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Transport and diagenesis of trace metals and organic matter in Palos Verdes shelf sediments affected by a wastewater outfall

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Abstract

Particles from the Whites Point/JWPCP outfalls operated by the Los Angeles County Sanitation District (LACSD) have been discharged onto the Palos Verdes (PV) shelf, Southern California, since the late 1930s. Since the early 1950s, they have made a significant contribution to the sedimentary deposits on the shelf. In order to study the transport and diagenesis of organic carbon (OC) and associated trace metals, replicate sediment cores were collected during 1996 and 1997 at four different sites at the ~60 m isobath on the PV shelf, and analyzed for OC, Ag, Al, Cd, Cr, Cu, Mn, Ni, Pb, and Zn. We conclude from these results that a significant fraction of OC and associated heavy metals were transported laterally on silt particles from shallower environments. Cross-shelf transport of sediments caused multiple peaks in measured profiles of OC and trace metals at site 6C, 2 km away from the outfall. The same mechanism is likely to contribute to a concentration decrease that is smaller than that expected from decreases from the Whites Point outfall emissions. Based on Pb/OC ratios in sediments, deposited in 1971, and comparisons to the outfall from the same year, we estimate that 50 ± 10% of the OC deposited in the early 1970s, now buried at 30–50 cm depth, had oxidized since that time, implying a half-life of about 26 years for the outfall-OC, as an upper limit. The average OC oxidation rate at peak depth (about 2 mg C $\mathrm{cm^{-2}}$ $\mathrm{year^{-1}}$) is, however, only about 10% of the present-day OC accumulation rate (20 mg C $\mathrm{cm^{-2}}$ $\mathrm{year^{-1}}$), which itself is adding not much more than 1% per year to the post-1950s OC inventory (~1500 mg $\mathrm{cm^{-2}}$). We furthermore estimate that the OC inventory in PV shelf sediments in 1971 was equivalent to about 35% of that emitted by the outfall. OC and trace metal inventories did not decrease in the period 1981 to 1997, contrary to those of other contaminants such as DDTs and PCBs. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Trace metals; Organic matter; Shelf sediments; Sediment transport; Sediment diagenesis; Palos Verdes shelf

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1. Introduction

Submarine discharges of sewage and wastewater on continental shelves are conducted by a number of large cities in the world. One such treated wastewater discharge is near Whites Point, on the Palos Verdes (PV) shelf near San Pedro, CA, operated by the Los Angeles County Sanitation District (LACSD). The currently used outfalls are located at a depth of about 60 m and below the pycnocline. The effluent is dispersed in a general northwest direction by the prevailing bottom currents. Before 1971, the sediments contained relatively high concentrations of a large number of pollutants such as the chlorinated hydrocarbon DDTs (Young et al., 1977; Eganhouse and Kaplan, 1982, 1988; Schafer, 1989; Lee, 1994; Eganhouse and Pontolillo, 2000; Eganhouse et al., 2000) and heavy metals (Morel et al., 1975; Finney and Huh, 1989; Huh et al., 1992). Fluxes of pollutants to the sediments have declined since about that time (e.g., Young et al., 1977; Schafer, 1977, 1989; Lee, 1994; Carry, 1996; Stull et al., 1996). Currently, the highest concentrations of these compounds are found buried at 30–50 cm below the sediment–water interface. Some of the concentrations and sediment inventories of organic compounds, such as DDTs, have declined since 1971 by 50% or more (Lee, 1994), possibly due to microbial degradation (Quensen et al., 1998). Marine sediments are thus expected to contain a record of these chemical inputs, possibly modified by microbially controlled diagenetic reactions related to organic carbon (OC) oxidation.

Previous studies have contributed a great deal to our understanding of the impact of these buried materials to the coastal environment. For example, the physical circulation (Hickey, 1992), geology (Gorsline, 1992; Huh et al., 1990), sediment geochronology (Finney and Huh, 1989; Huh et al., 1990, 1992; Wong et al., 1992), and organic matter cycling (Venkatesan and Kaplan, 1980; Williams et al., 1992) in the California Borderlands basins of the Southern California Bight have been described in the literature. Published accounts on the PV shelf area include also the effects of waste water disposal to the coastal waters of Southern California (for an overview, see Bascom, 1982; for ΣDDT compounds, and other organic chemicals, see Young et al., 1977; Venkatesan and Kaplan, 1980; Eganhouse and Kaplan, 1982, 1988; Stull et al., 1996; Venkatesan et al., 1996; Eganhouse and Pontolillo, 2000; Eganhouse et al., 2000 for trace metals, see Chow et al., 1973; Morel et al., 1975; Bruland et al., 1974; Stull and Baird, 1985; Finney and Huh, 1989; Huh et al., 1992; and for benthic ecosystem changes, see Stull et al., 1986, 1996; Swartz et al., 1986; Wheatcroft and Martin, 1996).

However, the fate of pollutants such as DDTs and heavy metals as well as organic carbon buried at 30–50 cm depth in these sediments is still controversial (Renner, 1998) and thus of great interest. The decreasing inventory and peak concentrations of ΣDDT in the sediment deposits has been taken as evidence for loss through the sediment surface, caused by deep bioturbation coupled to sediment resuspension (Drake et al., 1994; Niedoroda et al., 1996). If particle-reactive pollutants were lost by such a mechanism, heavy metal peak concentrations (at depth) and inventories would have had to decline as well. However, peak concentrations and inventories of metals at most locations on the shelf have not decreased since 1983 (LACSD, unpublished data, and discussed later), but those of ΣDDT did (Lee, 1994).

Santschi et al. (1999) investigated the fate of Hg buried in Lavaca Bay (Texas) sediments during the 1960s, and concluded that anthropogenically enhanced sedimentation and natural recovery are sufficiently fast so that Hg buried below 10 cm from the surface is part of the historical layer and not available for bioaccumulation and food chain transfer to the overlying water. Similarly, Santschi et al. (2000a), using natural and fallout radionuclides, demonstrated in a companion study to this paper that natural and anthropogenically enhanced sedimentation continues to bury the pollutants on the PV shelf, and thus, severely restricts transfer from depth to the surface.

In order to evaluate the various sources and pathways, as well as short-term and long-term oxidation rates of OC, we determined concentration profiles of OC, total nitrogen, sulfur, and various trace metals from a number of sediment core profiles on the Palos Verdes shelf, and compared these to each other as well as to similar profiles from the literature. By comparing trace metal and OC profiles in these outfall-affected sediments and relating them to their input functions, one can gain valuable insights not only about mechanisms of transport and deposition of these species, but also about possible post-depositional processes.

2. Methodology

2.1. Sampling

A total number of 13 boxcores and two vibracores were collected from the PV shelf on October 22, 1996 from sites 3C and 5C and on September 17–18, 1997 from sites 6C and 8C. In addition, subcores from a boxcore were also collected at sites 5C and 3C, and a vibracore was collected from site 3C, on October 22, 1996. Sampling locations are shown in Fig. 1 and listed in Table 1. Subcores taken from the box cores, in which possible sub-coring artifacts were minimal (Santschi et al., 2000b), and vibra cores were sectioned on board ship, or on the same day on-shore. Coring and smearing artifacts were minimized by removing the outer rims from each slice before further processing. Sediment samples from short and long cores were processed for radiochemical determinations (Santschi et al., 2000a), elemental analysis including organic carbon (OC), total N (TN), total S (TS) (Guo and Santschi, 1997), and trace metals (Warnken et al., 1999, 2000). Data from cores discussed in this paper were close (within 5–10%) to the nominal core depth of 60 cm. Therefore, they suffered very little from possible sub-coring artifacts during the box core sampling (Santschi et al., 2000b).

2.2. Analytical procedure for trace metals in sediments

2.2.1. Digestion

Approximately 2 g (~ 1.5 ml) of wet sediment was dried and homogenized. About 0.1 g of this dried and homogenized sediment was then weighed into 15-ml acid cleaned Teflon low-pressure vials. Concentrated Q-HCl acid (SEASTAR™) (5 ml) and 3 ml of concentrated Q-HNO_3 (SEASTAR™) were added. Vials were then sealed and placed on a hot

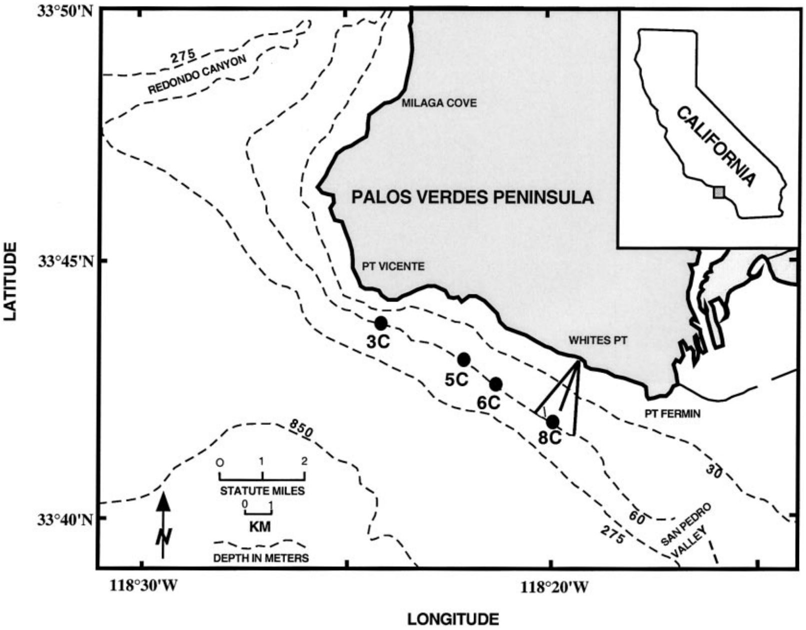

Fig. 1. Map of Palos Verdes shelf, showing sampling locations, and positions of Whites Point outfall pipelines.

