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The Effects of Tropical Storm Agnes on the Copper and Zinc Budgets of the Rappahannock River

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The Effects of Tropical Storm Agnes on the Chesapeake Bay Estuarine System

The Chesapeake Research Consortium, Inc.

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THE CHESAPEAKE RESEARCH CONSORTIUM, INC.

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Preface

During June 1972 Tropical Storm Agnes released record amounts of rainfall on the watersheds of most of the major tributaries of Chesapeake Bay. The resulting floods, categorized as a once-in-100-to-200-year occurrence, caused perturbations of the environment in Chesapeake Bay, the nation's greatest estuary.

This volume is an attempt to bring together analyses of the effects of this exceptional natural event on the hydrology, geology, water quality, and biology of Chesapeake Bay and to consider the impact of these effects on the economy of the Tidewater Region and on public health.

It is to be hoped that these analyses of the event will usefully serve government agencies and private sectors of society in their planning and evaluation of measures to cope with and ameliorate damage from estuarine flooding. It is also to be hoped that the scientific and technical sectors of society will gain a better understanding of the fundamental nature of the myriad and interrelated phenomena that is the Chesapeake Bay ecosystem. Presumably much of what was learned about Chesapeake Bay will be applicable to estuarine systems elsewhere in the world. Most of the papers comprising this volume were presented at a symposium held May 6-7, 1974, at College Park, Maryland, under the sponsorship of the Chesapeake Research Consortium,Inc., with support from the Baltimore District, U.S. Army Corps of Engineers (Contract No. DACW 31-73-C-0189). An early and necessarily incomplete assessment, *The Effects of Hurricane Agnes on the Environment and Organisms of Chesapeake Bay* was prepared by personnel from the Chesapeake Bay Institute (CBI), the Chesapeake Biological Laboratory (CBL), and the Virginia Institute of Marine Science (VIMS) for the Philadelphia District, U.S. Army Corps of Engineers. Most of the scientists who contributed to the early report conducted further analyses and wrote papers forming a part of this report on the effects of Agnes. Additional contributions have been prepared by other scientists, most notably in the fields of biological effects and economics.

The report represents an attempt to bring together all data, no matter how fragmentary, relating to the topic. The authors are to be congratulated for the generally high quality of their work. Those who might question, in parts of the purse, the fineness of the silk must keep in mind the nature of the sow's ears from which it was spun. This is not to disparage the effort, but only to recognize that the data were collected under circumstances which at best were less than ideal. When the flood waters surged into the Bay there was no time for painstaking experimental design. There were not enough instruments to take as many measurements as the investigators would have desired. There were not enough containers to obtain the needed samples or enough reagents to analyze them. There were not enough technicians and clerks to collect and tabulate the data. While the days seemed far too short to accomplish the job at hand, they undoubtedly seemed far too long to the beleaguered field parties, vessel crews, laboratory technicians, and scientists who worked double shifts regularly and around the clock on many occasions. To these dedicated men and women, whose quality of performance and perseverance under trying circumstances were outstanding, society owes an especial debt of gratitude.

It should be noted that the Chesapeake Bay Institute, the Chesapeake Biological Laboratory, and the Virginia Institute of Marine Science, the three major laboratories doing research on Chesapeake Bay, undertook extensive data-gathering programs, requiring sizable commitments of personnel and equipment, without assurance that financial support would be provided. The emergency existed, and the scientists recognized both an obligation to assist in ameliorating its destructive effects and a rare scientific opportunity to better understand the ecosystem. They proceeded to organize a coordinated program in the hope that financial arrangements could be worked out later. Fortunately, their hopes proved well founded. Financial and logistic assistance was provided by a large number of agencies that recognized the seriousness and uniqueness of the Agnes phenomenon. A list of those who aided is appended. Their support is gratefully acknowledged.

This document consists of a series of detailed technical reports preceded by a summary. The summary emphasizes effects having social or economic impact. The authors of each of the technical reports are indicated. To these scientists, the editors extend thanks and commendations for their painstaking work.

