

## **CHAPTER 5. SEDIMENT CHEMISTRY**

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### **I. INTRODUCTION**

The City of Los Angeles's Terminal Island Treatment Plant (TITP) discharges filtered secondary effluent into the Outer Los Angeles Harbor. The TITP NPDES permit mandates monitoring of receiving water throughout the Outer Los Angeles Harbor to determine the impact, if any, from the discharged secondary effluent from the Plant. The Plant's current NPDES permit became effective in March 1993. The program included chemical and physical characterization of sediments of the Outer Los Angeles Harbor stations to assess the accumulation of wastewater-related pollutants in the vicinity of TITP's outfall (EMD 1993 to 2002).

The TITP's NPDES mandated receiving water monitoring program, including the sampling stations, was modified several times during the period of 1994 -1995 (see Table 1-1 in Chapter 1). The modifications during this period were necessary to accommodate the continuous construction activities within the Outer Los Angeles Harbor associated with the construction of Pier 400, and changes in the configuration of the Plant's outfall.

By late July 1996, the new extended TITP outfall was in place and began discharging secondary effluent into the Outer Los Angeles Harbor near the southeast corner of Pier 400. At this time, the rock like construction enclosing the Increment 2 phase of Pier 400 created a new configuration for the Outer Los Angeles Harbor. These changes made necessary a complete re-evaluation of the TITP's entire receiving water monitoring program to better assess environmental impacts that could result from the TITP outfall discharge at its new terminus location. To address this, the TITP marine monitoring program was redesigned. The new program was submitted to the Regional Water Quality Control Board (RWQCB) in July 1996, and the Post-Pier 400 Monitoring Program was implemented in August 1996.

Since 1996, with the exception of the 1998 summer survey, the Los Angeles Harbor Annual Assessment Report (CLA, EMD 1996 to 2002, and this report) is based on the Post-Pier 400 Monitoring Program. In 1998, the City participated in the Southern California Bight '98 Regional Survey. To be able to participate in the Bight '98 Program, the City gained approval from the US Environmental Protection Agency (EPA) and the Los Angeles RWQCB to resource exchange a major portion of the Plant's NPDES permit required samples with those from the Bight '98 summer survey. To maintain continuity with historical data in 1998, only two sampling stations from the existing program were retained as compliance stations. During the summer of 2003, the City participated in the Southern California Bight '03 Regional Monitoring Survey. Eleven NPDES compliance benthic sampling stations were substituted for stations selected by the regional program via a resource exchange similar to the one conducted during the Bight '98 Survey. The same two sampling sites retained in 1998 Survey served as the compliance stations for TITP's NPDES mandated receiving water monitoring program in 2003.

Under the current NPDES mandated receiving water monitoring program, sediment collected from the thirteen receiving water stations in the Harbor are analyzed for grain size, total organic carbon, (TOC), dissolved sulfide, total organic halides (TOX), and selected inorganic and organic priority pollutants (nine metals, cyanide, and 89 organic compounds).

In this chapter, results of analyses of sediment samples collected at the two retained stations during the summer survey in 2003 are presented. These concentrations are compared with the levels found at stations in Santa Monica Bay (SMB), at harbors in the Southern California Bight and at one reference site. Whenever possible, historical trends were reviewed to assess temporal changes of pollutant levels in the vicinity of the City's outfall and in reference areas.

## **II. MATERIALS AND METHODS**

### **A. FIELD SAMPLING**

Single samples of sediment were collected from the outfall station HM3 in the Outer Harbor and station HM13 outside the Harbor (Figure 5-1) during the summer 2003 survey. 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.

