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# DISTRIBUTION OF COPPER AND ZINC IN OYSTERS AND SEDIMENTS FROM THREE COASTAL-PLAIN ESTUARIES

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## ABSTRACT

Copper and zinc were analyzed in oysters (*Crassostrea virginica*) from the Newport River estuary, North Carolina, and the Rappahannock River estuary, Virginia. Results indicated that a concentration gradient existed, higher concentrations of metals being found in animals living in fresher waters as was shown previously for oysters in the James, York, and Rappahannock estuaries in Virginia. Absorbed, precipitated-coprecipitated, and organic fractions of copper and zinc in the <63- $\mu\text{m}$  portion of the sediments from the Rappahannock and York rivers and estuaries were estimated from collections made in January 1972 and June 1973. These sediment data are discussed for both estuarine systems and are compared with metal concentrations in oysters. These comparisons indicated that the concentration gradient found in oysters does not appear to be related to the distribution of copper and zinc in the sediments. Alternative explanations for the inverse relationships between concentrations of copper and zinc in oysters and salinity are given.

The transport of trace metals from fresh waters through estuaries and eventually to the oceans has been studied by many investigators over the past several decades. The relative importance of the various mechanisms postulated has changed as hypotheses and analytical techniques have improved. Originally, calculations were mainly based on the solubility products of the metal sulfides or hydroxides. While such calculations are valid for a pure inorganic system, they may not always apply to conditions encountered in nature. Goldberg (1957), for instance, noted the importance of the biosphere in the budgets of metals; subsequently its role in the concentration, transport, and storage of these elements was shown. Turekian and Scott (1967) have shown that the role of inorganic suspended matter cannot be ignored in the metal budget of streams,

and they suggest that simple ion-exchange mechanisms for removing metals from solution to suspended sediments are not sufficient to explain their data but that coprecipitation may be. From the work of these men and others, we conclude that not only the solution chemistries but also the biological and surface chemistries must be considered in the routes and rates of metal transport in estuarine systems.

Scientists concerned with trace metals as environmental contaminants must take into account not only the total natural budgets of the elements but also, and most important, the biologically available fractions due to either natural or man-made inputs. This requires that analytical schemes be developed which will selectively identify the elements in question from individual phases in which they exist. Gibbs (1973) has recently developed a procedure that differentiates between metals in adsorbed, precipitated, and coprecipitated organic solids and crystalline phases. Huggett and Bender (1972) have reported another method yielding metals from inorganic-noncrystalline and organic sediment phases.

Even though the cation-exchange metal concentration for suspended matter is low (Turekian and Scott, 1967; Gibbs, 1973), metals in this form are easily mobilized by low pH. Such filter-feeding organisms as oysters eat suspended particles and pass them through their gut, which has a pH as low as 4 (Wilbur and Yonge, 1966). A portion of the adsorbed metal fraction of the sediment could be mobilized in the gut and made available to the animal. In the upper estuarine portion of the Rappahannock River in Virginia, oysters (*Crassostrea virginica*) have zinc concentrations of about 600 ppm (whole body, wet weight) (Huggett, Bender, and Slone, 1973). A calculation based on a 20-g animal, a pumping rate of up to 575 liters/day (Haven, 1973), a suspended-particle concentration of 30 mg/liter (Turekian and Scott, 1967) with an adsorbed zinc concentration of 2 ppm (this paper), and a 100% stripping efficiency by the animal shows that the animal could have reached its present body burden in about 1 year. Obviously the efficiency of stripping and assimilation by the animal is not 100%. However, it does serve to show that, if the adsorbed fraction is biologically available and even though the adsorbed concentration is small compared to the total concentration on the particle, it cannot be ignored and may be an important factor in bioconcentration by these animals since they may live for 10 years or more.

Characterized in this report are copper and zinc in sediments and oysters from two adjacent rivers and estuaries entering the Chesapeake Bay. One system, the Rappahannock River, is pristine in nature; the other, the York, receives acid mine drainage. The relationships between concentrations of metals in the sediments and those in the animals were investigated in an effort to define the biologically available fractions. Also reported here is research to confirm a previously demonstrated natural metal concentration gradient for oysters living in waters of different salinity.

