CHAPTER 8. TISSUE CHEMISTRY

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I. INTRODUCTION

The Terminal Island Treatment Plant (TITP) NPDES permit requires analyses of tissues of selected species of trawl–caught demersal fish to determine the bioaccumulation impact of discharged effluent from TITP. Demersal fishes are closely associated with the sea bottom throughout much of their lives, therefore are more likely to bioaccumulate pollutants from contaminated sediments or the prey living in the sediments than organisms living in the water column; consequently, the priority pollutant assessment of trawled organisms emphasizes an ecological concern. The level of chemical contaminants in fish tissues is an important indicator of potential health risks to humans who consume the seafood.

Until July 1996, secondary treated effluent was discharged through a six-meter deep outfall into the Outer Harbor south of Pier 300. Fishes were collected from two stations from 1993 to 1996: Cabrillo Pier and Horseshoe Kelp. The construction of Pier 400 in the mid-90's required relocation of the outfall. A new outfall, extending from the Terminal Island Treatment Plant to the area between Pier 400 and the breakwaters at a depth of 10 meters (Figure 8-1), began discharging effluent in late July 1996. TITP started to discharge over 15 MGD filtered secondary treated effluent through the new outfall in 1997 including about 5 MGD of tertiary treated wastewater into the Outer Los Angeles Harbor. In order to compare the pollutant level of fishes from different areas within and outside the Los Angeles Harbor, fishes have been collected from three areas since 1996: new outfall area (HT7), reference site outside Los Angeles Harbor (HT5) and Cabrillo Pier area (popular fishing site).

In summer 2002, priority pollutant levels in *Genyonemus lineatus* (white croaker), a widely distributed demersal fish in Southern California Bight, were analyzed for tissues collected from inside and outside the Los Angeles Harbor areas by trawling. The contamination levels in the fish tissues are assessed and compared with the results from previous years.

II. MATERIALS AND METHODS

A. FIELD SAMPLING

1. Sampling

During the summer of 2002, five white croakers each were collected by trawling at station HT5

(reference site outside of the breakwater of the Los Angeles Harbor) and station HT7 (located at the terminus of the TITP outfall) (Figure 8-1). Due to shallow water at the Cabrillo Pier area, it was not possible to catch white croaker by trawling (Figure 8-1). For a detailed description of this procedure see Chapter 7 (Trawl-Caught Fish and Invertebrates).

Upon capture, each target fish was examined for abnormalities, measured, and weighed. The selected fish specimens were frozen prior to dissection for muscle samples.

