

## VARIATIONS IN THE BIOACCUMULATION OF ZINC, COPPER, AND LEAD IN *Crassostrea virginica* AND *Ilyanassa obsoleta* IN MARINAS AND OPEN WATER ENVIRONMENTS

JAMES E. BYERS<sup>1</sup>

Duke University Marine Laboratory,  
Pivers Island, Beaufort, NC 28516

**Abstract:** The effect of marina-associated pollutants, specifically zinc, copper, and lead, on accumulation levels in the oyster, *Crassostrea virginica*, and the mud snail, *Ilyanassa obsoleta*, was studied. Oysters and mud snails living in marinas were found to have significantly increased levels of zinc and copper as compared to open water organisms. Lead values were significantly higher in open water oysters. *I. obsoleta* showed no differences in lead concentrations.

**Key Words:** lead; zinc; copper; marinas; *Crassostrea virginica*; *Ilyanassa obsoleta*.

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### INTRODUCTION

The effects of marina pollution on marine organisms are sparsely documented. The EPA states that marine plant and animal communities are sensitive to the effects of marina operation, but that the effects of low level pollutant discharges are poorly known (USEPA, 1984). Only recently has some data been presented to address marina contaminants (Marcus and Thompson, 1986; Adair, 1987). To this end, the present measurements attempt to document further the impact of marinas on the heavy metal accumulations of two organisms that live there.

It was hypothesized that Zn, Cu, and Pb would be enriched in the tissues of the marina organisms *Crassostrea virginica* and *Ilyanassa obsoleta* in comparison to conspecifics from open water environments.

Although some physical factors can influence the biological uptake of various metals in some marine organisms (Lloyd, 1965), given the small range and time frame over which *Crassostrea virginica* and *Ilyanassa obsoleta* were sampled, proximity to a marina was assumed to be the most influential factor. Zn, Cu, and Pb enter the marine environment at marinas in different ways. High levels of Cu used in antifouling paints on boat bottoms and channel markers are added to the water through dissolution. Cu and Pb are known to be outboard motor contaminants which enter the water during motor operation. As much as 55% of the original fuel can be discharged into the water (Jackivicz and Kuzminski, 1973). These rates of discharge, however, are probably decreasing due to increased efficiency of outboard motors and a decrease in the use of leaded gas. Sacrificial

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<sup>1</sup> Present address: Institute of Marine Sciences, University of North Carolina, Morehead City, NC 28557.

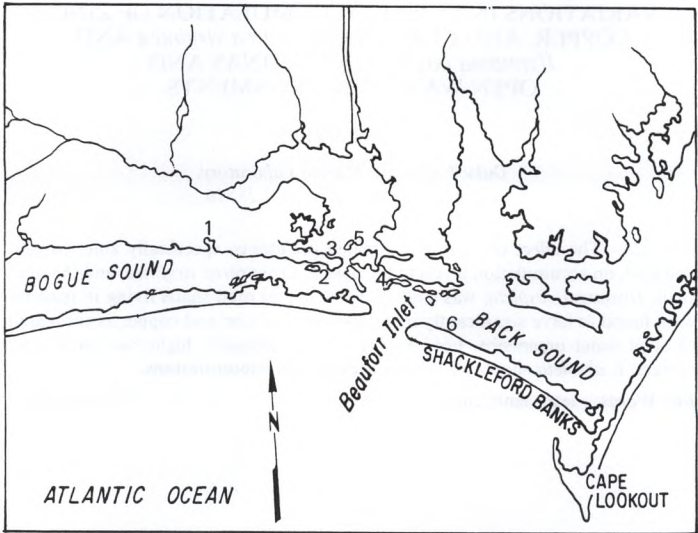


FIG. 1. Collection Sites. *Marinas*: 1—Peletier Creek; 2—Morehead City Waterfront; 3—Morehead City Yacht Marina. *Open Waters*: 4—Bird Shoal; 5—Phillip's Island; 6—Shackleford Banks.

