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CONTAMINANTS IN OCEAN FOOD WEBS

A marine food web is composed of a great many animals who are imagined to be living at various levels on a pyramid made of trophic steps. A few large animals at the pyramid's apex, such as sharks and swordfish, prey on those of the level immediately below them. These in turn eat large numbers of smaller fish on the next lower step, who themselves eat still smaller and more numerous creatures on lower levels.

The energy of numerous small creatures at the bottom is thought to flow upward to the few large animals at the top (see Mearns, this report). A much debated question is whether contaminating materials, such as metals or hydrocarbons that may bioaccumulate above natural concentrations in the lower level animals, also flow upwards, being biomagnified with each trophic step until they reach potentially toxic concentrations at the top of the food web.

Previous studies by this Project (Young *et al.*, 1975, 1978) show that most metals of concern do not biomagnify in marine ecosystems off southern California, but some scientists felt that these results were based on insufficient data. Therefore, in 1978, with the support of the National Science Foundation, we set out to make a new set of measurements of trace metals and chlorinated hydrocarbons in high and low trophic level animals from several food webs. Our goal was to determine whether there is biomagnification of contaminants in the muscle tissue (the part consumed by humans) of sea animals.

The study included measurement of the cesium/potassium ratio, shown to be a useful indicator of the "structure" or biomagnification potential of food webs (Young 1970; Isaacs 1972; Young *et al.* 1980).

We found the answer mixed. Most metals (chromium, copper, cadmium, silver and zinc) do not increase with trophic level (are not biomagnified) either in open water or in a contaminated coastal region. Nickel and lead concentrations are generally below detection limits (less than 0.05 and 0.1 mg/wet kg, respectively) except in zooplankton. The metalloids, arsenic, selenium, and antimony were also measured. All antimony concentrations were below the detection limit of 0.001 mg/kg, wet weight. Selenium showed no trend toward biomagnification; arsenic values were highest in sharks at higher trophic levels, but showed no trend when sharks were excluded.

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Table 1. Eastern Tropical Pacific Food Web (open ocean).
Mean concentrations (mg/wet kg)

Species	No. Samples	No. Animals/ Samples	Trophic Level	Cs/K		Total PCB	Total DDT	PCB in Lipid		DDT in Lipid		Organic Total		Dry wt %	Lipid wt %	As	Se
				Ratio x10 ⁶	Level			PCB	DDT	Lipid	Lipid	Hg	Hg				
Yellowfin tuna (50 kg)	5	10	4.82	13.3	<0.002	0.011	<0.217	1.20				0.88	29.1		0.92		
Silky shark	4	1	4.81	22.8	<0.001	0.007	<0.115	0.804	1.47			1.22	26.0		0.87	4.10	0.96
Skipped tuna	5	9	4.44	8.59	0.003	<0.001	0.462	<0.154	0.041	0.229	28.3	0.65	0.64	0.92	0.65	0.49	0.85
Yellowfin tuna (4 kg)	5	7	4.29	12.7	<0.002	<0.002	<0.308	<0.308	0.264	0.157	29.1	0.65	0.49	0.85	0.65	0.49	0.85
Frigate tuna	2	1	3.82	8.89	<0.001	0.005	<0.172	0.862	0.402	0.296	27.7	0.58			1.30	2.60	0.61
Squid	5	5	3.52	1.94	<0.001	<0.001	<0.169	<0.077	0.018	0.051	20.8	0.85	0.38	0.92	0.85	0.38	0.92
Flying fish	5	7	3.00	7.00	<0.002	<0.001	<0.235	<0.118	0.045	0.010	23.2	0.85	0.38	0.92	0.85	0.38	0.92
Zooplankton	5	>200	2.00	3.30	0.002	<0.001	0.016	<0.083	<0.003			0.016	13.8		1.21	0.77	0.82

Samples are muscle tissue except whole body was used for zooplankton.
— Values not determined.