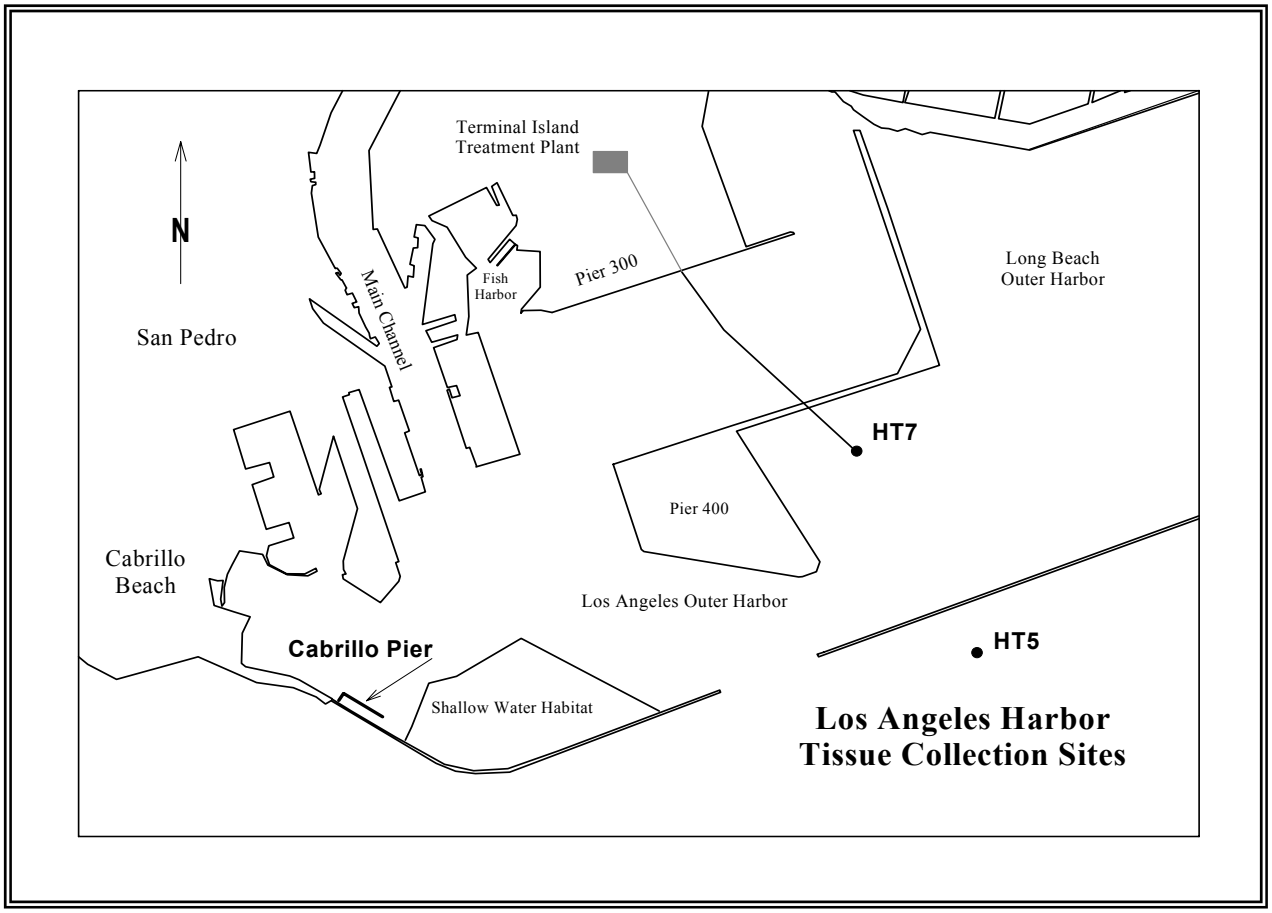

Figure 8-1. White croaker collection sites for tissue chemistry in Los Angeles Harbor.

2. Dissection

Dissections were performed in the laboratory following the methods of Lauenstein and Young (1986). Muscle tissue collected from each fish was divided into two equal portions. The first portion was transferred to an acid-washed plastic container for heavy metal analyses, the second to a methylene chloride-rinsed glass container for analyses of semivolatile organic pollutants. Samples were kept frozen until analyses.

B. LABORATORY ANALYSIS

Specific details regarding priority pollutant tissue analyses are provided (Appendix C). For heavy metal analyses, tissues were acid digested, then analyzed by Inductively Coupled Plasma (ICP) spectrometry or graphite furnace atomic absorption (GFAA) spectrometry. Tissues for organics were solvent extracted, and extracts were concentrated prior to analysis. Organochlorine pesticides and polychlorinated biphenyls (PCBs) were analyzed using a Gas Chromatograph (GC) with electron capture detectors (ECD). Base/Neutral and Acid extractible organic compounds (BNA) were analyzed by Gas Chromatograph/Mass Spectrometer (GC/MS). Total organic halides (TOX) were analyzed by Mitsubishi TOX analyzer.

III. RESULTS

All muscle tissue samples were analyzed for ninety-eight priority pollutants including nine heavy metals and eighty-nine organic compounds.

1. Metals

Of the nine priority pollutant metals, silver (Ag), arsenic (As), cadmium (Cd), chromium (Cr), copper (Cu), lead (Pb), and nickel (Ni) were not detected. Mercury (Hg) and zinc (Zn) were detected in all samples (Table 8-1).