Table 1
Sampling locations and ancillary parameters

Site/core[a]	Sampling location		Water depth (m)	Porosity (Ø)			Average recent sedimentation rate(cm year^{-1})[b]
	Latitude	Longitude		Surface	Max	Min	
8C(BC)	33°42.00′	118°20.05′	56	0.70	0.80	0.70	1.2
6C(BC)	33°42.51′	118°21.20′	59	0.70	0.78	0.70	1.3
6C(VC)	33°42.51′	118°21.20′	59	0.70	0.80	0.50	1.1
5C(BC)	33°42.91′	118°21.90′	58	0.70	0.78	0.50	1.5
3C(BC)	33°43.84′	118°24.13′	58	0.65	0.65	0.50	1.2
3C(VC)	33°43.84′	118°24.13′	58	0.68	0.65	0.47	1.1

[a] BC = box core; VC = vibra core.
[b] From Santschi et al. (2000b).

plate in a class-100 fume hood, and heated for ~24 h. After samples cooled down, each vial was placed on a hot plate for another 24 h after the addition of 2 ml of concentrated Q-HF (SEASTAR™). Then, 0.2 ml of concentrated perchloric acid (OPTIMA, Fisher) was added, and again heated for 24 h in a class-100 fume hood. For QA/QC purposes, digestion procedure blanks (a total of six), duplicate digestions (for 5% sample loads), two standard certified standard reference materials (NBS 1646 estuarine sediment and NIST 2704 Buffalo River sediment) were performed following the same procedures. Final digested samples were then transferred into acid cleaned 30-ml HDPE bottles and diluted to 30 ml with 18 MΩ ultrapure water. Agreement between measured and certified values for sediment standards was within the errors of the measurements (i.e., 1σ error $\leq 3\%$).

2.3. Analysis

Trace metal concentrations of digested samples in the 30 ml HDPE bottles were determined by a Perkin Elmer 5100 Atomic Absorption Spectrometer equipped with Zeeman background correction system and graphite furnace with pyrocoated L'vov platform tube. Instrument blank was frequently monitored and standard reference material (NIST 1643d, Trace Element in Natural Waters) was also analyzed as a sample during each measurement cycle. The quantitative analysis method with six point external calibration was used to determine the elements of

Table 2
Analytical procedural blanks and results from the analyses of certified standard reference materials

Elements	Analytical procedure blanks (ng)	NIST 1643d (trace elements in water)		NBS 1646 (Estuarine Sediment)		NIST 2704 (Buffalo River Sediment)	
		Measured (μg kg^{-1})	Certified (μg kg^{-1})	Measured (μg g^{-1})	Certified (μg g^{-1})	Measured (μg g^{-1})	Certified (μg g^{-1})
Ag	n.d.	7.60 ± 0.09	7.62 ± 0.25	–	–	–	–
Al	4.9 ± 1.8	50.8 ± 0.6	52.0 ± 1.5	$6.00 \pm 0.02\ 10^{4}$	$6.25 \pm 0.20\ 10^{4}$	$6.10 \pm 0.09\ 10^{4}$	$6.11 \pm 0.16\ 10^{4}$
Cd	n.d.	22.60 ± 0.20	22.79 ± 0.96	0.36 ± 0.02	0.36 ± 0.07	3.50 ± 0.16	3.45 ± 0.22
Cr	2.4 ± 0.6	38.65 ± 0.55	38.6 ± 1.6	74.8 ± 1.9	76 ± 3	133.7 ± 0.98	135 ± 5
Cu	1.3 ± 0.3	85.3 ± 0.4	85.2 ± 1.2	18.0 ± 1.2	18 ± 3	101.4 ± 2.1	98.6 ± 5.0
Fe	4.2 ± 1.5	32.2 ± 0.1	34.3 ± 1.6	$3.39 \pm 0.05\ 10^{4}$	$3.35 \pm 0.10\ 10^{4}$	$3.97 \pm 0.06\ 10^{4}$	$4.11 \pm 0.10\ 10^{4}$
Mn	1.2 ± 0.6	37.6 ± 0.5	37.66 ± 0.83	362 ± 7	375 ± 20	554 ± 7	555 ± 19
Ni	0.6 ± 0.5	28.3 ± 0.7	27.4 ± 0.8	33.6 ± 1.1	32 ± 3	44.3 ± 0.9	44.1 ± 3
Pb	1.1 ± 0.4	27.2 ± 0.8	27.89 ± 0.14	28.2 ± 1.8	27.69 ± 1.24	167.2 ± 0.1	161 ± 1.7
Zn	2.3 ± 1.2	51.0 ± 1.8	53.2 ± 1.1	136 ± 2	138 ± 6	433 ± 4	438 ± 12

interest. Selected metals at sites 3C and 5C were also analyzed by ICP-MS (Warnken et al., 1999, 2000). Table 2 documents the analytical precision and accuracy of trace metal analysis, as derived from analysis of standard reference materials.

2.4. Organic carbon and nitrogen analysis

Measurements of OC and nitrogen were carried out according to previously published procedures (Guo et al., 1996; Guo and Santschi, 1997). Sediments were first freeze dried on a Freeze Drier (LABCONCO, Model 77545) and then pulverized in a Mixer/Mill (SPEX 8000). A subsample from each sediment was measured for its total carbon and nitrogen concentrations on a CHNS/O elemental analyzer (PE 240 Series II). The CHNS/O Analyzer was calibrated using standard chemicals (acetanilide for C and N, and cystine for S) before measuring samples. Standard chemicals were also run as a sample at the beginning, in-between samples (after 10–15 samples), and at the end to ensure data qual-

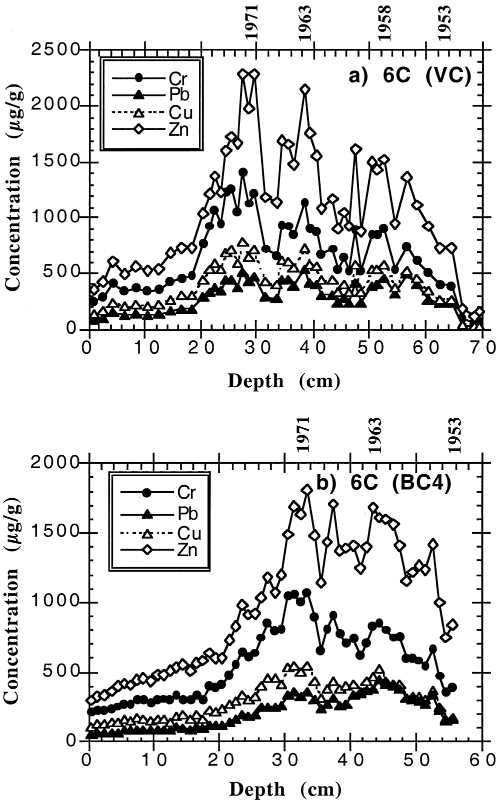

Fig. 2. Selected trace metal profiles at site 6C. Peaks were assigned to specific dates in accordance with radionuclide and organic carbon data (Santschi et al., 2000a).

