Columbia Environmental Research Center

Selenium and other trace elements in water, sediment, aquatic plants, aquatic invertebrates, and fish from streams in southeastern Idaho near phosphate mining operations: June 2000.

Final Report as part of the USGS Western U.S. Phosphate Project

October 10, 2002

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Abstract

Nine stream sites in the Blackfoot River watershed in southeastern Idaho were sampled in June 2000 for water, surficial sediment, aquatic plants, aquatic invertebrates, and fish. Selenium and other inorganic elements were measured in these aquatic ecosystem components, and a hazard assessment was performed on the data. Water quality characteristics such as pH, hardness, and specific conductance were relatively uniform among the nine sites examined. Of the aquatic components assessed, water was the least contaminated with selenium because measured concentrations were substantially below the national water quality criterion of 5 µg/L at 7 of the 9 sites. In contrast, selenium and several inorganic elements were elevated in sediment, aquatic plants, and aquatic invertebrates from several sites suggesting deposition in sediments and food web cycling through plants and invertebrates. Selenium was elevated to concentrations of concern in fish at seven sites (> 4 µg/g in whole body). A hazard assessment of selenium in the aquatic environment suggested low hazard at Trail Creek and Sheep Creek, moderate hazard at upper Slug Creek and lower Slug Creek, and high hazard at Angus Creek near the mouth, upper East Mill Creek, lower East Mill Creek, Dry Valley Creek, and lower Blackfoot River. Thus, the results of this study indicate that selenium concentrations from the phosphate mining area of southeastern Idaho were sufficiently elevated in several ecosystem components to cause adverse effects to aquatic resources in the Blackfoot River watershed.

