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Trace organic contaminants and their sources in surface sediments of Santa Monica Bay, California, USA

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1 2 3	Manuscript Number: MERE-D-09-0067R1 Revised and submitted to MER 12_22_09
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5	Trace organic contaminants and their sources in surface sediments of Santa Monica Bay,
6	California, USA.*
7	Camornia, Con.
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15	Abetweet
16	Abstract:
17 18	Spatial distribution of selected contaminants in the surface sediments of Santa Monica Bay (SMB), California was investigated. Sediments were analyzed for DDTs (DDT and
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	metabolites), polychlorinated biphenyls (PCBs), polycyclic aromatic hydrocarbons
20 21	(PAHs), linear alkylbenzenes (LABs) and coprostanol. Effluent samples from the Hyperion Treatment Plant (HTP), which discharges treated municipal wastewater
22	effluents into SMB, were also analyzed. The inter-correlation in the distribution trends of
23	contaminants was examined. The concentrations of contaminants were interpolated in a
24	geographic information system to visualize their spatial distribution in the Bay.
25	Inventories of the contaminants were also estimated.
26	The concentrations of coprostanol, LABs and PCBs are very high only in the vicinity of
27	the sewage outfall whereas PAHs and DDTs occur widespread in the Bay. The poor
28	correlation of DDTs with LABs, PAHs or coprostanol content confirms the historic
29	origin of DDTs and their absence in the contemporary wastewaters. Moderate correlation
30	of DDTs with PCBs implies historic deposits as a major origin of PCBs. There are hot
31	spots of DDTs at water depths of 60 and 100 meters and the inventory of DDTs in Bay
32	sediments is insignificant compared to that estimated in the Palos Verdes Shelf which
33	extends from the southern edge of Redondo Canyon around Palos Verdes Peninsula. The
34	concentration of toxic contaminants was examined according to published sediment
35	quality guidelines. About 20 stations contain p, p'-DDE and/or total DDTs above ERM
36	and, PCBs between ERL and ERM indicating potential for adverse biological effects.
37	and, I elbs between little and little indicating potential for adverse biological effects.
38	Keywords: DDT, polychlorinated biphenyls, polycyclic aromatic hydrocarbons, linear
39	alkylbenzenes, coprostanol, Santa Monica Bay, sediment pollution, organic compounds
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1. Introduction

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Coastal sediments in southern California receive organic pollutants from a variety of sources such as sewage outfalls, storm runoff, dredge disposal and industrial wastes from the adjacent major urban centers. Heavy contamination of sediments, particularly with DDTs in the southern California coast in the 1950-1970s, the Clean Water Act enforced in 1970-71 and the ban on DDTs in 1971 resulted in the development of contaminant monitoring programs (Brown et al., 1986; McDermott et al., 1974; Mearns et al., 1991; Young et al., 1977). Specifically, the Environmental Monitoring Division (EMD) of the City of Los Angeles' Hyperion Treatment Plant (HTP) began monitoring the quality of waste water discharged to SMB as well as the quality of sediments impacted by the outfall starting in the 1970's (i.e., CLA EMD, 1997;1999; SCCWRP Reports, 1972-1989). Heavily contaminated sediments, now buried in deeper strata below sediment-water interface, could however, be remobilized by periodic re-suspension events (Stull et al., 1996 and refs therein). This has been documented in the widespread presence of DDT metabolites in sediment cores from San Pedro, Santa Monica, Santa Barbara, Santa Cruz and San Nicolas Basins and in shallow waters in the Southern California Bight even after the ending of the discharges of wastes from the manufacturing company in 1970 (Shokes and Mankiewicz, 1979; Stull et al., 1986; Venkatesan et al., 1980; 1996; Zeng and Venkatesan, 1999). Designated historic deep ocean dumpsites could be yet another chronic source of DDTs to the sediments of the Santa Monica Basin (Chartrand et al., 1985; Venkatesan et al., 1996).

PCBs accumulating in sediments and their subsequent steady decline in the concentration profiles of the subsurface strata have also been recorded in several studies (Stull et al., 1986; 1988; Word and Mearns, 1979; Young and Heesen, 1978). More recent data on DDTs and PCBs in sediment cores from shallow and deeper Santa Monica and San Pedro basins, confirm the impact of ending of PCB uses and improved waste water technologies (Eganhouse and Pontolillo, 2000; Venkatesan, 1998). Multiple suites of new chemical markers have also been used to distinguish origins of different contaminant inputs to the Santa Monica Bay (SMB) waters (i.e., Chalaux et al., 1992). For example, linear alkylbenzenes (LABs) have been used in the synthesis of laundry detergents since the 1960s. The unreacted residual LABs are discharged to coastal areas almost exclusively from sewage outfalls and are considered reliable sewage tracers (Eganhouse et al., 1983; 1988; Eganhouse and Pontolillo, 2008). Coprostanol (5βcholestan-3β-ol) is another well-known sewage marker formed from the enteric reduction of cholesterol which is a major sterol in mammalian feces and discharged into the coastal environment via municipal wastewater outfalls (i.e., Takada and Eganhouse, 1998; Venkatesan and Kaplan, 1990).

Spatial and temporal distribution of some of the above listed contaminants have been examined in several, ²¹⁰ Pb dated, sediment box cores from Santa Monica Bay previously by Bay et al. (2003). As part of a multidisciplinary project conducted at UCLA on the Los Angeles Basin Watershed, surface sediments were collected in three successive years to establish current concentrations of a suite of contaminants from 42 stations encompassing the entire SMB (NCERQA Final report to EPA, 2002). Here, we present the concentrations of DDTs [o, p' and p, p' isomers of 1,1,1-Trichloro-2,2-bis(p-chlorophenyl)ethane, DDT] and the metabolites, DDE and DDD, polychlorinated

biphenyls (PCBs), polycyclic aromatic hydrocarbons (PAHs) and linear alkylbenzenes (LABs) in the surface sediments from SMB. Also presented here for the first time are the data on coprostanol (sewage marker) from these stations. The concentration data of contaminants were interpolated using a Geographic Information System (GIS). The interpolated data from three-year collection clearly illustrate the spatial trend in the Baywide distribution of the contaminants in surface sediments. The inter-correlation of the distribution trends among contaminants (especially with respect to DDTs) was investigated to infer their possible sources in the Bay. The spatial distribution of sedimentary contaminants established in this study is crucial to understanding the dynamics of the watershed and for wastewater management decisions and regulatory purposes because the sediments serve as transfer pathways of contaminants to higher trophic organisms.

2. Study location and sampling

Surface sediments were collected by the Hyperion Monitoring Program personnel from thirty NPDES (National Pollutant Discharge Elimination System) sediment chemistry stations during summer of 1997. Five stations were re-sampled during summer of 1998. Seventeen samples from selected NPDES stations and a few random stations were collected in 1999 (Fig.1). Some of the sampling sites were from the HTP 7-mile and 5-mile outfalls. Sewage sludge was disposed from the 7-mile outfall (positioned at head of the canyon) from 1957 to 1987 and this terminus is considered as a major historic source of contaminants to SMB (Schafer, 1989). 5-Mile outfall discharging treated wastewater began operation in 1959 and a full secondary treatment was commissioned effective from 1998.

The sediments were collected using a Van-Veen grab sampler from water depths of ~18 to 150 meters. The upper 2 cm (undisturbed layer) sediment from the top 10 cm was stored frozen in pre-cleaned I-Chem jars until analyses for the target compounds listed in Table 1. In addition, two (24-hr composite) grab samples of final effluent were collected in October of 1997 and March of 2001, respectively, from the plant (HTP). The effluents were analyzed only for LABs and sterols.

3. Methods

Solvent extraction and compound class separations were performed following the method of Venkatesan (1998). Thawed wet sediment (~20g) was equilibrated by sonication with a recovery surrogate spike mixture appropriate for the PAHs, LABs, chlorinated hydrocarbons and sterols (4-terphenyl-d₁₄, hexamethylbenzene, 1-phenyldodecane, 4,4'-dibromooctafluorobiphenyl, PCB BZ155 and $5\alpha[H]$ -androstanol). Sediments were extracted with methanol and then with methylene chloride (CH₂Cl₂) in a Virtis Homogenizer. The hexane layer partitioned from methanol phase and saturated sodium chloride solution was combined with the CH₂Cl₂ extract, rotary-evaporated, dried with anhydrous sodium sulfate and concentrated to 2 ml. Asphaltenes were precipitated with hexane and after elemental sulfur removal with activated copper granules, the concentrate was subjected to silica/alumina column chromatography to

isolate the aromatic fraction containing PCBs, chlorinated pesticides, LABs and PAHs and a polar fraction containing sterols including coprostanol and epicoprostanol ($(5\beta$ -cholestan- 3α -ol).

Two to 4 litre samples of final effluent were extracted with CH₂Cl₂ after breaking up the emulsion by adding sodium chloride. The filtered CH₂Cl₂ layer was then rotary-evaporated and processed as above for determination of LABs and sterols.

