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

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15

16 **Abstract:**

17 Spatial distribution of selected contaminants in the surface sediments of Santa Monica
18 Bay (SMB), California was investigated. Sediments were analyzed for DDTs (DDT and
19 metabolites), polychlorinated biphenyls (PCBs), polycyclic aromatic hydrocarbons
20 (PAHs), linear alkylbenzenes (LABs) and coprostanol. Effluent samples from the
21 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

38 **Keywords:** DDT, polychlorinated biphenyls, polycyclic aromatic hydrocarbons, linear
39 alkylbenzenes, coprostanol, Santa Monica Bay, sediment pollution, organic compounds
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46

47 1. Introduction

48

49 Coastal sediments in southern California receive organic pollutants from a variety
50 of sources such as sewage outfalls, storm runoff, dredge disposal and industrial wastes
51 from the adjacent major urban centers. Heavy contamination of sediments, particularly
52 with DDTs in the southern California coast in the 1950-1970s, the Clean Water Act
53 enforced in 1970-71 and the ban on DDTs in 1971 resulted in the development of
54 contaminant monitoring programs (Brown et al., 1986; McDermott et al., 1974; Mearns
55 et al., 1991; Young et al., 1977). Specifically, the Environmental Monitoring Division
56 (EMD) of the City of Los Angeles' Hyperion Treatment Plant (HTP) began monitoring
57 the quality of waste water discharged to SMB as well as the quality of sediments
58 impacted by the outfall starting in the 1970's (i.e., CLA EMD, 1997 ;1999; SCCWRP
59 Reports, 1972-1989). Heavily contaminated sediments, now buried in deeper strata below
60 sediment-water interface, could however, be remobilized by periodic re-suspension
61 events (Stull et al., 1996 and refs therein). This has been documented in the widespread
62 presence of DDT metabolites in sediment cores from San Pedro, Santa Monica, Santa
63 Barbara, Santa Cruz and San Nicolas Basins and in shallow waters in the Southern
64 California Bight even after the ending of the discharges of wastes from the manufacturing
65 company in 1970 (Shokes and Mankiewicz, 1979; Stull et al., 1986; Venkatesan et al.,
66 1980; 1996; Zeng and Venkatesan, 1999). Designated historic deep ocean dumpsites
67 could be yet another chronic source of DDTs to the sediments of the Santa Monica Basin
68 (Chartrand et al., 1985; Venkatesan et al., 1996).

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

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

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

105

106 **2. Study location and sampling**

107

108 Surface sediments were collected by the Hyperion Monitoring Program personnel
109 from thirty NPDES (National Pollutant Discharge Elimination System) sediment
110 chemistry stations during summer of 1997. Five stations were re-sampled during summer
111 of 1998. Seventeen samples from selected NPDES stations and a few random stations
112 were collected in 1999 (Fig.1). Some of the sampling sites were from the HTP 7-mile and
113 5-mile outfalls. Sewage sludge was disposed from the 7-mile outfall (positioned at head
114 of the canyon) from 1957 to 1987 and this terminus is considered as a major historic
115 source of contaminants to SMB (Schafer, 1989). 5-Mile outfall discharging treated
116 wastewater began operation in 1959 and a full secondary treatment was commissioned
117 effective from 1998.

118

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

125

126 **3. Methods**

127

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

139 isolate the aromatic fraction containing PCBs, chlorinated pesticides, LABs and PAHs
140 and a polar fraction containing sterols including coprostanol and epicoprostanol ((5 β -
141 cholestan-3 α -ol).

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

145 PAHs were quantitated by gas chromatography/mass spectrometry (GC/MS) from
146 the extracted ion current profiles using deuterated internal standard mixtures after
147 Venkatesan et al. (1987). A Finnigan 4000 Mass Spectrometer equipped with a 30 m DB-
148 5 fused silica capillary (0.25 mm I.D., 0.25 micron film, J&W Scientific) column was
149 used. GC/MS operating conditions are as follows: injector temperature 290°C; transfer
150 line temperature 280°C; initial oven temperature 35°C; initial hold time 6 min; 4°C/min
151 to 280°C; 2°C/min to 310°C. EM voltage: 1400v; electron energy: 70 eV. Source
152 temperature 240°C; scan speed 2s scan⁻¹ from 50 to 550 amu. A Galaxy 2000 for
153 Windows (Version 10.50, from Los Gatos Circuits (LGC), CA) data system was used to
154 acquire data. A five-point response factor calibration curve was established for
155 quantitation. Method detection concentrations (MDLs) of individual PAHs ranged from
156 0.1 to 1.0 ng/g with the exception of indeno(1,2,3-cd)pyrene which was 2 ng/g.

157 LABs were determined by GC/MS under conditions as above for PAH and
158 quantitated from extracted ion current profiles after Eganhouse et al. (1983) and Phillips
159 et al. (2001). MDL of individual LABs ranged from 0.05 to 0.1 ng/g.

160 Chlorinated hydrocarbons (pesticides and PCBs) were determined after Venkatesan
161 (1998) using a Varian 3500 GC (gas chromatograph) with dual electron capture detectors
162 (ECD) in the splitless mode using two columns, DB-5 and DB-1701, with same
163 specifications as above. The DB-5 was the working column and DB-1701 was the
164 confirmation column. GC/ECD operating conditions were as follows: injection
165 temperature 260°C, split open after 0.75 min; detector temperature 330°C; temperature
166 program 1 min at 60°C; 15°C/min to 150°C, hold 0.1 min; 2°C/min to 200°C, hold 10
167 min; 5°C/min to 280°C, hold 40 min. Hydrogen was used as carrier gas at 40 cm/sec.
168 Nitrogen at 30 ml/min was used as make-up gas. A four-point response factor calibration
169 curve was established. 2,4,5,6-tetrachloro-m-xylene and PCB BZ198 were used as
170 retention time markers. Because of the better resolution, some compounds, i.e. BZ 153,
171 105 and *o*, *p*'-DDT were always quantitated on DB-1701 column; all other compounds
172 were quantitated on DB-5. A Star Chromatography Workstation (Version 3.0, Varian
173 Analytical Instruments) was used to process the data. MDL of individual PCBs spanned
174 from 2 to 6 pg/g with the exception of BZ 8 which was 11 pg/g. Parent DDTs and the
175 metabolites exhibited MDLs ranging from 2 to 4 pg/g. Of the 16 chlorinated hydrocarbon
176 pesticides measured (including aldrin, dieldrin, heptachlor etc.), only the DDTs and the
177 metabolites will be discussed here. Discussion/interpretation will focus only on the total
178 DDTs, PCBs, LABs, PAHs and coprostanol + epicoprostanol.

