schiff 1999, Schiff and Gossett 1998) provided synoptic sampling of coastal portions of the SCB, excluding ports and harbors, for a subset of possible contaminants. The state Bay Protection and Toxics Cleanup Program (BPTCP) evaluated sediment quality within several coastal harbors and embayments (e.g., Fairey *et al.* 1998; Phillips *et al.* 1998). State and national Mussel Watch programs evaluated water quality at fixed but widely-spaced, nearshore locations along the coastline and inside ports and harbors (O'Connor 1996, Stephenson *et al.* 1995). Mearns *et al.* (1991) also characterized sediment quality within ports, harbors, and coastal portions of the SCB based on contaminant data from multiple studies conducted over a period of decades. Generally, however, these regional characterizations of sediment contaminant patterns have been limited by the lack of synopticity, methodological incompatibility, and spatially limited sampling. Therefore, the Bight'98 program provided a unique data set for evaluating input sources, pathways, and sinks of anthropogenic contaminants throughout the SCB.

This report evaluates spatial and compositional patterns in the Bight'98 sediment contaminant data using the multivariate techniques cluster analysis and PCA. Specifically, the objective was to identify sites with similar contaminant signatures and areal patterns that may infer sources and transport pathways. PCA and cluster analyses are particularly effective as exploratory tools for evaluating compositional patterns within large and complex data sets, and can reveal relationships among parameters and sampling locations that provide insight into contaminant sources and sinks. PCA was used previously by Phillips *et al.* (1997) to evaluate possible sources of sediment contaminants for the San Pedro Shelf area of the SCB, and cluster analysis was used by Anderson and

Gossett (1987) to evaluate patterns in sediment PAH concentrations at 24 sites in the SCB. Although sediment contaminant patterns at selected sites within the SCB have been well-characterized by previous studies, multivariate analyses are considered useful for interpreting larger scale spatial patterns that might be related to similar input sources or transport pathways. These results are also expected to provide a regional framework for interpreting sediment toxicity and biological community data.

METHODS AND MATERIALS

Sediment samples were collected from July through September, 1998, at 290 sites throughout the SCB (Figure C-1). The station array used for the Bight'98 Survey was based on a variable-density, stratified random sampling design described by Stevens (1997). Sites were assigned *a priori* to one of nine strata: large, publicly owned treatment work (LPOTW), small POTW (SPOTW), mid-shelf POTW, river, shallow shelf, mid-shelf, marina, port, and bay/harbor. Samples were from the top 0-2 cm of grabs (Van Veen grab) as representative of recently deposited sediments.

Analytical methods and data quality objectives for chemical analyses of sediment samples were described by the Bight+'98 Steering Committee (1998). Target analytes and corresponding ranges in method detection limits (MDL) are listed in Table C-1. Variations in MDLs for individual analytes reflected differences among participating laboratories in specific methods and capabilities. Although chemical analyses were performed by multiple laboratories, extensive intercalibrations were performed prior to and during the study to ensure data comparability.

A complete data matrix was prepared for individual and summed variables listed in Table C-2 and all 290 sites. Values corresponding to one-half of the reporting limits were substituted for non-detectable results. Values for summed variables (e.g., total DDTs) represented the summed concentrations of all detected components, while concentrations of non-detected components were treated as zero. In cases where all components of summed variables were below detection limits, values corresponding to one-half of the method detection limits for individual components were substituted, and surrogate values were summed. Prior to PCA, concentrations of individual variables were standardized by setting the mean to zero and variance to one. PCA then was performed on the correlation matrix, and factors were rotated using Varimax rotation to better align the directions of factors with the original variables, thereby making the factors more interpretable. Factor scores from the first four principal components were saved and analyzed by hierarchical cluster analysis using the Ward clustering option. The number of primary cluster groups was selected by visually inspecting the plot of cluster distance between successive cluster joins in the dendrogram and distributions of data points for bivariate plots of principal component scores. PCA and cluster analyses were performed using JMP software (SAS Institute 2001).

RESULTS

Cluster Analysis

The dendrogram obtained from cluster analysis of PCA scores indicated five primary cluster groups (Figure C-2) with varying numbers of sites per cluster (Table C-3). Spatial distributions of the cluster groups are shown in Figure C-1. The two largest cluster groups (Cluster Groups 1 and 2) accounted for 84% of the 290 sites and 96% of the corresponding study area, whereas the remaining three cluster groups combined accounted for only 46 of the sites and approximately 4% of the area. Mean concentrations of sediment contaminants associated with each site cluster are listed in Table 4.

Cluster Group 2, which contained the largest number of sites and accounted for the greatest proportion of the study area, comprised 148 shelf and 38 embayment sites consisting of shallow-shelf and mid-shelf (36%), LPOTW and SPOTW (13% and 16%, respectively), river (14%), and port/harbor/marina (21%) strata. All of the shallow-shelf and mid-shelf sites on the 30-m and 60-m depth contours, coinciding with locations sampled historically for the SCCWRP Reference Site Surveys (SCCWRP 1987, 1992), were part of this site cluster. Sediments were characterized by low proportions of fines, low total organic carbon (TOC) concentrations, and consistently lower contaminant concentrations than those of other cluster groups.

Cluster Group 1 comprised a relatively higher proportion of port, marina, and bay/harbor sites (21, 24, and 13%, respectively) and lower proportion of coastal (primarily mid-shelf, SPOTW, and river) sites, than Cluster Group 2. Many of the coastal sites included in this cluster were from a depositional region in the eastern Santa Barbara Channel characterized by relatively high proportions (46 to 99%) of fine-grained sediments, described previously by Kolpack (1986). Cluster Group 1 sediments contained higher average TOC content, and, with the exceptions of Ag and Sb, higher contaminant concentrations than those in Cluster Group 2. These differences may be attributable in large part to the relatively higher proportions of fines comprising Cluster Group 2 sediments and strong affinities of contaminants for fine-grained sediments.

With one exception (Station 2382 in Santa Monica Bay), Cluster Groups 3 and 4 consisted exclusively of industrialized harbor and marina strata sites. Cluster Group 3 contained three sites from Port of Los Angeles/Long Beach, two sites from San Diego Bay, and one site in Marina Del Rey. All of these sites were located in the inner portions of ports and harbors near industrial operations with limited circulation. Cluster Group 4 comprised 21 port, harbor, and marina sites in San Diego Bay; seven marina sites in Newport and Marina Del Rey harbors; six sites in the Port of Los Angeles/Long Beach, and one shallow-shelf site (Station 2382) that, unlike the Cluster Group 3 sites, was not confined to the inner portion of industrialized harbor areas. Cluster Groups 3 and 4 sediments contained elevated Cu, Hg, Pb, Zn, and Sb concentrations, whereas Cluster Group 3 sites also were distinguished by elevated LPAH, HPAH, PCB, and chlordane concentrations. Cluster Group 5 comprised five sites on the Palos Verdes Shelf (four

LPOTW and one shallow-shelf strata), generally northwest of the Joint Water Pollution Control Plant (JWPCP) outfalls, characterized by elevated DDT, PCB, Cd, and Ba concentrations.

Principal Components Analysis Results

The first four principal components of the PCA accounted for 67% of the total variance of the data set (Table C-5). Principal Components 1 and 2 (PC1 and PC2) explained 41 and 11%, respectively, of the variance, while PC3 and PC4 combined accounted for 16% of the variance. All other factors explained less than 5% of the variance and were not retained for further evaluation.

The highest PC1 loadings were for Cu, Hg, Zn, Pb, Al, and Fe. High factor loadings imply that these metals contributed to and strongly influenced the principal component (Zitko 1994). The highest scores for PC1 corresponded primarily to harbor and port strata sites, especially in San Diego Bay and the Port of Los Angeles/Long Beach, as well as marina strata sites within Newport and Marina Del Rey harbors and LPOTW strata sites near wastewater outfalls on the Palos Verdes Shelf. Factor scores give the positions of the samples in coordinates of the principal components, and the magnitude of scores corresponds to the extent to which individual sites reflect these attributes (i.e., elevated concentrations of metals with high loadings) and the amount of information for that site explained by the factor. High loadings for Fe and Al suggested that PC1 also included portions of the variance associated with natural patterns in sediment geochemistry (Schiff and Weisberg 1999).

The highest loadings on PC2 were for DDT, PCB, and Cd. High PC2 scores were, with minor exceptions, associated exclusively with LPOTW strata sites near the JWPCP and Hyperion Wastewater Treatment Plant (Hyperion) outfalls on the Palos Verdes Shelf and Santa Monica Bay, respectively. Low- and high-molecular-weight PAHs and, to a lesser extent, chlordane had the highest loadings on PC3. The highest PC3 scores were associated with port strata sites in San Diego Bay and the Port of Los Angeles/Long Beach and LPOTW strata sites associated with JWPCP and Hyperion outfalls. PC4 appeared to be associated mainly with Se, Ni, Ba, and fines, although the magnitude of the highest loading values were all less than 0.8. Sites with the highest PC4 scores corresponded to LPOTW, port, and marina strata, especially within San Diego Bay.

Bivariate plots of PCA scores shown in Figure 3 illustrate differences in sediment contaminant patterns for individual cluster groups. Density ellipses were computed from the bivariate normal distribution fits to the X and Y variables, and the ellipses delineate expected distributions of 95% of the data (PCA scores) for individual cluster groups. Relatively large ellipses associated with Cluster Groups 3 and 5 reflect the correspondingly large variances in contaminant concentrations. The plot of PC1 versus PC2 shows separation along PC1 for Cluster Groups 3 and 4, reflecting the elevated concentrations of highly loaded metals (e.g., Cu, Zn, and Pb) within these port and harbor

sites, and separation of Cluster Group 5 along PC2 associated with elevated concentrations of DDT, PCB, and Cd on the Palos Verdes Shelf. Although Cluster Group 2 overlapped with that of Cluster Group 1, the positive offset along PC1 reflected the consistently higher mean sediment metal concentrations associated with the Cluster Group 1 sites. Biplots of PC2 versus PC3 show considerable overlap along PC3 for all but Cluster Group 3, reflecting the presence of elevated PAH concentrations at these inner harbor sites.

DISCUSSION

Spatial patterns for sediment contaminants described by PCA and cluster analyses were internally consistent and, with some exceptions, in general agreement with results from previous site-specific and regional SCB studies (e.g., Mearns *et al.* 1991). PCA and cluster analyses indicated that the major portion (74%) of the SCB, primarily comprising areas of the open coast and shelf represented by Cluster Group 2, was characterized by sediments with generally low contaminant concentrations. The exception, represented by Cluster Group 5, reflected the uniqueness of the Palos Verdes Shelf compared to other shelf sites. A second group of sites represented by Cluster Group 1, comprising 22% of the SCB area, included harbor sites characterized by finer grained sediments with slightly higher contaminant concentrations than those for Cluster Group 2. Although the average concentrations were higher than those of Cluster Group 2 sites, the differences were consistent with the higher proportions of fine grained sediments and not necessarily due to greater contaminant inputs. Cluster Groups 3 and 4 represented subsets of port, harbor, and marina sites containing elevated sediment contaminant concentrations but, together with Cluster Group 5, represented less than 5% of the SCB area.

Although results from the multivariate analyses were consistent with previous studies, they did not indicate a close correspondence between cluster groups and the original site strata. Instead, primary distinctions appeared to be between relatively uncontaminated (Cluster Groups 1 and 2) and contaminated (Cluster Groups 3, 4, and 5) sites, while distinctions between Cluster Groups 1 and 2 appeared to be driven by differences in grain size and proportional differences in bulk contaminant concentrations. The background clusters included sites from all strata. Other than the JWPCP outfalls on the Palos Verdes Shelf, LPOTW strata sites near the Hyperion, Orange County Sanitation District (OCS), and Point Loma outfalls, and most SPOTW sites, were associated with Cluster Group 2 and, to a lesser extent, with Cluster Group 1. Associations of LPOTW sites near the OCS and Point Loma outfalls with the background coastal site cluster are reasonable based on the general absence of significant sediment contamination in the vicinity of these outfalls (Phillips *et al.* 1997; Zeng and Vista 1997). In contrast, sediments in the vicinity of the Hyperion outfall in Santa Monica Bay contained elevated Ag ($1.4\text{--}7.5\text{ }\mu\text{g g}^{-1}$), Hg ($0.13\text{--}0.7\text{ }\mu\text{g g}^{-1}$), and DDT (up to 100 ng g^{-1}) concentrations, and sites near the outfall terminus had high scores for PC2 and PC3. Similarly, during the 1994 SCBPP, approximately 80% of the sites in Santa Monica Bay were enriched in three or more metals, especially Ag, Cd, and Cr (Schiff and Weisberg 1999) that likely represented residual contamination from discontinued sludge discharges (Zeng and

Venkatesan 1999). Regardless, sediment contaminant patterns near the Hyperion outfall appeared to be more similar to those of other shelf areas described by Cluster Group 2 than to contaminant patterns associated with the Palos Verdes Shelf and Cluster Group 5. However, removal of outlier data associated with the Palos Verdes Shelf sites likely would have resulted in greater distinctions for cluster analysis between Hyperion and other LPOTW sites.

It is also noteworthy that, other than a single site near the mouth of the Los Angeles River in the Port of Long Beach, river strata sites occurred only in the background Cluster Groups 1 and 2, and sediments from river mouth locations did not exhibit any discernable chemical signatures (i.e., for the suite of measured contaminants) other than slightly elevated chlordane concentrations that might be associated with runoff. Chlordanes were moderately loaded on PC3, but this factor explained less than 10% of the total variance of the data set, and none of the river strata sites had particularly high scores for PC3. The absence of a strong runoff signal may be due in part to physical mixing processes that typically minimize deposition and accumulation of particle-associated contaminants at the mouths of coastal rivers. Regardless, this is contrary to expectations because previous studies have indicated that river discharges can be significant sources of runoff-derived pollutants as well as fine-grained sediments to coastal areas of the SCB (Schiff *et al.* 2000).

While Cluster Groups 1 and 2 were characterized as background sites for embayment and open coastal areas, respectively, it is useful to compare the area-weighted mean (AWM) concentrations calculated for these cluster groups to corresponding reference values reported previously for the SCB (Table C-5). Cluster Group 2 AWM values for metals and several organic contaminants were generally comparable to average concentrations reported for the 1985 and 1990 Reference Site Surveys (SCCWRP 1987, 1992), as well as AWM concentrations for reference site locations sampled as part of the Bight'98 program. The AWM metal concentrations for Cluster Groups 1 and 2 also show reasonably good agreement with values predicted using regression coefficients for baseline metal:iron relationships developed by Schiff and Weisberg (1999) for non-enriched sediments within the SCB. However, the AWM concentrations for Ag, Cd, and Pb in Cluster Group 2 sediments were up to several-fold higher than predicted baseline levels, indicating some degree of sewage- and/or runoff-derived contamination. Furthermore, sediments from Cluster Groups 1 and 2 typically contained measurable amounts of synthetic organic compounds (DDT, PCB, and chlordanes) which are not consistent with pollution-free conditions. For comparison, the SCBPP detected DDT in 89% of the SCB sediments during 1994 (Schiff *et al.* 2000), and Schiff and Weisberg (1999) concluded that 61% of SCB sediments contained elevated concentrations of one or more metals. Therefore, while the AWM concentrations reflected minimal contaminant inputs that characterize a large portion of the SCB, Cluster Groups 1 and 2 sediments were not "pollution-free."

In contrast with Cluster Groups 1 and 2, sites comprising Cluster Groups 3, 4, and 5 were characterized by elevated concentrations of various metals, PAHs, and organochlorines. Several of these sites, particularly in Cluster Groups 3 and 5, exhibited consistently high scores on one or more of the PCA factors. Regardless, the magnitude

of measured contaminant concentrations were consistent with those reported by previous studies and therefore were considered reasonable descriptions of SCB sediment contaminant patterns. In particular, the magnitude and distributions of contaminants such as DDT and PCB in Palos Verdes Shelf sediments have been well documented. Previous studies (Lee 1994, Eganhouse and Pontolillo 2000) concluded that histories of waste emissions to the Palos Verdes Shelf were recorded in the depositional chronologies of sediment cores. Further, surface contaminant concentrations on the Palos Verdes Shelf remain elevated despite large reductions in mass emissions. The presence of contaminants in surface sediments may be due to bioturbation and remobilization of historically buried sediments with elevated contaminant concentrations. Recent studies have also indicated that remobilized contaminants are subject to dispersion to other areas of the SCB (Zeng and Venkatesan 1999). As a result, the Palos Verdes Shelf represents a secondary source for DDT to other parts of the SCB, and may be responsible, in part, for the presence of measurable organochlorines in Cluster Group 2 sediments. Because the Palos Verdes Shelf is a reservoir for large quantities of DDT and PCB, and remobilization of contaminants represents an ongoing threat to biological resources and human health, sediment remediation and contaminant management projects are currently being developed to address these issues (Palermo *et al.* 1999).

Embayment sites contributing to Cluster Groups 3 and 4 were characterized by elevated concentrations of selected metals and PAHs that may be attributable to industrial input sources. Elevated metal (Cu, Hg, and Zn) concentrations can be associated with multiple source types that include industrial activities; hull cleaning and dissolution of anti-fouling hull paints in ports, harbors, and marinas; and urban runoff. Elevated PAH concentrations in sediments at Cluster Group 3 sites included both high- and low-molecular-weight compounds associated with both petroleum and combustion sources potentially derived from fuel spills and urban runoff. Sediment contaminants at the Cluster Group 3 sites likely reflect proximity to input sources as well as hydrological properties that promote deposition and accumulation of particulate-bound contaminants within the inner portions of industrialized harbors, such as commercial slips and dredged channels with limited circulation.

Compositional data for contaminant input sources to the Bight (e.g., POTW discharges, river and urban runoff, atmospheric deposition) are not presently available to support source apportionment estimates. However, future analyses of sediments for molecular markers, such as linear alkyl benzenes (LABs), are expected to provide information for more accurate assessments of contaminant contributions from specific sources. Additionally, it should be noted that while sediments collected for this program were from the surface 2-cm layer of grab samples, deposition rates are expected to vary considerably throughout the Bight. Also, some areas within harbors and marinas may have been dredged prior to sampling. Thus, contaminant levels measured at individual sites were not necessarily representative of inputs over a consistent period of time. Regardless, the overall patterns indicated by these results should be useful for interpreting patterns in biological communities, comparisons between bulk contaminant concentrations and effects thresholds, and sediment bioassay results from the Bight'98 program.

CONCLUSIONS

Of the five station groups delineated by cluster analysis, two groups comprising the majority of coastal and embayment sites, and representing 94% of the study area, were characterized by relatively low contaminant concentrations. The primary distinction between the two station groups appeared to be related to relatively finer sediment texture, and correspondingly higher contaminant concentrations, at embayment sites. The other three station groups were characterized by elevated concentrations of one or more contaminant classes but represented a relatively small portion of the total area of the SCB. Two of the cluster groups consisted almost exclusively of sites from enclosed portions of industrialized ports and marinas with high sediment trace metal and organic concentrations. The final site cluster comprised Palos Verdes Shelf sites, which reflected residual contamination from historical waste discharges. By contrast, other POTW and river sites lacked distinctive chemical signatures and were largely indistinguishable from other open-coastal background sites.

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Table C-1. Analytes and method detection limit (MDL) ranges for Bight'98 sediment samples.

Pest/PCBs	MDL (ng g ⁻¹)	PAHs	MDL (ng g ⁻¹)	Metals	MDL (µg g ⁻¹)
a -Chlordane	0.01-1	Naphthalene	5-36	Ag	0.06-0.2
? -Chlordane	0.01-1	1-Methylnaphthalene	5-39	Al	500
o,p'-DDD	0.02-1	2-Methylnaphthalene	5-39	As	0.08-0.62
o,p'-DDE	0.04-1	2,6-Dimethylnaphthalene	5-43	Ba	0.04-50
o,p'-DDT	0.02-1	1,6,7-Trimethylnaphthalene	5-39	Be	0.06-0.2
p,p'-DDD	0.03-1	Biphenyl	5-42	Cd	0.008-0.5
p,p'-DDE	0.02-1	Acenaphthene	5-42	Cr	1-16
p,p'-DDT	0.02-1	Acenaphthylene	5-25	Cu	1.9-7
PCB18	0.14-1	Fluorene	5-46	Fe	500
PCB28	0.24-1	Phenanthrene	5-37	Hg	0.005-0.2
PCB37	0.23-1.7	1-methylphenanthrene	5-29	Ni	1.2-4.2
PCB44	0.22-1	Anthracene	5-35	Pb	1-9.3
PCB49	0.17-1.3	Benz(a)anthracene	5-26	Sb	0.05-10
PCB52	0.27-1.6	Benz(a)pyrene	5-49	Se	0.11-1
PCB66	0.25-1	Benz(e)pyrene	5-48	Zn	1.4-30
PCB70	0.22-1	Fluoranthene	5-39		
PCB74	0.23-7.9	Pyrene	5-27		
PCB77	0.13-3.7	Chrysene	5-36		
PCB81	0.19-4.7	Benzo(ghi)perylene	5-63		
PCB87	0.1-1.8	Benzo(b)fluoranthene	5-44		
PCB99	0.18-4.1	Benzo(k)fluoranthene	5-49		
PCB101	0.2-1.2	Indeno(cd)pyrene	5-33		
PCB105	0.18-1	Dibenzo(ah)anthracene	5-33		
PCB110	0.1-1	Perylene	5-34		
PCB114	0.1-1				
PCB118	0.21-1.1				
PCB119	0.17-1.2				
PCB123	0.13-9.6				
PCB126	0.11-1.1				
PCB128	0.06-8.9				
PCB138	0.13-1.9				
PCB149	0.17-1.7				
PCB151	0.14-1.1				
PCB153	0.44-1.2				
PCB156	0.1-1.8				
PCB157	0.15-5.6				
PCB158	0.09-1.1				
PCB167	0.12-5.0				
PCB168	0.44-1.4				
PCB169	0.19-1.7				
PCB170	0.17-1.6				
PCB177	0.22-2.3				
PCB180	0.19-2.7				
PCB183	0.15-1.4				
PCB187	0.2-1.3				
PCB189	0.18-1.6				
PCB194	0.15-1.8				
PCB201	0.2-2.3				
PCB206	0.29-5.8				

Table C-2. Variables for PCA.

Metals	Ag, Al, As, Ba, Be, Cd, Cr, Cu, Fe, Hg, Ni, Pb, Sb, Se, Se, Zn
Total DDT	Summed concentrations of detected o,p'- and p,p'- isomers of DDT, DDE, and DDD
Total PCB	Summed concentrations of detected congeners: 18, 28, 37, 44, 49, 52, 66, 70, 74, 77, 81, 87, 99, 101, 105, 110, 114, 118, 119, 123, 126, 128, 138, 149, 151, 153, 156, 157, 158, 167, 168, 169, 170, 177, 180, 183, 187, 189, 194, 201, 206
Total Chlord	Summed concentrations of detected α - and γ -chlordane
Low	Summed concentrations of detected of two and three-ring PAHs:
Molecular	naphthalene, 1-methyl-, 2-methyl-, 2,6-dimethyl-, 1,6,7-trimethyl-
Weight PAH (LPAH)	naphthalenes, biphenyl, acenaphthene, acenaphthylene, fluorene, phenanthrene, 1-methyl-phenanthrene, anthracene
High	Summed concentrations of detected four and five-ring PAHs:
Molecular	fluoranthene, pyrene, chrysene, benzo(a)pyrene, benzo(e)pyrene,
Weight PAH (HPAH)	benzo(a)anthracene, benzo(b)fluoranthene, benzo(k)fluoranthene, indeno(1,2,3-cd)pyrene, dibenzo(ah)anthracene, perylene, benzo(ghi)perylene
TOC	Total organic carbon
Fines	Silts + clays: particle diameter <63 microns

Table C-3. Summary of cluster analysis results and characterizations of principal site cluster groups.

Cluster	No. Sites	Area		POTW	Proportion of Sites by Strata ^a			Description
		km ²	%		River	Ports/Harbor	Other Coastal	
1	62	704	22	14	8	58	19	Background Embayment
2	182	2,430	74	29	14	21	36	Background Coastal
3	6	8.7	0.3	0	17	84	0	Embayment – High Organics
4	35	89	3	0	0	97	3	Embayment – High Metals
5	5	47	1	80	0	0	20	Palos Verdes Shelf

^a POTW = LPOTW, SPOTW, and mid-shelf POTW strata; River = River and river-gradient strata; Ports/Harbor = Ports, harbors, marina, and other port strata; Other Coastal = Shallow-shelf, mid-shelf, and historical reference strata.

Table C-4. Mean concentration by cluster group of sediment fines (%), TOC (%), metals ($\mu\text{g g}^{-1}$), and organics (ng g^{-1}).

	Cluster 1	Cluster 2	Cluster 3	Cluster 4	Cluster 5
Fines	74	32	65	70	49
TOC	1.5	0.51	2.3	1.4	2.6
Ag	0.43	0.47	0.94	1.3	1.8
Al	25,000	10,600	23,200	31,800	15,500
As	11	4.4	11	8.8	9.6
Ba	228	75	114	112	605
Be	0.69	0.35	0.64	0.83	0.66
Cd	0.75	0.25	0.74	0.35	3.8
Cr	49	23	49	53	111
Cu	53	15	82	137	62
Fe	34,000	15,100	28,400	34,300	27,200
Pb	30	11	55	62	35
Hg	0.17	0.10	0.23	0.60	0.35
Ni	35	11	23	21	24
Sb	1.5	2.0	4.1	6.8	0.92
Se	1.4	0.48	0.47	0.59	0.99
Zn	136	49	211	205	130
Total Chlord	2.3	0.49	11	1.7	0.5
Total DDT	64	19	96	20	2,890
Total PCB	23	5.3	135	32	200
LPAH	88	19	1,030	80	126
HPAH	590	56	6,330	790	456

Table C-5. Rotated Factor Pattern for PCA Factors (PC 1-4).

	PC1	PC2	PC3	PC4
Ag	0.321	0.585	-0.032	0.053
Al	0.793	-0.057	0.159	-0.368
As	0.496	0.147	0.201	-0.063
Ba	-0.003	0.276	-0.032	-0.602
Be	0.464	0.081	0.058	-0.282
Cd	0.069	0.823	0.126	-0.355
Cr	0.551	0.639	0.165	-0.414
Cu	0.838	0.095	0.227	-0.078
Fe	0.706	0.075	0.177	-0.588
Hg	0.750	0.208	0.096	0.045
Ni	0.206	0.075	0.125	-0.643
Pb	0.734	0.244	0.299	-0.176
Sb	0.487	0.062	-0.118	0.301
Se	-0.012	0.086	0.096	-0.722
Zn	0.799	0.136	0.405	-0.285
Total Chlord.	0.093	0.016	0.594	-0.187
Total DDT	-0.034	0.874	0.035	-0.111
Total PCB	0.197	0.708	0.558	-0.123
LPAH	0.146	0.163	0.896	-0.046
HPAH	0.239	0.035	0.861	0.015
TOC	0.451	0.281	0.382	-0.534
Fines	0.577	-0.054	0.187	-0.607
% Total Variance	40.7	10.6	8.7	7.3

Table C-6. Comparisons of Bight '98 Cluster AWM and Baseline Concentrations.

