

Temporal and Spatial Patterns of Trace Elements in the Patuxent River: A Whole Watershed Approach

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ABSTRACT: Trace element distributions, partitioning, and speciation were examined at 15 sites in the Patuxent River watershed from May 1995 through October 1997 to determine possible sources of trace elements to the river and estuary, to examine the relationship of the trace element discharges to freshwater discharges as well as to land use and geographic region, to validate previous estimates of loadings to the river, and to provide baseline data for trace elements in the Patuxent River watershed and estuary. Six freshwater sites were examined, representing different basins and geographic provinces, and nine sites along the estuarine salinity gradient. Subregions within the watershed varied considerably in concentrations and areal yields for some elements. Concentrations of As, Cd, Ni, Pb, and Zn were elevated in the Coastal Plain sites compared to the Piedmont sites, while Cu and Hg were more evenly distributed. Cadmium, Cu, Hg, Ni, Pb, and Zn showed overall positive correlations with river flow while As and methylHg (meHg) showed negative correlations with river flow. Concentrations of trace elements in the estuarine portion of the river were generally low, and consistent with mixing between Patuxent River water with elevated concentrations and the lower concentrations of the Chesapeake Bay. Interesting features included a local Cd maximum in the low salinity region of the estuary, probably caused by desorption from suspended sediments, and a significant input of water containing high As concentrations from the Chesapeake Bay and from As being released from bottom sediments in summer. Comparisons between the estimated annual flux of trace elements and the estimates of suspected source terms (atmospheric deposition, urban runoff, and known point sources) suggest that, except for Hg, direct atmospheric deposition is small compared to fluvial loads. Current estimates of trace element inputs from point sources or from urban runoff are inadequate for comparison with other sources, because of inappropriate techniques and/or unacceptably high detection limits. A complete examination of trace element dynamics in the Patuxent River (and in other coastal systems) will require better data for these potential sources.

Introduction

Perceived declines in the health of the Chesapeake Bay ecosystem have led to attempts to define the role that toxic contaminants may play. The fact that there have been few systematic examinations of the concentrations of important contaminants (including trace elements) in the Bay, as well as a lack of evidence for direct effects of individual contaminants has prevented a consensus on the question of whether toxic compounds play a significant role. The importance of trace metals as one class of stressors among many, and the interactions

among these stressors are not understood. The Complexity And Stressors in Estuarine Systems (COASTES) project is being carried out to examine the effects of multiple stressors (nutrients, toxic trace elements, and low dissolved oxygen) and ecosystem complexity, using the Patuxent River as a model ecosystem (Breitburg et al. 1999). The Patuxent River has been used for some time as a model estuary for the study of nutrient enrichment (e.g., D'Elia et al. 1986; Sanders et al. 1987; Boynton et al. 1995). More recently, we have used the Patuxent as a model system in which to study trace metal behavior in estuaries (Riedel 1993; Sanders and Riedel 1993; Benoit et al. 1998). There is at least anecdotal evidence that concentrations of trace elements are high enough to cause some concern. For example, high concentrations of trace elements have been observed in the eastern oyster (*Crassostrea virginica*) from the Patuxent River for almost three decades (e.g., Roosenburg 1969; Riedel et al. 1995, 1998).

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We examined arsenic (As), cadmium (Cd), copper (Cu), mercury (Hg), methylmercury (meHg), nickel (Ni), lead (Pb), and zinc (Zn) in the estuarine and freshwater river from April 1995 through October 1997. The specific objectives of this component of the COASTES study were to estimate trace metal loading rates and determine possible sources to the river and estuary, to relate trace element fluxes to freshwater discharge rates and to relate areal yields of trace metals to land use patterns and geographic region, to describe trace metal behavior in the estuary, especially speciation and partitioning onto solids, and to provide baseline data for trace element exposure and concentration in the Patuxent River watershed and estuary. The fluvial loading data presented here, plus local estimates of atmospheric loading, were used to constrain metal budgets constructed using data from other sources such as point source data from utilities and industry and urban runoff estimates from U.S. Environmental Protection Agency.

Study Area

The Patuxent River drains the relatively heavily populated area between Washington, D.C. and Baltimore, Maryland, emptying through a partially mixed coastal plain sub-estuary into Chesapeake Bay (Fig 1). The drainage area of 2,393 km² (U.S. Environmental Protection Agency 1982) can be divided into three distinct geographic areas, the Piedmont region (foothills of the Appalachian Mountains); the Atlantic Coastal Plain, characterized by geologically recent unconsolidated sediments; and the tidal fresh and brackish estuarine region. Fifteen sites were selected for analysis, six in the freshwater region (one in tidal freshwater), and nine in the estuarine portion of the river. The five non-tidal sites were all located near U.S. Geological Survey gauging stations so that flow records could be obtained. Approximately 50% of the freshwater passes through these gauges. Much of the remainder enters the estuary through small streams along its flanks.

Freshwater sites were chosen on the mainstem of the Patuxent River and on its major tributaries to represent different land use types and geographic provinces. Land use in the Piedmont region is predominantly rural (both forested and agricultural) and light suburban. We sampled three sites in this region, one on the Main Branch above two reservoirs (site 1), one on the Main Branch at the fall line where the river reaches the Coastal Plain and immediately below the outlet of a reservoir (site 2), and a third at the fall line on the Little Patuxent River (site 3). The Coastal Plain of the Patuxent River is its most populated region, lying between the metropolitan regions of Balti-

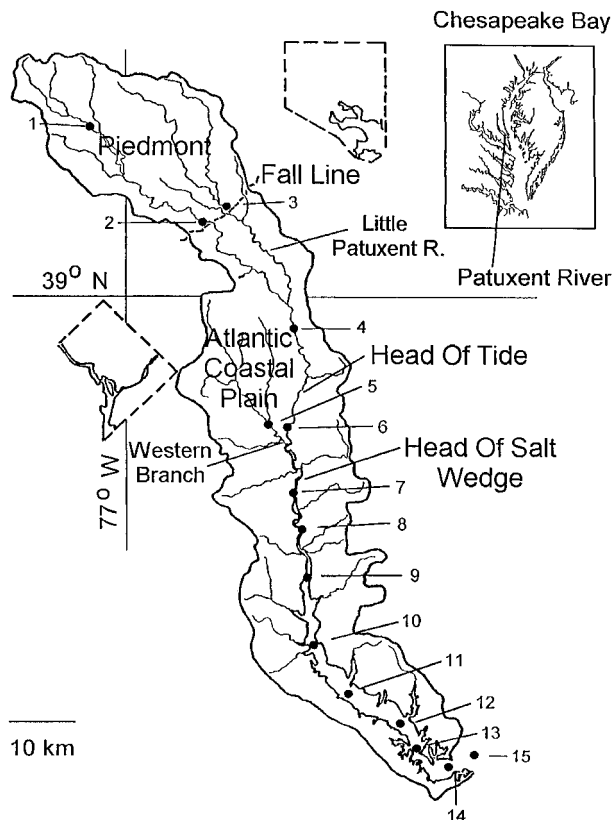


Fig. 1. Map of the Patuxent River watershed, showing the sampling sites, features, and regions referred to in text. Inset shows the location of the Patuxent River on Chesapeake Bay; dashed boxes represent metropolitan areas Washington, D.C. (left) and Baltimore, Maryland (upper).

more, Maryland and Washington, D.C. The Coastal Plain region also had three sampling sites, one located on the main Patuxent River (site 4), another located on the Western Branch of the Patuxent (site 5), and the third in the tidal freshwater near the head of the tide (site 6). In the Coastal Plain region, the Patuxent River receives the discharge from many wastewater treatment plants, including nine major municipal plants. The Western Branch of the Patuxent is the largest tributary in the Coastal Plain, and drains a relatively populated region near Washington, D.C. (Fig 1). Loading estimates to the estuarine Patuxent were based on flow and metal concentrations at stations 4 and 5, both near the head of tide.