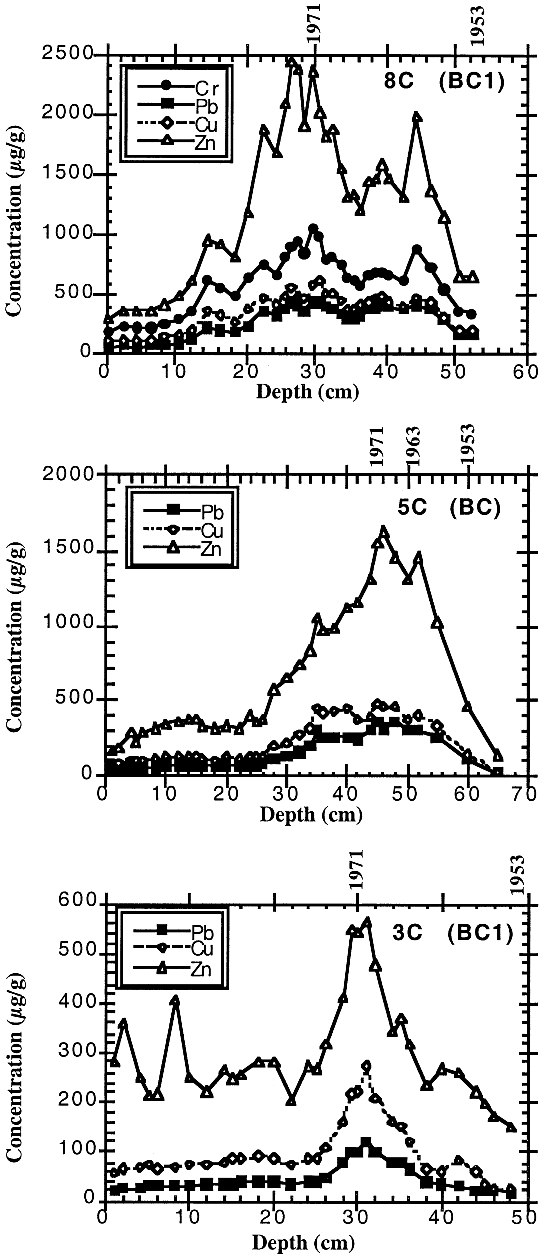

Fig. 3. Selected trace metal profiles from sites 8C, 5C and 3C. Peaks were assigned to specific dates in accordance with radionuclide and organic carbon data (Santschi et al., 2000a).

ity. Consistent QA and QC procedures were applied to all C, N and S analysis, with 10–20% of the samples run as replicates. Analytical precision was within 1% for carbon, 3% for nitrogen, and 5% for sulfur.

For OC analysis, freeze dried sediments were further treated with ~ 2 N HCl to remove inorganic carbon (e.g., Hedges and Stern, 1984; Guo and Santschi, 2000), dried again, and run for carbon analysis.

3. Results and discussion

3.1. Trace metal and OC profiles in sediments

Examples of trace metal profiles from sites 8C, 6C, 5C and 3C are given in Figs. 2 and 3, relationships between individual trace metals and OC at site 6C in Fig. 4, and relationships between OC, TN and TS in Fig. 5. Peak concentrations of trace metals and OC generally decrease in the direction 8C ≈ 6C > 5C > 3C. Concentrations of not only trace metals,

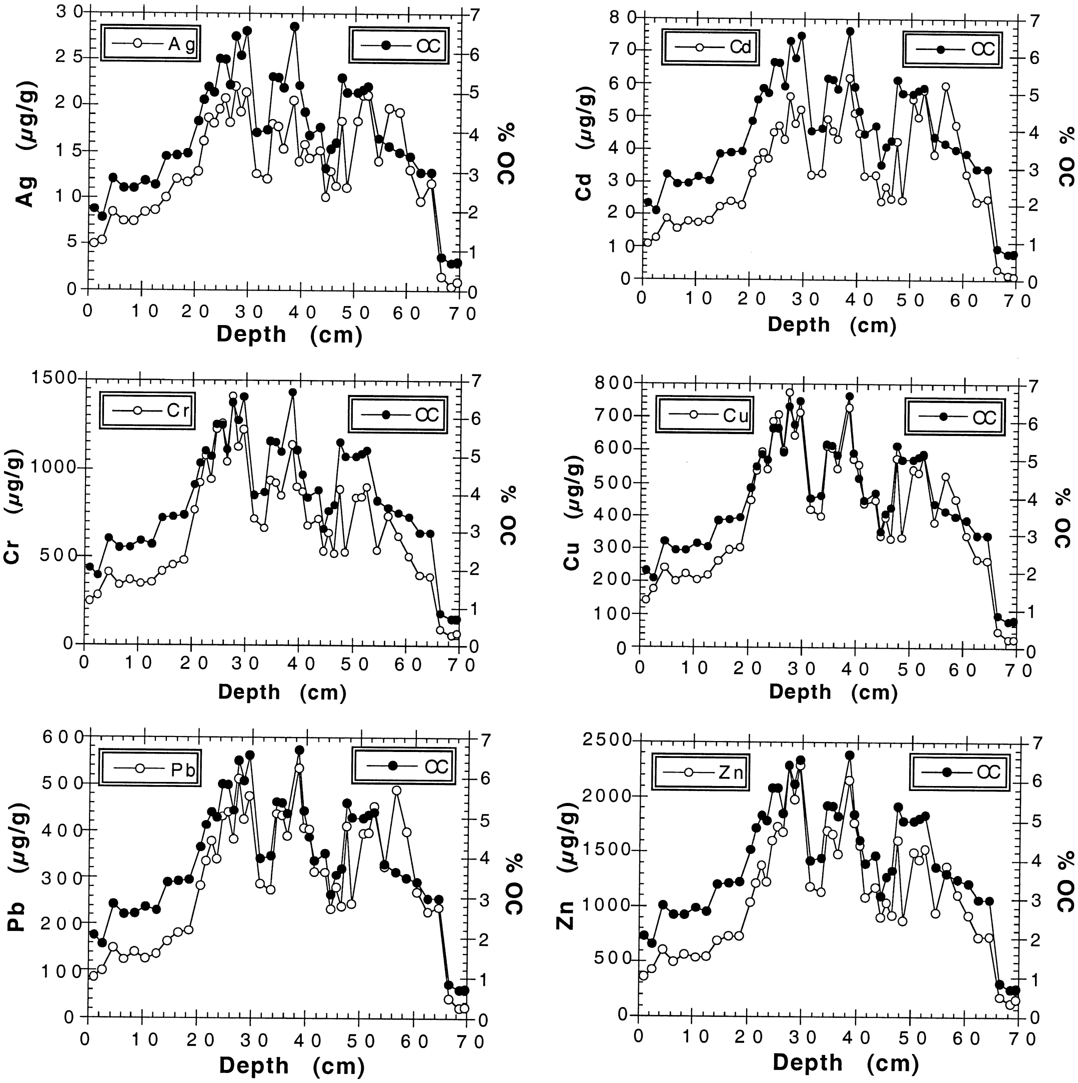

Fig. 4. Example of co-variation of trace metals and OC profiles in core 6CVC.

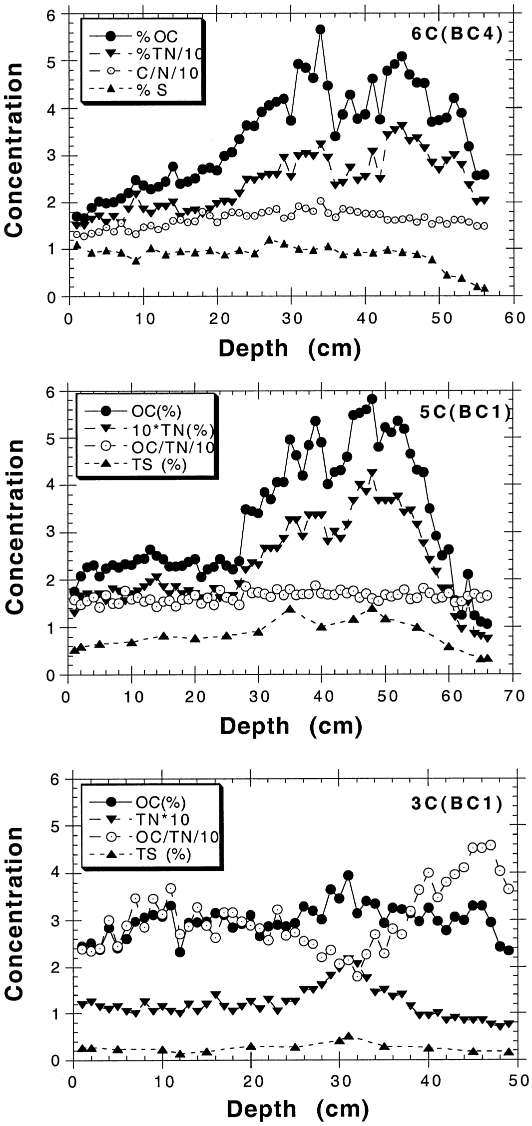

Fig. 5. Selected profiles of OC, total nitrogen (TN), OC/TN ratios, and total sulfur (TS).

but also of OC, TN and TS are relatively high, especially in the subsurface peak regions situated at 30–50 cm depth. High OC and sulfur (Fig. 5) values suggest an anoxic sediment, a fact that is further documented in Van Cappellen et al. (2000). Trace metal concentrations are enriched over the ambient background concentrations (Schiff and Weisberg, 1999) everywhere, except at the bottom of the deeper-reaching profiles, where they are very close to the baseline concentrations predicted by the linear relationship with iron concentrations (Schiff and Weisberg, 1999) of 3–4%.

The events causing multiple trace metal maxima (Figs. 2–4) were dated using multiple radioisotopic tracers (Santschi et al., 2000a). In 1971, OC emissions and sediment concentrations peaked (Finney and Huh, 1989; Stull et al., 1996; Paulsen et al., 1999), which allowed previous investigators to assign this year to the observed OC and tracer maxima (e.g., Eganhouse and Kaplan, 1982, 1988; Logan et al., 1989; Huh et al., 1992; Stull et al., 1996; Paulsen et al., 1999; Eganhouse and Pontolillo, 2000). In addition, the years 1963 and 1953 were used as the peak and beginning years of nuclear bomb fallout, respectively, as traced by Pu (Santschi et al., 2000a).