Several members of the staff of the Baltimore District, U.S. Army Corps of Engineers, worked with the editors on this contract. We gratefully acknowledge the helpful assistance of Mr. Noel E. Beegle, Chief, Study Coordination and Evaluation Section, who served as Study Manager; Dr. James H. McKay, Chief, Technical Studies and Data Development Section; and Mr. Alfred E. Robinson, Jr., Chief of the Chesapeake Bay Study Group.

The editors are also grateful to Vickie Krahn for typing the Technical Reports and to Alice Lee Tillage and Barbara Crewe for typing the Summary.

The Summary was compiled from summaries of each section prepared by the section editors. I fear that it is too much to hope that, in my attempts to distill the voluminous, detailed, and well-prepared papers and section summaries, I have not distorted meanings, excluded useful information or overextended conclusions. For whatever shortcomings and inaccuracies that exist in the Summary, I offer my apologies.

Jackson Davis
Project Coordinator

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-- Naval Ordnance Laboratory
-- Coastal River Squadron Two, Little Creek, Virginia
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-- Explosive Ordnance Disposal Unit Two, Fort Story, Virginia
-- Naval Ordnance Laboratory, White Oak, Maryland

U. S. Coast Guard
-- Reserve Training Center
-- Coast Guard Station, Little Creek, Virginia
-- Portsmouth Supply Depot
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THE EFFECTS OF TROPICAL STORM AGNES ON THE COPPER AND ZINC BUDGETS OF THE RAPPAHANNOCK RIVER[1]

Robert J. Huggett[2]
Michael E. Bender[2]

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 (Fig. 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 ppt. 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 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, 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.

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[1] Contribution No.759, Virginia Institute of Marine Science.

[2] Virginia Institute of Marine Science, Gloucester Point, Va. 23062

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 sides of the sampler.

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 $\geq$ 63μ 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 exact 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 0.45μ 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 Fig. 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 1μ since nearly the same size distribution for particles greater than 1μ exist in the estuarine portion of the stream (Nelson & Nichols, unpublished) From mile 10 to the mouth of the estuary the concentrations vary between 50 and 60 ppm.

The organic zinc concentrations are given in Fig. 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 Fig. 4. These data clearly show that shortly after 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 authors' belief that the increase was due directly to 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. It also appears unlikely that the copper was transported into the estuary from the Chesapeake Bay 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 storm's rain and runoff and were deposited in the estuary. This hypothesis is substantiated by the studies of Nichols, Nelson, and Thompson (this volume) which showed massive amounts of erosional products being swept into the Rappahannock estuary by 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 Fig. 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 1). Due to the extremely small sample sizes only this fraction could be extracted and analyzed. The data in Table 1 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.

Table 1. Copper in Suspended Sediments Collected During the Agnes Rappahannock River Flood

River Miles From Mouth	Date	Depth	HNO_3 ppm Cu
14.8	6/24/72	Bottom	180
14.8	6/27/72	Bottom	370
18	6/29/72	Surface	220
21	6/29/72	Surface	370
21	6/29/72	Bottom	280
27	6/29/72	Surface	230
27	6/29/72	Bottom	190
29	6/29/72	Surface	93
29	6/29/72	Bottom	400
31	6/29/72	Surface	100
31	6/29/72	Bottom	130
33	6/29/72	Surface	130
33	6/28/72	Bottom	57
36	6/28/72	Bottom	70
36	6/29/72	Surface	100
36	6/29/72	Bottom	95
39	6/29/72	Surface	84

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-precipitated 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.

The first assumption 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 this formula is valid only if the top 1 cm or 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 analyses 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 Fig. 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

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 were 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.

ACKNOWLEDGEMENTS

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.

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Huggett, R. J., M. E. Bender, and H. Slone. 1972. Sediment heavy metal relationships in the Rappahannock River sediments. In: Annual Report, June 1971-May 1972, Chesapeake Research Consortium, Inc., Baltimore, Maryland.

