Trace Elements in Streambed Sediment and Fish Liver at Selected Sites in the Upper Colorado River Basin, Colorado, 1995–96

By Jeffrey R. Deacon and Verlin C. Stephens

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FOREWORD

The mission of the U.S. Geological Survey (USGS) is to assess the quantity and quality of the earth resources of the Nation and to provide information that will assist resource managers and policymakers at Federal, State, and local levels in making sound decisions. Assessment of water-quality conditions and trends is an important part of this overall mission.

One of the greatest challenges faced by water-resources scientists is acquiring reliable information that will guide the use and protection of the Nation's water resources. That challenge is being addressed by Federal, State, interstate, and local water-resource agencies and by many academic institutions. These organizations are collecting water-quality data for a host of purposes that include: compliance with permits and water-supply standards; development of remediation plans for a specific contamination problem; operational decisions on industrial, wastewater, or water-supply facilities; and research on factors that affect water quality. An additional need for water-quality information is to provide a basis on which regional and national-level policy decisions can be based. Wise decisions must be based on sound information. As a society we need to know whether certain types of water-quality problems are isolated or ubiquitous, whether there are significant differences in conditions among regions, whether the conditions are changing over time, and why these conditions change from place to place and over time. The information can be used to help determine the efficacy of existing water-quality policies and to help analysts determine the need for and likely consequences of new policies.

To address these needs, the Congress appropriated funds in 1986 for the USGS to begin a pilot program in seven project areas to develop and refine the National Water-Quality Assessment (NAWQA) Program. In 1991, the USGS began full implementation of the program. The NAWQA Program builds upon an existing base of water-quality studies of the USGS, as well as those of other Federal, State, and local agencies. The objectives of the NAWQA Program are to:

- Describe current water-quality conditions for a large part of the Nation's freshwater streams, rivers, and aquifers.
- Describe how water quality is changing over time.
- Improve understanding of the primary natural and human factors that affect water-quality conditions.

This information will help support the development and evaluation of management, regulatory, and monitoring decisions by other Federal, State, and local agencies to protect, use, and enhance water resources.

The goals of the NAWQA Program are being achieved through ongoing and proposed investigations of 59 of the Nation's most important river basins and aquifer systems, which are referred to as study units. These study units are distributed throughout the Nation and cover a diversity of hydrogeologic settings. More than two-thirds of the Nation's freshwater use occurs within the 59 study units and more than two-thirds of the people served by public water-supply systems live within their boundaries.

National synthesis of data analysis, based on aggregation of comparable information obtained from the study units, is a major component of the program. This effort focuses on selected water-quality topics using nationally consistent information. Comparative studies will explain differences and similarities in observed water-quality conditions among study areas and will identify changes and trends and their causes. The first topics addressed by the national synthesis are pesticides, nutrients, volatile organic compounds, and aquatic biology. Discussions on these and other water-quality topics will be published in periodic summaries of the quality of the Nation's ground and surface water as the information becomes available.

This report is an element of the comprehensive body of information developed as part of the NAWQA Program. The program depends heavily on the advice, cooperation, and information from many Federal, State, interstate, Tribal, and local agencies and the public. The assistance and suggestions of all are greatly appreciated.

Robert M. Hirsch
Chief Hydrologist

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CONVERSION FACTORS AND VERTICAL DATUM

Multiply	By	To obtain
foot (ft)	0.3048	meter
inch (in.)	2.54	millimeter
mile (mi)	1.609	kilometer
square mile (mi^2)	2.59	square kilometer

ADDITIONAL ABBREVIATIONS:

micrometer (µm)
micrograms per gram (µg/g)

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Abstract

Trace elements were analyzed in streambed-sediment samples collected from 16 sites and in fish-liver samples collected from 14 sites in the Upper Colorado River Basin in Colorado as part of the National Water-Quality Assessment program. Sites sampled represented agricultural, mining, mixed, and urban/recreation land uses and background conditions. The results for 15 trace elements in streambed-sediment and in fish-liver samples are presented in this report. Fourteen of the selected trace elements were detected in streambed-sediment samples collected at all sites. Twelve of the selected trace elements were detected in fish liver at more than 50 percent of the sites. Cadmium, copper, selenium, and zinc were selected for a more detailed analysis.

Cadmium, copper, and zinc concentrations in streambed sediment were highest at mining land-use sites in the Southern Rocky Mountains physiographic province. Selenium concentrations in streambed sediment were highest at an agricultural land-use site in the Colorado Plateau physiographic province. The concentration of trace elements in streambed sediment generally increased as particle size decreased.

Concentrations of trace elements in fish liver generally did not follow the same relation to land use as concentrations in streambed sediment; however, cadmium concentrations in fish liver were highest at a mining land-use site in the Southern Rocky Mountains physiographic province, and selenium concentrations in fish liver were highest at an agricultural land-use site in the Colorado Plateau physiographic province. Copper and zinc concentrations in fish liver were highest at mixed land-use sites.

Comparison of streambed-sediment and fish-liver concentrations to two other similar NAWQA studies in the Rocky Mountain region generally indicated similar patterns in relation to land use for streambed sediment, but not for fish liver. Cadmium, copper, and zinc concentrations in streambed sediment were highest at sites affected by mining in all three study units. Selenium concentrations in streambed sediment did not indicate relations among the three study units when compared to land use. Cadmium in fish liver was highest at sites affected by mining in all three study units. Copper, selenium, and zinc in fish liver did not indicate relations among the three study units when compared to land use.

INTRODUCTION

The National Water-Quality Assessment (NAWQA) program is a long-term program of the U.S. Geological Survey (USGS) designed to describe the status and trends in the quality of the Nation’s surface- and ground-water resources and to provide an understanding of the natural and human factors that can affect the quality of these resources (Leahy and others, 1990). The program is interdisciplinary and integrates chemical, physical, and biological data to assess the Nation's water quality at local, regional, and national levels (Meador and Gurtz, 1994). One component of this integrative assessment is to examine the occurrence and distribution of selected organochlorine compounds and trace elements in streambed sediment, fish livers, and whole-body fish samples on a basin-wide scale. The NAWQA program emphasizes the use of consistent protocol methods for a nationwide approach. The program also strives for consistency of selected target taxa within and among study units.

Characterizing the geographic distribution of trace-element constituents with regard to background conditions and sources is one goal of the assessment. Concentrations of trace elements have been reported to be higher in streambed sediment and biota than in water (Lynch and others, 1988); thus, sampling streambed sediment and biota increases the probability of detecting trace amounts of these constituents in the environment. The use of streambed-sediment and biota analyses provides an understanding of the fate, distribution, and potential effects of these constituents. Measuring concentrations of trace elements in streambed sediment and in fish liver at the same site offers a more complete description, than just one sampling medium, of the occurrence and distribution of trace elements in a basin.

The Upper Colorado River Basin (UCOL) is 1 of 59 study units selected for the national assessment. A study to determine the occurrence and distribution of trace elements in streambed sediment and in fish liver was conducted in the UCOL between August and October 1995; one fish-liver sample was collected in August 1996. This report presents results of trace-element analyses for streambed sediment and fish livers. The results of occurrence and distribution analyses for organochlorine pesticides and polychlorinated biphenyls (PCB's) in streambed sediment and whole-body fish are discussed by Stephens and Deacon (1997).

Purpose and Scope

This report (1) identifies the occurrence and distribution of selected trace elements in streambed sediment and in fish liver at sampled sites; (2) determines the relation of trace elements in streambed sediment and fish liver to natural and human factors; (3) compares trace-element concentrations in different fish species; and (4) compares the results with those of two adjacent study units.

Description of Study Unit

The UCOL study unit has a drainage area of about 17,800 mi^2 with varied climate, geology, topography, and hydrology. The primary river in the study unit, the Colorado River, originates in the mountains of central Colorado and flows about 230 mi southwest into Utah (fig. 1). Its headwaters and most of the tributaries originate in the mountains that form the eastern and southern boundaries of the study unit (Driver, 1994).

The UCOL study unit is divided almost equally into two physiographic provinces: the Southern Rocky Mountains in the eastern part and the Colorado Plateau in the western part. A more detailed description of the two physiographic provinces and their environmental settings in the UCOL study unit is presented in Apodaca and others (1996).

Predominant land use in the UCOL is forest and rangeland (fig. 1). Within the forest and rangeland setting, other major land uses are mining, urban/recreation, and agriculture. Past and present mining activities have included the extraction of metals (copper, gold, lead, molybdenum, nickel, silver, vanadium, and zinc) and energy fuels (coal, gas, oil, and uranium). Urban/recreation is one of the smaller land uses in the study unit (fig. 1). A number of urban/recreation areas are associated with growth resulting from the expansion of the ski industry and from energy development in the 1980's. The Colorado Plateau physiographic province has agricultural and mixed (agriculture and urban) land-use sites. Agriculture includes the production of alfalfa, fruits, grains, hay, and vegetables (Apodaca and others, 1996). The Southern Rocky Mountains physiographic province has mining, urban/recreation, and mixed (mining and urban/recreation) land-use sites. Both physiographic provinces also have a background site.

