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METAL AND ORGANIC CONTAMINANTS IN SEDIMENTS AND ANIMALS

Few studies have been done to determine the assimilative capacity of the environment in terms of the relationship between bioaccumulation and biological effects. The purpose of this study was to provide an inventory of contaminant concentrations in sediments and animal tissues along a gradation of contamination. This would serve as a baseline for comparing the relationship between bioaccumulation and biological effects in this and other studies. Results from this study indicate that sediments were highly contaminated by DDTs, PCBs and metals at Palos Verdes (PV) Station 7-3, but relatively uncontaminated at Santa Monica Bay (SMB) Stations 6-4 and 2-3. Animal tissues were highly contaminated by DDTs and moderately contaminated by PCBs at PV 7-3, SMB 6-4, and SMB 2-3. The degree of contamination of animal tissues by DDTs was roughly proportional to the distance from PV 7-3. There was an inverse relationship between the concentrations of synthetic organic compounds and metal contaminants in tissues.

The present JWPCP outfall discharge near PV 7-3 contains nearly equal concentrations of highly lipid-soluble DDTs and PCBs (Schafer, this volume). The Hyperion outfall near SMB 6-4 discharges concentrations of PCBs similar to the JWPCP outfall, but much lesser amounts of DDTs. The JWPCP and Hyperion outfalls discharge nearly equal concentration of metals (Schafer, this volume).

The degree of accumulation of organic contaminants in sediments and animals around outfalls is more closely related to their lipid solubility than to the present wastewater concentration (Gossett et al. 1983). Metals may accumulate in sediments around outfalls but may show no increases in tissues (Brown et al. 1983).

Livers and gonads were chosen for analysis since these organs are important both in terms of bioaccumulation and biological effects. High concentrations of contaminants accumulate in the liver because it is a major site of detoxification. Female gonads may accumulate high concentrations of organics, as they contain substantial amounts of lipids that serve as a reservoir of nutrients for the developing embryo. The liver is important in terms of biological effects because it serves as a metabolic center in the organism; gonads serve to perpetuate the species.

The liver is not only a major site of detoxification but can also be a major site of toxicity. Once accumulated in the livers, organic chemicals are metabolized to highly reactive epoxides. These can be detoxified by glutathione, glucuronic acid, and sulfates or they can cause toxic effects if the capacities of detoxification systems are exceeded (Brown et al. 1984a). Toxicity in the liver can be manifested as tissue-level pathology, including hypertrophy and fatty vacuolation, and as molecular effects, including enzymatic changes and a reduction in the cell's capacity to produce metallothionein (Brown et al. 1982a, b; Perkins et al. 1982).

The relationship between accumulation of contaminants in gonads and reproductive failures has been studied for some fish species (von Westernhagen et al. 1981), although the ability of gonads to detoxify contaminants is unknown. It has been suggested that reproductive success is the most important biological effects parameter, since changes may directly cause any observed population declines.

Although the chemical analyses presented in this study were not always done on the same individuals as were used in the studies following on detoxification/toxification, reproduction, and liver histology, the results should serve as a point of reference for observed effects. However, it is acknowledged that any conclusions drawn with regards to bioaccumulation and biological effects in other fish must consider variability due to season, reproductive stage, and mobility.

Sediment concentrations of contaminants are also reported so that any relationship between environmental concentrations and bioaccumulation can be elucidated. Ultimately, it is envisioned that assimilative capacity can be related to contamiant effluent concentrations (Schafer 1984), contaminant physical-chemical properties (Gossett et al. 1983), sediment accumulation, bioaccumulation, detoxification/toxification, molecular effects, tissue-level histological and reproductive effects, and population changes (Bascom 1982).

MATERIALS AND METHODS

Fish and invertebrates were collected from Santa Monica Bay (SMB 2-3 and SMB 6-4) and Palos Verdes (PV 7-3) in December 1982, using a standard otter trawl. Surficial (0-2 cm deep) sediment samples were collected at the same time using a modified Van Veen grab sampler. Tissue and sediment samples for metal analysis were placed in clean polystyrene containers, while those for organics were placed in kiln-cleaned glass jars with aluminum lid-liners. All samples were immediately frozen on dry ice and stored at -20°C in the laboratory.

Tissue and sediment samples for trace metals were digested in hot nitric/hydrochloric acid for 3 hours, followed by filtration and dilution with deionized-distilled water (Young et al. 1981; Hershelman et al. 1981). Metals were analyzed on a Varian Techtron AA6 atomic absorption spectrophotometer with graphite furnace, flame, and deuterium-arc background correction, using the method of standard additions. The analytical methods for chlorinated hydrocarbons are described in Gossett et al. (this volume (b)).