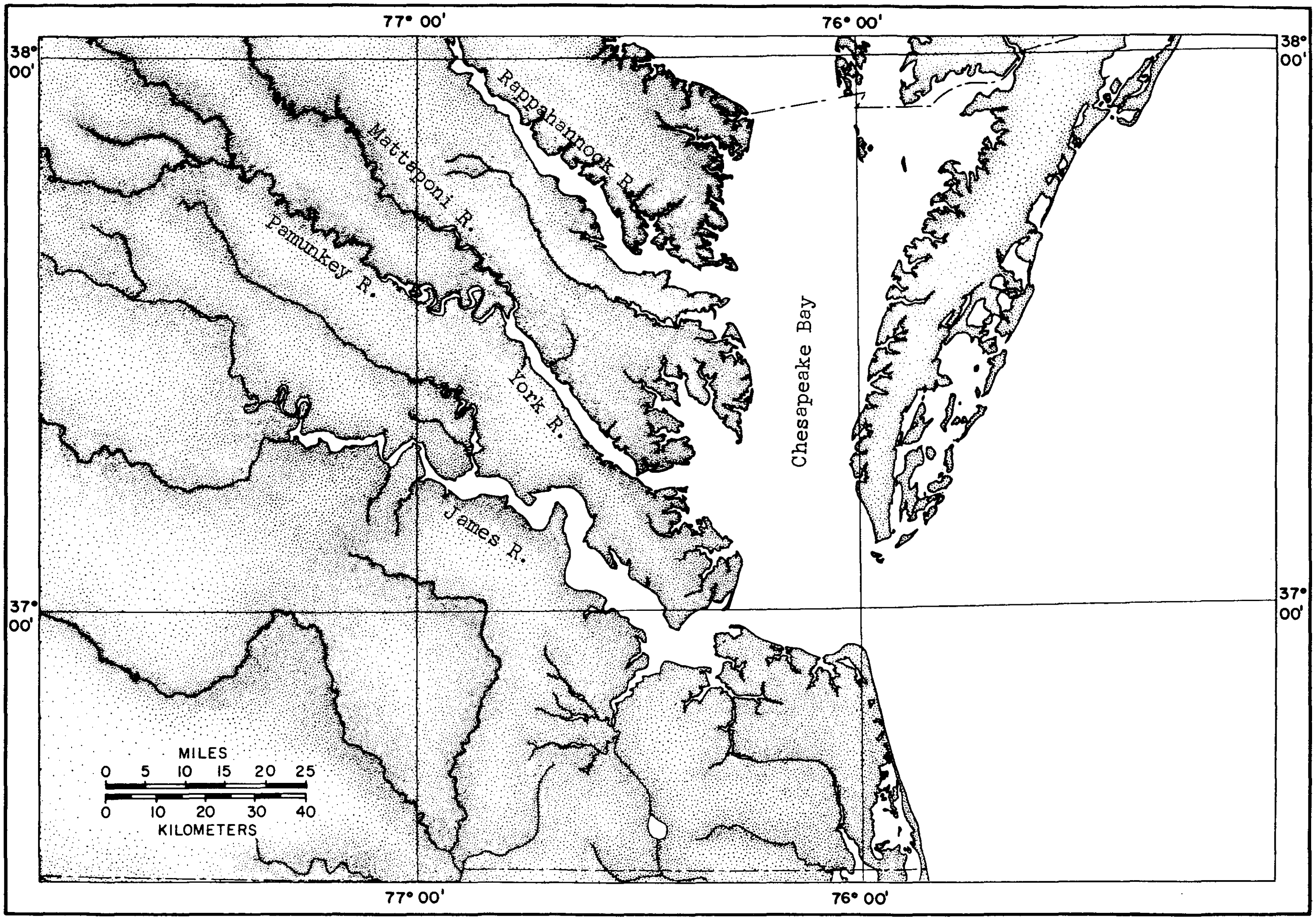

Figure 1. Map of the Chesapeake Bay.

