

# Chlorinated hydrocarbon pesticides and polychlorinated biphenyls in sediment cores from San Francisco Bay<sup>1</sup>

M.I. Venkatesan<sup>a,\*</sup>, R.P. de Leon<sup>a,2</sup>, A. van Geen<sup>b,3</sup>, S.N. Luoma<sup>c,4</sup>

<sup>a</sup> *Institute of Geophysics and Planetary Physics, University of California, Los Angeles, CA 90095-1567, USA*

<sup>b</sup> *Lamont-Doherty Earth Observatory of Columbia University, Palisades, New York, NY 10964, USA*

<sup>c</sup> *Water Resources Division, USGS, 345 Middlefield Road, Menlo Park, CA 94025, USA*

Received 31 July 1997; revised 26 June 1998; accepted 27 August 1998

## Abstract

Sediment cores of known chronology from Richardson and San Pablo Bays in San Francisco Bay, CA, were analyzed for a suite of chlorinated hydrocarbon pesticides and polychlorinated biphenyls to reconstruct a historic record of inputs. Total DDTs (DDT = 2,4'- and 4,4'-dichlorodiphenyltrichloroethane and the metabolites, 2,4'- and 4,4'-DDE, -DDD) range in concentration from 4–21 ng/g and constitute a major fraction (> 84%) of the total pesticides in the top 70 cm of Richardson Bay sediment. A subsurface maximum corresponds to a peak deposition date of 1969–1974. The first measurable DDT levels are found in sediment deposited in the late 1930's. The higher DDT inventory in the San Pablo relative to the Richardson Bay core probably reflects the greater proximity of San Pablo Bay to agricultural activities in the watershed of the Sacramento and San Joaquin rivers. Total polychlorinated biphenyls (PCBs) occur at comparable levels in the two Bays (< 1–34 ng/g). PCBs are first detected in sediment deposited during the 1930's in Richardson Bay, about a decade earlier than the onset of detectable levels of DDTs. PCB inventories in San Pablo Bay are about a factor of four higher in the last four decades than in Richardson Bay, suggesting a distribution of inputs not as strongly weighed towards the upper reaches of the estuary as DDTs. The shallower subsurface maximum in PCBs compared to DDT in the San Pablo Bay core is consistent with the imposition of drastic source control measures for these constituents in 1970 and 1977 respectively. The observed decline in DDT and PCB levels towards the surface of both cores is consistent with a dramatic drop in the input of these pollutants once the effect of sediment resuspension and mixing is taken into account. © 1999 Elsevier Science B.V. All rights reserved.

*Keywords:* chlorinated hydrocarbon pesticides; polychlorinated biphenyls; sediment cores; San Francisco Bay

## 1. Introduction

San Francisco Bay is a shallow epicontinental basin which receives drainage from about 40% of the total land area of the state of California; it is one of the largest estuaries in Western North America (Nichols et al., 1986). Chlorinated hydrocarbon contaminants have entered the catchment from a variety

\* Corresponding author. Tel.: +1-310-206-2561; Fax: +1-310-206-3051; E-mail: indira@igpp.ucla.edu

<sup>1</sup> Institute of Geophysics and Planetary Physics Contribution Number: 4214.

<sup>2</sup> Fax: +1-818-992-8940; E-mail: globalg1@haven.ios.com

<sup>3</sup> Fax: +1-914-365-8154; E-mail:

avangeen@ldeo.columbia.edu

<sup>4</sup> Fax: +1-650-329-4463; E-mail: snluoma@usgs.gov

of sources, including sewage and industrial outfalls (Hoffman and Meighan, 1984; Chapman et al., 1986), urban runoff (Law and Goerlitz, 1974), agricultural discharges (Bailey et al., 1967; Risebrough et al., 1968a), atmospheric fallout, harbor and shipping traffic and other anthropogenic inputs (Nichols et al., 1986). For example, Bailey et al. (1967) estimated that about 2 tonnes of DDT and its metabolites entered San Francisco Bay in 1967 from the drainage of agricultural lands in the region. Pereira et al. (1996) described a contamination gradient of DDTs in the Lauritzen Canal and Richmond Harbor in Central Bay that originated from a large DDT shipping facility active in the 1970's. Gilliom and Clifton (1990) found some of the highest bed sediment concentrations of DDTs amongst major rivers in the USA in the San Joaquin River, a major tributary to the Bay.

The massive usage of chlorinated hydrocarbons in the ~ 1950–~ 1975 period had significant ecosystem implications in the Bay Area, as it did elsewhere. Chlorinated hydrocarbon contamination spread to coastal waters outside the Bay, and DDTs and PCBs were detected in fish, collected along the lower continental slope down to water depths of 1000 m near the Farallon Islands (Melzian et al., 1987). Most notably the contamination threatened the survival of important piscivorous Pacific sea birds on the Pacific coast (Risebrough et al., 1967, 1968b, 1978; Long et al., 1990).

The widespread presence of chlorinated hydrocarbons and particularly PCBs in the Bay and Delta, as a result of the inputs described above, have been documented by determinations of chlorinated hydrocarbons in Bay sediments by various programs since the 1980's (Chapman et al., 1986; Spies et al., 1987; NOAA, 1987, 1988; Phillips and Spies, 1988; RMP, 1995, 1996). These studies provide a comparative data base against which modern concentrations of chlorinated hydrocarbons can be assessed. The history of chlorinated hydrocarbon contamination can also be followed using contaminant profiles from dated sediment cores, since sediments integrate and retain records of the influx of recalcitrant organic contaminants. Past studies of historical trends of pollutants levels have resulted in stringent laws as well as improved technologies in curtailing waste disposal into the ocean waters, especially since the

late 1970s. A comparison of the recent status of chlorinated hydrocarbon contamination with past contaminant concentrations has not been conducted in San Francisco Bay. Profiles of chlorinated hydrocarbon pesticides and polychlorinated biphenyls from dated sediment cores from the Richardson and San Pablo Bays, San Francisco are reported here. The data show distinct differences for the two classes of organic contaminant that can be attributed to different input histories and distributions in the watershed.

