Trace Element Speciation and Behavior in the Tidal Delaware River

Gerhardt F. Riedel[1]
James G. Sanders
The Academy of Natural Sciences
Estuarine Research Center
10545 Mackall Road
St. Leonard, Maryland 20685

ABSTRACT: Measurements of dissolved As, Cr, Cu, and Se using species-selective techniques were made in the tidal freshwater Delaware River at four sites in July 1991, January 1992, and March 1992. Concentrations of dissolved As, Cr, and Se were generally higher in July than in March or January. Copper concentrations were relatively constant. Both As and Cu increased in concentration in the region of Philadelphia. Measurements of As, Cd, Cr, Cu, Pb, Ni, Se, and Zn in seston were made during the July 1991 and March 1992 sampling using both a total digest and a series of sequential leaches. A large fraction of most of the elements, in the order Cd > Zn > Pb ≥ Cu > Ni ≥ As > Cr > Se, was solubilized by weak acid. The remainding fraction, for elements where the acid leach was not complete, was released by a rigorous digestion with concentrated acids. Based on estimates of similar rivers, Pb and Zn appear to be substantially enriched in Delaware River seston compared to other rivers draining the same geological provinces. Arsenic, Se, and Cd in seston may be moderately enriched.

Introduction

In 1991 the Delaware Estuary Program and United States Environmental Protection Agency sought information on the chemical and physical speciation of toxic trace metals and their possible influence on primary productivity in the tidal freshwater reaches of the Delaware River in order to better assess the transport, bioavailability, and toxicity of these metals. As part of this effort, data on the effects of toxic pollutants was reviewed, and a new set of water quality criteria for the Delaware River was promulgated (Delaware River Basin Commission 1994).

In particular, it was hypothesized that high trace element concentrations might be responsible for inhibition of phytoplankton growth in this region. To address these questions, we developed a two part program: first, to examine the speciation of a suite of metals and metalloids having the potential to be toxic to organisms of the Delaware Estuary, and which undergo geochemical and/or biogeochemical changes in speciation that can affect their reactivity and toxicity, and second, to examine the factors limiting primary productivity in the region. This paper reports on results on the first aspect of this study.

Previous studies of dissolved and particulate trace metal concentrations have been made in the Delaware River and Estuary (Sharp et al. 1982, 1984; Biggs et al. 1983; Church et al. 1988), and have been used to estimate input-export budgets

(Church et al. 1988). The Philadelphia metropolitan area was reported to be the source of a substantial fraction of the copper (Cu), nickel (Ni), zinc (Zn), and arsenic (As) inputs (Church et al. 1988). Dissolved concentration data on at least two other potentially toxic trace elements, chromium (Cr) and selenium (Se), were not available.

Existing dissolved and/or particulate partitioning data have shown that the river and/or estuary downstream from Philadelphia acts as a sink for many of the more particle-reactive metals (e.g., Zn and cadmium [Cd]), whereas some of the metals entering the river (e.g., Cu and Ni) show more conservative behavior (Church et al. 1988).

Toxic trace elements for which dissolved speciation is particularly important are As, Se, Cr, and Cu. The first two undergo biologically mediated methylation-demethylation reactions and changes in oxidation state. However, the methylation pathways and organisms involved in methylation are sufficiently different for each of these elements that one does not serve as an adequate model of the other. Chromium is commonly found in two different valences, +3 and +6, both of which are reasonably stable in natural waters, and which have very different toxicological and biogeochemical behaviors. Copper has been shown to be highly complexed by dissolved organic matter in many aquatic systems. Because the availability and toxicity of these four elements are dramatically different depending on the chemical speciation, it is important that environmental studies looking at these elements from a toxicological perspective consider their speciation.

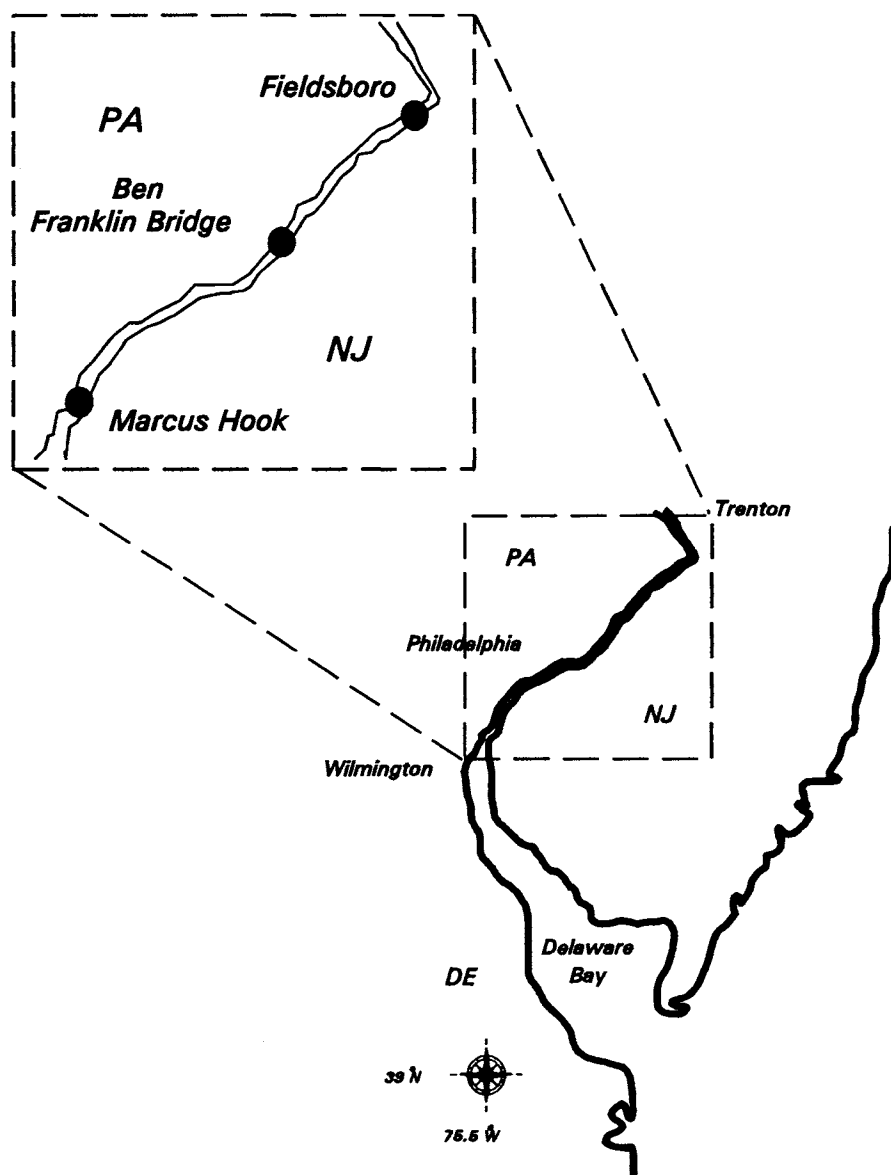[1] Corresponding Author; tele: 410 586-9700; fax: 410 586-9705; e-mail: friedel@acnatsci.org.

Fig. 1. Delaware River and Bay, showing the sampling locations in the tidal freshwater.

Methods and Materials

SAMPLING

Sampling Dates and Location

Sampling was carried out by small boat on three dates: July 24, 1991, January 14, 1992, and March 24, 1992. Three sites were chosen along the length of the tidal freshwaters of the Delaware River: at Marcus Hook, just above the most landward reach of saline water; near the Benjamin Franklin Bridge in Philadelphia; and at Fieldsboro, just below the maximum reach of the tide. Because of the possibility of salinity stratification at Marcus Hook, samples were taken at the surface and near the bottom. The sampling stations are shown in Fig. 1.

Sampling

Rigorous precautions for trace element sampling were followed. Sample bottles, filters, and sampling tubing were carefully acid-washed (Boyle and Huested 1983) and doubled bagged to prevent contamination. Water samples were taken using a peristaltic pump, using acid-washed polyvinyl chloride tubing for the sampling line and silicone tubing in the pump, and a plastic-covered weight to hold the intake end of the tubing at depth. To avoid contamination from the boat, samples were always collected facing into the current flow past the boat. Samples for dissolved trace elements analysis were pumped through acid-washed 0.2-μm

TABLE 1. Limits of detection (L.O.D.), mean process blank, and results for Standard Reference Materials (SRM) for dissolved trace element analysis (mean ± SD). N.D. = not detected. (L.O.D. based on 3σ of the process blanks, or of low standards when no blank is seen).

