



Temporal and spatial distributions of contaminants in sediments of Santa Monica Bay, California

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Abstract

Contaminant inputs from wastewater discharge, a major source of contamination to Santa Monica Bay (SMB), have declined drastically during the last three decades as a result of improved treatment processes and better source control. To assess the concomitant temporal changes in the SMB sediments, a study was initiated in June 1997, in which 25 box cores were collected using a stratified random sampling design. Five sediment strata corresponding to the time intervals of 1890–1920, 1932–1963, 1965–1979, 1979–1989, and 1989–1997 were identified using ²¹⁰Pb dating techniques. Samples from each stratum were analyzed for metals, 1,1,1-Trichloro-2,2-bis(p-chlorophenyl)ethane (DDT) and its metabolites (DDTs), polychlorinated biphenyls (PCBs), and total organic carbon (TOC). Samples from the 1965–1979, 1979–1989, and 1989–1997 strata were also analyzed for polycyclic aromatic hydrocarbons (PAHs) and linear alkylbenzenes (LABs). Sediment metal concentrations increased from 1890–1979 and were similar during the time intervals of 1965–1979, 1979–1989, and 1989–1997, although the mass emissions of trace metals from sewage inputs declined substantially during the same time period. Trace organic contamination in SMB was generally highest in sediments corresponding to deposition during the years of 1965–1979 or 1979–1989 and showed a decline in concentration in the 1989–1997 stratum. Temporal trends of contamination were greatest in sediments collected from areas near the Hyperion Treatment Plant (HTP) outfall system and on the slope of Redondo Canyon. The highest contaminant concentrations were present in sediments near

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the HTP 7-mile outfall in the 1965–1979 stratum. Elevated trace metal and organic concentrations were still present in the 1989–1997 stratum of most stations, suggesting that sediment contaminants have moved vertically in the sediment column since sludge discharges from the 7-mile outfall (a dominant source of contamination to the bay) ceased in 1987. The widespread distributions of DDTs and PCBs in SMB and highly confined distribution of LABs around the HTP outfall system were indicative of a dispersal mechanism remobilizing historically deposited contaminants to areas relatively remote from the point of discharge.

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1. Introduction

Santa Monica Bay (SMB) is located adjacent to the greater metropolitan Los Angeles area. It is an important ecological and economic resource for the area's population of more than 10 million people and has been subjected to numerous stresses as a result of rapid urbanization and industrialization. Contaminant sources include, but are not limited to, municipal wastewater, urban runoff, industrial facilities, direct waste dumping, oil spills, natural oil seeps, and atmospheric deposition. The contaminant contributions to SMB from these sources have changed dramatically over time, a combination of increased inputs due to population growth and reductions resulting from improved waste treatment procedures, enhanced source control efforts, changed waste disposal practices, and increased public awareness, among others.

Most monitoring and research efforts to assess the impact of the changing contaminant inputs on the sediment conditions of SMB only date back to the 1970s (Mearns et al., 1991). On the other hand, the contaminant inputs to SMB have been occurring since at least 1894, when raw sewage from the city of Los Angeles was first discharged into SMB. Analyses of sediment cores from deep-water basins offshore of southern California show increases in hydrocarbon contamination since the 1940s (Venkatesan, Brenner, Ruth, & Kaplan, 1980). The monitoring program administered by the Environmental Monitoring Division (EMD) of the city of Los Angeles' Hyperion Treatment Plant (HTP) has measured both the quality of municipal wastewater discharged to SMB and the quality of sediments receiving the effluents since the early 1970s (EMD, 1997, 1999); but these data have focused on the point of discharge and do not evaluate the SMB sediment conditions on a large spatial scale and do not describe temporal trends prior to 1970. Other studies have assessed the sediment conditions of SMB, but these studies have focused on either spatial distributions with no temporal assessment (Schiff & Gossett, 1998), studied temporal trends within a small area (SCCWRP 1995), or limited analysis of temporal trends to the period after 1970 (Mearns et al. 1991).

A study was initiated in June of 1997 to examine the temporal and spatial patterns of sediment contamination in SMB by analyzing multiple sediment cores collected throughout the bay. The concentrations of trace metals, DDTs, PCBs, PAHs, LABs,

and TOC were determined in core sections containing sediments deposited during five time periods: 1900, 1945, 1970, 1985, and 1997. While most of the analytes were selected due to their potential to cause toxicity, LABs were included as molecular markers of sewage inputs. The LABs are used as raw materials in detergent production and discharged to the coastal marine environment almost exclusively via sewage outfalls in southern California (Eganhouse, Blumfield, & Kaplan, 1983, Eganhouse, Olaguer, Gould, & Pinney, 1988).

2. Methods

2.1. Sample collection

Twenty-five sites in water depths between 16 and 182 m within SMB were sampled in June 1997 (Fig. 1). Twenty-one of these sites were selected using a stratified random design with the strata corresponding to three regions located at varying distances from the HTP 7-mile outfall. This outfall was used for the disposal of sewage sludge from 1957 to 1987 and is regarded as one of the dominant historical sources of contamination to SMB. The first stratum (designated as “Sludge” stratum) comprised a 12 km² area within a 2 km radius of the 7-mile outfall (Fig. 1). The second stratum (designated as “POTW” stratum) consisted of a 112 km² area outside of the sludge stratum and within 6.6 km of the 7-Mile outfall. The POTW stratum included

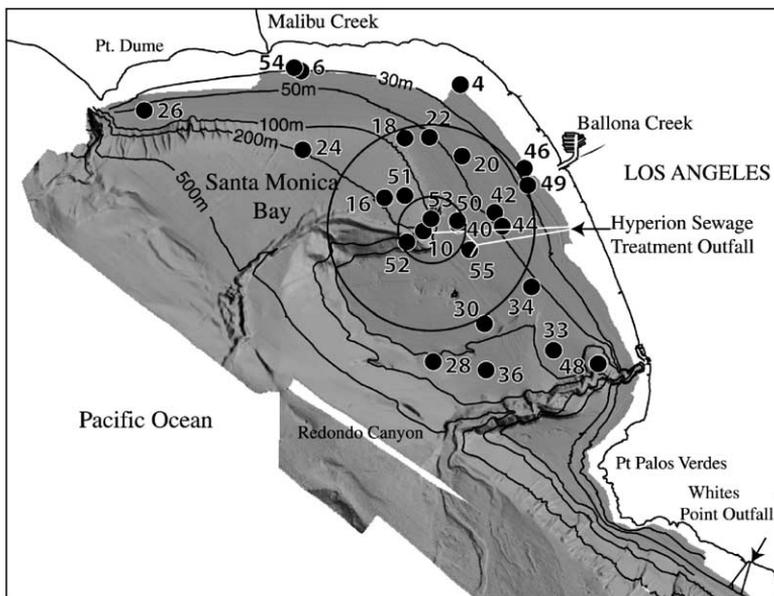


Fig. 1. Sampling sites in Santa Monica Bay, CA. The small and large circles indicate the boundaries of the Sludge and POTW strata, respectively.

the HTP 5-mile outfall, which was placed in operation in 1959 and currently discharges approximately 350 million gallons per day of treated wastewater from the city of Los Angeles. The third stratum (designated as “Other” stratum) consisted of the remainder of SMB north of the Redondo Canyon and comprised an area of 361 km². Sample sites were selected randomly within strata, but a systematic component was added to minimize clustering (Stevens, 1997). In this design, a hexagonal grid is placed randomly over a map of the sampling area, a subsample of hexagons is chosen from this population, and a random site is selected from each grid cell.