Table 2. Coastal Pelagic Food Web.
Mean concentration (mg/wet kg)

Species	No. Samples	Animals/ Trophic Sample Level	Cs/K Ratio x 10 ⁶	Total PCB	Total DDT	PCB in Lipid		DDT in Lipid		Organic Total		Ag	Cd	Cr	Cu	Ni	Pb	Zn	As	Se	%	%	
						PCB	DDT	Lipid	Lipid	Hg	Hg												
White shark	3R ¹	1	5.02	31.7	0.041	0.598	5.06	73.8	8.15	8.10	<0.002	0.004	0.145	0.27	<0.019	<0.056	5.05	3.18	0.45	22.3	0.81		
Mako shark	5	1	4.40	19.7	0.035	0.143	2.55	10.4	1.47	1.44	0.006	0.043	0.075	0.27	<0.037	<0.12	6.3	3.53	0.53	26.2	1.37		
Sea lion ²	5	1	4.02	10.7	1.22	24.8	84.7	1722	0.367	0.316								0.25	0.57	22.9	1.44		
Blue shark	5	1	4.00	13.7	0.016	0.107	1.86	12.4	0.506	0.710										18.8	0.86		
Swordfish	5	2	3.97	12.3	0.020	0.105	0.76	2.63	1.20	2.18	<0.002	0.078	0.018	0.35	<0.021	<0.064	6.44			25.3	3.99		
Thresher shark	5	3	3.82	25.5	0.016	0.094	1.48	8.7	0.642	0.661	<0.003	0.010	0.072	0.226	<0.072	<0.124	4.05			28.5	1.08		
Bonito	5	10	3.80	8.79	0.029	1.84	2.79	17.7	0.210	0.207	<0.003	0.010	0.037	0.481	<0.071	<0.12	3.91	0.27	2.11	27.2	1.04		
Barracuda	5	6	3.74	4.20	0.115	0.800	2.17	11.2	0.197	0.274										29.0	7.14		
Pacific mackerel	7	10	3.54	6.86	0.026	0.129	1.38	6.86	0.086	0.118	0.003	0.059	0.032	0.37	0.091	<0.10	4.4	0.54	0.58	28.7	1.88		
Market squid	5	12	3.52	3.32	0.012	0.014	<0.46	0.54	0.041	0.026	0.120	0.496	0.037	15.8	<0.018	<0.053	9.72	0.68	2.16	20.7	2.60		
Pacific hake	5	4	3.09	8.58	0.012	0.036	1.56	4.68	0.061	0.108	<0.002	0.003	0.073	0.20	<0.021	<0.063	2.59			19.3	0.77		
Jack mackerel	5	10	3.04	5.73	0.014	0.119	1.12	9.52	0.049	0.046								0.46	1.15	32.0	1.26		
Sardine	5	10	3.01	4.02	0.105	0.484	3.02	13.9	0.014	0.048	<0.003	0.021	0.035	0.335	<0.082	<0.153	3.94	0.81	0.78	30.6	3.48		
Basking shark	1	1	3.00	16.1	0.004	<0.005			0.065	0.096													
Blue whale	3R	1	3.00	11.0	0.003	0.050	0.20	3.33	0.034	0.021										0.19	0.68	25.2	1.50
Anchovy	5	35	2.82	1.87	0.008	0.047	0.500	2.94	0.022	0.033	0.010	0.172	0.068	0.39	<0.038	<0.12	7.6	1.66	0.54	22.8	1.60		
Zooplankton	5	1000	2.0	3.2	<0.003	0.011	0.278	1.08	<0.004	<0.034	0.044	0.83	0.114	1.12	0.294	0.384	10.5	1.32	0.48	11.6	1.02		

Samples are of muscle tissue except the whole body was used for zooplankton.

1 R means replicates of the same individual

2 Sea lion samples taken from terminally ill juveniles

— Values not determined.

Synthetic organic chemicals (DDT and PCB) and organic mercury do increase with trophic level; however, at the top trophic levels, animals from both control and contaminated areas have about the same concentrations of mercury. Unlike mercury, DDT and PCB concentrations were higher in animals from a contaminated ecosystem. Despite the elimination of the principal source of DDT (the Los Angeles County Outfall system, on the Palos Verdes shelf) over 10 years ago, 3 of the 4 species of fish examined from this region still had DDT levels greater than 5 mg/wet kg. Typical levels for chlorinated hydrocarbons in animals from the remote Eastern Tropical Pacific ecosystem are less than 0.01 mg/wet kg.

LIMITATIONS

Many factors in addition to trophic levels can alter or control the accumulation of contaminants. If our efforts to assign a precise trophic level value to each animal are successful, there could still be deviations in accumulation due to: (1) different physiological requirements of invertebrates, elasmobranchs, teleosts, and mammals; (2) different metabolic rates affecting the amount of prey consumed; (3) the age and life span of different organisms, and (4) variations in migratory ability that might subject animals to contaminant sources for differing amounts of time. The Project is presently studying other factors that may affect tissue concentrations; for example, the ability of the liver to accumulate and regulate some contaminants so that excesses are not found in muscle tissue.