## 2. Methods

### 2.1. Sampling and chronology

A box core and a gravity core from Richardson Bay and a gravity core from San Pablo Bay were investigated (Fig. 1). The Richardson Bay core was frozen soon after collection in 1992 and processed shortly thereafter; the San Pablo core was collected

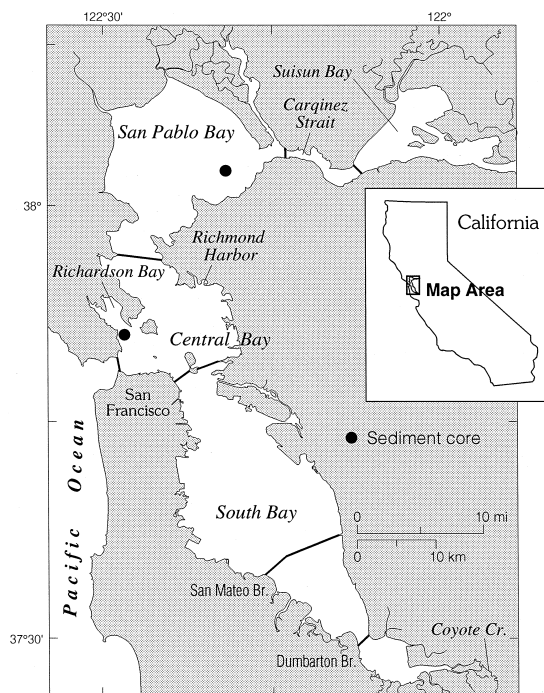


Fig. 1. Locations of sediment cores in San Francisco Bay. Richardson Bay: Box core-RB 92-3 (org)B, 35 cm; Gravity core-RB 92-3 (org), 148 cm. San Pablo Bay: Gravity core-SP 90-8 (org), 239 cm. Chronologies derived from RB92-3 (Fuller et al., 1999) after depth adjustment.

in 1990 and stored at 4°C in a cold room until analysis in 1992. The box core was sectioned at 5 cm and the gravity cores at 10 cm intervals. The core sections were air-dried in clean-baked aluminum pans covered with baked foil and dried in a hood away from the chemistry laboratory to avoid contamination. Dry samples were stored in organically-clean glass jars. Box and gravity cores were dated by  $^{210}\text{Pb}$  and  $^{234}\text{Th}$  activities (Fuller et al., 1999)  $^{14}\text{C}$  in mollusc shells and sediment  $^{10}\text{Be}$  (van Geen et al., 1999). Fallout isotope profiles ( $^{137}\text{Cs}$  and  $^{239,240}\text{Pu}$ ) were determined for comparison to the  $^{210}\text{Pb}$  chronology. A gravity core, RB92-3, from Richardson Bay was used for age-dating while another core, RB92-3(org) collected within a circle of diameter  $\leq 10$  m, was used for the analysis of organic constituents. Visual correlation of high-resolution density and magnetic susceptibility profiles in the two cores were used to transfer the chronology of RB92-3 to RB92-3org (Pereira et al., 1999). Strong vertical mixing of the sediments is indicated by the nearly constant excess  $^{210}\text{Pb}$  in the upper 25 cm, the depth of excess  $^{234}\text{Th}$  activity and the profiles of bomb fallout nuclides (Fuller et al., 1999). A chronology has, therefore, been developed by assigning the minimum age of deposition and a date of peak concentration to each depth. The minimum age of sediments at a given depth corresponds to the earliest date a contaminant could have been deposited. The depth interval with the highest concentration of the specific contaminant represents the peak year of input for that contaminant (Fuller et al., 1999).

Profiles of  $^{210}\text{Pb}$ ,  $^{137}\text{Cs}$  and  $^{239,240}\text{Pu}$  in the Pablo Bay core indicate considerably higher, albeit sporadic, sedimentation than in Richardson Bay over the past several decades (Fuller et al., 1999). A hiatus in the core suggested by the radionuclides and other properties is consistent with historical bathymetry data indicating a prolonged period of erosion in the area at the turn of the century. The San Pablo Bay core does not extend to sediment deposited before erosional disturbance of the watershed (van Geen et al., 1999).

## 2.2. Analytical procedures

The sediment sections were analyzed for chlorinated hydrocarbon pesticides and selected polychlorinated biphenyl congeners listed by NOAA NS

&T Program (Table 1). The analytical procedure is described by Venkatesan (1998) and Venkatesan et al. (1998). In the present study, the air-dried sediment samples were extracted with methylene chloride and processed; in the earlier work, on southern California sediments, the pore water was removed by methanol extraction of the wet sediments. All other steps are the same in both the studies.

Dry sediment (20–30 g) was sonicated for 15 min with 50 ml of methylene chloride and surrogates and then extracted by homogenization with 100 ml of methylene chloride three times. The concentrated extract was exchanged into hexane to precipitate asphaltene, treated with activated copper for elemental sulfur removal and then subjected to column chromatography on activated silica gel over alumina. The aromatic fraction (f2) containing target compounds eluted from the column was analyzed on a Varian 3500 gas chromatograph with electron capture detector (ECD) using a DB-5 (30 m) and a confirmation (DB-1701) column. Quantitation of all the target compounds listed in Table 1 was carried out.

GC/ECD operating conditions were optimized to yield the best possible resolution of all the compo-

Table 1  
List of target analytes

Pesticides	PCBs
Aldrin	BZ8
Alpha-chlordane	BZ18
Dieldrin	BZ28
Endrin	BZ44
Heptachlor	BZ52
Heptachlor epoxide	BZ66
Hexachlorobenzene	BZ77
Lindane (gamma-BHC)	BZ101
Mirex	BZ105
Trans-Nonachlor	BZ118
2,4'-DDE	BZ126
4,4'-DDE	BZ128
2,4'-DDD	BZ138
4,4'-DDD	BZ153
2,4'-DDT	BZ170
4,4'-DDT	BZ180
	BZ187
	BZ195
	BZ206
	BZ209

nents in both the columns. The conditions used are as follows: injection temperature 260°C; split open after 0.75 min; detector temperature 330°C; temperature program 10 min at 60°C; 15°C/min to 150°C, hold 0.1 min; 2°C/min to 200°C, hold 10 min; 5°C/min to 280°C, hold 40 min. Hydrogen at 40 cm/s was used as carrier gas. Nitrogen at 30 ml/min was used as make-up gas. A four-point response factor calibration was established to quantitate the target analytes. Selected samples were run by GC/MS for confirming compound identification and molecular weight of the biphenyls.

QA/QC procedures of the NOAA/NS&T Program were strictly adhered to throughout the project. A surrogate solution at a concentration of  $\sim 10 \times$  MDL [dibromooctafluorobiphenyl (DBOFB) and BZ #155] were added to the sediment before extraction. Internal standard BZ #103 and retention time markers tetrachloro-*m*-xylene (TCMX) and BZ #198 of appropriate concentration were used for accurate quantitation. With the analysis of every batch of field samples, a laboratory procedure blank, a matrix spike (sediment spiked with known amount of all the target analytes) and a reference sediment (SRM 1941, NIST, USA) were also processed. UCLA also took part in the interlaboratory calibration exercises conducted by NIST/NOAA.

All the box core sections were extracted, processed and analyzed in duplicate. Duplicate analysis was performed with selected sections from the gravity cores as well. Replicate instrumental analysis was also carried out for several fractions. The average recovery of the analytes from three matrix spike analyses ranged from 54–110% which was used to correct the data. Method detection limits were determined processing standard compounds at low levels (10 pg/ $\mu$ l), close to the estimated MDL (Federal Register, 1984). Limit of quantitation (LOQ) was calculated after Clesceri et al. (1989). LOQ was 2.5 times that of MDL.