In addition, four non-random sites were selected around specific contamination sources in SMB. The first two sites, Stations 10 and 55, were located near the terminus of each outfall and historically have been monitored by the City of Los Angeles (EMD Stations E6 and Z2, respectively). Two other non-random sites, Stations 49 and 54, were located at depths of 25 m immediately offshore from Ballona and Malibu creeks, the two largest sources of stormwater runoff to SMB.

Sediment samples were collected at each site using a standard NEL box corer, with a 20×30×60 cm box (Rosfelder & Marshall, 1967). Separate subcores for chemistry and geochronology measurements were taken by driving 8.7-cm outside diameter polycarbonate tubes into the intact box core sample at a constant speed with an electric actuator. Each geochronology subcore was extruded and sectioned into 2-cm-long samples on board the ship and transported to the laboratory for dating using radioisotope measurements (Alexander & Venherm, *this volume*). The chemistry subcores were stored at –20° C until the completion of dating. The chemistry subcores were then thawed and extruded; 2-cm sections were removed at the depths corresponding to the desired time horizons. Poor core penetration and/or rapid sediment accumulation rates at some of the stations prevented collection of sediment from the earliest time strata; in these cases, the bottom 2 cm of the core was analyzed if it was mathematically within 17 years of one of the target strata.

2.2. Sediment dating

Alexander and Venherm (*this volume*) identified five sediment strata in each geochronology subcore that corresponded to calculated ages of 1900, 1945, 1970, 1985, and 1997 (surface) using ²¹⁰Pb and ¹³⁷Cs. Sediment samples were prepared using the techniques described by Alexander, Smith, Schropp, Calder, and Windom, (1993) and summarized here. Sediments were ground to powders, sealed in 30-ml polypropylene jars, and equilibrated for 20 days to allow ingrowth of ²²²Rn. Activities of radionuclides were determined using intrinsic germanium detectors, computer-based multi-channel analyzers, and ORTEC Maestro software. Samples were counted for 24–72 h. Total ²¹⁰Pb activity was measured using 46.5 KeV gamma peak (Cutshall, Larsen, & Olsen, 1983). Supported levels of ²¹⁰Pb were determined by measuring the gamma activity of ²¹⁴Pb (295 and 352 KeV). Self-absorption corrections for ²¹⁰Pb were made on each sample following the techniques of Cutshall et al. (1983). ¹³⁷Cs activities were determined by measuring its 661.6-KeV gamma peak (Kuehl, Nittrover, & DeMaster, 1986).

2.3. *Measurements of metals*

Each sediment sample was mixed thoroughly in a plastic container and digested with concentrated nitric acid and hydrochloric acid at 95 °C using Method 3055 of the United States Environmental Protection Agency (US EPA) SW-846 protocols, Third Edition. The digestate was filtered and the filter paper loaded with particles was washed with hot hydrochloric acid and deionized water, and subjected to further digestion using hydrochloric acid. The filtrate from the second digestion was combined with that from the first digestion for instrumental analysis. Digested samples were analyzed using Method 6010 of the US EPA SW-846 protocols for most metals. Some metals expected to have low concentrations were analyzed with graphite furnace atomic absorption spectroscopy (US EPA Method 7010). Mercury was analyzed with a cold vapor method (US EPA Method 7471).

2.4. *Measurements of organics*

2.4.1. *Sample extraction*

Frozen sediment samples were thawed at room temperature and homogenized using a stainless steel spatula. An aliquot of ~20 g (wet weight) from each sample was transferred into a microwave Teflon-lined tube and was spiked with appropriate surrogate standards. The sample was extracted three times with 25 ml of methylene chloride each using a microwave-assisted solvent extractor (12 samples per batch), MSP 1000 Microwave Sample Preparation System (CEM Corporation, Matthews, NC), with the following procedure: the temperature was ramped to 120 °C in 15 min and held at 120 °C for another 15 min. After the tube was cooled to 35 °C or lower (in ~40 min), the organic layer was filtered through a long-stemmed glass funnel containing approximately 10 g of anhydrous sodium sulfate. The combined extract was concentrated to approximately 3 ml and solvent exchanged to hexane using a rotary evaporator at 30 °C and 650 mm Hg vacuum pressure. Activated copper was added to the extract for sulfur removal (in the dark overnight). The extract was transferred to a 1-dram vial and further concentrated to 2 ml under a gentle stream of ultra-high purity nitrogen.

One milliliter of each extract was transferred into a centrifuge tube, followed by an addition of 1 ml of concentrated sulfuric acid. The mixture was vigorously mixed using a vortex mixer set at speed 5 for approximately 1 min. After settling, the top organic layer was removed. The acid cleanup was repeated until a clean, cloudless organic layer was obtained. This layer was then transferred into a sample vial and internal standards (PCB 30 and PCB 205) were added; this extract was analyzed for DDTs and PCBs. The other 1 ml of extract was subjected to column cleanup/fractionation, and the final volume was adjusted to 1 ml; this extract was analyzed for PAHs and LABs.

2.4.2. *Instrumental parameters*

Six DDT components and 42 PCB congeners were measured using an HP 5890 II GC equipped with a ⁶³Ni electron capture detector (ECD) and a 60 m × 0.25 μm I.D. (0.25 mm film thickness) DB-5 silica fused capillary column (J&W Scientific,

Folsom, CA). Instrumental parameters were the same as those used previously (Zeng, Yu, & Tran, 1999).

Total PAHs was the sum of 29 PAH components and total LABs included all the individual compounds from phenyl decanes to phenyl tetradecanes (except for 1-phenyl isomers). The PAHs and LABs were measured using an HP 5890 II GC equipped with a 5970 mass spectrometer (MS) and a 60 m × 0.25 μm I.D. (0.25 mm film thickness) DB-5 silica fused capillary column. The chromatographic conditions are described in Zeng and Yu (1996) and Zeng and Vista (1997), respectively.