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

185 coprostanols from now on) will be discussed in detail here. MDLs of these two sterols are
186 4 and 5 ng/g respectively.

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

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

202

203 4. Results and discussion

204

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

210

211 4.1. Spatial distribution of DDTs in the Santa Monica Bay

212

213 Concentration of total DDTs (or DDTs = ΣDDT = Sum of DDT and metabolites,
214 *o, p'*- and *p, p'*-DDE, -and DDD) ranges from 1-157 ng/g dry sediment (Fig. 2, Table 2).
215 The ΣDDT contents from the NPDES and random stations analyzed in the current project
216 compare well with those reported from the Monitoring Division of HTP (CLA EMD
217 1997; 1999). However, it is important to recognize that the analytical protocol followed
218 in their laboratory is different from ours. The values from UCLA and HTP, for most of
219 the common stations, are of same order of magnitude and vary, at the most, by 30%. For
220 the remaining stations the values are within a factor of two. Sediments along the 30 m
221 contour contain lowest concentrations of DDTs, consistent with their coarse grain size of
222 the particles near-shore (CLA EMD 1997; 1999) as also evident from visual inspection of
223 the sediment. Concentrations of DDTs are high at stations B10, D2, D3, E3, E8 - E10
224 along the 100m isobath which are enriched in fine grain sediment. Concentration of
225 DDTs peaked at sediments from station E10 (157 ng/g, average of two years data).
226 Similar to the findings of Bay et al. (2003), stations around the HTP 7-mile outfall
227 terminus (ie., HR1, HR51 and E6) also contain high concentrations of DDTs. This
228 reflects the modest amount of DDTs manufacture wastes discharged in the past via HTP-
229 5 and 7-mile outfalls from the late 1950s when they commenced operation (Chartrand et
230 al., 1985; Schafer, 1989).

231 DDT 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,
239 effluent loading of DDTs from the HTP 5-mile in 1987-1997 was below 0.003 kg/day
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.
243 Apparently, historic DDTs (pre-1971) are still being chronically remobilized from the
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 Although DDTs were found in all samples, relatively greater accumulation of
247 DDTs is observed at a few stations in the Bay hot spots. There is no evidence to suggest
248 any illegal short dumping of DDT manufacturing wastes in the Bay similar to the ones
249 detected in the Santa Monica/San Pedro Basins (Chartrand et al., 1985; Venkatesan et al.,
250 1996). It is known that lipid components, having low water solubility, exhibit strong
251 affinities for fine-grained sediments and are redistributed by contaminant desorption,
252 current advection and re-deposition in near-shore bays as well as deeper waters of the
253 Basins (Noble et al., 2002; Jones et al., 2002). This could result in hot spots in the Bay
254 around water depths of 60 -100 meters with preferential deposition of organic
255 contaminants including DDTs. These stations are located in the southeastern region of the
256 SMB just north of Redondo canyon, i.e., E9, E10 and B10, farther away from the HTP
257 outfalls. Part of the DDTs could have been transported from Palos Verdes Shelf via
258 prevailing subsurface currents (California Countercurrent), advecting effluent particles up
259 the coast along the bathymetric contours (Hickey, 1993; Marchesiello et al., 2002; Stull et
260 al., 1996). Zeng and Venkatesan (1999) previously observed that the concentration of
261 *p, p'*-DDE in the surface sediments of Palos Verdes shelf 1) correlated well with those
262 of water column samples from the same stations and 2) exhibited a gradient from the
263 outfalls to offshore. They, therefore, suggested that historically deposited DDTs in the
264 Palos Verdes shelf have been remobilized upward in the sedimentary strata and
265 subsequently resuspended into the water column. This scenario is more likely,
266 considering that PVS sediments contain anomalously high concentrations of DDTs,
267 discharged in the past from LACSD (Los Angeles County Sanitation District) outfall
268 (Eganhouse et al., 2000; Stull et al., 1996). The contaminated particles from the deposits
269 on the Palos Verdes Shelf could be dispersed upward by bio-diffusion, crossing Redondo
270 canyon, and then removed to wider marine environment including SMB to the northwest
271 by strong flow events (Mearns et al., 1991; Nedoroda et al., 1996; Zeng and Venkatesan,
272 1999; Wiberg and Harris, 2002; Sherwood et al., 2002). In summary, DDTs are found at
273 different concentrations throughout the Bay and at relatively high concentration in the
274 proximity of the Hyperion outfall. There are hot spots of higher DDTs concentration from
275 transport of material most likely from the Palos Verdes Shelf into the sedimentary

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

278

279 4.2 Other anthropogenic marker compounds:

280

281 Total PCBs (or $\sum PCB$ = sum of the congeners, listed in Table 1)
282 concentrations in the sediments range from 2 to 136 ng/g. They are present in relatively
283 high amounts near the 7-mile outfall terminus (Fig. 3). Their concentrations decline
284 steeply away from the outfall terminus. Ten of the 42 stations (stations A1, A2, A3, B1,
285 B5, C5, C7, C8, D1 and FA20) have sediments containing less than 10 ng/g of PCBs.
286 Negligible loading or absence of PCBs is noted in the HTP 5-mile effluent collected in
287 1998 (CLA EMD, 1999). In contrast, $\sum PCB$ s concentrations are high in the sediments at
288 the 7-mile outfall (i.e., highest PCBs content in station E6 and HR51). This would imply
289 HTP historic deposits being the major source of PCBs in the Bay similar to that of DDTs.
290 PCBs were in large use especially in the early 1970; a ban on their production was
291 enforced in 1977 (U.S. EPA, 1984). Non-point sources such as refuse incineration,
292 atmospheric transport and industrial effluent runoff could also contribute PCBs to the
293 coastal zone (Atlas et al, 1986; Yasuhara and Morita, 1988). However, in SMB
294 sediments, contribution from these non-point sources appear to be not as important as that
295 from Hyp 7-mile deposits. There are no PCBs hot spots in the Bay unlike that of DDTs
296 which is consistent with the rapid deposition of PCBs at the discharge point. This
297 disparity in spatial distribution trends for PCBs and DDTs reiterates our earlier argument
298 requiring a second significant source for DDTs in SMB sediments farther away from
299 HTP discharges, especially, in the area near Redondo canyon.