Mercury (Hg) concentrations ranging from 0.072 mg/kg to 0.10 mg/kg in tissue samples were well below the "action levels" of 1.0 mg/kg for fish consumption set by the Food and Drug Administration (FDA). The Hg concentrations were also below the California State Department of Health Services advisory limit of 0.5 mg/kg. The FDA has not established the action levels for other metals. For some metals, an International Action Limit Median is widely used by other nations for a similar purpose (Mearns et al. 1991); these limits are included in Table 8-1. Our data indicate that the detected concentrations of Hg and Zn were well below the International Median values of 1.0 mg/kg and 70.0 mg/kg, respectively.

2. Organics

Among organic compounds analyzed, no semi-volatile pollutants or PCBs were detected in 2002. Three DDT derivatives (o,p'-DDE, p,p'-DDD, and p,p'-DDE) and TOX were detected in one or more white croaker muscle samples (Table 8-2). Among the detected organics, p,p'-DDE was detected in all samples and o,p'-DDE was detected in all samples at the outfall but was found in 4 out of 5 samples at the breakwater. DDT derivative, p,p'-DDD was detected only in one sample at the outfall and was found in 3 out of 5 samples at the breakwater. As shown in Table 8-2, the average concentrations of total DDT at the outfall and outside breakwater were above the

recommended limits of 0.1 mg/kg set by OEHHA (1991), but under the FDA's action level (5.0 mg/kg).

Table 8-1. Metals detected in white croaker muscle tissue collected inside and outside of the Los Angeles Harbor during 2002. Results are reported in mg/kg (ppm) wet weight.

	HT7 (Outfall)			HT5 (Outside Breakwater)			
	n=5 Aug. 2002			n=5 Aug. 2002			
	Freq. %	Average[1] mg/kg	Range mg/kg	Freq. %	Average[1] mg/kg	Range mg/kg	International Median mg/kg
Metals							
Ag	0	*	ND	0	*	ND	1.4
As	0	*	ND	0	*	ND	NA
Cd	0	*	ND	0	*	ND	NA
Cr	0	*	ND	0	*	ND	1.0
Cu	0	*	ND	60	1.75	ND-2.42	20.0
Hg	100	0.061	0.030-0.11	100	0.086	0.072-0.10	1.0
Ni	0	*	ND	0	*	ND	NA
Pb	0	*	ND	0	*	ND	NA
Zn	100	4.04	3.63-4.35	100	6.55	3.48-9.91	70.0

ND = Not Detected.
n = number of fish analyzed.
1 = Half of detection limit was used to calculate the average when the constituent was not detected
* Not Applicable, constituent either non-detect or detected in only one sample

Table 8-2. Organics detected in white croaker muscle tissue collected inside and outside of the Los Angeles Harbor during 2002. Results are reported in mg/kg (ppm) wet weight.

	HT7 (Outfall)			HT5 (Outside Breakwater)		
	n=5 Aug. 2002			n=5 Aug. 2002		
Constituents	Freq. %	Average[1] mg/kg	Range mg/kg	Freq. %	Average[1] mg/kg	Range mg/kg
Base/Neutral and Acids	0	*	ND	0	NA	ND
Pesticides & PCBs						
o,p'-DDE	100	0.024	0.0090-0.041	80	0.040	ND-0.12
p,p'-DDE	100	0.18	0.077-0.38	100	0.41	0.025-1.2
p,p'-DDD	20	*	ND-0.012	60	0.018	ND-0.075
Total DDT		0.22			0.47	
Total PCB	0	*	ND	0	*	ND
%Lipids	100	1.75	1.25-2.04	100	2.08	1.07-3.47
TOX	100	4.70	3.21-7.22	100	3.76	2.09-4.97

ND = Not Detected.
n = number of fish analyzed.
1 = Half of detection limit was used to calculate the average when the constituent was not detected
* Not Applicable, constituent either non-detect or detected in only one sample

