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Sediment Chemistry on the Mainland Shelf of the Southern California Bight

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ABSTRACT

Sediments represent one fate for contaminants that are discharged from urbanized areas and anthropogenic activities along the coast of the Southern California Bight (SCB). To understand large-scale ecological changes and cumulative effects from multiple contaminant sources, 248 sites between Point Conception and the U.S.-Mexico international border were sampled using a stratified-random study design. The objectives were to: 1) estimate the spatial extent and magnitude of sediment contamination, and 2) assess whether contamination was similar throughout the SCB or more severe in particular areas, such as sediments within Santa Monica Bay, in the vicinity of publicly owned treatment works (POTWs), or adjacent to river and creek mouths that discharge runoff from urbanized watersheds.

Eighty-nine percent of SCB sediments were found to contain evidence of anthropogenic contamination. Eighty-two percent of the SCB was contaminated with chlorinated hydrocarbons including total DDT (82%) and total PCB (46%). Utilizing iron as a conservative tracer of natural contributions for eight metals of interest, 50% of the SCB was estimated to be anthropogenically enriched in at least one trace metal.

Sediment quality screening level thresholds (effects range low [ERL], effects range median [ERM]) were used to assess the areal extent of potential biological effects for 13 constituents. Approximately 12% (433 km^2) of the SCB exceeded an ERM for at least one constituent, 55% (1,919 km^2) of the SCB exceeded an ERL, and 33% of the SCB was below all ERLs (1,169 km^2). The constituent that exceeded these screening level thresholds most often was total DDT. However, the predictive ability of screening level thresholds for total DDT was questionable because of a lack of correlation between sediment chemistry and biological indicators measured by other investigators, including sediment toxicity and the composition of benthic infaunal assemblages.

INTRODUCTION

The Southern California Bight (SCB) represents an important ecological, economic, and recreational resource for the nearly 15 million people who inhabit its coastal communities. This dense coastal human population, and accompanying rapid urbanization, has resulted in large ecological stresses affecting the marine ecosystem of the SCB. For example, several sources of pollutants are discharged to the SCB including treated municipal and industrial wastewater, stormwater runoff from urbanized areas, disposal of dredged materials, aerial fallout, oil and hazardous material spills, boating, and other sources (SCCWRP 1973). Sediments are often the fate of anthropogenic inputs, where they can reside for long periods of time (NOAA 1991, Finney and Huh 1989, Bertine and Goldberg 1977). Contaminant concentrations in sediments have been shown to covary with both wastewater and stormwater effluent emissions near their discharge locations (Phillips and Hershelman 1996, Bay and Schiff 1997).

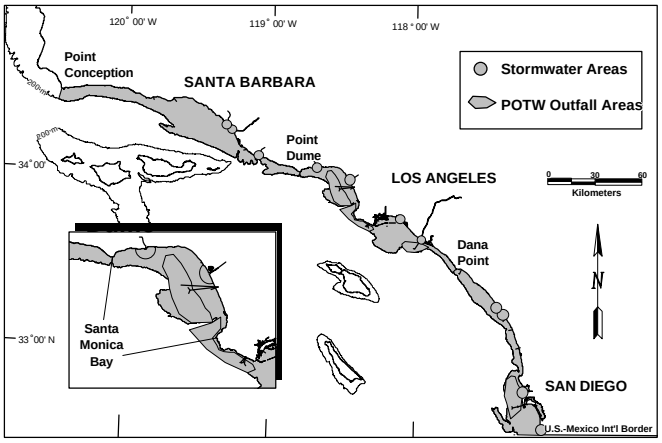
Sediment contamination has been shown to have both acute and chronic effects on the biological resources in the SCB. Monitoring programs for the largest publicly owned treatment works (POTWs) have observed a gradient of decreasing contaminants away from their outfalls (Stull *et al.* 1986a; Stull 1995, Diener *et al*. 1995). Statistical associations of sediment contaminant concentrations with changes in benthic community assemblages are used to identify whether their discharges alter the marine habitat. Furthermore, contaminants in sediments from southern California are correlated with toxicity observed in sediment-dwelling invertebrates (Swartz *et al*. 1985, Bay 1995) and bioaccumulation in flatfish (Schiff and Allen 1997, Young *et al*. 1991). Sediments have been implicated with reproductive impairment of at least two fish species (Hose *et al*. 1989) and historical deposits have resulted in the closure of commercial fishing in certain regions of the southern California mainland shelf.

While there may be a multitude of potential contaminant sources to the SCB, nearly all ocean monitoring

programs focus only on the impacts from single sources. As a result, less than 10% of the area on the mainland shelf of the SCB is actually being monitored on an ongoing basis (NRC 1990). Nearly $10 million is spent on ocean monitoring annually for regulatory compliance, but there are four different regulatory jurisdictions responsible for coastal discharges in the SCB. Consequently, these regulatory-based monitoring programs are a series of projects that do not necessarily analyze the same constituents, at similar frequencies, or with similar methodology, accuracy, or precision, making it difficult to merge data from disparate programs. Most monitoring programs are not designed to distinguish natural or anthropogenic changes that occur on a region-wide scale or assess cumulative impacts from multiple sources whose fates commingle.

