

# Silver and Copper Accumulation in Two Estuarine Bivalves, the Eastern Oyster (*Crassostrea virginica*) and the Hooked Mussel (*Ischadium recurvum*) in the Patuxent River Estuary, Maryland

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**ABSTRACT:** In order to assess the source of trace elements and to compare uptake between different bivalve species, oysters and mussels were transplanted to five sites in the upper Patuxent River estuary during 1988. Transplant sites were located above and below the discharge of Chalk Point Steam Electric Station (CPSES)—a historic point source for copper. Organisms were sampled approximately monthly for 1 yr and analyzed for copper and silver. During spring and summer, concentrations of silver and copper increased in oysters at the upstream stations. There was very little change in silver and copper concentrations in the mussels with either time or among stations. Copper concentrations accumulated by oysters approached those found during previous periods when CPSES used Cu-Ni alloy condenser tubes (1966–1987), suggesting that corrosion from the Cu-Ni condenser tubes was only a minor contributor to the copper burdens of oysters in the river nearby. The lack of accumulation by mussels at the same sites suggests that part of the reason for the accumulation by oysters may be a taxonomically specific physiological effect caused by the salinity regime in the upper Patuxent.

## Introduction

The Patuxent River in Maryland (Fig. 1) drains a portion of the Washington, D.C.–Baltimore corridor into the Chesapeake Bay, and consequently receives significant anthropogenic inputs from residential, agricultural, and industrial sources. Thus, there is considerable potential for pollutant impact on the organisms of the Patuxent River estuary and Chesapeake Bay. One of the most important commercial species in the Patuxent River estuary and Chesapeake Bay has been the eastern oyster, *Crassostrea virginica*. A nonmotile filter feeder, it is particularly subject to contamination by local pollution and, as a commercially utilized species, is especially suited to pass those pollutants on to man.

Historically, there has been a problem with copper contamination of oysters in the Patuxent River. Chalk Point Steam Electric Station (CPSES), a large coal- and oil-burning power plant, is located near the head of the Patuxent River estuary (Fig. 1). Unit 1 came on line in August 1964 and Unit

2 in March 1965. The original condensers were stainless steel and failed after a few months and were replaced with aluminum-bronze, which lasted less than a year (Roosenburg 1969). In 1966 copper-nickel (Cu-Ni) condensers were installed, and these remained with occasional replacement until 1987 when titanium (Ti) alloy tubes were installed. In the years following the first use of Cu-Ni alloy condenser tubes, a problem with 'greening' in oysters, caused by copper accumulation, was noted in the vicinity of CPSES. Concentrations of copper in oysters decreased downstream; in oysters transplanted to the discharge canal of the plant extremely high copper concentrations were found (Roosenburg 1969). Copper accumulation problems in oysters have long been observed near polluted sites around the world (e.g., Boyce and Herdman 1897; Orton 1923; Abbe 1982; Han and Hung 1990).

Because of the copper problems associated with plant operation, much interest has been focused on the trace element concentrations of oysters in the Patuxent River (Roosenburg 1969; Phelps et al. 1985; Abbe and Sanders 1986; Sanders et al. 1991;

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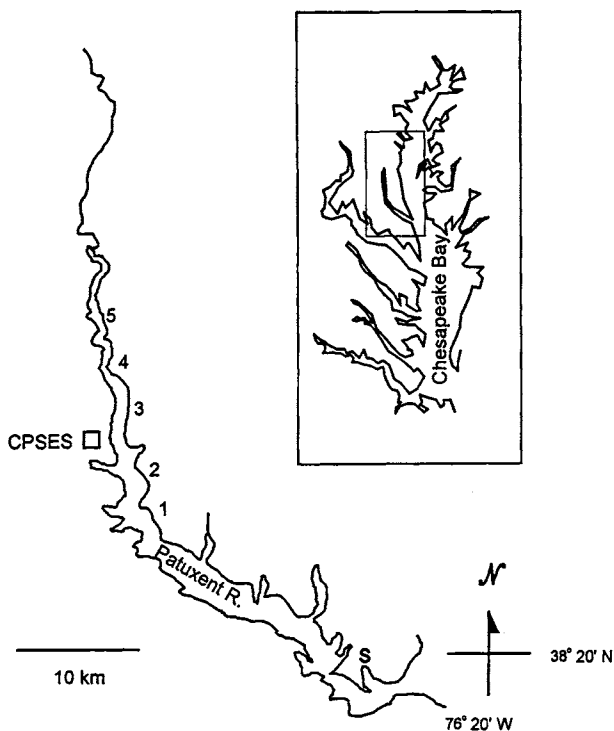


Fig. 1. Map of the Patuxent River, showing the five trans-plantation sites (1-5), Chalk Point Steam Electric Station (CPSES), and Solomons Harbor (S). Inset shows location of Patuxent River on Chesapeake Bay.

Wright and Zamuda 1991). During the period when Cu-Ni alloy condensers were used, it was estimated that  $600 \text{ kg yr}^{-1}$  of copper was released to the Patuxent River from Chalk Point by corrosion of the condensers (Eaton and Chamberlain 1982). At the time of this study, and through the present, no Cu-Ni alloy was used in the condensers of Units 1 and 2 at CPSES; however, other sources of copper may have been present in the plant, particularly copper tubing in the cooling towers of Units 3 and 4. Some water from these recirculating cooling systems is released into the discharge canal of CPSES daily (personal communication, David Bailey, Potomac Electric Power Company). This discharge is not routinely monitored for trace metals.

Our first objective was to determine whether metal concentrations in Patuxent River bivalves were still elevated following the switch to titanium alloy condensers at CPSES. In addition, we wished to examine similarities and/or differences in trace element uptake by organisms used as pollutant indicators. We approached these questions by transplanting eastern oysters (*Crassostrea virginica*) and another common, local bivalve species, the hooked mussel (*Ischadium recurvum*) to sites in the river below, at, and above the plant. We have also examined a long-term dataset of samples taken approx-

imately monthly from a natural oyster bar approximately 3 mi downstream of the plant; this dataset brackets the time period in question.