A piece of the butyrate core liner material, the same as that used for sediment subsampling was also analyzed for the target compounds. This sample did not contain detectable levels of any of the target analytes. However, small amounts of some phthalates were detected. Most of the target analytes were not detected in any of the procedure blanks either. A few PCBs (BZ #138, 153, 105, and 180) were

occasionally detected at the level of 1–2 picogram/ $\mu$ l of the blank sample injected. These analytes were present well above this limit in the field samples in which they could be quantitated. The possibility of extraneous contaminants being introduced during sample handling and processing is, therefore, minimal. A low level of contaminants was sporadically found very close to detection or quantitation limits in the pre-industrial horizons. For example, section 110–120 cm in RB92-3 contained no quantifiable pesticides but section 120–138 cm contained a measurable quantity of only hexachlorobenzene. These anomalous detections are probably the result of smearing of contaminated surface sediment along the walls of the liner during coring, and should probably be treated as field blanks. However, no attempt was made to correct for this effect.

### 3. Results

#### 3.1. Chlorinated hydrocarbon pesticides

##### 3.1.1. Richardson Bay

The total pesticides listed in Table 1 range in concentration from  $\sim 0.2$  (near detection limit)–22 ng/g dry weight and most of the box and gravity core sections exhibited nearly concordant values (Fig. 2). All concentrations are reported in ng/g dry weight and will be referred to as only ng/g from hereon. Horizons deposited before 1938 (deeper than 70 cm) contain very few pesticides (see field blanks discussed above). Pesticides begin to appear consistently from 60 cm upwards. In the sections above 60 cm (minimum age in the post-1940s) 80–93% of the total pesticides are DDTs. There is a subsurface maximum in total pesticide concentrations around 30–35 cm in the box core, corresponding to peak years of contaminant input from 1969–1974. Similarly, a subsurface maximum occurs at 20–30 cm in the gravity core with the 30–40 cm also containing near maximum value.

Total DDTs (sum of 2,4'- and 4,4'-DDE, DDD and DDT) range in concentration from  $< 0.2$  to 21 ng/g. They were detected in 3 sections between 80 and 110 cm in the pre-industrial horizon at the level of 30 to 70 times less than surface strata and the other sections contained none. DDTs are consistently detected in sediments deposited after 1938. Fig. 3

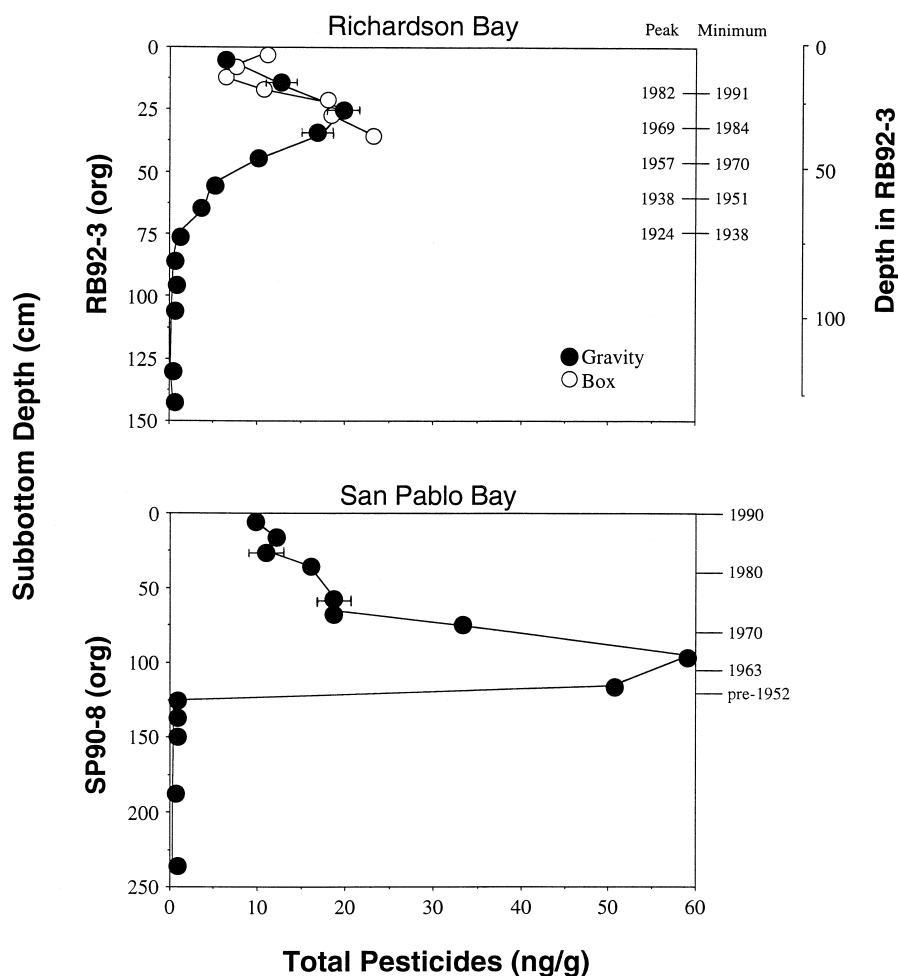


Fig. 2. Total pesticides in sediment cores from Richardson and San Pablo Bays: RB 92-3 (org)B and RB 92-3 (org) and SP 90-8. Total pesticides quantitated are the sum of those listed in Table 1. Horizontal bars represent standard deviation of replicate analyses. Also shown along the Y axis is the core used for dating from Richardson Bay (RB92-3). The peak year denotes the year of deposition with the greatest mass abundance for that depth. The minimum age represents the most recent date of deposition for sediment particles comprising a depth horizon (Fuller et al., 1999).

presents the downcore distribution of the DDTs and their metabolites, DDDs and DDEs. Except for DDTs in two sections, all other values of DDTs and the metabolites are concordant in both the box and gravity core sections. In general, DDTs and DDDs are greater in abundance than DDEs in many post-1940s intervals (Fig. 3, Table 2). The DDTs and the metabolites decline in concentration (to  $< 5$  ng/g) at the surface of the core, compared to the maximum concentrations deposited in the 1960's and 1970's.

### 3.1.2. San Pablo Bay

The total pesticides range in concentration from 0.3 (near detection limits) to 59 ng/g (Fig. 2) and DDTs constitute from 32 to 98% of the total pesticides in the core. Pesticides are absent or in concentrations close to detection in horizons below 120 cm (pre-1952 intervals). A sharp increase in the contaminants level is noticed above this boundary after the hiatus in the sediment chronology. A subsurface maximum in the profile centers at 90–100 cm (around