Zn, which is added to steel structures and steel boat bottoms to prevent rusting of the steel, contributes to elevated Zn levels in marinas. Finally, surface runoff, particularly from the marina work area, can contain high levels of Zn, Cu, and Pb and may significantly contaminate the water in marinas (USEPA, 1975; Shiver and Register, 1978). Sandblasting and painting debris contain high levels of these metals and are easily transported to the water (USEPA, 1984).

The levels of Cu are the best studied of these metals. Several studies in particular pertain directly to marinas. Nixon et al. (1973) found that benthic algae, fouling communities, and the sediments themselves all contained significantly higher Cu concentrations than in a nearby marsh. Adair (1987) also found significant enrichment in *C. virginica* for both Cu and Zn in marinas on the southern coast of North Carolina. It has been found that mussels in boat harbors exhibit significantly higher Cu concentrations as well (Young and Hessen, 1974; Young et al., 1975).

## MATERIALS AND METHODS

The American oyster, *Crassostrea virginica*, and the mud snail, *Ilyanassa obsoleta*, were collected from six different sites (Fig. 1) categorized as either marinas or open water sites. Three marina sites were chosen based on the assumption that each had a low flow rate of water and a permanent boat population. These areas included Peletier Creek (site 1), a marina with very low circulation, about 50

boats continually in the water, and a warehouse dry dock which holds about 225 more boats. The Morehead City waterfront (site 2) is an area protected from the sound by a well-developed longshore bar, but with strong tidal currents. At this site there are two marinas with a waterside gas station at one end and an additional 35 boats continually in the water. The Morehead City Yacht Marina (site 3) is located on the inland side of Morehead City with a fairly low water circulation and about 60 boats continually in the water.

Three open water sites were selected based on the assumption that each had a high tidal circulation of water and no permanent boat populations. These areas included the inlet side of Bird Shoal (site 4) which has some water circulation and is approximately 0.5 km from a marina or a permanent boat population. Phillip's Island (site 5) has a very high circulation of water and is approximately 1.5 km from a marina. Shackleford Island Jetty (site 6) has a very high circulation of water and is about 3 km from a marina; however, a large number of recreational boats do use this area in warmer weather.

Ten *C. virginica* and 60-70 *I. obsoleta* were collected from each site. The animals were collected within a relatively confined area of about ten meters radius at each collection site. An effort was made with *C. virginica* to select the largest organisms in order to ensure enough tissue with which to perform an analysis. Organisms were collected from late September through mid October and stored in a freezer until ready for use.

The adductors of *C. virginica* were weakened by prying the shell open using a stainless steel oyster knife, while avoiding contact with the tissue. The tissue was then removed with acid-washed plastic tongs and wet weight was recorded. An equal volume of a 10% solution of trichloroacetic acid (TCA) was added and the tissue was placed in a homogenizer and homogenized approximately four minutes (M. Brouwer, Research Associate Professor, Duke University Marine Lab, pers. comm.). As all acetates are soluble, metals released from the tissue were kept dissolved in solution by the TCA. Samples were then centrifuged 8-10 minutes. The supernatant was quantitatively extracted to acid-washed tubes and diluted with deionized water and then analyzed by an atomic absorption spectrometer (AAS).

The procedure for *I. obsoleta* was identical with the following exceptions. After removal of the tissue, 6 or 7 snails were added to a single tube in order to have enough tissue for analysis. Each tissue sample was then suspended in approximately 5 ml of "Instant Ocean," a commercial substance mixed with water to yield a sea water sample free from contaminants. The tubes were then centrifuged for 6 minutes. The "Instant Ocean" solution was decanted, more was added, and resuspension and centrifugation were repeated. Two parts of 10% TCA were added per gram of tissue in order to obtain enough sample volume with which to work.

The final data were then analyzed using a computer statistical analysis program (SAS) on IBM. The results are based on the Scheffe test for significance, a conservative test. The three marina sites were grouped together and its average was compared to the three open water sites grouped together. These categories were then split into individual sites and their averages were tested for significant differences. In the case of *C. virginica*, metal concentrations were tested to determine if they differed significantly with the weight of the organism. Weight was also

Table 1

Mean concentrations of metals in *C. virginica*. Values listed are micrograms/gram wet weight. \* indicates a value is significantly greater ( $p \leq 0.05$ ).

