

## CHAPTER 5

### SEDIMENT CHEMISTRY

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#### INTRODUCTION

The Terminal Island Water Reclamation Plant (TIWRP) has treated sewage from the Los Angeles Harbor portion of the City of Los Angeles since 1930. TIWRP discharges tertiary effluent into the Los Angeles Outer Harbor. The City of Los Angeles is mandated under the current TIWRP NPDES permit to monitor the receiving water throughout the Los Angeles Outer Harbor to assess the impact of TIWRP outfall on the health of the harbor. The city has fulfilled the NPDES mandate through a monitoring program that includes chemical and physical characterization of sediments of the Los Angeles Outer Harbor for the accumulation of wastewater-related pollutants in the vicinity of TIWRP's outfall. Sediment were collected from 11 receiving water stations in the Harbor and analyzed for grain size, total organic carbon (TOC), dissolved sulfide, total organic halides (TOX), and selected inorganic and organic priority pollutants (13 metals, cyanide, and 57 organic compounds).

In this chapter, results of these analyses on the sediment samples collected during the summers of 2006 and 2007 are presented. The data were examined for spatial patterns of contamination around the TIWRP outfall. The results also were compared with the background levels in the Southern California Bight and other urbanized areas. Historical trends were reviewed to assess temporal changes of pollutant levels in the vicinity of the City's Santa Monica Bay and the Los Angeles

Harbor outfalls and in the reference areas.

#### MATERIALS AND METHODS

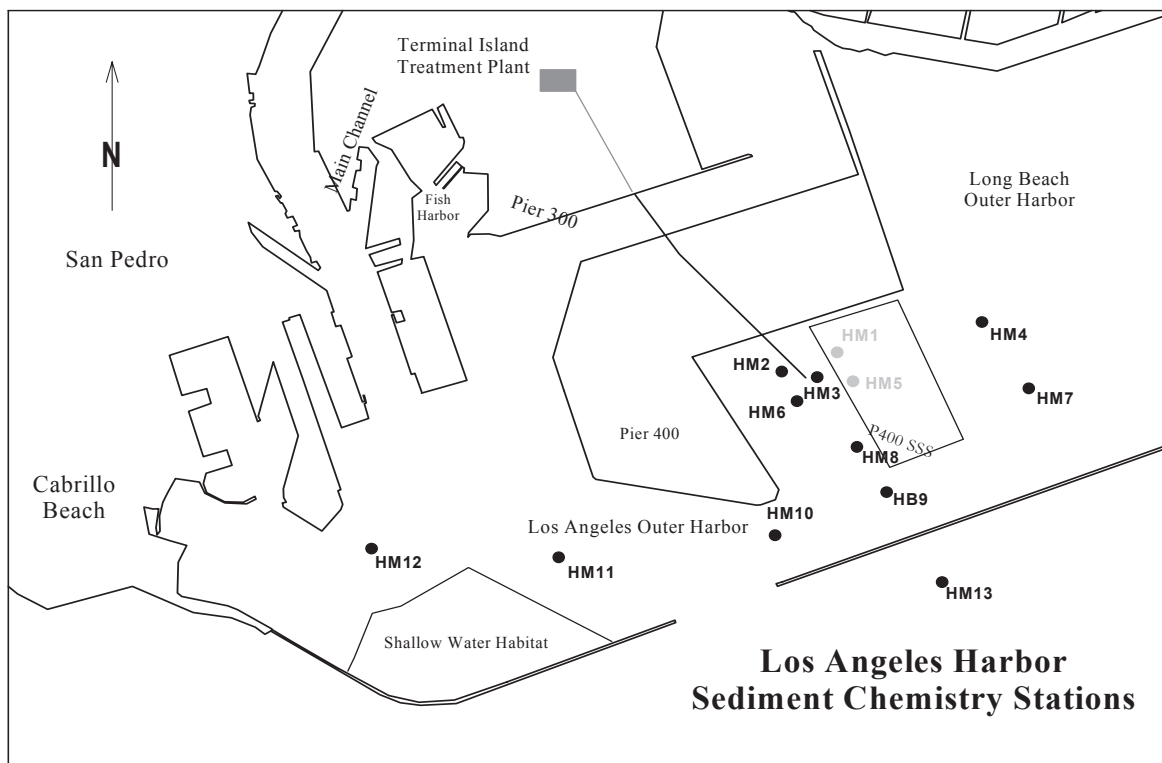
##### FIELD SAMPLING

Single samples of sediment were collected from the outfall stations HM2 – HM4 and HM6 – HM12 in the Outer Harbor and station HM13 outside the Harbor (Figure 5-1) during the summer 2006 and 2007 surveys. Details of sample collection, preservation, and storage are described in Appendix C along with precise descriptions of all analytical procedures. Only general procedures are mentioned below.

##### LABORATORY PROCEDURES

To assess the quality of the sediments, each sample was analyzed using the methods listed in this section.

Sediment grain size was measured using a Beckman Coulter LS 13-230 particle size analyzer. Analyses were performed to determine percentages of gravel (particles >2 mm), sand (particles 2 mm - 64  $\mu\text{m}$ ), silt (particles 63-4  $\mu\text{m}$ ), and clay (particles <4  $\mu\text{m}$ ).



**Figure 5-1.** Sediment chemistry sampling station locations in Los Angeles Harbor.

Dissolved sulfide was determined colorimetrically by the methylene blue method (APHA 1998, Part 4500-S<sup>2-</sup> D). Cyanide was measured by an extraction procedure (APHA 1998, Part 4500-CN<sup>-</sup> C&E). Total organic carbon (TOC) was analyzed using a TOC analyzer after persulfate digestion (APHA 1998, Part 5310 B).

Sediments for priority pollutant metals (except mercury) were digested in strong acids (EPA 1996, Method 3050B) and then analyzed using Inductively Coupled Plasma-Atomic Emission Spectrometry (EPA 1996, Method 6010B). Mercury was analyzed by Cold Vapor method (EPA 1994, Method 7471A). Sediments for organics were solvent-extracted and concentrated prior to analysis. Base/neutral and acid extractable organic compounds (BNA's) were analyzed using a gas chromatograph/mass spectrometer (GC/MS). Organochlorine pesticides and polychlorinated biphenyls (PCB's) were analyzed using a GC equipped with electron capture detectors (ECD). Total organic halides (TOX) were analyzed by Mitsubishi TOX analyzer using EPA Method

9020B and Method SW-846 (1994).

