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Balanus eburneus: A Sensitive Indicator of Copper and Zinc Pollution in the Coastal Zone

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The search for useful indicator organisms to monitor trace metal pollution in coastal areas has been ongoing for several years. Analysis of organisms that accumulate trace elements over time generally provides an integrated and more pertinent assessment of environmental quality than do attempts to measure variable and very low water metal concentrations. However, in coastal harbors and marinas, where the need is greatest, indicator organisms such as *Mytilus edulis* and *Crassostrea virginica* are often difficult to find. Furthermore, *Mytilus edulis* has been cited as too erratic in its uptake of Cu to be useful as an indicator for that trace element (PHILLIPS 1976). Although one specific organism may not represent the uptake behavior of all members of a local biotal community, hopefully the chosen organism will indicate metal stresses in the area. Several researchers have recently introduced the barnacle as a "potential" bioindicator for several trace metals (WALKER et al. 1975a; BARBARO et al. 1978). Our study of the ivory barnacle, *Balanus eburneus*, sought to test its sensitivity as an indicator of Cu and Zn pollution in the Florida coastal zone.

BARBARO et al. (1978) review the properties that organisms should have in order to be utilized as indicators of trace metal pollution as: (1) sessile living habits or at least restricted mobility, (2) ubiquitous occurrence and sufficient abundance in the area to be monitored, (3) availability in all seasons, (4) ease of sampling, (5) predisposition for a consistent uptake of one or more pollutants, (6) high capacity to accumulate metals above environmental levels, (7) predisposition for retaining the pollutants for a sufficient period after a reduction in the environmental levels. An organism's ability to tolerate brackish water also is certainly important. *B. eburneus* satisfies the properties reviewed above. It is sessile and the numerically dominant Cirripedia in our study location. Found in the area in all seasons, *B. eburneus* is easily collected from natural and artificial surfaces. It showed consistent uptake of Cu and Zn far above environmental levels during our study period and is highly tolerant of very low salinities (MOORE & FRUE 1959).

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MATERIALS AND METHODS

Barnacle and water samples were collected from eight sites in the Eau Gallie Harbor and Indian River Lagoon, Florida (FIGURE 1) during six separate field investigations between November 1978 and July 1979. Duplicate water samples were collected at each site from the bow of a small boat moving slowly upwind. Samples were obtained from approximately 15 cm below the surface by direct filling of acid-washed, 500 mL, conventional polyethylene bottles. Surface water temperature, salinity and pH were also measured at each location. Individuals from naturally occurring communities of _B. eburneus_ at each site were scraped from their substrata and placed in acid-washed polyethylene bags. All materials used in the collection and analysis of water and barnacles were cleaned in a manner similar to that described by PATTERSON & SETTLE (1976).

Immediately upon return to the laboratory, one water sample from each site was acidified with 0.25 mL of redistilled HNO_3. Suspended particulates were separated from the unacidified sample by filtration through preweighed, acid-washed, Nuclepore filters (47 mm diameter, 0.4 µm pore size). Suspended matter loads were quantified by reweighing the filters following drying/equilibration. The filters were stored in plastic petri dishes prior to particulate metal analysis. The filtrate was saved for analysis of dissolved Cu.

Total and dissolved Cu were determined separately by extracting the unfiltered and filtered samples respectively. The extraction process involved preconcentration of the metals by cobalt-ammonium pyrrollidine dithiocarbamate (APDC) coprecipitation (BOYLE & EDMOND 1975) and filtering the precipitate onto Nuclepore filters. Blanks and replicates were run to determine Cu contamination from the sample bottles, APDC, filters and distilled water. Filters from all samples (particulate, total and dissolved Cu) were placed in separate polystyrene vials and 0.5 mL of concentrated redistilled nitric acid was added to dissolve the precipitate and/or leach the particulates. The solutions were then brought to a final volume of 15 mL with distilled water and Cu was determined by direct aspiration into a Perkin Elmer model 460 atomic absorption spectrophotometer. The mean percent recovery of Cu determined from spiked samples was 90 %.

