

CHAPTER 8

TISSUE CHEMISTRY

RUEY HUANG

INTRODUCTION

The Terminal Island Treatment Plant (TITP) NPDES permit requires analyses of tissues from selected species of trawl-caught demersal fish to determine the bioaccumulation impact of discharged effluent from TITP. The annual survey addresses two questions. The first question: “Is the health of demersal fish in the vicinity of the discharge changing over time?” 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 second question: “Are seafood tissue concentrations below levels that will ensure public safety?” The level of chemical contaminants in fish tissues found during the annual survey 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 of the Outer Los Angeles Harbor between Pier 400 and the breakwaters at a depth of 10 meters (Figure 8-1), was placed in service in late July 1996. TITP has annually discharged about 15 MGD of tertiary treated wastewater through the new outfall beginning in 1997. 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, reference site outside Los Angeles Harbor (HT5), and Cabrillo Pier area (popular fishing site).

In 2003, the City of Los Angeles participated in the Southern California Bight Regional Monitoring Survey (Bight’03). All of the required NPDES permit tissue sampling in L.A. Harbor (LAH) was suspended in order to exchange the resources for the Bight’03 Survey.

The TITP NPDES permit was renewed in the summer of 2005. The major changes to the tissue bioaccumulation trend survey are the addition of liver samples from *Genyonemus lineatus* (white croaker) in the vicinity of the TITP discharge area and the muscle tissue analyses on a sport fish other than white croaker. The contamination levels in the collected fish tissues are assessed and compared with the results from previous years as well as the regulatory limits on seafood consumption

