Concentration, Distribution, and Comparison of Selected Trace Elements in Bed Sediment and Fish Tissue in the South Platte River Basin, USA, 1992–1993

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Abstract. During August–November 1992 and August 1993, bed sediment and fish liver were sampled in the South Platte River Basin and analyzed for 45 elements in bed sediment and 19 elements in fish liver. The results for aluminum, arsenic, cadmium, chromium, copper, iron, lead, manganese, selenium, silver, uranium, and zinc are presented here. All 12 trace elements were detected in bed sediment, but not all were detected in fish liver or in all species of fish. A background concentration of trace elements in bed sediment was calculated using the cumulative frequency curves of trace element concentrations at all sites. Arsenic, cadmium, copper, lead, manganese, silver, uranium, and zinc concentrations were greater than background concentrations at sites in mining areas or at sites that have natural sources of these elements. Trace element concentrations in fish liver generally did not follow the same patterns as concentrations in bed sediment, although concentrations of aluminum and cadmium were higher in fish liver collected at mountain sites that had been disturbed by mining. Concentrations of aluminum, arsenic, cadmium, chromium, copper, iron, lead, silver, and zinc increased in bed sediments in urban areas. Iron, silver, and zinc concentrations in fish liver also increased in urban areas. Concentrations of cadmium, copper, silver, and zinc in fish liver increased in the agricultural areas of the basin. Downstream changes in trace element concentrations may be the result of geological changes in addition to changes in land use along the river.

The U.S. Geological Survey's National Water-Quality Assessment (NAWQA) program uses an integrative (physical, chemical, and biological) approach to assess water quality in river basins (Gurtz 1994). One component of this integrative assessment is to examine the occurrence and distribution of selected organochlorine compounds and trace elements in bed sediment and biological tissue samples on a basinwide scale. The

occurrence and distribution of organochlorine compounds in these media were reported earlier in Tate and Heiny (1996). This paper presents the results of the NAWQA basinwide study of the occurrence and distribution of selected trace elements in bed sediment and fish liver in the South Platte River Basin.

Many trace elements such as arsenic, cadmium, copper, lead, and selenium can be toxic to aquatic biota (Eisler 1985, 1988a, 1988b; Jenkins 1981). Trace element concentrations in sediment are at least three orders of magnitude greater than the same elements in aqueous phases in part because fine-grained sediment acts as a transport agent for trace elements that coat particle surfaces or are adsorbed (Horowitz 1991). Trace elements are ingested with particulate matter (streambed sediment or suspended sediment in the water column) by benthic organisms and can then accumulate and move through the food chain. Analysis of trace element concentrations in the sediment aids in the interpretation of water quality and analysis of trace elements in fish tissue from the same locations as the bed sediment samples can indicate the bioaccumulation of trace elements by different species.

The objectives of this paper are to examine the concentration and distribution of selected trace elements in bed sediment and fish liver, to compare trace element concentrations in different fish species, to examine the relation of trace elements in bed sediment to geology, and to determine the relation of trace elements in bed sediment and fish liver to land use in the South Platte River Basin.

Description of Study Area

The South Platte River (Figure 1A) drains a 62,900 km² area, 79% of which lies in Colorado, 15% in Nebraska, and 6% in Wyoming (Dennehy *et al.* 1993). From its origin in the mountains of central Colorado, the South Platte River flows north along the Front Range Urban Corridor (Figure 1A) and then northeast across the Great Plains to the confluence with the North Platte River at North Platte, Nebraska.

The 23 sampling sites were categorized into 4 major rock groups that might affect the trace element concentrations detected in bed sediment and fish liver (Table 1, Figure 1B): Precambrian (PC), Cretaceous (K), and Tertiary (TD-Denver Formation and Dawson Arkose, TO-Ogallala Formation) rock groups were defined.

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Fig. 1. The South Platte River Basin. A, Location of the basin, hydrography, physiography, and site locations. B, Geology of the basin

	Site	Year				
Site Name	Number	Sample (Figure 1) Collected	Land use/ Land Cover	Elevation (meters)	Geology	Fish Species Collected
South Platte River below Chatfield Reservoir at Littleton, CO	1	1992	Built-up	1,643	Tertiary sedimentary rocks, TD	White sucker
Bear Creek at mouth at Sheridan, CO	2	1992	Urban	1,614	Tertiary sedimentary rocks, TD	White sucker
Clear Creek at Lawson, CO	3	1992	Built-up/Mining 2,475		Precambrian igneous and meta- morphic rocks, PC	Brown trout
Clear Creek at Golden, CO	$\overline{4}$	1993	Built-up/Mining 1,736		Precambrian igneous and meta- morphic rocks, PC	Brown trout
Cherry Creek at Denver, CO	5	1993	Urban	1,577	Tertiary sedimentary rocks, TD	None
South Platte River at Denver, CO	6	1993	Urban	1,576	Tertiary sedimentary rocks, TD	White sucker, common carp
Sand Creek near Denver, CO	7	1992	Urban	1,558	Tertiary sedimentary rocks, TD	None
South Platte River at Henderson, CO	8 ^a	1992	Mixed	1,525	Tertiary sedimentary rocks, TD	Common carp
North St. Vrain Creek near Allenspark, CO	9	1992	Forest	2,527	Precambrian igneous and meta- morphic rocks, PC	Brown trout
St. Vrain Creek at mouth near 10 Platteville, CO		1993	Mixed	1,445	Cretaceous sedimentary rocks, K Common carp	
Cache la Poudre River at mouth of canyon near Ft. Collins, CO	11 ^b	1992	Forest	1,591	Precambrian igneous and meta- morphic rocks, PC	Brown trout
Cache la Poudre River near Greeley, CO	12 ^a	1992	Mixed	1,405	Cretaceous sedimentary rocks, K White sucker, common carp	
Lonetree Creek at Carr, CO	13	1993	Rangeland	1,731	Cretaceous sedimentary rocks, K None	
Lonetree Creek near Greeley, 14 _{CO}		1993	Agriculture	1,411	Cretaceous sedimentary rocks, K None	
South Platte River at Kersey, 15 ^a CO		1992	Mixed	1,394	Cretaceous sedimentary rocks, K White sucker, common carp	
Crow Creek below North Fork near Silver Crown, WY	16	1992	Rangeland	1,943	Tertiary sedimentary rocks, TO	White sucker
South Platte River at Wel- dona, CO	17	1992	Agriculture	1,313	Cretaceous sedimentary rocks, K White sucker, common carp	
South Platte River at Coopers 18 Bridge near Balzac, CO			1992/1993 Agriculture	1,247	Cretaceous sedimentary rocks, K White sucker, common carp	
South Platte River at Jules- burg, CO	19	1992	Agriculture	1,051	Tertiary sedimentary rocks, TO	White sucker
South Platte River at North Platte, NE	20	1992	Agriculture	849	Tertiary sedimentary rocks, TO	White sucker, common carp
Milton Reservoir, CO	21	1992	Agriculture	1,463	Cretaceous sedimentary rocks, K Common carp	
Jackson Reservoir, CO	22	1992	Agriculture	1,353	Cretaceous sedimentary rocks, K Common carp	
Ft. Morgan Canal, CO	23	1992	Agriculture	1,327	Cretaceous sedimentary rocks, K None	