300 Total LABs (or $\sum LAB$ = sum of all the isomers from carbon number 11 to
301 14, Table 1) and coprostanols (sum of coprostanol and epicoprostanol) occur at
302 significant concentrations in sediments near the HTP 5-mile outfall, Z1 and Z2, and at
303 much higher concentrations at stations, HR1 and HR51 (near HTP 7-mile sludge disposal
304 site) with the latter containing the highest amounts. $\sum LAB$ concentrations in the Bay
305 ranges from <0.01 to 10 $\mu g/g$ (Fig. 4) and are comparable to the concentrations reported
306 by Bay et al. (2003). Coprostanol concentrations vary from 0.065 to 46 $\mu g/g$ (Fig. 5) with
307 highest concentrations at the 7-mile outfall and significantly high concentrations near the
308 5-mile outfall. The concentrations of LABs and coprostanols are much lower, by one to
309 two orders of magnitude, at other stations in SMB relative to the stations at the outfall
310 (i.e., E6, HR51). Less than 10 ng/g of LABs and coprostanols are found at stations, A1
311 and A2, at the 30 m water depth. While DDTs were found at trace concentrations or
312 mostly absent in the modern day (HTP 5 Mile) effluents, LABs and coprostanols occur at
313 significant concentrations in the effluents, i.e., 5.2 and 0.13 $\mu g/l$ of LABs and 154 and 5.2
314 $\mu g/l$ of coprostanols in 1997 and 2001 respectively (the values presented here being the
315 average of the two collections in the same year). The unusually high abundance of
316 coprostanol in the HTP effluents is comparable to those reported in partially treated
317 sewage (Fig. 5 in Takada and Eganhouse, 1998). Also note that the effluent collected
318 from HTP 5-mile in June of 1987 contained 158 $\mu g/l$ of coprostanol (Venkatesan and
319 Kaplan, 1990) which compares well with that of the 1997 samples in this study (Table 2).
320 The 2001 effluents reflect significantly reduced concentrations of the contaminants after
321 the full secondary treatment at HTP which became effective in 1998. This clearly

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

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

354 A sharp decline in coprostanols and LABs concentration with increasing distance
355 from the HTP outfall suggests a rapid deposition of sewage-derived organic components
356 in the vicinity of the discharge zone. The interpolated spatial distribution contours of
357 LABs and coprostanols originating from the outfalls are very similar in the Bay, attesting
358 to their common and exclusive major source from the HTP 5- and 7-mile discharges and
359 the similar properties controlling their transport. The absence of abnormally high
360 concentrations of wastewater-derived contaminants such as LABs or coprostanol at
361 stations farther away from the outfalls suggests that they are quickly deposited in the
362 outfalls vicinity, degraded and/or diluted before reaching the canyon. In contrast, the
363 wide spread occurrence of DDTs in the bay surface sediments at chronic levels, yet
364 exhibiting a gradient from the HTP outfall, would indicate resuspension of DDTs from
365 the discharge point (Zeng and Venkatesan 1999). This also implies that not all of the
366 DDTs in the hot spots could have originated from the historic Hyperion discharges and
367 that they should have been derived from an additional source as discussed in section 4.1.
368

369 Total PAHs (or $\Sigma\text{PAH} = \text{sum of PAH compounds listed in Table 1}$)
370 concentration ranges from 0.2 to 11 $\mu\text{g/g}$ and compares favorably with that reported by
371 Bay et al. (2003). The highest PAHs concentration occurs at the 7-mile outfall. No
372 consistent gradient in the total PAHs content was evident among other stations with
373 increasing distance from the HTP 5- and 7-mile outfalls (Fig.6). PAHs appear to be more
374 widespread in the Bay than any of the other components measured. This may be because,
375 in addition to that from HTP outfalls, PAHs could also be derived in varying proportions
376 from multiple sources such as Monterey shale erosion, natural oil seeps, petroleum
377 residues from storm runoff, harbors and urban drainage channels and from atmospheric
378 inputs (Cross et al., 1987; Eganhouse and Gossett, 1991; Eganhouse and Venkatesan,
379 1993). We found PCBs, LABs and PAHs in most of the sediments sampled. Although,
380 Bay et al. (2003) also found high concentration of these compounds near the outfalls,
381 they detected LABs only in one or two stations away from the outfall and PAHs only in
382 one station off Ballona Creek. This difference in observation between the two studies
383 may partly be due to the wider coverage of surface sediment sampling in the Bay in the
384 current investigation.

385

386 4.3: *Inter-correlation among contaminants:*

387

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

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

415 are more akin to that of the LABs and coprostanol than that of DDTs (Fig. 6). However,
416 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
419 moderate correlation between Σ DDT and Σ PCB has previously been found in sediments
420 from the southern region of San Pedro Shelf (Phillips et al., 1997). In contrast, Σ PCB
421 correlates strongly with Σ LAB, coprostanols and Σ PAH ($r=0.837, 0.812$ and 0.735
422 respectively; plots not shown) suggesting that most of the PCBs in sediments are also
423 mainly derived from HTP 7- and 5-mile outfalls. Concentrations of Σ PCB in the
424 sediments of Boston Harbor exhibited a high correlation with coprostanol concentrations
425 ($r^2=0.71$) 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
427 containing industrial wastes (Hom et al., 1974) and atmospheric transport (Atlas et al.,
428 1986). In summary, moderate to poor correlation of Σ DDT with all other contaminants
429 investigated here, calls for an additional source to explain the hot spots of DDTs at least
430 in some parts of SMB (Cf: 4.2).

431

432 4.4. Current emission of LABs and coprostanol to the Bay:

433

434 In 1997, approximately 6.7 kg/day of LABs and 215 kg/day of coprostanols were
435 discharged in the effluent from the HTP 5-mile (based on the average $\mu\text{g/l}$ of the
436 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
438 of 205 kg/day of coprostanol in the HTP 5-mile effluent collected in 1987 (Venkatesan
439 and Kaplan, 1990). The effluent samples collected in 2001 (Table 2), after the
440 introduction of full secondary treatment at HTP 5-mile (effective from 1998), contained
441 only < 1 and 5.2 kg/day respectively of LABs and coprostanols. This is one to two orders
442 of magnitude less than that discharged during '87-'97. No PAHs were detected in the
443 post-full secondary effluents (CLA EMD, 2001-2002). Although the surface sediments
444 from SMB were collected from 1997-1999, the presence of these sewage tracers in
445 significant amounts is clearly characteristic of their major origin prior to 1998 (i.e., pre-
446 full secondary treatment). The ^{210}Pb dating of sediment strata of sub cores corresponding
447 to calculated ages from 1900 to 1997 (surface) showed that sediment accumulation rates
448 could vary from 0.19 -0.37 cm/yr at stations in water depths greater than 50 m and farther
449 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
453 unknown proportion of these compounds in the Bay have their origin in the sludge field
454 by chronic remobilization and redistribution from the HTP 7-mile discharge site which
455 was terminated in 1987.