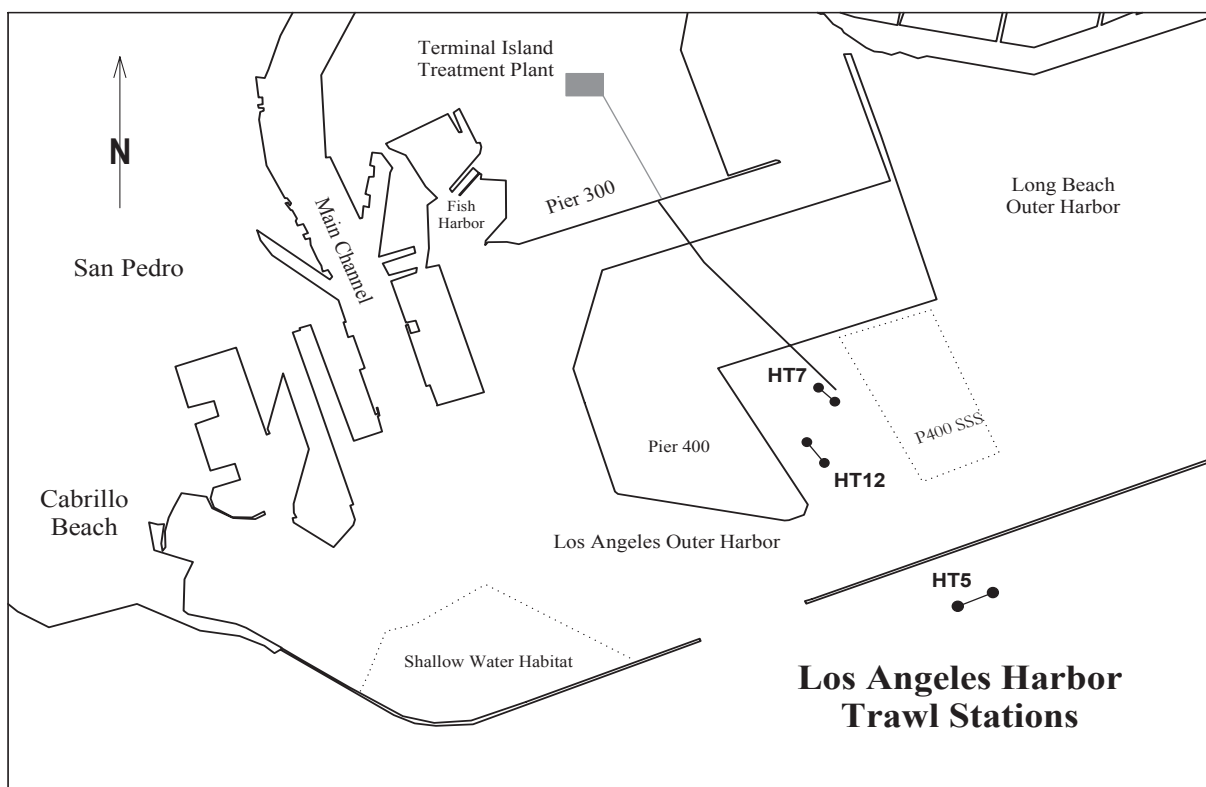


Figure 8-1. Trawl stations in Los Angeles Harbor during 2004 and 2005 survey.

MATERIALS AND METHODS

FIELD SAMPLING

Sampling

Five white croakers in 2004 and ten in 2005 were collected by trawling at station HT7 (located at the terminus of the TITP outfall) (Figure 8-1). Ten sportfish samples, queenfish, were collected at station HT12 (near TITP outfall) in 2005 for seafood safety study. Although sampling was conducted, no fish targeted for bioaccumulation were collected at station HT5 (reference site outside of the breakwater) during the 2004 and 2005 surveys. 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). The number of tissue samples collected is shown in Table 8-1. The liver

tissue samples from five croakers were composited into one liver sample.

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

Dissection

Dissections were performed in the laboratory following the method 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 analysis.

Table 8-1. Location and number of trawl and sport fish samples collected during 2004 and 2005.

	Station	2004	2005
		Summer	Summer
Trawl fish (white croaker)	HT5	0	0
	HT7	5	10
Sport fish (queenfish)	HT12	*	10

* Not required.

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. Mercury was analyzed by Cold Vapor analysis with Atomic Absorption Spectroscopy. 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.

RESULTS

All 2004 muscle tissue samples were analyzed for ninety-eight priority pollutants, including nine heavy metals and eighty-nine organic compounds. The muscle and liver tissue samples collected in 2005 were analyzed for total DDTs and six DDT derivatives, Total PCBs and seven PCB derivatives, and percent lipids based on the 2005 renewed NPDES permit.

METALS

Silver (Ag), cadmium (Cd), chromium (Cr), lead (Pb), and nickel (Ni) were not detected in muscle tissues collected in 2004 and 2005 surveys. Arsenic (As), copper (Cu), mercury (Hg) and zinc (Zn) were detected in all samples (Table 8-2). For each of the four detected metals, the average values in the collected samples at the outfall were higher in 2005 season.

Mercury (Hg) concentrations, ranging from 0.017 mg/kg to 0.11 mg/kg in fish muscle samples, were well below the “action levels” of 1.0 mg/kg for fish consumption set by the Food and Drug Administration (FDA) and 0.3 mg/kg for the Human Health Consumption level set by EPA (EPA 1994). 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, the International Action Limit Median is widely used by other nations for a similar purpose (Mearns et al. 1991). Our data indicate that the detected concentrations of mercury, copper, and zinc were well below the International Median values of 1.0 mg/kg, 20 mg/kg, and 70.0 mg/kg, respectively.

Silver, cadmium, and lead were not detected in muscle tissue of the sport fish, Queenfish, collected in 2005 (Table 8-3). The averages of arsenic, copper, mercury in Queenfish were lower

Table 8-2. Metals, cyanide, and organics found in muscle tissues of white croaker at HT7 in Los Angeles Harbor during 2004 to 2005 period. Bold numbers indicate DDT and PCB levels that exceeded the 0.1 mg/kg limit set by OEHHA (1991).