Table 1. Sampling sites, selected site characteristics, and fish species collected. TD = Tertiary Dawson Formation; PC = Precambrian; K = C retaceous; $TO = T$ ertiary Ogallala Formation

^a Field duplicate taken for bed sediment

^b Field duplicate taken for bed sediment and fish tissue

Land use/land cover within the South Platte River Basin is 41% rangeland, 37% agricultural, 16% forest, 3% urban or built-up, and 3% other (Fegeas *et al.* 1983). Rangeland covers the Great Plains Province away from the river courses. Rangeland has few sources of elements other than sediment input to the stream by bank erosion or aeolian deposition. Agricultural land is distributed throughout the Great Plains Province along river courses (Dennehy *et al.* 1993). Forests are in a north-south band in the Front Range. Interspersed within the forest are built-up areas (low-density population), mined areas, and an extensive network of gravel roads. Urban (high-density population) and built-up areas primarily occur along the Front Range Urban Corridor. Mixed land use describes sites that are in agricultural areas but are affected by upstream urban sources.

Materials and Methods

Sample Collection

Twenty-three sites were sampled throughout the basin (Table 1, Figure 1) during low flow conditions of August to November 1992 and August 1993. Bed sediment and fish samples were collected within the same 100- to 300-m reach at each site. At five sites, fish could not be collected in adequate numbers for element analysis (Table 1).

Bed sediments from stream channels were collected from undisturbed, continuously wetted, depositional zones. The collected streambed sediment was composited and sieved in the field, and the $<$ 63-µ-size fraction was retained for analysis of trace elements (Shelton and Capel 1994). Bed sediment was collected from three points within a reservoir (near inflow, near outflow, and at deepest point) by lowering an Ekman sampler over the side of a boat, collecting a grab of bottom material, and taking a subsample of the dredged material. The subsamples were composited and treated in the same manner as streambed sediment samples. Canals were sampled by lowering the Ekman sampler to the canal bottom and taking a subsample of the dredged material at five locations along the canal reach. The subsamples were composited and treated in the same manner as streambed sediment samples.

Fish were collected by electrofishing as described in Crawford and Luoma (1993). Species collected include brown trout (*Salmo trutta*), white sucker (*Catostomus commersoni*), and common carp (*Cyprinus carpio*) (Table 1). At each site, the livers were removed from five to nine fish, composited, frozen, and analyzed for elements. A composite fish liver sample consisted of a minimum of 10 g.

Sample Preparation and Analysis

In accordance with NAWQA protocols, bed sediment samples were analyzed for their total element concentrations by the U.S. Geological Survey Analytical Chemistry Services Group (ACSG), using total digestion procedures described in Arbogast (1990). Bed sediment samples were initially dried at ambient temperature and then ground to $<$ 150 μ using a Bico vertical grinder equipped with 6-in ceramic plates. A representative subsample $(1-3 \text{ oz})$ was then obtained using a riffle splitter, and the subsample was mixed for 20 min. Several analytical techniques were used to determine elements in bed sediment. Aluminum, chromium, copper, iron, lead, manganese, and zinc were determined by inductively coupled plasma-atomic absorption spectrophotometry (ICP-AES); cadmium and silver by flame atomic absorption spectrophotometry (flame AAS); arsenic and selenium by continuous flow hydride generation-atomic absorption spectrometry (HG-AAS); and uranium by delayed neutron activation analyses (DNAA).

In the ICP-AES decomposition procedures (Briggs 1990), a 0.2-g sample or standard is digested in a 30-ml Teflon bomb at 100°C using a combination of concentrated reagent-grade hydrochloric (3 ml), hydrofluoric (2 ml), and nitric (2 ml) acids, and concentrated double-distilled perchloric (1 ml) acid. A 100-µl aliquot of a 500-µg/ml lutetium internal standard also is added at the start of the decomposition. The solution is taken to dryness, and the residue is redissolved with 1 ml of aqua regia. A 1% nitric acid solution is added until a final mass of 10 g is obtained.

The digestion procedure for flame AAS is a modification of the method described by O'Leary and Viets (1986). In this procedure, a 0.5-g sample is digested with 5 ml of concentrated reagent-grade hydrofluoric acid and then taken to dryness. The residue is treated with concentrated reagent-grade hydrochloric acid (10 ml) and 30% hydrogen peroxide (1 ml) and heated until hydrogen peroxide and chlorine gases evolve. The mixture and a 4-ml ascorbic acid-potassium iodide solution (30–15% weight per volume) rinse are transferred to test tubes and mixed. After 20 min, 3 ml of methyl butyl ketone is added to the tubes, the tubes are capped, shaken for 5 min, and centrifuged. The organic layer is analyzed by flame AAS.