This study is unique in the SCB since it assesses the larger, regional-scale conditions of sediments on the mainland shelf and does not focus on site-specific locations. Not since 1976 has a bight-wide study of sediment chemistry been conducted (Word and Mearns 1979). That study, which was restricted to the 60m isobath, was the first to provide local monitoring agencies the opportunity to put their sampling sites in perspective of the entire SCB. However, there have been substantial changes in the magnitude of pollutant inputs, as well as significant changes in analytical chemistry techniques, over the last two decades. The objectives of this study were to provide up-to-date regional-scale perspectives and improve upon the earlier work by the addition of new study elements. To accomplish this goal, this study attempts to estimate the spatial extent and magnitude of sediment contamination on the mainland shelf of the SCB. Furthermore, this study attempts to measure if sediment contamination is similar throughout the SCB or more severe in particular areas, such as sediments within Santa Monica Bay, in the vicinity of POTWs, or adjacent to river and creek mouths that drain urbanized watersheds.

Figure 1. Areal extent of the subpopulations of interest.



METHODS

Two hundred and sixty-one sites were sampled on the continental shelf (defined as 10 to 200 m deep) from Point Conception, California, to the United States-Mexico international border between July 13 and August 22, 1994. Sites were selected using a stratified random design, with depth zone (the inner shelf from 10-25 m, the middle shelf from 26-100 m, and the outer shelf from 101-200 m), geography (Santa Monica Bay), and proximity to input sources (wastewater and stormwater outfalls) as the primary strata (Figure 1). The POTW wastewater stratum was defined as the area encompassed by the current NPDES ocean monitoring programs; the stormwater stratum was defined as the area within 3 km of the 11 largest river and creek mouths that drain directly to the SCB (Table 1). Details of site selection are provided in Bergen (1996) and Stevens (1997).

Of the 261 sites identified, only 248 yielded samples for sediment chemistry. For the 13 missing sites, 2 were the result of an incorrect sample frame (1 site in Mexico, 1 site deeper than 200 m); 10 were a result of substrate (i.e., rocks, cobbles, or hard-packed sand); and 1 was deleted due to improper vessel positioning. Sediment samples were obtained using a 0.1 m^2 modified Van Veen grab. Surficial sediments (top 2 cm) from undisturbed, representative samples were collected using a Teflon or HDPE scoop or syringe. Sediments not in contact with the wall of the grab were placed in separate pre-cleaned containers for analysis of grain size, TOC/TN, trace organics, and trace metals. Samples were transported on ice and then frozen (-20 ± 2^{o} C) prior to trace contaminant analysis or refrigerated (4 ± 1^{o} C) prior to grain size analysis.

Analytical Chemistry

Grain size analysis was performed using a Horiba Model LA-900 Laser Scattering Particle Size Distribution Analyzer which detects scattered (refracted and reflected) laser light to assess particle diameters. Data were reported as frequency (percent) of particles for 74 different diameters between 0.88 and 1,000 microns and the proportions less than 63 microns was summed to represent percent fines. Total organic carbon (TOC) and

TABLE 1. Areal extent of the Southern California Bight and subpopulations of interest.

		Area (km^2)
Entire SCB		3,520.3
Deep	(100 - 200 m)	827.1
Mid-depth	(30 - 100 m)	1,999.9
Shallow	(10 - 30 m)	701.5
Santa Monica Bay		457.4
Remaining SCB		3,071.1
Mid-depth Areas		
	Hyperion	100.9
	JWPCP	37.8
	OCSD	47.3
	Pt. Loma	106.8
	Sum POTW	292.8
	Non-POTW	1,707.1
Shallow Areas		
	Ventura River	8.1
	Santa Clara River	10.8
	Calleguas Creek	2.7
	Malibu Creek	10.8
	Ballona Creek	10.8
	San Gabriel River	8.1
	Santa Ana River	8.1
	Santa Margarita River	5.4
	San Luis Rey River	5.4
	San Diego River	10.8
	Sum Stormwater	81.1
	Nonstormwater	620.5

JWPCP = Joint Water Pollution Control Plant, Los Angeles County Sanitation District.
OCSD = Orange County Sanitation District.
POTW = Publicly owned treatment works.

total nitrogen (TN) analysis was performed using a Carlo Erba 1108 CHN Elemental Analyzer equipped with an AS/23 Autosampler (Castillo and Khan 1992).

Major and trace element analysis was performed for aluminum, antimony, arsenic, beryllium, cadmium, chromium, copper, iron, lead, mercury, nickel, selenium, silver, and zinc (Table 2). Sample preparation followed a modification of EPA Method 200.2 (U.S. EPA 1991) where approximately 0.5 g of freeze-dried, fine-ground sediment was digested using 5 mL of 1:1 trace metal grade nitric acid and 10 mL of 1:4 hydrochloric acid and heated to a gentle boil and swirled periodically for two hours. Solids were removed by centrifugation.

Inductively coupled plasma-mass spectroscopy (ICP-MS) was used to determine concentrations of aluminum, antimony, beryllium, cadmium, [total] chromium, copper, iron, lead, nickel, silver, and zinc from sample digest solutions utilizing a Hewlett Packard Model 4500 and following protocols established by EPA Method 200.8 (U.S. EPA 1991). The internal standard solution included scandium, gallium, rhodium, and bismuth. Graphite furnace atomic absorption spectrometry (GFAAS) was used for analysis of arsenic and selenium sample digest solutions utilizing a Perkin Elmer Model Z-3030 and Model 4100-Z instruments with Zeeman background correctors and following protocols established by EPA Method 200.9 (U.S. EPA 1991). Cold vapor atomic absorption spectrometry (CVAAS) was used for analysis of mercury from sample digest solutions utilizing a LDC Mercury Monitor equipped with a 30 cm absorption cell and volume reaction cell. In all methods, instrument blanks were run to identify sample carry-over and the Certified Reference Material was MESS-2 (National Research Council).

