

Nearshore Dredge-Spoil Dumping and Cadmium, Copper, and Zinc Levels in a Dermestid Shrimp

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Dumping of dredge spoil in nearshore waters is seen as an economically viable method of disposing of large volumes of essentially useless material. This method becomes especially attractive when examined in the perspective of an island situation where land is scarce, costly, and primarily limited to residential and other priority properties. The long-term impact of the operation on the ecological stability of aquatic communities, however, is uncertain. In light of man's growing use of the ocean as a repository for waste materials, the need to understand these impacts is increasingly urgent.

A dermestid shrimp of potential commercial importance, *Heterocarpus ensifer*, was chosen as an indicator organism to monitor possible changes in population characteristics and to observe potential changes in the retention of certain environmentally important metal residues. Ecological dynamics of this population are described elsewhere (CHAVE & MILLER 1977). Cadmium, copper, and zinc residue levels were evaluated in a control-site population and a dredge spoil dumping-site population over a period of two years active dumping to determine any modification in the bioaccumulation of these metals.

MATERIALS AND METHODS

Shrimp trapping stations were located at approximately 21°16'N and 157°57'W or 2 mi. south of the entrance to Honolulu Harbor, Oahu, Hawaiian Islands. Sampling was accomplished by setting strings of ten traps over the control and dump sites at an average depth of 230 fathoms (503 m). There were two sampling periods, one at the end of each year of active dumping. Animals collected during the first sampling period were segregated by sex and frozen for later analysis. Shrimp that were trapped during the second sampling period were fewer in number and remained in aggregate. Specimens analyzed for the first year's data were thawed, gravid females; the second year's group were fresh and of mixed sex.

All samples were oven dried at 104°F (40°C) for 60 h to insure thorough volatilization of all water and most of the lipid fraction. This effectually reduced the mass of an equivalent wet

sample to one-fifth. Destruction of organic matter in the samples was accomplished by wet digestion in the following manner (GORSUCH 1970). Animals from each trap were ground by mortar and pestle to a fine powder. Two 1 g aliquots from each trap were solubilized with hot nitric acid and hydrogen peroxide for oxidation. After final reflux and cooling, the samples were filtered through #40 filter paper and brought to volume with distilled water. Analyses for cadmium, copper, and zinc were performed under standard conditions using an atomic absorption spectrophotometer. Authentic metal standards were prepared daily.

RESULTS

Results from all analyses are summarized in Tables 1 and 2.

Table 1. Total Metals Recovered in ppm-Control and Dump Sites 1978 and 1979

	<u>1978</u>	<u>1979</u>
\bar{x} Copper control	103, s.d. 40	159, s.d. 32
\bar{x} Copper dumpsite	157, s.d. 36	180, s.d. 38
\bar{x} Zinc control	37, s.d. 17	65, s.d. 7
\bar{x} Zinc dumpsite	47, s.d. 12	59, s.d. 10
\bar{x} Cadmium control	7, s.d. 5	22, s.d. 6
\bar{x} Cadmium dumpsite	11, s.d. 6	23, s.d. 5
\bar{x} Sum Metals Recovered		
Control	147	245
Dumpsite	214	261

Table 1 shows the total concentration of copper, zinc, and cadmium recovered from the shrimp in the two sample periods. More total metals were recovered in the second year of sampling for each metal examined. The differences are not significant and can be attributed to the condition of the shrimp tissue at the time of preparation for analysis. The freezing of the first year's samples may have caused cell lysis, resulting in a loss of contents, and, therefore, a decrease in the amount of metals recovered after volatilization. To improve analytical sensitivity in the future, it is suggested that samples be dried and pulverized prior to freezing.

Taken alone, the amount of total metals recovered do not yield much insight into any dynamic ecological processes which may have been altered by the dredge spoil dumping. Table 2 breaks down the recovery by percent of each metal recovered, and the ratio of zinc and cadmium to the most abundant metal, copper.

