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Copper and zinc in bottom sediments and oysters, Crassostrea virginica, from Virginia's estuaries

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COPPER AND ZINC IN BOTTOM SEDIMENTS AND OYSTERS, *CRASSOSTREA VIRGINICA*, FROM VIRGINIA'S ESTUARIES.

The College of William and Mary in Virginia,
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Physical Oceanography

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COPPER AND ZINC IN BOTTOM SEDIMENTS AND OYSTERS, *CRASSOSTREA VIRGINICA*, FROM VIRGINIA'S ESTUARIES

A Dissertation
Presented to
The Faculty of the School of Marine Science
The College of William and Mary in Virginia

In Partial Fulfillment
Of the Requirements for the Degree of
Doctor of Philosophy

By
Robert James Huggett
1977

APPROVAL SHEET

This dissertation is submitted in partial fulfillment of

the requirements for the degree of

Doctor of Philosophy

Robert James Huggett

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DEDICATION

This work is dedicated to my wife, Lucy, whose love, encouragement and patience made this achievement possible.

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PREFACE

This dissertation consists of three manuscripts with a common, introduction, analytical methods and procedure evaluation, and conclusion. The first manuscript concerns concentrations of cadmium, copper and zinc in oysters, *Crassostrea virginica*, from the major estuaries in the Southern Chesapeake Bay. It has been published in Water Research. The second manuscript was published in Proceedings of a Symposium on Mineral Cycling in Southeastern Ecosystems and involves concentrations of copper and zinc in bottom sediments and oysters which live on those sediments. The third manuscript concerns concentrations of copper and zinc, in suspended and bottom sediments from the Rappahannock River before, during and after Tropical Storm Agnes. It has been published in The Effects of Tropical Storm Agnes on the Chesapeake Bay Estuarine System.

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I wish to thank my committee members, Dr. Robert J. Byrne, Mr. Dexter S. Haven, Dr. Joseph G. Loesch and Dr. Stephen C. Clement for their guidance and criticism of this manuscript.

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ABSTRACT

Oysters, *Crassostrea virginica*, were collected from 95 stations located on the western side of the southern Chesapeake Bay. Analysis of these samples for the trace metals, cadmium, copper and zinc indicated that concentration gradient existed for each of the three elements. Samples collected further up-stream (lower salinities) usually contained more of the metals than did those down-stream. The concentration gradients were utilized successfully to predict natural and/or anthropogenic metal concentrations in oysters from the study area.

Oyster samples collected from the Newport River estuary in North Carolina showed the same metal gradient as had been observed in the Chesapeake Bay.

Bottom sediments from the York and Rappahannock Rivers were collected and analyzed for copper and zinc by three chemical extraction methods followed by Atomic Absorption Spectrophotometry. Although trends of sediment-metals were observed they did not correlate with those present in oysters from the same estuaries.

Analysis of Rappahannock River bottom and suspended sediments before, during and after the run-off from Tropical Storm Agnes showed that the copper concentration in bottom sediments increased due to the storm. Since suspended sediments were also high, the assumption was made that deposition of the copper rich particulates accounted for the increase in bottom sediment copper. A deposition-mixing model was formulated and the amounts of deposition in the Rappahannock River Channel due to Tropical Storm Agnes were calculated.

COPPER AND ZINC IN BOTTOM SEDIMENTS AND OYSTERS, *CRASSOSTREA VIRGINICA*, FROM VIRGINIA'S ESTUARIES

INTRODUCTION

Significant effects of pollutants are related to their relative potency and the duration of their existence. The damage done by pollutants is less for those which have chemical half-lives. An obvious example of this is the difference in pollution potential of organo-phosphate and chlorinated hydrocarbon pesticides. Organo-phosphate pesticides have short lives in the environment, often on the order of days, and hence are important mainly through local direct acute exposure (Bender and Westmann, 1976). However, chlorinated hydrocarbons such as DDT can exist from between 10 and 15 years depending on the surrounding physical-chemical conditions and this long life time allows for global distribution and significance in the biosphere (MacMullan, 1968). The potential of ecological damage from a pollutant is directly proportional to its half-life. Extreme caution must be exercised in the release of a substance with an infinite half-life into the environment. Once in the environment its potential for harm remains until it loses its biological availability. Trace metals are examples of such pollutants.

Trace metals may be defined as those elements, usually the transition ones, which are found in trace quantities in the environment relative to the more abundant elements such as iron. From a chemical standpoint elements such as tin are non-metals but are accepted under the broad category of trace metals. Trace metals exist naturally in minerals and therefore there is a natural budget of these elements in aqueous systems. With the weathering of rocks, the elements reach the rivers, estuaries and eventually the oceans. The accompanying biological systems have evolved to cope with this natural occurrence. When a metal's budget is unbalanced by man-influenced augmentation, the biota must readjust to reach a new equilibrium and in the process the productivity of many organisms may be significantly affected.

Between 1953 and 1970, 46 persons died in the vicinity of Minamata Bay, Japan from the consumption of mercury contaminated shellfish (Nelson, 1971). More recent evidence indicates that cadmium contaminated rice crops in northern Japan killed more than 50 persons (McCaull, 1971). Improper waste disposal management was to blame in both cases. No longer can the axiom, "Dilution is the solution to pollution," be used in the selection of metal disposal methods and sites. The chemical and physical dynamics of aqueous systems are too complicated for such a naive approach. Proper management decisions concerning disposal of heavy metals in natural aqueous systems depend upon the determination of the questions to be answered and techniques required to arrive at the answers. The correct approach will be one which integrates the biological, chemical, and physical aspects yielding a measure of the ecological costs of various disposal alternatives. This information coupled with the sociological and economic costs can then be given to management agencies and a decision based on an enlightened cost-benefit analysis can be made. Unfortunately most of the necessary biological, chemical and physical aspects are unknown. Until the biological impacts of such additions can be accurately assessed and predicted, the sociological and economic ones cannot be determined.

The research reported in this manuscript involves attempts to determine the budgets of cadmium, copper and zinc in sediments and oysters, *Crassostrea virginica* from two eastern coastal plain estuaries, the York and Rappahannock (Figure 1).

Bottom sediments are mainly comprised of mineral grains, biogenic calcium carbonate, and organic matter, (the organic matter being either as discrete particles usually from partial decomposition of dead organisms, or as bacterial or algal coatings on mineral grains). In noncontaminated estuarine sediments from Virginia, the organic content as approximated by loss on ignition, commonly ranges between 1% and 15% on a dry weight basis (Brehmer, 1970; Virginia Institute of Marine Science, 1972). The moisture content of the sediment, as it comes up in the samples, varies depending on the average grain size. Sandy sediment will often contain between 60% and 80% solids, while those comprised mostly of silts and clays will have from 20% to 50% solids. Within an estuary, the particle size distribution may change greatly from one place to another depending on the current patterns, depth of the stream, and source of detrital material.

The metal content of any estuarine sediment is difficult to generalize because it depends on how the metals are extracted from the sediment and how the analyses are performed. A widely accepted characterization of sediment metals is one formulated by Gibbs (1973) in which there are four basic metal "locations" in sediments. One includes those metals which are incorporated into crystalline matrices. These may be either a part of the lattice or "trapped" in the lattice structure of clay or mica minerals. These metals are called crystalline metals. Another involves those metals scavenged into iron or manganese oxide-hydroxide coatings on the particles and are known as scavenged, or precipitated-coprecipitated, metals. A third type includes those metals adsorbed to the surface of the mineral grain which are called adsorbed metals. The fourth, called organic metals, are those incorporated in organic matrices either as coatings on the mineral or as biological debris. Three of these four types are directly related to the surface area of the sediment grains and hence, the particle size. With all other things being equal, one gram of a fine grained sediment will usually contain more of a metal than will an equal mass of a coarser one.

If the metals in untreated sediments are quantified by activation or equivalent analysis, all four "types" of a metal comprise the resulting value. There are advantages to this kind of analysis because solvent extractions to "strip" one type of metal relative to another are not well defined and undoubtedly extract metals from undesired locations. However, due to the expense of activation analyses and the point that crystalline metals are probably the least important with respect to their biological availability, extractions followed by atomic absorption spectrophotometric analyses are usually performed. The research reported in this manuscript was based on solvent extractions or "strips" followed by atomic absorption spectrophotometric quantitative analysis.

The organism chosen to compare the levels of cadmium, copper and zinc in adsorbed, precipitated-coprecipitated and organic phases in sediments to tissue level was the Eastern oyster, *Crassostrea virginica*. This species is abundant in the southern Chesapeake Bay and comprises a multi-million dollar per year industry in Virginia (Haven, 1977). They commonly inhabit waters with salinities between 7 o/oo and 30 o/oo where the bottom type is sufficiently hard to support the animals and the substrate to which they "set". They are filter feeders which can filter as much as 575 liters of water a day through their gills, efficiently removing particles between 2μ and 8μ for food (Haven, 1977). These particles are passed, by undulations of the cillia on the gills to the mouth and from there on into the stomach and gut (Galtstoff, 1964). Once in the gut the particles are subjected to digestive fluids which may have a pH as low as 4 (Wilbur and Yonge, 1966). The potential is there for metals which are bound to the particles and labile under reduced pH's to be mobilized under these conditions and incorporated into the oyster's tissues. Commonly oysters from non-polluted waters have metal concentrations which are four to five orders of magnitude above those in surrounding waters (Kopfler and Mayer, 1969) and one to ten times those in sediments (this manuscript). Therefore their ability to concentrate metals makes them an attractive choice for trace metal studies. Also since oysters are sessile, their metal content reflect levels in their immediate environment. This aspect of their ecology is essential if one is to compare concentrations of a substance in the animal with those in other segments of the ecosystem.

The objectives of the present study were to:

a) determine the concentrations of cadmium, copper and zinc in oysters from Virginia's tributaries entering the Chesapeake Bay;

b) develop a mechanism to determine whether the concentrations of cadmium, copper or zinc in oysters from various locations had been augmented by man's activities;

c) determine whether copper or zinc associated with bottom sediments is available to oysters that live on those sediments.

ANALYTICAL METHODS AND PROCEDURE EVALUATIONS

Virginia sediment and/or oyster samples were collected in the James, Nansemond, Elizabeth, Back, Poquoson, York, Pamunkey, Mattaponi, Severn, Ware, North, East, Piankatank and Rappahannock rivers. Oysters were also sampled from two beds in the Newport River Estuary and one in Bogue Sound, North Carolina (Figures 1 & 2).

Bottom sediments were sampled with a Ponar Grab Sampler. Upon reaching the boat, the top 1 cm of sediment was removed from the sampler with a stainless steel spatula. Care was taken to remove only that sediment which was not in direct contact with the sides of the sampler. The sediment samples were then placed in plastic bags and iced until returned to the laboratory. In the laboratory the samples were wet sieved, (U.S. standard sieve, No. 230, 63 μm openings) and that portion passing the sieve was saved for metal analysis. Subsequent re-sieving resulted in no discernable increase in the concentrations of either cadmium, copper or zinc.

The concentrations of metals in bottom sediment are probably a function of the surface area per unit mass of sediment as was mentioned in the introduction. Therefore sieving was necessary to normalize the surface areas per unit mass between sample locations. To exemplify the importance of sieving, copper and zinc concentrations and percent solids of bulk, non-sieved sediment samples taken from noncontaminated areas throughout the Chesapeake Bay are compared in Figure 3 and 4. Since fine grain samples always contain more water than do coarser ones, it was thought that a linear relationship might exist between per cent solids and metal levels which would allow comparisons of dissimilar sediments. As can be seen this proved to be the case. The relationship is a useful one when trying to correlate analyses performed on bulk sediment samples after a stripping technique has been employed. It does not, however, allow total normalization of one sample to another based on percent solids alone. Too, this relationship for copper and zinc may not hold for other metals. Differences between sample surface areas can be partially eliminated by analyzing a given particle size fraction of the sediments, thus equating surface areas between samples and reducing concentration differences due to particle surface area alone.

Once the samples were sieved, the $\overline{<}$63 μ portion was first air dried, then dried at 105°C, and saved for future metal extraction and analysis.

The procedures utilized to extract or "strip" metals in different phases from the sediments are given below:

A. Total non-crystalline metals

1. Place 0.500 g of dried, homogeneous sediment in a nitric acid washed centrifuge tube;
2. Add 5.0 ml of concentrated nitric acid and heat to fuming being careful not to lose sample by splashing due to boiling;
3. After cooling to room temperature an additional 5.0 ml of concentrated reagent grade nitric acid is added and the sample reheated to fuming;
4. The mixture is then centrifuged and the supernatant is separated and diluted to volume;

5. The diluted supernatant is then ready for metal analysis by Atomic Absorption Spectrophotometry.

Analyses of 10 fresh replicate samples showed this procedure to have a precision of ± 7% for copper and ± 5% for zinc. In most cases the sediments from the York and Rappahannock River systems contained cadmium at or near the detection level of the atomic absorption unit but due to high blank levels of cadmium in the nitric acid, this element was not quantified.

This technique is admittedly harsh and undoubtedly does remove some copper and zinc from crystalline sites. However, the procedure yields reproducible amounts of copper and zinc from fresh samples as evidenced by the above mentioned precisions of ±7% and ± 5%, respectively. Extractions and analyses were performed for these elements over a 20 month period, in portions from a large composite of sediment. The yields of copper and zinc were 11% and 7%, respectively (Table 1).

B. Precipitated-Coprecipitated Metals

1. Place 0.500 g of homogenized, dried sediment in a nitric acid washed centrifuge tube;
2. Add 25 ml of 0.10 molar reagent grade hydrochloric acid;
3. Shake for 60 minutes at room temperature and centrifuge;
4. Save the supernatant liquid for atomic absorption analyses.

This procedure yielded a precision of ± 4% for both copper and zinc on 10 replicate samples. It was found, however, that the reaction time, (the shaking time), is important in the yield. Also experiments indicate that the dilute hydrochloric acid probably attacks some of the organic and crystalline metals as well. This is exemplified in Figure 5 which shows the amount of zinc extracted by this method on a Rappahannock River sample with different extraction times. After approximately 45 to 60 minutes, there is a gradual increase which probably is due to the acid leaching metals from non-intended phases. Therefore a shaking time of 60 minutes was selected.

Cadmium concentrations in this sediment phase were unobtainable because reagent blank concentrations were too high (>50%) relative to sample concentration.

C. Adsorbed Metals

The adsorbed metals method was developed by Gibbs (1973) and involves replacement of copper and zinc adsorbed to sediments by magnesium chloride. The resultant mixture is centrifuged and the supernatant analyzed by Atomic Absorption Spectrophotometry. Again high blank cadmium levels negated determination of this element.

Organic concentrations were obtained by subtracting concentrations of precipitated-coprecipitated metals from total non-crystalline values for each sample.

D. Oysters

The analyses of oyster samples for cadmium, copper and zinc involved not only care in the digestion but also in the opening of the animal's shells and draining of the shell liquor. The entire scheme is given below:

1. Oysters are carefully washed to remove any adhering mud with particular attention given to the hinge.
2. A stainless steel oyster knife is inserted into the hinge and twisted causing the hinge to break. Caution must be

exercised not to stab or puncture the animal's flesh.

3. The oyster is held, hinge down, and shaken three times to drain shell liquor which is discarded.
4. The adductor mussel is cut and the oyster meat is placed into an acid washed and dried, 125 erlenmeyer flask and the wet weight recorded.
5. Approximately 20 ml of reagent grade concentrated nitric acid is added and the sample is allowed to digest for 24 hours at room temperature.
6. The sample is then heated to fuming or unitl a clear, dark red solution results.
7. The digest is cooled to room temperature and filtered through acid washed glass wool and the final filtered volume measured.
8. The sample is then ready for analysis by Atomic Absorption Spectrophotometry.

This method is relatively simple compared to most ashing methods. Sample splits which were sent by the National Marine Fisheries Service, Atlantic Estuarine Fisheries Center in Beaufort, North Carolina were analyzed by this procedure and compared to results on the splits extracted by them utilizing a dry ash method. The results were not significantly different for copper and zinc at the 0.001 significance level. They were not set-up to analyze for cadmium.

The extracts were analyzed for copper and zinc and where possible cadmium by Atomic Adsorption Spectrophotometry using a Varian AA-5 instrument. Conditions were as follow:

	Copper	Zinc	Cadmium
Fuel	Acetylene	Acetylene	Acetylene
Support	Air	Air	Air
Wavelength	324.8 nm	213.9 nm	228.8 nm
Slit	100 μ	100 μ	200 μ

Figure 1. Map of the Chesapeake Bay.

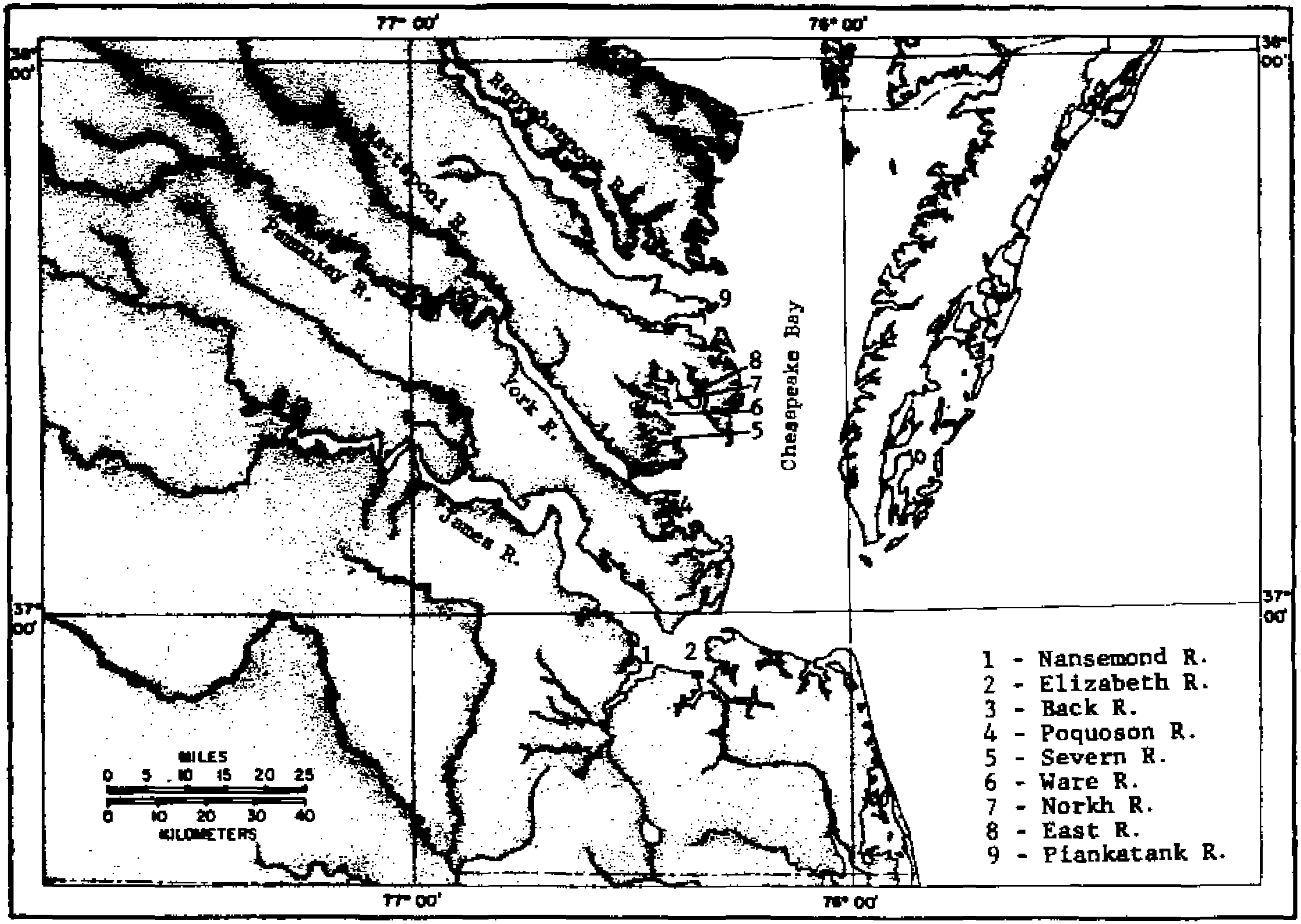
77° 00'
76° 00'
38° 00'
37° 00'
Rappahannock R.
Mattapony R.
Pamunkey R.
York R.
James R.
Chesapeake Bay
1
2
3
4
5
6
7
8
9
1 - Nansemond R.
2 - Elizabeth R.
3 - Back R.
4 - Poquoson R.
5 - Severn R.
6 - Ware R.
7 - Norkh R.
8 - East R.
9 - Piankatank R.
MILES
0 5 10 15 20 25
0 10 20 30 40
KILOMETERS

Figure 2. Map of the Newport Estuary and Bogue Sound, North Carolina.