Unlike grain size, TOC/TN, and trace metals which were analyzed by a single laboratory, five laboratories were used to analyze organic constituents. All laboratories quantified six DDT isomers and metabolites (o,p'-DDT, p,p'-DDT, o,p'-DDE, p,p'-DDE, o,p'-DDD, p,p'-DDD). Four of five laboratories quantified three Aroclor mixtures (Aroclor 1242, 1254, 1260). Two of five laboratories quantified 27 individual PCB congeners (Congeners 8, 18, 28, 29, 44, 50, 52, 66, 77, 87, 101, 104, 105, 118, 126, 128, 138, 153, 154, 170, 180, 187, 188, 195, 201, 206, 209). To compensate for the disparity in PCB analyses, total PCB was considered to be either the sum of all congeners or, alternatively, the sum of all Aroclors. All five laboratories reported 16 separate polynuclear aromatic hydrocarbons (PAH), however, there were differences among laboratories for detection limits that were accounted for by truncating all samples at the highest detection limit. A complete list of target analytes and reporting limits are summarized in Table 2.

Samples were thawed and homogenized with anhydrous sodium sulfate at room temperature, spiked with surrogate standards, and solvent extracted using either a soxhlet apparatus (SW-846, Method 3540) or roller table (Anderson and Gossett 1987), or by sonication. Extracts were then dried with anhydrous sodium sulfate, treated with copper or mercury for sulfur removal, and subjected to Florisil and/or alumina/silica gel packed columns for clean-up/fractionation (SW-846, Method 3620) (U.S. EPA 1986, 1983). Each extract was concentrated and internal standards were added to the final extract prior to instrumental analysis. Internal and surrogate standards varied between laboratories. No samples were reported as having matrix-related interferences.

Chlorinated pesticide and PCB measurements were conducted using gas chromatographs equipped with electron capture detectors (GC-ECD) (SW-846, Methods 8080 or 8081) (U.S. EPA 1986, 1983). Typically, DB-5

TABLE 2. Method reporting limits from regional monitoring of the Southern California Bight in 1994.

	Reporting Limits		Reporting Limits
Inorganics (ug/dry g)		**Polynuclear Aromatic Hydrocarbons (ng/dry g)**	
Aluminum	1,580	Acenaphthene	330
Antimony	0.1	Acenaphthalene	330
Arsenic	0.1	Anthracene	330
Beryllium	0.05	Naphthalene	330
Cadmium	0.05	Phenanthrene	350
Chromium	0.5	Dibenz[ah]anthracene	400
Copper	1	Benz[a]anthracene	400
Iron	1,000	Benzo[a]pyrene	330
Lead	0.5	Benzo[b]fluoranthene	550
Mercury	0.05	Benzo[ghi]perylene	990
Nickel	0.5	Benzo[k]fluoranthene	360
Selenium	0.05	Chrysene	330
Silver	0.05	Fluoranthene	330
Zinc	2	Fluorene	330
		Indeno[1,2,3-cd]pyrene	400
		Pyrene	330
Aroclor PCB (ng/dry g)		**Chlorinated Pesticides (ng/dry g)**	
PCB-1242	2	o,p - DDD	0.04
PCB-1254	2	o,p - DDE	0.02
PCB-1260	2	o,p - DDT	0.03
		p,p - DDD	0.04
Congener PCB (ng/dry g)		p,p - DDE	0.1
PCB-18,126,128,195,201,206,209	0.01	p,p - DDT	0.03
PCB-29,44,50,105,154	0.02		
PCB-87,101,180	0.03		
PCB-8,66,104,118,138,170,187	0.04		
PCB-28,188	0.05		
PCB-77	0.06		
PCB-52,133	0.07		

and DB-17/608/1701 columns were used for analyte identification and confirmation, respectively. The PAH compounds were measured using gas chromatography/ mass spectroscopy (GC-MS) equipped with DB-5 columns (SW-846, Method 8270) (U.S. EPA 1986, 1983). The chromatographic conditions varied among laboratories, but were chosen based upon the equipment used to provide sufficient separation efficiency for the target analytes.

Data Analysis

Data were analyzed in two ways: 1) calculation of mean parameter response (e.g., cadmium concentration) in the SCB and in various subpopulations (such as Santa Monica Bay); and 2) assessment of the fractional area within each population exceeding selected parameter thresholds of interest.

Mean parameter values were calculated using a ratio estimator (Thompson 1992):

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

where:

m = Mean concentrations for population j
p_i = Parameter value (e.g., concentration) at station i
w_i = Weighting for station i, equal to the inverse of the inclusion probablity for the site
n = Number of stations sampled in population j.

The ratio estimator was use in lieu of a stratified mean because an unknown fraction of each stratum was unsampleable (e.g., hard bottom). Thus, the estimated area, a random variable, was used as a divisor in place of the unknown true area. Standard error of the mean response was calculated as:

Standard Error = $$\sqrt{\frac{\sum_{i=1}^{n} ((p_i - m) \cdot w_i)^2}{\sum_{i=1}^{n} w^2_i}}$$

Confidence intervals were calculated as 1.96 times the standard error. Statistical differences between populations of interest were defined on the basis of nonoverlapping confidence intervals. 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 warranted based on preliminary examination of the data. The assumption is conservative in that its violation would lead to an overestimate of the confidence interval (Stevens and Kincaid 1997).