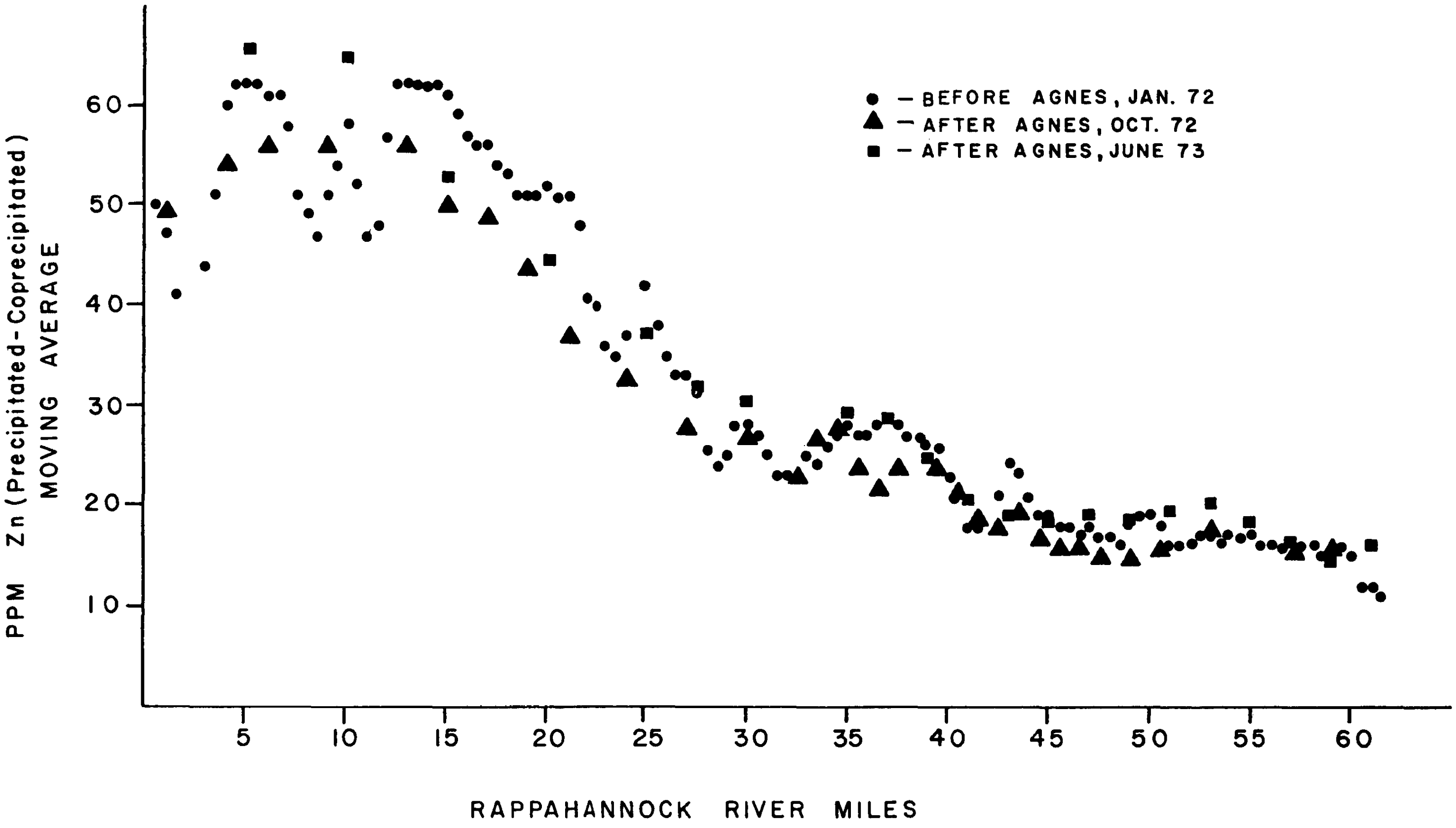

Figure 2. Precipitated-co-precipitated zinc in Rappahannock River sediments.