The estuarine portion of the Patuxent River has a volume of 597×10^6 m³, and covers an area of approximately 111 km². The average freshwater input is estimated to be 646×10^6 m³ yr⁻¹, and the residence time of freshwater in the estuary varies from about 30 to 110 d (Hagy et al. 2000). The estuary is generally shallow (mean depth approximately 5 m) and exhibits salinity-driven two layer

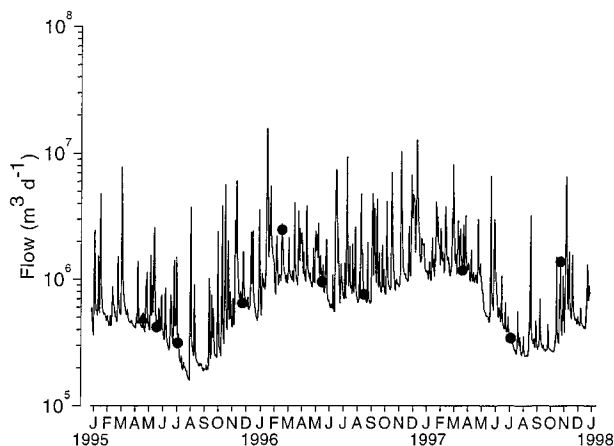


Fig. 2. Flow rate of the Main Branch of the Patuxent River at site 4 from 1995 through 1997. Closed circles mark the actual sampling times and flow rates (U.S. Geological Survey 1998), except for April 26, 1995, which is marked with a closed triangle, when only Hg samples were collected.

flow. Hypoxia and anoxia are often observed in summer at depths below 4–7 m (U.S. Environmental Protection Agency unpublished data).

Materials and Methods

SAMPLING METHODS

The nine estuarine sites were sampled by small boat, while the six freshwater riverine sites were sampled from the bank. Temperature and dissolved oxygen were measured in situ with a YSI model 51 dissolved oxygen meter and salinity was measured at the estuarine sites using a Beckman RS5–3 salinometer.

Trace elements were sampled on ten occasions from April 1995 through October 1997 (Fig. 2). Mercury and meHg were not sampled during the May 1995, May 1996, or October 1997, and Hg and meHg sampling alone was carried out in April 1995. In the estuary, Hg and meHg were sampled at only three sites; mid-estuary, near the turbidity maximum, and in tidal freshwater.

Trace elements were sampled using a 3-m plastic pole with a Teflon line reaching beyond the tip of the pole to reach away from the influence of the boat or the bank. When sampling from the boat, the boat was allowed to drift in the wind, and the pole oriented into the direction the boat was traveling; when sampling from the bank, the sampling tip was oriented upstream. The estuary was sampled from its mouth toward the freshwater end (sites 15 to 7), while the freshwater sites were sampled from the Piedmont down (sites 1 to 6). Filters were well rinsed (over 1 l by the time trace element samples were collected) with water from each new site before samples were taken so that carryover

between sites was minimized. The pumping system consisted of a Masterflex peristaltic pump using acid-washed C-Flex tubing, with acid-washed PFA Teflon line (Gill and Fitzgerald 1987; Flegal et al. 1991; Hurley et al. 1996). Field filtration blanks were taken prior to use of the filters with ambient waters, and duplicate samples were collected during every sampling to evaluate contamination and precision. Samples for Cd, Cu, Pb, Ni, and Zn were collected in acid-washed PFA Teflon bottles and preserved with 0.2% Baker Ultrex grade HCl, samples for Hg were collected in acid washed PFA Teflon bottles and preserved with 0.5% HCl (analyzed to determine best lot for low blanks), while samples for As were collected in acid-washed polyethylene bottles, and quick frozen in a dry ice/isopropanol mixture to preserve As speciation.

From February 1996, suspended particulate samples for most elements were collected at some stations; from August 1996, samples were collected at all the freshwater sites, and four estuarine sites, from the tidal freshwater to the mouth of the river. For suspended particulate metals, 8 l water samples were concentrated to approximately 100 ml using an A/G Technology UFP-500-E400 cross flow filter column (500,000 NMWC), and the particle concentrate filtered onto acid-washed 0.4 μm Nuclepore filters. Cross flow filter columns were cleaned with dilute bleach, 1% HCl, and rinsed with DI water, until the pH of the effluent water was > 5.0 .

ANALYTICAL METHODS

Samples for dissolved Cd, Cu, Pb, Ni, and Zn were pre-concentrated for analysis using APDC/ammonium DDDC chelation-chloroform extraction (Bruland et al. 1979; Nolting and de Jong 1994). Cadmium, Cu, Pb, and Ni were analyzed by graphite furnace atomic absorption spectrometry, while Zn was analyzed by flame atomic absorption spectrometry. These elements were analyzed using a Perkin Elmer 5100 ZL, using the method of standard additions for calibration. Standard Reference Materials (SRM) National Research Council of Canada (NRCC) SLEW-2 for estuarine samples, and NRCC SLRS-2 or SLRS-3 for freshwater samples were concentrated and analyzed along with each group of samples.

The seston samples were wet digested by $\text{HNO}_3/\text{HCl}/\text{HF}/\text{HClO}_4$ in an open Teflon vial (Van Loon 1985), and the resulting digestates were analyzed for As, Cu, Cd, Ni, and Zn by the same techniques cited for dissolved trace elements. A serious analytical interference occurred for the analysis of Pb in the seston, resulting in poor SRM and spike recoveries, so that Pb is not reported. This interference resulted from digestion of the polycarbonate membrane filter; digested sediment samples