Table 2. Metal As Percent Total Recovered and Ratio of Zinc and Cadmium to Copper

			<u>1978</u>			<u>Ratio</u>		
			<u>Cu</u>	<u>Zn</u>	<u>Cd</u>	<u>Cu</u>	<u>Zn</u>	<u>Cd</u>
Control								
n=9	% total		70.5	24.8	4.9	1	0.30	0.006
	s.d.		5.8	5.6	1.9		0.076	0.023
Dumpsite								
n=7	% total		73.1	22.0	4.7	1	0.36	0.068
	s.d.		3.6	4.7	1.7		0.11	0.028
			<u>1979</u>			<u>Ratio</u>		
			<u>Cu</u>	<u>Zn</u>	<u>Cd</u>	<u>Cu</u>	<u>Zn</u>	<u>Cd</u>
Control								
n=9	% total		64.4	26.8	8.8	1	0.42	0.14
	s.d.		4.8	3.0	2.2		0.083	0.047
Dumpsite								
n=7	% total		67.7	22.5	9.8	1	0.34	0.15
	s.d.		3.5	4.5	2.8		0.081	0.042

In both samples the distribution of metals is equivalent for the control and the dumpsite. The ratio of zinc and cadmium to copper is also essentially identical. For the animals examined in the second year at both sites there is a noticeable redistribution of metals, with cadmium displacing copper in the tissues. This substitution of cadmium for copper seen in the second sampling period effectively doubled the percentage of that metal found in the previous sample, while reducing the net copper content by 9%. The zinc content as a percentage of the total remained constant over the two year period. For the 1979 sample, the ratios of zinc and cadmium to copper increase because of the net decrease in the amount of copper. The increase in the ratio of cadmium to copper is active while that of zinc is passive. That is, zinc increases in relation to copper because the copper content decreases overall. The ratios for the control and dumpsite are negligibly different for both year's results.

DISCUSSION

Many organisms selectively accumulate a variety of trace elements that are thought to be essential to life processes. The metals discussed in this paper interact with marine biota, especially crustacea, in varied ways (EISLER 1972, JONES 1975, SAWARD 1975, NIMMO 1977). Some metals such as cadmium have no known role

in biological systems and may compete with, and displace, other metals that have known metabolic functions. A few metals such as copper and zinc participate in many physiological activities in the organism. Crustaceans employ copper as their respiratory pigment, hemocyanin. Zinc is commonly found in the tissues and has been suggested to be important in molting and muscle contraction, although its actions are, in general, not well understood. Accumulation of metals in fats and proteins can be expected to occur in organisms without viable mechanisms for elimination, such as crustaceans. In this case, the elements are conserved in ecosystems as they are passed throughout the food web. Those which are incorporated into the animal's skeleton have shorter lifetimes in an ecosystem and would be transferred to the bottom sediments instead (BOWEN 1966).

Sources of copper and zinc in dredge spoil and seawater are too varied and numerous to adequately delineate. It is unlikely that normal harbor operations would significantly add to the ambient levels of these metals either in the water or in the dredge spoil material. Cadmium however, is usually a contaminant in aquatic systems and is introduced by man. Cadmium is a common alloy of copper and zinc and is used in electroplating to impart corrosion-resistance to metal. It is also incorporated in anti-fouling marine paints to inhibit the growth of barnacles etc. on ships. Salt water is slightly acidic and it leaches cadmium as well as other metals.

Marine crustaceans regulate the concentrations of copper and zinc within their tissues. Copper content changes primarily with the amount of protein or solids in the blood. Zinc is distributed more widely and tissue concentrations remain fairly constant. To maintain zinc stasis, the metal is readily absorbed from the stomach and in some species, directly across the body surface. The ratio of zinc to copper is variable between species. The absolute zinc content in marine crustaceans has been estimated as 10^4 times that of an equal weight of ambient seawater (BRYAN 1968).

Cadmium is thought to interact with zinc and other metals of similar valence. Because cadmium is of group IIb in the periodic table, it is speculated that it is able to interfere with the metabolic function of zinc. Likewise, cadmium occurs in the ionic form as Cd^{+2} and binds to sulfhydryl moieties, as do other heavy metals including copper. It may be able to interfere with any common or essential divalent metal.

Since there was no apparent difference between the distribution of cadmium, zinc, or copper in either the control or the dumpsite groups it can be concluded that shrimp in the dumpsite area did not excessively accumulate these metals. Dredge spoil dumping may have had an effect on the relative distribution of

metals within the shrimp, with cadmium substituting for copper, but, likewise, the analyses may have detected a trend very independent of dredge spoil disposal in the area.

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