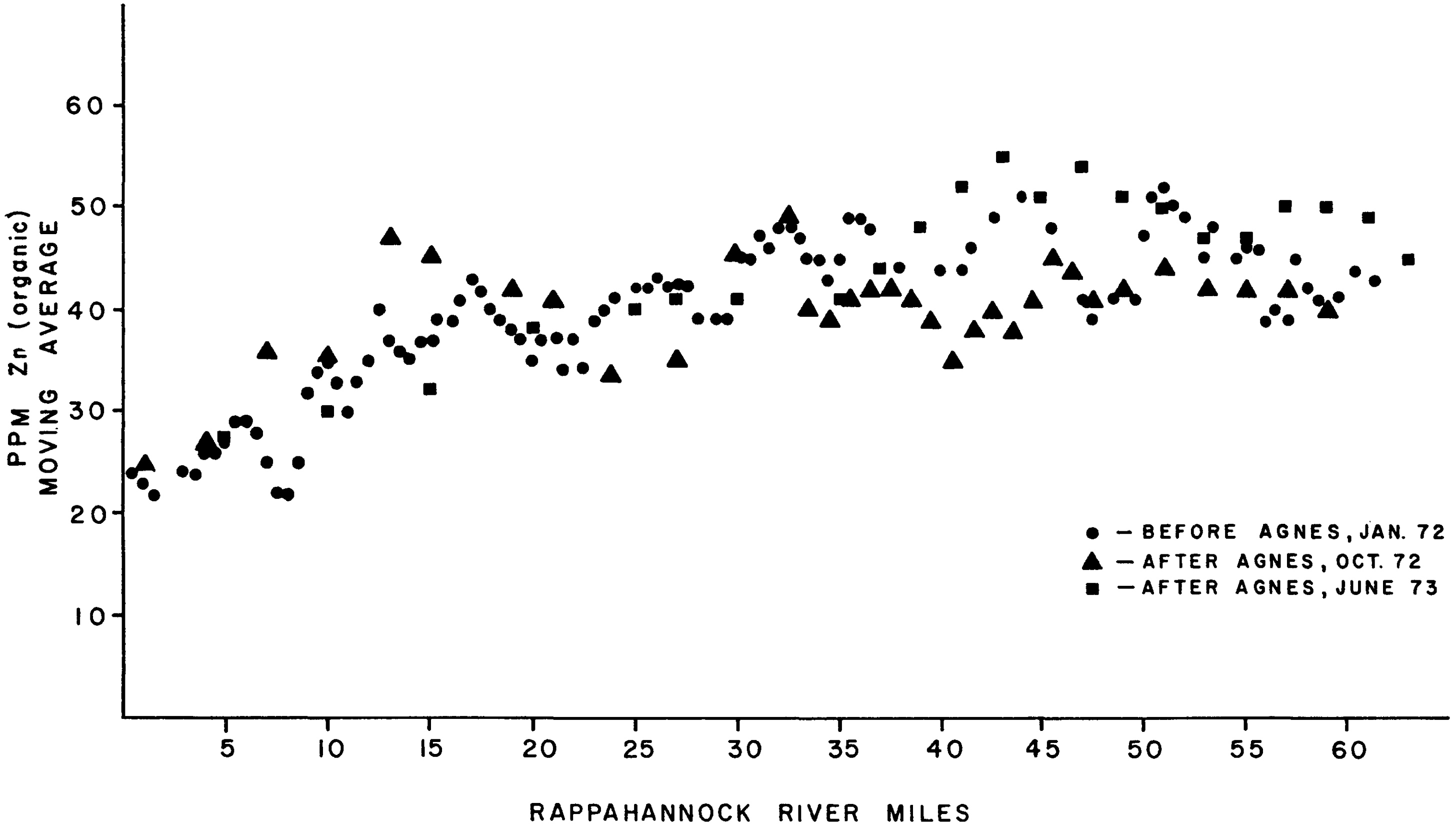

Figure 3. Organic zinc in Rappahannock River sediments.

