C-129

POLLUTANT FLOW THROUGH THE FOOD WEB OF LOS ANGELES HARBOR - A PILOT STUDY

A Report to

UNIVERSITY OF SOUTHERN CALIFORNIA
SEA GRANT INSTITUTIONAL PROGRAM

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November 28, 1979

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SUMMARY

Diets of four species of marine animals (gaper clam, Tresus nuttallii; Northern anchovy, Engraulis mordax; white croaker; Genyonemus lineatus; and California halibut, Paralichthys californicus) from western Los Angeles harbor, the site of an oil spill, were examined in order to make trophic level assignments for evaluating food web magnification or dimunition of inorganic and organic trace contaminants. In addition, muscle tissue of the animals, and blades of giant kelp (Macrocystis pyrifera), a primary producer, were analyzed for the cesium/potassium (Cs/K) ratio (a chemical index of trophic structure). A single brown pelican (Pelecanus occidentalis) was also included for analysis of benzo(a) pyrene.

There was little overlap in diets of the clam and fishes. Assignments, based on a conventional scale of I (primary producers) to V (tertiary carnivores), were: giant kelp (I); gaper clam (II-III); Northern anchovy (III); white croaker (III-IV); and California halibut (IV). Median Cs/K values increased with assigned trophic level (0.70, 1.84, 2.10, 2.92 and 3.49 $x10^{-6}$, respectively).

Trophic structure suitable for food web magnification was confirmed. Howe none of nine "non-volatile" trace elements measured (Ag, Cd, Cr, Cu, Fe, Mn, Ni, Pb and Zn) increased with trophic level; in fact, many decreased by as much as an order of magnitude. In contrast, concentrations of total mercury, total DDT and PCB 1254 did increase with trophic level. However, another organic contaminant, benzo(a)pyrene (a potent carcinogen), decreased with increase in trophic level; a comparison of this finding with previous studies suggests that benzo(a)pyrene may be more efficiently metabolized in the fishes and a sea bird than in invertebrates or seaweed and that the hydroxylase enzyme activity in these organisms should be measured in future studies. Overall, the benthic-based portion of the food web may be more important than the pelagic in terms of food web magnification, but this point needs further investigation.

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ACKNOWLEDGEMENTS

The impetus for this (and related) studies was provided by Professor J. D. Isaacs, Chairman of the SCCWRP Board of Consultants. Support was provided by the University of Southern California Sea Grant Institutional Program (NOAA, Office of Sea Grant, Department of Commerce #04 7 158 4113) and the University of Southern California Marine and Freshwater Bio-medical Center (NIEHS #1 P30 ESO 1965-01). Contribution No. 154 of the Southern California Coastal Water Research Project.

I. STRUCTURE IN THE FOOD WEB: A COMPARISON OF BIOLOGICAL AND CHEMICAL INDICIES.

A. Background:

There is considerable public and scientific apprehension about the potential ability of marine food chains to concentrate all or most toxic materials to hazardous levels. However, Isaacs (1972 and 1973) has suggested that marine food webs may be largely unstructured, i.e., the heterotrophs of the web do not occupy relatively well defined positions within a finite sequence of trophic steps. With the exception of certain materials such as the chlorinated pesticides, (Woodwell et al. 1967), there are relatively few reports which show that the degree of bioaccumulation of toxic residues is indeed correlated with trophic level. In fact, deGoeji et al. (1974) and others provide evidence that many trace metals exhibit no unnatural accumulation in bottomfish around coastal sewage outfalls. There is substantial data on pollutant residues in marine and estuarine animals (e.g., Reish et al. 1979) but these data are not in a form useful for examining specific food web relationships. In contrast, there is increasing information on the feeding habits of fishes and invertebrates (e.g., Simenstad and Lipovsky, 1977; Lipovsky and Simenstad, 1979) but few simultaneous analyses of trace contaminents.

The goal of this study is to determine what, if any, relationships exist between tissue concentrations of trace metals, chlorinated hydrocarbons and a potent carcinogenic petroleum hydrocarbon constituent (benzo(a)pyrene), and trophic levels of target organisms in highly urbanized Los Angeles Harbor.

The specific objective of this section is to identify likely dietary pathways leading to target organisms, assign trophic levels based on analysis of diet, and compare these assignments with tissue levels of the cesium/potassium (Cs/K) ratio, a useful indicator of trophic structure (Young, 1970; Young and Mearns, 1979). The following section of this report then compares these results to concentrations of specific pollutants.

Use of the Cs/K ratio as an index of trophic structure is a key element of this study. As described in more detail by Young (1970), Isaacs (1972), and Part II of this report, in a simplified linear food chain there is a 2 to 3 fold increase in the Cs/K ratio with each trophic step; thus, absence of such an increase suggests that the predator and its prey are involved in a largely homogenized, or unstructured, food web (Isaacs, 1972 and 1973). Utilizing this approach, Young and Mearns (1979) and Mearns and Young (1979) have concluded that certain marine food webs of southern California have intermediate levels of structure.

Below we report our approach, field methods, results of stomach analyses and assignment of trophic levels as well as a comparison of their trophic assignment to Cs/K ratios of target species from Los Angeles Harbor.

B. Methods

1. Description of the Study Area

Sampling was conducted in the western end of the Los Angeles Harbor, inside the San Pedro breakwater. This area is adjacent to (within 200-1000m) the site of an oil spill, (Sansinena tanker) which occurred in December 1976. The area (Figure 1) includes a sandy beach (Cabrillo Beach) on the west, commercial and recreation boat docks to the north, a dredged ship channel to the east and the San Pedro breakwater to the south. Maximum bottom depth is about 15 m (45 feet).

The area is in the general proximity of a variety of pollutant sources such as urban runoff, atmospheric fallout, vessel-related contaminants, ship yards, and municipal sewage. There is even a vector of pollutants from outside the harbor (discussed in more detail in Part II). With the possible exception of the historical Sansinena oil spill, the study area is probably not directly influenced by a point source of specific contaminants.

The area supports a variety of pelagic and benthic fishes, intertidal clam populations (gaper clam, *Tresus nuttallii*), both soft-bottom and hard substrate benthic invertebrate communities, and a small kelp bed (*Macrocystis pyrifera*). A fishing pier, adjacent to the breakwater, produces catches dominated by white croaker (*Genyonemus lineatus*), queenfish (*Seriphus politus*), California halibut (*Paralichthys californicus*), Pacific mackerel (*Scomber japonicus*) and several species of surf perch (Embiotocidae).

2. Preliminary Identification of Target Species

Our goal was to collect and analyze, in replicate

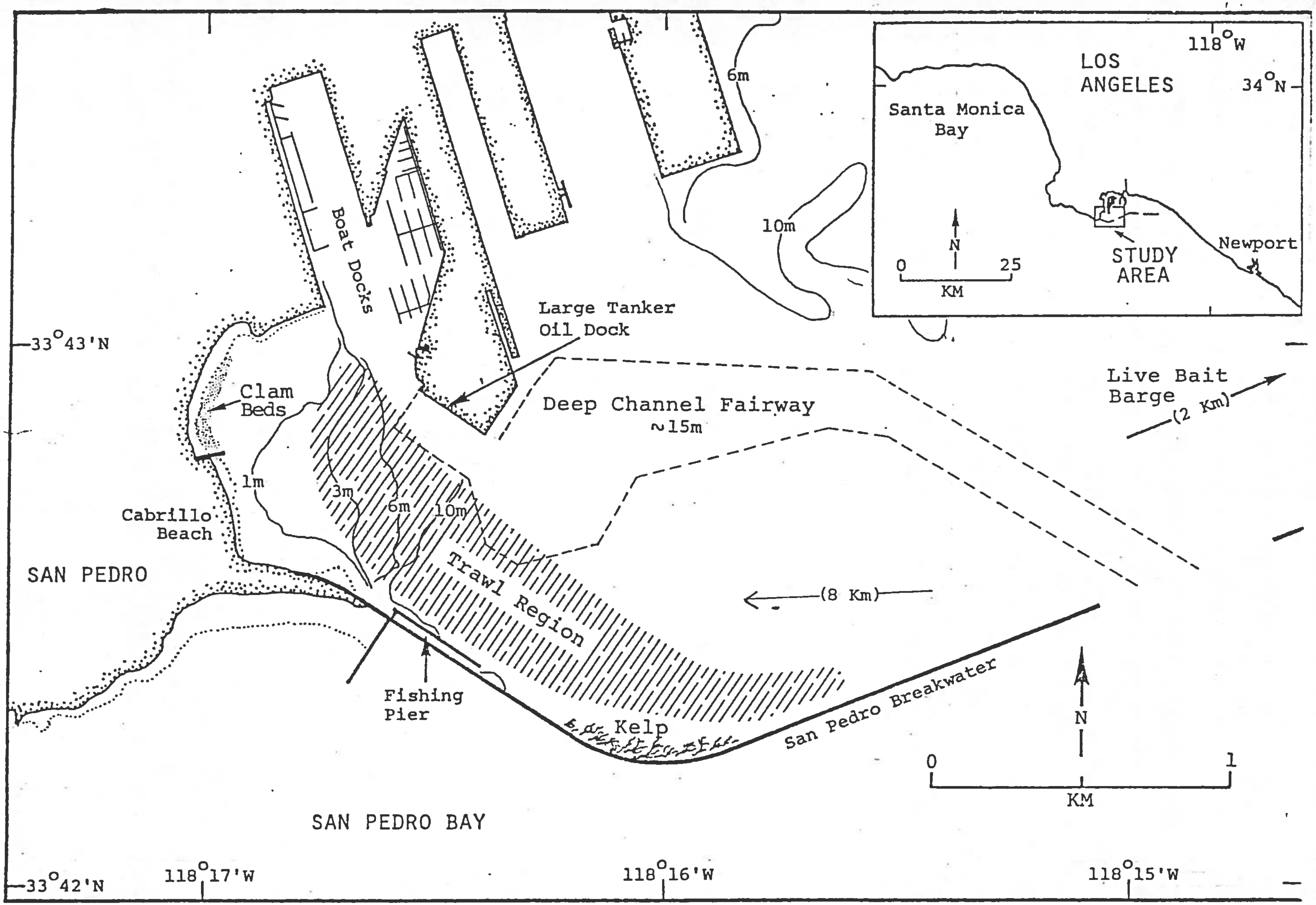

Figure 1: Collection sites in western Los Angeles Harbor, June-July, 1979. Shaded area was surveyed by otter trawl. The Large Tanker Oil Dock is the location of a major oil spill (December 1976 explosion of the tanker <u>Sansinena</u>).