Constituents Detected	Muscle Tissues of White Croaker					
	HT7 (Outfall) n= 5, August 2004			HT7 (Outfall) n= 10, August 2005		
	Frequency %	Average (mg/kg)	Range (mg/kg)	Frequency %	Average (mg/kg)	Range (mg/kg)
Metals						
Ag	0	ND	ND	0	ND	ND
As	100	0.85	0.49 - 1.1	100	1.1	0.57 – 1.5
Cd	0	ND	ND	0	ND	ND
Cr	0	ND	ND	0	ND	ND
Cu	100	0.33	0.20 - 0.60	100	0.37	0.21 – 1.0
Ni	0	ND	ND	0	ND	ND
Hg	100	0.038	0.017 - 0.054	100	0.065	0.022 - 0.11
Pb	0	ND	ND	0	ND	ND
Zn	100	2.8	2.7 - 3.0	100	3.4	3.4 - 3.8
Pesticides and PCBs:						
O,P'-DDE	0	ND	ND	50	0.028	ND – 0.071
P,P'-DDE	100	0.11	0.022 - 0.19	100	0.77	0.062 – 3.0
P,P'-DDD	40	0.0020	ND – 0.0028	0	ND	ND
P,P'-DDT	0	ND	ND	30	0.0016	ND – 0.0021
PCB 1254	60	0.053	ND – 0.068	20	0.032	ND – 0.034
PCB 1260	40	0.046	ND - 0.056	100	0.067	0.014 – 0.17
Base/Neutral/Acid Extractables:						
Isophorone	60	1.0	ND - 2.1	NR	NR	NR
4-nitrophenol	20	0.013	ND – 0.063	NR	NR	NR
Diethylphthalate	100	1.7	1.1 – 2.7	NR	NR	NR
Di-n-butylphthalate	80	0.28	ND – 0.38	NR	NR	NR
Bis(2-ethylhexyl)phthalate	40	0.40	ND – 0.40	NR	NR	NR
Total Organic Halides(TOX)	100	3.28	2.48 - 4.16	NR	NR	NR
Cyanide	0	ND	ND	0	ND	ND
Lipids (%)	100	1.22	0.98 - 1.35	100	2.26	1.48 – 2.92

n= Number of samples analyzed
 ND=Below Detection Limit
 NR=Not Required

Table 8-3. Metals, cyanide, and organics found in muscle tissues of queenfish at HT12 and liver tissues of white croaker at HT7 in Los Angeles Harbor during 2005 period. Bold numbers indicate DDT and PCB levels that exceed the 0.1 mg/kg limit set by OEHHA (1991).

Constituents Detected	Muscle Tissues of Queenfish n= 10, August 2005			Liver Tissues of White Croaker n= 2*, August 2005		
	Frequency %	Average (mg/kg)	Range (mg/kg)	Frequency %	Average (mg/kg)	Range (mg/kg)
Metals						
Ag	0	ND	ND	100	0.14	0.11, 0.17
As	100	0.46	0.39 - 0.52	100	2.4	2.12, 2.65
Cd	0	ND	ND	100	0.36	0.27, 0.45
Cr	100	1.4	0.040 – 6.9	0	ND	ND
Cu	100	0.31	0.24 - 0.44	100	11	9.2, 12
Ni	50	1.0	ND – 2.2	100	0.17	0.14, 0.20
Hg	100	0.11	0.070 - 0.16	100	0.080	0.080, 0.080
Pb	0	ND	ND	100	0.52	0.50, 0.54
Zn	100	6.2	4.9 – 7.1	100	26	23, 28
Pesticides and PCBs:						
O,P'-DDE	0	ND	ND	100	0.087	0.076, 0.097
P,P'-DDE	90	0.17	ND – 0.63	100	3.4	3.2, 3.7
P,P'-DDD	90	0.0023	ND – 0.0059	0	ND	ND
PCB 1016	0	ND	ND	100	0.042	ND, 0.084
PCB 1254	80	0.071	ND – 0.18	100	0.068	0.058, 0.078
PCB 1260	80	0.039	ND - 0.098	100	0.31	0.24, 0.38
Base/Neutral/Acid Extractables: NR						
Total Organic Halides(TOX)	NR					
Cyanide	0	ND	ND	50	0.15	ND – 0.30
Lipids (%)	100	2.41	1.95 - 2.98	100	18.6	17.8, 19.4

* Each was composited from 5 samples (only two values, range shows both)

n: Number of samples analyzed

ND : Below Detection Limit

NR: Not Required

than those of muscle tissues of trawl fish samples collected in 2004 and 2005. For two composite samples of white croaker liver tissues, all metals except chromium were detected at higher levels as compared to the metal levels of all muscle tissues samples. The liver tissue averages of copper, mercury, and zinc were still below the International Action Limit Median values.