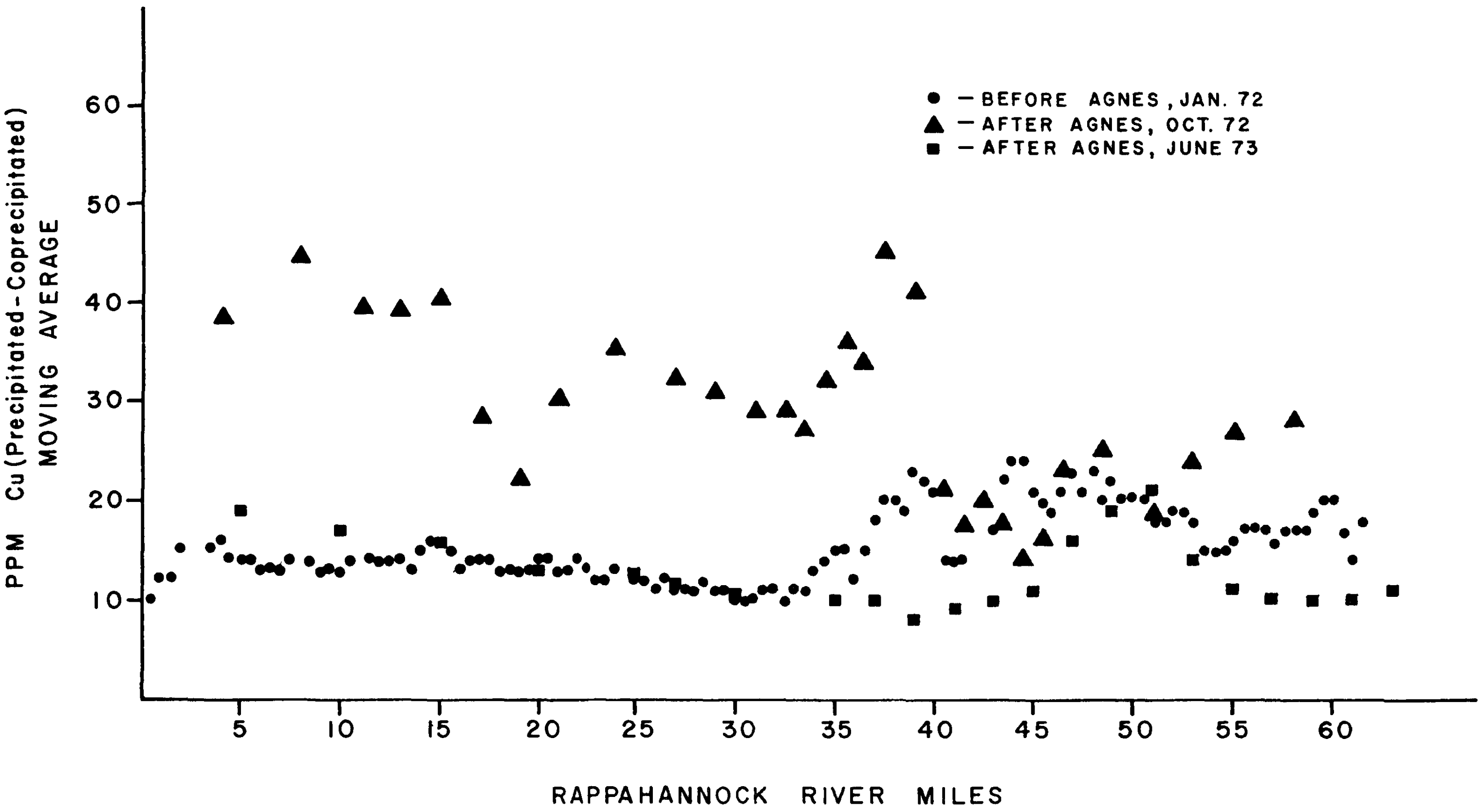

Figure 4. Precipitated-co-precipitated copper in Rappahannock River sediments.