PAHs were quantitated by gas chromatography/mass spectrometry (GC/MS) from the extracted ion current profiles using deuterated internal standard mixtures after Venkatesan et al. (1987). A Finnigan 4000 Mass Spectrometer equipped with a 30 m DB-5 fused silica capillary (0.25 mm I.D., 0.25 micron film, J&W Scientific) column was used. GC/MS operating conditions are as follows: injector temperature 290°C; transfer line temperature 280°C; initial oven temperature 35°C; initial hold time 6 min; 4°C/min to 280°C; 2°C/min to 310°C. EM voltage: 1400v; electron energy: 70 eV. Source temperature 240°C; scan speed 2s scan⁻¹ from 50 to 550 amu. A Galaxy 2000 for Windows (Version 10.50, from Los Gatos Circuits (LGC), CA) data system was used to acquire data. A five-point response factor calibration curve was established for quantitation. Method detection concentrations (MDLs) of individual PAHs ranged from 0.1 to 1.0 ng/g with the exception of indeno(1,2,3-cd)pyrene which was 2 ng/g.

LABs were determined by GC/MS under conditions as above for PAH and quantitated from extracted ion current profiles after Eganhouse et al. (1983) and Phillips et al. (2001). MDL of individual LABs ranged from 0.05 to 0.1 ng/g. Chlorinated hydrocarbons (pesticides and PCBs) were determined after Venkatesan (1998) using a Varian 3500 GC (gas chromatograph) with dual electron capture detectors (ECD) in the splitless mode using two columns, DB-5 and DB-1701, with same specifications as above. The DB-5 was the working column and DB-1701 was the confirmation column. GC/ECD operating conditions were as follows: injection temperature 260°C, split open after 0.75 min; detector temperature 330°C; temperature program 1 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 was used as carrier gas at 40 cm/sec. Nitrogen at 30 ml/min was used as make-up gas. A four-point response factor calibration curve was established. 2,4,5,6-tetrachloro-m-xylene and PCB BZ198 were used as retention time markers. Because of the better resolution, some compounds, i.e. BZ 153, 105 and o, p'-DDT were always quantitated on DB-1701 column; all other compounds were quantitated on DB-5. A Star Chromatography Workstation (Version 3.0, Varian Analytical Instruments) was used to process the data. MDL of individual PCBs spanned from 2 to 6 pg/g with the exception of BZ 8 which was 11 pg/g. Parent DDTs and the metabolites exhibited MDLs ranging from 2 to 4 pg/g. Of the 16 chlorinated hydrocarbon pesticides measured (including aldrin, dieldrin, heptachlor etc.), only the DDTs and the metabolites will be discussed here. Discussion/interpretation will focus only on the total DDTs, PCBs, LABs, PAHs and coprostanol + epicoprostanol.

An aliquot of the polar fraction was derivatized with BSTFA with 1% TMCS to silylethers and determined using a Varian Model 3400 GC equipped with a fused silica capillary column (DB-5 as above) using a Flame Ionization Detector following the method of Venkatesan et al. (1986). Compound identification of the derivatized fraction was confirmed by GC/MS under conditions described above for PAHs. Of the six sterols and coprostanone (Table 1), only coprostanol and epicoprostanol (known as

coprostanols from now on) will be discussed in detail here. MDLs of these two sterols are 4 and 5 ng/g respectively.

Quality control samples such as procedure blank, duplicate, matrix spike and Standard Reference Material (NIST) were processed with every batch of field samples to evaluate the accuracy of PAHs, PCBs and chlorinated hydrocarbons. Standard reference materials were unavailable for coprostanol and LABs at the time of this study. The data are reported in units of ng/g or $\mu g/g$. Target analytes are listed in Table 1.

Total concentration of contaminants in the sediments from all stations including replicate sampling at the same station in different years were mapped by the year after importing the data into ArcGIS® geographic information systems (GIS). To visualize their spatial distributions and patterns in the Bay, the concentration of the contaminants were interpolated in ArcGIS using an inverse distance weighted (IDW) interpolation method (Chang, 2008). The contaminant concentration between sampling stations was estimated from the station's sampling data and their contribution depends on their distance from the point under interpolation (Figs. 2-6). The extent of valid interpolation area is confined to the rectangle area bounded by all the sampling points. The interpolation near sampling points is more reliable than farther away from.

4. Results and discussion

The same stations sampled in two or three successive years (C1, C6, E3, E6, E10, B6 and Z2) exhibited concentrations of the target analytes which were similar or of same order of magnitude and hence, only the average data from analyses of those samples collected in multiple years are presented in Tables 2-4 for discussion. The spatial distributions of the contaminants in the Bay after interpolation are illustrated in Figs 2-6.

4.1. Spatial distribution of DDTs in the Santa Monica Bay

Concentration of total DDTs (or DDTs = Σ DDT = Sum of DDT and metabolites, o, p'- and p, p'-DDE, -and DDD) ranges from 1-157 ng/g dry sediment (Fig. 2, Table 2). The Σ DDT contents from the NPDES and random stations analyzed in the current project compare well with those reported from the Monitoring Division of HTP (CLA EMD 1997; 1999). However, it is important to recognize that the analytical protocol followed in their laboratory is different from ours. The values from UCLA and HTP, for most of the common stations, are of same order of magnitude and vary, at the most, by 30%. For the remaining stations the values are within a factor of two. Sediments along the 30 m contour contain lowest concentrations of DDTs, consistent with their coarse grain size of the particles near-shore (CLA EMD 1997; 1999) as also evident from visual inspection of the sediment. Concentrations of DDTs are high at stations B10, D2, D3, E3, E8 - E10 along the 100m isobath which are enriched in fine grain sediment. Concentration of DDTs peaked at sediments from station E10 (157 ng/g, average of two years data). Similar to the findings of Bay et al. (2003), stations around the HTP 7-mile outfall terminus (ie., HR1, HR51 and E6) also contain high concentrations of DDTs. This reflects the modest amount of DDTs manufacture wastes discharged in the past via HTP-5 and 7-mile outfalls from the late 1950s when they commenced operation (Chartrand et al., 1985; Schafer, 1989).

231 ΣDDT concentrations measured by the Hyperion laboratory during 1987-1999 and the 232 present study show that the DDTs in the sediment strata around the HTP-5 mile outfall 233 has not diminished significantly over the decade and has been fluctuating between 10 to 234 30 ng/g as found at stations Z1 and Z2 (CLA EMD, 1987 to 1997; 1999). Further, 235 relatively higher amounts of DDTs (50-100 ng/g) are still being detected in the sediments 236 from the vicinity of the HTP 7-mile sludge disposal terminus (stations E6, HR1 and 237 HR51), with sediments at station HR51 containing the highest concentration among the 238 three stations, even after a decade of the cessation of sludge discharge in 1987. However, effluent loading of DDTs from the HTP 5-mile in 1987-1997 was below 0.003 kg/day 239 240 and these compounds are not even detected in the effluent samples collected in 1998, 241 after commissioning full secondary treatment (CLA EMD, 1999). This confirms that 242 DDTs in the Bay sediments originate primarily, if not exclusively, from historic deposits. Apparently, historic DDTs (pre-1971) are still being chronically remobilized from the 243 244 sediments from the 7-mile sludge disposal site discharge point as previously noted 245 (Venkatesan in NCERQA Final report to EPA, 2002; Bay et al., 2003). 246

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Although DDTs were found in all samples, relatively greater accumulation of DDTs is observed at a few stations in the Bay hot spots. There is no evidence to suggest any illegal short dumping of DDT manufacturing wastes in the Bay similar to the ones detected in the Santa Monica/San Pedro Basins (Chartrand et al., 1985; Venkatesan et al., 1996). It is known that lipid components, having low water solubility, exhibit strong affinities for fine-grained sediments and are redistributed by contaminant desorption, current advection and re-deposition in near-shore bays as well as deeper waters of the Basins (Noble et al., 2002; Jones et al., 2002). This could result in hot spots in the Bay around water depths of 60 -100 meters with preferential deposition of organic contaminants including DDTs. These stations are located in the southeastern region of the SMB just north of Redondo canyon, i.e., E9, E10 and B10, farther away from the HTP outfalls. Part of the DDTs could have been transported from Palos Verdes Shelf via prevailing subsurface currents (California Countercurrent), advecting effluent particles up the coast along the bathymetric contours (Hickey, 1993; Marchesiello et al., 2002; Stull et al., 1996). Zeng and Venkatesan (1999) previously observed that the concentration of p, p'-DDE in the surface sediments of Palos Verdes shelf 1) correlated well with those of water column samples from the same stations and 2) exhibited a gradient from the outfalls to offshore. They, therefore, suggested that historically deposited DDTs in the Palos Verdes shelf have been remobilized upward in the sedimentary strata and subsequently resuspended into the water column. This scenario is more likely, considering that PVS sediments contain anomalously high concentrations of DDTs, discharged in the past from LACSD (Los Angeles County Sanitation District) outfall (Eganhouse et al., 2000; Stull et al., 1996). The contaminated particles from the deposits on the Palos Verdes Shelf could be dispersed upward by bio-diffusion, crossing Redondo canyon, and then removed to wider marine environment including SMB to the northwest by strong flow events (Mearns et al., 1991; Niedoroda et al., 1996; Zeng and Venkatesan, 1999; Wiberg and Harris, 2002; Sherwood et al., 2002). In summary, DDTs are found at different concentrations throughout the Bay and at relatively high concentration in the proximity of the Hyperion outfall. There are hot spots of higher DDTs concentration from transport of material most likely from the Palos Verdes Shelf into the sedimentary

regions in the SMB where conditions are conducive to organic matter accumulation (Lee and Wiberg, 2002).