Metal	Open Water Sites	Marina Sites
Cu	7.127	36.703*
Zn	204.89	593.54*
Pb	0.9355*	0.7647

tested for significance between individual sites and between marinas and open waters.

## RESULTS

When the three marina sites versus the three open water sites were compared, *C. virginica* showed significantly higher levels in both Cu and Zn concentrations in the marina samples (Table 1). The Pb concentration, however, was significantly higher in open water samples (Table 1). A breakdown of these groupings into individual sites shows how each site contributed to the composition of its category for Cu and Zn (Figs. 2 and 4). Peletier Creek (site 1) samples showed the highest Cu and Zn values and, comparatively, high Pb values as well.

Tissue weight of *C. virginica* was found to be significant only with Zn. Zn concentrations varied inversely with weight. A Student's *t* test of the mean weights of the marina and open water samples did not show that the weights were significantly different (Table 2); therefore, the fact that Zn varied with weight did not significantly affect these data. Comparison of the mean weight on a site by site basis also supported the same conclusion.

When comparing the three marina sites against the three open sites, *I. obsoleta* showed significantly higher levels of both Cu and Zn in the marina organisms (Table 3). Pb concentrations were not significantly different. From the mean concentrations by site, it can be seen that the Cu value was unusually high in the

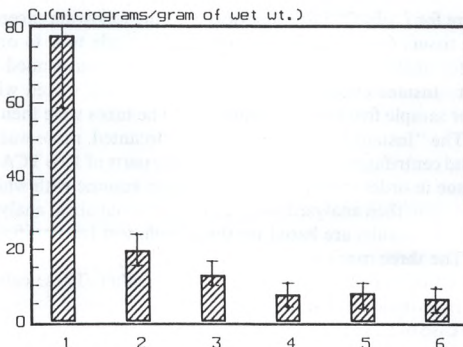


FIG. 2. Mean copper concentrations in *C. virginica* by site.

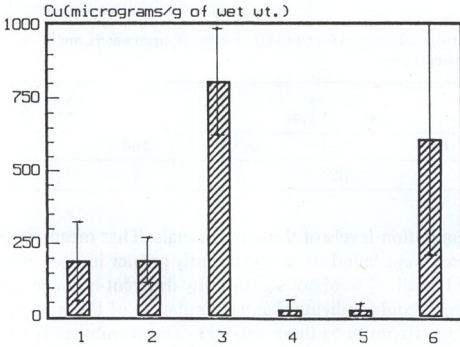


FIG. 3. Mean copper concentrations in *I. obsoleta* by site.

Shackleford Island (site 6) and Morehead City Yacht Marina (site 3) samples (Fig. 3).

### DISCUSSION

While this experiment was devised to provide a relative comparison between the open water and marina sites, the absolute values of the Zn and Cu concentrations do compare closely to the cited values in the existing literature (NOAA, 1989). The values achieved for Pb were not given much credibility as most values approached the detection limit of the AAS. The values are considerably higher than those in the literature and should be considered with caution.

The data failed to disprove the hypothesis that Zn and Cu are enriched in marinas. Increased human discharges in marinas, therefore, probably lead to the

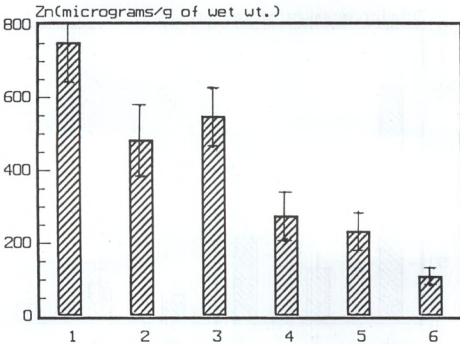


FIG. 4. Mean zinc concentrations in *C. virginica* by site.