## METHODS AND PROCEDURES

### Oysters

Samples of oysters, *Crassostrea virginica*, were collected by various standard methods (dredge, rake, tongs), depending on water depth and bottom type from the Rappahannock and the York river estuaries in Virginia and from the Newport River estuary and Bogue Sound in North Carolina. All samples were analyzed by atomic absorption spectrophotometry; however samples analyzed by the Virginia Institute of Marine Science (VIMS) were oxidized by wet digestion with concentrated acid and those prepared at the Atlantic Estuarine Fisheries Center (AEFC) were oxidized in a high-temperature oven. Specific preparative methods at each institution is given by Huggett and Bender (1973) and Cross and Brooks (1973).

### Sediments

Bottom sediments were collected from the channels of the Rappahannock River in 1972 and 1973 and from the York River in 1972. The samples were obtained with a Ponar grab sampler. The top 1 cm of undisturbed sediments was extracted from each sampler. The samples were stored in plastic bags on ice until returned to the laboratory (<8 hr), where the samples were immediately wet sieved (U. S. standard sieve, No. 230, 63- $\mu$ m openings). Subsequent resieving through the stainless-steel sieve resulted in no discernable increase of metal concentrations; therefore contamination from this source was negligible. The <63- $\mu$ m portion of each sample was air dried and saved for analysis. Since the concentration of the precipitated—coprecipitated and adsorbed fractions of the metals must be a function of the surface area per unit mass of the sediment grains and since the bottom sediments are not uniform in size distribution, this procedure was necessary to help normalize the samples.

Most samples were extracted in three ways to differentiate among the various biologically available fractions: adsorbed metals, precipitated—coprecipitated metals, and organic metals. Metals bound within the crystalline matrixes of minerals were considered unavailable to the biological community and were not measured. The adsorbed metals were obtained by extracting the sediments with 1.0N MgCl<sub>2</sub> (Gibbs, 1973). The precipitated—coprecipitated and adsorbed metals were extracted with 0.1N HCl, and the total noncrystalline metals were extracted with concentrated HNO<sub>3</sub> (Huggett and Bender, 1972). Analyses of replicate samples showed the nitric acid extraction to have a precision of  $\pm 7\%$  for copper and  $\pm 5\%$  for zinc; that of the hydrochloric acid procedure was  $\pm 4\%$  for both copper and zinc. These three extraction procedures allow a quantitative estimate of those metals adsorbed, coated (precipitated or coprecipitated), and organically bound in the bottom sediments. Obviously the reagents mobilize some metals from nonintended phases, but these are

considered to be negligible on the basis of replicate analyses and extraction efficiencies that are in turn based on reextractions of the same sample.

## RESULTS

### Oysters

In 1971 a survey of metal levels in oysters from the southern Chesapeake Bay indicated that a natural concentration gradient exists which is a function of, or is measured by, salinity (Huggett, Bender, and Slone, 1973). Animals living in fresher waters consistently contained more copper and zinc than those from a more saline environment (Fig. 1). This finding had not been shown previously and has not been tested since. It is extremely important, however, in light of environmental problems associated with anthropogenic additions of metals to the environment that effects of environmental variables on concentrations of metals in marine organisms be understood.

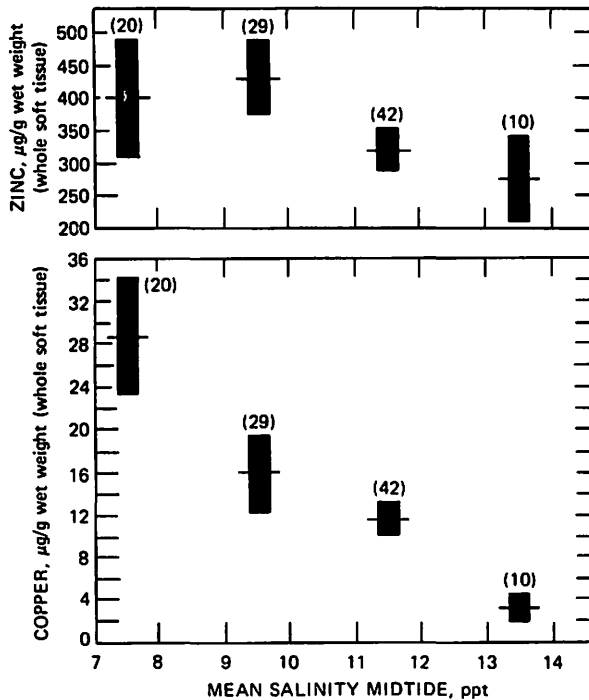


Fig. 1 Mean concentrations  $\pm 2$  standard errors of copper and zinc in oysters collected from the Rappahannock River estuary. The numbers in parentheses represent the individuals analyzed at each station.