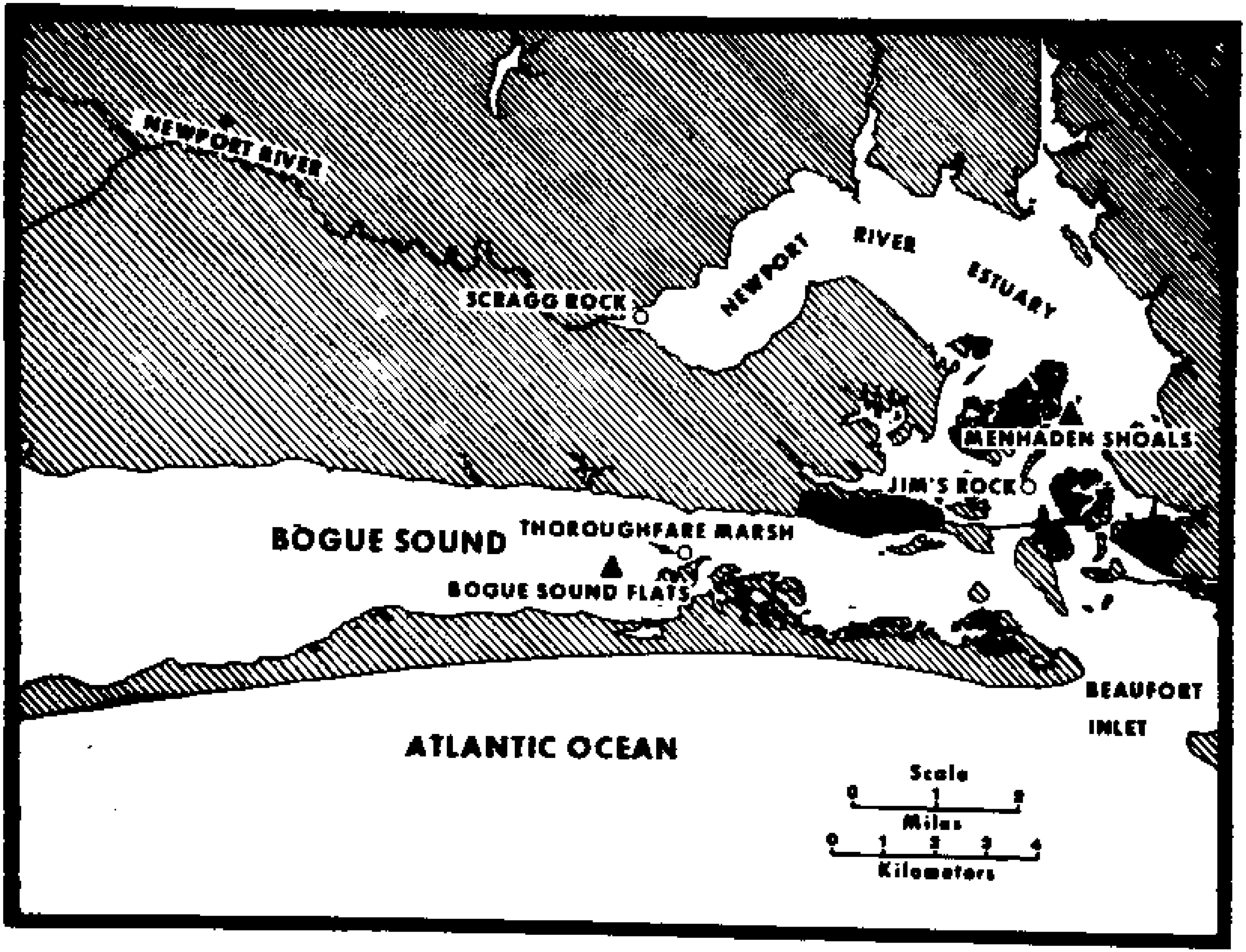
NEWPORT RIVER
SCRAGG ROCK
NEWPORT RIVER ESTUARY
MENHADEN SHOALS
JIM'S ROCK
BOGUE SOUND
THOROUGHFARE MARSH
BOGUE SOUND FLATS
BEAUFORT INLET
ATLANTIC OCEAN
Scale
0 1 2
Miles
0 1 2 3 4
Kilometers

Figure 3. Concentration of copper (nitric acid digestion) in sediments from noncontaminated areas throughout the Chesapeake Bay vs. percent solids.

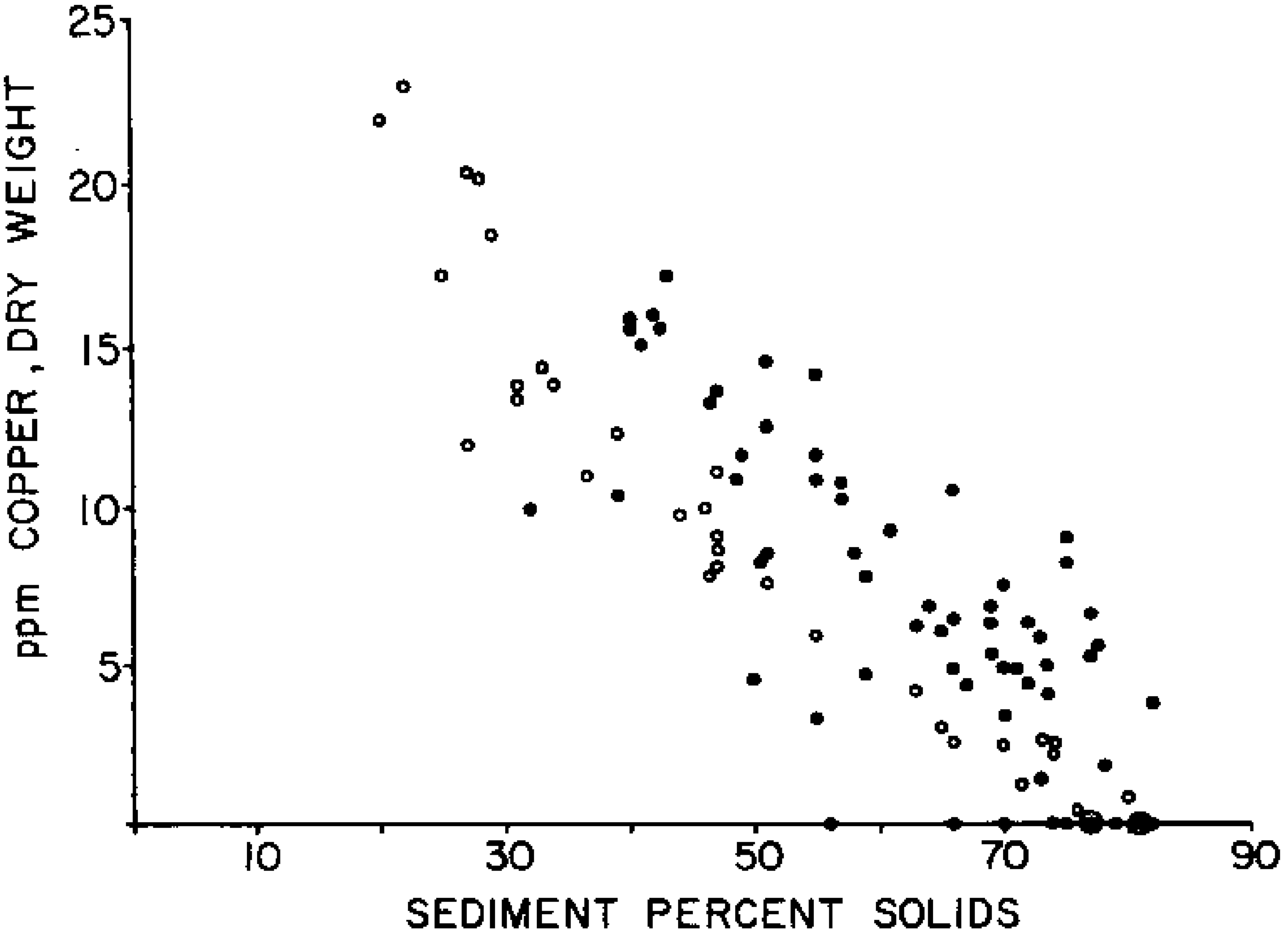
ppm COPPER, DRY WEIGHT
25
20
15
10
5
10
30
50
70
90
SEDIMENT PERCENT SOLIDS

Figure 4. Concentration of zinc (nitric acid digest) in sediments from noncontaminated areas throughout the Chesapeake Bay vs. percent solids.

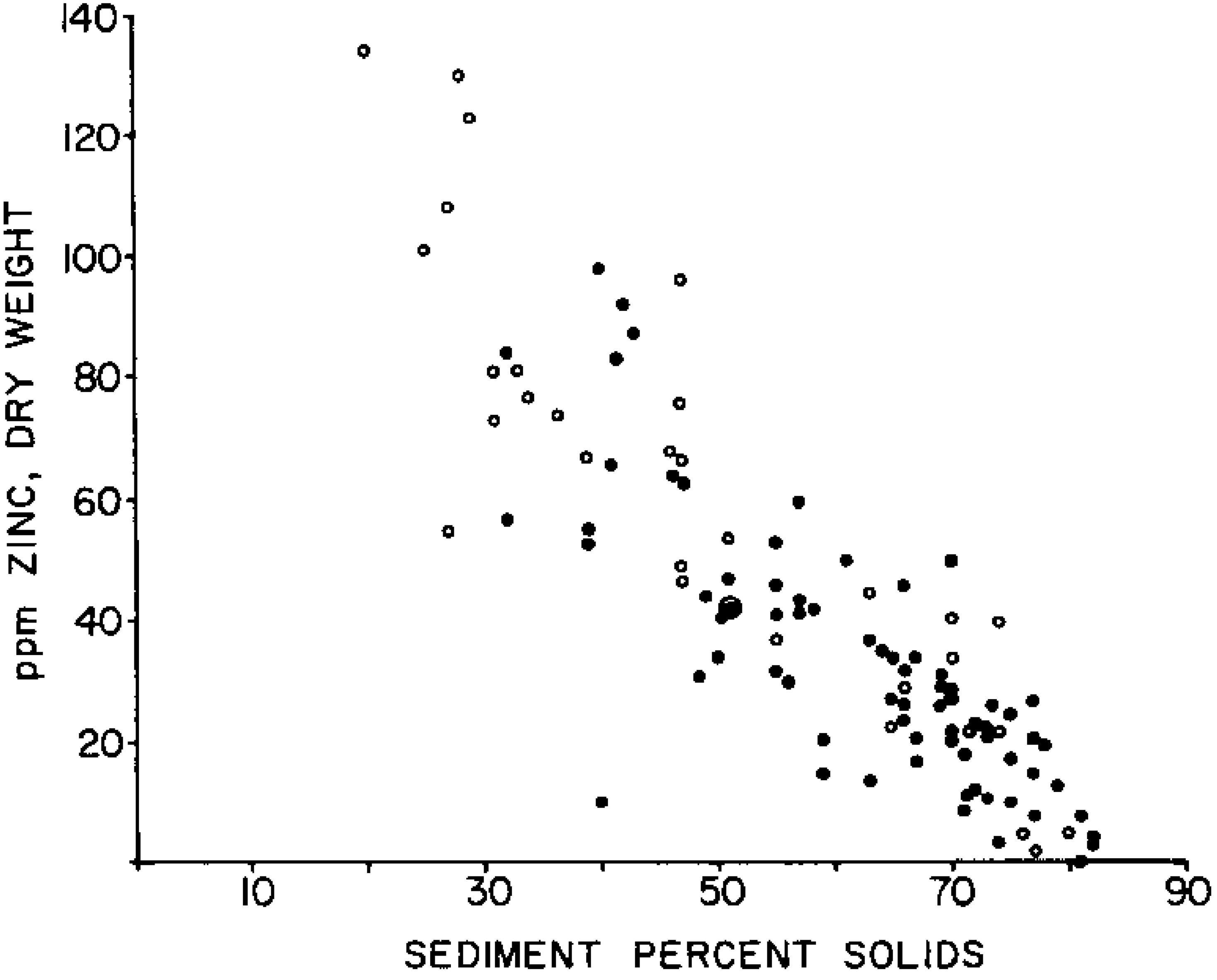
140
120
100
80
60
40
20
ppm ZINC, DRY WEIGHT
10
30
50
70
90
SEDIMENT PERCENT SOLIDS

Figure 5. Yield of zinc by 0.10 Molar Hydrochloric Acid vs. shaking time.

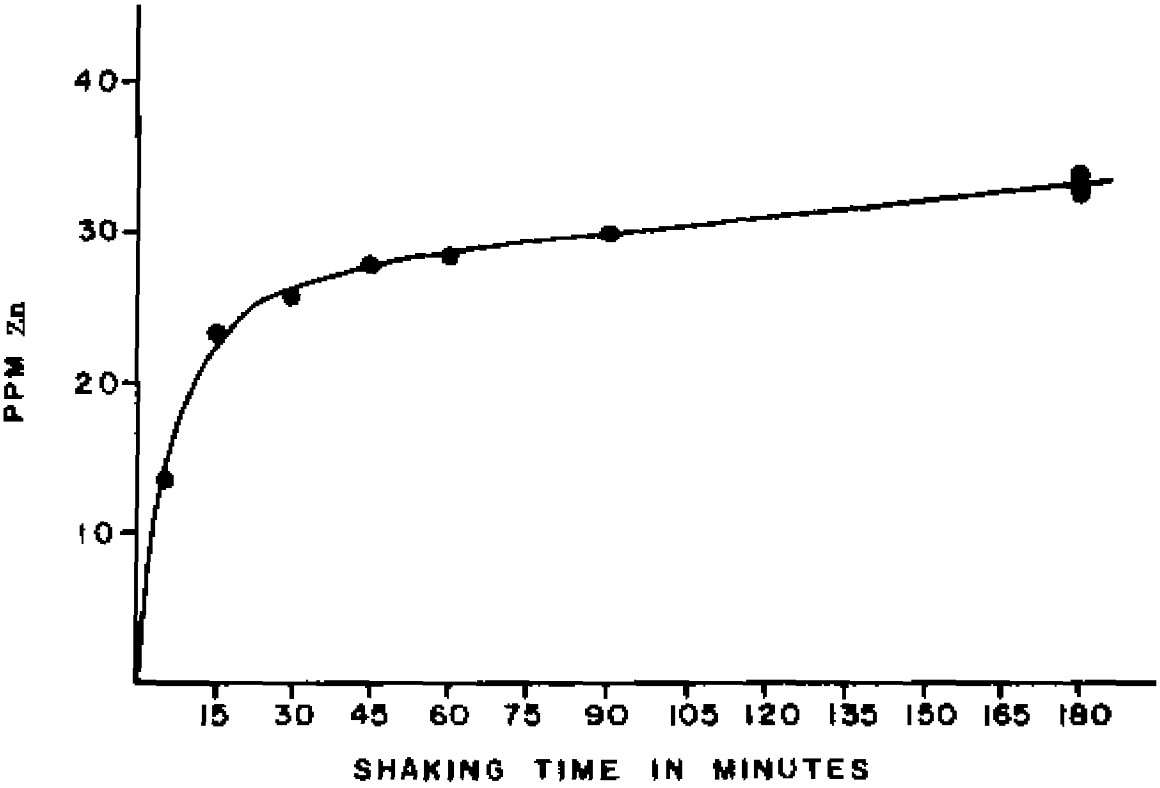
40
30
20
10
PPM Zn
15
30
45
60
75
90
105
120
135
150
165
180
SHAKING TIME IN MINUTES

TABLE 1

ZINC AND COPPER CONCENTRATIONS OBTAINED FROM A COMPOSITE OF RAPPAHANNOCK RIVER SEDIMENTS ANALYZED BY THE NITRIC ACID METHOD OVER A 20 MONTH PERIOD.

	mg kg^{-1} Dry Weight	
Date of Analysis	Zinc	Copper
February 1974	60	17
March 1974	60	18
May 1974		21
February 1975	64	20
May 1975	62	
May 1975	54	
June 1975	59	24
September 1975	66	20
	54	17
	53	17
	54	16
	56	18
	55	17
	$\bar{X} \pm sd = 58 \pm 4$	$\bar{X} \pm sd = 19 \pm 2$

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UTILIZING METAL CONCENTRATION RELATIONSHIPS IN THE EASTERN OYSTER (*CRASSOSTREA VIRGINICA*) TO DETECT HEAVY METAL POLLUTION

INTRODUCTION

The eastern oyster, *Crassostrea virginica*, inhabiting areas having salinities of 7-30 o/oo, is subjected to varying conditions with respect to both food and the chemical characteristics of the surrounding waters (Wilber and Yonge, 1969). The responses of these organisms as measured in terms of growth rate, survival, etc. to this gradient are of both commercial and scientific importance. One characteristic of filter feeding organisms, especially oysters, which is of considerable significance in this regard is their ability to concentrate a variety of compounds from the aqueous phase. Many substances, while not necessarily harming the organism, are concentrated in the animal's tissues.

The heavy metals, cadmium, copper and zinc are no exception and have been shown to be concentrated four to five orders of magnitude above that of the surrounding water (Kopfler and Mayer, 1969). Aside from the obvious public health and entrepreneurial aspects of this concentrating ability, the phenomenon may be used to detect pollution sources (Schuster and Pringle, 1969).

Previous workers have reasoned that if oysters from a given area contain more of a substance than a pre-set "Action-level" then a nearby source is indicated. Unfortunately, this reasoning can lead to erroneous conclusions and even at best can detect unnatural sources only after gross contamination has occurred.

The work described in this paper shows that the concentrations of the heavy metals, cadmium, copper and zinc in oysters are a function of not only source but also the animal's position in the estuary. The future use of concentration ratios is suggested which allows:

1. an indication whether metal concentrations in organisms be from natural or manmade sources;
2. recognition of problem areas before they reach nuisance levels;
3. prediction, with some certainty, of areas which would be adversely affected by unnatural additions of metals;
4. prediction of areas which could best tolerate unnatural additions of metals.

METHODS AND PROCEDURES

A total of 495 oysters were collected during the period of February-May 1971 from the areas indicated in Fig. 1. Salinities at the sampling locations ranged from 32 o/oo, for the ocean-side, Eastern Shore to 7 o/oo in the estuaries.

Five specimens from each site were removed from the shell without puncturing the body of the oyster, and the individual organisms, ranging in wet weight from 2 to 35 g, were completely digested in concentrated nitric acid (Reagent ACS, Fisher Scientific).

The dissolved samples were analyzed for cadmium, copper and zinc utilizing a Beckman Model 1301 Atomic Absorption System with a Model DB-G Grating Spectrophotometer.

