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Using trace element concentrations in *Corbicula fluminea* to identify potential sources of contamination in an urban river

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C. fluminea collected downstream of CFPPs had elevated tissue concentrations of trace elements.

Abstract

We used the biomonitor, *Corbicula fluminea*, to investigate the contributions of trace elements associated with different point sources and land uses in a large river. Trace elements were analyzed in tissues of clams collected from 15 tributary streams draining five land use or point source types: agriculture, forest, urban, coal-fired power plant (CFPP), and wastewater (WWTP). Clams from forested catchments had elevated Hg concentrations, and concentrations of arsenic and selenium were highest (5.0 ± 0.2 and 13.6 ± 0.9 μg g^{-1} dry mass (DM), respectively) in clams from CFPP sites. Cadmium concentrations were significantly higher in clams from urban and CFPP sites (4.1 ± 0.2 and 3.6 ± 0.9 μg g^{-1} DM, respectively). Non-metric multidimensional scaling (NMS) of tissue concentrations in clams clustered at CFPP and forest/agriculture sites at opposite ends of the ordination space, and the distribution of sites was driven by Cu, Zn, Cd, and Hg.

Keywords: *Corbicula fluminea*; Selenium; Arsenic; Urban; Coal

1. Introduction

Increased urbanization is associated with chemical, hydrological, and physical changes in rivers and streams. The term, urban stream syndrome, describes the patterns of chemical, physical, and biological change associated with increased urbanization in a catchment (Meyer et al., 2005). One component of the urban stream syndrome is elevated concentrations of metals (e.g., zinc, copper, mercury, cadmium) and metalloids (e.g., arsenic and selenium) which we collectively term trace elements, from various point and non-point sources including wastewater treatment plants, stormwater runoff, and industrial activities (Lenat and Crawford, 1994; Horowitz et al., 1999; Paul and Meyer, 2001). Elevated concentrations of copper, chromium, and lead in the water column have been associated with urban land use (Lenat and Crawford, 1994). Sediment-bound metals (e.g. copper, zinc, mercury) are also elevated in urban areas (Horowitz et al., 1999). During 1992–1995, the Chattahoochee River downstream of Atlanta, GA, and urban tributaries to this river were among the most impacted sites with respect to all streams (urban, agriculture, and forest) evaluated by the National Water-Quality Assessment (NAWQA) program nationwide (Frick et al., 1998). In the Chattahoochee River, high concentrations of fecal coliform bacteria are often cited as the primary water quality concern (Rose, 2002); yet, concentrations of lead and zinc are elevated in stream sediments in the metropolitan Atlanta area (Callender and Rice, 2000), and macroinvertebrates and fishes in the Chattahoochee River had elevated concentrations of copper, arsenic, cadmium, and mercury (Rosi-Marshall, 2002).

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Point sources of pollution in urban catchments include combined sewer overflows, storm sewer outfalls, wastewater treatment plants (WWTPs), coal-fired power plants (CFPPs), and other industrial activities (Carpenter et al., 1998). Pharmaceuticals, personal care products, nitrogen, and phosphorus have been found in effluent from WWTPs (Daughton and Ternes, 1999; Kolpin et al., 2002). Trace element concentrations were correlated with WWTP discharges in an urban river, and this correlation was attributed to decreased residence time in treatment during high flow events (Rozan and Benoit, 2001; Karvelas et al., 2003). Aquatic disposal of coal combustion waste products is a significant source of trace element inputs into rivers and streams (NRC, 2006). Froelich and Lesley (2001) observed elevated dissolved and particulate concentrations of arsenic and selenium in the Chattahoochee River near two CFPP effluent discharges, but these concentrations quickly decreased downstream (Froelich and Lesley, 2001). Knowledge of ecological effects of CFPP discharges in reservoirs is extensive (Hopkins et al., 2000; Rowe et al., 2001, 2002; Jackson et al., 2002; Lemly, 2002; Hopkins et al., 2004); however, very little is known about the impacts of CFPP effluent on biota in lotic systems (Lohner et al., 2001a,b).

Non-point sources of pollution into rivers include urban and agricultural runoff, septic tank leachate, and atmospheric deposition (Carpenter et al., 1998). During baseflow, urban streams had higher concentrations of ions compared to non-urban streams, but dilution during stormflow reduced the difference between the two stream types (Rose, 2002). Zinc concentrations were nearly an order magnitude higher in urban street runoff than runoff from shopping centers and suburban streets (Rose et al., 2001). Arsenic concentrations were elevated in soil and groundwater in cotton-producing regions, due to the use of arsenicals as herbicides and insecticides (Bednar et al., 2002). Elevated concentrations of arsenic, copper, and zinc have also been associated with poultry litter (Jackson and Bertsch, 2001; Jackson et al., 2003). Atmospheric deposition of mercury occurs through precipitation and adsorption to aerosol particles reaching remote areas far from the original source (Fitzgerald et al., 1998; Morel et al., 1998).

This study was designed to determine if the type and extent of trace element contamination in the tissue of a biomonitor, the Asiatic clam (*Corbicula fluminea*), varies with the type of point or non-point source in an urban river, which has elevated trace element content in aquatic insects and fishes (Rosi-Marshall, 2002). We measured trace element concentrations in soft tissues of *Corbicula fluminea* from tributary and mainstem sites primarily in the Chattahoochee River basin, but also in the Broad River basin in the Georgia Piedmont. The objectives of the study were to (1) quantify trace element concentrations in *Corbicula* tissues downstream of two types of point and three types of non-point sources; and (2) determine if the source type is correlated with tissue concentrations in the biomonitor. We hypothesized that: (1) clam tissues from sites receiving CFPP discharges (point source) would have elevated concentrations of arsenic, selenium, and cadmium, which are found in coal combustion wastes (Rowe et al., 2002); (2) clams downstream of WWTP discharges (point sources) would have elevated concentrations of zinc, cadmium, and lead (Karvelas et al., 2003); (3) clams from sites with highly urbanized catchments (non-point sources) would have elevated concentrations of copper, zinc, and cadmium since these metals are associated with urban runoff (Horowitz et al., 1999; Rose et al., 2001; Rose, 2002); and (4) clams from agricultural sites (non-point sources) would have elevated concentrations of arsenic based on the history of cotton-farming in the region and prevalence of poultry operations (Jackson and Bertsch, 2001; Bednar et al., 2002; Jackson et al., 2003).