IV. DISCUSSION

TITP Plant's NPDES permit mandates the monitoring of chemical contaminants in fish tissues inside and outside the Outer Los Angeles Harbor. Since 1993, the Environmental Monitoring Division (EMD) has monitored and assessed annually the tissue chemistry data of fish from the LA Harbor (CLA, EMD 1994 to 2001). However, the sampling sites inside and outside the Harbor have been changed due to construction and dredging activities associated with the construction of Pier 400, and relocation of TITP's outfall to its current position. In 1996, the newly extended TITP outfall was in place and began discharging secondary effluent into the Outer Los Angeles Harbor near the southwest corner of Pier 400 (Figure 8-1). To address the impact of effluent discharge at this new location, with approval from the Regional Water Quality Control Board in 1996, the receiving water monitoring program was modified, including the changes in field sampling sites (Table 8-3). Because of these changes, only chemistry data of tissues collected from 1996 to the present are used for outfall temporal or spatial trend assessment. In 1998, the City of Los Angeles participated in the Southern California Bight Regional Monitoring Survey (Bight'98). All of the required NPDES permit tissue sampling in L.A. Harbor was suspended in order to exchange the resources for the Bight'98 Survey.

Table 8-3. Temporal comparison[1] of pollutants and %lipid in white croaker tissues at TITP new outfall area (HT7) during 1999 to 2002 sampling years. Data are reported in mg/kg wet weight except lipid in %.

Muscle	8/99	8/00	8/01	8/02
As	0.75	0.66	ND	ND
Cu	ND	2.52	ND	ND
Hg	0.068	0.058	0.026	0.061
Pb	ND	ND	1.34	ND
Zn	3.01	3.33	3.15	4.04
Total DDT[2]	0.77	0.27	0.40	0.20
Total PCB[3]	ND	0.040	0.24	ND
% Lipid	1.74	1.10	2.06	1.75

ND: Constituent not detected.
1: The average data of monitored replicate results were used for comparison.
2: Sum of o,p'-DDE, p,p'-DDE, p,p'-DDD, and p,p'-DDT derivatives.
3: Sum of AR 1254 and AR 1260.

1. Temporal Patterns

Tables 8-3 and 8-4 show the temporal comparison of selected pollutants and %lipid from 1999 to 2002 at the outfall (HT7) and breakwater (HT5), respectively. Except arsenic, no significant changes were observed on the pollutant levels at the outfall area and outside breakwater (Figures 8-2 and 8-3) during the last four monitoring years. Arsenic was not detected at the outfall in 2001 and

2002. The concentrations of total DDTs in the white croaker collected at both outfall and breakwater exceeded the OEHHA action advisory level of 0.1 mg/kg.

There have been no samples collected at Cabrillo Pier since 1997 due to construction activities and inaccessibility to the sampling site. Cabrillo Pier is a popular fishing site, fishes caught in this area are in all probability consumed by local fishermen. In Sport Fish Consumption Advisories issued in June 2001 by OEHHA, white croaker collected at Cabrillo Pier was listed as "DO NOT CONSUME" in the site-specific consumption recommendation. An alternative method to collect fish samples from Cabrillo Pier area may be necessary in order to continue the monitoring of white croaker.

Table 8-4. Temporal comparison[1] of pollutants and %lipid in white croaker tissues collected outside the breakwater (HT5) during 1999 to 2002 sampling years. Data are reported in mg/kg wet weight except lipid in %.

Muscle	**8/99**	**8/00**	**8/01**	**8/02**
As	0.80	0.58	NA	ND
Cu	ND	1.19	NA	1.75
Hg	0.062	0.080	NA	0.086
Pb	ND	ND	NA	ND
Zn	3.80	3.86	NA	6.55
Total DDT[2]	1.73	0.60	NA	0.46
Total PCB[3]	ND	0.044	NA	ND
% Lipid	2.59	1.02	NA	2.08

ND: Constituent not detected.
NA: No samples collected in 2001.
1: The average data of monitored replicate results were used for comparison.
2: Sum of o,p'-DDE, p,p'-DDE, p,p'-DDD, and p,p'-DDT derivatives.
3: Sum of AR 1254 and AR 1260.

