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Temporal and Spatial Variations of Trace Metal Concentrations in Oysters from the Patuxent River, Maryland

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ABSTRACT: Concentrations of copper (Cu), silver (Ag), and cadmium (Cd) in eastern oysters (*Crassostrea virginica*) from the upper Patuxent River estuary analyzed since 1986 (Cd since 1991) were high relative to concentrations in other sites in the United States analyzed by the National Oceanic and Atmospheric Administration National Status and Trends program. Patuxent River oysters had above average concentrations of Ag and Cu, and unusually high concentrations of Cd. Metal concentrations were highest in summer, a period in which oyster meat condition index was relatively low. Copper values were highest in 1986–1987, likely elevated by erosion from Cu-Ni alloy condensers at a local power plant. Silver and Cd values exhibited more year-to-year variation. A number of factors were examined as candidates to explain the interannual differences, including river flow, salinity, and oyster condition, but none was able to explain the high and low years. Samples collected in spring and late summer of 1996 at a number of oyster bars located along the length of the Patuxent River showed that concentrations of all three metals increased with distance up-river. For Cd, the upstream increase was linear with distance, while for Ag and Cu, there was a secondary maximum near river km 16. A close correlation was observed between Ag and Cu for individuals at each site, with a poorer correlation between Cd and either Ag or Cu.

Introduction

High concentrations of trace elements, particularly copper (Cu), cadmium (Cd), and silver (Ag) are currently present in eastern oysters (*Crassostrea virginica*) in the upper Patuxent River estuary, Maryland, in the vicinity of the Chalk Point Steam Electric Station (CPSES). In the past, this power plant has been the focus of a number of studies that suggested high concentrations of Cu in oysters in the vicinity of the plant were due to Cu released from the plant by corrosion of Cu-Ni alloy condenser tubes (Roosenburg 1969; Abbe and Sanders 1986; Sanders et al. 1991; Wright and Zamuda 1991). For example, in 1982, oysters transplanted to the discharge canal of the plant accumulated Cu concentrations of approximately 1500 $\mu g\ g^{-1}$, whereas oysters transplanted to the Patuxent River near the plant intake and discharge accumulated approximately 300–400 $\mu g\ g^{-1}$ (Abbe and Sanders 1986). After the Cu-Ni condenser tubes were replaced by titanium alloy tubes (a process requiring 2 yr and completed in 1987), it was tacitly assumed the "problem" with elevated Cu levels in oysters in the upper Patuxent River was solved. However, Riedel et al. (1995) showed there was only a slight decline in Cu concentrations in oysters on a nearby bar after the condenser materials were changed.

Our objectives in this study were to determine the seasonal and interannual changes in Ag, Cu, and Cd concentrations in the Patuxent River oyster population, and examine how metal concentrations varied spatially along the length of the Patuxent River. Temporal changes were addressed by carrying out a long-term (11 yr) collection of oysters at one bar located near the top of the Patuxent River estuary at a site where high metal levels have been observed for more than 20 yr. The second objective was addressed by carrying out two samplings of oysters along the length of the Patuxent River estuary, in spring and summer of 1996.

Methods

SAMPLING SITE

The Patuxent River is the largest river contained completely within Maryland, and the seventh largest river entering Chesapeake Bay, with a drainage area of 2393 km^2. Located between Washington, D.C., and Baltimore, Maryland, the watershed is relatively heavily populated (490,000 in 1990; mean population density 205 km^{-2}, compared to the nearby Potomac River basin's 109 km^{-2}), with approximately 38% of the area in urban development (Hannawald 1990; Olsenholler 1991). The

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estuarine portion of the Patuxent River (Fig. 1) is generally shallow (mean depth ≅ 5 m), covers an area of approximately 111 km^2, and has a volume of 597 × 10^6 m^3. Given the average freshwater flow of 646 × 10^6 m^3 yr^{-1}, this yields a freshwater fill time of approximately 1 yr, but due to temporal variations in inputs and mixing, the residence time of fresh water in the estuary varies from 30 d to 100 d (Hagy 1996). The lower estuary exhibits salinity-driven, two-layer flow, and undergoes seasonal anoxia in some of the deepest sites. The watershed adjacent to the estuarine portion of the river is largely farmland or forest and lightly populated but is currently undergoing rapid population growth.

SAMPLING

Ten oysters between 70 mm and 90 mm shell length were collected approximately monthly from Holland Point bar (Fig. 1) in the Patuxent River, starting in February 1986, using an oyster dredge. Oysters were brought to the laboratory, scrubbed to remove sediment and external fouling, and placed overnight in filtered river water to allow them to empty their guts. They were then scrubbed again, rinsed with deionized water, measured, and weighed. The oysters were shucked with a stainless-steel oyster knife, and the tissues were blotted, placed in preweighed Pyrex beakers, and the wet weight determined. The tissues were dried to constant weight at 70°C, and the tissue dry weight was determined. The oyster shells were also dried and weighed so that the meat condition index (MCI, a measurement of the dry weight compared to the cavity volume) could be determined using the formula of Lawrence and Scott (1982):

$$\mathrm{CI} = \text{Dry Soft Tissue Weight (g)} \times 100 \div [\text{Whole Weight (g)} - \text{Shell Weight (g)}]$$

In May and September 1996, similar samples were collected from a number of oyster bars located along the length of the Patuxent River, and two bars in the Chesapeake Bay outside of the Patuxent River (Fig. 1). These samples were processed in the same manner as the monthly samples from Holland Point.