2. Methods

2.1. Study sites

Fifteen tributary study sites were selected based on either the percentage of different land uses in the catchment or the predominant effluent source. The sites represented one of three predominant land use types or two types of effluent: forest, agriculture, or urban land use; WWTP or CFPP effluent (Table 1). Fourteen sites were chosen in the Chattahoochee River basin and one forested site in the Broad River basin. We calculated land cover percentages using 1998 Landsat™ satellite imagery. Land cover for the study sites was characterized as percent urban (low and high density), agriculture (row crop and pasture), forest (deciduous, evergreen, and mixed), and other (golf course, clearcut, open water). The percent land cover was determined for the entire catchment upstream of the study site. Catchment boundaries were delineated from 30-m raster digital elevation models (USGS National Elevation Data Set), modified by lowering the elevation values of mapped steam channels to force flow direction maps to match existing 1:24,000 hydrography (e.g., King et al., 2005).

We surveyed six streams with forested catchments in the Chattahoochee River basin. Only two had *Corbicula fluminea*, so the third forested site was located in the Broad River basin. Catchment area for forested sites ranged from 64 to 1761 km^2, which encompassed the range of watershed sizes for the other land use categories (Table 1). Forested catchments in the Piedmont region were previously cotton fields until the early 1900s at which time the catchments were no longer used for agriculture and returned to a forested landscape (Frick et al., 1998; Paul et al., 2006).

The three agricultural tributaries empty into Lake Lanier, an impoundment on the Chattahoochee River. These watersheds were farmed for cotton in the 1800s; today poultry farms dominate the landscape. Catchment area ranged from 43 to 68 km^2, and agricultural land use ranged from 25 to 33% (Table 1). Forested land cover was high, ranging from 50 to 64%. In these catchments agricultural land use is primarily pasture that is used for disposal of poultry waste and cattle grazing, which is typical of agricultural watersheds in the Piedmont region (Paul et al., 2006).

The three urban streams were located within metropolitan Atlanta. The population density in the Nancy Creek and Peachtree Creek stream network was approximately 2400 people km^{-2} in 2000 (Rose et al., 2001). Population density in the Sope Creek catchment was 800 people km^{-2} (Meyer et al., 2005). These streams have flashy hydrographs and frequently overflow their banks during rain events. Catchment area ranged from 69 to 223 km^2 and urban land use ranged from 65 to 80% (Table 1).

The three CFPP sites were located in the mainstem of the Chattahoochee River, downstream of the effluent discharge. Plant McDonough and Plant Wansley each have one settling basin and Plant Yates has two basins. Settling basins from two of the plants discharge directly into the river and the third (Plant Wansley) discharges into Yellowdirt Creek just before its confluence with the Chattahoochee River. Discharges vary to maintain pond level in the settling basins. Energy generation capacity ranges from 490 to 1730 MW (Table 1).

We surveyed six streams receiving discharges from WWTPs; *Corbicula fluminea* was found in only three of them. The sampling sites in these streams were at the first access point (greater than 1000 m) downstream of the effluent

Table 1
Catchment area and land cover percentages for all 15 study sites

Site name	Site type	Point source[a]	Watershed area (km^2)	Urban (%)	Agriculture (%)	Forest (%)	Other (%)
Broad River	Forest	–	1761.4	8.1	24.3	58.2	9.4
Flat Shoals Creek	Forest	–	113.2	3.6	6.5	81.6	8.3
Snake Creek	Forest	–	63.6	8.1	10.0	70.9	10.9
East Fork Little River	Agriculture	–	43.0	8.8	33.0	50.5	7.7
Wahoo Creek	Agriculture	–	63.7	7.9	24.8	64.3	3.0
West Fork Little River	Agriculture	–	47.4	9.5	31.5	51.1	7.9
Nancy Creek	Urban	–	69.2	73.8	0.5	22.7	3.0
Peachtree Creek	Urban	–	223.0	79.7	0.4	18.7	1.2
Sope Creek	Urban	–	79.7	64.6	0.9	32.1	2.5
Plant McDonough	Coal	490	4120.5	26.1	10.7	53.8	9.4
Plant Wansley	Coal	1730	6620.5	25.3	10.2	56.6	8.0
Plant Yates	Coal	1250	6264.7	26.0	10.0	56.2	7.8
Anneewakee Creek	Wastewater	3.25	76.3	36.8	3.6	55.5	4.0
Big Creek	Wastewater	24	268.4	35.2	13.0	46.2	5.6
Suwanee Creek	Wastewater	2	109.3	33.2	8.2	51.2	7.4

Land coverage determined from 1998 Landsat™ imagery.

[a] Units for point sources are megawatts (coal) and million gallons per day (wastewater).

discharge. Catchment area ranged from 76 to 268 km^2 (Table 1). NPDES permit limits for the plants ranged from 2 to 24 million gallons per day (MGD).

2.2. Water quality

Each site was sampled once during the spring and summer of 2004. Temperature, specific conductance, pH, and dissolved oxygen were measured with a YSI sonde (Yellow Springs, OH). Whole water samples were collected in acid-washed polyethylene bottles and filtered in the field with pre-ashed (1 h at 260 °C (500 °F)) glass fiber filters (Whatman GFF). We measured total suspended solids by drying filters at 60 °C for 1 week and then weighing. Filtrate was retained for analysis of dissolved organic carbon (DOC), ammonium (NH_4^+), nitrate (NO_3^-), total dissolved phosphorus (TDP), total dissolved nitrogen (TDN). Concentrations of TDN and TDP were determined using the methods of Wetzel and Likens (2000). DOC was measured using a total carbon analyzer (Sievers Model 800 Turbo, Boulder, CO).