The multiple OC (and trace metal) peaks are unexpected, and while they have been observed before (Lee, 1994; Stull et al., 1996; Paulsen et al., 1999; LACSD, unpublished results), they have not been as common as single peaks (Eganhouse and Kaplan, 1988; Lee, 1994; Stull et al., 1996). If deposition were just a linear function of outfall conditions, smoother profiles would be expected. The highly significant correlations between OC and metals (Table 3), as well as many radionuclides (Santschi et al., 2000a), suggest that these multiple peak features were caused by additional sediment sources contributing to and interrupting the outfall related burial of these compounds (Santschi et al., 2000a). The multiple peaks of OC, trace metals, and radionuclides in these sediment cores thus point to an event-dominated depositional sedimentary environment on the PV shelf, whereby lower values could have been produced by enhanced depositional events caused, for example, by storm-related coastal erosion and river washloads (Inman and Jenkins, 1999; Inman et al., 2000). According to Inman et al., major storm events in the last 35 years occurred in 1969, 1978, 1980, 1983, 1993, and 1995. The 1969 storm could have been responsible for splitting the trace metal and OC peaks into two major peaks, which are evident not only in our profiles, but also in many of the trace metal profiles measured by LACSD (unpublished data; Fig. 6). Most importantly, our trace metal peak concentrations are very close to those measured by others (Galloway, 1972; LACSD, unpublished; Huh et al., 1990; List and Paulsen,

Table 3

(a) Correlation coefficients of trace metal and organic carbon concentrations in Core 6CVC ($P < 0.001$ for $R > 0.46$)[a]

	OC	Ag	Cd	Cr	Cu	Ni	Pb	Zn
OC	1	0.92	0.88	0.95	0.96	0.94	0.92	0.95
Ag	0.92	1	0.95	0.92	0.95	0.95	0.96	0.91
Cd	0.88	0.95	1	0.88	0.94	0.91	**0.98**	0.93
Cr	0.95	0.92	0.88	1	**0.99**	0.96	0.92	0.96
Cu	0.96	0.95	0.94	**0.99**	1	**0.97**	**0.97**	**0.98**
Ni	0.94	0.95	0.91	0.96	**0.97**	1	0.93	0.93
Pb	0.92	0.96	**0.98**	0.92	**0.97**	0.93	1	0.95
Zn	0.95	0.91	0.93	0.96	**0.98**	0.93	0.95	1

(b) Correlation coefficients of trace metal and organic carbon concentrations in Core 5CBC1 ($P < 0.001$ for $R > 0.53$)[a]

	OC	Ag	Cd	Cu	Ni	Pb	Zn
OC	1	**0.99**	0.91	**0.98**	0.95	**0.98**	**0.97**
Ag	**0.99**	1	0.92	**0.98**	0.95	**0.99**	**0.98**
Cd	0.91	0.92	1	0.87	0.83	0.94	0.95
Cu	**0.98**	**0.98**	0.87	1	0.96	**0.98**	0.96
Ni	0.95	0.95	0.83	0.96	1	0.93	0.93
Pb	**0.98**	**0.99**	0.94	**0.98**	0.93	1	**0.98**
Zn	**0.97**	**0.98**	0.95	0.96	0.93	**0.98**	1

(c) Correlation coefficients of trace metal and organic carbon concentrations in Core 3CBC1 ($P < 0.001$ for $R > 0.55$)[a]

	OC	Ag	Cd	Cu	Ni	Pb	Zn
OC	1	0.57	0.64	0.53	0.39	0.67	0.59
Ag	0.57	1	0.93	0.94	0.86	0.95	0.87
Cd	0.64	0.93	1	**0.97**	0.78	**0.98**	0.86
Cu	0.53	0.94	**0.97**	1	0.83	**0.98**	0.91
Ni	0.39	0.86	0.78	0.83	1	0.80	0.85
Pb	0.67	0.95	**0.98**	**0.98**	0.80	1	0.89
Zn	0.59	0.87	0.86	0.91	0.85	0.89	1

(d) Correlation coefficients (R), slopes and intercepts for the relationship between OC (%) and total nitrogen (TN, %), as $[\%\text{TN}] = a + b[\%\text{OC}]$

Core	R	Intercept a	Slope b
6CVC	0.99	0.031	0.058
6CBC1	0.97	0.035	0.063
6CBC3	0.97	0.049	0.054
6CBC4	0.96	0.053	0.055
6CBC5B	0.97	0.07	0.053
6CBC6	0.98	0.044	0.059
8CBC1	0.95	0.043	0.056
8CBC2	0.97	0.049	0.056
8CBC3B	0.97	0.083	0.055
5C	0.99	0.017	0.066
3C	0.67	−0.042	0.055

[a] Highest values indicated in bold.

2000). An example for this constancy of peak concentrations over time, as well as the presence of multiple peaks in previous profiles, is given for Pb in Fig. 6.

While Al and Fe concentrations were measured for all our cores, their concentrations did not reveal a consistent pattern in the different cores. Differences in relations of Al or Fe to porosity and OC (or trace

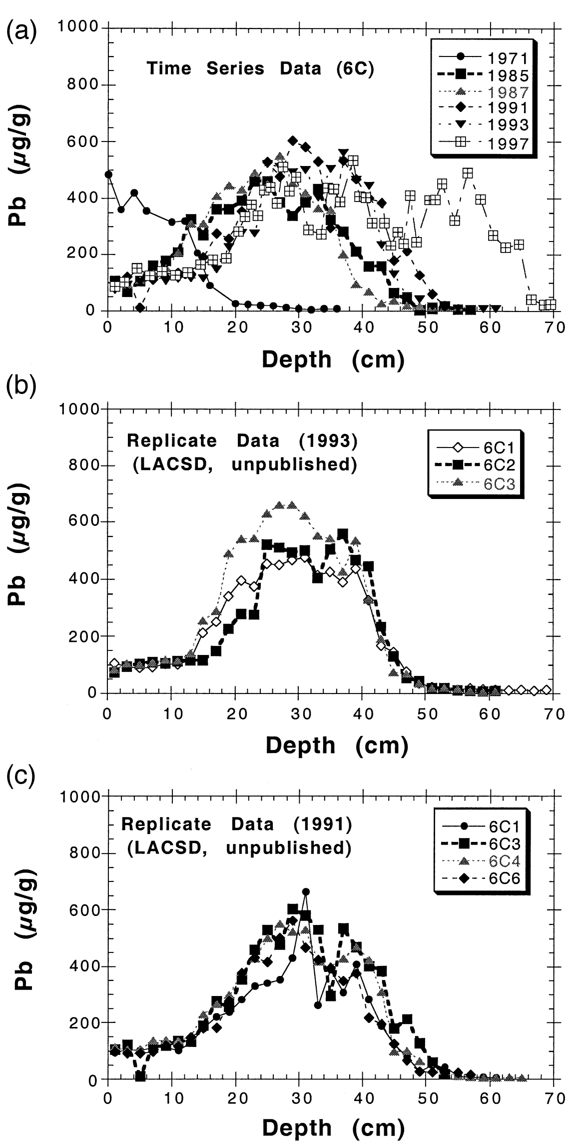

Fig. 6. Comparison with selected Pb profiles from site 6C (LACSD, unpublished). (a) Time series data, including the 1971 profile of Galloway (1972), and our 1997 profile; (b) replicate profiles from 1991; (c) replicate profiles from 1993.

metals) in just one core (Fig. 7), as well as between cores from the same site and from site to site, preclude any general interpretation in terms of episodic events. If these events were caused by episodic storm-related river washloads (Inman and Jenkins, 1999; Inman et al., 2000) and shore erosion, the deposited material from these events would likely be fine-grained as well, and thus, it would not be expected to reveal a consistent pattern. However, Al and porosity appear to increase at the beginning of the outfall period earlier than OC and porosity did, which agrees with our interpretation that some of the patterns were caused by climate related events.