ANALYSIS

Oyster tissues were dry ashed overnight at 550°C prior to digestion for analysis by atomic absorption spectrometry by (Van Loon 1985). The residue was dissolved in 15–20 ml of 1%/1% HNO_3/HCl. Two process blanks and samples of Standard Reference Materials (SRMs) were prepared in beakers, and carried through the digestion process with each group of 20–24 samples digested. Different SRMs were used at different times during the study depending on their availability, but for most of the study, NBS 1566 or NIST 1566a oyster tissue was used. Typical results for the analysis of the SRM are shown in Table 1.

Samples were analyzed by flame or graphite furnace atomic absorption spectrometry (FAAS or GFAAS). All Cu and Cd analyses were carried out by FAAS; Ag was analyzed by GFAAS through 1990 and by FAAS subsequently.

Results

Monthly means of metal concentrations in oysters from Holland Point, since 1986 for Cu and Ag and since 1991 for Cd, are shown in Fig. 2. Overall mean concentrations were 215 ± 71 $\mu g\ g^{-1}$ Cu, 3.7 ± 1.5 $\mu g\ g^{-1}$ Ag, and 24.1 ± 5.8 $\mu g\ g^{-1}$ Cd. There was considerable variability between individual oysters and between dates, however. Overall monthly means have been compiled in Fig. 3 and overall annual means in Fig. 4. Meat condition index has also been plotted on a monthly basis from 1986 though 1996 (Fig. 5), and on an overall monthly average basis (Fig. 5).

Interannual and intermonthly variability was examined using two-factor ANOVA, with collection month and year as classification variables. Bonferroni multiple comparisons (Neter and Wasserman 1974) were used to compare means for individual years and months (Table 2). There was significant ($p \le 0.05$) interannual variability for all three elements and for condition index. For Cu, the two highest years were 1986 and 1987, when CPSES still had Cu-Ni condensers, as had been observed previously (Riedel et al. 1995); 1993–1995 were the lowest years. For Ag, 1996 and 1992 were the highest years, and 1993–1995 were again the lowest years. Cd was similar to Ag, in that 1992 and 1996 were the two highest years; 1994, 1995, and 1991 were the lowest. Condition index was highest in 1986, 1990, 1994, and 1995, with notably low years occurring in 1987–1988 and 1992.

There was significant monthly variation for Cu, Cd, and condition index but not for Ag. The highest values of all metals occurred in the summer-fall period, beginning in June and ending in October. Average monthly condition index values decreased in summer, beginning in July, but recovered by November (Fig. 5). In the long-term dataset from Holland Point bar, weak, but highly significant, negative correlations existed between monthly mean condition index and the various trace element concentrations (Fig. 6). These relationships reflect the fact that concentrations of each of the metals peaked in late summer and fall, while the condition index was lowest during that period. It is tempting to speculate that when tissue mass was lost in summer to spawning, resulting in a lower