The percent of area exceeding a selected threshold was estimated in the same fashion after converting the data to a binomial form. For any sample observation, p_i was 1 if it exceeded the threshold value and 0 otherwise. The proportion of area that exceeded the selected threshold was taken as the mean of the indicator variable y_i.

Three thresholds were identified including anthropogenic enrichment of analytes and two screening levels of biological concern. Since chlorinated hydrocarbons are a synthetic pollutant, sediments were considered anthropogenically enriched wherever they were detected. Trace metals, however, are a naturally occurring component of marine sediments. Anthropogenic enrichment of trace metal constituents was assessed by conducting reference element normalization using iron (Schiff and Weisberg 1997). The two screening level thresholds of biological concern were developed by Long *et al*. (1995) (Table 3). One threshold, the effects range low (ERL) represents a concentration below which adverse biological effects should rarely observed. The second threshold, the effects range median (ERM), represents a concentration above which adverse biological effects may frequently be observed. The ERL and ERM are not regulatory sediment quality criteria; these thresholds are merely guidelines for assessing potential impacts resulting from contaminated marine or estuarine sediments. While these thresholds provide a useful benchmark for assessing relative resource condition, one cannot infer biological effects from an individual chemical exceedence since the guidelines were developed from locations with multiple chemical stressors, multiple biological endpoints, and various receiving water conditions (Long *et al.* 1998)

RESULTS

Eighty-nine percent of SCB sediments contained evidence of anthropogenic contamination (Table 4). Eighty-two percent of the SCB was contaminated with chlorinated hydrocarbons including total DDT (82%) and total PCB (46%). Utilizing iron as a conservative tracer of natural contributions for eight metals of interest, 50% of the SCB was estimated to be anthropogenically enriched in at least one trace metal. The three trace

TABLE 3. Screening level thresholds used for assessing the potential of adverse biological effects (Long *et al.* 1995).

	Effects Range Low (ERL)	Effects Range Median (ERM)
Organic Constituents (ng/dry g)		
Low Molecular Weight PAH	552	3,160
High Molecular Weight PAH	1,700	9,600
Total PAH	4,022	44,792
Total PCB	22.7	180
p,p' - DDE	2.2	27
Total DDT	1.58	46.1
Inorganic Constituents (ug/dry g)		
Arsenic	8.2	70
Cadmium	1.2	9.6
Chromium	81	370
Copper	34	270
Lead	46.7	218
Mercury	0.15	0.71
Nickel	20.9	51.6
Silver	1	3.7
Zinc	150	410

metals with the greatest spatial extent of contamination in SCB sediments were cadmium (31%), chromium (21%), and silver (20%). Anthropogenic enrichment was not confined to a specific location, but extended the entire length of the SCB, from Point Conception to the U.S.-Mexico international border (Figure 2).

Sediment screening level thresholds (Long *et al*. 1995) were used to assess the areal extent of potential biological effects for 13 constituents. Approximately 12% of the sediments in the SCB (433 km^2) exceeded ERM for at least one constituent. Nearly 55% of sediments in the SCB (1,9191 km^2) exceeded the ERL for at least one constituent, but were below the ERM. The remining 33% of the sediments in the SCB (1,169 km^2) were below all the ERLs evaluated.

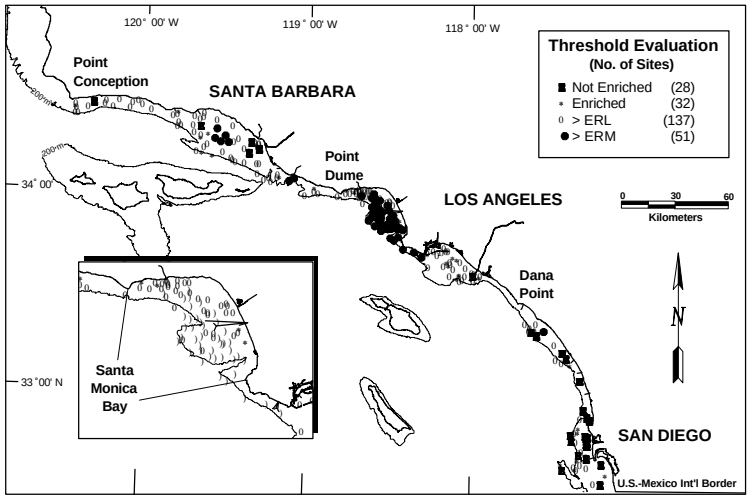
TABLE 4. Percent of area in the Southern California Bight exceeding contaminant thresholds in 1994. No iron:mercury baseline relationship existed to assess enrichment (see text).

	Detectable	Enriched	Effects Range Low	Effects Range Median
Arsenic	100.0	6.8	1.5	0.0
Cadmium	99.1	31.2	2.1	0.0
Chromium	100.0	21.4	7.3	0.0
Copper	100.0	16.4	6.8	0.0
Lead	100.0	16.5	0.5	0.0
Mercury	95.7	-	6.3	0.0
Nickel	99.9	3.2	3.2	1.8
Silver	98.5	20.2	7.3	1.0
Zinc	100.0	16.5	2.7	0.0
LMW PAH	0.0	0.0	0.0	0.0
HMW PAH	0.0	0.0	0.0	0.0
Total DDT	81.8	81.8	63.7	10.4
Total PCB	45.6	45.6	15.3	0.7
Any Trace Metal	100.0	50.1	13.7	2.8
Any Organic	82.1	82.1	63.7	10.4
Any Contaminant	100.0	89.0	66.8	12.3

Total DDT was the constituent that had the greatest areal extent for potential biological impairment (Table 4). Total DDT exceeded the ERL in 63.7% of the SCB (2,242 km^2); the ERM was exceeded in 10.4% of the SCB (366 km^2). The highest concentrations of total DDT occurred on the Palos Verdes shelf (Figure 3). Although emissions of total DDT are currently very low, this area was the site of historical discharges and a large reservoir of this contaminant still exists in subsurface sediments. The surficial sediment concentrations of total DDT decreased towards the north, declining as one approached Point Dume. North of Point Dume, and south of Palos Verdes, consistently lower level concentrations were observed.