Metal concentrations in surface sediments are currently 15–30% of the 1971 peak concentrations (Figs. 2 and 3), even though outfall mass emission rates of some of them have decreased to as low as 4–8% from their 1971 values (Fig. 8 and Carry, 1996). Ag emission rates from the Whites Point plant decreased from about 10 tons year^{-1} in 1971 to about 3 tons year^{-1} in 1995 (30% decrease of the 1971 value), while those of Cu decreased from about 270 tons year^{-1} in 1971 to less than 20 tons year^{-1} in 1995 (decrease to less than 8%), and those of Zn from 1400 tons year^{-1} in 1971 to less than 50 tons year^{-1} in 1995 (decrease to less than 4%) (Carry, 1996). It appears that the steeper decrease in Cu and Zn inputs from the outfall into coastal waters (as compared to Ag, for example) is not reflected in the sediments, thus suggesting that either recent Cu and Zn outfall loadings into coastal waters are presently deposited more efficiently than in the past, or that other sources exist for these metals. The latter explanation is more likely since Me/OC ratios in sediments close to the outfall are generally higher than the input ratios associated with the outfall (see below) and because the quantity of particulates emitted by the outfall has decreased by about an order of magnitude. Other metal sources include: other outfalls in the region, metals originating from lateral transport of more

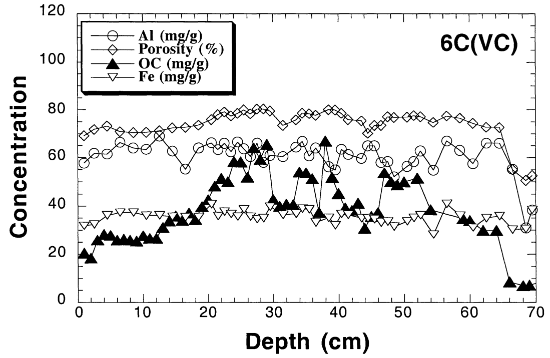

Fig. 7. Comparison of Al, Fe, porosity, and OC profiles from 6C(VC).

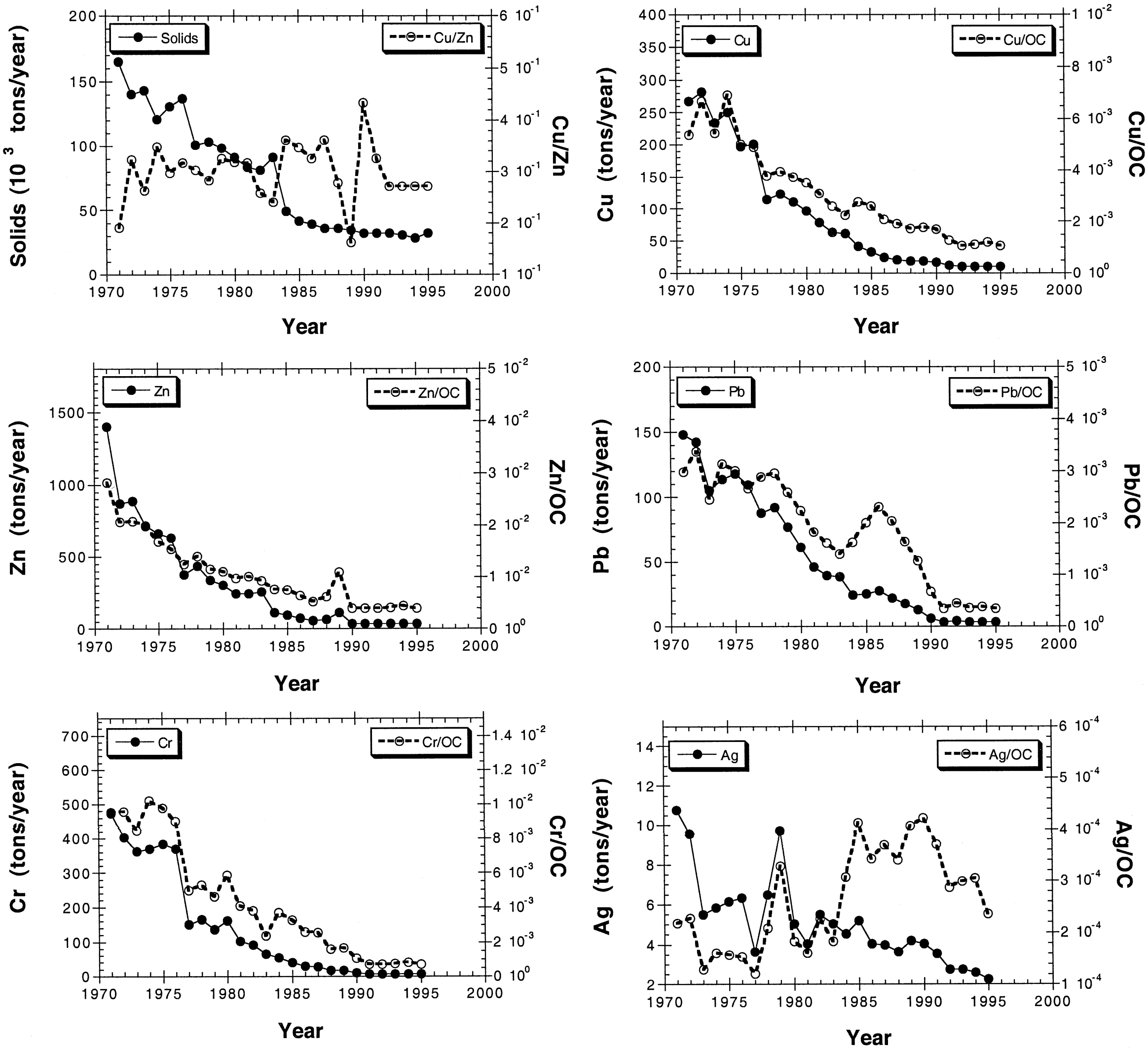

Fig. 8. Emission rates and Me/OC ratios in Whites Point's discharge are given for individual metals. OC input is equal to particle input times 0.3 (Myers, 1974; Sweeney et al., 1980).

shallower, more reworked deposits through sediment resuspension events, and river and storm water washloads. The persistence of the multiple peaks at site 6C (Figs. 2, 4 and 5) is congruent with the shallow mixed layer depths in the same cores (Santschi et al., 2000a), indicating that bioturbation has not been strong enough to obliterate these peaks.

While the outfall related OC input to the PV shelf sediments decreased by more than an order of magnitude since 1971 (Fig. 8), OC concentrations in the surface sediments only decreased by about a factor of 3 from the subsurface peak. Since sediment mixing below the upper 3–5 cm can be ruled out based on analysis of tracer profiles (Paulsen et al., 1999; Santschi et al., 2000b), sediment concentrations of trace metals and OC would be expected to closely track sediment inputs from the outfall and outfall-enhanced natural sedimentation. If the sediments had received OC and contaminants only during the late 1960s and early 1970s, and if there were no additional inputs (from lithogenic or biogenic sources), the concentrations of OC and contaminants in surface sediments should, according to a simple box model given in Santschi et al. (1999), have decreased with a half-life, $t_{1/2}$, of about 2 years.

$$t_{1/2} = \ln 2 * z_{\mathrm{m}}/S \approx (\ln 2) * 3\,\mathrm{cm}/(1\,\mathrm{cm}/\mathrm{year})$$

$$\approx 2\,\mathrm{years}$$

where z_{m} = mixed layer depth of ~3 cm, and S = sedimentation rate of ~1 cm year^{-1}. In other words, after 26 years, there should have been less than 0.01% of OC or trace contaminant left from the 1971 deposition in the surface sediment at 6C. Therefore, additional and continuing inputs of organic carbon (and contaminants) since 1971 are required to explain the near-constancy of OC and ΣDDT concentrations in surface sediments over the past 15 years (e.g., Lee, 1994; Drake et al., 1994).

The profiles of all trace metals closely resemble those of OC (Fig. 4). Indeed, there exist highly significant correlations between most measured sedimentary parameters, i.e., porosity, OC, TN, TS and trace metals. In addition, the various trace metals strongly correlate among each other (Table 3). Total nitrogen (TN), which has been measured by the US Geological Survey (USGS), the Southern California Coastal Water Research Project (SCCWRP) and the Los Angeles County Sanitation District (LACSD) more often than OC, proves to be an excellent predictor for OC concentrations, with, within the errors, identical TN/OC slopes of 0.058 (±0.005) for all the cores from sites 6C and 8C (Table 3d). Even with the high correlation coefficient, departures from the average the C/N ratio of 17 do occur, however, with extreme values in 1971 of approximately 15–20, and values at the sediment surface at 6C (and 8C, not shown) and 5C of about 14–16, and 24 at 3C (Fig. 5). The inverse OC/TN profiles at 3C, as compared to those at 6C (8C) and 5C, point to a system that is dominated by a greater proportion of terrestrial inputs at 3C than at the other stations.

This excellent correlation between OC and TN had already been previously pointed out by Eganhouse and Kaplan (1988). In our data, total sulfur also correlates with OC (Fig. 5). This close correlation between most parameters enhances the usefulness of many previous and incomplete data sets (e.g., Lee, 1994), which often only had TN data.

The highly significant correlations between trace metals and OC for sites 8C (not shown, but is the same), 6C, 5C, and 3C indicate that their burial was related to that of OC, and thus, these parameters can all be used as tracers of the outfall effluent particulates.

Trace metal to OC ratios in sediments are often significantly different from those of the outfall input, however. The likely reasons include: (1) fractionation processes in the water column (Paulsen et al., 1999); (2) diagenetic reactions (i.e., OC oxidation) in the sediments; and (3) trace metal remobilization from sediments. Due to the anoxic nature of these sediments (Smith and Greene, 1976; Van Cappellen et al., 2000), as is also evident from the high sulfur content (Fig. 5), remobilization of B-type metals (e.g., Ag, Pb) and many transition metals (e.g., Cu, Zn, Cd) is likely minimal (e.g., Shaw et al., 1990), because of their sequestration in iron sulfides (e.g., DiToro et al., 1992). If fractionation processes in the water can be constrained, metal/OC ratios might therefore be used to assess OC loss rates by oxidation.