RESULTS AND DISCUSSION

Sediments

Surficial sediments at PV 7-3 contained two to three orders of magnitude more DDTs and DDTols (oxygenated metabolites of DDTs) than those at SMB 6-4 and SMB 2-3 (Table 1). Concentrations of PCBs and PCBols were approximately one order of magnitude higher at PV 7-3 than at SMB 2-3 and 6-4; metals were one to two orders of magnitude higher. Concentrations of organic and metal contaminants were not markedly different between SMB 2-3 and 6-4. Analysis of total volatile solids (TVS) and dry/wet ratios indicated more deposition of particulate organic materials at PV 7-3 than at SMB 6-4 or 2-3.

The concentrations of contaminants in surficial sediments at PV 7-3 appear to be more reflective of historical (pre-1970) inputs than present-day inputs. This contention is made because the concentrations of PCBs and metals are much higher in surficial sediments at PV 7-3 than at SMB 6-4, even though wastewater concentrations at the two sites are nearly identical (Schafer 1984). In addition, the surficial sediment concentrations of total DDT at PV 7-3 are approximately two hundred-fold higher than at SMB 6-4, even though the wastewater discharges are only about fifteen times higher (mass emission rates of 422 and 30 kg/year, respectively). Thus, despite the present-day rate of deposition of organically enriched material at PV 7-3 of approximately 2.5 cm/year, bioturbation and mixing by wave action ensure that the deeper sediments containing DDT discharged in the past are present in surficial sediments*.

*Personal communication. July 1984. Tareah C. Hendricks, Physicist, SCCWRP.

Table 1. Concentrations of organic and metal contaminants in sediments at the stations sampled. Note that they are highest at PV 7-3 and much lower and similar to each other at SMB 2-3 and 6-4.

	Concentrations (mg/dry kg; mean ± standard error (n))		
	SMB 2-3	SMB 6-4	PV 7-3
Organics			
DDTs	0.12 ± 0.02(5)	0.10(1)	19.1 ± 3.6(5)
DDTols	0.80 ± 0.68(5)	0.38(1)	78.8 ± 18.2(5)
PCBs	0.018 ± 0.005(5)	0.044(1)	0.67 ± 0.27(5)
PCBols	6.7 ± 3.0(5)	6.5(1)	36.4 ± 33.3(5)
Metals			
Cadmium	0.34 ± 0.03(2)	0.70 ± 0.05(2)	33 ± 1(2)
Copper	16 ± 2(2)	25 ± 2(2)	340(2)
Zinc	70 ± 1(2)	54(2)	1150 ± 50(2)
Sediment Characteristics			
%<63µm	88	24	40
%dry wt	60	68	33
%TVS	4.7	2.1	18

The lack of any appreciable difference in surficial sediment contaminant concentration between SMB 2-3 and SMB 6-4 (Table 1) would appear to indicate some or all of the following: the Hyperion outfall discharge zone is remarkably clean relative to background; particulates released from the Hyperion outfalls do not settle in the immediate vicinity; deposition of present-day effluent is indistinguishable in a background of widespread, evenly dispersed contamination most likely originating from historical deposits.

The occurrence of high concentrations of oxygenated metabolites in relation to the total of metabolites and parent compounds (average: 91%) is in accordance with previous studies showing that organics are readily metabolized in marine sediments (Lee and Ryan 1978; Brown et al. 1984a). Oxygenated metabolites appear to represent the most prevalent form of synthetic chlorinated hydrocarbon contamination in the marine environment--and the form responsible for chronic effects in animals.

Fish Livers and Invertebrate Hepatopancreas

Fish livers and invertebrate hepatopancreas from PV 7-3 contained much

Table 2. Concentrations of contaminants in fish livers and invertebrate hepatopancreas. Organic contaminants increase from SMB 2-3 to PV 7-3, but metals frequently show a gradation in the opposite direction.