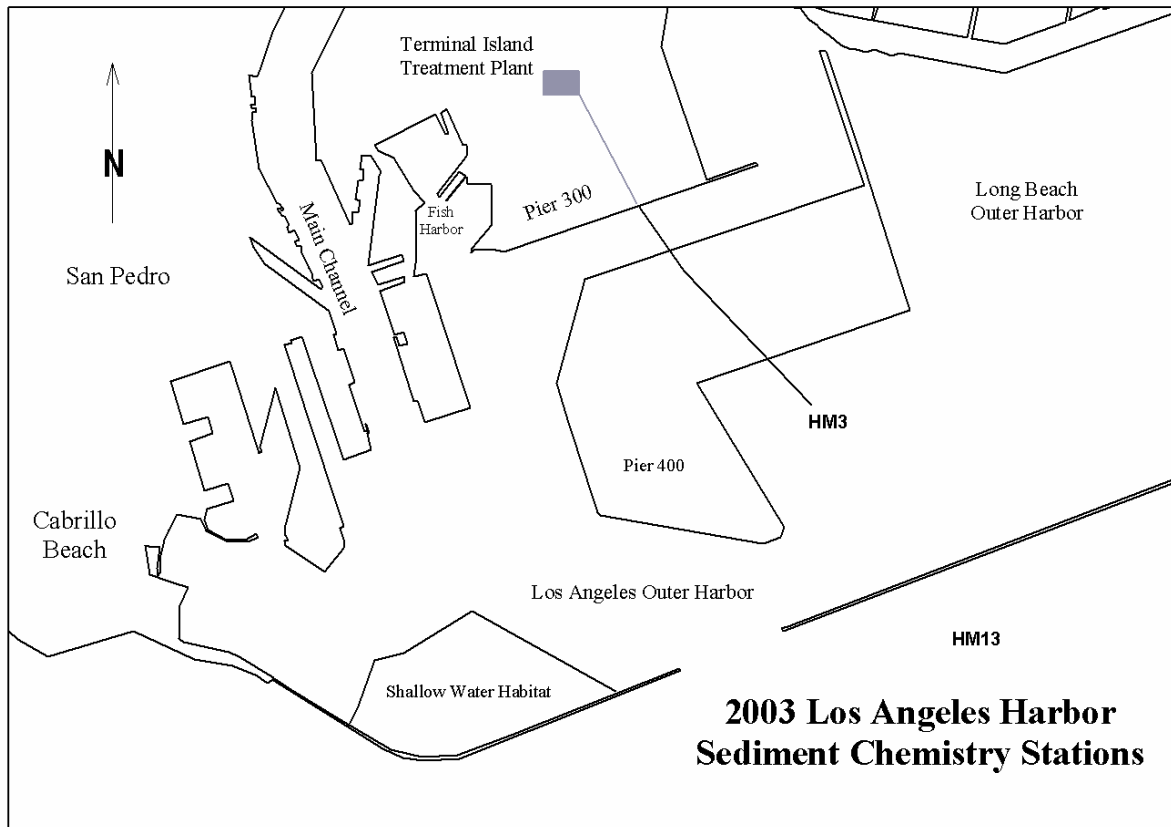
### **B. LABORATORY PROCEDURES**

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

A particle size analyzer determined sediment grain size. 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  $\mu\text{m}$ ).

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 were digested in acids and then analyzed using Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP) and electrothermal atomic absorption spectrophotometry (GFAA). 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 (SW-846, 1994).



**Figure 5-1.** Sediment chemistry sampling station locations.

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

### III. RESULTS

#### A. GRAIN SIZE

Sediments in the Los Angeles Harbor are heterogeneous (CLA, EMD 1998) and also as indicated by the 2003 results for the two compliance stations (Table 5-1), comprising different levels of sand, silt and clay. Fine grained sediments, mostly silt, were found at the TITP outfall station (HM3), inside the Harbor. Sands were dominant outside of the breakwater at station HM13, where grain size measurement showed sediments with 75.5% sand.

**Table 5-1.** Grain size distribution of sediments in Los Angeles Harbor surveyed in summer 2003.

STATION	Gravel	Sand	Silt	Clay	Fine Grain (Silt + Clay)
	%	%	%	%	%
HM3 (outfall)	0	35.9	52.9	11.3	64.2
HM13	0	75.5	20.0	4.49	24.5

#### B. TOTAL ORGANIC CARBON, TOTAL ORGANIC HALIDES, CYANIDE, AND DISSOLVED SULFIDE

Total organic carbon (TOC) and total organic halide (TOX) were detected at both sampling sites (Stations HM3 and HM13) (Table 5-2). Cyanide was detected only at Station HM3. Dissolved sulfides were not detected at either station.

