

## TROPHIC STRUCTURE AND POLLUTANT CONCENTRATIONS IN MARINE ECOSYSTEMS OF SOUTHERN CALIFORNIA<sup>1</sup>

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### ABSTRACT

The relationship between trace chemical concentrations and trophic level of fishes and several invertebrates was investigated in four southern California marine ecosystems: the Salton Sea, a saline lake; Newport Bay, a back-bay area; the Palos Verdes shelf, a waste-water contaminated coastal zone; and the San Pedro Channel, which contains a coastal pelagic food web. Feeding habits were investigated and used to assign assumed trophic levels to each species. These assignments were directly related to the cesium/potassium ratio (Cs/K), a possible chemical trophic step indicator. Trophic structure amenable to food web increases of pollutant concentrations was relatively strong in the Salton Sea and coastal pelagic ecosystems and was weaker in the nearshore ecosystems. As expected, organic mercury and the chlorinated hydrocarbons generally increased with increased trophic level; however, other trace metals did not.

### RESUMEN

La relación entre sustancias químicas a bajas concentraciones y el nivel trófico de peces y varios invertebrados fueron investigados y usados para asignar presuntos niveles tróficos a cada especie. Estas asignaciones fueron port, una bahía apartada; la plataforma submarina de Palos Verdes, una zona costera contaminada con aguas residuales; y el canal de San Pedro, que contiene una red alimenticia pelágica costera. Los hábitos de alimentación fueron investigados y usados para asignar presuntos niveles tróficos a cada especie. Estas asignaciones fueron directamente relacionadas con la proporción de cesio/potasio (Cs/K), que es posiblemente un indicador químico del grado trófico. La estructura trófica sujeta a incrementos de concentraciones de contaminantes en la red alimenticia fue relativamente fuerte en el Salton Sea y en ecosistemas pelágicos costeros, y más débil en los ecosistemas de cerca de la costa. Como se esperaba, el mercurio orgánico y los hidrocarburos clorinados generalmente aumentaron con el aumento en el nivel trófico; sin embargo, no aumentaron otros metales de bajas concentraciones.

### INTRODUCTION

The objective of the research described here was to determine the degree to which southern California marine

food webs are "structured," i.e. composed of species with distinct feeding relationships that can cause successively increased concentrations of some pollutants (Isaacs 1973). Public apprehension regarding the accumulation of pollutants in seafood is based largely in the assumption that such food chain or food web increases of organic and inorganic contaminants (Odum 1971), which has been demonstrated in certain terrestrial and freshwater systems, also occurs widely in marine ecosystems. However, in recent years, there have been an increasing number of reports that contradict this assumption, at least in part. The evidence obtained to date indicates that there is measurable structure to the coastal marine ecosystems of the Southern California Bight. Despite this structure, concentrations of most trace metals of present concern decrease with increase in presumed trophic levels. An important exception is organic mercury; this trace constituent, and the higher molecular weight chlorinated hydrocarbons—total DDT and PCB 1254—appear to increase in concentration with increase in trophic level.

### BACKGROUND

An unstructured food web is composed primarily of opportunistic, multidirectional feeders; under this condition, differences in pollutant concentrations in member organisms are not necessarily related to feeding relationships. Evidence supporting the unstructured food web hypothesis was obtained by Young (1970) in a comparative study of the distribution of two alkali metals, cesium (Cs) and potassium (K), in marine organisms from the Salton Sea in southern California and the Gulf of California. Potassium, an essential electrolyte, must be maintained at fairly constant levels in tissues; this is not the case for cesium, which is usually found in trace quantities. Increases in the ratio of cesium to potassium over known food chain links or trophic level steps (Odum 1971) can be expected because cesium has been found to have a biological half-life that is generally two to three times that of potassium. Thus, the relative values of the Cs/K ratio in organisms in a given ecosystem should give indication of the degree of trophic structure in that ecosystem, and thus indicate the potential for food chain increases of pollutant concentrations within the system.

The Salton Sea is a large saline lake with a very specialized and simplified food web (Walker 1961) that resembles the classical food chain situation. This structured ecosystem provided Young (1970) and Isaacs (1972, 1973) with an opportunity to measure cesium and potassium concentrations in the muscle tissues of widely

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differing marine fishes and to compare the Cs/K ratios for the fishes with those for their food. The results indicated median predator/prey increase factors of 2.2 for cesium and 2.5 for Cs/K ratio (Table 1). These values are in good agreement with those reported previously for various terrestrial and freshwater organisms (Anderson et al. 1957; McNeill and Trojan 1960; Green and Finn 1964; Pendleton 1964; Hanson et al. 1964; Pendleton et al. 1965; Hanson 1967; and Gustafson 1967). In addition, cesium concentrations and Cs/K ratios in muscle tissue of a given fish species were found to increase regularly with the number of trophic level steps in the food chain leading to that particular species (Table 2). The values, on the average, doubled with each step between the bottom (Level II) and the top (Level IV-V) of the trophic structure; these factor-of-two increases are consistent with the median predator/prey increase factor.

Subsequently, Young (1970) and Isaacs (1972) compared the Cs/K ratios for Salton Sea fishes with those for the same species in the Gulf of California and found that the latter did not show any major differences with increase in presumed trophic level (Table 3). This suggested that, in contrast to the Salton Sea community, the part of the food web sampled in the nearby Gulf of California was "homogeneous" in nature and unstructured, rather than characterized by structural feeding or trophic levels.<sup>1</sup>

On the basis of these and other findings, Isaacs (1972, 1973, 1976) has proposed that marine food webs are generally unstructured and has developed mathematical models applicable to such situations. However, since the limited investigation in the Gulf of California, no further field work has been done to test these models or the assumptions behind them. In view of the concern over increases of pollutant concentrations in marine food webs, particularly in those leading to man, it is important that such uncertainties be resolved.