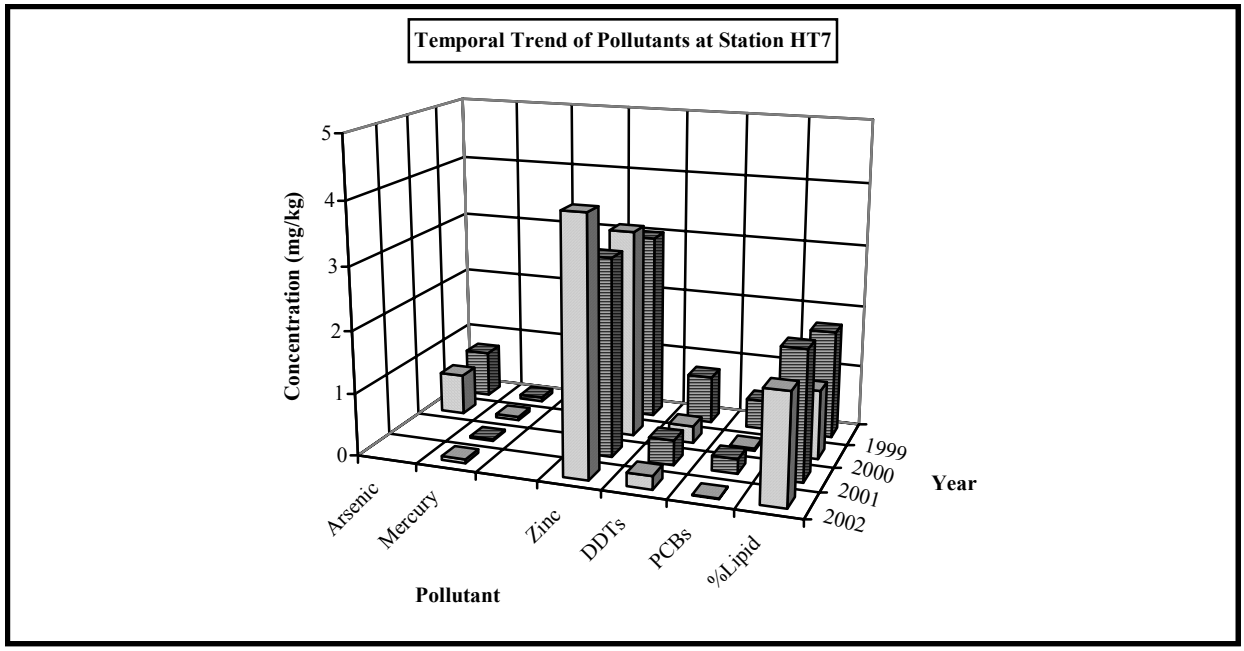

Figure 8-2. Temporal trend of %lipid and pollutants in muscle tissue of white croaker at the TITP outfall (HT7) from 1999 – 2002. Arsenic was not detected in 2001 and 2002.