Sediment TOC content was obtained from the difference between the measured concentrations of total carbon (TC) and total inorganic carbon (TIC). Wet sediment was homogenized and 3–5 g was removed for TC and TIC measurements. The wet sediment samples were dried for ~24 h at 50° C. Dried samples were ground with a ceramic mortar and pestle and stored in clean glass vials in a desiccator. An aliquot of each sample (~20 mg) was analyzed for TC on a carbon dioxide coulometer (System Model 5010; UIC, Inc.; sample was baked at 1000 °C for ~5 min and evolved CO₂ was measured by the coulometer). A separate aliquot of sediment (~20–100 mg) was analyzed for TIC on the carbon dioxide coulometer (sample was digested by heated, dilute perchloric acid and evolved CO₂ was measured by the coulometer). Replicates were run periodically (~15% of total samples) to monitor precision. The system was calibrated (both TC and TIC) by analyzing pure calcium carbonate as a standard. Blanks also were analyzed and subtracted from all analyses to remove background levels.

2.5. Data analysis

The mean concentration of each analyte within SMB strata at a specific time period was calculated by weighting the concentration at each station by the inverse of its inclusion probability as follows:

$$\text{Mean} = \frac{\sum_{i=1}^n p_i \times w_i}{\sum_{i=1}^n w_i},$$

where: p_i = concentration at station i ; and w_i = area weight for station i .

The potential biological significance of temporal changes in sediment contamination was evaluated by comparing concentrations to the effects range-median (ERM) and effects range-low (ERL) sediment quality guidelines (SQGs), which were developed by Long, MacDonald, Smith, and Carter, (1995) through the analysis of matching sediment chemistry and biological effects data. The ERL for a contaminant represents the concentration below which adverse effects upon sediment-dwelling fauna are expected to occur only infrequently. The ERM represents the concentration above which adverse effects have been observed to occur frequently. The percent of area exceeding the ERL or ERM was calculated as above with p_i equal to 1 if the concentration exceeded the guideline value. Contaminants included in these calculations were total PCB, total PAH, As, Cd, Cr, Cu, Pb, Hg, Ni, Ag, Zn, and total DDT

(ERL only). The ERM for total DDT (46.1 ng/g) was not used in these calculations as this value has been shown to have relatively low reliability (Long & MacDonald, 1998). In place of the DDT ERM, a value of 3000 ng/g was used. This value was calculated from the organic carbon normalized threshold for sediment toxicity due to DDT determined by Swartz et al. (1994), assuming 1% total organic carbon content.

Mean SQG quotients, the average of the ratios between the chemical concentrations in the sample and the respective SQG (ERM or DDT toxicity threshold), were calculated to indicate the potential for adverse effects based upon the mixture of contaminants present in each sample. These quotients were compared to criteria developed by Long and MacDonald (1998) to classify the samples into four categories representing different levels of concern. The PAH data were not used in calculation of the SQG quotients because no data were available for the 1900 and 1945 strata.

3. Results

Dating of the cores using ^{210}Pb profiles revealed that sediment accumulation rates vary throughout SMB. Sediment accumulation rates tended to be lowest (0.19–0.37 cm/year) at stations that were located in deeper water and distant from the HTP outfall system. The highest accumulation rate (2.28 cm/year) was measured at Station 53, located adjacent to the HTP 7-Mile Outfall. High accumulation rates were also present at shallow water locations offshore of Malibu and Ballona Creeks (1.1–1.37 cm/year).

The subcore sections representing each of the time strata usually contained sediments from multiple years, due to variations in accumulation rate, the presence of vertical sediment mixing, and the 1–2 cm thickness of the subcore sections. The calculated age of the sediments varied by up to 12 years over a 2 cm depth in some cores. In order to represent the variations in calculated age among the samples, each time stratum was identified by the range of ages calculated among all stations. These ranges were: 1890–1920, 1932–1963, 1965–1979, 1979–1989, and 1989–1997.

High accumulation rates and reduced penetration of the 50 cm deep box core due to coarse grain size at some locations prevented the collection of sediment samples corresponding to older strata at some stations. A total of 11, 17, 24, 24, and 25 samples were obtained for the 1890–1920, 1932–1963, 1965–1979, 1979–1989, and 1989–1997 time strata, respectively.

3.1. Temporal trends of sediment contamination

Concentrations of both metals and organics varied widely among the samples. A distinct temporal pattern was evident in many of the samples, especially those with the greatest concentrations of contaminants. The concentrations of most trace metals (As, Cd, Cr, Cu, Hg, Pb, Ni, and Zn) were highly correlated with each other (Pearson's correlation coefficients of >0.85 in most cases), indicating that these metals changed in a similar fashion over time. Correlations between Be or Ag and the other metals were low, which may have been due to the similar concentration of Be among the samples and the lack of detectable Ag in many samples.

Variation in Pb concentration for selected stations (Fig. 2) illustrates the temporal trends for most metals among the stations. The data for five stations are shown, each of which represents a different region or potential contaminant source in SMB: Station 10, adjacent to the HTP 7-mile outfall; Station 55, adjacent to the HTP 5-mile outfall, Station 36, on the slope of the Redondo Canyon; Station 49, offshore of Ballona Creek; and Station 26, located in northwestern SMB distant from most