## Materials and Methods

### EXPERIMENTAL DESIGN AND SAMPLING

Oysters (average initial length of 49.8 mm and dry soft tissue weight of 0.307 g) were obtained from Chesapeake Bay Oyster Culture of Shady Side, Maryland. These oysters were raised from parental stock specially selected for maximum growth. Mussels were dredged from the Patuxent River at the Holland Point oyster bar (Fig. 1, station 1), and averaged 51.8 mm long and 0.218 g dry soft tissue weight initially. All organisms were held in flowing unfiltered Patuxent River water before field deployment. Organisms were placed in vinyl-coated stainless-steel-mesh cages and placed on a platform of PVC pipe which held the cages 0.3 m above the bottom.

In April 1988, four platforms were set out, at the Holland Point (station 1, Fig. 1), Chalk Point discharge (station 3), Cedar Haven (station 4), and Deep Landing sites (station 5). Each platform contained 150 oysters and 200 mussels. Prior to setting the platforms, an initial sample of 20 of each organism was collected haphazardly from the entire pool of organisms to estimate average initial sizes, weights, and metal concentrations. On the first sampling date, the fifth platform was set out at the Teague Point site (station 2) to complete the geographic coverage, using organisms from the original group.

Sampling was carried out approximately monthly from June 1988 to May 1989. Ten organisms of each species were removed haphazardly from the cages and returned to the laboratory for analysis; this number was chosen to enable the detection of reasonably small differences between the sites (Wright et al. 1985). In some cases, less than 10 organisms were taken to allow more organisms in the final collection from that site. Organism mortality was not specifically monitored; however, in general, more organisms died in the more upstream stations, and consequently the time series for both oysters and mussels at some stations did not reach the full year. In at least two cases, oysters at station 5 and mussels at station 3, mortality was due to predation by crabs. A group of mussels recruited on the experimental platform at station 3 during the course of the experiment. These were sampled in October, after the transplanted mussels were gone, and were smaller than the transplants.

Salinity and temperature were measured in the bottom water at each site using a Beckman model RS5-3 portable salinometer, and dissolved oxygen

using a YSI model 57 oxygen meter. Water samples (1 l) were collected from the bow of the boat in acid-washed (Boyle and Huestad 1983) polyethylene bottles by holding the bottle under water as the boat advanced slowly through the water. Samples were returned to the laboratory for filtration and metal analysis.

Upon return to the laboratory, the bivalves were scrubbed to remove external fouling, and placed in aerated tanks of filtered Patuxent River water overnight to allow their guts to empty. The bivalves were scrubbed again, rinsed in de-ionized water, blotted dry, measured, and shucked. The tissues were blotted, placed in preweighed pyrex beakers, and the wet weights determined. The tissues were then dried at 70°C and reweighed.

In addition, native oysters in a fixed size range (70–100 mm length) have been collected approximately monthly from the Holland Point oyster bar since 1986 and analyzed for copper and silver (Sanders et al. 1991). These oysters are collected by oyster dredge. Preparation for analysis of these oysters is carried out in the same manner as for the oysters in the transplant study.

#### ANALYTICAL METHODS

Tissue samples for trace-element analysis were dry-ashed at 550°C (Van Loon 1985) and redissolved in 15 ml of a mixture of 1% HNO<sub>3</sub> and 1% HCl. All acids used were Baker trace-metal grade. Blanks were prepared using empty beakers carried through the digestion process. Tissue samples were analyzed for silver by graphite-furnace atomic absorption spectrometry (GFAAS), using D<sub>2</sub> background correction, on a Perkin Elmer 603 AAS equipped with an AS 400 graphite furnace and an AS 40 autosampler. Copper in the tissue digests was analyzed by flame atomic absorption spectrometry, using an air-acetylene flame and D<sub>2</sub> background correction, on a Perkin Elmer model 2380 AAS. Calibration for both elements was made using standards in a mixture of 1% HNO<sub>3</sub> and 1% HCl. Yields were monitored using samples of homogenized oyster tissue prepared in the laboratory and previously compared to NBS standard oyster material (NBS 1566). Recovery of NBS standard reference material 1566 (oyster) averaged 104 ± 10% for copper and 114 ± 13% for silver.

Water samples for copper (250 ml) were filtered through acid-washed (25% HNO<sub>3</sub>) GF/F filters (nominal pore size 0.7 μm) in an all-plastic acid-washed apparatus. They were concentrated using Chelex-100 resin into 12.5% HNO<sub>3</sub> following a K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> digest to oxidize dissolved and colloidal organics which can bind metals and reduce the extraction efficiency (Riedel et al. 1984). Analysis of these samples was carried out by GFAAS using stan-

dards in 12.5% HNO<sub>3</sub>. The efficiency of the pre-concentration and analysis procedures was checked by concentrating and analyzing duplicate 250 ml samples of NASS-1 and CASS-1 standard reference materials (National Research Council of Canada) with recoveries of 96% and 104%, respectively. Silver concentrations in water samples were not determined.

Sediment samples from the transplant stations were collected in summer of 1993, using a non-metallic box corer. The top 10 cm of sediment were mixed; screened through a 100-μm polypropylene mesh to remove large particles; digested in HNO<sub>3</sub>, HCl, HF, and HClO<sub>4</sub> (Van Loon 1985); and analyzed for copper and silver by flame and graphite-furnace atomic absorption spectrometry respectively. Estuarine sediment standard reference material (NBS 1646) was digested and analyzed with the sediment samples. Copper recovery averaged 80 ± 7%. This reference material is not certified for silver; however, we found values of 0.1 ± 0.01 μg g<sup>-1</sup>.