### ANALYTICAL PROCEDURES

The major problem facing us in the initial stages of this program was the development of a procedure for measuring, with sufficient precision, the very low concentrations of cesium that occur in marine organisms. Typical levels of this trace alkali metal in wet fish muscle are 10-50  $\mu\text{g}/\text{kg}$ , or parts per billion (ppb); this is near or below our detection limits for other metals of interest (e.g. chromium and nickel), using atomic absorption spectrometry (AAS) without chemical concentrations following sample digestion. Thus, it was necessary to develop a procedure by which cesium could be separated from the host of interfering compounds found in tissues and concentrated

<sup>1</sup>It should be noted that the *absolute* values for cesium and Cs/K ratios in the specimens from the Salton Sea and Gulf of California (or other truly marine ecosystems) are not comparable because of the different levels of cesium and potassium in the waters of these two saline environments. Rather, it is the *relative* values for specimens within a given ecosystem that should be examined in evaluating the degree of structure in the food web.

TABLE 1  
 Predator-to-prey Increases of Cesium Concentrations in Organisms from the Salton Sea in 1967.<sup>1</sup>

Organism	Major food	Ratio, Concentration in Organisms to Concentration in Major Food		Cs/K ratio $\times 10^6$
		Cesium	Potassium	
Corvina	Croaker	2.2	1.06	2.0
Croaker/sargo	Pile worm	5.6	1.00	5.6
Shad	Zooplankton	2.0	0.7	2.7
Mullet	Algal mat	2.3	1.02	2.3
	Median	2.2	1.01	2.5
	Mean	3.0	0.94	3.2

<sup>1</sup>After Young 1970.

TABLE 2  
 Variations in Muscle Tissue Concentration (Mean  $\pm 1$  Standard Error) of Cesium and Potassium and Cs/K Ratios with Differences in the Trophic Positions of Organisms from the Salton Sea in 1967.<sup>1</sup>

Organism	Assumed trophic level	Food chain to organism	Cesium ( $\mu\text{g}/\text{wet kg}$ )	Potassium ( $\text{g}/\text{wet kg}$ )	Cs/K ratio $\times 10^6$
Corvina	IV-V	Croaker: pile worm: detritus <sup>2</sup>	202 $\pm$ 22	3.52 $\pm$ 0.26	57.4
Croaker	III-IV	Pile worm: detritus <sup>2</sup>	98 $\pm$ 8	3.43 $\pm$ 0.20	31.4
Sargo	III-IV	Pile worm: detritus <sup>2</sup>	84 $\pm$ 5	3.58 $\pm$ 0.29	23.4
Shad	III	Zooplankton: phytoplankton	46 $\pm$ 3	3.07 $\pm$ 0.21	15.0
Mullet	II	Algal mat	30 $\pm$ 3	3.38 $\pm$ 0.25	8.9

<sup>1</sup>After Young 1970.

<sup>2</sup>Composed primarily of phytoplankton and zooplankton (Trophic levels I and II, respectively).

TABLE 3  
 Variations in Muscle Tissue Concentrations (Mean  $\pm 1$  Standard Error) of Cesium and Potassium and Cs/K Ratios with Differences in the Trophic Position of Organisms from the Upper (Nearshore) Gulf of California.<sup>1</sup>

Organism	Assumed trophic position	Cesium ( $\mu\text{g}/\text{wet kg}$ )	Potassium ( $\text{g}/\text{wet kg}$ )	Cs/K ratio $\times 10^6$
Corvina	High	39 $\pm$ 2.6	4.70 $\pm$ 0.10	8.3
Croaker	Intermediate	54 $\pm$ 2.5	4.20 $\pm$ 0.20	10.3
Sargo	Intermediate	36 $\pm$ 2.2	4.10 $\pm$ 0.06	8.8
Mullet	Low	51 $\pm$ 5.2	4.03 $\pm$ 0.09	12.6

<sup>1</sup>After Young 1970; Young and Folsom 1979.

sufficiently to permit AAS analyses that could clearly resolve two-fold differences in values at the 10-ppb level. This was accomplished by modifying a procedure that had been developed by Folsom and Sreekumaran (1970) and used by Young in the Salton Sea program described in the preceding section.

Basically, the technique involves digestion of wet tissue (6 to 10 grams) in nitric acid for about five hours. The digested material is then split into two equal portions, and enough cesium standard is added to one of the two replicate solutions to approximately double its estimated concentration. This technique, known as the method of standard additions, corrects for incomplete recovery of the target element and for "matrix" effects (biases introduced by the presence of other elements in the sample).

Next, the solubilized cesium atoms are concentrated on microcrystalline ammonium-12-molybdophosphate (AMP). This step separates the cesium from most of the other elements in the tissue, including much of the sodium and potassium, which greatly interfere with analysis. The AMP is then dissolved in ammonium hydroxide, and 2.5 to 5 microliters of this solution are injected into the carbon rod (Model 63) of a Varian Tectron AAS (Model AA6) equipped with a background corrector (Model BC-6). We have found it necessary first to condition the rod by firing and then injecting a procedural blank solution. To overcome problems of matrix effects and nonlinearity, an alternating series of aqueous cesium standard, sample, and cesium-spiked sample is then injected, and subsequently re-injected in reverse order. Replicate procedural blanks (including internal standards) are analyzed with each set of samples.