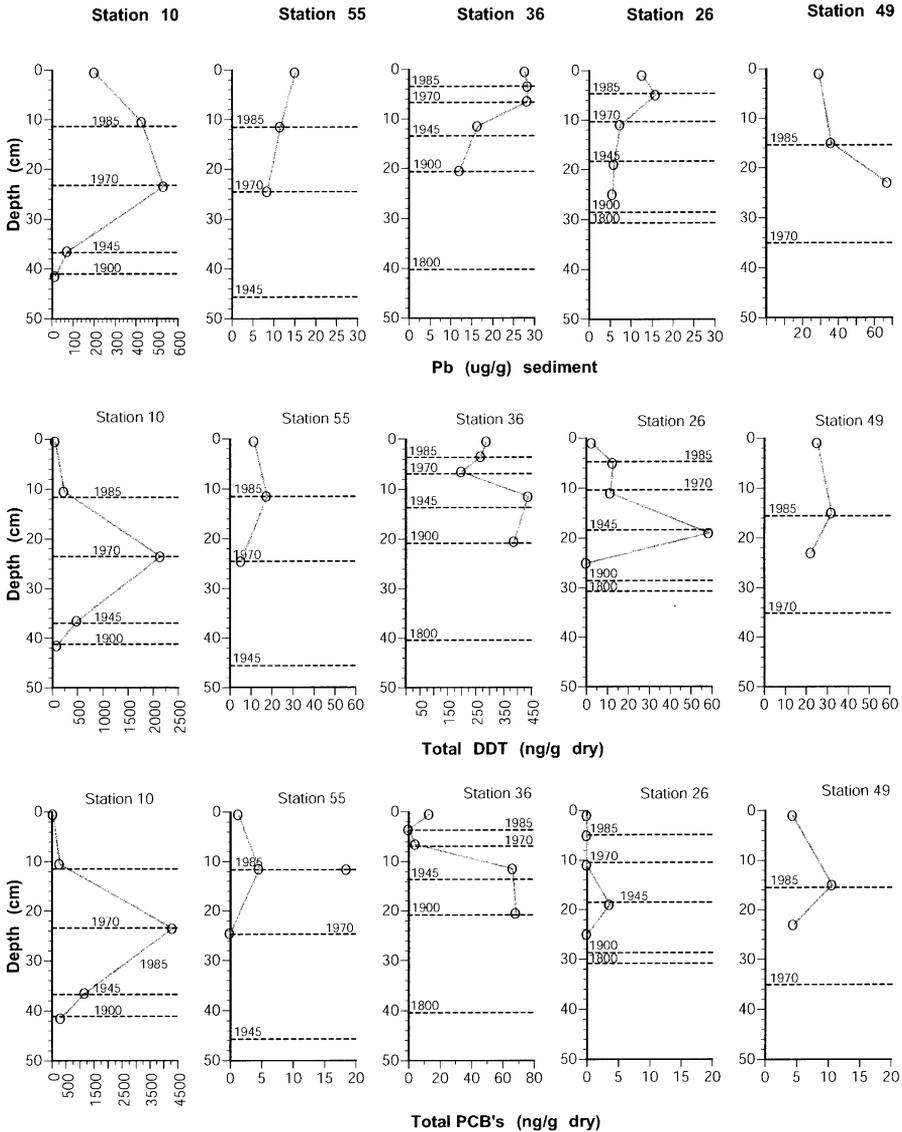


Fig. 2. Concentrations of lead, DDT, and PCB in sediments from five time strata at selected stations in Santa Monica Bay.

local contaminant discharges. The highest concentrations of Pb (and other metals) were usually present in samples collected near the 7-mile outfall, such as at Station 10. Relatively high concentrations were also measured at Station 49, offshore of Ballona Creek, the largest source of urban runoff to SMB. Pb concentrations at these two stations were highest in the 1965–1979 stratum and showed substantial declines in the 1979–1989 and 1989–1997 strata. Temporal patterns in metals were less distinct at those stations with lower Pb concentrations (e.g., Stations 55 and 26), but generally indicated higher concentrations in the 1965–1979 and later strata.

The DDTs were detected in all but two of the samples analyzed in the entire study. As with the metals, the most pronounced temporal trend was evident at stations with the highest concentrations, which were usually located near the 7-mile outfall (e.g. Station 10 in Fig. 2). The 1932–1963 or the 1965–1979 stratum usually contained the maximum concentration at a station. A dramatic decline in total DDT concentration between 1890–1979 strata and the 1989–1997 stratum was evident at many stations. Relatively high concentrations of DDTs were often present in samples from stations located on the slope of the Redondo submarine canyon (Stations 28, 36, and 48). The temporal pattern at Stations 36 and 28 was anomalous, showing relatively high concentrations of DDTs in the 1890–1920 stratum (Fig. 2).

The temporal patterns of total PCB among the stations were similar to those observed for total DDT (Fig. 2). Maximum PCB concentrations were usually found in the 1932–1989 strata and marked reductions in concentration were evident in the 1989–1997 stratum. Relatively high concentrations were found again in the 1890–1920 stratum from some of the stations located near the Redondo Canyon slope. Temporal patterns in PCBs could not be determined for approximately one-half of the stations because concentrations were below detection limits in many of the time strata.

Stations located near the HTP outfall system also showed temporal trends in the area-weighted average concentration of most contaminants (Table 1). For this analysis, data for the sludge and POTW strata were combined to represent the HTP outfall-influenced region. Among the metals, the mean concentrations of Cd, Cr, Cu, Pb, Hg, Ag, and Zn increased by at least a factor of three in the outfall region between the 1890–1920 and the 1965–1979 or 1979–1989 time strata. The average concentrations of As and Ni showed little temporal change in the Outfall (POTW + Sludge) stratum. Temporal changes in metal concentration were minor between the 1965–1979 and the 1989–1997 strata, however. The maximum concentration measured in each stratum also shows that substantial increases in metals contamination have occurred after the 1932–1963 stratum (Table 1). For every metal listed in Table 1, the lowest maximum concentration was present in the 1890–1920 stratum and the highest concentrations were present in the 1965–1979 to 1989–1997 strata. Average metal concentrations in the rest of SMB (“Other” stratum) showed little evidence of temporal change; an exception was Cu, which was not detected in any sample from the 1890–1920 stratum but ranged from 4.6 to 9.1 $\mu\text{g/g}$ in more recent sediments.

The average concentrations of chlorinated hydrocarbons (total DDT and total PCB) also showed large temporal variations (Table 1). Total DDT concentration in

Table 1

Area-weighted mean concentration of contaminants in sediment core samples from Santa Monica Bay. Values are shown for the Outfall (POTW + Sludge) and “Other” strata. Also shown are the maximum concentration values measured at any station in Santa Monica Bay for each time period

Stratum time interval	Area-weighted mean											
	Metals ($\mu\text{g/g}$)									Organics (ng/g)		
	As	Cd	Cr	Cu	Pb	Hg	Ni	Ag	Zn	DDTs	PCBs	PAHs
<i>Outfall stratum</i>												
1989–1997	6.3	3.4	87	55	32	0.5	22	5.5	106	31	26.6	157
1979–1989	6.3	4.4	110	70	34	0.4	24	4.6	127	459	27.2	103
1965–1979	6.3	4.9	109	60	37	0.5	22	3.6	128	113	201.4	214
1932–1963	5.1	1.2	46	5.8	13	0.2	17	1.9	63	140	86.1	na ^a
1890–1920	4.6	0.3	35	0	6	0.0	18	0.6	46	86	30.2	na
<i>Other stratum</i>												
1989–1997	6.5	0.9	58	8.1	19	0.2	18	0	58	68	2.5	0.3
1979–1989	5.0	0.5	65	9.1	19	0.2	24	0	60	73	0.6	0.0
1965–1979	6.2	0.8	57	6.7	17	0.2	19	0	58	62	1.0	0.4
1932–1963	6.2	0.8	52	4.6	15	0.2	21	0	57	221	40.8	na
1890–1920	4.9	0.7	48	0	9	0.1	19	0	50	135	20.3	na
<i>Maximum concentration</i>												
1989–1997	23.6	73.4	761	952	303	3.6	146	82	1447	290	924	5380
1979–1989	34.8	64.6	881	845	429	3.0	146	57	1149	369	391	2230
1965–1979	33.6	78.3	1114	875	532	5.1	150	59	1403	2150	4310	6910
1932–1963	10.5	12.0	128	80	74	0.6	34	34	208	591	1179	na
1890–1920	7.0	1.2	87	<21	22	0.3	28	10	64	388	318	na

^a No sample available for analysis.

the outfall stratum increased 430% between the 1890–1920 and 1979–1989 strata, while PCBs increased by 570% between the 1890–1920 and 1965–1979 strata. The mean concentrations of DDTs and PCBs also showed an approximately 4- or 7-fold decline, respectively, between the peak value and the 1989–1997 stratum. Total PAH concentrations in the outfall stratum also tended to decline after 1965–1979, but the change was relatively small (Table 1). The means for total DDT and total PCB in the rest of SMB (“Other” stratum) were highest in the 1932–1963 stratum and the 1890–1920 concentrations were greater than those measured in strata beginning in 1965 to the present.