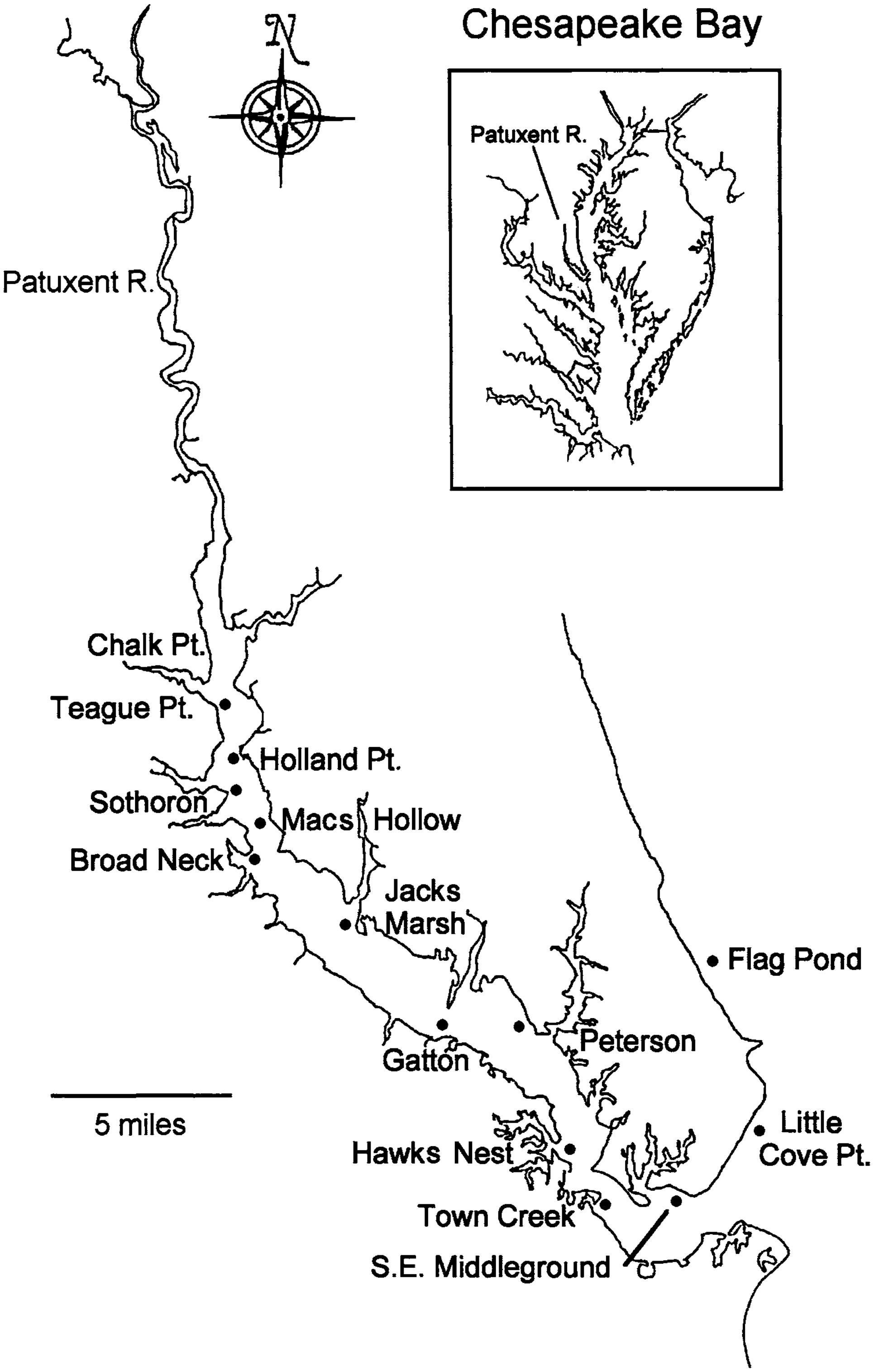

Fig. 1. Map of the Patuxent River (and Chesapeake Bay) showing sites where oysters were collected.

TABLE 1. Representative values (mean ± 1 SD) for Standard Reference Materials analyzed in conjunction with oyster samples.

Standard Reference Material	Ag ($\mu g\ g^{-1}$)	Cd ($\mu g\ g^{-1}$)	Cu ($\mu g\ g^{-1}$)
NIST 1566a (certified)	1.68 ± 0.15	4.15 ± 0.15	66.3 ± 4.3
NIST 1566a (found)	1.52 ± 0.24	4.35 ± 0.45	64.6 ± 3.2

meat condition index, accumulated metals remained behind, causing a temporary increase in metal concentrations until tissue mass was restored in late fall.

SPATIAL DISTRIBUTION OF TRACE ELEMENTS IN PATUXENT RIVER OYSTERS

The distribution of trace elements in oysters collected from natural bars along the length of the Patuxent River was a function of distance from Chesapeake Bay (Fig. 7). Cadmium in oysters increased essentially linearly with distance up the river, with slightly higher concentrations observed in the upriver sites in September than in May. For Cu and Ag, the pattern with distance from the mouth is not as clear as that for Cd. Both elements generally increased upstream, but both elements exhibited a secondary maximum at about river km 16 (Fig. 7), particularly during the September sampling. These results are quite similar to a 1987 transect (Sanders et al. 1991), suggesting that the spatial patterns for these elements have remained similar over the last decade.

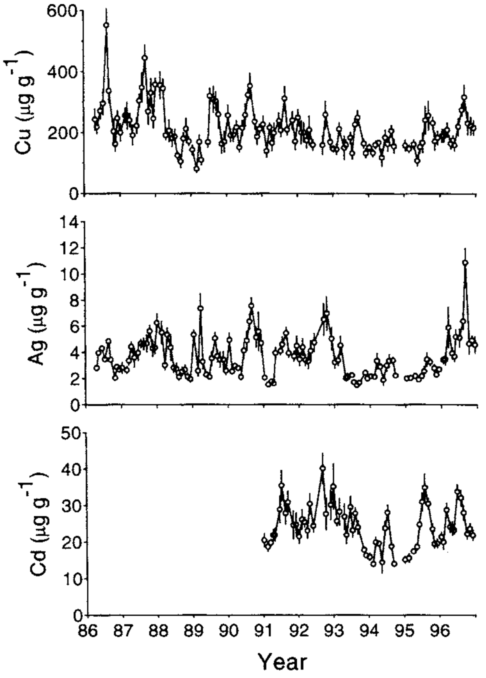

Fig. 2. Mean (±1 SE) concentrations of Cu, Ag, and Cd ($\mu g\ g^{-1}$ dry weight) in oyster samples collected monthly at Holland Point bar from 1986 to 1996.

INTERCORRELATIONS OF TRACE ELEMENTS

It is apparent from Fig. 7 that Ag and Cu correlate to a degree beyond the obvious relationship of both with distance up river. Among individual oysters collected at the same site at the same time, the correlation between Ag and Cu was surprisingly high; in the Patuxent transect dataset, the average correlation coefficient between Ag and Cu was 0.916, whereas the mean correlations between Ag and Cd or Cu and Cd were 0.468 and 0.491 respectively (Table 3). Similar correlations were found in the long-term dataset from Holland Point bar.

Discussion

RELATIVE CONTAMINATION OF PATUXENT RIVER OYSTERS

The question of whether the concentration of an element in an organism is high is a relative one. Different species, even within groups like the bivalves, may accumulate very different concentrations when exposed to the same environment (Riedel et al. 1995). Therefore, to determine whether

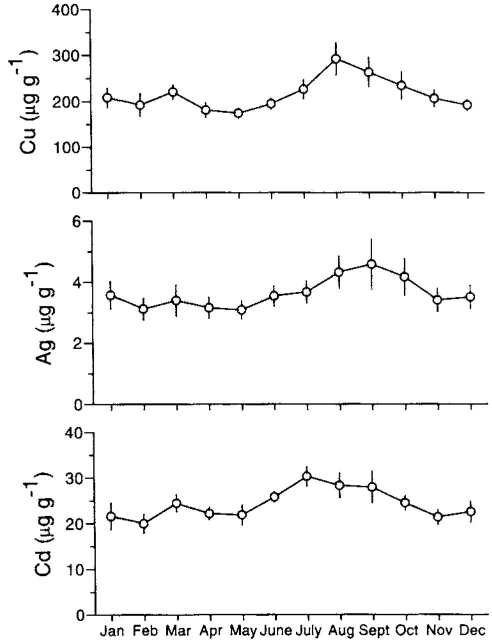

Fig. 3. Overall monthly mean (±1 SE) concentrations of Cu, Ag, and Cd ($\mu g\ g^{-1}$ dry weight) in oyster samples collected at Holland Point bar from 1986 to 1996.