To confirm earlier findings of Huggett, Bender, and Slone (1973) and Huggett and Bender (1973) that concentrations of copper and zinc decrease in oysters with increasing salinity and to compare analytical techniques between our two laboratories, we collected 50 oysters in January 1974 from each of two oyster beds in the Newport River estuary and one in Bogue Sound, N. C. One-half of the oysters from each of the three beds was sent to VIMS, and the remaining oysters were retained at AEFC and held in the same manner as the samples that were sent to VIMS. On the same day the oysters were opened by identical methods at each laboratory and then analyzed for concentrations of copper and zinc.

Results of these analyses (Fig. 2) show that concentrations of both copper and zinc decrease with increasing salinity in the Newport River estuarine system as described previously for the Rappahannock River estuary (Fig. 1), although absolute values are considerably lower in the Newport River estuarine system than in the Rappahannock. Similar relationships between concentrations of copper and zinc and salinity have been reported for the James and York river estuaries (Huggett, Bender, and Slone, 1973). In addition, statistical comparisons between concentrations of copper and zinc obtained at each laboratory were not significantly different at the 99.9% confidence level; thus the data from both laboratories are polled in Fig. 2.

## **Sediments**

The intent of this study was to delineate any trends in the sediment-metals concentrations which could be explained by natural estuarine variables, such as salinity and pH. Once these trends were established, they could be compared to the concentration trends found in the biota. The sediment results are given as moving averages between three adjacent stations in Figs. 3 to 7. This method was used because replicate sediment samples were not taken at each site, and no estimate of variability of a single station could be obtained. By averaging adjacent stations (moving averages), a better approximation is gained. This type of presentation does not change the trends but rather smooths out the data (Lewis, 1963).

## **Rappahannock River and Estuary**

### ***Copper***

The precipitated-coprecipitated metal concentrations in sediments (Fig. 3) from both sampling periods are almost identical from the mouth of the estuary up to the salt water-freshwater interface (normally between 55 and 70 km). The levels vary between 10 and 15 ppm from the mouth to 55 km. From 55 to 100 km from the mouth, the 1972 samples show an increase of approximately 100% over downstream samples. The 1973 samples show such an increase

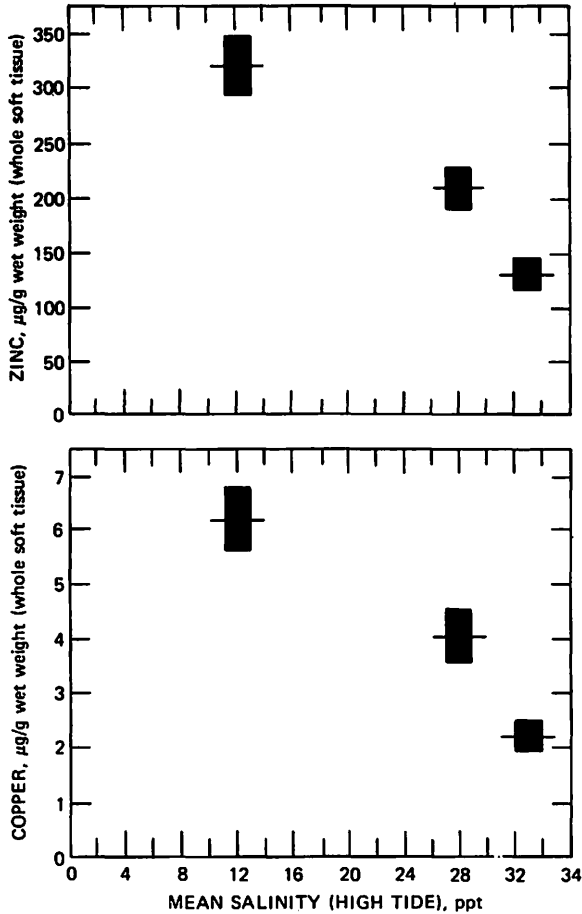


Fig. 2 Mean concentrations  $\pm$  standard errors of copper and zinc in oysters collected from Newport River estuary (12 and 28‰) and Bogue Sound (33‰). Each set of values represents the analysis of 50 individuals.

between 70 and 88 km from the mouth. The reason for these increases is unclear, but two possibilities arise:

1. The sorption reactions are controlled by salinity.
2. They result from sedimentation due to the flocculation at the turbidity maximum which occurs in this segment of the river (Nichols, 1974).

In addition, the organic copper concentrations (Fig. 3) are nearly constant (10 ppm) throughout the entire river and estuary sampled.