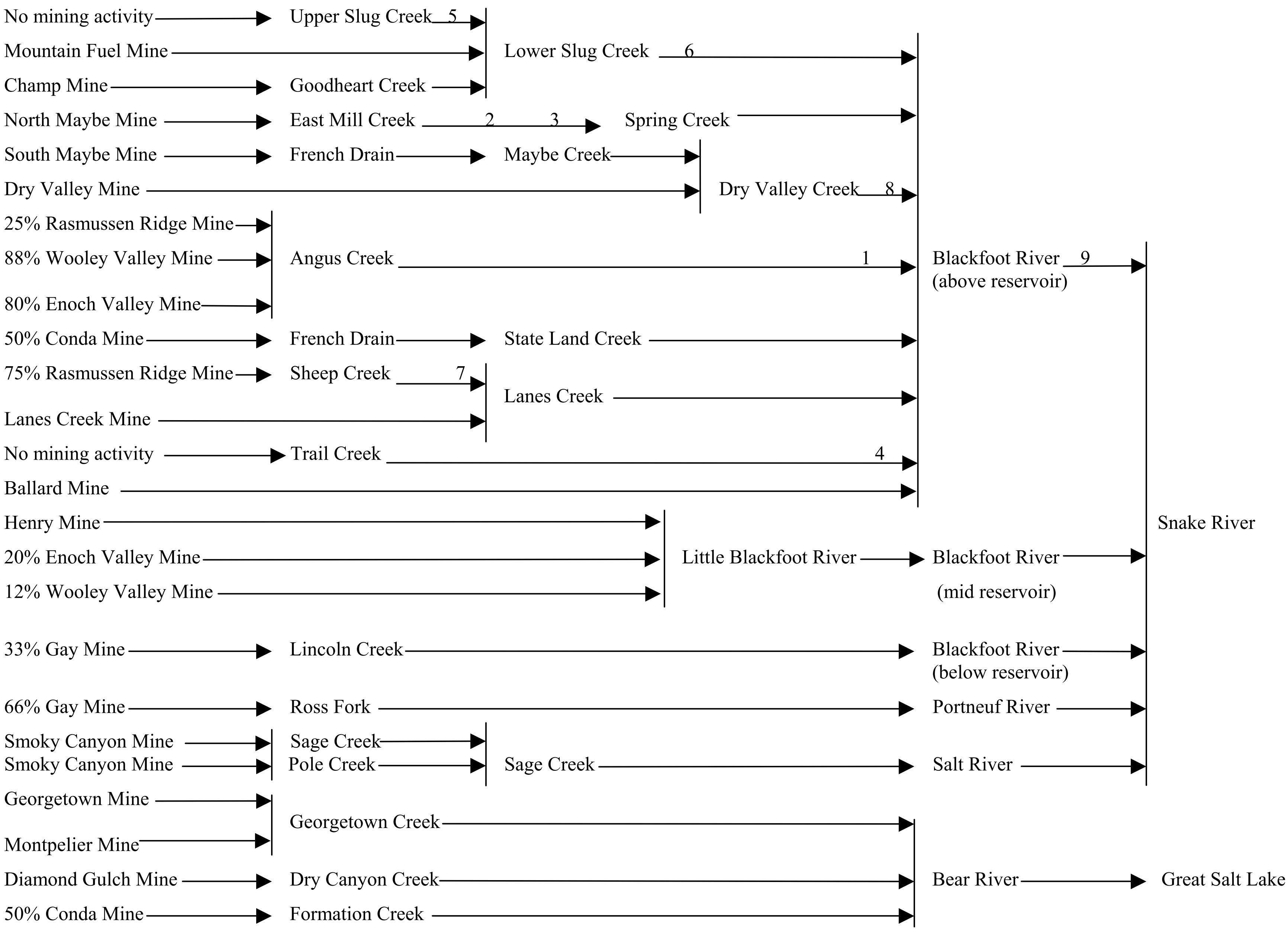
Introduction

Phosphorus is present in economically mineable quantities in organic-rich black shales of the Permian Phosphoria Formation, which constitutes the Western Phosphate Field. There are four active open pit mines in southeastern Idaho Phosphate District that produce phosphate from the Meade Peak Phosphatic Shale Member. In 1997 there were four active and 10 inactive mines in the Southeast Idaho Phosphate Resource Area (Montgomery Watson 1999). Most mining of these phosphatic shales is by open-pit surface mining, and waste materials are generally disposed of on the surface in tailings piles, ponds, landfills, and dumps. Many of the waste piles have drainage systems to move surface water and groundwater away from waste piles after which it reaches other surface waters, eventually draining into tributaries, and later, the Blackfoot River and Blackfoot Reservoir. Thus, water movement releases toxic trace elements to aquatic and terrestrial ecosystems.

The Blackfoot River watershed has several active and inactive phosphate mines that potentially could adversely affect aquatic resources in several tributaries of the Blackfoot River (Figure 1). As early as 1970-1976 concerns about contamination of the Blackfoot River and its tributaries by inorganic elements released from phosphate mining activities were expressed (Platts and Martin 1978). Recent concerns about the potential impact on aquatic and terrestrial ecosystems from phosphate mining activities have been the subject of several reports (Montgomery Watson 1999, 2000, 2001a, 2001b). Several investigations by the U.S. Geological Survey (USGS) have reported the chemical composition of weathered and less weathered strata of the Meade Peak phosphoatic shale (Desborough et al. 1999, Herring et al. 2000a, 2000b). Other USGS investigations have reported trace element concentrations in aquatic bryophytes and terrestrial plants that were influenced by mining activities (Herring and Amacher 2001, Herring et al. 2001).

Release of toxic trace elements from mining activities and accumulation in the food chain

Figure 1. Diagram of surface and ground water flow from phosphate mines to drains, creeks, and rivers in southeastern Idaho. Numbers are sample locations: 1 Angus Creek, 2 upper East Mill Creek, 3 lower East Mill Creek, 4 Trail Creek, 5 upper Slug Creek, 6 lower Slug Creek, 7 Sheep Creek, 8 Dry Valley Creek, 9 lower Blackfoot River.



has resulted in the adverse biological effects. In recent years, seven horses in the Dry Valley and Woddall areas were euthanized, and 60-80 sheep were found dead on the Caribou National Forest on the old Stauffer Mine site due to selenium poisoning according to toxicologist and veterinarian reports (Caribou County Sun 1999). Twenty-six dead sheep were found at the south end of Rasmussen Ridge Mine near a spring or seep at an overburden ore site. Elevated concentrations of selenium and other trace elements have been reported in limited samples of fish fillets and aquatic invertebrates (Montgomery Watson 1999). A recent USGS report suggested that selenium concentrations in fish and wildlife were sufficiently elevated to cause adverse effects in sensitive fish species (Piper et al. 2000).

The purpose of this study was to determine the concentrations of selenium and other trace elements in water, surficial sediment, aquatic plants, aquatic invertebrates, and fish from streams in southeastern Idaho near phosphate mining operations. This information was used in a hazard assessment of the potential effects of selenium and other inorganic elements on aquatic resources in areas of the Blackfoot River watershed that are potentially impacted by phosphate mining activities.

Methods and Materials

Samples of water, surficial sediment, aquatic plants, aquatic invertebrates, and fish were collected from nine sites in the Blackfoot River watershed located in southeastern Idaho (Figures 2 and 3, Table 1). Samples were collected in June 2000.

Site description

The collection sites were:

1. The Angus Creek near mouth site was located at the crossing of the creek by Forest Route 095 (U.S. Forest Service map, Caribou National Forest, Montpelier and Soda Springs Districts, 1988), and was approximately a half km above the confluence with the Blackfoot River. The land on either side of the road was managed by the Idaho Department of Fish and Game and was composed primarily of grassland habitat with sparse forbs and very limited grazing activity. Sample collection was primarily on the upstream side of the road crossing.

2. The upper East Mill Creek site was located near an unmaintained dirt road (Forest Route 309) about 2 miles from the intersection of Forest Route 102 and Forest Route 309, and was approximately 8 km above the confluence with the Blackfoot river. The land was owned by the U.S. Forest Service and was composed of pine forest with some sagebrush in open areas. Sample collection was in a generally open area of forbs, grass, and spare pine trees with very limited grazing activity.

3. The lower East Mill Creek site was located at the crossing of the creek by Forest Route 102. The site was located approximately 4 km below the upper East Mill Creek site and about 4 km above the confluence with the Blackfoot River. The site was on private land (Bear lake Grazing Company) accessed by landowner permission (Ms. Joan Bunderson). The land on either side of the road was composed of grass and sagebrush and had moderate grazing activity. Sample collection was about equally distributed upstream and downstream of the road crossing.