## DATA ANALYSIS

Four sets of data were generated from sediment sample analyses:

1. grain size;
2. cyanide, sulfide, total organic carbon, and total organic halides;
3. priority metal pollutants; and
4. organic priority pollutants.

Sediment data were normalized using methods described by NOAA (1988) in their National Status and Trends Program. Following this technique, raw data were normalized by dividing the raw concentrations by the weight of silt and clay (particles less than 64  $\mu\text{m}$  in diameter). Data were not normalized when the silt and clay fraction of the sediment was less than 20% (therefore priority pollutants at HM13 for 2007 were not normalized).

**Table 5-1.** Grain size distribution of sediments in Los Angeles Harbor surveyed in summer 2006 and 2007.

STATION	PERCENT COMPOSITION							
	GRAVEL		SAND		SILT		CLAY	
	2006	2007	2006	2007	2006	2007	2006	2007
HM2	0.0	0.0	50.5	51.9	38.6	40.3	10.4	7.96
HM3 (outfall)	0.0	0.0	31.2	21.5	53.0	65.1	15.5	13.4
HM4	0.0	0.0	18.0	18.8	61.7	66.2	19.9	14.9
HM6	0.0	0.0	21.7	20.3	60.4	66.5	17.4	13.2
HM7	0.0	0.0	34.0	38.0	49.3	49.7	16.4	12.2
HM8	0.0	0.0	52.8	36.1	35.8	52.4	11.0	11.5
HM9	0.0	0.0	20.0	15.4	59.1	68.9	20.7	15.7
HM10	0.0	0.0	32.9	42.5	51.3	47.2	15.0	10.3
HM11	0.0	0.0	17.5	21.7	61.7	64.0	20.7	14.3
HM12	0.0	0.0	4.95	7.50	65.3	70.1	29.4	22.4
HM13 (outside breakwater)	0.0	0.0	76.9	82.1	18.4	14.9	4.29	2.94

This was done to prevent misleadingly high values in sandy samples (NOAA 1988).

## RESULTS

### GRAIN SIZE

The composition of grain size in the sediments collected at these 11 Los Angeles Harbor stations in 2006 and 2007 is similar to that reported for the last biannual monitoring program (CLA, EMD 2004-2005). In the 2006 and 2007 surveys, the sediment was found to be comprised mainly of silt and sand with no gravel (Table 5-1). Sand was dominant at stations HM2, HM8 (close to the TIWRP outfall) and HM13 (outside the harbor). Sandy silt was found at the rest of the stations.

### TOTAL ORGANIC CARBON

Over the 2006-2007 monitoring period, uniform levels of TOC were detected within Los Angeles Harbor (Table 5-2) with the exception of HM8 in 2006 and HM12 in 2007, where levels were high at 23566 mg/kg dry-wt and 25360 mg/kg dry-wt, respectively. There was a 17% increase at HM3 (from 15919 mg/kg dry-wt in 2006 to 18635 mg/kg dry-wt in 2007). TOC level at the breakwater (HM13) was much lower in 2007 than in 2006. Substantially higher TOC concentrations were measured at HM6,

HM9, and HM12 in 2007.

### CYANIDE, DISSOLVED SULFIDE, AND TOTAL ORGANIC HALIDES

In 2006, TOX and dissolved sulfide were not detected; cyanide was detected only at HM10 (Table 5-3). TOX, dissolved sulfide, and cyanide were not analyzed in 2007.

### PRIORITY POLLUTANTS: METALS AND ORGANICS

Out of a total of 70 priority pollutants (see Appendix D), 18 were detected in 2006 and 17 in 2007.

### METALS

In 2006, eight of the 13 metals of interest were found in Los Angeles Harbor sediments. Detected at all sites were arsenic, cadmium, chromium, copper, lead, mercury, nickel, and zinc (Table 5-3). Silver was not detected at any of the sites.

In 2007, all eight priority pollutant metals found in 2006 were detected at all sites; silver was detected at all stations, but not HM13. When detected, the level of silver was low (<0.6 mg/kg dry-wt).

In the 2006 and 2007 summer surveys, the metal with

**Table 5-2.** TOC (mg/kg dry-wt) in Los Angeles Harbor sediment in the summers of 2006 and 2007.

STATION	TOC mg/kg	
	2006	2007
HM2	13046	10812
HM3(outfall)	15919	18635
HM4	13988	15800
HM6	13780	17648
HM7	15353	15772
HM8	23566	17159
HM9	14455	20632
HM10	16205	14703
HM11	15514	16325
HM12	16555	25360
HM13(outside breakwater)	15383	3097

the highest concentration at all 11 stations was zinc; zinc concentrations ranged from 42.1 to 184 mg/kg dry-wt. Mercury had the lowest concentration, ranging from 0.038 to 0.401 mg/kg dry-wt.

In the 2006 survey, station HM13 measured the highest total metals concentration and station HM10 showed the lowest (Figure 5-2). In the 2007 survey, the results were different. Station HM12 had the highest total metals concentration while HM13 had the lowest (the metal concentration were not normalized due to silt and clay fraction of the sediment was less than 20%).

## PESTICIDES AND PCB'S

Out of the 26 pesticides and PCBs tested, only six were detected in 2006 and four of the six in 2007 (Table 5-4).

In 2006, three of the pesticides, *o,p'*-DDE, *p,p'*-DDE, and *p,p'*-DDD, were detected at the HM3 (outfall), and six other monitoring stations (Table 5-4). Their levels were comparable to or lower than those at the HM13 (outside breakwater). *p,p'*-DDE was detected at all 11 stations, and *o,p'*-DDE was detected at all stations but HM8 and HM12. *p,p'*-DDD was not detected at HM4 and HM9. *p,p'*-DDT was only detected at HM12 and HM13 and

not at HM3 (outfall). The highest levels of total DDT were at HM12 and HM13 and the lowest at HM8 (Figure 5-3). PCB Aroclor 1254 and Aroclor 1260 were detected at HM4 and HM7, respectively.