Despite these uncertainties we believe the elevated concentration of DDT's, PCB's, and organic mercury can be attributed principally to trophic structure.

SELECTION OF FOOD WEBS

Our previous food web studies have focused on ecosystems in protected and inland waters: Los Angeles Harbor, Newport Bay, and the Salton Sea (Young and Mearns 1978; Mearns and Young 1980; Young *et al.* 1980; Mearns *et al.* 1981). This report deals with both coastal and open ocean food webs. We selected organisms for sampling that not only represent a range of trophic levels, but which also are significant components of a given ecosystem.

The Eastern Tropical Pacific is a center for tuna fishing and tuna research. At our request, the Inter-American Tropical Tuna Association sampled seven pelagic groups of animals in the area 70-800 kilometers off Central America (Table 1). This remote, offshore region is not known have any point sources of contaminants.

The nearshore area off southern California is a great source of commercial fishing that makes Los Angeles one of the largest fresh fish ports in the United States. The eight species of bony fish, four species of sharks, and market squid sampled from this ecosystem constitute over 80%, by weight, of commercial landings in the Los Angeles area. We also sampled other members representing widely different trophic positions: zooplankton, 2 species of mammals, and 2 uncommon species of sharks (Table 2) (figure 1).

Much has been learned about the ecosystem off Palos Verdes Peninsula through monitoring and research efforts, because this soft bottom region is the site of a major wastewater outfall system. The kinds of fish and invertebrates in this food web have been extensively studied (SCCWRP Annual Reports, 1974-1981; LASCDC, 1980-81). Although this region is of limited importance as a commercial fishery, some of the species found there are commercially important in other areas. In this area there are great numbers of mysids and small decapod shrimps which live on, and just above, the bottom that are important prey items for many animals. The