The adsorbed phase, as indicated by magnesium chloride extraction, shows that in the estuary the adsorbed fraction of copper is low compared to the other

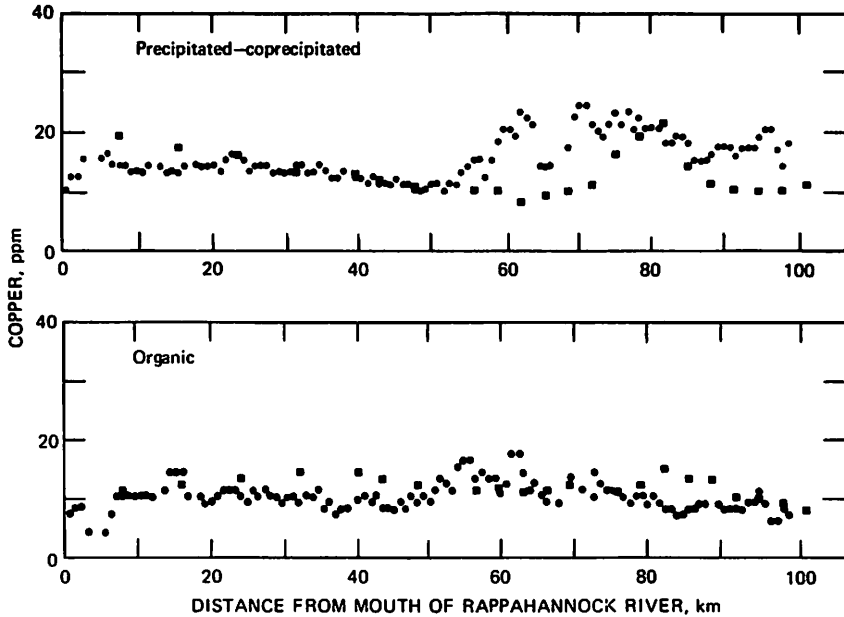


Fig. 3 Moving averages (3) of concentrations of precipitated-coprecipitated and organic copper in the  $<63\text{-}\mu\text{m}$  fraction of sediments from the Rappahannock River and estuary collected in January 1972 ( $\bullet$ ) and June 1973 ( $\blacksquare$ ). Zero kilometers represents the mouth of the estuary.

two fractions (Fig. 4). Because magnesium is an abundant element in seawater, estuarine sediments have already been "stripped" of some adsorbed metallic ions. The variations in adsorbed concentrations in the freshwater portions (55 km upstream) are probably due to either surface area or mineralogical changes in the sediments as a result of sedimentation parameters (particle density, flocculation, current velocity, etc.). This is somewhat confirmed by the lower concentrations found in samples taken in areas of scour in the river. The increase in copper toward the mouth of the estuary is probably due to particle-size differences, smaller particles being deposited downstream.

### Zinc

The precipitated-coprecipitated zinc concentrations increased toward the mouth of the estuary while the organic phases decreased (Fig. 5). The range of concentrations was approximately the same for both sampling periods.

To our knowledge there are no man-made sources of zinc in the Rappahannock River. The three-fold increase in precipitated-coprecipitated zinc from freshwater to the estuary mouth may be explained, in part, by the particle sizes of the bottom sediments. Under normal conditions the carrying

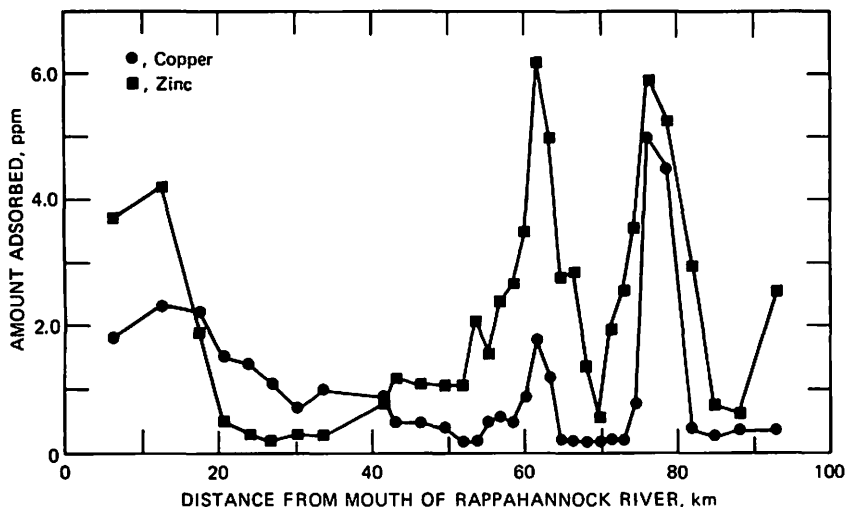


Fig. 4 Moving averages (3) of concentrations of adsorbed copper and zinc in the  $<63\text{-}\mu\text{m}$  fraction of sediments from the Rappahannock River and estuary collected in January 1972. Zero kilometers represents the mouth of the estuary.