4. The Trail Creek site was located at the crossing of the creek by Trail Creek Road (Forest Route 124), and was approximately 8 km above the confluence with the Blackfoot River. The site was on private land accessed by landowner permission (Mr. Val Bloxham). The land

Figure 2. Map of study area. (Map source: modified from Herring et al. 2001).

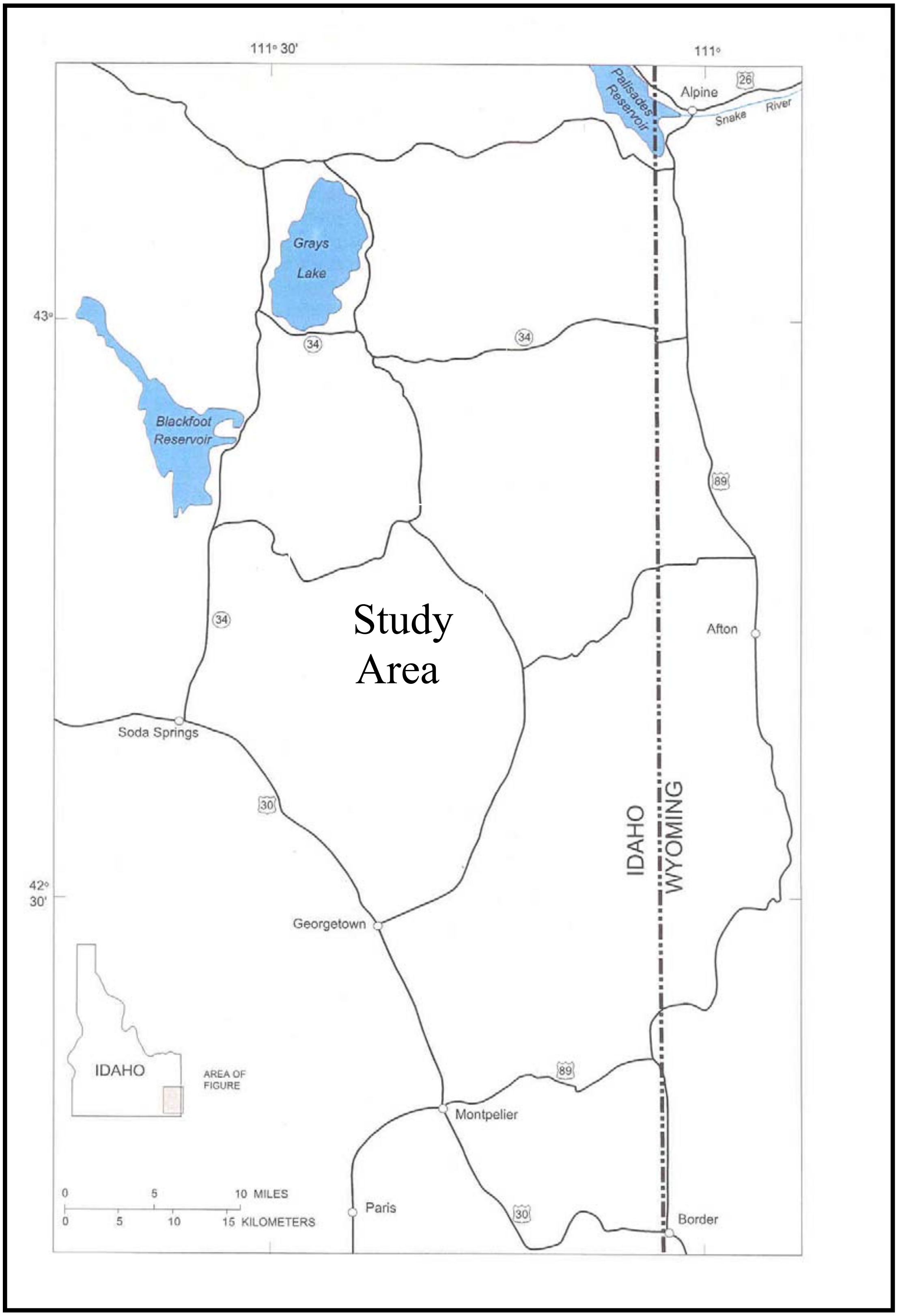


Figure 3. Map of sample sites: 1: Angus Creek, 2: upper East Mill Creek, 3: lower East Mill Creek, 4: Trail Creek, 5: upper Slug Creek, 6: lower Slug Creek, 7: Sheep Creek, 8: Dry Valley Creek, 9: lower Blackfoot River. (Map source: Bureau of Land Management, BLM/ID/GI-94/026+421A0 and BLM/GI-94/026+421A).