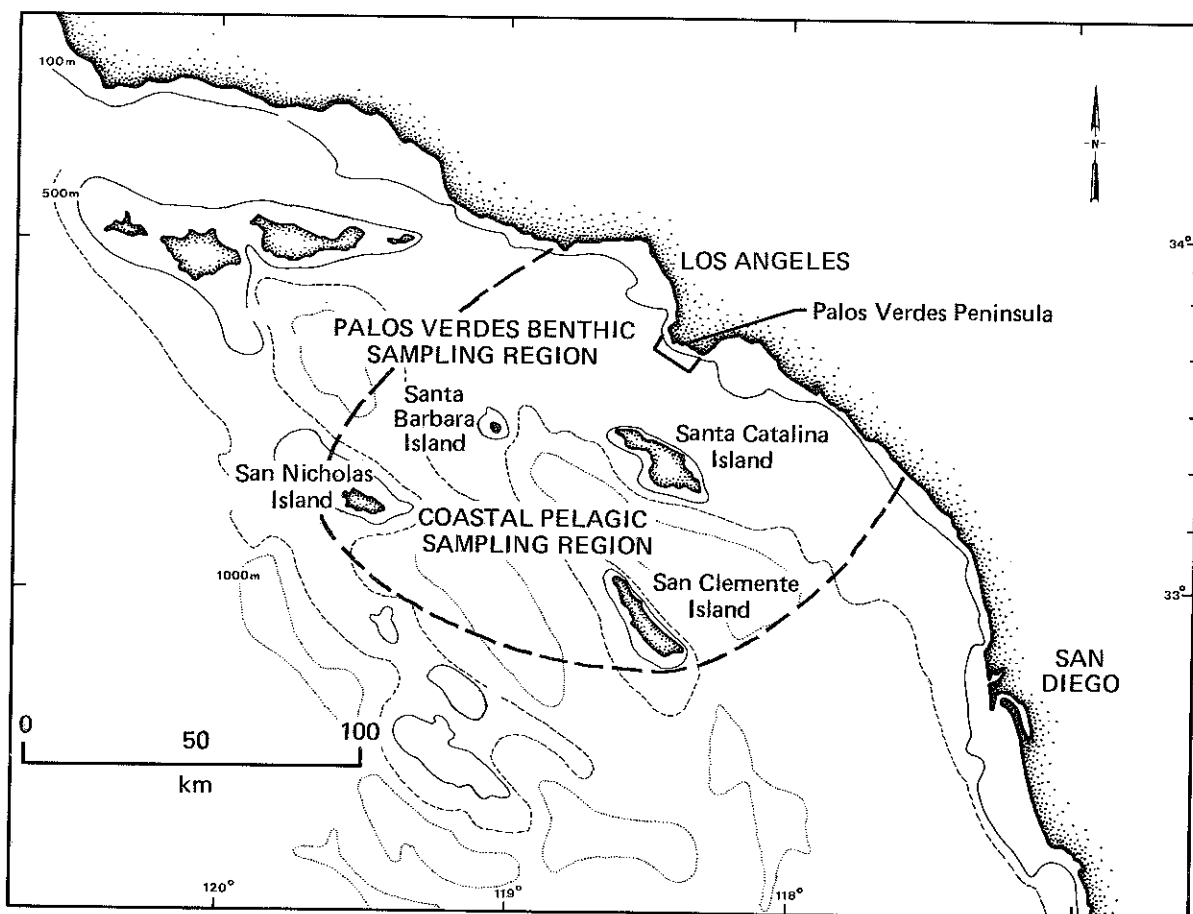


Figure 1. Sampling regions for the Coastal Pelagic and Palos Verdes Benthic food webs off southern California. The remote Eastern Tropical Pacific food web sampled was centered approximately 500 kilometers off Costa Rica, 5° North and 90° West.

organisms sampled to represent this region are listed in Table 3. This area is unique because past discharges of pesticides and trace metals have left in the sediments some of the highest concentrations reported for an open coastal region.

Methods of collection and trophic level assignments for the animals sampled from these three ecosystems are discussed by Mearns in this Biennial Report.

TISSUE SELECTION AND PREPARATION

Under some circumstances it may be best to use whole organisms when studying predator-prey relationships, but this is impractical when working with large animals. In the larger animals, muscle was selected as the representative tissue for the following reasons:

1. Of all the body tissues, muscle generally constitutes the highest proportion of an organism's mass.
2. Pollution concerns usually are greatest for the edible portion of an organism.

TABLE 3. Palos Verdes Epibenthic Food.
Mean concentrations (mg/wet kg)

Species	No. Samples	No. Animals/ Sample	Trophic Level	Cs/K Ratio $\times 10^6$	Total PCB in DDT in										Mean concentrations (mg/wet kg)				
					Total PCB	DDT	Lipid	DDT in Lipid	Organic Hg	Total Hg	Ag	Cd	Cr	Cu	Ni	Pb	Zn	% Dry	% Lipid
Scorpionfish	5	2	4.53	6.22	0.044	0.268	0.56	34.4	0.247	0.247	<0.002	<0.006	<0.015	0.194	<0.030	<0.062	2.54	21.1	0.78
Spiny dogfish	5	1	4.16	31.3	5.12	65.5	41.9	537	1.48	1.53	<0.002	0.018	0.031	0.097	<0.021	<0.058	3.86	27.6	12.2
Dover sole	5	10	3.52	3.62	0.279	7.17	16.1	414	0.024	0.046	<0.002	0.006	<0.018	0.181	<0.020	<0.059	2.86	19.9	1.73
White croaker	5	10	3.36	2.85	0.383	7.63	22.9	454	0.063	0.071	<0.002	<0.002	<0.012	0.240	<0.023	<0.064	2.10	22.1	1.68
Ridgeback prawn	5	10	3.33	3.04	0.061	0.327	5.81	22.7	0.047	0.072	<0.001	0.012	0.138	5.49	<0.019	<0.058	12.0	24.4	1.05
Mysids & decapods	5	~200	2.78	13.8	0.032	0.323	2.22	22.4	-	0.006	0.167	0.108	1.17	5.41	1.07	0.330	9.11	15.5	1.44
Sediments	2	1	?	840	1.64	27.8	273	4633	-	-	11.4	27.1	802	387	73	223	993	37.8	0.60

Samples are of muscle tissue except the whole body was used for mysid and decapod shrimp.

— Values not determined.

3. Because of the early emphasis placed on radiometal accumulation in muscle tissue by radioecological and health physics studies, more is known of the cycling characteristics of such metals in muscle than other tissues.

For very small organisms such as plankton and microcrustaceans, we analyzed the entire organism.

In order to achieve an adequate statistical base, we attempted to obtain five composites of each species selected. Each composite was composed of ten individuals where possible. Very large or rare species had fewer analyses and fewer individuals per composite. Composites of small organisms had many more than 10 individuals per sample.

Generally, samples were immediately frozen upon collection; then dissected in the laboratory while partially thawed: Mysids and decapod shrimp samples were hand-sorted to remove debris before freezing. Muscle tissue from large fish and mammals usually was taken from the dorsal region just behind the head and then frozen as soon as possible. Samples for metals were kept in plastic containers and samples for organics were kept in cleaned, foil-covered glass jars.