RESULTS

Examination of the data showed that oysters from the same sampling location often differed in metal concentration as much as 100 per cent and occasionally 300 per cent. Such variability of metal concentrations in oysters from the same location is not unique to Chesapeake Bay. Fitzgerald and Skaven (1963) and Kopfler and Mayer (1969) reported like findings for oysters collected from various areas along the Atlantic and Gulf Coasts. These variable concentrations are assumed to be normally distributed around some population mean, therefore the sample mean from each location should approximate the population mean. The use of means, however, weakens the statistical computation since the degrees of freedom are reduced and the probability of rejecting a null hypothesis is greater. Before using the means, an attempt was made to find whether or not the variability of concentrations from the same sampling location could be explained by the oyster's age. The individual organism zinc data from the James River are expressed in Fig. 2 and there appeared to be no correlation between the age of the oyster, as indicated by weight, and the metal concentration. This indicates that the oysters are in steady state equilibrium with respect to the available metals and that sample mean can be used if necessary.

In this study, means were used only to ascertain the areal distribution of metals in the various river systems. The means showed that a concentration gradient existed in all systems and that each metal increased in concentration as fresh water was approached (Figs. 3, 4 and 5).

Several assumptions were made at this point, these were:

1. that the metals (Cu, Cd and Zn) available to oysters in non-industrialized areas are from the natural weathering of rocks;
2. that the ratio of copper to zinc in the weathering rocks is relatively constant within a drainage basin;
3. that oysters accumulate a constant percentage of each element available to them.

If these assumptions are valid then there should be a linear relationship between the zinc and copper concentrations in oysters taken from areas which have similar drainage basins. To test this hypothesis, all samples from rivers which extend above the fall line and in which there is no known zinc or copper source are plotted in Fig. 6.

The method of least squares was employed to obtain a best fit line for this data with an equation:

$$Y = -1.9 + 0.09\,X$$

Preliminary analysis of the cadmium and zinc data indicate that a linear relationship exists for these metals as well.

DISCUSSION

Analyses of these data show that there is an apparent linear relationship between the levels of copper and zinc, and zinc and cadmium in uncontaminated oysters. If samples originating from areas which have known or highly probable unnatural metal sources are from calculations, then background conditions are approached as in Fig. 6. Ideally, confidence intervals producing confidence bands would give investigators a statistical probability of whether samples taken elsewhere are from the same "non-contaminated" population. A sample which falls outside these bands would indicate either an unnatural source of zinc or of copper depending on which side it falls. Unfortunately the use of normal confidence intervals necessitates that there be an independent and a dependent variable. If the assumptions outlined in the results section are correct, then both variables are independent, i.e. the zinc concentration does not control the copper levels found in the oysters.

The statistical approach should be that of a normal bivariate distribution. This would allow confidence intervals which would form an ellipse at a given significance level around the mean. The mean of all samples, however, is not realistic since, at least in this study, it is weighted due to the more numerous high salinity sampling areas. The authors have placed a band, consisting of two straight lines, around the least squares line. This band encompasses 95 per cent of the points and can be thought of as an approximate confidence band. The equations for the two lines are :

$$Y = -33 + 0.07\ X$$

$$Y = +30 + 0.11\ X$$

The remaining data from areas of suspected unnatural inputs, as well as those falling outside the lines in Fig. 6, are plotted along with the confidence band in Fig. 7. Those points falling outside the band indicate unnatural contamination and these areas are shown in Fig. 8.

It appears that the Elizabeth River and Hampton Roads, both highly industrialized, are contaminating the oysters in this area as well as the lower reaches of the James River with zinc. Oysters from one station in the Elizabeth River averaged over 6000 ppm in zinc. Bottom sediments from the Elizabeth confirmed this source (or sources) Fig. 9.

The upper James appears to have an unnatural source of copper as indicated by points falling on the copper side of the band in Fig. 7.

The cause of the concentration banding is, at the writing of this manuscript, unknown. The concentration of the metals (whatever the form) may be greater in low salinity waters. We have, however, analyzed centrifuged water samples from the York River, with stations 0.5 mile apart from the mouth to 10 miles above the salt-fresh water interface, and found no significant difference in the concentrations of metals analyzed (copper, cadmium and lead).

We have also analyzed bottom sediments from the James and the levels of metals in these sediments have no relationship to the levels in the oysters.

The authors feel that the form of the metal in solution governs the concentration banding phenomenon. Chelating by humic acids in the low salinity areas may make the metals more available to the organism either directly or through the food chain.

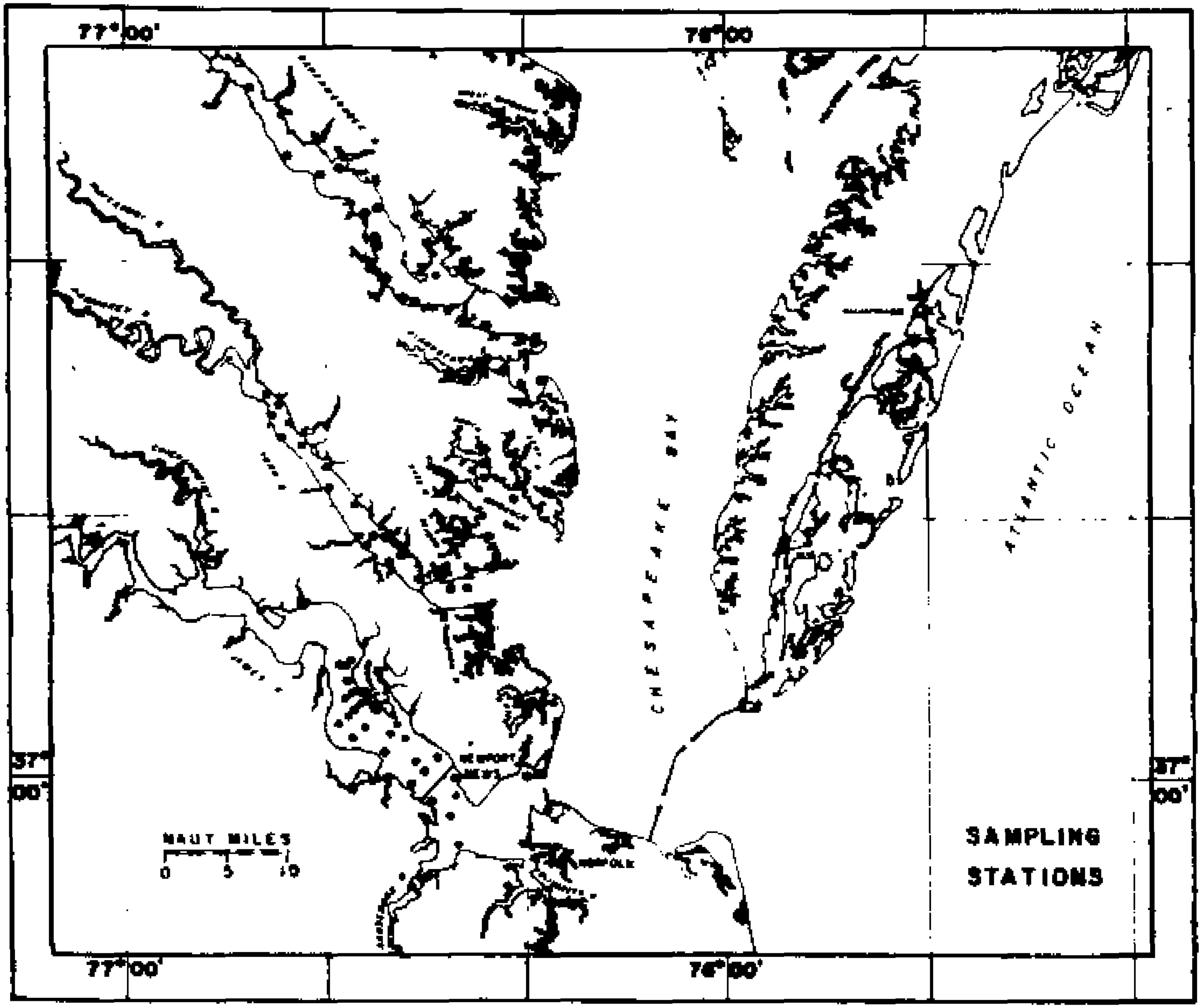
At present laboratory investigations are being conducted to determine the cause of the banding phenomenon.

CONCLUSIONS

The distribution of the metals, copper, cadmium and zinc, with respect to the salinity regimes, Figs. 3, 4 and 5 allows the prediction of areas that would be most affected by unnatural additions of metals. A source in the low salinity areas would be potentially more dangerous to the oysters and those that consume them than one in high salinity.

It is apparent that no single concentration for an "Action-level" can be set for cadmium, copper or zinc in oysters which will definitely indicate pollution sources. However, the approach described in this manuscript has been proven valid in the Chesapeake Bay and may be of use elsewhere.

Figure 1. Location of sampling stations.



SAMPLING STATIONS

Figure 2. Oyster weight vs. zinc concentration for James River oysters.

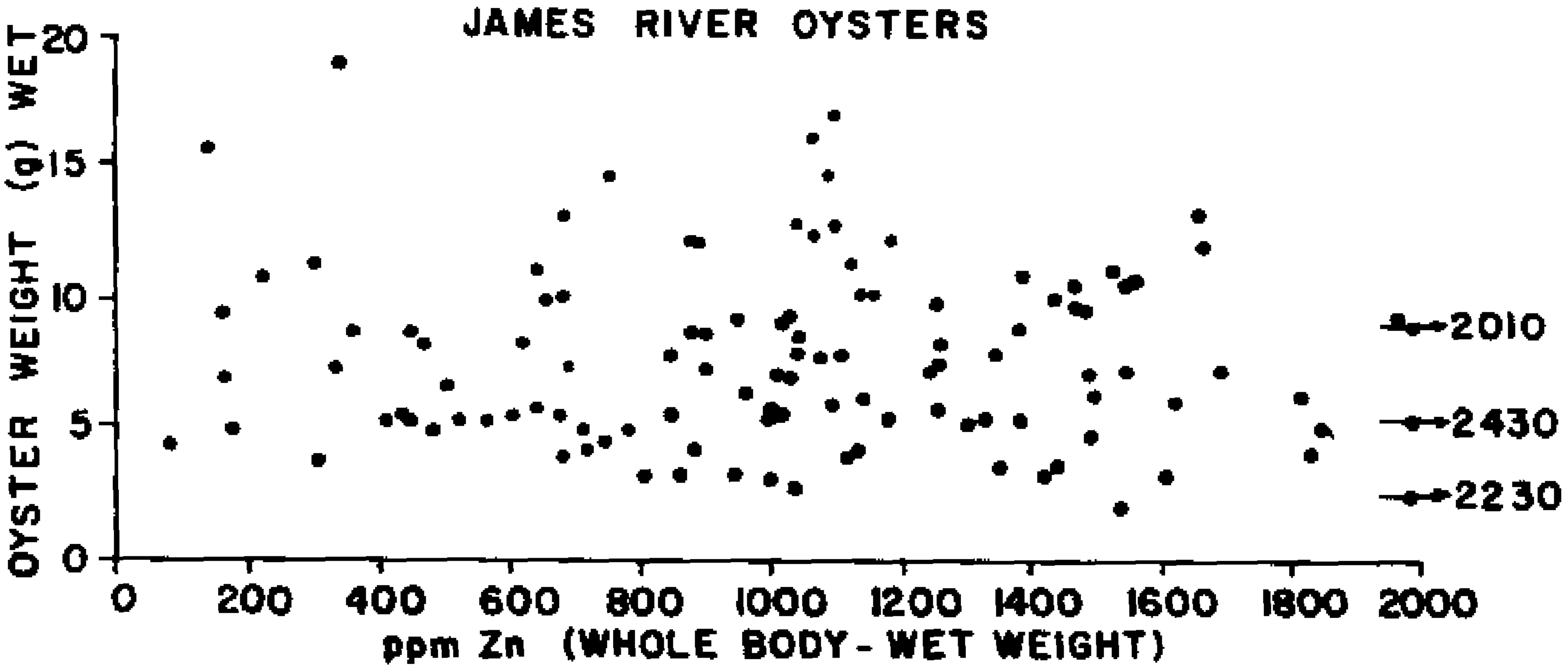

JAMES RIVER OYSTERS
OYSTER WEIGHT (g) WET
20
15
10
5
0
0
200
400
600
800
1000
1200
1400
1600
1800
2000
ppm Zn (WHOLE BODY - WET WEIGHT)
2010
2430
2230

Figure 3. The distribution of zinc in oysters from Virginia's major rivers.

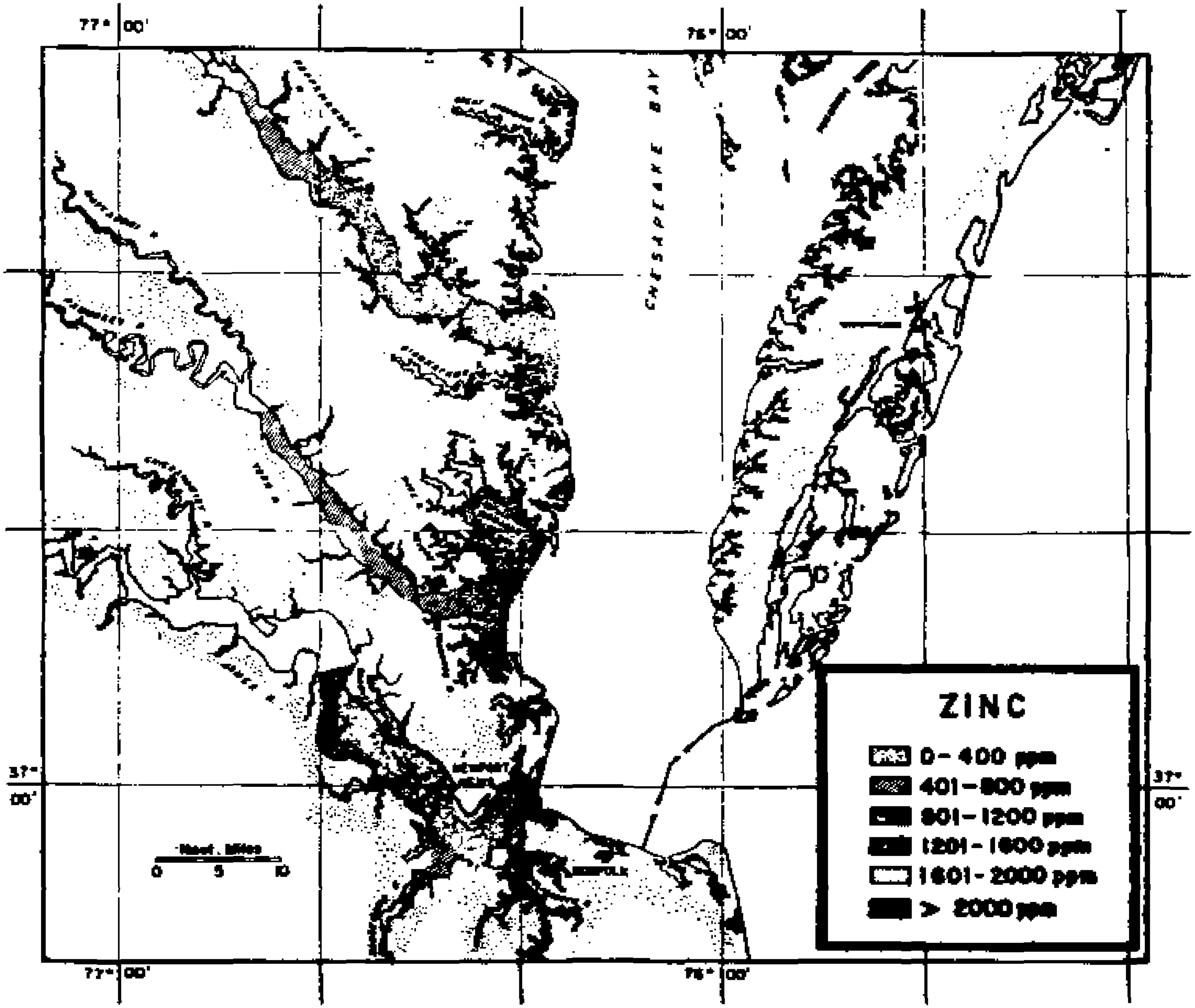

77° 00'
76° 00'
37° 00'
CHESAPEAKE BAY
NEWPORT NEWS
NORFOLK
YORK R.
JAMES R.
Naut. Miles
0 5 10
ZINC
0 - 400 ppm
401 - 800 ppm
801 - 1200 ppm
1201 - 1600 ppm
1601 - 2000 ppm
> 2000 ppm

Figure 4. The distribution of copper in oysters from Virginia's major rivers.

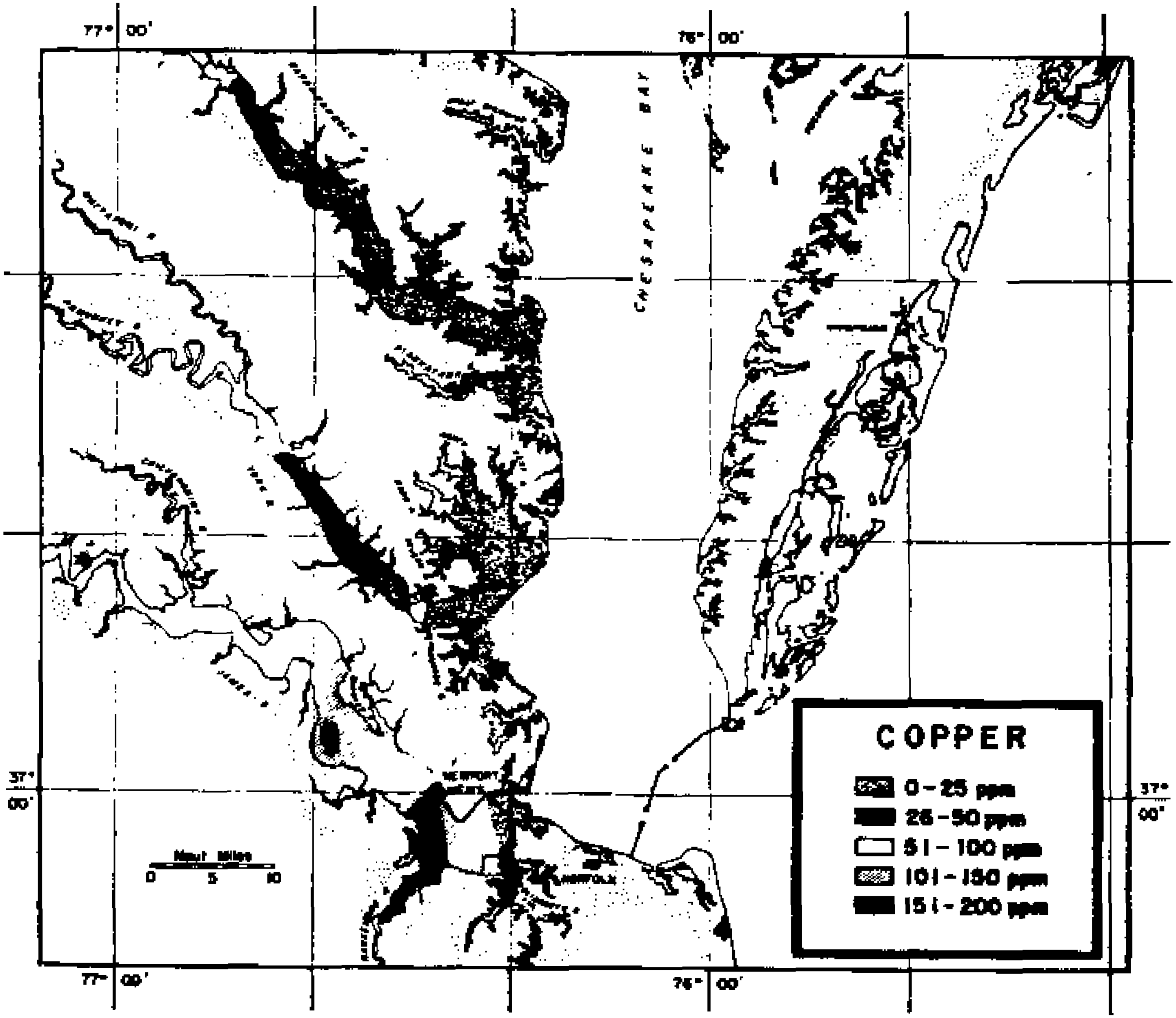

COPPER
0 - 25 ppm
26 - 50 ppm
51 - 100 ppm
101 - 150 ppm
151 - 200 ppm
CHESAPEAKE BAY
YORK R
JAMES R
NEWPORT NEWS
NORFOLK
Naut. Miles
0
5
10
77° 00'
76° 00'
37° 00'

Figure 5. The distribution of cadmium in oysters from Virginia's major rivers.