In 2007, total DDT concentration level was low at HM13 compared to the rest of the harbor stations. At HM3 (outfall), for example, the levels of *p,p'*-DDE and *o,p'*-DDE were two times higher than those at HM13. *p,p'*-DDD was detected at HM4, HM6, HM9, and HM11 while *p,p'*-DDT was detected only at HM4. The highest levels of total DDT were detected at HM2, HM9, and HM12 (Figure 5-3). The lowest concentration of total DDT was detected at HM13. *p,p'*-DDD and *p,p'*-DDT were not detected at HM3 and HM13. No PCBs were detected at any stations in 2007.

## BASE/NEUTRAL AND ACID EXTRACTABLE COMPOUNDS (BNAS)

Out of 31 BNAs targeted in this monitoring program, only isophorone, di-*n*-butylphthalate, di-*n*-octylphthalate, diethylphthalate, and bis(2-ethylhexyl)phthalate were detected in the 2006 and 2007 monitoring periods (Table 5-4). Isophorone was found only at HM10 in 2006. Diethylphthalate was detected at all stations except at HM12 in 2006 and HM6, HM8, HM11, and HM12 in 2007. Di-

**Table 5-3.** Cyanide, dissolved sulfide, TOX, and metals (mg/kg dry-wt) detected in sediments at stations HM2-HM4 and HM6-HM13 of Los Angeles Harbor in the summers of 2006 and 2007. Concentrations were normalized against the fine grain fraction (except HM13 in 2007).

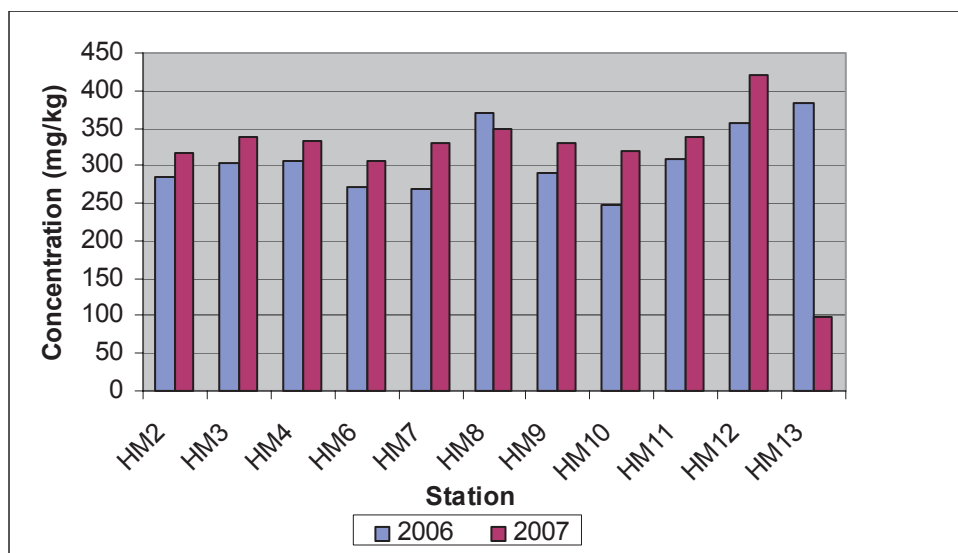
POLLUTANTS	STATIONS										
	HM2	HM3	HM4	HM6	HM7	HM8	HM9	HM10	HM11	HM12	HM13
<b>2006</b>											
<b>Metals (mg/kg):</b>											
Arsenic	5.22	4.82	3.16	4.54	6.35	7.31	4.21	4.06	7.27	5.43	18.4
Cadmium	4.53	4.67	4.39	4.42	4.06	5.98	4.40	4.27	4.33	4.67	6.87
Chromium	57.1	58.2	57.7	52.7	51.0	72.0	58.9	51.3	59.7	64.7	83.7
Copper	45.9	57.5	60.5	53.2	50.4	73.1	56.9	44.5	63.6	92.9	39.2
Lead	5.86	5.62	11.1	5.87	9.74	2.48	9.07	3.32	5.16	11.1	14.4
Mercury	0.231	0.247	0.306	0.231	0.260	0.248	0.239	0.184	0.244	0.096	0.310
Nickel	30.2	35.0	31.4	30.3	27.4	50.0	32.7	29.6	37.6	34.9	37.4
Zinc	135	137	137	122	120	159	124	112	131	144	184
<b>Others (mg/kg):</b>											
TOX	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Cyanide	ND	ND	ND	ND	ND	ND	ND	0.45	ND	ND	ND
Dissolved sulfide	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
<b>2007</b>											
<b>Metals (mg/kg):</b>											
Arsenic	8.70	8.45	7.00	7.42	7.98	8.92	8.56	9.08	10.3	10.1	4.06
Cadmium	1.26	1.53	1.25	1.36	1.24	1.83	1.55	1.27	1.28	1.36	0.37
Chromium	62.2	65.9	61.6	60.7	63.0	68.2	66.8	60.4	66.2	73.8	22.0
Copper	48.9	61.8	62.5	56.6	58.2	63.2	62.1	49.2	68.4	114	8.96
Lead	21.8	21.0	27.9	19.1	28.3	19.2	27.1	39.0	19.0	28.5	11.9
Mercury	0.183	0.208	0.265	0.186	0.401	0.154	0.234	0.197	0.185	0.289	0.038
Nickel	31.3	37.3	31.7	32.9	31.3	41.2	35.5	34.1	39.3	38.0	9.0
Silver	0.207	0.408	0.395	0.364	0.323	0.501	0.473	0.313	0.434	0.584	ND
Zinc	143	141	141	128	140	146	129	127	133	156	42.1
<b>Others (mg/kg)</b>											
TOX	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
Cyanide	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
Dissolved sulfide	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
<b>ND=Not detected</b>											
<b>NA=Not analyzed</b>											

n-octylphthalate was found in sediment collected from station HM2 and HM3 in 2007.

## DISCUSSION

### PATTERNS OF GRAIN SIZE AND TOC IN 2006 AND 2007

Distribution of fine grained sediments and TOC in the 2006 and 2007 sampling years are shown in Figures 5-4 and 5-5, respectively. The fine grain (silt + clay) percentages were greater than 45% at all stations except HM13, which is outside the harbor. TOC varied the most at station HM12; the concentration increased significantly from 16555 to 25360 mg/kg dry-wt.



**Figure 5-2.** Total metals (mg/kg dry-wt) in Los Angeles Harbor sediment in 2006 and 2007. Concentrations were normalized against fine grain fraction.