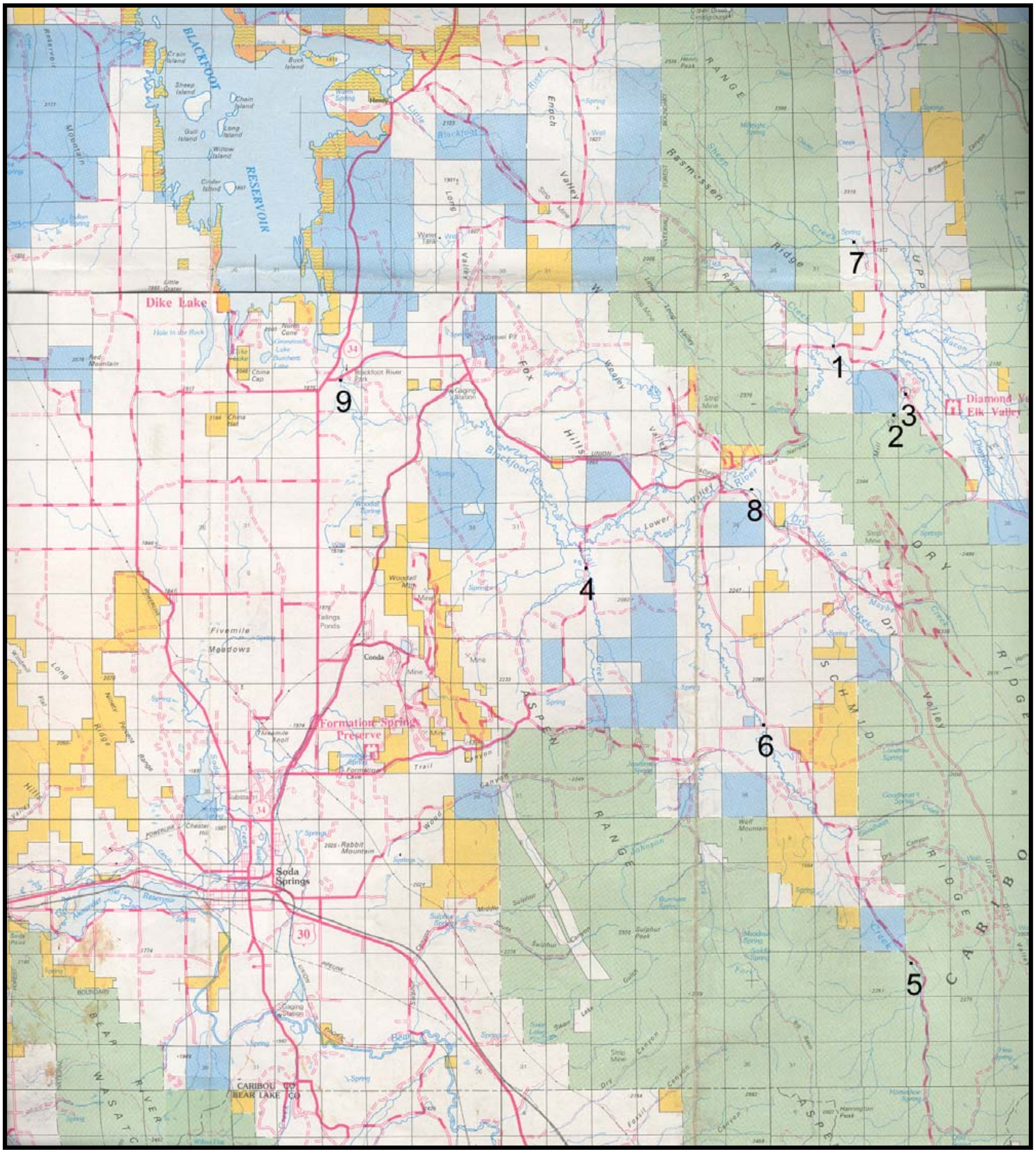


Table 1. Latitude and longitude of nine sites sampled in southeastern Idaho near Soda Springs, Idaho.

Site name & ID	Location[1]	
Angus Creek near mouth (ACM)	N42º49'42.24" W111º20'15.04"	±11m
Upper East Mill Creek (UEMC)	N42º48'26.74" W111º18'38.82"	±14m
Lower East Mill Creek (LEMC)	N42º48'53.56" W111º18'25.98"	±11m
Trail Creek (TC)	N42º45'29.82" W111º26'47.53"	±8m
Upper Slug Creek (USC)	N42º37'50.85" W111º18'20.51"	±14m
Lower Slug Creek (LSC)	N42º42'23.79" W111º22'03.89"	±9m
Sheep Creek (ShpC)	N42º51'46.92" W111º20'00.53"	±18m
Dry Valley Creek (DVC)	N42º46'58.71" W111º22'26.47"	±14m
Lower Blackfoot River (LBR)	N42º49'12.49" W111º33'09.33"	±10m

[1]Global positioning system: Rockwell International, type HNV-560C, Cedar Rapids, Iowa (readings courtesy of Phil Moyle, USGS, GD).

on either side of the road was grazed grassland. Sample collection was primarily downstream of the crossing in an area with light grazing activity, whereas the upstream side of the crossing had moderate to heavy grazing activity.

5. The upper Slug Creek site was located about 2 km inside the U.S. Forest Service boundary on Slug Creek Road (Forest Route 095) and approximately a quarter mile off the gravel road that paralleled the stream. The site was located above the influence of mining activities and >20 km above the confluence with the Blackfoot River. The land was owned by the U.S Forest Service. The vegetation around the stream was primarily willow-type shrubs with sparse grass, but there was a substantial amount of sagebrush and quaking aspen trees nearby. The site had light grazing activity. This site was considered the reference site.