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461 4.5. *Inventories of the contaminants:*

462

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

484

485 4.6. *Sediment toxicity estimates:*

486

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

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

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

518
519

520 **5. Conclusions**

521

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

540

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542

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554 **7. References**

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

558 Ballschmiter, K., Zell, M., 1980. Analysis of polychlorinated biphenyls by capillary gas
559 chromatography. *Fresenius' Zeitschrift fur Analytische Chemie* 302, 20-31.

560 Bay, S. M., Zeng, E. Y., Lorenson, T. D., Tran, K., Alexander, C., 2003. Temporal and
561 spatial distributions of contaminants in sediments of Santa Monica Bay, California.

562 *Marine Environmental Research* 56, 255-276.

563 Brown, D.A., Gossett, R.W., Hershelman, G.P., Ward, C. F., Wescott, A. M., Cross, J.
564 N., 1986. Municipal wastewater contamination in the southern California Bight: Part I -
565 Metal and organic contaminants in sediments and organisms. *Marine Environmental*
566 *Research* 18, 291-310.

567 Chaux, N. Bayona J. M., Venkatesan M. I., J. Albaiges. 1992. Distribution of
568 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
574 of Past Practices, Potential Adverse Impacts, and Recommendations for Future Action.
575 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.

579 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
581 near Los Angeles, California. *Marine Environmental Research* 23, 307-323.

582 Eganhouse, R. P., Venkatesan, M. I., 1993. Chemical Oceanography and Geochemistry,
583 in: Dailey, M. D., Reish, D. J., Anderson, J. W. (Eds.), *Ecology of the southern*
584 *California Bight: A synthesis and interpretation*. Univ. California Press, Berkeley, USA.
585 pp. 71-189.

586 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.

589 Eganhouse, R. P., Olaguer, D. P., Gould, B. R., Finney, C. S., 1988. Use of molecular
590 markers for the detection of municipal sewage sludge at sea. *Marine Environmental*
591 *Research* 25, 1-22.

592 Eganhouse, R. P.; Gossett, R. W., 1991. Historical deposition and biogeochemical fate of
593 polycyclic aromatic hydrocarbons in sediments near a major submarine wastewater
594 outfall in southern California., Baker, R. A. (Ed.) *Organic Substances in Sediments and*
595 *Water*. Lewis Publishers: Chelsea. Michigan, Vol. 2, pp 191-220.

596 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
599 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 *situ* Transformation rates and geochemical fate. *Environmental Science & Technology* 42,
602 6392-6398.
- 603 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.
- 606 Greenstein, D., Bay, S., Jirik., Brown. J., Alexander, C. 2003. Toxicity assessment of
607 sediment cores from Santa Monica Bay, California. *Marine Environmental Research*. 56,
608 277-297.
- 609 Hickey, B. M., 1993. Physical Oceanography, in: Dailey, M. D., Reish, D. J., Anderson,
610 J. W. (Eds.), *Ecology of the southern California Bight: A synthesis and interpretation*.
611 Univ. California Press, Berkeley, USA. pp.19-70.
- 612 Hom, W., Risebrough R. W., Soutar A., Young D. R., 1974. Deposition of DDE and
613 polychlorinated biphenyls in dated sediments of the Santa Barbara Basin. *Science* 184,
614 1197-1199.
- 615 Jones, B. H., Noble, M. A., Dickey, T. D. 2002. Hydrographic and particle distributions
616 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 California: an overview.
620 *Continental Shelf Research* 22, 835-840.
- 621 Long, E. R., MacDonald, D. D., 1998. Perspective: recommended uses of empirically
622 derived, sediment quality guidelines for marine and estuarine ecosystems. *Human and*
623 *Ecological Risk Assessment* 4, 1019-1039.
- 624 Long, E. R., MacDonald, D. D., Smith, S. L., Calder, F. D., 1995. Incidence of adverse
625 biological effects within range of chemical concentrations in marine and estuarine
626 sediments. *Environmental Management* 19, 81-97.
- 627 MacGregor, J. S., 1976. DDT and its metabolites in the sediments off Southern
628 California. *Fisheries Bulletin* 74, 27-35.
- 629 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.
- 632 Marchesiello, P., McWilliams, J. C., Shchepetkin, A., 2002. Equilibrium Structure and
633 Dynamics of the California Current System. *Journal of Physical Oceanography* 33, 753-
634 783. H., J.
- 635 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.
- 641 Noble, M. A., Ryan, H. F., Wiberg, P. L., 2002. The dynamics of subtidal poleward flows
642 over a narrow continental shelf, Palos Verdes, CA. *Continental Shelf Research* 22, 923-
643 944.
- 644 Niedoroda, A. W., Swift, D. J. P., Reed, C. W., Stull, J. K., 1996. Contaminant dispersal
645 on the Palos Verdes continental margin: III. Processes controlling transport, accumulation

- 646 and re-emergence of DDT-contaminated sediment particles. *The Science of the Total*
647 *Environment* 179, 109-133.
- 648 Phillips, C. R., Venkatesan, M. I., Bowen, R., 1997. Interpretations of contaminant
649 sources to San Pedro Shelf sediments using molecular markers and principal component
650 analysis, in: Eganhouse, R. P. (Ed.), *Molecular markers in environmental chemistry*
651 1997, American Chemical Society, Washington, D.C. pp. 242-260.
- 652 Phillips, C. R., Venkatesan, M. I., Lin., T. 2001. Linear alkylbenzenes in muscle tissues
653 of white croaker near a large ocean outfall in southern California, USA. *Environmental*
654 *Toxicology and Chemistry* 20, 231-238.
- 655 Quensen, J. F., Tiedje, J. M., Jain, M. K., Mueller, S. A. 2001. Factors controlling the
656 rate of DDE dechlorination to DDMU in Palos Verdes margin sediments under anaerobic
657 conditions. *Environmental Science & Technology* 35, 286-291.
- 658 SCCWRP annual or biannual reports, 1972-1989. Southern California Coastal Water
659 Research Project, Long Beach, California.
- 660 Schafer, H., 1989. Improving Southern California's coastal waters. *Journal of the water*
661 *Pollution Control Federation* 61, 1395-1401.
- 662 Sherblom, P. M., Henry, M. S., Kelly, D., 1997. Questions remain in the use of
663 coprostanol and epicoprostanol as domestic waste markers: Examples from coastal
664 Florida. in: Eganhouse, R. P. (Ed.), *Molecular markers in environmental chemistry* 1997,
665 American Chemical Society, Washington, D.C. pp.320-331.
- 666 Sherwood, C. R., Drake, D. E., Wiberg, P. L., Wheatcroft, R. A., 2002. Prediction of the
667 fate of *p,p'*-DDE in sediment on the Palos Verdes shelf, California, USA. *Continental*
668 *Shelf Research* 22, 1025-1058.
- 669 Shokes, R. F., Mankiewicz, P. J., 1979. Natural and anthropogenic fluxes of chemicals
670 into the Southern California Bight as related to the potential impacts of offshore drilling.
671 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
673 accumulation in Santa Monica Bay, California. *Marine Environmental Research* 56, 151-
674 176.
- 675 Stull, J. K., Baird, R.B., Heesen, T. C., 1986. Marine sediment core profiles of trace
676 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
679 organic matter distributions in marine sediment cores near a major California wastewater
680 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.
684 *The Science of the Total Environment* 179, 73-90.
- 685 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*
689 *challenges: An EPA Perspective*, U.S. EPA, Office of Management Systems and
690 Evaluation, Washington, D.C., pp. 93-101.