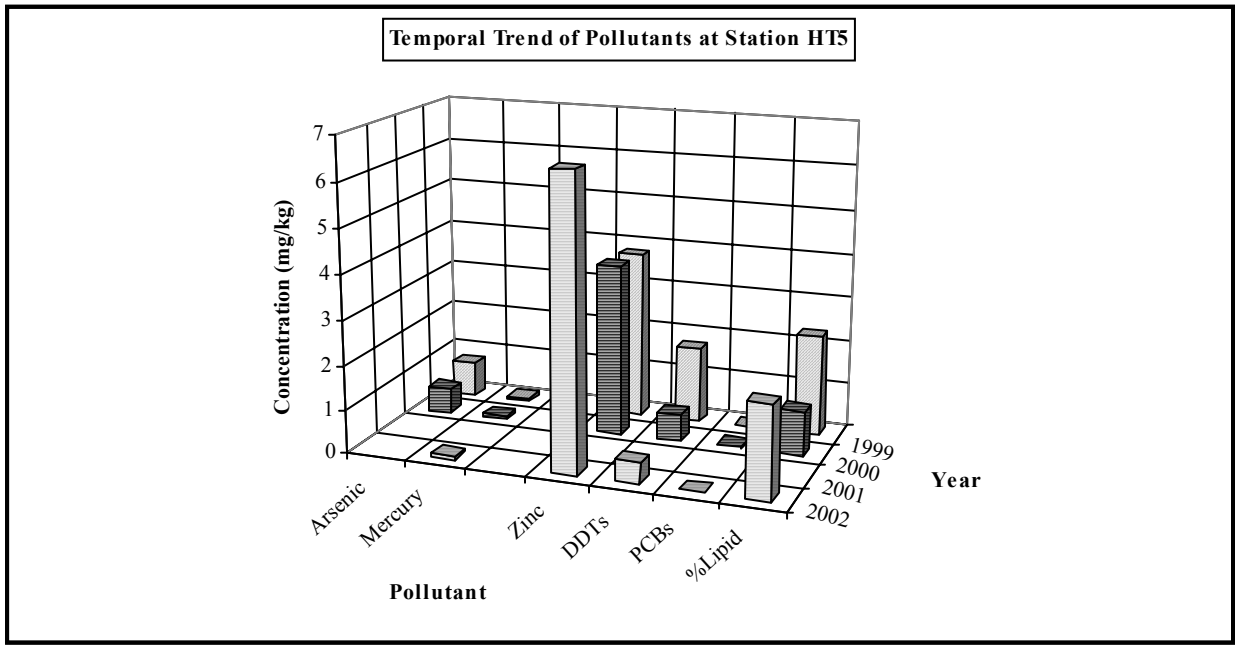

Figure 8-3. Temporal trend of %lipid and pollutants in muscle tissue of white croaker outside breakwater (HT5) from 1999 – 2002. Arsenic was not detected in 2001 and 2002.

2. Spatial Patterns

The last sample collection at Cabrillo Pier was conducted in 1996. In 2001, no samples were collected outside the breakwater. The selected pollutant levels found at Cabrillo Pier in August 1996, the averages at the new outfall and the averages outside the harbor site from 1999 to 2002 are shown in Table 8-5. Mercury was found in the muscle tissue at the outfall and breakwater, but not at Cabrillo Pier. The levels of Cu, Zn, total PCB, and %lipid were lower at Cabrillo Pier than outside breakwater and TI outfall. However, total DDT levels were found higher at Cabrillo Pier. This four-year assessment did not show any significant impact on the pollutant levels in fish tissues within the study areas by the wastewater discharge.

Table 8-5. Spatial comparison[1] of pollutants and % lipid in white croaker tissues at Cabrillo Pier (1996 only), TITP new outfall (HT7), and outside breakwater (HT5) during 1999 – 2002 sampling years. Data are reported in mg/kg wet weight except lipid in %.

Muscle	Cabrillo Pier 1996	Outfall[2] (HT7) 1999 – 2002	Outside breakwater[2] (HT5) 1999 - 2002
As	0.65	0.66	0.58
Cu	0.46	1.17	1.47
Hg	ND	0.050	0.083
Zn	3.3	3.51	5.21
Total DDT[3]	0.62	0.30	0.55
Total PCB[4]	0.18	0.095	0.027
% Lipid	1.52	1.64	1.55

ND: Constituent not detected.
1: The average data of monitored replicate results were used for comparison.
2: The averages of data from 1999 to 2002.
3: Sum of o,p'-DDE, p,p'-DDE, p,p'-DDD, and p,p'-DDT derivatives.
4: Sum of AR 1254 and AR 1260.

3. Impact from the pollution in sediment

To assess the impact of sediment pollution on the ecosystem of the Harbor, the pollutant concentrations in muscle tissues of white croaker collected at the outfall and the breakwater are compared with the pollutant concentrations in sediments near the outfall and outside the breakwater during 2002 sampling year (Table 8-6 and Figure 8-4). For sediment samples, station HM3 is located at the new outfall, while station HM13 is outside the breakwater (Figures 5-1 and 8-1).