6. The lower Slug Creek site was located at the intersection of Slug Creek Road (Forest Route 095) and Old Mill Road (Forest Route 124). The site was in the road right-of-way, and about 10 km above the confluence with the Blackfoot River. The land around the stream was primarily grassland and was heavily grazed in one area downstream and lightly grazed in two other areas upstream. Sample collection was upstream of the heavily grazed area in a stream section with little grazing activity.

7. The Sheep Creek site was located on private land (Sheep Creek Guest Ranch) about 3 km upstream of the crossing of the creek by Forest Route 095. The site was accessed with landowner permission (Mr. Phil Baker). The land along the stream was primarily pine forest with some forbs, shrubs, and grass. Sample collection for water, sediment, and fish was upstream of most animal and human activity at the end of a private road and about 2 km above Lanes Creek, which flowed into the Blackfoot River about 4 km downstream. Aquatic plants and one fish species were collected about 1.5 km downstream of the primary sample collection site and near the stream crossing with Forest Route 095 in an area of sagebrush and grass with moderate grazing activity.

8. The Dry Valley Creek site was located on private land (Hunsacker Ranch) about a half km from Forest Route 122 and accessed along a railroad track that paralleled the creek. The site was about 0.75 km above the confluence with the Blackfoot River. The land was accessed with landowner permission (Mr. and Mrs. Keith Hunsacker). The land along the stream was primarily grassland with some shrubs nearby and moderate grazing activity.

9. The lower Blackfoot River site was located on county parkland on the upstream side of a large steel and concrete bridge located on Blackfoot River Road about 0.5 km east of State Highway 34. The site was located approximately 1 km above the confluence with Blackfoot Reservoir. The land was accessed by landowner permission (Caribou County Commissioner Carol Davids-Moore). The land along the river was primarily riparian with some grass and light camping activity.

Sample Collection

Samples of water, surficial sediment, aquatic plants, aquatic invertebrates, and fish were collected at each of nine stream sites. Sample bottles used for water collection were conditioned by immersion in site water three times. Sample container conditioning and sample collection of water collected by the USGS Water Resources Discipline (WRD) technicians (Jay Bateman and Don Cole, Idaho Falls, ID) followed procedures of the WRD (USGS 1998). Water samples were collected using width and depth integrated sampling techniques. For each sample site, one set of samples was unfiltered, and a second set filtered through a 0.45 µm polycarbonate filter using standard sampling techniques of the WRD. One filtered water sample was collected for measurement of major cations and anions. A 200-ml sample of each filtered site water was collected in an acid-cleaned polyethylene bottle for analysis of selenium concentrations and a second bottle collected for analysis of inorganic element concentrations. A reagent blank was collected for analysis of selenium and inorganic element concentrations. The reagent blank consisted of deionized water from a mobile laboratory combined with the acid preservative. Water samples for selenium analysis were acidified with ultrapure HCl and those for inorganic elements were acidified with ultrapure HNO_3. All samples for inorganic element analyses were stored frozen.

Sediment was collected using a plastic scoop to gently acquire surficial sediments including detritus, but not pebbles or plant material. The scoop and sample container were rinsed in ambient water for sufficient time to condition the equipment to ambient conditions prior to sample collection. After sediments settled, excess water was removed and the sample stored frozen. One sample was used for analysis of selenium and mercury concentrations, and a second sample used for analysis of inorganic element concentrations.

Submerged aquatic plants (white-water buttercup, *Ranunculus longirostris*) were collected from each site. Plants were collected by hand. The sample consisted of leaf whorls removed from stems using plastic or stainless steel forceps. Two sets of plant samples were collected from each site, squeezed to remove excess water, weighed, bagged in Whirl-Pak bags, labeled, and stored frozen. One composite set was analyzed for selenium concentrations and the other set analyzed for inorganic element concentrations.

Aquatic invertebrates were sieved from bed substrate materials collected either by D-frame kick nets or removing large stones with attached invertebrates. Substrate was placed in large polypropylene trays and invertebrates separated from substrate using forceps or glass tubes with suction bulbs. Two sets of invertebrate samples were collected from each site, separated by taxa group, weighed, bagged in Whirl-Pak bags, labeled, and stored frozen. Each composite invertebrate sample contained half of the available taxa weight. One composite set was analyzed for selenium concentrations and the other set analyzed for inorganic element concentrations. An opportunistic sample of crane fly nymphs was collected at the head of Angus Creek at the base of a valley fill. This sample was split for analysis of selenium concentrations and inorganic element concentrations similar to the other aquatic invertebrates collected.

Fish were by collected by electrofishing using a Coffelt Mark-10 electroshocker. The anode and cathode wands were rinsed in ambient water for sufficient time to condition the equipment to ambient conditions. Equipment and operators (Bill Janowski and Larry Michelson) were provided by the U.S. Forest Service, Caribou National Forest, Soda Springs, ID. Two sets of fish samples were collected from each site, euthanized with MS-222 (tricaine methanesulfonate), identified to species (assistance provided by Jim Mende, Idaho Department of Fish and Game, Pocatello, ID), measured for total length and weight, bagged in Whirl-Pak bags, samples labeled with identification information, and stored frozen. One set of fish was analyzed for selenium concentrations in whole body and the other set analyzed for inorganic element concentrations in whole body. A specimen of each species was retained to confirm identification.