CHEMICAL METHODS

The concentrations of most metals in this study were determined by atomic absorption spectroscopy. For silver, cadmium, chromium, copper, nickel, lead, and zinc, 1 to 2 grams of sample were dissolved in hot nitric and hydrochloric acids, filtered and diluted, and analyzed on a Varian Techtron (model AA-6) spectrophotometer. Internal standard addition and blank corrections were made. Analytical details for the above metals are reported in Young and Jan (1978).

Cesium, which occurs at very low levels in tissues, required a special digestion using a larger sample size of 5-10 grams, followed by a concentrating step. The cesium in a 100 ml sample solution was collected on ammonium-12-molybdophosphate microcrystals, which were then separated by filtration. The crystals were then redissolved in a small volume (4 ml), thereby concentrating the cesium so that it could be readily detected by carbon rod atomic absorption spectroscopy. Potassium concentrations were determined by atomic emission spectroscopy by aspiration into an air-propane flame. Analytical details for cesium and potassium are reported by Young *et al.* (1980).

Total mercury concentrations were determined by a hot acid digestion in a closed reflux apparatus. After cooling, ionic mercury in the sample solution was reduced to elemental mercury. Quantification was done by purging the volatile metallic mercury through a Laboratory Data Control cold vapor atomic absorption spectrophotometer. Organic mercury was measured in a similar manner, but a sample was first subjected to a benzene extraction, followed by a cysteine back extraction. Analytical details are reported by Eganhouse (1975).

Chlorinated hydrocarbon analyses employed an acetonitrile/hexane extraction procedure, followed by a Florisil clean-up step. The extract is injected into a Tracor MT 220 gas chromatograph equipped with a Nickel ⁶³ electron capture detector.

Quantification is based on external standards by comparison of peak heights. Analytical details are given in Young *et al.* (1976).

Arsenic, selenium, and antimony concentrations were determined by nuclear activation analysis at the TRIGA Mark 1 nuclear reactor facility at the University of California, Irvine. For analyt-