Total PCB was the next constituent with the greatest areal extent of potential biological impairment. Total PCB exceeded the ERL in 15.3% of the SCB; the ERM was exceeded in 0.7% of the SCB. Every trace metal evaluated exceeded the ERL, but the amount of area varied from metal to metal. The differences ranged from 0.5 to 7.3% of the SCB for lead and chromium, respectively. However, only nickel (1.8% of the SCB) and silver (1.0% of the SCB) exceeded the ERM.

Figure 2. Spatial distribution of relative sediment contamination on the mainland shelf of the southern California Bight in 1994.



Evaluation of Subpopulations

Santa Monica Bay

Mean sediment concentrations inside of Santa Monica Bay were higher for every constituent measured than sediment concentrations outside of Santa Monica Bay (Table 5). Both regions had similar grain sizes (44.8 *versus* 42.2 % fines), indicating the composition and texture of the sediments were

FIGURE 3. Spatial distribution of total DDT in sediments on the mainland shelf of the southern California Bight in 1994.

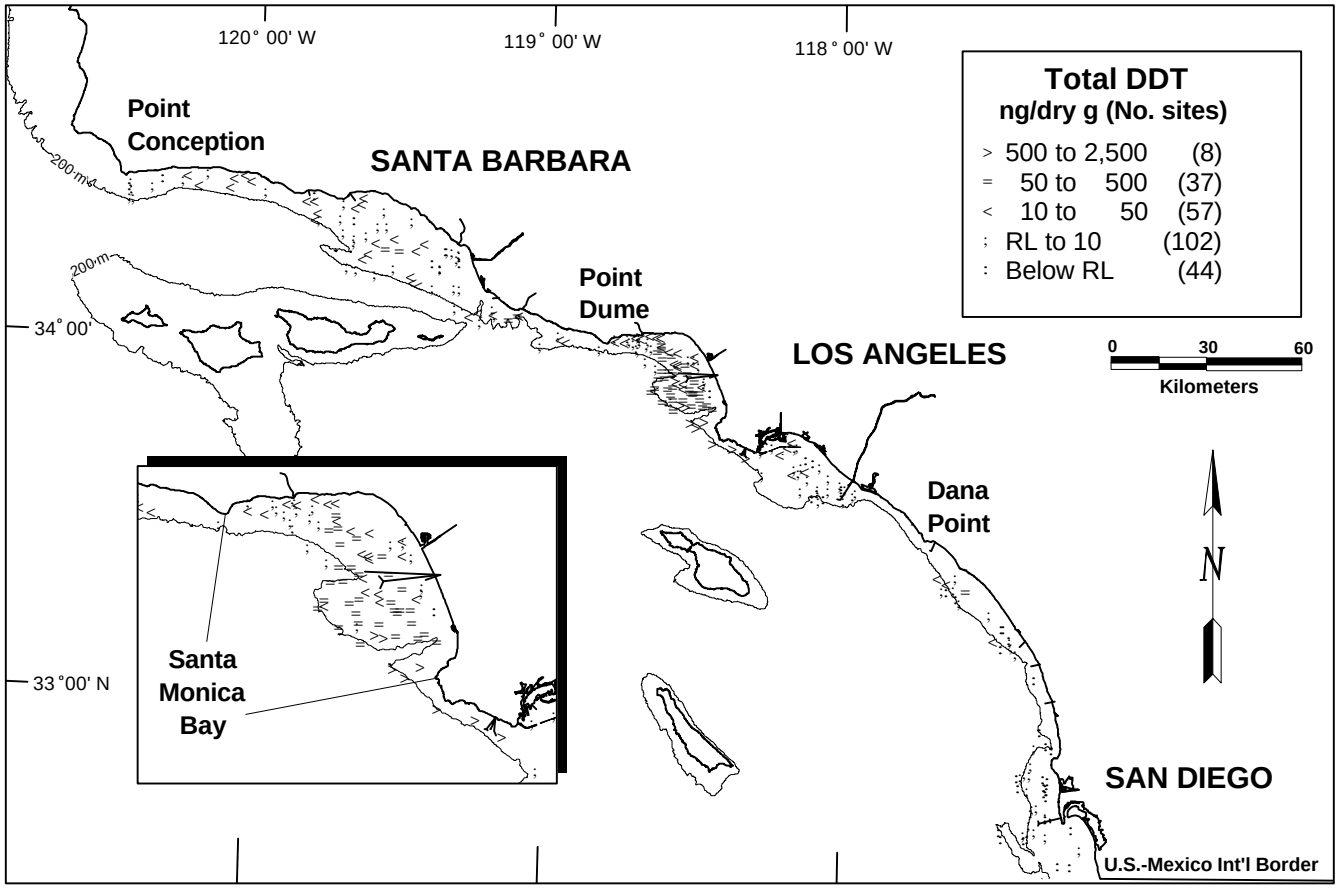


TABLE 5. Area-weighted mean sediment concentration (95% confidence intervals) in the Southern California Bight and for three subpopulations including Santa Monica Bay (SMB), publicly owned treatment works (POTWs), and stormwater. The (*) numbers indicate significantly greater concentrations.