The digestion procedure for analyses by HG-AAS is described in Welsch *et al.* (1990). A 0.25-g sample is weighed into a Teflon bomb and moistened with 1 mL 1% reagent-grade nitric acid. A mixture of reagent-grade nitric (9 ml) and hydrofluoric (10 ml) acids and double-distilled perchloric (6 ml) acid is added and the sample is heated to 105–110°C until the solution volume is reduced to 2 ml. A 25-ml aliquot of 50% (volume per volume) hydrochloric acid solution is added, and the digestate is heated for 30 min. The solution is transferred to polyethylene bottles and distilled water is added to make 54 g. The solution then is analyzed by HG-AAS.

The DNAA procedure is described in McKown and Knight (1990). A 2-dram polyvial is filled with 5 to 10 g of sample. Samples are briefly irradiated in a constant flux of neutrons. The samples are transported from the reactor to the spectrum analyzer where delayed neutrons emanating from the sample are counted. Using appropriate calibration standards, the raw counting data are converted to uranium concentration values.

Elements in fish liver were determined by the U.S. Geological Survey's National Water-Quality Laboratory (NWQL) using a method similar to the USEPA method 200.3 described by McDaniel (1992). Fish livers were dried at 65°C and samples were then digested in concentrated reagent-grade nitric acid (85°C), oxidized by careful additions of hydrogen peroxide (30% solution), evaporated to incipient dryness, reconstituted with 5% nitric acid, filtered (Whatman #41), and diluted to 100 ml. The acid digestate tissue samples were analyzed by inductively coupled plasma-mass spectrophotometry (ICP-MS, Faires 1993) for concentrations of aluminum, chromium, copper, iron, manganese, and zinc, and ICP-AES (Fishman and Friedman 1989) for concentrations of arsenic, cadmium, lead, selenium, silver, and uranium.

Quality control procedures for elements in bed sediment included analyses of a reference material GXR-2 (enriched soil) and an analytical duplicate for each batch of samples analyzed. There was less than 10% difference between lab duplicates for the 21 sets of lab duplicates analyzed. With the exception of aluminum, ACSG values for elements in GXR-2 reference material were within quality assurance guidelines of ± 3 standard deviations (SD). The percent difference between field duplicates of bed sediments was less than 15% except for manganese (15–35%).

Quality control procedures for elements in fish liver included analyses of blank samples and two standard reference materials (SRM), National Institute of Standards and Technology (NIST) oyster tissue (SRM 1566A), and NIST bovine liver (SRM 1577A), with each batch of fish liver samples. Tissue blank samples that followed the same preparation procedure as all other samples had concentrations much lower than the detection limits. With the exception of aluminum in NIST oyster tissue, NWQL values were within ± 3 SD of NIST certified values. The lower recovery of aluminum in NIST oyster tissue is attributed to the presence of sediment in the standard reference material that is not decomposed by the NWQL acid-extraction procedure (Hoffman 1996). Low recoveries for iron by the NWQL method also were attributed to the sediment contribution. The percentage difference between the field duplicates of liver from brown trout was less than 40% except for zinc (45%). The high percent differences may occur because these are not true duplicates in that there was a month between collections due to a lack of enough fish for duplicates at the initial time of sampling.

Data Analysis

Although 45 major and trace elements in bed sediment samples were quantified, many element concentrations were near or less than the method detection limits or indicated little variation across the basin. Element concentrations in fish liver were reported for 19 elements, with the number of detectable elements varying by site and fish species. Twelve trace elements were selected for discussion on the basis of concentration variability, distribution throughout the basin, and detection in bed sediment and fish liver. A complete list of all elements and their concentrations in bed sediment and fish liver at these sites is in the U.S. Geological Survey's National Water Information System (NWIS) data base. Concentrations (including duplicates) are listed in the tables

Table 2. Background concentrations for selected trace elements in soils and bed sediment. All values are in μ g/g dry weight unless noted as percent $(%)$; 23 bed-sediment samples were analyzed and used to compute background concentrations and geometric means for this study; $\frac{1}{1}$ = not available

Element	Jenkins $(1981)^{a}$	Salomans and Forstner $(1984)^{a}$	Shacklette and Boerngen $(1984)^{a}$	Severson and Tourtelot $(1994)^{b}$	This Study Background Concentration	This Study Geometric Mean Concentration	This Study Range of Concentration
Aluminum (%)			5.80	18.6	7.20	6.30	$5.10 - 7.40$
Arsenic	$1.80 - 6.60$	_	5.50	22.0	7.80	5.70	$2.80 - 31$
Cadmium	0.06	0.62			3.30	0.77	$0.1 - 22$
Chromium	100	84.0	41.0	130	60.0	49	$33 - 71$
Copper	20.0	25.8	21.0	74.0	104	46	18–480
Iron $(\%)$		3.20	2.10	9.90	4.90	3.20	$2.10 - 6.80$
Lead	$10.0 - 40.0$	29.2	17.0	130	100	44	$19 - 270$
Manganese		760	380	850	1260	880	410-6700
Selenium	0.20	_	0.23	_	2.88	1.50	$0.30 - 3.80$
Silver					1.20	0.61	$0.20 - 5.7$
Uranium			2.50		9.00	8.60	$5.50 - 25$
Zinc		59.8	55.0	190	454	190	82-3700

^a Background concentrations established for Western U.S. soils

^b Geochemical data for soils in the Front Range Urban Corridor, Colorado

in Appendixes A and B (at the end of this article) for the selected trace elements under discussion. Geometric mean trace element concentrations were calculated using a value of one-half the method detection limit for fish liver samples with concentrations below the method detection limit.