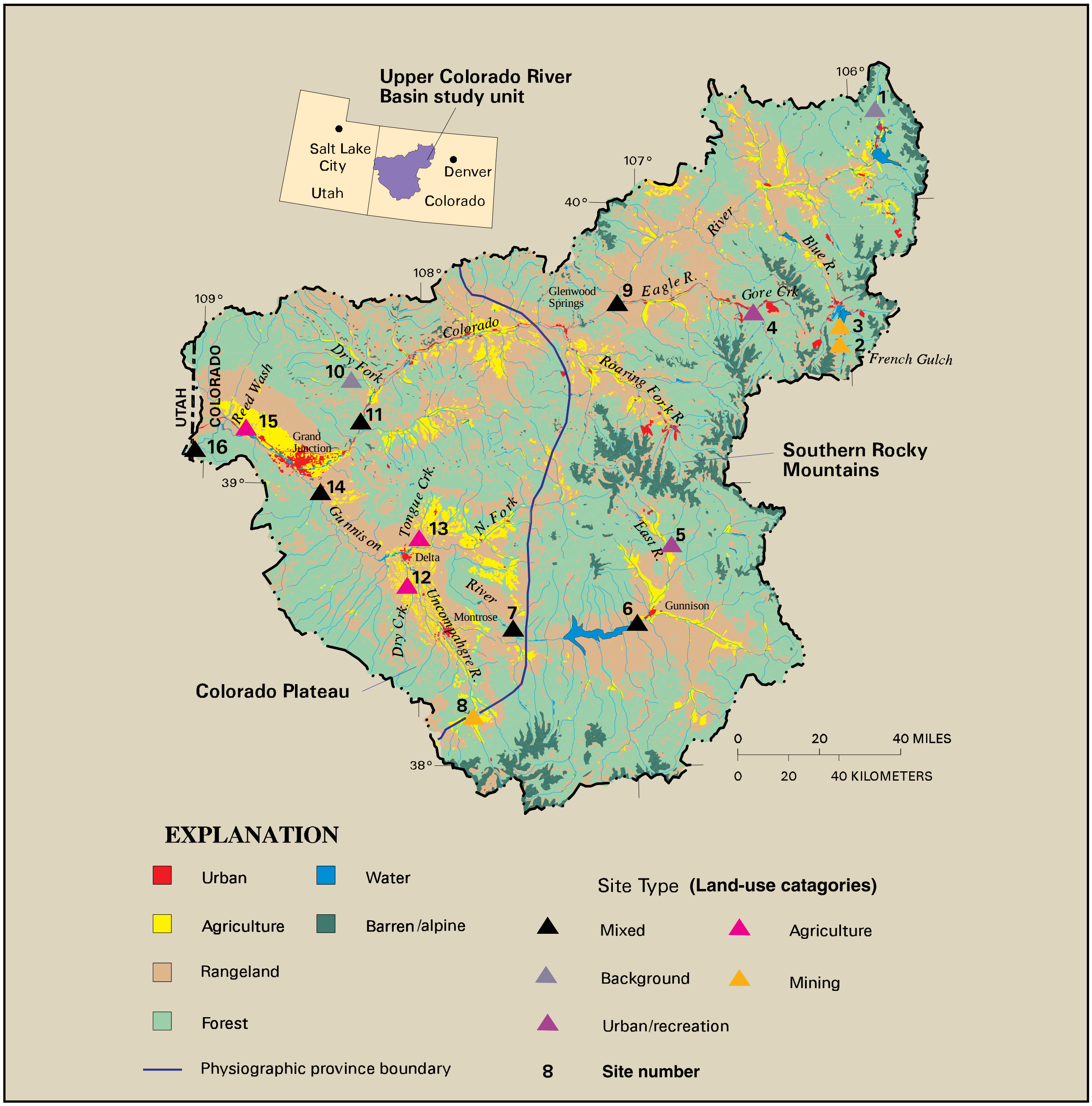

Figure 1. Location of sites for collection of streambed-sediment and fish-liver samples in the Upper Colorado River Basin study unit.

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SAMPLE COLLECTION AND ANALYSIS

Collection and field processing of streambed-sediment and fish-liver samples for analysis of trace elements followed established NAWQA protocols (Crawford and Luoma, 1993; Shelton and Capel, 1994). Streambed-sediment samples were collected at 16 sites throughout the UCOL study unit (fig. 1; table 1). Streambed sediments were collected from undisturbed, continuously wetted, depositional zones in the stream channel. Depositional zones were selected to represent upstream effects and various flow regimes. Sampling was confined to the upper three-fourths inch of streambed sediment to insure that the most recent deposition was being sampled. Each depositional zone at a sampling site was subsampled at several locations, and the sub-samples were composited. Field processing of streambed sediment included wet sieving samples through a 63-μm sieve for the trace-element analysis (Shelton and Capel, 1994). Streambed-sediment samples were analyzed for trace elements at the USGS, Branch of Geochemistry Analytical Services Group Laboratory, Denver, Colorado. The constituents included in streambed-sediment analyses and the lower levels of determination (LLD) (Arbogast, 1990) are listed in table 2.

Fish collection was done by electrofishing a stream reach that was 450 to 600 ft long at wadeable sites and 1,500 to 3,000 ft long at nonwadeable sites. The fish taxa collected for analyses were selected from a National Target Taxa List (NTTL) that consists mostly of bottom-feeding fish and nonmigrating game fish (Crawford and Luoma, 1993). The NTTL was established to provide consistency within the NAWQA program. Trace elements in fish liver were analyzed at the USGS National Water Quality Laboratory, Arvada, Colorado (Hoffman, 1996). The constituents included in fish-liver analyses and the minimum reporting limits (MRL) (Timme, 1995) are listed in table 2. Results
of selected trace-element analyses for streambed sediment and for fish liver are listed in tables 3 and 4. Trace-element data for streambed sediment and fish liver are stored in the USGS National Water Information System (NWIS) data base.

Replicate samples were collected for streambed sediment and triplicate samples were collected for fish liver for quality assurance/quality control. The difference between field replicate samples for streambed sediment ranged from 10 to 15 percent. The difference between field triplicate samples for fish liver ranged from 10 to 30 percent. Therefore, more variability in analysis was associated with the fish-liver samples.

TRACE ELEMENTS IN STREAMBED SEDIMENT

Trace elements are unevenly distributed in the aquatic environment and, by the process of adsorption, tend to be associated with fine-grained sediment. Many trace elements, such as arsenic, cadmium, copper, lead, mercury, selenium, and zinc, can be toxic to aquatic biota (Jenkins, 1981; Ames and others, 1987). The concentration of trace elements in streambed sediment is strongly affected by the particle-size distribution of the sample (Rickert and others, 1977; Wilbur and Hunter, 1979).

Fourteen of the 15 selected trace elements (table 3) were detected in streambed sediment at all sites. Molybedenum was the only trace element that was not detected at all sites. Because of their concentrations in the study unit and their toxicity to aquatic biota, cadmium, copper, selenium, and zinc were selected for detailed analysis.

One approach to evaluate elevated concentrations is by comparison to other studies in the Western United States (Jenkins, 1981; Salomons and Forstner, 1984; Shacklette and Boerngen, 1984; Severson and Tourtelot, 1994; Carter, 1997; Heiny and Tate, 1997) (table 5). To determine the extent of contamination in an aquatic system by means of the trace elements in streambed sediment, the natural level (or the background concentration) needs to be established. A basin-specific background concentration for cadmium, copper, selenium, and zinc was determined by plotting cumulative frequency curves (Velz, 1984) for the UCOL study unit for data from 16 streambed-sediment samples. The concentration at the first break point (change in slope) was designated as the background concentration (fig. 2). Cadmium and copper had determined background concentrations of 0.70 and 43 μg/g (fig. 2; table 5). Trace-element concentrations greater than the background concentration were considered elevated and may have been affected by natural or human activities. Sites 1 and 10 (sites chosen to represent background conditions) had lower

Table 1. Description of sampling sites in the Upper Colorado River Basin study unit