**Table 5-2.** Cyanide, dissolved sulfide, TOC, and TOX in sediments collected from Los Angeles harbor in summer 2003. Concentrations were normalized against fine grain fractions.

STATION	Cyanide	Dissolved Sulfide	TOC	TOX
	mg/kg	mg/L	mg/kg	mg/kg
HM3 (outfall)	0.500	ND	8520	16.6
HM13	ND	ND	12700	14.7

## C. PRIORITY POLLUTANTS METALS AND ORGANICS

Out of 99 priority pollutants tested, 15 were detected from sediment samples collected at the two sampling sites during summer 2003 (Tables 5-3 and 5-4). A complete list of priority pollutants analyzed is presented in Appendix D.

### 1. Metals

Sediment samples were analyzed for nine priority pollutant metals, with eight detected at both sampling sites (Table 5-3). Silver was not detected at either station. Except copper, all detected concentrations of metals were higher at the station HM13 located outside of the breakwater relative to TITP outfall station HM3.

**Table 5-3.** Metals detected in sediments at stations HM3 and HM13 of the Los Angeles harbor in summer 2003. Concentrations were normalized against fine grain size.

Pollutants	Stations	
	HM3	HM13
<b>Metals (mg/kg)</b>		
<b>Arsenic</b>	6.78	19.6
<b>Cadmium</b>	1.93	2.49
<b>Chromium</b>	51.3	83.1
<b>Copper</b>	50.3	38.5
<b>Lead</b>	4.35	20.6
<b>Mercury</b>	0.14	0.24
<b>Nickel</b>	40.3	45.5
<b>Silver</b>	ND	ND
<b>Zinc</b>	140	192

ND - Not Detected

### 2. Pesticides and PCB's

In addition to p,p'-DDT, three derivative products of the pesticide DDT (o,p'-DDE; p,p'-DDE; and p,p'-DDD) were detected in the sediments collected from TITP outfall station HM3. Of the four derivatives, p,p'-DDE reached a concentration of 80.3 µg/kg dry weight. At station HM13 (outside of breakwater), o,p'-DDE and p,p'-DDE were found at higher levels as compared to the concentrations at the station HM3 (Outfall), however p,p'-DDD and p,p'-DDT were not detected (Table 5-4). No PCB's were detected in 2003 survey.

### 3. Base/neutral and Acid Extractable Compounds (BNA's)

Of the 57 BNA's analyzed, diethylphthalate, di-n-butylphthalate and bis(2-ethylhexyl)phthalate were detected at station HM13 and only diethylphthalate was measured at the station HM3 (Outfall) (Table 5-4) in 2003 survey.

**Table 5-4.** BNA and pesticides detected in sediments at HM3 and HM13 of the Los Angeles Harbor in summer 2003. Concentrations were normalized against fine grain fraction.

Pollutants	Stations	
<b>Base Neutral Acids (mg/kg)</b>	<b>HM3</b>	<b>HM13</b>
Diethylphthalate	5.38	8.86
Di-n-butylphthalate	ND	2.46
Bis-(2-ethylhexyl)phthalate	ND	3.89
<b>Pesticides (µg/kg)</b>		
o, p'-DDE*	10.0	21.7
p, p'-DDE	80.3	173
p, p'-DDD	6.00	ND
p, p'-DDT	20.5	ND
ND – Not Detected		
* Not a priority pollutant		

## IV. DISCUSSION

### A. TEMPORAL PATTERNS OF GRAIN SIZE, TOC, and TOX

The five-year temporal trends of grain size, TOC, and TOX from 1999 to 2003 sampling years are shown in Table 5-5. The percentage of fine grains (silt + clay) at both stations was the lowest in 2001. The highest percentage of fine grains at station HM3 was in 1999 and was at station HM13 in 2000. TOC levels were the lowest in 2002 at both stations but in 2003 increased almost to the same levels of 2001. The TOX concentration was more than doubled at HM3 in 2003 as compared to the level of 2002. However, the level of TOX at HM13 decreased from 30.2 mg/kg in 2002 to 14.7 mg/kg in 2003.