To identify elevated trace element concentrations, a background concentration for the study area is required. One approach is comparison of element concentrations in soil samples from the Western United States (Jenkins 1981; Salomans and Forstner 1984; Shacklette and Boerngen 1984; Table 2). A basin-specific background concentration for each trace element was determined by plotting cumulative frequency curves of trace element concentrations for the 23 samples (after Velz 1984). Aluminum had a monotonic cumulative frequency curve (Figure 2B) and the background concentration was taken as the concentration at the 95th percentile. All other trace elements had bimodal cumulative frequency curves, and the curve for zinc is shown as an example in Figure 2A. For these distributions, the concentration at which the line reaches maximum curvature (changes slope) was taken as the background concentration. Element concentrations greater than the background concentration are elevated.

Results

Element Occurrence and Relative Concentration

Arsenic, cadmium, chromium, copper, iron, lead, manganese, selenium, and zinc in bed sediment all exceeded background concentrations (Figure 3, Table 2) at two to three sites. The background concentration for aluminum in bed sediment was exceeded only at one site (Figure 3, Table 2), whereas the background concentrations for silver and uranium (Figure 3, Table 2) were exceeded at six and five sites, respectively. Cadmium, chromium, copper, iron, manganese, selenium, silver, and zinc were detected in fish liver at all sites (Figure 3).

With the exceptions of cadmium, copper, selenium, silver, and zinc, trace element concentrations are at least an order of magnitude higher in bed sediment than in fish liver (Figure 3). Selenium concentrations are higher in fish liver than bed sediment by an order of magnitude (Figure 3), and cadmium, copper, silver, and zinc have similar concentrations in bed

Fig. 2. Sample cumulative frequency curves used to determine background element concentrations. (A) Bimodal cumulative frequency curve for zinc, with background concentration taken where the slope changes most dramatically (the 90th percentile in this example). (B) Monotonic cumulative frequency curve for aluminum, with background concentration taken at the 95th percentile

sediment and fish liver (Figure 3). Aluminum and iron concentrations are measured in percent in bed sediment, therefore concentrations of these elements are several orders of magnitude higher in bed sediment than fish tissue.

There is an order of magnitude difference between the highest and lowest concentrations of arsenic, copper, lead, manganese, selenium, silver, and uranium in bed sediment (Figure 3, Table 2). Of these, copper, silver, and zinc in fish liver display at least an order of magnitude difference between the highest and lowest concentrations (Figure 3, Table 3). There are two orders of magnitude difference between the highest and lowest concentrations of cadmium in bed sediment and fish liver (Figure 3, Tables 2, 3), zinc in bed sediment (Figure 3, Table 2), and aluminum in fish liver (Figure 3, Table 3).

Comparison of geometric mean concentrations of trace elements in bed sediment and fish liver indicates variability between media analyzed, as well as within fish species. Because of differences in media analyzed, this discussion will include only white sucker and common carp that were collected at the same sites (6, 12, 15, 17, 18, and 20; Table 1). Nondetection of aluminum, arsenic, chromium, lead, and uranium in white sucker or common carp at some of these sites also excludes these elements from comparisons (Table 3). Concentrations of cadmium and zinc are an order of magnitude higher in common carp than white sucker, whereas concentrations of copper, iron, manganese, selenium, and silver are similar in white sucker and common carp (Figure 3).

Distribution of Elements

Selected trace element concentrations in bed sediment and fish liver for sampling sites on the mainstem of the South Platte River were plotted in downstream order beginning with site 1 (Table 1), which is about 150 km downstream from the South Platte River headwaters (the confluence of the North and South Forks of the South Platte River) and about 25 km upstream from site 6 in Denver (Table 1, Figures 4, 5). Aluminum, arsenic, chromium, and lead concentrations in bed sediment increase to a maximum at, or just downstream from, the Denver urban area (about 190 km; Figure 4) and gradually decrease downstream through mixed and agricultural land use areas (Figure 4).

Concentrations of cadmium, copper, iron, silver, and zinc in bed sediment also increase to a maximum at, or just downstream from, Denver (about 190 km; Figure 5), then gradually decrease downstream. Concentrations of cadmium, copper, and zinc in fish liver exhibit an opposite pattern with lower concentrations in the urban area followed by increasing concentrations downstream (Figure 5). Iron concentrations in fish liver were highest in Denver (at 190 km; Figure 5), and remained relatively stable downstream of the urban area. Concentrations of silver in fish liver increased dramatically downstream of the urban area (from about 200 to 400 km) and then decreased across the plains (Figure 5).

Effect of Geology on Trace Element Concentrations

Precambrian igneous and metamorphic rocks outcrop in the Front Range. The Precambrian rocks are not easily eroded; however, some minerals are more readily soluble than others and bed sediment samples from those source areas might be enriched in aluminum, iron, and uranium (Sharp and Aamodt 1976). Tertiary volcanic rocks intrude into the Precambrian in an area known as the Mineral Belt and encompass all of the upper Clear Creek watershed (including sites 3 and 4, Figure 1).

Cretaceous sedimentary rocks outcrop along the eastern slope of the Front Range. Cretaceous rocks vary from sandstones to shales and siltstones, are more easily eroded than the igneous and metamorphic rocks, and are enriched in iron, selenium, and uranium (Nunes 1978; Trexler 1978; Schultz *et al.* 1980).

Tertiary sedimentary rocks outcrop in the Great Plains Province. These rocks are easily eroded and contain easily solubilized minerals, such as iron, uranium, and manganese (Nunes 1978; Trexler 1978).

Trace element concentrations in bed sediment and fish liver were averaged by rock group in the basin (Table 4). Geometric mean concentrations of aluminum and selenium were highest in bed sediment in rock group TD, whereas concentrations of arsenic, cadmium, copper, iron, lead, manganese, silver, uranium, and zinc in rock group TO generally are two to four times the concentrations in the other rock groups (Table 4). Results of a Kruskal-Wallis test indicate significant statistical differences in concentration among the four rock groups for aluminum, chromium, iron, and uranium ($p < 0.05$). Limited sample sizes exclude the use of statistical tests on element concentrations in fish liver compared to rock groups.