Potassium is analyzed by aspirating into an air-propane flame both unspiked and potassium-spiked aliquots of the tissue digestion solution, which has been diluted by a factor of 250 in deionized distilled water. Additional details of these analytical procedures will be reported elsewhere.

To test the accuracy of our procedures for cesium and potassium analysis, we have analyzed the Standard Reference Material No. 1571 (orchard leaves) of the National Bureau of Standards (NBS) for these metals. The uncertified cesium value listed by NBS is 0.04 mg/dry kg; in our triplicate analyses, we obtained mean and standard deviation values of  $0.048 \pm 0.0067$  mg/dry kg, suggesting agreement within about 20%. Our corresponding values for potassium were  $14.4 \pm 0.15$  mg/dry kg, which agree within 2% with the NBS certified potassium values of  $14.7 \pm 0.03$  mg/dry kg.

The precision of our cesium and potassium measurements was evaluated by making five blank determinations and analyzing six replicates of composite sample muscle tissue from 10 albacore caught off San Diego in summer 1978. The results, summarized in Table 4, indicated coefficient-of-variation values for cesium and potassium in fish muscle of about 14 and 3%, respectively. The uncertainty associated with the cesium blank correction is  $\pm 2$  ppb, which corresponds to an uncertainty of approximately 5 to 20% in the net values presented in this paper.

We have previously reported other analytical procedures used in the work described here. Methods for analysis of nonvolatile trace metals are given in Young and Jan (1979), Eganhouse (1975), and Eganhouse and Young (1978); and procedures for analyses for chlorinated hydrocarbons are given in Young et al. (1976). Lipid content determinations were made using the procedures of Bligh and Dyer (1959).

TABLE 4  
 Precision of Cesium and Potassium Measurements as Indicated by Five Blank Determinations and Analyses of Six Aliquots of Homogenized Fish Muscle.

	Cesium (ug/wet kg)	Potassium (g/wet kg)
Fish muscle tissue:		
Median .....	48.0	3.67
Mean .....	48.4	3.65
Standard deviation .....	6.7	0.094
Coefficient of variation .....	14%	2.6%
Procedural blanks:		
Median .....	11.0	0.03
Mean .....	10.8	0.03
Standard deviation .....	1.9	-
Coefficient of variation .....	18%	-

### ECOSYSTEMS INVESTIGATED

To date, four different marine ecosystems have been investigated using the Cs/K ratio as a trophic step indicator. In March 1978, we participated with Mr. Glenn Black, California Department of Fish and Game, in a sampling of the North Shore region of the Salton Sea. Specimens of most of the same fish species collected there by Young in 1967 were obtained by gill net and beach seine. These included orange-mouth corvina (*Cynoscion xanthulus*), Gulf croaker (*Bairdiella icistia*), sargo (*Anisotremus davidsoni*), and threadfin shad (*Dorosoma petenense*). However, striped mullet (*Mugil cephalus*) were not obtained; therefore, we collected specimens of sailfin molly (*Poecilia latipinna*), which—like the mullet—feed near the bottom of the food web. All specimens were wrapped in plastic bags and frozen under dry ice in the field.

In July 1978, we collaborated with Dr. Michael Horn, California State University Fullerton, in collecting fishes with gill net, beach seine, and bottom trawl from Newport Bay. This is a major back bay of southern California that harbors a fauna not unlike that of the Salton Sea and also provides an important breeding area for coastal marine organisms. The inclusion of this second study area provided an opportunity to examine fundamental aspects of food web structure and corresponding increases in pollutant concentrations. The species taken from the back bay were striped bass (*Morone saxatilis*), spotted sand bass (*Paralabrax maculatofasciatus*), yellowfin croaker (*Umbrina roncadorensis*), topsmelt (*Atherinops affinis*), and large and small striped mullet.

The third ecosystem investigated was that exposed to the submarine discharge of primary-treated municipal effluent off Palos Verdes Peninsula by Los Angeles County Sanitation Districts. Over the last two to three decades, this discharge zone has received large quantities of trace metals, chlorinated hydrocarbons, and other

waste-water constituents, which have caused extensive contamination of the bottom sediments (Young et al. 1975). Thus, inclusion of this region as a study area provided opportunity to investigate the degree to which toxic trace metals and high-molecular-weight chlorinated hydrocarbons from a major waste-water source are distributed through a coastal marine food web whose structure we have evaluated. The species selected were important seafood organisms that had been collected from the discharge zone during 1975-77 and maintained under frozen storage; these included bocaccio (*Sebastes paucispinis*), California scorpionfish (*Scorpaena guttata*), Pacific sanddab (*Citharichthys sordidus*), ridgeback prawn (*Sicyonia ingentis*), yellow crab (*Cancer anthonyi*), black abalone (*Haliotis cracherodii*), and purple-hinged scallop (*Hinnites multirugosus*).

Finally, we obtained samples of pelagic fishes taken by commercial fishermen from a relatively uncontaminated section of the Southern California Bight, the San Pedro Channel. The fishes thus obtained included several top carnivores such as albacore (*Thunnus alalunga*), and blue shark (*Prionace glauca*). Also sampled were several primary carnivores, including market squid (*Loligo opalescens*), Pacific mackerel (*Scomber japonicus*), and Pacific bonito (*Sarda chiliensis*), as well as a plankton feeder—northern anchovy (*Engraulis mordax*). The size of the animals selected varied by over three orders of magnitude, ranging from 5-gram northern anchovy to 20-kg blue sharks. Small specimens were frozen whole and returned to the laboratory for dissection. Larger fishes were weighed; a 1-kg sample of white muscle tissue was then taken and frozen in a clean plastic bag for subsequent analysis.