## Results

#### ENVIRONMENTAL VARIABLES

Water temperatures at the sample sites ranged from about 2°C in December to 32°C in July. All the sampling sites were within 5°C of each other at any sampling. Usually the Chalk Point discharge (station 3) was the warmest site, presumably due to the thermal plume of the discharge, and station 1 was the coolest (Fig. 2A). At the start of the study, salinities averaged about 5 on the practical salinity scale. Salinities increased to approximately 15 through October 1988, then decreased through the study (Fig. 2B). Usually, salinity decreased consistently upriver, with a notable exception occurring in May 1989 when a storm event diluted the salinity in a large creek near station 2 and caused the salinity at that site to fall below the stations upstream. Dissolved oxygen showed a strong negative correlation with temperature, with low values (3–6 mg l<sup>-1</sup>) occurring in July and high values (14–15 mg l<sup>-1</sup>) occurring in December (Fig. 2C). Except in mid-summer, all stations had very similar dissolved oxygen concentrations.

#### WATER-COLUMN COPPER CONCENTRATIONS

Measured values of dissolved copper during the sampling period ranged from 0.5 μg l<sup>-1</sup> to 3.1 μg l<sup>-1</sup> (Fig. 3). Differences between stations were not large or systematic, except that station 1 was generally higher and much more variable; we suspect, but cannot verify, that some of these samples were contaminated. Means for individual stations ranged from 1.0 μg l<sup>-1</sup> at station 2 to 1.6 μg l<sup>-1</sup> at station 1. A plot of the copper concentrations ver-

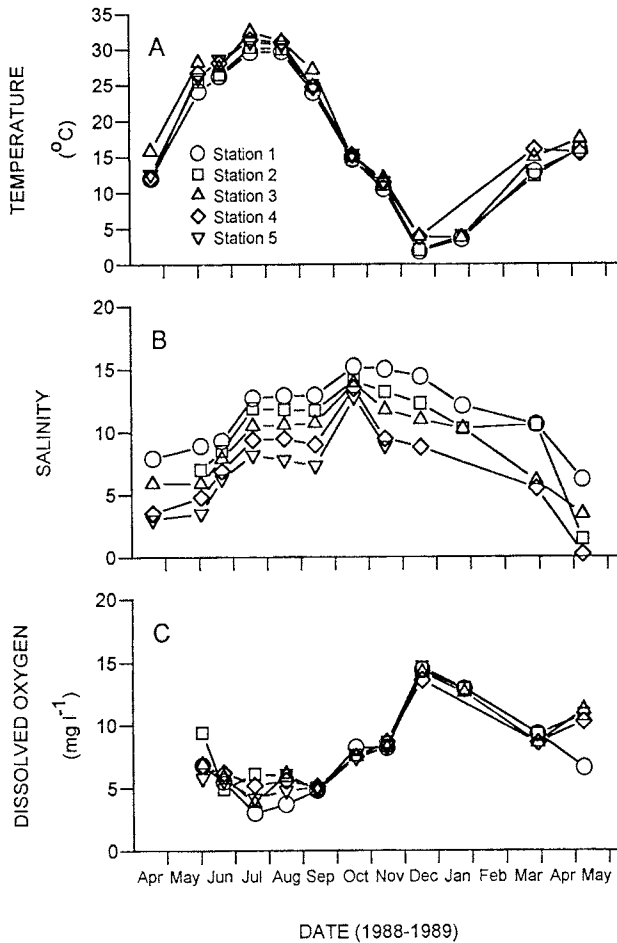


Fig. 2. Environmental variables at the time of organism collection: A) temperature, B) salinity, C) dissolved oxygen.

sus salinity (Fig. 3; inset) shows no strong relationship to salinity.

#### SEDIMENT METAL CONCENTRATIONS

Sediment concentrations of copper and silver are presented in Table 1. Copper concentrations in sediment of the upper Patuxent River in 1993 were approximately 20–25  $\mu\text{g g}^{-1}$  throughout the study area, with no significant geographic trends. Silver, however, showed a trend, with the highest concentrations recorded at the furthest upstream stations.

#### ORGANISM GROWTH AND CONDITION

Throughout the experiment these oysters were subadult, and did not produce gonads or spawn. Growth of oysters was strongly affected by the location to which they were transplanted (Fig. 4A, B). Oysters grew from early June through October or November. The downstream stations grew most rapidly. Oysters at station 5 did not grow at all,

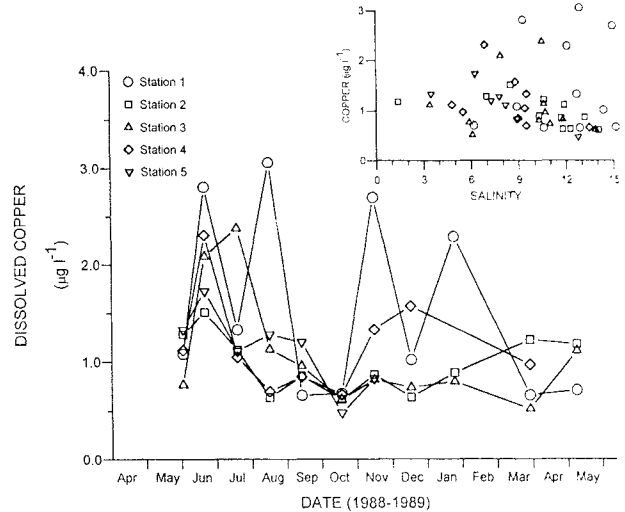


Fig. 3. Dissolved copper concentrations ( $\mu\text{g l}^{-1}$ ) in the Patuxent River at the time of transplanted organism collection. Inset shows the same data plotted versus salinity at the time of collection.