	Concentrations (mg/wet kg; mean ± standard error (n))		
	SMB 2-3	SMB 6-4	PV 7-3
DDTs			
Yellowchin sculpin[a]	13 ± 4(4)	20 ± 9(5)	74 ± 13(4)
Longspine combfish[b]	12 ± 4(4)	22 ± 4(6)	86 ± 18(7)
Pacific sanddab[c]	42 ± 8(5)	71 ± 15(6)	610 ± 105(4)
Red pointer crab[d]	5(1)	17 ± 8(4)	44 ± 38(3)
Ridgeback prawn[e]	12 ± 9(2)	13 ± 6(6)	49 ± 5(6)
DDTols			
Yellowchin sculpin	NA[f]	78 ± 43(3)	69 ± 68(3)
Longspine combfish	ND[g]	14 ± 3(6)	63 ± 27(7)
Pacific sanddab	17 ± 7(4)	9 ± 7(3)	263 ± 244(3)
Red pointer crab	49(1)	NA	140 ± 27(3)
Ridgeback prawn	NA	NA	NA
PCBs			
Yellowchin sculpin	1.2 ± 0.5(4)	2.3 ± 0.8(5)	2.3 ± 0.4(4)
Longspine combfish	1.3 ± 0.3(4)	4.0 ± 0.9(6)	5.9 ± 1.3(7)
Pacific sanddab	4.8 ± 0.9(5)	16 ± 2(6)	14 ± 3(4)
Red pointer crab	0.5(1)	1.9 ± 0.4(4)	4.7 ± 0.7(3)
Ridgeback prawn	3.0 ± 2.0(2)	3.1 ± 0.7(6)	1.8 ± 0.2(6)
PCBols			
Yellowchin sculpin	NA	21 ± 6(3)	36 ± 31(3)
Longspine combfish	ND	0.26 ± 0.17(6)	210 ± 147(7)
Pacific sanddab	19 ± 14(4)	290 ± 135(6)	120 ± 40(3)
Red pointer crab	49(1)	NA	44 ± 9(3)
Ridgeback prawn	NA	NA	NA
Cadmium			
Yellowchin sculpin	0.79 ± 0.11(4)	0.26 ± 0.05(5)	0.15 ± 0.05(3)
Longspine combfish	3.2 ± 0.7(5)	0.57 ± 0.15(6)	1.2 ± 0.5(6)
Pacific sanddab	0.87 ± 0.18(5)	0.66 ± 0.14(5)	1.8 ± 1.0(6)
Red pointer crab	30.5 ± 7.5(2)	12.2 ± 3.1(4)	3.9 ± 0.7(6)
Ridgeback prawn	8.8 ± 0.5(2)	9.5 ± 5.9(3)	0.23 ± 0.02(6)
Copper			
Yellowchin sculpin	6.7 ± 3.6(4)	3.2 ± 0.5(5)	9.8 ± 3.7(3)
Longspine combfish	224 ± 82(5)	111 ± 53(6)	30 ± 12(6)
Pacific sanddab	2.0 ± 0.3(5)	6.2 ± 1.1(5)	4.3 ± 1.2(6)
Red pointer crab	35 ± 14(2)	66 ± 16(4)	27 ± 4(6)
Ridgeback prawn	222 ± 133(2)	151 ± 44(3)	90 ± 14(6)
Zinc			
Yellowchin sculpin	136 ± 22(4)	62 ± 5(5)	55 ± 13(3)
Longspine combfish	126 ± 8(5)	86 ± 14(6)	86 ± 4(6)
Pacific sanddab	20 ± 4(5)	28 ± 8(5)	26 ± 2(6)
Red pointer crab	81 ± 14(2)	55 ± 10(4)	64 ± 6(6)
Ridgeback prawn	72 ± 27(2)	50 ± 17(3)	98 ± 19(6)

[a] *Icelinus quadriseriatus*.
[b] *Zaniolepis latipinnis*.
[c] *Citharichthys sordidus*.
[d] *Mursia gaudichaudii*.
[e] *Sicyonia ingentis*.
[f] Not analyzed.
[g] Not detected.

higher concentrations of DDTs than those from SMB 6-4 (Table 2). This finding corresponded with the levels in sediments. However, whereas sediment concentrations of DDTs were similar at SMB 6-4 and 2-3 (Table 1), liver and hepatopancreatic DDTs were consistently higher at SMB 6-4 than SMB 2-3. This indicates that liver and hepatopancreatic concentrations of DDTs were more a reflection of the distance the fish was collected from PV 7-3 than the sediment concentration at the place of collection. This pattern is apparent for both mussels (total tissue) and fish livers collected from SMB 2-3 to PV 7-3 (Figure 1) and in scorpionfish livers collected over a much larger range (Figure 2). Results for fish could indicate that they swim in and out of the zone of influence of PV 7-3, but results for mussels indicate a water column distribution of DDTs that does not reflect sediment concentrations.

Although sediment concentrations of PCBs were much higher at PV 7-3 than at SMB 6-4 (Table 1), there was very little difference in liver and hepatopancreatic PCB values between these two stations (Table 2). Thus, unlike those for DDT, PCB tissue concentrations do not appear to reflect distance from sediment sources, but rather may reflect the relatively similar present-day effluent sources at PV 7-3 and SMB 6-4.

Like sediments, oxygenated metabolites represented a large portion (average: 66%) of contamination of livers and hepatopancreas by organics (Table 2). The source of oxygenated metabolites in animal tissues may be from either sediments or metabolism within the animals. PCBs are metabolized in both sediments (Lee and Ryan 1978) and fish (Franklin et al. 1980). However, whereas DDT is known to be metabolized in sediments (Lee and Ryan 1978), it may not be metabolized in some fish species (Addision et al. 1977). Therefore, DDT metabolites in fish may originate either from the sediments (Brown et al. 1984b) or from animals lower in the food web that obtained DDT from the sediments.