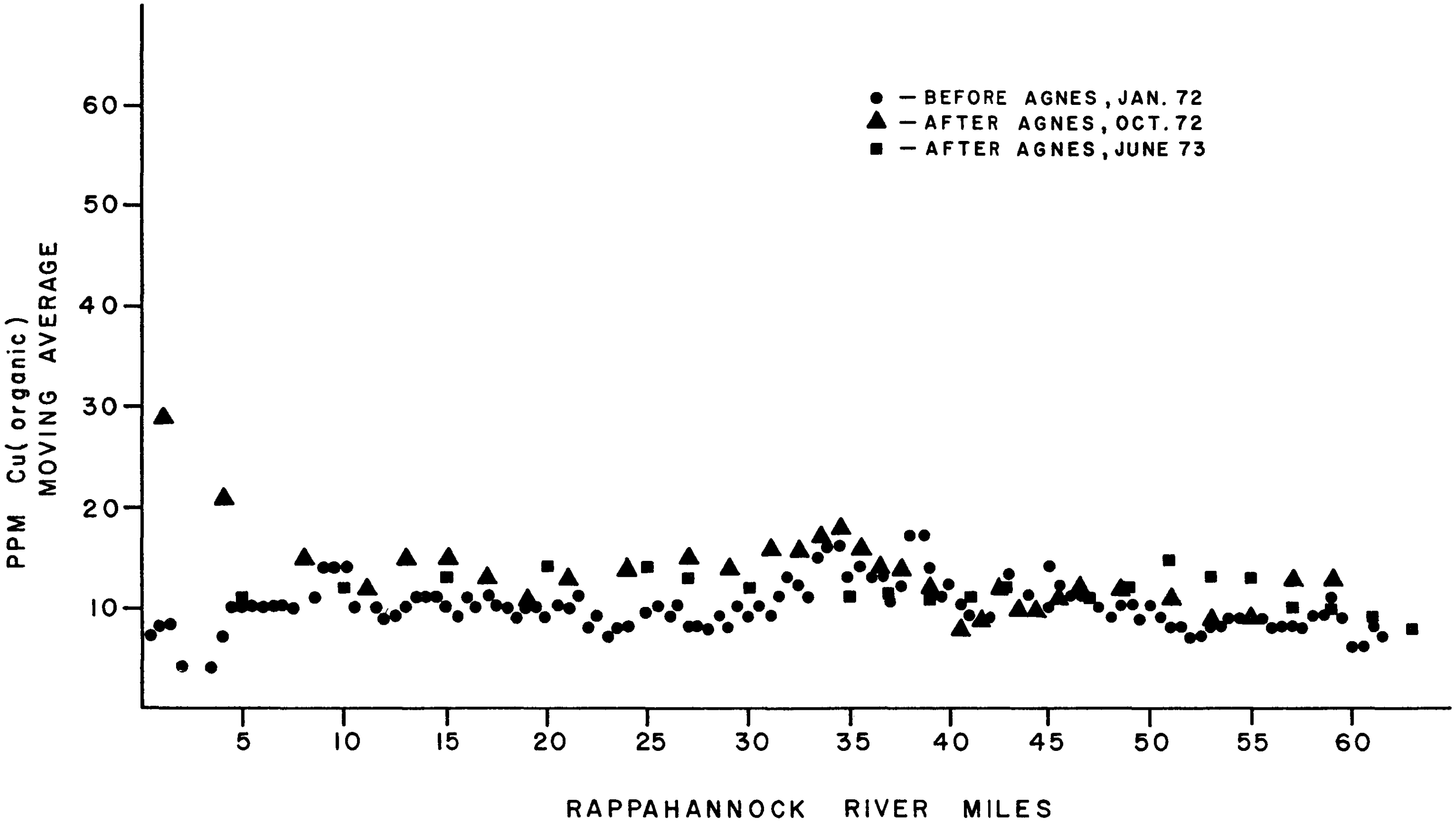

Figure 5. Organic copper in Rappahannock River sediments.