Arsenic in rock group TO and selenium in rock group TD are the only instances where concentrations in both white sucker and common carp are highest compared to other rock groups (Table 4). For other elements, correlations between rock group and concentration in different fish species are difficult to determine. Many factors might account for variations in trace element concentration in fish liver, including geochemistry, surface-water chemistry, species, and laboratory methods. Elements with concentrations greater in fish liver than in bed sediment are marked with an asterisk (*) in Table 4 and are indicative of bioaccumulation in these fish species in the South Platte River Basin. Other analytical procedures such as the U.S. Environmental Protection Agency (USEPA) method 200.1 or the U.S. Geological Survey In-Bottle digestion procedure for whole water-recoverable elements may be more useful for determining true bioavailability of trace elements (G. L. Hoffman, National Water Quality Laboratory, written commun., 1996).

Discussion

Comparison of Trace Element Concentrations to Established Guidelines

At this time, no State or Federal guidelines exist for concentrations of trace elements in bed sediment, and the authors do not know of any established guidelines for trace element concentrations in fish liver. However, the Ontario (Canada) Ministry of Environment and Energy has developed Provincial Sediment Quality Guidelines (PSQG) for trace elements considered most toxic to aquatic life (Persaud *et al.* 1993). Background trace element concentrations for bed sediment in the South Platte River Basin are all greater than the PSQG lowest effect level

Fig. 3. Concentrations of elements in bed sediment and fish liver for all sites in the South Platte River Basin. Sites are grouped by location and type; mountains, plains tributary, plains mainstem, and reservoir and canal. See Table 1 and Figure 1 for names and locations of sites. The solid line labeled background is the background element concentration for bed sediment for the South Platte River Basin as determined in this study. Stars indicate sites where no fish were collected. Blanks indicate the element was not detected in fish liver at that site

Fig. 3. *Continued*

Table 3. Geometric means, maximum, and minimum trace element concentrations for fish liver samples in the South Platte River Basin. Concentrations are in $\mu g/g$. *n* = number of samples; geo. mean = geometric mean concentration; nd = nondetection values below reporting limit

	Brown Trout $(n = 4)$		White Sucker $(n = 10)$		Common Carp $(n = 10)$	
Element	Geo. Mean	(Range)	Geo. Mean	(Range)	Geo. Mean	(Range)
Aluminum	4.39	$(<1.0 - 32.45)$	0.60	$(<1.0-2.91)$	0.99	$(1.18 - 5.06)$
Arsenic	0.40	$(<0.1 - 0.68)$	0.34	$(<0.1 - 0.76)$	0.27	$(<0.1 - 0.87)$
Cadmium	3.88	$(0.30 - 22.7)$	0.26	$(0.26 - 0.49)$	1.79	$(0.48 - 19.1)$
Chromium	0.67	$(0.55 - 0.90)$	0.51	$(<0.1 - 0.71)$	0.32	$(<0.1 - 0.57)$
Copper	194	$(46.0 - 318)$	82.6	$(39.7 - 126)$	73.3	$(10.9 - 166)$
Iron	445	$(300 - 777)$	379	$(125 - 655)$	358	$(160 - 912)$
Lead	nd	(nd)	nd	(nd)	0.25	$(<0.1 - 0.58)$
Manganese	5.20	$(3.21 - 8.61)$	7.64	$(5.26 - 10.4)$	5.02	$(2.77 - 7.29)$
Selenium	17.9	$(10.1 - 31.4)$	6.29	$(4.40 - 10.4)$	8.13	$(3.08 - 16.0)$
Silver	2.11	$(1.06 - 3.62)$	1.04	$(0.43 - 3.29)$	1.19	$(0.26 - 2.85)$
Uranium	nd	(nd)	0.16	$(<0.1 - 0.48)$	nd	(nd)
Zinc	93.9	$(72.5 - 130)$	101	$(60.9 - 139)$	628	$(320 - 1321)$

(LEL), which is defined as a level of contamination that has no effect on the majority of the sediment-dwelling organisms and is considered clean to marginally polluted in the PSQG (Table 5). Several elements exceed the severe effect level (SEL), which is defined in the PSQG as heavily polluted sediment that is likely to affect the health of sediment-dwelling organisms. According to the PSQG, sites with concentrations greater than the SEL are considered highly contaminated and require further testing and monitoring. Thus, sites 3 and 4, which are on Clear Creek and are affected by acid mine drainage (Lehnertz 1991), would require further monitoring.

Comparison of Bed Sediment Trace Element Concentrations to Background Concentrations

Many trace elements in bed sediment in the South Platte River occur at much higher concentrations than the suggested back-

Fig. 4. Concentrations of elements in bed sediment along the mainstem of the South Platte River, from a site downstream from Chatfield Reservoir, Colorado, at about 150 km river distance to a site at North Platte, Nebraska, at about 700 km river distance. Land use varies along the mainstem from urban to mixed urban and agriculture, and then to agriculture

ground concentrations for Western soils (Table 2). In contrast, the Front Range Urban Corridor background concentrations (Table 2) for soils generally are higher than bed sediment concentrations in the South Platte River Basin.

Soils data are analyzed on the \leq 2-mm-size fraction, whereas bed sediment samples from this study are analyzed on the $<$ 63-µ-size fraction. The large surface area of small sedimentary particles will tend to adsorb some soluble elements to a greater extent than larger particles (Horowitz 1991). Smaller particles can become suspended in the water column more easily than larger particles, which will facilitate their ability to scavenge soluble elements in the water column. Also, geochemical processes are different on land than in the stream channel, such as bacterial-mediated processes, iron reduction, ion substitution, and chelation, creating different suites of elements in the wetted environment. For these reasons, background concentrations in soils used for data analysis and comparisons to concentrations of elements in bed sediment need to be carefully chosen.