(5 composites of at least 10 organisms each), species representing the widest possible range of trophic levels. This included primary producers (by convention, Trophic Level I), herbivores (Trophic Level II) and primary, secondary and tertiary carnivores (Trophic Level III, IV and V). Data from previous surveys and food habits studies were reviewed and a possible list of primary and alternative target species were selected (Table 1). Seining, bottom trawling, clamming, gill netting, and scuba diving were required to capture species on the list.

3. <u>Field Sampling</u>

Bottom trawls were taken in the area (Figure 1) on 5 and 14 June, 1979, using a 7.6m head rope length otter trawl fitted with a 1.2cm stretch mesh cod-end liner and towed astern of the launch <u>Golden West</u> (University of Southern California Institute for Marine and Coastal Studies) at 2.5 knots for 10 minutes. Depths sampled ranged from 3 to 12m. Fish and invertebrates were placed in holding tanks and specimens of target species, alternate species and other abundant species were selected, measured, and frozen. Non-target fishes and invertebrates were identified, counted and returned to the harbor.

Northern anchovies (<u>Engraulis mordax</u>) are abundant in the harbor but were rare in the trawls. To obtain an adequate supply, we purchased 0.5-1.0kg of live anchovies from a live-bait boat. The vessel's skipper confirmed that the anchovies were caught by purse seine in the harbor about 2km east of the center of our trawl area.

During June we dove and fished for the target herbivorous fish, Opaleye perch (<u>Girella nigricans</u>) without success and were unable to add replicates to a single specimen caught by trawl.

Table 1: Target and alternate species of marine plants and animals selected for food web study

Trophic Level	Primary Target	Alternate
V	California sea lion (Zalophus californianus)	Pacific electric ray (Torpedo californica) Very large halibut (Paralichthys californicus)
IV	California halibut (Paralichthys californicus)	Large white croaker (Genyonemus lineatus Queenfish (Seriphus politus) California bonito (Sarda chiliensis) Kelp bass (Paralabrax clathratus) Barred sandbass (Paralabrax nebulifer) Rockfish (Sebastes sp.)
III	Northern anchovy (Engraulis mordax)	Small water column fish (white croaker, queenfish, rockfish)
II	Opaleye perch (Girella nigricans)	Halfmoon (Medialuna californiensis) Gaper clam (Tresus nuttallii)
I	Giant kelp (Macrocystis pyrifera)	Other macroscopic seaweeds.

We therefore decided to substitute the gaper clam (Tresus nuttallii). Twenty gaper clams were dug from Cabrillo Beach, just west of the trawl area, and frozen.

Approximately 1kg of giant kelp (Macrocystis pyrifera) blades were removed from a small bed at the breakwater, washed of adhering silt in the ambient water, and frozen.

During our visit to collect anchovies, a Brown Pelican (Pelecanus occidentalis) was found freshly impaled on wire mesh of the bait barge. The stomach contained Northern anchovy and the bird was then frozen for chemical analysis.

4. Dissections: Examination of Stomach Contents

Dissections were performed in the laboratory using partially thawed specimens. After reviewing our inventory, we elected to dissect and analyze 5 composites of giant kelp (a primary producer), gaper clam (a suspension feeder), Northern anchovy (a plankton feeder), white croaker (a benthic feeder), and 4 composites of California halibut (a piscivore).

Stomachs and intestines from all specimens of California halibut and 14 specimens of white croaker were removed and preserved in formalin for stomach content analysis. We decided not to examine stomachs of anchovy from the bait barge because their confinement may have inhibited feeding or caused them to take items not normally encountered. Earlier (Fall, 1978) we did examine stomachs of Northern anchovy from San Pedro Bay, a few kilometers outside the breakwater, and used these data to represent their feeding habits.

Fine, greenish-brown silty material in gaper clam digestive tracts was briefly examined during their dissection.

Our stomach observations were complimented with data from the literature and unpublished reports (Phillips *et al*. 1972; Ware, 1979; Haaker, 1975; Miller, 1971).

Contents of stomach and intestines were removed and items sorted by major taxa under a dissecting microscope and each item identified. Volumes of prominent food items were estimated from dimensions (mm) of whole and nearly whole representatives. These data were used to compute the Index of Relative Importance (Pinkas *et al*. 1971) for each food item:

$$IRI = \%F \ (\%N + \%V)$$

where: %F = percent of predators with food item,

%N = percent contribution of food item by number,

%V = percent contribution of food item by volume.

IRI's were then summed and the % contribution to total IRI by each food item computed and used to identify the most important food items in the predators.

C. Findings

1. Field Sampling

Of 21 trawl tows, 18 successfully captured bottomfish and several invertebrates. Overall, the hauls captured 2317 fish of 21 species (Table 2) and the average trawl took 129 fish (±107,SD) and 6.3 species (±1.84, SD). White croaker (*Genyonemus lineatus*), white sea perch (*Phanerodon furcatus*) and California tonguefish (*Symphurus atricauda*) accounted for 75% of the abundance and were among the most frequently caught fish (Table 2). Two species of perch (*Embiotoca jacksoni* and *Cymatogaster aggregata*) and Pacific pompano (*Peprilus simillimus*) were the next most abundant fishes (Table 2). California halibut (*Paralichthys californicus*) and Northern anchovy (*Engraulis mordax*) accounted for 2.0 and 1.8 per-

Table 2: Abundance and frequency of occurrence of fishes in 18 positive bottom trawls from western Los Angeles Harbor, June, 1979

	Common Name	Scientific Name	Abundance No.	Abundance %	Freque[ncy] %
1	White croaker	Genyonemus lineatus	1073	60	89
2	White sea perch	Phanerodon furcatus	719	40	67
3	California tonguefish	Symphurus atricauda	110	6.1	44
4	Pacific pompano	Peprilus simillimus	96	5.3	39
5	Black perch	Embiotoca jacksoni	74	4.1	44
6	Shiner perch	Cymatogaster aggregata	60	3.3	28
7	California halibut	Paralichthys californicus	36	2.0	72
8	Northern anchovy	Engraulis mordax	32	1.8	28
9	Barred sand bass	Paralabrax nebulifer	30	1.7	44
10	Calico rockfish	Sebastes dallii	27	1.5	17
11	Specklefin midshipman	Porichthys myriaster	26	1.4	33
12	Queenfish	Seriphus politus	13	0.7	28
13	California lizardfish	Synodus lucioceps	9	0.5	33
14	Hornyhead turbot	Pleuronichthys verticalis	3	0.2	17
15	Pile perch	Damalichthys vacca	2	0.1	11
16	Walleye surfperch	Hyperprosopon argenteum	2	0.1	11
17	California scorpionfish	Scorpaena guttata	1	<0.1	6
18	Cabezon	Scorpaenichthys marmoratus	1	<0.1	6
19	Onespot fringehead	Neoclinus uninotatus	1	<0.1	6
20	Opaleye	Girella nigricans	1	<0.1	6
21	Bay goby	Lepidogobius lepidus	1	<0.1	6
	TOTAL	21 species	2317 individuals		

widely distributed (second most frequently caught fish).

Few invertebrates were captured in the trawls; included were 10-20 small shrimp (Crangon).

All fish examined appeared lively and healthy; none showed signs of external diseases such as fin erosion, tail erosion or tumors which have been observed in the past in other portions of the harbor and offshore (Mearns and Sherwood, 1977; EQA and MBC, Inc, 1978).

2. Characterization of Target Organisms

As noted above, members of 5 species of organisms were selected for further analysis and confirmation of trophic level. From the gaint kelp plants we sampled blades from actively growing tips near the sea surface. The blades were about 30-40cm long, 10cm wide and about 2-4cm thick. We were unable to measure the size of whole plants but inspection suggests they were well over 10kg and 3m long.

The animals sampled ranged from small Northern anchovy (3 to 11g) to large California halibut (111 to 586g) (Table 3). The 20 gaper clams were randomly grouped into 5 composites of 4 clams each. Despite our randomization, mean clam weight per composite ranged two-fold from 202g to 408g. The mean shell length of these clams ranged from 108 to 137mm. According to published accounts (Wendell et al. 1976), gaper clams with valve (shell) lengths over 80mm would be over 4 years old. However, Mr. Eric Knaggs (California Department of Fish and Game, Long Beach, personal communication) has determined that southern California gaper clams, including those from Cabrillo Beach, grow much faster than more northerly populations and rarely exceed an age of 5 years. Based on Knaggs age-length data (unpublished) our clams were approximately 2 to 3 years old.

Forty-one small (3 to 11g) Northern anchovies were grouped into 5 composites as shown in Table 3. The fish ranged from 68-104mm (standard length) and based on published age-length curves (Sunada, 1976) are all less than 1 year old (1979 year class). Specimens were randomized so that mean fish size per composite varied less than 17 percent about the median of 5.57g.

Previous data suggested that both white croaker and California halibut can change their diets (and therefore trophic levels) with size during juvenile and subadult stages. Accordingly, we composited samples of these 2 species by size. This resulted in a two-fold range in mean fish weight for white croaker (from 22.9 to 44.2g) and a 3.5-fold range in mean fish weight for California halibut (from 151 to 524g).