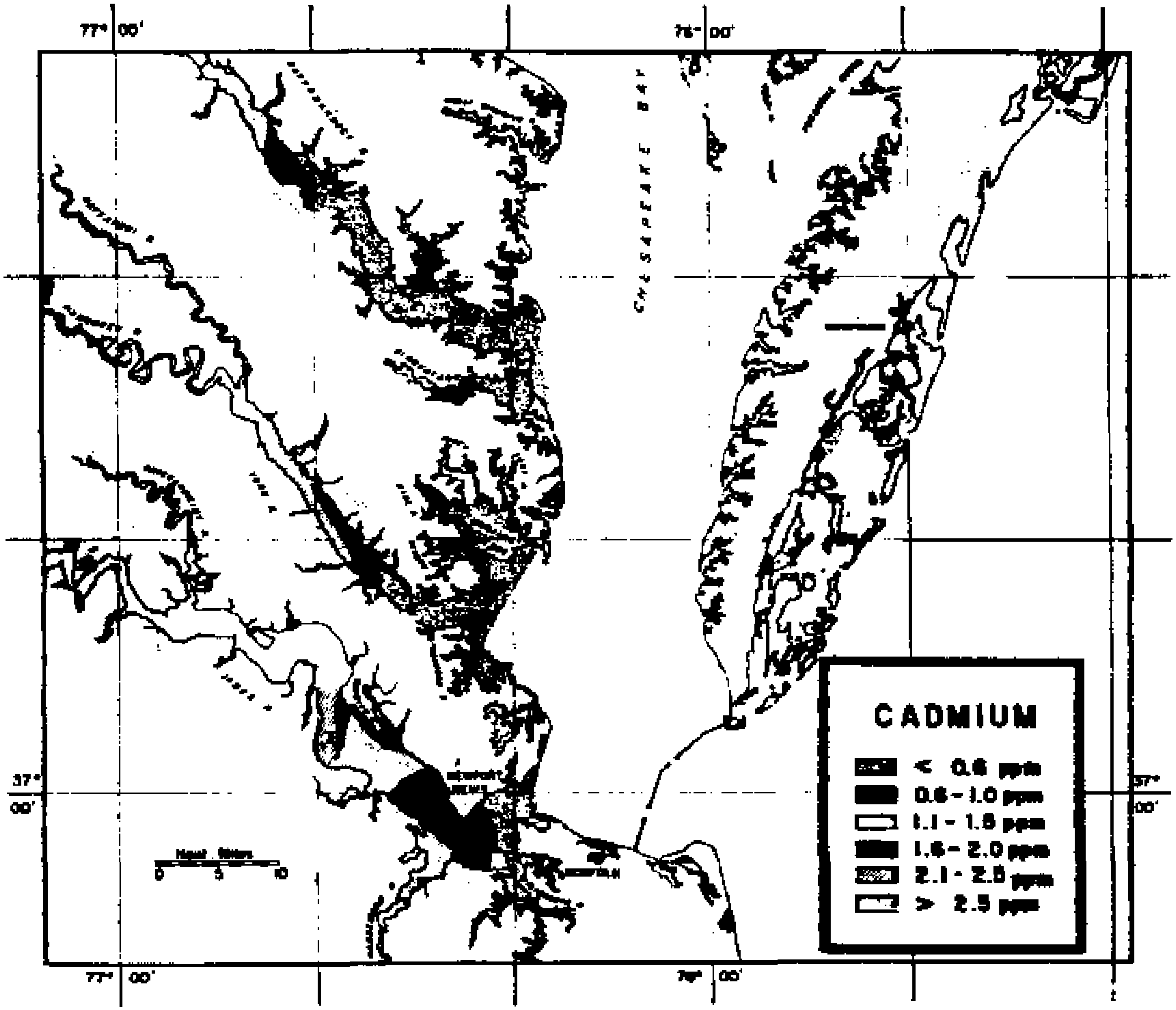

77° 00'
76° 00'
37° 00'
CHESAPEAKE BAY
NEWPORT NEWS
NORFOLK
0 5 10
CADMIUM
< 0.6 ppm
0.6 - 1.0 ppm
1.1 - 1.5 ppm
1.6 - 2.0 ppm
2.1 - 2.5 ppm
> 2.5 ppm

Figure 6. Relationship between zinc and copper in oysters from Virginia's major rivers.

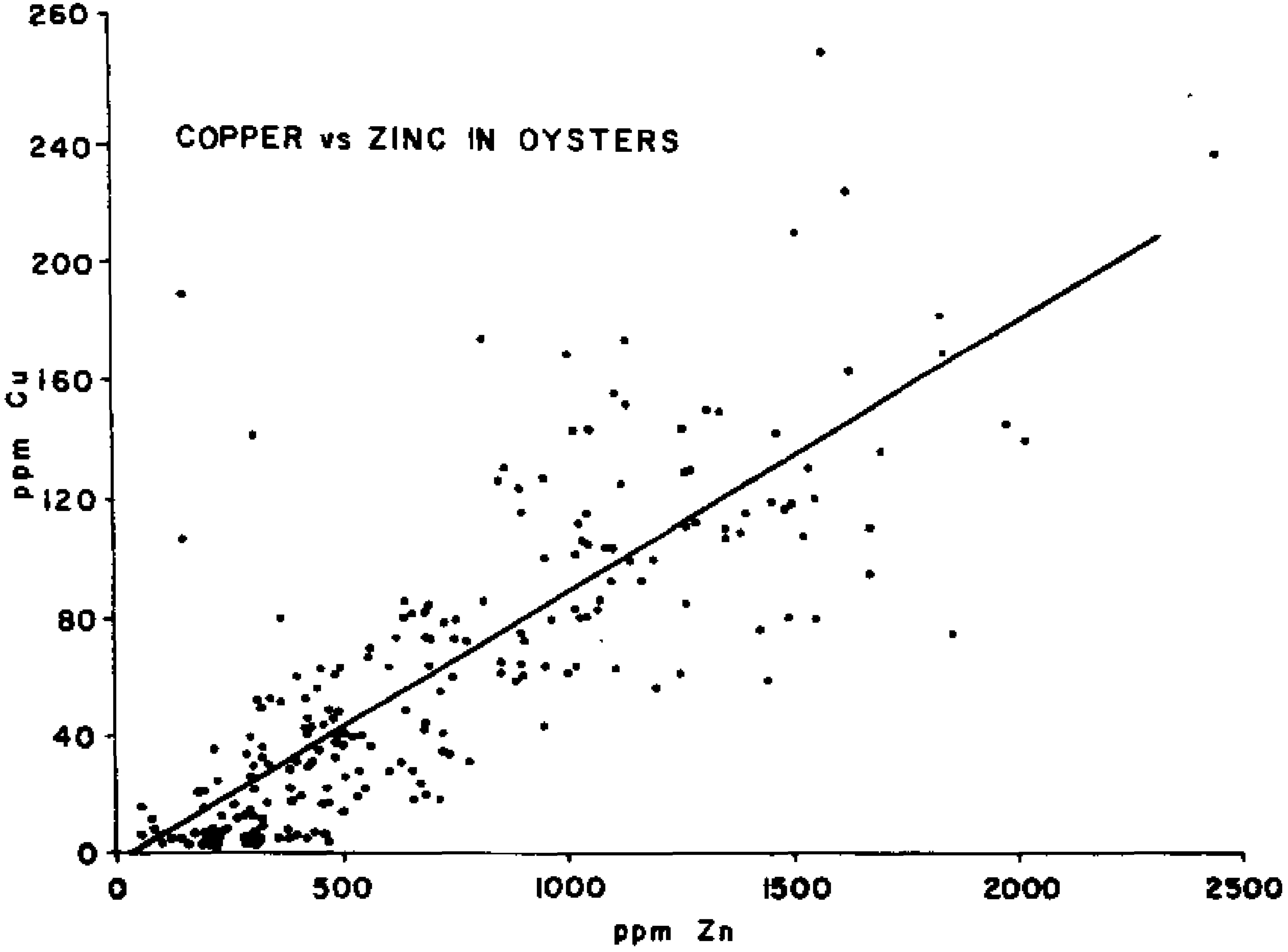

COPPER vs ZINC IN OYSTERS
ppm Cu
260
240
200
160
120
80
40
0
0
500
1000
1500
2000
2500
ppm Zn

Figure 7. Oyster data indicating unnatural metal inputs.

OYSTER DATA INDICATING UNNATURAL METAL INPUTS

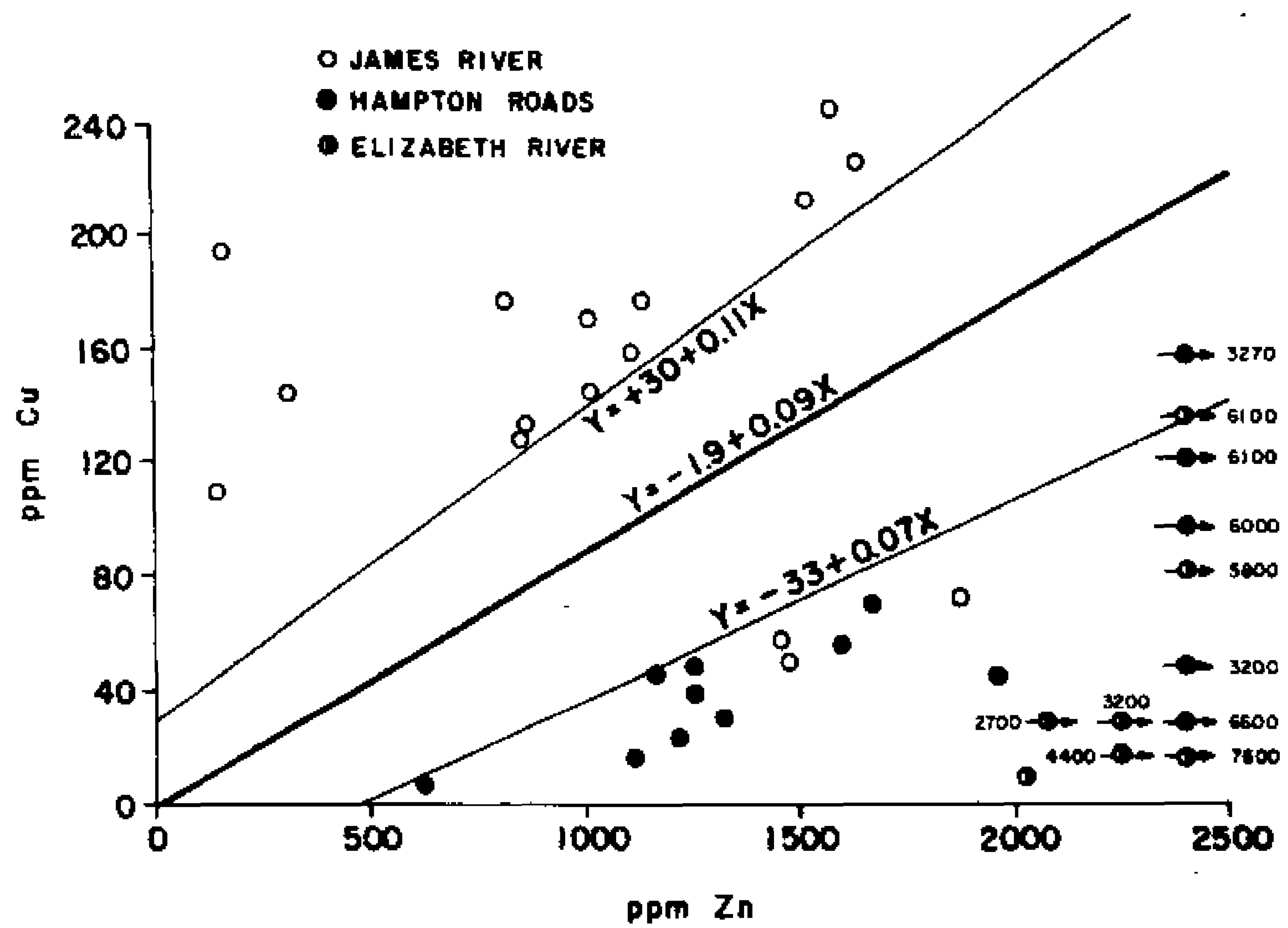


Figure 8. The distribution of unnatural zinc and copper levels in oysters from Virginia.

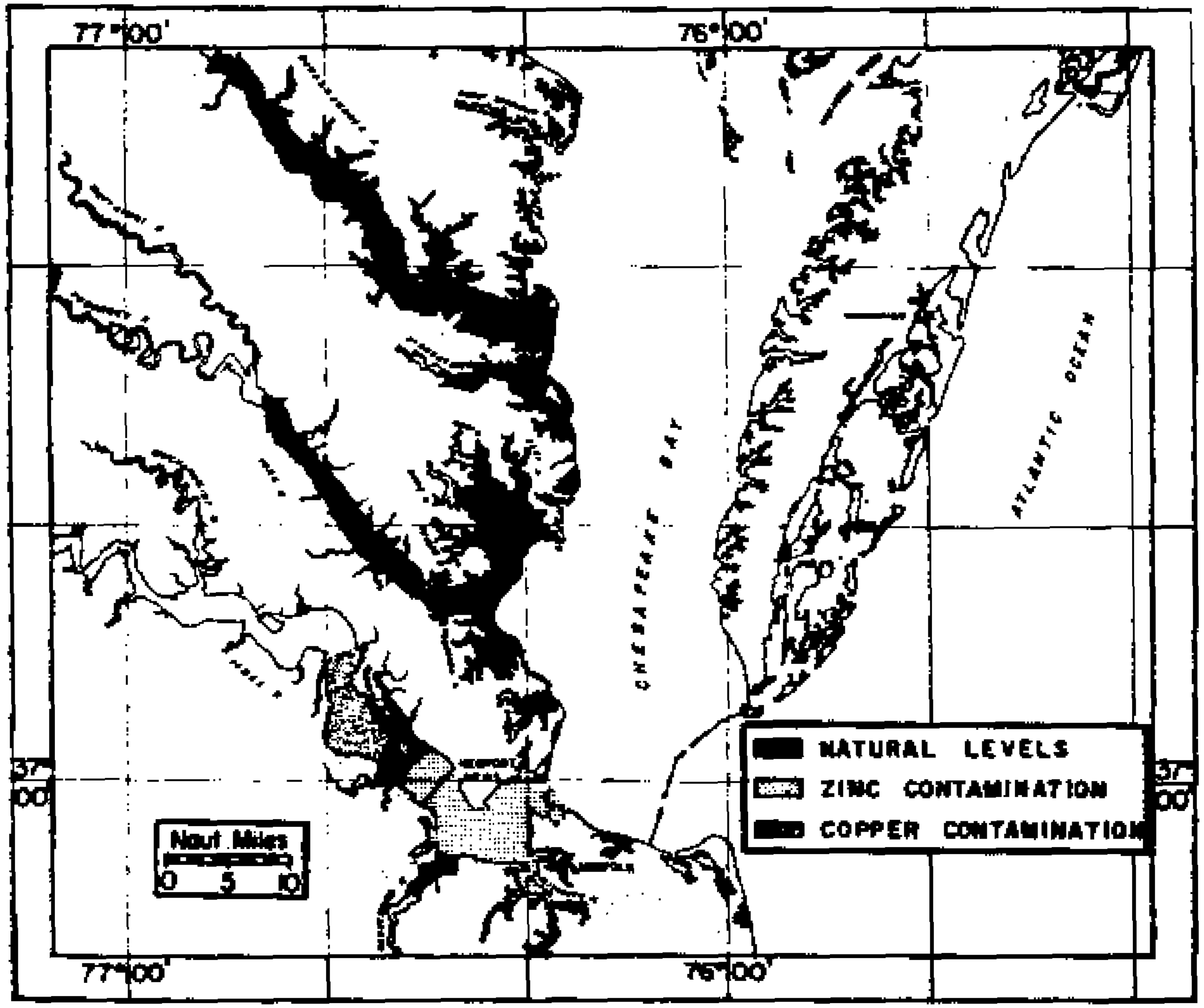
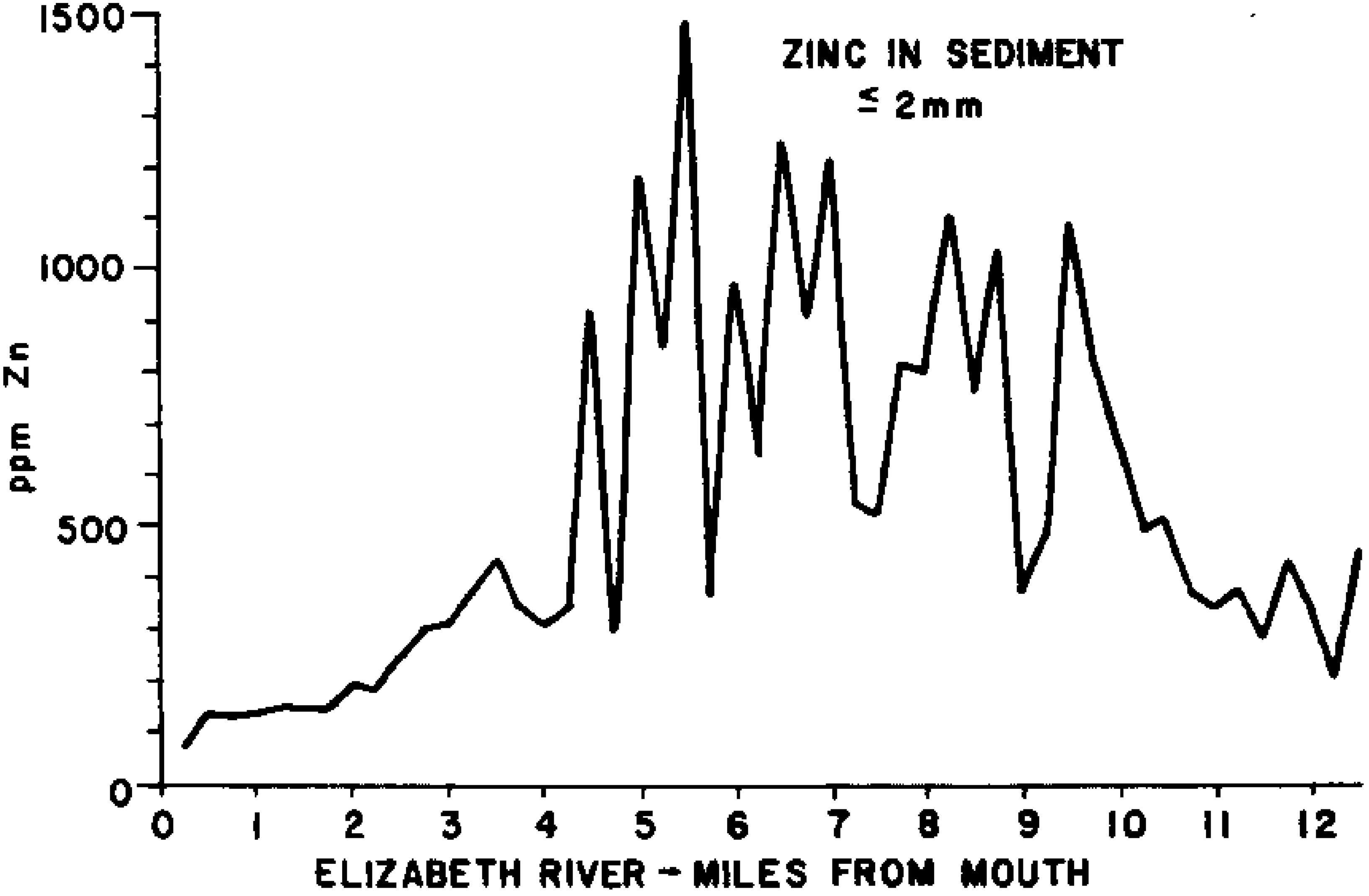

77°00'
76°00'
37°00'
CHESAPEAKE BAY
ATLANTIC OCEAN
NATURAL LEVELS
ZINC CONTAMINATION
COPPER CONTAMINATION
Naut Miles
0 5 10

Figure 9. Zinc levels in Elizabeth River sediments.