Site number (fig. 1)	Site name	Site identification	Site type	Elevation (feet)	Physiographic province	Fish species collected
1	Colorado River below Baker Gulch	09010500	Background	8,750	Southern Rocky Mountains	Brown trout
2	French Gulch near Breckenridge	09046530	Mining	9,485	Southern Rocky Mountains	None
3	Blue River near Breckenridge	392944106024400	Mining	9,480	Southern Rocky Mountains	Brown trout
4	Gore Creek at mouth near Minturn	09066510	Urban/recreation	7,730	Southern Rocky Mountains	Brown trout
5	East River below Cement Creek	09112200	Urban/recreation	8,006	Southern Rocky Mountains	Brown trout
6	Gunnison River at County Road 32	383103106594200	Mixed	7,570	Southern Rocky Mountains	Brown trout
7	Gunnison River below Gunnison Tunnel	09128000	Mixed	6,526	Southern Rocky Mountains[1]	Brown trout
8	Uncompahgre River near Ridgway	09146200	Mining	6,878	Southern Rocky Mountains	Brown trout; white sucker
9	Colorado River at Dotsero	09070500	Mixed	6,130	Southern Rocky Mountains	Brown trout; white sucker
10	Dry Fork at upper station near DeBeque	09095300	Background	5,385	Colorado Plateau	None
11	Colorado River near Cameo	09095500	Mixed	4,813	Colorado Plateau	Bluehead sucker
12	Dry Creek at Begonia Road near Delta	09149480	Agriculture	5,215	Colorado Plateau	Bluehead sucker; white sucker
13	Tongue Creek at Cory	09144200	Agriculture	5,030	Colorado Plateau	Brown trout; white sucker
14	Gunnison River near Grand Junction	09152500	Mixed	4,628	Colorado Plateau	Bluehead sucker
15	Reed Wash near Mack	09153290	Agriculture	4,505	Colorado Plateau	Flannelmouth sucker
16	Colorado River near Colorado-Utah State line	09163500	Mixed	4,325	Colorado Plateau	Bluehead sucker; common carp

[1]Site 7 is physically located in the Colorado Plateau but is hydrologically represented as a Southern Rocky Mountain sampling site.

Table 2. Constituents included in the streambed-sediment and fish-liver analyses

[Values in micrograms per gram dry weight, unless expressed as a percentage (%)]

Streambed sediment Trace elements and major metals (lower level of determination)[1]				
Aluminum (0.005%)	Chromium (1)	Lithium (2)	Potassium (0.05%)	Tin (10)
Antimony (0.1)	Cobalt (1)	Magnesium (0.005%)	Scandium (2)	Titanium (0.005%)
Arsenic (0.1)	Copper (1)	Manganese (4)	Selenium (0.1)	Uranium (0.05)
Barium (1)	Gallium (4)	Mercury (0.02)	Silver (0.1)	Vanadium (2)
Beryllium (1)	Gold (8)	Molybedenum (2)	Sodium (0.005%)	Ytterbium (1)
Bismuth (10)	Holmium (4)	Neodymium (4)	Strontium (2)	Yttrium (2)
Cadmium (0.1)	Iron (0.005%)	Nickel (2)	Sulfur (0.05%)	Zinc (4)
Calcium (0.05%)	Lanthanum (2)	Niobium (4)	Tantalum (40)	
Cerium (4)	Lead (4)	Phosphorus (0.005%)	Thorium (4)	
Carbon (lower level of determination)				
Carbonate (0.01%)	Total carbon (0.01%)	Total organic carbon (0.01%)		

Fish livers Trace elements and major metals (minimum reporting limit)[2]			
Aluminum (1)	Cadmium (0.1)	Manganese (0.1)	Silver (0.1)
Antimony (0.1)	Chromium (0.5)	Mercury (0.1)	Strontium (0.1)
Arsenic (0.1)	Cobalt (0.1)	Molybedenum (0.1)	Uranium (0.1)
Barium (0.1)	Copper (0.5)	Nickel (0.1)	Vanadium (0.1)
Beryllium (0.1)	Iron (1)	Selenium (0.1)	Zinc (0.5)
Boron (0.2)	Lead (0.1)		

[1]The lower level of determination is three times the standard deviation of the blank added to the average of the blank (Arbogast, 1990).

[2]The minimum reporting limit is the smallest measured concentration of a constituent that may be reliably reported using a given analytical method (Timme, 1995).

concentrations of cadmium, copper, selenium, and zinc than the background concentrations for the basin.

Because of the extent of mineralized areas in the UCOL study unit, the concentrations of cadmium, copper, selenium, and zinc could represent natural conditions at some sites. Seven sites exceeded background concentrations for the UCOL for cadmium; three sites exceeded background concentrations for the UCOL for copper; seven sites exceeded background concentrations for the UCOL for selenium; and six sites exceeded background concentrations for the UCOL for zinc (tables 3 and 5). Sites affected by mining (2, 3, and 8) generally exceeded the background concentrations by orders of magnitude for cadmium and zinc. Site 15, an agricultural land-use site, had about four times the background concentration for selenium.

There currently are no State or Federal guidelines or standards for concentrations of trace elements in streambed sediment. 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. Two assessment values were calculated: a lower value, referred to as the threshold effect level (TEL), and an upper value, referred to as the probable effect level (PEL). The TEL represents the concentration below which adverse effects to aquatic biota are expected to occur rarely. The PEL defines the level above which adverse effects to aquatic biota are predicted to occur frequently. These two assessment values refer to the total concentration of a chemical in bulk sediment (Environment Canada, 1995) (table 6). Therefore, comparison of the concentrations for the smaller than 63-μm fraction size in this study to these guidelines may overestimate concentrations that adversely affect aquatic life. The concentration of trace elements on streambed materials is strongly affected by the particle-size distribution of the sample. The concentration of trace elements on streambed materials, generally, increases as particle size decreases (Brook and Moore, 1988). Selenium was not in the PSQG; therefore, a protocol for aquatic hazard assessment of selenium was used as a guideline (Lemly, 1995). Lemly (1995) uses several assessment categories to determine levels of selenium that have high, moderate, low, and no hazard effects. The lower level of <1 μg/g (no identifiable hazard) and an upper level of >4 μg/g (high hazard) are

Table 3. Concentrations of selected trace elements in streambed-sediment samples collected from sites in the Upper Colorado River Basin study unit

[Values in micrograms per gram dry weight unless expressed as percentage (%); --, less than lower limit of determination (table 2)]

Site	Aluminum (%)	Arsenic	Cadmium	Chromium	Copper	Iron (%)	Lead	Manganese	Mercury	Molybdenum	Nickel	Selenium	Silver	Uranium	Zinc
1	7.5	7.1	0.5	58	25	4.6	23	1,100	0.04	--	20	0.8	0.4	14	150
2	7.3	36	57	53	210	4.9	1,800	4,400	.25	7.0	28	2.1	6.7	6.3	9,000
3	7.6	23	11	75	110	4.6	640	1,600	.25	7.0	32	1.1	3.7	9.6	3,000
4	6.5	3.0	.4	73	36	3.5	31	570	.07	--	30	1.3	1.0	12	190
5	6.5	17	4.3	57	32	3.3	51	770	.05	2.0	25	1.9	.5	6.1	610
6	6.1	8.9	1.9	39	26	3.7	40	1,600	.06	--	17	1.2	.5	5.6	310
7	7.0	7.8	.7	51	43	4.6	42	960	.08	--	21	.9	.3	6.2	180
8	7.4	20	2.5	29	290	4.8	130	1,300	.04	3.0	16	1.1	2.2	3.9	790
9	6.0	7.3	1.2	62	25	2.9	31	590	.03	--	29	1.8	.3	6.4	330
10	5.3	8.9	.2	35	18	2.2	12	380	.02	--	15	.5	.1	4.9	71
11	6.2	6.9	.6	44	25	2.7	23	400	.03	--	21	.6	.4	4.8	120
12	6.2	8.3	.6	41	25	2.5	31	510	.03	--	19	1.1	.4	4.9	120
13	6.2	11	.6	63	20	2.7	21	320	.03	2.0	26	2.1	.1	4.1	110
14	6.0	9.4	.7	53	25	2.6	26	450	.03	2.0	24	2.5	.2	4.9	120
15	5.5	14	1.8	57	30	2.5	19	280	.02	6.0	32	5.6	.2	5.4	130
16	5.5	8.0	.6	47	18	2.4	24	410	.03	--	20	1.7	.2	5.0	100

Table 4. Concentrations of selected trace elements in fish-liver samples collected from sites in the Upper Colorado River Basin study unit

[Values in micrograms per gram dry weight; --, less than minimum reporting level (table 2); species code: bt, brown trout; bs, bluehead sucker; ws, white sucker; fs, flannelmouth sucker; cc, common carp]