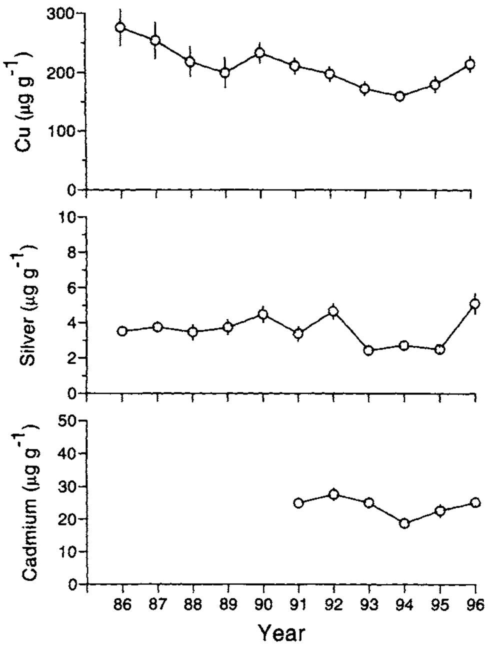

Fig. 4. Overall annual mean (±1 SE) concentrations of Cu, Ag, and Cd (µg g^{-1} dry weight) in oyster samples collected at Holland Point bar from 1986 to 1996.

concentrations are above normal requires a comparison to a reasonable cross section of the population. Fortunately, the National Oceanic and Atmospheric Administration (NOAA) National Status and Trends "Mussel Watch" program has been analyzing trace elements in various organisms, including the eastern oyster, from a large number of sites from the East and Gulf coasts of the United States since 1983. To demonstrate whether oysters from the upper Patuxent River have unusually high trace metal concentrations, we have plotted the "Mussel Watch" *C. virginica* data from 1986 to 1993 (O'Connor 1994) as a relative frequency diagram (Fig. 8), along with the monthly means from Holland Point (individual values from the "Mussel Watch" data are composites of 10 or more oysters).

The results of this comparison clearly show that mean Cu concentrations in Holland Point oysters (215 ± 71 µg g^{-1}) were higher than in "Mussel Watch" oysters (164 ± 163 µg g^{-1}), but that the two distributions overlap considerably. The same pattern was generally true for Ag (Holland Point mean = 3.4 ± 1.7 µg g^{-1} compared to 2.1 ± 1.5 µg g^{-1} for the "Mussel Watch"). However, for Cd, the two distributions barely overlap (Holland Point mean = 24.1 ± 5.8 µg g^{-1} compared to 4.0 ± 2.9 µg g^{-1} for the "Mussel Watch"), leading to the conclusion that Cd concentrations in oysters from this area are unusually high.

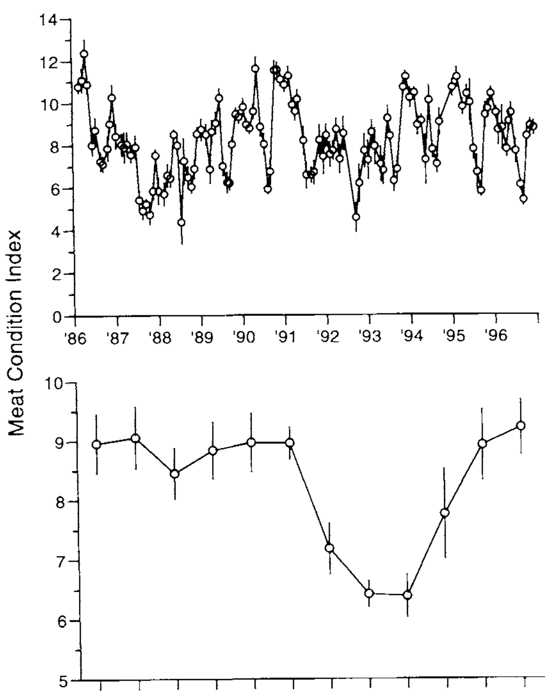

Fig. 5. Meat condition index for oysters collected from Holland Point bar, 1986–1996. Top: Monthly means (±1 SE) through time. Bottom: Overall monthly means.

SPATIAL DISTRIBUTION OF METALS IN OYSTERS, AND THE SOURCES OF METALS TO OYSTERS

There are two obvious factors which contribute to the increase of trace element concentrations in oysters with distance up river. The first is that concentrations of the trace elements are generally higher in the fresh water entering the head of the Patuxent River estuary than in the Chesapeake Bay water that enters from the south. In 1995 and 1996, Riedel et al. (unpublished data) carried out a series of quarterly measurements of dissolved trace elements throughout the Patuxent River watershed, with six sites in the fresh water region and nine sites in the estuarine region. Copper averaged 1.14 ± 0.24 µg l^{-1} (18 ± 4 nM) in the tidal fresh water, and 0.74 ± 0.23 µg l^{-1} (12 ± 4 nM) at the mouth of the river. Average Cd concentration in the tidal fresh water was 0.045 ± 0.030 µg l^{-1} (0.40 ± 0.27 nM), and 0.017 ± 0.005 µg l^{-1} (0.15 ± 0.04 nM) at the river mouth. However, a local maximum in average Cd concentrations [0.079 ± 0.028 µg l^{-1} (0.70 ± 0.25 nM)] occurred near the head of the estuary, near the CPSES, and just above the upper range of oysters in the Patuxent River. This is also near the location of the region where fresh and salt water begin to mix; thus the maximum may result from the desorption of Cd from particles as salinity increases. Dissolved Ag concentra-

TABLE 2. Results of the two-way Analysis of Variance on the Holland Point Bar oyster data using month and year. All pair-wise comparisons between months and years were tested for significance using Bonferroni multiple comparisons. Months and years were ranked from high to low, and bars drawn under groups not significantly different from one another.