ZINC IN SEDIMENT
≤ 2mm
ppm Zn
1500
1000
500
0
0
1
2
3
4
5
6
7
8
9
10
11
12
ELIZABETH RIVER – MILES FROM MOUTH

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SCHUSTER, C. N. and B. H. PRINGLE. 1969. Trace metal accumulation by the American Eastern oyster, *Crassostrea virginica*. Proceedings of the National Shellfisheries Ass., Vol. 59.

WILBER, K. M. and C. M. YONGE. 1969. Physiology of Molluscs, 645 pp. Academic Press, New York.

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

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-μm 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.

INTRODUCTION

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 hypothesis 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-μm 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-μm 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 $MgCl_2$ (Gibbs, 1973). The precipitated-coprecipitated and adsorbed metals were extracted with 0.1N HCl, and the total noncrystalline metals were extracted with concentrated HNO_3 (Huggett and Bender, 1972). Analyses of replicate samples showed the nitric acid extraction to have a precision of ±7% for copper and ±5% for zinc; that of the hydrochloric acid procedure was ±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 graident 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.

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 pooled 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 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. The 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 two fractions (Fig. 4). Because magnesium is an abundant element in seawater, estuarine sediments have already been "stripped" of some absorbed 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 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 mechanisms 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 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 1900's. 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 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 μm membrane filters, have not been satisfying. Two methods were tried, each with limited success: aniodic stripping voltametry and organic chelation and extraction. Each has the limitation of matrix 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 particular 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 environmentalong 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 of zinc for binding sites in the soft tissue. 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}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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This manuscript is Virginia Institute of Marine Science Contribution No. 631.

Figure 1. Mean concentration ± 2 standard errors of copper and zinc in oysters collected from the Rappahannock River Estuary. The number in parentheses represents the individuals analyzed at each station.

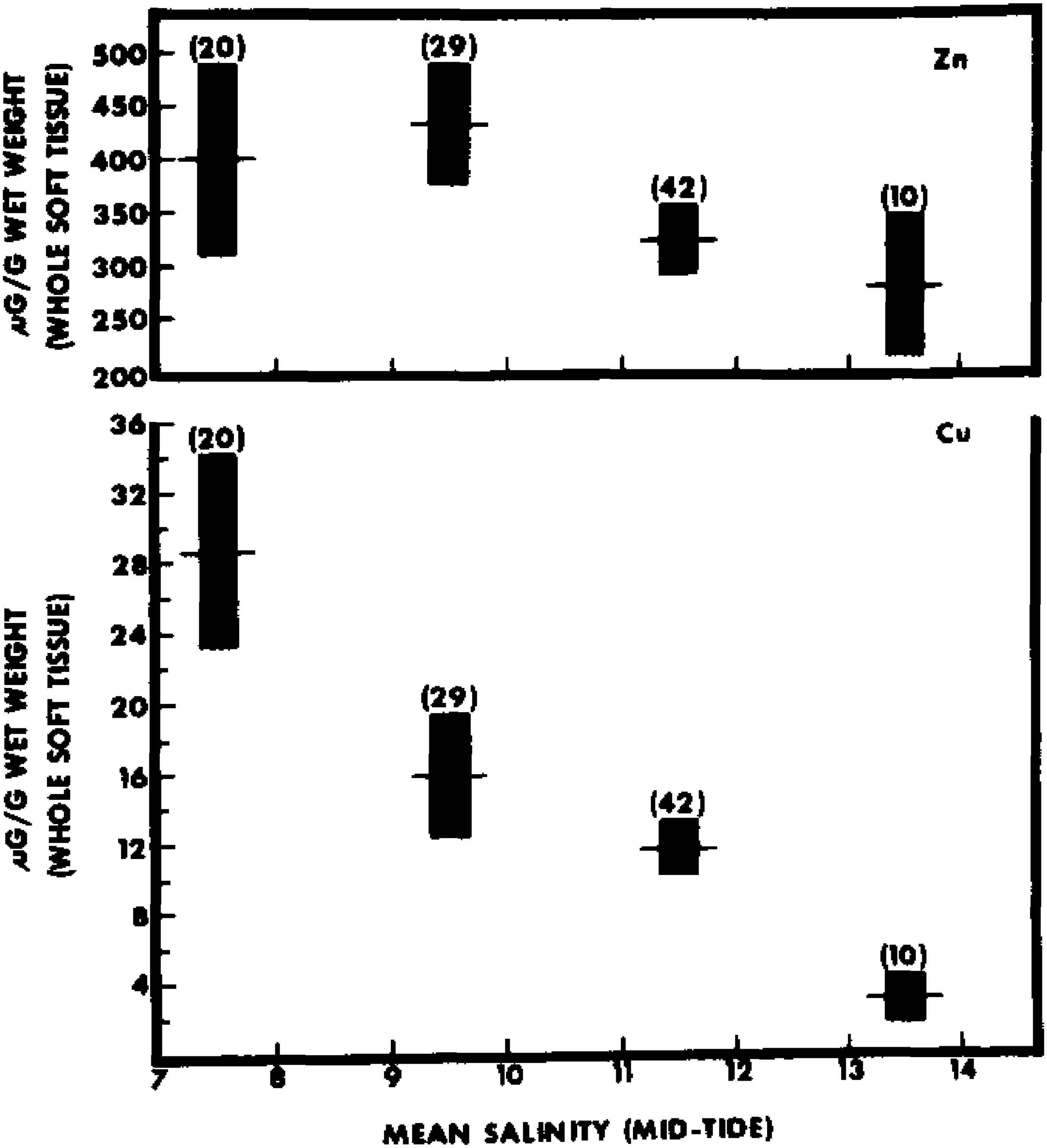

Zn
Cu
(20)
(29)
(42)
(10)
µG/G WET WEIGHT (WHOLE SOFT TISSUE)
200
250
300
350
400
450
500
4
8
12
16
20
24
28
32
36
7
8
9
10
11
12
13
14
MEAN SALINITY (MID-TIDE)

Figure 2. Mean concentrations ± 2 standard errors of copper and zinc in oysters collected from Newport River Estuary (12 and 28 o/oo) and Bogue Sound (33 o/oo). Each set of values represents the analysis of 50 individuals.

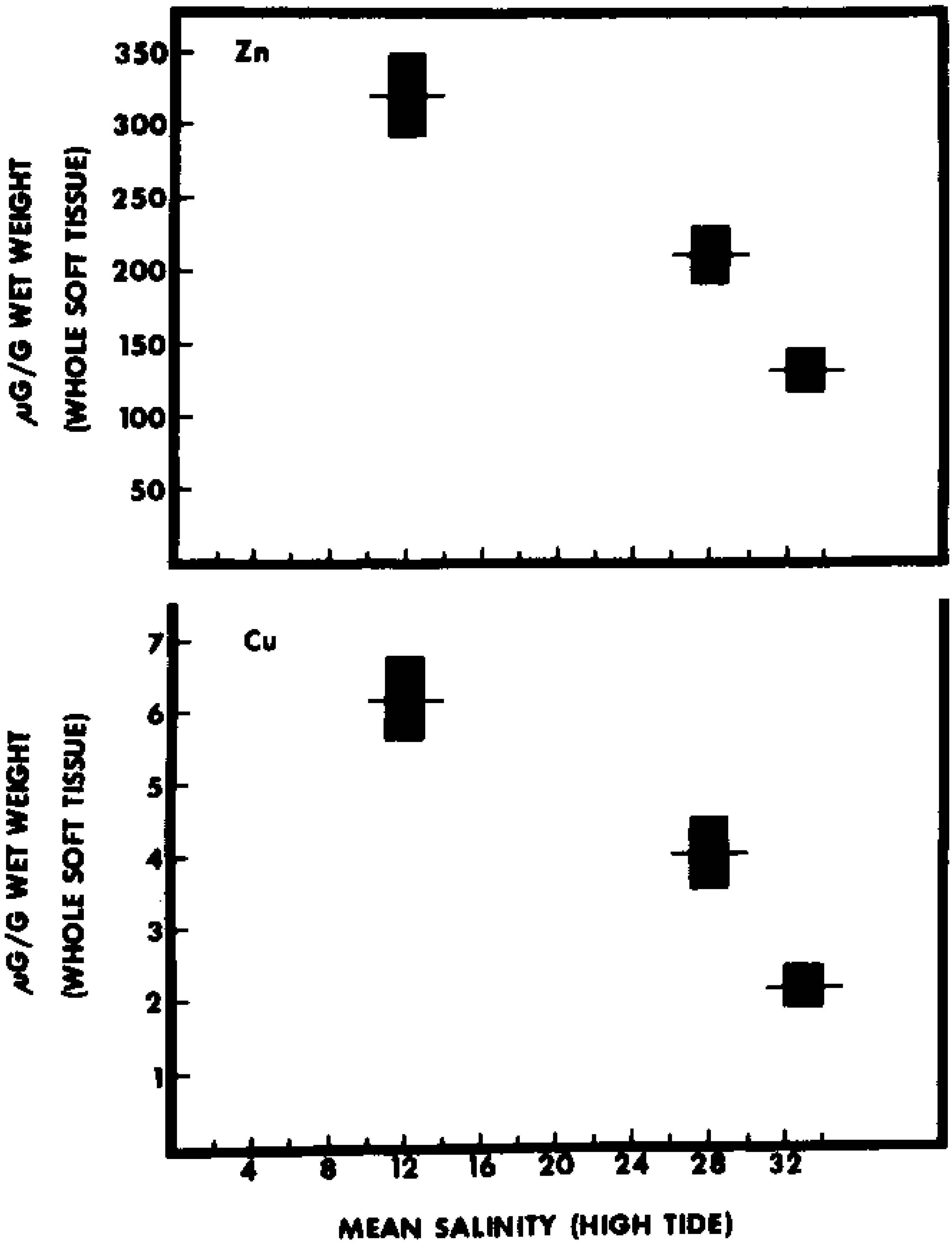

Zn
Cu
μG/G WET WEIGHT
(WHOLE SOFT TISSUE)
350
300
250
200
150
100
50
7
6
5
4
3
2
1
4
8
12
16
20
24
28
32
MEAN SALINITY (HIGH TIDE)

Figure 3. Moving averages (3) of concentrations of precipitated-coprecipitated and organic copper in the ≤63 μm fraction of sediments from the Rappahannock River and estuary collected in January 1972 (●) and June 1973 (■). Zero kilometers represent the mouth of the estuary.

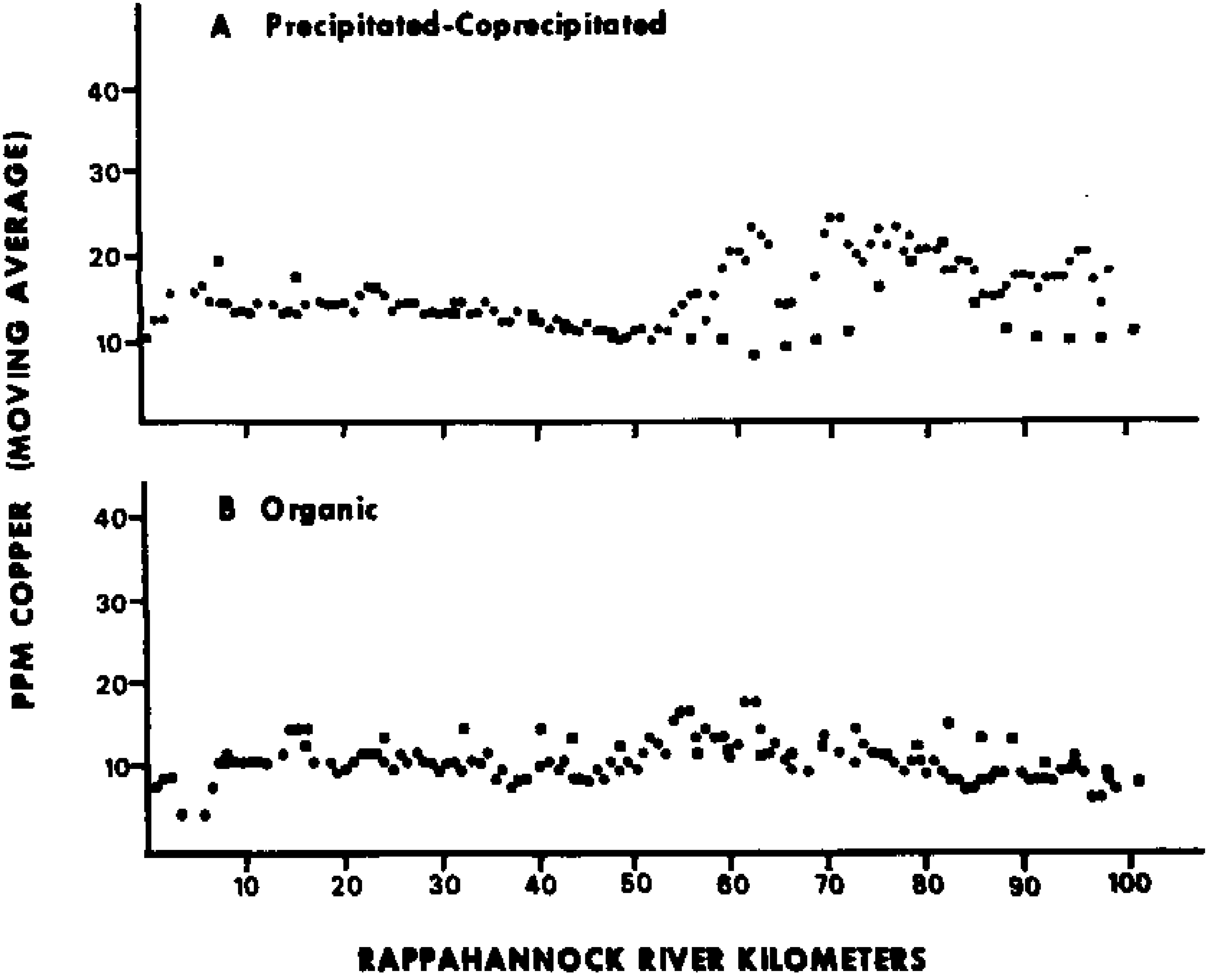

A Precipitated-Coprecipitated
B Organic
PPM COPPER (MOVING AVERAGE)
40
30
20
10
40
30
20
10
10
20
30
40
50
60
70
80
90
100
RAPPAHANNOCK RIVER KILOMETERS

Figure 4. Moving averages (3) of concentrations of adsorbed copper and zinc in the ≤63 μm fraction of sediments from the Rappahannock River and estuary collected in January 1972. Zero kilometers represent the mouth of the estuary.

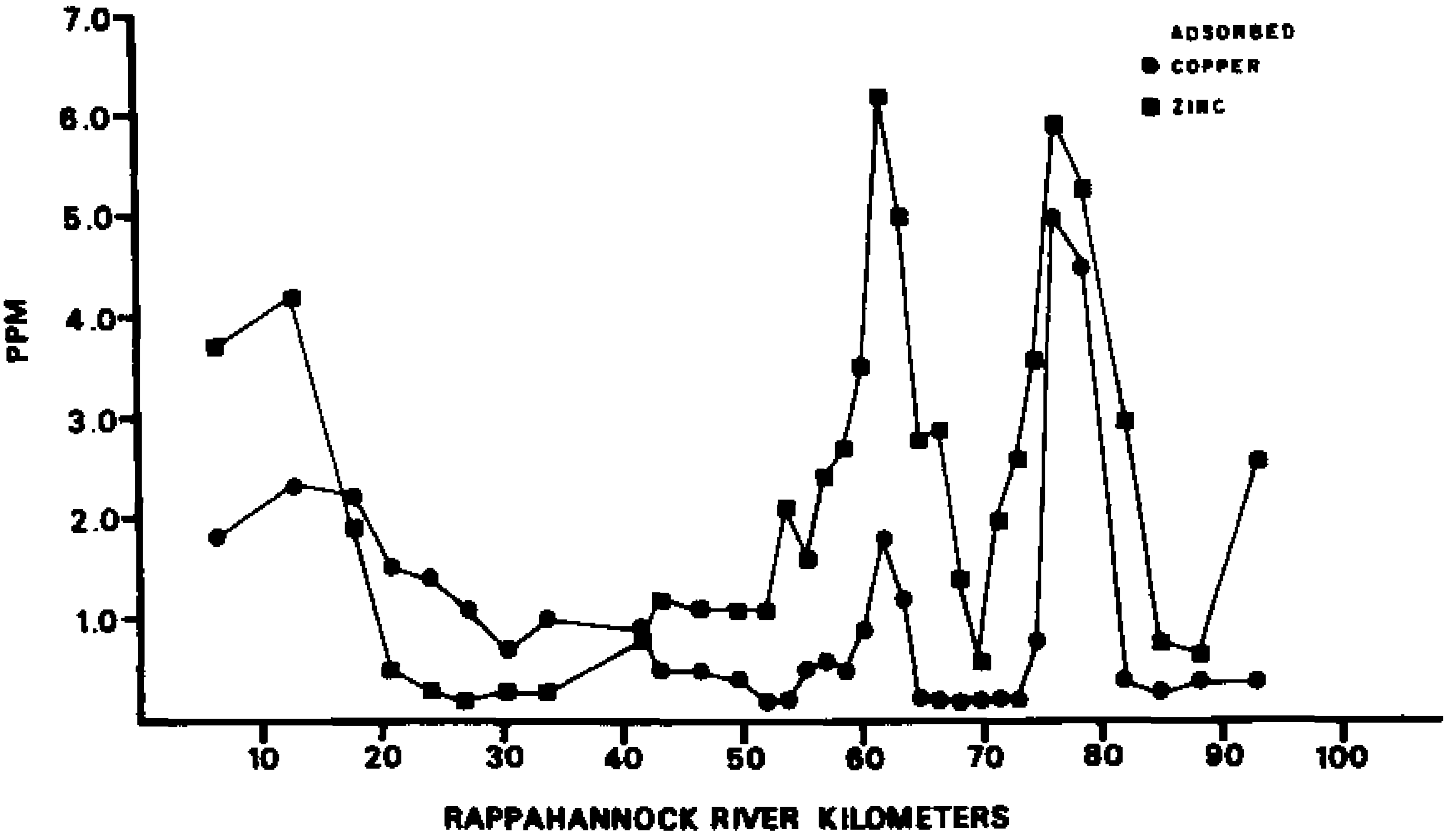

ADSORBED
● COPPER
■ ZINC
PPM
7.0
6.0
5.0
4.0
3.0
2.0
1.0
10
20
30
40
50
60
70
80
90
100
RAPPAHANNOCK RIVER KILOMETERS

Figure 5. Moving averages (3) of concentrations of precipitated-coprecipitated and organic zinc in the ≤ 63 μm fraction of sediments from the Rappahannock River and estuary collected in January 1973 (•) and June 1973 (■). Zero kilometers represent the mouth of the estuary.