Age-length curves developed for San Pedro Bay-Los Angeles Harbor white croaker by Phillips et al.(1972) indicates that most of the July 1979 specimens were 1 year old juvenile fish (1979 year class). Inspection of published age-weight-length nomograms for California halibut (Hulbrock, 1974) indicate that the specimens were juveniles and subadults ranging from about 1 to not more than 2 and one-half years old (1976 to 1978 year classes). Most of the fish had small but developing gonads and each composite contained fish of both sexes.

3. Analysis of Feeding Habits and Trophic Level Assignments

a. Giant Kelp

We know of no information which suggests that kelp or other seaweeds are not autotrophic; by convention, we consider kelp a primary producer and assign it to Trophic Level I.

b. Gaper Clam

Intestines of our thawed gaper clams contained a greenish-brown material. According to Reid (1971) stomach contents of

Table 3: **Weights, lengths, estimated ages, muscle concentration of cesium (Cs) and potassium (K) and Cs/K ratio in composites of gaper clams (<u>Tresus nuttallii</u>) and 3 species of fishes from western Los Angeles harbor, June-July 1979.**

SPECIES	Composite No.	No. in Composite ♂	0	Σ	Weight (g)* mean ± S.D.	Range	Shell or Stand. Length (mm)* mean ± S.D.	Range	Est. Age Years	μg/dry kg Cs	g/dry kg K	Cs/K (x 10^{-6})
California halibut	1(220)	4	4	8	151 ± 24.5	111-178	214 ± 7.25	208-225	1+	61.9	23.3	2.66
	2(221)	4	4	8	213 ± 9.6	194-228	243 ± 5.39	235-252	1+	67.8	22.7	2.99
	3(222)	1	3	5	355 ± 42.1	296-408	287 ± 12.6	274-305	2	85.4	21.4	3.99
	4(223)	4	2	6	524 ± 48.4	471-586	318 ± 11.6	304-327	2+	123.0	21.9	5.62
White croaker	1(258)	-	-	15	22.9 ± 2.31	18.2-26.5	103 ± 3.51	98-109	0-1	54.5	17.9	3.04
	2(257)	-	-	12	24.6 ± 3.09	21.4-30.0	109 ± 4.49	104-116	1	73.2	18.2	4.02
	3(256)	-	-	12	32.0 ± 3.91	25.3-37.1	115 ± 4.51	107-122	1	52.8	18.1	2.92
	4(255)	-	-	12	35.1 ± 4.55	29.1-43.7	121 ± 4.92	115-130	1	48.6	18.4	2.64
	5(254)	-	-	12	44.2 ± 5.07	38.2-55.0	128 ± 7.30	119-145	1-2	46.8	17.9	2.61
Northern anchovy	1(230)	-	-	10	4.90 ± 1.18	3.0-5.9	78.2 ± 5.85	68-83	<1	16.1	7.68	2.10
	2(231)	-	-	14	5.24 ± 0.89	4.0-7.5	81.6 ± 3.48	76-90	<1	35.6	17.6	2.02
	3(228)	-	-	9	5.57 ± 1.26	3.9-7.8	82.1 ± 9.06	75-90	<1	39.2	23.6	1.66
	4(229)	-	-	8	6.26 ± 1.29	4.3-7.9	85.0 ± 6.00	76-93	<1	48.8	20.8	2.35
	5(227)	-	-	11	6.54 ± 2.26	3.6-11.0	86.7 ± 9.37	75-104	<1	51.6	22.8	2.26
Gaper clam	1(245)	-	-	4	202 ± 36	155-238	108 ± 8.5	101-120	2	23.2	12.6	1.84
	2(247)	-	-	4	286 ± 108	206-441	113 ± 12.5	104-131	2	17.2	12.5	1.38
	3(246)	-	-	4	315 ± 127	215-498	122 ± 12.8	110-137	2	27.6	12.0	2.30
	4(248)	-	-	4	344 ± 76	277-451	120 ± 7.1	113-130	2+	18.8	11.3	1.66
	5(244)	-	-	4	408 ± 202	107-536	137 ± 33.0	89-160	1-3+	53.0	25.2	2.10

* S.D. = Standard Deviation

suspension feeding clams are characteristically green or brown due to the preponderance of phytoplankton (<100μ in size) during periods of phytoplankton blooms; sand grains would be indicative of deposit and sand-grain feeders. We did not determine whether or not sand grains were present in our clams so we cannot exclude the possibility that our *T. nuttallii* were feeding on surface detritus or surface sediment. Reid (1969) carefully inspected stomach contents of the related horse clams, (*Tresus capax*) from a British Columbia population. These clams contained small phytoplankton (*Fragilaria*, *Melosira*, *Meridian*, *Gomphonema*), detritus and a variety of other diatoms and flagellates. They did not contain larger organisms (peridinians, *Coscinodiscus*, *Gyrosigma* or *Chaetocerus*) even though these were blooming at the time. His clams also contained bacteria (a spirochaete, *Cristispira*). In the winter, when phytoplankton blooms were frequent, stomachs contained only detritus and spirochaetes, with no zooplankton present. MacGinitie (1935) concluded that Elkhorn Slough (central California) gaper clams were feeding on detritus. At the California Department of Fish and Game Laboratory at Granite Canyon, young *T. nuttallii* are fed a mixture of small chrysomonacds (*Isochrysis galvanica*) and diatoms (non-chain forming *Chaetocerus gracilis*); although they feed well, growth is slow (Mr. Arthur Hazeltine, California Department of Fish and Game, personal communication).

These observations suggest that at least 2 clams of the genus *Tresus* feed on detritus (intermediate Trophic Level I-II) and phytoplankton (Trophic Level I) but not zooplankton (Trophic Level II). We therefore assign the Los Angeles harbor gaper clam to intermediate trophic level II-III with a bias toward II because of the suggestive importance of phytoplankton.

c. Northern Anchovy

Analysis of stomachs and intestines from 9 Northern anchovies caught in San Pedro Bay in October 1978 indicated that they were mainly feeding on zooplankton particulates rather than phytoplankton.

The anchovy we examined had a median length of 83mm (range 78 to 95 SL) and a median weight of 5.3g (range 4.5 to 6.9g); thus, the fish were about the same weight but were slightly shorter than the 5.6g 82.1mm specimens taken for chemical analysis from the bait barge in 1979.

A total of 20 classes of food items were enumerated in the anchovy stomach contents (Appendix A). Identifiable items were dominated by parts (appendages) of small crustaceans. Identifiable crustaceans included cypris, zoea, nauplii larval stages, copepods, and juvenile euphausids. Also present were salps, tiny bivalves (presumably pelagic; possibly Mytilus sp.), hydroids (medusae) and insect wings. Phytoplankton such as diatoms and dinoflagellates were rare but it is possible they were eaten but destroyed during freezing, thawing and subsequent preservation. Sand grains were not observed. Eggs (or particles that resembled eggs) and small fibrous "sticks" were present.

Relative volumes of each food class were roughly estimated by comparative inspection; i.e., relative to the mass of material on a slide, unidentifiable particulates appeared to account for 70 percent of the bulk (Appendix A and Table 4). From these estimates plus data on numbers and frequencies of occurence of food item types, we calculated IRI's (Appendix A and Table 4). A summary of IRI's of major classes of food items suggested that unidentifiable particulates and crustaceans (whole and parts) were most important (68 and 31% of total IRI, respectively) and all other

Table 4: Summary of indicies of relative importance (IRI) for six major classes of food items from nine Northern anchovy (*Engraulis mordax*) from San Pedro Bay, 1978.

Category	IRI	%IRI
Unidentified Particulates	13290.0	68.20
Crustaceans (whole, parts)	5980.0	30.70
Eggs	202.0	1.04
Other identifiable zooplankton	4.4	0.02
"Sticks"	1.1	<0.01
Phytoplankton (confirmed)	17.0	0.09
Σ IRI	19494.5	100.00

items, including identifiable phytoplankton were relatively unimportant (Table 4). Loukashkin (cited in Miller, 1971) examined stomachs of 926 anchovies taken throughout central and southern California and off northern Baja California at different seasons. According to Miller (1971) his data indicates that the Northern anchovy "is strictly a plankton feeder" eating both phytoplankton and zooplankton but showing a "preference percentage-wise for zooplankton." Clearly our anchovy were feeding to a moderate extent on zooplankters (Trophic Level II). Accordingly, we first assigned these anchovy to Trophic Level III. The unidentifiable material could, however, include detritus derived from zooplankton and phytoplankton(Trohpic Level I). Accordingly, we then reassigned these Northern anchovy to intermediate Trophic Level II-III (but with a bias toward III).

d. White Croaker

Stomachs of 14 small (average 20g and 100mm SL) white croaker from the specimens selected for chemical analysis (at least 1 fish from each composite) contained a variety of benthic and epibenthic crustaceans (caprellids, cumaceans, cladocerans, shrimp and ostracods), small clams, remains of small fishes (scales, spines) and remains of a few polychaetes and gastropods. Crustacean were numerically dominate and occurred in all fish and these, in turn, were domianted by caprellid amphipods (Appendix B and Table 5).

Estimates of relative volume of whole food items (bottom, Appendix B), which give considerable weight to fish, suggested that fish could be quite important. However, when IRI's were calculated, the initial importance of small epibenthic crustacenas was not diminished; overall, crustaceans accounted for nearly half of the important food items, clams about one-quarters, and fish about

Table 5: Summary of indicies of relative importance (IRI) for 6 major classes of items in stomachs of 14 white croaker (Genyonemus lineatus) from western Los Angeles Harbor, June-July, 1979. Mean weight 27.6g (22.2-39.2), mean S.L., 110mm (98-145mm). From Appendix B.