	Measured AWM		Predicted ^a		1985 and 1990 Reference Site Surveys ^b				Bight '98 Historical Sites ^c		Pollution-Free Baseline ^d
	Cluster 1	Cluster 2	Cluster 1	Cluster 2	30 m	60 m	30 m	60 m	30 m	60 m	
Ag	0.18	0.38	0.22	0.10	0.01	0.03	0.1	0.25	0.30	0.30	0.4
As	8.7	4.3	7.2	4.3					3.2	4.3	
Cd	0.57	0.25	0.30	0.15	0.13	0.14	0.26	0.24	0.21	0.18	0.4
Cr	39	22	50	24	18	25	17	26	14	20	25
Cu	24	8.7	20	9.0	5.7	10	5.3	9.2	5.6	9.1	9
Fe	30,205	14,837					11,000	18,000	10,600	15,400	
Pb	15	11	14	7.3	2.9	4.8	4.4	6.9	7.0	5.2	10
Ni	50	12	29	14	9.0	13	8.0	11	7.3	11	15
Zn	95	40	93	45	31	48	29	45	29	39	44
Total DDT	42	18			9.1	19	5.4	13	3.9	6.9	
Total PCB	6.5	4.6			11	19	7.1	12	0.5	1.2	
LPAH	29	15							20	20	
HPAH	195	27			39	20	24	26	32	29	

^a Predicted values based on baseline regression coefficients (slope and intercept) for metal:iron relationships in SCB sediments from sites distant from known point and non-point sources of pollution developed by Schiff and Weisberg (1999). ^b Average values for 30-m and 60-m sites sampled in 1985 and 1990 for the SCCWRP Reference Site Surveys (SCCWRP 1987, 1992); total DDT is the sum of five isomers, total PCB is sum of two Aroclors, and HPAH represents sum of 30 LPAH and HPAH. ^c Averages for historical 30-m and 60-m sites corresponding to SCCWRP Reference Site Survey locations.

^d from Katz and Kaplan (1981). Area-weighted mean (AWM) concentrations for individual station clusters were calculated as

$$\text{follows: } m = \frac{\sum_{i=1}^n (p_i * w_i)}{\sum_{i=1}^n w_i}, \text{ where } m = \text{Area weighted mean concentration for population } j, \quad p_i = \text{Parameter value (e.g., concentration) at station } i, \quad w_i = \text{area weight for station } i, \text{ equal to the inverse of the inclusion probability, } n = \text{Number of stations in population } j.$$

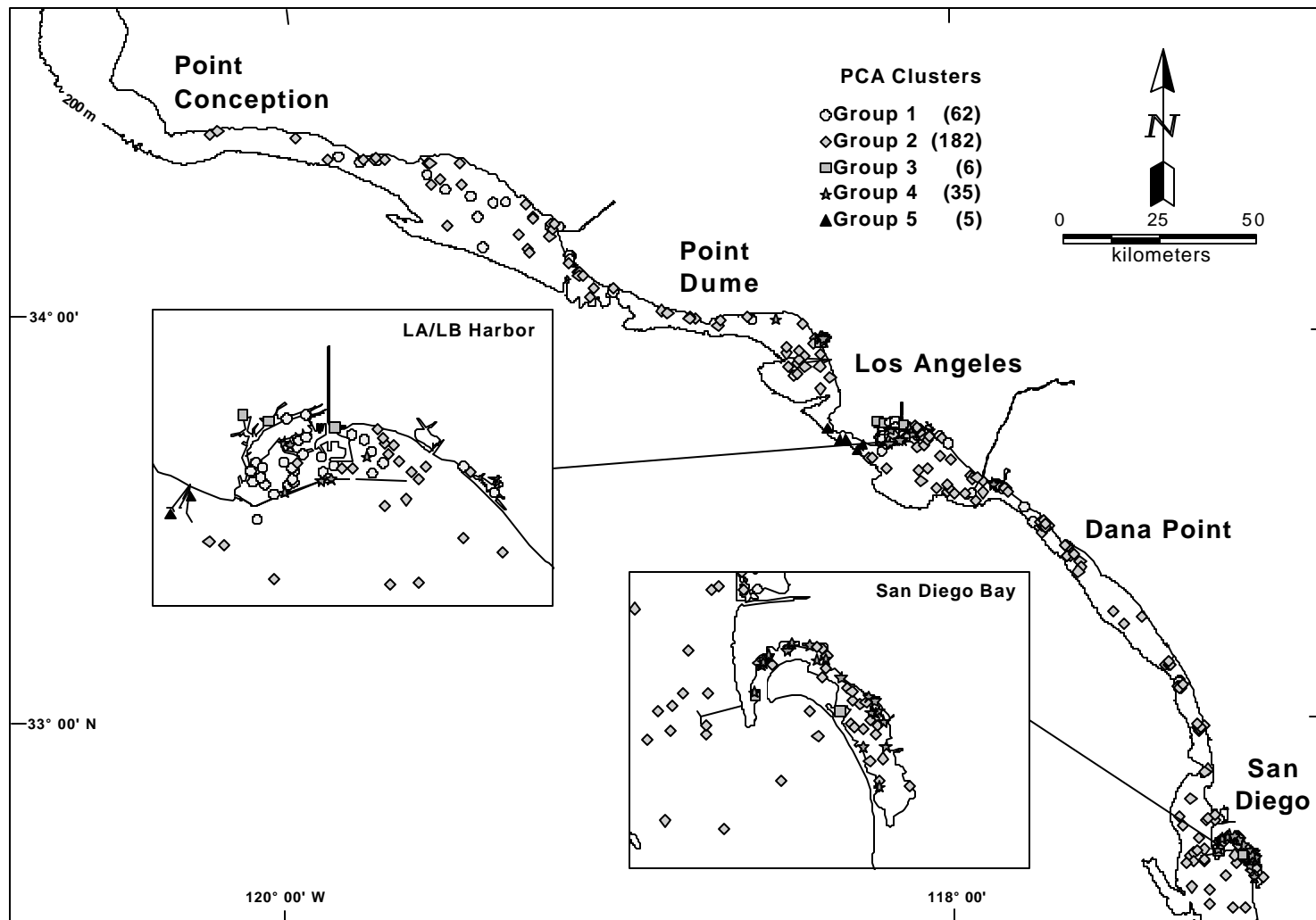


Figure C-1. Spatial distributions of site clusters.

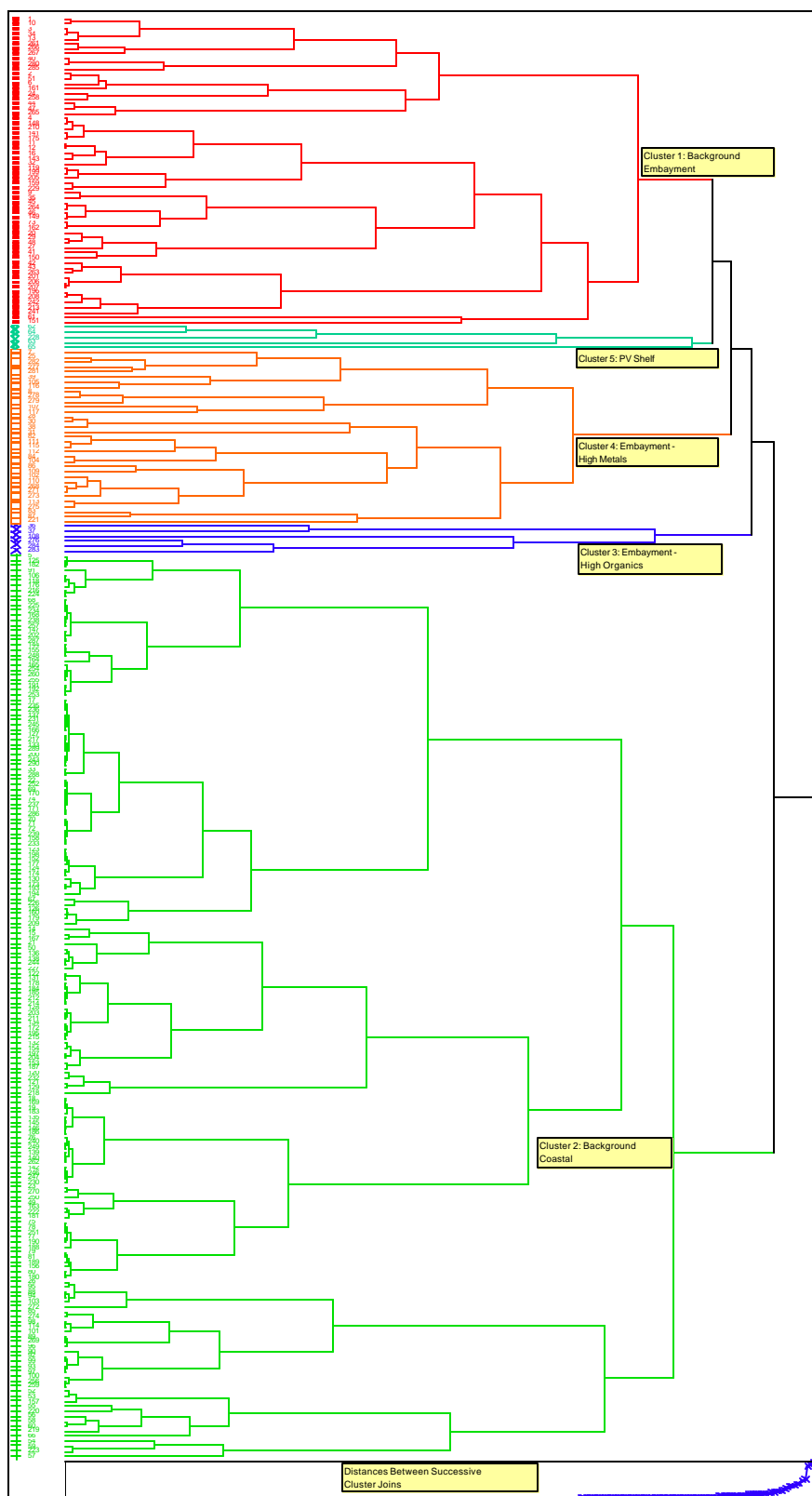
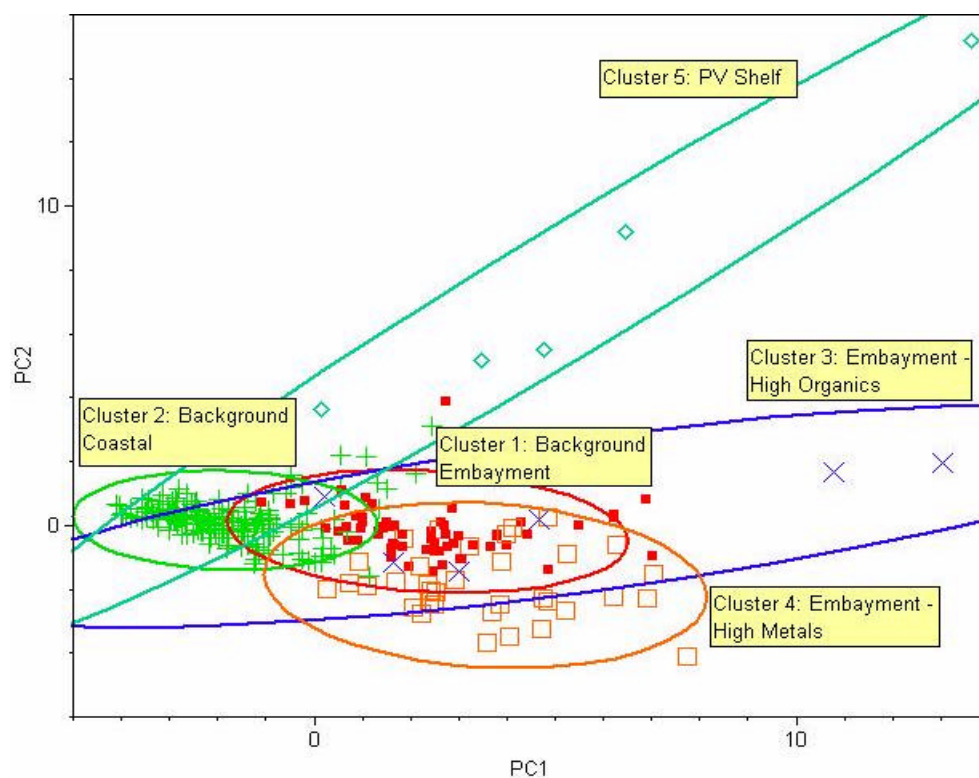


Figure C-2. Dendrogram from cluster analysis of PCA scores. Cluster distances between successive cluster joins are shown beneath the dendrogram.

a)



b)

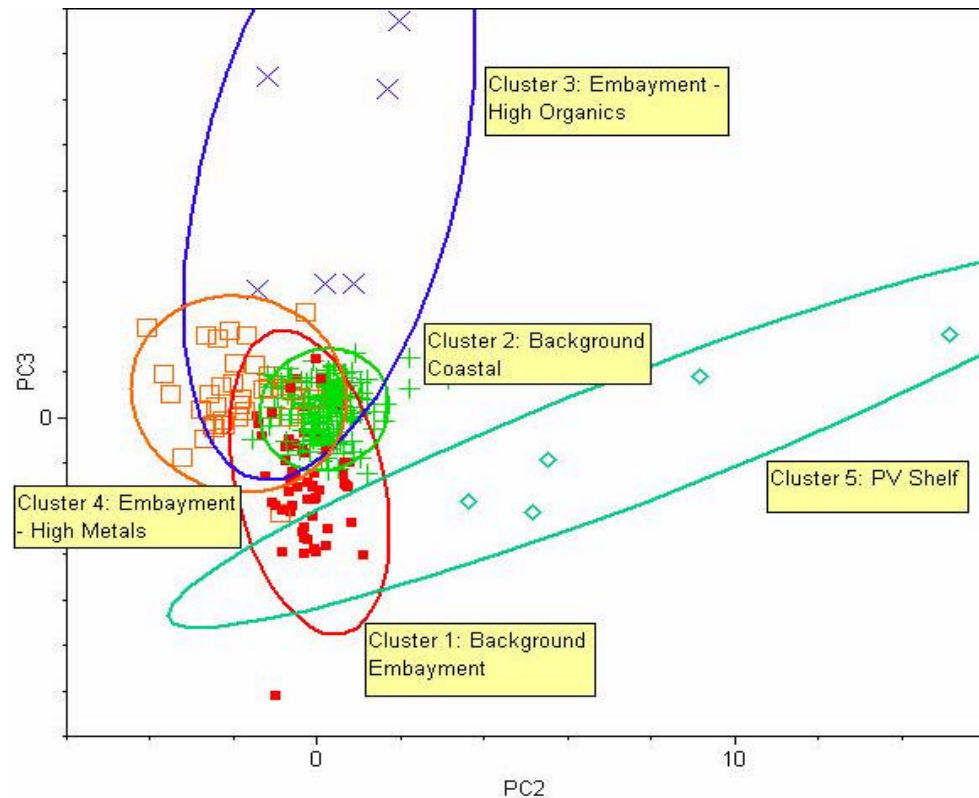


Figure C-3. Bivariate plots of principal component scores: a) PC1 vs PC2 and b) PC2 vs PC3. 95% density ellipses are shown for individual site clusters.

APPENDIX D

Supplemental Sediment Quality Guideline Quotient
Information and Calculations

INTRODUCTION

Several assessment tools were investigated for use in evaluating the potential for adverse biological impacts associated with the sediment contamination measured during the Bight'98 Survey. Among the assessment approaches explored were two relatively recent methods involving the calculation of mean sediment quality guideline quotients. The first method is the National Oceanic and Atmospheric Administration (NOAA) mean effects range median quotient (ERMQ) approach as described most recently in Long *et al.* 1998. The method for calculating ERMQ is described in the methods section of this report. The second approach investigated is a new very similar sediment quality guideline quotient (SQGQ) method developed by Fairey *et al.* (2001). This method uses a subset of nine sediment quality parameters that was found to produce the greatest success in predicting sediment acute toxicity. The method was developed using synoptic sediment chemistry and toxicity data from 3,584 samples from different regional monitoring studies nation-wide. The data used included more than 600 samples from the California Bay Protection and Toxic Clean-up Program. In their study, Fairey *et al.* (2001) examined many combinations of sediment quality guidelines in common use, and identified the parameters that produced the best predictive ability for sediment acute toxicity to amphipods.

Data are presented herein that evaluate the efficacy of these two approaches for assessing the potential for acute toxicity in the sediment of the Southern California Bight (SCB). The two approaches were compared to determine the value of the new SQG approach versus the more commonly used ERMQ approach.

METHODS

The ERMQ values for each station were calculated using 24 parameters including 13 individual PAHs, total PCB (42 congeners), total DDT (6 compounds), and 9 trace metals. In some analyses, DDT was excluded because it tended to skew the data without having any impact on the assessment. The related method developed by Fairey *et al.* (2001), uses a subset of nine parameters including five metals (cadmium, copper, silver, lead, and zinc), and four organic compound groups--total PAH (13 compounds), total chlordanes (5 isomers), total PCB (18 congeners), and dieldrin.

In this study, eight of the nine parameters identified by Fairey *et al.* (2001) were used for calculating the SQGQ values; one of the parameters, the chlorinated pesticide dieldrin, was not a target analyte in the Bight'98 Survey. Three of the chlordane isomers, and three of the PCB congeners were also not Bight'98 target analytes. Inclusion of DDT elevated only five stations above the Level II range for the ERMQ calculations: three stations into Level III, and two stations into Level IV. Only four of these stations were tested for toxicity, and only one was toxic (16% survival).

RESULTS AND DISCUSSION

There was a total of 241 stations with complementary toxicity and sediment chemistry results. A comparison of the amphipod toxicity and Quicksed test results from the Bight'98 Sediment Toxicity Study and the corresponding ERMQ values calculated from the sediment chemistry results are shown in Figures D-1 and D-2, respectively. The plots show a poor correlation between observed toxicity and ERMQ values for both the amphipod and Quicksed tests.

These results are consistent with the predicted performance of the assessment model. All of the Bight'98 station fall within the lowest two ERMQ ranges; within these ranges, the model predicts only 11 and 30% of the samples will be toxic for MERMQ Levels I and II, respectively. Table D-1 presents a comparison of the predicted number of toxic samples to the actual percent of samples found to be toxic within each MERMQ range. The toxicity results are comparable to those predicted by the ERMQ model. Therefore, although the relationship between the sediment chemistry and toxicity is poor, the model is performing correctly. The fact is that the sediment contamination in the SCB is in the range where the predictive ability of the available toxicity models is poor.

In order to determine whether a reduced parameter set would improve the predictive ability of the sediment quality guideline approach, the mean SQGQs were calculated. The Bight'98 toxicity data were plotted versus mean SQGQ values and compared to the empirical relationship derived by Fairey *et al.* (2001). The results of this comparison are shown in Figure D-3. As for the MERMQ approach, a poor correlation was found between the amphipod toxicity and mean SQGQ although the model was functioning correctly. All of the samples from the Bight'98 Survey fell toward the lower end of the SQGQ range. The percent of samples found to be toxic as a function of SQGQ was compared to the percent of samples expected to be toxic from the empirical model, and the results are shown in Figure D-4. Again, there was good agreement between the toxicity and the model on a percentage basis. As can be seen from Figure D-4, in the SQGQ range of most of the SCB, the predictive ability of the model is poor.

The available empirical toxicity models were all developed using mortality as the endpoint. It is clear from these calculations that the vast majority of the SCB is at a low risk for acute toxicity. Even at the high end of the ERMQ range for the Bight'98 samples, the models predict that 30 to 50 % of the samples should be toxic. A comparison of the Bight'98 toxicity and chemistry data gives results that are consistent with the percent of samples expected to be toxic based on correlations derived with national synoptic sediment chemistry-toxicity databases. The empirical models are therefore useful for predicting the percent of the SCB samples, and hence the area at risk for acute toxicity. This analysis is shown as a cumulative distribution function (CDF) in Figure D-5. However, due to the relatively low levels of contamination, the models are not useful for predicting toxicity on a site-by-site basis.

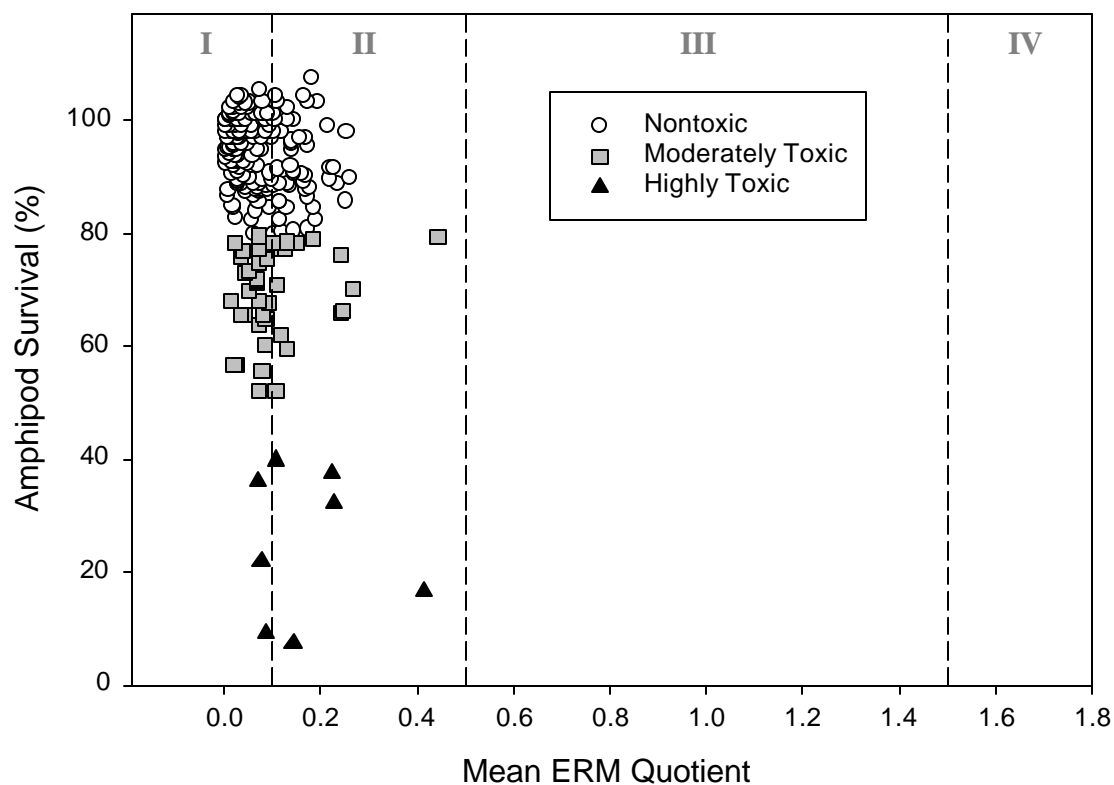


Figure D-1. Comparison of sediment amphipod toxicity results with the calculated ERM quotients from the sediment chemistry results. The ERM quotient values were calculated excluding DDT. The toxicity designations are those defined in the Bight'98 Sediment Toxicity Report (Bay *et al.* 2000). The ERM quotient ranges (roman numerals) are those defined by Long *et al.* 1998.

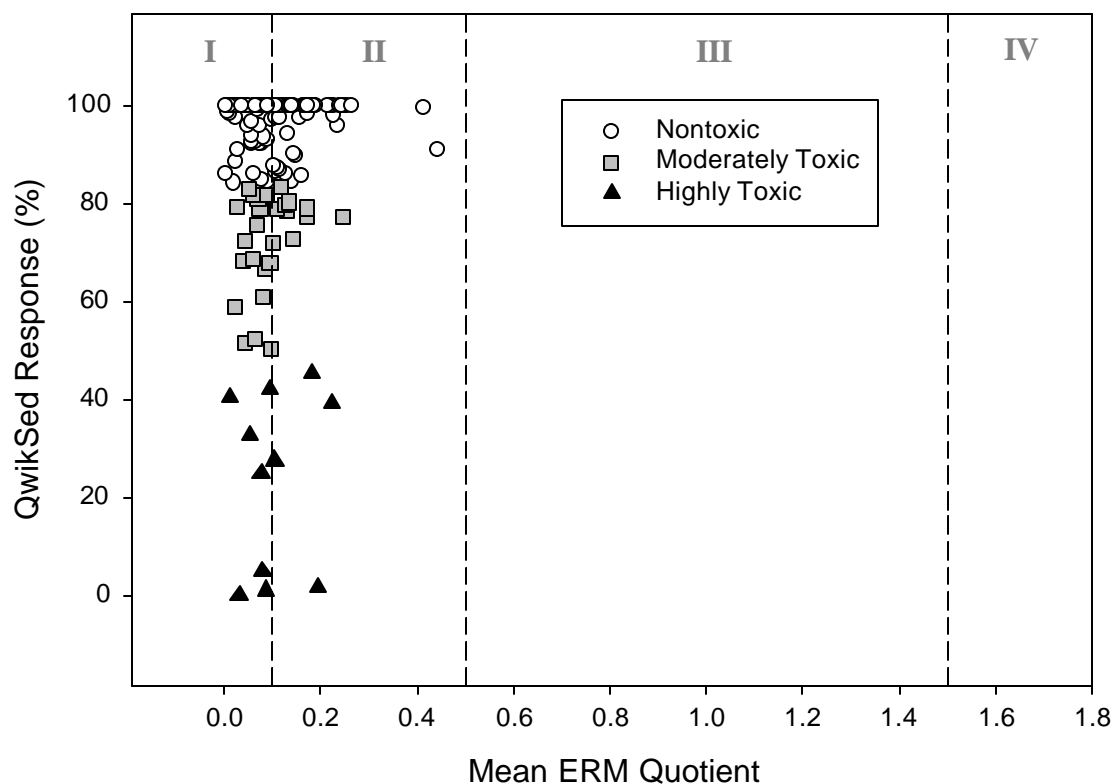


Figure D-2. Comparison of sediment Qwiksed test toxicity results with the calculated ERM quotients from the sediment chemistry results. The ERM quotient values were calculated excluding DDT. The toxicity designations are those defined in the Bight'98 Sediment Toxicity Report (Bay *et al.* 2000); see report for a description of the Qwiksed elutriate test. The ERM quotient ranges (roman numerals) are those defined by Long *et al.* 1998.

Table D-1. A comparison of the predicted percent of toxic samples as a function of ERM quotient range based on the data from Long *et al.* 1998, versus the number of samples actual found to be toxic to amphipods as reported in the Bight'98 Sediment Toxicity Report (Bay *et al.* 2000).

Mean ERM Quotient Priority Level	Predicted % of Samples Toxic	% of Samples Toxic in Bight '98 Toxicity Report
	Long <i>et al.</i> (1998) (n=1,068)	Bay <i>et al.</i> (2000) (n=241)
Level I: <0.10	11	17.1 (29/170)
Level II: 0.11 – 0.50	30	28.2 (20/71)
Level III: 0.51 – 1.50	46	No Samples
Level IV: > 1.50	75	No Samples

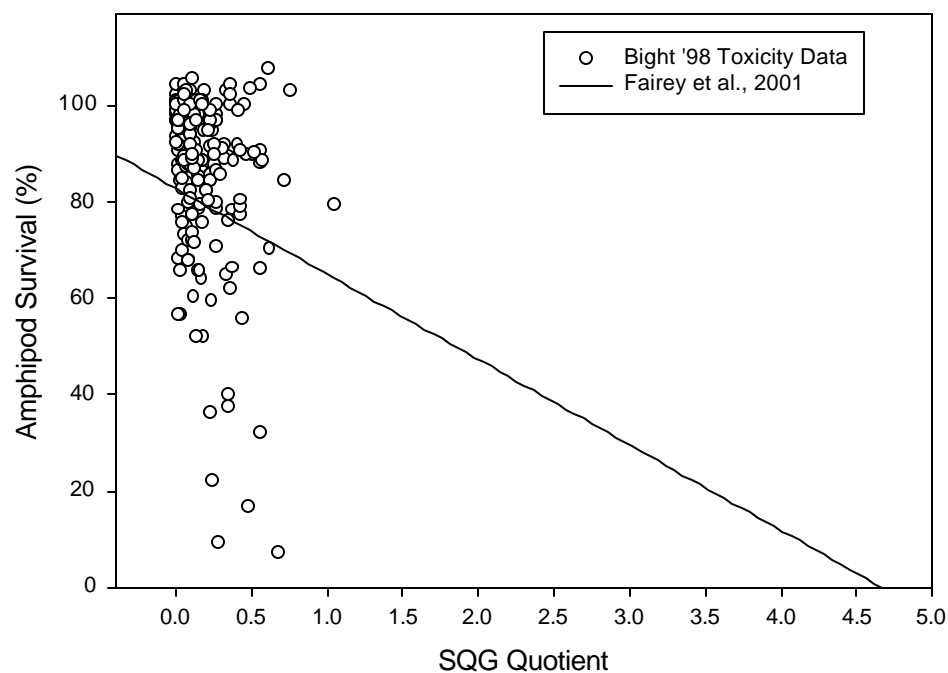


Figure D-3. A comparison of the Bight'98 sediment toxicity results as a function of the optimum sediment quality guideline quotient (SQG) to the model linear relationship developed by Fairey *et al.* 2001.