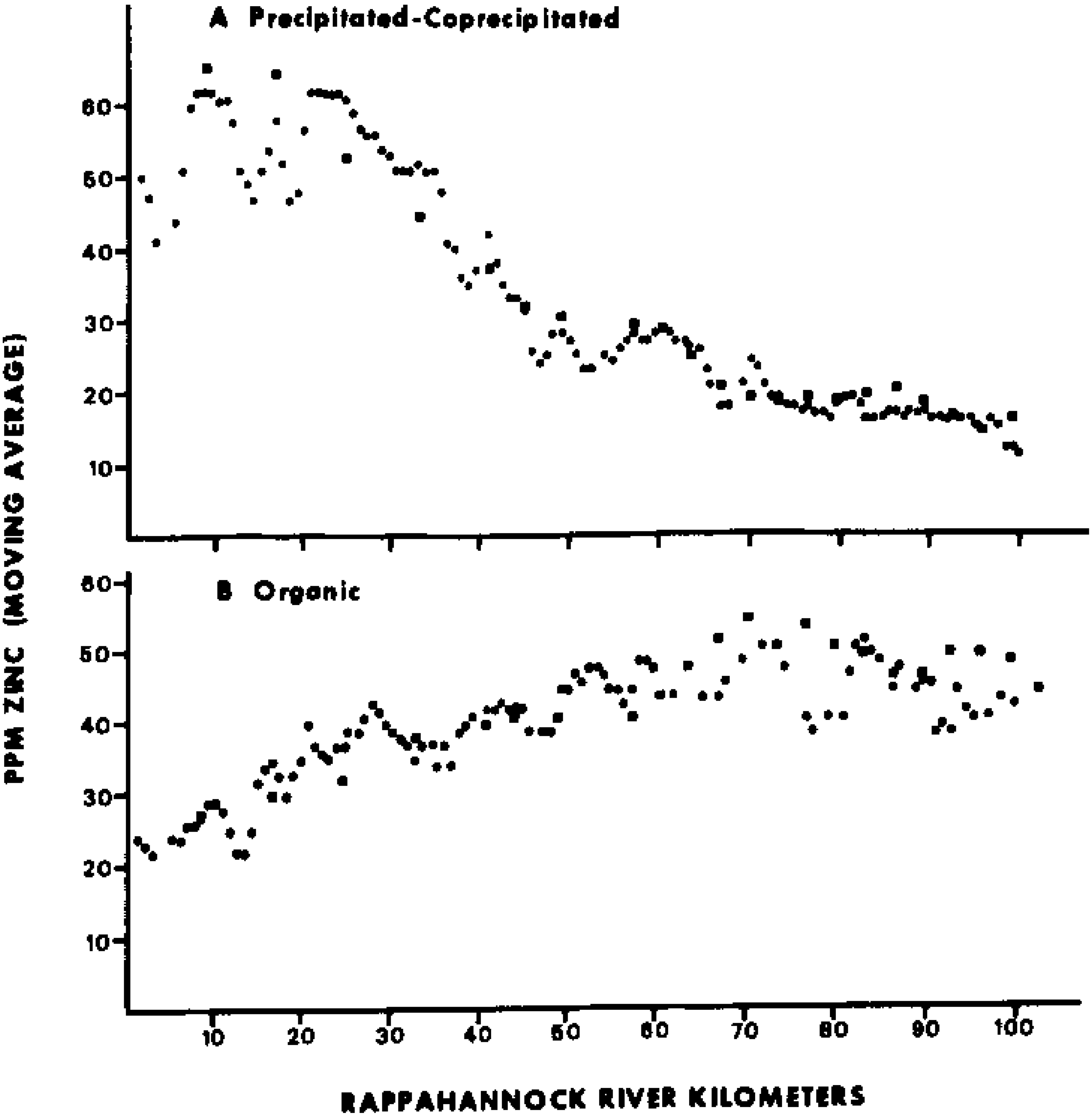
A Precipitated-Coprecipitated
B Organic
PPM ZINC (MOVING AVERAGE)
10
20
30
40
50
60
10
20
30
40
50
60
70
80
90
100
RAPPAHANNOCK RIVER KILOMETERS

Figure 6. Moving averages (3) of concentrations of precipitated-coprecipitated and organic copper in the ≤63 μm fraction of sediments from the York River and estuary collected in June 1973: · , York River. ·· , Mattaponi River. ● , Pamunkey River.

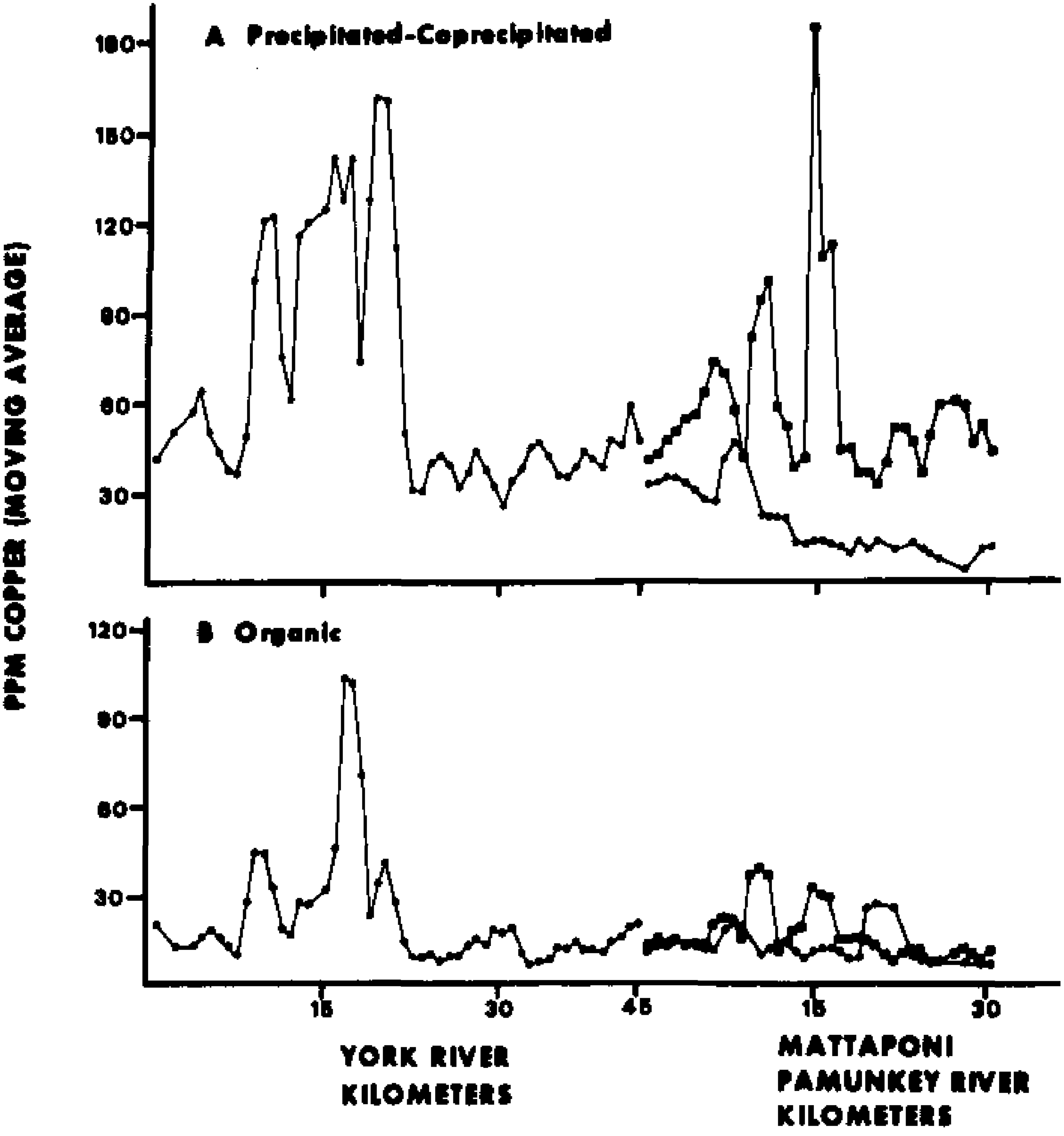
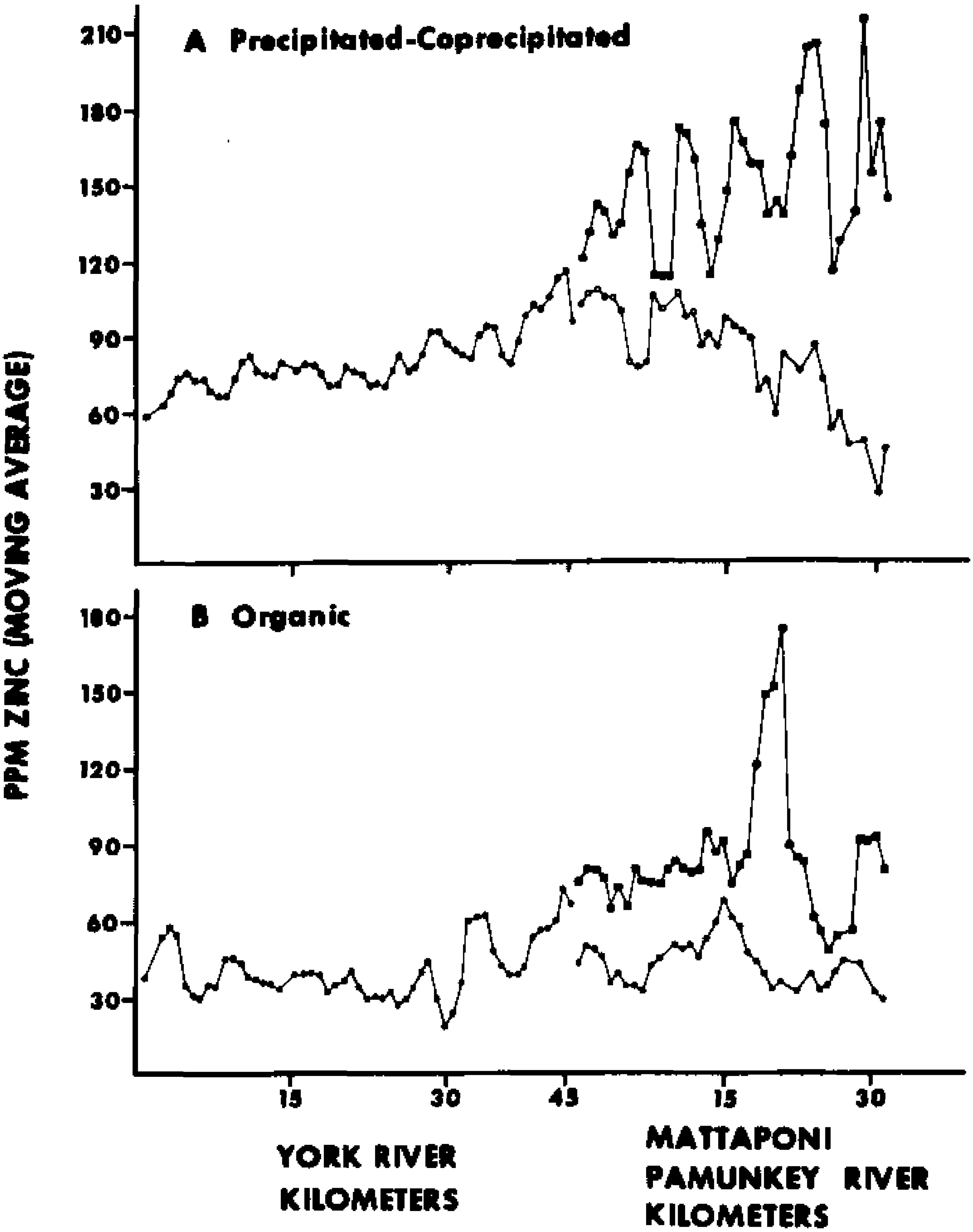

PPM COPPER (MOVING AVERAGE)
A Precipitated-Coprecipitated
180
150
120
90
60
30
B Organic
120
90
60
30
15
30
45
15
30
YORK RIVER
KILOMETERS
MATTAPONI
PAMUNKEY RIVER
KILOMETERS

Figure 7. Moving averages (3) of concentrations of precipitated-coprecipitated and organic zinc in the ≤63 μm fraction of sediments from the York River and estuary collected in June 1973: ● , York River. ○, Mattaponi River. ■ , Pamunkey River.



PPM ZINC (MOVING AVERAGE)
A Precipitated-Coprecipitated
210
180
150
120
90
60
30
B Organic
180
150
120
90
60
30
15
30
45
15
30
YORK RIVER
KILOMETERS
MATTAPONI
PAMUNKEY RIVER
KILOMETERS

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THE EFFECTS OF TROPICAL STORM AGNES ON THE COPPER AND ZINC BUDGETS OF THE RAPPAHANNOCK RIVER

Abstract

The metals copper and zinc were analyzed in bottom sediments (top 1 cm) from the Rappahannock River before and after Tropical Storm Agnes. By extracting the sediments with various techniques (HNO_3, HCl) the nature of the metal speciation can be estimated. Data show that the inorganic copper was increased by a factor of 2 to 3 in the normally saline portion of the river as a result of Agnes but returned to before-Agnes levels within one year.

Metal analyses of suspended sediments collected during the Agnes flooding allows an estimate of sedimentation indicating at least 7.5 mm of new sediments at mile 40, decreasing nearly linearly to 1 mm at mile 15.

Introduction

The Rappahannock River is a coastal plane estuary located on the Chesapeake Bay (Figure 1). It is tidal for approximately 100 nautical miles (185 kilometers) with the first 45 miles (80 kilometers) at normal river flows being estuarine having salinities greater than 0.4 parts per thousand. This system is relatively pristine in nature in its estuarine portion with occasional agricultural development along its banks. To the authors knowledge there are no man-induced trace metal sources in the river with the possible exception of drainage and sewage from Fredericksburg, Virginia, located at the fall line, 185 kilometers upstream.

In an attempt to define and understand the trace metal budgets of large coastal plane estuaries, the Rappahannock River was extensively sampled in 1972 and 1973. During this period three major sampling runs were conducted: one in January 1972, one in October 1972 and one in June 1973. The first sampling was approximately six months before Tropical Storm Agnes passed over the system, the second was two months and the third was 12 months after.

The work reported here was originally intended to describe the background levels of copper and zinc in the top 1 cm of Rappahannock River bottom sediments and to correlate the concentrations found to the normally analyzed estuarine variables of the pH and salinity. Six months after such a background study Tropical Storm Agnes passed through the system.

To ascertain the effects of this deluge on the sediment metals budget on the Rappahannock River for which we had good background data, the system was resampled and analyzed. Since some changes were noted, the system was sampled again 12 months after the storm to note recovery if any.

The authors wish to acknowledge the assistance of H. D. Slone and J. Lunz of the Virginia Institute of Marine Science in this project and Dr. B. Nelson of the University of South Carolina and Dr. M. Nichols of the Virginia Institute of Marine Science who graciously supplied suspended sediment samples for this project.

This project was funded through the Chesapeake Research Consortium by the National Science Foundation - RANN Program Grant G. I. 34869.

Methods and Procedures

The original sampling was in January 1972 and consisted of samples taken in the channel at 0.5 nautical mile intervals from the mouth to 20 miles above the freshwater-saltwater interface. In all, 63 miles of the stream were sampled, yielding a total of 126 samples. After Agnes in October 1972, the samples were taken at 2 mile intervals from the mouth to approximately 30 miles upstream and then at 1 mile intervals up to mile 60. The last sampling was conducted in June 1973, approximately one year after Agnes and consisted of samples taken at 5 mile intervals from the mouth to mile 35 and then at 2 mile intervals up to mile 63. The sampling intervals increased with each subsequent sampling because we were initially unaware of the natural variations; therefore as many samples as we could analyze were taken. As more was learned about the system, fewer samples were taken.

The samples were collected with a ponar grab sampler which was lowered slowly to the bottom. When tension was released on the wire, the sampler closed and was returned to the boat, opened and the top 1 centimeter of sediment was removed, being careful not to collect material which had come in contact with the sampler's sides.

Each sample was wet sieved and only the less-than or equal-to 63 micron portion was saved for analysis. Since the concentrations of metals sorbed or coated to sediment grains is a function of the surface area per unit mass of the grains, the sieving was necessary to help normalize the samples.

After the $\overline{<}63$ μ fractions were obtained from the samples, they were dried first in air and then at 105°c. Each dried sample was then split and one portion was extracted with 0.1N HCl at room temperature for one hour and another portion was extracted with fuming (not boiling) concentrated HNO_3. The extact details of the extractions are given by Huggett, Bender and Slone (1972).

The various methods of extraction yield two distinct metal fractions: the HCl should release non-crystalline metals which are bound to the sediments by absorption, precipitation and co-precipitation reactions. The HNO_3 extraction should release these metals as well as those bound within organic matrices. The difference between the HNO_3 and HCl yields should approximate the organic metals.

The extracts were all analyzed by standard Atomic Absorption techniques.

Suspended sediments were obtained from Dr. B. Nelson (University of South Carolina) and Dr. M. Nichols (Virginia Institute of Marine Science) who collected them from the Rappahannock River during the Agnes flooding. The suspended sediments were separated on 0.45 micron membrane filters by filtration.

The suspended matter was scraped from the filters with a glass rod and extracted for copper by the previously mentioned HNO_3 procedure. Since the suspended sediments had been stored approximately 18 months before analysis, it was feared that the samples may have lost their integrity with respect to organic-inorganic copper phases. Therefore the HNO_3 extract, which should extract both, was used.

Results and Discussion

The precipitated-co-precipitated zinc data are graphically displayed in Figure 2. The concentrations at a station are nearly the same for all three sampling periods. In the normally freshwater portion of the river (above mile 45), the concentrations are relatively constant at approximately 18 ppm. From mile 45 downstream to mile 10 there is an increase to between 50 and 60 ppm. This increase may be due to either an increase in pore-water pH towards the mouth of the estuary (Nelson, 1973) or an increase in surface area of the downstream sediment grains. If such a sediment grain surface area increase is true, it must be for particles below 1 μ since nearly the same size distribution for particles greater than 1 μ exist in the estuarine portion of the stream (Nelson and Nichols, 1973). From mile 10 to the mouth of the estuary the concentrations vary between 50 and 60 ppm.

The organic zinc concentrations are given in Figure 3. As in the case of the precipitated-co-precipitated zinc fraction, the levels of organic zinc are nearly the same for all three sampling periods. From mile 45 to mile 60, the values range between 40 and 50 ppm but decrease from about 45 ppm beginning at mile 45 to 20 ppm at the mouth of the estuary at mile 0. This decrease is gradual but quite linear and opposite the trend observed for the precipitated-co-precipitated zinc fraction. This suggests that the metal bound inorganically is not available for organic reactions.