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4.2 Other anthropogenic marker compounds:

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Total PCBs (or PCBs= Σ PCB=sum of the congeners, listed in Table 1) concentrations in the sediments range from 2 to 136 ng/g. They are present in relatively high amounts near the 7-mile outfall terminus (Fig. 3). Their concentrations decline steeply away from the outfall terminus. Ten of the 42 stations (stations A1, A2, A3, B1, B5, C5, C7, C8, D1 and FA20) have sediments containing less than 10 ng/g of PCBs. Negligible loading or absence of PCBs is noted in the HTP 5-mile effluent collected in 1998 (CLA EMD, 1999). In contrast, ΣPCBs concentrations are high in the sediments at the 7-mile outfall (i.e., highest PCBs content in station E6 and HR51). This would imply HTP historic deposits being the major source of PCBs in the Bay similar to that of DDTs. PCBs were in large use especially in the early 1970; a ban on their production was enforced in 1977 (U.S. EPA, 1984). Non-point sources such as refuse incineration, atmospheric transport and industrial effluent runoff could also contribute PCBs to the coastal zone (Atlas et al, 1986; Yasuhara and Morita, 1988). However, in SMB sediments, contribution from these non-point sources appear to be not as important as that from Hyp 7-mile deposits. There are no PCBs hot spots in the Bay unlike that of DDTs which is consistent with the rapid deposition of PCBs at the discharge point. This disparity in spatial distribution trends for PCBs and DDTs reiterates our earlier argument requiring a second significant source for DDTs in SMB sediments farther away from HTP discharges, especially, in the area near Redondo canyon.

Total LABs (or LABs = Σ LAB=sum of all the isomers from carbon number 11 to 14, Table 1) and coprostanols (sum of coprostanol and epicoprostanol) occur at significant concentrations in sediments near the HTP 5-mile outfall, Z1 and Z2, and at much higher concentrations at stations, HR1 and HR51 (near HTP 7-mile sludge disposal site) with the latter containing the highest amounts. ΣLAB concentrations in the Bay ranges from <0.01 to 10 µg/g (Fig. 4) and are comparable to the concentrations reported by Bay et al. (2003). Coprostanol concentrations vary from 0.065 to 46µg/g (Fig. 5) with highest concentrations at the 7-mile outfall and significantly high concentrations near the 5-mile outfall. The concentrations of LABs and coprostanols are much lower, by one to two orders of magnitude, at other stations in SMB relative to the stations at the outfall (i.e., E6, HR51). Less than 10 ng/g of LABs and coprostanols are found at stations, A1 and A2, at the 30 m water depth. While DDTs were found at trace concentrations or mostly absent in the modern day (HTP 5 Mile) effluents, LABs and coprostanols occur at significant concentrations in the effluents, i.e., 5.2 and 0.13 µg/l of LABs and 154 and 5.2 µg/l of coprostanols in 1997 and 2001 respectively (the values presented here being the average of the two collections in the same year). The unusually high abundance of coprostanol in the HTP effluents is comparable to those reported in partially treated sewage (Fig. 5 in Takada and Eganhouse, 1998). Also note that the effluent collected from HTP 5-mile in June of 1987 contained 158 µg/l of coprostanol (Venkatesan and Kaplan, 1990) which compares well with that of the 1997 samples in this study (Table 2). The 2001 effluents reflect significantly reduced concentrations of the contaminants after the full secondary treatment at HTP which became effective in 1998. This clearly

indicates that LABs and fecal sterols in the surface sediments in SMB derive mainly from pre-1998 wastewater effluents in addition to the possible remobilization from the surface sediments, contaminated from former Hyp 7-mile sludge discharges.

Percent coprostanol in total sterols in the sediments ranges from 3 to 58. Stations A1, A2, A3, B1, B3, B8, C1 and C4 which are in shallow waters (~30 m or less) and mostly coarse-grained, exhibit values between 3 and 8%. All other stations especially from water depths between 60 and 100 m have values > 20\% with even higher percentage values in the sediments near the outfall vicinity and in fine grain sediments. Sediments from stations E6 and HR51 exhibit highest ratios (58 and 53% respectively). The range in values clearly demonstrates sewage impact in all of the bay sediments and the high values at E6 and HR51 are consistent with the report of Venkatesan and Kaplan (1990). They found that the sewage sludge and the sediment samples collected near HTP 7-mile discharge point contained total sterols as much as 2 mg/g of dry sediment, of which coprostanols constituted a high percentage, between 50 and 70%. The higher the percentage of coprostanol in total sterols, greater is the proportion of sewage-derived carbon in the sediments. With the exception of station A1 where epicoprostanol is absent, all stations exhibit coprostanol /epicoprostanol ratio ranging from 2.1 to 15.9 and the effluent samples had ratios between 4 and 5. These values compare favorably with those measured by Venkatesan and Santiago (1989) and Venkatesan and Kaplan (1990) for Santa Monica Basin sediments and HTP effluents who attributed ratios close to or larger than one (greater proportion of coprostanol) to human wastes. Based on their study of sterols in different marine mammalian feces which contained epicoprostanol predominating over coprostanol, Venkatesan and Santiago (1989) also concluded that marine mammalian feces, especially from baleen whales contributed to the unique sterol profiles in the Antarctic sediment cores from Bransfield Strait and McMurdo Sound. Later, questions have been raised regarding the utility of this ratio in differentiating marine and terrestrial sources or *in situ* processes, especially when these sterols are present at low concentrations (Sherblom et al., 1997). However, when coprostanol data and the above discussed ratios in SMB sediments are considered along with distribution of LABs, which are synthetic compounds/ sewage markers, it is clear that the coprostanols in the sediments of SMB are mainly characteristic of municipal wastes and sludge rather than from marine mammals.

A sharp decline in coprostanols and LABs concentration with increasing distance from the HTP outfall suggests a rapid deposition of sewage-derived organic components in the vicinity of the discharge zone. The interpolated spatial distribution contours of LABs and coprostanols originating from the outfalls are very similar in the Bay, attesting to their common and exclusive major source from the HTP 5- and 7-mile discharges and the similar properties controlling their transport. The absence of abnormally high concentrations of wastewater-derived contaminants such as LABs or coprostanol at stations farther away from the outfalls suggests that they are quickly deposited in the outfalls vicinity, degraded and/or diluted before reaching the canyon. In contrast, the wide spread occurrence of DDTs in the bay surface sediments at chronic levels, yet exhibiting a gradient from the HTP outfall, would indicate resuspension of DDTs from the discharge point (Zeng and Venkatesan 1999). This also implies that not all of the DDTs in the hot spots could have originated from the historic Hyperion discharges and that they should have been derived from an additional source as discussed in section 4.1.

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Total PAHs (or PAHs= Σ PAH = sum of PAH compounds listed in Table 1) concentration ranges from 0.2 to 11 µg/g and compares favorably with that reported by Bay et al. (2003). The highest PAHs concentration occurs at the 7-mile outfall. No consistent gradient in the total PAHs content was evident among other stations with increasing distance from the HTP 5- and 7-mile outfalls (Fig.6). PAHs appear to be more widespread in the Bay than any of the other components measured. This may be because, in addition to that from HTP outfalls, PAHs could also be derived in varying proportions from multiple sources such as Monterey shale erosion, natural oil seeps, petroleum residues from storm runoff, harbors and urban drainage channels and from atmospheric inputs (Cross et al., 1987; Eganhouse and Gossett, 1991; Eganhouse and Venkatesan, 1993). We found PCBs, LABs and PAHs in most of the sediments sampled. Although, Bay et al. (2003) also found high concentration of these compounds near the outfalls, they detected LABs only in one or two stations away from the outfall and PAHs only in one station off Ballona Creek. This difference in observation between the two studies may partly be due to the wider coverage of surface sediment sampling in the Bay in the current investigation.

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4.3: Inter-correlation among contaminants:

Scatter plots between the suite of chemical markers and correlation coefficients obtained by linear regression help confirm the source of different contaminants (Fig. 7). As expected, the poor correlation between ΣDDT and ΣLAB or coprostanols (r = 0.302) and 0.318 respectively), confirms the major historic origin of DDTs and their absence in the contemporary sewage effluents. Similar poor correlation between ΣDDT and ΣLAB $(r^2=0.14, Fig. 4. in Phillips et al., 1997)$ was also found in sediments from the southern region of San Pedro Shelf, indicative of different sources for the DDTs and LABs. Percent DDEs in Σ DDT in the surface sediments is uniformly high (71-91), which is similar to that reported ~ 30 years ago by MacGregor (1976) and later in the study of Zeng and Venkatesan (1999). Our findings on DDTs distribution in SMB are also consistent with the elegant dechlorination studies of DDE on the Palos Verdes Shelf (Eganhouse and Pontolillo (2008). Their field data suggest that p, p'-DDE is persistent on a decadal scale and that in situ rates of reductive dechlorination of p, p'-DDE is much lower than, by factors of 2 to 4, those observed by Quensen et al. (2001) in comparable laboratory microcosm experiments. The presence of DDTs and the metabolites in the surface sediments of SMB in the current study demonstrates that historic discharges from the HTP outfalls are still being remobilized by bioturbation as well as physical processes such as sediment mixing and resuspension.