3.2. Spatial patterns of sediment contamination

The spatial distribution of trace metals in SMB was dominated by contributions from the HTP outfall system. The influence of the outfalls can be seen in plots of Pb concentration for the 1932–1963, 1965–1979, 1979–1989, and 1989–1997 strata (Fig. 3). The highest concentration of Pb and other metals in each of these strata was almost always found near the 7-mile outfall (Stations 10 or 53). Other stations located

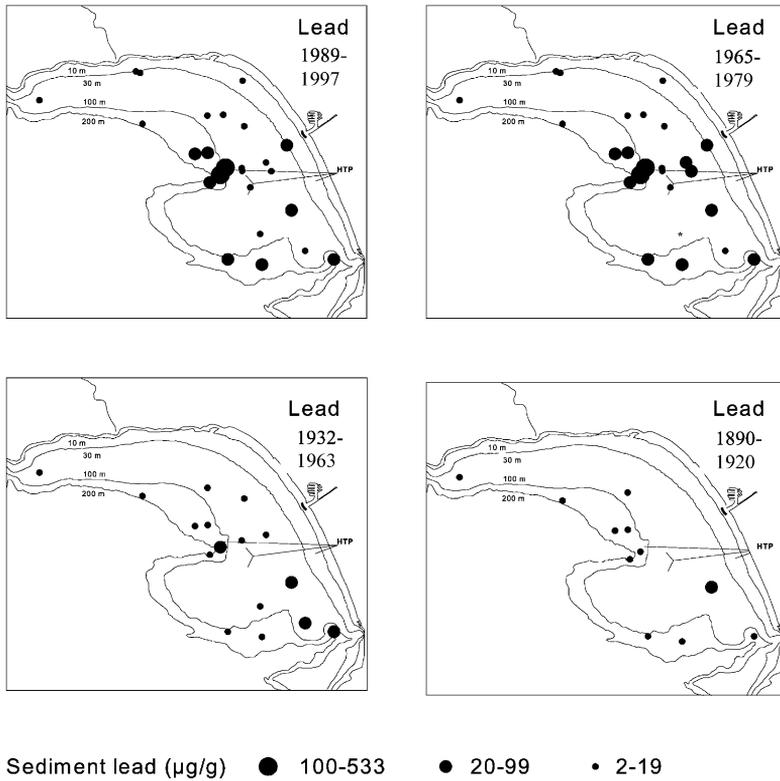


Fig. 3. Concentration of lead in sediment samples from four time strata in Santa Monica Bay sediment cores.

relatively close to the outfall system tended to have higher metal concentrations compared to locations in the northern region of SMB. Moderately elevated metal concentrations were also present in most strata at stations located near Redondo Canyon (Fig. 3). Metal concentrations were generally low and lacked a spatial pattern in the 1890–1920 stratum. Sediments corresponding to the 1890–1920 stratum were obtained from less than one-half of the stations and were distributed primarily in depths of greater than 100 m, limiting the ability to discern a spatial pattern.

Spatial patterns of trace organic contaminants in the 1932–1963, 1965–1979, 1979–1989, and 1989–1997 strata also appeared to be most influenced by two areas: the HTP outfall system (Stations 10, 50, 51, 53, and 55) and the area on the slope of Redondo Canyon, represented by Stations 28, 33, 36, and 48 (Figs. 4 and 5). The greatest concentrations of total DDT and total PCB were found in samples from sludge stratum corresponding to the 1965–1979 stratum. The concentrations of DDTs and PCBs at these stations decreased substantially in more recent sediment strata. In the area on the slope of Redondo Canyon, the sediments in the strata of 1890–1920 and 1932–1963 generally contained higher DDT and PCB concentrations than those in the other strata.

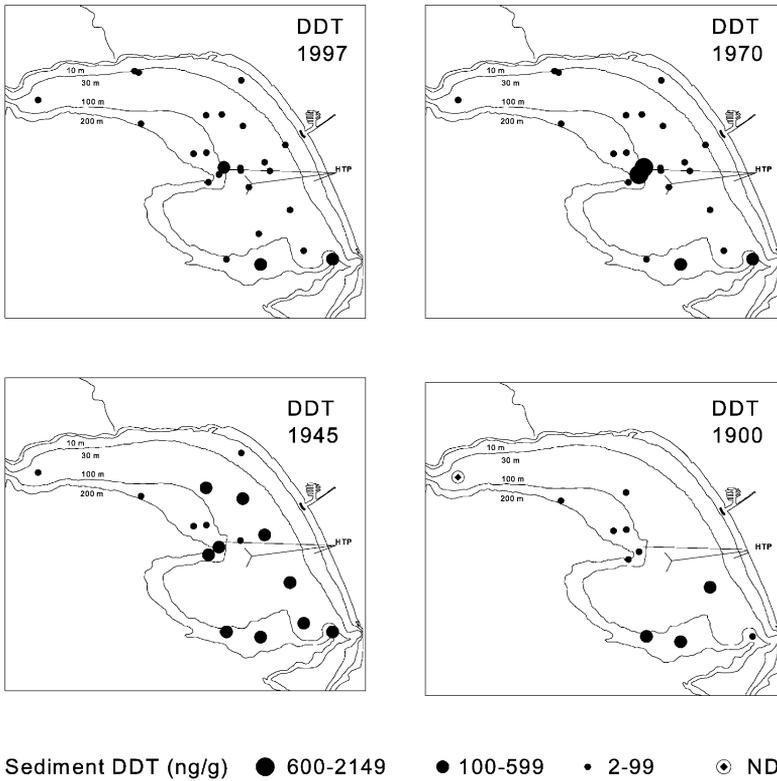


Fig. 4. Concentration of total DDT in sediment samples from four time strata in Santa Monica Bay sediment cores.

While DDT components were found in almost every sample and PCB congeners were present in about half of the samples, LAB and PAH compounds were only detected near the HTP outfalls and, for PAHs only, close to the mouth of Ballona Creek. High concentrations of LABs (848–61,500 ng/g) were present in the samples collected from Stations 10 and 53 near the HTP 7-mile outfall in the 1965–1979, 1979–1989, and 1989–1997 sediment strata (Fig. 6). No consistent temporal trend was evident in LAB concentrations among the stations. At Station 10, the highest concentration (16,000 ng/g) occurred in the 1979–1989 stratum and was an order of magnitude higher than those in the 1965–1979 and 1989–1997 strata. In contrast, the LAB concentrations in the Station 53 samples were all within the same order of magnitude with the highest value occurring in the stratum of 1989–1997.