rather the mean dry weights and mean lengths decreased (due to shell erosion) and most of the oysters died during June and July. Mortality appeared to be caused largely by mud crab predation, as indicated by holes in the shells of the dead oysters, and presence of mud crabs in the cages (McDermott 1960). The mussels were mature when planted and produced gonads in spring and spawned in summer, and did not grow in length during the study, although they appeared to add weight during the spring and fall and lose weight during summer (Fig. 4C, D)

#### BIVALVE METAL ACCUMULATION

Copper concentrations in oysters dropped substantially between the transplantation date and the first sampling at all the stations. This may represent depuration of Cu taken up at the hatchery they were obtained from. Station 1 exhibited a decreasing trend in oyster copper concentration over the entire course of the study. In contrast, by June concentrations at stations 2–5 had begun to rise again, reaching means of approximately 450  $\mu\text{g g}^{-1}$  by mid July. Stations 3 and 4 remained elevated

TABLE 1. Concentrations of copper and silver in the sediments from the experimental sites.

Station	Copper ( $\mu\text{g g}^{-1}$ )	Silver ( $\mu\text{g g}^{-1}$ )
1	19.7	0.26
2	22.8	0.27
3	25.9	0.35
4	21.9	0.42
5	26.8	0.49

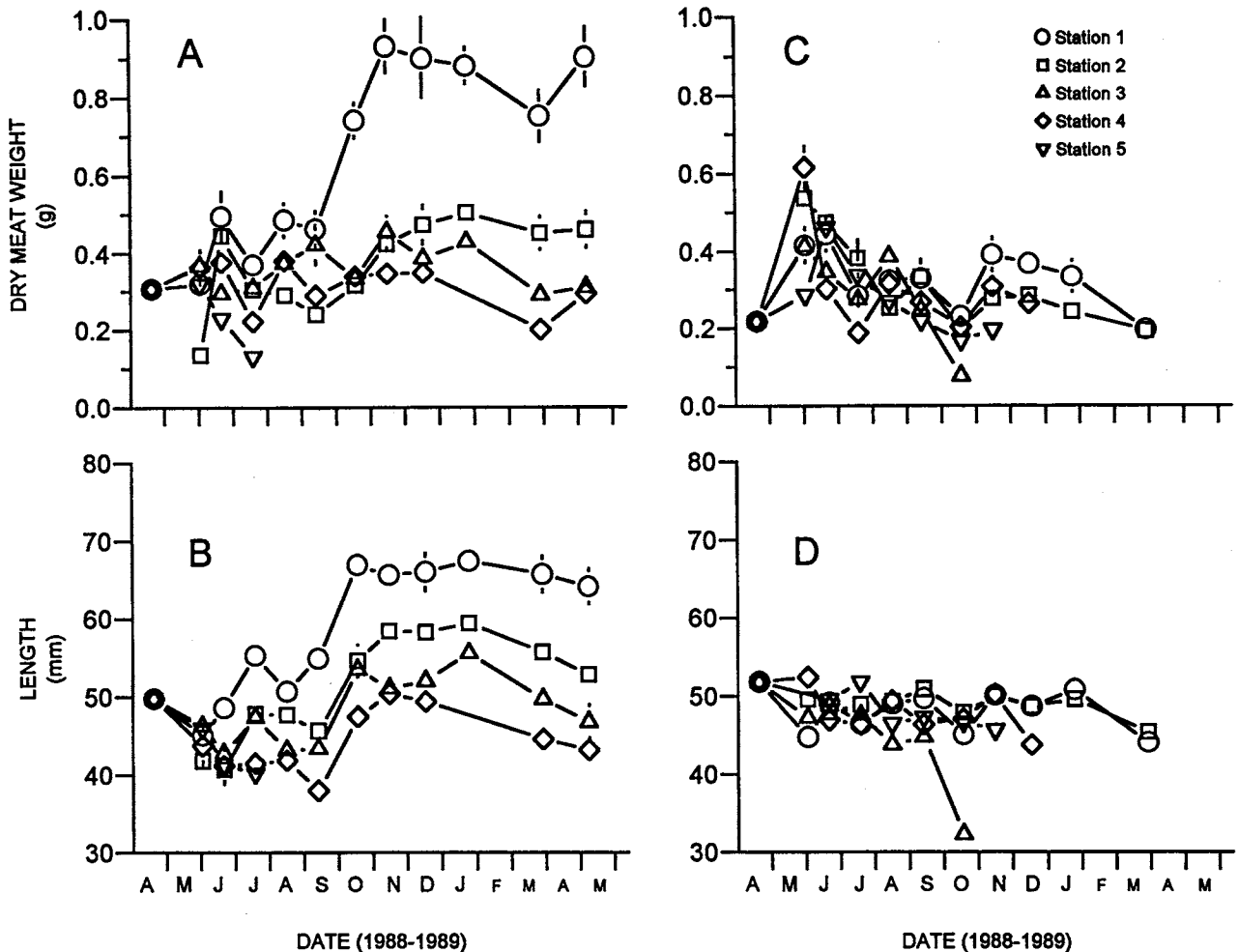


Fig. 4. Growth of organisms transplanted to different sites in the Patuxent River estuary. Each point shows mean  $\pm$  SE of sample: A) oyster dry meat weight, B) oyster mean shell length, C) mussel dry meat weight, D) mussel shell length.

through winter but dropped substantially by May, declining to or below initial levels (Fig. 5A); station 2 declined throughout the fall. Copper concentrations in the transplanted mussels were much lower than in the oysters. Concentrations at all stations (but less so at station 1) showed a slight rise through September and October, and a decline to initial values by January (Fig. 5B). The highest concentrations in mussels (above  $40 \mu\text{g g}^{-1}$ ) were found at station 2 in October; however, concentrations decreased at this station, as for the other stations, during the winter.