capacity of an estuary for suspended sediments decreases with increasing salinity. This should result in the downstream deposition of finer grained sediments. If the concentrating mechanism for inorganic zinc is dependent on sediment surface area, then the increase may be expected.

The decrease in organic zinc may be a result of one or more of the following:

1. Zinc's being bound inorganically and hence made unavailable to be bound organically.
2. A decreasing concentration of organic material toward the mouth of the estuary.

The decreasing trend follows that found for zinc in oysters from this stream (Huggett, Bender, and Slone, 1973).

The adsorbed fraction follows the same trend as that of copper and is generally slightly higher in concentration, suggesting this element to be more favored in adsorption reactions or more abundant in the incoming waters. (Fig. 4).

### York River

The York River is situated between the James and Rappahannock rivers and is unique in that it bifurcates approximately 45 km upstream from its mouth, the Pamunkey River being the southern tributary and the Mattaponi River the

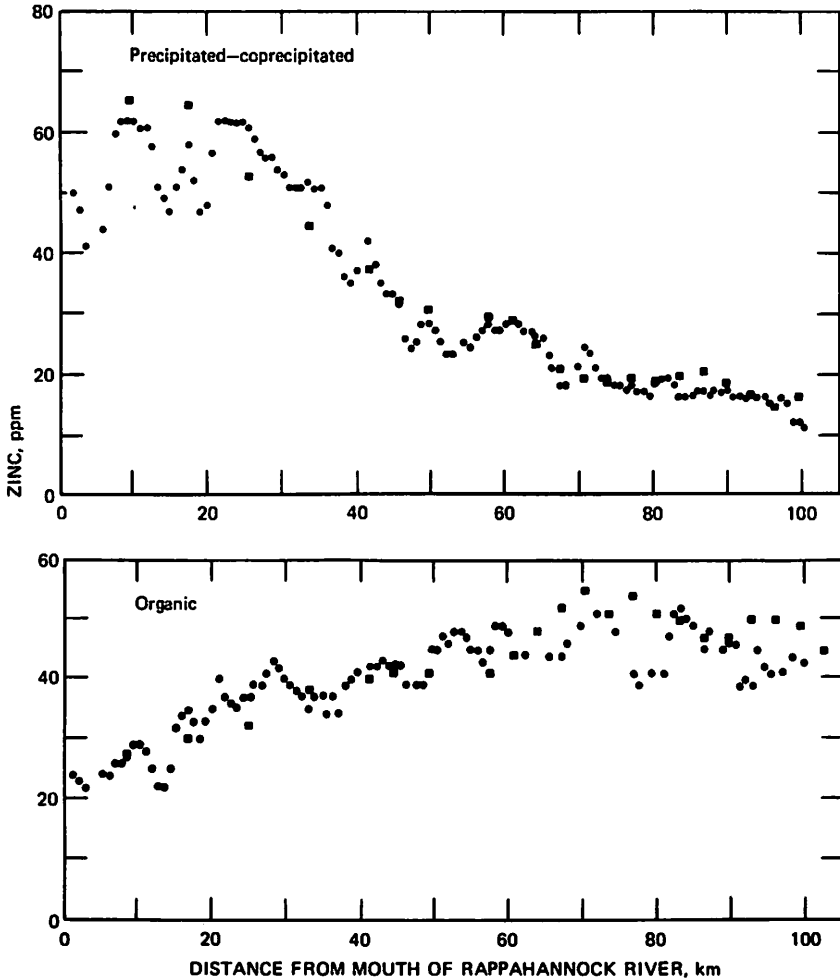


Fig. 5 Moving averages (3) of concentrations of precipitated-coprecipitated and organic zinc in the  $<63\text{-}\mu\text{m}$  fraction of sediments from the Rappahannock River and estuary collected in January 1973 (●) and June 1973 (■). Zero kilometers represents the mouth of the estuary.

northern tributary. Under normal conditions the freshwater-salt water interface is located approximately 7.5 km above the bifurcation point. The two tributaries are almost identical in size, drainage basin, and bordering vegetation. One exception, however, is that the Pamunkey River receives mine drainage from abandoned pyrite mines that were operated from the middle of the last century up until the early 1900s. This drainage enters the stream approximately 130 km

above the bifurcation point. As will be shown, this abandoned mine has affected the metals budgets of the stream and that of the parent river.