Dissections were carefully performed according to an established protocol for trace contaminant analyses (Jan et al. 1977). White muscle tissue was excised and examined for cesium, potassium, chlorinated hydrocarbons (total DDT and several PCB's), and all or part of a suite of trace metals (silver, cadmium, chromium, copper, iron, total and organic mercury, manganese, nickel, lead, and zinc). If the individuals of a given species were large, we analyzed one sample from at least three specimens of similar size; for smaller organisms, three composites from a large number of individuals of the species were used. In a number of cases, additional analyses for total and organic mercury were conducted.

The relatively large number of constituents selected for investigation in this initial survey of four different ecosystems severely limited the number of replicates that could be analyzed. Therefore, to reduce the effect of outlying values that are commonly seen in trace analysis, we used the median rather than the mean as a measure of central tendency in summarizing and comparing our tissue concentration data.

There are a number of reports on the feeding habits of many of the organisms used in this study. To begin the work of assigning trophic positions, we examined this literature as well as our records of the gut contents of individuals of each species; we then attempted to assign each organism to one of five levels of trophic categories:

- I, plants, including phytoplankton;
- II, herbivores, zooplankton;
- III, primary carnivores, including some infaunal feeders;
- IV, secondary carnivores (many fish);
- V, tertiary carnivores (e.g. large predatory fishes and sharks).

Most organisms and samples did not fit this scheme well and were then assigned intermediate positions. For example, Salton Sea detritus, which is food for several fish species considered, was composed of dead phytoplankton (Level I) and zooplankton (Level II) and therefore was assigned Trophic Level I-II; fish feeding primarily on the detritus were assigned to Level II-III (Young 1970). Similarly, we found algae (I), suspension-feeding bryozoans (II-III), and amphipods and small crabs (perhaps Level III) in the stomachs of yellowfin croaker (SCCWRP unpublished); as there is no evidence that this species is able to digest the algae, we assigned the fish to Trophic Level III-IV.

The resulting trophic level assignments are not meant to imply that specific organisms at a certain trophic level are necessarily prey for those placed at the next higher level. The assignments are mainly used as indicators of broad differences in food preference.

Collections of individuals of each species have been archived for detailed gut analyses.

## GENERAL SUMMARY OF FEEDING HABITS

Available data indicate that we sampled animals representing low, medium, and relatively high trophic levels in each ecosystem (Table 5). In the Salton Sea and the coastal pelagic food webs, we collected organisms known to form strong predator/prey pairs (e.g. corvina ← shad and small croaker; bonito and mackerel ← anchovy). In Newport Bay and at Palos Verdes, we sampled animals that did not necessarily feed on one another but were otherwise readily separated into lower and higher trophic levels, which are estimated in the second column of Table 5.

## SALTON SEA STUDY

The chemical data from our 1978 Salton Sea survey are presented in Table 6. Also listed are the median values obtained for percent dry weight and percent lipid weight of the wet muscle samples analyzed. The data show a distinct relationship between the estimated trophic position of the fishes surveyed and their muscle tissue concentrations of cesium and potassium. For ex-

TABLE 5  
 General Feeding Habits and Preliminary Trophic Level Assignments of Organisms from Four Marine Ecosystems.

Predator	Trophic assignment	Primary Prey <sup>1</sup>	Secondary Prey <sup>1</sup>	Data source
<b>Salton Sea</b>				
Corvina	IV-V	Fish (croaker, goby, shad)	Polychaete	Walker 1961; Young 1970; SCCWRP <sup>2</sup>
Croaker	III-IV	Bottom-dwelling polychaetes	Barnacles, copepods	Walker 1961; Young 1970
Sargo	III-IV	Polychaetes, barnacles		Walker 1961; Young 1970
Shad	III	Plankton (barnacle cypris)	Phytoplankton	Walker 1961; SCCWRP <sup>2</sup>
Molly	II-III	Algae and detritus		Moyle 1976
<b>Newport Bay</b>				
Sandbass	IV-V	Crabs, ghost shrimp, small fish		Feder et al. 1974
Striped bass	IV-V	Crustaceans, fish		Moyle 1976
Croaker	III-IV	Epibenthic invertebrates	Small fish, algae	Joseph 1962; Skogsberg 1939; SCCWRP <sup>2</sup>
Topsmelt	III-IV	Small benthic crustaceans	Polychaetes, gastropods	Lane 1975; Mitchell 1953
Mullet	II	Benthic diatoms, algae, detritus	Microinvertebrates	Walker 1961; Young 1970; Moyle 1976
<b>Palos Verdes</b>				
Bocaccio	IV-V	Small fish (rockfish, anchovy), pelagic red crab, squid		Fitch and Lavenberg 1971
Scorpionfish	IV-V	Fish, crab, shrimp, squid, octopus		Feder et al. 1974; SCCWRP <sup>2</sup>
Sanddab	III-IV	Epibenthic crustaceans, polychaetes	Small fish	SCCWRP <sup>2</sup>
Crab	III-IV	Omnivore: molluscs, detritus		Frey 1971
Prawn	III-IV	Crustaceans; possibly polychaetes, clams		Frey 1971; J.Q. Word <sup>3</sup>
Scallop	II-III	Phytoplankton		Assumption (rocky bottom filter feeder)
Abalone	II	Microalgae, macroalgae		Cox 1962
<b>San Pedro Channel</b>				
Blue shark	IV-V	Fish (anchovy, mackerel), squid	Small fish, euphausiids	Morejohn et al. 1978; Sciarrotta and Nelson 1977
Albacore	IV-V	Pelagic, mesopelagic fish (saury), anchovy, squid		Pinkas et al. 1971
Bonito	IV	Anchovy, squid		Pinkas et al. 1971; SCCWRP <sup>2</sup>
Pacific mackerel	III-IV	Anchovy, euphausiids, squid, young fish		Feder 1974; Miller 1970; SCCWRP <sup>2</sup>
Anchovy	II-III	Zooplankton and phytoplankton		Miller 1976; SCCWRP <sup>2</sup>