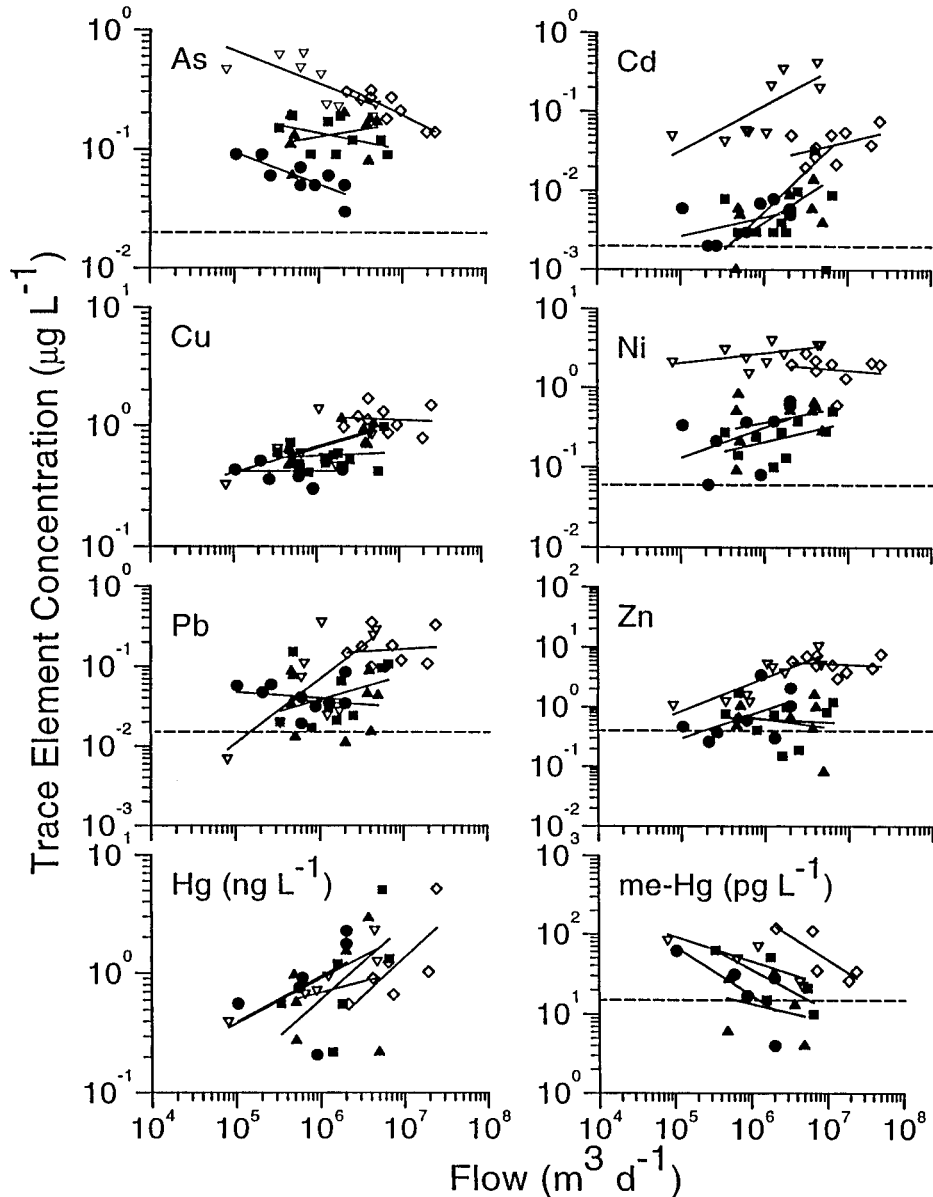


Fig. 3. Scatter/regression plots of concentrations of dissolved trace elements in the five flow monitored freshwater sites versus average flow rate on the date of collection. Site 1 closed circle, site 2 closed triangle, site 3 closed square, site 4 open diamond, site 5 open inverted triangle. Piedmont sites were assigned solid symbols, Coastal Plain sites were assigned open symbols. The lower limit of detection ($3 \times \text{SD}$ of the blanks) is denoted by a dotted line.

without filters showed good SRM and spike recoveries.

Water samples for total Hg and total dissolved Hg were analyzed following the methods of Gill and Fitzgerald (1987) and Bloom and Fitzgerald (1988). Particulate Hg was determined by subtraction from total Hg in filtered and unfiltered samples, and the concentration of suspended matter. Methylmercury was determined by distillation (Horvat et al. 1993a,b), ethylation, trapping and

concentration on Tenax, chromatographic separation, followed by pyrolysis, and detection by cold vapor atomic fluorescence spectroscopy (Bloom 1989). Methylmercury analyses were also carried out on both filtered and unfiltered samples; however, in the majority of cases, the difference between filtered and unfiltered samples was insufficient for an adequate estimation of particulate meHg.

Arsenic was analyzed by hydride generation,

TABLE 1. Results for statistical analysis of trace element concentrations versus daily average stream flow on sampling date. Top, simple correlation coefficient of trace element concentration with stream flow at each site (* $p < 0.05$, ** $p < 0.01$). Bottom, results of two-way ANOVA of site and log transformed stream flow on log transformed trace element concentration, p value for significance of variable in ANOVA. ANOVA run with interaction term, but re-analyzed without the interaction term if $p > 0.25$ for the interaction.

Site	As	Cd	Cu	Hg	meHg	Ni	Pb	Zn
1	-0.76*	0.50	0.12	0.85*	-0.72	0.76*	0.14	0.42
2	-0.41	0.44	0.11	0.30	-0.89*	0.60	0.36	0.12
3	-0.42	0.16	0.42	0.63	-0.47	0.68*	0.44	0.17
4	-0.86**	0.60	0.00	0.78	-0.58	-0.03	0.26	0.10
5	-0.73*	0.72*	0.36	0.84*	-0.76	0.57	0.61	0.80**
Variable				p-value				
Flow	0.000	0.007	0.065	0.002	0.000	0.031	0.012	0.071
Site	0.000	0.060	0.000	0.558	0.000	0.000	0.168	0.196
Flow \times Site	>0.25	0.200	>0.25	>0.25	>0.25	>0.25	0.130	0.154

cryogenic trapping, chromatographic separations, and detection using a hydrogen-burning quartz cuvette (Andreae 1977; Braman et al. 1977; Riedel 1993) in a Perkin Elmer 2380 atomic absorption spectrometer. This method determines arsenate, arsenite, monomethylarsenic (MMA), and dimethylarsenic (DMA).

DATA ANALYSIS

To calculate the flux of trace elements out of watershed areas, the log-log regression between flow and concentration was used to estimate daily concentrations from daily flows (U.S. Geological Survey 1998, unpublished data). Estimated daily concentrations were multiplied by the flow rate at each site to give the daily yield, and the daily yields were summed over the interval January 1, 1995 through December 31, 1997 to estimate the annual yield of each of the five non-tidal watershed sites for each trace element. The annual areal yield ($\text{g km}^{-2} \text{yr}^{-1}$) for each sub-basin was determined from the area of the watersheds (U.S. Geological Survey 1998). To estimate the contribution of suspended trace elements to the estuary, the log-log regressions between seston and flow rate, and the daily flows from 1995 through 1997 were used to estimate daily seston loads, which were summed over each year for 1995 to 1997. Because of the likelihood that some extremely high suspended matter concentrations would accompany certain flood conditions, and because we did not sample bed load, our estimates of particulate inputs and particulate trace metal inputs should be regarded as low estimates. For purposes of calculating regressions with flow, and watershed yields, any values less than the method detection limit were set to one half the detection limit (Clarke 1998).

Results and Discussion

DISSOLVED TRACE ELEMENTS IN THE RIVERINE PATUXENT RIVER

Dissolved trace element concentrations in the riverine portion of the Patuxent River showed clear

differences between the Piedmont sites and the Coastal Plain for several elements, with lower mean concentrations at stations above the fall line. Differences can be seen in Fig. 3 which shows trace element concentrations plotted against river flow, by site. Most striking was Cd, which averaged $0.006 \pm 0.006 \mu\text{g l}^{-1}$ at the three stations above the fall line and $0.081 \pm 0.091 \mu\text{g l}^{-1}$ at the three freshwater stations below the fall line, for a Coastal Plain/Piedmont ratio of approximately 13:1. Arsenic, Cu, Hg, meHg, Ni, Pb, and Zn had Coastal Plain/Piedmont ratios of 2.4, 1.7, 1.2, 2.0, 6.3, 3.3, and 7.9, respectively.