2.3. Trace element sampling and analysis

Water samples were filtered in the field using GHP Acrodisc GF 25 mm syringe filters with GF/0.45 μm GHP membranes (Pall Life Sciences, East Hills, NY, USA) for dissolved trace element concentrations. Filtered water samples were acidified with trace-metal grade nitric acid prior to freezing. Field blanks using deionized-distilled water were treated in the same manner. Analysis of water samples is described below and dissolved concentrations are reported in Peltier (2006).

Clams from all sites were approximately 15–25 mm in length, and we collected at least 15 clams from an area approximately 500 m^2 in size from each location. Clams were kept in aerated site water for 24 h for gut depuration, placed in plastic bags, and frozen. After thawing, clams were measured for length, total weight, and soft tissue weight (wet). Soft tissues were then frozen in sterile microcentrifuge tubes, freeze-dried, and dry tissue mass (DM) recorded.

Tissue from nine similarly sized individuals (18.40 ± 0.13 mm length) from each site was analyzed for trace element concentrations. We chose to analyze a subset of nine individuals to minimize the effects of variation in size among sites and cost of analysis. As demonstrated in Bilos et al. (1998) size of *Corbicula fluminea* and trace element concentration are correlated, and by eliminating size variation, we chose to focus on the relationship between trace element concentrations in the river and accumulation in *Corbicula fluminea*. Approximately 20–60 mg DM of clam tissue was used for digestion. Trace metal grade nitric acid (2.5 ml) was added to the samples prior to digestion in a microwave (CEM Corporation, Matthews, NC, USA) with heating steps of 60, 60, 70, 80% microwave power for 10, 10, 15, and 20 min, respectively. After digestion, 0.5 ml of trace metal grade hydrogen peroxide was added to the samples and microwaved at the same power and duration as the first digestion. Samples were brought to a final volume of 10 ml with high-purity deionized water. All trace element analyses were performed using an inductively coupled plasma mass spectrometer (ICP-MS) (Perkin Elmer, Norwalk, CT). We measured total concentrations of V, Mn, Fe, Co, Ni, Cu, Zn, As, Se, Sr, Cd, Hg, and Pb. Concentrations of V, Mn, Fe, Co, Ni, Sr, and Pb are not reported in this manuscript, but all trace element concentrations for tissues and water are presented in Peltier (2006). Certified reference materials of appropriate matrix (Riverwater and Tort 2; NRC, Ottawa, Canada), replicates, and blanks were included in the digestion and analysis procedures for QA/QC purposes. Mean percent recoveries for trace elements in tissues and water reference material ranged from 89 to 125%.

2.4. Statistical analyses

All tissue concentrations are reported as means ± 1 standard error for each site ($N = 9$). We tested the normality of trace element concentrations at each site with the Shapiro–Wilk's test, and transformed them using $\log_{10}(x + 1)$. Shell lengths of clams were compared with a one-way ANOVA followed by Tukey–Kramer post hoc tests. We intended to compare means of trace elements among site types (e.g., agriculture, urban). However, sites categorized within a site type differed significantly in trace element concentrations, so all comparisons were among 15 sites rather than five site types. Multivariate analysis of variance (MANOVA) was used to test for differences in log-transformed trace element concentrations among the 15 study sites. Elements that were significantly different among the 15 sites were subsequently analyzed with one-way ANOVAs followed by Tukey–Kramer post hoc tests. Significant differences were reported at the $p < 0.05$ level of confidence. Pearson's correlation coefficient (r) was used to examine relationships among log-transformed trace element concentrations across all study sites. JMP 5.0.1 or SAS 9.1 (SAS Institute, Cary, NC, USA) were used for statistical analyses.

Overall variation in trace element tissue concentrations among the study sites was examined using non-metric multidimensional scaling (NMS) ordination with Sorenson distance measure using the statistical package PC-ORD (MJM Software Design, Glenden Beach, OR, USA). NMS uses an iterative search for low stress (<10 is ideal). Stress is measured as the relationship between ranked distances in the original multi-dimensional space and ranked distances in the reduced dimensions of the ordination. NMS is commonly used to compare ecological community composition across multiple sites

(Roy et al., 2003; Dodson et al., 2005). We used this indirect ordination technique to determine site similarity based on overall trace element concentrations in *Corbicula fluminea* tissue. We used mean trace element concentrations of Ni, Cu, Zn, As, Se, Sr, Cd, Hg, and Pb in the tissues of clams from each study site to position sites in ordination space. Correlation coefficients of NMS axes with measured environmental or land cover variables and with individual trace elements were calculated to determine factors associated with each axis.

3. Results

3.1. Water quality

All study sites were sampled during baseflow except Nancy Creek and Broad River. Nancy Creek was sampled during the rising limb of the hydrograph and Broad River was sampled several days after a large rain event. Total suspended solids concentration was highest at Nancy Creek, likely due to increasing flow and runoff associated with the increasing precipitation (Table 2). Specific conductance differed among sites, and the highest values were from CFPP and urban sites whereas forested sites had the lowest values (Table 2). Dissolved organic carbon (DOC) ranged between 2.01 and 12.10 mg l^{-1} with the highest concentrations at the CFPP and urban sites. However, regressions between mean tissue concentration of trace elements and DOC concentration at each site were only significant for Zn, Cd, and Hg ($p < 0.05$). Nutrient concentrations ranged widely among the study sites. TDP and TDN concentrations were lowest at Flat Shoals Creek (forest) (Table 2). West Fork Little River (agriculture) and Nancy Creek (urban) had the highest TDN and TDP concentrations, respectively (Table 2).