Water quality analyses and flow measurement

Ambient water samples at each study site were collected by WRD technicians and analyzed for general water quality characteristics according to standard methods (APHA et al. 1995). Site water was analyzed *in situ* for the following general water quality characteristics: conductivity, pH, temperature, and dissolved oxygen concentration.

Immediately after arrival of the test water at the mobile laboratory, the following water quality characteristics were measured: conductivity, pH, alkalinity, hardness, calcium, magnesium, and temperature. A subsample of 200ml water was collected and stored at 4ºC with no preservative, and transported to the CERC Field Research Station, Yankton, South Dakota, for analysis of sulfate and chloride. A second subsample of 125 ml water was collected, acidified with 0.5 ml concentrated H_2SO_4, and transported to Yankton for analysis of ammonia concentrations. All water quality characteristics were measured according to standard methods (APHA et al. 1995), except ammonia and chloride. Ammonia was measured using ion-selective electrodes and following the procedures for low concentration measurements of the electrode manufacturer (Orion Research 1990, 1991; ATI Orion 1994). Chloride was measured using a Buchler digital chloridometer.

WRD technicians also collected and measured water quality characteristics as part of WRD water sample collection efforts (pH, conductivity, alkalinity, bicarbonate, carbonate, dissolved oxygen, percent saturation, and water temperature). This duplication of effort allowed the Yankton FRS (Biological Resources Discipline: BRD) to cross check measurement analyses of water quality characteristics.

Inorganic Element Analysis

Water, surficial sediment, aquatic plants, aquatic invertebrates, and fish were analyzed for selenium concentrations by atomic absorption spectroscopy-hydride generation (AA-HG). Analyses were conducted at the Environmental Trace Substances Laboratory (ETSL), University of Missouri, Rolla, MO. Analyses incorporated appropriate quality assurance/quality control (QA/QC) procedures such as standardizing equipment with certified reference material, determination of limit of detection, analysis of reagent blanks, spiked samples (termed % recovery of digested spike), duplicate analysis samples (termed % relative standard deviation, RSD), certified reference materials, reference materials spiked before digestion (termed % recovery of reference material), and reference material spiked after digestion (termed % recovery of reference standard). Analysis of selenium concentrations was based on U.S. Environmental Protection Agency (USEPA) method 7000 (USEPA 1983), and results were reported on a dry weight basis.

A subsample of sediment was digested using a four acid procedure and analyzed for concentrations of selenium by AA-HG and mercury by cold vapor AA at the USGS, Geologic Discipline (GD) Laboratory at the Denver Federal Center, Denver, CO. All analyses incorporated QA/QC of the GD including standardizing analytical instruments using certified reference materials, determination of the limit of detection, and analysis of certified reference standards. Results were reported on a dry weight basis.

Water, surficial sediment, aquatic plant, aquatic invertebrate, and fish samples were analyzed for inorganic element concentrations by inductively-coupled argon plasma (ICP) spectrophotometry (aluminum, arsenic, barium, beryllium, boron, cadmium, chromium, copper, iron, lead, magnesium, manganese, molybdenum, nickel, strontium, vanadium, and zinc). Analyses were conducted by the ETSL, and incorporated appropriate QA/QC described above. Analysis of inorganic elements by ICP was based on USEPA method 6010 (USEPA 1983) and results were reported on a dry weight basis.

A subsample of sediment was digested using a four acid procedure and analyzed for concentrations of inorganic elements by ICP (major elements: calcium, magnesium, phosphorus, potassium, and sodium; trace elements: aluminum, antimony, arsenic, barium, beryllium, bismuth, cadmium, cerium, cesium, chromium, cobalt, copper, gallium, iron, lanthanum, lead, lithium, manganese, molybdenum, nickel, niobium, rubidium, scandium, silver, strontium, thallium, thorium, titanium, uranium, vanadium, yttrium, zinc). Analysis was conducted at the USGS, GD Laboratory at the Denver Federal Center, Denver, CO. All analyses incorporated QA/QC of the GD including standardizing analytical instruments using certified reference materials, determination of the limit of detection, and analysis of certified reference standards. Results were reported on a dry weight basis.

Statistical analyses

Data were analyzed using computer programs (SAS 1990) to determine the relation between various measures made during the study. Correlation analyses were used to test for relations among water quality characteristics, and selenium concentrations in water, sediments, aquatic plants, aquatic invertebrates, and fish. For fish residue data for each sample location, the geometric mean was used in correlation analyses with other variables. The Pearson correlation coefficients are reported.

Results

Water quality

Water quality characteristics measured by BRD were given in Table 2 and those measured by WRD were given in Table 3. The measurements for pH, conductivity, and alkalinity were similar between the two groups. The Pearson correlation coefficient between the two measures for pH were r=0.77 (P=0.02, n=9), conductivity r=0.99 (P<0.0001, n=9), and alkalinity r=0.99 (P<0.0001, n=9).