ORGANICS

Among organic compounds analyzed, trace levels of five semi-volatile pollutants were detected in white croaker muscle tissue in 2004 (Table 8-2). Two DDT derivatives (p,p'-DDE, and p,p'-DDD) and TOX were detected in one or more white croaker muscle samples. Among the detected organics, p,p'-DDE was detected in all samples with an average of 0.11 mg/kg, which is above 0.1 mg/kg limit set by OEHHA (1991). The PCB derivatives, PCB 1254 and PCB 1260, were detected in 2004 and 2005 white croaker muscle tissues with the total concentration below 0.1 mg/kg limit each year.

O,p'-DDE, p,p'-DDE, and p,p'-DDT were detected in muscle tissues of white croaker in 2005 (Table 8-2). The average of p,p'-DDE in 10 samples reached 0.77 mg/kg with the maximum of 3.0 mg/kg. Overall, the concentrations of total DDT in 2004 and 2005 muscle tissues collected at the outfall 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).

An average of 0.17 mg/kg and 0.0023 mg/kg of two DDT derivatives, p,p'-DDE, and p,p'-DDD, respectively, were detected in muscle tissues of the sport fish, queenfish, during the 2005 survey (Table 8-3). PCB 1254 and PCB 1260 were detected in queenfish muscle tissue in 2005 with averages of 0.071 mg/kg and 0.039 mg/kg, respectively.

O,p'-DDE and p,p'-DDE were detected in liver tissues of white croaker in 2005 (Table 8-3). The average of p,p'-DDE was at 3.4 mg/kg, more than

4 times the average (0.77 mg/kg) in muscle tissue. PCB 1016, PCB 1254, and PCB 1260 were found in liver tissues at significant higher levels than those in muscle tissues.

The metal and organic pollutant levels in liver tissues showed a high bioaccumulation effect. The level of total PCB in liver tissues was almost 4 times the level in muscle tissues. The high bioaccumulation effect is associated with high lipids levels in liver tissues. The average lipids level (18.6%) in liver tissues of white croaker was almost 9 times of the average level (2.26%) in muscle tissues.

DISCUSSION

Since 1993, the Environmental Monitoring Division (EMD) has monitored annually and assessed the tissue chemistry data of fish from the LA Harbor (LAH) (CLA, EMD 1994 to 2003). 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 changes in field sampling sites. The chemistry data of tissues collected from 2000 to present are used for 5-year outfall temporal trend assessment (Figure 8-2). Since no samples were collected at HT5 (reference site outside the breakwater) during the 2004 and 2005 surveys, spatial trend was not assessed.

Table 8-4. Selected metals and organics found in muscle tissues of white croaker in Los Angeles Harbor and Santa Monica Bay during 2005. Bold numbers indicate DDT and PCB levels that exceed the 0.1 mg/kg limit set by OEHHA (1991).

Constituents Detected	Los Angeles Harbor n= 10, August 2005			Santa Monica Bay n= 3, March 2005		
	Frequency %	Average (mg/kg)	Range (mg/kg)	Frequency %	Average (mg/kg)	Range (mg/kg)
Metals						
As	100	1.1	0.57 – 1.5	100	0.20	0.26 – 0.39
Cu	100	0.37	0.21 – 1.0	100	0.49	0.40 – 0.61
Hg	100	0.065	0.022 - 0.11	100	0.056	0.080 - 0.12
Pb	0	ND	ND	33	0.070	ND – 0.22
Zn	100	3.4	3.4 - 3.8	100	2.4	2.4 - 2.5
Pesticides and PCBs:						
O,P'-DDE	50	0.028	ND – 0.071	33	0.0013	ND – 0.0067
P,P'-DDE	100	0.77	0.062 – 3.0	100	0.028	0.013 – 0.077
P,P'-DDT	30	0.0016	ND – 0.0021	0	ND	ND
PCB 1254	20	0.032	ND – 0.034	67	0.031	ND – 0.086
PCB 1260	100	0.067	0.014 – 0.17	67	0.034	ND – 0.11
Lipids (%)	100	2.26	1.48 – 2.92	100	1.01	1.59 – 1.78