Species	IRI	%IRI
Polychaetes	340	3.9
Pelecypods	2208	25.3
Gastropods	223	2.6
Crustaceans (7 major taxa)	4129	47.4
Fish	1802	20.7
Inanimate objects	11	0.1
Σ IRI	8713	100.0

one-fifth (Table 5). The identity of several organisms confirmed the fish were feeding near or on the bottom; confirmed benthic organisms include the tube-dwelling polychaete Cistena californica and tellinid clams. Epibenthic organisms included the amphipod Photis sp. and the ostarcod Euphilomedes sp. Phillips et al (1972) sampled stomachs of 52 white croaker collected in San Pedro Bay and concluded that the diets shift from zooplankton to the benthos as the fish grows. Fish between 60 and 80mm SL fed almost exclusively on zooplankton (euphausids, zoea, nauplii, megalops, chaetognaths, larval polychaetes, cyprids, copepods and larval fish) but contained a few epibenthic crustacean (cladocerans, amphipods, ostracods, mysids). Seven fish 82-121mm SL were more transitional, containing a complete mixture of zooplankton and benthic invertebrates; 32 fish larger than 105mm SL, contained exclusively benthic organisms (polychaetes, pea crabs, shrimp, clams, amphipods, mysids and ostracods). Ware (1979), in a study of feeding habits of white croaker near and away from a Los Angeles Harbor cannery waste discharge also concluded white croaker are omnivores which shift their diet with size. He identified 132 invertebrates and 1 fish (Engraulis mordax). Planktonic crustaceans decreased and benthic and epibenthic invertebrates increased in importance as fish grew from juveniles to subadults. The composition of benthic diets changed seasonally with changes in availability. Fish (Engraulis mordax) were important components of the diet of adult croakers.

Overall, we conclude that the young white croakers were feeding on or near the bottom, mainly on epibenthic and benthic crustaceans and clams. We assume the crustaceans and clams are mainly detritus (Trophic Level I-II) feeders and thus assign them to intermediate Trophic Level II-III. In turn, we initially assigned white croaker to the intermediate Trophic Level III-IV. However, considering the possible importance of fish (i.e., Trophic Level III or higher) in the diet, we conclude that these croakers are closer to Trophic Level IV than to III.

e. California halibut

Stomachs of 15 of the 27 California halibut used for chemical composites contained indentifiable food items. Of the 19 items, 18 were fish or fish remains and of these, there were 8 northern anchovy (20-80mm long), 3 gobies (Family Gobiidae) and remains of 7 unidentifiable fish. One small halibut contained eyestalks, presumably from a shrimp (Appendicies C and D) but none had remains of any other invertebrates.

Analysis of the stomach content data, including computation of estimates of IRI, clearly indicate that fish, particularly Northern anchovy, were the most important food items (Table 6, Appendicies C and D). The preponderance of anchovy suggests the California halibut were feeding mainly on small water column plankton-eating fish (Trophic Level II → III). However, the occurrence of mud, sand grains, remains of one shrimp and gobies (which are bottom dwelling fish that feed on the bottom and on epibenthic crustaceans, e.g., MacDonald, 1975) suggests the halibut were obtaining a significant part, (one-quarter to one-third) of their diet from epibenthic and benthic invertebrates and fish

Table 6: Summary of indicies of relative importance (IRI) for food items in stomachs of 27 California halibut (Paralichthys californicus) from western Los Angeles Harbor, June-July, 1979.

Composite No.	Weight (g) mean ± S.E.*	%IRI Shrimp	%IRI Fish**
220	151 ± 8.7	1.9	98.1
221	213 ± 3.4	0	100
222	348 ± 19	0	100
223	524 ± 20	0	100
	TOTAL	0.8	99.2

* Standard error

** Northern anchovy, 48.2; goby, 7.6; unidentified fish, 43.4

(i.e., Trophic Level III → IV). Gobies were the most frequently encountered food item in California halibut from Anaheim Bay (Haaker, 1975). A purely anchovy diet would place our halibut at Trophic Level III → IV (closer to IV than III) while a purely benthic fish diet would place them at Trophic Level IV → V (closer to V than to IV). Accordingly, we generally assigned those halibut to intermediate Trophic Level IV↔V with a bias toward IV because of the dominance of anchovy.

As noted above, there was a considerable size range among the halibut composites (151 to 524g/fish). Inspection of stomach contents data indicated the single shrimp eyestalk was found in one of the smaller halibut (129g, 210mm SL). Adult California halibut feed almost exclusively on fish (Feder, 1974). However, Haaker (1975) found that California halibut in Anaheim Bay (adjacent to Los Angeles-Long Beach harbors) changed diet with size: "California halibut less than 55mm SL" ate mostly small benthic crustaceans "and gobies (Clevelandia, Quietula and young Gillichthys)"; "fish between 55 and 230mm SL ate larger crustacean and fishes." "California halibut over 230mm SL were almost totally piscivorous" with very few large crustaceans found in the gut (Haaker, 1975). Thus, while young white croaker are shifting from a water column to benthic feeding mode with size, young California halibut are shifting from a benthic or epibenthic feeding mode toward a nekton feeding mode with size.

These observations suggested our California halibut specimens had recently passed through the transition stage from smaller epibenthic organisms to larger nekton.

4. Overall Trophic Structure and Comparison to Chemical Indicators

As stated above the specific objective of this section of the report were to: 1) identify likely dietary pathways leading to target organisms, 2) assign trophic levels based on analysis of diet, and 3) compare these assingments with tissue cesium/potassium ratios.

Data on feeding habits and trophic level assignments were used to construct a general flow diagram showing the approximate position of each target organism and its principle prey (defined by indicies of relative importance). In constructing the diagram, we also considered the relative position of man (i.e., recreational fishermen) and the pelican (Figure 2).

Our diagram (Figure 2) indicates 2 principle routes of material flow from primary producers; one path through the benthos to white croaker and a second path through the water column and Northern anchovy to the halibut and California pelican. Recreational fishermen crop organisms from both routes, but unlike the pelicans, we believe fishermen do not directly capture and consume Northern anchovy. Thus, organisms at the top of this portion of the food web are each exposed to different routes of transfer of trace materials.

This study focuses on only a part of the harbor food web. As noted above, other fish, such as the perches, Pacific mackerel and bonito are abundant in the harbor area and should be included in future studies.

Based on feeding habits data, we assigned target organisms to the following trophic levels: (I) giant kelp; (II-III) gaper clam; (II→III) Northern anchovy; (III→IV) white croaker; and (IV↔V) California halibut. The arrows in these assignments indicate that organisms of intermediate trophic levels should be biased toward the indicated level (rather than exactly half-way between).

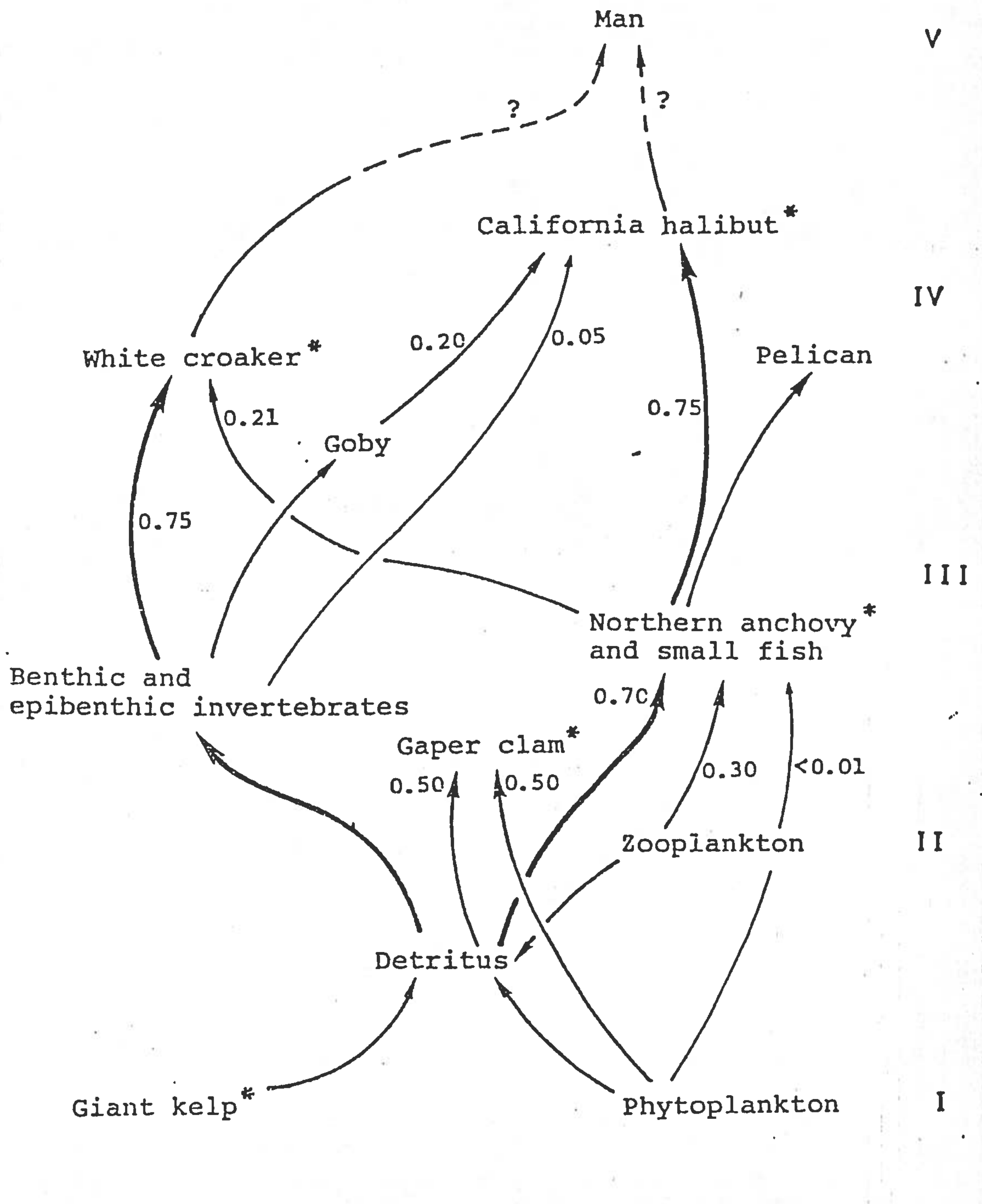

Figure 2: Principal feeding relationships and estimated trophic levels of organism investigated. Asterisk indicates target species sampled in this study, numbers are fractions of indicies of relative importance from food habit analyses. Roman numerals indicate conventional trophic level.