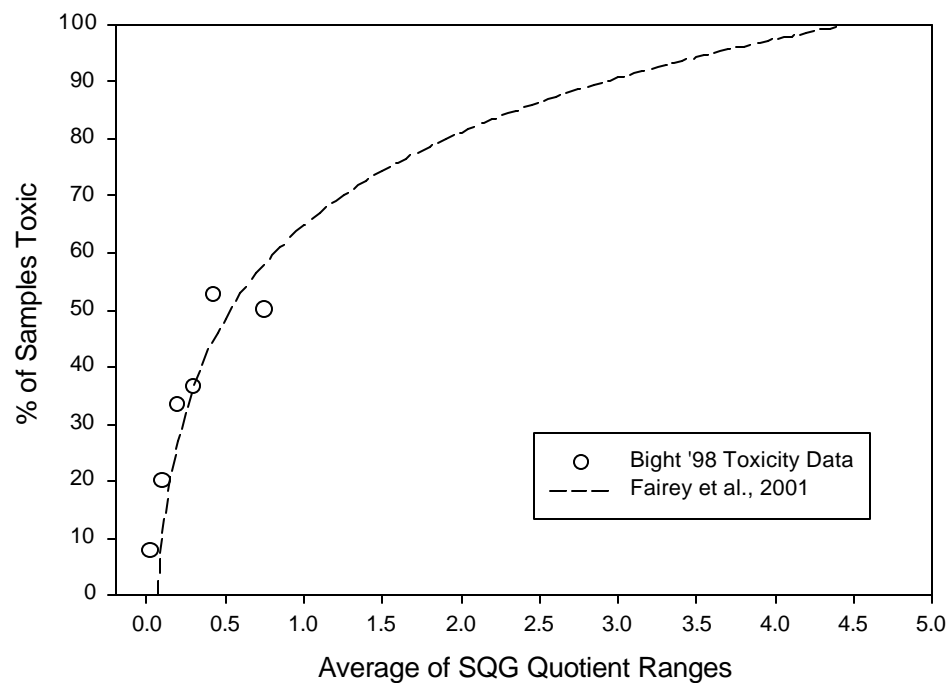


Figure D-4. The Bight'98 percent of toxic samples as a function of the optimum sediment quality guideline (SQG) ranges compared to the prediction of the model relationship developed by Fairey *et al.* 2001.

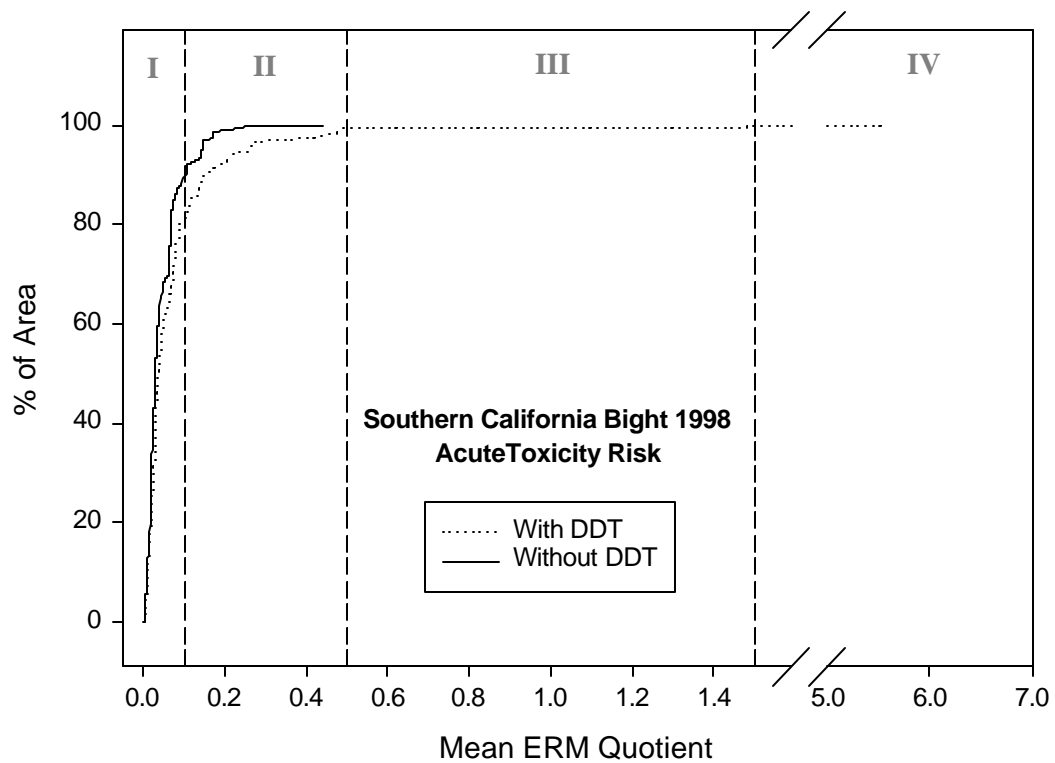


Figure D5. Cumulative distribution function (CDF) showing the percent of the Southern California Bight within each of the mean ERM quotient ranges described by Long *et al.* 1998. There are CDF's shown for calculations done with and without inclusion of DDT. These plots confirm that inclusion of DDT in the ERM quotient calculations has no significant impact on the assessment results.

APPENDIX E

A Comparative Evaluation of Sediment Contamination in the
Southern California Bight Using Multiple Equilibrium
Partitioning (EqP) – Based Assessment Tools

A Comparative Evaluation of Sediment Contamination in the Southern California Bight Using Multiple Equilibrium Partitioning (EqP) – Based Assessment Tools

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INTRODUCTION

Evaluation of sediment contamination with respect to its potential effects on benthic organisms can be made by using various sediment quality guidelines that generally have been derived from correlative studies (Long et al. 1995, 1998), direct exposure of organisms to chemicals (U.S. EPA, 2000a, 2000b, Di Toro and McGrath, 2000) or a combination of both approaches (Swartz 1999). This study uses the direct exposure approach that is essentially an application of EPA's water quality criteria (WQC) to the interstitial water (IW) environment inhabited by benthic organisms. The development of WQC demonstrated that the exposure route of most aquatic organisms to chemicals was through the freely dissolved form (Sunda and Guillard, 1976). Therefore, the promulgated WQCs are based on freely dissolved concentrations below which 95% of water-living organisms could be indefinitely exposed without detriment (U.S. EPA, 1999). The WQC database was expanded to include laboratory exposure data for sediment dwelling organisms and freely dissolved concentrations were established for polynuclear aromatic hydrocarbons (PAHs) and metals that if exceeded in IW would be detrimental to most benthic organisms. These water concentrations are referred to as the final chronic values (FCVs) and can be related to sediment concentrations through the use of EqP.

The toxic unit concept evolved out of WQC database development and helped explain the apparent additivity of multiple chemicals to observed toxicity. A toxic unit (TU) of a chemical was defined as the concentration that is present at that chemical's LC50 (Sprague, 1970). It was found that fractional TUs (the ratio of the chemical's concentration to its TU) from different chemicals of similar modes of action, when added together would be proportional to an organism's response. This additivity has been interpreted as the accumulation of toxicants (body burden) within organisms to a critical concentration that is present at the exposure LC50 (Di Toro, et al., 2000). Quantitative structure activity relationships (QSARs) were also found that related the K_{ow} of organic compounds to their LC50s (Könemann, 1981), thus allowing the LC50s and TUs of untested chemicals to be calculated. Therefore, to evaluate the extent of sediment contamination it would be necessary to determine the Σ TUs in the IW coming from chemicals of the same mode of action (Swartz et al., 1995; Di Toro et al., 2000; Di Toro and McGrath, 2000; U.S. EPA, 2000a).

Rather than sampling IW directly, the concentrations of chemicals freely dissolved in the IW can be computed from bulk sediment concentrations. Justification for this indirect approach to

determining IW concentrations and thus organism exposure is the acceptance of the concept of equilibrium partitioning of chemicals among the various phases that are present in their immediate environment (Di Toro et al., 1991). For organic chemicals, the organic matter in the sediment is thought to control their IW concentrations, whereas, for divalent cationic metals, it is the sulfidic solid phases primarily (Di Toro et al., 1990) and, to a lesser extent, the organic matter.

The approach taken with regard to organic contaminants calculates the sediment concentration in equilibrium with a TU of chemical, freely-dissolved in sediment IW using the following relationships:

$$TU_{sed} = K_{oc} * TU_{IW} \quad (1)$$

where the units of TU_{sed} , K_{oc} (carbon-normalized partition coefficient), and TU_{IW} are $\mu\text{g/kg-OC}$ (organic carbon), L/kg-OC , and $\mu\text{g/L}$, respectively. Carbon-normalized sediment concentrations of these chemicals are divided by their individual TU_{sed} s and the resulting fractional TUs (TU_s) are summed. A similar approach for metal contaminants is to determine bulk sediment metal and sulfide concentrations to assess whether there is sufficient sulfide to render the metals biologically inactive.

METHODS

This study applies a variety of equilibrium partitioning-based assessment tools to the results of the comprehensive chemical and biological sampling design of the Southern California Bight 1998 Regional Monitoring Program. Six approaches which are based on the extrapolation of laboratory or field exposure results using EqP to the assessment of sediment contamination were used in this section. The ÓPAH model (Swartz et al., 1995) was used to compute the probabilities of 3 levels of acute toxicity due to 13 PAHs. Two similar methods based on EqP and the target lipid narcosis model (U.S. EPA 2000a; Di Toro and McGrath 2000) were used separately and in combination to compare sediment PAH and polychlorinated biphenyl (PCB) concentrations to those that would be considered of no concern by the EPA. Sediment concentrations of the isomers of DDT and its metabolites (DDTs) were compared to concentrations that were found to be associated with acutely toxic sediments and those with altered amphipod abundance (Swartz et al., 1994). Lastly, IW and bulk sediment concentrations of 5 metals were assessed using EPA saltwater Water Quality Criteria (U.S. EPA, 1999) and consideration of the relative concentrations of sulfide and metals released from sediment following extraction by a weak solution of non-oxidizing acid, HCl (Di Toro et al., 1992; Allen et al., 1993).

The ÓPAH Model

Swartz et al. (1995) published the ÓPAH model for predicting the acute toxicity of PAH contaminated sediments. This model was based on a QSAR of LC50 vs. K_{OW} for three PAHs. The QSAR was used to compute LC50s of 13 PAHs that are looked for and often found to co-occur in contaminated sediments. The TU concept and additivity were combined through the summation of fractional toxic units computed from the bulk sediment concentrations using EqP, or using concentrations determined in the IW (Ozretich et al. 2000, 2002). The QSAR used to compute the LC50s of the individual 13 PAHs is:

$$\log LC50_{IW} = 5.92 - 1.33 * \log K_{ow} \quad (2)$$

where $LC50_{IW}$ is the IW concentration (iM) that would be lethal to 50% of the exposed animals (if present, would be equivalent to 1.0 IW TU), and K_{OW} is the octanol/water partition coefficient of the compound. The carbon-normalized sediment concentration that would be in equilibrium with this IW concentration was computed with the following:

$$(C_{sed} / f_{OC}) = LC50_{IW} * MW * K_{OC} * (10^{-3} \text{ kg-OC/g-OC}) = 1.0 \text{ sediment TU} \quad (3)$$

where C_{sed} is the sediment concentration ($\mu\text{g/kg-dry}$), f_{OC} is the fraction of organic carbon (OC) in the sediment (kg-OC/kg-dry), MW is molecular weight (ig/imole) and K_{OC} is the carbon-normalized equilibrium partition coefficient (L/kg-OC). The units of sediment TUs are $\mu\text{g/g-OC}$, and the K_{OC} of organic compounds has been shown to be related to the compound's K_{OW} ($\log K_{OC} = 0.983 * \log K_{OW}$; Di Toro et al. 1991). An example of a computed TU can be found in Table E-1. The TU_f from an individual compound would be computed by dividing its carbon-normalized bulk sediment concentration by its sediment TU. The $\acute{O}TU_f$ from the 13 PAHs were then used to compute the probability of three levels of toxicity (not toxic, uncertain or acute toxicity) to infaunal amphipods using the following relationships:

Percent of samples with:

$$\text{mortality} > 24\% = 60.64 + 76.09 * \log \acute{O}TU_f \quad (4)$$

$$\text{mortality} > 13\% = 77.13 + 65.32 * \log \acute{O}TU_f \quad (5)$$

In this model, sediments with mortality $> 24\%$ would be considered toxic; the percent of nontoxic sediments would be 100% minus equation 5 and the percent of sediments of uncertain toxicity would be equation 5 minus equation 4. Although equations 4 and 5 were developed using

Rhepoxinius abronius, *Eohaustorius estuarious* (the amphipod used in this study of Southern California sediments (Bay et al., 2000)) was among 6 amphipod species that were used in generating the QSAR of Equation 2. It must be noted that an outcome of this model is that $\acute{O}TU_S$ of 0.15 have an ~25% probability that a sample would have mortalities exceeding 13%. In addition, a 100% probability for a response of >13% and >24% mortality would be predicted at $\acute{O}TU_S$ of 2.2 and 3.3, respectively.

As not all 13 PAHs were detected in all samples, the $\acute{O}TU_f$ were computed as though all were present by dividing the $\acute{O}TU_S$ of the reported compounds by the average percentage of $\acute{O}TU_f$ from them that was found by Swartz et al. (1995) in sediments contaminated by PAHs. For example, if the sum of fractional TUs from compounds X, Y and Z was 0.10 TU and on average, they were responsible for 33% of the TU_f s in Swartz et al. (1995), then $\acute{O}TU_{f \text{ to } 13}$ ($\acute{O}TU_f$ adjusted to 13 compounds) for the sample would be 0.30. Following Swartz et al. (1995), from each sample's $\acute{O}TU_{f \text{ to } 13}$, a probability in each of the three mortality categories was computed. For the study, the probabilities, as fractional stations were added to represent the number of stations expected to be found in the mortality categories.

Table E-1. Examples of Toxic Unit and Equilibrium Partitioning Sediment Guideline values.

Compound	MW	K _{ow}	Swartz ¹ TU only (mg/g-OC)	EPA ² ESG (mg/g-OC)	Di Toro ESG (mg/g-OC)
Chrysene	228.3	5.71	2136	844	1426 ³
PCB 101	326	6.38	NA	NA	2257 ⁴

¹ from Swartz et al. (1995)

² equilibrium partitioning sediment guidelines from U.S. EPA (2000a)

³ from Di Toro and McGrath (2000)

⁴ from Di Toro et al. (2000)

Target Lipid Narcosis Model

An analysis of the entire WQC database (156 chemicals with 33 species) was performed by Di Toro et al. (2000) for Type I narcotic chemicals. Di Toro et al. determined that among the chemicals sharing the same mode of action there were differences in the intensity of the responses that were associated with chemical. For example, compared to the average, base narcotic chemical, it took 0.57, 0.57, and 0.5 of the halogenated compounds, ketones, and PAHs,

respectively to elicit the same acute response. Using only the PAH data from the WQC database, U.S. EPA (2000a) provided a rationale for computing concentrations of commonly quantified PAHs, that if exceeded would be detrimental to benthic organism survival over long periods of time.

These concentrations became the EPA equilibrium partitioning sediment guidelines (ESGs) for PAHs. Although EPA and Di Toro et al. utilized the same universal slope of the QSAR relating LC50 (mM) and compound K_{OW} ($\log LC50 = -0.945 * \log K_{OW}$), they arrived at different critical body burdens of PAHs present at the LC50. The reason for this was that the WQC data used by EPA was only for PAH exposures, a small subset of the entire database, whereas, Di Toro et al. (2000) utilized the entire database. Given this difference in sources for critical body burdens, the EPA body burden associated with the FCV, (i.e., the C_{tiss}^*) of each PAH, was 2.24 $\mu\text{mol/g-lipid}$ which compared well to the 3.78 $\mu\text{mol/g-lipid}$ from Di Toro and McGrath (2000) that came from a baseline FCV with a PAH chemical class correction. The C_{tiss}^* present at the final chronic value were computed by EPA and Di Toro et al. from different final acute values (FAV) using acute-to-chronic ratios of 4.16 for PAHs (EPA) and 5.09 for all narcotic chemicals (Di Toro et al.). FCV and FAV represent concentrations that would be considered protective of 95% of benthic species from adverse chronic or acute effects, respectively. The FCV for individual PAHs can be computed from the following:

$$\log FCV = \log C_{tiss}^* - 0.945 * \log K_{ow} + \log \ddot{A}c \quad (6)$$

where FCV has units of $\mu\text{mol/L}$, and $\ddot{A}c$ is the chemical class correction. In computations of FCV for PAHs, the EPA C_{tiss}^* value of 2.24 was used with no class correction. To assess the contribution of PCBs, the general narcosis response of Di Toro et al. (2000) was used where the baseline C_{tiss}^* of 6.94 was used with a halogenated compound class correction of 0.570. EPA would not consider carbon-normalized sediment concentrations of individual PAHs at and above those in equilibrium with their FCVs suitable for sustained benthic life. Following the concept of additivity, neither would sediments whose sum of fractional FCVs equaled or exceed 1.0! Conversion of these protective FCVs into sediment concentrations (ESGs) was accomplished using EqP in the following:

$$\log C_{ESG} = 0.038 * \log K_{OW} + \log C_{tiss}^* - \log \ddot{A}c \quad (7)$$

where C_{ESG} has units of $\mu\text{mol/g-OC}$ and the factor 0.038 incorporates the universal slope of equation 6 with the conversion of K_{OW} to K_{OC} of Di Toro et al. (1991). As in equation 6, different C_{tiss}^* values were used to compute ESGs for PAHs and PCBs. Taking the antilog of equation 7 and multiplying by a compound's molecular weight converts the result to $\mu\text{g/g-OC}$ which was used to divide the carbon-normalized PAH and PCB concentrations of the sediment samples to compute fractional ESGs (ESG_f) that were summed, $\sum ESG_f$. Computed C_{ESG} s for a PAH and PCB are

found in Table E-1.

In this study 24 individual, hydrocarbon compounds were looked for by the participating laboratories. These included the 23 PAHs of NOAA's National Status and Trends list of analytes (NOAA, 1991) and biphenyl which, because its phenyl groups are not fused is not considered a PAH. However, the concentrations attributed to biphenyl were included in the fractional toxic unit summaries

of this study. In recognition of the PAHs that are likely to be present in samples and that are not on a laboratory's analyte list, U.S. EPA (2000a) proposed a factor of 4.14 to convert a sample list of 23 PAHs to what they would consider "total PAHs." Total PAHs consist of 18 individual unsubstituted compounds and 16 groups of "parent" PAHs with alkyl substitutions, yielding "34" PAHs (U.S. EPA 2000a). This factor was used to correct the ÓESG_f from 24 compounds of this study to those expected from the "total PAHs" ($\text{ÓESG}_{f \text{ to total}}$) that are likely to be present with a 95% certainty. Those samples where $\text{ÓESG}_{f \text{ to total}} < 1.0$ would be considered by EPA as acceptable for the protection of benthic organisms.

Although EPA has not proposed ESGs for PCBs, as additive narcotic chemicals, PCBs should behave similarly to PAHs. ESG_f s were computed for PCBs using K_{ow} 's from Hawker and Connell (1988) and their sums were evaluated with respect to those coming from PAHs. No factor was used to convert the target list of 41 PCB congeners in this study to "total PCBs" to account for unmeasured congeners.

Total DDTs

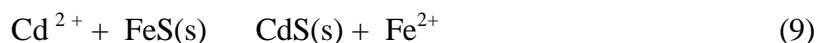
From studies of DDT contaminated field sediments, Swartz et al. (1994) reported a mean LC50 for the sum of carbon-normalized DDTs of 2040 $\mu\text{g/g-OC}$ for *E. estuarius*. *E. estuarius* the amphipod used in bioassays of sediments from this study (Bay et al., 2000). In addition, a threshold of 100 $\mu\text{g/g-OC}$ was reported for effects on amphipod populations which would be a chronic effects threshold. Organic carbon-normalized concentrations of the sum of these chlorinated compounds were compared to the LC50 and threshold values.

IW metals, AVS and SEM

Anaerobic conditions common in fine-grained sediments lead to the formation of hydrogen sulfide that in the presence of ubiquitous iron will form solid iron monosulfide in the following chemical equilibrium:

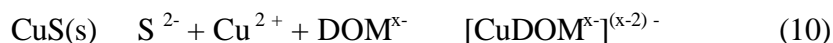


With the addition of other metals in sufficient quantities to exceed their sulfide solubility products, solid sulfides of the additional metals would form at the expense of FeS if the metals bond more strongly to the sulfide ion than does the iron of FeS. This is illustrated in the following equilibrium after the addition of divalent cations of cadmium to anaerobic, iron-rich sediment:



This displacement behavior is expected of the cations of cadmium, copper, lead, nickel, and zinc (Di Toro et al., 1992) with the formation of metal sulfides in a Me:S molar ratio of 1:1. The solubility products of these sulfides are so small that if the metal was present and there was sufficient sulfide present, essentially, all the mass of these metals would be present as their sulfides. The formation of sulfides makes these metals, essentially, not bioavailable.

In natural waters, freely dissolved cations are also in equilibrium with dissolved organic and inorganic ligands:



where DOM^{x-} depicts a multi-dendate molecule of dissolved organic matter, and $[\text{CuDOM}^{x-}]^{(x-2)-}$ depicts a copper DOM complex that remains in solution but the copper of the complex may not be bioavailable (Sunda and Guillard, 1976). The presence of metal sulfides with their exceedingly small solubility products (10^{-10} to 10^{-20}) may control the freely-dissolved metal but the total dissolved metal can be considerably more elevated due to the formation of some metal-ligand complexes with stability constants of the order of 10^{13} and 10^{17} for copper and nickel, respectively (Donat et al., 1994). Although the stability constants of the complexes of these metals and commonly-occurring inorganic ligands are fairly well known allowing for the computation of freely-dissolved metal concentrations in artificial seawater, it is problematic to computationally include naturally-occurring organic ligands with poorly known concentrations and stability constants that can be so large and varying.

Assessment of organism exposure in sediments containing metal contaminants rests on determining the likelihood that freely dissolved metal is present in the IW at high enough concentrations to affect benthic organisms. EPA has published WQC for saltwater (Table E- 2) that effectively accounts for metal-inorganic ligand complexes (U.S. EPA, 1999). However, only indirectly, as a footnote, does EPA acknowledge the possible confounding effects of metal-organic complexes on the saltwater metal WQC, and only for copper. EPA has developed procedures for establishing site-specific, freshwater WQCs for copper that could be adapted for use in saltwater

IW and for other metals (U.S. EPA, 2001). However, the bioassay endpoint and metal spiking protocols for application to IW are less far along in development than are the chemical endpoint methods for direct determination of freely dissolved metal concentrations in natural water (Donat et al., 1994; Gordon et al., 1996; Bruland et al., 2000). Although these direct chemical methods are being actively pursued, to date, the methods are not readily applicable outside academic research laboratories. In this study, individual metal concentrations of cadmium, copper, nickel, lead and zinc were compared to their WQC for short-term exposure (CMC) and continuous exposure (CCC). OCMC_f and OCCC_f values were computed as though the metal effects were additive.

Table E-2. National recommended water quality criteria for freely-dissolved priority metal pollutants (U.S. EPA, 1999).

Priority Pollutant	Saltwater (µg/L)	
	CCC ¹	CMC ²
cadmium	9.3	42
copper	3.1	4.8
lead	8.1	210
nickel	8.2	74
zinc	81	90

¹Criterion Continuous Concentration is the highest indefinite exposure without an unacceptable effect.

²Criteria Maximum Concentration is the highest 1-hr exposure without an unacceptable effect.

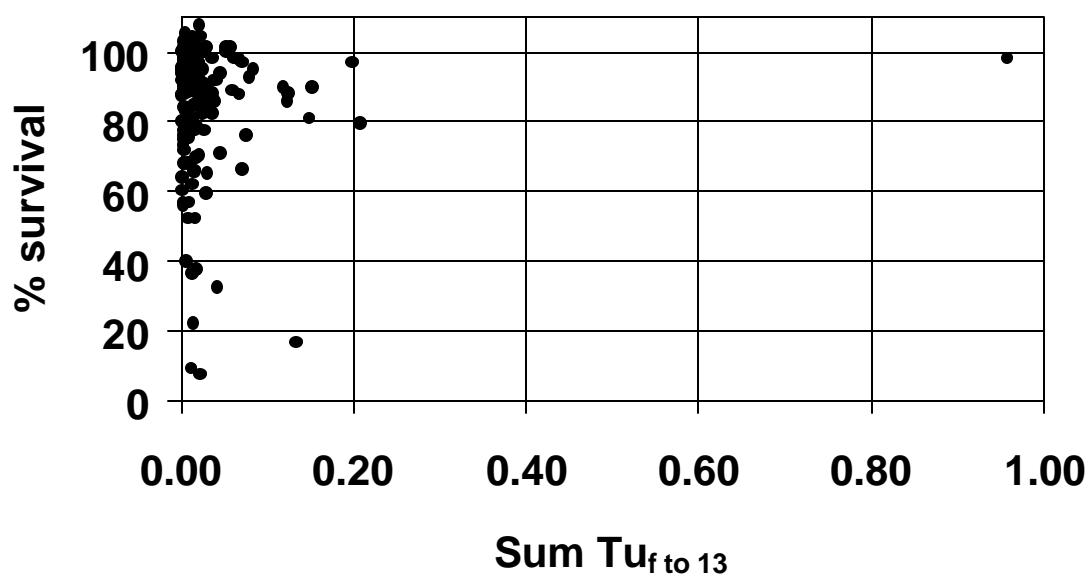
The uncertainty of the biological consequences from applying WQC in IW compelled EPA to choose analysis of the sulfide and metal content of the solid phase as the preferred regulatory method for assessing metal contamination of sediments (U.S. EPA 2000b). Allen et al. (1993) determined that the sulfides of these metals are readily hydrolyzed by dilute solutions of HCl yielding gaseous hydrogen sulfide (acid volatile sulfide, AVS) and the released metals in solution (simultaneously extracted metals, SEMs). In experimentally amended and field-contaminated sediments, when SEM was found to exceed AVS (but not before), ppm concentrations of metals were found in the IW and exposed benthic animals died (U.S. EPA, 2000b). EPA established an ESG for metal mixtures such that if the molar AVS concentration was less than the molar SEM concentration such sediments would be protective against any adverse effects of cadmium, copper, lead, nickel or zinc. However, if $SEM - AVS \geq 1.0$ and $(SEM - AVS)/f_{oc} \geq 130 \text{ } \mu\text{mole/g-OC}$ (to account for metal organic matter interactions) such sediments would not be suitable for the sustained health of benthic organisms (U.S. EPA, 2000b). In this study, the carbon-normalized difference between SEM and AVS of the samples were compared to the metal ESG of 130 $\mu\text{mole/gOC}$.