Table 2

Mean weight of *C. virginica* in grams (wet weight), marinas vs. open waters, and by site. 95% Confidence interval given in parentheses.

Site #	Marinas 2.62 ± (0.394)			Open Water 3.437 ± (0.451)		
	1.87	3.50	2.52	2.64	3.83	3.84
Site #	1	2	3	4	5	6

increased accumulation levels of these two metals. That mean concentrations of Pb in *C. virginica* were found to be significantly greater in open water organisms and *I. obsoleta* Pb values were not significantly different between open water and marina organisms, could indicate that accumulation of Pb in these organisms is not enhanced by proximity to these marinas. The possibility is thus raised that some mechanism other than water-transported Pb is responsible for accumulation levels in *C. virginica* and *I. obsoleta*. Fallout from atmospheric Pb perhaps has a greater effect on biological accumulation than water-transported Pb. The possibility remains, however, that the data for Pb in this experiment is an analytical artifact.

Several comments should be made about the results attained from specific sites. The high values of Cu, Zn, and Pb in *C. virginica* at Peletier Creek suggest that the bioaccumulation of metals is increased there (Figs. 2 and 4). Bird Shoal (site 4) values for Pb in *C. virginica* seemed unusually high for a supposed open water site. This finding remains unexplained. The Cu and Pb values for *I. obsoleta* at Shackleford (site 6) were unusually high (Fig. 3). In addition, the standard deviations were also high, suggesting that a few aberrant snails could have influenced the mean at this site. These unexpected high values could be due to the high population of boats which utilize the area around Shackleford. Many boats which utilize this area are often dragged onto the sand beach near the collection site. This results in the scraping off of some boat paint, which often leaves visible

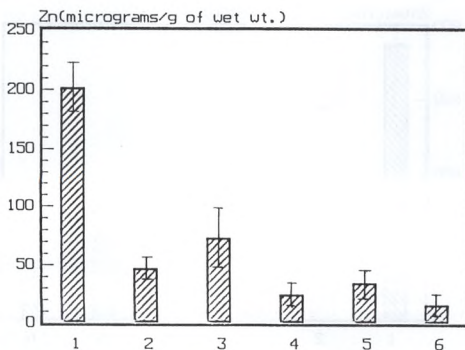


FIG. 5. Mean zinc concentrations in *I. obsoleta* by site.

Table 3

Mean concentrations of metals in *I. obsoleta*. Values listed are micrograms/gram wet weight. \* indicates a value is significantly greater ( $p \leq 0.05$ ).

Metal	Open Water Sites	Marina Sites
Cu	219.5	402.2*
Zn	24.94	103.76*
Pb	3.617	4.337

streaks of paint in the sand. Even a single snail from the sample that had ingested only a small particle of this paint-containing sand would significantly alter the results by exhibiting much higher levels of Cu and possibly Pb as well.

Differences in Zn and Cu concentrations between oysters and snails quite probably reflect the differences in their feeding strategies. The oyster, a filter feeder, is more indicative of suspended or dissolved particles, while the snail, a sediment surface detritus feeder, reflects the presence of less soluble particles. Significantly higher values ( $p \leq 0.05$ ) of Cu in snails compared to oysters and significantly higher values ( $p \leq 0.05$ ) of Zn in oysters compared to snails appear to indicate that Cu is far less soluble in seawater than Zn. Differences in feeding strategies could, therefore, be an important factor when selecting a biological monitor of marina pollutant activity in future studies or projects.

The results presented here compare closely to similar findings of heavy metal enrichment in marina organisms (Wolfe 1970; Young et al., 1979; Marcus and Thompson, 1986; Adair, 1987). The data, when added to this existing literature on heavy metal contaminants, provides further evidence of an existing trend of significant Zn and Cu bioaccumulation in certain marine invertebrates in marinas.

*Acknowledgments:* I thank William Kirby-Smith and Marius Brouwer for their consultation and guidance, especially in my procedure set-up. Also I thank Thea Brouwer for her guide to the technical equipment used and Mike Kingston for his aid with the programming of the SAS statistical program.

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Received 25 June 1992