**Table 5-5.** Temporal trends of fine grain percentage, TOC, and TOX at Stations HM3 and HM13 from 1999 to 2003.

	<b>1999</b>	<b>2000</b>	<b>2001</b>	<b>2002</b>	<b>2003</b>
<b><u>Silt + Clay (%)</u></b>					
<b>HM3</b>	85.2	62.6	58.1	83.2	64.2
<b>HM13</b>	26.5	38.4	24.5	25.8	24.5
<b><u>TOC (mg/kg)</u></b>					
<b>HM3</b>	33870	24574	9914	5724	8520
<b>HM13</b>	16470	23911	12408	7279	12700
<b><u>TOX (mg/kg)</u></b>					
<b>HM3</b>	ND	ND	14.4	7.02	16.6
<b>HM13</b>	ND	ND	26.8	30.2	14.7
ND – Not Detected					

## **B. SPATIAL PATTERNS OF METALS AND ORGANICS**

In general, the concentration levels of metals and organics detected in 2003 survey were higher at Station HM13 located outside of the breakwater than at Station HM3 (outfall) with the exception of copper, p,p'-DDD, and p,p'-DDT (Table 5-3 and 5-4). The concentration of arsenic at HM13 was almost three times higher than the value at HM3. Lead concentration of HM13 reached five times of that at HM3. Chen et al. (1974) reported that metals, absorbed onto effluent particles, concentrated in sediments near outfalls. Additionally, these metals could be introduced into the Harbor from other sources including aerial fallout, storm drains, and other outfalls (Chen and Lu 1974).

Table 5-6 shows the comparison of pollutant levels at LA Harbor in 2003 with the average levels in ports at Southern California Bight in 1998. Except cadmium, nickel, and total DDT, all other metals and PCBs detected at LA Harbor in 2003 were lower than the average levels of pollutants found in ports at Southern California Bight of 1998 (SCCWRP 2003).

**Table 5-6.** Concentrations of metals and organic pollutants in Los Angeles Harbor, summer 2003 with comparison to concentrations in ports of Southern California Bight (SCB) in 1998.

	<b>LA Harbor (2003)*</b>	<b>Ports at SCB (1998)**</b>
<b>Metals (mg/kg)</b>		
<b>Arsenic</b>	6.78	10.1
<b>Cadmium</b>	1.93	0.4
<b>Chromium</b>	51.3	51.8
<b>Copper</b>	50.3	107
<b>Lead</b>	4.35	44.9
<b>Mercury</b>	0.14	0.39
<b>Nickel</b>	40.3	21.5
<b>Silver</b>	ND	1.1
<b>Zinc</b>	140	180
<b>Total DDT (µg/kg)</b>	117	30.8
<b>PCB (µg/kg)</b>	ND	38.3
ND - Not Detected		
* Concentrations normalized against fine grain fraction and sample was collected at TITP Outfall Station HM3		
** Area-weighted means.		

Los Angeles Harbor is an enclosed harbor and is quite different from open bays. A comparison was made in an attempt to evaluate the degree of contamination compared to the other reference sites (Table 5-7). When compared to Stations Z2 (HTP Outfall) and C1 of Santa Monica Bay, TITP outfall had a higher level of most of the priority pollutants except lead. Silver and PCBs were not detected at TITP Outfall and SMB Station C1 in the 2003 survey. However when compared to Dana Point reference site (NOAA 1988), TITP outfall showed a lower degree of contamination with the exception of cadmium, copper and nickel.