RESULTS

The ÓPAH Model

The ÓPAH model was applied only to the 241 stations that had *E. estuarius* amphipod bioassays performed. One or more of the 13 PAHs used in this model exceeded the laboratories' detection limits (DL) in 163 samples; none were detected in 78 samples. The $\acute{O}TU_{f\ to\ 13}$ s of the 163 samples were computed and a $\acute{O}TU_{f\ to\ 13}$ of 0.0 was assigned to the 78. The probability of each sample being placed in the three model toxicity categories was computed and summed by category for the 241 stations. These summations are compared to those found from the *E. estuarius* amphipod bioassay results (Bay et al., 2000) in Figure E-1 and Table E-3.

Figure E-1. *E. estuarius* survival (Bay et al., 2000) and $STU_{f\ to\ 13}$.



Target Lipid Narcosis Model

This model was applied to the PAH and PCB sediment concentrations. Of the 290 samples analyzed for these compounds, PAHs did not exceed the detection limit in 72, and PCBs in 131. $\Sigma\text{ESG}_{f \text{ to total}}$ and ΣESG_f were computed for the PAHs and PCBs, respectively. $\Sigma\text{ESG}_{f \text{ to total}}$ for “total” PAHs exceeded 1.0 at 10 stations with 8 coming from the ports and industrial waterway strata (Table E-4). The average $\Sigma\text{ESG}_{f \text{ to total}}$ was 2.7 with a maximum of 9.6. ΣESG_f from PCBs averaged only 0.4% $\pm 0.06\%$ (mean \pm SE) of the fractional units coming from PAHs, with a maximum of 8%.

Total DDTs

One or more of the isomers of DDT and its metabolites were detected in 220 of the 290 samples. In only 4 samples did DDTs exceed 100 $\mu\text{g/g-OC}$, the concentration above which chronic effects on amphipod populations would be expected (Table E-4). The maximum carbon-normalized concentration was 185 $\mu\text{g/g-OC}$.

IW Metals, AVS and SEM

Only 108 samples had sufficient water content to harvest IW for dissolved metals; AVS and SEM were determined on these samples as well. WQCs of only copper and nickel were exceeded in any of the IW samples. Two samples had both copper and nickel exceeding their CCCs and there were 35 samples where one or the other CCC was exceeded (Table E-5).

If metal CCC_f are additive (U.S. EPA, 2000b) as TU_s appear to be for organic compounds, then the ECCC_f from 79 stations exceeded 1.0 and, without qualification, might be considered unsuitable for some benthic organisms. On average copper, nickel and zinc contributed 61%, 30%, and 4%, and 82%, 9% and 8%, respectively, of the ΣCCC_s and ΣCMC_f s in this study. The EPA-proposed ESG for metals in sediment of 130 $\mu\text{mole (SEM-AVS)/g-OC}$ was exceeded in only 8 samples with SEM-AVS from 27 stations exceeding 0.0 $\mu\text{mole/g}$ (Table E-6).

Table E-3. Number of stations with predicted and observed categories of acute toxicity.

Bioassay Response	Number of Stations	
	Predicted ¹	Observed ²
>87% survival	192	170
between 76% and 87% survival	36	34
<76% survival	13	37

¹ Using equations 2-5

² Bay et al., 2000

Table E-4. Stations exceeding sediment guidelines for total PAHs and DDTs.

Strata (% of 3259 km²area)	Number of Stations	PAHs SESGf to total >1.0	DDTs >100mg/gOC
Ports/Industrial (1.9%)	37	8 (0.4%)	0
POTW outfalls (5.5%)	71	1 (0.04%)	4 (0.6%)
Marinas (2.7%)	39	1 (0.07%)	0
Shallow (30%)	41	0	0
Mid-Depth (58%)	34	0	0
River (1%)	31	0	0
Other Harbors (1.6%)	37	0	0
Total: (% of area):	290 (100%)	10 (0.5%)	4 (0.6%)

Table E-5. Stations exceeding sediment interstitial water quality criteria for dissolved metals.

Strata (% of area)	Stations	Copper		Nickel		SCCC_f	ΣCMC_f
		>CCC	>CMC	>CCC	>CMC	>1.0	>1.0
Ports/Industrial (1.5%)	28	5	1	2	1	19	3
POTW outfalls (1.3%)	8	3	2	1		6	2
Marinas (2.6%)	35	15	9	3		28	10
Shallow (13%)	3					2	
Mid-Depth (81%)	10	2	2			7	2
River (0%)	0						
Other Harbors (1.2%)	24	5	4			17	4
Total:	108	30	18	6	1	79	21
% of area:	100%	18%	17%	1%	<1%	70%	18%

Table E-6. Stations exceeding ESG for bulk sediment metals.

Strata (% of area)	Stations	(SEM-AVS)/OC >130 μmole/g-OC	SEM-AVS >0 μmole/g
Ports/Industrial (1.5%)	28	2 (0.1%)	8 (0.4%)
POTW outfalls (1.3%)	8		2 (0.2%)
Marinas (2.6%)	35	3 (0.1%)	5 (0.2%)
Shallow (13%)	3		
Mid-Depth (81%)	10		7 (56%)
River (0%)	0		
Other Harbors (1.2%)	24	3 (0.1%)	5 (0.2%)
Total:	108	8	27
% of area:	100%	0.3%	57%

DISCUSSION

Acute Toxicity

As the highest bulk PAH concentrations (Table E-7) were generally associated with the highest total organic carbon (TOC) concentrations (2428 μ g/kg w/ 2.5% OC), the resulting low carbon-normalized values caused the Σ PAH Model output to predict few samples to be acutely toxic or of uncertain toxicity. These results were generally reflected in the *E. estuarius* bioassay results (Table E-3) although the higher than predicted number of acutely toxic samples suggests that toxicants other than PAHs were present in some of the samples.

DDT and its metabolites were detected in most samples of this study but the maximum carbon-normalized concentration for total DDT was 185 μ g/g-OC, less than the 300 μ g/g-OC for the 10-day bioassay toxicity (Swartz et al., 1994). In addition there was no relationship between the survival of *E. estuarius* in the bioassays and the concentrations of DDT (Figure E-2).

The expectation of analyzing metals in IW was that if SEM >AVS or if the carbon-normalized differences between these parameters exceeded 130 μ mole/gOC there would be elevated dissolved metal concentrations. Neither of these expectations was realized in the several samples where these chemical conditions were found (Figure E-4).

Table E-7. PAH and TOC statistics from 290 stations.

Parameter	mean	SE	n	maximum	minimum
PAHs (ng/g-dry wt)	56	2.5	3305	2428	0.9
TOC (%)	0.91	0.04	290	3.64	0.05

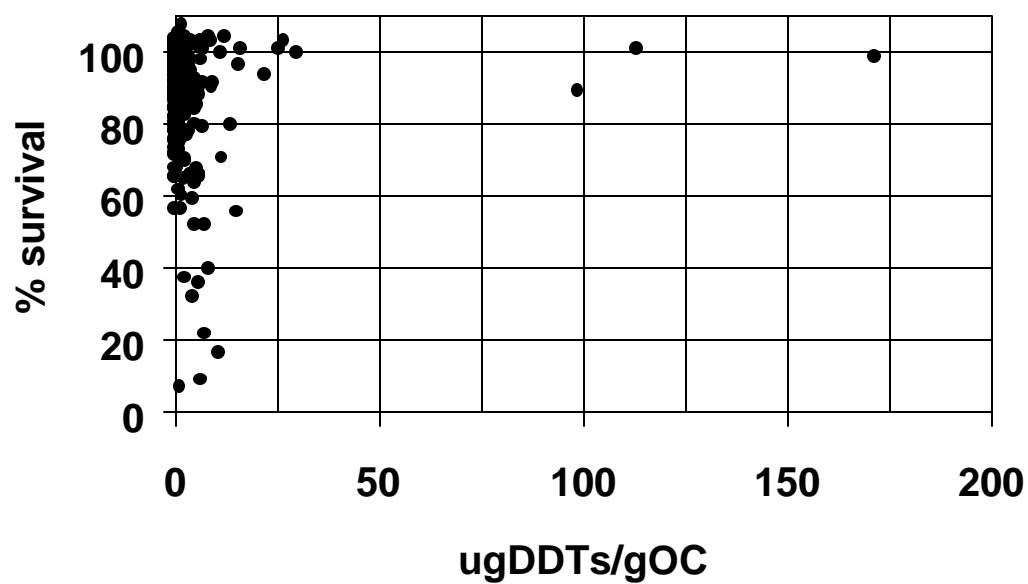


Figure E-2. *E. estuarius* survival (Bay et al., 2000) and concentrations of DDTs.

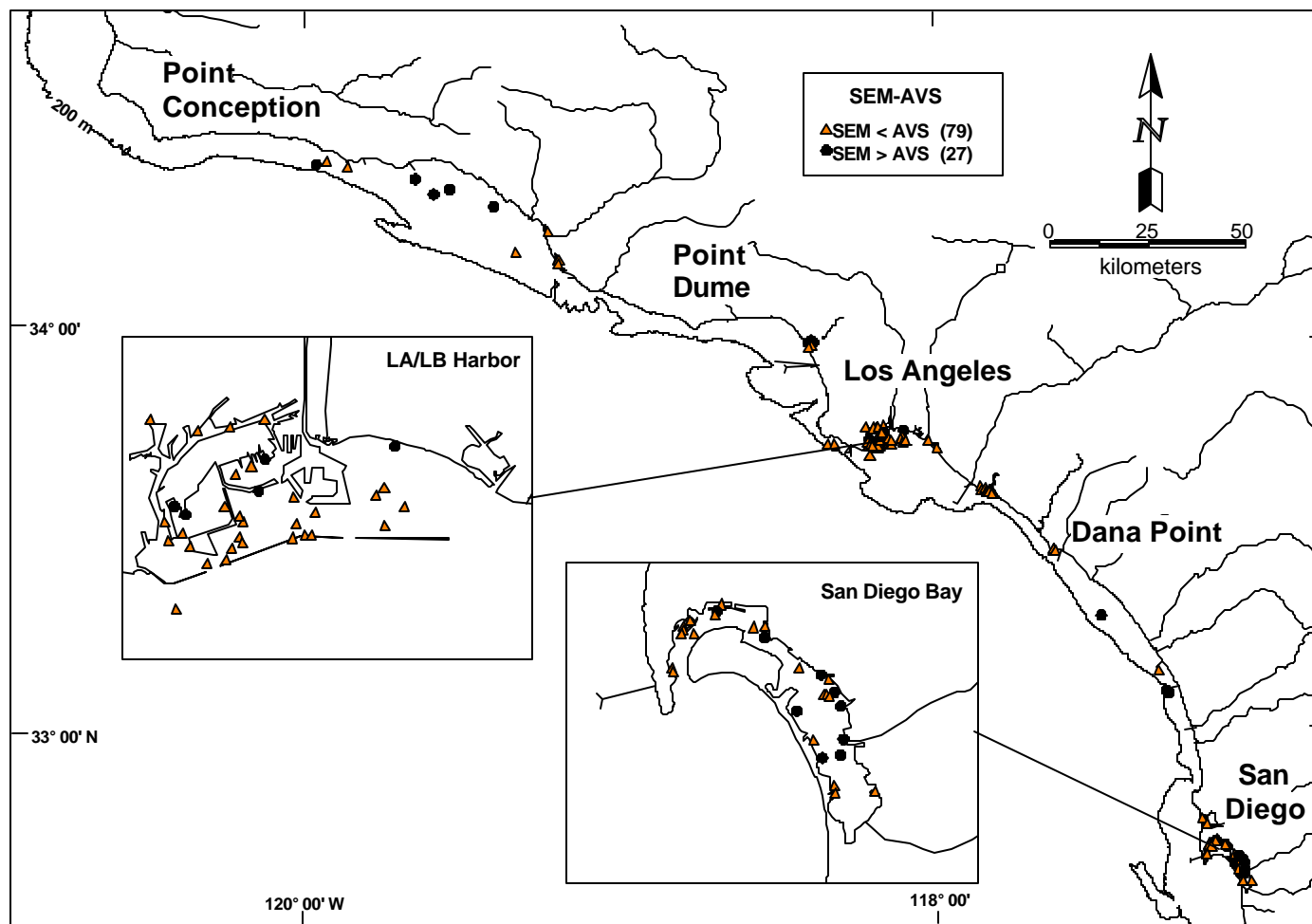


Figure E-3. The Bight '98 sediment chemistry stations (108) evaluated for potential toxicity using the SSEM-AVS approach.

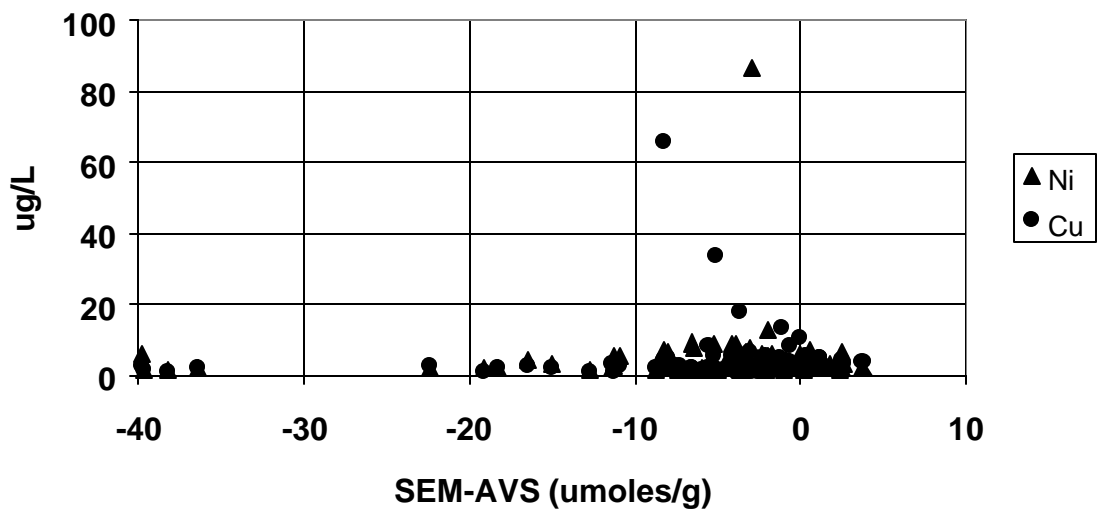


Figure E-4. Concentrations of nickel and copper associated with the difference between SEM and AVS.

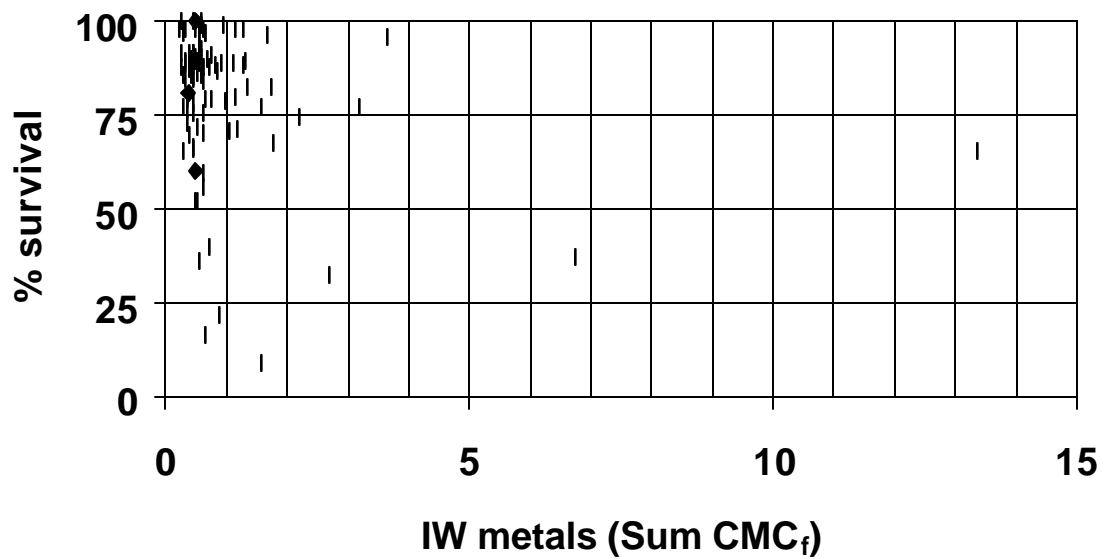


Figure E-5. *E. estuarius* survival and the summation of the ratio of CMC to metal

concentration for cadmium, copper, lead, nickel, and zinc.

Although the CMC concentrations for short-term exposure were exceeded individually by copper and nickel, and the ΣCMC_f s across the five metals exceeded 1.0 in many samples (Table E-5), these exceedences were distributed fairly evenly among the toxic and non toxic samples (Figure E-4).

The likely explanation for these elevated metal concentrations not being acutely toxic is that, although they are dissolved, the majority of the metals are sequestered by dissolved organic matter in the IW (Sunda and Guillard, 1976). Skrabal et al. (1997) reported that organic ligands on the order of 0.05-0.2% of the dissolved organic carbon (DOC) in the IW of Chesapeake Bay sediments (6-24 mgC/L, Burdige and Homstead, 1994) were capable of interacting with copper. Skrabal et al. (1997) found freely-dissolved concentrations of copper to be <0.1 % to 3% of the total and that the measured copper was associated with only 2.5% to 35% of the ligands that were capable of sequestering copper with stability constants on the order of 10^{15} . This suggests that in IW there can be relatively large reservoirs of organic ligands that are capable of sequestering divalent metal species. The concentrations of total metals dissolved in IW of this study are a likely consequence of natural organic complexes interacting with the metal sulfides to enhance the IW concentrations of these metals, especially copper and nickel, but rendering the dissolved metals biologically inert.

The association of significant mortality with low levels of contamination (by conventional suite of chemical analytes) has been reported in several studies (Swartz et al., 1995 (25% >13% mortality); Swartz et al., 1994 (100% - 23% mortality); Long and McDonald, 1998 (10% >20% mortality)). These levels of mortality have been attributed to unmeasured contaminants, natural sediment features, or interactions between several parameters (Swartz et al., 1994, O'Connor and Paul, 2000). Toxicity identification evaluation (Ho et al., 1997 and Burgess, 2000) of the sediments of this study might help identify the origin of this background toxicity.

Chronic Toxicity

From EPA's perspective, those stations containing PAHs at such levels that their $\Sigma\text{ESG}_{f \text{ to total}}$ s are greater than one would be considered sites of concern and, in this study, the concern would be extended to the statistically sampled grid that the individual stations represent (U.S. EPA, 2000d). These sediment guidelines for PAHs are based on the assumption that extractable PAHs are in equilibrium with IW. This assumption is questionable when soots, coal fragments, or other solid products of petroleum combustion are suspected to be in sediment (Ozretich, et al., 2000, 2002) and is one justification for developing site-specific ESGs (U.S. EPA, 2000c). The 10 stations that exceed this PAH ESG represent ~0.5% of the study area but ~22% of the ports and industrial strata (Table E-4). Although these stations would be considered of concern they would be strong

candidates for developing site-specific ESGs for PAHs, as these types of water bodies can be heavily used by vessels propelled by diesel marine engines known for their soot-laden stack discharges. As the threshold for benthic community effects attributable to DDT contamination was found at concentrations of ~100 µg/g-OC (Swartz, et al., 1994), modified benthic communities might be expected at the 4 sites near POTW outfalls representing 0.6% of the study area and ~6% of the outfall strata (Table E-4).

Summary

The concentrations of organic and inorganic contaminants for which sediment guidelines have been proposed were sufficiently low that no stations would have been expected to be acutely toxic. Also, few stations would be expected to manifest the effects of concentrations exceeding those expected to cause changes in the benthic community structure. Although concentrations of total metals in the IW from stations of this study exceeded acute and chronic criteria, the criteria likely do not represent the bioavailable concentrations in the IW and are thus, without additional information, overly conservative.

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APPENDIX F

Comparison of P450 HRGS Assay Results and
Sediment Chemistry Data

INTRODUCTION

Portions of sediment extracts from the 290 U.S. stations of the Southern California Bight 1998 Regional Monitoring Survey (Bight'98 Survey) were analyzed with using the P450 Human Reporter Gene System (HRGS) Assay (EPA Method 4425). The P450 HRGS assay is an analytical method that measures the presence of compounds that induce a toxic response in a modified line of human liver cells. The test responds primarily to carcinogenic compounds such as dioxins, furans, co-planar PCBs, and certain PAHs (Kim *et al.* 1997, Jones and Anderson 1999, Jones *et al.* 2000, McCoy *et al.* 2002). The target analytes from the Bight'98 Survey that are known to induce a response in the P450 HRGS assay are shown in Table F-1. Correlations between adverse biological impacts and P450 HRGS response have also been identified (Anderson *et al.* 1999a, 1999b, 1999c). Therefore, the P450 HRGS system can, in principle be used to both screen for presence of chemical contamination and to estimate the potential for biological impacts in sediments containing toxic and carcinogenic compounds.

In this study, the P450 HRGS assay response (in Benzo[a]pyrene equivalents or B[a]P Eq) is compared to measured sediments concentrations of the Bight'98 target analytes known to induce a P450 response (i.e., PAHs and PCBs). The responses from the assay were assessed relative to total and organic carbon-normalized concentrations, as well as a subset of the known P450 inducing compounds. Relationships between assay response and sample subpopulations are also be explored.

METHODS

A description of the methods and materials used in conducting a typical P450 HRGS assay has been reported elsewhere (Anderson *et al.* 1995, APHA 1998, ASTM 1999, EPA 2000). The specific details on the procedures used in the Bight'98 Survey can be found in the Bight'98 Sediment Toxicity Report (Bay *et al.* 2000) and in the Methods sections of this report. It is important to note that different target analytes have different induction kinetics. A 16-h exposure period was used in this study to maximize the combined response for PAHs and PCBs. The maximum induction for PAHs is achieved 6-8 h after exposure to the cells, whereas PCBs require 16 hours to achieve the maximum response. The response due to PAHs declines by approximately 70% from 6-16 h after exposure. In contrast, the induction from a mixture of PAHs and PCBs increases more than 100% between 6 and 16 h. Therefore, the 16-h exposure time is a compromise to enhance the potential contribution from both PCBs and PAHs.

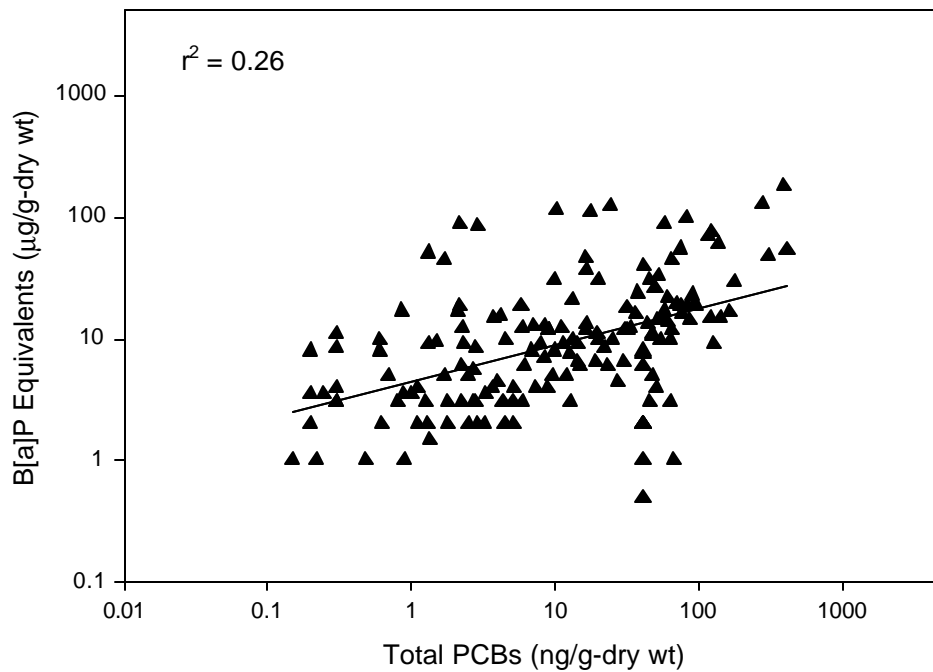
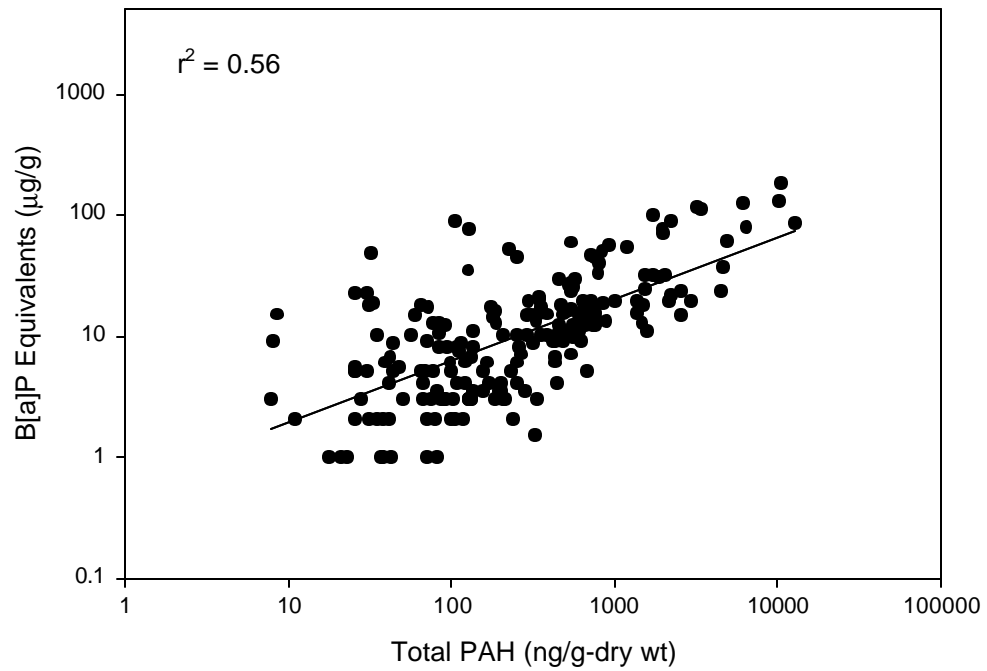


Figure F-1. P450 HRGS assay results plotted versus sediment total PAH (circles) and total PCB (triangles) concentrations.