The PAH compounds were detected only in samples collected from Stations 10, 49, 51, and 53. Three of these stations are near the HTP 7-mile outfall and one is in shallow water offshore of Ballona Creek. The greatest PAH concentration in each of the three strata occurred in the sample collected from Station 53. No consistent temporal pattern was evident among the stations.

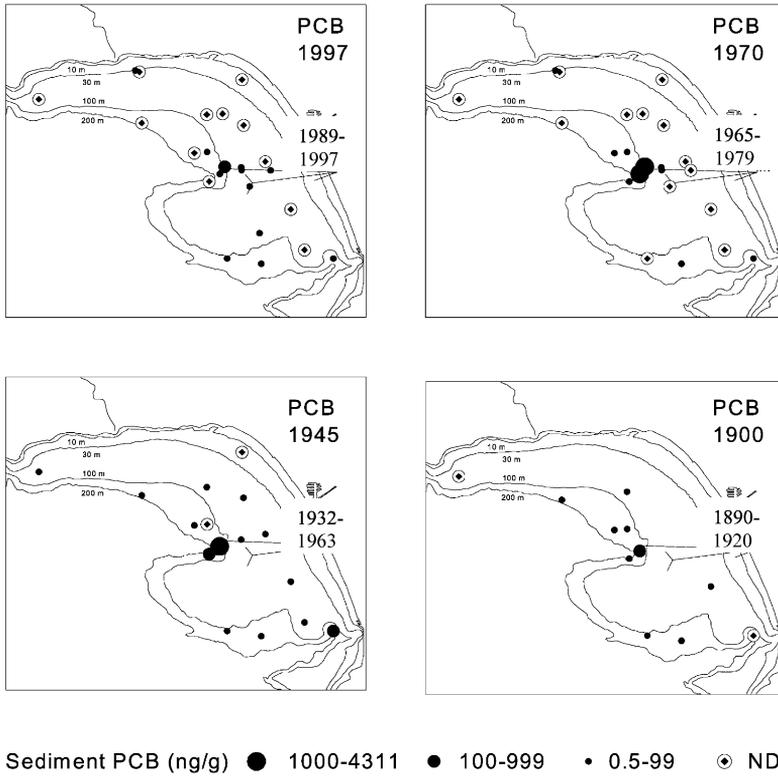


Fig. 5. Concentration of total PCB in sediment samples from four time strata in Santa Monica Bay sediment cores.

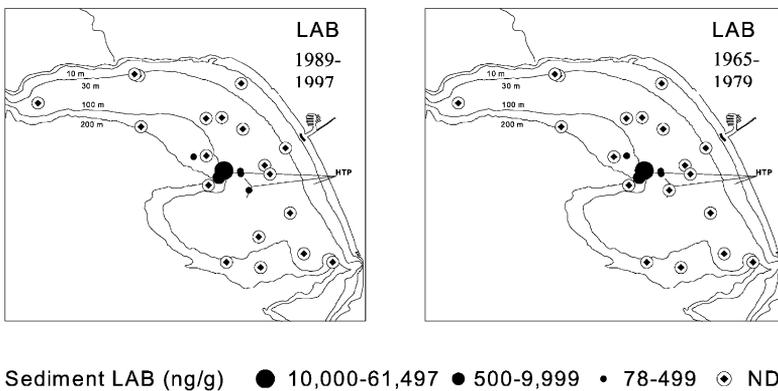


Fig. 6. Concentration of linear alkylbenzenes (LABs) in sediment samples from two time strata in Santa Monica Bay sediment cores.

3.3. Comparison with sediment quality guidelines

A comparison of SMB trace metal concentrations with national sediment quality guideline (SQG) values revealed an exceedence of at least one ERM (indicating the potential for adverse effects) in each of the five time strata. In the 1890–1920 stratum, only the ERM for Ag was exceeded at one location (Station 10). Two ERMs (Ag and Cd) were exceeded in the 1932–1963 stratum, while the ERM for every metal except As was exceeded in at least one station for the 1965–1979, 1979–1989, and 1989–1997 strata. ERM exceedences for Hg, Ni, and Ag were measured at multiple sites located in the vicinity of the HTP outfall system, while exceedences for the other metals were limited to Stations 10 and 53.

The spatial extent of potentially adverse sediment trace metal contamination, expressed as the percent of area with an ERM exceedence, increased in the 1965–1979, 1979–1989, and 1989–1997 strata (Table 2). One or two percent of SMB exceeded the ERM for metals in the 1890–1920 and 1932–1963 strata, respectively, while the area of exceedence was 6–10% in the 1965–1997 strata. A similar pattern was evident in comparisons to ERL values, which represent the concentration above which adverse effects are occasionally observed (Table 2). The percent of area exceeded at least one metal ERL increased from 36% in the 1890–1920 stratum to 75% in the 1989–1997 stratum. The ERL was exceeded for multiple metals in each of the time strata.

Exceedences of SQGs for organics in SMB were much less prevalent compared with trace metals (Table 2). Thresholds indicating adverse effects (ERM or DDT toxicity threshold) were exceeded only for PCBs at one or two stations (10 and 53) in each time stratum. These exceedences accounted for approximately 1% of SMB. The ERL exceedences were much more prevalent; all the samples analyzed from the 1932–1963, 1965–1979, 1979–1989, and 1989–1997 strata contained at least one organic contaminant with a concentration higher than the ERL. The DDT ERL was exceeded in 88–100% of the area at each time stratum, including the 1890–1920 stratum (Table 2). The PCB ERL was exceeded in 1–53% of the area, with the greatest areas of exceedence occurring in the 1932–1963 and 1890–1920 strata.

Comparison of the mean SQG quotient for each sample showed that stations in the sludge stratum contained the greatest overall magnitude and severity of contamination (Table 3). The quotients for two stations (10 and 53) frequently exceeded 1.5, the criterion indicating a high potential for adverse effects (Long & MacDonald, 1998). The temporal pattern of quotients in the sludge stratum was similar to that observed for individual contaminants, with maxima usually occurring in the 1965–1979 or 1979–1989 strata.

The severity of contamination was much less in the POTW stratum, where the mean SQG quotients ranged from 0.07 to 0.71 (Table 3). Only one station (16) within this stratum was classified in the medium-high concern category, defined as a mean SQG quotient in the 0.51–1.5 range. As in the Sludge stratum, maximum mean SQG quotients were usually measured in the 1965–1979, 1979–1989, and 1989–1997 strata. Mean SQG quotients varied little among the time strata at most stations in the POTW stratum, however.