 Σ LAB and coprostanols, in contrast to DDTs, covary with each other exhibiting excellent correlation (r=0.955) corroborating their common origin from HTP 7- and 5-mile outfalls (Fig.7). Eganhouse and Sherblom, (2001) examined the sources of contaminants in Boston Harbor along similar lines. They found that Σ LAB and coprostanol were highly correlated indicating that they both derive from sewage treatment plant that discharged sludge into the harbor. Σ PAH are also highly correlated with Σ LAB and coprostanol (r=0.877 and 0.827, respectively, Fig.7) in SMB sediments, but were only moderately correlated with DDTs (r=0.514, plot not shown). This is consistent with the previous observation (Cf: 4.2) that the distribution contours of PAHs

- are more akin to that of the LABs and coprostanol than that of DDTs (Fig. 6). However,
- PAHs in SMB sediments could reflect a mixed input from HTP 7-Mile as well as HTP 5-
- 417 Mile outfalls and other varied multiple sources as discussed above (Cf 4.2). The
- 418 concentration of Σ PCB correlates only moderately with Σ DDT (r=0.587). Similar
- moderate correlation between ΣDDT and ΣPCB has previously been found in sediments
- 420 from the southern region of San Pedro Shelf (Phillips et al., 1997). In contrast, ΣPCB
- 421 correlates strongly with Σ LAB, coprostanols and Σ PAH (r=0.837,0.812 and 0.735
- respectively; plots not shown) suggesting that most of the PCBs in sediments are also
- mainly derived from HTP 7- and 5-mile outfalls. Concentrations of Σ PCB in the
- sediments of Boston Harbor exhibited a high correlation with coprostanol concentrations
- 425 (r²=0.71) suggesting sewage as a major source of PCBs (Eganhouse and Sherblom,
- 426 2001). A portion of PCBs in SMB also probably derives from non-point sources
- containing industrial wastes (Hom et al., 1974) and atmospheric transport (Atlas et al.,
- 428 1986). In summary, moderate to poor correlation of ΣDDT with all other contaminants
- investigated here, calls for an additional source to explain the hot spots of DDTs at least
- in some parts of SMB (Cf: 4.2).

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4.4. Current emission of LABs and coprostanol to the Bay:

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- In 1997, approximately 6.7 kg/day of LABs and 215 kg/day of coprostanols were
- discharged in the effluent from the HTP 5-mile (based on the average $\mu g/l$ of the
- component present in the two effluent collection (Cf: Table 2) multiplied by the average
- 437 24 hr composite flow for the days of collection). This compares favorably with the value
- of 205 kg/day of coprostanol in the HTP 5-mile effluent collected in 1987 (Venkatesan
- and Kaplan, 1990). The effluent samples collected in 2001 (Table 2), after the
- introduction of full secondary treatment at HTP 5-mile (effective from 1998), contained
- only < 1 and 5.2 kg/day respectively of LABs and coprostanols. This is one to two orders
- of magnitude less than that discharged during '87-'97. No PAHs were detected in the
- post-full secondary effluents (CLA EMD, 2001-2002). Although the surface sediments
- from SMB were collected from 1997-1999, the presence of these sewage tracers in
- significant amounts is clearly characteristic of their major origin prior to 1998 (i.e., pre-
- full secondary treatment). The ²¹⁰Pb dating of sediment strata of sub cores corresponding
- to calculated ages from 1900 to 1997 (surface) showed that sediment accumulation rates
- could vary from 0.19 -0.37 cm/yr at stations in water depths greater than 50 m and farther
- removed from the outfall, to 2.28 cm/yr close the outfall vicinity (Bay et al., 2003). Since
- 450 the samples analyzed here are 2 cm surface grab sediment cuts collected from 1997 to
- 451 1999 and not fine resolution core sections, they would reflect an integrated value of
- 452 contaminants in the sediment horizon a few years predating 1997. It is also likely that an
- 432 Contaminants in the sediment norizon a few years predating 1997. It is also fixely that an
- 453 unknown proportion of these compounds in the Bay have their origin in the sludge field
- by chronic remobilization and redistribution from the HTP 7-mile discharge site which
- was terminated in 1987.

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4.5. Inventories of the contaminants:

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Inventories of selected contaminants in the top 2 cm of the SMB sediments were estimated from the concentration data (Table 2) and extrapolated to the entire bay assuming a surface area of 550 km² (Sommerfield and Lee, 2003). The calculations show that, on an average, about 0.6 metric tons of total DDTs could be present in the top 2 cm of the entire Bay as presented in Table 3. Assuming the same concentration of DDTs, it is estimated that, on an average, at least about 3 metric tons of total DDTs could be present in the top 10 cm of the entire Bay (range: 0.08-12.5 m. tons). This is relatively insignificant compared to that estimated to be present in the Palos Verdes Shelf. For example, in 1989, ~210 tons of DDTs was estimated to be present in the Palos Verdes Shelf and the slope and that an average of 6.3 tons/year was being remobilized and reintroduced into the marine environment (Niedoroda et al., 1996). They also estimated that ~ 0.6 tons/year of the 6.3 tons/year, released from the zone of loss, may account for the increase in sediment DDTs to the northwest of Palos Verdes Peninsula, along the shelf towards SMB. This could explain the source of the hot spots of DDTs detected in the southeastern region of the SMB near Redondo canyon as discussed earlier (Cf: 4.1). The inventory of total PCBs is comparable to DDTs and the maximum inventory is found at station E6 which is in the vicinity of the 7-mile outfall, documenting its major origin in the historic discharges. Inventories of PAHs and LABs are two orders of magnitude greater than that of DDTs and PCBs and their maximum inventories at HR51 correlates with their source in the sludge discharge until 1987 and in modern sewage effluents (Table 2).

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4.6. Sediment toxicity estimates:

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The concentration of toxic contaminants was examined according to the sediment guidelines suggested by Long et al. (1995) from their results on laboratory and field tests conducted throughout the country. The two guideline values, ERL and ERM, delineate three concentration ranges for a particular chemical or a group of chemicals (Table 4). Concentrations of a chemical below ERL define the range where adverse biological effects to living resources would rarely be observed. Concentrations equal to or above the ERL, but below the ERM would signify that such effects would occasionally occur. Finally. > ERM values would imply the range within which such effects would frequently occur. Long and MacDonald (1998), however, noted that for most substances the incidence of adverse biological effects ranged from 0 to 16%, while total DDTs were exception for which 48% of the incidences showed adverse biological effects at levels below threshold effects concentrations. Caution should, therefore, be exercised in the interpretation of the ERM concentrations of DDTs. Applying these criteria to the SMB sediments, 16 to 20 stations (generally from 100-m contours, most of which are located in the southeast of the Bay and a few close to the HTP outfalls), contain p, p'-DDE and/or total DDTs above the ERM (indicating potential for adverse biological effects). Based on the arguments of Long and MacDonald (1998), described above, this may be considered as a very conservative estimate of ERM with respect to DDTs. More than 50% of the stations sampled exhibit concentrations of DDTs between ERL and ERM. Slightly less than 50% of the stations contain total PCBs at concentrations between the ERL and ERM

where adverse biological effects could occur occasionally. This needs serious consideration, especially, in view of the findings of Greenstein et al.(2003) who reported significant negative correlation between sea urchin fertilization and the concentration of PCBs in sections of sediment cores from SMB. Most of the stations contain individual and total PAHs below ERL, signifying generally better sediment quality in SMB with respect to PAHs relative to DDTs and PCBs.

Total DDT concentrations in SMB sediments are at least an order of magnitude less than in the sediments of Palos Verde Shelf. It is not clear from the comparison of the decadal data (CLA EMD Reports from 1987-2002; this study) whether the contaminants would be gradually buried in the subsurface strata of the Bay in the next few decades, when they will no longer be bioavailable.

5. Conclusions

The distribution contours of LABs and coprostanols are very similar, clearly indicating their common origin in contemporary municipal wastes and a similar dynamics of transport in SMB sediments. The spatial distribution of PAHs and PCBs are, however, somewhat different from wastewater markers implying varied mixed input sources in addition to that from municipal wastes and historic deposits. DDTs are found throughout the Bay and at relatively high concentration in the proximity of the Hyperion outfall. The widespread distribution of the contaminants in SMB reflects their lateral transport. DDTs can be obviously linked to HTP historical discharges. However, the disparity in the spatial distribution trends between DDTs and PCBs as well as DDTs hotspots near Redondo canyon are likely related to the remobilization /dispersal of DDTs from Palos Verdes shelf. Generally DDTs are found at lower concentrations in SMB sediments relative to the Palos Verdes Shelf. Yet, nearly 50% of the stations sampled in SMB contain DDTs concentrations greater than ERM and PCBs concentrations between ERL and ERM. Therefore, chemical analyses of major environmental compartments (i.e., water, sediments and fauna) in SMB must be continued to establish the presence, concentration and loading of the target contaminants to assess the status/health of the ecosystem. Such an integrated approach will lead to an understanding of possible pathways toxicants might take which will help in future pollution control measures.