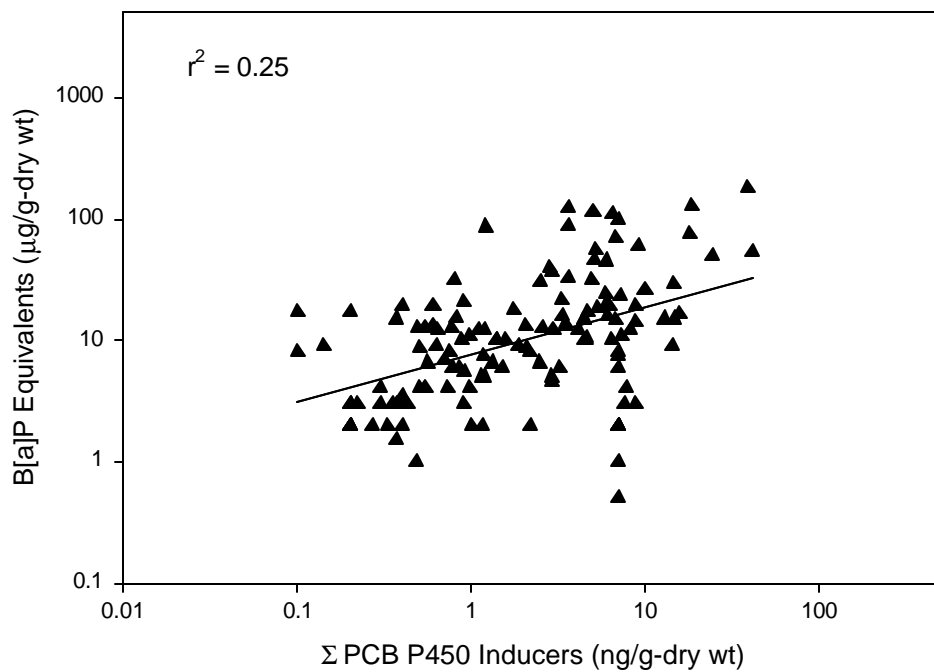
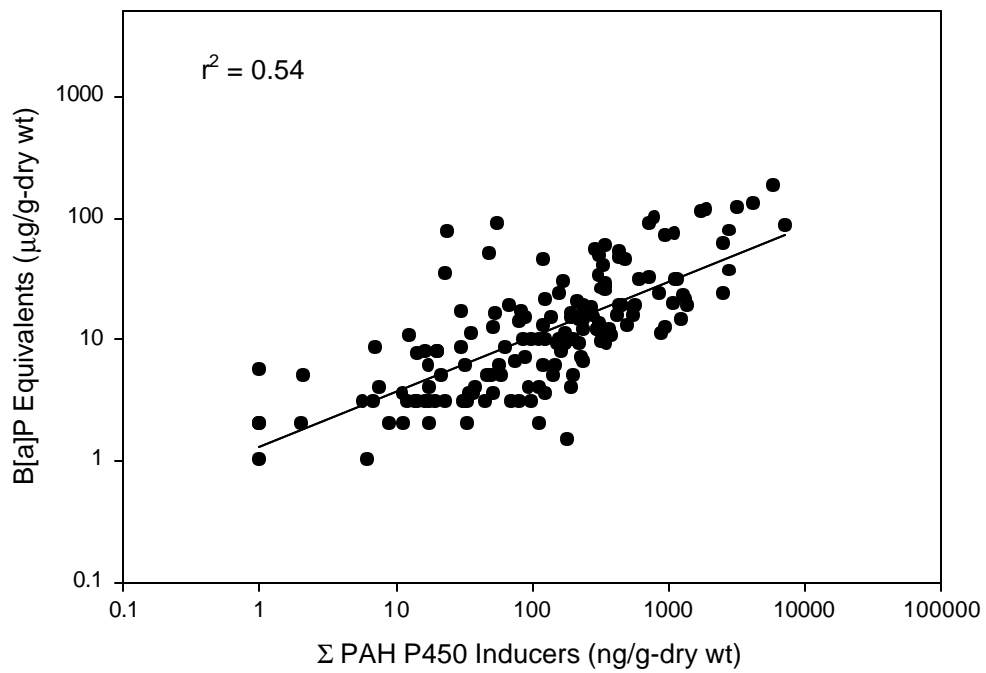


Figure F-2. P450 HRGS assay results plotted versus total sediment concentrations of P450 inducing PAHs (circles) and PCBs (triangles).

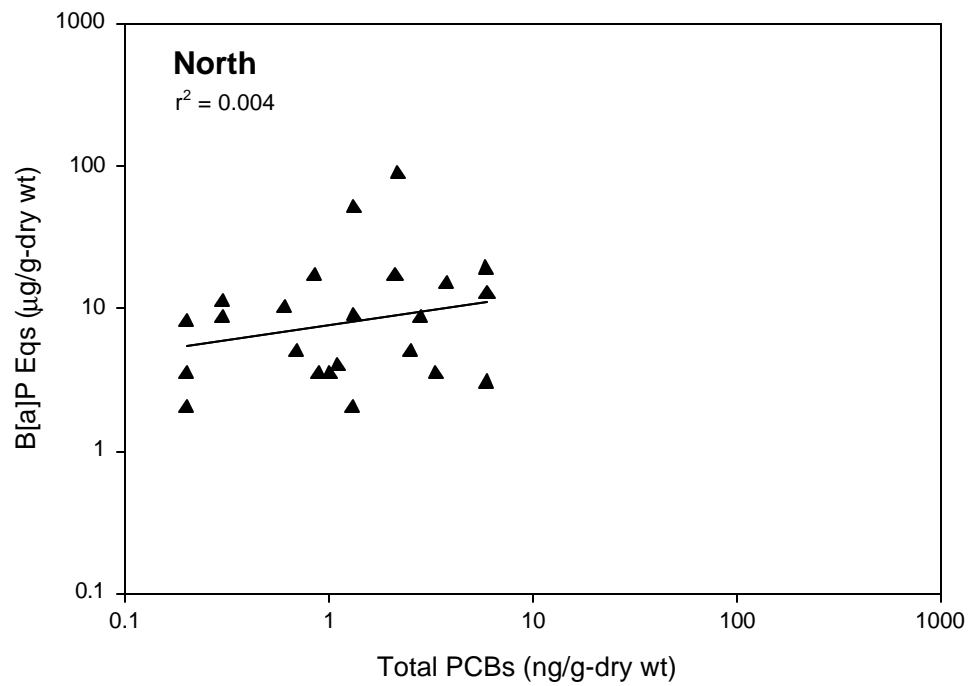
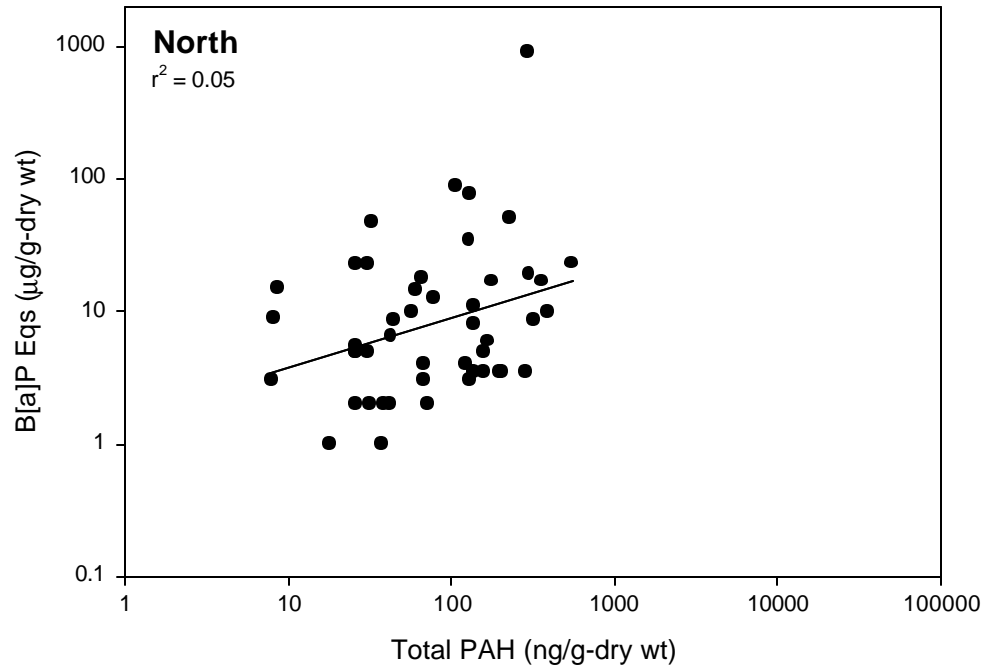


Figure F-3. P450 HRGS results plotted versus sediment total PAH (circles) and PCB (triangles) concentrations on a dry weight basis for samples from northern section of the Southern California Bight.

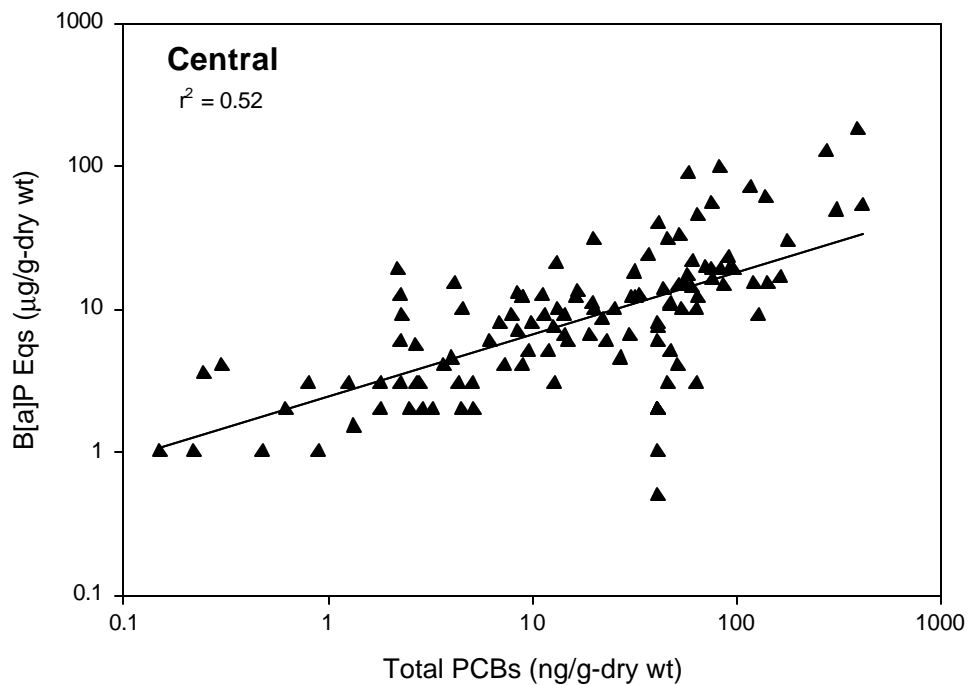
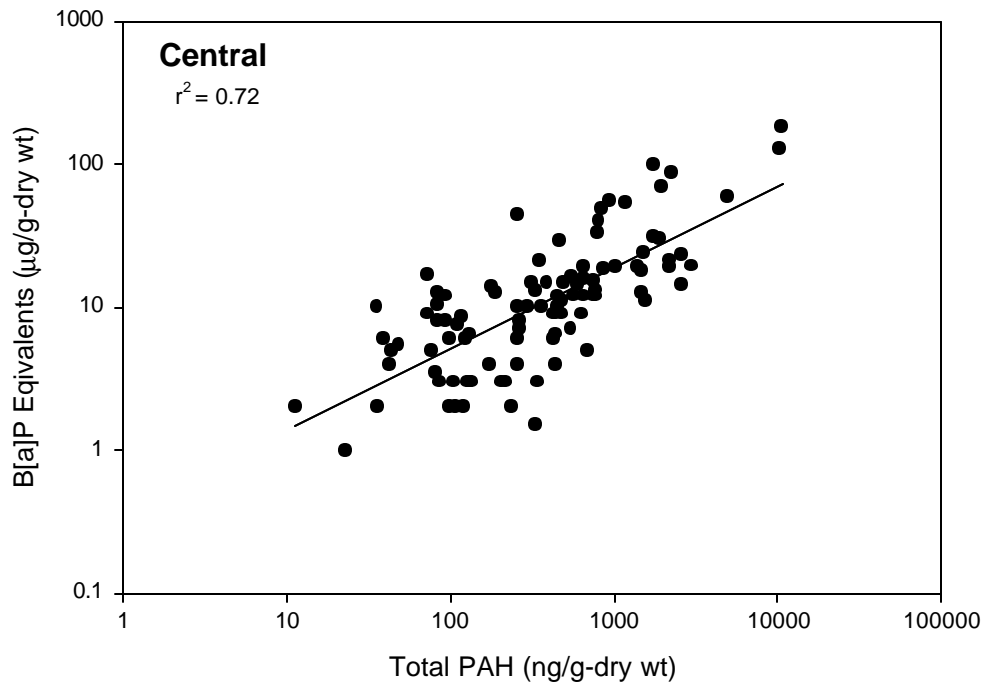


Figure F-4. P450 HRGS results plotted versus sediment total PAH (circles) and PCB (triangles) concentrations on a dry weight basis for samples from central section of the Southern California Bight.

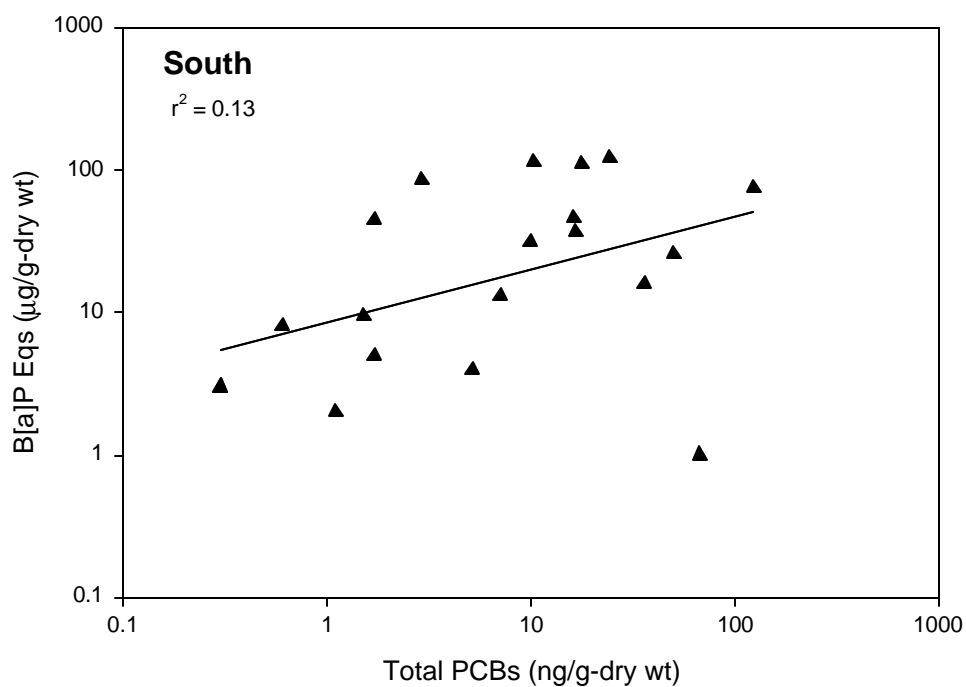
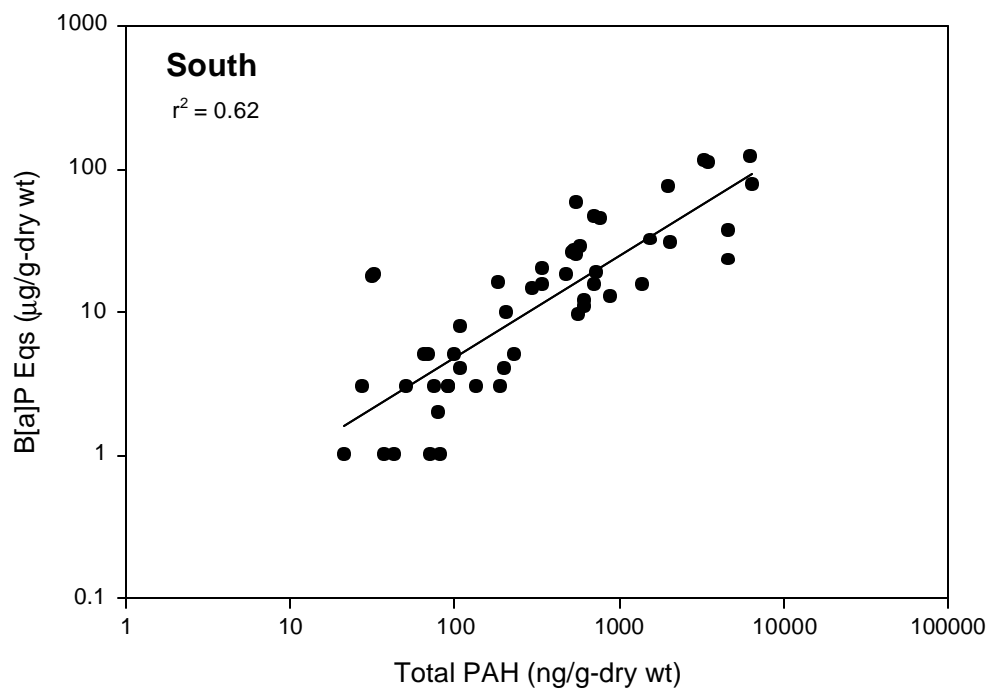


Figure F-5. P450 HRGS results plotted versus sediment total PAH (circles) and PCB (triangles) concentrations on a dry weight basis for samples from southern section of the Southern California Bight.

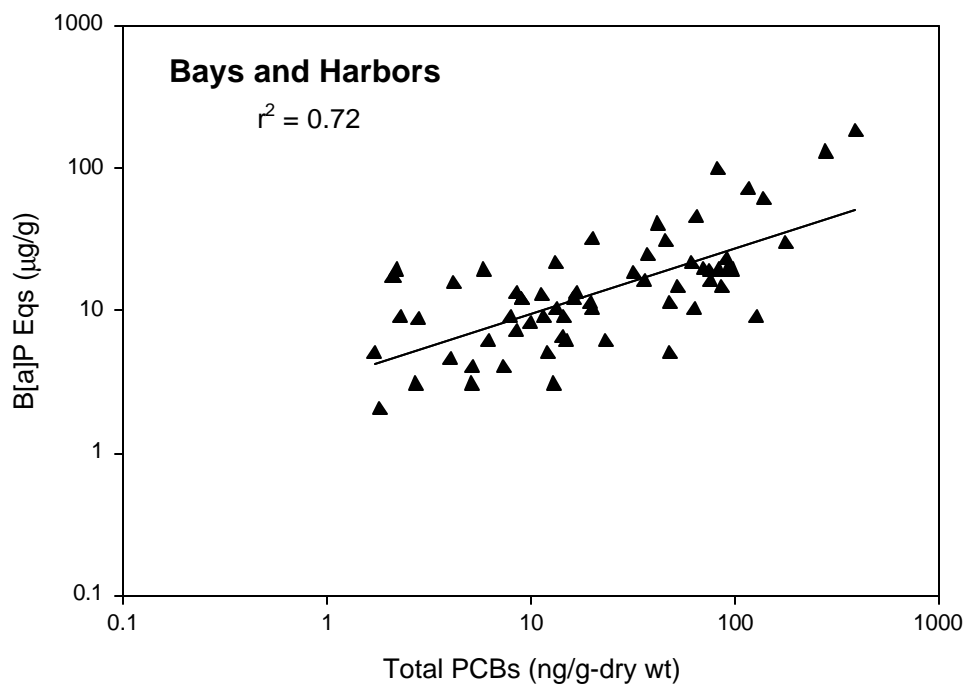
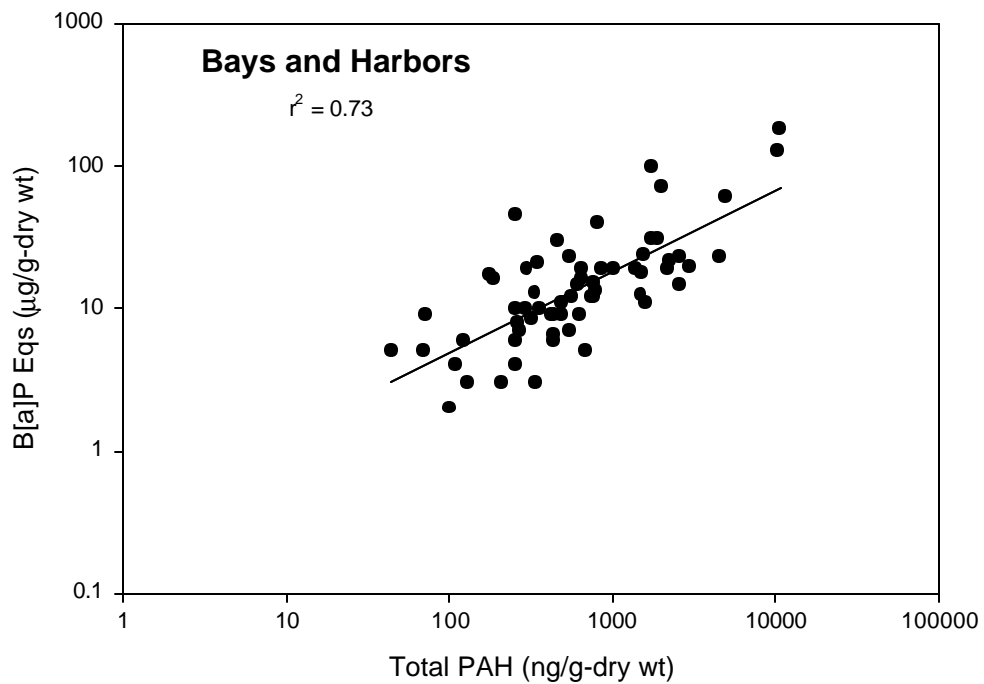


Figure F-6. P450 HRGS results plotted versus sediment total PAH (circles) and PCB (triangles) concentrations on a dry weight basis for samples from all the bay and harbor areas except San Diego Bay.

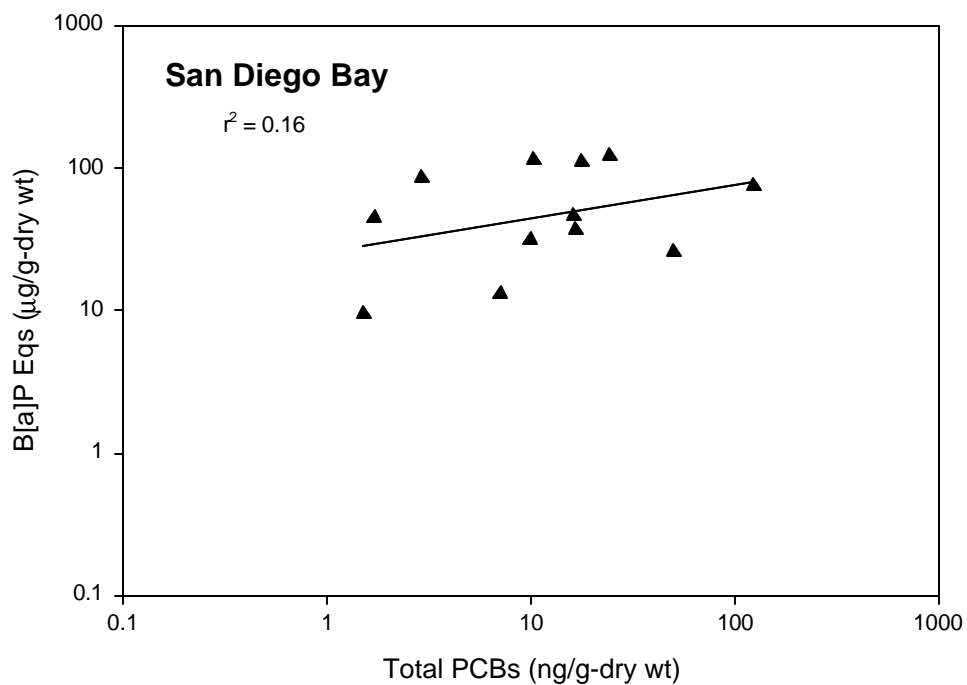
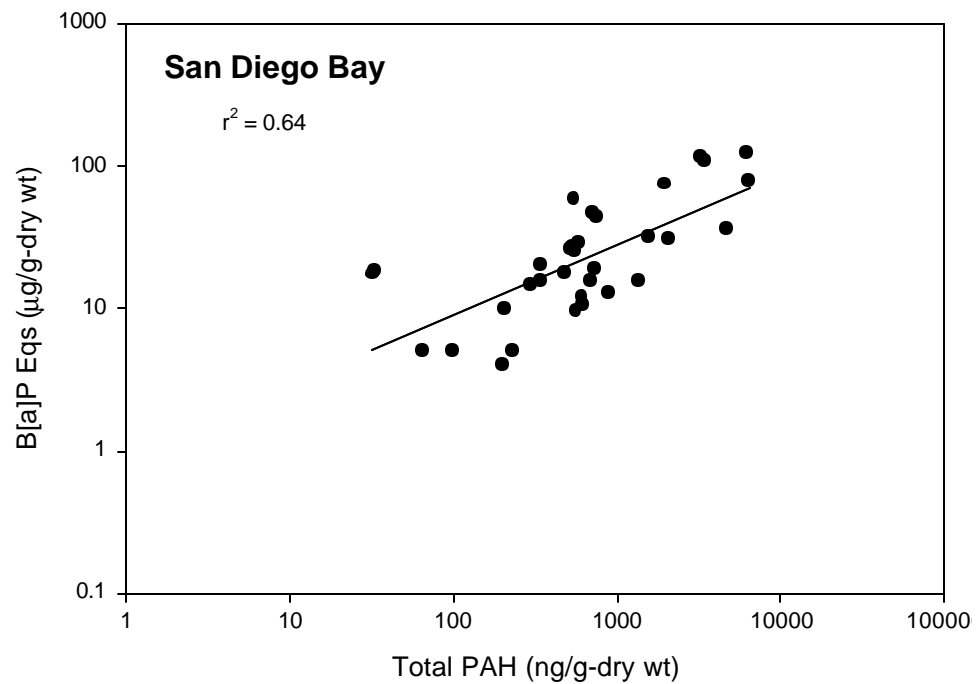


Figure F-7. P450 HRGS results plotted versus sediment total PAH (circles) and PCB (triangles) concentrations on a dry weight basis for samples from San Diego Bay.

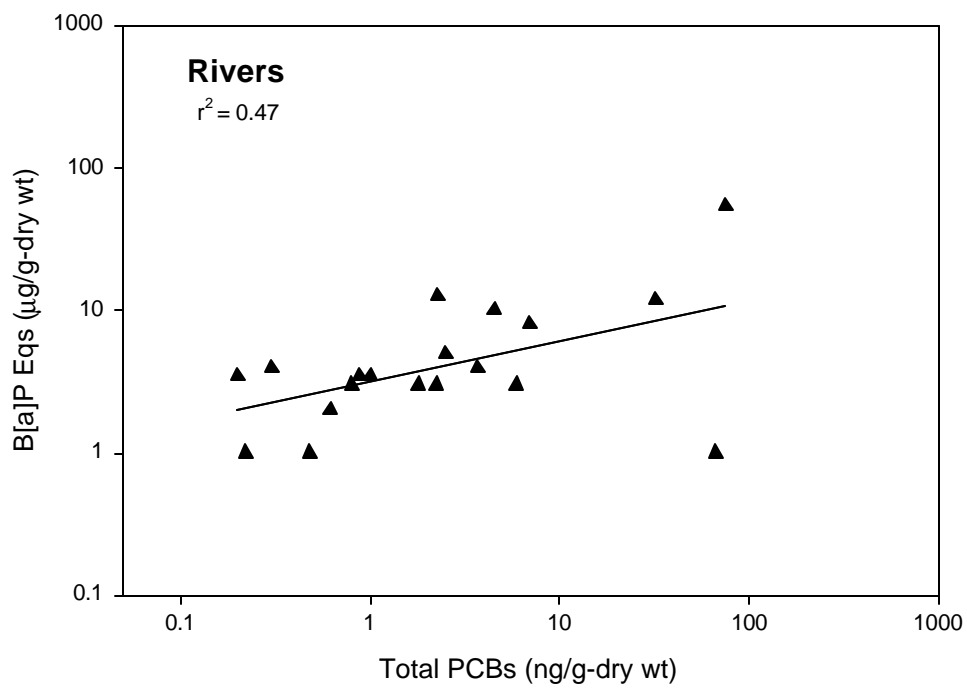
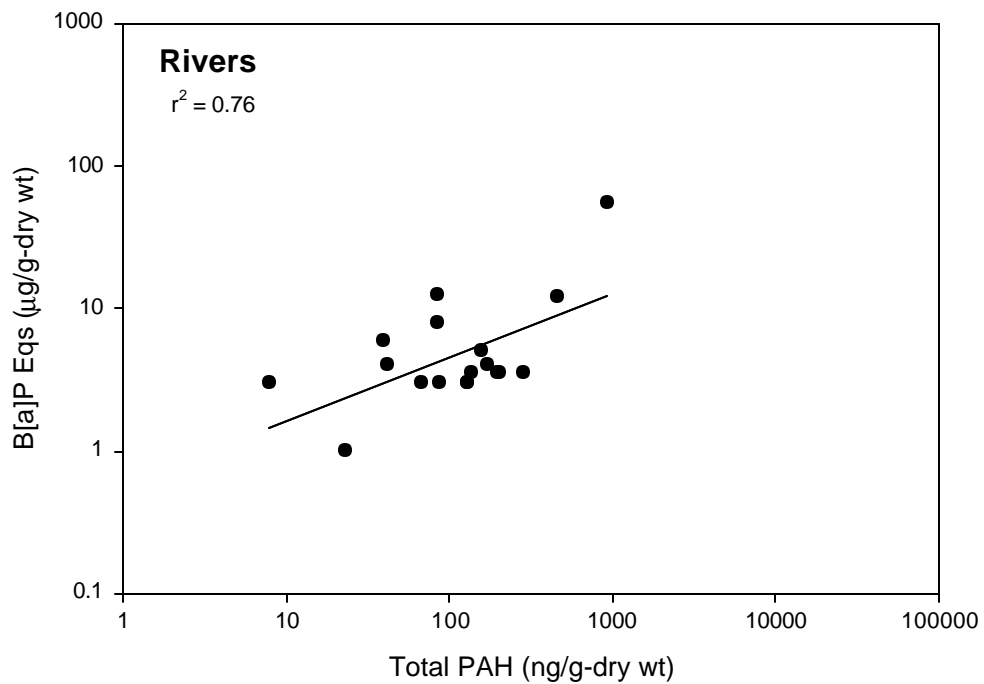


Figure F-8. P450 HRGS results plotted versus sediment total PAH (circles) and PCB (triangles) concentrations on a dry weight basis for samples from river discharges areas.