n=Number of samples analyzed
ND=Below Detection Limit

TEMPORAL PATTERNS

To address the question: “Is the health of demersal fish in the vicinity of the discharge changing over time?”, Figure 8-2 shows the temporal comparison of selected pollutants and percent lipid from 2000 to 2005 at the outfall (HT7). Samples were not collected in 2003 due to the resource exchange to Bight’03 monitoring. No clear patterns are observed in Figure 8-2. The concentrations of mercury, zinc, and percent lipid showed no significant changes. Except the high level in 2000, the concentrations of copper are very consistent. Total DDTs range from 0.11 mg/kg in 2004 to 0.80 mg/kg in 2005. Total PCBs range from 0.010 mg/kg in 2002 to 0.24 mg/kg

in 2001. Percent lipid levels have no significant changes over the five-year period.

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 of collecting fish samples from the Cabrillo Pier area may be necessary in order to continue monitoring white croaker in this area.

Table 8-5. Concentrations of pollutants in muscle tissues of white croaker and sediment near the TITP outfall stations, HT7 and HM3, respectively, during 2004 and 2005 period.

Constituents	Muscle Tissue at HT7		Sediment at HM3	
	2004 (mg/kg)	2005 (mg/kg)	2004 (mg/kg)	2005 (mg/kg)
Metals				
Ag	ND	ND	0.09	ND
As	0.85	1.1	6.0	6.4
Cd	ND	ND	1.7	4.2
Cr	ND	ND	50	40
Cu	0.33	0.37	57	47
Ni	ND	ND	35	29
Hg	0.038	0.065	0.13	0.16
Pb	ND	ND	4.1	10
Zn	2.8	3.4	100	100
Pesticides and PCBs:				
O,p'-DDE	ND	0.028	ND	ND
P,p'-DDE	0.11	0.77	0.084	0.060
P,p'-DDD	0.0020	ND	ND	ND
P,p'-DDT	ND	0.0016	ND	ND
PCB 1254	0.053	0.032	ND	ND
PCB 1260	0.046	0.067	ND	ND
Base/Neutral/Acid Extractables:				
Isophorone	1.0	NR	ND	ND
4-nitrophenol	0.013	NR	ND	ND
Diethylphthalate	1.7	NR	ND	ND
Di-n-butylphthalate	0.28	NR	ND	ND
Bis(2-thylhexyl)phthalate	0.40	NR	ND	ND
Total Organic Halides (TOX)		NR	7.4	7.0

ND : Below Detection Limit
NR: Not Required

In order to compare the pollutant levels in white croakers at different locations, Table 8-4 shows the concentrations of selected pollutants in muscle tissues of white croaker collected in the Los Angeles Harbor and Santa Monica Bay (SMB) in 2005. All white croaker samples were collected at the vicinities of the outfalls, HT5 in LAH and

5-Mile in SMB. Copper, mercury, and zinc were detected in all white croaker samples from LAH and SMB with comparable levels. For pesticides and PCBs, o,p'-DDE, p,p'-DDE, PCB1254, and PCB1260 were the common pollutants found in the samples from both locations. The levels of detected organic pollutants were higher in LAH,