How do we compare these biologically derived assignments to our initially assumed levels (Table 1) and to the chemical indicator Cs/K? One approach is shown in Table 7 which indicates the size of our target organism, our trophic assignments assumed before the study began, trophic levels assignments based on feeding habits and numerical values for trophic levels and Cs/K. These data indicate that organism size is unrelated to trophic level or to Cs/K and that, with the exception of white croaker our assigned trophic levels are similar to assumed trophic levels. Thus, specific feeding habits data served to fine-tune trophic level assignments.

The conventional trophic level system (i.e., I, II, III, IV, and V) is discontinuous and was obviously not intended to be correlated directly with continuous data such as increases or decreases in trace materials. However, to compare trophic level assignments with tissue chemical data, some sort of numerical value still needs to be placed on each target species and its prey. One approach is shown in the fifth column of Table 7 ("numerical" assignment) in which linearity is assumed and trophic levels are given direct numerical units to the nearest quarter trophic step (range 1.00 for giant kelp to 4.25 for California halibut). In addition, both the trophic level system and the chemical tracer need a common starting point. The approach we took was to normalize all Cs/K data to kelp, our primary producer, yielding the set of "adjusted" Cs/K ratios listed in the last column of Table 7. The correlation between these normalized Cs/K values and the numerical trophic level assignments is high ($r = 0.998$), indicating that there is indeed a strong relationship between trophic level assignments based on feeding habits and corresponding relationships inferred from the Cs/K ratios. Work is being focused on understanding the nature of this correlation in this and other food webs.

Table 7: Comparison of assumed and assigned trophic levels, Cs/K ratios, and Trophic Level I adjusted Cs/K ratios for target organisms from western Los Angeles Harbor, June-July, 1979

Predator	Size (g)	Assumed Trophic Level	Assigned Trophic Level*	Numerical Trophic Level Assignment	Median Value (x10⁻ Cs/K	Median Value (x10⁻ Adjusted Cs/K
California halibut	284.0	IV	IV ← V	4.25	3.49	4.98
White croaker	32.0	III	III → IV	3.75	2.92	4.17
Northern anchovy	5.6	III	II → III	2.75	2.10	3.00
Gaper clam	315.0	II	II - III	2.50	1.84	2.63
Giant kelp	>10,000.0	I	I	1.00	0.70	1.00

* Arrow direction shows bias toward the indicated level rather then exactly half way between.

II. BIOMAGNIFICATION AND BIODIMUNITION OF TRACE METALS AND CHLORINATED HYDROCARBONS

A. Background

1. Introduction

Public apprehension regarding the accumulation of pollutants in seafood and other marine organisms is based largely on the assumption that food chain magnification of inorganic and organic contaminants, which has been demonstrated in certain terrestrial and freshwater systems, also occurs in marine ecosystems. However, in recent years there have been an increasing number of reports that contradict this assumption, at least in part. As described in the preceeding section, one of the objectives of this pilot program was to determine whether or not there is evidence that the food web in Los Angeles harbor is "structured", i.e., composed of distinct feeding relationships that can cause successively increased concentrations of some pollutants.

2. Trophic Step Index

As an improvement upon studies conducted during the 1950's and 1960's, Young (1970) and Isaacs (1973, and 1972) developed a chemical indicator for the degree of structure in marine food webs. The technique utilizes distributions of two alkali metals, cesium (Cs) and potassium (K); this pair of elements is of interest regarding biomagnification because Cs has been shown to have a biological half-life that is 2 to 3 times that of K, and essential electrolyte (Pendleton, 1964). Thus under equilibrium conditions the Cs/K ratio in a given organism with a specific diet should be amplified by a factor of 2-3 over this ratio in its food. Similarly, the Cs/K ratio should increase by approximately this factor over every trophic level step of a truely linear food chain.

84 m tons of copper annually are applied with antifouling paints to vessel bottoms in the harbor. Clearly, not all this copper is released to the ecosystem; nevertheless, the quantity applied is on the same order as the 116 m tons released during 1977 from the Joint Water Pollution Control Plant, Los Angeles County Sanitation District (JWPCP) municipal wastewater outfalls, 8 km to the west of the Harbcr's western entrance (Schafer, 1979). Other metals, such as cadmium, chromium, mercury, lead, and zinc also have been used as toxicants or pigments in vessel paints and primers (Young et al. 1979). Similarly, the use of zinc as anodes in cathodic protection devices for recreational vessels may well be a major source of this metal to harbor waters of the Bight--an estimated 160 m tons are used in this manner in southern California (SCCWRP, 1973; Young, 1979).

Such vessel-related uses of toxic trace metals appear to have been an important cause of the distinct contamination of water, sediments, and lower organisms which have been observed in Los Angeles harbor. In a survey of subsurface seawater collected from the westernmost mouth, we measured concentrations of dissolved chromium, copper, and nickel which, on the average, were an order-of-magnitude above estimated baseline concentrations (McDermott and Heesen, 1975; Young et al. 1978). Chen and Lu (1974) reported clearly elevated levels of a variety of trace elements in harbor sediments, and we found elevated levels of copper and other metals in whole soft tissues of the bay mussel Mytilus edulis collected there (Alexander et al. 1976; Young et al. 1979).

In addition to trace metals, 2 types of higher molecular weight chlorinated hydrocarbons occur in relatively high concentrations in Los Angeles harbor. DDT and its residues were released for up to two decades in massive quantities to the JWPCP outfall by one of the world's largest manufacturers of the pesticide (Young et al. 1976; Young et al. 1977; Young and Heesen, 1978), and polychlorinated biphenyls (PCB's) are reported to have been used extensively in paints and hydraulic fluids (Jensen, 1970; Nisbet and Sarofim, 1972). As a result, levels of total DDT and total PCB in mussels collected from the harbor in 1974 ranged up to 1.0 and 0.6 mg/wet kg (Young and Heesen, 1974; McDermott et al. 1975), and specimens collected near the western entrance concentrated these synthetic organics approximately 100,000 times above levels in the water (Young et al. 1980). In addition, the median levels of total DDT and PCB 1254 obtained from ten samples of surface seawater collected at this harbor entrance over a full tidal cycle in 1974 were 8.0 ng/liter and 2.2 ng/liter, respectively. These values are 1-4 orders of magnitude above those measured by Risebrough et al. (1976) in waters of the Pacific Ocean off Baja California and central Mexico.

B. Procedures

1. Sampling

The study area and sampling program have already been described in Part I. To minimize uncertainties caused by biological variation, the chemical program was based on the premise that, whenever possible, 5 composites of 10 or more individual organisms of the target species would be analyzed. Muscle tissue of the animals was selected as the target tissue because: 1) it is a common tissue that constitutes a significant proportion of total body mass; 2) it could be clearly separated from contaminating sediments; 3) it could be obtained in sufficient quantities from all animals for the various trace analyses to be conducted; and 4) it is the important tissue in the food chain affecting man. In addition, fronds of the giant kelp were selected for the Trophic Level I sample because, in contrast to phytoplankton, an adequate mass could be collected and washed of adhering sediment in the field.

Upon collection, the samples were placed in new polyethylene bags, labeled, sealed and returned to the laboratory within a few hours where they were frozen. Subsequently, they were weighed while still frozen, and dissected under clean conditions before thawing. Details are presented in Appendicies G and I.

2. Analysis

Four types of analytical procedures were employed in this study. The cesium analyses were made by carbon rod atomic absorption spectrometry (AAS), and required a special chemical separation and concentration procedure developed in the SCCWRP laboratory (Jan and Young, in preparation); this is summarized (along with that for potassium) in Appendix F. Analyses for the relatively non-volatile trace metals (silver, cadmium, chromium, copper, iron, manganese, nickel, lead, and zinc) were conducted by AAS (generally using the carbon rod) following hot acid digestion without subsequent chemical concentration (Appendix G). The total mercury analyses were conducted utilizing cold-vapor AAS (Appendix H), and DDT and PCB residues were measured by electron-capture gas chromatography (Appendix I).

C. Findings

1. Cs/K Ratio

Results of the individual composite analyses (Appendix E) are summarized in Table 8. The data are presented on a dry weight basis to remove effects of varying water content. Although

Table 8: Concentrations of cesium (Cs) and potassium (K) in muscle tissue of animals and fronds of kelp from western Los Angeles Harbor, June-July, 1979.

Organism	Trophic Level+	No. of Composite	Median Wt.++ (kg)	Value	Cs (µg/dry kg)	K (g/dry kg)	Cs/K ($x10^{-6}$)
California halibut	IV ← V	4	0.3	Median	76.6	22.3	3.49
				Mean	84.5	22.3	3.82
				S.E.*	13.8	0.4	0.66
White croaker	III → IV	5	0.03	Median	52.8	18.1	2.92
				Mean	55.2	18.1	3.05
				S.E.*	4.7	0.1	0.26
Northern anchovy	II → III	5	0.006	Median	39.2	20.8	2.10
				Mean	38.3	18.5	2.08
				S.E.*	6.3	2.9	0.12
Gaper clam	II - III	5	0.3	Median	23.2	12.5	1.84
				Mean	28.0	14.7	1.86
				S.E.*	6.5	2.6	0.16
Giant kelp	I	5	>10.0	Median	25.0	35.6	0.70
				Mean	23.2	33.2	0.71
				S.E.*	3.8	2.1	0.12

\+ Arrow shows bias toward the indicate level rather than exactly half way between.
++ Of whole specimens
* S.E. = Standard error

we believe that medians are better representations of central tendency of trace constituents than are means, the latter values and their standard errors also are listed to provide some indication of variation in the final concentrations. It is seen that both the concentrations and the Cs/K ratios increase monatomically with the trophic level assignments obtained independently using classical ecological techniques. Overall, the median Cs/K ratio increases by a factor of 5.0 over the 3-4 step interval between Levels I (kelp) and IV+V (halibut), indicating substantial structure in this ecosystem. Thus, both the classical trophic level approach and the newer trophic step index approach suggest the potential for food web magnification of contaminents in western Los Angeles harbor.