In general, Dry Valley Creek had the highest conductivity, hardness, calcium, magnesium, chloride, and sulfate concentrations of the nine sites examined. The other stream sites had generally similar water quality characteristics to each other, except sulfate was greater at Angus Creek mouth and lower at upper Slug Creek than the other sites. The nine sites were well oxygenated at the time of sampling as revealed by the high dissolved oxygen concentration and high percent saturation of dissolved oxygen (Table 3).

Inorganic elements

The QA/QC measures by AA-HG at ESTL for the determination of selenium concentrations in water, surficial sediment, aquatic plant, aquatic invertebrate, and fish samples are given in Table 4. In general the limit of detections (LOD) were 0.2 µg/g for analysis of surficial sediment, aquatic plant, aquatic invertebrate, and fish matrices and 0.5 µg/L for analysis of water. The procedure blank had background concentration less than the LOD, which indicated no contamination from reagents or sample handling. The percent relative standard deviation

Table 2. Water quality characteristics measured in water collected from nine sites in the Blackfoot River watershed. Number of samples (n) in brackets. If n>1, water quality measure is the mean; "<" indicates below limit of measurement.

	Location[1]								
Measure	ACM	UEMC	LEMC	TC	USC	LSC	DVC	ShpC	LBR
pH	8.2 [2]	8.1 [1]	8.3 [1]	8.3 [2]	8.1 [1]	8.2 [1]	7.9 [2]	8.2 [1]	7.9 [2]
Conductivity (µmhos/cm)	393 [1]	370 [1]	367 [1]	380 [1]	398 [1]	402 [1]	611 [1]	371 [1]	412 [1]
Hardness (mg/L as $CaCO_3$)	198 [2]	187 [1]	188 [1]	188 [2]	202 [1]	204 [1]	284 [2]	191 [1]	212 [2]
Calcium (mg/L)	61 [2]	55 [1]	55 [1]	57 [2]	59 [1]	59 [1]	86 [2]	58 [1]	59 [2]
Magnesium (mg/L)	11 [2]	12 [1]	12 [1]	11 [2]	13 [1]	14 [1]	17 [2]	11 [1]	16 [2]
Alkalinity (mg/L as $CaCO_3$)	170 [2]	178 [1]	179 [1]	183 [2]	206 [1]	198 [1]	186 [2]	182 [1]	204 [2]
Chloride (mg/L)	4.9 [1]	2.0 [1]	1.9 [1]	6.1 [1]	3.5 [1]	5.3 [1]	8.8 [1]	1.5 [1]	2.5 [1]
Sulfate (mg/L)	27.5 [1]	13.2 [1]	13.0 [1]	7.1 [1]	<5.0 [1]	9.9 [1]	96 [1]	12.8 [1]	10.2 [2]
Un-ionized ammonia (mg/L NH_3-N)	0.001 [1]	<0.001 [1]	<0.001 [1]	<0.001 [1]	<0.001 [1]	0.001 [2]	<0.001 [1]	0.001 [1]	<0.001 [1]
Total ammonia (mg/L as N)	0.02 [1]	0.02 [1]	<0.01 [1]	0.01 [1]	0.01 [1]	0.02 [2]	<0.01 [1]	0.03 [1]	<0.01 [1]

[1]ACM: Angus Creek near mouth, UEMC: Upper East Mill Creek, LEMC: Lower East Mill Creek, TC: Trail Creek, USC: Upper Slug Creek, LSC: Lower Slug Creek, DVC: Dry Valley Creek, ShpC: Sheep Creek, LBR: Lower Blackfoot River.

Table 3. Water quality characteristics measured in water collected from nine sites in the Blackfoot River watershed. Data from WRD, Idaho Falls, ID.

	Location[1]								
Measure	ACM	UEMC	LEMC	TC	USC	LSC	DVC	ShpC	LBR
pH	8.4	8.3	8.4	8.3	8.2	8.1	8.1	8.3	7.8
Conductivity (µmhos/cm)	380	357	353	362	388	399	548	359	407
Alkalinity (mg/L as $CaCO_3$)	170	180	178	184	208	196	186	184	210
Bicarbonate (mg/L)	198	210	206	215	244	234	227	214	256
Carbonate (mg/L)	4.3	4.3	5.3	4.8	4.3	2.4	0	5.3	0
Dissolved oxygen (mg/L)	8.5	9.1	8.7	10.9	9.3	10.6	10.2	9.6	9.1
% Saturation dissolved oxygen	93	84	85	102	86	111	111	87	98
Water temperature (°C)	20.1	12	23	12	12	22	19	11	19
Discharge (cfs)	1.63	1.48	0.78	3.08	0.92	2.96	0.80	5.03	87.5

[1]ACM: Angus Creek near mouth, UEMC: Upper East Mill Creek, LEMC: Lower East Mill Creek, TC: Trail Creek, USC: Upper Slug Creek, LSC: Lower Slug Creek, DVC: Dry Valley Creek, ShpC: Sheep Creek, LBR: Lower Blackfoot River.