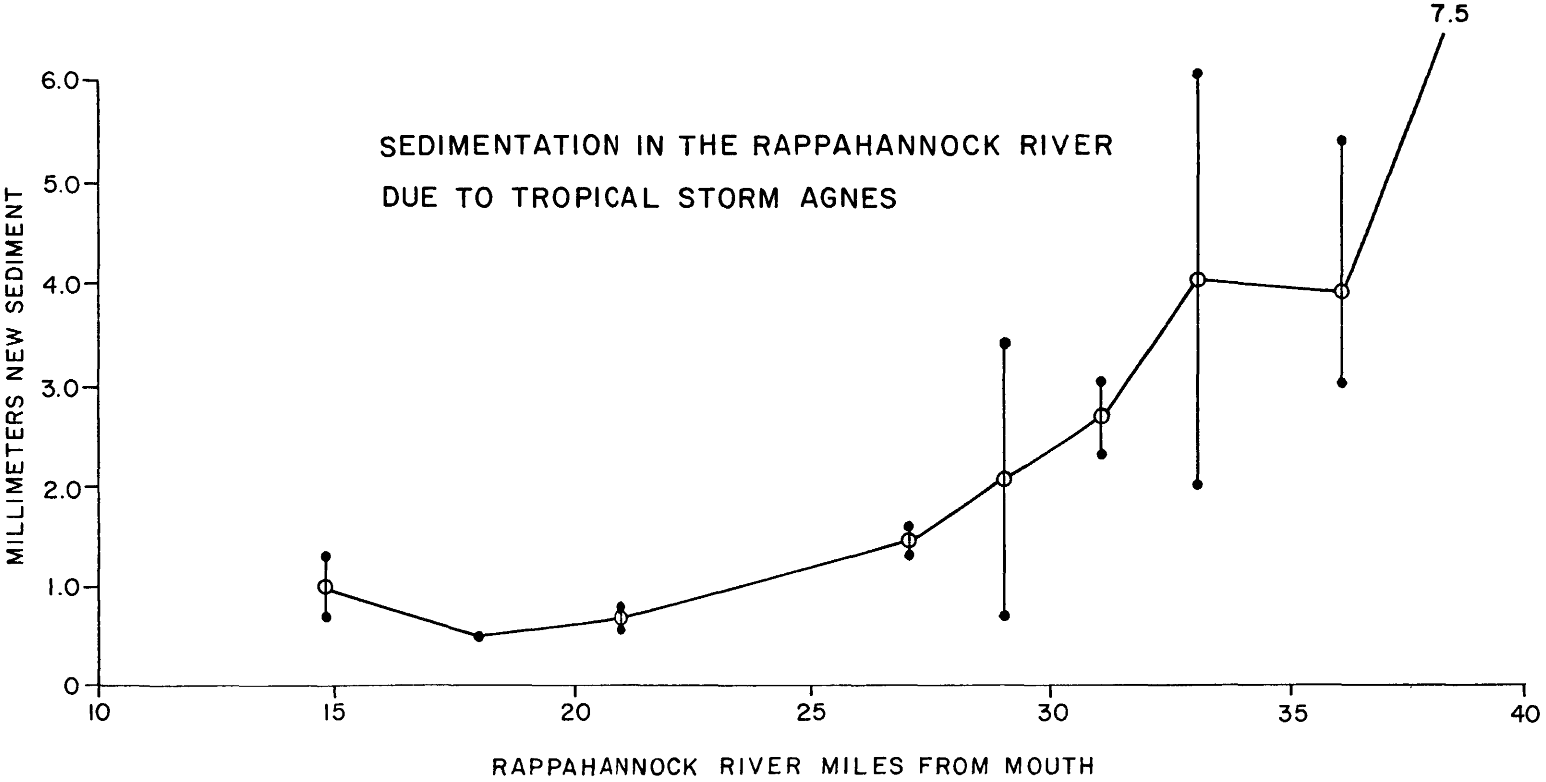

Figure 6. Sedimentation in the Rappahannock River due to Agnes.