Table 2
Percent area in Santa Monica Bay with contaminant concentrations exceeding sediment quality guideline values in each time interval

	Above ERL						Above ERM					
	Value ($\mu\text{g/g}$)	1890–1920	1932–1963	1965–1979	1979–1989	1989–1997	Value ($\mu\text{g/g}$)	1890–1920	1932–1963	1965–1979	1979–1989	1989–1997
As	8.2	0	10	18	1	9	70	0	0	0	0	0
Cd	1.2	1	22	30	18	32	9.6	0	1	1	1	1
Cr	81	12	1	22	30	20	370	0	0	1	1	1
Cu	34	0	2	14	14	13	270	0	0	1	1	1
Pb	46.7	0	1	2	1	1	218	0	0	1	1	1
Hg	0.15	24	58	74	67	75	0.71	0	0	2	6	2
Ni	20.9	36	35	38	38	35	51.6	0	0	1	10	1
Ag	1.0	2	2	10	10	12	3.7	1	2	6	5	9
Zn	150	0	1	1	1	1	410	0	0	1	1	1
Any metal		36	58	74	67	75		1	2	6	10	9
DDT	0.002	88	100	100	100	100	3.00 ^a	0	0	0	0	0
PCB	0.023	38	53	1	6	1	0.18	1	1	1	1	1
PAH	4.022	na ^b	na	1	0	1	44.80	na	na	0	0	0
Any organic		88	100	100	100	100		1	1	1	1	1

^a Not an ERM, value from Swartz *et al.* (1994).

^b No sample analyzed.

Table 3

Mean sediment quality guideline (SQG) quotients for sediment metals and organics in five dated sediment core strata. Also shown is the percent area in each of four categories of concern regarding the potential for adverse effects based on the mean SQG quotient (Long & MacDonald 1998). The SQG quotient is the sample concentration divided by the guideline value for each analyte (ERM for nine metals and total PCB or DDT threshold value)

Stratum	Station or category	1890–1920	1932–1963	1965–1979	1979–1989	1989–1997
<i>SQG quotient</i>						
Sludge	10	0.68	1.81	6.40	3.51	1.85
Sludge	40	na ^a	na	0.23	0.26	0.14
Sludge	50	na	0.30	0.20	0.11	0.11
Sludge	53	na	na	4.41	2.99	4.96
POTW	16	0.24	0.12	0.46	0.71	0.58
POTW	18	0.27	0.10	0.07	0.08	0.16
POTW	20	na	0.09	0.10	0.11	0.09
POTW	22	na	na	0.07	0.09	0.09
POTW	42	na	0.12	0.13	0.12	0.11
POTW	44	na	na	0.12	0.15	0.12
POTW	51	0.30	0.27	0.45	0.46	0.39
POTW	52	0.10	0.19	0.38	0.36	0.42
POTW	55	na	na	0.14	0.20	0.23
Other	4	na	na	0.07	0.05	0.06
Other	6	na	na	0.11	0.09	0.11
Other	24	0.12	0.10	0.11	0.11	0.12
Other	26	0.08	0.10	0.09	0.18	0.10
Other	28	0.39	0.12	0.12	0.12	0.13
Other	30	na	na	na	na	0.12
Other	33	na	0.15	0.10	0.09	0.11
Other	34	0.63	0.16	0.09	0.07	0.08
Other	36	0.91	0.19	0.18	0.19	0.20
Other	48	0.08	0.22	0.17	0.15	0.16
Other	49	na	na	0.28	0.11	0.09
Other	54	na	na	0.12	0.10	0.09
<i>Percent area in category</i>						
	Lowest (≤ 0.1)	62	33	42	39	29
	Medium-low (0.11–0.5)	38	65	56	56	66
	Medium-high (0.51–1.5)	0	0	0	4	3
	Highest (> 1.5)	0	2	2	1	1

^a No sample analyzed.

Greater variation in the mean SQG quotients was present among the remaining stations, located in the “Other” stratum. This stratum contained the greatest percentage of samples with mean SQG quotients in the lowest concern category (≤ 0.1), but also contained two stations in the medium-high concern category (Table 3). The greatest mean SQG quotients in this stratum were measured at stations located

either near the mouth of Ballona Creek or near the Redondo Canyon. Unlike the Sludge and POTW strata, maximum mean SQG quotients were usually present in the 1890–1920 or 1932–1963 stratum.

Calculation of the percent of area within each of four mean SQG quotient categories shows a pattern of reduced sediment quality in SMB after deposition of the 1890–1920 stratum. In the 1890–1920 stratum, 62% of SMB was classified as having contamination levels indicating the lowest level of concern (Table 3). The percent of area of low concern declined by about one half in the 1932–1963, 1965–1979, 1979–1989, and 1989–1997 strata, as more stations were classified in categories of greater concern. The two most contaminated stations (10 and 53) stayed in the highest concern category in strata dated from 1932 to 1997.

4. Discussion

4.1. Temporal variation of sediment contamination in Santa Monica Bay

Large temporal changes in sediment contaminant concentrations were measured in SMB, which reflect changes in the characteristics and magnitude of inputs to the bay during the last century. Some of the most significant events have been the production and use of DDTs and PCBs, expansion of the HTP outfall system and discharge volume in response to a burgeoning Los Angeles population, and reductions in contaminant inputs due to source control, advanced sewage treatment, and the termination of sludge disposal in the bay. The influence of these events and the dominant role played by wastewater inputs is shown by changes in the mean contaminant concentrations within the outfall stratum (Table 1). Concentrations of both trace metals and organics rose sharply after the 1890–1920 time stratum and usually reached maximum values in the 1965–1979, or 1979–1989 strata. Similar results were obtained in a previous study of sediment cores from a smaller number of stations in SMB (SCCWRP, 1995). These temporal changes correspond with significant changes in wastewater treatment and disposal practices by the City of Los Angeles, such as the disposal of sewage sludge within the bay (1957–1987), operation of the 5-mile outfall (1959–present), and recent operational upgrades at the HTP to provide full secondary treatment (1987–1998).

A decline of approximately an order of magnitude in the concentrations of DDT in the sediments near the outfall was evident in strata dated between 1979–1989 and 1989–1997, whereas PCB concentrations dropped by an order of magnitude between the 1965–1979 and later strata. However, few changes in metal concentrations were observed. Several factors may account for the difference in temporal patterns between these contaminant groups. First, the mass inputs of trace metals from wastewater have not fallen to the same extent as DDTs and PCBs. Total DDT and PCB inputs from wastewater into the Southern California Bight have declined by 3–4 orders of magnitude since 1970, while metal inputs have declined by 1–2 orders of magnitude over the same time (Raco-Rands, 1999). In addition, other significant sources of trace metals to SMB still exist, such as urban runoff and atmospheric

deposition. The mass from these nonpoint source inputs has been estimated to exceed current wastewater inputs into SMB (Schiff, 1997), thus moderating the decline in sediment concentrations resulting from improved wastewater treatment.