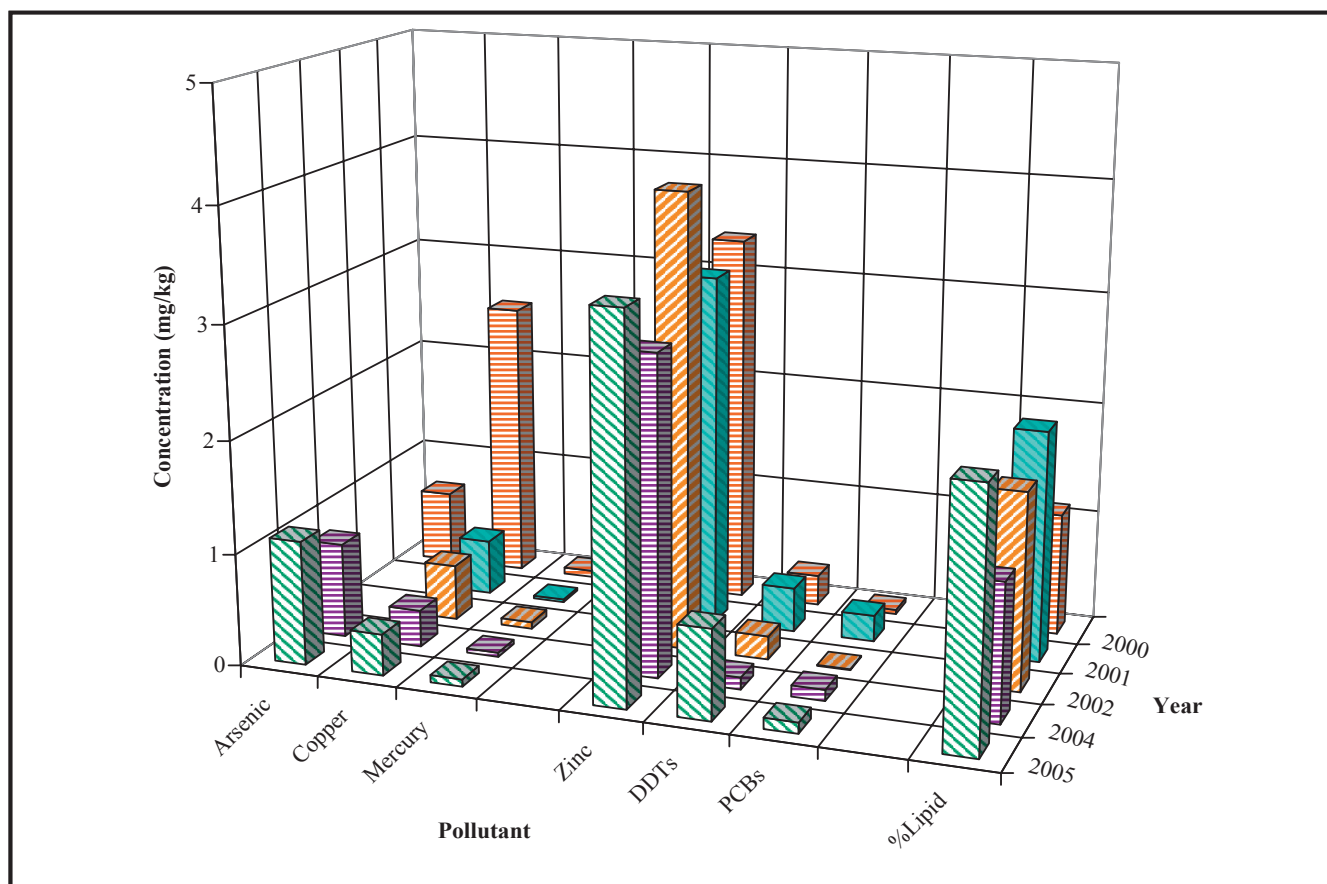


Figure 8-2. Temporal trend of selected pollutants and %lipid in muscle tissue of white croaker at the TITP outfall (HT7) from 2000 – 2005. Arsenic was not detected in 2001 and 2002.

especially p,p'-DDE, which was found at an average of 0.77 mg/kg in LAH versus an average of 0.028 mg/kg in SMB.

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 (HT7) are compared with the pollutant concentrations in sediments near the outfall (HM3) (see Chapter 5) during 2004 and 2005 sampling years (Table 8-5).

Arsenic, copper, mercury, and zinc were detected both in white croaker muscle tissue and sediment samples from the TITP outfall area during the 2004 and 2005 surveys. However, cadmium, chromium,

nickel, and lead were found in sediment, but not in muscle tissue. For organics, several BNA, pesticide, and PCB compounds were found in muscle tissue but undetected (except p,p'-DDE) in sediment. P,p'-DDE was detected in sediment samples collected near the outfall at 0.084 mg/kg in 2004 and at 0.060 mg/kg in 2005.

The fact that arsenic, copper, mercury, zinc, and DDE were detected in tissue and sediment at the outfall indicates that these pollutants 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 (CLA, EMD 1994 to 2003), the TITP wastewater discharge seems to have very little impact on the pollutant burden of white croakers in the Harbor.