2. Trace Metals

Despite this fact, the data for the relatively non-volatile trace metals listed in Table 9 indicate just the opposite effect. In all cases, the measurable concentrations of metals in the highest organism (halibut, Level IV-V) are an order of magnitude below those in the lowest organism (kelp, Level I). Restriction of the comparison to animals (halibut muscle vs. clam siphon) yields the same trend, although the magnitude of the concentration differences is reduced for some metals. Further restriction of the comparison to muscle tissue of halibut and anchovy, which are at least 1 trophic level apart and also constitute a distinct predator:prey relationship, yields the following measurable consumer:diet "increase factors" (based on median values).

Cadmium	<0.8
Chromium	0.9
Copper	0.3
Iron	0.2
Mangenese	0.2
Zinc	0.5

Table 9: Concentrations (μg/dry kg) of nine trace metals in muscle tissue of animals and fronds of kelp from western Los Angeles harbor, June-July, 1979.

Organism	Trophic Level+	Value	Ag	Cd	Cr	Cu	Fe*	Mn*	Ni	Pb	Zn*
California halibut	IV ← V	Median	< 9	< 9	120	700	3.5	0.42	<160	<280	9.8
		Mean	< 9	<10	150	890	3.7	0.45	<140	<280	10
		S.E.	-	3	40	230	0.42	0.08	-	-	1.1
White croaker	III → IV	Median	19	19	80	2400	14	1.0	<160	<280	16
		Mean	21	30	90	2100	14	1.0	<160	<280	16
		S.E.	2	-	20	240	0.6	0.16	-	-	0.5
Northern anchovy	II → III	Median	<8	12	130	2300	16	2.3	<140	<240	18
		Mean	<8	36	130	2500	19	2.3	<150	<250	21
		S.E.	-	-	4	180	3.6	0.07	-	-	1.8
Gaper clam	II - III	Median	54	110	360	2700	27	1.1	740	<310	44
		Mean	81	190	360	3200	32	1.2	800	<310	46
		S.E.	30	79	30	550	4.9	0.12	150	-	2.8
Giant kelp	I	Median	62	1500	1600	6800	85	16	<560	<730	80
		Mean	64	1600	1600	6700	106	15	<900	<920	77
		S.E.	6	140	80	600	13	1.2	-	-	6.5

+ Arrow shows bias toward the indicate level rather than exactly half way between

* mg/dry kg

S.E. = Standard error

Thus, it appears that these relatively non-volatile trace metals do not biomagnify in the food web of western Los Angeles harbor, but instead are characterized by decreasing concentrations with increasing trophic position.

The one exception to this pattern occurs for total mercury (Table 10). In this case, there is a general pattern of increasing concentration with increasing trophic level. This is consistent with our findings in other ecosystems (Young and Mearns, 1979; Mearns and Young, 1979). In particular the halibut muscle contains 4.6 times as much total mercury as does muscle tissue of the anchovy, and 3.3 times as much total mercury as siphons of the gaper clam.

3. DDT's and PCB's

Increasing concentrations of the higher molecular weight chlorinated hydorcarbons with trophic position also was observed (Table 10). For example, levels of total DDT measured in halibut and white croaker (approximate Level IV) on both dry weight and lipid weight basis were 2 orders of magnitude above those in kelp fronds, and PCB 1254 concentrations were 1 to 2 orders of magnitude higher. These fishes also had dry weight concentrations of DDT and PCB residues that were 5-20 times above average levels measured in the clam and anchovy, and the halibut:anchovy increase factors on the two bases were:

	Dry Weight	Lipid weight
Total DDT	3.9	2.9
1254 PCB	3.7	3.0

These increase factors are very similar to those observed for total mercury. Our previous studies of nearshore exosystems (Young and Mearns, 1979) have shown that virtually all of the measurable

Table 10: Concentrations of total mercury, total DDT, and PCB 1254 in muscle tissues of animals and fronds of kelp from western Los Angeles harbor, June-July, 1979.

Organism	Trophic Level+	Value	μg/dry kg			μg/g lipid		Dry/Wet Wt. (%)	Lipid/Wet (%)
			Total Hg	Total DDT	1254 PCB	Total DDT	1254 PCB		
California halibut	IV ← V	Median	400	1800	590	27	9.6	22	1.4
		Mean	410	1800	570	29	9.1	22	1.4
		S.E.*	39	110	73	2.7	1.2	0.2	0.06
White croaker	III → IV	Median	180	2500	2100	37	29	21	1.6
		Mean	210	3900	2400	52	36	21	1.5
		S.E.*	41	1600	410	15	5.4	0.1	0.2
Northern anchovy	II → III	Median	88	460	160	9.4	3.2	25	1.2
		Mean	98	490	160	10	3.3	25	1.2
		S.E.*	15	56	9	1.4	0.25	0.7	0.04
Gaper clam	II - III	Median	120	190	39	4.7	0.93	19	0.75
		Mean	128	190	53	4.9	1.5	19	0.77
		S.E.*	12	15	13	0.62	0.52	0.4	0.07
Giant kelp	I	Median	110	16	51	0.36	1.3	8.0	0.28
		Mean	110	22	49	0.60	1.4	7.9	0.30
		S.E.*	15	9	4.4	0.22	0.26	0.5	0.04

+ Arrow shows bias toward the indicate level rather than exactly half way between

* S.E. = Standard error

mercury in such samples is in an organic form. This may explain the similarities observed between our measurement of total mercury, total DDT, and PCB 1254.

III. LEVELS OF BENZO(a)PYRENE

A. Background

Oceans serve as repositories for various organic compounds which occur as environmental contaminants. The levels of these pollutants in the ocean and marine animals are important because of detrimental effects directly on marine ecosystems and because of possible public health implications to man by virtue of his consumption of contaminated seafoods (Dunn and Stich, 1975). Of particular interest are those compounds known to be carcinogenic to mammals. The most widely studied carcinogen is benzo(a)pyrene (BaP), perhaps due to its ubiquitous presence in our environment. Wide spread accumulation of BaP has resulted from its synthesis as an unavoidable by-product of incomplete combustion. Sources of BaP contamination of oceans include: shipping (exhaust, creosoted pilings), oil (spills, natural seepage), atmospheric fall-out, and land run-off (National Academy of Sciences, 1972; Dunn and Young, 1976; Pancirov and Brown, 1977).

BaP is a member of a class of compounds termed polycyclic aromatic hydrocarbons (PAH) which requires metabolism by a mixed-function oxidase (MFO) enzyme system to its active, ultimate carcinogenic form. MFO normally functions in the metabolism and eventual excretion of endogenous substances such as steroids, and xenobiotics such as pesticides and PAH (Conney, 1967; Gelboin, 1967). However, MFO (or aryl hydrocarbon hydroxylase {AHH} when pertaining to PAH) produce reactive intermediates known as diol epoxides which bind to cellular macromolecules such as DNA to exert their carcinogenic action (Grover and Sims, 1973; DePierre and Ernster, 1978).

BaP has been measured in a wide variety of marine organisms and sediments around the globe (Zobell, 1971). Reports also vary extensively as to levels of BaP, ranging from near the limit of detectibility, 0.1 parts per billion (ppb), up to 2200 ppb in invertebrates (Dunn and Young, 1976; Piccinetti, 1967). Plankton and seaweeds varied tremendously as to BaP content ranging from traces up to 440 ppb dry weight (Mallet and Priou, 1967; Niaussat and Auger, 1970). Flounder and menhaden caught in the Atlantic Ocean contained less than 2 ppb wet weight while angler fish inhabiting the Adriatic Ocean had BaP levels of 40 ppb dry weight (Pancirov and Brown, 1977; Piccinetti, 1967).

Preliminary studies of mussels (*Mytilus californianus*) within the Los Angeles arbor revealed high levels of BaP in their soft tissues. Levels of BaP ranged from 1 ppb (μg/kg wet tissue) in mussels when sampled from areas of relatively clean waters up to 250 ppb in mussels collected in intertidal areas contaminated with oil products (unpublished data).

The possibility of biomagnification of BaP within the food chain has not been previously reported although other hydrocarbons (such as DDT) do tend to biomagnify through the trophic levels from water and plants to higher predators (Keith and Hunt, 1966; Woodwell *et al*. 1967; Young and Mearns, 1979). The problem of possible BaP biomagnification was addressed in this study by measuring the levels of BaP in selected organisms representative of trophic levels I through IV-V collected within the western Los Angeles Harbor area.

B. Methods

Organisms and sediments were collected as described in Part I. Tissues were protected from light, frozen and stored at -10°C prior to analysis. The analytical procedure was that of Dunn (1976) with the exception of the following modifications. The sample material was thawed and aliquot (3-4g) was placed in an oven (60°C) for 48 hours to determine water content. Digestion of the samples was accomplished in a KOH/ethanol mixture with refluxing for 1.5 hours. This digestion mixture was then extracted with 4 x 50ml hexane. The hexane extracts were combined, washed and rotary evaporated to 10ml for column chromatography. The column (15 x 300mm) with a coarse fritted disc was prepared with 6 g silica (activated with 2% water) covered by 2g Na_2SO_4 in hexane. The sample was passed through and washed with 30ml hexane. BaP and other PAH were eluted with 40ml toluene. The toluene was reduced to 5ml by rotary evaporation, 25ml methanol was added and again reduced to 5ml, 25ml hexane was added and finally reduced to 5ml.

This 5ml hexane was extracted with 3 x 5ml DMSO and back extracted into 2 x 10ml hexane. This hexane extract was reduced to 0.1ml, applied to a thin layer plate, and developed for 5 hours in a vacuum developing tank. BaP was visualized under long-wave fluorescence and eluted into methanol.