- 691 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.
- 695 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.
- 698 Venkatesan, M. I., and Santiago, C. A., 1989. Sterols in ocean sediments: novel tracers to
699 examine habitats of cetaceans, pinnipeds, penguins and humans. *Marine Biology* 102,
700 431-437.
- 701 Venkatesan, M. I., Brenner, S., Ruth, E., Bonilla, J., Kaplan, I. R., 1980. Hydrocarbons
702 in age-dated sediment cores from two basins in southern California Bight. *Geochimica et*
703 *Cosmochimica Acta* 44, 789-802.
- 704 Venkatesan, M. I., Ruth, E., Kaplan, I. R., 1986. Coprostanols in Antarctic marine
705 sediments-a biomarker for marine mammals and not human pollution. *Marine Pollution*
706 *Bulletin* 17, 554-557.
- 707 Venkatesan, M. I., Ruth, E., Steinberg, S., Kaplan, I. R., 1987. Organic Geochemistry
708 of sediments from the continental margin off southern New England, USA-Part II.
709 *Lipids. Marine Chemistry* 21, 267-299.
- 710 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.
- 712 Wiberg, P. L., Harris, C. K., 2002. Desorption of *p,p'*-DDE from sediment during events
713 on the Palos Verdes Shelf, California: a modeling approach. *Continental Shelf Research*
714 22, 1005-1023.
- 715 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.
- 718 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.
- 721 Young, D. R., Heesen, T. C., 1978. DDT, PCB and chlorinated benzenes in the marine
722 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
- 725 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).**

730

731

732

733 **Figure captions**

734

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 \sum 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 \sum 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 \sum 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. \sum DDT, parent DDT and

754 metabolites; \sum LAB, linear alkylbenzenes; Cops, coprostanol + epicoprostanol.; \sum PAH,

755 polycyclic aromatic hydrocarbons; \sum PCB, polychlorinated biphenyls. For list of

756 compounds summed, see Table 1.

757

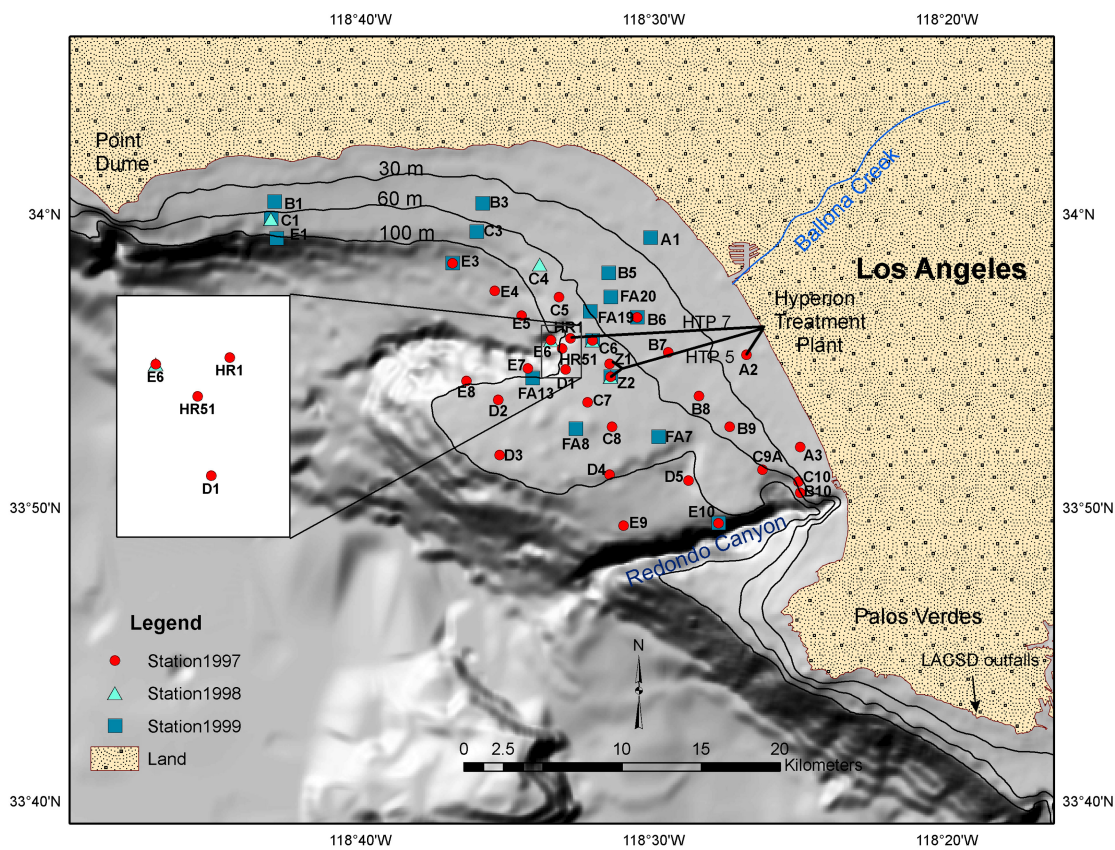
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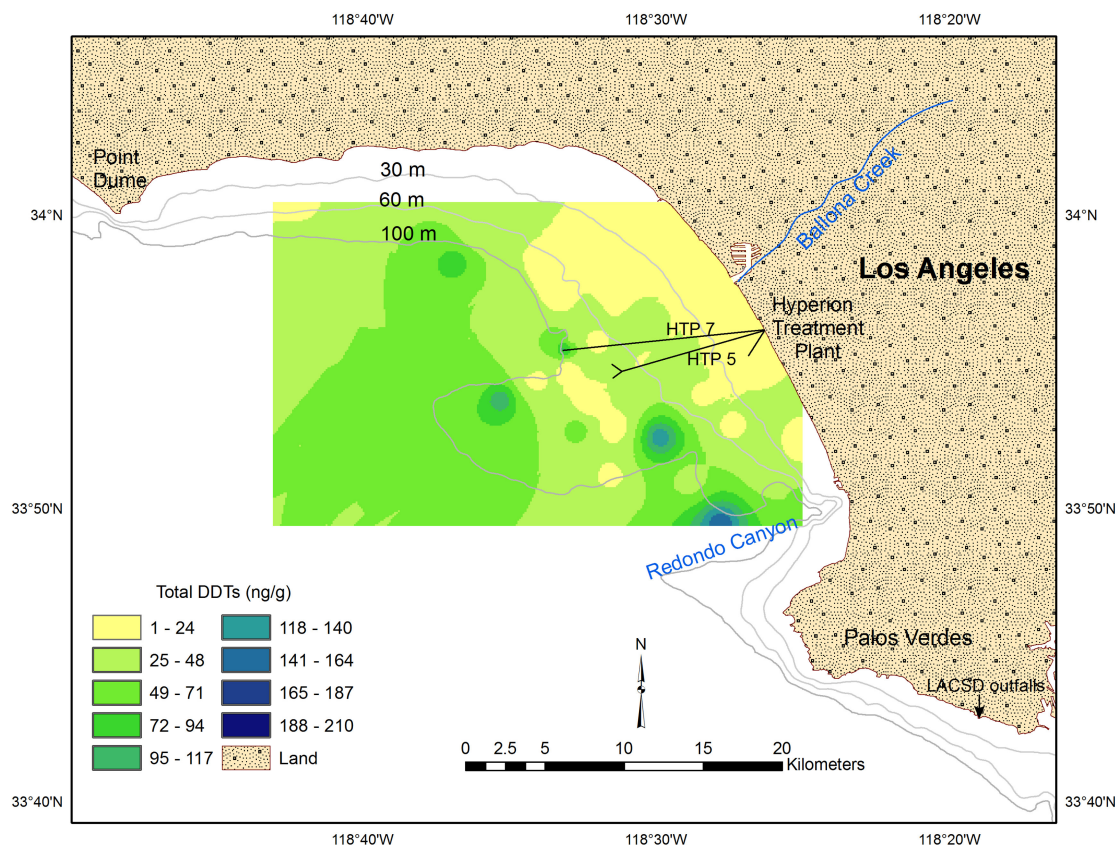
759 **Figures 1-7 (See attached folder of Tiff or excel files.**

