

RESEARCH NOTES



Updates on research progress of timely interest to the marine community

PARTITIONING OF COPPER AND ORGANIC CARBON IN THE PATUXENT RIVER ESTUARY

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Each year thousands of tons of metals enter the Chesapeake Bay as a result of man's activities: lead, iron, zinc and copper among others are discharged from heavy industry and power treatment plants, and in run-off from farm lands and urban development; in addition, airborne contaminants from other parts of the country, carried aloft by winds, settle into Bay waters from rain and snow. How harmful are these metals to the biota? There are no simple answers. Metals occur naturally and all organisms make use of them; but like too much of any good thing, high concentrations can be lethal or can affect one organism in a trophic level and thereby affect other organisms indirectly. In recent years, scientists have shown that there is a complex relationship between the concentration of metals and their toxicity. To predict the toxicity of a particular metal, it is necessary to know its chemical form or species--particulate, dissolved, free ionic, complexed. In a series of experiments on the bioavailability of one metal, copper, Craig Zamuda, Dave Wright, James Sanders and Richard Smucker collected water samples periodically between June 1981 and August 1982 at various stations in the Patuxent River. Their aim: to determine the spatial distribution of copper concentration and dissolved organic carbon by size fraction and seasonal variations (which are influenced by environmental and man-made conditions). Such an understanding of bioavailability is a prerequisite for understanding uptake of copper and other metals by organisms like the commercially important American oyster and for developing management strategies that will limit the effects of metals in the Chesapeake Bay.

--The Editors

INTRODUCTION

The bioavailability and toxicity of trace metals to estuarine organisms is affected by the chemical speciation of the metal. For example, Zamuda and Sunda (1982) have reported that accumulation of dissolved copper by the American oyster *Crassostrea virginica* is controlled by the cupric ion activity, and not the total

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copper concentration. Within estuarine systems, the chemical forms of copper and, thus, the bioavailability may change substantially due to changes in salinity, pH and concentration and composition of dissolved organic ligands. At the present time, however, very little is known concerning the quantitative changes in speciation of trace metals and their effect upon controlling trace metal bioavailability within estuarine systems. Nevertheless, there is little doubt that the bioavailability of metals is continually changing in estuaries as a result of biogeochemical processes.

Naturally occurring dissolved organic compounds significantly affect the chemical speciation of copper. Studies have indicated that in estuarine systems greater than 90% of the dissolved copper is complexed by dissolved organic ligands. Thus, the biological availability and potential toxicity of copper in natural waters depend not only upon total copper concentration but also on the nature and abundance of available complexing organic ligands.

During the past year we have characterized the particulate, soluble and colloidal-phase copper fractions in the Patuxent River. The physicochemical speciation of copper has been examined for several sampling locations to quantify changes in copper and carbon on a temporal and spatial basis. Ultrafiltration has been employed to determine the distribution of dissolved organic matter and organic-copper complexes among well-defined molecular size fractions.

METHODS AND MATERIALS

Water samples (10 L each) were collected from several stations in the Patuxent River from Holland Cliff to Solomons Island near the mouth of the Patuxent River (Fig. 1). Samples were taken throughout the year and represent a range in seasonal salinity conditions. All samples were collected at 0.5 m depth in acid-washed, polyethylene carboys. Samples were returned to the laboratory, filtered through glass-fiber filters in acid-washed plasticware and the retentate subsequently analyzed for particulate metal. The filtrate was transferred to 4 liter polypropylene jugs for ultrafiltration. An aliquot of each river sample was not ultrafiltered to provide total values for dissolved organic carbon (DOC) and copper. Dissolved organic carbon analysis employed the persulfate oxidation techniques of Menzel and Vaccaro (1964) and were performed in triplicate. Standard carbon samples were prepared using oven-dried potassium bithalate.