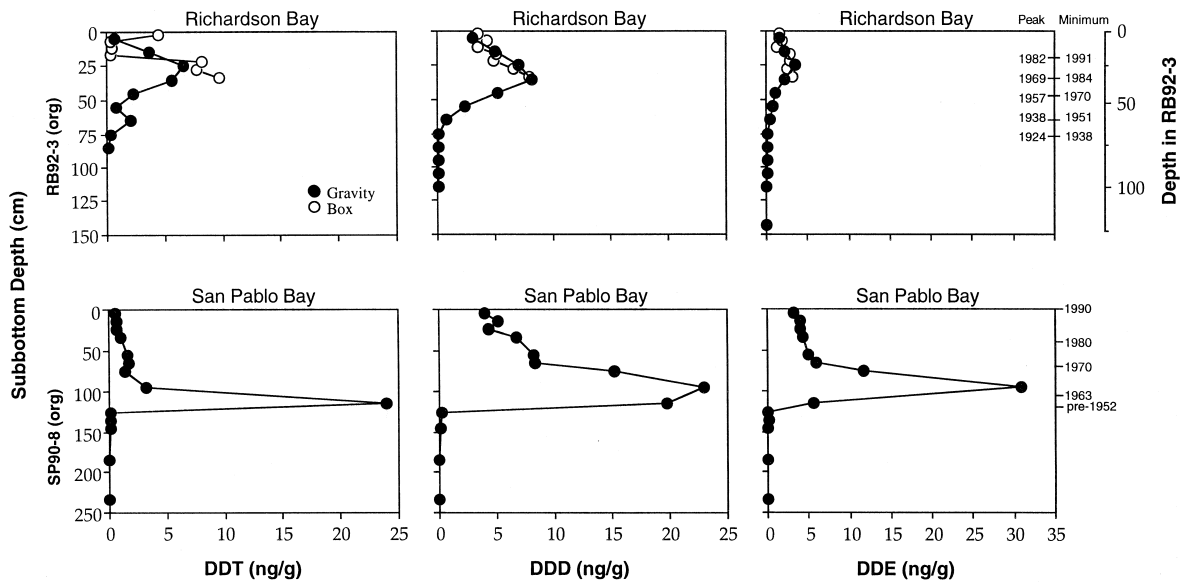


Fig. 3. DDTs and metabolites in sediment cores from Richardson and San Pablo Bays; RB 92-3 (org)B and RB 92-3 (org) and SP 90-8.

1965), above which there is a decrease in the pesticides content.

Total DDTs content spans from 0.1 (close to detection limits) to 57 ng/g and the core profile of

Table 2

Selected parameters from the distribution of chlorinated pesticides in the sediment cores

Core section (cm)	Non-DDT pesticides (%)	DDTs in total DDTs (%)	DDD <sub>s</sub> /DDE <sub>s</sub>
<i>Richardson Bay</i>			
RB 92-3(org)			
0–10	13	14	1.9
10–20	13	39	2.1
20–30	11	40	2.0
30–40	8	34	2.9
40–50 <sup>a</sup>	12	26	4.6
50–60 <sup>a</sup>	15	20	3.1
60–70 <sup>b</sup>	15	62	1.7
<i>San Pablo Bay</i>			
SP 90-8(org)			
0–10	21	8	1.2
10–20	18	7	1.3
20–30	18	9	1.1
30–40	22	9	1.6
50–60	21	11	1.4
60–70	19	5	1.4
70–80	13	5	1.3
90–100	4	6	0.8
110–120 <sup>c</sup>	2	49	3.5

<sup>a</sup>Corresponds to 1940s–1960s (Peak years of deposition).

<sup>b</sup>Corresponds to 1930s–1940s (Peak years of deposition).

<sup>c</sup>Start of pre-1952.

the total DDTs mimics that of the total pesticides. The contaminants are either not detected or close to detection/quantitation limits of 0.1–0.3 ng/g in the pre-1952 intervals. Above 120 cm the levels of DDTs begin to rise sharply. A subsurface maximum around 1965 centers at 90 to 100 cm, similar to the total pesticides (Fig. 2). Most of the sections in San Pablo Bay, in contrast to Richardson Bay, are uniformly enriched in DDEs and DDDs relative to DDTs (Fig. 3, Table 2). In only one section (110–120 cm) are DDTs slightly higher than DDDs. This skews the subsurface maximum in the DDTs profile towards a slightly lower horizon than those of DDDs and DDEs.

### 3.2. Non-DDT pesticides in Richardson and San Pablo cores

The concentration of non-DDT pesticides (Total Pesticides – DDTs) in Richardson Bay ranges from below detection limits to 2.2 ng/g. They are either not detected or almost at detection limits below 70 cm in RB92-3, similar to the total pesticides. Alpha-chlordane is the most dominant component in most of the sections in the post-1940s interval. Total non-DDT pesticides in San Pablo Bay range in content from < 1 to 4 ng/g. Pre-1952 strata contain about 0.2–0.5 ng/g (close to detection limits) of the total components.

### 3.3. Polychlorinated biphenyls (PCBs)

#### 3.3.1. Richardson Bay

Total PCBs (sum of all the congeners listed in Table 1) content ranges from 0.8 (near detection limits) to 32 ng/g. Traces of PCB were found at the level of 0.8–2 ng/g below 80 cm in the cores. The topmost section (0–5 cm) in the box core was nearly two-fold enriched in PCBs compared to the gravity core. However, all other corresponding sections from box and gravity core exhibited concordant abundance of PCBs (Fig. 4). A similar enrichment of total pesticides and DDTs in the surface section of the box core was also noted. Both core sections have been analyzed in duplicate and the results were reproducible. Subsurface maxima occur around 1969 and 1982.

Non- and mono-*ortho* coplanar PCBs (i.e., BZ 77, 105 and 118) constitute between 0 to 22% of the

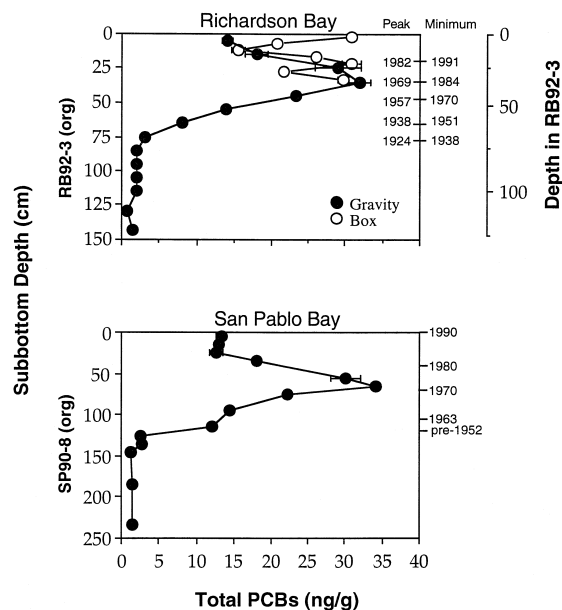


Fig. 4. Total polychlorinated biphenyls (PCBs) in sediment cores from Richardson and San Pablo Bays. Total PCBs quantitated are the sum of those listed in Table 1. Horizontal bars represent standard deviation of replicate analyses.

total PCBs measured. These are considered to be the most toxic of the PCBs analyzed here. BZ 110 could coelute with BZ 77 on DB-5 column. But, generally the DB-5 column gave lower quantitation numbers than DB-1701 column for BZ 77 in the samples, suggesting that other unknown compounds could be coeluting with this PCB in the latter column as well. This prompted us to use the DB-5 value for BZ 77. Because of the coelution problem in both the columns, the concentration of BZ 77 should be considered as an upper limit in all the samples. The quantitation of BZ 105 and 153 was done on the DB-1701 column where they were better resolved than in DB-5 (Venkatesan, 1998). The fourth PCB (non-*ortho*), BZ 126, which is also considered toxic was not detected in any of the samples.