3.2. Implications for transport and fractionation processes

One of the metals that appears to preserve its effluent input ratio is Ag. According to Flegal et al. (1995), Ag is an excellent tracer for sewage OC. As can be seen from Fig. 8, the effluent ratio of (1–4) × 10^{-4} Ag/OC (g/g) is relatively constant, and appears to have been better preserved in the 6C and 8C sediments (Fig. 9) than those of other metals. Ag/OC ratios at 6C and 8C are at the upper end of the input range, ratios at 5C are in the middle, and ratios at 3C are at the lower end (Fig. 9) of the effluent ratio (Fig. 8). In other words, Ag/OC ratios in sediments decreased with increasing distance from the source. Similar trends were also observed for other Me/OC ratios, such as Pb/OC ratios (Fig. 9). However, the decrease of Me/OC ratios with increasing distance from the outfall source is possibly less for Cu and Zn, indicating other sources for Cu and Zn, or different rates of transfer from the water to sediments for these metals.

Unlike the temporally (1971 to present) decreasing input ratios of Pb, Cr, Cu and Zn to OC (Fig. 8),

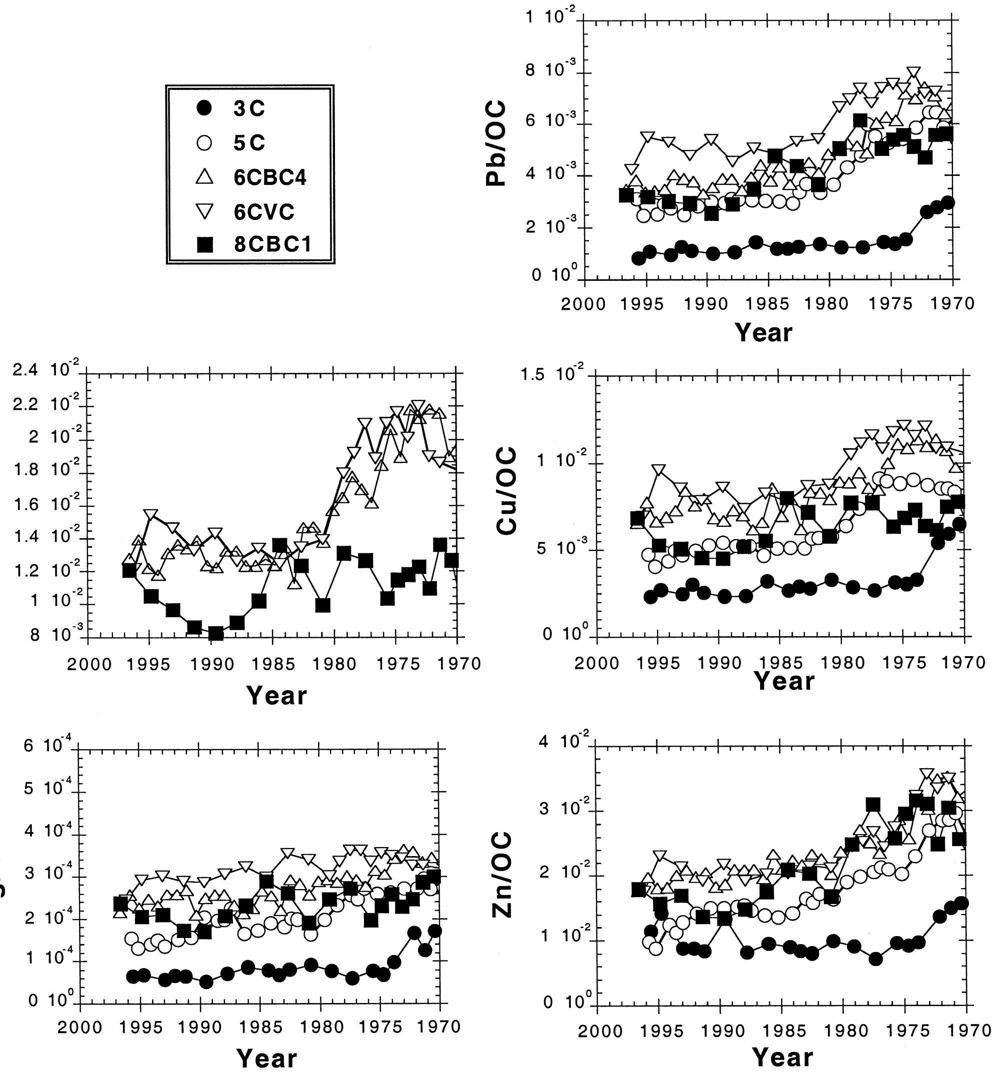

Fig. 9. Changes of metal to OC concentration ratio with depth in Palos Verdes shelf sediments.

the ratios of these metals to OC in the PV sediments usually decrease by less than a factor of two over the same time period (Fig. 9), which is much less than the input ratios (Fig. 8). For example, ratios of Zn, Pb, Cr to OC in the inputs all decrease by about 90%, while sedimentary ratios decrease by only about 50% or less (Fig. 9). It also appears that with increasing distance from the source, metal (Me) to OC ratios systematically decrease, with the highest ratios at 6C, and the lowest ones at 3C. If particle and OC inputs into the sediments are supplemented by secondary sources such as primary production in the water column, winnowed sediments from shallower sites, erosion from the palisades and toe of the Portuguese Bend landslide (Drake et al., 1994; Santschi et al., 2000b), and metals and OC from other sewage outfalls, rivers (Inman and Jenkins, 1999) and atmospheric sources, Me/Me and Me/OC ratios would consequently differ from those in the outfall. Since present-day OC loadings from the outfall are lower by an order of magnitude than in 1971, but OC concentrations in sediments only de-

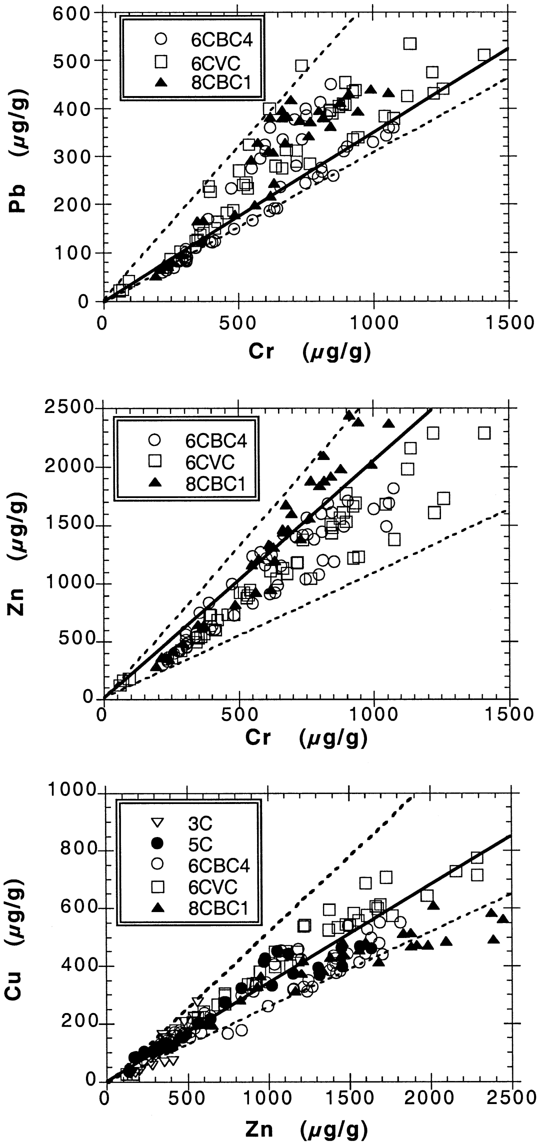

Fig. 10. Correlations between metals in Palos Verdes shelf sediments. The solid and dotted lines in (a,b) are the main trend lines and boundaries of data spread in all core data from Huh et al. (1992), to which our data favorably compare. In (c), the lines are from LACSD (unpublished data).

creased by a factor of 3 since then, most of the recent OC must therefore be supplied by other sources.

Ratios of metals to Zn or to Cr have also been used to deduce transport mechanisms in the water or sediments by using a comparison of these ratios in sediments with those from surface sediment ratios in 1971 (Galloway, 1972), and with ocean outfall sources (Katz and Kaplan, 1981). Ratios of Pb/Cr and Zn/Cr (slopes in Fig. 10) in 6C and 8C sediments vary by less than a factor of two, indicating only moderate fractionation between these three metals in these cores. Fractionation could occur, for example, by association to different sized particles with different settling rates. Furthermore, Zn/Cr and Pb/Cr ratios at 6C are very similar to those reported by Huh et al. (1992) (solid trend lines in Fig. 10), and to the emission ratios (Fig. 8). As is also evident from Fig. 10, the spread in our data is identical to that in Huh et al. (1992) and LACSD (unpublished data; Fig. 6). An additional atmospheric source has been proposed for Pb on the PV shelf (e.g., Chow et al., 1973; Huh et al., 1992), which would affect Pb profiles on the PV shelf as well.