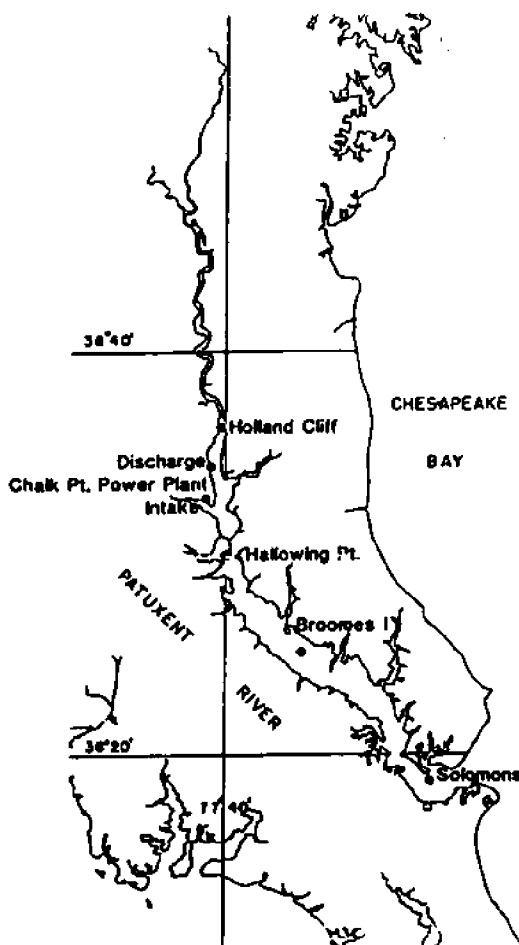


Figure 1. Sampling locations in the Patuxent River.

Copper analysis employed a solvent extraction-preconcentration technique similar to Kinrade and Van Loon (1973); samples were extracted in duplicate and analyzed for copper by graphite-furnace absorption spectrophotometry.

RESULTS AND DISCUSSION

Dissolved copper concentrations generally decreased with distance downriver; this was true for total dissolved copper levels, as well as copper concentrations in the various molecular weight fractions (<10,000 m.w., <100,000 m.w.) that we examined. Ultrafiltration results indicate that the highest concentrations of dissolved copper were in the less than 10,000 molecular weight fractions (Table 1). The distribution of copper among various size fractions does differ on a spatial basis, particularly in the region of Chalk Point and Hallowing Point. Within these regions, there is an increase in the colloidal-phase copper complexes. Greater seasonal variability in the distribution of copper also was recorded for these sites. Thus, there appears to be a region, of limited geographical range, in which measurable changes in the physicochemical speciation of copper occur.

The spatial pattern of copper concentrations in the Patuxent River indicates an additional source of copper in the region of the Chalk Point Power Plant. The magnitude of the impact of the power plant on copper cycling can be estimated from comparisons of copper concentrations in the intake and discharge waters. Our measurements indicate that the amount of copper added to the estuarine system from power plant operations is between 1.0 and 3.7 $\mu\text{g Cu L}^{-1}$. The impact of the plant will be a function of the relative contribution of power plant cooling water demands to total river discharge. Under conditions of low river discharge and high cooling water demand, the contribution of the power plant to copper cycling would be expected to increase. This is consistent with the seasonal maximum in copper concentrations recorded in August. Salinities were high, river discharge was low and, due to peak electrical production, cooling water demand was maximum.

Table 1. Partitioning of dissolved copper (<0.45 μm) among distinct size fractions in the Patuxent River.

| STATION | Copper ($\mu\text{g Cu L}^{-1}$) | Percent of Total Dissolved Copper | | |
|-----------------|---------------------------------------|-----------------------------------|----------------------|----------------------------------|
| | | <10,000 M.W. | 10,000< > 100,000 | 100,000< > 0.45 μm |
| HOLLAND CLIFF | 2.7 \pm 0.5 | 74.8 \pm 2.6 | 10.3 \pm 2.2 | 15.0 \pm 2.2 |
| CHALK POINT | 3.6 \pm 0.4 | 73.0 \pm 1.8 | 10.5 \pm 2.4 | 16.5 \pm 2.2 |
| HALLOWING POINT | 2.3 \pm 0.2 | 73.0 \pm 4.6 | 14.4 \pm 2.7 | 12.6 \pm 2.9 |
| BROOMES IS. | 1.8 \pm 0.3 | 80.6 \pm 2.3 | 8.0 \pm 1.5 | 11.4 \pm 1.7 |
| SOLOMONS IS. | 1.8 \pm 0.3 | 77.4 \pm 2.2 | 8.9 \pm 1.2 | 13.5 \pm 1.8 |

Elevated copper levels in May and June have been recorded near the mouth of the Patuxent River at Solomons Island. We postulate that the elevated levels may be due to anthropogenic inputs of copper from the numerous marinas located in the area. During the spring, extensive scraping and repainting of boats occurs, with the usual application of a copper-based antifouling bottom paint. Leaching of this copper on a continuous basis reduces fouling while also contributing copper to the aquatic environment.