#### 3.3.2. San Pablo Bay

Total PCBs content ranges from 1.2 to 34 ng/g in the San Pablo core with levels in the pre-1952 intervals around 1 ng/g, similar to concentrations found in Richardson Bay (Fig. 4). Significant amounts of PCBs are first detected above 120 cm and the contaminants level maximizes at 60–70 cm. Thus, maximum deposition of PCBs occurred more

recently (in ~ 1975) than maximum deposition of DDTs. Non- and mono-*ortho* coplanar PCBs are almost at detection limits below 120 cm and constitute 4 to 36% of the total PCBs in the post-1952 intervals following a depth distribution similar to the total PCBs.

## 4. Discussion

### 4.1. Chlorinated hydrocarbon pesticides

As a consequence of major source control effected by the Clean Water Act of 1970–1971, the sale and use of DDT were banned by the US Environmental Protection Agency in 1972. California had already curbed the sale and use of DDT two years earlier in 1970. The use of DDT in the USA peaked in the late 50s and early 60s (Mearns et al., 1991). In addition to the large urban/industrial area surrounding the Bay, which historically included an active DDTs shipping facility, the majority of the catchment of the San Francisco Estuary consists of the agriculturally productive Central Valley which drains into the Sacramento and San Joaquin Rivers. So significant agricultural and industrial development in the watershed provide potentially important sources of the chlorinated hydrocarbons in this aquatic ecosystem (Phillips and Spies, 1988).

#### 4.1.1. DDTs in Richardson Bay

The historic trends in the DDTs profile in the well constrained RB92-3 core document the history of DDTs use described above. DDTs are present in only trace amounts in sediments deposited before the 1930s. They are first detected in sediments deposited in late 1930s and early 40s. Concentrations increase slightly in sediments deposited around 1950–1955, with a subsequent rapid increase to a maximum, in the sediment horizon at 30–35 cm, between 1969 to 1974. The latter observations are consistent with the time when DDTs were in common agricultural use as a major pesticide (Fig. 3). The maximum concentrations of DDTs and the metabolites found in RB92-3 are lower by several orders of magnitude than found in sediments from Palos Verdes Shelf and Santa Monica/San Pedro basins off southern California coast (Word and Mearns, 1979; Venkatesan,

1998). But the concentrations in Richardson Bay are comparable to the levels detected in the San Francisco region by the NS&T Program and from other coastal areas such as Puget Sound (Washington coast) and Boston Harbor (Massachusetts) (Phillips and Spies, 1988; NOAA, 1991). The gradual decline in DDTs observed in recent years reflects the ban of the compound.

The detection of chronic levels of DDTs around 6–9 ng/g in the surface sediments of Richardson and San Pablo Bays, despite the ban, could be due to continuing agricultural inputs or to resuspension and redistribution. The mixing/accumulation model of Fuller et al. (1999) for Richardson Bay indicates that even if all new inputs of these contaminants had abruptly ended in 1970, surface sediment would still contain about 50% of the maximum levels of input. On the other hand, agricultural soils could also provide a reservoir of DDT which is released to the aquatic environments through soil erosion and storm runoff. In 1983 DDT was detected at levels exceeding National Academy of Sciences guidelines for predator protection in fish from seven rivers and streams in the agricultural watershed of the Bay, including the San Joaquin River at Vernalis. Anton et al. (1986) suggest that a combination of the mixing of DDT into the soil column and soil erosion rates will result in continued release of DDT well into the 21st century in the Central valley.

The sum of 2,4'- and 4,4'-DDT in RB92-3 constitutes about 5–62% of the total DDTs from 1930–present; in the last two decades, these average about 20% of the total DDTs. The enhanced levels of parent DDTs and DDDs compared to DDEs in the Richardson Bay core is in contrast to observations in deeper waters off the southern California Basins. While parent DDTs are the dominant isomers in some isolated sites from the Santa Monica/San Pedro basins, most likely originating from chemical dumpsites located nearby (Venkatesan et al., 1996), most sites were characterized by relatively more DDEs than the other compounds (MacGregor, 1974, 1976; Venkatesan, 1998).

The dominance of DDDs over DDEs in sediments (Table 2) might imply reductive dechlorination of DDTs to DDDs under anaerobic conditions (Wedemeyer, 1967; Baxtor, 1990). However, it is unlikely that significant DDDs could have been



formed from DDTs in the well-aerated sediments typical of San Francisco Bay. DDTs are metabolized to DDEs by dehydrochlorination under aerobic conditions (Aguliar, 1984). This suggests the possibility of an additional source for DDDs. Technical DDD was, indeed, used as a commercial insecticide in agriculture and its runoff could have contributed to the enrichment of DDDs in the sediments. More likely, however, is a contribution from the DDTs shipping facility in Lauritzen Canal, within the Richmond Harbor of Central San Francisco Bay. In an intensive study of the sediments of the Canal and Richmond Harbor, Pereira et al. (1996) concluded that both *p,p'*-DDT and *p,p'*-DDD were processed at the site, and that both degradation of *p,p'*-DDT and direct input of *p,p'*-DDD were responsible for the contamination. They found DDD concentrations in Bay sediments, adjacent to Richmond Harbor, that were more than double the concentrations determined at all other sites in the Bay. They concluded that DDD from Lauritzen Canal had entered the Bay via resuspension and gradual mixing or transport of fine grained suspended material. Physical re-entrainment of surface sediments across substantial distances, by strong currents and storm events, was responsible for the dispersal of DDTs in Palos Verdes shelf, southern California (Young et al., 1977; Niedoroda et al., 1996). It is conceivable that similar processes could have moved DDDs into Richardson Bay from Richmond Harbor, especially given the complex nature of long term sediment transport in the Bay (Conomos, 1979). The ratio of DDDs/DDEs down to 70 cm in the Richardson Bay core are close to 2 or above (Table 2). This ratio is highest (3.1–4.6) in the 40–60 cm horizon which corresponds to the peak years of deposition during 1940–1960, but also coincides with the activities of the DDDs packaging site. The much lower ratios (0.4–1.7) below 60 cm might reflect aerobic degradation of DDTs into DDEs (Aguliar, 1984). The lack of anaerobic conditions as well as the absence of data on DDMU preclude further interpretation of degradation processes (e.g., Quensen et al., 1998).