Analyte	L.O.D. μg l^{-1}	Blank μg l^{-1}	SRM	SRM Found μg l^{-1}	SRM Certified μg l^{-1}
As	0.01	N.D.	CASS-1	1.04 ± 0.05	1.04 ± 0.07
			SLRS-2	0.76 ± 0.13	0.77 ± 0.09
Cu (total)	0.06	0.00	SLRS-2	2.54 ± 0.29	2.77 ± 0.17
Cu (C$_{18}$)	0.18	0.00			
Cr (VI)	0.10	0.02			
Cr (total)	0.15	0.05			
Se (IV)	0.01	N.D.			
Se (IV + VI)	0.01	N.D.			
Se (total)	0.06	0.03			

polysulfone cartridge filters directly into acid-washed sample bottles. Each bottle was rinsed three times with sample prior to final filling. After filling, bottles were repackaged in plastic bags for transport to the laboratory. For each of these analyses, two samples were collected for analysis.

Water samples for As were collected in 250-ml polyethylene bottles, and frozen in the field in a mixture of isopropyl alcohol and dry ice. Water samples for Cr analysis were collected in 250-ml acid-washed polypropylene bottles. Chromium (VI) samples were refrigerated at natural pH prior to the concentration step (described below). Total dissolved Cr samples were held for 48 h in the same way prior to concentration. Concentrated samples were held refrigerated, and were analyzed by graphite furnace atomic absorption spectrometry (GFAAS) within 2 wk of the concentration step. Samples for total Cu analysis were stored in 250-ml acid-washed polyethylene bottles, acidified to pH < 2 using high purity HNO$_3$ and held at 4°C until concentration and analysis. Samples for Se analysis were collected in the field in 250-ml acid-washed (20% HCl) polyethylene bottles, acidified to pH 1.5–2.0 using high purity HCl, and refrigerated.

For collection of suspended particles, 20-l acid-washed polyethylene carboys were filled using the sampling pumps without the cartridge filter and brought to the laboratory for separation of the particles by settling, centrifugation, and filtration. Particles were also taken by the same methods from large tanks of water collected at the same time for a related productivity study (Sanders and Riedel unpublished data).

ANALYTICAL TECHNIQUES

Dissolved Speciation of Trace Elements

Arsenic was measured by hydride generation, subsequent cryogenic trapping, chromatographic separation of forms (Braman et al. 1977), and detection by atomic absorption spectrometry using a

hydrogen-burning quartz cuvette (Andreae 1977). Samples of the standard reference material (SRM) CASS-1 or SLRS-2 (both from National Research Council of Canada) were run as a benchmark for the analysis. Results for blanks and SRMs for dissolved trace element analyses are given in Table 1.

Chromium species in water were analyzed using a modification of the technique of Osaki et al. (1983). Chromium as Cr(VI) in 250 ml water samples was reacted with s-diphenyl carbazide, extracted onto XAD-2 or C$_{18}$ resin with the aid of 2-napthalene sulfonate, eluted with 5 ml methanol and analyzed by graphite furnace atomic absorption spectrometry (GFAAS). No SRMs are available for Cr speciation in natural water, therefore, we standardized Cr speciation measurements with spiked samples. Total dissolved Cr was analyzed by the same procedure, following oxidation of Cr(III) to Cr(VI) with potassium persulfate.

Total dissolved Cu was concentrated (from aqueous samples using Chelex-100 resin) into a small volume of high purity HNO$_3$ (Riley and Taylor 1968; Evans et al. 1977; Kingston et al. 1978; Riedel 1984a) for analysis by GFAAS. Two process blanks of 250 ml of deionized (DI) water were prepared and analyzed along with the samples, as well as 250-ml samples of the riverine SRM SLRS-2 from National Research Council of Canada.

Nonpolar, organically-bound Cu was determined directly after concentration onto C$_{18}$ resin (SEP-PAK, Waters), elution with methanol and HCl, and GFAAS (Mills et al. 1982). Samples were taken in 125-ml acid-washed, conventional polyethylene bottles and refrigerated pending extraction.

In the January and March samplings, we also measured the strength and extent of Cu complexation using an EDTA-ligand exchange technique (Sunda and Hanson 1987). Briefly, various levels of Cu and EDTA were added to natural water samples, allowed to equilibrate for 24 h, and extracted on C$_{18}$ resin. In the absence of EDTA, extracted Cu increases as the Cu added is complexed. EDTA,

TABLE 2. Mean process blanks, limits of detection (L.O.D.) for the trace element digests of seston, in $\mu g\ g^{-1}$ dry weight, and results of analysis of particulate standard reference materials and certified value (mean $\pm$ SD, n = 4). Blanks and L.O.D. calculations assume 0.05 g sample weight. Limit of detection calculated as 3σ of the digestion blank. All results are in $\mu g\ g^{-1}$ dry weight.

Element	Blank	L.O.D.	BCSS-1 Found	BCSS-1 Certified	NBS 1646 Found	NBS 1646 Certified
As	0.12	1.7	10.4 ± 0.9	11.1 ± 1.4	9.4 ± 0.4	11.6 ± 1.3
Cd	0.08	0.30	0.31 ± 0.03	0.25 ± 0.04	0.40 ± 0.02	0.36 ± 0.07
Cu	0.6	1.3	14.9 ± 0.8	18.5 ± 2.7	16.2 ± 2.0	18.0 ± 3.0
Cr	0.6	1.8	91 ± 6	123 ± 14	67 ± 5	76 ± 3
Ni	1.5	3.4	50.6 ± 6.8	55.3 ± 3.6	34.1 ± 2.6	32.0 ± 3
Pb	0.3	0.7	23.8 ± 2.9	22.7 ± 3.4	24.7 ± 4.7	28.2 ± 1.8
Se	0.1	0.3	0.33 ± 0.23	0.43 ± 0.06	0.29 ± 0.09	Not Certified
Zn	4	15	108 ± 6	119 ± 12	126 ± 11	138 ± 6

a strong chelator of Cu whose Cu-complex is not extracted by C_{18} resin, competes with the natural organic compounds for Cu and decreases the Cu extracted by the resin. From the relationship between various Cu additions extracted with and without EDTA, and the known affinity of EDTA for Cu, it should be possible to calculate the concentration and apparent Cu complexation constant of Cu-binding ligands. For these experiments we used 100-ml water samples with Cu additions ranging from 30 nM to 1,000 nM, and EDTA additions of 0.1 μM to 100 μM.

From the difference between the amount of total Cu required to produce a particular C_{18}-Cu level in the presence and absence of EDTA, this difference being assumed to equal the concentration of CuEDTA in the sample with EDTA, the Cu free ion concentration is calculated by

$$[Cu^{2+}] = [CuEDTA][Ca^{2+}]K_{CaEDTA}$$
$$\cdot \{([EDTA_{total}] - [CuEDTA])K_{CuEDTA}\}^{-1} \quad (1)$$

This formula is modified from Sunda and Hanson (1987) by excluding the effect of Mg^{2+}, which at the ratio of Ca to Mg found in the Delaware River does not substantially affect the apparent CuEDTA equilibrium constant. Because other elements which compete for EDTA must be included in the calculations, we measured Ca and Mg in the river water using ion chromatography.

Selenium was measured by hydride generation, cryogenic trapping, and hydrogen flame atomic absorption spectrometry, a technique similar to the one used for As (Cutter 1978, 1983), that distinguishes selenate (Se(VI)), selenite (Se(IV)), and organic Se.

Particulate Trace Elements

Speciation of the particulates was carried out using selective sequential leaches. A sample of the particulates was leached for 24 h with 5 ml of 1.0 N high purity HCl, rinsed three times with 5 ml of 1 N HCl, and the combined supernatant analyzed for weak acid-leachable metals. This was consid-

ered to be a reasonable measure of biologically available trace elements (Luoma and Jenne 1976; Luoma and Bryan 1978). The remaining particles were further leached with 5 ml of 1 N HCl with 1% hydroxylamine HCl at 60°C for 24 h to solubilize iron and manganese oxides and associated metals, rinsed three times with 5 ml of 1 N HCl with 1% hydroxylamine HCl, and the combined supernatant analyzed for hydroxylamine reducible metals. The particles remaining from this step were digested with concentrated HNO_3:HCl:HF (modified from Van Loon 1985) for a measurement of the residual particulate metal. A separate pair of samples was subjected only to the same total digestion as a direct measure of total particulate elements. A pair of process blanks and SRMs (National Biological Service 1646 and National Research Council of Canada BCSS-1) were carried out along with the sequential leach for each batch of samples.