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7. References

554555

- 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.
- Ballschmiter, K., Zell, M., 1980. Analysis of polychlorinated biphenyls by capillary gas
- chromatography. Fresenius' Zeitschrift für Analytische Chemie 302, 20-31.
- Bay, S. M., Zeng, E. Y., Lorenson, T. D., Tran, K., Alexander, C., 2003. Temporal and
- spatial distributions of contaminants in sediments of Santa Monica Bay, California.
- Marine Environmental Research 56, 255-276.
- Brown, D.A., Gossett, R.W., Hershelman, G.P., Ward, C. F., Wescott, A. M., Cross, J.
- N., 1986. Municipal wastewater contamination in the southern California Bight: Part I -
- Metal and organic contaminants in sediments and organisms. Marine Environmental
- 566 Research 18, 291-310.
- 567 Chalaux, N. Bayona J. M., Venkatesan M. I., J. Albaiges. 1992. Distribution of
- surfactant markers in sediments from Santa Monica Basin, Southern California. Marine
- 569 Pollution Bulletin 24, 403-407.
- 570 Chang, K., 2008. Introduction to Geographic Information Systems, 4th ed. McGraw-Hill
- 571 Companies, Boston, USA, pp. 334.
- 572 Chartrand, A. B., Moy, S., Safford, A. N., Yoshimura, T., Schinazi, L. A., 1985. Ocean
- 573 Dumping Under Los Angeles Regional Water Quality Control Board Permit: A Review
- of Past Practices, Potential Adverse Impacts, and Recommendations for Future Action.
- Report from California Regional Water Quality control Board, pp. 47.
- 576 CLA EMD, (1987-2002). (City of Los Angeles. Environmental Monitoring Division).
- 577 Santa Monica Bay Annual or Biennial Assessment Report: Hyperion Treatment Plant,
- 578 Los Angeles, CA, USA.
- Cross, J. N., Hardy, J. T., Hose, J. E., Hershelman, G. P., Antrim, L. D., Gossett, R. W.,
- 580 Crecelius, E.A., 1987. Contaminant concentrations and toxicity of sea-surface microlayer
- near Los Angeles, California. Marine Environmental Research 23, 307-323.
- Eganhouse, R. P., Venkatesan, M. I., 1993. Chemical Oceanography and Geochemistry,
- in: Dailey, M. D., Reish, D. J., Anderson, J. W. (Eds.), Ecology of the southern
- California Bight: A synthesis and interpretation. Univ. California Press, Berkeley, USA.
- 585 pp. 71-189.
- Eganhouse, R. P., Blumfield, D. L., Kaplan, I. R., 1983. Long-chain alkylbenzenes as
- 587 molecular tracers of domestic wastes in the marine environment. Environmental Science
- 588 & Technology 17, 523-530.
- Eganhouse, R. P., Olaguer, D. P., Gould, B. R., Finney, C. S., 1988. Use of molecular
- markers for the detection of municipal sewage sludge at sea. Marine Environmental
- 591 Research 25, 1-22.
- Eganhouse, R. P.; Gossett, R. W., 1991. Historical deposition and biogeochemical fate of
- 593 polycyclic aromatic hydrocarbons in sediments near a major submarine wastewater
- outfall in southern California., Baker, R. A. (Ed.) Organic Substances in Sediments and
- Water. Lewis Publishers: Chelsea. Michigan, Vol. 2, pp 191-220.
- Eganhouse, R. P., Pontolillo, J., Leiker, T. J., 2000. Diagenetic fate of organic
- 597 contaminants on the Palos Verdes Shelf, California. Marine Chemistry 70, 289-315.
- 598 Eganhouse, R. P., Pontolillo, J., 2000. Depositional history of organic contaminants on
- the Palos Verdes Shelf, California. Marine Chemistry 70, 317-338.

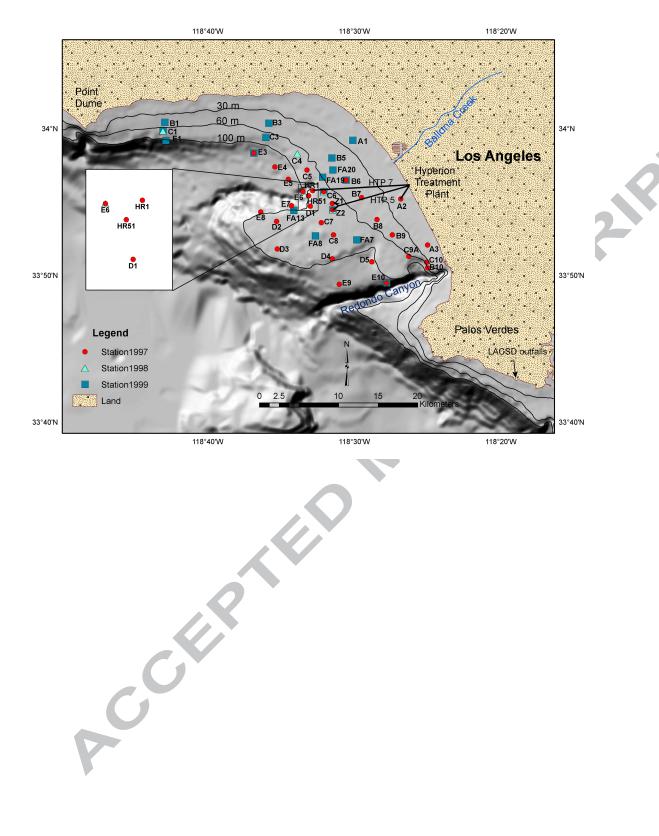
- 600 Eganhouse, R. P., Pontolillo, J., 2008. DDE in sediments of the Palos Verdes Shelf: *In*
- 601 situTransformation rates and geochemical fate. Environmental Science & Technology 42,
- 602 6392-6398.
- Eganhouse, R. P., Sherblom, P. M., 2001. Anthropogenic organic contaminants in the
- 604 effluent of a combined sewer overflow: Impact on Boston Harbor. Marine Environmental
- 605 Research 51, 51-74.
- Greenstein, D., Bay, S., Jirik., Brown. J., Alexander, C. 2003. Toxicity assessment of
- sediment cores from Santa Monica Bay, California. Marine Environmental Research. 56,
- 608 277-297.
- Hickey, B. M., 1993. Physical Oceanography, in: Dailey, M. D., Reish, D. J., Anderson,
- J. W. (Eds.), Ecology of the southern California Bight: A synthesis and interpretation.
- Univ. California Press, Berkeley, USA. pp.19-70.
- 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,
- 614 1197-1199.
- Jones, B. H., Noble, M. A., Dickey, T. D. 2002. Hydrographic and particle distributions
- over the Palos Verdes Continental Shelf: spatial, seasonal and daily variability.
- 617 Continental Shelf Research 22, 945-965.
- 618 Lee, H. J., Wiberg, P. L., 2002. Character, fate and biological effects of contaminated,
- 619 effluent-affected sediment on the Palos Verdes margin, southern Califronia: an overview.
- 620 Continental Shelf Research 22, 835-840.
- Long, E. R., MacDonald, D. D., 1998. Perspective: recommended uses of empirically
- derived, sediment quality guidelines for marine and estuarine ecosystems. Human and
- 623 Ecological Risk Assessment 4, 1019-1039.
- Long, E. R., MacDonald, D. D., Smith, S. L., Calder, F. D., 1995. Incidence of adverse
- biological effects within range of chemical concentrations in marine and estuarine
- sediments. Environmental Management 19, 81-97.
- MacGregor, J. S., 1976. DDT and its metabolites in the sediments off Southern
- 628 California. Fisheries Bulletin 74, 27-35.
- McDermott, D. J., Heesen, T. C., Young, D. R., 1974. DDT in bottom sediments around
- 630 five southern California outfall systems. Tech. memorandum 217. SCCWRP, El
- 631 Segundo, CA pp. 54.
- Marchesiello, P., McWilliams, J. C., Shchepetkin, A., 2002. Equilibrium Structure and
- Dynamics of the California Current System. Journal of Physical Oceanography 33, 753-
- 634 783. H., J.
- Mearns, A. J., Matta, M., Shigenaka, G., MacDonald, D., Buchman, M., Harris, H.,
- 636 Golas, J., Lauenstein, G. G., 1991. Contaminant trends in the Southern California Bight:
- 637 Inventory and assessment. NOAA Tech. Mem. NOS ORCA 62, Seattle, Washington.
- 638 NCERQA Final Report to EPA. 2002. "Integrated Urban Watershed Analysis: The Los
- 639 Angeles Basin and Coastal Environment". UCLA Institute of the Environment Report
- 640 #02-02(August 2002). EPA Grant Number: R82-5831, pp 129-136.
- Noble, M. A., Ryan, H. F., Wiberg, P. L., 2002. The dynamics of subtidal poleward flows
- over a narrow continental shelf, Palos Verdes, CA. Continental Shelf Research 22, 923-
- 643 944.
- 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