<sup>1</sup>Specific to size of fish analyzed.  
<sup>2</sup>SCCWRP, unpublished data based on collection during 1978 and 1979.  
<sup>3</sup>J.Q. Word, SCCWRP, personal communication.

ample, the median Cs/K ratios for the molly (Levels II-III), the shad (III), the sargo/croaker group (III-IV), and the corvina (IV-V) are 14.3, 17.1, 19.8, and  $32.0 \times 10^{-6}$ , respectively. Thus, the ratio increased by a factor of 2.2 over two trophic level steps. Although this increase is not as large as that observed by Young in 1967 (Table 2), these results nevertheless show a substantial structure in the part of the Salton Sea food web under study.

The manner in which the trace metals and chlorinated hydrocarbons of concern are distributed through this structured food web is of particular interest. As shown in Table 6, there is no evidence of generally increasing muscle tissue concentrations of most of the target trace metals with increase in trophic level or Cs/K ratio. For example, when we compared the median values for seven metals in the highest and lowest trophic levels sampled (the corvina, representing Level IV-V, and the molly, representing Level II-III), we obtained the following overall increase factors for the two trophic level steps:

Silver	<1.5	Iron	0.4
Cadmium	<1.5	Manganese	<0.1
Chromium	0.5	Zinc	0.6
Copper	1.0		

All values for two other metals, nickel and lead, were below the limits of detection and could not be compared.

TABLE 6  
 Median Concentrations of Cesium, Potassium, Trace Metals, Total DDT, and PCB 1254 in Wet Muscle Tissue of Organisms Collected from the Salton Sea in March 1978.

	Organism and Estimated Trophic Level				
	Corvina, Level IV-V	Croaker, Level III-IV	Sargo, Level III-IV	Shad, Level III	Molly, Level II-III
Number of Samples	4	3	3	3 <sup>1</sup>	3 <sup>1</sup>
Median weight (kg)	0.84	0.16	0.48	0.035	0.003
Cesium (µg/kg)	116	84.6	76.8	59.9	43.7
Potassium (g/kg)	3.63	4.05	4.07	3.50	3.06
Cs/K ratio $\times 10^{-6}$	32.0	20.9	18.8	17.1	14.3
Other trace metals (mg/kg)					
Silver	<0.003	0.002	0.002	0.003	0.002
Cadmium	<0.003	0.001	0.001	0.006	0.002
Chromium	<0.016	0.018	0.028	0.024	0.030
Copper	0.30	0.46	0.62	0.56	0.30
Iron	2.1	4.4	8.4	4.8	5.2
Manganese	0.046	0.41	0.23	1.3	0.70
Nickel	<0.04	<0.03	<0.03	<0.03	<0.02
Lead	<0.04	<0.04	<0.03	<0.06	<0.04
Zinc	3.1	3.2	3.5	3.9	5.3
Mercury					
Organic	0.030	0.009	0.012	NA <sup>2</sup>	0.008
Total	0.016	0.009	0.005	0.008	0.005
Chlorinated hydrocarbons (mg/kg)					
Total DDT	0.20	0.064	0.19	0.24	0.040
PCB 1254	0.014	0.002	0.008	0.040	0.000
Weight of samples					
% dry weight	25.0	23.7	27.0	31.3	24.5
% lipid weight	2.0	1.8	8.0	18.8	5.5

<sup>1</sup>Composites containing 10-12 individuals; shad collected March 1979  
<sup>2</sup>Not analyzed.

Similar overall increase factors were obtained by combining, where possible, the shad and molly data for Levels II-III and comparing them with the Level IV-V data. The results of this survey provide a substantial argument against increases in concentrations of these particular metals with trophic level in marine ecosystems.

The results for a tenth metal—mercury—were very different (Table 7). Median values for total concentrations of this metal in the molly (Level II-III), shad (III), sargo/croaker (III-IV), and corvina (IV-V) are 0.005, 0.008, 0.007, and 0.016 respectively, suggesting that concentrations tend to increase with trophic level. Application of the nonparametric, one-sided Mann-Whitney U-Test indicated that the difference between the corvina and sargo/croaker concentrations of total mercury were statistically significant ( $P < 0.01$ ). We therefore sought additional information by analyzing these samples for organic mercury. There appeared to be a systematic error in our results in that concentrations of organic mercury were often slightly higher than those for total mercury. However, the same general relationships between median concentration and trophic level were observed (Table 7). Again, the difference between values for Level III-IV and Level IV-V was found to be statistically significant ( $P < 0.01$ ). Thus, these two sets of independent analyses indicate that, on a wet-weight basis, muscle tissue concentrations of mercury increase threefold with a presumed two-step increase in trophic level in this ecosystem.