Silver concentrations in the transplanted oysters exhibited a pattern similar to that of copper. Silver concentrations in the transplanted oysters (Fig. 6A) remained similar to initial concentrations through the June sampling. The concentration in station 1 oysters remained approximately the same through the study. However, silver concentrations in the oysters from stations 3, 4, and 5 had a sharp

increase in July, from about  $6 \mu\text{g g}^{-1}$  to about  $12 \mu\text{g g}^{-1}$  in 1 mo. Concentrations in oysters from station 2 had also increased but not as rapidly. By August, stations 2, 3, and 4 had become essentially indistinguishable. Concentrations at these stations leveled off in September but remained elevated through March. All three stations had substantial decreases in concentration between March and May. Silver concentrations in the transplanted mussels remained close to the initial concentrations, about  $1 \mu\text{g g}^{-1}$ , throughout the experiment (Fig. 5B). No patterns, either spatial or temporal, are apparent.

Results of copper and silver analyses from native oysters from the Holland Point oyster bar for the period 1986-1991 are shown in Fig. 7. Annual mean copper concentrations fell from  $270 \mu\text{g g}^{-1}$  and  $289 \mu\text{g g}^{-1}$  in 1986 and 1987 before removal of the Cu-Ni condensers, to  $218 \mu\text{g g}^{-1}$ ,  $204 \mu\text{g g}^{-1}$ ,  $230 \mu\text{g g}^{-1}$ , and  $202 \mu\text{g g}^{-1}$  in 1988, 1989, 1990,

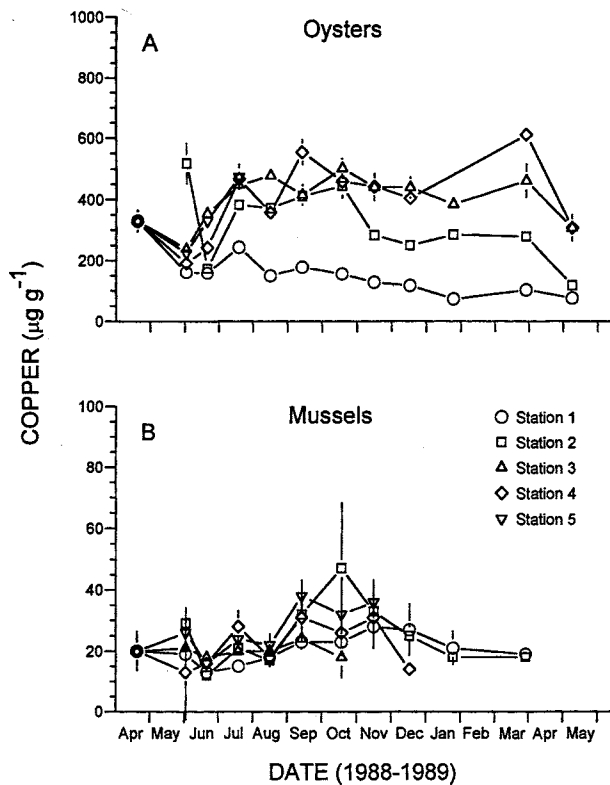


Fig. 5. Concentration of copper ( $\mu\text{g g}^{-1}$  dry weight) in organisms transplanted to different sites in the Patuxent River estuary. Each point shows mean  $\pm$  SE of sample: A) oysters, B) mussels.

and 1991, respectively, after the change to titanium condensers. Analysis of variance with a randomized block design (Neter and Wasserman 1974), using collection months as a block variable, revealed a significant difference ( $p < 0.05$ ) among years, and a contrast of the means of years prior to removal of the Cu-Ni condensers to the years after their removal shows a significant difference ( $p < 0.05$ ). A similar analysis of the silver data showed no significant differences among annual means ( $p > 0.1$ ). A seasonal pattern of change in metal concentration is also apparent, with maximum values occurring in July through September (Sanders et al. 1991). For copper this seasonal effect is significant in the analysis of variance ( $p < 0.05$ ), while it is not significant for silver ( $p > 0.1$ ).

## Discussion

### TRACE ELEMENT SOURCES

Several sources of copper (and other trace elements) to the study area exist other than CPSES. United States Environmental Protection Agency (1994) reported waste-water treatment plant and industrial copper loadings to the Patuxent River over the period 1987–1992 to be approximately

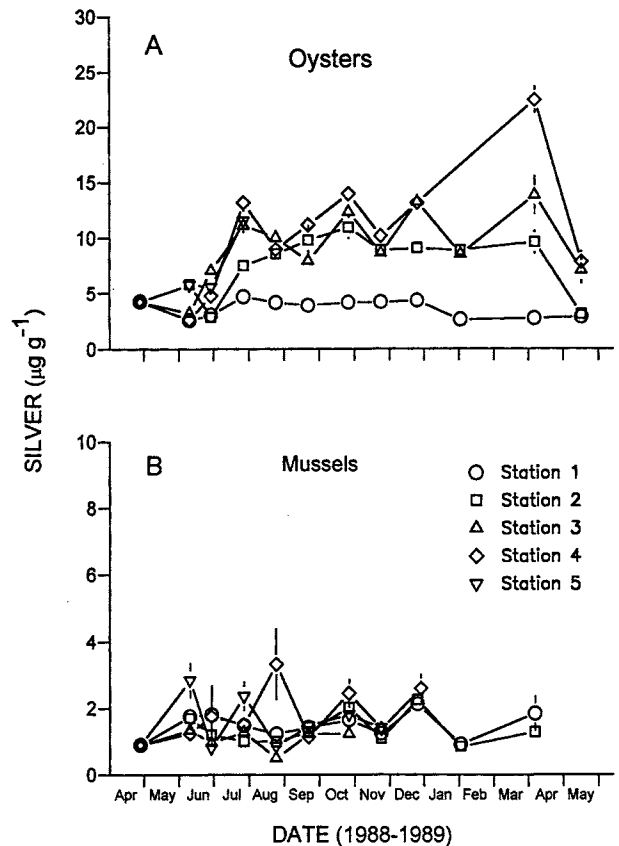


Fig. 6. Concentration of silver ( $\mu\text{g g}^{-1}$  dry weight) in organisms transplanted to different sites in the Patuxent River estuary. Each point shows mean  $\pm$  SE of sample: A) oysters, B) mussels.