Comparison of Trace Element Concentrations with Other Studies

The element concentrations in bed sediment in this study are generally higher than the concentrations found in an environmental contaminants study of the agricultural area in the South Platte River by DeWeese *et al.* (1993). DeWeese *et al.* (1993) used the entire bed sediment sample for analysis (in comparison to the ≤ 63 -µ-size fraction of this study), which would tend to dilute the concentrations of elements.

Steele and Doerfer (1983) evaluated selected trace element concentrations in bed sediment in the Denver area and determined that trace element concentrations increased through the urban area and decreased downstream from Denver. Similar trends occurred in this study for aluminum, arsenic, cadmium, chromium, copper, iron, lead, silver, and zinc (Figures 3, 4, 5).

Caution should be used when comparing results of different fish tissue studies because of differences in detection limits, lab methodologies, and types of tissue analyzed (fish livers compared to whole fish). Because the liver concentrates cadmium, copper, lead, and zinc (Weatherly *et al.* 1980; Wachs 1985) compared to muscle (Crawford and Luoma 1993), comparisons of results from other studies that analyzed different fish tissue to results from this study of the South Platte River Basin should not be made.

Relation of Trace Elements in Bed Sediment and Fish Liver to Land Use

Geology of the sediment source areas is an important influence on trace element concentrations in bed sediment in the South Platte River Basin because the total digestion method was used. However, elevated concentrations of some trace elements can be related to land use by observing patterns of downstream increases in concentration within a rock group. Trace elements in bed sediment that might be related to urban land use include aluminum, arsenic, cadmium, chromium, copper, iron, lead, silver, and zinc (Figures 4, 5), because concentrations increase after the river flows through the Denver urban area (in TD rock group). In addition, other studies (Severson and Tourtelot 1994) report increases in concentration of arsenic, copper, lead, silver, and zinc in the Denver area.

Another source of increased trace element concentrations in bed sediment and fish tissue are mining practices in the headwaters of tributaries to the South Platte River. Comparison of results at sites 3 and 4 in mountain sites with mining influence to sites 9 and 11 in mountain sites without mining influence (all sites in rock group PC) indicate higher concentrations of cadmium, copper, lead, manganese, silver, and zinc at the mined sites (Figures 3, 4, 5). In contrast, concentrations of chromium, iron, selenium, and uranium are higher in bed sediment at the sites not influenced by mining (Figures 3, 4, 5), indicating a naturally high concentration of these elements in the PC rock group.

Increasing concentrations of aluminum, cadmium, copper, silver, and zinc in fish liver in agricultural land use areas

- Bed sediment -White sucker - Common carp

Fig. 5. Concentrations of elements in bed sediment and fish liver along the mainstem of the South Platte River from a site downstream from Chatfield Reservoir, Colorado, at about 150 km river distance to a site at North Platte, Nebraska, at about 700 km river distance. Land use varies along the mainstem from urban to mixed urban and agriculture, and then to agriculture

downstream from Denver (greater than 200 km; Figure 5) may be influenced by a change from rock group K to rock group TO (Table 4) or by changing land use. Aluminum and cadmium concentrations are high in brown trout liver in the mined mountain sites (3 and 4, Figure 3), whereas copper, iron, selenium, and silver occur at higher concentrations in the non-mined mountainous areas (sites 9 and 11, Figures 4, 5).

Summary

Trace element concentrations need to be measured in bed sediment and fish liver for a more complete picture of the relation between bedrock geology, element composition in bed sediment, bioaccumulation of elements in fish liver, and land use. Trace elements are naturally present in all bed sediment samples, but they do not accumulate at the same rates in different fish species. Different patterns of trace element concentration occur between bed sediment and fish liver; thus, measuring concentrations in bed sediment alone will not determine which trace elements bioaccumulate in fish liver. If trace element concentrations are measured only in fish liver, then the natural distribution of trace elements in the basin will not be known.

Because geology influences trace element concentration and distribution in bed sediment in the South Platte River Basin,

					\mathbf{r}						
	PC		K			TD			TO		
Element	BS $(n = 10)$	ВT $(n = 4)$	BS $(n = 3)$	WS $(n = 4)$	CC $(n = 7)$	BS $(n = 6)$	WS $(n = 3)$	CC $(n = 2)$	BS $(n = 4)$	WS $(n = 3)$	CC $(n = 1)$
Aluminum	6.32	4.39	5.54		1.10	6.82		1.20	6.31	0.90	
Arsenic	5.72	0.32	4.69	0.20	0.20	5.50	0.20	0.10	10.2	0.60	0.90
Cadmium	0.59	$3.89*$	0.27	0.30	$1.60*$	1.01	0.20	0.70	2.07	0.20	$11.0*$
Chromium	50.5	0.67	33.0	0.60	0.40	48.9	0.50		58.5	0.50	
Copper	34.9	194*	27.2	$103*$	$73.0*$	57.6	$89.0*$	$62.0*$	94.8	58.0	$109*$
Iron	2.85	445	2.26	478	398	3.42	324	296	5.38	324	253
Lead	33.7		25.2		0.20	64.4		0.30	74.5		
Manganese	712	5.2	792	8.20	5.20	882	8.20	4.80	1573	6.50	4.50
Selenium	1.43	$17.9*$	1.00	$5.50*$	$8.00*$	2.26	$7.90*$	8.70*	1.01	$6.00*$	$7.80*$
Silver	0.57	$2.11*$	0.23	$1.50*$	$1.10*$	0.84	$1.10*$	$1.30*$	0.99	0.60	$1.50*$
Uranium	6.82		7.20	0.10		7.86			20.2		
Zinc	138	93.9	90.5	118*	748*	230	102	454*	575	82.0	354

Table 4. Geometric mean concentrations of elements in bed sediment and fish liver by rock group. Concentrations are in μ g/g, except aluminum and iron in bed sediment are in percent. PC = Precambrian; K = Cretaceous; TD = Tertiary Dawson Arkose; TO = Tertiary Ogallala Formation; BS = bed sediment; $BT =$ brown trout; $WS =$ white sucker; $CC =$ common carp; n = number of samples; $\frac{1}{100}$ = not detected