#### 4.1.2. DDTs in San Pablo Bay

The post-1952 profile of DDTs in SP90-8 reflects what we would expect to be the history of riverine inputs from agricultural runoff during the period of

intensive DDT usage, as well as declining concentrations during the period of source control (Phillips and Spies, 1988). DDT, DDD and DDE concentrations are substantially higher in the San Pablo Bay core than in Richardson Bay, at their maximum. Surface sediment concentrations are similar in the two cores (i.e., the decline of DDTs concentrations from their maximum, since the ban of the compound, is larger in the San Pablo core than in the Richardson Bay). The higher maximum concentrations could reflect closer proximity of San Pablo Bay to agricultural inputs of DDTs. The strong influence of river inflows at this site is verified by a higher content of terrigenous alkanes (biomarkers of terrigenous plant input) in SP90-8 than in RB92-3 (Hostettler et al., 1999). An enhanced influx of agricultural DDTs might also explain the higher ratio of DDE/DDD in SP90-8 compared to RB92-3 at the time of maximum input. The TOC concentrations in post-1952 sediments of San Pablo Bay (1.4–1.7%) are slightly greater than in Richardson Bay (0.74–1.28%) (Pereira et al., 1999) and grain size is finer in bulk sediments. Both could enhance organic contaminant concentrations in SP90-8 compared to RB92-3. However, it is unlikely that this influence dominated, otherwise it would have affected surface sediments similar to the buried horizons.

Percentage of DDTs in total DDTs as well as the ratio of DDDs to DDEs are nearly constant throughout the post-1952 horizons (Table 2). It is not surprising that the industrial DDD signature was not evident in SP90-8, given the greater distance from Lauritzen Canal, and more landward location of this site compared to RB92-3. The high concentrations of DDTs, at their maximum, in San Pablo Bay, suggest that agricultural inputs had a greater regional influence on sediment contamination than did the industrial site.

#### 4.1.3. Non-DDT pesticides in Richardson and San Pablo Bays

Chlordane, dieldrin and aldrin are among the chlorinated polycyclic hydrocarbons (Table 1) formerly used as pesticides primarily in the control of soil pests (Mearns et al., 1991). In Richardson Bay, these components vary from 8 to 21% of the total pesticides, stabilizing in the last two decades around 11–15%. Similarly in San Pablo Bay, the post-1952

horizons contain these compounds at the level of 2–22% of the total with the last two decades containing around 20% of the total. They were at the lowest level of 2–4% during the 1950s and 1960s when DDTs probably were used the most. Alpha-chlordane is the dominant compound of the non-DDT pesticides in the post-1940 horizon in both sites. The depth profiles of the non-DDT pesticides roughly correspond to those of the DDTs in terms of onset as well as decline from the peak levels (figure not shown here).

#### 4.2. Polychlorinated biphenyls (PCBs)

The historic trends in the usage of PCBs are widely documented (i.e., Bopp et al., 1982; Olsen et al., 1984). Studies from the Hudson River and estuary, New York, show that PCBs first appeared in sediments deposited in the late 1930s and their concentrations exhibit subsurface maxima from the late 1960s through the early 1970s with declining trends in the recent years. Hom et al. (1974) observed a steady increase in PCBs content from 1945 through 1967 in a dated core from the anoxic sediments of Santa Barbara Basin collected in 1970, but no data exists from this site to document recent trends.

PCBs are first detected in sediment deposited during the 1930's in Richardson Bay. The subsurface maximum suggests the peak years of deposition were between 1969 and 1974 in RB92-3; the subsurface maximum in SP90-8 is approximately 1975. Maximum concentrations in both cores correspond to the period when PCB usage was at a maximum. However, the upper level of PCBs detected in the two sites from San Francisco Bay is at least an order of magnitude less than that reported for southern California sediments (Young et al., 1977; NOAA, 1991; Venkatesan, 1998). Concentrations are comparable to other data from the general region of San Francisco Bay and coastal areas of Florida and Oregon (Phillips and Spies, 1988; NOAA, 1991). The comparability of PCBs concentrations between SP90-8 and RB92-3 indicate that inputs were diffusely associated with development (perhaps atmospheric and/or from a large number of discharges into a well mixed Bay), in contrast to the distinct differences in DDTs concentrations between the cores during the period of maximum usage.

The decrease in PCBs content in recent years are consistent with the ban on production in 1977 (Mearns et al., 1991; Valette-Silver, 1993). Wastewater treatment technology also improved to reduce solids and toxic wastes emissions beginning in the 1970s due to the Clean Water Act of 1970–1971. The depth profile in RB92-3 is similar for both total and selected toxic PCBs and is analogous to profiles observed previously for Santa Monica/San Pedro Basin cores (Venkatesan, 1998) and other regions. The elevated level of PCBs in the topmost section from box core and the post-1970s excursions in the PCBs signal cannot be fully justified by sediment mixing.

The onset of DDTs contamination in RB92-3 lagged by almost a decade that of PCBs. This difference coincides with the earlier start of the usage of PCBs. The subsurface maximum concentrations of DDTs and subsequent decline precedes the maximum and decline in PCB concentrations in both cores. This lag also coincides with the relative timing in source control measures which became effective in 1970 and 1977 respectively for DDTs and PCBs. The extent of the decline in PCBs content in recent years (post 1980s) in both cores attests to the effectiveness of the source control measures.

Because the histories of DDTs and PCBs input are better known than for most contaminants, their profiles may also be informative with regard to sedimentation processes in the cores. Because the chlorinated hydrocarbon profiles in the post-industrial horizon in the Richardson Bay core follow usage so closely, they also provide an independent constraint on the age of the core horizons, and help validate the age model based on radiochronology (Fuller et al., 1999). The decline in the DDTs from their maximum is larger in the surface horizon of the SP90-8 relative to Richardson Bay. This is consistent with more rapid sediment deposition at SP90-8, especially if there was less vertical mixing (Fuller et al., 1999).

#### 4.3. Non- and mono-ortho PCBs

The ratios of the total PCBs to non- and mono-ortho PCBs fall within a narrow range of values, from 5–8 and 3–8 in the post-industrial sediments from both the sites. Ratios from pre-industrial horizons are

Table 3  
Inventories of chlorinated hydrocarbon contaminants in San Francisco Bay (ng/cm<sup>2</sup>)<sup>a</sup>

Core interval in years	Total DDTs	Total DDDs	Non-DDT pesticides	Total PCBs
<i>Richardson Bay</i>				
RB 92-3(org)				
1950s–1992	557	286	76	1154
1930s–1992	618	320	90	1391
<i>San Pablo Bay</i>				
SP 90-8(org)				
1952–1990	3453	1582	369	4069

<sup>a</sup>Mass/area = Measured concentration (ng/g) × Bulk density (g/cm<sup>3</sup>) × Thickness of the interval (cm). See Fuller et al. (1999).

sporadic covering a range from 3- $\alpha$  where all PCBs except three congeners (BZ 8,18 and 28) are close to LOQ or MDL. In a recent study of historical trends of these highly toxic PCBs in cod liver oils, the concentration of congener BZ 77 was found to decline in concurrence with total PCB levels in cod and thus appears to be metabolized and/or excreted in cod compared to the other congeners, BZ 126 and 169 (Falandysz et al., 1994). In view of this finding, our data was examined to infer trends in the degradation of the toxic PCBs in the sediment cores. Although we did not detect BZ 126 and measure 169, the other toxic PCBs including BZ 77, BZ 105 and 118 apparently covary with the total PCBs down to 60 cm in the core and, therefore, are at least as stable as all other PCBs (assuming their ratio of output has remained historically the same as that measured in the sediments).