In many cases, stream flow was correlated with the dissolved concentration of trace elements (Table 1, Fig. 3), positively in most cases, but negatively in the case of As and meHg. To determine whether there was a significant overall effect of flow across sites, the concentration data were analyzed by two-way ANOVA (Table 1), using site as a block variable (Neter and Wasserman 1974). Because of the wide variation in values, both concentration and flow data were log transformed to stabilize the variance. Overall, Cd, Cu, Ni, Hg, and Pb yielded significant positive correlations with river flow, while As and meHg yielded significant negative correlations. A positive correlation of dissolved trace elements with flow suggests that the source of the trace element is more available at higher flows; for example, material in near-surface waters and overland flows, or derived from the movements of soil or sediment at high flows. Such sources are generally diffuse non-point sources. A negative correlation would result from a relatively fixed source, such as ground water, or a point source whose output of the element in question is independent of flow (Neal et al. 1996). In some cases (e.g., Cd, Pb, and Zn), there is a non-negligible interaction ($p < 0.25$) between site and flow rate, which suggests that the relationship between flow and concentration varies between different sites. This is evident in several plots. In par-

TABLE 2. Estimated annual yields (SD) of dissolved trace elements in five areas of the Patuxent River drainage. CP:P ratio = Coastal Plain: Piedmont. All elements have units of $\text{g km}^{-2} \text{yr}^{-1}$ except meHg which is $\text{mg km}^{-2} \text{yr}^{-1}$.

Site	Drainage Area (km^2)	As	Cd	Cu	Hg	meHg	Ni	Pb	Zn
1	90	22 (10)	2.8 (2.3)	210 (140)	0.66 (0.61)	7.5 (2.1)	170 (150)	19 (11)	590 (610)
2	342	31 (25)	3.7 (4.3)	220 (210)	0.30 (0.32)	3.4 (2.2)	180 (190)	15 (16)	186 (168)
3	255	53 (23)	1.6 (0.7)	290 (160)	1.1 (1.0)	3.9 (0.3)	150 (100)	42 (34)	300 (160)
4	901	70 (22)	20 (12)	450 (210)	0.92 (0.68)	14 (3)	660 (280)	69 (35)	2,000 (900)
5	232	100 (25)	140 (60)	380 (140)	0.72 (0.29)	11 (3)	1,400 (500)	140 (70)	3,700 (1,600)
CP:P ratio		2.5	31	1.8	1.3	2.7	6.5	4.4	8.2

ticular, site 2 often shows less relationship with flow than other sites, either positive or negative, while site 5 shows the strongest relationship with flow. Site 2 is immediately downstream from a reservoir, and increased flow into the reservoir displaces older water from the reservoir, delaying, and dampening the effect of increased flow considerably. The same argument applies to a lesser extent to site 4, which lies further down the Main Branch, but which also receives water from the Little Patuxent River, and coastal plain drainage on the Main Branch. The area upstream of site 5 is the most heavily urbanized region of the watershed. The difference between the positive correlation for total Hg with flow and the negative correlation for meHg (Table 1, Fig. 3) suggests that their sources are largely separate.

AREAL YIELDS

Differences in loading among the various drainage basins of the Patuxent River is also reflected

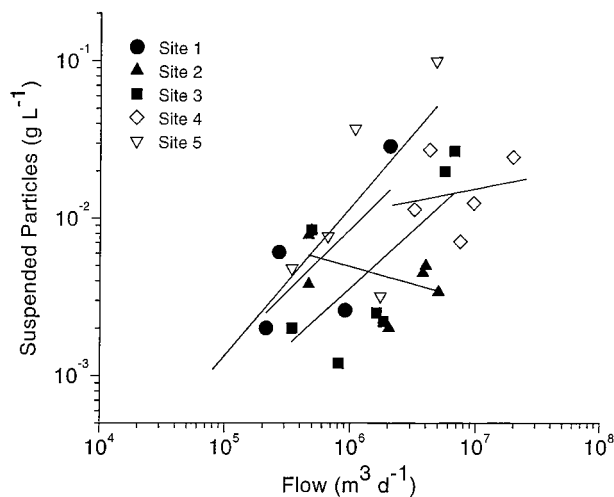


Fig. 4. Scatter/regression plots of concentrations of suspended particulate material in the five flow monitored freshwater sites versus average flow rate on the date of collection. Site 1 closed circle, site 2 closed triangle, site 3 closed square, site 4 open diamond, site 5 open inverted triangle. Piedmont sites were assigned solid symbols, Coastal Plain sites were assigned open symbols.

in the areal yields of the sampled tributaries. The areal yields for several elements, notably Cd, Pb, As, and Zn, show substantial differences from basin to basin (Table 2). For all elements, the mean of the three Piedmont sites show lower yields than the mean of the two Coastal Plain sites. Cadmium is again the most extreme case, with a factor of 31 between their means, while the difference is least for Hg. Yields of Ni, Pb, and Zn were also substantially greater in the Coastal Plain than in the Piedmont. Of the metals examined, Hg concentrations exhibited the narrowest range in yield among basins, and were most significantly correlated with flow. These patterns suggest more diffuse sources than other metals, probably dominated by atmospheric deposition.

Moreover, even within the Coastal Plain sites, Cd yield is uneven. The Western Branch of the Patuxent is so enriched in Cd that it yields more dissolved Cd (33.3 kg yr^{-1}) than the Main Branch of the Patuxent at site 4 (20.4 kg yr^{-1}), despite the fact that its total discharge is approximately one fourth that of the Main Branch, which also has a greater area of Coastal Plain drainage, plus additional drainage from the Piedmont, and the output of 8 major municipal waste water treatment plants. We are currently investigating the possibility that the high levels of Cd (and also As, Ni, and Zn) in the drainage area of the Western Branch is due to the extensive surface outcropping of a metalliferous sediment, greensands of the Aquia and Nanjemoy formations (McCartan et al. 1998).

SUSPENDED PARTICULATE TRACE ELEMENTS

Concentrations of suspended particles in the riverine Patuxent River varied by region and by the flow. Concentrations of suspended particles at site 3 and site 5 were significantly correlated ($p < 0.05$) with river flow, site 1 was weakly correlated ($p < 0.1$), while the relationships with flow in the Main Branch immediately below the reservoirs (site 2) and the main branch above the tidal region (site 4) were not significant ($p > 0.2$) (Fig. 4).

Concentrations of trace elements in the suspended particles varied geographically as well. Ar-

TABLE 3. Concentrations of trace elements in seston (SD) collected from the Patuxent River watershed. See Fig. 1 for site locations. All elements have units of $\mu\text{g g}^{-1}$ except Hg which is ng g^{-1} .

Site	As	Cd	Cu	Ni	Zn	Hg
1	5.4 (0.7)	0.2 (0.1)	39 (14)	53 (6)	148 (18)	100 (60)
2	9.9 (3.7)	0.4 (0.2)	40 (15)	51 (17)	123 (37)	87 (42)
3	6.4 (0.9)	0.3 (0.2)	31 (5)	43 (10)	196 (75)	123 (65)
4	7.6 (1.0)	0.7 (0.2)	33 (4)	38 (5)	196 (31)	132 (64)
5	22.5 (4.7)	7.3 (7.2)	18 (3)	41 (12)	230 (58)	120 (119)
6	10.8 (3.8)	2.9 (1.3)	22 (11)	49 (28)	188 (79)	128 (55)
7	12.9 (0.9)	2.6 (1.1)	20 (6)	34 (9)	181 (86)	129 (111)
8	13.4 (1.0)	2.3 (0.4)	24 (5)	40 (4)	172 (49)	94
9	13.2 (2.9)	1.7 (1.0)	24 (2)	42 (4)	204 (81)	104 (64)
10	14.1 (3.3)	1.6 (0.8)	23 (3)	51 (20)	171 (31)	116
15	17.2 (11.8)	0.6 (0.3)	17 (4)	30 (9)	141 (36)	78

senic was highest at site 5, followed by the estuarine sites (from the Bay end up, following the concentrations of filterable As in the water), followed by the remaining river sites (Table 3). The highest concentrations of Cd in suspended particles were also found at site 5, followed by the tidal freshwater and upper estuarine sites. The Piedmont sites had the lowest concentrations of Cd in suspended particles. In contrast, the highest values of Cu in particles were found in the Piedmont stations (sites 1–3) and the estuarine sites (sites 6–15); the Western Branch (site 5) had the second lowest Cu, similar to the values at the mouth of the Patuxent River. Nickel and Zn values were not significantly different between sites ($p = 0.098$ and $p = 0.053$, respectively), but the highest values also tended to be among the Piedmont sites, and the lowest values at the mouth of the estuary. Total Hg in suspended particles was relatively constant, at around 100 ng g^{-1} , and was not significantly different between sites.