After return to the laboratory, barnacles were thoroughly rinsed with distilled water to remove excess detritus. Whole soft parts were removed, weighed and pooled according to site for each determination. Replicate determinations of percent water in _B. eburneus_ yielded 83.6 $\pm$ 3.0%. Samples (0.5-3.0 g wet weight) were placed in acid washed 180 mL tall-form Pyrex beakers and digested with redistilled HNO_3 and 30% H_2O_2. The resulting clear solution was brought to a volume of 25 mL with distilled water. Procedural blanks were prepared following the same methods used for the barnacle digestions. Copper and Zn in all the barnacle samples and blanks were determined by atomic absorption spectrophotometry.

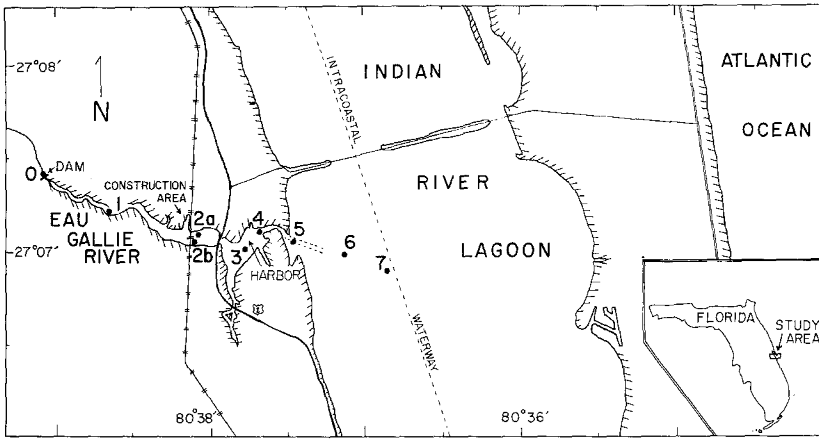

FIGURE 1. Map of Eau Gallie River and Indian River Lagoon.

STUDY AREA

The eight sampling sites studied (FIGURE 1) were located strategically throughout the Eau Gallie/Indian River area. Site 0, at the western extremity of the lower river, is the primary source of freshwater to the upper harbor. Site 2 was chosen to determine the effects of sewage effluent and a railway trestle spanning the harbor on the levels of Cu and Zn. Site 3, located in the center of the harbor turning basin, represents a possible loading area for Cu from antifouling paints. Intermixing of harbor and estuarine waters were the focal points of Sites 4 and 5. Values observed at Sites 6 and 7 in the Indian River Lagoon serve as a useful reference to the data obtained from the harbor waters.

Average values for surface water temperature, pH, salinity, and suspended matter concentrations during the entire period are plotted according to site number in FIGURE 2. Temperature varied seasonally from 23 to 34° C with minor variations throughout the study area. Water pH values showed similar uniformity with an overall average of 7.6 $\pm$ 0.2. Salinity increases steadily throughout the harbor basin from approximately 1 ‰ in the upper harbor waters to 24 ‰ at the Indian River sites. Suspended matter concentrations showed significant intersite variation, with an overall range from 1.3 mg/L at Site 6 to 42.5 mg/L at Site 2.

RESULTS AND DISCUSSION

Data on trace metal accumulation in barnacles collected from their natural environment have only recently been recorded (IRELAND 1973; WALKER et al. 1975b; WALKER 1977; BARBARO et al. 1978). These available data show barnacle Cu ranges from 46 to 3750 µg/g (dry wt.) and Zn variations of 500 to 23,000 µg/g (dry wt.). CLARKE (1947) determined Cu levels in *B. eburneus* to be 8 to 16 µg/g (dry wt.) where water concentrations were between 10 and 30 µg/L. When exposed to 140 µg/L dissolved cupric citrate under experimental conditions, *B. eburneus* accumulated the metal to a level of 1090 µg/g (dry wt.) after only 15 days. When next