Site[1]	Species	Aluminum	Arsenic	Cadmium	Chromium	Copper	Iron	Lead	Manganese	Mercury	Molybdenum	Nickel	Selenium	Silver	Uranium	Zinc
1	bt	--	0.3	--	0.8	344	608	--	10.2	0.35	1.3	--	51.8	1.7	--	105
3	bt	2.2	.2	81.3	.7	482	773	1.0	6.6	.25	1.5	0.2	13.9	6.2	--	138
4	bt	8.6	--	3.5	.8	493	504	--	4.7	.14	1.2	--	32.2	19.7	--	87.9
5	bt	1.6	--	4.6	.7	402	492	--	3.7	--	.6	--	38.8	3.1	--	93.5
6	bt	--	.3	.6	.8	543	345	--	5.7	.3	.7	--	31.8	.6	--	93.4
7	bt	1.7	.2	2.9	.6	519	437	--	4.2	.2	.9	--	32.2	1.9	--	75.1
8	bt	3.2	--	3.0	.7	147	214	--	4.5	--	.6	--	63.2	1.4	--	81.2
8	ws	22.3	.3	4.9	.6	136	1,700	.8	6.8	.1	1.3	.2	6.1	.7	--	123
9	bt	--	--	.6	.7	269	464	--	4.0	.13	1.8	.5	66.5	3.5	--	96.6
9	ws	--	.3	.4	--	52.7	353	--	6.0	--	1.3	.2	3.1	.9	--	55.8
11	bs	19.6	1.3	.4	--	9.2	449	.3	4.5	--	1.3	.4	4.2	--	--	42.8
12	bs	6.8	.8	.8	--	12.5	656	--	9.4	--	2.0	.6	6.6	--	--	63.3
12	ws	1.4	--	--	--	28.4	490	--	5.2	--	1.0	--	7.2	.3	--	69.4
13	bt	--	--	.4	.7	299	332	--	3.6	.17	1.3	--	166	1.7	--	130
13	ws	--	.3	.4	.6	51.2	391	--	6.6	--	1.6	.2	11.9	.7	--	97.7
14	bs	25.2	1.1	--	--	12.6	417	--	6.0	--	.8	--	8.9	--	--	60.4
15	fs	2.5	--	1.4	--	38.6	386	.3	2.4	--	.9	--	12.3	--	--	136
16	bs	206	1.3	--	1.0	17.8	950	--	12.9	.13	1.8	--	11.1	--	--	73.2
16	cc	43.8	.5	3.0	.5	76	553	.4	7.7	.14	1.3	--	14.2	1.0	--	858

[1]Sites 2 and 10 did not contain fish.

Table 5. Background concentrations for selected trace elements in soils and streambed sediment

[All values in micrograms per gram dry weight. Sixteen streambed-sediment samples were analyzed and used to compute background concentrations for this study; --, no data available]

Element	Jenkins (1981)[1]	Salomons and Forstner (1984)[1]	Shacklette and Boerngen (1984)[1]	Severson and Tourtelot (1994)[2]	Streambed sediments from the South Platte NAWQA study[3]	Streambed sediments from the Rio Grande NAWQA study[4]	Streambed sediments from this study[5]	Range of concentrations from this study
Cadmium	0.06	0.62	--	--	3.30	1.20	0.70	0.2–57
Copper	20.0	25.8	21.0	74.0	104	55.0	43	18–290
Selenium	.20	--	.23	--	3.0	.60	1.3	0.5–5.6
Zinc	--	59.8	55.0	190	454	150	190	71–9,000

[1]Background concentrations established for Western United States soils.
[2]Geochemical data for soils in the Front Range urban corridor, Colorado.
[3]Background concentration established for the South Platte NAWQA study (Heiny and Tate, 1997).
[4]Background concentration established for the Rio Grande NAWQA study (Carter, 1997).
[5]Background concentrations determined from technique described by Velz (1984) for this study.

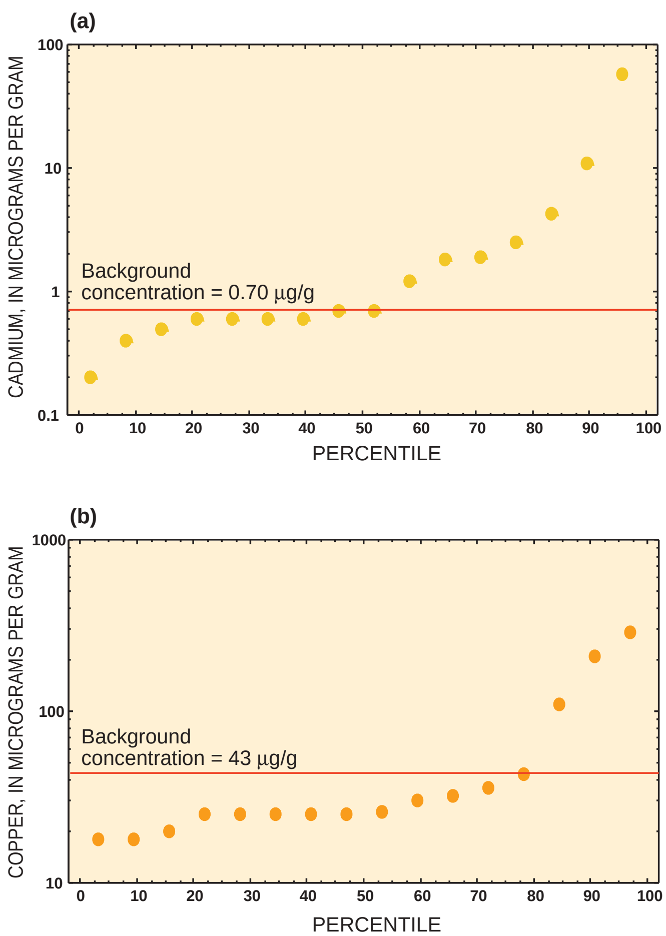

Figure 2. Example of a cumulative frequency curve used to determine the background concentration of (a) cadmium and (b) copper.

compared to streambed-sediment concentrations from the UCOL study in table 6.

A total of six sites have concentrations that are greater than the PEL or high hazard level for one or more of the four trace elements selected for detailed analysis (table 6). Elevated concentrations from sites 2, 3, and 8 may be a result of natural and human factors. Natural factors include weathering of carbonate, igneous, metamorphic, and volcanic rocks; and human factors include metal mining (Apodaca and others, 1996). The concentrations of cadmium, copper, and zinc at mining sites are higher than the PEL and concentrations at other sites (tables 3 and 6). Although site 5 represents urban/recreation land use, it also had past mining activities in the upper part of the watershed. Site 9 represents a mixed land-use site and receives water from a mining-affected river just upstream from the sampling site. Elevated concentrations of some trace elements at site 5 and site 9 also may be a combination of natural and human factors. Site 15, an agricultural land-use site in the Colorado Plateau physiographic province, had the highest concentration of selenium. The underlying geology, consisting mainly of Mancos Shale of Cretaceous age, and the irrigation return flows upstream are likely contributing factors to the elevated selenium concentration. Selenium is present naturally in the shale bedrock of the middle and lower reaches of the basin and is present in the surface and ground water (Apodaca and others, 1996).

Table 6. Comparison of guidelines and trace-element concentrations determined in streambed sediment in this study

[Values in micrograms per gram dry weight]

Trace element	Threshold effect (TEL)[1]	Probable effect level (PEL)[2]	Sites with concentrations above PEL[3]
Cadmium	0.59	3.53	2, 3, 5
Copper	35.7	197	2, 8
Zinc	123	315	2, 3, 5, 8, 9

Trace element	No identifiable hazard level[4]	HIgh hazard level	Sites with concentrations above the high hazard level[3]
Selenium	1	4	15

[1]Represents the concentration in bulk sediment below which adverse biological effects are expected to occur rarely (Environment Canada, 1995).

[2]Represents the concentration in bulk sediment above which adverse biological effects are predicted to occur frequently (Environment Canada, 1995).

[3]Sites from this study for the less than 63-micrometer fraction.

[4]Source is a protocol for aquatic hazard assessment of selenium (Lemly, 1995).

Particle-size determination of the samples indicated that the mining sites (sites 2, 3, and 8) in the Southern Rocky Mountains physiographic province contained a larger percentage of silt/clay particles than other sites in the Southern Rocky Mountains physiographic province (fig. 3). Human disturbances at the mining land-use sites may have contributed to the larger percentages of silt/clay particles. The weathering of the rocks in the Southern Rocky Mountains physiographic province does not produce large amounts of small particulates (silt/clay). Higher percentages of silt/clay particles in combination with mining land use at sites 2, 3, and 8 may be a factor for higher concentrations of trace elements at these sites. Site 15, an agricultural land-use site, with the highest concentration of selenium, had one of the highest percentages of silt/clay particles of the sites in the Colorado Plateau physiographic province. Overall, sites in the Colorado Plateau physiographic province contained larger percentages of silt/clay particles than sites in the Southern Rocky Mountains physiographic province (fig. 3). Weathering of the sedimentary rocks in the Colorado Plateau physiographic province is one contributing factor to larger percentages of silt/clay particles at these sites.

Sites in the Southern Rocky Mountains physiographic province had higher concentrations of cadmium, copper, and zinc than sites in the Colorado Plateau physiographic province, which are indicative of mining land use and the mineralized areas (carbonate, igneous, metamorphic, and volcanic rocks) in upper parts of the basin (fig. 4). Sites in the Colorado Plateau physiographic province generally had higher concentrations of selenium than sites in the Southern Rocky Mountains physiographic province, which are indicative of agricultural land-use practices and the sedimentary deposits (Mancos Shale) (Butler and others, 1996).