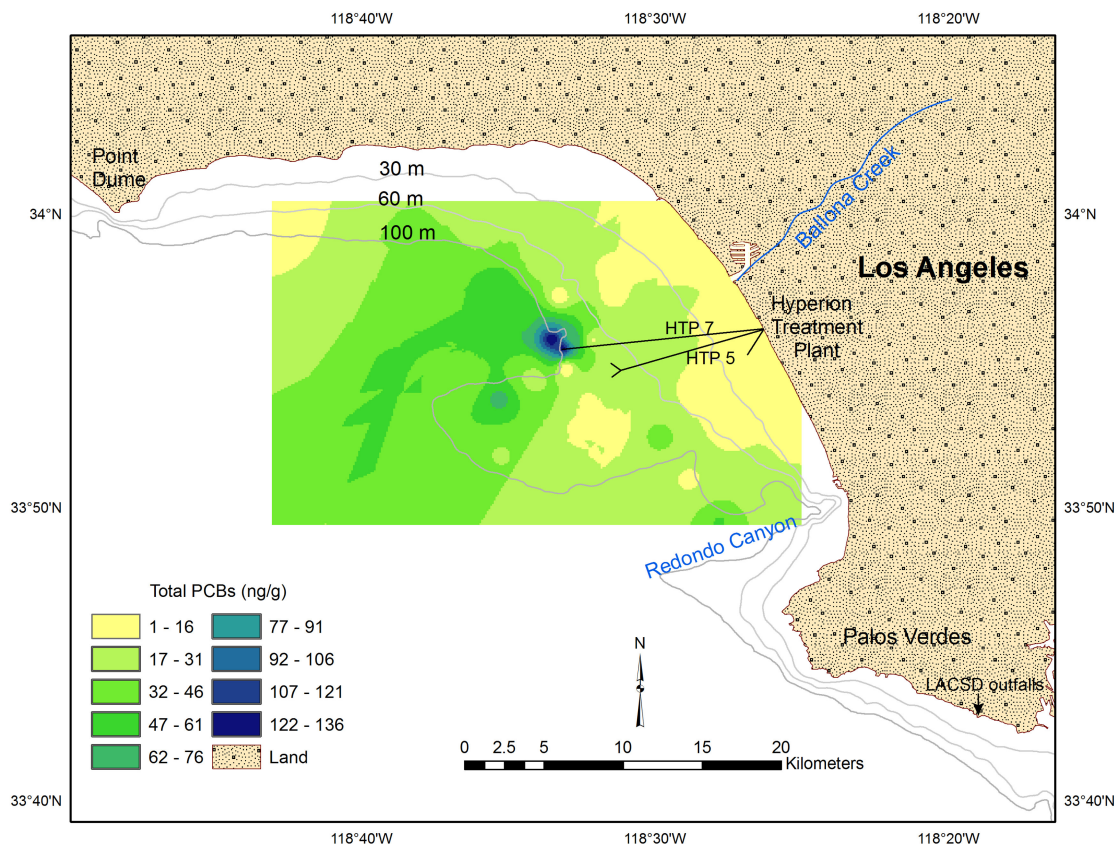
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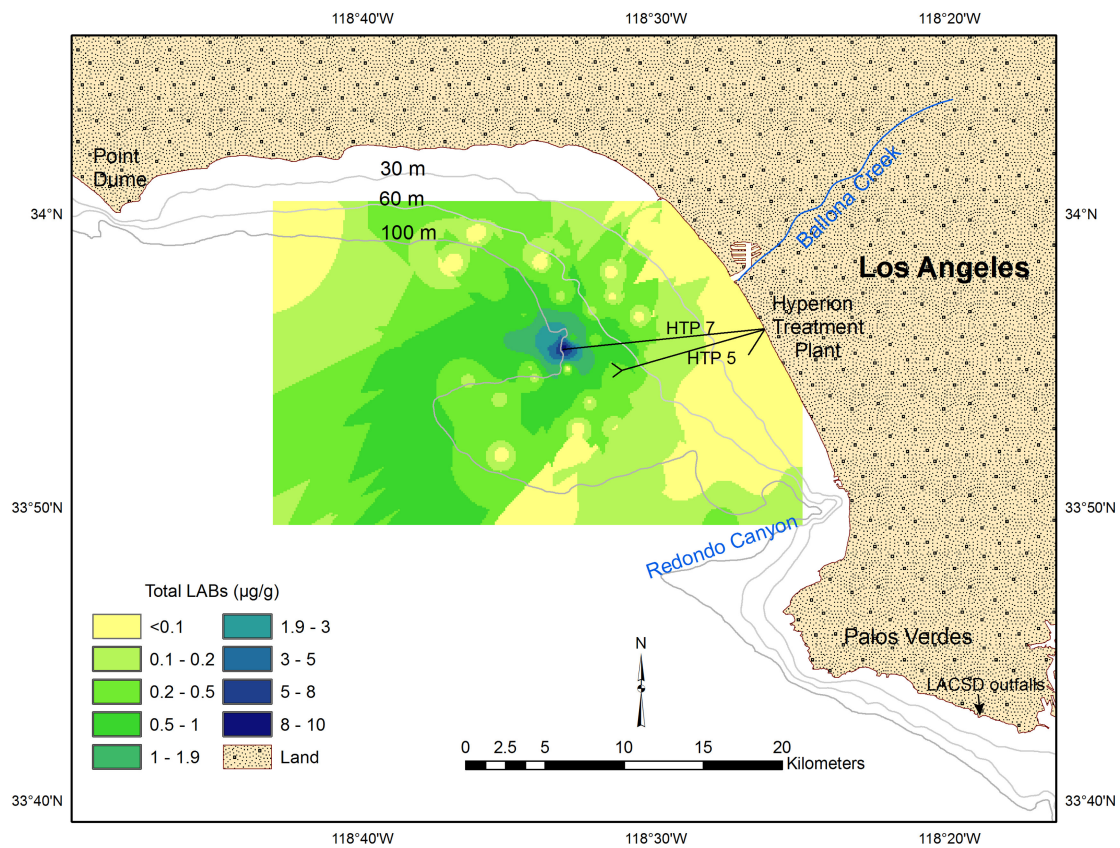
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