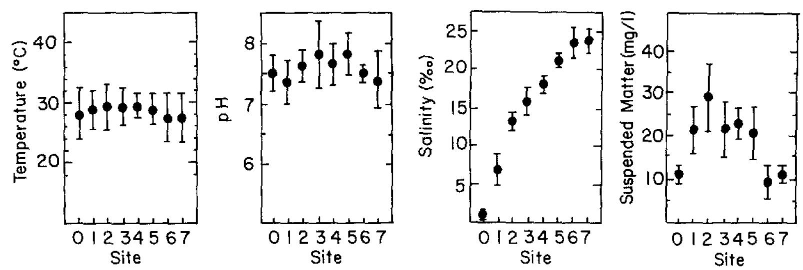

FIGURE 2. Surface water parameters for each site. Averages with standard deviations given for all six sampling periods.

placed in fresh seawater for 18 days, the level of Cu in the barnacle soft tissue dropped to 390 µg/g (dry wt.).

In our study, Cu tissue levels for <u>B. eburneus</u> range from 11 to 64 µg/g (dry wt.) where ambient dissolved Cu concentrations were 0.4 to 1.6 µg/L. Average barnacle Cu concentrations (FIGURE 3) consistently show a dramatic increase on approach to Site 3 from either Site 0 or Sites 6 and 7. However, within-site seasonal variations were surprisingly slight. Uniformity was especially pronounced at Sites 6 and 7 where the mean of 14.6 $\pm$ 0.6 µg/g may well define natural Cu levels in barnacle tissues of this region. The high barnacle Cu concentrations at Sites 2b and 3 (FIGURE 3) suggest a source of biologically available Cu near these areas.

Dissolved Cu concentrations ranged from 0.4 to 1.6 µg/L and total Cu ranged from 0.8 to 2.7 µg/L (FIGURE 4). Dissolved Cu concentrations were highest at Site 3, four times greater than those in the open estuary. These data indicate a Cu source in the marina area with subsequent dilution of the Site 3 peak level by mixing with lower Cu containing freshwater or seawater end-members.

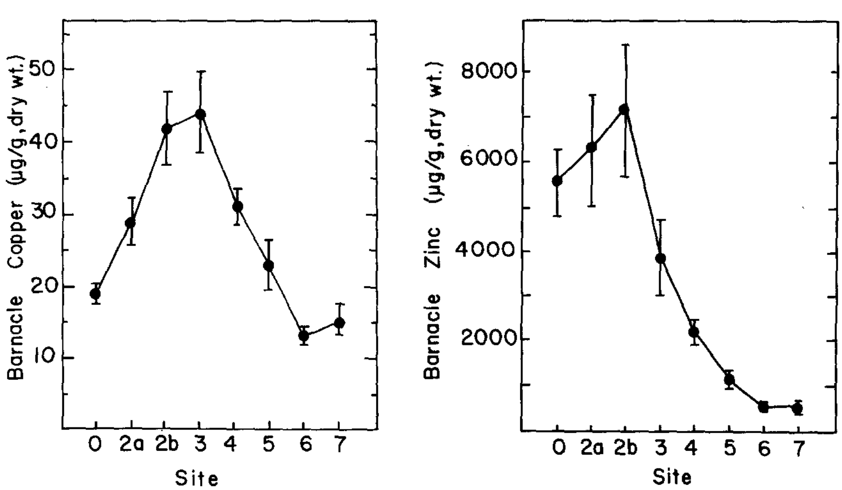

FIGURE 3. Barnacle soft tissue Cu and Zn concentrations (overall means with standard deviations) for each site.

Site 3 (FIGURE 1), near marinas in the harbor turning basin, is an area where the use of antifouling paints on the hulls of boats moored there is a source of Cu to the harbor waters. These antifoulants usually contain 50 to 60% cuprous oxide. To be effective, the leaching rate must be greater than 10 μg Cu cm^{-2} day^{-1} (GOLDBERG, 1976) with the Cu released in a biologically available form.