### SPATIAL PATTERNS OF METALS AND ORGANICS IN 2006 AND 2007

In 2006, the concentrations of all metals (except copper) were lower at all stations inside the harbor than at HM13 (outside breakwater); the nickel concentration was higher at HM8 and HM11 than at HM13. In 2007, all metal concentrations were lower at HM13 than that at stations inside the harbor (Table 5-3). This reversed trend could be the result of low percent silt and clay in sediment collected at HM13 in 2007 (Table 5-1). Tables 5-3 and 5-5 show that in 2006, all metals concentrations (except mercury, nickel, and zinc) at HM3 (outfall) were lower than the average concentrations across all 11 stations. Concentrations of arsenic, copper, lead, and mercury were lower at HM3 than the average of all 11 stations in 2007.

Table 5-4 shows the concentrations of BNA and pesticide compounds detected in the Los Angeles Harbor sediments collected in 2006 and 2007. In 2006, di-n-butylphthalate and bis(2-ethylhexyl)phthalate were not detected at HM3 but were at HM13 (outside the harbor). Only diethylphthalate was detected at HM3. Isophorone was not detected either at HM3 or HM13.

In 2007, four BNAs were detected at HM3 while only di-n-butylphthalate and diethylphthalate were found outside the harbor at HM13. Di-n-butylphthalate was found at HM3 at a level higher than the average of the 11 stations but not HM13; the concentrations at HM13 in 2006 exceeded the 11-station average but not in 2007 (Table 5-6).

In 2006, o,p'-DDE, p,p'-DDE, and p,p'-DDD were detected at HM3. o,p'-DDE and p,p'-DDE were found at concentrations lower than the average of the 11 stations (Table 5-6). p,p'-DDD level was comparable to the average and less than that at HM13. All four pesticides, including p,p'-DDT, were detected at HM13 and all but p,p'-DDT exceeded the 11-station average. In 2007, only o,p'-DDE and p,p'-DDE were found at both HM3 and HM13; both below the 11-station average.

A comparison of total DDTs at the outfall station HM3 and the outer harbor station HM13 from 2003 to 2007 (Table 5-9) indicate that the total DDTs in sediment at HM13 is higher than at HM3. This most likely is due to HM13 being physically closer to the major source of DDT associated with the White Point (Palos Verdes) discharge than is the TWRP outfall (Eganhouse and Pontolillo, 2000).

Except for copper, mercury, lead, and silver (not

**Table 5-4.** BNA (mg/kg dry-wt) and Pesticides/PCBs ( $\mu\text{g}/\text{kg}$  dry-wt) detected in sediments at station HM2 - HM4 and HM6 - HM13 of Los Angeles Harbor in the summers of 2006 and 2007. Concentrations were normalized against the fine grain fraction (except HM13 in 2007).

POLLUTANTS	STATIONS										
	HM2	HM3	HM4	HM6	HM7	HM8	HM9	HM10	HM11	HM12	HM13
<b>2006</b>											
<b>Base Neutral Acids (mg/kg):</b>											
Isophorone	ND	ND	ND	ND	ND	ND	ND	3.6	ND	ND	ND
Di-n-Butylphthalate	0.6	ND	0.7	ND	0.5	ND	ND	0.6	0.6	ND	1.4
Diethylphthalate	1.4	1.2	1.7	6.0	1.4	2.1	2.6	3.1	1.1	ND	3.3
Bis(2-ethylhexyl)-phthalate	0.9	ND	2.7	ND	2.2	ND	17.5	3.1	1.2	0.7	7.4
<b>Pesticides/PCBs (<math>\mu\text{g}/\text{kg}</math>):</b>											
o,p' - DDE	29.3	11.7	12.0	12.7	15.6	ND	12.7	16.6	13.4	ND	32.6
p,p' - DDE	126	56.6	65.4	75.9	87.2	43.3	77.2	82.6	76.2	91.6	179
p,p' - DDD	6.2	5.3	ND	4.8	5.5	3.6	ND	7.7	4.6	14.4	6.2
p,p' - DDT	ND	ND	ND	ND	ND	ND	ND	ND	ND	119	8.0
Arochlor 1254	ND	ND	ND	ND	95.6	ND	ND	ND	ND	ND	ND
Arochlor 1260	ND	ND	39.2	ND	ND	ND	ND	ND	ND	ND	ND
<b>2007</b>											
<b>Base Neutral Acids (mg/kg):</b>											
Di-n-Butylphthalate	11.9	7.6	0.7	1.8	0.6	4.2	2.6	0.8	5.6	6.8	0.4
Diethylphthalate	1.2	0.6	1.4	ND	2.1	ND	1.6	2.2	ND	ND	1.0
Bis(2-ethylhexyl)-phthalate	4.4	0.7	0.8	ND	ND	0.8	0.8	0.9	3.2	0.8	ND
Di-n-octylphthalate	2.3	1.6	ND	ND	ND	ND	ND	ND	ND	ND	ND
<b>Pesticides (<math>\mu\text{g}/\text{kg}</math>):</b>											
o,p' - DDE	39.0	18.0	14.5	20.3	17.4	19.6	26.9	18.9	20.6	33.4	8.9
p,p' - DDE	139	82.3	75.4	101	84.6	86.4	135	85.2	105	147	48.3
p,p' - DDD	ND	ND	7.5	9.7	ND	ND	8.1	ND	9.9	ND	ND
p,p' - DDT	ND	ND	8.0	ND	ND	ND	ND	ND	ND	ND	ND

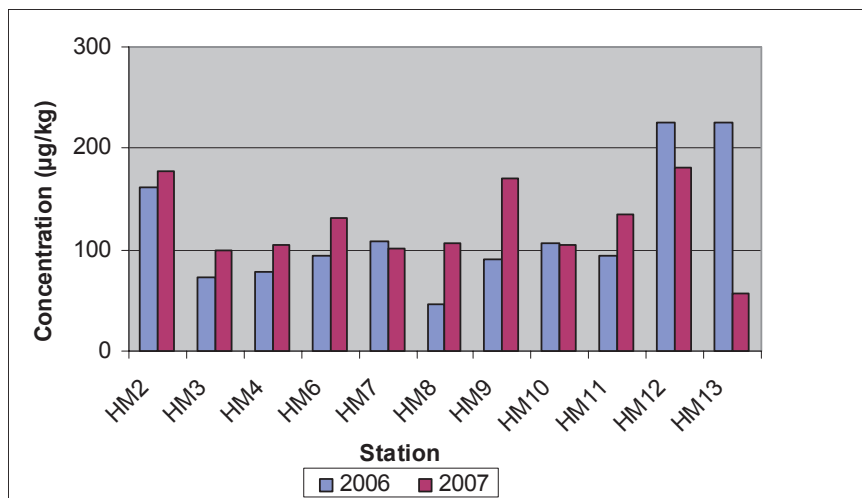
ND=Not detected

detected in 2006), the average concentrations of the pollutants at the Los Angeles Harbor were higher than the average found in Southern California Bight ports in 2003 (SCCWRP 2006; Table 5-7).