Only mercury and zinc were detected in the white croaker samples at the outfall (HM7) and copper, mercury, and zinc were detected at outside the breakwater (HM5). All metals except silver were found at the outfall (HM3) and 7 metals (excluding silver and arsenic) were found outside the breakwater (HM13) . PCBs were not detected in muscle tissue of white croaker and sediment samples at both locations, while DDT was detected in both tissues and sediments. The fact that mercury, zinc, and DDT were detected in tissues and sediments inside and outside the harbor

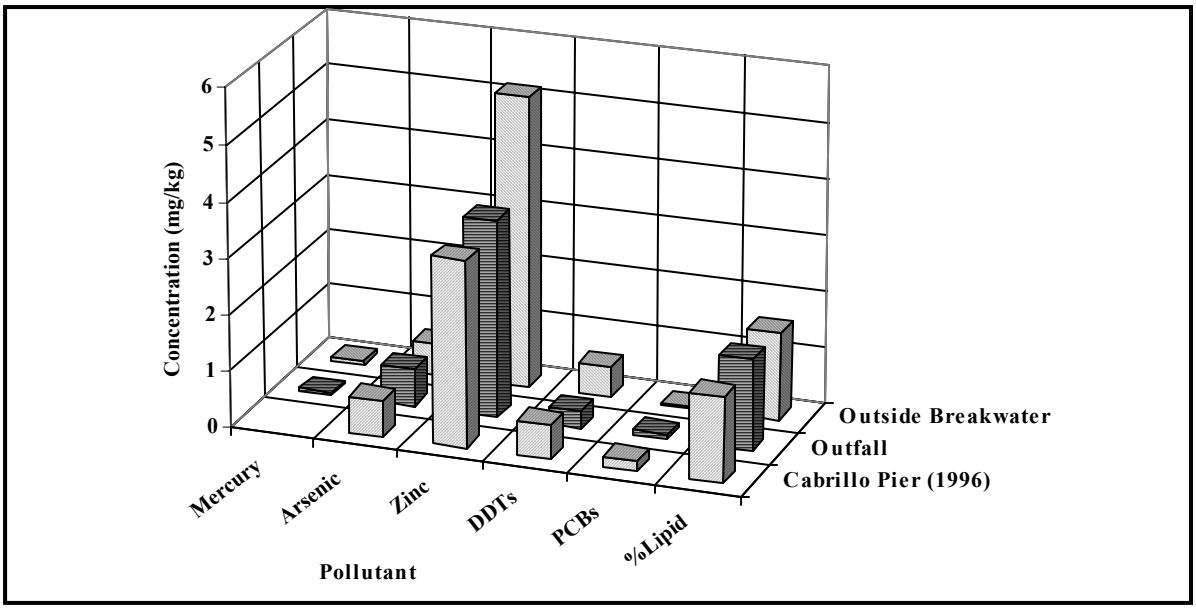

Figure 8-4. Spatial trend of %lipid and pollutants in muscle tissue of white croaker at Cabrillo Pier (1996 only), outfall (HT7), and outside breakwater (HT5) from 1999 – 2002. Mercury was not detected at Cabrillo Pier in 1996.

indicates that mercury, zinc, and DDT may have accumulated in the ecosystem. However, based on the previous spatial and temporal patterns of the pollutants in fish tissues, and the relationship with sediment pollutants, the TITP wastewater discharge means to have very little impact on the pollutant burden of white croakers in the Harbor.

Table 8-6. Concentrations of pollutants in muscle tissues of white croaker and sediments near the new outfall (HT7) and outside breakwater (HT5) during 2002 sampling season.