In all of the samples of suspended particles, Cd, Cr, Cu, Pb, and Ni were analyzed by GFAAS, and Zn was analyzed by flame atomic absorption spectrometry (FAAS). Arsenic and Se in particulate samples were determined using hydride generation analyses described above. For the analysis of Se, the subsamples were carefully dried at low temperature to remove HNO_3, redissolved in 4 N HCl, and digested with $K_2S_2O_8$ to convert all Se present to Se(IV) for analysis (Cutter 1978).

Blanks, estimated lower limits of detection for the total particulate trace element analysis, and results for analysis of the sediment-certified reference materials using the total digest are shown in Table 2.

Results

DISSOLVED TRACE ELEMENTS

Arsenic

In the July sampling, dissolved As averaged 1.04 $\pm$ 0.25 $\mu g\ l^{-1}$, and station means ranged from 0.76 $\mu g\ l^{-1}$ to 1.30 $\mu g\ l^{-1}$; in the January sampling, it
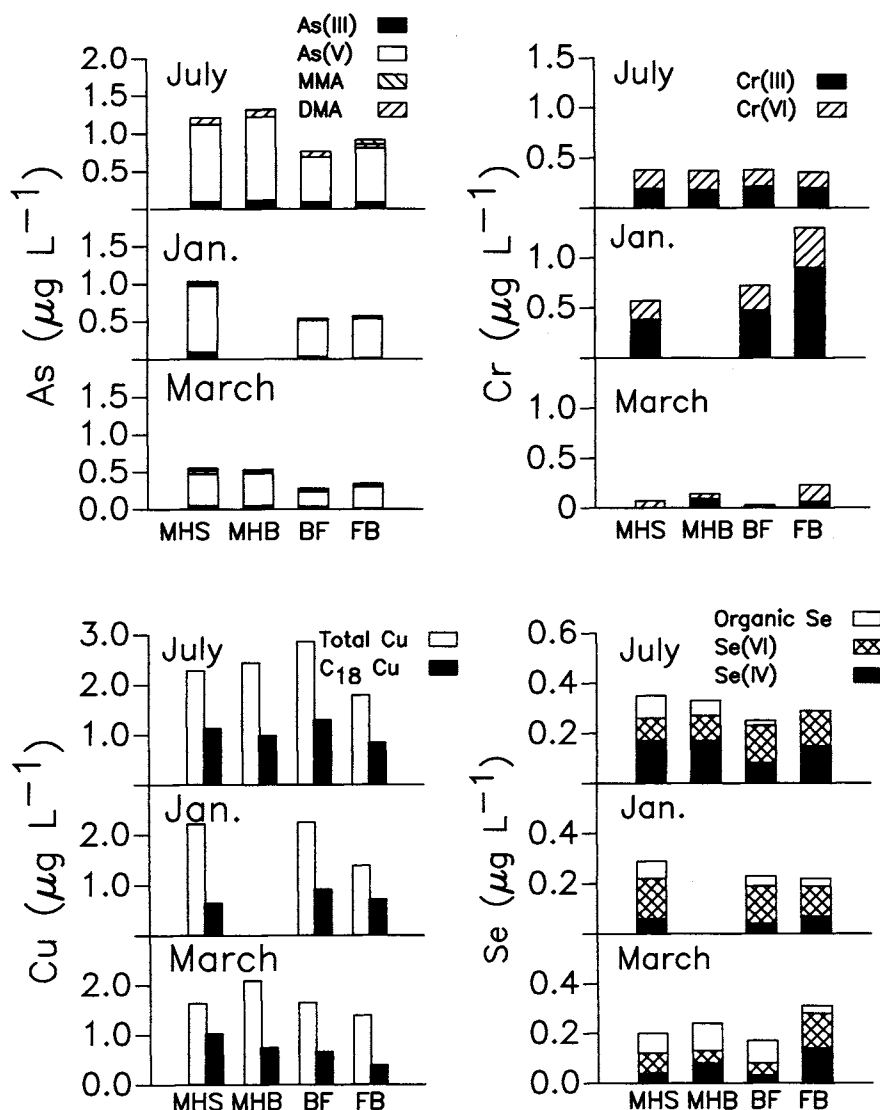
Fig. 2. Concentration and speciation of dissolved As, Cr, Cu, and Se in the tidal Delaware River at four sites (MHS = Marcus Hook surface, MHB = Marcus Hook bottom, BF = Benjamin Franklin Bridge, FB = Fieldsboro), on three dates (July 24, 1991, January 14, 1992, and March 24, 1992). Upper left, As; upper right, Cr; lower left, Cu; lower right, Se.

averaged 0.70 ± 0.28 μg l^{-1}, and ranged from 0.53 μg l^{-1} to 1.03 μg l^{-1}; and in the March sampling, it averaged 0.42 ± 0.13 μg l^{-1} and ranged from 0.28 μg l^{-1} to 0.55 μg l^{-1} (Fig. 2). In all cases the majority of the As was present as As(V) (arsenate), with overall averages of 84%. Minor amounts were present as As(III) (arsenite), monomethylarsenic (MMA), and dimethylarsenic (DMA). At all three sampling times, the As concentrations in the two Marcus Hook samples were the highest, and the Benjamin Franklin Bridge the lowest, largely due to differences in As(V). In the July sampling, As(III) was approximately constant, averaging 9%, while MMA was the dominant methyl species, averaging 7%. In January, the fraction of As as

As(III) increased in the downstream direction, from 2% at Fieldsboro to 8% at Marcus Hook. In March, As(III) composed 10–14% of As at the three downstream stations but only 3% at Fieldsboro. Methyl species ranged from 4% to 8% each.

Chromium

Dissolved Cr concentrations varied from 0.03 μg l^{-1} to 1.30 μg l^{-1}. In July 1991, total Cr concentrations ranged from 0.36 μg l^{-1} to 0.38 μg l^{-1}, with Cr(III) composing $52 \pm 2\%$ of the total (Fig. 2). In the January 1992 sampling, total Cr concentrations ranged from 0.57 μg l^{-1} at Marcus Hook to 1.30 μg l^{-1} at Fieldsboro. In this case, Cr(III) was again the dominant species, composing $67 \pm 2\%$
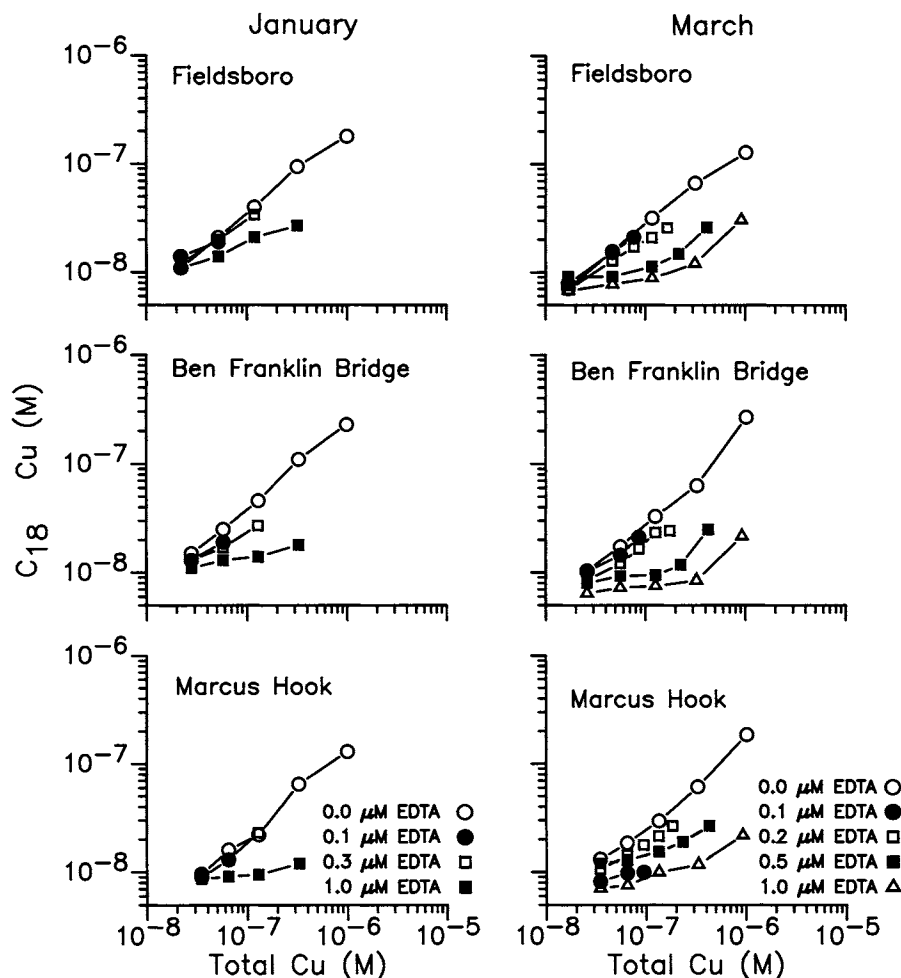
Fig. 3. C_{18}-extractable Cu in the Cu-EDTA ligand exchange experiments carried out after the January 14, 1992, and March 24, 1992, samplings.