The precipitated-co-precipitated copper data are presented in Figure 4. These data clearly show that shortly after Tropical Storm Agnes passed over the Rappahannock River, the precipitated-co-precipitated copper was a factor of 2 to 3 times higher in the normally saltwater portion of the river than either six months before or one year after. In the normally freshwater section the values did not significantly change during the eighteen months of study. It is the author's belief that the increase was due directly to Tropical Storm Agnes. The estuarine section of the river was turned nearly fresh by the deluge and since this section showed elevated copper but the normally freshwater portion did not, a salinity controlled reaction for the precipitated-co-precipitated copper appears possible. However, the investigators did not note such a phenomenon even after subjecting Rappahannock River sediments to various salinities and dissolved copper concentrations in the laboratory. Another possibility is that elevated dissolved copper was brought into the system from upstream runoff. This appears unlikely since the concentrations did not change at the upstream stations. The likelihood that the copper was transported into the estuary from the Chesapeake Bay also appears unlikely since the net flow of the stream was into the Bay during this period.

The final and most likely explanation of the increase is that new sediments high in copper were transported from the land to the river during the storms' rain and runoff and were deposited in the estuary. This hypothesis is substantiated by the studies of Nichols, Nelson and Thompson (1974) which showed massive amounts of erosional products being swept into the Rappahannock estuary by Tropical Storm Agnes runoff. Further substantiation will be presented later in the discussion of copper analysis of suspended sediments collected after Agnes in the Rappahannock River.

The organic copper concentrations are given in Figure 5. The levels are nearly the same for all sampling periods ranging between 10 and 15 ppm. The elevated precipitated-co-precipitated copper previously mentioned was not evident in the organic fraction suggesting that the inorganically bound metals are not readily available for organic reactions.

The suspended sediments collected during the Agnes runoff period were analyzed for organic copper (Table I). Due to the extremely small sample sizes only this fraction could be extracted and analyzed. The data in Table I show that the copper concentrations tend to increase for samples taken closer to the estuary's mouth. This is explained by the fact that the suspended sediments should have a greater surface area the further downstream they travel since larger particles would be settling out.

If the hypothesis that the elevated copper concentrations (Fig. 4), were due to Agnes-induced new sediments is true, then by comparing the pre-Agnes sediment copper concentrations with the after-Agnes values and the suspended sediment copper levels, an estimate of sedimentation can be obtained. In order to do this several assumptions must be made:

1) That all the suspended materials were of the same or similar origin with respect to their precipitated-co-precipiated copper concentrations.
2) That the copper concentrations did not significantly change from time of deposition until sampling.
3) That the suspended sediments collected at any one place were similar with respect to copper as those deposited at that point.
4) That the new sediments were not mixed below 1 cm by either biological or physical factors.

Assumption one appears valid since samples collected on different days from the same locations had similar copper concentrations. The second assumption may not be entirely valid. Since samples collected one year after the storm showed copper levels to have returned to normal it is logical that the re-equilibration started soon after the waters returned to normal (~1 month before the October sampling). This would result in the sedimentation estimates being low. The third assumption is probably valid since the river is tidal and therefore the suspended sediments move up and downstream depending on the tide stage. This assumption would probably not be true if the system were non-tidal. The fourth assumption, if not true, would again result in a lower estimate of sedimentation. The authors know of no way to check this assumption.

With these assumptions, the before-Agnes and after-Agnes bottom sediment copper data and the suspended sediment copper values, the percent of the top 1 cm of bottom sediment due to Agnes can be calculated at each location for which all these values are known by the following formula:

$$X = \frac{a-c}{a-b}10$$

It must be noted that this formula is valid only if the top 1 cm of bottom sediment is sampled. In this equation "x" is the millimeters of new sediment in the top 1 cm of the bottom material after-Agnes; "a" is before-Agnes sediment concentration; "b" is the suspended sediment concentration and "c" is the after-Agnes sediment concentration.

The data used for these calculations were the raw sediment rather than the moving averages presented in the previous figures. The moving average technique was used to smooth out "noise" in the data but still show trends. The un-averaged data must be used in the sedimentation calculations to assure accurate estimates at each location. The results are presented in Figure 6. In this figure the range of values as well as the means are given for each location in which there were suspended sediment samples. The data show that at least 7.5 millimeters of new sediment were deposited in the channel at mile 39. The amount of new material decreases nearly linearly to about 1 millimeter at mile 15. This trend is logical and may be thought of as a proof of the calculations because more sediments should have been deposited upstream since these areas are closer to the source of the suspended sediments.

A year after the storm the sediment copper levels were back to normal. This could be due to: migration of the sediments upstream on the estuarine salt wedge; bottom sediments being resuspended and carried seaward in the surface waters; mixing of the new sediments with old underlying material by burrowing animals or chemical re-equilibration of copper to normal with the return of stable salinity and pH structure. The authors do not know the exact mechanism; perhaps a combination of all.

Conclusions

Tropical Storm Agnes caused a 2 to 3 fold increase in the precipitated-co-precipitated copper content of the estuarine surface sediments of the Rappahannock River. The sediments did, however, return to "normal" within one year after the storm. The organic copper and zinc and the precipitated-co-precipitated zinc levels were not affected by the storm.

A calculation based on the deposition of suspended material, high in precipitated-co-precipitated copper on material relatively low in this copper phase, resulting in a sediment with a copper content between the two, shows that at least 7.5 millimeters of new sediment was deposited at mile 39 with amounts decreasing downstream to about 1 millimeter at mile 15. This technique appears extremely sensitive to small sedimentation amounts and may prove useful to other investigators.

Figure 1. Map of the Chesapeake Bay.

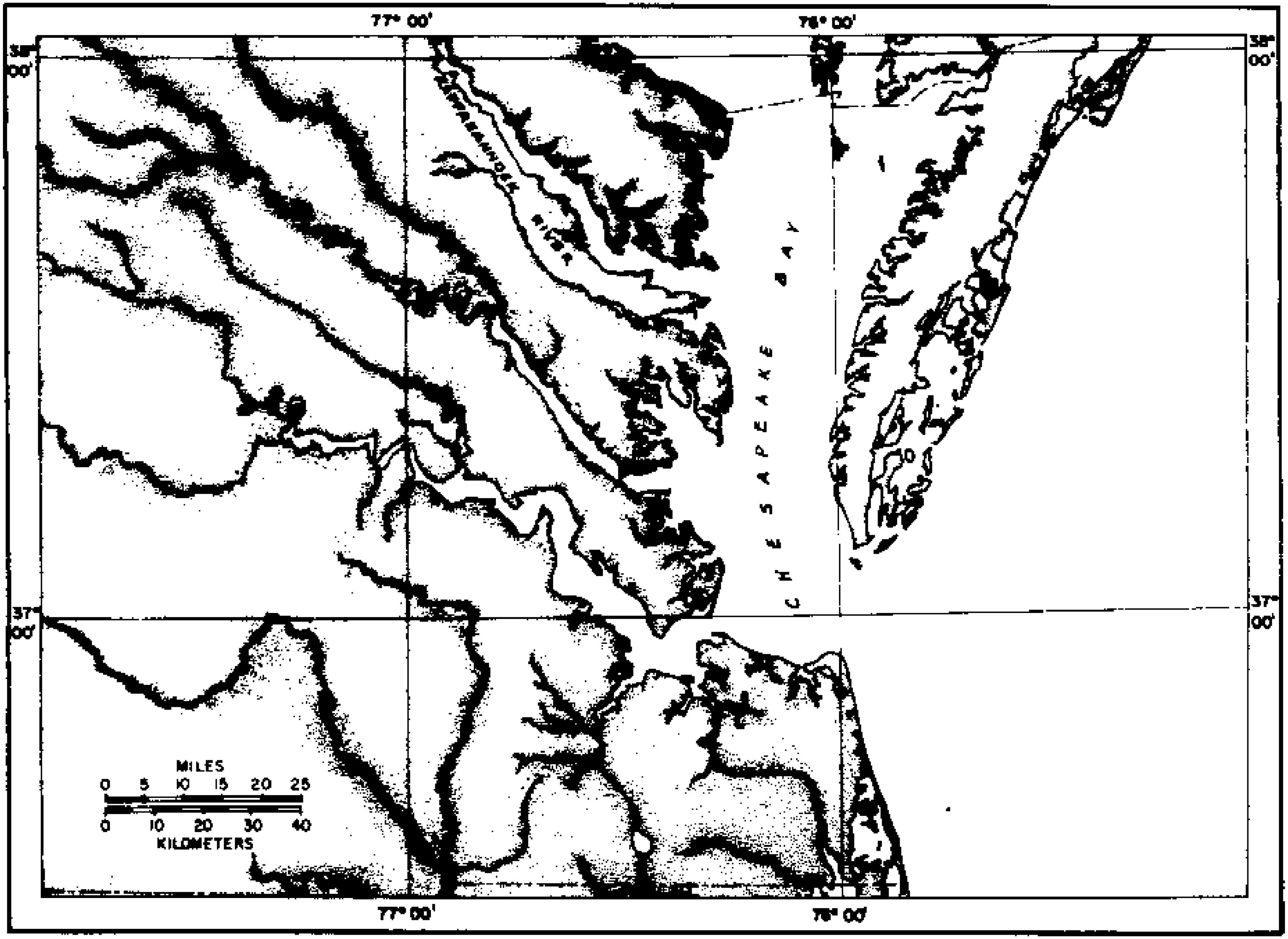

77° 00'
76° 00'
38° 00'
37° 00'
RAPPAHANNOCK RIVER
CHESAPEAKE BAY
MILES
0 5 10 15 20 25
0 10 20 30 40
KILOMETERS

Figure 2. Precipitated-coprecipitated zinc in Rappahannock River sediments.

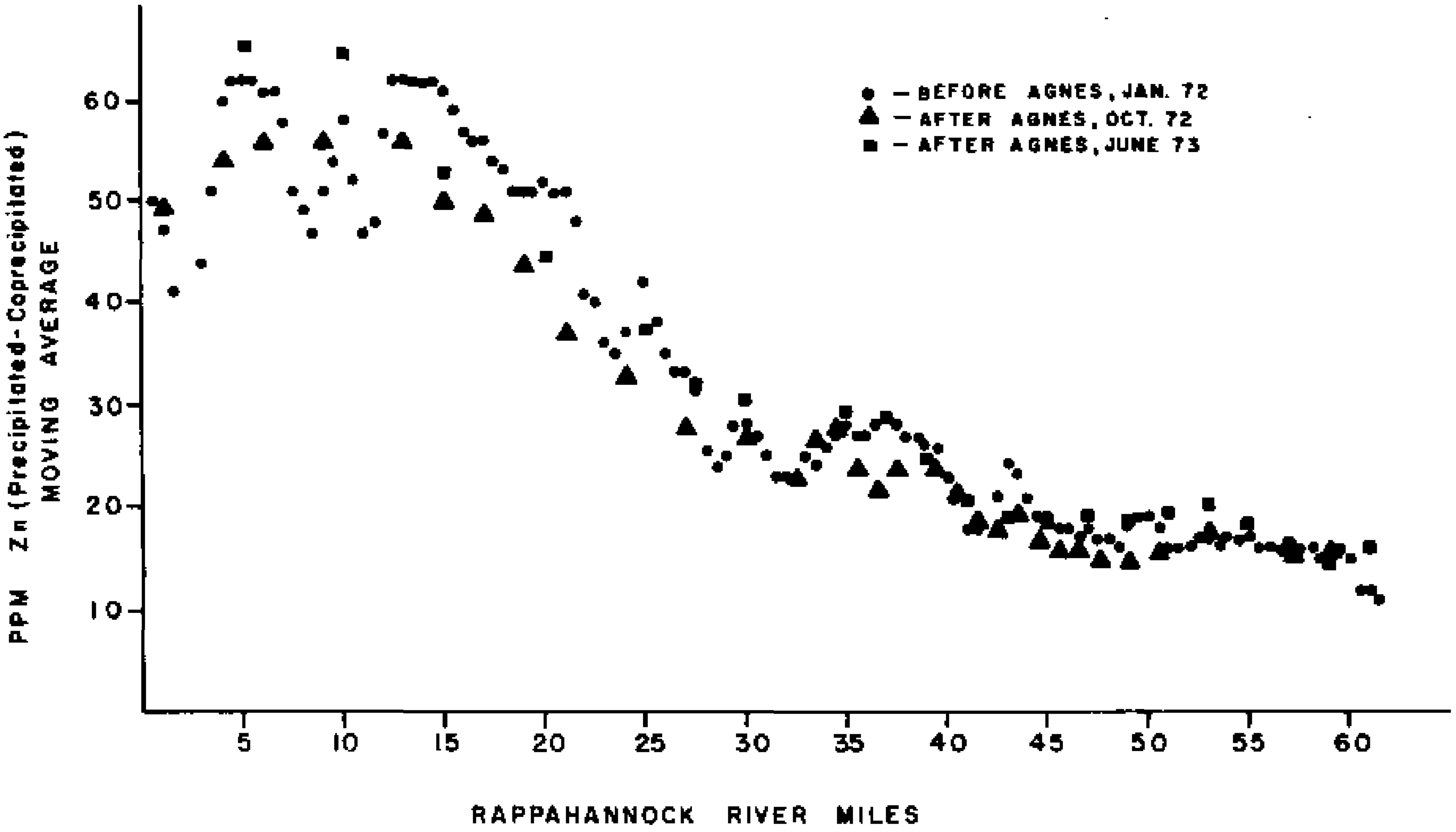

● — BEFORE AGNES, JAN. 72
▲ — AFTER AGNES, OCT. 72
■ — AFTER AGNES, JUNE 73
PPM Zn (Precipitated - Coprecipitated) MOVING AVERAGE
60
50
40
30
20
10
5
10
15
20
25
30
35
40
45
50
55
60
RAPPAHANNOCK RIVER MILES

Figure 3. Organic zinc in Rappahannock River sediments.

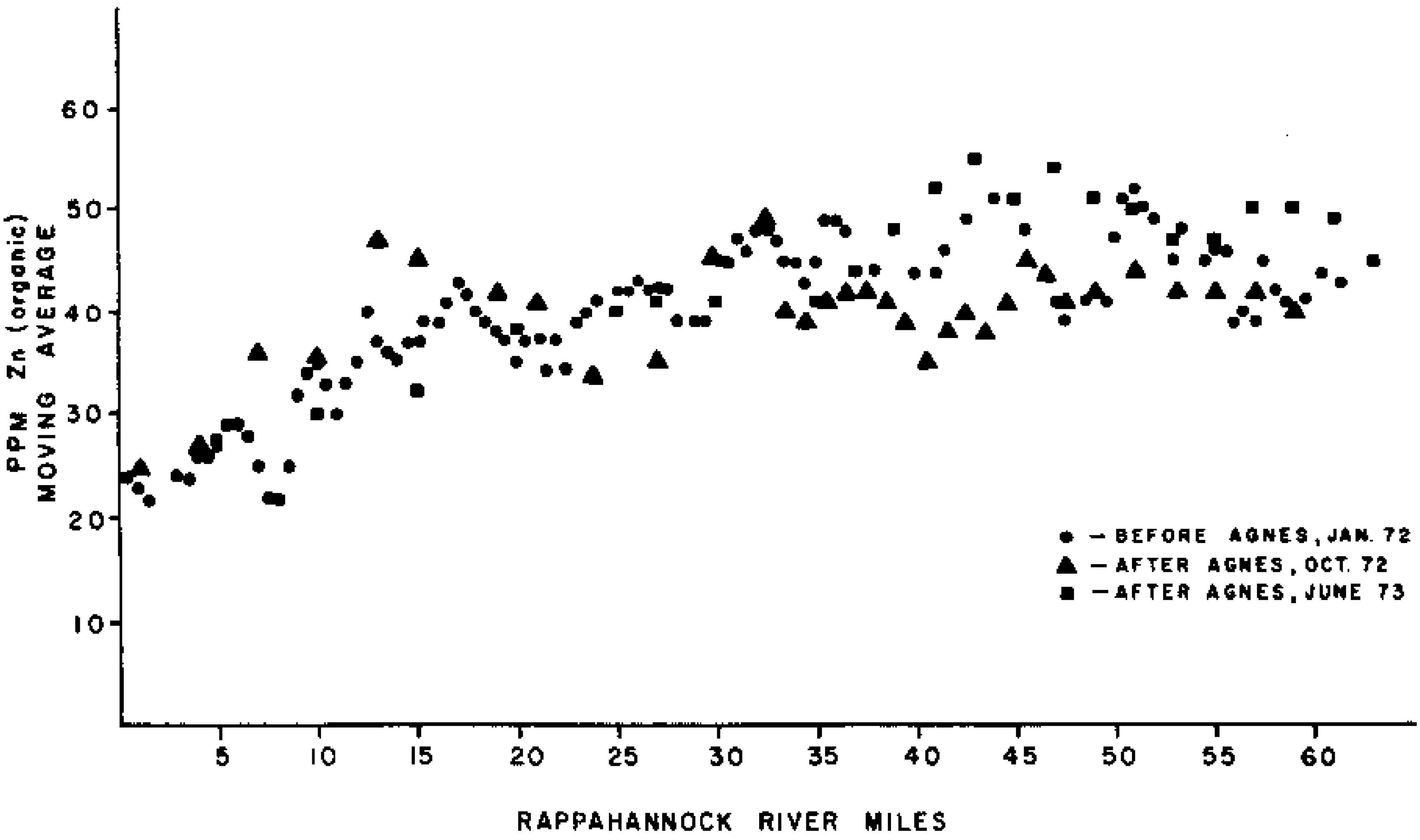
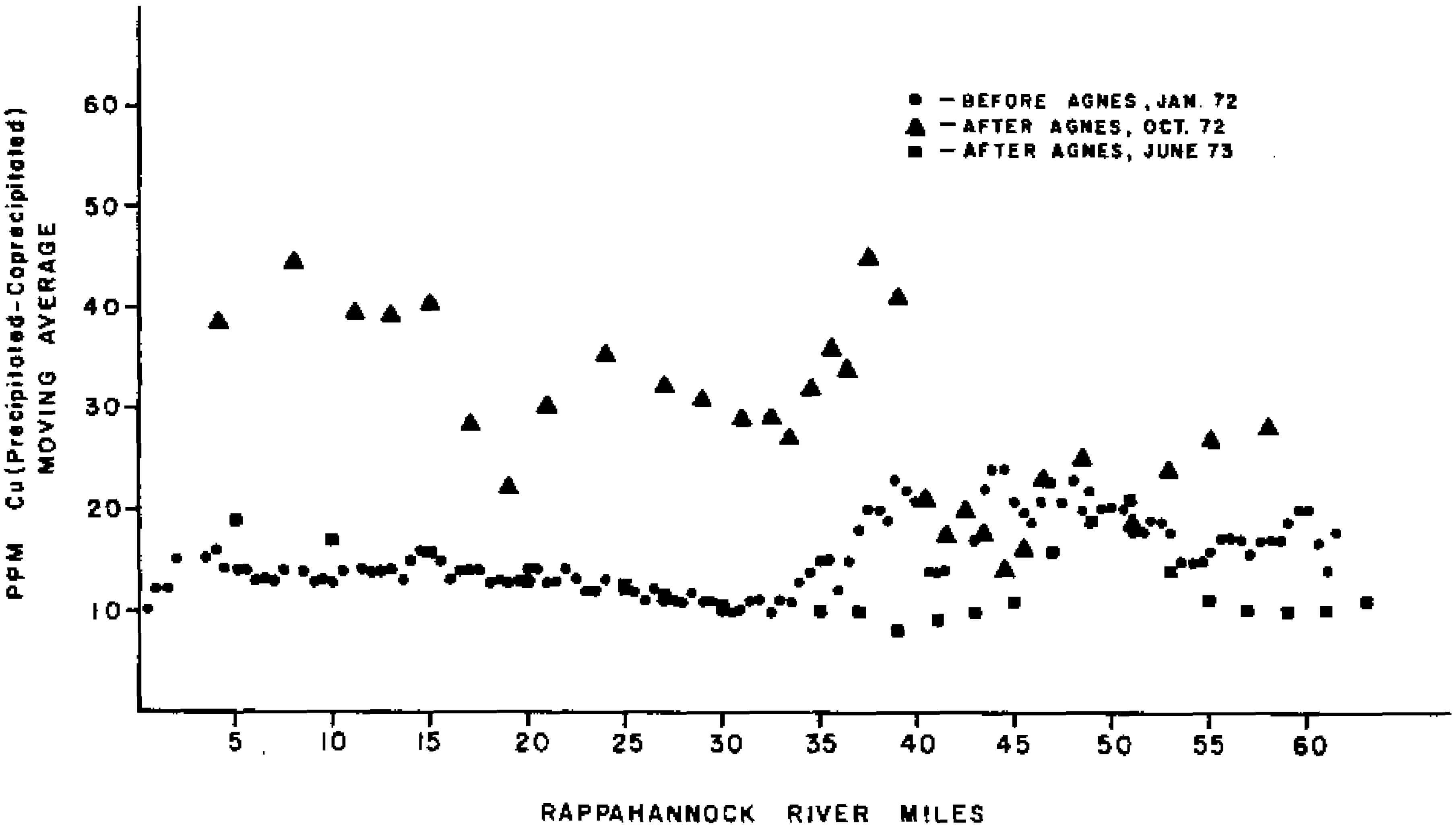

PPM Zn (organic)
MOVING AVERAGE
60
50
40
30
20
10
5
10
15
20
25
30
35
40
45
50
55
60
RAPPAHANNOCK RIVER MILES
● — BEFORE AGNES, JAN. 72
▲ — AFTER AGNES, OCT. 72
■ — AFTER AGNES, JUNE 73

Figure 4. Precipitated-coprecipitated copper in Rappahannock River sediments.