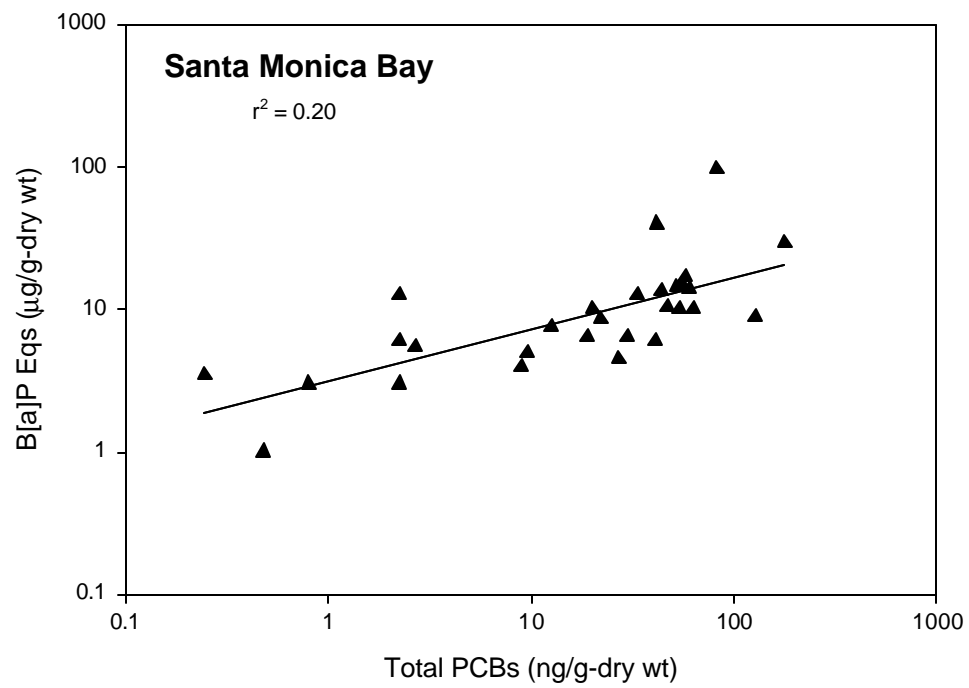
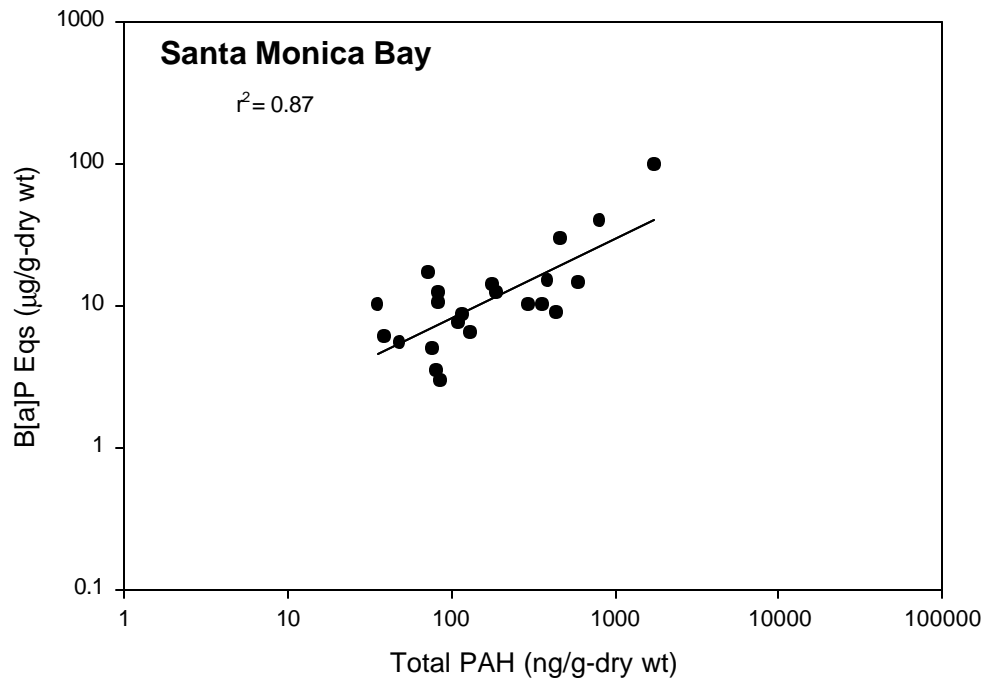


Figure F-9. P450 HRGS results plotted versus sediment total PAH (circles) and PCB (triangles) concentrations on a dry weight basis for samples from Santa Monica Bay.

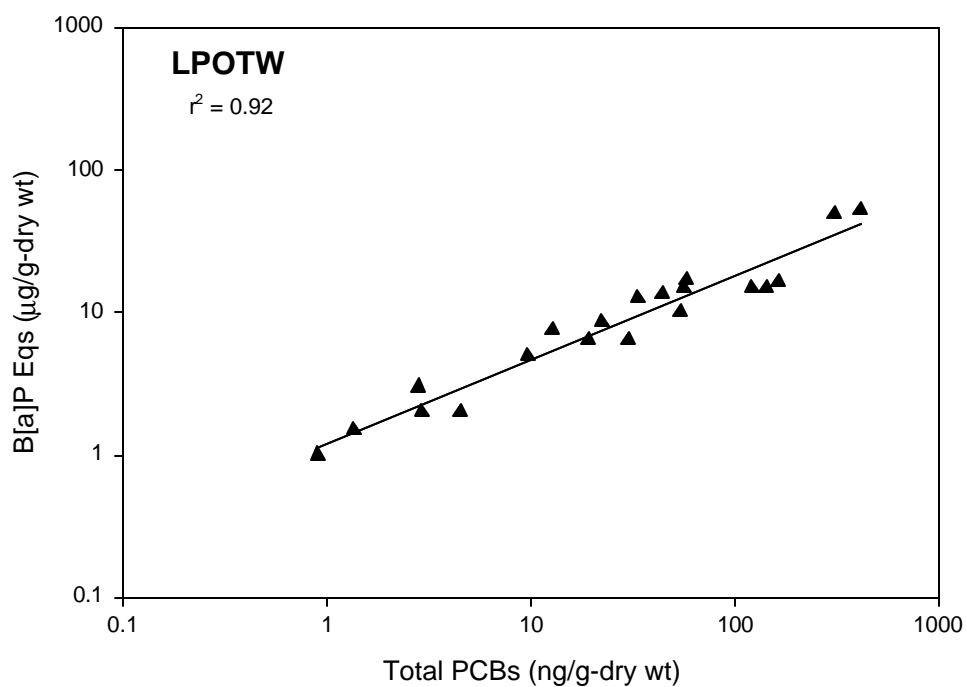
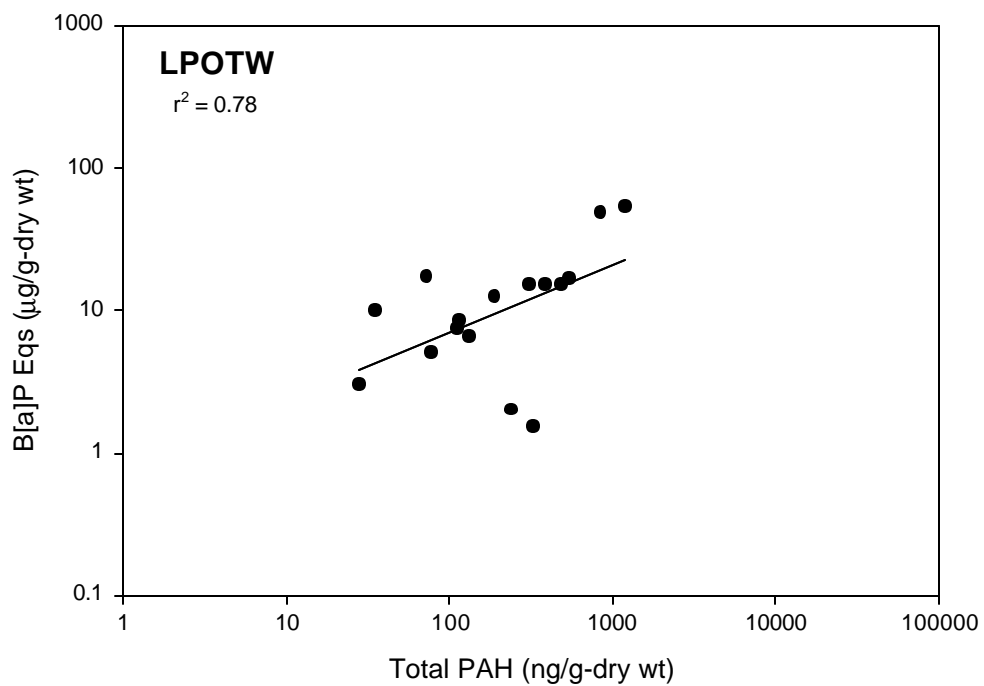


Figure F10. P450 HRGS results plotted versus sediment total PAH (circles) and PCB (triangles) concentrations on a dry weight basis for samples in proximity to large POTW outfalls.

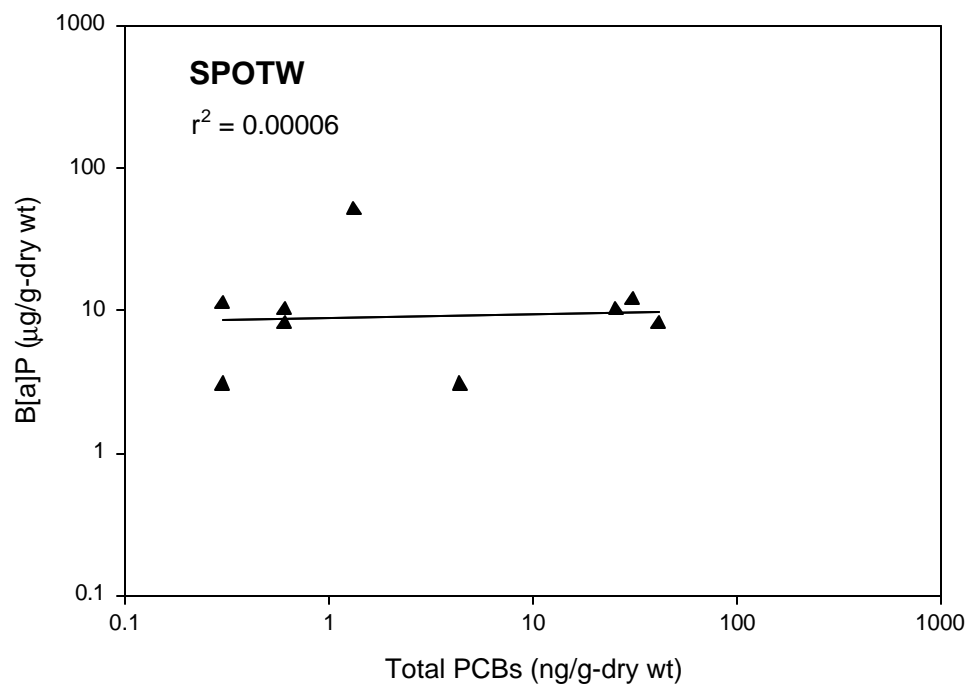
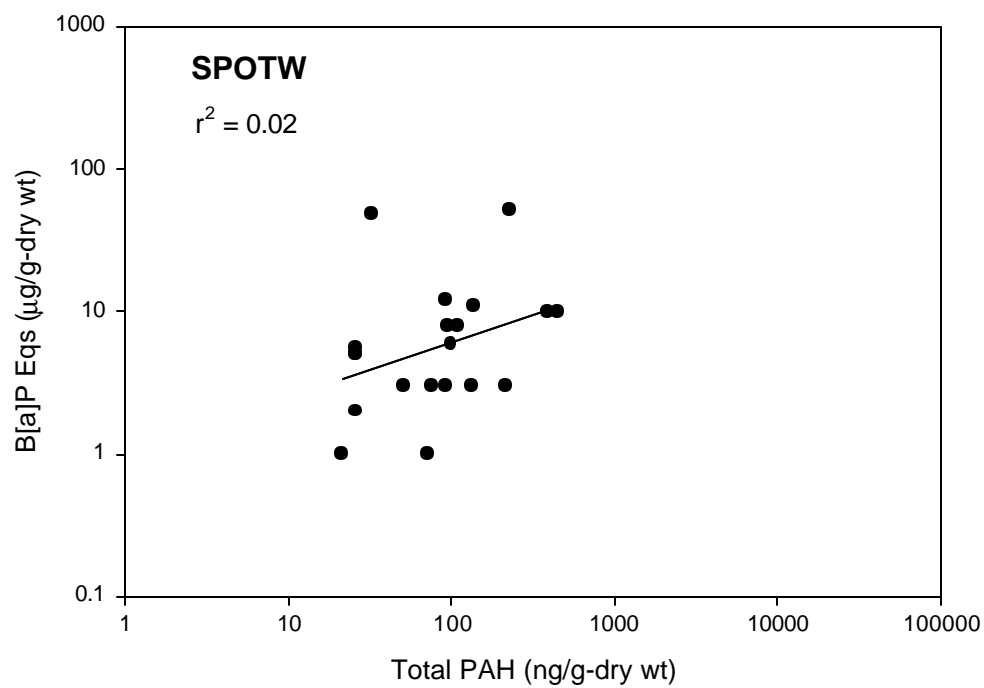


Figure F-11. P450 HRGS results plotted versus sediment total PAH (circles) and PCB (triangles) concentrations on a dry weight basis for samples in proximity to small POTW outfalls.

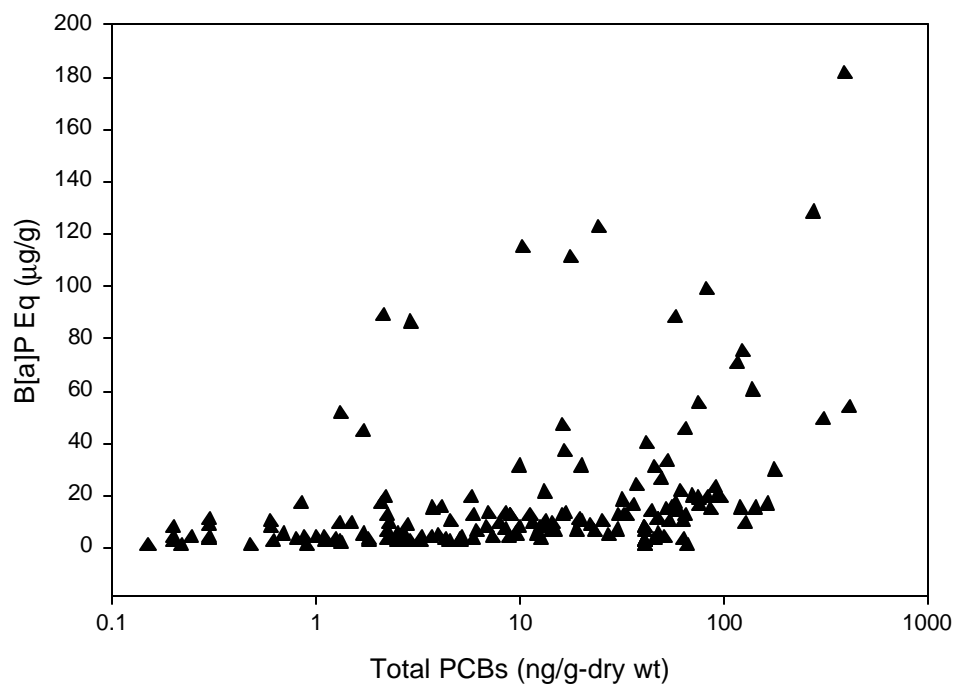
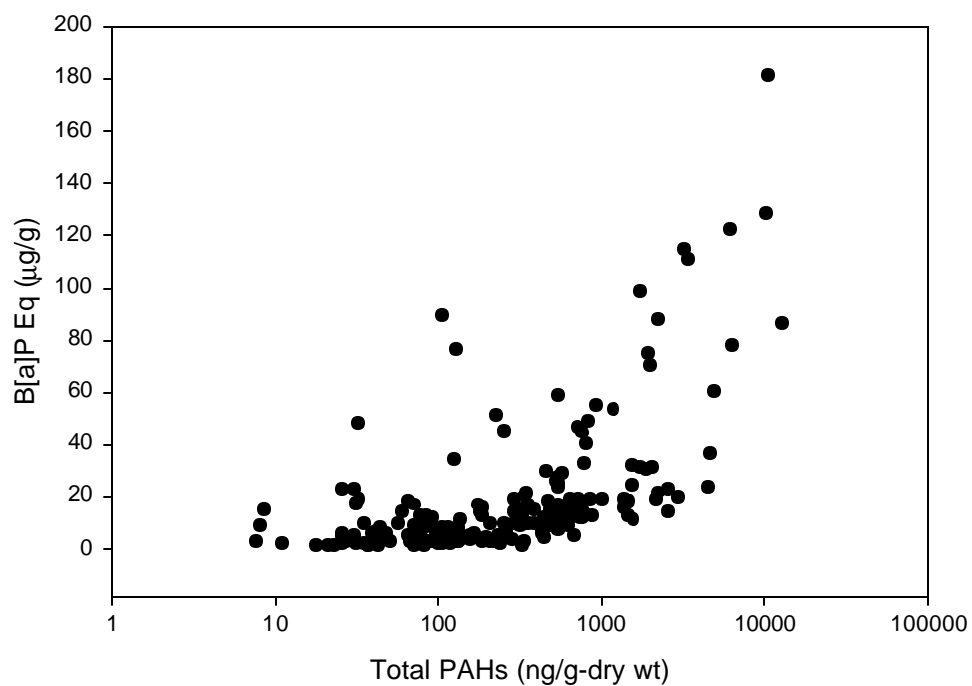


Figure F-12. Bight'98 P450 HRGS results on semi-log plots versus sediment total PAH (circles) and PCB (triangles) concentrations on a dry weight basis. The single station with an extremely high assay response (~1000 B[a]P Eq) has been omitted for graphical clarity.

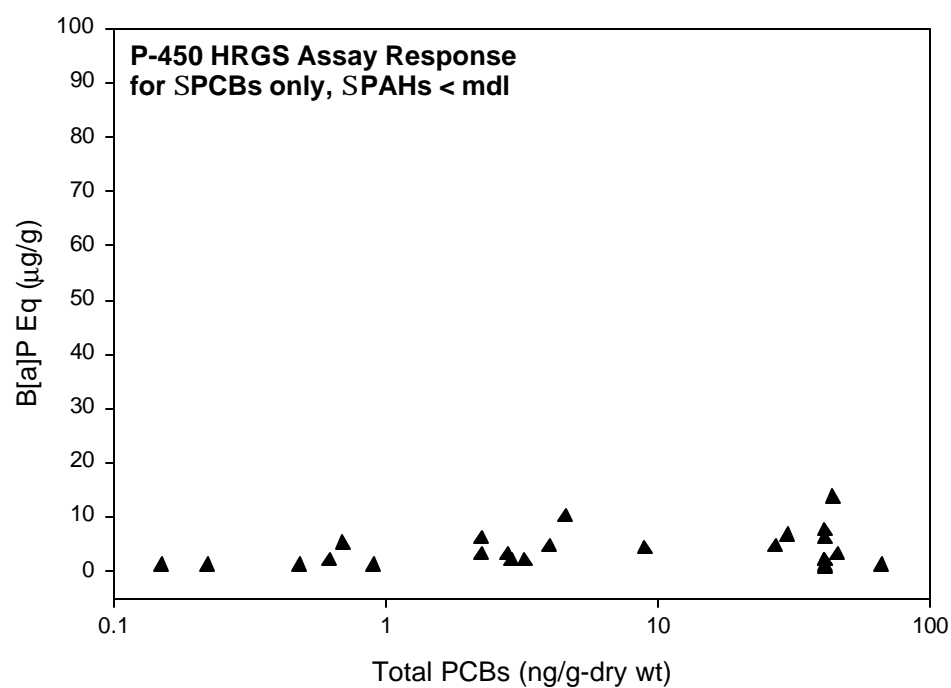
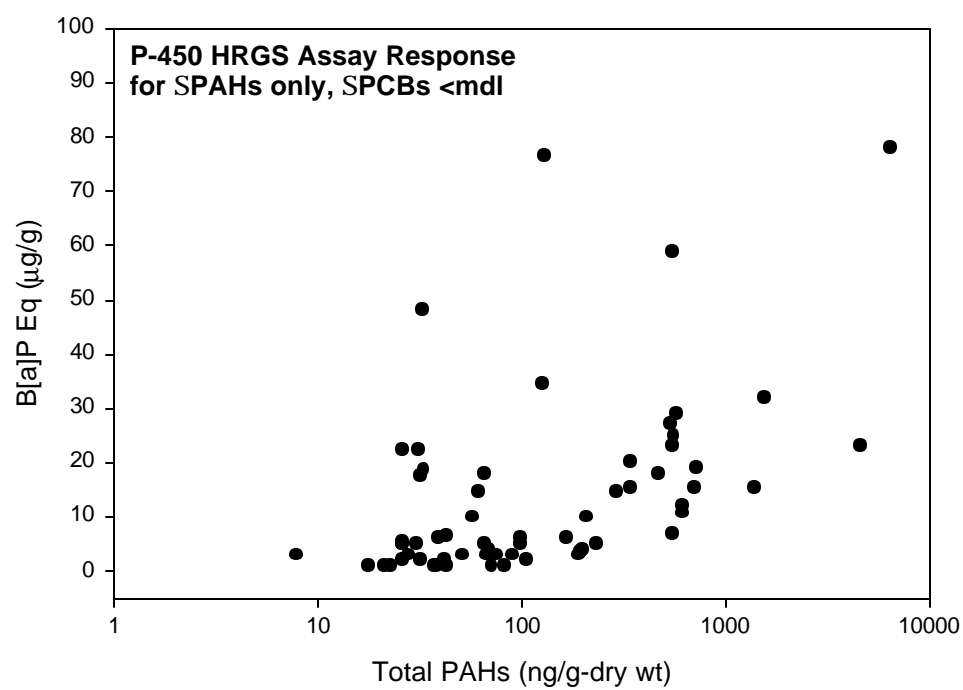


Figure F-13. The P450 HRGS results plotted on a semi-log scale relative sediment total PAH (circles) and PCB (triangles) concentrations on a dry weight basis, for samples with measurable levels of only PAHs and PCBs, respectively.

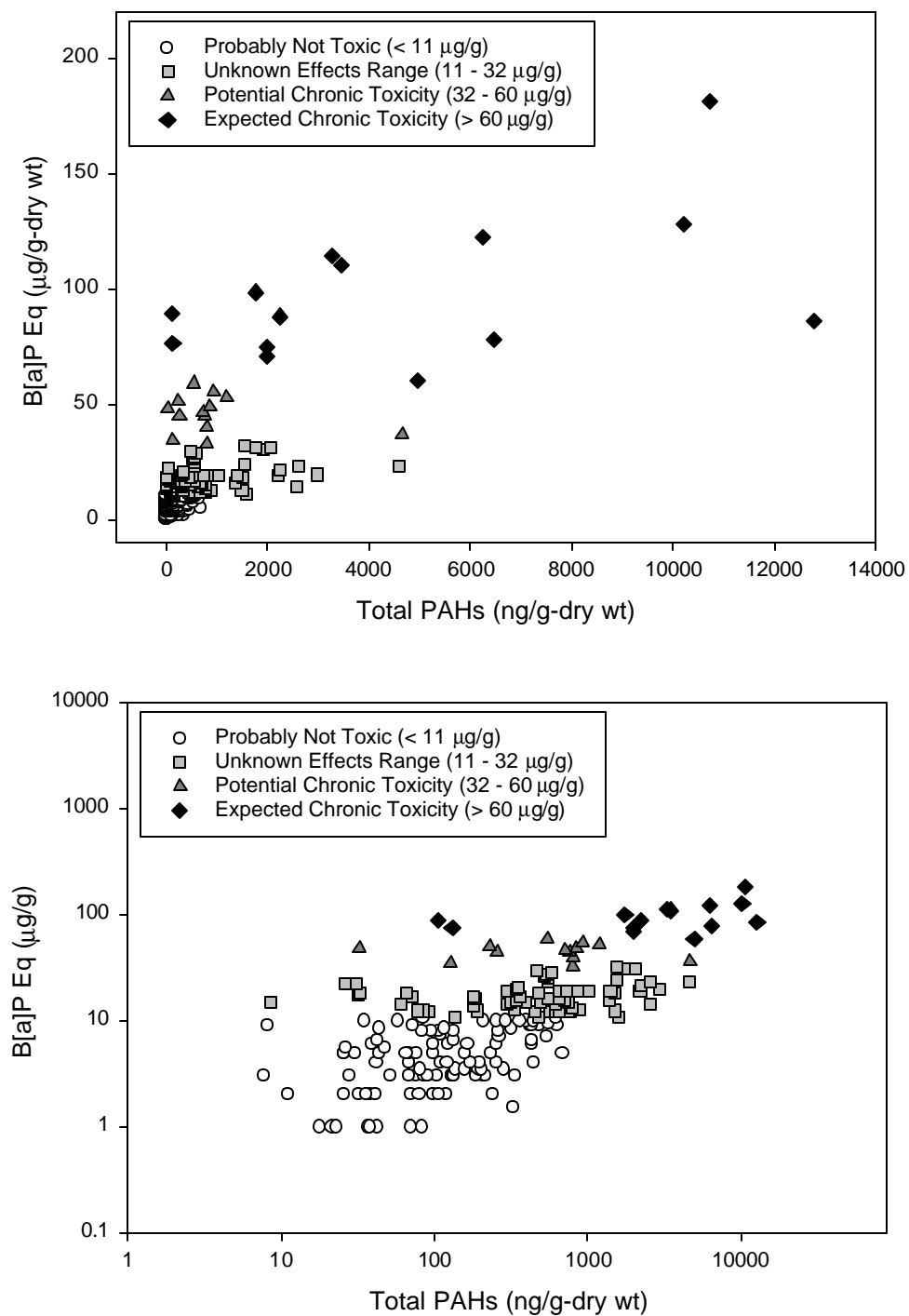


Figure F14. P450 HRGS results and the associated predicted toxicity versus sediment total PAH concentrations on a dry weight basis plotted on linear scale and log-log plots.