The Mann-Whitney statistical test was performed on the streambed-sediment data to determine if the selected trace elements were significantly different between the two physiographic provinces. The Mann-Whitney test is a nonparametric test

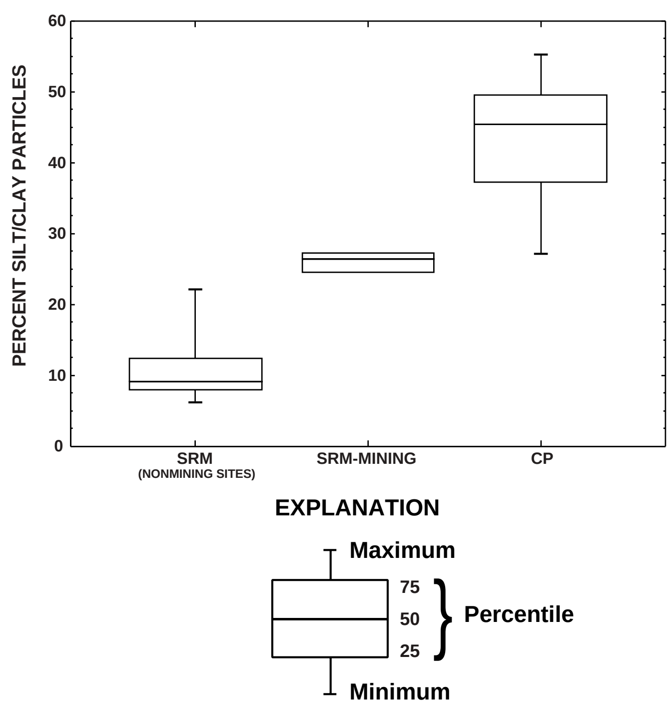

Figure 3. Comparison of particle-size percentages between sites in the Southern Rocky Mountains (SRM) and the Colorado Plateau (CP) physiographic provinces.

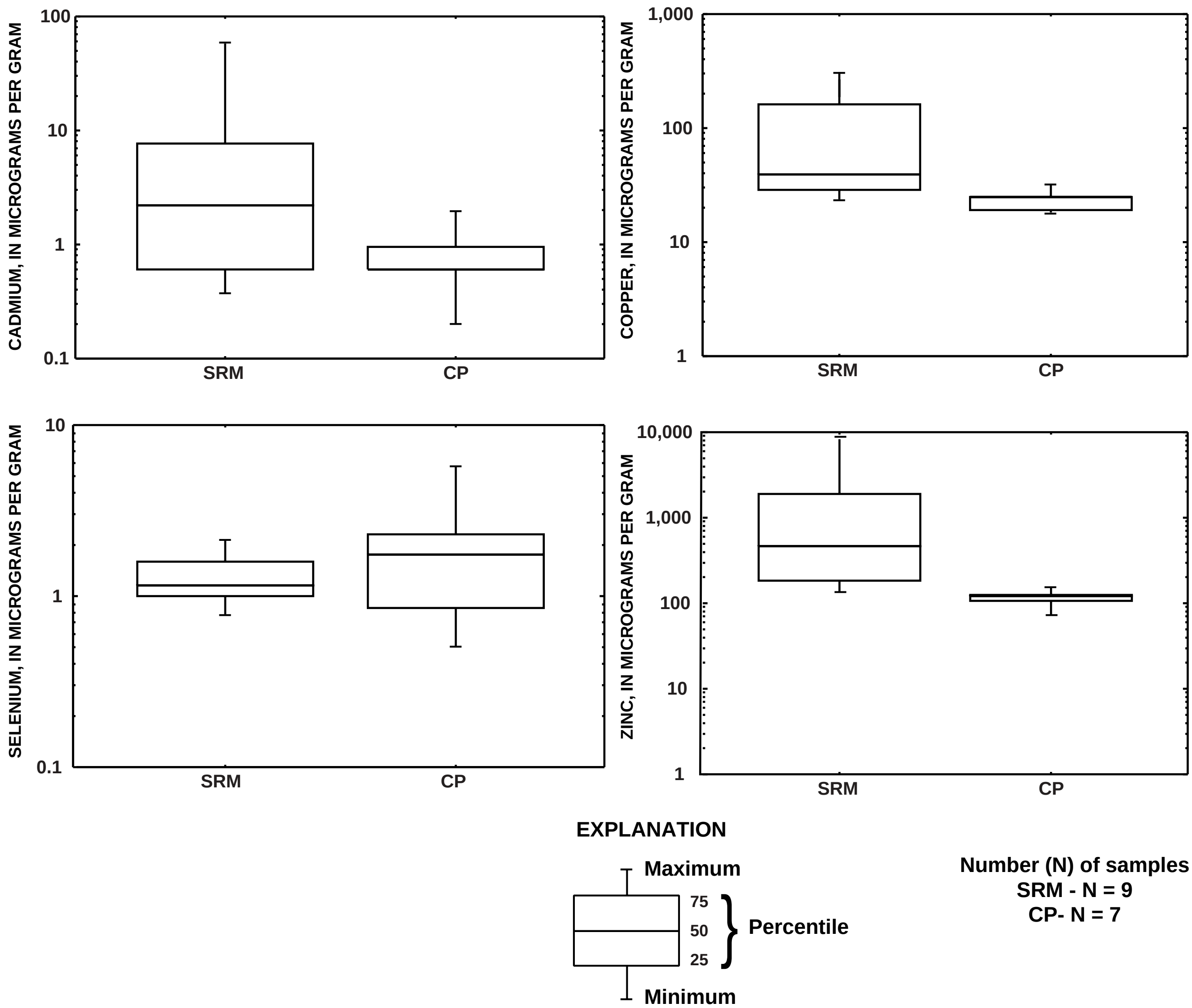

Figure 4. Range of concentrations for cadmium, copper, selenium, and zinc in streambed sediment for the Southern Rocky Mountains (SRM) and the Colorado Plateau (CP) physiographic provinces.

that tests for statistical differences between two independent groups of data (Helsel and Hirsch, 1992). Results from the tests indicated significant differences ($p < 0.05$) in the concentrations between the two physiographic provinces for copper and zinc. Concentrations of cadmium and selenium were not significantly different ($p > 0.05$) between the two physiographic provinces.

Mean concentrations of the four selected trace elements compared to the different land-use categories in the UCOL study unit are shown in figure 5. Cadmium, copper, and zinc concentrations were highest at mining land-use sites. Although natural background concentrations of trace elements may be high in the mineralized areas where mining occurs, mining land-use practices can cause increased concentrations of trace elements (Axtmann and Luoma, 1991). Selenium concentrations were highest at agricultural land-use sites. Irrigation practices near agricultural land-use sites may be mobilizing and redistributing selenium (Butler and others, 1996).