#### 4.4. Inventories of contaminants in San Francisco Bay

Integrated concentration (mass/area) of selected contaminants deposited at the core sites after 1950 were calculated using the bulk density derived from total density profile (Fuller et al., 1999). Values were assigned to 'missing' intervals from interpolation of the two adjacent horizons. For core RB92-3(org), depth intervals were first adjusted based on density analysis by Gamma Ray Attenuating Porosity Evaluator (GRAPE) to account for apparent difference in sedimentation rate between cores. Since sediment density was not measured in SP90-8, a value of 1.11 g/cm<sup>3</sup> was used for calculating mass/area over the upper 120 cm. The total DDTs and DDDs burden

from the 1950s onward in SP90-8 is about 6 times greater than in RB92-3(org) (Table 3). The integrated mass/area of non-DDT pesticides and total PCBs are also high, 5 and 4 times larger respectively, in San Pablo Bay than in the other site. The difference in the PCB content is about the equivalent of the difference in sedimentation rates between the two sites (0.9 vs. 4.0 cm/year). Thus, like concentrations, the inventories suggest a source(s) (i.e., atmospheric inputs, discharges into a well mixed Bay) that is distributed relatively uniformly across the Bay Area, as has been reported elsewhere (Atlas et al., 1986; Erickson, 1992). The difference in the inventory of total DDD and DDTs exceeds the difference in sedimentation rates and appears to verify the importance of riverine inputs containing agricultural runoff.

## 5. Conclusion

The sediment downcore profiles of chlorinated pesticides and PCBs from the Richardson and San Pablo Bays clearly mimic the trends in the anthropogenic activities of the 1900s. The subsurface maxima in the 1960–1970s, and the subsequent decline of the contaminant levels in the surface strata, coincide with the period of maximum urban, industrial and agricultural use of these chemicals and the effectiveness of recent source control of contaminants and improved water management practices. Whereas both the Bays are impacted by human activities, the core from San Pablo Bay, apparently, has preserved the historic imprints of contamination best because of the higher resolution in its chronology than that from Richardson Bay. The lag in the subsurface maximum

between the core profile of DDTs and PCBs coincides well with the relative timing in source control measures adopted for these compound classes. The onset of organic contamination evident at the beginning of the industrial horizon in the Richardson Bay core, despite the lack of very fine resolution, provides a constraint on the age of the sediment, especially in the upper 50 cm, independent of the age model based on radiochronology.

The larger mass of total DDDs and DDTs accumulated in San Pablo than in Richardson Bay can be accounted for by closer proximity of the former to the freshwater inflows from Sacramento and San Joaquin Rivers draining agricultural lands. Subtle differences in the relative distribution of DDTs and the metabolites between the sediments from the two Bays indicate some industrial input of DDD to Richardson Bay. PCBs are more uniform in concentration and follow sediment deposition more closely than do the DDTs, suggesting sources more uniformly associated with the urbanization/industrialization of the Bay area.

### Acknowledgements

We thank E. Ruth for the GC/ECD analysis, X. Ouyang, L. Wei and S. Bhalla for technical assistance, S. Bhalla for data reduction, R. Anima, C. Fuller, F. Hostettler and W. Pereira for samples and/or pertinent information. This work was funded by USGS award #1434-93-A-1016 as part of the NOAA/NS&T Program.

### References

Aguliar, A., 1984. Relationship of DDE/DDT in marine mammals to the chronology of DDT input into the ecosystem. *Canadian J. Fish. Aquatic Science* 41, 840–844.

Anton, E.C., Lininger, M., Youngerman, J.M., Agee, B.A., 1986. DDT in the Salinas Valley. A special report on the probable source of Technical grade DDT found in the Blanco Drain near Salinas, California. Special Water Quality Monitoring Report No. 86-2 WQ. pp 49.

Atlas, E., Bidleman, T., Giam, C.S., 1986. Atmospheric transport of PCBs to the ocean. In: Waid, J.S. (Ed.), *PCBs and the Environment*, CRC Press, Boca Raton, FL, pp. 79–100.

Bailey, T.E., Acse, A.M., Hannum, R.R., 1967. Distribution of pesticides in California. *J. Sanit. Eng. Div. Am. Soc. Eng.* 93, 27–43.

Baxtor, R.M., 1990. Reductive dechlorination of certain chlorinated organic compounds by reduced haematin compared with their behaviour in the environment. *Chemosphere* 21, 451–458.

Bopp, R.F., Simpson, H.J., Olsen, C.R., Trier, R.M., Kostyk, N., 1982. Chlorinated hydrocarbons and radionuclide chronologies in sediments of the Hudson River and estuary, New York. *Environ. Sci. Technol.* 16, 666–676.

Chapman, P.M., Dexter, R.N., Cross, S.F., Mitchell, D.G., 1986. A field trial of the sediment quality triad in San Francisco Bay. NOAA Tech. Mem. NOS OMA 25. National Oceanic and Atmospheric Administration, Rockville, MD, USA.

Clesceri, L.S., Greenberg, A.E., Trussell, R.R., 1989. Standard methods for the examination of water and wastewater, 17th edn. Publication Office, American Public Health Association, Washington, DC, pp. 18–20.

Conomos, T.J. (Ed.), 1979. San Francisco Bay: The urbanized estuary. American Association for the Advancement of Science, San Francisco, CA, pp 493.

Erickson, M.D., 1992. Analytical Chemistry of PCBs. Lewis Publ., Boston, 508 pp.

Federal Register, 1984. Vol. 49, No. 209, pp. 198–199.

Falandysz, J., Kannan, K., Tanabe, S., Tatsukawa, R., 1994. Concentrations, clearance rates and toxic potential of Non-ortho coplanar PCBs in cod liver oil from the southern Baltic Sea from 1971 to 1989. *Mar. Pollut. Bull.* 28, 259–262.

Fuller, C.C., van Geen, A., Baskaran, M., Anima, R., 1999. Sediment chronology in San Francisco Bay, California, defined by  $^{210}\text{Pb}$ ,  $^{234}\text{Th}$ ,  $^{137}\text{Cs}$ , and  $^{239,240}\text{Pu}$ . *Mar. Chem.* 64, 7–27, (this issue).

Gilliom, R.J., Clifton, D.G., 1990. Organochlorine pesticide residues in bed sediments of the San Joaquin River. *CA. Wat. Res. Bull.* 26, 11–23.

Hoffman, R.W., Meighan, R.B., 1984. The impact of combined sewer overflows from San Francisco on the western shore of central San Francisco Bay. *J. Water Pollut. Control Fed.* 56, 1277–1285.

Hom, W., Risebrough, R.W., Soutar, A., Young, D.R., 1974. Deposition of DDE and polychlorinated biphenyls in dated sediments of the Santa Barbara Basin. *Science* 184, 1197–1199.

Hostettler, F.D., Pereira, W.E., Kvenvolden, K.A., van Geen, A., Luoma, S.N., Fuller, C.C., Anima, R., 1999. A record of hydrocarbon input to San Francisco Bay as traced by biomarker profiles in surface sediment and sediment cores. *Mar. Chem.* 64, 115–127, (this issue).