Relative sediment quality throughout SMB, as determined by comparisons with SQGs, has not shown much improvement in the last 30 years, which is contrary to expectations given the documented reductions in contaminant inputs. The percent of SMB classified as having the best sediment quality (i.e., lowest potential for adverse effects) was similar in the 1932–1963 and 1989–1997 strata: 33 and 29%, respectively. The severity of contamination is not great, when assessed using the classification system described by Long and MacDonald (1998); most of the potentially impaired sediments in the 1989–1997 stratum (66% of SMB) are in the medium-low priority category and only 4% of SMB is classified in more severe categories (Table 3). The temporal reductions in SMB contamination (Fig. 2 and Table 1) did not result in improved SQG scores for two reasons. First, most of the improvements occurred at stations near the 7-mile outfall that account for only a small percentage of the area of SMB. Second, trace metals drive the SQG exceedences in SMB to a large extent and average sediment trace metal concentrations have not changed appreciably in SMB since the 1970s.

Calculation of SQG exceedences and quotients provide a comparison to contamination levels associated with toxicity in other studies, but they may not necessarily accurately predict the occurrence of toxic effects in SMB. These parameters are primarily intended to provide a benchmark for evaluating the potential for concern at a site and for selecting sites for further study (Long & MacDonald, 1998). Toxicity tests conducted as part of this study detected reduced amphipod survival and inhibited sea urchin egg fertilization at several sites, with the sea urchin test showing the best correspondence with sediment contaminant concentrations (Greenstein, Bay, Jirik, Brown, & Clark, 2000).

4.2. Vertical transport of contaminants

The presence of detectable concentrations of DDTs and PCBs in the 1890–1920 and 1989–1997 strata is not the result of concurrent waste disposal activities, as these compounds were not in use during these two time intervals. Rather, these data reflect the influence of physical and biological processes on the vertical distribution of sediment contamination in SMB.

A possible mechanism leading to the upward and downward spreading of historically discharged materials such as DDT is bioturbation (Niedoroda, Swift, Reed, & Stull, 1996; Zeng & Venkatesan, 1999). The typical surface mixing depth by biota is ~8–20 cm (Wheatcroft & Martin, 1996). A study at a site in San Francisco Bay (California) with a high rate of biological mixing, age-modeled by Fuller, van Geen, Baskaran, and Anima, (1999), measured mixing of surface sediments down to 33 cm. Fuller et al. (1999) calculated that, with this degree of mixing, only about 3% of the sediment present at a discrete depth was deposited within a single year. The mixing depths are 2–6 cm in SMB based on ^{234}Th data which integrated the effects of mixing on monthly timescale and about 2–8 cm based on ^{210}Pb measurements which

integrated the effects of mixing on century timescales (Alexander and Venherm, this volume). Bioturbation in Santa Monica Bay could mix the sedimentation record from several to 40 years, since the accumulation rates measured in our study ranged from 0.2 to 2.3 cm per year.

Sediment contamination from adjacent depths can also be mixed as the result of physical processes, including diffusion and resuspension. Thus, the date and chemical composition of a stratum reflects the average condition resulting from past and present biological, chemical, and physical processes. This issue is significant when high concentrations of contaminants such as DDT are deposited on top of cleaner sediments. A small amount of mixing over a period of several decades can contaminate cleaner underlying sediments and provide a misleading indication of surface sediment conditions in the past. The influence of these processes depends upon the location. They are less significant in anoxic deep-water basins, where there is little bioturbation and resuspension, but are important on the continental shelf, as in SMB.

The occurrence of contaminants in strata from time periods expected to be free of such chemicals does not indicate a flaw in the analysis, but rather illustrates that core profiles must be interpreted with caution in physically and biologically dynamic areas such as SMB.

4.3. *Lateral transport of contaminants*

The widespread distribution of sediment contamination throughout SMB at all the time intervals studied (Figs. 3–5) suggests a lateral transport mechanism at work. There was evidence of two major spatial patterns in the concentration data: one reflecting HTP outfall-related inputs and the other suggesting a source near the Redondo Canyon. DDT and PCB concentrations in Redondo Canyon slope sediments had an unusual temporal pattern, suggesting a different source than HTP discharge. Near the HTP outfall, total DDT concentrations generally peaked in the 1965–1979 stratum and decreased substantially in later strata (Fig. 2). Surprisingly, total DDT concentrations remained relatively high in the top sediment layers on the slope of Redondo Canyon. This distribution pattern was not found with the PCB concentrations (Fig. 2). Since DDTs and PCBs are similar in hydrophobicity, the disparity in the spatial distribution patterns for DDTs and PCBs was likely indicative of a second significant source of DDTs besides the HTP 7-mile outfall. Supporting this hypothesis was the absence of LABs in the sediments collected from the slope of Redondo Canyon, since LABs found in SMB sediments are almost exclusively discharged from the HTP outfall system.

Urban runoff is often considered a significant source of coastal sediment contamination. Some evidence of urban runoff influence was observed in SMB. Elevated contaminant levels were measured at Station 49 (offshore of Ballona Creek), producing relatively high SQG quotients, but no influence was detected at nearby stations. These results are similar to those obtained in a recent study of stormwater discharge effects in SMB (Bay, Jones, & Schiff, 1999), where the detectable influence of Ballona Creek runoff on sediment contamination did not extend more than 2 km

upcoast or downcoast of the discharge. Although urban stormwater discharges are now estimated to contribute more trace metals to the Southern California Bight than municipal wastewater discharges (Schiff, 1997), the transport and resuspension of stormwater contaminants by SMB currents and waves appear to disperse this material so widely that spatial contamination patterns are not distinct. Sensitive molecular markers of runoff particles are needed to enable the fate of contaminants discharged in stormwater to be tracked in SMB.

Surface runoff to SMB is unlikely to be the cause of the abundant DDT concentrations on the slope of Redondo Canyon. Sediments collected from station 49 adjacent to Ballona Creek and from Stations 6 and 54 close to Malibu Creek contained low concentrations of both DDTs and PCBs, as compared with sediments collected from the slope of Redondo Canyon. The opposite would have occurred if these creeks were major contributors of DDTs and PCBs to SMB. Atmospheric deposition could also contribute to the sediment contamination in SMB, but that would yield an even distribution of both DDT and PCB concentrations in a relatively small region like SMB. A more viable mechanism to explain the occurrence of high-level DDTs in Redondo Canyon is the long-range transport of DDTs from the Palos Verdes Shelf. Sediments on the Palos Verdes Shelf contain high levels of DDTs (Eganhouse, Pontollillo, & Leiker, 2000; Lee 1994; Stull et al., 1996) due to the historical discharge of DDT-containing wastes from the Los Angeles County Joint Water Pollution Control Plant. This hypothesis has been suggested by Mearns et al. (1991) in a spatial analysis of sediment contamination data from the Southern California Bight that showed elevated sediment DDTs to the north of PVS, in the direction of prevailing ocean currents. Validation of such a mechanism requires further investigations and is beyond the scope of the present study, however.

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