Levels of BaP were measured fluorimetrically in hexadecane. Losses during procedures were calculated by counting the recovery of the internal tracer of radioactive BaP added at initiation of the assay. These correction factors were used to determine the net amount of BaP following analysis by fluorimetry. All procedures were conducted under yellow filtered (ultraviolet absorbing) light.

Radioactively labelled benzo(a)pyrene (G-^{3}H-benzo(a)pyrene) with a specific activity of 25 Ci/mmole was obtained from Amersham/Searle. Silica Gel60 (70-140 mesh) and the 20 x 20cm thin layer plates (30% acetylated 0.1mm) on plastic were acquired from Macherey and Nagel Company. KOH and Na_2SO_4 were reagent grade. All solvents were spectrograde from Burdick and Jackson.

C. Findings

Results of the assays are summarized in Table 11. Levels of BaP are expressed on both a dry and a wet weight basis in parts parts per billion (ppb). However, BaP is discussed in dry weight terms since there is variation in water content between different samples and from handling methods; also BaP which is highly lipophilic is associated with the dry tissue fraction and not the water portion. Wet weight values are included for comparison to previous studies.

From these data (Table II) there exists an inverse relationship between the levels of BaP (dry weight) and the trophic level. That is, decreasing amounts of BaP are found in predators in the higher trophic levels, when compared to amounts found in either plants or filter-feeding organisms. Also within bony fishes there is a significant difference in the content of BaP in the zooplankton-feeding anchovy (55.1 ppb) versus benthic and nekton-feeding fish such as croaker or halibut, (8.1 and 7.0 ppb respectively) This finding is in agreement with the work of Piccinetti (1967) who reported BaP in higher amounts and in a higher percentage of plankton feeders than in higher trophic level feeders. However, these results differ from the direct relationship of increasing quantities of certain hydrocarbons (such as DDT) with increasing trophic levels. We speculate that these findings may correlate with the ability of each organism to metabolize BaP to water-soluble forms (which are not measured by this assay) for excretion.

Inert sediments tend to accumulate BaP from several sources, although recent evidence suggests that microorganisms present in polluted areas possess the ability to metabolize BaP (Farrington and Meyers, 1975). Mussels (Mytilus edulis) have been shown not to actively metabolize BaP, although such bivalves release this

Table II: Concentrations[+] of BaP in sediments and tissue of organisms from western Los Angeles Harbor, June-July, 1979.

Sample	Tissue Analyzed	Trophic Level+	% Dry Weight++	Number of Determinations*	BaP Wet Weight	BaP Dry Weight**
California halibut (*Paralichthys californicus*)	muscle	IV ← V	21.3±0.4	4(20)	1.5±0.3	7.0±1.7
	liver	"	21.4±0	2(10)	3.4±0.4	15.9±2.0
	GI tract	"	20.7	1(5)	1.4	6.9
Brown pelican (*Pelecanus occidentalis*)	muscle	III → IV	33.0±0.5	1(1)	0.1	0.2
White croaker (*Genyonemus lineatus*)	muscle	III → IV	21.5±0.8	5(25)	1.7±1.0	8.1±4.9
Northern anchovy (*Engraulis mordax*)	muscle	II → III	32.7±8.4	3(45)	18.7±8.8	55.1±25
Gaper clam (*Tresus nuttallii*)	siphons muscle	II - III	20.6±1.5	5(25)	8.8±2.5	43.0±15
Giant kelp (*Macrocystis pyrifera*)	fronds	I	7.7±0.2	5(5)	5.4±2.8	69.1±24
Sediments	upper 2 cm	-	45.6±1.6	3(3)	148.5±41	343.9±124

\+ Error

++ Mean ± standard deviation.

* Total number of organisms or samples composited for determinations is indicated in parenthesis, eg.: 5(25) indicates 5 determinations, each determination is a composite of 5 samples.

** Expressed as part per billion (ppb) or micrograms per kilogram tissue weight.

compound when transferred to clean waters (Lee et al. 1972; Dunn and Stich, 1976). Thus clams (also members of the class Mollusca) would show higher levels of BaP because they bioaccumulate it by filter feeding and do not metabolize this compound. There is a dearth of investigation of BaP hydroxylase activity in plants, although one paper reports no activity in phytoplankton (Malins, 1977). Coupling this with the possibility that certain plants (algae) are able to biosynthesize BaP and other PAH, the high levels in kelp are plausible (Borneff et al, 1968).

The NIEHS laboratory (Triangle Park, N. Carolina) has characterized BaP hydroxylase activity in many organisms on the east coast, particularly in crustaceans and fishes. Their studies indicate that more primitive fishes (such as elasmobranchs) generally have lower BaP hydrozylating activities than do more evolved (e.g. bony) fishes (Bend et al. 1977). Also, due to its inducible nature, BaP hydroxylase activity may be increased in individuals exposed previously to numerous contaminants such as PAH (Bend et al. 1978). Anchovy are relatively less evolved in comparison to halibut and may possess less activity in metabolizing hydrocarbons, leading to an accumulation of BaP in its tissue. Also white croaker and California halibut, due to their feeding contact with sediments high in contaminants (such as PCB and DDT), may live in a perpetually induced state which increases their ability to alter BaP (James and Bend, 1977).

One pelican sample available for analysis contained the lowest levels of BaP (0.2 ppb). This low concentration is reasonable when considering a study on the class Aves (chicken embryo) which found the BaP hydroxylating activity to be comparable to that of mammals (Jellinck and Smith, 1973). However, these speculations require substantiation by measuring AHH activity in those organisms sampled in correlation to their BaP levels. This will be essential in light of the varying exposures to inducing agents that each fish may encounter.

In conclusion benzo(a)pyrene was measured in marine sediments and organisms representing trophic levels I-IV near Cabrillo Beach in the western Los Angeles Harbor. Data indicate an inverse relationship exists between levels of BaP and the trophic levels of the organisms. Decreasing values of BaP in organisms of higher trophic levels may be related to their increasing ability to actively metabolize BaP for excretion.

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Appendix A: Summary of abundance(N), frequency(F), estimated relative volume(V) and indicies of relative importance (IRI)* of items in stomachs of 9 northern anchovy (Engraulis mordax) from San Pedro Bay, 1978.

Item	Abundance		Frequency		Estimated relative volume	Indicies o of relative importance (IRI)
	N	%N	F	%F	%V	N
Unidentifiable Particulates	4448	62.9	9	100	70.0	13290.0
Crustacea parts	2301	32.5	9	100	25.0	5750.0
Whole Crustaceans						
Unidentifiable	9	0.13	5	56	<0.01	7.84
Juvenile Euphausids	41	0.58	8	89	1.0	141.0
Copepods	35	0.44	8	89	0.1	53.0
Cladocerans	20	0.28	8	89	1.0	113.9
Shrimplike crustaceans	3	0.04	3	33	0.1	4.62
Zoea	3	0.04	3	33	0.01	1.65
Nauplii	5	0.07	2	22	0.01	1.76
"Square" copepod	1	0.01	1	11	<0.01	.22
Insect wings	4	0.06	3	33	0.1	5.28
Sticks	3	0.04	2	22	0.01	1.11
Eggs	136	1.92	9	100	0.1	202.0
Salps	3	0.04	3	33	0.01	1.65
Bivalves	4	0.06	3	33	0.01	2.31
Gastropods	1	0.01	1	11	0.01	.22
Hydroids (medusa)	1	0.01	1	11	0.01	.22
Phytoplankton						
Filamentous algae	4	0.06	4	44	0.001	2.68
Diatoms	22	0.31	4	44	0.001	13.68
Dinoflagellates	2	0.02	2	22	0.001	0.46
Total	7076					19592.0

* IRI = %F (%N + %V)
where %F = percent of predators with food item
%N = percent of contribution of food items by number
%V = percent contribution of food items by volume

Appendix B: Summary of abundance(N), frequency(F) estimated relative volume(V), and indicies of relative importance (IRI)*of items in stomachs of 14 white croaker (Genyomenus lineatus) from western Los Angeles harbor. Mean weight 27.6g (22.2-39.2g), mean standard length (S.L.), 110mm (100-122mm).

Item	Abundance		Frequency		Estimated Volume**		Indicies of Relative Importance	
	N	%N	F	%F	V	%V	IRI	%IRI
Polychaetes (b)	27+	5.0	7	50.0	270	1.8	340	3.9
Pelecypods (c)	36+	6.6	10	71.0	3600	24.5	2208	25.3
Gastropods (c)	9	1.7	4	28.6	900	6.1	223	2.6
Crustaceans:	464	85.1	14	100.0	3883	26.5	4129	47.4
Unidentifiable	1+	0.2	1	7.1	N.C.			
Cladocerans (a)	64+	11.7	7	50.0	64	0.4	605	6.9
Ostracods (a)	29+	5.3	6	42.9	29	0.2	236	2.7
Cumaceans (b)	81+	14.9	4	28.6	810	5.5	583	6.7
Caprellid (b)	249+	45.7	5	35.7	2490	17.0	2238	25.7
Amphipods (b)	8	1.5	5	35.7	80	0.5	71	0.8
Mysids (c)	1	0.2	1	7.1	100	0.7	6	<0.1
Shrimp (c)	31+	5.7	7	50.0	310	2.1	390	4.5
Fish (d)	6+	1.1	6	42.9	6000	40.9	1802	20.7
Thread/Metal (b) (artifats)	3	0.6	3	14.3	30	0.2	11	0.1
Total	545				14683		8713	

* IRI = %F (%N + %V)
where %F = percent of predators with food item
%N = percent of contribution of food items by number
%V = percent contribution of food items by volume

** Relative volume estimated by assigning scores as follows
(a) "small" crustaceans, etc. = 1
(b) "medium" crustaceans, etc. = 10
(c) "large" crustaceans, etc = 100
(d) "fish" = 1000

Appendix C: Summary of abundance(N), frequency(F), estimated relative volume(V) and indicies of relative importance (IRI)* of items in stomachs of 27 California halibut (Paralichthys californicus) from western Los Angeles harbor. Mean weight 204g (111-586), mean standard length (S.L.) 265mm (208-327).