	Ag	Cu	Cd
Years	96 92 90 87 89 86 88 91 94 95 93	86 87 90 88 96 91 89 92 95 93 94	92 96 93 91 95 94
Months	8 9 10 3 1 7 12 11 6 2 4 5	8 9 10 7 3 1 11 6 2 12 4 5	7 8 9 6 10 3 12 4 5 1 11 2

tions were not measurable in the estuary (below the lower limit of detection of 0.002 μg l^{-1} (0.02 nM).

However, for both Cu and Cd, the annual delivery of the metals to the top of the estuary is not constant through time. The concentrations of Cu and Cd in the freshwater Patuxent River correlate positively with river flow; hence higher river flows in winter and spring lead to higher volumes of fresh water, with higher metal concentrations being delivered to the top of the estuary. With temperatures rising and oysters starting to feed, this is an optimal situation for the accumulation of the metals by oysters.

The apparent local maximum in Ag and Cu in oysters near river km 16 correlates spatially with a small community on the river (Broomes Island) which has a number of marinas where boats painted with Cu-based antifouling paint are moored during the summer. It is not, however, immediately evident why this area should be contaminated with Ag. Silver has been strongly associated with sewage (Sañudo-Wilhelmy and Flegal 1992), primarily due to its use in photography. This region is not connected to a municipal sewage plant, but uses septic tank disposal, and thus it is unlikely that sewage is the source for this peak. However, the whole Patuxent River is heavily influenced by municipal

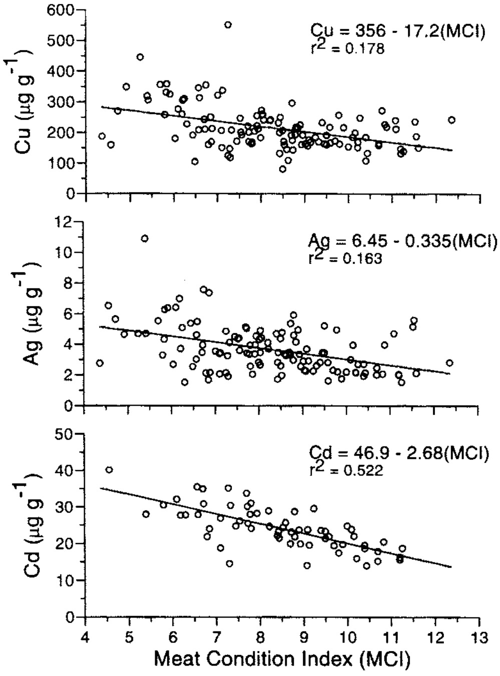

Fig. 6. Average monthly meat condition index in the long-term dataset from Holland Point bar plotted against the metal concentrations.

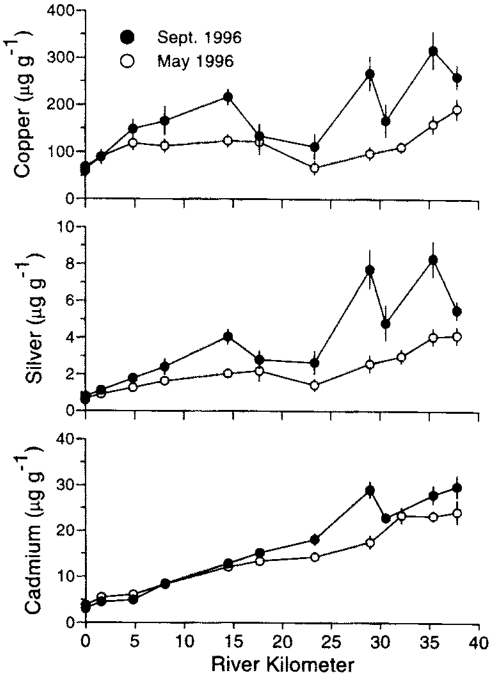

Fig. 7. Mean (±1 SE) concentrations of Cu, Ag, and Cd (μg g^{-1} dry weight) of oyster samples collected from various natural oyster bars in the Patuxent River in May and September 1996.

TABLE 3. Correlation of Ag, Cd, Cu, and meat condition index (MCI) among oysters collected from 13 oyster bars in and outside of the Patuxent River.

	Ag-Cu r	Ag-Cd r	Cu-Cd r	Ag-MCI r	Cu-MCI r	Cd-MCI r
Mean of sites—Spring	0.916	0.457	0.491	−0.285	−0.265	−0.399
SD	±0.089	±0.253	±0.254	±0.388	±0.397	±0.308
Mean of sites—Fall	0.929	0.111	0.071	−0.078	0.016	−0.559
SD	±0.050	±0.324	±0.362	±0.312	±0.288	±0.358
Spring data combined	0.867	0.759	0.524	0.186	−0.025	0.285
Fall data combined	0.913	0.726	0.568	−0.193	−0.284	−0.167
All data combined	0.912	0.718	0.548	−0.209	−0.258	−0.059

sewage; nine large sewage systems enter the freshwater portion of the Patuxent River. During low flow periods approximately half the river flow can be accounted for as wastewater treatment plant outflow. Thus it seems likely that sewage may contribute to the elevated levels of Ag in oysters at the top of the estuary.

A second factor contributing to the rise in oyster metal concentrations up river is the salinity gradient. Oysters take up Ag, Cd, and Cu from solution more rapidly at lower salinities (Engel et al. 1981; Wright and Zamuda 1987; Abbe and Sanders 1990; Amiard-Triquet et al. 1991). To some extent this simply reflects a decrease in thermodynamic activity of the free ion due to the increase of ionic strength and complexation by seawater ions. However, at least in the case of Cu, the increase in uptake with decreasing salinity is greater than can be accounted for by thermodynamic factors alone (Wright and Zamuda 1987).