of the total. In March 1992, dissolved Cr concentrations ranged from 0.03 μg l^{-1} to 0.23 μg l^{-1}, with the highest values at Fieldsboro.

Copper

Over the course of the study dissolved Cu ranged from 1.07 μg l^{-1} to 2.86 μg l^{-1} (Fig. 2). Overall, the highest values were recorded in July 1991, and the lowest values in March 1992. In each sampling period, the Fieldsboro station recorded the lowest values, ranging from 1.07 μg l^{-1} in March to 1.79 μg l^{-1} in July. Among the other three stations, there was no other consistent variation in dissolved Cu with time, or in the case of the two Marcus Hook stations, with depth.

C_{18}-extractable Cu ranged from 0.39 μg l^{-1} to 1.3 μg l^{-1}, and from 29% to 63% of the total dissolved Cu. Overall, there was a statistically significant positive correlation (r^2 = 0.530, d.f. = 9, p < 0.05)

between total dissolved Cu and C_{18}-extractable Cu over all sites and samplings.

The ligand exchange experiments suggested that considerably more than 30–60% of the Cu was complexed by organic matter. The amount of C_{18}-extracted Cu rose as Cu additions (in the absence of EDTA) increased to 1000 nM (Fig. 3). Additions of EDTA suppressed but did not eliminate C_{18}-extracted Cu, implying that the organic compounds present in the water competed with EDTA at concentrations as high as 1000 nM. Moreover, when higher levels of EDTA (up to 1000 μM) were added in the absence of added Cu, very little suppression of the amount of Cu extracted by the C_{18} resin was observed, suggesting that at ambient Cu concentrations, Cu was bound by a ligand stronger than EDTA, or that the natural ligands were very stable kinetically. These results are qualitatively in agreement with results of Sunda and Hanson

(1987), which showed the presence of two ligands in Narragansett Bay water, a high affinity ligand at concentrations comparable to ambient Cu concentrations, and a low affinity ligand present at much higher concentrations.

Attempts to calculate the concentration and affinity of the natural ligands were unsuccessful, because calculations from Eq. (1) did not result in a unique relationship between calculated $[Cu^{2+}]$ and C_{18}-extracted Cu over all concentrations of EDTA used.

The inability of the ligand exchange technique to identify a distinct set of Cu-complexing ligands may be due the presence of other metals complexing both natural organics and EDTA, as suggested by Sunda and Hanson (1987), or to slow dissociation kinetics of the Cu-complexes present in freshwater and estuarine environments (Rate et al. 1993; Chakrabartl et al. 1994). Significantly, another ligand exchange technique, using diethylenetriaminepentaacetic acid (DPTA)/solvent extraction coupled with cathodic stripping voltammetry, which found discrete classes of ligands in open ocean water, failed to produce consistent results in estuarine waters (Miller and Bruland 1994).

SELENIUM

Total dissolved Se ranged from 0.17 μg l^{-1} to 0.35 μg l^{-1} over the course of the study (Fig. 2). The highest values at each site were recorded in July 1991, and with only one exception, the lowest values at each site were recorded in March 1992. In general, inorganic Se dominated the total. In the July 1991 sampling, the fraction as Se(IV) was greater than that of Se(VI) at three of four stations (the exception was from the Ben Franklin Bridge). Selenite averaged 46 $\pm$ 9% of total Se, while Se(VI) averaged 42 $\pm$ 16%. Organic Se ranged from immeasurable at Fieldsboro to 25% (Fig. 2). In the January sampling, Se(VI) dominated the speciation of Se, averaging 60 $\pm$ 5% of total Se, with Se(IV) averaging 23 $\pm$ 7%, and organic Se 17 $\pm$ 6% of the total Se. In March 1992, all three forms were almost equal, organic Se averaged 37 $\pm$ 18%, Se(VI) 31 $\pm$ 8%, and Se(IV) 32 $\pm$ 17%.

TRACE ELEMENTS IN SESTON

Results for the analysis of total trace elements in suspended particles for both July and March are shown graphically in Fig. 4. In general, similar values were obtained from the two samplings for each element, suggesting relatively constant composition of the particles. Trends among stations were not strong; however, in all cases either the Ben Franklin or the Fieldsboro station had the highest values for an element. The results of both samplings were tested for a significant effect of station by Friedman two-way ANOVA by ranks (Daniel 1978). In the July sampling, there were significant differences between stations ($p < 0.05$), and in pairwise comparisons the Ben Franklin station ranked significantly higher than the two Marcus Hook stations ($p < 0.10$), with the remaining comparisons being insignificantly different from one another ($p > 0.10$). In the March sampling, over all elements, the differences among stations were just short of significant ($0.10 > p > 0.05$).

The composition of the seston, as observed in the sequential leach experiment, are shown in Table 3. A large fraction of most of the elements, in the order Cd > Zn > Pb $\geq$ Cu > Ni $\geq$ As > Cr > Se, was solubilized by 1 N HCl. The 1 N HCl: 1% hydroxylamine leach, was in most cases, a very small fraction. The remainder was released by the same rigorous digestion with concentrated acids to which the total seston samples were subjected. In the majority of cases the sum of the three extracts was within $\pm$20% of the result of the digest for total suspended particles (Fig. 5).

Discussion

DISSOLVED TRACE ELEMENT CONCENTRATION AND SPECIATION
Arsenic

Church et al. (1988) observed concentrations of dissolved As from about 0.8 μg l^{-1} to 2.0 μg l^{-1} in the tidal freshwater Delaware River below Philadelphia. Arsenite concentrations ranged from undetectable to about 0.15 μg l^{-1}. They suggested significant sources of As in the Philadelphia area. Our data showed a consistent significant increase ($p < 0.05$, two-way ANOVA) of approximately 30–50% in total dissolved As concentration below the Benjamin Franklin Bridge Station, and thus our data concur with their findings.

Our findings, as well as those of Church et al. (1988) suggest that As concentrations in the Delaware River are reduced in winter (high flow) compared to summer (low flow). In a recent study of trace elements in the Patuxent River, Maryland, we observed a negative relationship between dissolved As and flow (Riedel et al. unpublished data). The negative relationship between concentration and flow suggests that sources of As are relatively fixed; that is, the amount of As available does not increase proportionally with stream flow. This would be the case if the source of As were fixed point sources, or a diffuse source less affected by increased flow, such as groundwater inputs.