Unlike DDTs and PCBs, concentrations of metals were frequently lower in liver and hepatopancreatic tissue collected near suspected sources of effluent and sediment contamination at PV 7-3 and SMB 6-4. In fact, although sediment metal concentrations were one to two orders of magnitude higher at PV 7-3 than at either SMB 6-4 or 2-3 (Table 1), liver and hepatopancreatic concentrations were frequently depressed by this much at PV 7-3 (Table 2). This phenomenon most likely does not reflect reduced water column availability of contaminants, because metals were not depressed in mussels (Figure 3). Rather, the concentrations of metals in fish livers and invertebrate hepatopancreas tended to be reduced as the concentration of organic contaminants increased. Statistical analysis indicated that the reduced levels of metals were inversely proportional to the concentration of oxygenated metabolites of organics contaminants rather than parent compounds (Figure 4). This

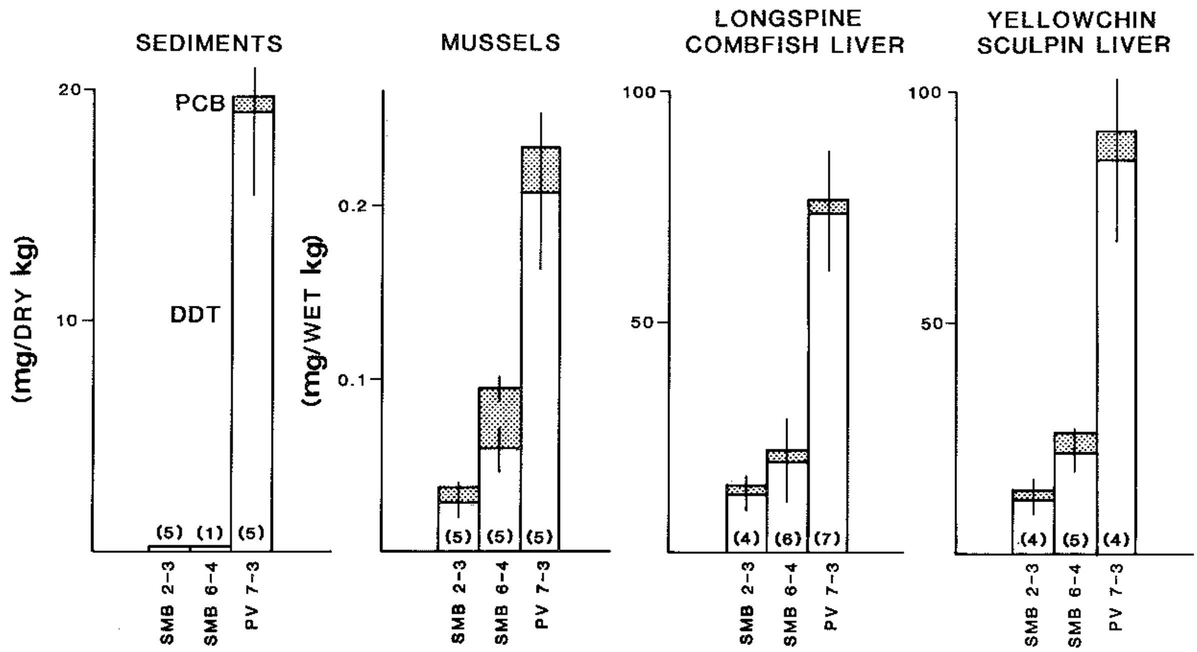

Figure 1. Concentrations (mean ± 1 standard error (n)) of chlorinated hydrocarbons in sediments, mussels (total tissue), and fish livers at the sampled stations (mussel values are seasonal means from onshore sites adjacent to offshore stations (data from Brown et al. 1982c)).

inverse relationship is in accordance with previous studies indicating that oxygenated metabolites, not parent compounds, are responsible for biological effects (Brown et al. 1982a, b; 1983; 1984a, b). Trace metal deficiencies are suspected to result from the effect of oxygenated metabolites on metallothionein metal binding (Brown et al. 1982a, b; this volume). Trace metal depressions have been linked to some disease processes, including cancer (Brown et al. 1980).

Fish Gonads

The concentrations of organics and metals in gonads followed patterns similar to liver tissue (Table 3). DDTs were markedly higher in gonads from PV 7-3 relative to SMB 6-4 and 2-3. PCBs showed a less clear relationship to distance from PV 7-3. Oxygenated metabolites represented a substantial portion (average: 77%) of the total contamination by organics. Metals were sometimes depressed in gonads of fish from PV 7-3.