3.2. Clams

Clam lengths were not significantly different among forest, agriculture, urban, and CFPP sites (ANOVA, $p > 0.05$), and clam sizes collected were representative of clams observed at all sites. Clams from wastewater treatment plant sites were significantly larger than clams from the other site types; however their lengths remained within the range of 15–20 mm. Regressions between trace element concentrations and clam length were negative and significant ($p < 0.05$) only for Cd. However, length only explained 3–9% of the variance in trace element concentration. Therefore size differences among clams did not explain the differences in trace element concentrations among sites.

Trace element concentrations in clams differed significantly among the study sites (MANOVA, $p < 0.05$). Of the 15 study sites, clams from nine sites had significantly different concentrations of Cu, Zn, As, Se, Cd, and Hg than the other six study sites. Mean concentrations of all six trace elements from each site are shown in Table 3.

Mean As concentrations in tissues were highest at the Plant Wansley (CFPP) site and lowest at the East Fork Little River (agriculture) site (Table 3). Se concentrations were highest in clams from the two CFPP sites (Plant Wansley and Plant Yates), and the lowest concentrations were found in those from a WWTP site (Anneewakee Creek) (Table 3). The highest concentrations of Cd in clams were found at the Peachtree Creek (urban) site (Table 3). Hg concentrations were the highest at one of the forested sites, Flat Shoals Creek (Table 3).

3.3. Relationship to land cover

We compared tissue concentrations of all trace elements at each study site with percentage of urban, forest, and agricultural land cover at that site. Mean tissue concentrations of Hg were positively correlated with percent forested land cover ($r^2 = 0.34$, $p = 0.02$). Percent urban land cover was not significantly (positively or negatively) related to tissue concentrations of any of the trace elements reported here (in all cases $r^2 < 0.19$, $p > 0.10$).

Table 2
Water quality parameters and sampling dates for the 15 study sites

Site name	Site type	Date (m/d/y)	Temperature (°C)	Specific conductance (mS cm^{-1})	pH	DOC (mg l^{-1})	TSS (mg l^{-1})	Total P (μg l^{-1})	Total N (mg l^{-1})
Broad River	Forest	6/28/2004	22.9	0.05	7.2	4.7	4.6	78.2	0.8
Flat Shoals Creek	Forest	9/6/2004	22.7	0.05	7.5	2.3	56.4	5.4	0.3
Snake Creek	Forest	6/18/2004	22.6	0.03	7.4	2.2	9.8	60.2	0.4
East Fork Little River	Agriculture	4/2/2004	10.5	0.11	7.8	3.9	2.6	34.4	1.1
Wahoo Creek	Agriculture	9/6/2004	21.5	0.06	7.6	2.0	8.5	19.4	0.6
West Fork Little River	Agriculture	3/23/2004	6.6	0.14	7.9	3.9	3.3	27.9	2.1
Nancy Creek	Urban	4/26/2004	13.9	0.34	7.5	7.4	130.5	107.9	1.0
Peachtree Creek	Urban	3/18/2004	14.1	0.23	7.9	12.1	3.6	51.8	0.8
Sope Creek	Urban	3/18/2004	19.4	0.22	7.6	7.7	3.0	49.1	0.7
Plant McDonough	Coal	3/5/2004	15.8	0.30	7.6	6.9	2.6	40.0	1.8
Plant Wansley	Coal	3/3/2004	12.7	1.44	8.0	10.8	11.0	65.1	0.3
Plant Yates	Coal	3/3/2004	NA	NA		6.4	9.2	49.5	1.7
Anneewakee Creek	Wastewater	6/18/2004	25.7	0.09	7.5	3.8	7.1	45.5	1.3
Big Creek	Wastewater	3/29/2004	17.0	0.24	8.0	7.2	5.2	40.0	0.9
Suwanee Creek	Wastewater	6/18/2004	24.9	0.15	7.6	3.3	9.8	36.7	1.5

NA indicates no data was collected.

Table 3
Concentrations (mean ± 1SE) of trace elements (μg g^{-1} dry mass) in *Corbicula fluminea* ($N = 9$) from each study site

Site name	Landuse	Cu	Zn	As	Se	Cd	Hg
Broad River	Forest	32.0 ± 1.9	189.4 ± 8.5	3.1 ± 0.1	3.9 ± 0.1	0.8 ± 0.0	0.13 ± 0.0
Flat Shoals Creek	Forest	35.6 ± 1.4	245.8 ± 10.4	2.8 ± 0.1	4.6 ± 0.1	2.1 ± 0.1	0.56 ± 0.0
Snake Creek	Forest	37.7 ± 2.4	334.4 ± 23.5	3.2 ± 0.2	3.7 ± 0.2	2.6 ± 0.1	0.36 ± 0.1
East Fork Little River	Agriculture	38.2 ± 1.0	244.1 ± 9.3	2.1 ± 0.1	3.4 ± 0.1	2.2 ± 0.2	0.26 ± 0.0
Wahoo Creek	Agriculture	37.2 ± 1.8	246.9 ± 7.5	2.5 ± 0.1	4.3 ± 0.1	1.1 ± 0.1	0.31 ± 0.0
West Fork Little River	Agriculture	36.5 ± 1.0	305.1 ± 12.0	2.2 ± 0.1	3.7 ± 0.1	1.5 ± 0.2	0.29 ± 0.0
Nancy Creek	Urban	36.7 ± 1.3	303.3 ± 23.0	3.0 ± 0.2	3.3 ± 0.1	1.5 ± 0.1	0.13 ± 0.0
Peachtree Creek	Urban	63.6 ± 2.1	467.5 ± 31.7	2.7 ± 0.1	4.7 ± 0.1	4.1 ± 0.2	0.21 ± 0.0
Sope Creek	Urban	42.4 ± 1.6	296.1 ± 29.0	3.3 ± 0.1	4.8 ± 0.1	2.6 ± 0.1	0.21 ± 0.0
Plant McDonough	CFPP	61.2 ± 3.3	509.5 ± 35.7	2.3 ± 0.1	4.5 ± 0.2	2.0 ± 0.2	0.12 ± 0.0
Plant Wansley	CFPP	40.4 ± 1.9	544.0 ± 17.6	5.0 ± 0.2	9.8 ± 0.3	2.3 ± 0.1	0.13 ± 0.0
Plant Yates	CFPP	87.7 ± 8.0	380.8 ± 27.7	3.5 ± 0.1	13.6 ± 0.9	3.6 ± 0.9	0.17 ± 0.0
Anneewakee	WWTP	35.4 ± 7.0	236.2 ± 43.5	2.4 ± 0.4	2.6 ± 0.5	1.3 ± 0.2	0.24 ± 0.0
Big Creek	WWTP	38.4 ± 1.3	360.2 ± 15.9	2.8 ± 0.1	3.5 ± 0.1	1.4 ± 0.1	0.12 ± 0.0
Suwanee Creek	WWTP	33.5 ± 2.2	288.3 ± 21.9	3.0 ± 0.2	4.3 ± 0.3	1.6 ± 0.1	0.18 ± 0.0