Byrd (1990) surveyed the As concentration in 17 rivers from the east coast of the United States and Canada, and found concentrations ranging from 0.02 μg l^{-1} to 0.5 μg l^{-1}. Thus, concentrations of
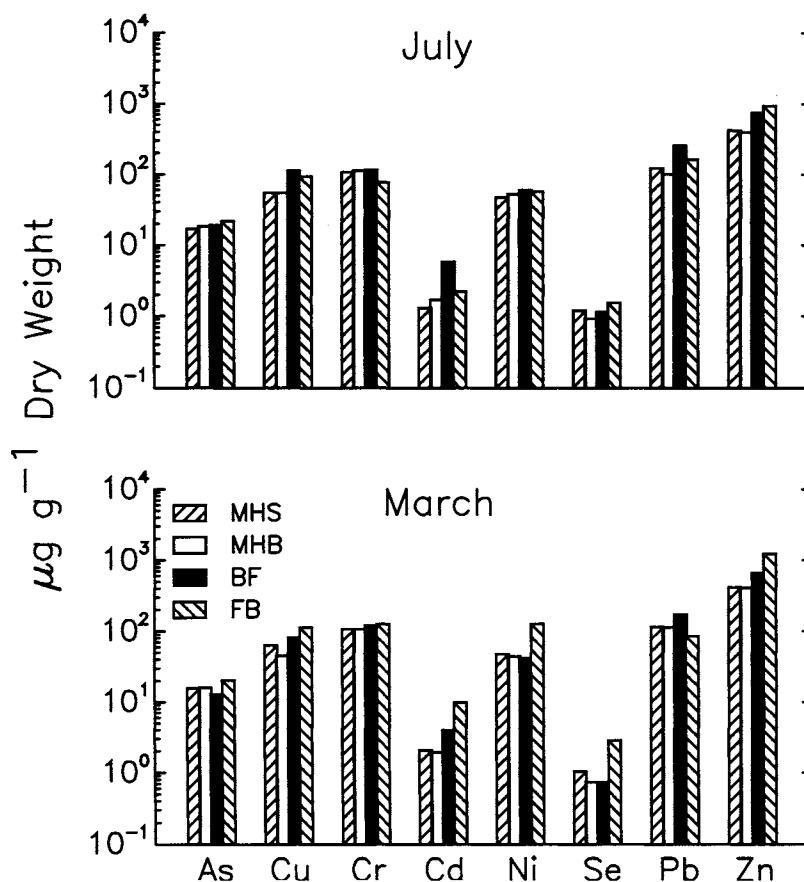
Fig. 4.   Concentration of several trace elements in seston from the July 24, 1991, and March 24, 1992, samplings at four sites (MHS = Marcus Hook surface, MHB = Marcus Hook Bottom, BF = Benjamin Franklin Bridge, FB = Fieldsboro).

As found in the tidal freshwater of the Delaware appear to be somewhat enriched in As.

The values reported by Church et al. (1988) and this study may reflect some anthropogenic sources of As to the Delaware River. However, the concentrations in this river are low compared to some heavily impacted rivers and estuaries, such as some in mining areas of Britain where concentrations may run as high as 200 μg l^{-1} (Langston 1983), or the Schelde Estuary of Belgium with concentrations approaching 20 μg l^{-1} (Andreae and Andreae 1989).

In our studies, As(III) and methyl As species, while commonly detected, were relatively minor components. In other systems, greater diversity of As speciation has been observed, with reduced and methylated forms occasionally dominating (Howard et al. 1982, 1988; Sanders 1985; Riedel 1993). The apparent paucity of reduced and methyl species may be due to insufficient sampling (missing brief peaks of abundance in the river; e.g., Riedel 1993), or because the tidal freshwater Delaware lacks certain characteristics that favor methylation. In particular, periods of high phytoplankton

growth and rapid declines in phosphate concentrations or phosphate limitation seem to favor algal reduction and methylation of As (Sanders and Windom 1980; Wangberg and Blanck 1990; Riedel 1993; Sanders and Riedel 1993; Sanders et al. 1994). In the production study carried out simultaneously with this study (Sanders and Riedel unpublished data), phosphate, while often potentially limiting by atomic ratio, was present at concentrations of 1.4–3.9 μM and did not appear to limit the growth of phytoplankton. Growth was most consistently shown to be light limited.

Chromium

Chromium concentrations have not been reported for the Delaware River, or for similar rivers on the East Coast. Abu-Saba and Flegal (1995) studied the speciation of Cr in a transect of San Francisco Bay and observed dissolved Cr(VI) concentrations of approximately 0.1 μg l^{-1} through the estuary, while Cr(III) concentrations ranged from 0 μg l^{-1} at the seaward end of the estuary to 0.35 μg l^{-1} in the low salinity regions of the San Joaquin River. In several fresh and saltwater sites

TABLE 3.   Results of the sequential fractionation on seston. Results for all three sites averaged in each time period.

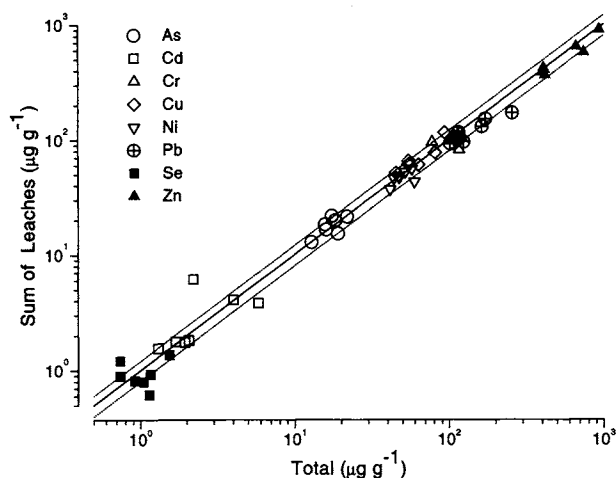| Element and Sampling Date	% Acid Leachable	% Hydroxylamine Reducible	% Residual
As			
July 1991	86 ± 1	4 ± 1	10 ± 1
March 1992	79 ± 2	10 ± 1	11 ± 2
Cd			
July 1991	97 ± 1	1 ± 1	2 ± 1
March 1992	98 ± 2	1 ± 2	1 ± 2
Cr			
July 1991	65 ± 7	7 ± 1	28 ± 7
March 1992	52 ± 3	10 ± 2	38 ± 4
Cu			
July 1991	93 ± 1	1 ± 0	6 ± 1
March 1992	90 ± 3	2 ± 2	5 ± 1
Ni			
July 1991	89 ± 2	0 ± 0	11 ± 2
March 1992	71 ± 7	2 ± 1	27 ± 7
Pb			
July 1991	93 ± 2	1 ± 1	6 ± 2
March 1992	94 ± 3	2 ± 2	4 ± 3
Se			
July 1991	31 ± 21	1 ± 1	68 ± 22
March 1992	41 ± 10	13 ± 3	46 ± 14
Zn			
July 1991	95 ± 3	1 ± 1	4 ± 4
March 1992	95 ± 2	4 ± 1	1 ± 1

Fig. 5.   A comparison of the total particle digests for suspended particles to the sum of the selective leaches for the same samples. Central line shows 1:1 relationship, outer dotted line shows ±20%.

in the southeastern United States, Kaczynski and Kieber (1993) found mean concentrations of Cr ranging from 0.02 μg l^{-1} to 0.16 μg l^{-1}, with fractions of Cr(III) ranging from 38% to 100%.

Copper

Values similar to ours for total dissolved Cu in the tidal freshwater Delaware are reported by Culberson et al. (1987a, b) and Church et al. (1988). As with this study, higher concentrations of Cu were often found in the regions of the river below Philadelphia, suggesting a source of Cu in the region.

Selenium

Cutter (1989a) has reviewed Se concentrations and speciation in fresh waters worldwide. Excluding extremely contaminated systems, such as the San Luis Drain in California and the Scheldt Estuary in Belgium, dissolved Se in rivers and streams ranged from 0.02 μg l^{-1} to 0.7 μg l^{-1}, with Se(IV) ranging from undetectable to 0.2 μg l^{-1}, Se(VI) from undetectable to 0.6 μg l^{-1}, and organic Se from undetectable to 0.06 μg l^{-1}. Generally, Se(VI) is the dominant form. Given the range of Se concentrations and forms encountered in the other rivers, the Delaware River does not stand out as

being unusual in either total Se concentration or speciation. As with As and Cr, measured concentrations of Se were highest during the July 1992 sampling, suggesting dilution by river flow.

Both Se(VI) and Se(IV) are readily accumulated by phytoplankton (Foe and Knight 1986; Riedel et al. 1991) and incorporated into organic compounds, which are readily passed up food chains (Ogle et al. 1988; Fisher and Reinfelder 1991; Rienfelder and Fisher 1991; Luoma et al. 1992).