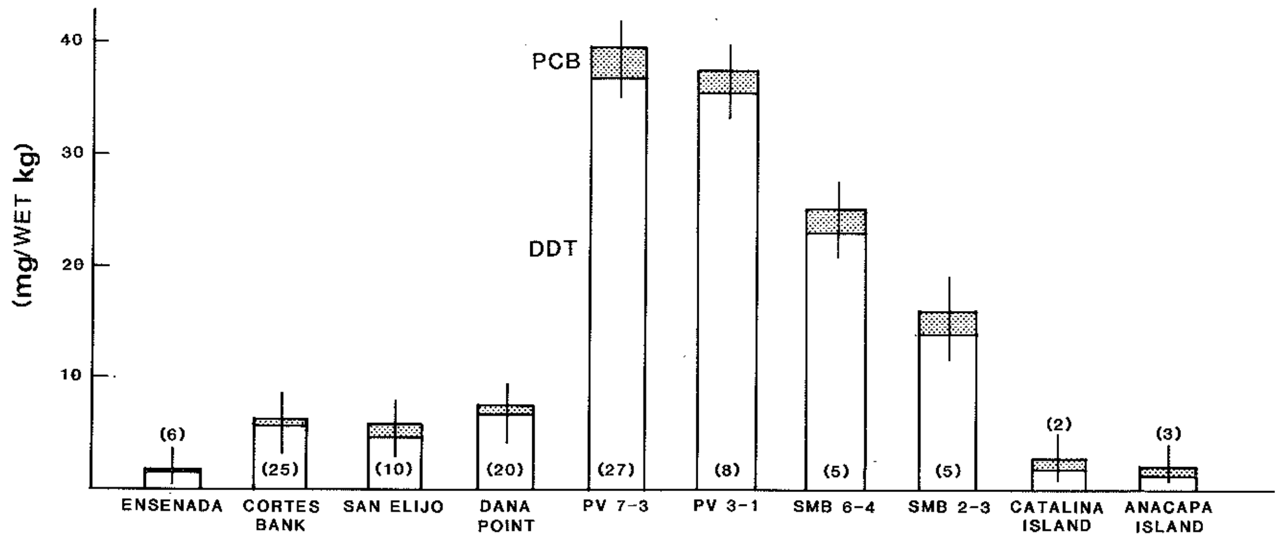

Figure 2. Concentrations (mean ± 1 standard error (n)) of chlorinated hydrocarbons in scorpionfish livers from sites along the coasts of southern California and Mexico (lows ranged from 1.5 mg/wet kg at Anacapa Island to 40 mg/wet kg at PV 7-3; concentrations were roughly proportional to distance from PV 7-3).