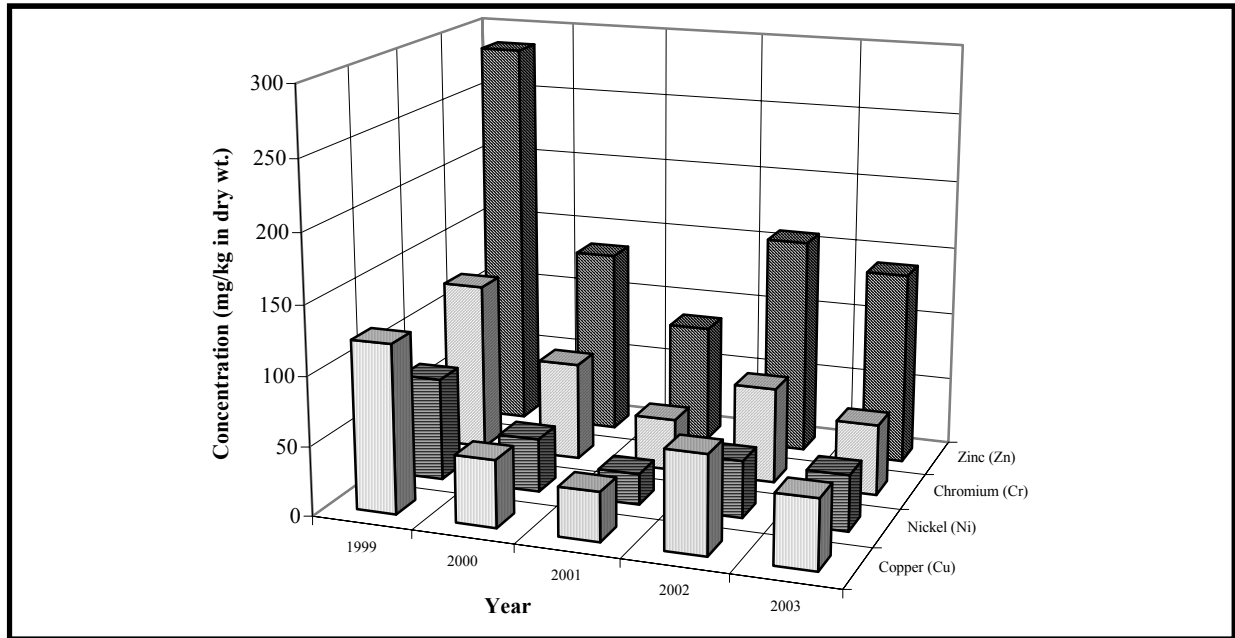
**Table 5-7.** Comparison of contaminant levels at TITP outfall, stations in Santa Monica Bay during summer 2003, and a reference site. Concentrations were normalized against fine grain fractions.

Contaminants	Los Angeles Harbor	SMB		Reference Site
	TITP Outfall*	Z2 <sup>a</sup>	C1 <sup>b</sup>	Dana Point <sup>c</sup>
<b>Metals (mg/kg)</b>				
Arsenic	6.78	1.2	0.56	29.8
Cadmium	1.93	0.77	0.71	1.37
Chromium	51.3	40	40	141
Copper	50.3	26	15	30.2
Lead	4.35	7.9	8.5	51.4
Mercury	0.14	0.24	0.13	0.63
Nickel	40.3	10	22	25.5
Silver	ND	1	ND	1.87
Zinc	140	50	60	169
<b>Pesticides &amp; PCB (µg/kg):</b>				
Total DDT	117	33.9	57.8	NA
PCBs	ND	32.8	ND	20.3
ND - Not Detected; NA - Not Available.				
* TITP Outfall Station HM3				
a HTP Outfall				
b Station near Point Dume				
c 1984-1987 Reference Site Survey (NOAA 1988)				