		Southern California Bight		Geographic Subpopulation: Santa Monica Bay		NonSanta Monica Bay	
		Mean	95% CI	Mean	95% CI	Mean	95% CI
Fines	% dry	42.5	4.0	44.8	5.1	42.2	4.5
TOC	% dry	0.748	0.088	**1.200***	0.209	0.682	0.094
TN	% dry	0.051	0.004	**0.093***	0.012	0.045	0.005
Arsenic	ug/dry g	5.1	0.3	5.6	0.7	5.0	0.4
Cadmium	ug/dry g	0.33	0.04	**0.66***	0.19	0.28	0.04
Chromium	ug/dry g	39	4	**85***	16	32	3
Copper	ug/dry g	15	2	**30***	6	12	2
Lead	ug/dry g	10.9	1	**22***	3	9	0
Mercury	ug/dry g	0.050	0.007	**0.146***	0.024	0.036	0.006
Nickel	ug/dry g	18.1	1.9	**24***	3	17	2
Silver	ug/dry g	0.30	0.08	**1.58***	0.48	0.16	0.03
Zinc	ug/dry g	59	5	**84***	10	55	5
Total DDT	ng/dry g	40.8	18.3	**120.5***	48.0	29.2	19.5
Total PCB	ng/dry g	13.3	3.0	**57.6***	17.8	6.8	2.4

comparable. However, 12 of the remaining 13 constituents, including TOC, TN, cadmium, chromium, copper, lead, mercury, nickel, silver, zinc, total DDT, and total PCB were significantly higher (50% to 1,000% higher) inside than outside of the Bay.

The spatial extent of sediment contamination inside of Santa Monica Bay was much greater relative to the extent of contamination outside of Santa Monica Bay (Figure 4). One hundred percent of the area inside of Santa Monica Bay was enriched in at least one sediment contaminant. Thirteen percent of the area outside Santa Monica Bay was not enriched in any contaminant. Moreover, the magnitude of Bay-wide sediment contamination was also greater (Figure 4). Fifty percent of the area inside the Bay contained sediments with at least one constituent that exceeded the ERM. In contrast, only 7% of the areas outside the Bay contained sediment concentrations that exceeded the ERM. Finally, where contamination was observed, sediments inside the Bay were far more frequently contaminated by more than one constituent. We found 35 sites in this study that were anthropogenically enriched in 9 to 10 parameters (including As, Cd, Cr, Cu, Pb, Ni, Ag, Zn, total DDT, and total PCB) and all were located in Santa Monica Bay. Three of these sites were contaminated by 9 to 10 constituents at levels that exceeded the ERL. Finally, eight sites were observed to exceed the ERM for multiple constituents. Once again, all eight were located inside Santa Monica Bay.

POTW Outfall Areas

Mean sediment concentrations within POTW outfall zones were higher for 10 of 14 constituents than sediment concentrations outside POTW outfall zones at similar depths (25 - 100 m)(Table 5). Although not significantly different among zones, grain size within POTW outfall zones differed by 20% relative to non-outfall zones (47.9% *versus* 40.8% fines, respectively). However, concentrations of copper, mercury, silver, total DDT, and total PCB were disproportionately higher in sediments nearest POTW outfalls. Mean sediment concentrations were significantly higher and were 100% to 1,000% greater for these constituents relative to mean sediment concentrations in non-POTW zones. Mean concentrations of TOC, TN, cadmium, chromium, and lead were higher in sediments inside POTW outfalls zones, but they were not significantly different from sediments in non-POTW zones. In contrast, sediment concentrations of arsenic, nickel, and zinc were higher outside POTW outfall zones than inside; mean concentrations of arsenic and nickel were significantly higher.

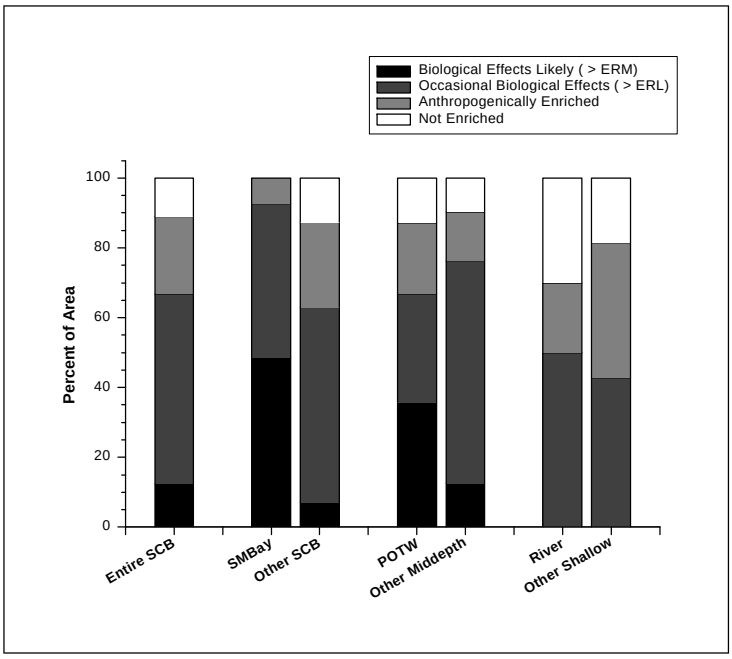
Approximately 90% of the mid-depth (25 - 100 m) area inside and outside POTW outfalls zones were enriched in at least one sediment contaminant (Figure 4). Although this relative extent of sediment contamination was similar between subpopulations, the relative magnitude of the sediment contamination inside POTW outfall zones was greater. For example, nearly 35% of the POTW outfall zone was enriched above the ERM for at least one constituent compared to less than 13% of the area outside POTW outfall zones.