### Copper

The distribution of precipitated-coprecipitated copper in the York riverine and estuarine sediments does not resemble that in the Rappahannock River (Fig. 6). There appears to be an unnatural source of copper between 7.5 and

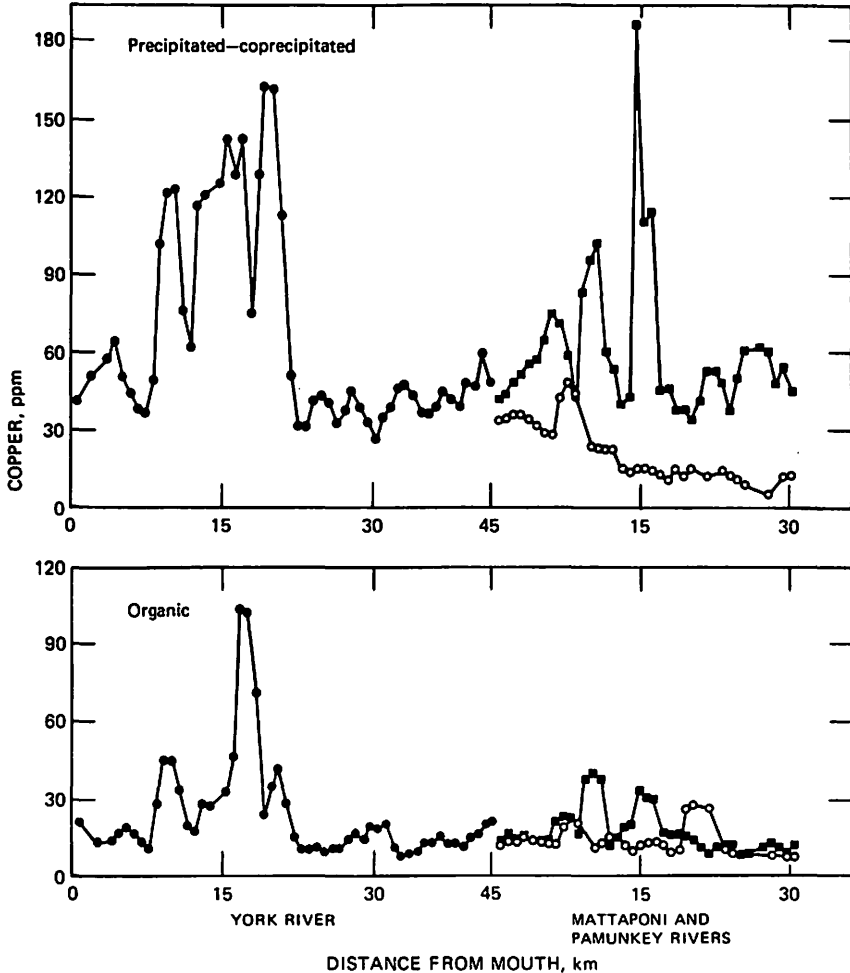


Fig. 6 Moving averages (3) of concentrations of precipitated-coprecipitated and organic copper in the  $<63\text{-}\mu\text{m}$  fraction of sediments from the York River and estuary collected in June 1973: ●, York River. ○, Mattaponi River. ■, Pamunkey River.

22 km from the mouth. At this segment of the river, the concentrations are three to four times higher than those on either side. Within this area there are at least two possible sources for this metal. One source is a primary sewage outfall located approximately 6 km upstream, and the other is the Naval Weapons Station located approximately 16 km upstream. In addition, the effect of the abandoned mines draining into the Pamunkey River is evident. The concentrations are 100 to 200% higher in this stream relative to its counterpart, the Mattaponi River.

The organic copper concentrations reflect the unnatural input into the lower river but otherwise do not appear greatly different than the Rappahannock River sediments (Fig. 6). The levels in the Mattaponi and Pamunkey rivers are similar, indicating that the inorganic copper from mine drainage is not greatly manifested in the organic phases.