* Indicates concentrations in fish liver that are greater than concentrations in bed sediment

Table 5. Comparisons between Provincial Sediment Quality Guidelines (PSQG) and element concentrations determined in bed sediment in this study. Concentrations are in µg/g except for iron, which is in percent. 23 sites were sampled in this study; see Table 1 for site names and Figure 1 for site locations

Element	Lowest Effect Level (LEL) ^a	Severe Effect Level $(SEL)^b$	Established Background Concentration ^c	Sites with Concentration Above SEL
Arsenic	6.0	33	7.80	0
Cadmium	0.6	9.5	3.30	3, 4
Chromium	26	110	60.0	0
Copper	16	110	104	3, 4, 8
Iron	2.12	4.38	4.90	2, 3, 4, 9
Lead	31	250	100	4
Manganese	460	1,100	1,260	3, 4, 15, 17, 18, 20
Zinc	120	820	454	3.4

^a Marginally contaminated sediments (Persaud et al. 1993)

^b Highly contaminated sediments (Persaud et al. 1993)

^c This study

patterns of trace element concentration with respect to land use must be carefully differentiated. A different method of bed sediment analysis, such as the mild acid solubilization procedure USEPA method 200.1 or the U.S. Geological Survey in-bottle digestion procedure for whole water recoverable elements, would be more useful for determining elements that have been added to the sediments and their bioavailability. Observed patterns of increased concentrations of aluminum, arsenic, cadmium, chromium, copper, iron, lead, silver, and zinc in bed sediment in the Denver urban area, with no change in geology, are related to land use. Elevated concentrations of cadmium, copper, lead, manganese, silver, and zinc in bed sediment in some tributaries in the mountains are caused by mining practices. However, elevated concentrations of chromium, iron, selenium, and uranium in bed sediment in nonmined mountain tributaries appear to be natural phenomena unrelated to land use effects. It is much harder to relate trace element concentrations in fish liver to land use. Some elements occur at higher concentrations in fish liver from the mined sites (aluminum and cadmium), but other elements occur at higher concentrations in fish liver from the non-mined sites (chromium, copper, iron, selenium, and silver), and these patterns differ from those observed for bed sediment. Increasing concentrations of cadmium, silver, and zinc in fish liver in agricultural areas may relate to geology or land use. The concentrations of trace elements in fish liver are related to concentrations of elements in ingested food, water, and sediment, along with the rates of bioaccumulation and depuration, and these factors differ for different elements and fish species.

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Appendix A. Trace element concentrations (µg/g, dry weight, unless noted as percent) in bed sediment, percent carbon, and size fraction of bed sediment in the South Platte River Basin. [See Figure 1 and Table 1 for site locations and names.]

Site	Aluminum (%)	Arsenic	Cadmium	Chromium	Copper	Iron $(\%)$	Lead	Manganese	Selenium	Silver
1	6.1	4.8	0.2	$42\,$	24	2.2	28	910	0.9	0.2
2	6.9	5.2	0.7	50	45	4.4	58	860	2.0	0.3
3	7.0	6.0	21	45	250	5.0	170	6,700	1.1	2.8
4	6.4	31	$22\,$	70	480	6.0	270	3,900	0.7	5.7
5	6.7	6.1	1.5	51	82	3.3	100	690	2.8	0.9
6	6.7	5.6	2.4	59	80	3.8	98	1,000	2.8	1.7
7	7.4	4.5	0.6	38	47	3.6	45	870	3.8	1.3
8	7.2	7.2	3.5	57	110	3.7	100	1,000	2.5	3.0
8	6.9	6.5	2.7	51	91	3.3	87	720	1.8	2.5
9	5.2	3.3	0.2	54	24	6.8	28	330	1.5	0.3
10	6.5	6.5	0.4	60	26	3.0	28	580	1.0	0.6
11	6.8	3.6	0.2	69	28	4.1	24	710	0.9	0.2
11	7.0	2.8	0.3	71	28	4.1	$27\,$	460	0.9	0.2
12	6.7	7.9	0.1	59	29	3.0	24	410	1.2	0.5
13	6.1	6.9	0.4	39	18	2.7	24	690	1.2	0.2
14	6.5	6.6	0.4	48	18	2.7	19	480	0.4	0.2
15	6.3	6.7	0.7	52	49	3.0	41	1,300	1.9	0.7
15	6.3	6.0	1.1	53	48	3.0	39	1,100	1.8	0.7
16	6.3	5.2	0.1	33	30	2.5	28	550	0.3	0.2
17	6.0	5.4	1.2	46	50	2.7	49	1,100	2.2	0.8
18	5.9	4.4	0.8	43	39	2.6	34	1,100	1.7	0.6
19	5.3	4.3	0.5	33	28	2.2	26	820	1.5	0.3
20	5.1	4.6	0.4	33	24	2.1	22	1,100	2.2	0.2
21	6.4	3.6	1.7	60	59	2.9	58	560	3.0	1.5
22	6.0	4.7	0.5	48	31	2.7	29	540	2.9	0.5
23	6.9	5.9	1.5	55	63	3.3	54	900	$2.0\,$	1.1
Site	Uranium		Zinc	Organic Carbon (%)			Inorganic Carbon (%)		63 μm (%)	Percent Less than
1	7.11		82	1.14		$0.02\,$			8.45	
\overline{c}	8.10		180	3.1		0.15			14.1	
3	17.8		3,200	2.59		0.15			18.5	
4	23.0		3,700	5.1		$0.10\,$			3.60	
5	7.30		320	11.0		1.30			8.60	
6	8.90		460	8.0		1.00			5.80	
7	7.24		160	1.89		0.48			18.3	
8	8.69		430	2.96		0.19			14.4	
8	8.40		380	2.11		0.16			34.6	
9	24.6		84	8.94		0.02			18.1	
10	6.60		100	$8.8\,$		0.50			23.5	
11	16.5		110	4.77		0.02			14.7	
11	16.4		110	4.45		0.02			20.9	
12	5.52		110	1.8		0.84			21.2	
13	6.50		89	11.0		3.30			10.0	
14	5.10		89	5.6		1.90			21.4	
15	6.13		190	3.2		0.94			16.4	
15	6.88		190	3.22		0.97			22.6	
16	5.22		84	1.62		1.44			31.7	
17	6.25		190	3.53		1.57			14.0	
18	6.94		140	$2.2\,$		1.60			26.4	
19	7.96		97	1.97		3.25			17.5	
20	8.99		91	3.12		2.98			16.8	
21	8.41		220	2.61		1.93			25.8	
22	10.6		120	2.81		3.24			6.20	
23	7.65		220	2.66		0.94			10.2	