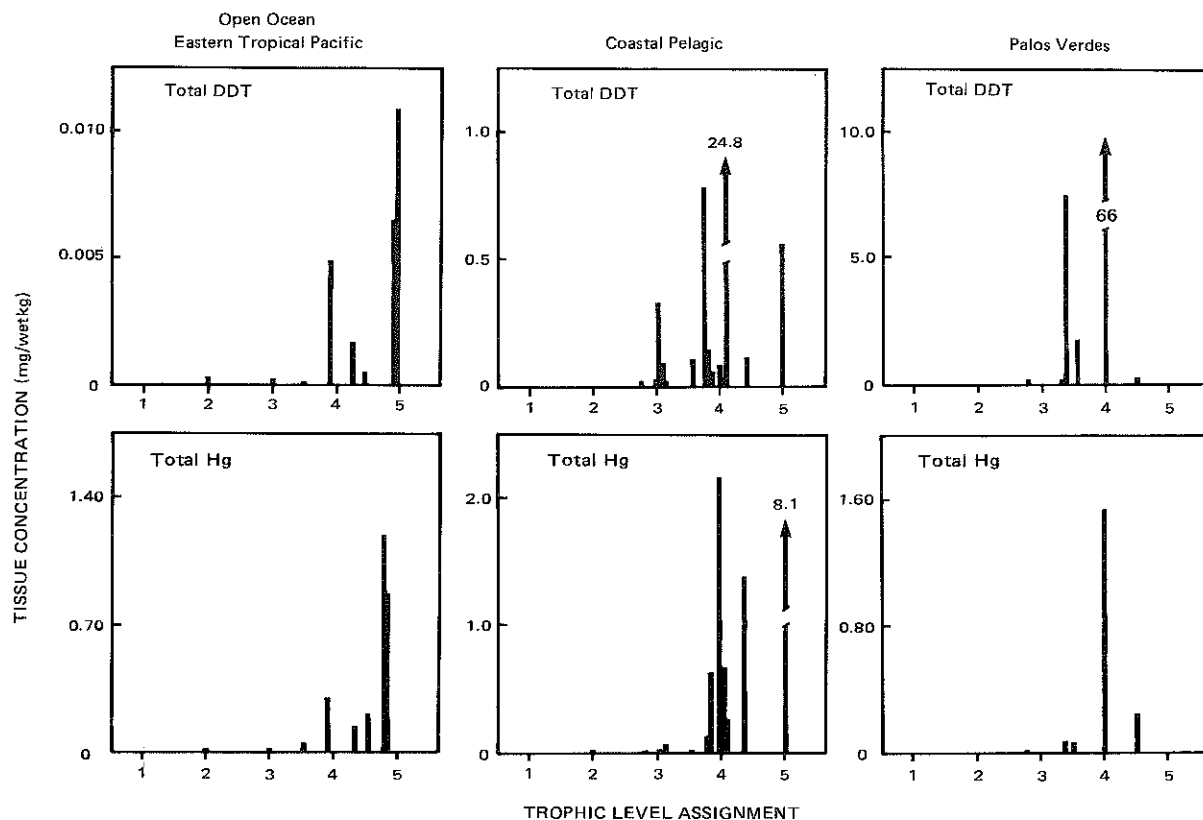


Figure 2. Examples of contaminants that increase with increasing trophic level. Species for various trophic level assignment are given in tables 1-3.

ical details see De Goeij *et al.* (1974).

Dry weight and lipid determinations were done by freeze drying followed by a chloroform/methanol extraction, according to the procedures of Bligh and Dyer (1959).

RESULTS

Eastern Tropical Pacific

The chemical results are presented in Table 1, and bar graphs for some chemical concentrations are shown in Figures 2, 3, and 4.

Most of the DDT and PCB measurements were at or near detection limits. Because so many of the PCB values were below detection, no relationship to trophic level could be determined. The quantifiable DDT values did show a trend of increasing concentration with trophic level. There was at least a factor of 10 increase (<0.001 to 0.011 mg/wet kg) between low trophic level fish and invertebrates and top trophic level sharks and tuna.

Total mercury concentrations ranged from 0.010 mg/wet kg for the lower trophic level organisms to over 1.2 mg/wet kg for the higher level fish. This increase with assigned trophic level is