WATER QUALITY CRITERIA FOR DISSOLVED TRACE ELEMENTS

The current recommended chronic water criterion for the protection of aquatic life in the Delaware Estuary is 190 μg l^{-1} for As(III) (no value given for As(V)), or 9.19 μg l^{-1} as a systemic toxicant (Delaware River Basin Commission 1994; Table 4). Phytoplankton are among the most sensitive organisms to As, due to its chemical similarity to phosphate. Concentrations of arsenate as low as 5 μg l^{-1} have been shown to inhibit the growth of particular phytoplankton species (Sanders and Riedel 1987), and to alter the phytoplankton community composition in mesocosm experiments (Sanders and Cibik 1985). While an argument could be made for an arsenate criterion based on the protection of phytoplankton communities, it is unlikely that present levels would exceed such a standard. One final water quality criterion is recommended for As in the Delaware River: as a carcinogen, fish and water ingestion and fish ingestion only of 0.018 μg l^{-1} and 0.144 μg l^{-1} have been proposed (Delaware River Basin Commission 1994). Given the prevailing concentrations of As in

TABLE 4. Comparison of the Delaware water quality criteria (Delaware River Basin Commission 1994) to concentrations found in this study.

Analyte	Delaware River (This Study) ($\mu g\ l^{-1}$)	Criteria for Protection of Aquatic Life		Criteria for Systemic Toxicants	
		Acute ($\mu g\ l^{-1}$)	Chronic ($\mu g\ l^{-1}$)	Fish & Water Ingestion ($\mu g\ l^{-1}$)	Fish Ingestion Only ($\mu g\ l^{-1}$)
As (III)	0.01–0.10	360	190		
Total As	0.28–1.32			9.19	73.4
Cr (III)	0.00–0.90	1,065–1,535[1]	130–180[1]	33,000	673,000
Cr (VI)	0.03–0.40	16	11	166	3,370
Cu	1.39–2.25	10.1–15.4[1]	7.1–10.4[1]		
Se	0.17–0.35	20	5.0	100	2,020

[1] Calculated based on hardness values for the Delaware River cited in Delaware River Basin Commission (1994).

the Delaware, it (and indeed many other United States rivers) will often exceed these criteria.

The recommended chronic criterion of Cr(VI) for the Delaware River is 11 $\mu g\ l^{-1}$ (Delaware River Basin Commission 1994, Table 4)), or from 130 μg l^{-1} to 180 $\mu g\ l^{-1}$ total Cr. Levels found in this study were more than one order of magnitude below this. Hexavalent Cr is the species most toxic to most organisms. Riedel (1984b, 1985) showed that uptake and toxicity of Cr(VI) to phytoplankton is inversely proportional to sulfate concentrations. Thus, it is much more toxic in fresh water than in saline waters, and can inhibit growth to some species of algae at $\mu g\ l^{-1}$ concentrations in fresh water (Frey et al. 1983; Riedel 1989).

Chronic criteria for Cu for the protection of aquatic life in the Delaware River depend on water hardness, and are estimated to vary between 7.1 $\mu g\ l^{-1}$ and 10.4 $\mu g\ l^{-1}$ (Delaware River Basin Commission 1994; Table 4). Thus, of the elements reported here, measured Cu concentrations most closely approach regulatory thresholds, with the chronic criteria exceeding the ambient values by factors of 3 to 6.

The question of Cu toxicity is complicated by the issue of complexation by organic compounds. It has been well established that Cu toxicity to phytoplankton is controlled by the cupric free-ion concentration (Sunda and Guillard 1976), and that the Cu free-ion concentration is determined by the interaction of Cu with both inorganic and organic complexes. Our measurements of C_{18}-extractable Cu suggest a minimum of 30% to 60% of the Cu is complexed by organic matter. The ligand exchange studies, while not successful in measuring the concentrations and binding strengths of organic ligands, points to the existence of at least two ligands, a relatively low affinity ligand that competes weakly with EDTA at concentrations up to at least 1,000 nM, and a ligand that competes strongly with EDTA at concentrations comparable to the ambient dissolved Cu. This is in agreement with a number of studies of Cu and Zn in natural waters which show two distinct classes of ligand, and high

organic complexation at ambient metal concentrations (e.g., Coale and Bruland 1988; Bruland 1989). The existence of these ligands in the Delaware River suggests the current concentrations of Cu are largely nontoxic due to complexation by the strong ligand class, while Cu additions above the current levels would be complexed by the weak ligand class, and thus be more bioavailable and hence toxic, though not as toxic as it would be in the absence of complexing agents.

The chronic criterion for Se in the Delaware River is 5 $\mu g\ l^{-1}$ Se (Delaware River Basin Commission 1994; no form specified, Table 4), well above the concentrations measured here. However, some lake systems receiving little more Se than this chronic criterion have had severe problems with fish populations due to the effect of Se on fish reproduction (Cumbie and Van Horn 1978; Hodson 1990).

TRACE ELEMENTS IN SESTON

The concentrations of the total trace elements in suspended particles found in this study are compared to other Delaware River results, and other river systems in Table 5. Of the elements examined, Pb appeared to be the most enriched compared to expected values for the geological provinces, and compared to similar rivers. Culberson et al. (1987a, b) have also found very similar values for Pb in seston from the tidal freshwaters of the Delaware River.

Three other elements, As, Cd, and Zn, were present at concentrations that suggested some elevation. The other elements, Cr, Cu, Ni, were found at levels measured in similar systems, where data are available. Few data are available for Se in seston, but the data here overlap results reported by Cutter (1989b) from San Francisco Bay.

From the results of the speciation experiments, it is clear that for most trace elements the majority of the element is present in an acid-labile form, and may be bioavailable (Luoma and Bryan 1978). With respect to the 1 N HCl leach, potential availability fell along a gradient Cd > Zn > Pb $\geq$ Cu

TABLE 5. Comparison of the seston trace element concentrations of this study with other values from the Delaware River, mean values of other rivers from the geological provinces the Delaware River drains, and other values. Values are given in $\mu g\ g^{-1}$ dry weight as mean ± SD or (minimum–maximum).

Element	This Study	Other Delaware	Average Coastal[1]	Average Piedmont[1]	Average Appalachian[1]	Other Values
As	16.9 ± 2.8					(5–14)[2]
	(10.9–21.8)					(9–45)[3]
Cd	2.8 ± 1.6	7.8[4]	0.7	0.6	1.1	(0.6–0.8)[5]
	(0.84–6.47)	11.7 ± 12.5[6]				
Cr	110 ± 13					100[7]
	(78–130)					(67–82)[5]
Cu	71 ± 24	78[4]	25	150	75	(27–34)[5]
	(44–11)	118 ± 140[6]				
Ni	49 ± 8	74[4]	75	100	150	(42–51)[6]
	(38–60)	89 ± 45[6]				
Pb	149 ± 55	202 ± 114[6]	10		30	(29–34)[5]
	(91–267)					
Se	1.00 ± 0.28					(0.3–1.2)[7]
	(0.61–1.54)					
Zn	543 ± 188	304[4]	200	300	300	
	(394–937)	652 ± 358[6]				

[1] Windom (1990)—20 eastern United States Coast Rivers.
[2] Wasleuchuk and Windom (1978)—Ogeechee River, Georgia.
[3] Seyler and Martin (1990)—Gironde, Loire, and Rhone rivers, France.
[4] Church et al. (1986)—Mean Delaware values for zero salinity.
[5] Trefry et al. (1986)—Mississippi River.
[6] Culberson et al. (1987a, b)—Freshwater Delaware, results from stations with salinity less than 1.0.
[7] Wedpohl (1960)—Mean crustal abundance.

> Ni ≥ As > Cr > Se, with the first four elements greater than 90% mobilized, and Ni and As not far behind. Only Cr (approximately 60%) and Se (approximately 40%) appear exceptional in their resistance to the acid leach.

Recent studies of the assimilation of trace elements from phytoplankton demonstrate that the issue of bioavailability is quite complex, and suggest that no simple chemical leach will adequately predict assimilation of different trace elements by a wide variety of aquatic organisms with differing digestive strategies. For example, assimilation efficiencies of individual trace elements from phytoplankton by the mussel *Mytilus edulis* have been shown to vary greatly among different species of algae, as well as the time it takes food to pass through the digestive system (Wang et al. 1995; Decho and Luoma 1996; Wang and Fisher 1996). Selenium assimilation efficiencies from phytoplankton have been shown to be relatively high for a variety of aquatic organisms and this has been linked to a relatively large fraction of Se present in the cytoplasm (Reinfelder and Fisher 1991, 1994; Luoma et al. 1992; Wang and Fisher 1996). The issue is further clouded in a real system like the Delaware River by the simultaneous presence of phytoplankton, nonliving organic debris, and mineral particles.