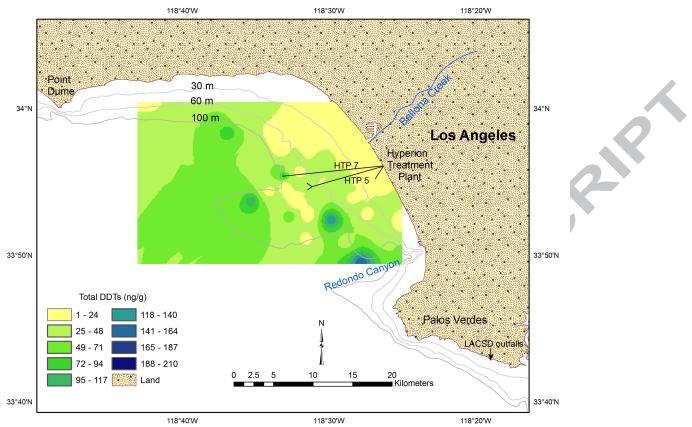
- and re-emergence of DDT-contaminated sediment particles. The Science of the Total
- 647 Environment 179, 109-133.
- Phillips, C. R., Venkatesan, M. I., Bowen, R., 1997. Interpretations of contaminant
- sources to San Pedro Shelf sediments using molecular markers and principal component
- analysis, in: Eganhouse, R. P. (Ed.), Molecular markers in environmental chemistry
- 651 1997, American Chemical Society, Washington, D.C. pp. 242-260.
- Phillips, C. R., Venkatesan, M. I., Lin., T. 2001. Linear alkylbenzenes in muscle tissues
- of white croaker near a large ocean outfall in southern California, USA. Environmental
- Toxicology and Chemistry 20, 231-238.
- Ouensen, J. F., Tiedje, J. M., Jain, M. K., Mueller, S. A. 2001. Factors controlling the
- rate of DDE dechlorination to DDMU in Palos Verdes margin sediments under anaerobic
- conditions. Environmental Science & Technology 35, 286-291.
- 658 SCCWRP annual or biannual reports, 1972-1989. Southern California Coastal Water
- Research Project, Long Beach, California.
- Schafer, H., 1989. Improving Southern California's coastal waters. Journal of the water
- Pollution Control Federation 61, 1395-1401.
- Sherblom, P. M., Henry, M. S., Kelly, D., 1997. Questions remain in the use of
- coprostanol and epicoprostanol as domestic waste markers: Examples from coastal
- Florida. in: Eganhouse, R. P. (Ed.), Molecular markers in environmental chemistry 1997,
- American Chemical Society, Washington, D.C. pp.320-331.
- Sherwood, C. R., Drake, D. E., Wiberg, P. L., Wheatcroft, R. A., 2002. Prediction of the
- fate of p,p'-DDE in sediment on the Palos Verdes shelf, California, USA. Continental
- 668 Shelf Research 22, 1025-1058.
- Shokes, R. F., Mankiewicz, P. J., 1979. Natural and anthropogenic fluxes of chemicals
- into the Southern California Bight as related to the potential impacts of offshore drilling.
- Report to Bureau of Land Management, benthic year 2. Vol. II, Rep. 24.0, pp. 96.
- 672 Sommerfield, C. K., Lee, H. J., 2003. Magnitude and variability of Holocene sediment
- accumulation in Santa Monica Bay, California. Marine Environmental Research 56, 151-
- 674 176.
- Stull, J. K., Baird, R.B., Heesen, T. C., 1986. Marine sediment core profiles of trace
- constituents offshore of a deep wastewater outfall. Journal of Water Pollution Control
- 677 Federation 58, 985-991.
- 678 Stull, J. K., Baird, R., Heesen T., 1988. Trace metal, chlorinated hydrocarbon and
- organic matter distributions in marine sediment cores near a major California wastewater
- discharge, in: Wolfe D. A., O'Connor, T. P., (Eds.), Ocean Processes in Marine
- 681 Pollution. Krieger Press.
- 682 Stull, J. K., Swift, D., Niedoroda, A., 1996. Contaminant dispersal on the Palos Verdes
- 683 continental margin. I. Sediments and biota near a major California wastewater discharge.
- The Science of the Total Environment 179, 73-90.
- Takada, H.; Eganhouse, R. P., 1998. Molecular markers of anthropogenic waste. In
- 686 Encyclopedia of Environmental Analysis and Remediation, Meyers, R. A., (Ed.) John
- 687 Wiley & Sons: New York, pp 2883-2938.
- 688 U.S. EPA., 1984. Toxic chemicals: An overview, in: Environmental Progress and
- challenges: An EPA Perspective, U.S. EPA, Office of Management Systems and
- 690 Evaluation, Washington, D.C., pp. 93-101.

- Venkatesan, M. I., 1998. II. Historical trends in the deposition of organic pollutants in the
- 692 southern California bight, in: Historical contamination in the southern California Bight.
- 693 U.S. Dept. Comm., NOAA Tech. Memo. NOS ORCA 129, Silver Spring, Maryland,
- 694 pp. 35.
- Venkatesan, M. I., Kaplan, I. R., 1990. Sedimentary coprostanol as an index of sewage
- 696 addition in Santa Monica Basin, Southern California. Environmental Science &
- 697 Technology 24, 208-214.
- Venkatesan, M. I., and Santiago, C. A., 1989. Sterols in ocean sediments: novel tracers to
- examine habitats of cetaceans, pinnipeds, penguins and humans. Marine Biology 102,
- 700 431-437.
- Venkatesan, M. I., Brenner, S., Ruth, E., Bonilla, J., Kaplan, I. R., 1980. Hydrocarbons
- in age-dated sediment cores from two basins in southern California Bight. Geochimica et
- 703 Cosmochimica Acta 44, 789-802.
- Venkatesan, M. I., Ruth, E., Kaplan, I. R., 1986. Coprostanols in Antarctic marine
- sediments-a biomarker for marine mammals and not human pollution. Marine Pollution
- 706 Bulletin 17, 554-557.
- Venkatesan, M. I., Ruth, E., Steinberg, S., Kaplan, I. R., 1987. Organic Geochemistry
- of sediments from the continental margin off southern New England, USA-Part II.
- 709 Lipids. Marine Chemistry 21, 267-299.
- Venkatesan, M. I., Greene, G. E., Ruth, E., Chartrand, A. B., 1996. DDTs and dumpsite
- 711 in the Santa Monica Basin, California. The Science of the Total Environment 179, 61-71.
- Wiberg, P. L., Harris, C. K., 2002. Desorption of *p,p*'-DDE from sediment during events
- on the Palos Verdes Shelf, California: a modeling approach. Continental Shelf Research
- 714 22, 1005-1023.
- Word, A. W., Mearns, A. J., 1979. 60-meter control survey off southern California. Tech.
- 716 Mem. 229. Southern California Coastal Water Research project, El Segundo, California,
- 717 pp. 58.
- Yasuhara, A., Morita, M., 1988. Formation of chlorinated aromatic hydrocarbons by
- 719 thermal decomposition of vinylidene chloride polymer. Environmental Science &
- 720 Technology 22, 646-650.
- Young, D. R., Heesen, T. C., 1978. DDT, PCB and chlorinated benzenes in the marine
- ecosystem off southern California, in: Jolley, R. L., Gorchev, W. H., Hamilton, Jr., D. H.
- 723 (Eds.), Water chlorination: Environmental Impact and health effects, Ann Arbor science
- 724 Publishers, Ann Arbor, MI, pp. 267-290
- Young, D. R., McDermott-Ehrlich D. J., Heesen, T. C., 1977. Sediments as sources of
- 726 DDT and PCB. Marine Pollution Bulletin 8, 254-257.
- 727 Zeng, E., Venkatesan, M. I., 1999. Dispersion of sediment DDTs in the coastal ocean off
- 728 Southern California. The Science of the Total Environment 229, 195-208.