Table F-1. Bight'98 target analytes known to induce a response from the P450 HRGS assay.

Polynuclear Aromatic Hydrocarbons (PAHs)	Polychlorinated Biphenyls (PCBs)
Benzo(k) fluoranthene	PCB #81
Dibenzo(a,h)anthracene	PCB #126
Benzo(b)fluoranthene	PCB #77
Indeno(1,2,3-cd)pyrene	PCB #114
Benzo(a)pyrene	PCB #118
Benzo(a)anthracene	PCB #123
Chrysene	PCB #169

RESULTS AND DISCUSSION

The P450 HRGS data from all 290 stations relative to total PAH and total PCB is shown in Figure F-1. The linear correlation coefficient (r^2) for PAHs is fair, and the r^2 for PCBs is rather poor. In an effort to improve the linear relationship between the assay response and the concentrations of the target analytes, the assay results were plotted against a subset of the chemistry data limited to the sums of the known P450 inducing compounds (Figures F-2). Using the sums of only the known P450 inducers produced modest increases in the r^2 values for PAHs. In contrast, the r^2 values for the assay response with respect to PCBs decreased. This result implies that the correlation of the P450 HRGS response with PCB concentrations may in most cases be due to the co-occurrence of PCBs with other inducing compounds (e.g., PAHs) and not the PCBs directly.

The response of the P450 HRGS assay for the Bight'98 subpopulations in relation to sediment total PAH and PCB concentrations is shown in Figures F-3 through F11. The data for different strata have all been plotted on the same scale to facilitate comparisons. In general, this analysis shows there is a better correlation of the P450 HRGS results with

PAHs than with PCBs. The one striking exception is the results for LPOTWs, where the r^2 value was 0.92 for the correlation of assay response with PCB concentration, the best of all the subpopulation comparisons. In contrast, the correlation of assay response with total PAH concentration for the LPOTW stratum was not as impressive, but was still quite good, with an r^2 of 0.78.

Data from the northern, central, and southern regions of the SCB are compared in Figures F-3 through F-5. Correlations are good for the central and moderate to poor for the southern sections of the Bight. The correlation is very poor for the northern Bight. It is noteworthy, however, that the highest response in the survey was for a station in the northern Bight near Coal Oil Point (~ 1000 BaP Eq). The high assay responses for a few samples from the northern Bight could not be explained by any of the target analytes in Bight'98 Survey. These results suggest the presence of some unknown compound(s) inducing a strong P450 response in human liver cells. The bay and harbor areas had very good correlations of assay response with both PAH and PCB concentrations. In contrast, rivers and SPOTWs had very poor correlations.

Another interpretation of data for the P450 HRGS assay response versus total PAH and total PCB was obtained by re-plotting the results on a semi-log scale (Figures F-12 and F-13). The assay response increases dramatically when the total PAH is = ~1000 ng/g-dry wt (i.e., ~1 ppm). A similar trend is apparent when total PCB is = ~100 ng/g-dry wt, but there are fewer data so the results are less compelling. Because the P450 HRGS assay can respond to several different classes of compounds, it is never clear what compounds are actually inducing the response. In order to address this problem, stations were identified which had only one of the Bight target analytes groups known to induce a P450 response, i.e., PAHs and PCBs. Reviewing the 290 Bight'98 stations analyzed, 63 stations had measurable levels of PAHs, but no PCBs. Conversely, 26 stations had detectable PCBs, but no PAHs. The assay responses for these stations are shown in Figure F-13.

The data in these plots generally support the trends observed in Figure F-12; however, they also reveal several interesting points. First, the assay response to PAHs may begin as low as 100 ng/g-dry weight for total PAH. Second, the total PCB analysis shows that any significant assay response observed below 100 ng/g-dry wt is not due to PCBs. Lastly, these data show that some of the high responses observed are not due to either PAHs or PCBs measured in this program. This last point exemplifies one of the real advantages of the P450 HRGS assay, which is to detect the presence of toxic chemicals not on the target analyte list for a given study. It should be noted that studies have demonstrated (Jones and Anderson 1999) that the induction measured in human cells by this approach may be much stronger for certain PAHs (e.g., benzo(k)fluoranthene) and PCBs (e.g., Congeners 81 and 126) than for other members of these compounds groups. This is important because the mixtures of specific chemicals in sediment samples from various locations are seldom the same.

Overall, the data show that the P450 HRGS assay works very well where there is significant sediment contamination. The low degree of correlation observed for all of

the Bight'98 data taken together is due to the fact that much of the Bight has sediments that are relatively clean. The linear relationships are also confounded by the fact that the assay responds to compounds that are not on the Bight'98 target analyte list. The good linear correlation observed for areas with higher levels of contamination (e.g., bays and harbors and LPOTWs), and the poor correlation for areas of lower contamination (e.g., SPOTWs) support this assessment of the assay performance.

A summary plot of all the P450 HRGS response data versus total PAH concentration is shown in Figure F-14. The data are also presented as a function of potential toxicity to benthic organisms, as determined from previous studies (Anderson et al, 1999; Fairey *et al.* 1996). A general trend is apparent where a greater percentage of the samples induce an increasing assay response and are at a higher risk for chronic toxicity with increasing PAH concentrations. This plot points to the value of the P450 HRGS assay as a rapid, inexpensive screening tool for assessing both sediment contamination and the associated potential for chronic toxicity to benthic organisms. As with other analytical and assessment tools, the variability in the results decreases as sediment concentrations increase. The response of the P450 HRGS assay appears particularly good for total PAH and PCB concentrations above one part-per-million.

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APPENDIX G

Sediment Grain Size and Station Location Information

Table G-1. Sediment grain size parameters and station location data for samples analyzed for the sediment chemistry component of the Bight '98 Survey.

Station ID	%Fines	%Clay	%Gravel	%Sand	%Silt	MeanPhi	MedianPhi	Sorting	Skewness	Kurtosis	Area Weight	Strata	Depth	Region	Lat deg	Lat min	Long deg	Long min
2128	94	35	0	4	59	6.84	6.98	1.81	-0.07	0.18	2.44	marina	S	N	34	14.766	119	15.565
2129	79	23	0	21	56	5.66	5.32	2.29	0.15	-0.64	2.44	marina	S	N	34	10.396	119	13.681
2130	91	31	0	9	60	6.40	6.56	2.08	-0.08	-0.18	2.44	marina	S	N	34	10.313	119	13.392
2131	93	29	0	9	64	6.26	6.05	2.15	0.10	-0.27	2.44	marina	S	N	34	9.814	119	13.453
2132	0	0	0	99	0	1.57	1.87	0.76	-0.39	0.86	29.37	bath-30	S	N	34	9.311	119	13.657
2134	77	13	0	22	64	5.12	4.94	2.02	0.09	-0.10	2.44	marina	S	C	33	42.926	118	3.731
2136	89	30	0	13	59	6.25	6.63	2.22	-0.17	-0.14	2.44	marina	S	C	33	37.133	117	55.632
2137	85	29	0	16	56	6.07	6.35	2.31	-0.12	-0.40	2.44	marina	S	C	33	36.780	117	55.432
2138	95	30	0	6	65	6.43	6.45	1.94	-0.01	-0.02	2.44	marina	S	C	33	36.845	117	54.847
2141	86	25	0	11	61	6.06	6.39	2.10	-0.16	-0.11	2.44	marina	S	C	33	36.683	117	54.127
2142	88	24	0	10	64	6.01	5.84	2.05	0.08	-0.30	2.44	marina	S	C	33	36.464	117	54.602
2143	90	26	0	8	64	6.21	6.18	1.98	0.02	-0.16	2.44	marina	S	C	33	36.418	117	54.380
2144	81	22	0	19	59	5.62	5.60	2.22	0.01	-0.51	2.44	marina	S	C	33	36.448	117	54.034
2145	87	24	0	13	63	5.92	6.08	2.09	-0.08	-0.31	2.44	marina	S	C	33	36.229	117	53.321
2146	63	17	0	35	46	4.72	4.57	2.66	0.06	-0.76	2.44	marina	S	C	33	36.116	117	53.243
2147	84	23	0	13	61	5.88	5.81	2.05	0.03	-0.54	2.44	marina	S	C	33	36.079	117	53.560
2148	20	5	8	70	15	2.28	1.48	2.44	0.33	0.69	2.44	marina	S	C	33	35.670	117	52.773
2149	32	7	1	68	25	2.35	1.42	2.94	0.32	-0.58	2.44	marina	S	S	33	27.664	117	42.264
2150	42	8	0	57	34	3.51	2.60	2.39	0.38	0.03	2.44	marina	S	S	33	27.719	117	42.251
2151	77	18	0	24	59	5.26	5.52	2.46	-0.11	-0.46	2.44	marina	S	S	33	27.593	117	41.821
2152	68	13	0	32	55	4.80	4.19	2.06	0.29	-0.30	1.80	other	S	C	33	45.559	118	9.760
2153	37	9	0	63	28	3.40	2.48	2.46	0.37	0.09	1.80	other	S	C	33	45.207	118	9.455
2154	33	8	0	66	25	3.46	2.50	2.34	0.41	0.43	1.80	other	S	C	33	44.941	118	9.352
2155	90	22	0	12	68	5.90	5.57	2.01	0.16	-0.31	1.80	other	S	C	33	44.602	118	10.063
2156	89	23	0	10	66	6.03	5.71	1.96	0.16	-0.32	1.80	other	S	C	33	44.398	118	10.280
2157	47	9	0	52	38	3.30	2.86	2.93	0.15	-0.92	1.80	other	S	C	33	44.539	118	9.191
2158	80	18	0	17	62	5.58	5.35	2.05	0.11	-0.43	1.80	other	S	C	33	43.698	118	12.518
2159	71	16	0	26	55	5.21	4.99	2.21	0.10	-0.47	1.80	other	S	C	33	43.352	118	12.623
2160	73	16	0	26	57	5.16	5.20	2.33	-0.01	-0.46	1.80	other	S	C	33	43.414	118	12.281
2161	77	16	0	21	61	5.34	5.20	2.15	0.06	-0.42	1.80	other	S	C	33	43.444	118	12.136
2162	91	19	0	10	72	5.75	4.91	1.99	0.42	0.37	1.80	other	S	C	33	42.807	118	14.504

Table G-1. Continued.

Station ID	%Fines	%Clay	%Gravel	%Sand	%Silt	MeanPhi	MedianPhi	Sorting	Skewness	Kurtosis	Area Weight	Strata	Depth	Region	Lat deg	Lat min	Long deg	Long min
2163	75	18	0	24	57	5.42	5.19	2.16	0.11	-0.63	1.80	other	S	C	33	43.676	118	10.010
2164	22	6	0	79	16	2.87	1.32	2.06	0.75	1.89	1.80	other	S	C	33	43.820	118	4.957
2167	87	18	0	14	69	5.66	5.26	2.02	0.20	0.01	1.80	other	S	C	33	44.134	118	9.459
2168	79	17	0	18	62	5.45	5.04	2.04	0.20	-0.36	1.80	other	S	C	33	42.711	118	15.041
2169	83	23	0	16	60	5.80	5.93	2.28	-0.06	-0.24	1.42	port	S	C	33	46.094	118	16.701
2170	78	22	0	21	56	5.57	5.33	2.30	0.10	-0.59	1.42	port	S	C	33	45.859	118	15.360
2172	56	13	1	43	43	4.41	3.90	2.31	0.22	-0.17	1.42	port	S	C	33	44.953	118	14.561
2173	69	18	0	29	51	5.22	4.89	2.28	0.14	-0.73	1.42	port	S	C	33	44.847	118	14.237
2174	40	9	0	59	31	3.33	2.51	2.77	0.29	-0.80	1.42	port	S	C	33	44.055	118	15.993
2175	71	13	0	29	58	4.91	4.31	2.01	0.30	-0.35	1.42	port	S	C	33	44.453	118	13.607
2176	97	27	0	4	70	6.40	6.05	1.84	0.19	-0.21	1.42	port	S	C	33	43.850	118	15.671
2177	84	25	0	15	59	5.99	5.79	2.27	0.09	-0.35	1.42	port	S	C	33	44.072	118	14.553
2178	86	21	0	13	65	5.84	5.78	2.03	0.03	-0.36	1.42	port	S	C	33	43.680	118	16.262
2179	88	19	0	11	69	5.77	5.40	1.98	0.19	0.06	1.42	port	S	C	33	44.337	118	12.617
2182	76	14	0	23	62	5.04	4.15	2.12	0.42	0.56	1.42	port	S	C	33	43.429	118	15.740
2184	88	21	0	11	67	5.86	5.71	1.97	0.08	-0.34	1.42	port	S	C	33	43.264	118	16.142
2185	82	17	0	17	65	5.48	5.10	2.02	0.19	-0.32	1.42	port	S	C	33	43.991	118	11.985
2186	50	10	0	48	40	4.30	3.39	2.07	0.44	0.02	1.42	port	S	C	33	43.882	118	11.580
2187	49	9	0	51	40	4.23	3.22	2.02	0.50	0.24	1.42	port	S	C	33	43.871	118	11.041
2188	86	18	0	14	68	5.61	5.30	1.96	0.16	-0.26	1.42	port	S	C	33	44.030	118	5.328
2189	17	2	1	79	15	1.60	0.79	2.47	0.33	-0.31	4.39	LPOTW	M	C	33	57.144	118	33.601
2190	32	5	0	65	27	3.52	2.52	1.77	0.56	1.51	4.39	LPOTW	M	C	-99	-99.000	-99	-99.000
2191	16	2	0	83	14	2.28	1.36	1.85	0.49	1.29	4.39	LPOTW	M	C	33	56.175	118	33.670
2192	35	5	0	63	30	3.68	2.42	1.61	0.78	2.01	4.39	LPOTW	M	C	33	56.639	118	31.178
2194	41	5	0	60	36	3.65	3.08	1.77	0.32	1.75	4.39	LPOTW	M	C	33	55.209	118	31.244
2195	41	4	0	56	37	3.69	2.97	1.66	0.44	2.16	4.39	LPOTW	M	C	33	54.653	118	31.471
2196	17	2	15	65	15	1.06	-0.02	2.68	0.40	-0.25	4.39	LPOTW	M	C	33	54.185	118	33.202
2197	55	7	0	44	48	4.23	2.75	1.81	0.82	2.95	4.39	LPOTW	M	C	33	54.211	118	30.053
2198	20	2	0	76	18	2.50	1.72	1.90	0.41	0.74	4.39	LPOTW	M	C	33	53.254	118	31.465
2199	15	2	3	81	13	1.06	-0.51	2.35	0.67	1.10	4.39	LPOTW	M	C	33	52.959	118	32.084
2200	50	10	0	48	40	4.32	3.12	2.17	0.55	0.75	4.39	LPOTW	M	C	33	44.873	118	25.745

Table G-1. Continued.

Station ID	%Fines	%Clay	%Gravel	%Sand	%Silt	MeanPhi	MedianPhi	Sorting	Skewness	Kurtosis	Area Weight	Strata	Depth	Region	Lat deg	Lat min	Long deg	Long min
2201	62	9	0	34	53	4.58	4.11	2.04	0.23	0.00	4.39	LPOTW	M	C	33	43.226	118	23.550
2202	73	14	0	27	59	4.99	4.17	2.08	0.39	0.28	4.39	LPOTW	M	C	33	43.328	118	22.350
2204	65	9	1	32	56	4.59	4.34	2.06	0.12	0.55	4.39	LPOTW	M	C	33	41.811	118	20.341
2205	40	7	0	59	33	3.95	2.85	1.91	0.58	0.47	4.39	LPOTW	M	C	33	40.613	118	18.351
2206	26	5	0	74	21	3.37	2.01	1.78	0.76	1.58	4.39	LPOTW	M	C	33	40.509	118	17.598
2207	7	0	0	95	7	1.94	0.62	1.24	1.07	6.17	4.39	LPOTW	M	C	33	36.757	118	3.953
2208	18	4	0	81	14	2.92	1.71	1.77	0.69	3.14	4.39	LPOTW	M	C	33	36.151	118	3.408
2209	25	2	0	75	23	3.27	2.02	1.39	0.90	2.81	4.39	LPOTW	M	C	33	35.511	118	3.777
2210	24	2	0	74	22	3.24	1.98	1.41	0.89	2.66	4.39	LPOTW	M	C	33	35.413	118	2.473
2211	27	2	0	73	25	3.33	2.15	1.41	0.83	2.26	4.39	LPOTW	M	C	33	35.281	118	0.602
2212	37	3	0	62	34	3.65	2.54	1.51	0.73	1.51	4.39	LPOTW	M	C	33	35.372	117	59.343
2213	9	0	0	89	9	2.10	0.99	1.29	0.86	4.25	4.39	LPOTW	M	C	33	34.323	117	58.703
2214	53	3	0	48	50	3.98	3.06	1.48	0.62	0.88	4.39	LPOTW	M	S	32	41.392	117	18.065
2215	55	3	0	47	52	4.00	3.11	1.47	0.60	0.87	4.39	LPOTW	M	S	32	40.874	117	18.600
2216	42	3	0	58	39	3.72	2.68	1.48	0.70	1.47	4.39	LPOTW	M	S	32	40.571	117	19.322
2217	45	2	0	53	43	3.76	2.85	1.37	0.66	1.24	4.39	LPOTW	M	S	32	39.759	117	18.636
2218	45	3	0	55	42	3.84	2.90	1.57	0.59	0.61	4.39	LPOTW	M	S	32	39.986	117	16.787
2219	37	3	0	64	34	3.63	2.60	1.64	0.63	0.73	4.39	LPOTW	M	S	32	39.288	117	19.885
2220	40	2	0	60	38	3.66	2.71	1.46	0.65	0.91	4.39	LPOTW	M	S	32	39.581	117	16.801
2221	69	6	0	32	63	4.56	4.08	1.66	0.29	-0.62	2.49	sdmari	S	S	32	43.671	117	12.307
2222	72	9	0	26	63	5.02	4.75	1.82	0.15	-1.02	2.49	sdmari	S	S	32	43.127	117	13.551
2223	77	9	0	24	68	5.09	4.97	1.81	0.06	-0.94	2.49	sdmari	S	S	32	42.925	117	13.831
2224	40	4	0	58	36	3.55	2.81	1.95	0.38	-0.33	2.49	sdmari	S	S	32	42.785	117	14.046
2225	57	13	0	44	44	4.48	3.99	2.36	0.21	-0.69	2.49	sdmari	S	S	32	42.804	117	13.812
2226	91	9	0	8	82	5.50	5.33	1.51	0.11	-0.72	2.49	sdmari	S	S	32	42.667	117	13.899
2227	50	5	0	49	45	4.10	3.47	1.88	0.34	-0.71	2.49	sdmari	S	S	32	43.424	117	12.482
2228	45	3	0	54	42	3.79	2.84	1.55	0.61	0.96	2.49	sdmari	S	S	32	43.444	117	10.690
2229	43	13	1	56	30	3.71	3.02	2.81	0.25	-0.85	1.10	sdother	S	S	32	42.537	117	10.562
2230	10	1	0	89	9	2.24	0.82	1.33	1.07	5.50	1.10	sdother	S	S	32	42.151	117	10.724
2231	31	9	3	65	22	2.43	1.32	3.10	0.36	-0.53	1.10	sdother	S	S	32	41.681	117	9.391
2233	36	9	0	61	27	3.82	2.65	2.24	0.52	0.02	1.10	sdother	S	S	32	41.149	117	9.110

Table G-1. Continued.

Station ID	%Fines	%Clay	%Gravel	%Sand	%Silt	MeanPhi	MedianPhi	Sorting	Skewness	Kurtosis	Area Weight	Strata	Depth	Region	Lat deg	Lat min	Long deg	Long min
2235	45	7	0	56	38	3.82	3.16	2.25	0.29	-0.88	1.10	sdothor	S	S	32	38.448	117	8.216
2238	57	9	0	42	48	4.52	4.10	2.08	0.20	-1.08	1.10	sdothor	S	S	32	37.525	117	7.719
2239	34	4	0	67	30	3.36	2.41	2.03	0.47	-0.27	1.10	sdothor	S	S	32	40.944	117	8.706
2240	44	13	0	56	31	3.80	3.14	2.79	0.24	-0.93	1.10	sdothor	S	S	32	40.052	117	9.245
2241	18	3	0	81	15	2.74	1.24	1.74	0.87	2.44	1.10	sdothor	S	S	32	40.216	117	8.189
2242	31	4	0	66	27	3.35	2.30	1.97	0.53	-0.04	1.10	sdothor	S	S	32	39.898	117	8.985
2243	35	5	0	65	30	3.42	2.47	2.08	0.45	-0.34	1.10	sdothor	S	S	32	39.870	117	8.559
2244	20	3	0	78	17	3.00	1.53	1.59	0.93	3.05	1.10	sdothor	S	S	32	39.583	117	7.909
2245	60	15	1	40	45	4.54	4.47	2.61	0.03	-0.87	1.10	sdothor	S	S	32	39.050	117	8.562
2247	44	8	0	55	36	3.95	3.23	2.25	0.32	-0.90	1.10	sdothor	S	S	32	38.540	117	7.484
2249	72	10	0	27	62	4.91	5.00	2.05	-0.05	-0.57	1.10	sdothor	S	S	32	37.280	117	7.687
2251	72	10	0	27	62	4.91	5.06	2.10	-0.07	-0.62	1.88	sdport	S	S	32	42.138	117	9.724
2252	16	5	0	83	11	1.66	-0.02	2.46	0.69	1.29	1.88	sdport	S	S	32	41.512	117	9.171
2253	66	9	0	33	57	4.68	4.49	2.05	0.09	-0.95	1.88	sdport	S	S	32	41.286	117	8.285
2254	35	9	1	62	26	3.43	2.41	2.54	0.40	-0.23	1.88	sdport	S	S	32	40.635	117	9.794
2255	59	8	0	40	51	4.38	4.14	2.21	0.11	-1.00	1.88	sdport	S	S	32	40.678	117	7.764
2256	67	9	0	34	58	4.70	4.49	2.04	0.10	-0.98	1.88	sdport	S	S	32	40.611	117	8.152
2257	77	11	0	23	66	5.18	5.14	1.88	0.02	-0.99	1.88	sdport	S	S	32	40.610	117	8.045
2258	71	11	0	29	60	4.93	5.02	2.12	-0.04	-0.97	1.88	sdport	S	S	32	40.555	117	7.928
2259	68	15	3	28	53	4.71	5.14	2.62	-0.16	-0.17	1.88	sdport	S	S	32	40.213	117	7.484
2260	27	4	0	72	23	3.22	2.00	1.87	0.65	0.65	1.88	sdport	S	S	32	40.031	117	7.799
2262	74	12	0	25	62	5.12	4.99	1.94	0.07	-1.06	1.88	sdport	S	S	32	39.090	117	7.376
2263	73	9	0	25	64	5.02	4.93	1.89	0.05	-0.95	1.88	sdport	S	S	32	42.963	117	10.559
2264	73	10	0	27	63	5.00	4.85	1.91	0.07	-0.98	1.88	sdport	S	S	32	41.120	117	7.970
2265	13	4	0	87	9	1.95	0.22	2.07	0.83	2.94	1.88	sdport	S	S	32	41.033	117	8.418
2266	51	6	0	48	45	4.12	3.27	1.81	0.47	-0.05	1.39	SPOTW	M	N	34	23.885	119	49.325
2267	17	1	0	85	16	2.79	1.59	1.30	0.93	3.62	1.39	SPOTW	S	N	34	24.338	119	49.543
2268	27	3	0	73	24	3.10	1.87	1.74	0.70	1.27	55.28	bath-120	M	N	34	24.069	119	48.680
2269	40	13	0	58	27	3.68	2.83	2.74	0.31	-0.75	1.39	SPOTW	S	N	34	23.824	119	40.080
2272	21	6	0	76	15	2.87	1.29	2.07	0.76	1.91	1.39	SPOTW	S	N	34	23.888	119	39.572
2273	27	4	0	72	23	3.05	1.74	1.72	0.76	2.46	1.39	SPOTW	S	N	34	7.848	119	11.909
2274	4	0	0	94	4	1.94	1.50	0.99	0.45	5.60	1.39	SPOTW	S	N	34	7.430	119	11.821

Table G-1. Continued.

Station ID	%Fines	%Clay	%Gravel	%Sand	%Silt	MeanPhi	MedianPhi	Sorting	Skewness	Kurtosis	Area	Weight	Strata	Depth	Region	Lat deg	Lat min	Long deg	Long min
2275	7	0	0	93	7	2.02	1.23	1.19	0.66	4.21	1.39		SPOTW	S	N	34	7.872	119	11.748
2276	5	0	0	92	5	1.95	1.54	1.13	0.36	2.74	1.39		SPOTW	S	N	34	7.445	119	10.990
2277	56	8	0	43	48	4.07	3.27	1.99	0.40	1.22	1.39		SPOTW	M	C	33	30.447	117	45.898
2278	53	7	0	46	46	3.94	3.10	1.95	0.43	1.63	1.39		SPOTW	M	C	33	30.283	117	45.835
2279	20	2	0	80	18	2.86	2.11	1.47	0.51	3.22	1.39		SPOTW	S	C	33	30.927	117	46.019
2280	69	11	0	28	58	4.77	3.66	1.99	0.56	1.15	1.39		SPOTW	M	C	33	30.517	117	46.145
2281	58	8	0	41	50	4.14	3.61	2.06	0.26	1.03	1.39		SPOTW	M	S	33	26.019	117	41.949
2282	19	2	0	81	17	3.24	1.90	1.15	1.16	6.64	1.39		SPOTW	S	S	33	26.165	117	40.751
2283	56	8	0	45	48	4.09	3.27	1.96	0.42	1.33	1.39		SPOTW	M	S	33	25.898	117	41.341
2284	51	8	0	49	43	4.10	3.12	1.92	0.51	1.51	1.39		SPOTW	M	S	33	26.098	117	41.846
2285	66	9	0	34	57	4.53	3.81	1.93	0.37	0.29	1.39		SPOTW	M	S	33	9.547	117	23.877
2286	21	2	0	78	19	3.22	1.96	1.19	1.07	5.63	1.39		SPOTW	S	S	33	9.995	117	23.299
2287	58	8	0	40	50	4.27	3.31	1.91	0.51	0.84	1.39		SPOTW	M	S	33	9.548	117	23.376
2288	69	11	0	28	58	4.77	3.66	1.99	0.56	1.15	1.39		SPOTW	M	S	33	9.517	117	23.061
2289	61	8	0	38	53	4.36	3.43	1.85	0.50	1.17	1.39		SPOTW	M	S	33	6.147	117	21.509
2290	80	13	0	18	67	5.25	4.86	1.88	0.21	-0.25	1.39		SPOTW	D	S	33	6.974	117	21.528
2291	61	8	0	38	53	4.37	3.27	1.80	0.61	1.22	1.39		SPOTW	M	S	33	5.991	117	21.156
2292	80	13	0	20	67	5.15	5.02	2.00	0.06	0.07	1.39		SPOTW	D	S	33	7.157	117	21.389
2293	0	0	0	100	0	0.04	-0.30	0.68	0.50	2.24	1.39		SPOTW	S	S	32	59.972	117	17.535
2294	41	6	0	56	35	3.79	2.56	1.74	0.71	1.95	2.22		SPOTW	M	S	33	0.169	117	18.286
2295	35	5	0	63	30	3.60	2.23	1.70	0.80	2.73	2.22		SPOTW	M	S	32	59.424	117	17.919
2296	18	2	0	78	16	3.10	1.76	1.24	1.08	5.32	2.22		SPOTW	M	S	32	59.937	117	17.828
2297	79	21	0	21	58	5.58	5.25	2.24	0.15	-0.53	2.22		SPOTW	S	C	33	43.371	118	14.119
2298	70	14	0	30	56	5.01	4.44	2.12	0.27	-0.37	1.39		SPOTW	S	C	33	43.735	118	14.039
2299	64	13	0	34	51	4.83	4.29	2.13	0.25	-0.62	1.39		SPOTW	S	C	33	43.220	118	14.019
2300	89	22	0	13	67	5.84	5.58	2.06	0.13	-0.22	1.39		SPOTW	S	C	33	43.096	118	14.339
2301	24	6	0	75	18	3.19	1.80	1.94	0.72	2.09	1.39		SPOTW	S	N	34	24.058	119	49.999
2302	80	15	0	22	65	5.13	4.03	2.12	0.52	0.77	1.08		River	M	C	33	30.599	117	46.581
2303	72	11	0	28	61	4.82	3.75	1.97	0.54	1.06	1.08		River	M	C	33	31.122	117	46.912
2304	0	0	0	97	0	0.64	0.56	0.72	0.11	0.67	1.08		River	S	C	33	31.279	117	46.177
2305	7	0	0	90	7	2.51	2.94	1.01	-0.42	3.15	1.08		River	S	C	33	58.549	118	28.261
2306	0	0	1	97	0	0.30	0.06	0.78	0.31	2.24	1.08		River	S	C	33	56.157	118	27.155

Table G-1. Continued.