Windom (1990) compared the trace element concentrations of suspended particulate matter from 20 North American east coast rivers, and de-

termined that particulate matter from the Piedmont and Coastal Plain differed in their overall composition, with the Piedmont having higher concentrations of Cu, Ni, and Zn, but nearly identical concentrations of Cd compared to the Coastal Plain. Our results follow this trend, as the (potentially) much less contaminated Piedmont sites tended to have higher Cu and Ni content. Our results for Cd do not agree, and suggest that Cd in suspended material from the Coastal Plain samples in the Patuxent basin are unusually high, particularly at site 5.

In the estuarine region, our values for trace elements in suspended particles are similar to values previously reported for bottom sediments in the Patuxent River Estuary (Table 4). The suspended particles in the Patuxent estuary probably consist largely of suspended bottom sediments, modified somewhat by the relatively high phytoplankton biomass often found in the Patuxent Estuary.

TRANSFER OF TRACE ELEMENTS TO THE PATUXENT RIVER ESTUARY

The estuary receives and integrates water (and associated materials) with a residence time of 30–

TABLE 4. Concentrations (SD) of trace elements in seston compared to sediments collected from similar regions of the Patuxent River Estuary. All elements have units of $\mu\text{g g}^{-1}$ except Hg which is ng g^{-1} .

	As	Cd	Cu	Ni	Zn	Hg	Reference
Upper Estuary (Sites 6–9)							
Seston	13 (2)	2.4 (1.0)	22 (6)	40 (13)	174 (55)	113 (63)	This paper
Sediment			23 (3)			116 (54)	Benoit et al. 1998
Sediment	21 (5)	2.7 (0.8)	22 (6)	34 (14)	140 (40)	56 (15)	Riedel et al. 1995
Sediment							Eskin et al. 1996
Middle Estuary (Sites 10–11)							
Seston	14 (3)	1.6 (0.8)	23 (3)	51 (20)	171 (31)	90 (43)	This paper
Sediment						145 (13)	Benoit et al. 1998
Sediment	31 (10)	0.5 (0.5)	26 (6)	38 (6)	165 (22)	70 (31)	Riedel et al. 1995
Sediment							Eskin et al. 1996
Lower Estuary (Sites 12–15)							
Seston	17 (12)	0.6 (0.3)	17 (4)	30 (9)	141 (36)	78 (13)	This paper
Sediment						103 (13)	Benoit et al. 1998
Sediment	10 (2)	0.5 (0.1)	26 (3)	21 (3)	165 (20)		Riedel unpublished data
Sediment	39 (22)	1.1 (0.7)	25 (5)	34 (12)	140 (30)	70 (20)	Eskin et al. 1996

TABLE 5. Monthly mean estimated combined inputs of dissolved trace elements to the Patuxent River estuary from the Main Branch and Western Branch of the Patuxent River. All elements have units of kg except Hg and mHg which are g.

Month	Cu	Cd	Ni	Pb	Zn	Total As	Hg	mHg
January	48	7.2	97	12.0	310	8.3	87	1.4
February	59	5.0	100	10.0	290	9.1	160	1.5
March	60	6.3	110	12.0	330	9.9	120	1.7
April	45	3.7	81	7.7	230	8.0	74	1.4
May	45	4.9	85	8.9	250	8.1	75	1.4
June	29	2.9	58	5.2	160	6.1	38	1.1
July	36	2.9	62	6.3	180	6.2	85	1.2
August	26	1.8	45	4.2	130	5.0	39	1.0
September	28	1.8	48	4.5	140	5.3	50	1.0
October	40	4.7	77	8.3	230	7.1	78	1.3
November	55	6.4	102	12.0	310	8.9	130	1.5
December	56	6.3	102	11.0	300	8.3	150	1.3

110 d (Hagy et al. 2000), depending on flow. To examine the inputs of trace elements to the estuary on a useful timescale we have summed the calculated daily loads of dissolved and particulate trace elements over individual months for 1995–1997 from the sites of the Patuxent closest to the head of tide (sites 4 and 5), and averaged the years, to produce a signal of typical monthly input to the head of the estuary (Table 5). Note that in the Patuxent River approximately half of the freshwater inputs enters below sites 4 and 5, the gauged stations on the Main and Western Branch of the Patuxent (Hagy et al. 2000), much of this from small streams entering the estuary from the side. These Coastal Plain streams have not been sampled, and their contribution to trace elements in the Patuxent is unknown. Largely because of the winter/summer difference in river flow, but also in part due to the relationships between trace element concentrations and flow, trace element inputs into the head of the Patuxent River estuary can be nearly two to five times as great in winter as in summer.

CONCENTRATIONS OF TRACE ELEMENTS IN THE ESTUARINE PATUXENT RIVER

Dissolved trace element concentrations in the estuarine portion of the Patuxent River are plotted versus salinity (Fig. 5), to help display the relationship between riverine and Chesapeake Bay end members and the concentrations in the estuary.

Arsenic concentrations entering the head of the Patuxent River estuary ranged from slightly below 0.2 to just over 0.5 $\mu\text{g l}^{-1}$, with higher concentrations at time of lower flow. Upon entering the estuary, over the course of the initial mixing of salt and freshwater from a salinity of 0 to 2, a significant increase of As was usually observed (Fig. 5). This probably results from inputs from the Western Branch, which enters the estuary between sites 6 and 7, and which usually contains higher As con-

centrations than the Main Branch of the Patuxent. Similar patterns of concentration and dilution through estuaries have been observed in many rivers (Byrd 1990).

The speciation of As within the estuary varies greatly throughout the year (Fig. 6). While arsenate [As(V)] can dominate during summer and early fall, in the winter and early spring methylated As forms comprise the majority of the As, particularly in the lower reaches of the estuary. This corresponds to the time of year when dense blooms of a dinoflagellate known to produce methylated As occur (Sanders 1985; Sanders and Riedel 1993), as well as a period when nutrient conditions in the Patuxent River are often potentially phosphate limiting (D'Elia et al. 1986; Riedel 1993), a condition which favors As uptake and methylation by phytoplankton (Blum 1966; Sanders and Windom 1980; Riedel 1993; Sanders and Riedel 1993). However, substantial concentrations of both MMA and DMA are also present in the summer period, with the highest concentrations at or near the river mouth, suggesting that it is formed biologically in the mesohaline portions of the Chesapeake Bay and the Patuxent River. Widespread dinoflagellate and microflagellate blooms are also typical in the Chesapeake Bay and Patuxent River during this time period (Tyler and Seliger 1978; Sanders 1985; Sellner et al. 1991).