● —BEFORE AGNES, JAN. 72
▲ —AFTER AGNES, OCT. 72
■ —AFTER AGNES, JUNE 73
PPM Cu (Precipitated-Coprecipitated)
MOVING AVERAGE
60
50
40
30
20
10
5
10
15
20
25
30
35
40
45
50
55
60
RAPPAHANNOCK RIVER MILES

Figure 5. Organic copper in Rappahannock River sediments.

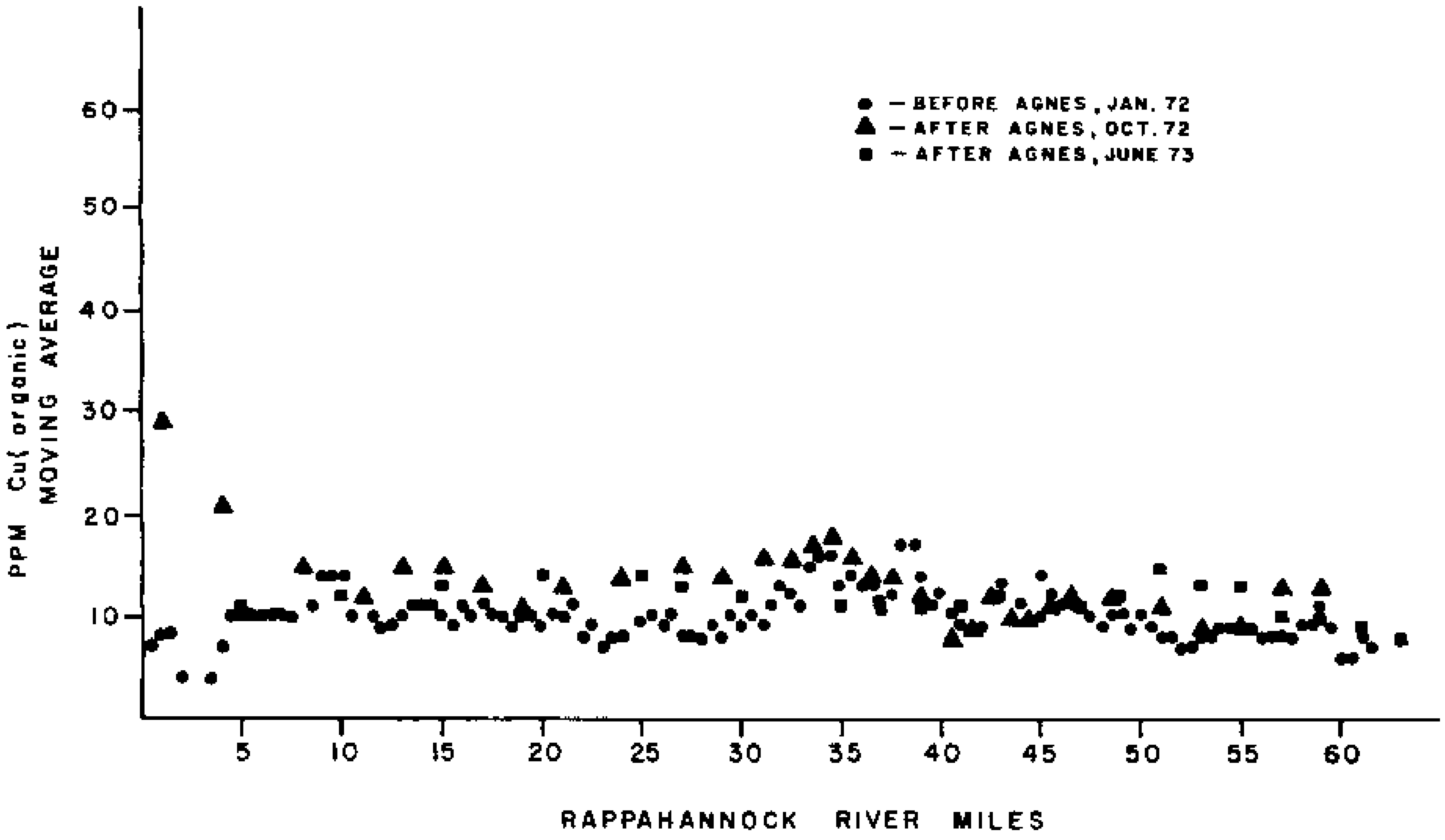
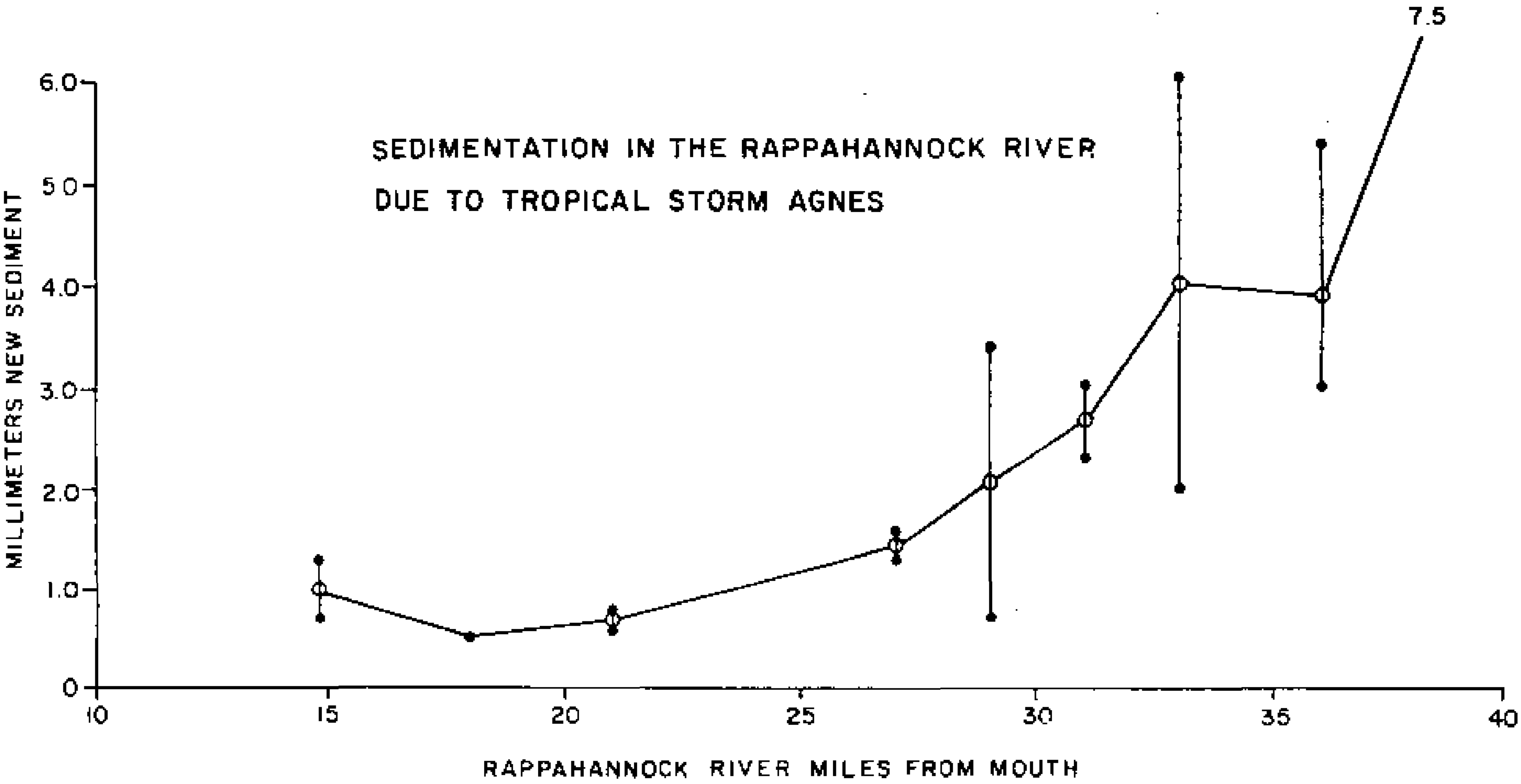

● — BEFORE AGNES, JAN. 72
▲ — AFTER AGNES, OCT. 72
■ — AFTER AGNES, JUNE 73
PPM Cu(organic)
MOVING AVERAGE
60
50
40
30
20
10
5
10
15
20
25
30
35
40
45
50
55
60
RAPPAHANNOCK RIVER MILES

Figure 6. Sedimentation in the Rappahannock River due to Tropical Storm Agnes.



SEDIMENTATION IN THE RAPPAHANNOCK RIVER
DUE TO TROPICAL STORM AGNES

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Nelson, B. and M. Nichols. 1973. Unpublished data.

Nichols, M. M., B. Nelson, and G. Thompson. 1974. Responses and Recovery to Sediment Influx in Virginia Estuaries. In: Proceedings of the Symposium on the Effects of Tropical Storm Agnes on the Chesapeake Bay Estuarine System, May 6-7, 1974, College Park, Maryland.

CONCLUSIONS

Data herein show that concentration gradients of cadmium, copper and zinc exist in oysters Crassostrea virginica from Virginia and North Carolina estuaries. Recently MacKay, et al., (1975) reported a similar gradient for oysters, Crassostrea commercialis in estuaries of New South Wales, Australia. These gradients allow a crude predictive mechanism of metal concentrations in oysters as a function of their position in the estuary. Animals living further upstream (i.e., in lower salinities) have higher concentrations of cadmium, copper and zinc than those downstream. Therefore, since this relationship has been shown for animals from a significant portion of the Atlantic Coast of the United States as well as from Australia, it appears that the relationship is fundamental in the ecology of estuaries.

Many investigators have attempted to determine the average concentration of a metal in oysters from an estuary for public health regulatory purposes. In doing so samples have been taken from throughout the estuary or in some cases the region and results averaged (Proceedings of the 7th National Shellfish Sanitation Workshop, 1971). The results reported here clearly show that this procedure is risky in that the obtained averages will not be realistic because the natural concentration gradients have been ignored. A better indication of oysters contaminated by cadmium, copper and zinc is obtained by utilizing the concept of natural concentration gradients and the resulting linear relationship between copper and zinc, cadmium and zinc, and cadmium and copper concentrations in oysters from the same location. The use of the copper-zinc relationship to detect heavy metal pollution is documented in this manuscript and Bender and Huggett, (1977) showed that similar use of copper-cadmium and cadmium-zinc is possible.

Another consideration often omitted in the design of sampling strategies for determining metals in oysters involves the natural varability of metal concentrations within a given population or sampling station. Concentrations of cadmium, copper and zinc in oysters from Virginia which are collected from the same location or bed commonly differ by factors of 1 to 3. Therefore to determine the mean concentrations for a given location one must either collect and analyze a number of replicates or blend a number of replicates together and then analyze the blend (Shellfish Sanitation, 1976). The problem with the latter alternative is that there is no measure of variation thus no statistical tests of significance can be made. If, however, the objective of a survey of metals in oysters from an area is only to obtain a general idea of concentrations with minimum cost, a few replicates or blends can be used (Colby, Cross and Huggett, 1977).

The available data on cadmium, copper or zinc levels in solution in coastal plain-estuarine systems do not indicate that there are concentration gradients similar to those found in oysters. These analyses were based on the assumption that a constituent in solution was one which was present in the water after filtering through a 0.45 μm filter. The procedures were such that only total concentration of a "dissolved" metal was analyzed. Therefore it is possible that metals in solution, defined by these constraints could have been associated with collodial particles less than 0.45 μm or that they existed in several speciated forms in true solution (i.e. hydrated, complexed, etc.). Yet, since no total solution metal gradient was evident it is probable that the concentrations of cadmium, copper, and zinc in oysters are not directly due to total dissolved metals.

Analyses of bottom sediments from two estuaries, the York and Rappahannock Rivers, for the trace metals copper and zinc were conducted to determine whether similar gradients of metal concentrations exist in sediments and oysters living on those sediments. Sediment samples were extracted for metals in several ways to obtain the fractions associated with organic, oxide coatings and absorbed phases in or on the sediments. The results of these analyses showed that gradients did exist but that they were different than those observed in the oysters. For instance, the concentrations of zinc associated with oxide-hydroxide coatings in Rappahannock River sediments increased with increasing salinity while copper associated with this phase remained almost constant throughout the saline portion of the river. The oyster "metal" gradient for this river decreased with increasing salinity. The fractions of copper and zinc which was adsorbed to the surface of the particles decreased greatly at the freshwater-salt water interface from as high as 6 $mgkg^{-1}$ in fresh water to near 1 $mgkg^{-1}$ in low salinity waters. In the saline portion of the river the levels increased towards the mouth. These changes can be attributed to two basic phenomenon in estuaries. The sharp decrease from fresh to salt water is likely due to the abundance of magnesium ions in seawater, which replace the adsorbed copper and zinc. The following increase towards the mouth of the estuary may be due to increasing surface area per unit mass of the ≤63 μm fraction of the sediment because of finer particles being deposited further downstream. Nichols (1977), however, has found that the average particle sizes in this portion of the Rappahannock River to be nearly constant. These "adsorbed" trends were opposite from those encountered in oysters from the river.

The sediment zinc which was organic in nature decreased toward the mouth of the estuary while "organic" copper remained almost constant. This zinc fraction showed the only trend which corresponded to the gradients in oysters. However since the oyster gradients exist over large geographical areas and for cadmium, copper and zinc, it is logical that if sediments serve as the direct source to oysters of these metals then the same metal gradients for oysters and sediments should exist for all the metals. This is not the case.

The sediment metals in the York-Pamunkey-Mattaponi system showed different gradients than did the Rappahannock. As in the Rappahannock the trends were inconsistent with those observed in oysters. The York-Pamunkey-Mattaponi system clearly showed the influence of acid mine drainage entering the system in the upper Pamunkey River. The concentrations of copper and zinc in sediments were 2 to 10 times higher in the Pamunkey River than in the Mattaponi. Since, both the rivers drain similar strata and have similar sized drainage basins the metal levels should be similar if it were not for the acid mine drainage. This authropogenic source has also augmented the copper and zinc in the sediments of the York River. This can be concluded since there is continuity in sediment copper and zinc concentrations from the York to the Pamunkey whereas there appears to be dicontinuity from York to the Mattaponi. The data also show an unexplained abundance of copper in sediments of the York from 7 to 22 km from the mouth. The oyster samples taken in this segment of the river do not indicate above normal levels of copper which supports the hypothesis that, at least for copper, sediment metal concentrations do not directly control the metal concentrations in oysters.

Therefore it appears that little relationship exists between the concentration gradients observed in oysters, and the concentrations of total dissolved metals and/or metals in sediments. Several other possibilities are apparent. One of these is that since concentrations of dissolved calcium in estuarine waters are dependent on salinity and since oysters must obtain calcium for shell deposition, those animals living in fresher waters must either pump more water than animals in saltier water to remove needed calcium, or be more efficient than those living in higher salinities at removing calcium from the same amount of water. Either of these mechanisms for calcium uptake could result in concurrent increases in other dissolved cations such as cadmium, copper, or zinc (Wolf and Stillings, 1975).

Another possible explanation for the oyster gradients is that if the dissolved concentrations of copper, cadmium and zinc are nearly constant throughout the estuary they may be outcompeted for binding sites by more abundant cations from seawater (magnesium, calcium, etc.) at higher salinities.

A third possibility involves chelation and/or complexation of the dissolved metals by humic substances, particularly fulvic acids. It has been shown that fulvic acids are efficient complexing and chelating agents for cations (Jenne, 1968; Shapiro, 1964; Hair and Bassett, 1973). Since these substances originate from decaying plant material on land it is probable that their concentrations would increase with decreasing salinity. This trend was noted by Hair, et al. (1973). Therefore if the dissolved metal concentrations for copper, cadmium and zinc are constant throughout the estuary but the fulvic acid decreases from fresh water-seaward due to dilution by the humate poor seawater, then there should be a gradient of complexed or chelated metals decreasing in a seaward direction. This would be the same type of gradient as observed in oysters from the estuaries. It is possible that by complexing or chelating the metals their biological availability is increased by direct partitioning of the substances from estuarine water into the body mucus of the oysters.

During the period of this research, Tropical Storm Agnes passed over the drainage basin of the Rappahannock River and the resulting rains washed large quantities of sediments into the estuary. Analysis of the bottom sediments of the Rappahannock River soon after the deluge showed that the precipitated-coprecipitated copper concentrations of the estuarine sediments were elevated by a factor of 3 to 4 relative to before the storm. Subsequent analyses of the sediments approximately twelve months later indicated that the copper concentrations had returned to pre-Agnes levels. Suspended sediment samples collected in the Rappahannock River during the Agnes run-off period were analyzed for copper and showed concentrations as much as 40 times those observed in the underlying bottom sediments. By assuming that the increase in sediment copper, immediately after Agnes was due to deposition of erosion products (suspended sediments) a 1:1 mixing model was used to calculate the amount of sediments deposited in the Rappahannock Estuary as a result of the tropical storm. The calculations indicated that approximately 7.5 mm of new sediments were deposited in the channel at kilometer 38 on the Rappahannock decreasing almost linearly towards the mouth of the estuary to about 1 mm at kilometer 15. These estimations of deposition are supported by measurements of suspended sediment concentrations obtained by Nichols and Nelson during the run-off period (Nichols, 1975).

In summary, oysters from non-contaminated estuaries in Virginia and North Carolina have concentrations of cadmium, copper and zinc which can vary depending their position in the estuary. Animals living in less saline waters will contain more of the metal than those living downstream. These gradients can be used to detect unnatural levels of these metals in oysters and to determine anthropogenic sources.

Analyses of copper and zinc concentrations in bottom sediments yield data which when interpreted suggest that the abundance of these metals does not correlate with the levels of these elements in oysters. Therefore, the reason for the trace element gradients in oysters may be either related to the biological functions of the animals as a function of salinity or the speciation or chemistry of the metal in solution as a function of salinity.

Metal analysis of bottom and suspended sediment before and after major erosional events may be used to estimate deposition of new sediments in the estuary resulting from the event.

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