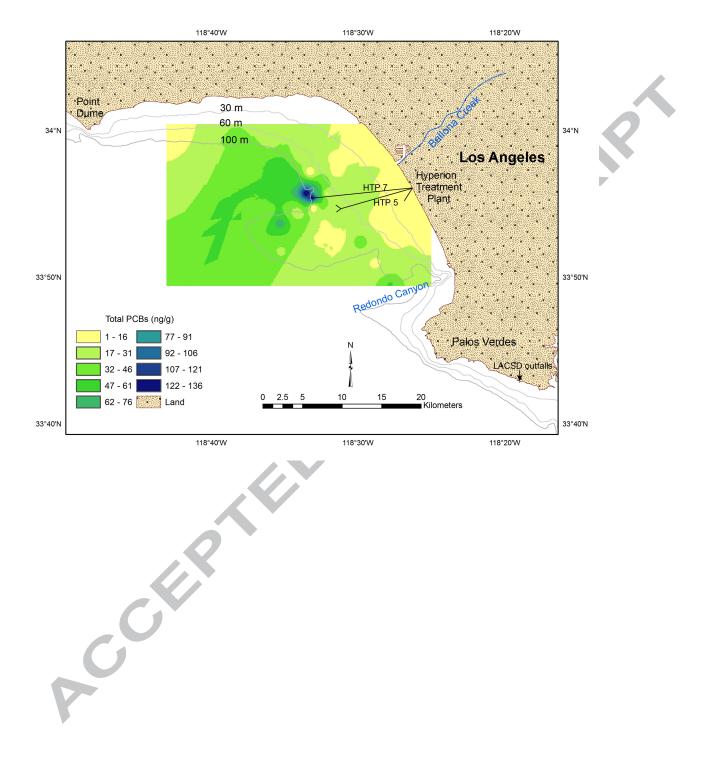
729	Tables 1-4 (See attached folder of excel Files).
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733	Figure captions
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735	Fig.1. Station locations of surface sediments from Santa Monica Bay.
736	HTP 7 and HTP 5 = Hyperion Treatment Plant 7-mile and 5-mile outfall respectively;
737	LACSD outfalls = Los Angeles County Sanitation District; Sediments were collected
738	from stations C6 and Z2 in all three years; from station B6, E3 and E10 in 1997 and
739	1999; from station C1 in 1998 and 1999 and from E6 in 1997 and 1998. Note that the
740	coordinates of the same station from year to year collection overlapped/coincided within
741	the size of a given symbol.
742	Fig.2. Interpolated concentration of Σ DDT in Santa Monica Bay.
743	Total concentration of contaminants in the sediments of all stations including replicate
744	sampling at the same station in different years were plotted for interpolation by
745	Geographic Information System in figs 2 to 6. For a list of contaminants which were
746	summed, see Table 1.
747	Fig.3. Interpolated concentration of Σ PCB in Santa Monica Bay.
748	Fig.4. Interpolated concentration of $\sum LAB$ in Santa Monica Bay.
749	Fig.5. Interpolated concentration of Coprostanol + epicoprostanol (coprostanols) in Santa
750	Monica Bay.
751	Fig.6. Interpolated concentration of Σ PAH in Santa Monica Bay.
752	Fig.7. Scatter plots of total concentration of contaminants in the sediments of Santa
753	Monica Bay. Correlation coefficient 'r' included on the plot. ∑DDT, parent DDT and
754	metabolites; Σ LAB, linear alkylbenzenes; Cops, coprostanol + epicoprostanol.; Σ PAH,
755	polycyclic aromatic hydrocarbons; Σ PCB, polychlorinated biphenyls. For list of
756	compounds summed, see Table 1.
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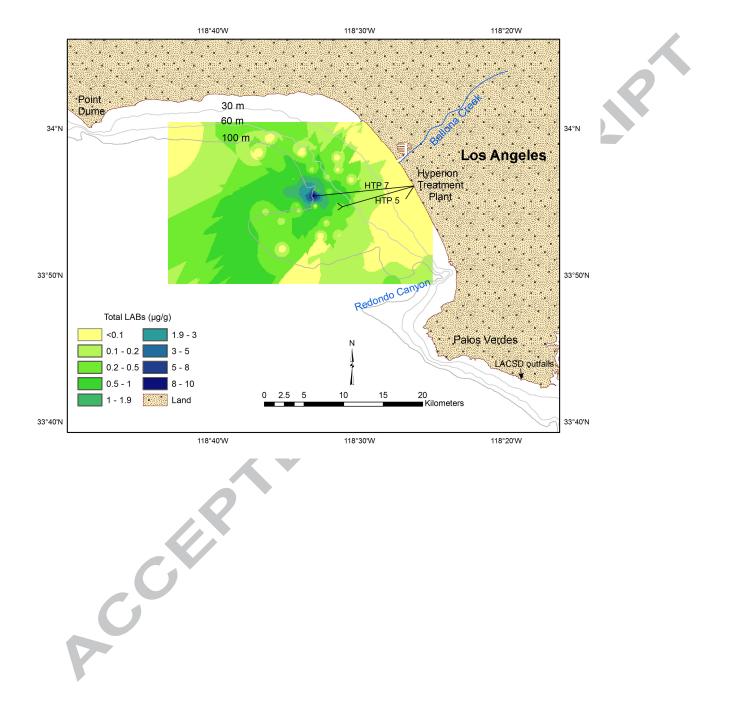
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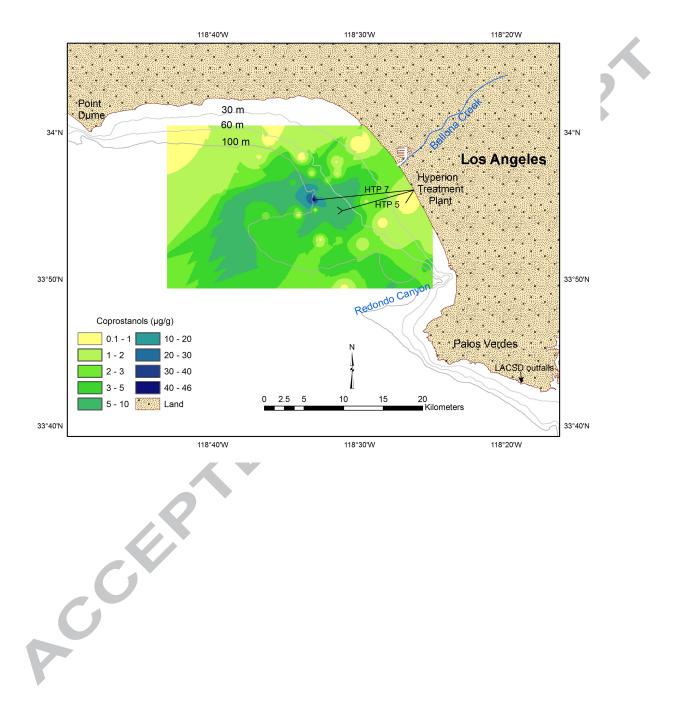


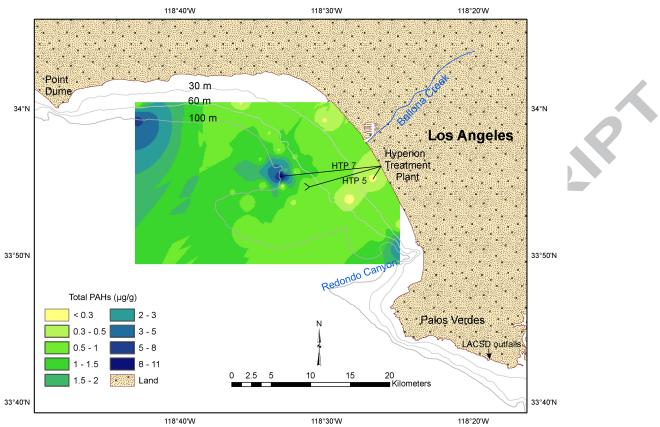














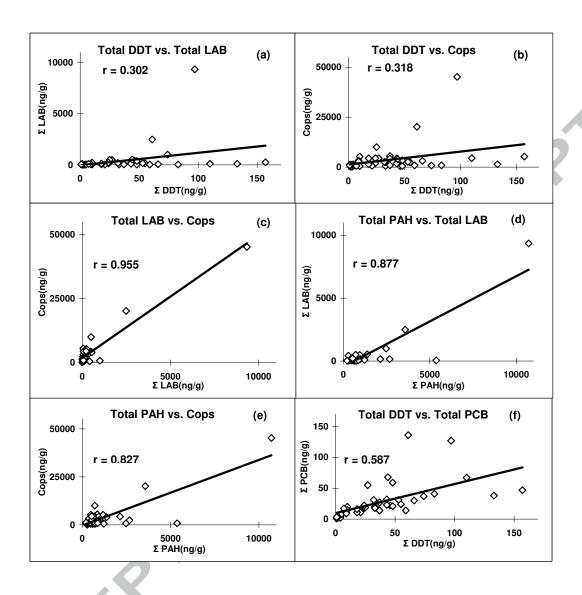


Table 1.