Law, L.M., Goerlitz, D.F., 1974. Selected chlorinated hydrocarbons in bottom material from streams tributary to San Francisco Bay. *Pestic. Monit. J.* 8, 33–36.

Long, E.R., Buchman, M.F., Bay, S.M., Carr, R.S., Chapman, P.M., Hose, J.E., Lissner, A.L., Scott, J., Wolfe, D.A., 1990. Comparative evaluation of five toxicity tests with sediments from San Francisco Bay and Tomales Bay, California. *Environ. Toxicol. Chem.* 9, 1193–1214.

MacGregor, J.S., 1974. Changes in the amount and proportions of DDT and its metabolites, DDE and DDD, in the marine environment off southern California. 1949–72. *Fish. Bull.* 72, 275–293.

- MacGregor, J.S., 1976. DDT and its metabolites in the sediments off Southern California. *Fish. Bull.* 74, 27–35.
- Mearns, A.J., Matta, M., Shigenaka, G., MacDonald, D., Buchman, M., Harris, H. Golas, J., Lauenstein, G., 1991. Contaminant trends in the southern California Bight: Inventory and assessment. NOAA Technical Memorandum NOS ORCA 62. Seattle, WA. pp 423.
- Melzian, B.D., Zoffman, C., Spies, R.B., 1987. Chlorinated hydrocarbons in lower continental slope fish collected near the Farallon Islands, California. *Mar. Pollut. Bull.* 18, 388–393.
- Nichols, F.H., Cloern, J.E., Luoma, S.N., Peterson, D.H., 1986. The modification of an estuary. *Science* 231, 567–573.
- Niedoroda, A.W., Swift, D.J.P., Reed, C.W., Stull, J.K., 1996. Contaminant dispersal on the Palos Verdes continental margin: III. Processes controlling transport, accumulation and re-emergence of DDT-contaminated sediment particles. *The Science of the Total Environ.* 179, 109–133.
- NOAA, 1987. National Status and Trends Program for Marine Environmental Quality. Progress report and preliminary assessment of findings of the benthic surveillance project-1984. National Oceanic and Atmospheric Administration, Rockville, MD, USA.
- NOAA, 1988. Status and trends in concentrations of contaminants and measures of biological stress in San Francisco Bay. NOAA Technical Memorandum NOS OMA 41, Seattle, WA. 268 pp.
- NOAA, 1991. Second summary of data on chemical concentrations in sediments from the National Status and Trends Program. NOAA Tech. Mem. NOS OSMA 59. National Oceanic and Atmospheric Administration, US Dept. of Commerce.
- Olsen, C.R., Larsen, I.L., Brewster, R.H., Cutshall, N.H., Bopp, R.F., Simpson, H.J., 1984. A geochemical assessment of sedimentation and contaminant distributions in the Hudson-Raritan Estuary. NOAA Technical report, NOS/OMS,2, pp 101.
- Pereira, W.E., Hostettler, F.D., Rapp, J.B., 1996. Distributions and fate of chlorinated pesticides, biomarkers and polycyclic aromatic hydrocarbons in sediments along a contamination gradient from a point-source in San Francisco Bay, California. *Mar. Environ. Res.* 41, 299–314.
- Pereira, W.F., Hostettler, F.D., Luoma, S.N., van Geen, A., Fuller, C.C., Anima, J., 1999. Sedimentation record of anthropogenic and biogenic polycyclic aromatic hydrocarbons in San Francisco Bay, California. *Mar. Chem.* 64, 99–113, (this issue).
- Phillips, D.J.H., Spies, R.B., 1988. Chlorinated hydrocarbons in the San Francisco estuarine ecosystem. *Mar. Pollut. Bull.* 19, 445–453.
- Quensen, J.F. III, Mueller, S., Jain, M.K., Tiedje, J.M., 1998. Reductive dechlorination of DDE to DDMU in marine sediment microcosms. *Science* 280, 722–724.
- Regional Monitoring Program for trace Substances, 1995. 1995 Annual Report, San Francisco Estuary Institute. 324 pp. with appendices.
- Regional Monitoring Program for trace Substances, 1996. 1996 Annual Report, San Francisco Estuary Institute. 299 pp. with appendices.
- Risebrough, R.W., Menzel, D.B., Martin, D.J. Jr., Olcott, H.S., 1967. DDT residues in Pacific sea birds: a persistent insecticide in marine food chains. *Nature* 216, 589–591.
- Risebrough, R.W., Hugget, R.J., Griffin, J.J., Goldberg, E.D., 1968a. Pesticides: transatlantic movements in the northeast trades. *Science* 159, 1233–1236.
- Risebrough, R.W., Rieche, P., Peakall, D.B., Herman, S.G., Kirven, M.N., 1968b. Polychlorinated biphenyls in the global ecosystem. *Nature* 220, 1098–1102.
- Risebrough, R.W., Chapman, J.W., Okazaki, R.K., Schmidt, T.T., 1978. Toxicants in San Francisco Bay and Estuary. Report of the Association of Bay Area Governments, Berkeley, CA, USA.
- Spies, R.B., Andersen, B.D., Rice, D.W. Jr., 1987. Benzothiazoles in estuarine sediments as indicators of street runoff. *Nature* 327, 697–699.
- Valette-Silver, N.J., 1993. The use of sediment cores to reconstruct historical trends in contamination of estuarine and coastal sediments. *Estuaries* 16 (3B), 577–588.
- van Geen, A., Valette-Silver, N.J., Luoma, S.N., Fuller, C.C., Baskaran, M., Tera, F., Klein, J., 1999. Constraints on the sedimentation history of San Francisco Bay from <sup>14</sup>C and <sup>10</sup>Be. *Mar. Chem.* 64, 29–38, (this issue).
- Venkatesan, M.I., 1998. Part II. Historical trends in the deposition of organic pollutants in the Southern California Bight. NOAA Technical Memorandum NOS ORCA 129. National Oceanic and Atmospheric Administration, US Dept. Commerce, Silver Spring, MD, USA, 136 pp.
- Venkatesan, M.I., Mirsadeghi, F., Ruth, E., 1998. Historic record of the deposition of organic pollutants in the sediments from southern California Bight. To be submitted to *Mar. Env. Res.*
- Venkatesan, M.I., Greene, G.E., Ruth, E., Chartrand, A.B., 1996. DDTs and dumpsite in the Santa Monica Basin, California. *Science of the Total Environment* 179, 61–71.
- Wedemeyer, G., 1967. Dechlorination of 1,1,1-trichloro-2,2-bis(*p*-chlorophenyl)ethane by *Aerobacter aerogenes*. *Applied Microbiol.* 15, 569–574.
- Word, J.W., Mearns, A.J., 1979. 60-meter control survey off southern California. Tech. Mem. 229, Southern California Coastal Water Research Project, El Segundo, CA, 58 pp.
- Young, D.R., McDermott-Ehrlich, D., Heesen, T.C., 1977. Sediments as sources of DDT and PCB. *Mar. Pollut. Bull.* 8, 254–257.