### *Zinc*

The precipitated—coprecipitated zinc levels in this system are greatly elevated over those of the Rappahannock (Fig. 7). This is apparently due to the input from the previously mentioned abandoned mines. The concentrations decrease in a linear manner from the most upstream station on the Pamunkey River to the mouth of the York River. The lower stations on the York River have nearly the same concentrations as do those at the mouth of the Rappahannock (40 to 60 ppm). The levels in the Mattaponi River increase downstream as did those in the unpolluted Rappahannock.

The organic zinc concentrations are similar to those found in the Rappahannock except that the Pamunkey levels are apparently being affected by the mine drainage (Fig. 7). The general trend is a decrease in organic zinc with increasing salinity to about 10 ppt (32 km upstream) and then steady to the mouth of the York River.

### **Discussion**

A concentration gradient exists in the oyster samples from the Newport River estuarine system, with progressively higher concentrations of either copper or zinc being found in progressively fresher waters. This gradient, which also has been shown in the Rappahannock and York estuaries, suggests that a natural phenomenon is responsible. One explanation might be that those animals in fresher waters are closer to the source, if the metals are supplied from the natural weathering of rocks. Thus a gradient should exist for concentrations of copper and zinc in solution in the river waters similar to that found in oysters. The efforts at VIMS to analyze the copper and zinc content of Rappahannock River water, passed through 0.45- $\mu\text{m}$  membrane filters, have not been satisfying. Two methods were tried, each with limited success: anodic stripping voltametry and organic chelation and extraction. Each has the limitation of matrix

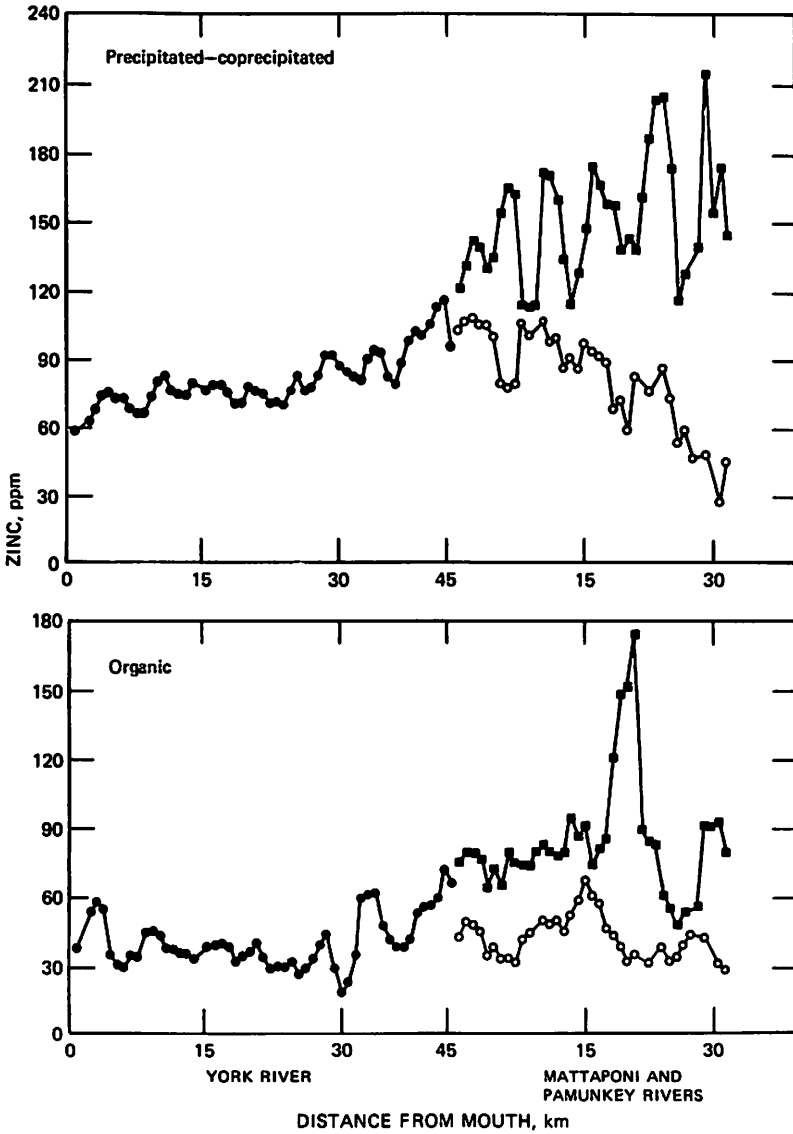


Fig. 7 Moving averages (3) of concentrations of precipitated-coprecipitated and organic zinc in the  $<63\text{-}\mu\text{m}$  fraction of sediments from the York River and estuary collected in June 1973: ●, York River. ○, Mattaponi River. ■, Pamunkey River.

interferences as salinities change. Even so the limited data obtained do not show a concentration gradient for copper, cadmium, or zinc. Recently Cronin et al. (1974) reported on metal-water data from samples collected in the upper Chesapeake Bay. As in the case of the Rappahannock River samples, no consistent metal trends were shown in these samples as a function of salinity. Similarly, Cross, Duke, and Willis (1970) report that concentrations of zinc in unfiltered water samples were constant throughout the Newport estuary, North Carolina. These data imply that the concentration gradients found in the oysters are not a result of a similar gradient in the water.