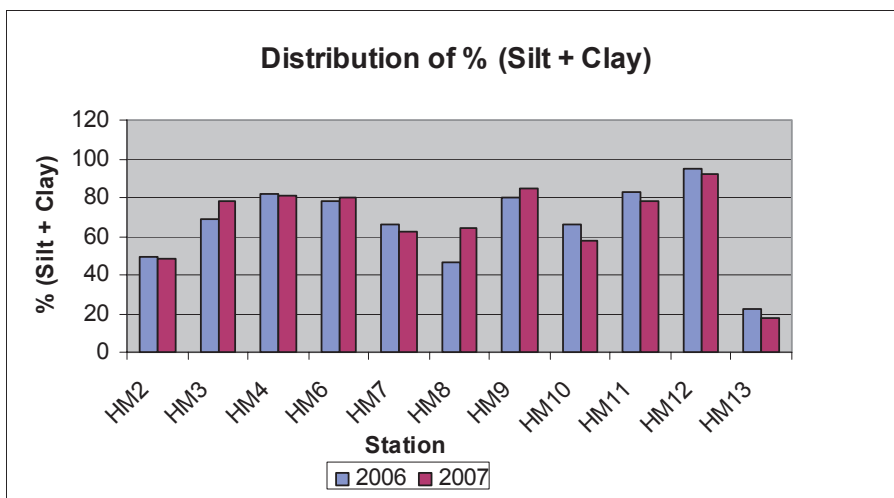
Los Angeles Harbor is an enclosed harbor that contains the TIWRP outfall (HM3). It is, therefore, informative to compare the health of the receiving water at HM3 with similar sites along the Southern

California Coast. To this end the concentrations of the priority pollutants at HM3 are compared with concentrations at the Hyperion Waste Water Treatment Plant (HTP) outfall station (Z2) and two reference sites (C1 and Dana Point, Table 5-8).

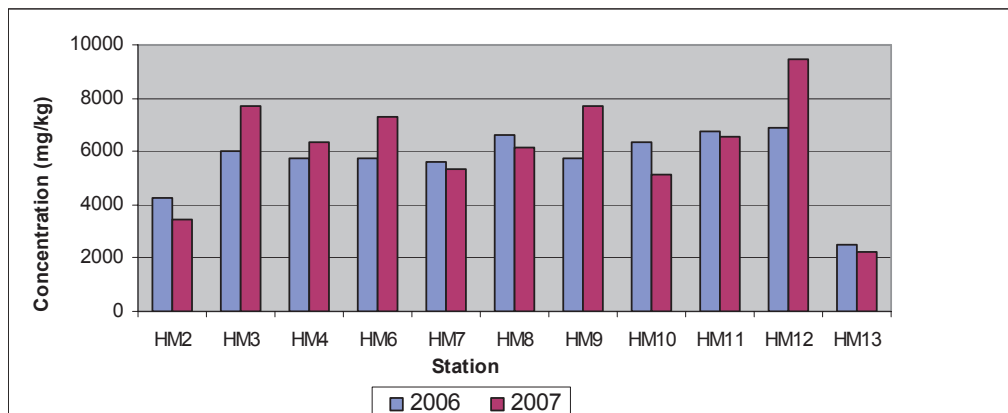
In 2006, concentrations of cadmium, chromium, and mercury at HM3 were found to be twice the concentrations at Z2; similar ratios were found for



**Figure 5-3.** Total DDT ( $\mu\text{g}/\text{kg}$  dry-wt) in Los Angeles Harbor sediment in 2006 and 2007.



**Figure 5-4.** Distribution of % (Silt + Clay) in Los Angeles Harbor in 2006 and 2007.



**Figure 5-5.** TOC in Los Angeles Harbor sediment in 2006 and 2007.

**Table 5-5.** Metals (mg/kg dry-wt) in sediments of Los Angeles Harbor in the summers of 2006 and 2007. Concentrations were normalized against the fine grain fraction (except HM13 in 2007).

POLLUTANTS	L.A. Harbor (2006)			L.A. Harbor (2007)		
	#	Ave.*	Range	#	Ave.*	Range
<b>Metals (mg/kg):</b>						
Arsenic	11	6.4	3.2-18.4	11	8.7	7.0-10.3
Cadmium	11	4.8	4.1-6.9	11	1.4	1.2-1.8
Chromium	11	60.6	51.0-83.7	11	64.9	60.4-74
Copper	11	58.0	39.2-92.9	11	64.4	48.9-114
Lead	11	7.6	2.5-14.4	11	25.1	19.0-39.0
Mercury	11	0.24	0.1-0.3	11	0.21	0.04-0.4
Nickel	11	34.2	27.4-50.0	11	35.2	31.3-41.2
Silver	0	ND	ND	10	0.36	0-0.58
Zinc	11	137	112-184	11	138	127-156

#Number of stations where metals were detected

\*Average of 11 stations. Concentrations below detection limit were taken as zero.

**Table 5-6.** BNA (mg/kg dry-wt) and Pesticides ( $\mu\text{g}/\text{kg}$  dry-wt) detected in sediments of Los Angeles Harbor, in the summers of 2006 and 2007. Concentrations were normalized against fine grain fraction (except HM13 in 2007).