277  $\text{kg yr}^{-1}$  (CPSES is not included in this list). Using an average flow of the Patuxent River from 1987 through 1992 of  $810,000 \text{ m}^3 \text{ d}^{-1}$  (data from United States Geological Survey Surface Water Information Department, Towson, Maryland), we calculate potential additions of copper in the freshwater Patuxent River from these sources alone to be approximately  $0.9 \mu\text{g l}^{-1}$ , with monthly values

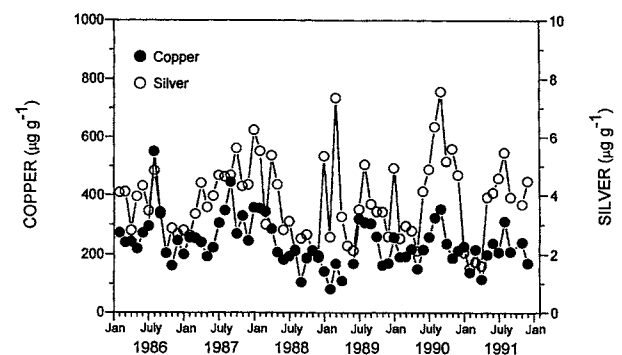


Fig. 7. Concentration of copper and silver from oysters collected from the Holland Point oyster bar from 1986 to 1991.

ranging from  $0.24 \mu\text{g l}^{-1}$  to  $3.6 \mu\text{g l}^{-1}$  depending on the flow conditions. This is consistent with our measurements of dissolved copper concentrations in the Patuxent.

Atmospheric deposition of metals is another potential source for trace elements in the Patuxent River. Atmospheric deposition of copper in the Chesapeake area has been estimated to be  $660 \mu\text{g m}^{-2} \text{yr}^{-1}$  (Scudlark et al. 1994). The Patuxent River drainage area is  $2,269 \text{ km}^2$ , thus the depositional flux to the drainage is approximately  $1,500 \text{ kg yr}^{-1}$ . Clearly, atmospheric deposition has the potential to be a major factor in the copper budget of the Patuxent River. However, it is not known what fraction of atmospherically deposited trace elements are trapped by the landscape, and not transmitted to the river. Atmospheric inputs would be concentrated in the freshwater regions of the Patuxent, as most of the input would be onto the watershed and not the estuary surface, and thus the contribution of the atmospheric inputs at a particular station would be closely related to the salinity at the site.

Another potentially significant, but difficult to quantify, source of copper is the copper oxide-based antifouling paint applied to virtually all of the recreational and work boats moored in the area. Copper leaching from such paints can be a significant source of copper pollution, particularly in poorly flushed waters with significant boat traffic (Claisse and Alzieu 1993). A copper leach rate of  $100 \text{ mg m}^{-2} \text{d}^{-1}$  is required to maintain antifouling protection (Zamuda 1984). A survey of the town of Benedict (near Holland Point bar, and the first concentration of boats downstream of fresh water), revealed about 100 vessels (average length about 6 m) moored during the summer season, for a total surface area of approximately  $1,000 \text{ m}^2$ . That surface area would produce a leach rate of  $100 \text{ g d}^{-1}$  and, further assuming that the vessels are in the water an average of 6 mo, a total loading of about  $18 \text{ kg yr}^{-1}$ . Even allowing for greater than minimum leach rates, a greater number of boats (there are many boats located at private docks), longer periods in the water, and possible errors in our estimate of average boat size, this source does not appear to be an important source in the upper Patuxent. However, boat paint is likely an important source of copper in a budget for the entire Patuxent; Zamuda (1984) estimated that the harbor at Solomons (Fig. 1) released  $3,015 \text{ kg yr}^{-1}$  to the Patuxent River near its confluence with Chesapeake Bay. With the ban on tin antifouling paints and a large increase in the numbers of boats anchored in Solomons, current inputs may be significantly higher.

Our data on dissolved copper show no evidence for a gradient of dissolved copper in the upper

Patuxent to account for the observed differences in copper concentrations of the oysters, and the measured concentrations are within values that upstream loadings, wet atmospheric deposition, or antifouling paint alone could produce if the copper were efficiently transmitted downstream or upstream. Mean dissolved copper concentrations were not significantly different among the different stations ( $p > 0.10$ , one-way ANOVA), suggesting that this was not a significant source of the variation in oyster uptake, and the station with the highest mean dissolved copper (station 1), had the lowest copper uptake on both a per organism and biomass basis.

Silver concentrations and sources in the Patuxent River are much less well documented than copper. There are few published values for dissolved silver in the Patuxent River, or the Chesapeake Bay area in general. United States Environmental Protection Agency (1994) reports a single point source for silver of  $4 \text{ kg yr}^{-1}$  in the Patuxent River. Atmospheric deposition of silver has not been examined in the Chesapeake Bay area.