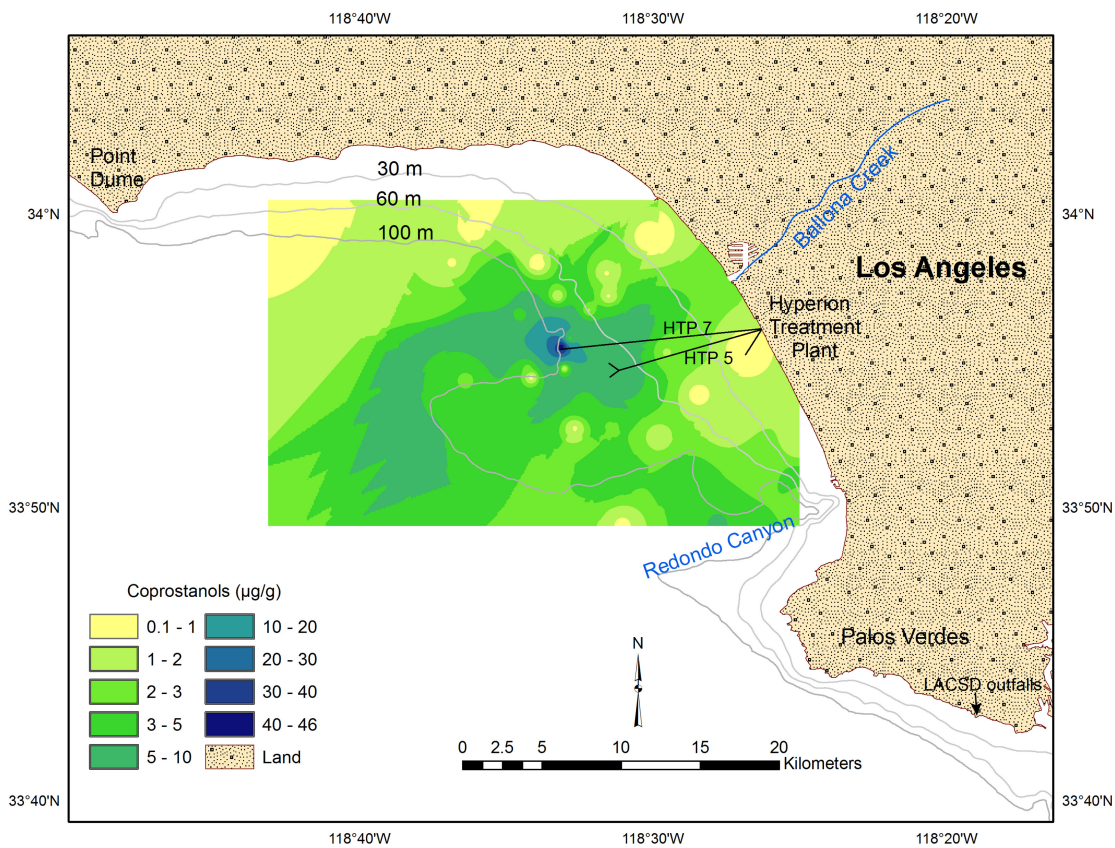
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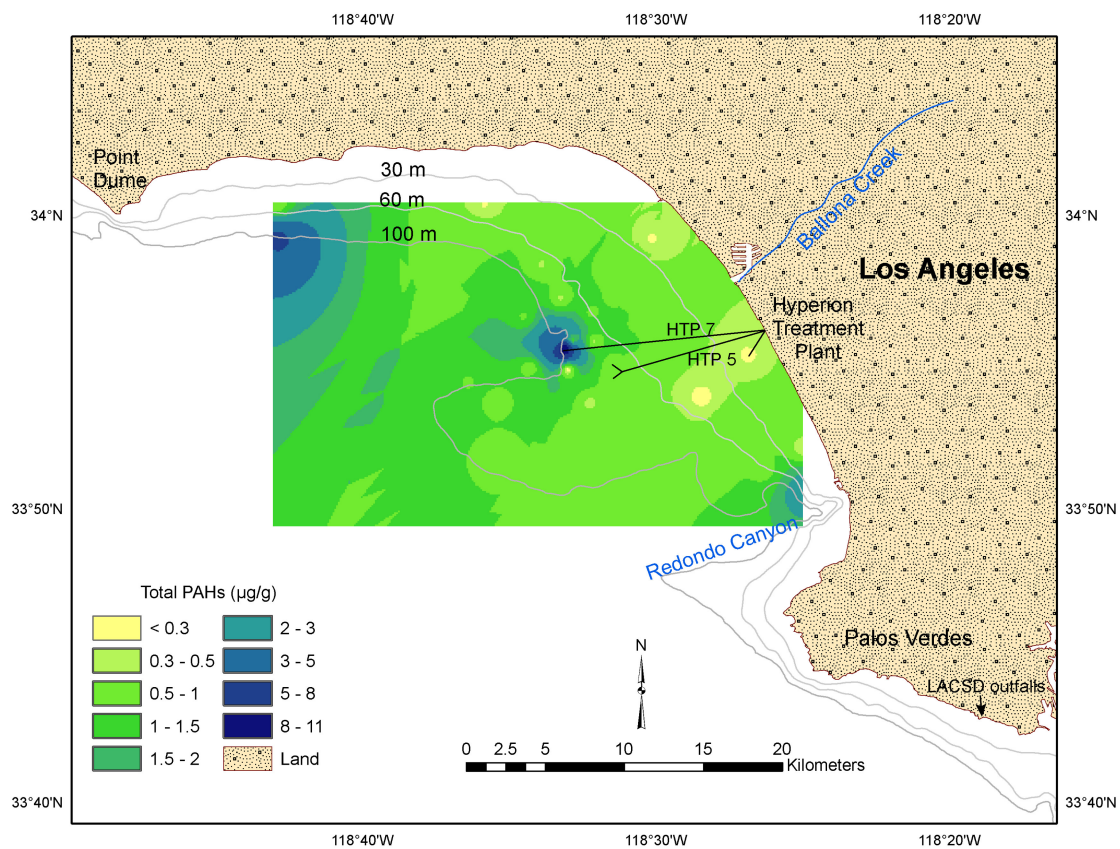