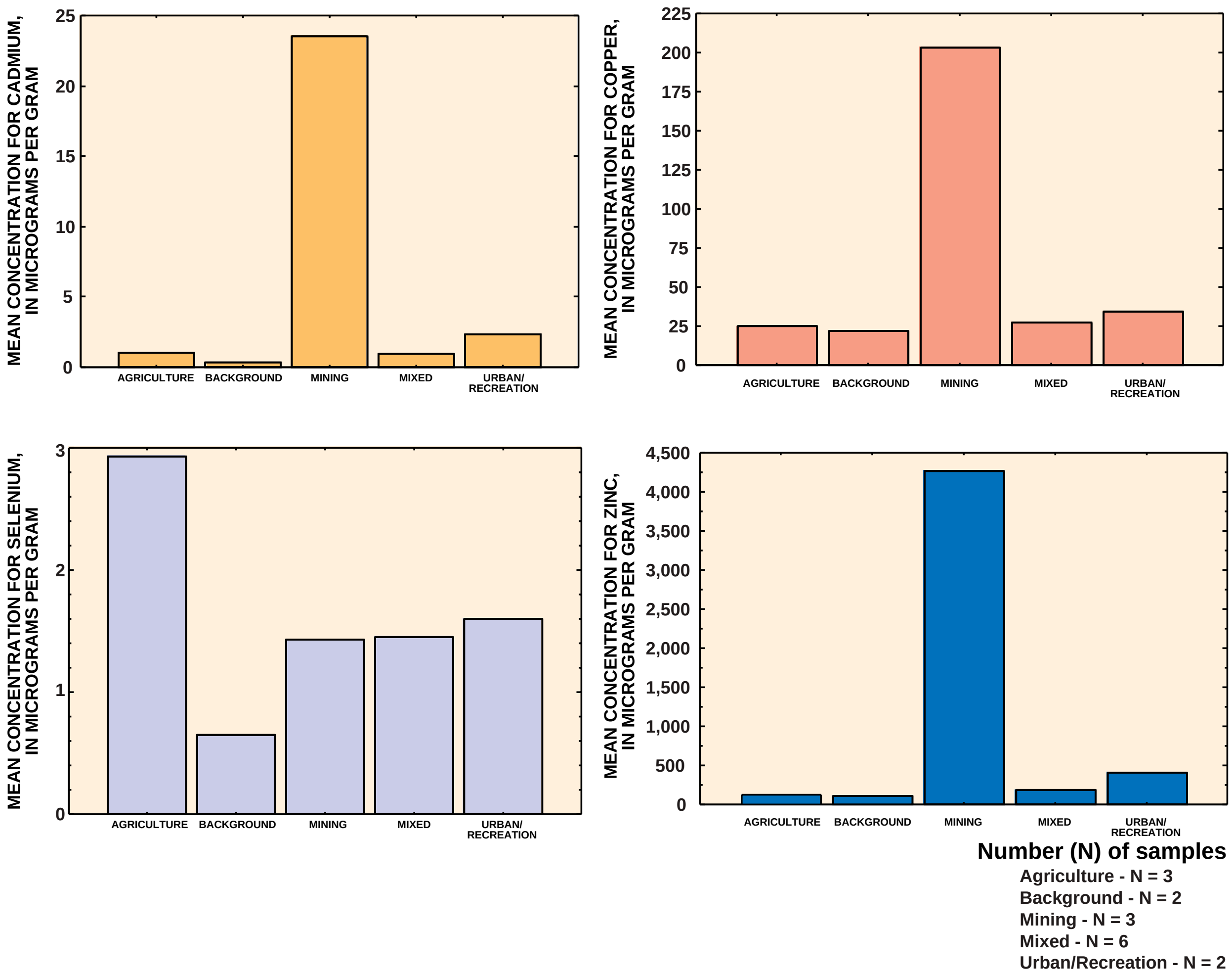

Figure 5. Mean concentrations of cadmium, copper, selenium, and zinc in streambed sediment for land-use categories in the Upper Colorado River Basin study unit.

TRACE ELEMENTS IN FISH LIVER

The quantification of potential contaminants in biological tissues can be an important part of water-quality assessment programs. Determination of contaminants in tissue can be used to provide information about (1) direct threats to human health and ecosystem integrity and (2) the occurrence and distribution of potential contaminants in the environment. The analysis of fish tissue in the NAWQA program concentrates on the second objective.

Four important attributes of tissue analysis are: (1) To increase the likelihood of detecting contaminants that are undetectable in water and sometimes streambed sediment; (2) to obtain a time-integrated estimate of contaminants in the environment; (3) to indicate bioaccumulation; and (4) to provide the opportunity for integrating tissue concentrations with those in water and sediment to assess contaminant fate, distribution, and effects (Crawford and Luoma, 1993). A major limitation to tissue analysis is that a single species is not available at all sites in a large basin. Therefore, comparisons among different species are questionable because accumulation rates among species can differ. Migration and mobility of fish add to variability when comparing concentrations at sites to land use. Measuring concentrations of trace elements in streambed sediment and in fish liver at the same site offers a more complete description than just one sampling medium.

The most common taxa present at most of the sampling sites were brown trout, white sucker, and bluehead sucker (table 1). At this time, there are no established guidelines for trace-element concentrations in fish liver. Twelve of the selected trace elements (table 4) were detected at more than 50 percent of the sites. Lead, nickel, and uranium were detected at less than 50 percent of the sites.

Relating trace-element concentrations in fish liver to land use is more difficult than with streambed sediment, probably because of not having the same species at all sites. Individual samples of cadmium were highest in both sampling media at mining land-use sites, whereas selenium was highest in both sampling media at agricultural land-use sites. Copper and zinc were highest in streambed sediment at mining land-use sites, whereas copper and zinc were highest in fish liver at mixed land-use sites.

Brown trout and white suckers were the only taxa that were collected in both physiographic provinces; therefore, these taxa were used for comparisons between the two physiographic provinces. The highest mean concentrations of cadmium and copper were found in brown trout fish-liver samples at sites in the Southern Rocky Mountains physiographic province. The highest mean concentrations of selenium and zinc were found in brown trout fish-liver samples at sites in the Colorado Plateau physiographic province (fig. 6).

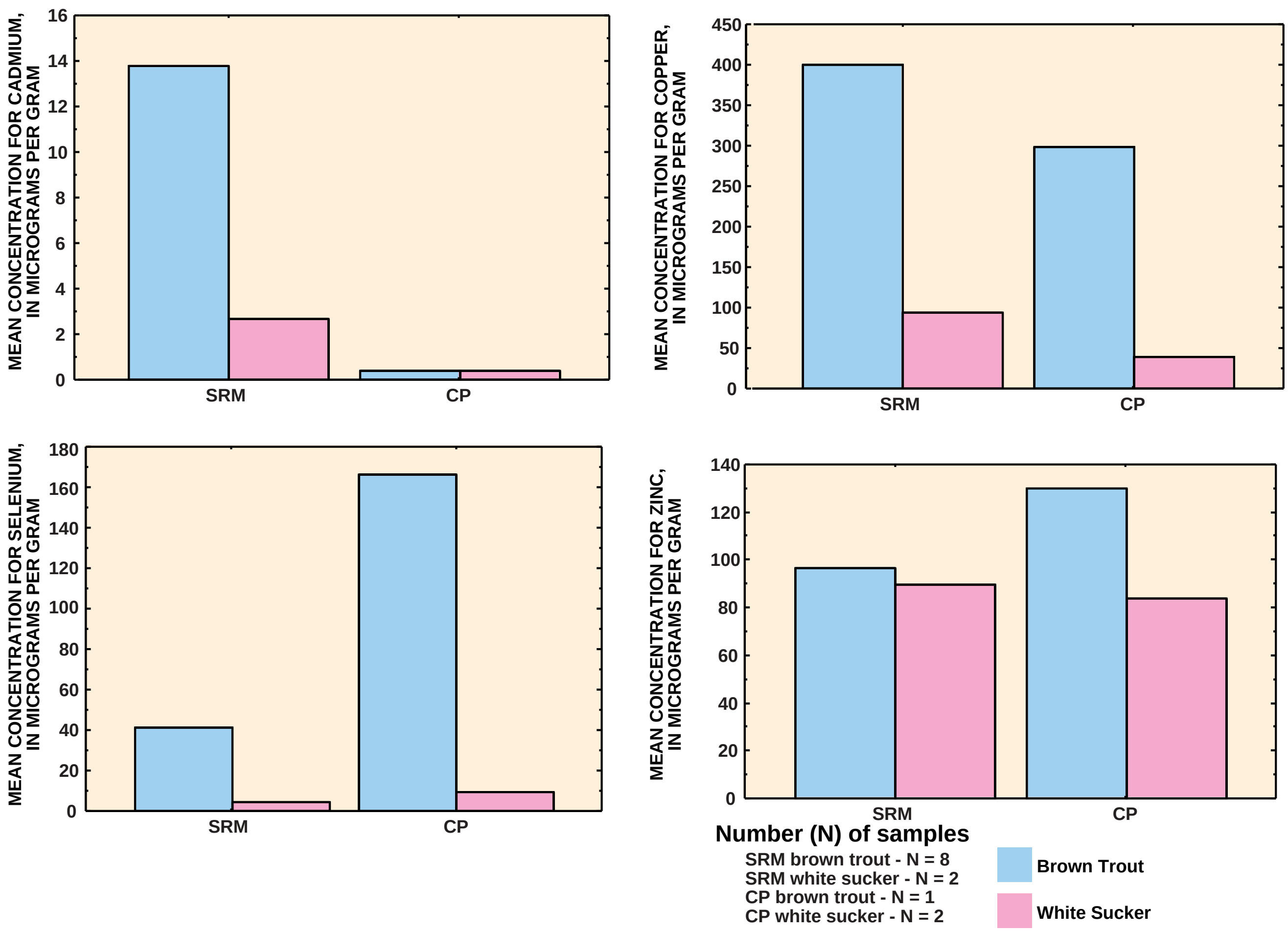

Figure 6. Range of concentrations for cadmium, copper, selenium, and zinc in fish liver (brown trout and white sucker) in the Southern Rocky Mountains (SRM) and Colorado Plateau (CP) physiographic provinces.

The highest concentration of cadmium was in a brown trout liver sample at site 3, a mining land-use site, in the Southern Rocky Mountains physiographic province (table 4). The highest concentration of copper was in a brown trout liver sample at site 6, a mixed land-use site, in the Southern Rocky Mountains physiographic province. The highest concentration of zinc was in a common carp liver sample at site 16, a mixed land-use site, in the Colorado Plateau physiographic province, which was the most downstream site in the basin. Schmitt and Brumbaugh (1990) reported that common carp had higher whole-body zinc concentrations than any other fish species analyzed during the U.S. Fish and Wildlife Service National Contaminant Biomonitoring Program. The highest concentration of selenium was in a brown trout liver sample from site 13, an agricultural land-use site in the Colorado Plateau physiographic province. NAWQA studies in the South Platte River Basin (SPLT) and the Rio Grande Valley (RIOG), both with sampling sites in Colorado, also reported liver tissue from brown trout with higher concentrations of cadmium, copper, and selenium than liver tissue from other fish species (Carter, 1997; Heiny and Tate, 1997).