POLLUTANTS	L.A. Harbor (2006)			L.A. Harbor (2007)		
	#	Ave.*	Range	#	Ave.*	Range
<b>Base Neutral Acids (mg/kg):</b>						
Di-n-Butylphthalate	6	0.4	ND-1.36	11	3.9	0.4-11.9
Diethylphthalate	10	2.2	ND-6.0	7	0.9	ND-2.2
Bis(2-ethylhexyl)phthalate	8	3.2	ND-17.5	8	1.1	ND-4.4
<b>Pesticides (<math>\mu\text{g}/\text{kg}</math>):</b>						
o,p' - DDE	9	14.2	ND-32.6	11	21.6	8.9-39.0
p,p' - DDE	11	87.4	43.3-179	11	99.1	48.3-147
p,p' - DDD	9	5.3	ND-14.4	4	3.2	ND-9.9
p,p' - DDT	2	11.5	ND-119	1	0.7	ND-8.0

# Number of stations where detected

\* Average of 11 stations. Concentrations below detection limit were taken as zero.

zinc and mercury at HM3 versus C1. At HM3, the concentrations of copper were three times, nickel four times, and total DDT six times higher than of those at Z2. Silver was not detected at any of these stations in 2006. Copper at HM3 was three times its levels at C1; whereas, the total DDT level at HM3

was comparable to that found at C1.

In 2007, the concentrations of arsenic, lead, and mercury at HM3 were twice of those found at Z2, while those of cadmium and chromium were three times, copper and total DDT four times, and zinc

**Table 5-7.** Concentrations of metals (mg/kg dry-wt) and organic pollutants ( $\mu\text{g}/\text{kg}$  dry-wt) in Los Angeles Harbor during the summers of 2006 and 2007 with a comparison to concentrations in Southern California Bight (SCB) ports in 2003.

Contaminant	LA Harbor		SCB Ports
	2006	2007	2003
<b>Metals (mg/kg)</b>			
As	6.43	8.7	4.3
Cd	4.78	1.4	0.86
Cr	60.6	64.9	39
Cu	58.0	64.4	70
Hg	0.24	0.21	0.28
Pb	7.61	25.1	29
Ni	34.2	35.2	18
Ag	ND	0.4	0.2
Zn	137	138	128
<b>Total DDT (<math>\mu\text{g}/\text{kg}</math>)</b>	118	125	25
<b>PCBs (<math>\mu\text{g}/\text{kg}</math>)</b>	12.3	ND	7.7

ND=Not detected

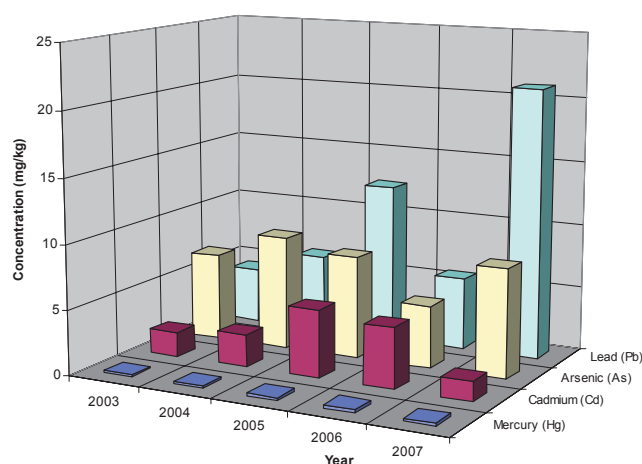
and nickel five times the levels at Z2. Compared to C1, the concentration of cadmium was double and copper was three times higher at HM3.

Total DDT was detected at all three sites (HM3, Z2 and C1). PCB Aroclors were not detected at HM3 in either year, but was detected at Z2 and C1 in 2006. Except cadmium, copper, nickel, and total DDT, the levels of all contaminants detected were lower at HM3 than at the Dana Point reference site (NOAA 1988, Table 5-8).

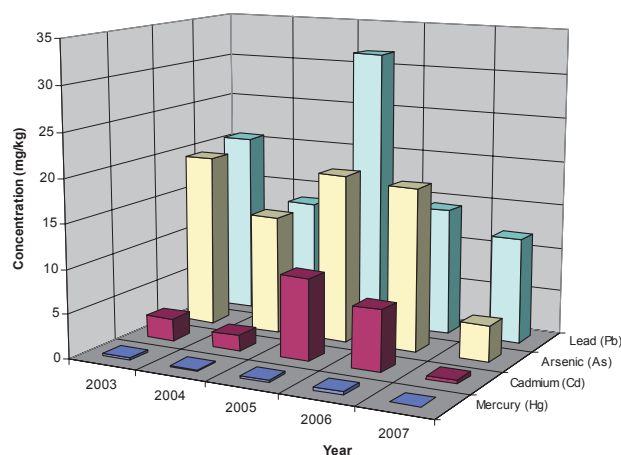
### TEMPORAL PATTERNS OF METALS AND ORGANICS IN 2006 AND 2007

Five years of priority pollutant metals data were examined for temporal patterns. Mercury (Figures 5-6 and 5-7) and silver (not shown) have maintained the same low level concentrations over the years. The concentrations of other metals have fluctuated within the last five years at both stations, HM3 and HM13 (Figures 5-6 through 5-9).

Zinc concentration at HM3, varied the least over the five-year period (Figure 5-8). The concentration ranged from the lowest level (124 mg/kg dry-wt)



**Figure 5-6.** Trends of mercury, cadmium, arsenic, and lead at Station HM3 from 2003 to 2007.



**Figure 5-7.** Trends of mercury, cadmium, arsenic, and lead at Station HM13 from 2003 to 2007.

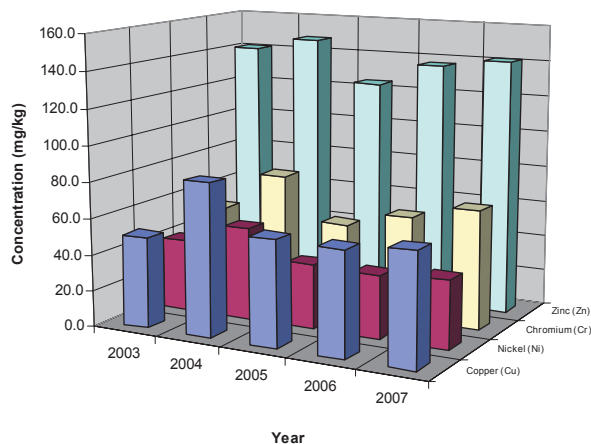
in 2005 to the highest (148 mg/kg dry-wt) in 2004. Cadmium and lead at HM3 fluctuated the most among all the metals (Figure 5-6). The concentration of cadmium, at 1.5 mg/kg dry-wt in 2007, was only one-third its value of 5.2 mg/kg dry-wt in 2005. Lead concentration quadrupled from 4.4 mg/kg dry-wt in 2003 to 12.4 mg/kg dry-wt in 2005, then decreased to 5.6 mg/kg dry-wt in 2006 before it peaked at 21.0 mg/kg dry-wt in 2007 (Figure 5-6). Silver was rarely detected in the last five years; it was detected only in 2004 (0.1 mg/kg dry-wt) and 2007 (0.4 mg/kg dry-wt). Overall, the highest concentrations of all metals (except cadmium and lead) were measured in 2004.