Another potential source of trace elements for filter-feeding bivalves could be suspended particles, which in the case of a highly turbid estuary such as the upper Patuxent River, consists largely of re-suspended sediments. Sediment copper concentrations from the study area do not reflect severe copper contamination either upstream in general, or in the vicinity of CPSES. Values measured in the Patuxent River are approximately equivalent to current values for mainstem Chesapeake Bay sediments or sediments of several of the less impacted Chesapeake tributaries (R. Eskin, Maryland Department of the Environment, personal communication). Silver concentrations in the Patuxent River sediment do increase upstream, suggesting a possible source of dissolved silver for uptake by oysters in the upper Patuxent. Silver adsorbed to phytoplankton or sediment particles is not available to oysters (Abbe and Sanders 1990). However, silver is strongly complexed by chloride, and silver adsorbed to particles can be desorbed by increasing the salinity (Sanders and Abbe 1987, 1989). Thus, in the course of estuarine mixing, silver could be desorbed from the particles (thus lessening the concentration in the resulting sediment) and made available for uptake by organisms. The decrease in silver in sediment downstream may also simply result from mixing with low-silver concentration sediment from further down the estuary.

#### SALINITY

Negative correlations between salinity and metal concentrations are often observed in field studies with bivalves (e.g., Huggett et al. 1973; Phillips

1976; George et al. 1978; Phelps et al. 1985; Sanders et al. 1991). But, it is often unclear whether the relationship is due to a direct effect of salinity or is caused by dilution of the higher levels from the freshwater source with lower concentrations in the saline end-member. In laboratory studies, a direct effect of salinity on the uptake of dissolved copper and silver in oysters has been observed (Wright and Zamuda 1987; Abbe and Sanders 1990; Amiard-Triquet et al. 1991).

Increasing salinity decreases the thermodynamic activity of dissolved metals by both inorganic complexation and increased ionic strength. Zamuda and Sunda (1982) demonstrated that at a fixed salinity, the uptake of dissolved copper by *C. virginica* was determined by the activity of the free copper ion. Similarly, complexation of silver by the chloride ion in seawater has been shown to regulate the uptake of silver by phytoplankton, zooplankton, and sediment (Engel et al. 1981; Sanders and Abbe 1987; Sanders and Abbe 1989). However, the effect of salinity on copper accumulation by oysters is not consistent with changes in the cupric ion activity alone (Wright and Zamuda 1987); accumulation at lower salinity is greater at equivalent copper ion activities than at higher salinities. In this study, our five stations have a more or less constant gradient of salinity, from the downstream to the upstream stations, with an average salinity drop of about 1 unit with each station further upstream. Our trace-element accumulation data do not show this gradient. Rather, the most downstream station is quite different from the other upstream stations, which are more or less similar.

One factor arguing against the role of salinity as the sole factor determining trace-element concentrations in oysters was the seasonal pattern of trace-element accumulation. Trace-metal concentrations in the transplanted oysters and, to a much lesser extent, mussels were highest during the summer months, when salinities were highest (suggesting a suppression of trace element uptake as discussed above). Thus, focusing on a single site over an annual cycle, it could appear that metal uptake was positively correlated to salinity. The same pattern is observed for copper, but not silver, in the long-term survey of oysters from Holland Point bar.

We therefore hypothesize that there is a physiological response of oysters to temperature which alters trace metal (particularly copper) regulation in oysters such that, all other factors being equal (dissolved metal concentration, salinity, etc.), metal concentrations will be greater in the warm seasons than the cold seasons. This is a testable hypothesis, but it is beyond the scope of this paper.

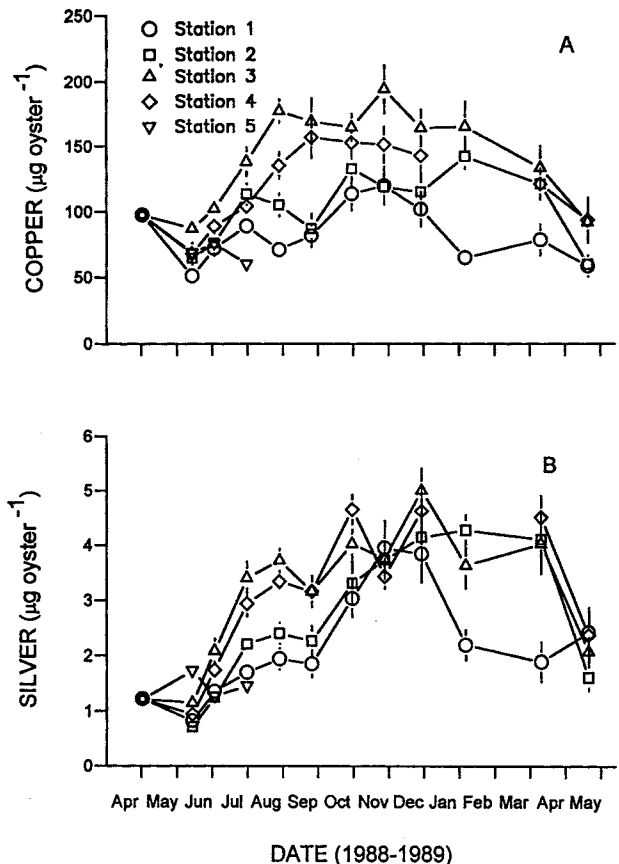


Fig. 8. Body burden ( $\mu\text{g oyster}^{-1}$ ) of metals in transplanted oysters transplanted to different sites in the Patuxent River estuary. Each point shows mean  $\pm$  SE of sample: A) copper, B) silver.

#### GROWTH RATE

Another significant variable among stations was the growth rate of the oysters. Oysters grew most rapidly at the furthest downstream station, station 1. Salinity stress was a major factor during the course of the growing season. *C. virginica* requires an average salinity of at least 5 for sporadic feeding, and 7.5 for sustained feeding and normal growth (Loosanoff 1953; Galtsoff 1964). For station 5, the salinity did not exceed 7.5 until October, when oyster mortality was complete.