	Abundance		Frequency		Estimated Volume		Indicies of Relative Abundance	
Item	N	%N	F	%F	V**	%V	IRI	%IRI
Shrimp	1	5.3	1	3.7	1.0	2.2	43.5	0.8
Anchovy	8	42.1	6	22.2	20.0	43.4	2762.0	48.2
Gobies	3	15.8	3	11.1	7.5	16.3	433.0	7.6
Unidentified fish	7	36.8	8	29.6	17.5	38.0	2488.0	43.4
Total Fish	18	94.7	15	55.6	45.0	97.8	5683.0	99.2

* IRI = %F (%N + %V)
where %F = percent of predators with food item
%N = percent of contribution of food items by number
%V = percent contribution of food items by volume

** Assumed average weight (volume) of 30 to 80g small fish = 2.5g (2.5ml).

Appendix D: Summary of mean standard lengths (S.L.), mean weights (g), abundance(N) frequency(F), estimated relative volume(V) and indicies of relative importance (IRI)* items in stomachs of California halibut (*Paralichthys californicus*) from west Los Angeles harbor. Fish food items were: anchovy, (8, 20 to 80mm); gobies (3, 35mm) and 7 unidentifiable small fish remains.

	Composite Identification Number (quantity in composite)			
	220 (8)	221 (8)	222 (5)	223 (6)
SL	214.4	243.0	287.0	318.0
S.E.	±2.56	±1.91	±5.6	±4.7
g **	151.1	213.0	348.1	524.0
S.E.	±8.67	±3.38	±18.5	±19.8
Fish				
N (%)	7(87.5)	¢(100%)	2(100%)	3(100%)
F (%)	5(63%)	5(63%)	2(40%)	3(50%)
V (%)	17.5(94.6)	15(100)	5(100%)	7.5(100%)
Crustacean				
N (%)	1(12.5)	0	0	0
F (%)	1(12.5)	0	0	0
V (%)	1(5.4)	0	0	0
IRI Fish				
IRI Fish	11472.0	12600	8000	10,000
IRI Crustacean	224.0	0	0	0
%IRI Fish	98.1	100	100	100
%IRI Crustacean	1.19	0	0	0

* IRI = %F (%N + %V)
where %F = percent of predators with food item
%N = percent of contribution of food items by number
%V = percent contribution of food items by volume

** S.E. = Standard error

Appendix E: Sample description and corresponding muscle tissue concentration (dry weight basis) for organisms from western Los Angeles harbor, June-July, 1979.

Composite Identification Number	Common Name	Scientific Name	Date Collected	Method of Collection	Standard length* (cm)	Total length* (cm)	Total weight* (g)	Number of individuals	Dry weight (%)	Lipid (%)
220	California	Paralichthys	6-05-79	Bottom trawl	21.8	25.8	167	8	21.5	1.45
221	Halibut	californicus	6-14-79		24.4	27.8	214	8	21.1	1.20
222					28.2	33.4	365	5	21.9	1.45
223					31.6	37.0	507	6	21.9	1.39
254	White	Genyonemus	6-14-79	Bottom trawl	12.6	14.9	43.6	12	21.8	2.03
255	Croaker	lineatus			12.0	14.4	34.2	12	21.0	0.83
256					11.4	13.6	32.4	12	21.4	1.73
257					10.8	13.0	24.6	12	21.6	1.17
258					10.4	12.0	23.6	15	21.3	1.57
227p	Northern	Engraulis	7-11-79	Bait Barge	8.6	10.0	5.9	11	-	-
228p	Anthovy	mordax			8.2	9.8	5.5	9	-	-
229p					8.6	10.4	6.6	8	-	-
230p					8.0	9.4	5.3	7	-	-
231p					8.2	9.9	5.4	9	-	-
227g					7.6	9.1	4.8	19	25.4	1.14
228g					8.4	9.8	5.6	12	22.2	1.34
229g					8.2	9.8	5.2	10	25.0	1.18
230g					8.0	9.4	4.8	10	25.4	1.19
231g					8.2	9.8	5.4	14	26.7	1.17
244	Gaper Clam	Tresus	7-10-79	Hand Collected	-	15.0	494	4	18.3	0.66
245		nuttallii			-	10.6	207	4	19.4	0.82
246					-	12.0	273	4	20.3	0.60
247					-	10.8	248	4	20.3	1.01
248					-	11.9	324	4	18.6	0.75
249	Giant Kelp	Macrocystis	7-10-79	Hand Collected	-	-	-	-	8.09	0.41
250					-	-	-	-	9.52	0.24
251					-	-	-	-	6.48	0.28
252					-	-	-	-	7.98	0.36
253					-	-	-	-	7.59	0.22

* -median value

Appendix E (Continued)

Composite Identification Number	Cs (µg/kg)	K (g/kg)	Cs/K ($x10^{-6}$)	Total Hg (mg/kg)	p,p[1]-DDE (mg/kg)	Total DDT (mg/kg)	1254 PCB (mg/kg)	Total PCB (mg/kg)
220	61.9	23.3	2.66	0.340	1.60	1.78	0.730	0.883
221	67.8	22.7	2.99	0.346	1.74	2.08	0.630	0.734
222	85.4	21.4	3.99	0.457	1.68	1.84	0.553	0.663
223	123.0	21.9	5.62	0.493	1.47	1.53	0.384	0.580
254	46.8	17.9	2.61	0.206	9.23	10.2	3.87	4.29
255	48.6	18.4	2.64	0.143	1.74	2.01	2.14	2.39
256	52.8	18.1	2.92	0.178	2.50	2.97	2.28	2.51
257	73.2	18.2	4.02	0.162	1.38	1.56	1.37	1.67
258	54.5	17.9	3.04	0.371	2.06	2.54	2.12	2.44
227p	51.6	22.8	2.26	-	-	-	-	-
228p	39.2	23.6	1.66	-	-	-	-	-
229p	48.8	20.8	2.35	-	-	-	-	-
230p	16.1	7.68	2.10	-	-	-	-	-
231p	35.6	17.6	2.02	-	-	-	-	-
227g	-	-	-	0.083	0.650	0.689	0.181	0.401
228g	-	-	-	0.140	0.428	0.495	0.162	0.284
229g	-	-	-	0.092	0.408	0.464	0.132	0.144
230g	-	-	-	0.075	0.366	0.441	0.169	0.220
231g	-	-	-	-	0.318	0.352	0.142	0.262
244	53.0	25.2	2.10	0.082	0.219	0.235	0.055	0.055
245	23.2	12.6	1.84	0.144	0.160	0.196	0.031	0.077
246	27.6	12.0	2.30	0.123	0.163	0.172	0.103	0.206
247	17.2	12.5	1.38	0.099	0.118	0.143	0.039	0.049
248	18.8	11.3	1.66	0.140	0.156	0.188	0.038	0.113
249	13.6	38.1	0.36	0.087	0.004	0.006	0.032	0.343
250	15.8	28.3	0.56	0.063	0.005	0.008	0.051	0.246
251	34.0	35.6	0.96	0.154	0.039	0.056	0.056	0.216
252	27.6	28.1	0.98	0.113	0.014	0.016	0.051	0.376
253	25.0	35.7	0.70	0.119	0.017	0.026	0.055	0.146

Appendix E (Continued)

Composite Identification Number	Ag (mg/kg)	Cd (mg/kg)	Cr (mg/kg)	Cu (mg/kg)	Fe (mg/kg)	Mn (mg/kg)	Ni (mg/kg)	Pb (mg/kg)	Zn (mg/kg)
220	<0.009	0.014	0.256	1.58	3.48	0.684	<0.17	<0.29	13.6
221	<0.009	<0.005	0.104	0.720	4.95	0.460	0.095	<0.28	8.86
222	<0.009	0.014	0.132	0.575	3.00	0.388	<0.16	<0.27	9.54
223	<0.009	<0.005	0.105	0.689	3.48	0.283	<0.15	<0.26	10.1
254	0.028	0.009	0.096	2.50	14.9	1.05	<0.16	<0.27	15.9
255	0.024	0.024	0.167	1.68	11.9	0.519	<0.16	<0.27	15.7
256	0.019	0.093	<0.06	1.35	12.0	1.49	<0.17	<0.29	13.8
257	0.019	0.019	0.079	2.53	14.0	1.19	<0.16	<0.28	16.2
258	0.014	<0.005	0.070	2.35	14.5	0.920	<0.16	<0.28	16.5
227	<0.008	0.004	0.118	3.09	12.2	2.34	<0.14	<0.24	26.5
228	<0.009	<0.005	0.135	2.20	14.6	2.54	<0.16	<0.28	17.4
229	<0.008	0.012	0.128	2.20	16.2	2.44	<0.14	<0.25	18.1
230	<0.008	0.039	0.142	2.74	17.3	2.20	<0.14	<0.24	18.2
231	<0.007	0.120	0.127	2.30	32.5	2.21	0.165	<0.23	24.0
244	0.175	0.104	0.361	2.74	50.3	1.68	0.557	<0.33	41.6
245	<0.010	0.082	0.325	5.28	25.7	1.04	1.25	<0.31	44.0
246	0.128	0.108	0.493	3.45	23.7	1.26	0.744	<0.30	51.8
247	0.039	0.138	0.350	2.29	27.0	1.09	1.03	<0.28	39.1
248	0.054	0.500	0.430	2.36	35.0	1.10	0.425	<0.33	53.6
249	0.062	1.48	1.56	5.78	85.3	13.2	<0.82	<0.68	64.4
250	0.042	1.29	1.40	4.99	78.6	11.6	<0.35	<0.60	59.6
251	0.062	2.02	1.40	8.13	15.2	17.9	<0.56	1.11	92.7
252	0.075	1.42	1.82	6.84	100.0	16.0	<0.43	<0.73	80.0
253	0.079	1.86	1.65	7.85	112.0	17.5	2.34	1.48	88.1