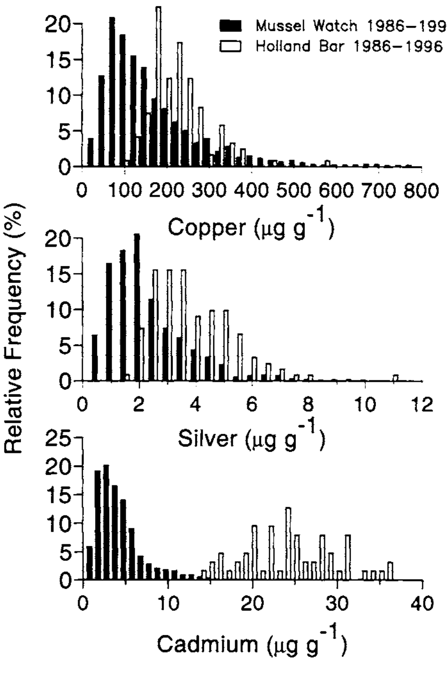

Fig. 8. Relative frequency distributions for monthly mean concentrations of Cu, Ag, and Cd (μg g^{-1} dry weight) in oysters collected at Holland Point bar (1986–1996) compared to samples of oysters collected nationwide by the National Oceanic and Atmospheric Administration (NOAA) National Status and Trends program, 1986–1993. National Status and Trends data obtained from the NOAA/ORCA web site (http://www-orca.nos.noaa.gov).

Another potential source of variation in the metal concentrations of oysters is from diet. Modeling of accumulation of an number of metals by *C. virginica* and *Mytilus edulis* from both water and suspended particles suggests that for the majority of these elements, including Cd and Cu, food is the predominant pathway (Thomann et al. 1995). Similar modeling of Ag uptake by mussels (*M. edulis*) in laboratory and field conditions has produced a range of results. Fisher et al. (1996) suggested that Ag has a relatively low absorption efficiency from food (2–4% in the field and 12–19% when fed labeled phytoplankton), and that uptake from water is probably more important. Later results reported assimilation efficiencies of Ag from natural seston of 5–18% (Wang et al. 1996). Recent studies (Reinfelder et al. 1997) suggest assimilation efficiencies of oysters fed labeled algae (44% for Ag and 69% for Cd) are substantially higher than those of *M. edulis* (13% for Ag and 37% for Cd). Thus, diet may be the predominant source of both elements for oysters.

In the Patuxent, Ag, Cd, and Cu in sediment all show significant upward trends from the mouth to the top of the estuary (Riedel et al. 1995; Eskin et al. 1996), with Cd showing the greatest increase. Similar trends have been observed for metal concentrations of suspended particles in the Patuxent (Riedel unpublished data). While not directly addressing whether food or water is the major source of metals to filter-feeding bivalves in the Patuxent River estuary, this does demonstrate that from either source, concentrations are higher near the top of the estuary, suggesting those metals are entering the estuary from upstream. Until good mathematical models of the uptake and loss of metal by oysters are available, studies with natural populations will be correlative and not quantitative, and often multiple factors will have strong correlations.

CORRELATIONS OF TRACE ELEMENTS AND MCI

The fact that Cu and Ag correlate so highly among individual oysters strongly suggests variations in individual concentrations are not random, but that they are the result of some physiological variability among the oysters in response to metal loadings, the result of "micro" environmental differences between the habitats for oysters, or simply the effect of some other physiological variable on metal concentrations. One factor possibly accounting for the degree of correlation between Ag and Cu is that they share a similar storage mechanism in the oyster. Both Ag and Cu are predominantly stored in sulfide granules within the amoebocytes and basement membranes of the digestive tubules (Ruddell 1971; Ruddell and Rains 1975; Lytton et al. 1985; Berthet et al. 1992). Copper and Ag-sulfide granules are eliminated from the oyster by extrusion of the metal-bearing amoebocytes through the gills (Berthet et al. 1992). In contrast, a substantial fraction of Cd (about 20%) is stored in metallothionein in the gill tissue, while much of the remainder is found in the cytosol (Roesijadi 1994). Metallothioneins are long-term storage/detoxification proteins, from which very little Cd is lost through time. Perhaps other, unknown physiological differences between oysters at a given site that impact storage of Ag and Cu will also tend to influence both metals, but not Cd, similarly.

A large degree of variation among individual oysters has been observed before (e.g., Phelps et al. 1985). However, in most cases where oysters (and indeed most aquatic organisms) are analyzed, several oysters from a site are pooled for analysis. While this is the most economical method of reducing the potential error due to individual variability, it bypasses an important element of the variation. Comparing sites using composited or overall mean data could give very different information than from data derived from individual oysters. For example, in the spring transect, Cd for each individual site generally has a negative correlation with MCI, implying that oysters in poorer physiological condition tend to have higher Cd concentrations (mean r = −0.399 ± 0.308). When considered over all sites in spring, however, there is a weak positive association between Cd and MCI (Fig. 9). This resulted from the oysters in the upper end of the estuary having had both higher Cd concentrations and MCI than the oysters near the river mouth. Thus, an analysis of the influence of physiological condition on Cd concentrations (or vice versa) based on composite samples would suggest that oysters in good physiological condition would have higher Cd concentrations. In the fall sampling, the within site variation gave similar negative results (mean r = −0.559 ± 0.358), but the overall relationship was also weakly negative (r = −0.284), largely because physiological condition of the oysters in the upper end of the estuary was generally lower than oysters at the lower end. Two-factor ANOVA (Neter and Wasserman 1974) using Site and MCI, showed that MCI was a significant factor in the concentration of all three metal levels in the oysters from both spring and fall transects ($p < 0.05$ in all cases).