The data listed in Table 6 show no apparent relationship between the wet-weight concentrations of total DDT and PCB 1254 in the muscle tissue of the study organisms and their assumed trophic levels. However, these synthetic compounds are often found in higher concentrations in lipid-rich tissues. Therefore, we normalized these parameters in a lipid-weight basis and obtained the median concentrations given in Table 8. With one exception, the muscle tissue concentrations of total DDT and PCB 1254 on a lipid-weight basis increase both with increase in Cs/K value and with increase in estimated trophic level.

### NEWPORT BAY STUDY

In contrast to the situation observed in the Salton Sea, the alkali metal results obtained from the Newport Bay survey (Table 9) indicated that there was considerably less structure in the food web of this marine ecosystem. The median Cs/K ratios from small mullet (Level II), topsmelt/yellowfin croaker (Level III-IV), and spotted sandbass/striped bass (IV-V) were quite similar: 3.6, 4.6, and  $5.2 \times 10^{-6}$ , respectively.

We have excluded the large mullet from this comparison because the median weight for these specimens (2.7 kg) was an order of magnitude above those of the other species. However, a comparison of the cesium and po-

tassium data for the small and large mullet does provide useful information regarding the effect of specimen size on the results. Because mullet are primarily herbivorous and do not appear to change their diet as they grow, they are useful organisms with which to evaluate the effect of size alone on muscle concentrations of various trace chemicals. Although the large mullet were four to five times as heavy as the small mullet, the median cesium concentrations and Cs/K ratios for the two groups of fish were similar (Table 9). This suggests that, in the absence of differences in food at different growth stages, values for cesium and the Cs/K ratio in muscle tissue of a fish species are not strongly dependent on size. Concentrations of most of the other metals analyzed also did not

TABLE 7  
 Variations in Muscle Tissue Median Concentrations of Mercury (mg/wet kg) with Differences in Trophic Position of Organisms from Three Marine Ecosystems.

Area and species-group	Assumed trophic level	Organic mercury	Total mercury
Salton Sea:			
Corvina . . . . .	IV-V	0.030	0.016
Sargo/croaker . . . . .	III-IV	0.010	0.007
Shad . . . . .	III	NA <sup>1</sup>	0.008
Molly . . . . .	II-III	0.008	0.005
Newport Bay:			
Sandbass/bass . . . . .	IV-V	0.32	0.28
Topsmelt/croaker . . . . .	III-IV	0.073	0.050
Small mullet . . . . .	II	0.014	0.017
Palos Verdes:			
Scorpionfish/bocaccio . . . . .	IV-V	NA <sup>1</sup>	0.26
Crab/prawn/sanddab . . . . .	III-IV	NA <sup>1</sup>	0.080
Abalone/scallop . . . . .	II-III	NA <sup>1</sup>	0.033

<sup>1</sup>Not analyzed.

TABLE 8  
 Variations in Median Muscle Tissue Concentrations of Chlorinated Hydrocarbons, on Wet and Lipid Weight Bases, with Increase in Trophic Position of Organisms from Three Marine Ecosystems.

Area and species group	Assumed trophic level	Cs/K ratio $\times 10^{-6}$	Total DDT (mg/kg)		PCB 1254 (mg/kg)	
			Wet weight	Lipid weight	Wet weight	Lipid weight
Salton Sea:						
Corvina	IV-V	32.0	0.20	10	0.014	0.70
Croaker	III-IV	20.9	0.064	3.6	0.002	0.11
Sargo	III-IV	18.8	0.19	2.4	0.008	0.10
Shad	III	17.1	0.24	1.3	0.040	0.21
Molly	II-III	14.3	0.040	0.7	0.000	0.00
Newport Bay:						
Sandbass/bass	IV-V	5.2	0.62	64	0.24	25
Topsmelt/croaker	III-IV	4.6	0.18	20	0.040	4.7
Small mullet	II	3.6	1.00	25	0.12	3.0
Palos Verdes:						
Scorpionfish/bocaccio	IV-V	15.1	2.1	270	0.23	31
Crab/prawn/sanddab	III-IV	11.2	1.5	290	0.19	37
Abalone/scallop	II-III	6.4	0.008	11	0.01	1.1

increase greatly with increase in mullet size; however, the median cadmium concentration for the larger mullet was ten times the value for the small mullet, and the copper and iron values for the larger fish were twice as high.

As was the case in the Salton Sea results, trace metal values for Newport Bay specimens did not generally increase with increase in presumed trophic level. Comparison of median concentrations for the highest and lowest comparable groups (sandbass/bass, Level IV-V, and small mullet, Level II) yields the following overall increase factors for this presumed two-to-three step increase in trophic level:

Silver	1.5	Iron	1.0
Cadmium	>1.5	Manganese	1.0
Chromium	>0.6	Zinc	1.4
Copper	1.1		

Because the concentrations of silver and cadmium were very low, the significance of the factors listed for these metals is questionable. Nickel and lead concentrations in Newport Bay specimens also were low, as they were in Salton Sea samples. Another similarity between the two sets of data was that distinct increases of total and organic mercury with increase in presumed trophic level were found in both areas (Table 7). Over the two-to-three step increase in trophic position between Levels II and IV-V, total and organic mercury concentrations increased by about a factor of 20.