**Table 5-8.** Comparison of contaminant levels at TIWRP outfall, stations in Santa Monica Bay and a reference site at Dana Point. Concentrations were normalized against the fine grain fraction.

Contaminants	LA Harbor		SMB		Reference Site		
	TIWRP Outfall*		Z2	C1	Dana Point		
	2006	2007	2006	2007	2006	2007	
<b>Metals (mg/kg):</b>							
Arsenic	4.8	8.4	4.0	3.7	3.1	5.7	29.8
Cadmium	4.7	1.5	2.0	0.5	3.8	0.8	1.37
Chromium	58.2	65.9	29.1	26.3	64.1	66.5	141
Copper	57.5	61.8	14.4	14.8	20.2	19.6	30.2
Lead	5.6	21.0	4.9	9.6	7.2	19.1	51.4
Mercury	0.2	0.2	0.1	0.1	0.1	0.2	0.63
Nickel	35.0	37.3	9.4	6.8	33.7	30.3	25.5
Silver	ND	0.4	ND	1.2	ND	0.8	1.87
Zinc	137	141	39.6	30.2	89.1	78.5	169
<b>Pesticides &amp; PCB (µg/kg):</b>							
Total DDT	73.7	100	11.8	24.2	82.5	103.5	NA
Total PCB	ND	ND	71.4	ND	161	ND	20.3
ND – Not Detected; NA – Not Available							
* TIWRP Outfall Station HM3							
Z2 – HTP Outfall							
C1 – Station near Point Dume							
Dana Point – 1984-1987 Reference Site Survey (NOAA 1988)							

**Table 5-9.** Temporal pattern of total DDT and metals concentrations at HM13 (outside breakwater of the Harbor) and HM3 (outfall). Concentrations were normalized against fine grain fraction.

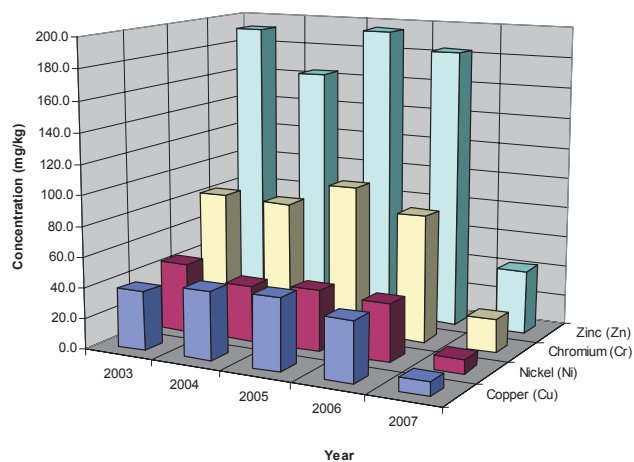
	TOTAL DDT (µg/kg)		TOTAL METALS (mg/kg)	
	HM3	HM13	HM3	HM13
2003	117	194	295	402
2004	84.3	278	375	354
2005	71.5	163	294	442
2006	73.7	226	303	384
2007	100	57.0	338	98.4



**Figure 5-8.** Trends of chromium, copper, nickel, and zinc at Station HM3 from 2003 to 2007.

The concentrations of metals at station HM13 (outside breakwater) exhibited higher variation than HM3. The lowest concentration of cadmium was 0.4 mg/kg dry-wt measured in 2007 and the highest was 9.3 mg/kg dry-wt detected in 2005—two orders of magnitude higher. All metals concentrations except silver varied from two to five times within the five-year period. Silver was not detected at HM13 in the last five years. In 2007, all metals concentrations detected at HM13 were low, which appears to be related to their low silt and clay percent (17.8%).

Among organic priority pollutants, DDTs were repeatedly detected in the Los Angeles Harbor surveys. At Station HM3 (ITWRP outfall), the concentration of DDTs declined from a high of 117  $\mu\text{g}/\text{kg}$  dry-wt in 2003 to a low of 71.5  $\mu\text{g}/\text{kg}$  dry-wt in 2005, but increased to 100  $\mu\text{g}/\text{kg}$  dry-wt in 2007, its second highest level in the five-years surveyed (Table 5-9). In general, station HM13 (outside breakwater) exhibited higher DDTs concentrations than HM3 and has been maintaining similar levels from 2003 to 2006. The lowest concentration of total DDT during this period was 163  $\mu\text{g}/\text{kg}$  dry-wt detected in 2005 and the highest was 278  $\mu\text{g}/\text{kg}$  dry-wt measured in 2004. In 2007, the total DDT level detected at HM13 was exceptionally low (57.0  $\mu\text{g}/\text{kg}$  dry-wt) as a results of the data were not normalized by fine grain fraction. When the silt and clay content is less than 20%, the DDTs data are not normalized. PCBs had not been detected in the last



**Figure 5-9.** Trends of chromium, copper, nickel, and zinc at Station HM13 from 2003 to 2007.

five years at either station.

Over the five-year period, the concentration of total metal contaminants detected at HM3 remained constant at  $321 \pm 35$   $\mu\text{g}/\text{kg}$  dry-wt. A similar pattern at a slightly higher concentration of total metal is observed at HM13 between 2003 and 2006 ( $396 \pm 37$   $\mu\text{g}/\text{kg}$  dry-wt). In 2007 the total concentration of metals is again abnormally low because these concentrations are not normalized by grain size fraction.

## CONTAMINATION ASSESSMENT IN LOS ANGELES HARBOR

To assess the biological impact of sediment contaminants of the Los Angeles Harbor, the metals, DDTs, and PCBs levels in the sediments were compared with the Effective Range-Low (ER-L), and the Effective Range-Median (ER-M) values (Long et al 1995). The ER-L and ER-M values correspond, respectively, to bulk sediment concentrations below which effects to benthic organisms are rarely observed (ER-L) and levels above which effects are frequently observed or expected (ER-M).