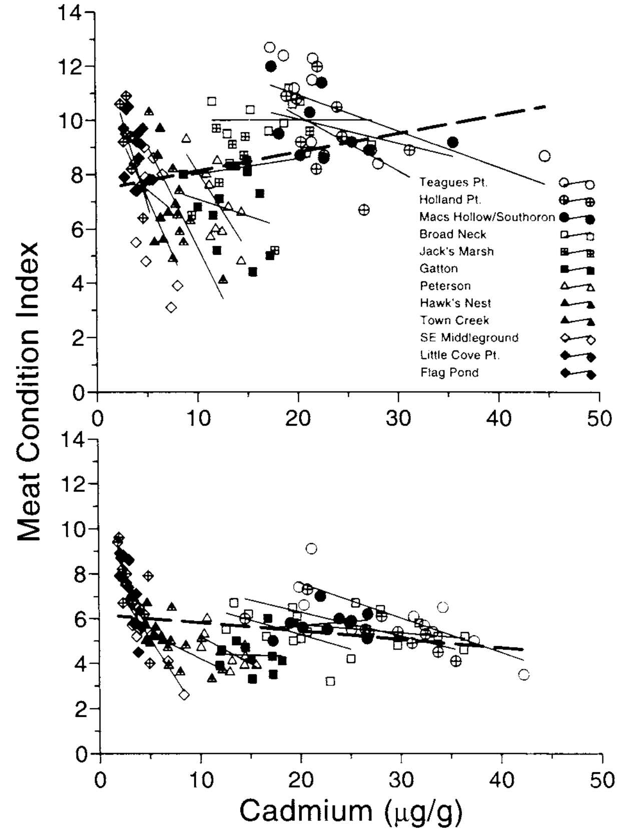

Fig. 9. Meat condition index (MCI) versus Cd concentration for individual oysters from 12 sites in the Patuxent River and Chesapeake Bay. Light solid lines show the regression of Cd versus MCI within a given site, heavy dashed line shows regression for all data combined. Top: Samples collected in May 1996. Bottom: Samples collected in September 1996.

TEMPORAL CHANGES IN METAL CONCENTRATIONS IN OYSTERS

Both Cu and Cd have a significant annual cycle of metal concentration, with higher concentrations in the late summer and fall. Silver shows a similar trend, but the variation is not statistically significant. The rise in metal content of the oysters corresponds to the decrease in oyster meat condition, which is caused by loss of tissue due to spawning (Haven 1962; Galtsoff 1964; Abbe and Sanders 1988), disease (Ray et al. 1953; Burreson 1991; Ditman 1993), poor environmental conditions (Beaven 1946; Galtsoff 1964), or fouling organisms (Lunz 1941; Engle and Chapman 1953). Two diseases, MSX and Dermo, have devastated Chesapeake Bay oyster populations in recent years (Abbe 1992; Smith and Jordan 1993). In particular, large mortalities occurred in 1986–1988 and 1992, years when condition index was declining or unusually low (Fig. 5). High values of meat condition index are due to the storage of large quantities of glycogen in the oyster (Shumway 1996), which are lost during periods of stress such as high temperatures, low salinity, disease, and during spawning. We hypothesize that loss of glycogen due to stress and spawning are not necessarily accompanied by loss of proportional amounts of metal, causing an increase in metal concentrations during these periods.

The interannual variation of Cu can be largely ascribed to the change in the operation of the Chalk Point Steam Electric Station, which replaced Cu-Ni condensers with Ti alloy condensers in 1986–1987, resulting in the annual average Cu in oysters decreasing from 265 $\mu g\ g^{-1}$ during 1986–1987 to 199 $\mu g\ g^{-1}$ from 1988 to 1996. During 1993–1995, and particularly 1994, all three metal levels in oysters were relatively low (Fig. 4). We have examined a number of possible sources of long period variation for all the elements (Table 4), including annual river flow (a potential indicator of variation in the input of metals into the estuary), mean summer-fall salinities (a potential indicator of variation in the uptake of metals by the oyster), and annual mean condition index (an indicator for a potential source of variation in the physiologic state of the oysters). None of these indexes explained a significant fraction of the interannual variation in metal concentrations in oysters. It seems likely that all these factors likely have some influence, and that determining which of these factors are important at any given time will require a predictive model for trace metal accumulation by oysters, as well as good environmental data for the system.

HUMAN HEALTH CONSEQUENCES OF ELEVATED METAL CONCENTRATIONS IN OYSTERS

In humans, Cd is accumulated primarily in kidney tissue, the target organ of cadmium toxicity, where it has a biological half-life of 14–38 yr. While there is not a strict permissible limit on the concentrations of Cd (or Cu or Ag) in seafood in the United States, there is a method for calculating a "level of concern" (Adams et al. 1993). Using national average shellfish consumption data, a general level of concern of 3.7 μg Cd g^{-1} wet weight, or approximately 18.5 $\mu g\ g^{-1}$ dry weight, was determined. As is evident from Fig. 8, oysters from the upper Patuxent River commonly exceed this value. Using the mean value of Cd in Holland Point bar oysters of 24.1 $\mu g\ g^{-1}$ (dry), a mean tolerable daily oyster intake of 11.2 g wet weight $person^{-1}\ d^{-1}$, or 4.1 kg $person^{-1}\ yr^{-1}$, can be determined. This corresponds to approximately 370 typical market-size oysters annually.