As was the case with Salton Sea specimens, there is no apparent relationship between the wet weight concentration of total DDT or PCB 1254 in Newport Bay samples and the presumed trophic levels of the specimens. However, a more distinct pattern is revealed when the data are normalized on a lipid-weight basis, as shown in Table 8. The Group IV-V fishes contained distinctly higher lipid weight concentrations of total DDT and PCB 1254 than did fishes at lower levels. In view of the apparent increase in chlorinated hydrocarbon concentrations with mullet size (Table 9) and the fact that the median weight for the small mullet was two to five times higher than the corresponding weight for the other two groups, the correlation with trophic level might have been clearer if fish specimens of approximately equal weight had been available for study.

### PALOS VERDES STUDY

Chemical and size data from the benthic/epibenthic marine ecosystem in the waste-water discharge zone of Palos Verdes Peninsula are presented in Table 10. The median Cs/K ratios for specimens at Trophic Levels II-III, III-IV, and IV-V are 6.5, 11.2, and 15.1  $\times 10^{-6}$ , respectively. This represents an increase in the ratio by a factor of 2.3 over the presumed two trophic level steps. Again, with the exception of total mercury, there was no apparent increase in levels of toxic trace metals with in-

TABLE 9  
 Median Concentrations of Cesium, Potassium, Trace Metals, Total DDT, and PCB 1254 in Wet Muscle Tissue of Organisms Collected from Newport Bay in July 1978.

	Organism and Estimated Trophic Level					
	Striped bass Level IV-V	Spotted sand bass, Level IV-V	Yellowfin croaker, Level III-IV	Topsmelt, Level III	Mullet, Level II	
					Large	Small
Number of specimens	3	3	3	3	3	3
Median weight (kg)	0.25	0.31	0.21	0.05	2.7	0.60
Cesium ( $\mu\text{g}/\text{kg}$ )	21.7	22.6	19.8	12.4	16.8	16.1
Potassium (g/kg)	4.39	4.10	3.58	3.36	3.76	4.49
Cs/K ratio $\times 10^{-6}$	4.94	5.51	5.53	3.69	4.47	3.59
Other trace metals (mg/kg)						
Silver	0.003	0.003	0.003	0.002	0.002	0.002
Cadmium	0.003	0.003	0.002	0.002	0.020	<0.002
Chromium	<0.009	0.014	0.008	<0.010	0.016	0.018
Copper	0.27	0.26	0.26	0.20	0.55	0.24
Iron	1.7	2.2	2.4	1.9	4.2	2.0
Manganese	0.17	0.093	0.28	0.36	0.068	0.13
Nickel	<0.03	<0.04	<0.03	<0.03	<0.04	<0.03
Lead	<0.04	<0.04	<0.03	<0.04	<0.04	<0.04
Zinc	4.1	4.3	5.8	14	3.3	2.9
Mercury						
Organic	0.36	0.27	0.054	0.092	0.017	0.014
Total	0.41	0.20	0.050	0.051	0.010	0.017
Chlorinated hydrocarbons (mg/kg)						
Total DDT	0.75	0.48	0.20	0.15	4.4	1.00
PCB 1254	0.29	0.19	0.042	0.039	0.47	0.12
Weight of samples						
% dry weight	24.5	23.8	24.4	24.8	28.2	27.3
% lipid weight	0.91	1.07	1.2	0.67	8.6	4.0

TABLE 10  
 Median Concentrations of Cesium, Potassium, Trace Metals, Total DDT, and PCB 1254 in Wet Muscle Tissue of Organisms Collected from the Palos Verdes Shelf, 1975-77.

	Bocaccio, Level IV-V	Scorpion-fish Level IV-V	Sanddab, Level III-IV	Yellow crab, Level III-IV	Prawn, Level III-IV	Scallop, Level II-III	Abalone, Level II
	Number of specimens	3	2	3	2	3	3
Median weight (kg)	0.37	0.34	0.073	0.58	0.024	0.095	0.54
Cesium ( $\mu\text{g}/\text{kg}$ )	77.4	54.4	48.1	21.1	37.3	21.4	24.3
Potassium (g/kg)	4.66	4.01	3.98	3.24	3.33	3.93	3.19
Cs/K ratio $\times 10^{-6}$	16.6	13.6	12.1	6.5	11.2	5.4	7.6
Other trace metals (mg/kg)							
Silver	0.008	0.022	0.005	0.095	<0.004	<0.003	0.028
Cadmium	<0.002	0.004	0.003	0.004	0.032	0.803	0.041
Chromium	<0.010	0.036	0.032	0.080	<0.019	0.255	0.95
Copper	0.15	0.15	0.19	7.84	2.0	0.24	3.35
Nickel	0.058	0.15	0.056	0.26	<0.03	0.046	0.68
Lead <sup>1</sup>	0.08	0.64	0.02	0.14	<0.01	<0.04	<0.12
Zinc	4.7	3.9	3.2	25.2	9.8	19.8	6.1
Total mercury	0.14	0.38	0.081	0.064	0.080	0.056	0.010
Chlorinated hydrocarbons (mg/kg)							
Total DDT	0.61	3.5	6.1	1.5	0.15	0.16	0.001
PCB 1254	0.072	0.39	0.38	0.19	0.058	0.012	0.006
Weight of samples							
% dry weight	28.0	23.0	21.0	20.0	24.0	24.0	25.0
% lipid weight	1.47	0.69	0.88	0.52	1.27	0.76	0.94

<sup>1</sup>Measurable lead values may indicate contamination of sample.

crease in trophic level or Cs/K ratio. Comparison of median concentrations for specimens at Level IV-V and those at Level II-III yields the following overall increase factors:

Silver	1.0	Copper	0.08
Cadmium	<0.01	Nickel	0.3
Chromium	<0.04	Zinc	0.3

However, as in the previous two studies, there was a correlation between wet-weight concentrations of total mercury and trophic level, as shown in Table 7 (organic mercury was not measured in these samples). There also was some indication of a relationship between total DDT and PCB 1254 concentrations, and trophic level and Cs/K ratio (Table 8).