Summary

In general, dissolved trace element speciation and concentrations in the tidal freshwater Dela-ware River suggest several elements (e.g., As, Cr, and Cu) may be elevated above natural background levels by anthropogenic inputs. However, the levels found are not in excess of the current water quality criteria for the system. Furthermore, based on studies of the effects of specific forms of trace elements to phytoplankton, it does not appear likely that these elements are having any significant impact on phytoplankton production. Neither do these elements attain concentrations known to inhibit sensitive phytoplankton species, and thus alter the phytoplankton community. Thus, the current water quality criteria for these elements appear adequate to protect this community. For Se, comparable data from similar systems are scarce. Although the concentrations of dissolved Se found do not suggest an immediate problem, freshwater systems with little more Se than the current criteria have been severely affected by Se bioaccumulation. Thus, a re-examination of the Se criteria may be warranted.

Concentrations of trace elements in seston further suggest certain other elements (e.g., Cd, Pb, Zn) are enriched in the tidal freshwater Delaware compared to less impacted rivers draining the same geological areas.

ACKNOWLEDGMENTS

this effort. William Yates, Brian Albright, Roger Thomas, Louis Sage, Deborah Connell, Dorothea Ferrier, and Laura Cole assisted in the field with sample collection. Deborah Connell, Laura Cole, and Flodia Traore assisted with the chemical analyses. Without these contributions this work would not have been possible.

LITERATURE CITED

ABU-SABA, K. E. AND A. R. FLEGAL. 1995. Chromium in San Francisco Bay: Superposition of geochemical processes causes complex spatial distributions of redox species. *Marine Chemistry* 49:189–199.

ANDREAE, M. O. 1977. Determination of arsenic species in natural waters. *Analytical Chemistry* 49:820–823.

ANDREAE, M. O. AND T. W. ANDREAE. 1989. Dissolved arsenic species in the Schelde Estuary and watershed, Belgium. *Estuarine Coastal and Shelf Science* 29:421–434.

BIGGS, R. B., J. H. SHARP, T. M. CHURCH, AND J. M. TRAMONTANO. 1983. Optical properties, suspended sediments, and chemistry associated with the turbidity maxima of the Delaware estuary. *Canadian Journal of Fisheries and Aquatic Science* 40(Supplement 1):172–179.

BOYLE, E. A. AND S. HUESTED. 1983. Aspects of the surface distributions of copper, nickel, cadmium, and lead in the North Atlantic and North Pacific, p. 379–394. *In* C. S. Wong, E. A. Boyle, K. W. Bruland, J. D. Burton, and E. D. Goldberg (eds.), Trace Metals in Seawater. Plenum Press, New York.

BRAMAN, R. S., D. L. JOHNSON, C. C. FOREBACK, J. M. AMMONS, AND J. L. BRICKER. 1977. Separation and determination of nanogram amounts of inorganic arsenic and methylarsenic compounds. *Analytical Chemistry* 49:621–625.

BRULAND, K. W. 1989. Complexation of zinc by natural organic ligands in the central North Pacific. *Limnology and Oceanography* 34:269–285.

BYRD, J. T. 1990. Comparative geochemistries of arsenic and antimony in rivers and estuaries. *Science of the Total Environment* 97/98:301–314.

CHAKRABARTI, C. L., Y. YU, D. C. GRÉGOIR, M. H. BACK, AND W. H. SCHROEDER. 1994. Kinetic studies of metal speciation using Chelex cation exchange resin: Application to cadmium, copper, and lead speciation in river water and snow. *Environmental Science & Technology* 28:1957–1967.

CHURCH, T. M., J. M. TRAMONTANO, AND S. L. MURRAY. 1986. Trace metal fluxes through the Delaware Bay Estuary. *Rapports et Procès-Verbaux des Réunions Conseil International pour l'Exploration de la Mer* 186:271–276.

CHURCH, T. M., J. M. TRAMONTANO, J. R. SCUDLARK, AND S. L. MURRAY. 1988. Trace metals in the waters of the Delaware estuary, p. 93–115. *In* S. K. Majumdar, E. W. Miller, and L. E. Sage (eds.), Ecology and Restoration of the Delaware River Basin. Pennsylvania Academy of Sciences, Philadelphia, Pennsylvania.

COALE, K. H. AND K. W. BRULAND. 1988. Copper complexation in the northeast Pacific. *Limnology and Oceanography* 33:1084–1101.

CULBERSON, C. H., A. FRAKE, J. H. SHARP, J. R. PENNOCK, S. E. PIKE, B. W. LEE, J. R. SCUDLARK, R. B. BIGGS, AND J. M. TRAMONTANO. 1987b. Data from the SALT Cruises: September 1980–July 1981. University of Delaware Oceanographic Data Report Number 3, University of Delaware, Newark, Delaware.

CULBERSON, C. H., J. R. PENNOCK, B. E. LEE, R. B. BIGGS, T. M. CHURCH, AND J. H. SHARP. 1987a. Data from the YABLED Cruises: September 1981–July 1984. University of Delaware Oceanographic Data Report Number 4, University of Delaware, Newark, Delaware.

CUMBIE, P. M. AND S. L. VAN HORN. 1978. Selenium accumulation associated with fish mortality and reproductive failure. *Proceedings of the Annual Conference of the Southeastern Association of Fisheries and Wildlife Agencies* 32:612–624.

CUTTER, G. A. 1978. Species determination of selenium in natural waters. *Analytica Chimica Acta* 98:59–66.

CUTTER, G. A. 1983. Elimination of nitrite interference in the determination of selenium by hydride generation. *Analytica Chimica Acta* 149:391–394.

CUTTER, G. A. 1989a. Freshwater systems, p. 243–262. *In* M. Ihnat (ed.), Occurrence and Distribution of Selenium. Chemical Rubber Company, Boca Raton, Florida.

CUTTER, G. A. 1989b. The estuarine behavior of selenium in San Francisco Bay. *Estuarine Coastal and Shelf Science* 28:13–34.

DANIEL, W. W. 1978. Applied Nonparametric Statistics. Houghton Mifflin Company, Boston, Massachusetts.

DECHO, A. W. AND S. N. LUOMA. 1996. Flexible digestion strategies and trace metal assimilation in marine bivalves. *Limnology and Oceanography* 41:568–572.

DELAWARE RIVER BASIN COMMISSION. 1994. Recommended implementation policies and procedures: Phase I TMDLs for toxic pollutants in the the Delaware River Estuary: Final Report of the Water Quality Advisory Committee. Estuary Toxics Management Program, Delaware River Basin Commission, West Trenton, New Jersey.

EVANS, D. W., N. H. CUTSHALL, F. A. CROSS, AND D. A. WOLFE. 1977. Manganese cycling in the Newport River Estuary, North Carolina. *Estuarine and Coastal Marine Science* 5:71–80.

FISHER, N. S. AND J. R. REINFELDER. 1991. Assimilation of selenium in the marine copepod *Acartia tonsa* studied with a radiotracer ratio method. *Marine Ecology Progress Series* 70:157–164.

FOE, C. AND A. W. KNIGHT. 1986. Selenium bioaccumulation, regulation, and toxicity in the green alga *Selenastrum capricornutum* and dietary toxicity of contaminated alga to *Daphnia magna*, p. 77–88. *In* J. Slecum (ed.), Selenium in the Environment. California State University, Fresno, California.

FREY, B. E., G. F. RIEDEL, A. E. BASS, AND L. F. SMALL. 1983. Sensitivity of estuarine phytoplankton to hexavalent chromium. *Estuarine Coastal and Shelf Science* 17:181–187.

HODSON, P. V. 1990. Indicators of ecosystem health at the species level and the example of selenium effects on fish. *Environmental Monitoring and Health* 15:241–254.

HOWARD, A. G., S. C. APTE, S. D. W. COMBER, AND R. J. MORRIS. 1988. Biogeochemical control of the summer distribution and speciation in the Tamar Estuary. *Estuarine Coastal and Shelf Science* 27:427–443.

HOWARD, A. G., M. H. ARBAB-ZAVAR, AND S. APTE. 1982. Seasonal variability of biological methylation in the estuary of the river Beaulieu. *Marine Chemistry* 11:493–498.

KACZYNSKI, S. E. AND R. J. KIEBER. 1993. Aqueous trivalent chromium photoproduction in natural waters. *Environmental Science & Technology* 27:1572–1576.