Another interesting feature of the As cycle of the Patuxent River estuary is the apparent input of arsenate in the mid-estuarine area during mid-summer (Fig. 6). We have recently examined the seasonal cycle of As at a single site (near site 10) in the Patuxent River in some detail (Riedel 1993), which showed a distinct summer peak of arsenate. The highest values of this peak are greater than can be produced by the conservative mixing of the two end members, Patuxent River freshwater, and Atlantic Ocean coastal surface waters. Combining the results of the previous study with the current

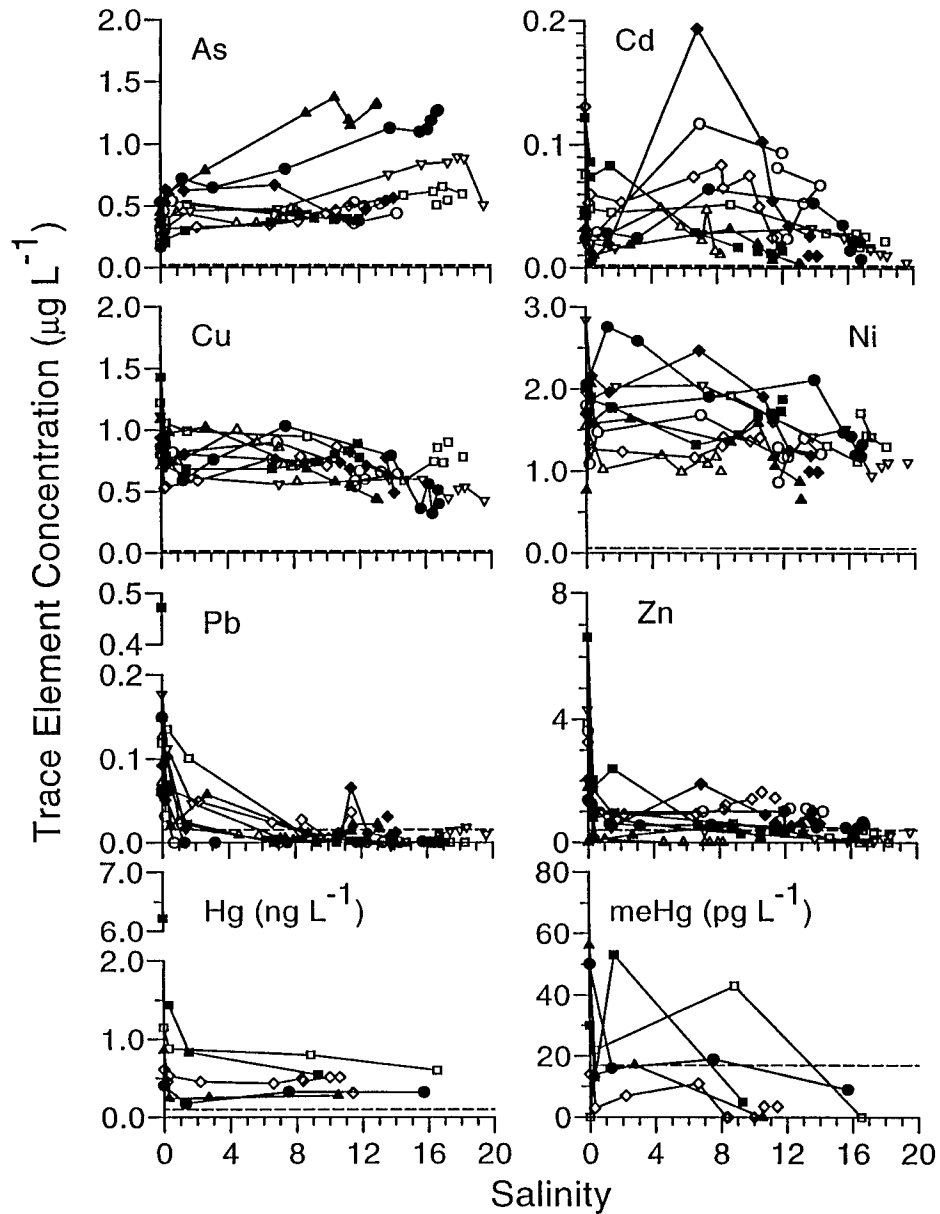


Fig. 5. Concentration of dissolved trace elements at the tidal freshwater and estuarine sites plotted as a function of salinity. May 1995 (April 1995 for Hg samples) open circles, August 1995 closed circles, November 1995 open squares, February 1996 closed squares, May 1996 open triangles, August 1996 closed triangles, March 1997 open diamond, July 1997 closed diamond, October 1997 open inverted triangle. The lower limit of detection ($3 \times \text{SD}$ of the blanks) is denoted by a dotted line.

study, we believe there is strong evidence that the peak in arsenate in summer results from cycling within the Patuxent River. We believe that flux of As from the sediment occurs in summer into the hypoxic and periodically anoxic bottom water as it moves up the Patuxent River (Riedel et al. 1997, 1999). This bottom water is transported up-river to the mixing zone, where it is mixed into the surface water, forming the observed mid-estuarine As maximum in surface water. Similar estuarine distribu-

tion patterns have been observed for Mn, which has redox behavior similar to As (Evans et al. 1977; Eaton 1979).

Cadmium concentrations entering the Patuxent River estuary ranged from 0.02 to $0.13 \mu\text{g l}^{-1}$, with higher concentrations entering in high flow periods. In virtually every transect, a substantial loss in Cd (0.02 to $0.07 \mu\text{g l}^{-1}$) occurred between the final freshwater stations, and the lowest station with a salinity greater than 0.1 (Fig. 5), suggesting sorp-

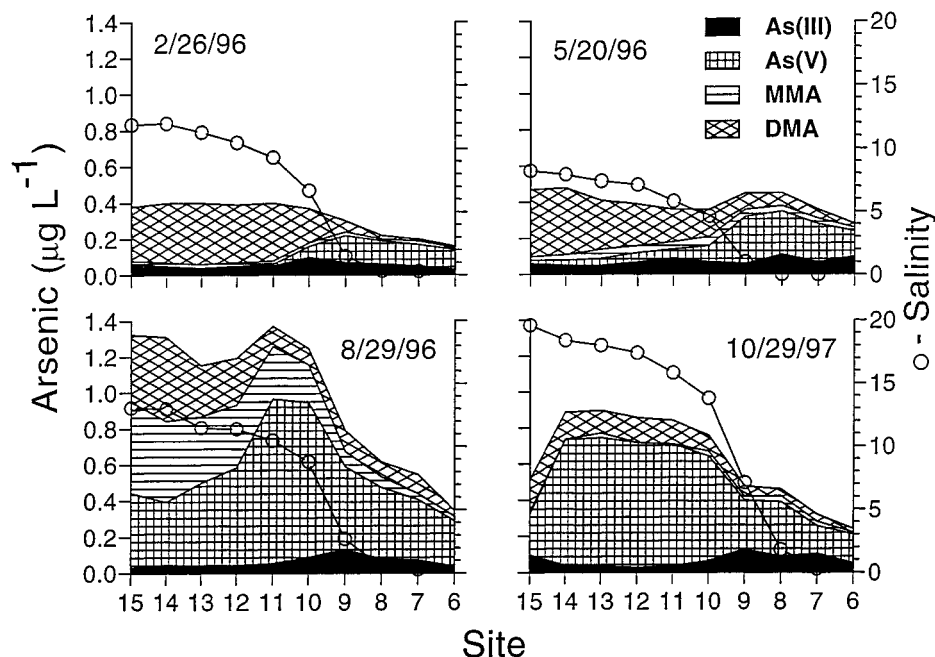


Fig. 6. Speciation of As in the Patuxent River Estuary on four occasions.