TABLE 4. Top. Annual mean values of Cu, Ag, and Cd, and mean meat condition index (MCI) of Holland Point Bar oysters, annual total Patuxent River flow (data for Patuxent River at Bowie for water year [August 1–July 31] obtained from United States Geological Survey, Towson, Maryland), and mean summer salinity near Holland Bar (June–October for station RET 1.1, 3 m, obtained from Environmental Protection Agency Chesapeake Bay Program, Annapolis, Maryland). Bottom, Correlation coefficients for the correlation between each parameter.

Year	Annual Mean Cu ($\mu g\ g^{-1}$)	Annual Mean Ag ($\mu g\ g^{-1}$)	Annual Mean Cd ($\mu g\ g^{-1}$)	Annual Mean MCI	Annual River Flow ($\times 10^6\ m^3$)	Mean Summer Salinity
1986	276	3.51		9.40	189	13.4
1987	253	3.74		6.78	238	12.3
1988	218	3.46		6.71	309	11.0
1989	200	3.73		8.17	376	7.9
1990	233	4.48		9.37	328	8.7
1991	212	3.38	25.0	8.68	295	11.9
1992	198	4.66	27.7	7.40	199	9.8
1993	173	2.44	25.1	8.22	422	9.7
1994	160	2.71	18.7	8.89	419	8.1
1995	181	2.50	22.7	9.26	221	14.3
1996	215	5.26	25.2	8.22	451	6.6

	Cu r	Ag r	Cd r	MCI r	Flow r	Salinity r
Cu	1.000					
Ag	0.428	1.000				
Cd	0.691	0.574	1.000			
MCI	−0.073	−0.208	−0.757	1.000		
Flow	−0.503	0.018	−0.354	0.047	1.000	
Salinity	0.343	−0.480	0.029	0.077	−0.805	1.000

Until the recent decline in oysters throughout Chesapeake Bay, thought to be due to a combination of habitat loss, overfishing, and the two diseases MSX and Dermo (Abbe 1992; Smith and Jordan 1993; Burreson and Rugone Calvo 1996), the Patuxent River supported a commercial oyster fishery. Even now, a reduced level of fishing for personal consumption and for local restaurants continues. Many area residents consume local shellfish, and it is possible that some could exceed the tolerable average daily intake.

While Cu accumulated in oysters can be toxic to humans (Chang 1962; O'Shaghnessy 1966; Pringle et al. 1968), Cu does not present a long-term bioaccumulation hazard in the same way as Cd. High levels of Cu in oyster tissue cause a characteristic green coloration, and an unpleasant taste (Roosenburg 1969; Han and Hung 1990). Thus, it is unlikely that Cu accumulation in oysters represents a significant human health threat. However, Cu accumulation presents a significant threat to an oyster fishery because it can make the oysters undesirable. Silver in oyster tissue is not known to represent a significant human health threat.

CONSEQUENCES OF ELEVATED METAL CONCENTRATIONS TO OYSTERS

Certainly, oysters are susceptible to acute metal toxicity (Orton 1923; Pringle et al. 1968), but the concentration at which toxicity occurs has been demonstrated to be high compared to what is commonly found in the environment (Engel and Fowler 1979; George et al. 1983; Berthet et al. 1992). For example, Japanese oysters (*Crassostrea gigas*) in southwestern Taiwan exposed to 5–25 $\mu g\ l^{-1}$ Cu developed Cu tissue concentrations of up to 4400 $\mu g\ g^{-1}$ dry weight without apparent ill effect (Han and Hung 1990). Clearly, the storage and depuration mechanisms are responsible for ameliorating the toxicity of the metals. However, very little is known about the ecotoxicological consequences of the accumulations of metals by oysters.

SUMMARY

Unusually high concentrations of Ag, Cd, and Cu were found in oysters collected monthly from 1986 to 1996 from a natural oyster bar in the upper Patuxent River estuary. In 1996, oysters collected from natural oyster bars located along the length of the river showed that concentrations of these elements increased up river, almost linearly in the case of Cd. The increase for Ag and Cu was nonlinear and both had a secondary maximum approximately 16 km from the mouth of the river.

Concentrations of all three elements were generally elevated compared to levels typical of oysters collected on the East and Gulf coasts. For Ag and Cu, the concentrations were in the high range of values reported for oysters in the United States by the NOAA National Status and Trends program, and for Cd, the values found were almost exclusively higher than those found elsewhere. Cadmium levels are sufficiently high that public health concerns may be warranted.

Although a general correlation between all three metals existed, in part due to the increase in all metals up river, a particularly tight correlation existed between Ag and Cu. This extended to correlations among individual oysters collected at the same site and time, suggesting that similar processes were controlling the concentrations of these metals. We suggest that Ag and Cu share a similar storage and depuration mechanism: production and ejection of sulfide granules, which may lead to their being closely coupled. In contrast, Cd is stored primarily in metallothionein.

For Ag and Cd there were significant differences between collection years, with 1993, 1994, and 1995 having lower mean concentrations than 1992 and 1996. There were also significant monthly differences for Cd and Cu, with higher values occurring in the late summer-fall period, a time when oyster tissue condition was low.

Sources of the metals to the oysters are not presently clear, but both dissolved and suspended metals are elevated in the upper end of the estuary. Prior to 1988, a power plant with Cu-Ni condensers contributed significant Cu to the oysters in the area. A decrease in Cu in oysters was observed after Cu-Ni condensers were replaced by Ti alloy condensers. For Cd, the highest concentrations were found just down river from a maximum of dissolved Cd in the upper estuary. These high dissolved concentrations may have resulted from desorption from suspended particles at the fresh water-brackish water interface, and relatively high concentrations of dissolved Cd are observed in the fresh waters of the Patuxent River during high flow periods. Urban runoff or waste water treatment plants from the freshwater region may be responsible for elevated trace elements in the upper Patuxent River estuary.

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