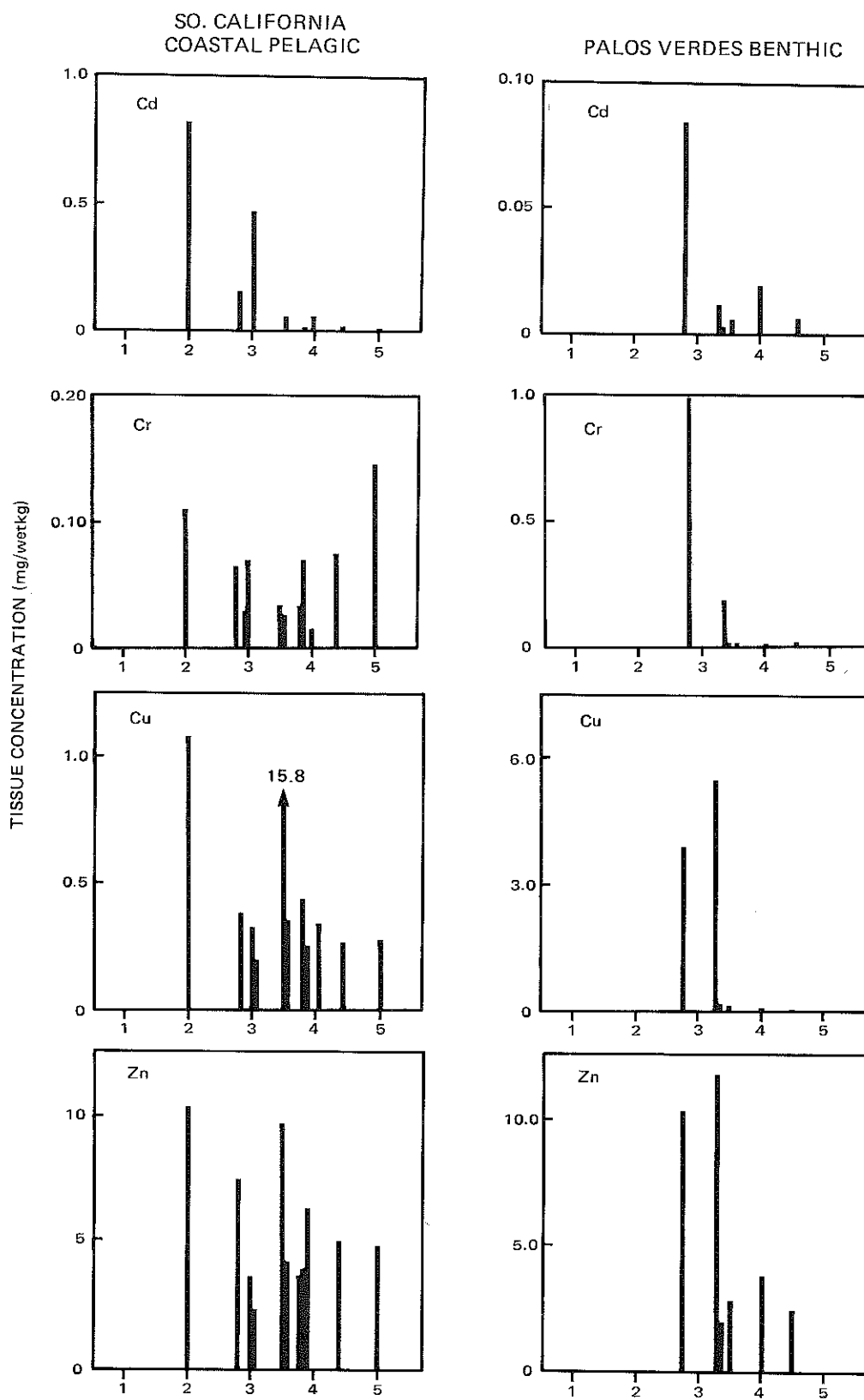


Figure 3. Examples of contaminants that appear not to increase in concentration with increasing trophic level. Two invertebrates, zooplankton and squid that seem to be anomalous are at trophic levels 2.0 and 3.52 (see text for explanation). The remaining trophic values are for vertebrates listed in tables 1-3.

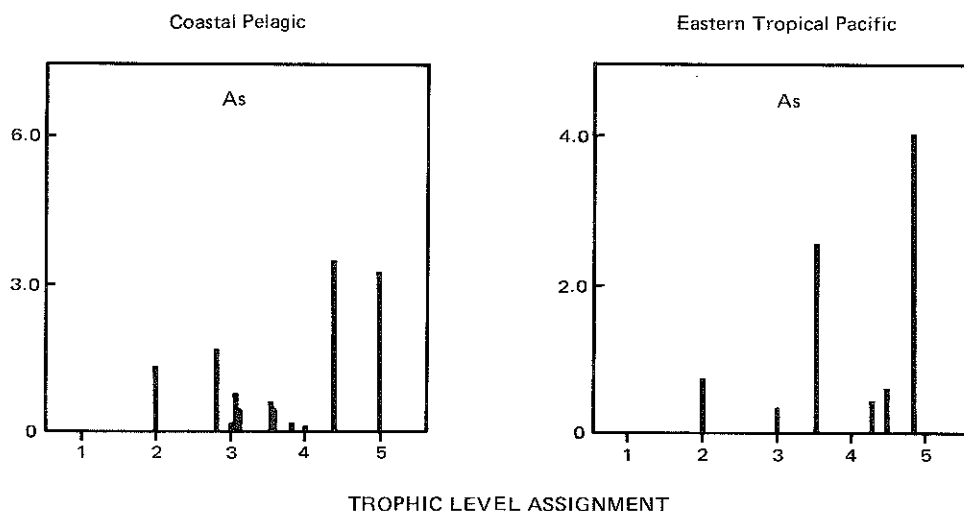


Figure 4. Arsenic concentrations showing high levels in top trophic level sharks.

statistically significant at $p < 0.05$. Generally, organic mercury is the major component of total mercury measurements, especially in higher trophic level organisms.

Trace metal samples for this food web are currently being stored for future analysis. However, at this time, in view of the following results from a highly contaminated region, we have no reason to believe that the trace metals measured will accumulate with increasing trophic levels.

Southern California Coastal Pelagic

The chlorinated hydrocarbon data are given on a wet weight and lipid weight basis due to their affinity for lipids and the lipid content variation among organisms.

Wet weight values ranged from < 0.005 to 24.8 mg/wet kg for DDT and < 0.003 to 1.22 mg/wet kg PCB. Excluding the sea lion data, both DDT and PCB are significantly correlated to trophic level assignments ($p < 0.05$; lipid basis). Our sea lion samples were of young, ill animals collected by the L.A. County Veterinarian at various beaches in the county. These animals were yearlings, thus the anomalously high values may reflect nursing on lipid rich milk and their physical condition. Values in non-ill adult sea lions may be very different. With the exception of sea lions, none of the DDT or PCB values exceeded 1 mg/wet kg.