tion of Cd to particles after the transition across this boundary. Most of the transects show a substantial rise in dissolved Cd at a salinity ranging from 2 to 9. In some cases this rise is substantial, from c. 0.02 to $0.20 \mu\text{g l}^{-1}$ in July 1997, and from 0.02 to $0.12 \mu\text{g l}^{-1}$ in May 1995. This peak is located near the turbidity maximum in the Patuxent River; however, it is also near the outfall of a large coal-burning power plant (Chalk Point Steam Electric Station) (Riedel et al. 1995, 1998). Because of the substantial decrease we observe in the average Cd concentration of suspended particles down the estuary (see below), we strongly suspect that the primary source of the Cd in the mid-estuarine maximum is desorption or regeneration from suspended particles; benthic flux, exogenous inputs (such as the power plant), or minor tributaries cannot be excluded. Similar mid-estuarine Cd maxima have been observed in several other estuaries world-wide where they are often at least partially ascribed to desorption from particles (e.g., Elbaz-Poulichet et al. 1987; Bewers and Yeats 1989; Flegal et al. 1991; Ng et al. 1996).

Concentrations of Cd on particles in the tidal freshwater of the Patuxent appear to be sufficient to cause the observed mid-estuarine Cd peak. Concentrations of suspended particulate matter in the tidal freshwater of the Patuxent average approximately 30 mg l^{-1} , but may exceed 200 mg l^{-1} (U.S. Environmental Protection Agency unpublished data). The difference between Cd concentrations on particles in the tidal freshwater and the mouth

of the river is approximately $2.0 \mu\text{g g}^{-1}$ (Table 3). In a simplistic calculation assuming that desorption from particles is responsible for the difference in Cd concentration, desorption could result in a dissolved Cd concentration rise of $0.06 \mu\text{g l}^{-1}$ on average, and as much as $0.4 \mu\text{g l}^{-1}$ in extreme conditions. This is sufficient to explain the observed mid-estuarine Cd maxima.

Below the mid-estuarine maximum area, Cd concentrations usually declined to values of $0.02 \mu\text{g l}^{-1}$ or below at the Patuxent River mouth. These values are typical of previous measurements of Cd in the main-stem of the Chesapeake Bay collected with clean analytical techniques (Culberson and Church 1988; Donat 1996, unpublished data).

Copper concentrations entering the head of the Patuxent River Estuary ranged from c. 0.7 to $1.4 \mu\text{g l}^{-1}$ (Fig. 5). As with Cd, there was a significant decline in Cu concentrations from the final freshwater site to the first slightly saline site. Thereafter, Cu concentrations were rather stable, averaging about $0.8 \mu\text{g l}^{-1}$. In a few cases (August 1995, February 1996, May 1996, and August 1996), there was some suggestion of a mid-estuarine maximum in the salinity range of 3–10, however given the variability in the inputs, this is quite uncertain. Concentrations of Cu at the mouth of the River ranged from c. 0.4 to $0.8 \mu\text{g l}^{-1}$, consistent with other measurements of Cu from that region of main-stem Chesapeake Bay (Culberson and Church 1988; Donat 1996, unpublished data; Skrabal et al. 1997). The Cu concentrations reported here rep-

represent a significant change from the 1970s and early 1980s when Cu inputs from the Chalk Point Steam Electric Station raised Cu levels in the upper Patuxent River estuary to as much as $2.5 \mu\text{g l}^{-1}$ (Abbe and Sanders 1986; Wright and Zamuda 1991). In 1986–1987, this plant installed titanium alloy condensers which reduced the loads of Cu to the estuary (Riedel et al. 1995).

Other elements (Ni, Pb, and Zn) also exhibited decreases with increasing salinity (Fig. 5). Nickel followed a pattern similar to Cu, with a gradual decrease in concentration with salinity, suggestive of conservative mixing behavior. As with Cd, both Pb and Zn showed substantial decreases between sites 6 and 7 despite the fact that the Western Branch, which generally has higher concentrations of these elements than the Main Branch, empties into the estuary between these two sites. The region between sites 6 and 7 is a shallow tidal freshwater wetland area. We believe that this wetland is a significant sink for trace elements transiting the upper estuarine Patuxent River system, as observed in a freshwater wetland by Lung and Light (1996).

Total dissolved Hg concentrations in the estuarine Patuxent River (Fig. 5) ranged from 0.2 to 6 ng l^{-1} . The highest concentrations were found in tidal freshwater during the highest flows, with most remaining values below 1 ng l^{-1} . Like Cd, Ni, Pb, and Zn, losses of Hg usually occurred between the tidal freshwater site on the main-stem Patuxent (site 6) and the first station with significant salinity (site 7). Nevertheless, higher Hg concentrations were found in the estuary during periods of high flow, reflecting riverine inputs. Methylmercury concentrations were generally highest at the lowest salinities, suggesting a riverine or tidal freshwater source. Mixing behavior is difficult to assess because concentrations in the estuarine Patuxent were mostly below the calculated detection limit, $< 20 \text{ pg l}^{-1}$. Measured concentrations below this detection limit are shown in Figs. 3 and 5 to show potential trends and as an estimate of error. Methylmercury represents a larger fraction of total Hg in the freshwater river (6% of filterable and 3% of total) than in the estuary (estimated at 4% of filterable and 2% of total). Throughout the system, a larger fraction of meHg is found in the dissolved phase than in total Hg. A further description of the seasonality and behavior of Hg, meHg, and dissolved gaseous Hg in the estuary is given in Benoit et al. (1998).

COMPARISONS WITH OTHER ESTIMATES OF TRACE ELEMENT LOADING IN THE PATUXENT RIVER

Potential sources for the trace elements found in the Patuxent River include atmospheric deposition (wet and dry), point sources, urban runoff,

groundwater, sediment efflux, and tidal exchange with Chesapeake Bay. A compilation of loading data from a variety of sources is reported in Table 6. To compare the potential impact of these sources to the Patuxent River to measured concentrations in the Patuxent River, we have listed these values, along with our own estimate of the yields from the main branch of the Patuxent River (site 4) and the Western Branch (site 5) in dissolved and particulate form (Table 6). We have also shown the results of a previous survey of trace element loads to the Patuxent River, which consisted of two samplings, spring and fall, in 1994 (U.S. Environmental Protection Agency 1996). This survey was also done with appropriate trace element sampling and analytical techniques. This study generally agrees with our estimates within the annual variation due to differences in runoff, which suggests that for rough material budgeting purposes, a simple survey may be adequate. For elements where concentrations are highly flow dependant, or the elements are highly associated with particles (which are also strongly flow dependant), such estimates are at best simplistic.

Estimates of atmospheric deposition were taken from Scudlark et al. (1994), Baker and Clarke (1995), and Mason et al. (1997). Direct atmospheric deposition to the water surface is generally 5–10 times lower than fluvial inputs for most metals. Mercury is an exception for which the loadings are comparable. For the majority of metals, atmospheric deposition to the land, and subsequent transmission to the river could supply ample trace elements, requiring watershed transmission efficiencies ranging from 7.9% for Hg to 65% for As.