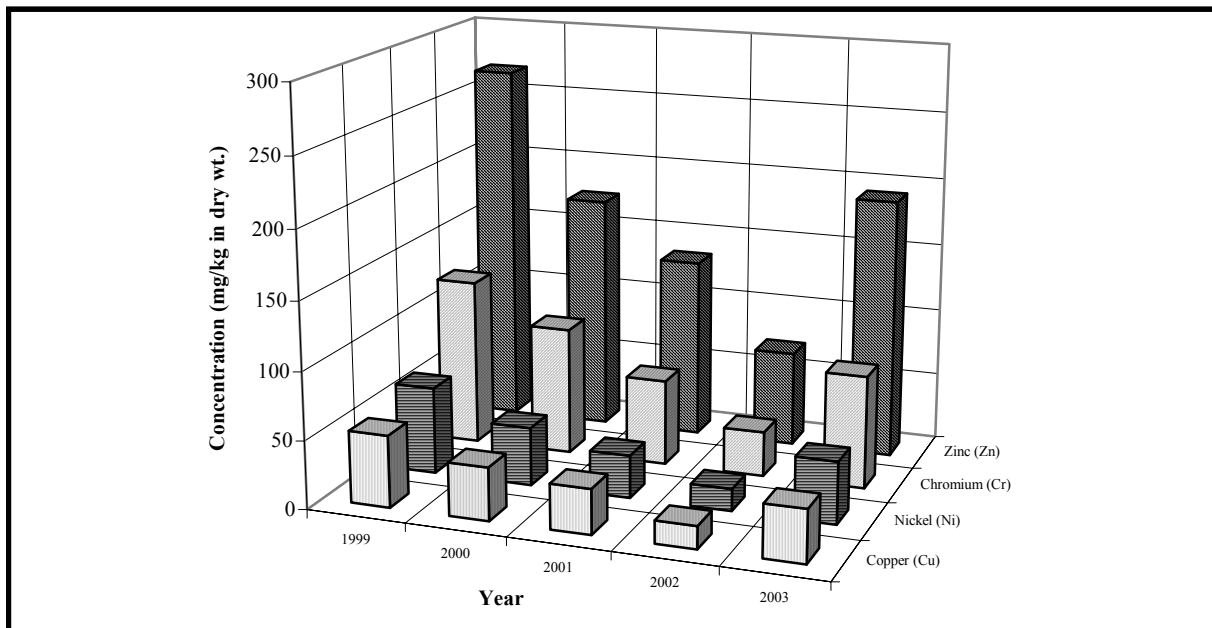
### C. TEMPORAL PATTERNS

The five-year temporal trends of priority pollutant metals are shown in Figures 5-2, 5-3, 5-4, and 5-5. Silver had not been detected in any station. In general, there was a declining trend in the degree of contamination at both Station HM3 (outfall) and HM13 (outside the breakwater) over the past five years. The few exceptions at Station HM13 were arsenic, nickel, and zinc. The most significant decline in the concentration of metals was lead. The contamination level reduced from 27.9 mg/kg (the highest) in 2002 to 4.4 mg/kg (the lowest) in 2003 survey at the Station HM3. At Station HM13, the concentration of lead reduced from 40.3 mg/kg (the highest) measured in 1999 to 20.6 mg/kg (the second lowest) in 2003. The temporal pattern of nickel, zinc and cadmium varied.

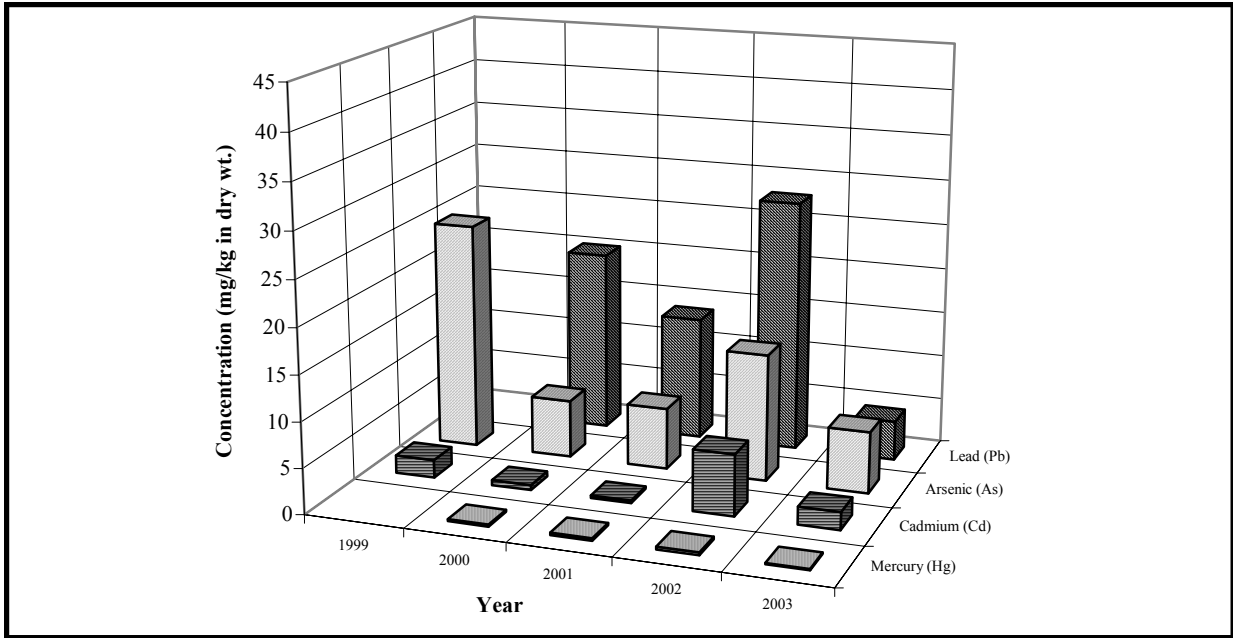
The contamination levels of nickel and zinc of both Stations declined gradually from 1999 to 2001 but went back up to 2000 level in the 2002 and 2003 surveys. The cadmium concentration had been reducing from 1999 to 2001 but jumped to triple the value of 1999 in 2002 then declined back to 1999 level in the 2003 survey at Station HM3. Cadmium measurement at Station HM13 was more consistent than HM3. Chromium and copper showed a more consistent declining trend than any other metals. Their contamination levels had reduced almost by half since 1999 survey for both Stations HM3 and HM13. Mercury had been maintaining the same low concentration level over the years.