If trace-metal uptake and oyster growth are not tightly coupled, we can get an alternative view of metal uptake, one not influenced by the effect of dilution of the tissue by growth, by examining the amount of metal per organism (rather than per unit weight). Thus, increases represent net uptake of metal and decreases net loss of metal. Figure 8 (A, B) show the copper and silver burdens of the sampled oysters. On this basis, from May to September the oysters from station 3, the Chalk Point Discharge site, added copper and silver most rap-



idly, with station 4 oysters nearly equivalent. Finally, both copper and silver burdens declined in spring, from March to May. Interestingly, this view of the data shows that, copper and, in most months, silver body-burdens at any given sampling are highest at station 3, the Chalk Point discharge site. This suggests that the plant may remain a significant source of copper to the oysters in the Patuxent River after the switch from Cu-Ni to Ti alloy condenser tubes. If a combination of lower salinities, reduced growth rates, and an upstream source were responsible for higher metal accumulation, we would expect the station 4 oysters to have the highest body burdens. However, as we have previously noted we did not see analytical evidence of higher concentrations of copper at station 3.

The maximum copper concentrations attained by the oysters near CPSES in this study ( $500 \mu\text{g g}^{-1}$  at station 3) are similar to values reported during the period when the plant used Cu-Ni condenser tubes. Roosenburg (1969) reported 1,200–1,300  $\mu\text{g g}^{-1}$  Cu on a dry weight basis in oysters from the discharge canal but only 500–800  $\mu\text{g g}^{-1}$  in the river nearby, close to our station 3. Abbe and Sanders (1986) found concentrations near the same site of up to about  $500 \mu\text{g g}^{-1}$  in 1982. Oysters in the vicinity of the plant, but not in the discharge canal, did not appear to respond to the removal of the Cu-Ni condenser tubes with a substantial reduction in copper concentrations.

#### INTERSPECIFIC DIFFERENCES

Clearly, interspecific differences between organisms play an important role in metal accumulation. The mussel *I. recurvum*, while exposed to the same water and phytoplankton community and possibly feeding on the same food as the oysters, showed much lower concentrations and little consistent variation in the concentration of either silver or copper, either spatially or temporally. Worldwide, a variety of mussel and oyster species are used for environmental monitoring (e.g., *Mytilus edulis*, *M. californianus*, *M. galloprovincialis*, *Crassostrea gigas*, and *Saccostrea cucullata*; Davies and Pirie 1978; Eganhouse and Young 1978; Goldberg et al. 1983; Johnson and Lack 1985; Lutten et al. 1986; National Oceanic and Atmospheric Administration 1987; Roper et al. 1991; Berthet et al. 1992; Peerzada and Kozlick 1992). A similar large difference in copper, silver, and zinc accumulation between *C. virginica* and the mussel *Mytilus edulis* at several common sites in Long Island Sound in the long-term "mussel watch" program (O'Connor 1994) further suggests that the difference between oysters and mussels in our study may not be due to a particular property of the mussel *I. recurvum*.

Berthet et al. (1992) suggested that different

groups of bivalves handle toxic trace elements by different strategies. Studies have shown that oysters and scallops sequester large quantities of metals in their amoebocytes in metal sulfide granules (Ruddell 1971; Ruddell and Rains 1975; Lytton et al. 1985; Amiard-Triquet et al. 1991; Berthet et al. 1992). In clams and mussels, which do not store large quantities of metals in their amoebocytes, bioaccumulation must be regulated by another, unknown process. If this is true, much biomonitoring data using oysters as bioaccumulation monitors may need to be reexamined. While the bioaccumulation by oysters is real, and thus important for its own impact, under some conditions, particularly low salinities, uptake by oysters may not reflect trace-metal loadings and biological accumulation of other species.

A combination of factors appear to be controlling trace-metal concentrations in oysters to produce large concentrations (in the absence of unusual loadings) in the oyster populations in the upper end of the Patuxent River estuary. First, lower salinity makes cationic trace elements such as copper and silver more available to uptake. It probably also alters the storage of metals in oyster (but not mussel) tissue in a way that increases the accumulation at a constant exposure (Zamuda and Sunda 1982; Amiard-Triquet et al. 1991; Berthet et al. 1992). Second, extremely low salinity values reduce oyster growth rates at the fresher sites, resulting in greater uptake per unit biomass and, thus, in even higher concentrations. Third, a seasonal effect on metal concentrations in oysters adds an annual pattern of variation that can conceal the effects of salinity at a single site.

#### SUMMARY

Based on these observations, it seems likely that metal loads from the Cu-Ni condensers of units 1 and 2 of CPSES may have been responsible for only a fraction of the accumulation of copper by oysters in the upper portion of the Patuxent River. Several other sources, including atmospheric deposition, waste-water treatment plants, and anti-fouling paint, may each introduce as much or more copper to the Patuxent River. The current and past metal concentrations in oysters are probably a combination of continued loadings from other sources, reduced growth rates in upstream stations, and an exaggerated accumulation by oysters caused by the low-salinity regime.

In contrast to the oyster, the hooked mussel, *I. recurvum*, maintains nearly constant trace-element concentrations throughout this region of the estuary. The discrepancy between metal accumulation of these two organisms, in a common environment and with a common food source, suggests

that the mechanisms of metal accumulation and regulation of these two bivalves deserve further study considering both the variations in loading and environmental conditions (particularly salinity and temperature) the organisms experience.

#### ACKNOWLEDGMENTS

We thank the following people for their assistance with this project: Bill Yates and Tim Thoman for platform construction and sampling, and Deborah Connell, Lorraine Curran, Lori Cole, Doug Talaber, and Linda Smith for laboratory and analytical work. The study was supported by the Patuxent River Endowment and the Academy of Natural Sciences. We also appreciate comments and suggestions from Guri Roesjadi, Dave Wright, Ken Paynter, and two anonymous reviewers.

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Received for consideration, September 9, 1994  
accepted for publication, February 21, 1995