3.4. Correlations among trace elements

Several of the trace element concentrations in tissues of individual clams were highly correlated across study sites (Table 4). We found strong positive correlations between Cu, Zn, As, Se, and Cd (Table 4). Tissue concentrations of Hg were not highly correlated with any of the trace elements reported here. Tissue concentrations were not correlated with dissolved concentrations of any trace element.

3.5. NMS ordination

A two-dimensional ordination of the 15 sites defined by nine trace elements was recommended from comparison of real and randomized data in NMS. The best NMS solution had a stress value of 0.958. Axis 1 accounted for 91% of the variation and axis 2 contributed an additional 8.5% for a total of 99.5% of variance accounted for by the ordination. Two forest sites, two agriculture sites, and one WWTP site (Anneewakee Creek) grouped together on the forest/agriculture side of ordination space (Fig. 1). All three CFPP sites and one urban site (Peachtree Creek) clustered together on the opposite end of the ordination space. Two environmental variables (DOC and conductivity) and three land cover variables (% urban, % agriculture, and % forest) were correlated ($r^2 > 0.30$) with the grouping of sites (Fig. 1). DOC, conductivity, % urban, and % agriculture were correlated ($r^2 > 0.30$) with axis 1 whereas % urban and % forest were negatively correlated with axis 2 ($r^2 > 0.40$) (Table 5). Cu, Zn, and Cd concentrations in clams were positively correlated with axis 1 and Hg concentrations were positively correlated with axis 2 (Table 5).

Table 4
Pearson's correlations (r) between trace element concentrations in clam tissues across all study sites

	Cu	Zn	As	Se	Cd	Hg
Cu	1.0000	–	–	–	–	–
Zn	**0.7342**	1.0000	–	–	–	–
As	**0.5216**	**0.5908**	1.0000	–	–	–
Se	**0.6783**	**0.5856**	**0.7107**	1.0000	–	–
Cd	**0.5406**	0.4820	0.3349	0.4102	1.0000	–
Hg	0.0702	−0.0853	0.0300	−0.0427	0.1821	1.0000

Bold type indicates $r \geq 0.50$. Significant correlations ($p < 0.05$) for $r \geq 0.17$.

4. Discussion

4.1. Site characterization

The patterns we saw among sites are evidence of the inherent variability in water chemistry, biological activity, and geomorphology in streams across the landscape. In addition, historical differences in land use, efficiency of instream processes, and loading of pollutants leads to variability in the chemistry of urban streams (Walsh et al., 2005). Historical legacy influences forested catchments since extensive agriculture (primarily cotton) dominated the region before the forested areas returned (Frick et al., 1998; Roy et al., 2003; Paul et al., 2006). In the southern Appalachians, stream invertebrate assemblages in two forested catchments were more similar to macroinvertebrate communities in agricultural catchments reflecting agricultural land use 50 years earlier (Harding et al., 1998). Streams can be categorized based upon land cover or catchment area, but streams within these categories still vary considerably. Assuming an ''urban'' stream in one catchment will function in a similar manner as another ''urban'' stream in a neighboring catchment ignores the uniqueness and variability just described.

4.2. Trends in trace element concentrations

Despite the differences within site type categories, we were able to draw conclusions about overall trends in trace element concentrations. Clams from the reference (forested) sites had the highest tissue concentrations of Hg. Natural and anthropogenically derived Hg is distributed through atmospheric

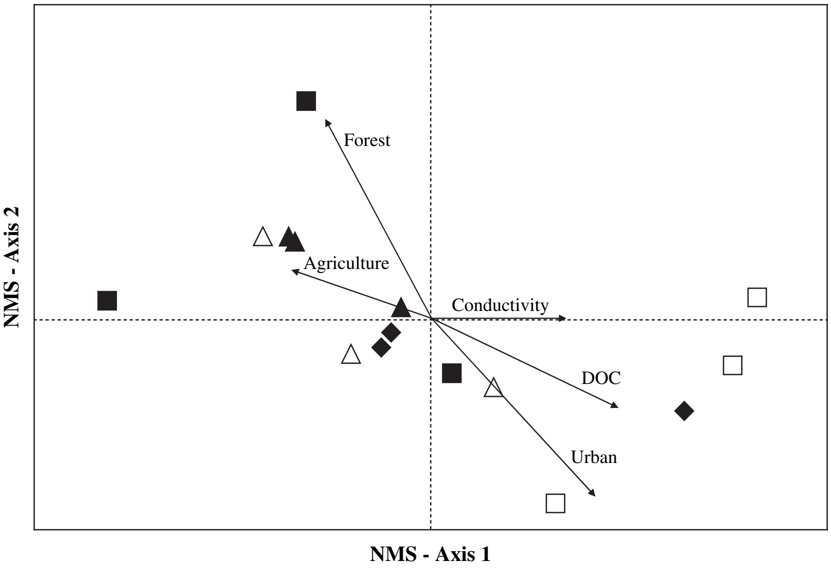

Fig. 1. NMS ordination of mean trace element concentrations in clams at each site plotted with environmental variables that are correlated with the ordination axes. Filled squares = forest sites, filled triangles = agricultural sites, filled diamonds = urban sites, open squares = coal sites, and open triangles = wastewater sites. Labeled arrows indicate environmental and land cover variables correlated with the axes. The length of the line corresponds to the strength of the correlation with NMS space; correlations range from $r^2 = 0.34$ to $r^2 = 0.50$.