POTW Subpopulation				Stormwater Subpopulation			
Outfall		Nonoutfall		Stormwater		Nonstormwater	
Mean	95% CI	Mean	95% CI	Mean	95% CI	Mean	95% CI
40.8	5.2	47.9	6.1	31.7	9.2	20.2	5.5
1.051	0.273	0.734	0.103	0.330	0.105	0.212	0.038
0.065	0.009	0.053	0.006	**0.034***	0.010	0.022	0.005
4.5	0.4	**5.7***	0.5	4.1	0.7	3.9	0.7
0.43	0.13	0.30	0.05	0.21	0.06	0.15	0.06
48	9	39	6	**27***	6	18	3
21*	4	13	2	**11***	3	6	1
14	2	11	1	**12***	4	6	1
0.100*	0.023	0.037	0.005	0.032	0.013	0.028	0.008
14	2	**21***	3	15	4	10	3
0.90*	0.28	0.21	0.04	0.15	0.10	0.06	0.01
60	7	61	8	51	13	34	6
146.8*	96.3	15.3	4.3	5.1	3.0	4.1	2.2
43.0*	16.2	8.0	2.7	4.3	3.6	3.9	3.1

Stormwater Discharge Areas

Mean sediment concentrations in zones near stormwater discharges were higher for every constituent measured compared to sediments outside stormwater discharge zones at similar depths (10 - 25 m) (Table 5). Sediments inside stormwater discharge zones were 50% finer than sediments outside (31.7 *versus* 20.2 % fines, respectively). Likewise, the mean TOC and TN contents of these stormwater-influenced sediments were 50% higher than sediments outside stormwater discharge zones. Trace metal concentrations averaged 60% higher in sediments inside stormwater discharge zones; mean sediment concentrations of chromium, copper, and lead were significantly higher than mean sediment concentrations outside stormwater discharge zones. Mean concentrations of total DDT and total PCB were only marginally higher inside stormwater discharge zones than mean sediment concentrations outside.

FIGURE 4. Relative extent of sediment contamination in the southern California Bight (SCB) and associated geographic or anthropogenic subpopulations in 1994.



The magnitude and extent of sediment contamination near stormwater discharge zones was similar relative to other shallow water areas of the SCB (70 *versus* 82%, respectively) (Figure 4). Approximately half of the sediments within or outside stormwater discharge zones were enriched in at least one contaminant beyond the ERL. Unlike the Santa Monica Bay or POTW outfall subpopulation comparisons, no shallow water areas, either within or outside stormwater discharge zones, exceeded the ERM for any constituent.

DISCUSSION

The spatial extent of sediment contamination was widespread in the SCB and the majority of area on the coastal mainland shelf has been influenced by man's activities. Total DDT, total PCB, and trace metals were each found to be enriched in over half of the SCB sediments. The magnitude of this enrichment increased near areas where inputs of contaminants were greatest. Santa Monica Bay for example, adjacent to metropolitan Los Angeles, receives a multitude of inputs from one of the most densely populated coastal regions in the country. In turn, sediments in Santa Monica Bay had higher sediment contaminant concentrations, a greater proportion of sediments that exceeded sediment quality screening thresholds for biological impairment, and a greater frequency of exceedences by multiple constituents compared to sediments outside the Bay.

The most prevalent sediment contaminant in the SCB was total DDT. The highest sediment concentrations were measured on the Palos Verdes Shelf. This location is the subject of an EPA Superfund site investigation as a result of historical discharges by Montrose Chemical Corporation which, until 1971, sent DDT manufacturing waste through Los Angeles County's ocean outfall from the Joint Water Pollution Control Plant. Although estimates of up to 1,800 metric tons of total DDT were discharged by Montrose per annum prior to 1971 (Chartrand 1988), current POTW emissions are extremely low or nondetectable (Raco-Rands 1996). The sediment concentrations resulting from these historical discharges steadily declined moving northward, through Santa Monica Bay and beyond, which is the net direction of the oceanic currents in the region (Hickey 1993). Sediment concentrations of total DDT remained uniformly low to the south of Palos Verdes. Other examples of constituents that showed spatial patterns relative to large POTWs were total PCB, silver, and cadmium (Schiff and Gossett 1998). Although large quantities of these constituents have been discharged through POTW outfalls since the early 1970's, more than 99% of the mass emissions occurred between 1972 and 1988; less than 1% has been discharged over the last 10 years (Raco-Rands 1996). Historical discharges of some contaminants have accumulated in sediments near POTW outfalls and can

TABLE 6. Areal extent of sediment contamination for total DDT in the Southern California Bight (SCB) utilizing various threshold values.