Cu/Zn emission ratios were 0.3 (±0.1) from 1971 till 1977 (Schafer, 1977; Katz and Kaplan, 1981), as well as afterwards (Fig. 8). Such ratios were also found in the surface sediments at that time (Katz and Kaplan, 1981; Kettenring, 1981). For example, that ratio was 0.30 ± 0.01 in sediments at a site near 6C in 1971 (Galloway, 1972). Cu/Zn ratio of 0.3 is also close to the 1971 value in several of our cores except at 3C (Fig. 11), despite the fact that sedimentary Cu/Zn ratios (e.g., Fig. 11, and slopes in Fig. 10) vary as much in different cores from one site (e.g., site 6C) as they vary down-core in the profiles and in-between sites. Katz and Kaplan (1981) noted that surface sediment Cu/Zn ratios at station 7C, which is closest to the outfall but does not

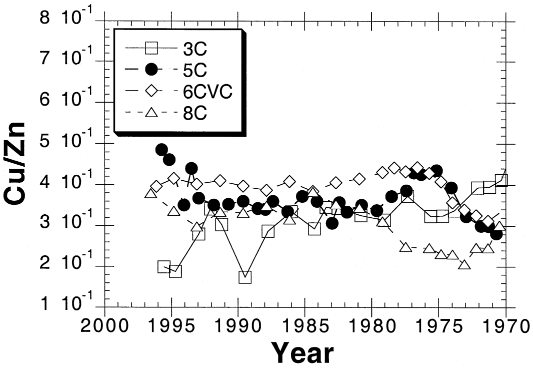

Fig. 11. Cu/Zn ratio profiles in sediments from sites 8C and 6C.

underlie it, were identical in 1977 to the average outfall ratios of 0.31 ± 0.02 between 1974 and 1977. They also mentioned that all other stations further away from the outfall had surface sediment Cu/Zn ratios that were larger than the emission ratio. This is also reflected in our data, which show highest values in 1971 at site 3C, furthest away from the outfall. However, since the 1980s, the Cu/Zn ratios at 3C are anomalously low. This suggests some fractionation between the two metals, likely related to the differential sorption behavior of these metals in the effluent plume. In addition, the characteristics of the particles likely have changed over time. Cu and Zn are currently still being buried at Cu/Zn ratios ranging from 0.2 to 0.5 (Fig. 11), close to the emission ratio of 0.3 ± 0.1.

3.3. Sedimentary OC oxidation processes

Since lateral inputs of sediment could affect OC peak concentrations in sediment cores taken over time, another way to calculate OC oxidation rates is needed. Table 4 compares Me/OC ratios in the peak region of sediments (Figs. 2–4 and 9) to those in effluents (Fig. 8). Such an approach requires that the metal is little fractionated (Faisst, 1976), nor solubilized to any large degree before or during burial. As pointed out before, the high levels of hydrogen sulfide and total sulfur in the sediments would assure that most heavy metals would be present as an insoluble sulfide (DiToro et al., 1992). Low levels of solubilization and association with more rapidly sinking particles (Faisst, 1976; Katz and Kaplan, 1981) make Pb a good tracer for deducing OC oxidation rates in PV sediments. Another suitable metal is Cr. Because metals such as Cu and Zn appear to have been partly fractionated by being associated with different sized particles (Faisst, 1976) or solubilized (Katz and Kaplan, 1981) in the water column, or supplied from other sources, they might be less useful for such a purpose.

Organic matter oxidation rates for the year 1971 could be calculated from the difference between the OC maximum concentration at 6C in 1971 (12%) (Myers, 1974; Sweeney et al., 1980) and in 1997 (6%). Peak OC concentrations at 6C were about twice as high in 1971 as they were in 1996/1997, suggesting a half-life of about 26 years. An improved approach is to use differences in the metal/OC ratios, such as Pb/OC and Cr/OC, be-

Table 4
Comparison of trace metal ratios (Me/Me) and trace metal to organic carbon (Me/OC) ratios ($\mu g\ g^{-1}$ OC)

Core, site, or year	Cr/Zn in 1971 peak	Pb/Cr in 1971 peak	Cr/OC in 1971 peak	Pb/OC in 1971 peak	% OC[a] remaining of 1971 sediment, based on Cr	% OC[a] remaining of 1971 sediment, based on Pb	Reference
6CBC4	0.59	0.34	19,000	6400	62	60	This work
6CVC	0.62	0.36	22,000	8000	57	47	This work
8CBC1	0.36	0.50	13,600	5600	87	67	This work
5C	–	–	–	7120	–	53	This work
3C	–	–	–	3725	–	100	This work
All cores	–	–	20,000 (6C only)	7600	~ 40	~ 50	This work
PV shelf	0.5	0.41	–	–	–	–	Huh et al., 1992
6C sediment surface in 1971	0.42–0.48	0.41–0.49	8190	3720	–	–	Galloway, 1972; Myers, 1974
3C 1971 peak in 1981/3	–	–	12,740	–	–	–	LACSD, unpubl., Eganhouse and Kaplan, 1988
Outfall in 1971	0.32	0.32	8823	2833	–	–	Schafer, 1977; Stull and Baird, 1985

[a] Calculated as (input ratio/core ratio)/0.75, with 0.75 being the fraction of particle-associated OC from the outfall that is not lost via oxidation in the water column prior to deposition (Myers, 1974; Sweeney et al., 1980).

tween sediment and effluent particles to estimate the OC oxidation rates more accurately. A comparison of the metal (e.g., Cr, Pb) to OC ratios in the sediment layer with maximum OC concentration in 1971 to that in 1996/1997 (Table 4), reveals that about 40–60% of the OC emitted by the JWPCP plant and deposited onto the PV shelf sediments at 6C (and 67–87% at 8C) is still present in the 1971 layer where the OC and metal concentrations peaked. This confirms the half-life of 26 years for outfall-OC deduced above, as an upper limit. A half-life of that magnitude is close to the half-life of DDE on the PV shelf of about 20 years (List and Paulsen, 2000; Drake et al., 1994), suggesting a possible link between DDE disappearance and OC degradation. A half-life of 26 years would require an OC degradation rate of about 1.5–3 mg C cm^{-2} $year^{-1}$ (average 2 mg C cm^{-2} $year^{-1}$), depending on assumptions of reaction order.

Experimental and field observations indicate that about 25% of the OC emitted by the Whites Point outfall is degraded in the water before burial (Myers, 1974; Sweeney et al., 1980), and that outfall particles, as they come out the pipe, contained about 30–35% OC. From these observations, one can also estimate that about 50% ($12\%/0.325/0.75 \approx 50\%$) of the particles deposited on the PV shelf in 1971 originated from the outfall, in agreement with previous estimates (Myers, 1974; Sweeney et al., 1980). Thus, approximately 37% ($\approx 6/(12/0.75) * 100\%$) of the OC resident on a particle discharged from the outfall in 1971 presently resides on that particle in its sediment repository. Given that the sediment layer deposited in 1971 at site 6C currently has a porosity of about 80%, and likely was deposited over a 1.5–2 cm interval (Logan et al., 1989; Paulsen et al., 1999; Santschi et al., 2000b), the 1971 layer therefore lost about 54 mg C cm^{-2} ($= 60$ mg C $g^{-1} * 0.5$ g $cm^{-3} * 1.75$ cm) in 26 years, or, if oxidation would have been a continuous process, about 2 mg cm^{-2} $year^{-1}$. The assumption of continuous organic matter oxidation, even at 30–50 cm depth, is likely not fulfilled, however. As DOC, Fe and Mn concentrations in the pore waters from sites 6C and 8C (Van Cappellen et al., 2000) show, early diagenesis of organic matter, Fe and Mn is most intense in the upper 10 cm of sediment. DOC in the pore water peaks near the sediment surface, Mn at 7 cm, and Fe at 10 cm depth at 6C, with similar depth profiles at 8C. Rates of diagenesis 26 years ago, are, however, not known. Therefore, this half-life of OC of 26 years for outfall-derived OC in PV sediments is a long-term average.

While other sources of OC were clearly of minor importance in 1971, this is not the case at the present time. Therefore, a different approach is needed to estimate present-day OC oxidation rates. Van Cappellen et al. (2000) have estimated OC oxidation rates at site 6C to be about 1130 μmol C cm^{-2} $year^{-1}$, or 13 mg cm^{-2} $year^{-1}$, from modeling pore water profiles of oxygen, sulfate, sulfide, alkalinity, pH, Fe, Mn, nitrate and ammonia. Given the recent sediment accumulation rate of about 0.8–0.9 g cm^{-2} $year^{-1}$ at that site (Santschi et al., 2000a), this would amount to about 15 mg C g^{-1} of sediments or about 1.5% OC, which would presently be lost from the sediments during early diagenesis. Organic carbon oxidation at 6C is, however, significantly accomplished by sulfate reduction (Van Cappellen et al., 2000: 80% at 6C; Berelson et al., 2000: 30% at a nearby site). The higher value of the OC oxidation rates in recently deposited sediments than in the layer deposited in 1971 is likely related to the fact that freshly produced OC is more degradable than the residual fraction of refractory OC from outfall inputs.