deposition (Mason et al., 1994; Fitzgerald et al., 1998; Morel et al., 1998). Forests are efficient in collecting Hg-containing aerosols and particulates, which may later be washed out during precipitation events (Kolka et al., 1999a,b; Grigal et al., 2000). Other studies have shown higher concentrations of Hg in aquatic organisms associated with surrounding forested land cover (Sonesten, 2001, 2003). Hg concentrations in fish (*Perca fluviatilis* and *Rutilus rutilus*) were higher in lakes with forested catchments; higher humic acids and DOC in these systems likely contributed to this relationship (Sonesten, 2001, 2003). The percentage of forested land cover in the agricultural sites was similar to forest cover in the forested catchments, and clams from agricultural sites also had higher concentrations of Hg relative to the other site types. In the Albemarle–Pamlico drainage basin, tissue concentrations of Hg in *Corbicula fluminea* from highly forested catchments ranged between 0.02 and 0.22 μg g^{-1} WM (0.08–0.88 μg g^{-1} DM, assuming 75% moisture content) (Ruhl and Smith, 1996) compared to 0.13–0.56 μg g^{-1} DM from forested and agricultural catchments in this study. Hence clams from Chattahoochee River forested and agricultural tributaries had similar mercury concentrations in their tissue as clams from other forested tributaries in the southeastern United States.

Table 5
Results of the NMS ordination

Variable	Axis 1	Axis 2
Copper	(+)0.35	(−)0.45
Zinc	(+)0.97	−
Arsenic	−	−
Selenium	−	−
Cadmium	(+)0.37	−
Mercury	−	(+)0.42
% urban	(+)0.39	(−)0.45
% agriculture	(−)0.34	−
% forest	−	(−)0.47
DOC	(+)0.50	−
Conductivity	(+)0.34	−

Correlation of trace element concentrations and environmental variables with NMS axes ($r^2 > 0.30$ reported). Direction of the relationship noted in parentheses.

Clams from the Peachtree Creek (urban) site had elevated tissue concentrations of Cd, Cu, and Zn. Concentrations of Cd and Zn in clams from urban sites (1.6–4.0 and 296–468 μg g^{-1} DM) were higher than observed in the Río de la Plata (0.5–1.9 and 118–316 μg g^{-1} DM) and the Paraná River (1.6 and 163 μg g^{-1} DM), which are located in a highly industrialized watershed in Argentina (Bilos et al., 1998; Villar et al., 1999). *Corbicula fluminea* can feed both from the water column and the sediments (Hakenkamp et al., 2001), and their tissue concentrations reflect trace element concentrations in the water and sediments over time rather than simply at the time of sampling. Tissue concentrations are an integrated measure of the trace elements that are bioavailable in the system rather than a single measurement of dissolved trace element concentration.

We predicted that clams downstream of the three CFPPs would have elevated tissue concentrations of trace elements, and these predictions were supported. CFPP discharges in the Chattahoochee River were associated with higher concentrations of As and Se in the tissues of *Corbicula fluminea*. Clams from the Plant Wansley (CFPP) site had the highest concentrations of Zn, As, and Se (Table 3). Of the three CFPP sites, Plant McDonough had the highest concentrations of Cu in clams (Table 3). All three plants burn eastern bituminous coal so the differences among plants are not likely related to the type of coal burned. However, the differences may simply be related to energy generation capacity (Wansley > Yates > McDonough, Table 1) rather than specific combustion processes. Arsenic concentrations in clams from CFPP sites follow the pattern of energy generation capacity, and Se concentrations were lower at McDonough site compared to Plants Wansley and Yates. The mean Se concentrations (9.8 and 13.6 μg g^{-1} DM) in clams from two CFPP sites in the Chattahoochee River were slightly higher than mean Se concentrations (8.7 μg g^{-1} DM) found in clams in the ash basins of a small CFPP in South Carolina (Nagle et al., 2001). However, mean As and Cd concentrations from the two CFPP Chattahoochee sites (Table 3) were lower than As and Cd concentrations (13 and 4 μg g^{-1} DM, respectively) in the South Carolina study (Nagle et al., 2001).

4.3. NMS ordination

NMS ordination of sites based on mean trace element concentrations in clams was consistent with the observation that nine of the 15 sites had significantly higher or lower trace element concentrations than the other six sites (Fig. 1). All three CFPP sites and one urban site (Peachtree Creek) grouped together along the ordination axis correlated with conductivity and DOC. High concentrations of Zn, Cu, and Cd in clam tissues characterized clam tissues from those four sites (Tables 3 and 5). As discussed earlier, forested and agricultural sites had similar percentages of forested land cover in their catchments, and forested catchments were probably used for agriculture a century ago. Thus, it is not surprising that two of the agricultural and two of the forested catchments cluster together in the NMS ordination. Higher concentrations of Hg characterized those agricultural and forested sites (Tables 3 and 5). Anneewakee Creek (WWTP) also clustered with the four forest/agriculture sites, which may reflect the high percentage of forested land cover in its catchment (Table 1). The other two WWTP sites were located closer to downtown Atlanta than Anneewakee Creek, but the % urban cover was similar among the three WWTP sites (Table 1). The six sites (two WWTP, two urban, one forested, and one agricultural) where trace element concentrations exhibited intermediate concentrations (Table 3) were located in the center of the NMS ordination (Fig. 1).