Point sources to the Patuxent River in Table 6 were estimated in two ways. First, U.S. Environmental Protection Agency has assembled an inventory of actual measured inputs from known discharges using National Pollution Discharge Elimination System (NPDES) permits (U.S. Environmental Protection Agency 1999). This inventory is rather incomplete; of nine large waste water treatment plants on the Patuxent River, data from only three are included in trace element loading estimates. Much of the data consists of non-detects with rather high limits of detection. Default trace element detection limits for the calculation of point source loadings are $0.9 \mu\text{g l}^{-1}$ As, $5 \mu\text{g l}^{-1}$ Cd, $3 \mu\text{g l}^{-1}$ Cu, $7 \mu\text{g l}^{-1}$ Hg, $10 \mu\text{g l}^{-1}$ Pb, $5 \mu\text{g l}^{-1}$ Ni, and $2 \mu\text{g l}^{-1}$ Zn (U.S. Environmental Protection Agency 1999). For a second estimate we used actual volume discharge reports from the point sources on the Patuxent River from 1984–1994 (Maryland Department of the Environment unpublished data), and estimated the trace element concentration of their effluents from a sur-

TABLE 6. A comparison of potential sources of trace elements to the Patuxent River drainage. All elements have units of kg yr⁻¹.

Source	As	Cd	Cu	Ni	Hg	Pb	Zn
Atmospheric Deposition ^{a,b}							
Total Watershed Area	510	201	2,300	3,000	35	3,800	12,000
Water Surface	48	27	220	270	4.7	358	1,100
Point Sources Estimates							
EPA Inventory ^c	0–7.6	3.5–37	150–180	79–260	0–1.5	20–140	420–460
NOAA Estimate ^d	980	370	1,200		12	1,400	103,000
Urban Runoff ^e	140	84	810	580	12	1,100	6,500
Fall Line Load ^f							
Filterable	69 (32)	35 (5)	590 (460)	730 (82)	No data	91 (93)	2,000 (36)
Particulate	No data	22 (8)	52 (64)	110 (115)		34 (19)	400 (415)
Filterable Yield (this study) ^g	93	54	540	980	1.1	103	2,900
Main Branch	70 (22)	21 (12)	450 (210)	660 (290)	0.9 (0.7)	69 (35)	2,000 (900)
Western Branch	23 (6)	33 (15)	90 (30)	330 (120)	0.2 (0.1)	33 (14)	900 (400)
Particulate Yield (this study) ^h							
	240	66	380	600	1.9		3,300
Main Branch	50 (30)	5 (2)	220 (120)	260 (140)	0.9 (0.5)	No data	1,400 (700)
Western Branch	190 (100)	61 (30)	150 (80)	340 (170)	1.0 (0.5)		1,900 (1,000)

^a Elements other than Hg from U.S. Environmental Protection Agency (1999), based on Scudlark et al. (1994), calculated assuming 38% urban coverage, and water surface area assuming 10% urban coverage.

^b Hg data only from U.S. Environmental Protection Agency (1999), data derived from Mason et al. 1997.

^c Estimates of known point sources from U.S. Environmental Protection Agency (1999); ranges include high and low estimates based on reported concentrations.

^d Estimated from reported discharges (Maryland Department of the Environment unpublished data) and estimated concentrations from National Pollution Discharge Elimination System (NPDES) waste water survey (National Oceanic and Atmospheric Administration 1993).

^e U.S. Environmental Protection Agency (1999), based on rainfall models and a Chesapeake Bay regional survey of NPDES discharge results.

^f U.S. Environmental Protection Agency (1996). These data were sampled near site 4. Calculation used mean concentration of spring and fall sampling, and 1994 total discharge from site 4 (U.S. Geological Survey). Results are the mean (SD) of samples from spring and fall sampling.

^g Filterable loads were calculated using the regression of concentration on flow, calculating daily loads, and summing them annually. Results are mean (SD) of annual estimates.

^h Particulate yields were calculated using the regression of seston on flow, calculating daily loads using mean concentrations of metals in seston, and summing them annually. Results are mean (SD) of annual estimates.

vey of trace elements concentrations in similar treatment plants in the mid-Atlantic area (National Oceanic and Atmospheric Administration 1993).

The known point sources are insufficient to supply the annual trace element loadings for most elements; using the National Oceanic and Atmospheric Administration (1993) estimates of discharge concentrations, the point source estimates are much higher, resulting in point source estimates which substantially exceed the annual trace element loadings, from 129% for Cu to 1,679% for Zn. In this estimate it is likely that the same inadequate analytical techniques that result in the non-detects in the point source data have resulted in an overestimate of the contribution from typical treatment plants.

Urban runoff was also taken from U.S. Environmental Protection Agency (1999). This data was calculated from NPDES storm water discharge measurements in the Chesapeake Bay region for a number of trace elements and rainfall models. As with the point sources data, the very high detection limits in the NPDES measurements is a signif-

icant problem with these estimates. Setting aside this caveat, urban runoff estimates are generally similar in magnitude to our load estimates (36% for Ni to 105% for Zn), except for Hg, where runoff substantially exceeds our load estimate (433%).

Several potentially important source of trace elements to the river have not been evaluated, including soil erosion, groundwater inputs, sediment efflux, and exchange with Chesapeake Bay. Although erosion is responsible for much of the particulate loads to the river, the concentrations of trace elements in soils and the geographic source of the particles are unknown. Similarly, groundwater is the dominant source of water in the river during base flow periods and we are unaware of any systematic estimates of groundwater contributions of trace elements to this system. The As data suggest that sediment efflux is an important process in the estuarine Patuxent River during summer. We have also conducted sediment flux experiments using Patuxent River sediment, and observed significant efflux of Cd, Cu, Ni, and Zn (Sanders et al. 1998) as well as Hg (Benoit et al.

1998). More systematic work will be necessary to characterize sediment flux over the estuary. Finally, tidal exchange with the Bay is undoubtedly a large term in any materials budget of the Patuxent River, since the exchange of water with the Bay is approximately ten times greater than fluvial input (Hagy et al. 2000). A direct estimate of the net exchange of trace metals with the Chesapeake Bay would be difficult, given the small differences in concentrations between the exchanging waters.

This compilation further clearly illustrates that current estimates of point sources loading and urban runoff loadings which use the current NPDES methods and data are inadequate for the purpose of understanding trace element loadings to the Patuxent (and by extension to many similar systems). The analytical methods by which these loadings estimates were collected were designed to determine whether individual point source lead to concentrations that result in acute or chronic toxicity to aquatic life, or endanger human health, not to determine how these sources impact the loadings in a complex hydrological system like the Patuxent River.

Conclusions

This study provides a relatively comprehensive set of measurements of the concentrations of a suite of dissolved and particulate trace elements in the Patuxent River watershed and estuary through a three year period, 1995 through 1997. From this data set we conclude that the loadings of trace elements into the Patuxent River estuary are controlled in large part by the loadings from various sub-watersheds, which can vary substantially between geographic areas (e.g., Piedmont versus Coastal Plain). The concentrations of metals in runoff vary with flow, and the relationship between flow and concentrations varies between elements and within a particular element depending on the region. Concentration and speciation of trace elements in the Patuxent River estuary are highly dependent upon internal processes, including adsorption and desorption to sediments or suspended particles, benthic flux, and biological uptake and transformation. Loadings estimates based on NPDES data or other data derived from similar poor sensitivity methods are inadequate to understand the contributions and consequences of anthropogenic loadings to this and similar systems.

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