Target analytes measured in Santa Monica Bay sediments ^a

Target analytes measured in Santa	Monica Bay sediments. ^a	
PAH	PAH (continued)	PCBs ^d
naphthalene	benzo(k)fluoranthene	BZ8
C ₁ -naphthalenes	benzo(b)fluoranthene	BZ18
2-methylnaphthalene	benzo(e)pyrene	BZ28
1-methylnaphthalene	benzo(a)pyrene	BZ44
C ₂ -naphthalenes	9,10-diphenylanthracene	BZ52
2,6-dimethylnaphthalene	perylene	BZ66
C ₃ -naphthalenes	indeno(1,2,3-cd)pyrene	BZ77
2,3,5-trimethylnaphthalene	dibenz(a,h)anthracene	BZ101
C ₄ -naphthalenes	picene	BZ105
biphenyl	benzo(ghi)perylene	BZ118
acenaphthylene	anthanthrene	BZ126
acenaphthene	coronene	BZ128
fluorene	1,2,4,5-dibenzopyrene	BZ138
2-methylfluorene	C ₁ -C ₂₀ H ₁₂ aromatics	BZ153
C ₁ -fluorenes	C ₂ -C ₂₀ H ₁₂ aromatics	BZ170
C ₂ -fluorenes	C ₃ -C ₂₀ H ₁₂ aromatics	BZ180
C ₃ -fluorenes	C ₄ -C ₂₀ H ₁₂ aromatics	BZ187
phenanthrene		BZ195
1-methylphenanthrene		BZ206
anthracene	LABs ^c	Chlorinated pesticides
C ₁ -phenanthrenes/anthracenes	5-phenylundecane	2,4'-DDE
C ₂ -phenanthrenes/anthracenes	4-phenylundecane	4,4'-DDE
3,6-dimethylphenanthrene	3-phenylundecane	2,4'-DDD
C ₃ -phenanthrenes/anthracenes	2-phenylundecane	4,4'-DDD
C ₄ -phenanthrenes/anthracenes	6-phenyldodecane	2,4'-DDT
2,3-benzofluorene	5-phenyldodecane	4.4'-DDT
1,1'-binaphthalene	4-phenyldodecane	Sterols
dibenzothiophene ^b	3-phenyldodecane	Coprostanole
C1-dibenzothiophenes ^b	2-phenyldodecane	Epicoprostanol ^e
C ₂ -dibenzothiophenes ^b	7-and/or 6-phenyltridecane	Coprostanone
C ₃ -dibenzothiophenes ^b	5-phenyltridecane	Cholesterol
C ₄ -dibenzothiophenes ^b	4-phenyltridecane	Cholestanol
fluoranthene	3-phenyltridecane	Campesterol
pyrene	2-phenyltridecane	β-Sitosterol
C ₁ -fluoranthenes/pyrenes	7-phenyltetradecane	p chocore.
C ₂ -fluoranthenes/pyrenes	6-phenyltetradecane	
C ₃ -fluoranthenes/pyrenes	5-phenyltetradecane	
	, ,	
C ₄ -fluoranthenes/pyrenes	4-phenyltetradecane	
benz(a)anthracene	3-phenyltetradecane	
chrysene/triphenylene	2-phenyltetradecane	
Cchrysenes/triphenylenes		
C ₂ -chrysenes/triphenylenes		
C ₃ -chrysenes/triphenylenes		
C ₄ -chrysenes/triphenylenes		

 $[^]a\Sigma$ PAH=all parent PAHs+C₁ to C₃ or C₄ homologs; Σ LAB, Σ PCB, chlorinated pesticides (Σ DDT) or Σ sterols=sum of the compounds listed under that category.

^bRecovery not reliable due to activated copper treatment.

^cThe number refers to the position of phenyl substitution along the linear alkyl chain.

^dThe numbering of PCB congeners follows the system of Ballschmiter and Zell (1980).

^eCoprostanols, in this paper, refers to the sum of concentration of coprostanol and epicoprostanol.

Table 2. Average concentration of contaminants in Santa Monica Bay sediments collected from 1997 to 1999.

Sediment Station		Total DDT ^a	Total PCB ^a	Total PAH ^a	Total I AB ^a	Coprostanolsa
ocamion otation	meters	ng/g	ng/g	μg/g	ng/g	µg/g
A1	18	2	2	0.28	3	0.07
A2	18	3	4	0.28	3	0.07
A3	18	4	4	0.30	3	1.34
B1	45	4	2	0.59	23	0.54
B3	45	46	22	0.29	420	0.48
B5	45	5	8	0.67	41	0.92
<u>B6^b</u>	45	37	27	0.85	56	5.54
B7	45 45	24	18	0.58	138	1.89
B8	45	21	11	0.23	38	0.64
B9	45	18	11	0.72	42	1.45
B10	45	55	24	2.67	148	2.44
<u>C1</u>	60	48	21	0.74	25	0.6
C3	60	33	20	0.68	32	0.6
C4	60	10	20	0.48	33	0.47
C5	60	2	4	0.45	99	1.22
<u>C6</u>	60	10	15	0.48	225	5.31
<u>C7</u>	60	9	10	0.38	81	3.31
C8	60	9	9	0.59	99	2.82
C9A	60	33	18	0.85	45	2.41
C10	60	43	23	2.14	151	4.33
D1	75	1	1	0.21	29	1.23
D2	80	110	67	0.70	107	4.5
D3	80	66	30	0.78	59	3.13
D4	80	18	16	0.52	118	4.4
D5	80	37	14	0.66	70	4.3
E1	150	37	14	5.37	45	8.58
<u>E3</u>	150	83	41	0.69	28	8.71
<u>E3</u> E4	150	48	59	1.27	374	3.44
E5	150	27	55	0.94	485	4.41
<u>E6</u>	150	61	136	3.57	2490	20.18
E7	150	32	31	0.54	186	2.57
E8	150	53	31	0.97	150	2.64
E9	150	74	37	2.47	997	7.68
<u>E10</u>	150	157	47	1.18	252	5.27
FA7	58	133	38	0.72	113	1.41
FA8	65	59	14	0.72	35	0.91
FA13	80	7	17	1.22	89	5.73
FA19	53	43	32	0.87	105	1.88
FA20	48	1	3	0.87	64	0.93
Z1	60	25	19	0.71	495	9.99
<u>Z2</u>	60	24	22	0.53	215	4.5
HR1	100	44	68	1.38	531	3.99
HR51	153	97	127	10.71	9342	45.26
Effluent samples			*		μg/l	μg/l
10/4/1997		NA	NA	NA	5.7	140
10/5/1997		NA	NA	NA	4.7	168
3/12/2001		NA	NA	NA	0.15	4.2
3/13/2001		NA	NA	NA	0.11	6.2
^a For compounds summed up refer to Table 1						

^aFor compounds summed up refer to Table 1.

The above total contaminant concentrations are averages of two to three year collection for samples when the station was resampled. But, note that total concentration of contaminants in the sediments of all stations including replicate sampling at the same station in different years were plotted for interpolation by GIS to determine the spatial trend in figs from 2 to 6.

NA: Not analyzed.

^b Stations which were sampled in more than one year underlined; refer to Fig. 1 for details.

Table 3. Inventories of selected contaminants in the top 2 cm of sediments in Santa Monica Bay.

Inventory (ng/cm ²) ^a							
Contaminant	p,p'-DDE	Total DDT	Total PCB	Total PAH	Total LAB		
Minimum ^b	0.8(D1) ^d	2.9(D1)	2.9(D1)	609(D1)	8.7(A1-A3)		
Maximum ^b	322(E10)	455(E10)	394(E6)	31059(HR51)	27091(HR51)		
Average ^c	83	111	80	3484	1219		
	Baywic	de Inventory (me	etric tons) ^e				
Minimum	0.004	0.016	0.016	3.35	0.048		
Maximum	1.77	2.5	2.2	177	149		
Average ^c	0.46	0.61	0.44	19.2	6.7		

^aMass accumulation was calculated by multiplying the concentration/g dry sediment by sediment bulk density and then by the sampling depth of 2 cm.

Sommerfield and Lee (2003) reported a bulk density between 1.3 and 1.6 for the sediments at sediment- water interface in SMB. The average value of that range (1.45)

is assumed to be the bulk density of the top 2 cm in this study.

^b Minimum and maximum concentration of the contaminant measured in the study.

^c The contaminant concentrations presented in Table 2 were averaged to compute the average inventory per square cm.

^d Station No. in parenthesis. See Fig. 1 for station location.

^e Inventory for the top 2 cm of the entire SM Bay, extrapolated from ng/cm² from this study and SMB area of 550 km² from the report of Sommerfield and Lee (2003).

Table 4.

PAHs, DDTs and PCBs in the top 2 cm of sediment in Santa Monica Bay: Sediment quality guidelines.

Chemical	ERL ^a (ng/g)	ERM ^b (ng/g)	<erl<sup>c</erl<sup>	>ERL <ermc<sup>c</ermc<sup>	>ERM ^c
	400	0.4.0.0	40		
naphthalene	160	2100	49	3	
2-methylnaphthalene	70	670	47	4	1
acenaphthylene	44	640	52		
acenaphthene	16	500	51	1	
fluorene	19	540	51	1	
phenanthrene	240	1500	52		
anthracene	85	1100	52		
fluoranthene	600	5100	52		
pyrene	665	2600	52		
benz(a)anthracene	261	1600	52		
chrysene/triphenylene	384	2800	52		
benzo(a)pyrene	430	1600	51	1	
dibenz(a,h)anthracene	63	260	52		
Total PAH	4000	44700	40	3	
	4022	44792	49		
p, p'-DDE	2	27	6	26	20
Total DDTs	2	46	2	34	16
Total PCBs	23	180	29	23	
			_ ==	7	

^a Effects range-low; ^b Effects range-median after Long et al., 1995.

^c Number of Santa Monica Bay sediments exhibiting contaminant concentrations in the window of ERL, ERM or in-between.