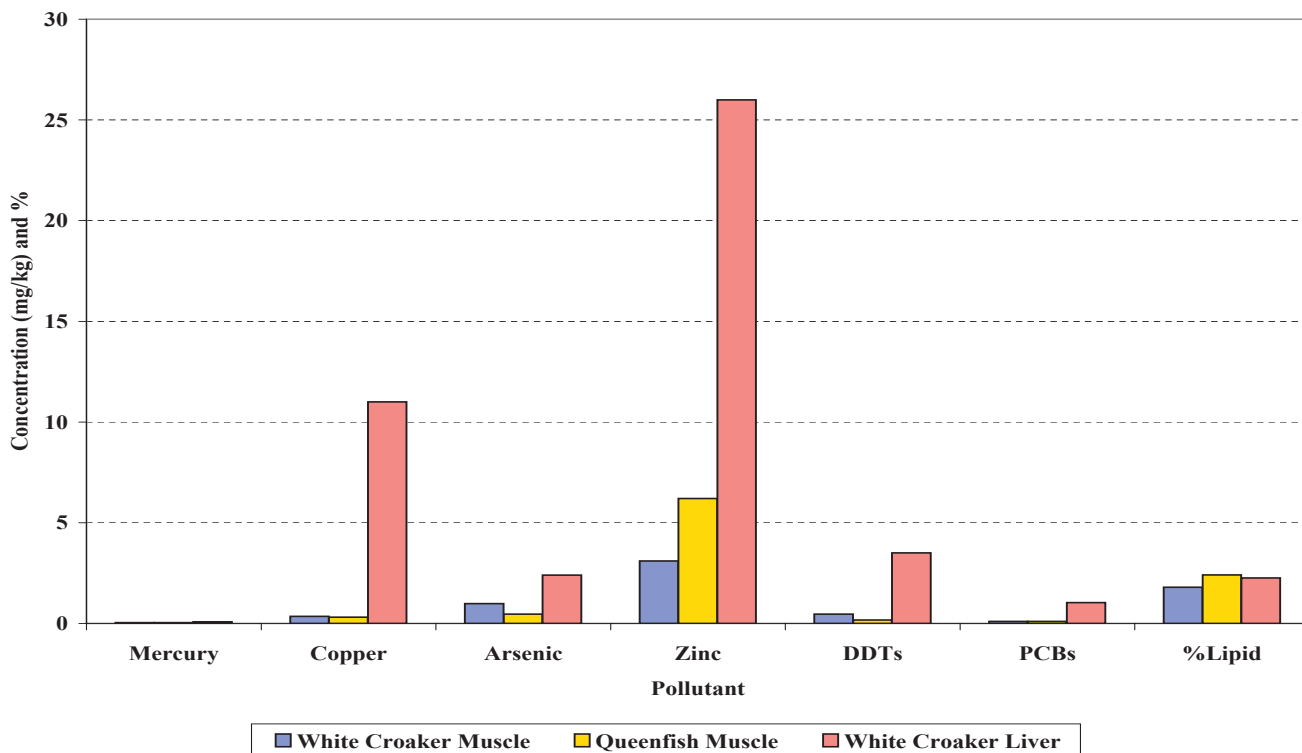


Figure 8-3. Concentrations of selected pollutants in muscle and liver tissues near the TITP outfall during the 2004 and 2005 sampling seasons.

SEAFOOD SAFETY

Tables 8-2 and 8-3 contain the concentrations of detected pollutants in white croaker and queenfish tissue collected during the 2004 and 2005 surveys to address the question: “Are seafood tissue concentrations below levels that will ensure public safety?” The levels of mercury and other detected metals were under all regulatory limits and proposed action levels. However, the total DDT levels in both white croaker and Queenfish tissues have exceeded the recommended 0.1 mg/kg limit of DDT and PCB levels set by California OEHHA. The total PCB level in liver tissues of Queenfish also exceeded the 0.1 mg/kg limit. Figure 8-3 shows the average levels of selected pollutants in muscle and liver tissue of white croaker and in muscle tissue of Queenfish in the 2004 and 2005 sampling seasons. The liver tissues clearly accumulate more pollutants than muscle tissues.

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