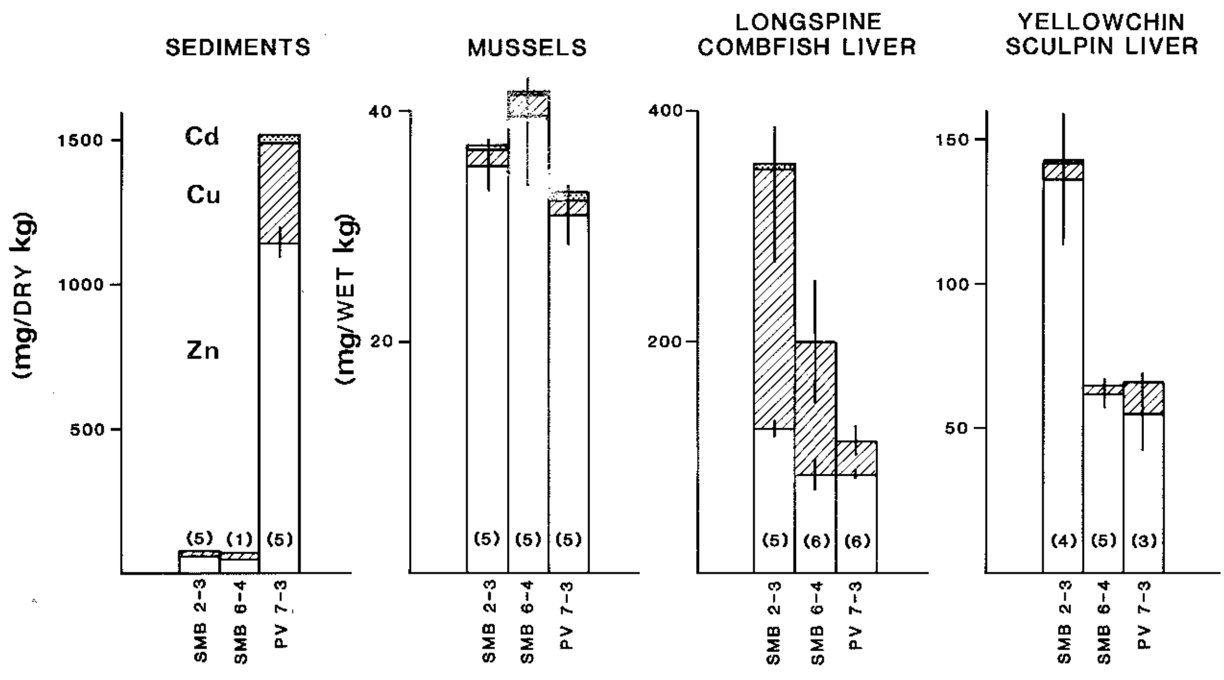

Figure 3. Concentrations (mean ± 1 standard error (n)) of metals in sediments, mussels (total tissue), and fish livers at the sampled stations (mussel values are seasonal means from onshore sites adjacent to offshore stations (data from Brown et al. 1982c)). Concentrations of metals at PV 7-3 were higher in sediments, but lower in fish livers.

Table 3. Concentrations of organics and metals in fish gonads. The trends are similar to those in livers, with highest concentration of organics and lowest metals in those from PV 7-3.

	Concentrations (mg/wet kg; mean ± 1 standard error (n))		
	SMB 2-3	SMB 6-4	PV 7-3
DDTS			
Yellowchin sculpin	0.059(1F)	0.003 ± 0.003(1F,4M)	4.4(1F)
Longspine combfish	0.73 ± 0.38(3F,2M)	1.1 ± 0.4(3F,2M)	2.6 ± 0.8(3F,2M)
Pacific sanddab	0.33 ± 0.07(4F,1M)	1.6 ± 0.3(1F,2M)	15 ± 6(4F,1M)
DDTols			
Yellowchin sculpin	NA[a]	NA	NA
Longspine combfish	NA	31 ± 29(3F,2M)	0.78 ± 0.5(3F,2M)
Pacific sanddab	9.3 ± 6.4(4F,1M)[b]	NA	35 ± 16(4F,1M)
PCBs			
Yellowchin sculpin	0.23(1F)	ND(1F,4M)	0.022(1F)
Longspine combfish	0.022 ± 0.018(3F,2M)	0.19 ± 0.07(3F,2M)	0.16 ± 0.05(3F,2M)
Pacific sanddab	0.018 ± 0.008(4F,1M)	0.20 ± 0.09(1F,2M)	0.88 ± 0.34(4F,1M)
PCBols			
Yellowchin sculpin	NA	NA	NA
Longspine combfish	NA	0.11 ± 0.09(3F,2M)	43 ± 29(3F,2M)
Pacific sanddab	15 ± 4(4F,1M)	NA	600 ± 370(4F,1M)
Cadmium			
Yellowchin sculpin	0.36 ± 0.21(2F)	0.36 ± 0.09(1F,1M)	0.08 ± 0.06(2M)
Longspine combfish	0.05 ± 0.01(3F)	0.56 ± 0.20(3F,1M)	0.39 ± 0.16(2F,2M)
Pacific sanddab	0.06 ± 0.02(4F)	0.03 ± 0.01(4F)	0.10 ± 0.005(5F,1M)
Copper			
Yellowchin sculpin	12.5 ± 1.5(2F)	6.0 ± 1.2(1F,1M)	1.2 ± 0.2(2M)
Longspine combfish	5.8 ± 1.6(3F)	8.8 ± 1.2(3F,1M)	6.1 ± 2.2(2F,2M)
Pacific sanddab	1.2 ± 0.3(4F)	1.0 ± 0.2(4F)	0.6 ± 0.1(5F,1M)
Zinc			
Yellowchin sculpin	102 ± 38(2F)	50 ± 9(1F,1M)	29 ± 6(2M)
Longspine combfish	38 ± 11(3F)	58 ± 9(3F,1M)	69 ± 15(2F,2M)
Pacific sanddab	85 ± 19(4F)	97 ± 15(4F)	92 ± 916(5F,1M)

[a]Not analyzed.
[b]F=female; M=Male.

Table 4. Concentrations of organic contaminants in livers of Pacific sanddab and Dover sole collected from sites at Palos Verdes and Santa Monica Bay between 1976 and 1984. Note that concentrations have increased since the mid-1970's in Pacific sanddab livers but have decreased in livers of Dover sole.