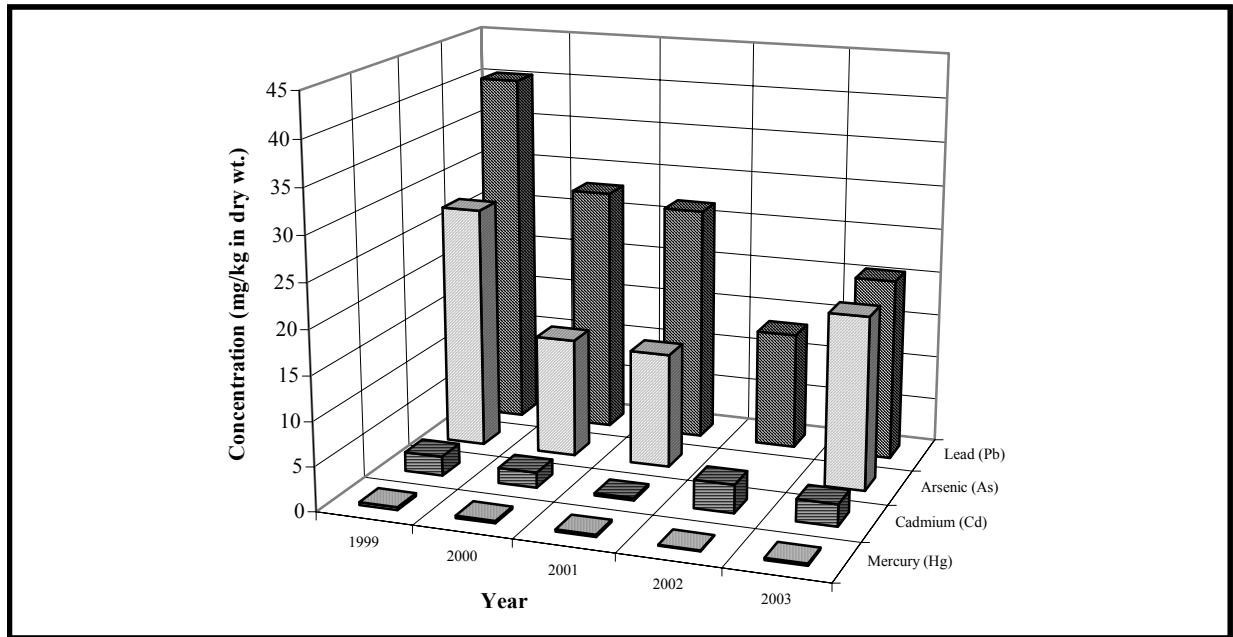
**Figure 5-2.** Trends of chromium, copper, nickel, and zinc at Station HM3 from 1999 to 2003.