Based on trophic level assignment, chlorinated hydrocarbon concentrations in some animals deviated from expected values. Squid, a mid-trophic level organism, had very low values on both a wet weight and lipid weight basis. Also, swordfish concentrations on a lipid weight basis were equal to, or lower than, their chief prey, Pacific hake or anchovy (as determined by this study). We speculate that this could be due to migrations from areas with less contamination.

Total mercury and organic mercury are significantly related to trophic level ($p < 0.05$). Inspection of the data reveals that mercury concentrations show few deviations in expected values based on trophic level assignment. However, white shark values were unusually high, possibly due to age. Although the concentrations for organic mercury in swordfish appear as expected,

the measurement for total mercury seems high compared to literature values. Organic mercury has been shown in other studies to comprise 80 to 90% of total mercury (Officer and Ryther 1981).

There is no evidence of biomagnification of the seven other heavy metals measured. Generally, squid and zooplankton accounted for the highest concentrations. Some of the higher values can be attributed to physiological differences, for example, copper-based hemocyanin circulatory systems in molluscs and crustaceans. Also, for zooplankton, entire organisms, rather than just muscle tissue, were analyzed.

Selenium concentration did not increase with trophic level, and, although the highest arsenic value was found in sharks, its relationship to trophic level was not statistically significant.

Palos Verdes Epibenthic

The chlorinated hydrocarbon data from Palos Verdes is complicated by very low values in the highest trophic level animal, scorpionfish. Possible explanations include: (1) migration from a cleaner area, (2) feeding on prey with low levels of contaminants, and (3) a greater ability to keep chlorinated contaminants out of the muscle tissue. We compared DDT and PCB on a lipid weight basis because of large variations in lipid content (0.60-12.2%). With the exclusion of scorpionfish, both DDT and PCB are significantly correlated with assigned trophic level ($p < 0.05$). On a lipid basis, there is at least a factor of ten increase between low and high trophic level animals. Excluding scorpionfish, concentrations in muscle tissue of the target fishes exceeded 5 mg/wet kg DDT and spiny dogfish exceeded 5 mg/wet kg PCB.

Both organic and total mercury were significantly correlated to trophic level, if we eliminate scorpionfish. Mercury concentrations for the mysids and decapod shrimp were the lowest values (0.006 mg/wet kg) in both the Palos Verdes and southern California coastal pelagic food webs. The ridgeback prawn, white croaker, and Dover sole, which are about 1 trophic step above the mysids and decapod shrimps, had concentrations about ten times higher (0.04-0.07 mg/wet kg). The top trophic level organisms, scorpionfish and spiny dogfish, had the highest mercury concentrations, 0.25 and 1.53 mg/wet kg respectively.

Cadmium, chromium, copper, and zinc were above detection limits in both the high and low trophic level animals. Only in mysids and decapod shrimps were silver, nickel, and lead measurable. Generally, the highest concentrations of metals measured were found in mysids and decapod shrimps. Again, this may be due to the use of whole organisms in the analysis. When only muscle tissue is considered the ridgeback prawn had much higher concentrations than the fish, although cadmium concentrations were approximately equal. There is no significant correlation between these metal concentrations and assigned trophic levels.

CONCLUSION

The concentrations of chlorinated hydrocarbons depend both on exposure to a source and trophic position. All three of these food webs have shown an increase of DDT concentrations in muscle tissue with trophic level. However, concentrations in the top trophic level animals from the Central America site were equivalent to the lowest trophic level animals (zooplankton) off southern California. The lowest trophic level animals on the soft bottom Palos Verdes out-fall area are 30 times higher in DDT than the Coastal Pelagic zooplankton.

Although DDT and PCB do accumulate in pelagic seafood species off southern California, typical concentrations were 10 times less than Food and Drug Administration guidelines for human consumption.

Epibenthic animals at Palos Verdes show increased chlorinated hydrocarbon concentrations with trophic level, and excessive concentrations of DDT in some mid-and high trophic level fish.

Of any contaminant measured in this study, mercury showed the closest relationship with trophic level. All three food webs showed about the same mercury concentration (1.5 mg/wet kg) in their top predators with the exception of the white shark (8 mg/wet kg). Unlike other metals, mercury concentrations in the low trophic level invertebrates are lower or equal to low trophic level vertebrates.

The remaining metals measured in the Coastal Pelagic and Palos Verdes Benthic ecosystems showed no tendency to increase with trophic level. Thus, the results of this study of marine foodwebs support the hypothesis that DDT, PCB, and organic mercury do biomagnify. However, other metals measured do not.

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