5. Conclusion

Inputs from CFPPs and urbanized tributaries are contributing trace elements to the Chattahoochee River. The tissue concentrations of trace elements in *Corbicula fluminea* indicate the potential for bioavailability to higher trophic levels in these aquatic food webs. In urban rivers receiving effluent from coal-fired power plants, evaluation of the extent of trace element contamination in the food web is warranted. It is imperative to determine the effects on aquatic organisms, which may lead to detrimental impacts on human health through the consumption of fish and other biota from these rivers.

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References

Bednar, A.J., Garbarino, J.R., Ranville, J.F., Wildeman, T.R., 2002. Presence of organoarsenicals used in cotton production in agricultural water and soil of the southern United States. Journal of Agricultural and Food Chemistry 50, 7340–7344.

Bilos, C., Colombo, J.C., Presa, M.J.R., 1998. Trace metals in suspended particles, sediments and Asiatic clams (*Corbicula fluminea*) of the Rio de la Plata Estuary, Argentina. Environmental Pollution 99, 1–11.

Callender, E., Rice, K.C., 2000. The urban environmental gradient: anthropogenic influences on the spatial and temporal distributions of lead and zinc in sediments. Environmental Science & Technology 34, 232–238.

Carpenter, S.R., Caraco, N.F., Correll, D.L., Howarth, R.W., Sharpley, A.N., Smith, V.H., 1998. Nonpoint pollution of surface waters with phosphorus and nitrogen. Ecological Applications 8, 559–568.

Daughton, C.G., Ternes, T.A., 1999. Pharmaceuticals and personal care products in the environment: agents of subtle change? Environmental Health Perspectives 107, 907–938.

Dodson, S.I., Lillie, R.A., Will-Wolf, S., 2005. Land use, water chemistry, aquatic vegetation, zooplankton community structure of shallow lakes. Ecological Applications 15, 1191–1198.

Fitzgerald, W.F., Engstrom, D.R., Mason, R.P., Nater, E.A., 1998. The case for atmospheric mercury contamination in remote areas. Environmental Science & Technology 32, 1–7.

Frick, E.A., Hippe, D.J., Buell, G.R., Couch, C.A., Hopkins, E.H., Wangsness, D.J., Garrett, J.W. 1998. Water quality in the Apalachicola-Chattahoochee-Flint River Basin, Georgia, Alabama, Florida, 1992–1995. USGS Circular Report 1164.

Froelich, P.N., Lesley, P., 2001. Tracing germanium contamination from coal-fired power plants along the Chattahoochee River-Apalachicola River: implications for the toxic metalloids arsenic and selenium. In: Hatcher, K.J. (Ed.), Proceedings of the Georgia Water Resources Conference. Institute of Ecology, University of Georgia, Athens, GA.

Grigal, D.F., Kolka, R.K., Fleck, J.A., Nater, E.A., 2000. Mercury budget of an upland-peatland watershed. Biogeochemistry 50, 95–109.

Hakenkamp, C.C., Ribblett, S.G., Palmer, M.A., Swan, C.M., Reid, J.W., Goodison, M.R., 2001. The impact of an introduced bivalve (*Corbicula fluminea*) on the benthos of a sandy stream. Freshwater Biology 46, 491–501.

Harding, J.S., Benfield, E.F., Bolstad, P.V., Helfman, G.S., Jones, E.B.D., 1998. Stream biodiversity: the ghost of land use past. Proceedings of the National Academy of Sciences of the United States of America 95, 14843–14847.

Hopkins, W.A., Snodgrass, J.W., Roe, J.H., Jackson, B.P., Gariboldi, J.C., Congdon, J.D., 2000. Detrimental effects associated with trace element uptake in lake chubsuckers (*Erimyzon sucetta*) exposed to polluted sediments. Archives of Environmental Contamination and Toxicology 39, 193–199.

Hopkins, W.A., Staub, B.P., Snodgrass, J.W., Taylor, B.E., DeBiase, A.E., Roe, J.H., Jackson, B.P., Congdon, J.D., 2004. Responses of benthic fish exposed to contaminants in outdoor microcosms – examining the ecological relevance of previous laboratory toxicity tests. Aquatic Toxicology 68, 1–12.

Horowitz, A.J., Meybeck, M., Idlafkih, Z., Biger, E., 1999. Variations in trace element geochemistry in the Seine River Basin based on floodplain deposits and bed sediments. Hydrological Processes 13, 1329–1340.

Jackson, B.P., Bertsch, P.M., 2001. Determination of arsenic speciation in poultry wastes by IC-ICP-MS. Environmental Science & Technology 35, 4868–4873.

Jackson, B.P., Allen, P.L.S., Hopkins, W.A., Bertsch, P.M., 2002. Trace element speciation in largemouth bass (*Micropterus salmoides*) from a fly ash settling basin by liquid chromatography-ICP-MS. Analytical and Bioanalytical Chemistry 374, 203–211.

Jackson, B.P., Bertsch, P.M., Cabrera, M.L., Camberato, J.J., Seaman, J.C., Wood, C.W., 2003. Trace element speciation in poultry litter. Journal of Environmental Quality 32, 535–540.

Karvelas, M., Katsoyiannis, A., Samara, C., 2003. Occurrence and fate of heavy metals in the wastewater treatment process. Chemosphere 53, 1201–1210.

King, R.S., Baker, M.E., Whigham, D.F., Weller, D.E., Jordan, T.E., Kazyak, P.F., Hurd, M.K., 2005. Spatial considerations for linking watershed land cover to ecological indicators in streams. Ecological Applications 15, 137–153.

Kolka, R.K., Grigal, D.F., Verry, E.S., Nater, E.A., 1999a. Mercury and organic carbon relationships in streams draining forested upland peatland watersheds. Journal of Environmental Quality 28, 766–775.