Site	Fish Species	Aluminum	Arsenic	Cadmium	Chromium	Copper	Iron	Lead	Manganese	Selenium
$\mathbf{1}$	White sucker	nd	0.57	nd	0.64	122	125	nd	9.56	7.66
\overline{c}	White sucker	nd	0.50	0.31	0.71	88.2	601	nd	8.35	6.08
3	Brown trout	6.58	0.68	22.7	0.60	46	544	nd	6.08	10.1
4	Brown trout	32.45	nd	16.0	0.69	252	300	nd	8.06	10.4
6	White sucker	nd	nd	0.30	nd	64.4	453	nd	6.81	10.4
6	Common carp	2.65	nd	1.06	nd	75.2	367	0.29	5.28	10.3
8	Common carp	nd	0.29	0.48	nd	51.5	239	0.28	4.35	7.34
9	Brown trout	3.49	$0.62\,$	1.70	0.90	318	777	nd	4.35	31.4
10	Common carp	3.74	nd	2.90	0.55	160	523	0.48	8.28	15.2
11	Brown trout	nd	nd	0.30	0.55	317	361	nd	3.21	24.7
11	Brown trout	nd	0.49	0.44	nd	447	257	nd	3.68	37.3
12	White sucker	nd	0.58	nd	0.53	77.6	588	nd	8.35	6.52
12	Common carp	nd	0.39	0.79	0.52	103	912	nd	5.72	7.92
15	White sucker	nd	nd	0.37	0.55	99.6	332	nd	6.99	4.94
15	Common carp	1.18	0.46	2.46	nd	81.3	373	0.58	4.59	7.73
16	White sucker	nd	0.76	0.43	0.69	65.2	416	nd	7.08	4.40
17	White sucker	nd	0.40	0.49	0.61	126	409	nd	7.18	5.36
17	Common carp	nd	0.65	19.1	nd	141	267	0.36	6.13	8.78
18	White sucker	2.91	nd	0.47	0.62	116	655	nd	10.4	5.46
18	Common carp	5.06	nd	8.92	0.57	166	545	0.35	7.29	16.0
19	White sucker	nd	0.49	nd	nd	39.7	206	nd	5.26	6.12
20	White sucker	nd	0.44	0.26	0.57	73.3	397	nd	7.31	7.87
20	Common carp	nd	0.87	10.9	nd	109	253	nd	4.52	7.75
21	Common carp	nd	0.27	0.52	nd	31.2	380	nd	3.61	5.38
22	Common carp	nd	nd	nd	nd	10.9	160	nd	2.77	3.08
Site	Species	Silver	Uranium	Zinc	Moisture (%)	Average Standard Length (mm)		Average Weight (g)	Average Age (yr)	Number of Fish
1	White sucker	1.23	nd	95.0	78.7	161		80	1.7	9
\overline{c}	White sucker	0.89	nd	112	76.9	291		401	3.2	8
3	Brown trout	1.06	nd	127	78.2	693		323	2.8	5
4	Brown trout	3.38	nd	130	75.4	207		172	1.5	5
6	White sucker	1.33	nd	100	68.2	301		450	4.4	8
6	Common carp	1.54	nd	643	69.0	417		1,764	5	8
8	Common carp	1.15	nd	320	68.3	342		1,149	3.4	8
9	Brown trout	3.62	nd	72.5	74.9	201		139	$\overline{2}$	8
10	Common carp	1.80	nd	1,003	75.9	467		2,340	4.8	8
11	Brown trout	1.25	nd	79.8	72.6	216		160	2.1	8
									2.4	8
11	Brown trout	1.84	nd	50.3	78.8	289		379		
12	White sucker	1.13	nd	99.1	77.1	242		249	4	8
12	Common carp	1.07	nd	874	76.0	374		1,328	3.8	8
15	White sucker	0.87	nd	111	74.8	219		192	3.3	7
15	Common carp	0.82	nd	514	75.9	379		1,427	3.8	8
16	White sucker	0.43	nd	99.1	78.5	186		152	$2.3\,$	6
17	White sucker	1.50	nd	125	76.1	240		265	4.1	7
17	Common carp	2.11	nd	893	75.9	489		3,250	4.9	8
18	White sucker	3.29	0.48	139	72.4	195		132	2.9	$10\,$
18	Common carp	2.85	nd	1,321	75.0	490		2,650	5.1	8
19	White sucker	0.77	nd	60.9	71.7	234		291	2.8	8
20	White sucker	0.66	nd	89.6	79.8	223		228	4.5	8
20	Common carp	1.48	nd	354	75.8	422		1,948	4.2	8
21 22	Common carp Common carp	0.87 0.26	nd nd	570 434	70.1 67.8	526 445		3,261 2,357	4.7 4.2	8 8

Appendix B. Trace element concentrations (µg/g, dry weight) in fish liver in the South Platte River Basin and fish characteristics. [See Figure 1 and Table 1 for site locations and descriptions; $nd =$ below detection limit.]

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