Source	Units	Total DDT Threshold Number		Percent of SCB Exceeding Threshold	
		Low	High	Low	High
Long *et al.* 1995 (ERL/ERM)	ng/dry g	1.58	46.1	63.7	10.4
MacDonald *et al.* 1996 (TEL/PEL)	ng/dry g	3.89	51.7	49.2	9.1
Daskalakis and O'Conner 1995 (COSED High/5xHigh)	ng/dry g	22	110	19.1	5.1
MacDonald *et al.* 1994b (Sediment Effect Criterion)	ng/dry g	7.12	-	41.7	-
	ug/g TOC	199	-	71.5	-
Swartz et al. 1994	ug/g TOC	300	-	63.6	-
Chapman, 1996	ng/dry g	8.51	-	40	-
	ug/g TOC	269	-	65	-

remain there for decades (Zeng *et al*. 1995, Stull *et al*. 1986b).

Currently, stormwater discharges from urbanized watersheds are potentially the largest contributor of trace metals to the SCB (Schiff 1997). We observed a 60% increase in sediment concentrations of common runoff metals such as chromium, copper, lead, nickel, and zinc near these discharges. Not only did the magnitude of sediment contamination increase, but we also observed an equally large increase in the extent of sediment contamination; approximately 50% more area inside stormwater zones were anthropogenically enriched in trace metals than outside stormwater zones.

Use of Screening Level Thresholds

Although we observed widespread sediment contamination, these large changes in the extent and magnitude of chemical contamination do not automatically infer widespread biological impact. Chemical concentration thresholds help us to evaluate the potential for biological impairment, but establishing numerical thresholds at which sediment contaminants are in excess and detrimental to marine life has been the subject of extensive debate for many years (Chapman 1989; DiToro *et al*. 1991; Hoke *et al*. 1994; U.S. EPA 1993a, b, c). At the time of this study, no regulatory sediment quality criteria had been promulgated by the State of California for which to compare our results and assess the extent of sediment contamination in the SCB. Therefore, this study utilized several pollutant thresholds of increasing severity to assess the extent and magnitude of sediment contamination that equated with: 1) were contaminants measurable above background levels or naturally occurring concentrations (anthropogenically enriched); and 2) did the contaminants exceed screening level values that may indicate occasional biological effects (> ERL) or values that may indicate frequent biological effects (> ERM). The extent of sediment contamination derived from these thresholds is valid only if the predictability of the threshold is reliable.

Long *et al*. (1998) and Daskalakis and O'Conner (1995) have developed and evaluated the predictive ability of the ERL and ERM for the constituents that were assessed in this study. The screening level values appear to be highly reliable for adverse biological effects from some constituents including PAH, arsenic, cadmium, chromium, copper, lead, silver, and zinc. The screening level values for other constituents assessed in this study were less reliable for adverse biological effects including total DDT, total PCB, mercury, and nickel. One consequence of unpredictability is an increase in Type I errors; a false positive would indicate a potential for biological impairment when none may actually occur. This lack of reliability affects assessments of sediment contamination in the SCB, particularly since total DDT was such a widespread contaminant and often exceeded the screening level values for adverse biological effects.

Accompanying studies in the SCB consisted of more ecological indicators than just sediment chemistry. Several biological indicators were measured at the same sites

examined in this paper and these indicators did not demonstrate widespread adverse biological effects, despite the increased probability of observing them as indicated by sediment quality threshold exceedances. None of the 71 whole sediment samples from the SCB tested with the amphipod *Ampelisca abdita* exhibited acute toxicity (Bay 1996), although 17 of these samples exceeded the ERM for at least one constituent. Eleven of these 17 samples exceeded the ERM solely for total DDT. Approximately 90% of the SCB area was determined to have ecologically healthy benthic community assemblages indicative of reference areas (Bergen *et al.* 1998). The remaining 10% of the SCB was characterized by a low degree of impact and there was a low correspondence between changes in benthic community assemblages and exceedances of the ERM at individual sites.

There are several potential reasons why the ERL and ERM screening level thresholds do not correspond to the biological indicators assessed by these accompanying studies. One reason might be that the biological indicators are not sensitive to contaminant changes. In the case of sediment toxicity tests, *Ampelisca* was less sensitive than toxicity tests using the purple sea urchin (*Strongylocentrotus purpuratus*) (Bay 1996). A second explanation might be that the local organisms may have physiologically or genetically adapted to local contaminants as they have in other locations (Weis and Weis 1989). A third explanation might be that either the thresholds are not good predictors of adverse biological effects or that local conditions (such as bioavialability or presence of other contaminants) are not similar to those when threshold exceedences result in biological effects.

Since the reliability of the ERL and ERM screening level thresholds of adverse biological effects for total DDT was questionable, several alternative thresholds taken from the literature were applied to our distribution of sediment total DDT in the SCB (Table 6). Despite the fact that these alternative thresholds encompassed a wide variety of approaches, locations, and endpoints, the widespread distribution of total DDT in sediments of the SCB at levels of concern remained. The frequency of contaminant threshold exceedence was high and the estimate of aerial extent for potential biological impact due to total DDT was consistently large (> 40% of SCB).

Regardless of whether the thresholds were good predictors of biological impacts at individual sites, total DDT and total PCB are bioavailable and are concentrated up the food chain. Accompanying studies found widespread bioaccumulation of total DDT and total PCB in livers of three flatfish species (Pacific sanddab [*Citharichthys sordidus*], longfin sanddab [*Citharichthys xanthostigma*], and Dover sole [*Microstomus pacificus*]) throughout the SCB (Schiff and Allen 1997). Each of these species is intimately associated with sediments and feeds upon resident infaunal invertebrates. Total DDT was detected in all 78 liver tissue samples analyzed representing the majority of each species range in the SCB. Finally, fish tissue concentrations were significantly correlated to concentrations measured in sediments near each specimen's collection site, regardless of species.

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