KINGSTON, H. M., I. L. BARNES, T. J. BRADY, T. C. RAINS, AND M. A. CHAMP. 1978. Separation of eight transition elements from alkali and alkaline earth elements in estuarine and sea water with chelating resin and their determination by graphite furnace atomic absorption spectrometry. *Analytical Chemistry* 50:2064–2070.

LANGSTON, W. J. 1983. The behavior of arsenic in selected United Kingdom estuaries. *Canadian Journal of Fisheries and Aquatic Sciences* 40(supplement 2):143–150.

LUOMA, S. N. AND G. W. BRYAN. 1978. Factors controlling the availability of sediment-bound lead to the estuarine bivalve *Scrobicularia plana. Journal of the Marine Biological Association of the United Kingdom* 58:793–802.

LUOMA, S. N. AND E. A. JENNE. 1976. Estimating bioavailability of sediment-bound trace metals with chemical extractants, p. 343–351. *In* D. D. Hemphill (ed.), Trace Substances in Environmental Health: Proceedings of University of Missouri's 10th Annual Conference on Trace Substances in Environmental Health. University of Missouri, Columbia, Missouri.

LUOMA, S. N., C. JOHNS, N. S. FISHER, N. A. STEINBERG, R. S.

Oremland, and J. Reinfelder. 1992. Determination of selenium bioavailability to a benthic bivalve from particulate and solute pathways. *Environmental Science & Technology* 26:485–491.

Miller, L. A. and K. W. Bruland. 1994. Determination of copper speciation in marine waters by competitive ligand equilibration/liquid-liquid extraction: An evaluation of the technique. *Analytica Chimica Acta* 284:573–586.

Mills, G. A., G. L. Gill, A. K. Hanson, J. G. Quinn, W. R. Lamella, and N. D. Chasten. 1982. Chemical studies of copper-organic complexes isolated from estuarine waters using C_{18} reverse phase liquid chromatography. *Marine Chemistry* 11:355–377.

Ogle, R. S., K. J. Maier, P. Kiffney, M. J. Williams, A. Brasher, L. A. Melton, and A. W. Knight. 1988. Bioaccumulation of selenium in aquatic ecosystems. *Lake and Reservoir Management* 4:165–173.

Osaki, S., T. Osaki, and Y. Takashima. 1983. Determination of chromium(VI) in natural waters by the sorbtion of chromium-diphenyl carbazone with XAD-2 resin. *Talanta* 30:683–686.

Rate, A. W., R. G. McLaren, and R. S. Swift. 1993. Response of copper(II)-humic acid dissociation kinetics to factors influencing complex stability and macromolecular conformation. *Environmental Science & Technology* 27:1408–1414.

Reinfelder, J. R. and N. S. Fisher. 1991. The assimilation of elements ingested by marine copepods. *Science* 251:794–796.

Reinfelder, J. R. and N. S. Fisher. 1994. The assimilation of elements ingested by marine planktonic bivalve larvae. *Limnology and Oceanography* 39:12–20.

Riedel, G. F. 1984a. Trace metals in the Columbia River Estuary following the 18 May 1980 eruption of Mount St. Helens. *Pacific Science* 38:340–349.

Riedel, G. F. 1984b. Influence of salinity and sulfate on the toxicity of chromium(VI) to the estuarine diatom *Thalassiosira pseudonana*. *Journal of Phycology* 20:496–500.

Riedel, G. F. 1985. The relationship between chromium(VI) uptake, sulfate uptake and Chromium(VI) toxicity in the estuarine diatom *Thalassiosira pseudonana*. *Aquatic Toxicology* 7:191–204.

Riedel, G. F. 1989. Interspecific and geographical variation of the chromium sensitivity of algae, p. 537–548. *In* G. W. Suter and M. A. Lewis (eds.), Aquatic Toxicology and Environmental Fate: Eleventh Volume, ASTM STP 1007. American Society for Testing and Materials, Philadelphia, Pennsylvania.

Riedel, G. F. 1993. The annual cycle of arsenic in a temperate estuary. *Estuaries* 16:533–540.

Riedel, G. F., D. P. Ferrier, and J. G. Sanders. 1991. Uptake of selenium by freshwater phytoplankton. *Water, Air and Soil Pollution* 57-58:23–30.

Riley, J. P. and D. Taylor. 1968. Chelating resin for the concentration of trace metals from seawater and their conjunction with atomic absorption spectrophotometry. *Analytica Chimica Acta* 40:479–485.

Sanders, J. G. 1985. Arsenic geochemistry in Chesapeake Bay: Dependence on anthropogenic inputs and phytoplankton species composition. *Marine Chemistry* 17:329–340.

Sanders, J. G. and S. J. Cibik. 1985. Adaptive behavior of euryhaline phytoplankton to arsenic stress. *Marine Ecology Progress Series* 22:199–205.

Sanders, J. G. and G. F. Riedel. 1987. Control of trace element toxicity by phytoplankton, p. 131–149. *In* J. A. Saunders, L.

Kosak-Channing, and E. E. Conn (eds.), Recent Advances in Phytochemistry, Volume 21, Phytochemical Effects of Environmental Compounds. Plenum Press, New York.

Sanders, J. G. and G. F. Riedel. 1993. Trace element transformation during the development of an estuarine algae bloom. *Estuaries* 16:521–531.

Sanders, J. G., G. F. Riedel, and R. W. Osman. 1994. Arsenic cycling and impact in estuarine and coastal marine ecosystems, p. 289–308. *In* J. Nriagu (ed.), Advances in Environmental Science and Technology: Arsenic in the Environment. John Wiley and Sons, New York.

Sanders, J. G. and H. L. Windom. 1980. The uptake and reduction of arsenic species by marine algae. *Estuarine and Coastal Marine Sciences* 10:555–567.

Seyler, P. and J. M. Martin. 1990. Distribution of arsenite and total dissolved arsenic in major French estuaries: Dependance on biogeochemical processes and anthropogenic inputs. *Marine Chemistry* 29:277–294.

Sharp, J. H., C. H. Culberson, and T. M. Church. 1982. The chemistry of Delaware estuary. General considerations. *Limnology and Oceanography* 27:1015–1028.

Sharp, J. H., J. R. Pennock, T. M. Church, J. M. Tramontano, and L. A. Cifuentes. 1984. The estuarine interaction of nutrients, organics and metals: A case study in the Delaware estuary, p. 241–259. *In* V. S. Kennedy (ed.), The Estuary as a Filter. Academic Press, New York.

Sunda, W. G. and R. R. L. Guillard. 1976. Relationship between cupric ion activity and toxicity of copper to phytoplankton. *Journal of Marine Research* 34:511–529.

Sunda, W. G. and A. K. Hanson. 1987. Measurement of free cupric ion concentration in seawater by a ligand competition technique involving copper sorption onto C_{18} SEP-PAK cartridges. *Limnology and Oceanography* 32:537–564.

Trefry, J. H., T. A. Nelsen, R. P. Trocine, S. Metz, and T. W. Vetter. 1986. Trace metal fluxes through the Mississippi River Delta system. *Rapports et Procès-Verbaux des Réunions Conseil International pour l'Exploration de la Mer* 186:277–288.

Van Loon, J. C. 1985. Selected Methods of Trace Metal Analysis: Biological and Environmental Samples. John Wiley and Sons, New York.

Wang, W. X., N. S. Fisher, and S. N. Luoma. 1995. Assimilation of trace elements by the mussel *Mytilus edulis*: Effects of algal food abundance. *Marine Ecology Progress Series* 139:165–196.

Wang, W. X. and N. S. Fisher. 1996. Assimilation of trace elements and carbon by the mussel *Mytilus edulis*: Effects of food composition. *Limnology and Oceanography* 41:197–207.

Wangberg, S. and H. Blanck. 1990. Arsenate sensitivity in marine periphyton communities established under various nutrient regimes. *Journal of Experimental Marine Biology and Ecology* 139:119–134.

Waslenchuk, D. G. and H. L. Windom. 1978. Factors controlling the estuarine chemistry of arsenic. *Estuarine and Coastal Marine Science* 7:455–464.

Wedepohl, K. H. 1960. Spurenanalatische Untersuchungen an Tiefseetonen aus dem Atlantik. *Geochimica et Cosmochimica Acta* 18:200–231.

Windom, H. L. 1990. Flux of particulate metals between east coast North American rivers and the North Atlantic Ocean. *Science of the Total Environment* 97/98:115–124.