Kolka, R.K., Nater, E.A., Grigal, D.F., Verry, E.S., 1999b. Atmospheric inputs of mercury and organic carbon into a forested upland bog watershed. Water, Air and Soil Pollution 113, 273–294.

Kolpin, D.W., Furlong, E.T., Meyer, M.T., Thurman, E.M., Zaugg, S.D., Barber, L.B., Buxton, H.T., 2002. Pharmaceuticals, hormones, other organic wastewater contaminants in US streams, 1999–2000: a national reconnaissance. Environmental Science & Technology 36, 1202–1211.

Lemly, A.D., 2002. Symptoms and implications of selenium toxicity in fish: the Belews Lake case example. Aquatic Toxicology 57, 39–49.

Lenat, D.R., Crawford, J.K., 1994. Effects of land-use on water-quality and aquatic biota of 3 North-Carolina Piedmont streams. Hydrobiologia 294, 185–199.

Lohner, T.W., Reash, R.J., Willet, V.E., Rose, L.A., 2001a. Assessment of tolerant sunfish populations (*Lepomis* sp.) inhabiting selenium-laden coal ash effluents–1. Hematological and population level assessment. Ecotoxicology and Environmental Safety 50, 203–216.

Lohner, T.W., Reash, R.J., Williams, M., 2001b. Assessment of tolerant sunfish populations (*Lepomis* sp.) inhabiting selenium-laden coal ash effluents–2. Tissue biochemistry evaluation. Ecotoxicology and Environmental Safety 50, 217–224.

Mason, R.P., Fitzgerald, W.F., Morel, F.M.M., 1994. The biogeochemical cycling of elemental mercury – anthropogenic influences. Geochimica et Cosmochimica Acta 58, 3191–3198.

Meyer, J.L., Paul, M.J., Taulbee, W.K., 2005. Stream ecosystem function in urbanizing landscapes. Journal of the North American Benthological Society 24, 602–612.

Morel, F.M.M., Kraepiel, A.M.L., Amyot, M., 1998. The chemical cycle and bioaccumulation of mercury. Annual Review of Ecology and Systematics 29, 543–566.

Nagle, R.D., Rowe, C.L., Congdon, J.D., 2001. Accumulation and selective maternal transfer of contaminants in the turtle *Trachemys scripta* associated with coal ash deposition. Archives of Environmental Contamination and Toxicology 40, 531–536.

NRC, 2006. Managing Coal Combustion Residues in Mines. The National Academies Press, Washington, DC.

Paul, M.J., Meyer, J.L., 2001. Streams in the urban landscape. Annual Review of Ecology and Systematics 32, 333–365.

Paul, M.J., Meyer, J.L., Couch, C.A., 2006. Leaf breakdown in streams differing in catchment land use. Freshwater Biology 51, 1684–1695.

Peltier, G.L. 2006. Trace element accumulation in lotic systems: implications for aquatic organisms and human health. PhD thesis, University of Georgia, Athens, GA.

Rose, S., 2002. Comparative major ion geochemistry of Piedmont streams in the Atlanta, Georgia region: possible effects of urbanization. Environmental Geology 42, 102–113.

Rose, S., Crean, M.S., Sheheen, D.K., Ghazi, A.M., 2001. Comparative zinc dynamics in Atlanta metropolitan region stream and street runoff. Environmental Geology 40, 983–992.

Rosi-Marshall, E.J. 2002. Quality of suspended fine particulate matter and its role as a conduit for metals in riverine food webs. PhD thesis, The University of Georgia, Athens, GA.

Rowe, C.L., Hopkins, W.A., Congdon, J.D., 2002. Ecotoxicological implications of aquatic disposal of coal combustion residues in the United States: a review. Environmental Monitoring and Assessment 80, 207–276.

Rowe, C.L., Hopkins, W.A., Zehnder, C., Congdon, J.D., 2001. Metabolic costs incurred by crayfish (*Procambarus acutus*) in a trace element-polluted habitat: further evidence of similar responses among diverse taxonomic groups. Comparative Biochemistry and Physiology C Toxicology & Pharmacology 129, 275–283.

Roy, A.H., Rosemond, A.D., Paul, M.J., Leigh, D.S., Wallace, J.B., 2003. Stream macroinvertebrate response to catchment urbanisation (Georgia, USA). Freshwater Biology 48, 329–346.

Rozan, T.F., Benoit, G., 2001. Mass balance of heavy metals in New Haven Harbor, Connecticut: predominance of nonpoint sources. Limnology and Oceanography 46, 2032–2049.

Ruhl, P.M., Smith, K.E., 1996. Water-quality assessment of the Albemarle-Pamlico drainage basin, North Carolina and Virginia – trace elements in Asiatic clam (*Corbicula fluminea*) soft tissues and redbreast sunfish (*Lepomis auritus*) livers, 1992–93. Open-File Report, 96–334.

Sonesten, L., 2001. Mercury content in roach (*Rutilus rutilus* L.) in circumneutral lakes - effects of catchment area and water chemistry. Environmental Pollution 112, 471–481.

Sonesten, L., 2003. Catchment area composition and water chemistry heavily affects mercury levels in perch (*Perca fluviatilis* L.) in circumneutral lakes. Water, Air and Soil Pollution 144, 117–139.

Villar, C., Stripeikis, J., D'Huicque, L., Tudino, M., Troccoli, O., Bonetto, C., 1999. Cd, Cu and Zn concentrations in sediments and the invasive bivalves *Limnoperna fortunei* and *Corbicula fluminea* at the Rio de la Plata basin, Argentina. Hydrobiologia 416, 41–49.

Walsh, C.J., Roy, A.H., Feminella, J.W., Cottingham, P.D., Groffman, P.M., Morgan, R.P., 2005. The urban stream syndrome: current knowledge and the search for a cure. Journal of the North American Benthological Society 24, 706–723.

Wetzel, R.G., Likens, G.E., 2000. Limnological Analyses, third ed. Springer, New York.