	Concentrations (mg/wet kg; mean ± 1 standard error)			
	Santa Monica Bay		Palos Verdes	
Pacific sanddab liver				
Date collected	May 1977[a]	Dec 1982[b]	June 1980[c]	Dec 1982[d]
Total DDT	26.2 ± 4.0	71.4 ± 14.8	126	610 ± 105
Total PCB	22.3 ± 5.1	15.7 ± 2.6	5.7	14 ± 3
(n)	(6)	(6)	(5[e])	(5)
DDT/PCB ratio	1.2	4.6	22	44
Dover sole liver				
Date collected	May 1977[a]	July 1984[a]	Nov 1976[d,f]	Sep 1983[d]
Total DDT	13 ± 1	2.6 ± 1.8	240 ± 34	46 ± 12
Total PCB	5.6 ± 3.5	0.82 ± 0.44	18 ± 3	1.5 ± 0.2
(n)	(12)	(11)	(6)	(15)
DDT/PCB ratio	2.3	3.2	13	31

[a] SMB 7-mile pipe.
[b] SMB 6-4.
[c] PV 3-1.
[d] PV 7-3.
[e] Five composites of 10 fish each.
[f] Data from Young et al. (1984).

Temporal Trends

On the basis of data presented in Table 4, it appears as though concentrations of organics have increased in Pacific sanddab livers and decreased in Dover sole livers from both SMB and PV since the mid-1970's. Some caution must be exercised in interpreting data since fish were not always collected from exactly the same station in the mid-1970's as in the early 1980's. However, the influence of this difference should be minimal since fish are mobile and probably spend part of their time away from the collection site. These data support the contention that organic contaminants have reached a state of equilibrium in southern California coastal waters (Young et al. 1984).

Comparison With Other Contaminated Marine Sites

A major supposition at the initiation of this study was that SMB 2-3 was a relatively uncontaminated control site. This assumption was made on the basis of sediment chemistry data (similar to that in Table 1) and infaunal trophic index (SMB 2-3 was rated 93 by Word and Mearns (1979)). Sediment chemistry data showed that, in comparison to PV 7-3, SMB 2-3 did indeed appear to be a relatively clean reference area (Figures 1 and 3). However, comparison of our sediment data with data (Malins et al. 1980; 1984) from both the Port Madison/Case Inlet, Puget Sound, Washington, control sites and areas in Puget Sound (Elliot Bay and Commencement Bay) considered to be highly contaminated shows that SMB 2-3 sediments are relatively contaminated (Figure 5). A comparison of chlorinated hydrocarbon concentrations from fish livers in both areas (Figure 5) provides an even stronger case: mean values recorded for English sole from Elliot Bay and Commencement Bay were

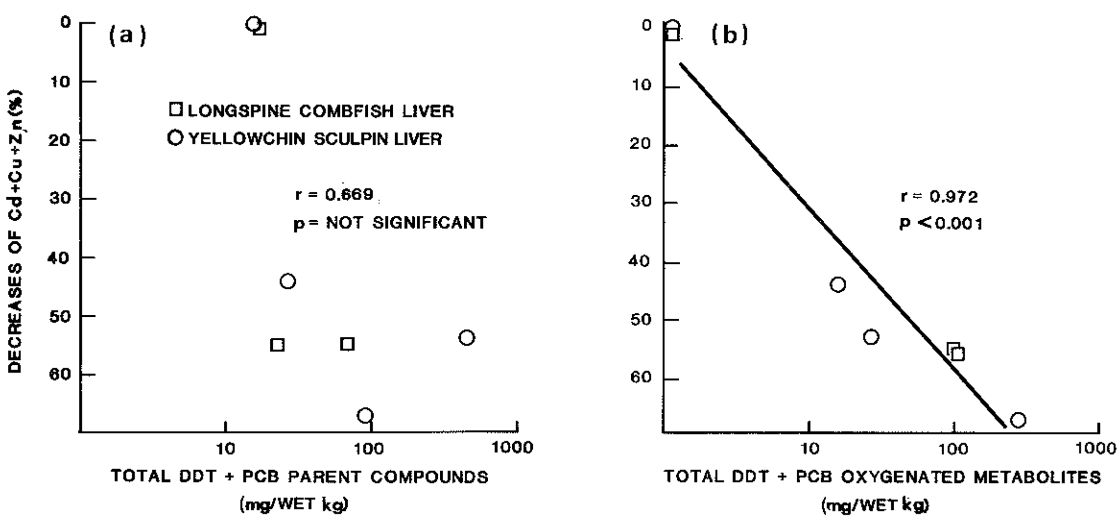

Figure 4. Percent decreases of cadmium, copper, and zinc in fish livers versus total concentrations of a) DDT and PCB parent compounds and b) DDTol and PCBol. The reductions of trace metals in fish livers were inversely correlated with total DDTols and PCBols, but not with DDT and PCB.