Station ID	%Fines	%Clay	%Gravel	%Sand	%Silt	MeanPhi	MedianPhi	Sorting	Skewness	Kurtosis	Area Weight	Strata	Depth	Region	Lat deg	Lat min	Long deg	Long min
2307	14	0	0	84	14	3.03	2.20	0.83	1.00	6.07	1.08	River	S	C	33	57.753	118	28.561
2308	59	15	0	40	44	4.67	3.75	2.27	0.40	-0.26	1.08	River	M	N	34	5.047	119	5.441
2310	35	6	0	63	29	3.69	1.93	1.70	1.04	4.29	1.08	River	S	N	34	5.492	119	5.341
2311	71	17	0	28	54	5.17	4.84	2.27	0.15	-0.64	1.08	River	S	C	33	45.330	118	11.100
2312	60	10	0	38	50	4.45	3.47	2.10	0.47	1.26	1.08	River	S	C	34	1.228	118	39.880
2314	14	3	0	85	11	2.86	1.29	1.49	1.06	5.45	1.08	River	S	C	34	1.632	118	40.808
2315	0	0	0	100	0	0.50	0.04	0.69	0.65	1.68	1.08	River	S	S	32	46.171	117	16.183
2317	0	0	5	94	0	0.04	0.08	0.86	-0.05	0.88	1.08	River	S	S	32	46.024	117	16.539
2318	12	1	0	89	11	2.69	1.62	1.26	0.85	4.73	1.08	River	S	C	33	43.422	118	7.614
2319	64	4	0	34	60	4.33	3.84	1.63	0.30	-0.33	1.08	River	S	C	33	44.227	118	8.610
2320	6	1	0	94	5	2.00	-1.11	1.34	2.33	28.02	1.08	River	S	C	33	43.978	118	7.289
2321	26	2	0	74	24	2.81	1.93	1.78	0.49	0.85	1.08	River	S	C	33	43.759	118	8.008
2325	16	0	0	83	16	3.03	1.90	0.92	1.22	7.15	1.08	River	S	C	33	37.668	117	59.261
2326	17	0	0	83	17	2.98	1.93	0.96	1.09	6.19	1.08	River	S	C	33	37.359	117	57.374
2328	40	3	0	59	37	3.58	2.43	1.42	0.81	2.64	1.08	River	S	N	34	13.183	119	17.300
2329	0	0	0	100	0	2.29	2.24	0.21	0.26	2.35	1.08	River	S	N	34	14.967	119	16.548
2330	35	1	0	64	34	3.28	2.51	1.21	0.63	2.17	1.08	River	S	N	34	14.381	119	16.817
2331	93	7	0	9	86	5.04	4.47	1.41	0.40	0.09	1.08	River	S	N	34	14.736	119	17.307
2335	17	0	0	83	17	2.97	1.93	0.98	1.06	5.69	1.08	River	S	S	32	32.682	117	9.288
2338	23	3	0	77	20	3.26	1.79	1.45	1.02	3.77	1.08	River	S	N	34	16.164	119	20.448
2339	73	5	0	27	68	4.46	3.87	1.56	0.38	0.44	1.08	River	S	N	34	15.141	119	17.097
2340	13	1	0	86	12	2.93	1.55	1.07	1.29	7.49	1.08	River	S	N	34	15.919	119	20.460
2341	26	2	0	74	24	3.30	2.00	1.23	1.06	4.55	1.00	Hist30	S	N	34	5.352	119	9.016
2342	38	5	0	60	33	3.70	2.70	1.89	0.53	0.15	1.00	Hist60	M	N	34	4.233	119	9.601
2343	6	0	0	94	6	2.01	0.78	1.19	1.03	6.66	1.00	Hist30	S	N	34	1.493	118	51.129
2344	35	3	0	63	32	3.59	2.46	1.58	0.71	1.34	1.00	Hist60	M	N	34	1.143	118	51.379
2345	71	4	0	28	67	4.39	3.67	1.45	0.49	0.36	1.00	Hist30	M	C	33	30.401	117	46.108
2346	73	4	0	26	69	4.46	3.79	1.45	0.46	0.18	1.00	Hist60	M	C	33	29.619	117	46.601
2347	59	3	0	42	56	3.94	2.96	1.33	0.74	2.29	1.00	Hist30	M	S	33	24.315	117	39.244
2348	74	4	0	26	70	4.48	3.86	1.46	0.42	0.05	1.00	Hist60	M	S	33	23.689	117	39.856
2350	29	2	0	72	27	3.35	2.21	1.40	0.81	2.21	1.00	Hist60	M	S	32	53.318	117	16.662
2351	22	4	16	59	18	1.34	0.10	2.89	0.43	-0.12	1.00	Hist60	M	S	32	49.290	117	19.214

Table G-1. Continued.

Station ID	%Fines	%Clay	%Gravel	%Sand	%Silt	MeanPhi	MedianPhi	Sorting	Skewness	Kurtosis	Area Weight	Strata	Depth	Region	Lat deg	Lat min	Long deg	Long min
2352	0	0	0	98	0	0.87	0.77	0.67	0.15	1.82	1.00	Hist30	M	S	32	32.512	117	11.417
2353	0	0	4	94	0	-0.17	-0.25	0.76	0.11	0.94	1.00	Hist60	M	S	32	33.128	117	15.825
2354	17	2	0	83	15	2.82	1.39	1.41	1.01	3.90	29.37	bath-30	S	N	34	27.540	120	18.768
2355	11	2	0	86	9	2.72	1.06	1.29	1.29	6.79	29.37	bath-30	S	N	34	27.111	120	20.203
2356	30	4	0	68	26	3.28	2.15	1.88	0.60	0.46	55.28	bath-120	M	N	34	26.862	120	4.431
2357	73	10	0	25	63	5.06	4.98	1.91	0.04	-0.95	55.28	bath-120	M	N	34	24.385	119	56.450
2358	42	6	0	57	36	3.93	3.13	2.06	0.39	-0.64	55.28	bath-120	M	N	34	23.805	119	58.381
2359	21	5	0	81	16	2.96	1.55	1.94	0.73	2.59	29.37	bath-30	S	N	34	23.923	119	51.888
2360	49	13	0	49	36	4.12	3.63	2.59	0.19	-0.71	55.28	bath-120	M	N	34	23.639	119	52.514
2361	13	1	0	85	12	3.06	1.61	0.98	1.48	9.59	29.37	bath-30	S	N	34	23.970	119	34.190
2362	71	9	0	28	62	4.78	5.36	2.40	-0.24	-0.73	55.28	bath-120	M	N	34	22.099	119	40.061
2363	0	0	0	99	0	1.28	1.48	0.45	-0.44	2.39	55.28	bath-120	M	N	34	21.340	119	37.694
2364	21	3	0	78	18	2.75	1.35	1.94	0.72	1.14	55.28	bath-120	M	N	34	20.622	119	39.422
2365	56	8	0	45	48	4.50	4.04	2.02	0.23	-1.05	55.28	bath-120	M	N	34	20.692	119	33.739
2366	46	6	0	54	40	4.01	3.37	2.12	0.30	-0.92	55.28	bath-120	M	N	34	19.852	119	36.651
2367	98	11	0	1	87	6.03	5.93	1.24	0.08	-0.38	55.28	bath-120	M	N	34	19.069	119	32.026
2368	99	11	0	1	88	5.92	5.75	1.28	0.13	-0.47	55.28	bath-120	M	N	34	18.052	119	27.800
2369	96	10	0	4	86	5.59	5.32	1.42	0.19	-0.53	55.28	bath-120	M	N	34	18.212	119	25.498
2370	21	1	0	80	20	3.14	1.91	1.04	1.18	6.52	29.37	bath-30	S	N	34	17.914	119	21.715
2371	95	9	0	5	86	5.50	5.22	1.41	0.20	-0.35	55.28	bath-120	M	N	34	15.917	119	30.595
2372	39	4	0	60	35	3.74	2.64	1.61	0.68	0.97	55.28	bath-120	M	N	34	14.395	119	36.122
2373	71	4	0	28	67	4.36	3.46	1.43	0.62	1.36	29.37	bath-30	S	N	34	13.226	119	23.129
2374	74	10	0	24	64	5.15	5.04	1.85	0.06	-1.03	55.28	bath-120	M	N	34	11.282	119	29.466
2375	61	10	0	37	51	4.52	3.10	1.97	0.72	1.82	29.37	bath-30	S	N	34	11.262	119	21.332
2376	52	8	0	49	44	4.16	2.37	1.83	0.98	3.82	29.37	bath-30	S	N	34	10.762	119	20.774
2377	11	1	0	88	10	2.85	1.58	1.00	1.26	8.11	29.37	bath-30	S	N	34	2.338	118	56.386
2378	14	2	0	84	12	3.07	1.55	1.17	1.30	7.21	29.37	bath-30	S	N	34	1.963	118	55.358
2379	3	0	0	95	3	1.89	1.01	1.08	0.82	6.77	29.37	bath-30	S	N	34	1.154	118	50.220
2380	29	5	0	70	24	3.45	2.24	1.79	0.68	2.72	29.37	bath-30	S	C	34	1.104	118	45.578
2381	59	10	0	37	49	4.54	3.31	2.02	0.61	1.26	55.28	bath-120	M	C	34	0.186	118	46.126
2382	45	8	0	56	37	4.02	2.82	1.89	0.63	1.67	29.37	bath-30	S	C	34	1.543	118	35.250
2383	19	1	0	80	18	3.19	2.12	0.93	1.16	7.67	29.37	bath-30	S	C	34	0.682	118	30.789

Table G-1. Continued.

Station ID	%Fines	%Clay	%Gravel	%Sand	%Silt	MeanPhi	MedianPhi	Sorting	Skewness	Kurtosis	Area Weight	Strata	Depth	Region	Lat deg	Lat min	Long deg	Long min
2384	50	7	0	47	43	4.23	2.71	1.82	0.83	2.90	55.28	bath-120	M	C	33	55.842	118	30.263
2385	5	0	0	92	5	2.61	1.73	0.71	1.22	9.55	29.37	bath-30	S	C	33	54.387	118	27.429
2386	5	0	0	91	5	2.51	2.47	0.78	0.05	5.16	29.37	bath-30	S	C	33	52.690	118	25.473
2387	45	9	0	54	36	4.14	2.69	2.05	0.71	2.17	55.28	bath-120	M	C	33	50.894	118	27.136
2388	64	13	0	34	51	4.83	4.14	2.03	0.34	-0.36	29.37	bath-30	S	C	33	44.900	118	8.922
2389	6	0	0	91	6	1.88	1.27	1.28	0.47	3.11	29.37	bath-30	S	C	33	42.566	118	19.310
2390	60	13	0	39	47	4.43	4.25	2.49	0.07	-0.58	29.37	bath-30	S	C	33	41.609	118	15.874
2391	52	8	0	49	44	3.92	3.18	2.14	0.35	0.52	29.37	bath-30	S	C	33	42.562	118	8.259
2392	18	2	0	79	16	2.68	1.80	1.59	0.56	2.38	29.37	bath-30	S	C	33	42.305	118	9.321
2393	0	0	0	98	0	1.01	1.09	0.74	-0.11	0.44	29.37	bath-30	S	C	33	40.968	118	5.297
2394	14	2	0	82	12	2.94	1.79	1.39	0.83	4.36	55.28	bath-120	M	C	33	39.064	118	14.941
2395	6	0	0	91	6	2.69	2.39	0.84	0.35	4.50	29.37	bath-30	S	C	33	40.363	118	3.240
2396	15	2	0	83	13	3.11	1.68	1.25	1.14	5.22	55.28	bath-120	M	C	33	38.883	118	8.966
2397	23	4	0	75	19	3.47	1.91	1.50	1.05	3.96	29.37	bath-30	S	C	33	39.001	118	7.563
2398	13	2	0	84	11	3.03	1.56	1.21	1.23	6.67	55.28	bath-120	M	C	33	37.155	118	8.579
2399	12	0	0	86	12	3.04	2.15	0.80	1.11	7.23	29.37	bath-30	S	C	33	38.085	117	59.690
2400	22	4	0	75	18	3.31	1.89	1.62	0.88	3.20	55.28	bath-120	M	C	33	36.225	118	5.718
2401	44	9	0	53	35	4.15	2.94	1.95	0.62	0.80	55.28	bath-120	M	C	33	35.494	117	57.440
2402	48	8	0	50	40	3.87	3.17	2.19	0.32	0.62	29.37	bath-30	S	C	33	33.451	117	49.794
2403	76	12	0	24	64	4.94	4.24	1.89	0.37	0.03	55.28	bath-120	M	C	33	31.117	117	48.173
2404	37	5	0	64	32	3.72	1.72	1.59	1.26	7.60	29.37	bath-30	S	S	33	25.329	117	39.535
2405	65	8	0	32	57	4.51	3.45	1.75	0.60	1.17	55.28	bath-120	M	S	33	17.677	117	33.514
2406	28	2	0	72	26	3.27	2.16	1.22	0.90	4.50	29.37	bath-30	S	S	33	16.884	117	28.313
2407	58	8	0	41	50	4.27	3.27	1.86	0.54	1.24	55.28	bath-120	M	S	33	15.619	117	31.421
2408	60	8	0	40	52	4.35	3.22	1.80	0.62	1.24	55.28	bath-120	M	S	33	6.307	117	21.710
2409	1	0	0	98	1	1.05	0.69	0.72	0.50	1.54	29.37	bath-30	S	S	33	0.243	117	16.920
2410	47	9	1	51	38	3.95	2.96	2.31	0.43	1.20	55.28	bath-120	M	S	32	46.329	117	21.273
2411	53	3	0	47	50	4.01	3.18	1.52	0.54	0.49	55.28	bath-120	M	S	32	45.153	117	20.579
2412	48	3	0	53	45	3.90	2.97	1.52	0.61	0.78	55.28	bath-120	M	S	32	43.285	117	17.776
2413	29	2	0	72	27	3.22	2.18	1.57	0.66	1.21	55.28	bath-120	M	S	32	41.427	117	16.701
2414	0	0	0	99	0	2.16	2.21	0.24	-0.23	0.40	29.37	bath-30	S	S	32	40.619	117	11.387
2415	8	0	0	93	8	2.45	1.42	0.96	1.06	6.34	29.37	bath-30	S	S	32	39.524	117	10.937

Table G-1. Continued.

Station ID	%Fines	%Clay	%Gravel	%Sand	%Silt	MeanPhi	MedianPhi	Sorting	Skewness	Kurtosis	Area Weight	Strata	Depth	Region	Lat deg	Lat min	Long deg	Long min
2417	0	0	0	99	0	2.19	2.25	0.27	-0.21	1.21	29.37	bath-30	S	S	32	37.498	117	12.876
2418	24	2	0	75	22	3.00	1.85	1.66	0.69	1.20	55.28	bath-120	M	S	32	35.718	117	18.888
2419	11	1	0	90	10	0.79	-0.75	2.04	0.76	1.83	55.28	bath-120	M	S	32	35.365	117	15.817
2421	85	11	0	14	74	5.43	5.36	1.68	0.04	-0.88	2.44	marina	S	C	33	45.975	118	14.454
2423	42	2	0	57	40	3.61	2.91	1.68	0.42	-0.10	2.44	marina	S	S	32	46.841	117	14.948
2424	8	0	0	93	8	1.65	0.21	1.35	1.07	5.38	2.44	marina	S	S	32	45.987	117	14.848
2425	68	4	0	30	64	4.54	4.19	1.65	0.21	-0.66	2.44	marina	S	S	32	46.035	117	14.137
2426	38	3	0	62	35	3.61	2.56	1.55	0.68	1.29	1.80	other	S	C	33	44.049	118	13.886
2427	89	8	0	11	81	5.19	4.77	1.52	0.27	-0.41	1.80	other	S	C	33	43.852	118	14.130
2428	100	14	0	0	86	6.16	5.83	1.30	0.25	-0.20	1.80	other	S	C	33	43.126	118	15.550
2430	83	8	0	16	75	5.12	4.81	1.61	0.19	-0.53	1.42	port	S	C	33	46.146	118	13.469
2431	78	8	0	22	70	5.03	4.79	1.74	0.14	-0.76	1.42	port	S	C	33	45.202	118	13.445
2432	94	11	0	6	83	5.68	5.58	1.49	0.06	-0.73	1.42	port	S	C	33	45.048	118	13.822
2433	71	7	0	28	64	4.83	4.53	1.78	0.17	-0.87	1.10	sdothor	S	S	32	43.341	117	12.553
2434	45	4	0	56	41	3.85	2.90	1.62	0.59	0.52	1.10	sdothor	S	S	32	43.494	117	11.018
2435	49	4	0	51	45	3.83	3.21	1.88	0.33	-0.48	1.10	sdothor	S	S	32	42.692	117	13.375
2436	55	13	0	43	42	4.26	3.95	2.65	0.12	-0.97	1.10	sdothor	S	S	32	42.902	117	10.987
2438	68	20	1	31	48	5.06	5.23	2.65	-0.06	-0.64	2.49	sdmari	S	S	32	37.338	117	6.102
2439	53	4	0	48	49	4.08	3.49	1.81	0.32	-0.62	1.88	sdport	S	S	32	43.566	117	11.371
2440	38	4	0	64	34	3.43	2.59	2.04	0.41	-0.44	1.88	sdport	S	S	32	43.109	117	10.489
2441	79	7	0	20	72	5.05	4.81	1.66	0.14	-0.78	1.88	sdport	S	S	32	41.468	117	14.278
2442	79	9	0	22	70	5.10	4.92	1.77	0.10	-0.87	1.88	sdport	S	S	32	41.348	117	14.225
2443	86	29	0	15	57	6.14	6.51	2.33	-0.16	-0.22	1.14	marina	S	C	33	58.978	118	27.344
2444	91	22	0	9	69	6.01	5.79	1.97	0.11	-0.02	1.14	marina	S	C	33	58.965	118	26.918
2445	82	23	0	19	59	5.77	5.65	2.21	0.05	-0.55	1.14	marina	S	C	33	58.643	118	27.303
2446	57	13	0	42	44	4.48	3.82	2.26	0.29	-0.48	1.14	marina	S	C	33	58.650	118	26.533
2447	77	14	0	21	63	5.21	4.91	1.97	0.15	-0.45	1.14	marina	S	C	33	58.600	118	26.862
2448	57	13	0	43	44	4.55	4.02	2.31	0.23	-0.75	1.14	marina	S	C	33	58.158	118	26.821
2449	60	10	0	38	50	4.45	3.47	2.10	0.47	1.26	1.14	marina	S	C	33	57.956	118	27.264
2450	70	11	0	30	59	4.73	4.46	2.07	0.13	-0.07	1.00	river-gradient	S	C	33	45.615	118	11.962
2451	63	13	1	34	50	4.65	4.45	2.28	0.09	0.05	1.00	river-gradient	S	C	33	45.113	118	10.454
2453	29	2	0	70	27	3.38	2.21	1.06	1.10	6.84	1.00	river-gradient	S	C	33	37.675	117	58.493

Table G-1 Continued.

Station ID	%Fines	%Clay	%Gravel	%Sand	%Silt	MeanPhi	MedianPhi	Sorting	Skewness	Kurtosis	Area Weight	Strata	Depth	Region	Lat deg	Lat min	Long deg	Long min
2454	18	4	0	80	14	2.81	1.50	1.77	0.74	3.15	1.00	river-gradient	S	C	33	30.545	117	45.314
2455	34	6	0	64	28	3.63	2.32	1.80	0.73	1.80	1.00	SPOTW-permit	M	S	33	6.584	117	20.813
2456	28	4	0	70	24	3.47	2.05	1.55	0.92	3.21	1.00	SPOTW-permit	M	S	33	0.608	117	18.135
2457	32	4	0	68	28	3.51	1.97	1.40	1.10	5.33	1.00	SPOTW-permit	S	S	33	26.473	117	41.450

Table G-2. Sediment grain size and station location data for the samples collected in Mexico as part of the Bight '98 Survey.

StationID	% Coarse	% Fines	Area Weight	STRATA	Lat deg	Lat min	Long deg	Long min
2555m	63.8	36.2	21.28	Mexico-Central	32	12.147	116	56.586
2556m	82.5	17.5	21.28	Mexico-Central	32	11.760	116	55.664
2558m	61.7	38.3	62.50	Mexico-North	32	20.004	117	7.109
2559m	75.4	24.6	21.28	Mexico-Central	32	9.911	116	57.540
2560m	85.9	14.1	62.50	Mexico-North	32	18.278	117	6.504
2561m	74.7	25.3	21.28	Mexico-Central	32	14.220	117	0.407
2563m	94.1	5.9	32.26	Mexico-South	31	47.078	116	48.499
2565m	78.7	21.3	32.26	Mexico-South	31	46.002	116	43.285
2567m	88.9	11.1	62.50	Mexico-North	32	31.715	117	8.633
2568m	97.1	2.9	62.50	Mexico-North	32	27.629	117	15.784
2569m	81.5	18.5	21.28	Mexico-Central	32	10.769	116	55.828
2570m	92.8	7.2	62.50	Mexico-North	32	23.087	117	7.492
2572m	80.6	19.4	21.28	Mexico-Central	31	58.599	116	52.128
2574m	86.2	13.8	21.28	Mexico-Central	32	14.528	116	58.246
2575m	89.9	10.1	62.50	Mexico-North	32	17.818	117	12.360
2576m	98.8	1.2	62.50	Mexico-North	32	23.984	117	10.667
2577m	96.1	3.9	32.26	Mexico-South	31	51.628	116	46.829
2578m	70.0	30.0	21.28	Mexico-Central	32	3.836	116	54.114
2579m	59.5	40.5	32.26	Mexico-South	31	47.294	116	43.564
2582m	83.6	16.4	32.26	Mexico-South	31	49.144	116	42.437
2583m	98.0	2.0	62.50	Mexico-North	32	31.756	117	16.430
2584m	95.1	4.9	62.50	Mexico-North	32	27.473	117	17.901
2585m	51.4	48.6	62.50	Mexico-North	32	13.835	117	5.333
2587m	98.5	1.5	62.50	Mexico-North	32	27.081	117	11.859
2588m	38.2	61.8	62.50	Mexico-North	32	14.757	117	6.505
2589m	57.8	42.2	21.28	Mexico-Central	32	13.116	117	1.709
2590m	98.3	1.7	32.26	Mexico-South	31	58.222	116	49.835
2591m	62.3	37.7	21.28	Mexico-Central	32	8.808	116	56.223
2592m	99.3	0.7	62.50	Mexico-North	32	28.947	117	9.110
2593m	94.7	5.3	62.50	Mexico-North	32	21.068	117	6.326
2594m	56.4	43.6	32.26	Mexico-South	31	49.344	116	44.528
2595m	96.0	4.0	62.50	Mexico-North	32	6.144	117	5.047
2596m	66.4	33.6	21.28	Mexico-Central	32	8.208	116	56.236
2597m	72.7	27.3	32.26	Mexico-South	31	59.900	116	47.292
2599m	95.7	4.3	32.26	Mexico-South	31	45.066	116	39.850
2601m	68.2	31.8	21.28	Mexico-Central	32	13.358	116	57.382
2602m	84.7	15.3	62.50	Mexico-North	32	21.148	117	10.827
2603m	87.9	12.1	21.28	Mexico-Central	32	1.817	116	54.902
2604m	99.2	0.8	62.50	Mexico-North	32	30.391	117	13.149
2606m	82.1	17.9	62.50	Mexico-North	32	13.999	117	10.534
2607m	96.3	3.7	32.26	Mexico-South	31	49.765	116	49.299
2608m	65.6	34.4	32.26	Mexico-South	31	50.524	116	40.426

Table G-2. Continued.

StationID	% Coarse	% Fines	Area Weight	STRATA	Lat deg	Lat min	Long deg	Long min
2609m	87.4	12.6	32.26	Mexico-South	31	47.508	116	39.597
2610m	90.6	9.4	32.26	Mexico-South	31	47.097	116	38.363
2611m	38.2	61.8	62.50	Mexico-North	32	13.088	117	4.199
2613m	97.8	2.2	21.28	Mexico-Central	32	2.049	116	54.010
2614m	95.2	4.8	32.26	Mexico-South	31	53.442	116	47.844
2615m	97.6	2.4	32.26	Mexico-South	31	52.081	116	45.631
2616m	98.9	1.1	62.50	Mexico-North	32	26.074	117	16.848
2617m	86.8	13.2	62.50	Mexico-North	32	32.941	117	20.014
2618m	76.9	23.1	21.28	Mexico-Central	32	6.526	116	56.325
2620m	61.2	38.8	32.26	Mexico-South	31	49.617	116	39.063
2621m	59.1	40.9	62.50	Mexico-North	32	23.907	117	16.532
2622m	77.5	22.5	21.28	Mexico-Central	32	12.437	116	57.125
2623m	97.5	2.5	62.50	Mexico-North	32	16.539	117	2.507
2624m	94.3	5.7	62.50	Mexico-North	32	19.328	117	4.072
2625m	68.4	31.6	21.28	Mexico-Central	31	57.184	116	50.438
2628m	98.2	1.8	62.50	Mexico-North	32	15.190	117	8.905
2630m	98.5	1.5	62.50	Mexico-North	32	27.779	117	13.184
2631m	92.9	7.1	32.26	Mexico-South	31	51.244	116	50.707
2633m	57.5	42.5	21.28	Mexico-Central	32	6.041	116	55.705
2634m	98.9	1.1	32.26	Mexico-South	31	53.710	116	45.086
2636m	68.0	32.0	32.26	Mexico-South	31	48.992	116	46.548
2637m	33.8	66.2	62.50	Mexico-North	32	21.500	117	16.299
2638m	65.0	35.0	32.26	Mexico-South	31	56.253	116	47.436
2639m	86.2	13.8	32.26	Mexico-South	31	55.163	116	46.329
2641m	95.7	4.3	21.28	Mexico-Central	32	5.284	116	54.000
2643m	86.6	13.4	62.50	Mexico-North	32	20.504	117	13.784
2644m	88.0	12.0	21.28	Mexico-Central	32	0.789	116	53.886
2645m	85.3	14.8	32.26	Mexico-South	31	48.078	116	41.754