Dissolved organic carbon (DOC) concentrations in the Patuxent River decreased as a function of increasing salinity. Maximum DOC values were recorded in the fall (November) with a seasonal minimum during summer (August). Elevated levels in November may result from terrestrial runoff of dissolved organic compounds originating from decomposing fall vegetation. On the other hand, Sigleo et al. (1980) and Sigleo and Helz (1981) have suggested that the organic fraction is derived primarily from in situ aquatic microorganisms, and not from terrestrial runoff. The arguments for their conclusion were based on analysis of summer and winter samples from the Patuxent River in which: (1) the colloid material consists of carbohydrate and proteinaceous polymers, known extracellular products from phytoplankton; (2) detailed amino acid analyses failed to find any of those amino acids indicative of soil bacteria; (3) there were no traces of lignin, or other evidence of woody plants. Unfortunately, no analysis was conducted during the fall when one would expect the greatest input of carbon from terrestrial sources. It is possible that the estuarine biological production of dissolved organic carbon predominates throughout the year with a shift to terrestrial input occurring in the fall.

Ultrafiltration was employed to determine the distribution of dissolved organic carbon among distinct size fractions. Results indicate that within the Patuxent River much of the carbon is associated with compounds of small molecular weight--approximately 80% of the total DOC has a normal size of less than 10,000 m.w. Annual means of total DOC values and the relative contribution of various molecular weight fractions indicate little spatial variation in partitioning of carbon within the Patuxent River (Table 2).

Table 2. Partitioning of dissolved organic carbon (0.45 μm) among distinct size fractions in the Patuxent River.

| STATION | TOTAL DOC (mg C L ⁻¹) | <10,000 | 10,000 < >100,000 | 100,000 < >0.45 μm |
|-----------------|--------------------------------------|----------------|-------------------|-------------------------------|
| HOLLAND CLIFF | 5.9 \pm 0.9 | 85.0 \pm 2.6 | 6.6 \pm 1.7 | 8.4 \pm 1.5 |
| CHALK POINT | 5.0 \pm 0.7 | 79.6 \pm 4.5 | 10.6 \pm 3.1 | 10.6 \pm 2.1 |
| HALLOWING POINT | 4.9 \pm 0.6 | 80.4 \pm 2.3 | 8.5 \pm 1.9 | 11.1 \pm 1.9 |
| BROOMES IS. | 4.7 \pm 0.6 | 79.1 \pm 2.0 | 6.9 \pm 1.5 | 13.9 \pm 2.5 |
| SOLOMONS IS. | 4.4 \pm 0.6 | 77.2 \pm 2.9 | 10.4 \pm 2.6 | 12.5 \pm 2.1 |

It appears that naturally occurring organic compounds are important in effecting the chemical speciation of copper in the Patuxent River. As indicated previously, greater than 99% of the dissolved copper is estimated to be bound to dissolved organics, and this chemical association with trace metals is a major factor that controls metal ion activities and thus bioavailability. The addition of chlorine to cooling waters by power plants to minimize biofouling of condenser tubes may have a major influence on estuarine carbon and trace metal chlorine chemistry. Carpenter and Smith (1978) have reported that chlorine degradation can lead to reduction of the copper complexation capacity of marine system, suggesting that the organic fraction involved in the complexation of copper may be the same fraction oxidized during chlorine breakdown. Thus the oxidation of carbon by chlorination could result in increased bioavailability and toxicity of copper to aquatic organisms. A comparison of carbon levels in samples from the intake and discharge canal indicates that DOC levels were consistently lower in the discharge canal. The apparent loss of DOC ranged from 0.10 to 1.50 mg C L⁻¹ with a mean of 0.51 mg C L⁻¹ or a mean apparent loss of 12.5% of the initial DOC. The quantity of carbon oxidized appears small in comparison to the total complexation capacity of Patuxent River water, although the combined effects of reduced organic complexation and increased dissolved copper levels may have important consequences with regard to bioavailability of copper in the region of the power plant.

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Crassostrea virginica

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