Present-day accumulation of OC to the shelf of about 20 mg cm^{-2} $year^{-1}$ (calculated from values given in Paulsen et al., 1999 and Santschi et al., 2000b) is, while an order of magnitude higher than the outfall-derived OC oxidation rate, still only adding a little more than 1% per year to the OC (and trace metal) inventory.

Sediment inventories of trace metals and OC of different cores at different sites, shown in Table 5, provide for spatial and temporal comparisons. Our measured trace metal inventories for the different sites are at the high end of the range of composite values reported by Huh et al. (1992), but very similar to those determined by LACSD (unpublished data), as shown in Table 5. Interestingly, inventories of the different trace metals have remained quite constant over the past decades, indicating that the majority of the inventory was deposited in the 1960s and 1970s. Our OC inventories are, however, significantly higher than some of the previous estimates. For example,

Table 5

Comparison of sediment inventories for trace metal (mg cm^{-2}), organic carbon (OC, mg-C cm^{-2}) and total nitrogen (TN, mg-N cm^{-2}) at sites 3C, 5C, 6C and 8C (calculated down to a depth which was deposited at around 1953; this is 65 cm for the vibracore, or shorter for the other cores, where the core bottom depth was dated to around 1953 using radiochemical methods by Santschi et al., 2000a,b)

Site/Core[a]	[Zn]	[Pb]	[Ni]	[Cu]	[Cr]	[Cd]	[Ag]	[OC]	[TN]	Reference[b]
3C-BC (1996)	14	3	2	5	–	0.3	0.1	1500	60	1
5C-BC (1996)	29	7	2.4	10	–	0.25	0.3	1505	107	1
8C-BC1 (1997)	34.3	7.6	2.4	10.0	17.0	0.95	0.4	1491	94	1
6C-BC4 (1997)	34.6	7.5	2.3	10.8	20.1	0.9	0.4	1225	87	1
6C-VC (1997)	43.9	11.6	3.0	16.4	26.4	1.3	0.55	1557	105	1
6C (1983)	32.5	–	1.8	10.2	18.1	0.8	–	–	–	2
6C (1993)	31.7 ± 2.0	8.5 ± 0.6	2.0 ± 0.3	11.2 ± 0.8	17.4 ± 1.6	1.0 ± 0.06	–	–	122 ± 11	2 ($n = 3$)
6C (1992)	–	–	–	–	–	–	–	1514	–	3
3C (1981)	–	–	–	–	–	–	–	924	–	4
3C (1983)	10.9	–	1.2	5.4	9.6	0.25	–	–	–	2
3C (1993)	10.8 ± 1.1	3.0 ± 0.6	1.4 ± 0.3	4.7 ± 0.8	8.0 ± 1.2	0.3 ± 0.08	–	–	74 ± 9	2 ($n = 3$)
3C (1992)	–	–	–	–	–	–	–	767	–	3

[a] BC = box core; VC = vibra core.

[b] 1: This work; 2: LACSD (unpublished data), which had possibility for core top loss (Lee, 1994); 3: USGS (Lee, 1994); 4: Eganhouse and Kaplan (1988), with possible core top loss.

Myers (1974) estimated OC inventories of about 0.15, 0.25, 0.25, and 0.7 g cm^{-2} for sites 3C, 5C, 6C and 8C, respectively, in 1972, when a large fraction of the total outfall-OC should have already been deposited. Our inventories in cores collected in 1996 at site 3C are also higher than those published by Eganhouse and Pontolillo (2000) for site 3C, collected in 1992/1993. Our data, however, indicate that OC inventories for sites 3C, 5C, 6C and 8C are consistently high, about 1.5 g cm^{-2} (Table 3). A similar value can also be calculated for a site 6C core collected in 1992 by USGS (Table 5). Thus, it appears that some of the previous data underestimated the OC inventory. Given the fact that the OC peak region from our 6C cores likely lost about 50% of the outfall-OC due to oxidation, the discrepancy between the two estimates appears even larger. Non-outfall sources of OC deposited since the early 1980s, the use of low sediment densities used by Myers (1974) for OC inventory calculations, sediment loss during coring (Lee, 1994), and/or sediment heterogeneity could be reasons for the high OC inventories determined in 1996/1997.

It is also important to know what fraction of OC emitted by the outfall was deposited onto PV sediments in 1971. This can be estimated from an average sediment accumulation rate of 0.8 g cm^{-2} year^{-1} (Paulsen et al., 1999; Santschi et al., 2000b), and an observed OC concentration of 6% to 12% (Sweeney et al., 1980) in 1971 in surface sediments covering an area of about 40 km^2 (Lee, 1994; Drake et al., 1994), i.e., 0.8 g cm^{-2} year^{-1} $\times$ (0.06 to 0.12) $\times$ 40 $\times 10^{10}$ cm^2 = 1.9 to 3.8 $\times 10^7$ kg OC year^{-1} for 1971. This estimate can be compared to the OC emission rate from the wastewater outfall in the early 1970s (Fig. 8), which was 165 $\times 10^6$ (kg year^{-1}) $\times$ 0.3 (kg C (kg sewage particles)$^{-1}$) = 5.5 $\times 10^7$ kg C year^{-1}. The fraction of total outfall-OC that was buried in the PV sediments in the early 1970s was therefore at least 35% of the OC outfall discharge. Our estimate for the year 1971 falls in between those of Huh et al. (1992) (12–20%) and Farley (1990) (63%) for the sediments within 20 km from the outfall. These estimates are, however, significantly higher than other estimates (Galloway, 1972; Myers, 1974; Katz and Kaplan, 1981).

4. Summary and conclusions

Not only are a large fraction (~ 35%) of OC and trace metal emissions deposited on the Palos Verdes shelf, the resulting sediment inventories have been relatively constant over the past 10 to 15 years (Table 3), thus indicating that recent additions and losses must have been relatively small, or balance each other. Changes of OC/metal ratios in sediments and comparison to input ratios could therefore be used to estimate an outfall-OC oxidation rate of about 2 mg cm^{-2} $year^{-1}$ since 1971. The half-life of 15–26 years for this outfall-derived OC at sites 3C and 6C, respectively, is surprisingly close to the DDE half-life on the PV shelf (List and Paulsen, 2000), suggesting a possible relationship between the disappearance of DDE and OC degradation. Present-day accumulation of OC to the shelf is about 20 mg cm^{-2} $year^{-1}$ (Paulsen et al., 1999; Santschi et al., 2000b). While this is an order of magnitude higher than outfall-OC oxidation, because most of the OC inventory is deeply buried, it still adds only a little more than 1% per year to the OC (and trace metal) inventory. Due to the close correlation of OC with heavy metals and other contaminants (e.g., DDTs), the same argument likely applies to them, too, despite the fact that they have different sources. While there has been a decrease in OC concentrations buried in the sediments in 1971, no such decrease has been observed for trace metals at site 6C.

While inventories and surface layer concentrations of OC show only small or no differences in the direction away from the outfall (e.g., between 6C and 3C, which are about 5 km apart), trace metal, nitrogen and sulfur inventories and surface concentrations significantly decrease from 6C to 3C, likely indicating multiple sources of OC to the Palos Verdes sediments: (1) aquagenic OC derived from nutrient-enhanced primary productivity in the overlying water column; (2) riverine OC, especially during storms; (3) OC associated with eroded shore-line material; (4) OC from the wastewater outfall; and (5) scavenging of OC from the ocean waters to the underlying sediments. OC from the wastewater outfall is likely also an important contributor (directly or indirectly) to reduced S and N, as well as trace metals, explaining the decreasing concentrations and inventories away from the outfall. OC and trace metal inventories have been remarkably constant since 1981/1983, contrary to reported declines in inventories of other contaminants such as DDTs and PCBs (Lee, 1994; Eganhouse and Pontolillo, 2000) on the Palos Verdes Shelf.

The multiple-source explanation is consistent with the fact that surface concentrations in recently deposited sediments are higher than expected from the outfall emission records. In addition, this explanation accounts for the multiple maxima and minima in the OC, N, S and trace metal profiles. If deposition is modulated by cross-shelf transport processes, which mix and erode sediment previously deposited in shallower parts of the shelf, and re-deposit these sediments in somewhat deeper waters, then the strong correlations we observed between chemical constituents in the PV sediment profiles would be expected. Therefore, the multiple-source and cross-shelf transport explanation provides the most coherent accounting of the complex, and sometimes difficult to recreate, observations from the effluent-affected sediment profiles on the Palos Verdes Shelf.

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