Pollutant Levels in Fishes and Sediments Collected from the Harbor

Unit = mg/kg

Metal	White Croaker[1]		Sediment[1]	
	HT7 (outfall)	HT5 (outside breakwater)	HM3 (outfall)	HM13 (outside Breakwater)
Ag	ND	ND	ND	ND
As	ND	ND	11.0	ND
Cd	ND	ND	5.29	2.50
Cr	ND	ND	54.7	26.1
Cu	ND	1.75	56.0	13.0
Hg	0.061	0.086	0.232	0.066
Ni	ND	ND	32.4	12.9
Pb	ND	ND	21.9	10.4
Zn	4.04	6.55	124	55.4
PCB & DDT				
Total DDT[2]	0.20	0.46	0.0341	0.0283
Total PCB[3]	ND	ND	ND	ND

Note: Concentrations in sediments are based on dry weight.
ND: Constituent not detected.
NA: Not available.
1: The average data of monitored replicate results were used for comparison.
2: Sum of o,p'-DDE, p,p'-DDE, p,p'-DDD, and p,p'-DDT derivatives.
3: Sum of AR 1254 and AR 1260.

IV. LITERATURE CITED

CLA, EMD. See City of Los Angeles, Environmental Monitoring Division.

City of Los Angeles, Environmental Monitoring Division. 1994. Marine Monitoring in the Los Angeles Harbor: Annual Assessment Report for the Period March 1993 through December 1993. 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 9-4 + appendices.

City of Los Angeles, Environmental Monitoring Division. 1995. Marine Monitoring in the Los Angeles Harbor: Annual Assessment Report for the Period January 1994 through December 1994. 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 9-8

City of Los Angeles, Environmental Monitoring Division. 1996. Marine Monitoring in the Los Angeles Harbor: Annual Assessment Report for the Period January 1995 through December 1995. 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 9-12

City of Los Angeles, Environmental Monitoring Division. 1997. Marine Monitoring in the Los Angeles Harbor: Annual Assessment Report for the Period January 1996 through December 1996. 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

City of Los Angeles, Environmental Monitoring Division. 1998. Marine Monitoring in the Los Angeles Harbor: Annual Assessment Report for the Period January 1997 through December 1997. 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

City of Los Angeles, Environmental Monitoring Division. 1999. Marine Monitoring in the Los Angeles Harbor: Annual Assessment Report for the Period January 1998 through December 1998. 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 7-20

City of Los Angeles, Environmental Monitoring Division. 2000. Marine Monitoring in the Los Angeles Harbor: Annual Assessment Report for the Period January 1999 through December 1999. 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

City of Los Angeles, Environmental Monitoring Division. 2001. Marine Monitoring in the Los Angeles Harbor: Annual Assessment Report for the Period January 2000 through December 2000. 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 8-11

City of Los Angeles, Environmental Monitoring Division. 2002. Marine Monitoring in the Los Angeles Harbor: Annual Assessment Report for the Period January 2001 through December 2001. 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 8-15

EPA. See Environmental Protection Agency

Environmental Protection Agency, 1993, Proceedings of the U.S. Environmental Protection Agency's National Technical Workshop "PCB's in Fish Tissues", U.S. EPA, Washington, DC. pp 4-1 - 4-16.

Environmental Protection Agency, 1994, Guidance For Assessing Chemical Contaminant Data For Use In Fish Advisories, Vol. II: Risk Assessment And Fish Consumption Limits. Office of Water, U.S. EPA, Washington, DC.

Lauenstein, G. G. and D. R. Young. 1986. National Status and Trends Program for Environmental Quality. Benthic Surveillance Project: Cycle III Field manual. NOAA Technical Memorandum NOS OMA 28. Rockville, Maryland, pp. 26.

Mearns, A.J., M. Matta, G. Shigenaka, D. MacDonald, M. Buchman, H. Harris, J. Golas, and G. Lauenstein. 1991. Contaminant Trends in the Southern California Bight Inventory and Assessment. NOAA Technical Memorandum NOS ORCA 62, Seattle, Washington, pp. 389.

OEHHA. See Office of Environmental Health Hazard Assessment.

Office of Environmental Health Hazard Assessment. 1991. A Study of Chemical Contamination of Marine Fish from Southern California, Volume II: Comprehensive Study, California Environmental Protection Agency, Sacramento, California, pp. 116.