In 2006, as shown in Table 5-10, the average concentrations of all metals and the organics except total DDT were consistently below the corresponding ER-M values. Average concentration of total DDT

**Table 5-10.** Concentrations of metals and organic pollutants in sediments of Los Angeles Harbor, summer 2006 and 2007, with comparison to Effective Levels\* (ER-L and ER-M). Concentrations were normalized against fine grain fraction.

Contaminants	LA Harbor (2006)		LA Harbor (2007)		ER-L*	ER-M*
	Ave**	HM3***	Ave**	HM3***		
<b>Metals (mg/kg):</b>						
Arsenic	6.4	4.8	8.7	8.5	8.2	70.0
Cadmium	4.8	4.7	1.4	1.5	1.2	9.6
Chromium	60.6	58.2	64.9	65.9	81.0	370
Copper	58.0	57.5	64.4	61.8	34.0	270
Lead	7.6	5.6	25.1	21.0	46.7	218
Mercury	0.2	0.2	0.2	0.2	0.2	0.7
Nickel	34.2	35.0	35.2	37.3	20.9	51.6
Silver	ND	ND	0.4	0.4	1.0	3.7
Zinc	137	137	138	141	150	410
<b>PAHs (µg/kg):</b>	ND	ND	ND	ND	4,022	44,792
<b>Pesticides and PCB (µg/kg):</b>						
Total DDT	118	73.7	125	100	1.58	46.1
Total PCB	12.3	ND	ND	ND	22.7	180

ND= Not detected

\* Source: Long et.al. (1995).

\*\* Average of 11 stations. Concentrations below detection limit were taken as zero

\*\*\* TIWRP outfall station

in the Harbor sediments was higher than both ER-L and ER-M values. At the outfall station, HM3, the concentrations of all metals were all below the corresponding ER-M values, but the concentrations of cadmium, copper, nickel, and total DDT were above their respective ER-L values.

In 2007, as shown in Table 5-10, average concentrations of all metals and the organics except total DDT were consistently below the corresponding ER-M values. Average concentration of priority metals in the Harbor sediments was lower than ER-M values but higher than ER-L with the exception of arsenic (2006 only), chromium, lead, silver, and zinc (Table 5-10). At the outfall station HM3, the concentrations of metals were all below the corresponding ER-M values, but the concentrations of arsenic (2007 only), cadmium, copper, nickel, and total DDT were above their respective ER-L values.

Based on their concentrations with respect to ER-L and ER-M, metals and PCBs are expected to have little or no biological impact on benthic organisms at TIWRP outfall, but total DDT is expected to have some biological impact.

## LITERATURE CITED

- APHA. See American Public Health Association.
- American Public Health Association. 1998. Standard Methods for the Examination of Water and Wastewater, 20th ed. American Public Health Association, Washington, DC, pp. 1-1 to 10-161 + plates.
- CLA, EMD. See City of Los Angeles, Environmental Monitoring Division.

- City of Los Angeles, Environmental Monitoring Division. 2003. Marine Monitoring in the Los Angeles Harbor: Annual Assessment Report for the Period January 2002 through December 2002. Report submitted to EPA and RWQCB (Los Angeles). Department of Public Works, Bureau of Sanitation, Terminal Island Treatment Plant, San Pedro, California, pp. 1-1 to 8-12 + appendices.
- City of Los Angeles, Environmental Monitoring Division. 2004-2005. Marine Monitoring in the Los Angeles Harbor: Biennial Assessment Report for the Period January 2004 through December 2005. Report submitted to EPA and RWQCB (Los Angeles). Department of Public Works, Bureau of Sanitation, Terminal Island Treatment Plant, San Pedro, California, pp. 1-1 to 8-12 + appendices.
- Eganhouse, RP. and Pontolillo, J. 2000. Depositional History of Organic Contaminants on the Palos Verdes Shelf, California. *Marine Chemistry* 70, 317-338.
- EPA. See United States Environmental Protection Agency.
- United States Environmental Protection Agency. 1996. Acid Digestion of Sediments, Sludges, and Soils. EPA Method 3050B Revision 2, National Technical Information Services, Springfield, VA (<http://www.epa.gov/SW-846/pdfs/3050b.pdf>).
- United States Environmental Protection Agency. 1996. Inductively Coupled Plasma-Atomic Emission Spectrometry. EPA Method 6010B. Region 8-Biosolids Documents. (<http://www.epa.gov/region8/water/biosolids/biosolidsdown/method/6010B.pdf>).
- United States Environmental Protection Agency. 1994. Mercury in Liquid Waste (Manual Cold-Vapor Technique)' EPA Method 7471A Revision 1 (<http://www.epa.gov/testmethods/pdfs/7470a.pdf>).
- United States Environmental Protection Agency. 1994. Total Organic Halides (TOX)' EPA Method 9020B Revision 2. (<http://www.epa.gov/epaoswer/hazwaste/test/pdfs/9020b.pdf>).
- United States Environmental Protection Agency. 1994. Test Methods for Evaluating Solid Waste. EPA SW-846, Volume 1B: Laboratory Manual Physical/Chemical Methods; 3rd Edition, Revision 2., Office of Solid Waste and Emergency Response, Washington, DC, unpagged.
- Long E.R., McDonald D. D., Smith, S.L. and Calder, F.C. 1995. Incidence of Adverse Biological Effects Within Ranges of Chemical Concentrations in Marine and Estuarine Sediments. *Environ. Manage.* 19: 81-97.
- NOAA. See National Oceanic and Atmosphere Administration.
- National Oceanic and Atmosphere Administration. 1988. National Status and Trends Program for Marine Environmental Quality. A Summary of Selected Data on Chemical Components in Sediments Collected During 1984, 1985, 1986 and 1987. NOAA Technical Memorandum NOS OMA 44. NOAA Office of Oceanography and Marine Assessment, Rockville Maryland, 15 pp. + appendices.
- SCCWRP. See Southern California Coastal Water Research Project.
- Southern California Coastal Water Research Project. 2006. Schiff, K., Maruya, K. and Christenson, K. Southern California Bight 2003 Regional Monitoring Program: II. Sediment Chemistry. Garden Grove, California, 27 pp. + appendices.