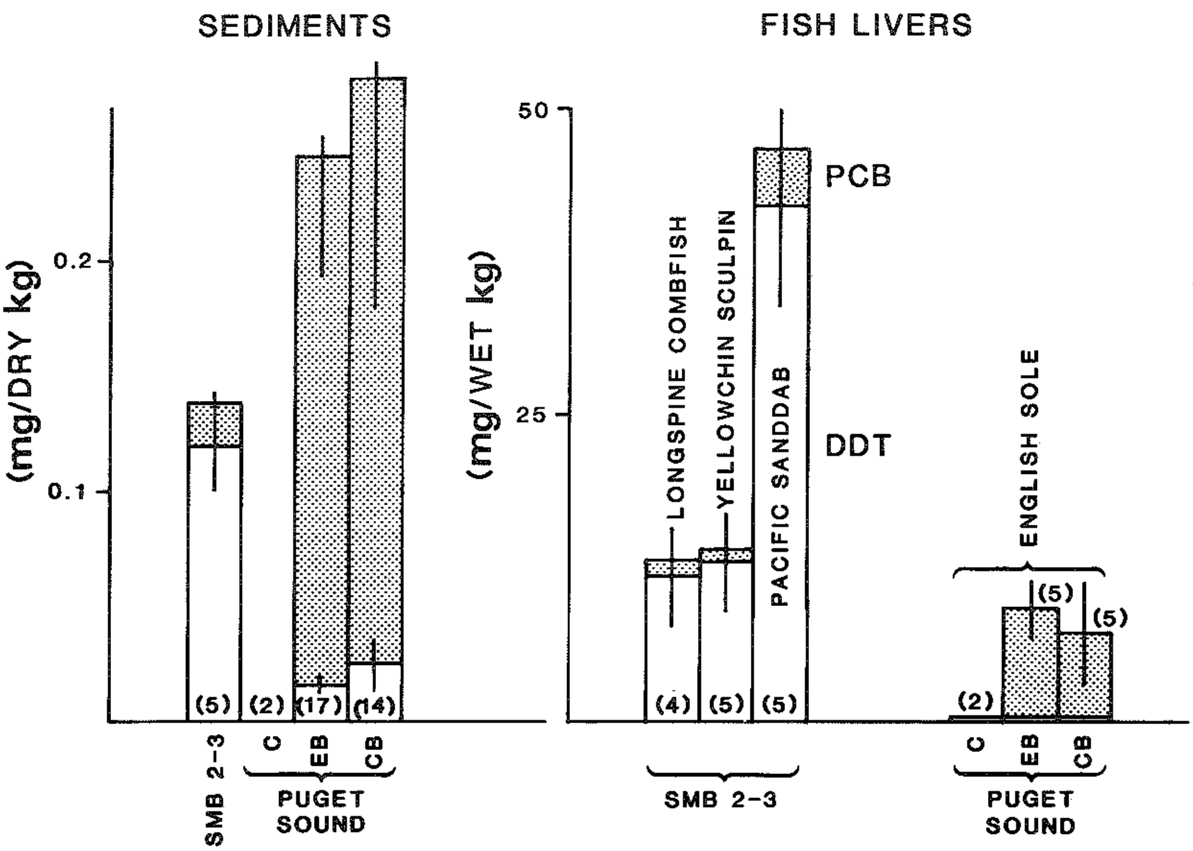

Figure 5. Comparison of sediment and fish liver concentrations (mean ± 1 standard error (n)) of chlorinated hydrocarbons found in the SMB 2-3 site with concentrations found in Puget Sound, Washington (Port Madison and Case Inlet are controls; Elliot Bay and Commencement Bay are contaminated). Concentrations of chlorinated hydrocarbons in SMB 2-3 fish livers were higher than the highest values found in Puget Sound fish livers (Puget Sound data from Malins et al. 1980; 1984).

9.2 and 7.4 mg/wet kg, respectively, while the values we measured from SMB 2-3 fish ranged from 14 to 47 mg/wet kg (Table 2). Since the Puget Sound values are the highest ever found there, it is concluded that SMB 2-3 is not an adequate control site. Based on our search for uncontaminated scorpionfish (Figure 2), it may be that no area in the southern California Bight is adequately clean to be considered as a control site.

Implications for Biological Effects

The concentrations of chlorinated hydrocarbons found in the livers of fish from PV 7-3 and SMB 6-4 and 2-3 are in excess of those thought to result in pathology in other fish species (Malins et al. 1983; 1984).

The concentrations of chlorinated hydrocarbons in gonads from these fish are within the range shown to result in reproductive impairment (von Westernhagen et al. 1981). The metal reductions shown in livers and gonads of fish from PV 7-3 and SMB 6-4 relative to SMB 2-3 are believed to represent a toxic effect of oxygenated metabolites on metallothionein synthesis.

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