**Figure 5-3.** Trends of chromium, copper, nickel, and zinc at Station HM13 from 1999 to 2003.



**Figure 5-4.** Trends of mercury, cadmium, arsenic, and lead at Station HM3 from 1999 to 2003. Lead and mercury were not detected in 1999.



**Figure 5-5.** Trends of mercury, cadmium, arsenic, and lead at Station HM13 from 1999 to 2003. Arsenic was not detected in 2002.

Among organic priority pollutants, DDTs were repeatedly detected in the Los Angeles Harbor surveys. At Station HM3 (TITP outfall), the concentration of DDTs gradually declined from 113  $\mu\text{g}/\text{kg}$  detected in 1999 to 58.4  $\mu\text{g}/\text{kg}$  detected in 2002 then increased to 117  $\mu\text{g}/\text{kg}$  in 2003 survey, highest in the last five years (Table 5-8). Station HM13 (Outside breakwater) followed a similar pattern of HM3 only the concentration was overall higher than HM3 but concentrations of total DDT

was second lowest in the last five years. PCBs had not been detected at Station HM3 since 2001 and at Station HM13 since 2000.

**Table 5-8.** Temporal pattern of total DDT and PCB concentrations at HM13 (outside breakwater of the Harbor) and HM3 (outfall). Concentrations were normalized against fine grain fraction.

Contaminants	HM3 (Outfall)					HM13 (Outside Breakwater)				
	1999	2000	2001	2002	2003	1999	2000	2001	2002	2003
<b>Total DDT (µg/kg)</b>	113	102	73.7	58.4	117	231	198	247	125	194
<b>PCB (µg/kg)</b>	31.3	28.1	ND	ND	ND	60.6	ND	ND	ND	ND

ND – Not Detected.

The declining trend of priority pollutants shown in LA Harbor surveys can be attributed to the joint effort of EPA and TITP. With the ever-stringent EPA criteria, TITP had to improve treatment process and seek for innovative treatment technologies to comply with the latest NPDES permit. The result of the improvement was higher effluent quality and a cleaner LA Harbor.

#### D. CONTAMINATION ASSESSMENT OF THE LOS ANGELES HARBOR

To assess the biological impact of the sediment contaminants of the Los Angeles Harbor, the metals, DDTs and PCBs levels of 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). As shown in Table 5-9, 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 in the Harbor sediments was higher than both ER-L and ER-M values. At the outfall station HM3, the concentrations of metals were all below the corresponding ER-M values and only the concentrations of cadmium, copper, nickel and total DDT were above their respective ER-L values.

The distribution of contaminants in the Outer Harbor will change due to natural processes coupled with any resumption of dredge and fill operations. As additional construction activities continue in the vicinity of the TITP outfall, the recovery process for the marine communities would take place gradually over several years. As the effluent discharge continues, it will take long-term monitoring surveys to document any changes that may occur in sediment chemistry at and around the outfall due to the effluent discharge.

**Table 5-9.** Concentrations of metals and organic pollutants in sediments of Los Angeles Harbor, summer 2003 with comparison to Effective Levels\* (ER-L and ER-M). Concentrations were normalized against fine grain fraction.

DETECTED POLLUTANTS	L.A. Harbor		ER-L*	ER-M*
	Ave**	HM3***		
<b>Metals (mg/kg)</b>				
Arsenic	13.2	6.78	8.2	70
Cadmium	2.21	1.93	1.2	9.6
Chromium	67.2	51.3	81	370
Copper	44.4	50.3	34	270
Lead	12.5	4.35	46.7	218
Mercury	0.193	0.14	0.15	0.7
Nickel	42.9	40.3	20.9	51.6
Silver	ND	ND	1	3.7
Zinc	166	140	150	410
<b>Pesticides and PCB (µg/kg)</b>				
Total DDT	156	117	1.58	46.1
AR 1254	ND	ND	22.7	180
ND= Not detected				
* Source: Long et.al. (1995).				
** Average of 2 stations. Concentrations below detection limit were taken as zero				
*** TITP Outfall station				

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