### STUDY OF PELAGIC FISHES (SAN PEDRO CHANNEL)

Only the alkali metals were analyzed for the pelagic ecosystem; results are summarized in Table 11 in the same format used to present the 1967 Salton Sea survey results (Table 1). The data indicate distinct structure for both ecosystems. Increase in Cs/K ratios for hypothesized predator/prey relationships in the pelagic ecosystem range from 1.6 to 3.2, with a median value of 2.3. This is in agreement with the corresponding median value of 2.5 (range was 2.0 to 5.5) obtained by Young in the 1967 survey of the inland, quasi-marine ecosystem of the Salton Sea.

### CONCLUSIONS

The results of the studies reported here suggest that Cs/K ratios in organisms from a marine ecosystem can indeed provide a useful indication of the degree of trophic structure in the food web of that environment. Although physiological differences between individual species or groups of species considered may cause distinct variations, the information obtained suggests that, in a structured situation, this ratio should approximately double over a single trophic level step. The fact that an increase of this magnitude was not observed over the presumed trophic level steps of the two nearshore marine ecosystems studied to date (Newport Bay and Palos Verdes shelf) is consistent with the hypothesis that such systems experience considerable "homogenization" of energy flow as a result of the opportunistic (i.e. unstructured) feeding patterns of member organisms.

Nevertheless, all four types of "marine" ecosystems investigated (saline lake, back bay, benthic discharge zone, and coastal pelagic community) exhibited measurable food web structure. In the Salton Sea, the Cs/K ratio increased by a factor of 2.2 over two presumed trophic steps. This ratio increased by only about a factor of 1.5 over two to three presumed trophic level steps in upper Newport Bay, and an increase factor of 2.3 was observed over two presumed steps on the Palos Verdes

shelf. This latter value was also the median increase factor measured for several specific predator/prey (single-step) relationships in the coastal pelagic food web of the Bight.

We have completed analyses of trace contaminants in specimens from three of the four study areas. The degree of structure in the food webs of the three systems varied. However, we found no evidence of increase in concentrations of nine of ten trace metals with increase in trophic level within any system. In fact, in the benthic/epibenthic system within the waste-water discharge zone of Palos Verdes Peninsula, concentrations of these metals were considerably lower in the high-level predatory fishes than in the lower level infaunal and filter-feeding organisms. Thus, although the large point-source input of metal wastes from municipal waste-water discharge has previously been shown to result in elevated levels of metals in certain of the invertebrates that occupy the lower trophic levels (Jan et al. 1977), we did not find that this contamination is passed up the food web to fishes situated at higher trophic levels.

In contrast, there were very distinct increases in mercury and total DDT and PCB 1254 concentrations with increase in trophic level in the three ecosystems. Independent measurement of total and organic mercury verified this finding and suggested that most of the mercury in the muscle tissue of the fish specimens investigated was in an organic form. Concentrations increased from the lowest to the highest trophic levels sampled by up to a factor of 20.

There is no question that DDT and PCB 1254 residues are foreign chemicals which occur at significantly higher concentrations in the Palos Verdes marine food web than at distant control sites. However, the results from our control zone surveys (Jan et al. 1977) show that mercury concentrations are normally higher in higher trophic level organisms. We have found no evidence that the waste-water mercury released from the Palos Verdes outfalls is contributing to the increased concentrations of this metal in the marine food web of that region.

TABLE 11  
 Comparison of the Concentrations of Cesium and Potassium and Cs/K Ratios (on a Wet-Weight Basis) in the Muscle Tissue of Pelagic Fishes from the Southern California Bight with Those in Their Food.

Organism	Major food	Ratio, concentration in organism to concentration in major food		Cs/K ratio $\times 10^{-6}$
		Cesium	Potassium	
Pacific mackerel	Anchovy	1.90	1.16	1.64
Pacific bonito	Anchovy	2.56	1.26	2.03
Albacore	Anchovy, mackerel	1.77	0.91	1.94
Blue shark	Bonito	2.21	0.89	2.48
Blue shark	Mackerel	2.98	0.97	3.08
Blue shark	Anchovy, mackerel, bonito	3.12	0.99	3.15
Median		2.38	0.98	2.26
Mean		2.42	1.03	2.39



The clearest relationship between total DDT and PCB 1254 concentration and trophic position usually was obtained when the concentrations in wet tissue were normalized to a lipid-weight basis. Order of magnitude increases were observed in several cases.

The increases in mercury, total DDT, and PCB 1254 concentrations with trophic level may well be the result of relatively long biological half-lives of organic mercury and the synthetic organics in muscle tissues of the species analyzed. If a substance has a sufficiently long half-life, the existence of any structure in a food web will result in an increased concentration of the substance with increase in trophic position. Because the resulting increase factors are dependent on the degree to which equilibrium has been reached in any one step and the effect of growth and physiological conditions (such as percent lipid), we are not yet able to quantitatively relate increases in the Cs/K ratios with corresponding increases in the concentrations of trace pollutants that result from the feeding process. However, we believe that the results reported here represent a significant increase in our understanding of trophic position and the problem of food web increases of pollutant concentration in marine ecosystems.

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