Multiple fish taxa were collected at sites 8, 9, 12, 13, and 16 (table 4). Comparison of selected trace-element concentrations in fish liver among the different taxa at the same sites indicated that trace-element bioconcentration may be species dependent. Brown trout liver samples at sites 8, 9, and 13 generally had higher concentrations of cadmium, copper, selenium, and zinc than white sucker liver samples. The white sucker liver sample at site 12 had higher concentrations of copper, selenium, and zinc than the bluehead sucker liver sample. At site 16, the common carp liver sample had higher concentrations of cadmium, copper, selenium, and zinc than the bluehead sucker liver sample. The concentrations of trace elements in fish liver are related to concentrations of trace elements in ingested food, water, and sediment, along with the rates of bioaccumulation and depuration, and these factors differ for different trace elements and fish species (Heiny and Tate, 1997).

COMPARISON OF SELECTED TRACE ELEMENTS IN STREAMBED SEDIMENT AND FISH LIVER TO THOSE FROM OTHER NAWQA STUDY UNITS IN THE ROCKY MOUNTAIN REGION

Selected trace-element concentrations in streambed-sediment and fish-liver samples collected from the UCOL NAWQA were compared to concentrations from two other NAWQA study units (fig. 7) in the Rocky Mountain region that had similar geology and land uses. The range in concentrations in streambed-sediment samples for cadmium, copper, selenium, and zinc in the UCOL, SPLT, and RIOG NAWQA study units is shown in figure 8. The range in concentrations for white-sucker fish-liver samples for the three study units is shown in figure 9. White sucker was used for comparison among the study units because it was the only species where at least four samples were collected in each study unit.

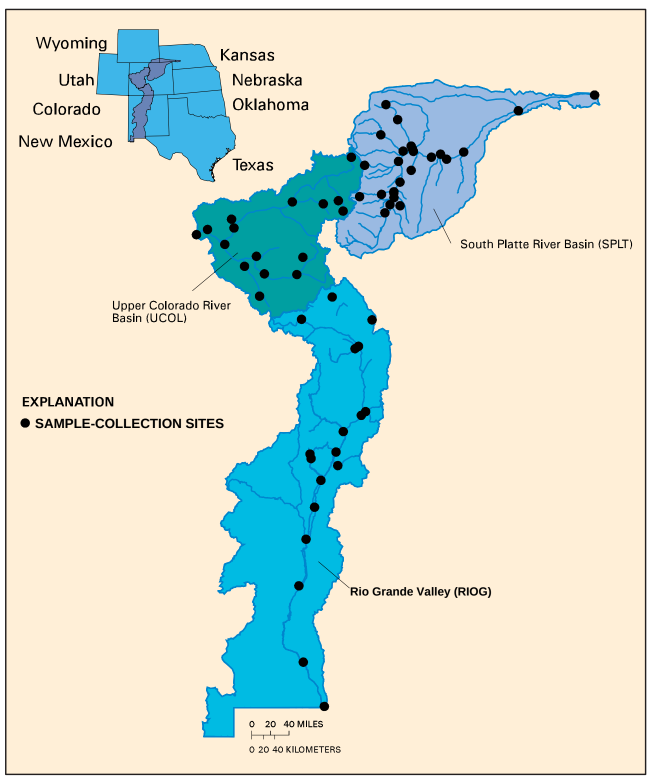

Figure 7. Location of National Water-Quality Assessment program sample-collection sites in the Upper Colorado River Basin (UCOL), the South Platte River Basin (SPLT), and the Rio Grande Valley (RIOG) study units.

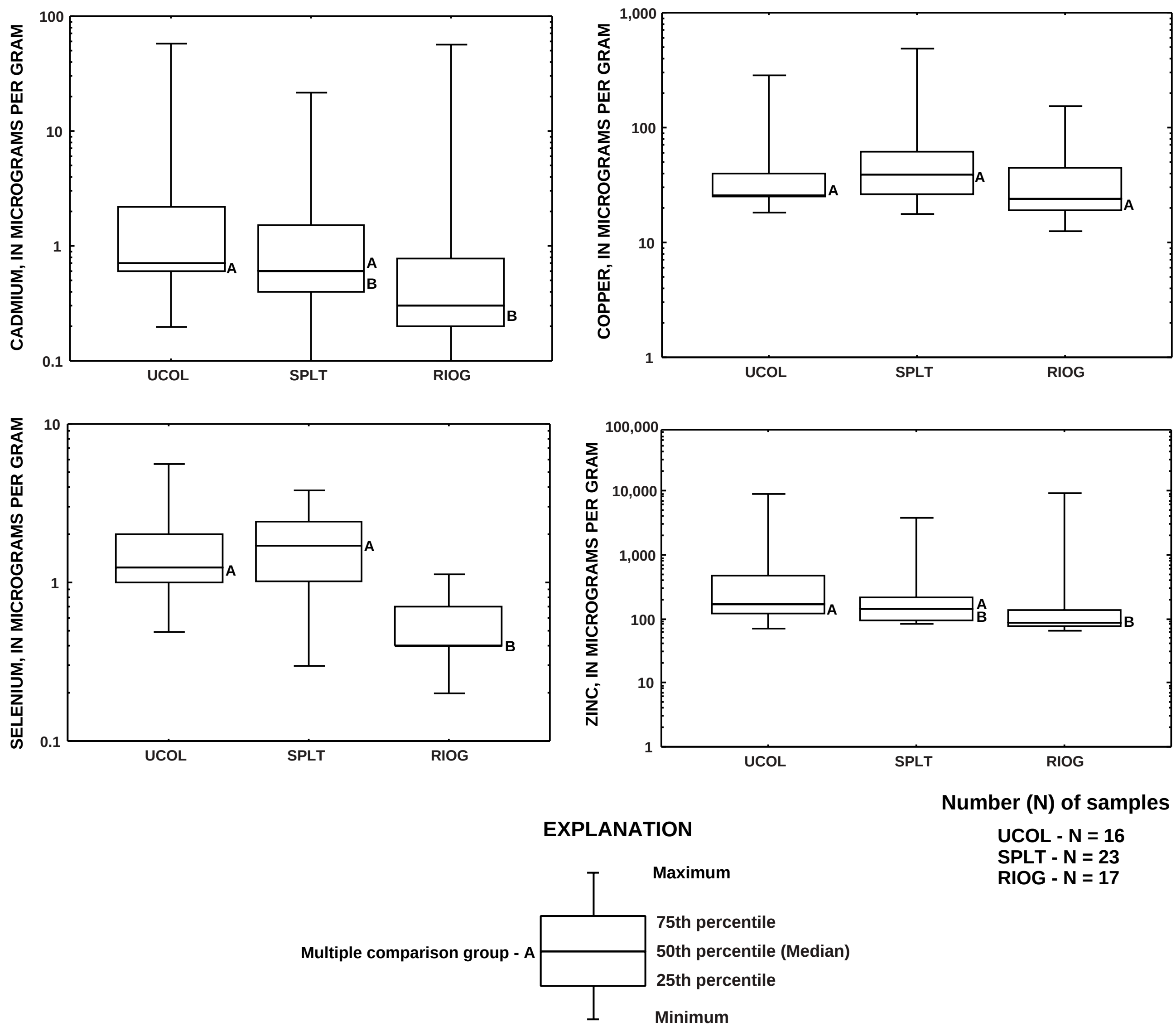

Figure 8. Comparison of concentrations for cadmium, copper, selenium, and zinc in streambed sediment for the Upper Colorado River Basin (UCOL), the South Platte River Basin (SPLT), and the Rio Grande Valley (RIOG) study units.

The Kruskall-Wallis statistical test (Helsel and Hirsch, 1992) was performed on the streambed-sediment and fish-liver data to determine if there were significant differences in the trace-element concentrations among the three study units. Comparison of streambed-sediment-sample concentrations for the three study units indicated significant differences for cadmium, selenium, and zinc ($p < 0.05$) and indicated that copper ($p > 0.05$) was not significantly different among the three study units. Comparison of fish-liver-sample concentrations indicated significant differences for copper, selenium, and zinc ($p < 0.05$) and indicated that cadmium ($p > 0.05$) was not significantly different among the three study units.

When results from the Kruskall-Wallis test indicated significant differences, a Tukey's multiple comparison test (Helsel and Hirsch, 1992) was used to determine which groups were significantly different. The letters A and B were assigned to each boxplot to denote significant statistical differences in the data sets. Boxplots that had the same letter were not significantly different, and boxplots that had different letters were significantly different.