Another possible explanation is that sediments serve as a source of copper and zinc to oysters, and thus sediments may control directly the levels of metals found in these filter-feeding organisms. The sediment data presented in this paper, however, tend to dispute this hypothesis. Even though the sediments were extracted by several techniques and concentration trends were noted, they were not similar to those found in the oysters except for organic zinc in sediments from the Rappahannock estuary. Concentrations of copper in this fraction, however, remained constant throughout the estuary. If this fraction was controlling directly the availability of copper and zinc to the oysters, we would expect both metals to decrease in sediments with salinity, as is shown for oysters.

The precipitated-coprecipitated zinc concentrations in the Rappahannock River sediments decreased with decreasing salinity, and the same phase of copper remained relatively constant in the estuarine portion of the river. But the copper and zinc concentration in oysters from the same river increased with decreasing salinity. Comparison of all the various sediment metal fractions with the metals in oysters in this manner showed no consistent relationships. Cronin et al. (1974) conclude that trace-metal concentrations in oysters do not depend on the concentration of the metals on suspended material. This confirms our findings if the assumption is made that suspended material is similar in nature and composition to the fine surface sediments at any point in an estuarine system.

If gradients in concentrations of dissolved and particulate copper and zinc are eliminated as possible factors controlling the inverse relationship between salinity and concentrations of copper and zinc in oysters, we are left with the following explanations:

1. In his attempt to explain the high concentrations of zinc found in oysters relative to other marine organisms, Wolfe (1970) postulated that zinc may be assimilated from the environment along with calcium by a relatively nonspecific ion-transport mechanism to satisfy the organisms' large calcium requirements for shell deposition. Because concentrations of calcium in seawater are dependent on salinity, oysters may have to extract calcium from seawater more efficiently at lower salinities and may also concentrate greater quantities of other inorganic cations such as copper and zinc during this process of maintaining adequate calcium reserves for shell deposition (Wolfe and Stillings, 1975).

2. At higher salinities the more abundant cations in seawater (magnesium, calcium, etc.) may be outcompeting the less abundant metals such as copper or zinc for binding sites in the soft tissues. Although copper and zinc form more stable chelates with proteins than do magnesium, manganese, or calcium (Pringle et al., 1968), the greater concentrations of these less abundant ions at higher salinities may overwhelm this relationship. Romeril (1971) showed, for example, that the uptake of  $^{65}\text{Zn}$  in the oyster, *Ostrea edulis*, was decreased by the addition of iron and cobalt.

3. Another explanation for the observed metal concentration gradients in oysters could be that chelation or complexation of the metals in solution by natural organics, such as fulvic acids, make the elements more available to oysters. These humic substances are believed to be derived from decaying plant materials on land and are leached and washed away by surface or subsurface waters, eventually reaching the estuaries (Swanson and Palacas, 1965). This means that the concentrations of fulvic acids should decrease with increasing salinity (because of dilution) as do the levels of zinc and copper in the oysters. Metal complexes and chelates of humic substances have been found and studied by many investigators (Jenne, 1968; Shapiro, 1964), and an excellent review on the subject was written by Schnitzer and Khan (1972). One logical mode of uptake of the organometals by the oysters would be by direct partitioning of the substances from solution into the body mucus and then into the tissues. Without further research, however, none of these three hypotheses can be proved.

This discussion illustrates our lack of knowledge of the environmental processes controlling the availability of trace metals to estuarine biota. Yet this aspect of estuarine biogeochemistry is receiving very little effort at the present time. This is an unfortunate situation because our estuarine systems are being subjected to environmental modifications (dredging, filling, etc.) and anthropogenic inputs of contaminants.

Without adequate basic information on bioavailability of metals to organisms, the consequences of increased releases of metals into estuarine systems cannot be predicted by management agencies, and hence the proper management of estuarine ecosystems is impossible.

## ACKNOWLEDGMENTS

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