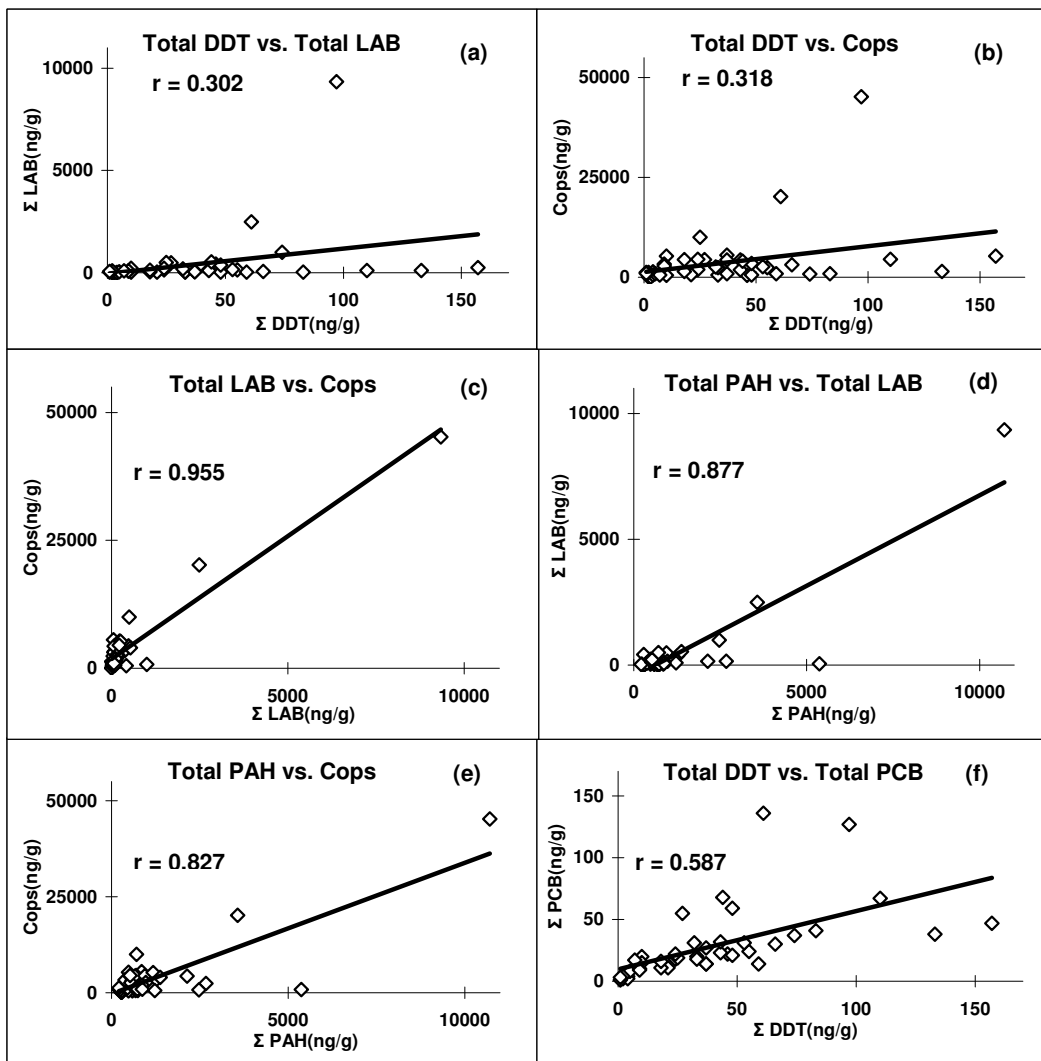


Table 1.

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	Coprostanol ^e
C ₁ -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	
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	
C ₁ -chrysenes/triphenylenes		
C ₂ -chrysenes/triphenylenes		
C ₃ -chrysenes/triphenylenes		
C ₄ -chrysenes/triphenylenes		

^aΣPAH=all parent PAHs+C₁ to C₃ or C₄ homologs; ΣLAB, ΣPCB, chlorinated pesticides (ΣDDT) or Σsterols=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	Water depth meters	Total DDT ^a ng/g	Total PCB ^a ng/g	Total PAH ^a µg/g	Total LAB ^a ng/g	Coprostanols ^a 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	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
C7	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	0.58	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
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	0.73	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
<u>Effluent samples</u>					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

^aFor compounds summed up refer to Table 1.

NA: Not analyzed.

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.

^bStations 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	<i>p,p'</i> -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
Baywide Inventory (metric 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 ^c	>ERL	<ERM ^c	>ERM ^c
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	4022	44792	49	3		
<i>p, p'</i> -DDE	2	27	6	26		20
Total DDTs	2	46	2	34		16
Total PCBs	23	180	29	23		

^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.