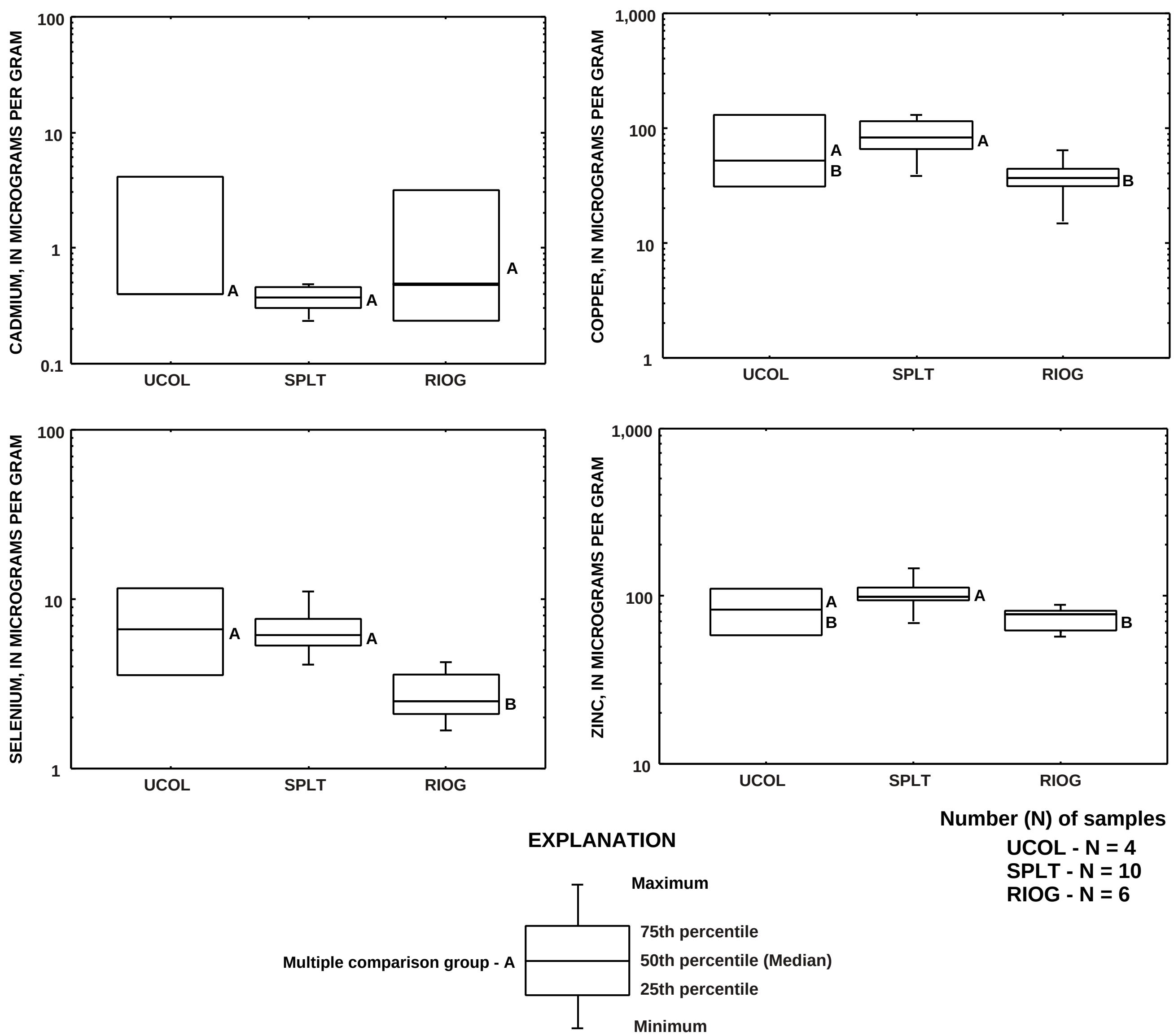

Figure 9. Comparison of concentrations for cadmium, copper, selenium, and zinc in fish liver (white sucker) for the Upper Colorado River Basin (UCOL), the South Platte River Basin (SPLT), and the Rio Grande Valley (RIOG) study units.

Regional similarities in streambed-sediment concentrations occurred more often than regional differences among the three study units. More relations were observed between two study units rather than among all three study units. For example, the UCOL and the SPLT study units were similar for all four trace elements. The SPLT and RIOG were similar for cadmium and zinc. All three study units were similar for copper (fig. 8).

Similarities for fish-liver concentrations existed between the UCOL and SPLT for all four trace elements. The UCOL and RIOG were similar for copper and zinc. All three study units were similar for cadmium (fig. 9).

All three study units have agricultural, mining, and urban land use. The highest concentrations for cadmium, copper, and zinc in streambed sediment for all three study units were at sites affected by mining. The only relation between fish-liver samples and land use for the four selected trace elements in the three study units was for cadmium. The highest concentrations for cadmium in fish-liver samples in the three study units were at sites affected by mining.

Streambed sediment is a better indicator than fish liver for assessing the occurrence and distribution of trace elements on a basinwide scale in the UCOL study unit and for developing relations between study units and land use. Streambed sediment is a consistent sampling medium among sites, which lessens the variability. However, fish-liver data do provide an indication of bioaccumulation of trace elements.

SUMMARY

The U.S. Geological Survey's National Water-Quality Assessment program is a long-term interdisciplinary program that is designed to integrate chemical, physical, and biological data to assess the Nation's surface- and ground-water quality. One component of this integrative assessment is to examine the occurrence and distribution of selected trace elements in streambed sediment and in tissues of aquatic organisms on a basin-wide scale. Sixteen sites in the Upper Colorado River Basin (UCOL) were sampled for trace elements in streambed sediment. Fourteen of the 16 sites also were sampled for trace elements in fish livers. Sites sampled represented agriculture, mining, mixed (mining and urban/recreation or agriculture and urban), and urban/recreation land uses and background conditions.

A total of six sites had concentrations that were greater than the PEL or high hazard level for one or more of the four trace elements selected for detailed analysis. Five sites in the Southern Rocky Mountain physiographic province exceeded the PEL for cadmium, copper, or zinc. Elevated concentrations at these sites may be a result of natural and human factors. One site in the Colorado Plateau exceeded the high hazard level for selenium.

The Southern Rocky Mountains physiographic province consists of geologic formations containing carbonate, igneous, metamorphic, and volcanic rocks, which contribute trace elements to water and sediment through processes of weathering. Particle-size determination of the samples indicated that sites chosen to represent mining land-use in the Southern Rocky Mountains physiographic province contained a larger percentage of silt/clay particles than other sites located in the Southern Rocky Mountains physiographic province. Generally, as particle size decreases, concentrations of trace elements increase. The geology in the middle to lower parts of the UCOL study unit consists mainly of sedimentary deposits. Mancos Shale of Cretaceous age is a predominant geologic formation in this area and contributes selenium concentrations to streambed sediment. Irrigation return flows also can enhance the transport of this naturally occurring element to surface waters. Cadmium, copper, and zinc concentrations in streambed sediment were highest at sites located in the Southern Rocky Mountains physiographic province, particularly at sites representing mining land-use settings. The highest selenium concentration was at an agricultural land-use site located in the Colorado Plateau physiographic province.

Collection of the same fish species on a basin-wide scale often is difficult. Because different species can bioconcentrate certain trace elements at different rates, multiple taxa in a study unit are sometimes difficult to compare. Migration and mobility of fish also add to variability when comparing sites and land use. Although there is a strong relation between trace elements in streambed sediment and land use, relations of trace-element concentrations in fish liver to land-use effects are not as obvious.

Similar patterns were indicated for streambed-sediment concentrations between the RIOG, the SPLT, and the UCOL study units. The highest concentrations of cadmium, copper, and zinc in streambed sediment were at sites affected by mining. Selenium concentrations in streambed sediment did not have similar land-use patterns among the three study units. Comparison of concentrations of copper, selenium, and zinc in fish-liver samples to land use indicated that the relations among the three study units did not have similar patterns. The only similarity among fish-liver samples and land use in the three study units was for cadmium concentrations. The highest concentrations for cadmium in fish liver in the three study units were at sites affected by mining.

Streambed sediment is a better indicator than fish liver for assessing the occurrence and distribution of trace elements on a basinwide scale in the UCOL study unit and in developing relations between the UCOL, the SPLT, and the RIOG study units. It is a consistent sampling medium among sites, which lessens the variability in analysis. The fish-liver data in the UCOL study unit and relation to the SPLT and the RIOG study units provided less comparable data to land use than the streambed-sediment data.

The combined use of streambed-sediment and biota analyses does, however, provide an understanding of the fate, distribution, and potential effects of contaminants. Measuring concentrations of trace elements in streambed sediment and fish liver at the same site offers a more complete description, than just one sampling medium, of the occurrence and distribution of trace elements in a study unit.

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