A significant correlation between the barnacle tissue and dissolved Cu concentrations (FIGURE 4) suggests that dissolved Cu is the key to Cu accumulation in barnacle soft tissues and that Site 3 is the major source area. More striking is the sensitivity of B. eburneus to changes in dissolved Cu. As Figure 4 shows, a 1 $\mu g/L$ increase in dissolved Cu induces a 36 $\mu g/g$ increase in tissue Cu. Equally important are the observed minimum Cu levels in both tissue and water samples at the extremes represented by Sites 0 and Sites 6 and 7.

BARBARO et al. (1978) noted that suspended particulates may also be an important source of Cu to the barnacle. Our study shows that particulate Cu concentrations decrease from 1 to 2 $\mu g/L$ at the Site 1 area to 0.1 to 0.3 $\mu g/L$ at Sites 6 and 7. However, no relationship was found between barnacle Cu concentrations and particulate Cu levels, suggesting a minor role for suspended matter in barnacle tissue Cu accumulation.

Zinc concentrations in the barnacle soft tissues ranged from 360 to 12,000 $\mu g/g$ (dry wt.) with harbor values 14 to 29 times higher than the relatively uniform baseline levels observed (530 $\pm$ 150 $\mu g/g$, dry wt.). Within site seasonal variations in barnacle Zn concentrations were relatively low as depicted by the standard deviations plotted in FIGURE 3. Mean Zn concentrations show a similar trend to that found for Cu (FIGURE 3), however a slight upstream shift in site of maximum concentrations was observed. Unlike the defined point source for Cu (vessel related), the data

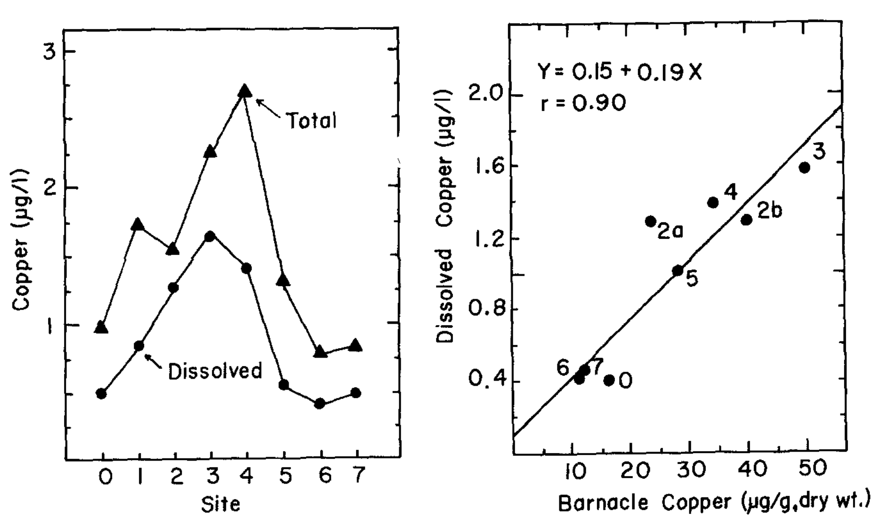

FIGURE 4. Total and dissolved Cu values for the study area; and dissolved Cu versus barnacle Cu concentrations.

suggest non-point sources for Zn throughout the upper harbor.

Relative to the data of previous investigators and our baseline concentrations, the barnacles of the Eau Gallie Harbor waters are moderately high in Cu and Zn and indicative of polluted conditions. Our data suggest that a 1 ppb increase in dissolved Cu brings about a 36 ppm increase in tissue Cu levels and that B. eburneus is a sensitive indicator of Cu and Zn pollution. Yet, this readily identifiable pollution is non-detectable 1 km away in the barnacles of the Indian River Lagoon. This suggests minimal input or rapid dilution of these metals in the Indian River waters and raises concern for pollutant enrichment in restricted coastal embayments.

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