Table 4. Quality assurance and quality control measures of selenium analysis of water, sediment, aquatic plants, aquatic invertebrates, and fish collected at nine sites in the Blackfoot River watershed. N=1 for water, sediment, aquatic plants, and aquatic invertebrates; n=2 for fish (mean and standard error in parentheses). Analyses at ESTL, Rolla, MO.

	Matrix				
Measure	Water	Sediment	Aquatic Plant	Aquatic Invertebrate	Fish
Limit of detection (LOD) (µg/L or µg/g)	0.5	0.2	0.2	0.2	0.2 (0)
Procedural blank	<LOD	<LOD	<LOD	<LOD	<LOD
% RSD[1]	<LOD	2.0	6.2	1.6	2.5 (1.3)
% Recovery of certified material	94[2]	NG[3,4]	81[5]	90[5]	92[5] (2)
% Recovery of digested spike	95	88	85	103	101 (3)
% Recovery of reference material	96	95	95	94	88 (2)
% Recovery of reference standard	96	94	94	94	94 (0)

[1]%RSD: percent relative standard deviation for duplicate preparation and analysis.
[2]National Institute of Standards and Technology (NIST) standard reference material 1643d (water).
[3]NG: not given.
[4]NIST standard reference material 2704 (Buffalo River sediment).
[5]National Resource Council of Canada standard reference material DORM-2 (dogfish muscle).

(duplicate preparation and analysis) ranged from <LOD to 6.2%, which indicated consistent sample handling during preparation, digestion, and analysis. Percent recovery of selenium from certified material ranged from 81 to 94%, which indicated the digestion and analysis procedure accurately measured selenium concentrations. Percent recovery of selenium from samples spiked before digestion ranged from 85 to 103%, which indicated the digestion procedure did not alter the amount of spiked selenium in the sample, i.e., suggested no loss of selenium during digestion. Percent recovery of selenium spiked in reference material before digestion ranged from 88 to 96%, which indicated the digestion procedure did not alter the amount of spiked selenium in the reference material. Percent recovery of selenium spiked in reference material after digestion ranged from 94 to 96%, which indicated little interference by other elements during the selenium analysis.

The QA/QC measures by ICP at ESTL for the determination of inorganic element concentrations in water, surficial sediment, aquatic plant, aquatic invertebrate, and fish samples are given in Table 5. In general the LOD, procedural blanks, relative standard deviation of duplicate preparation and analysis, and spike recoveries were comparable to those in the selenium analysis.

The QA/QC measures for the determination of mercury by cold vapor AA and selenium by AA-HG at the GD lab involved analysis of three reference materials. The recovery of mercury from reference materials ranged from 82 to 102% and for selenium ranged from 107 to 109%.

The QA/QC measures by ICP at the GD lab for the determination of inorganic element concentrations in sediment are given in Table 6. In general the LOD, percent relative standard deviation for duplicate preparation and analysis, and percent recovery of elements in standard reference materials was comparable between the GD lab and ESTL.

Water

Selenium concentrations in water from seven sites were less than the LOD (<0.5 µg/L) (Table 7). However, selenium in water was elevated at upper East Mill Creek, which had 30 µg/L, and at lower East Mill Creek, which had 15 µg/L.

Concentrations of inorganic elements in water were generally similar among the nine sites (Table 8). Although upper and lower East Mill Creek had elevated selenium concentrations, they were not among the highest in other inorganic element concentrations, except for strontium. Dry Valley Creek, relative to the other eight sites, had elevated aluminum, copper, iron, and magnesium.

Sediment

Selenium concentrations in surficial sediment were relatively low at five sites (<2 µg/g), moderately elevated at the Dry Valley Creek and lower Blackfoot River (2.1-5.2 µg/g), and very elevated at the upper and lower East Mill Creek (33-52 µg/g) (Tables 7 and 9). Sheep Creek and Trail Creek had the lowest selenium concentrations in surficial sediment. Mercury did not seem to be elevated at the nine sites (Table 9).

Concentrations of inorganic elements in surficial sediments followed a similar pattern as selenium in sediments (Tables 10-11). Upper and lower East Mill Creek tended to have the highest concentrations of antimony, cadmium, chromium, copper, molybdenum, nickel, silver, vanadium and zinc, whereas Dry Valley Creek had a moderate amount of these elements relative

Table 5. Quality assurance and quality control measures of analyses of inorganic elements in water (W), sediment (S), aquatic plants (P), aquatic invertebrates (I), and fish (F) collected at nine sites in the Blackfoot River watershed. N=1 for water, sediment, aquatic plants, and aquatic invertebrates; n=2 for fish (mean and standard error in parentheses). Analyses at ESTL, Rolla, MO.

	LOD[1]			% RSD[2]				
Element	W (µg/L)	S, P, I, F (µg/g)	Procedural blank	W	S	P	I	F
Aluminum	20	6	<LOD	0.2	4.3	6.4	9.4	6.0 (2.6)
Arsenic	10	2	<LOD	11	3.2	7.0	12.2	<LOD
Barium	0.7	0.07	<LOD	5.3	4.9	2.6	2.6	5.4 (0.6)
Beryllium	0.8	0.08	<LOD	<LOD	8.7	<LOD	<LOD	<LOD
Boron	4	0.4	<LOD	7.0	1.1	0.7	9.3	3.2 (1.7)
Cadmium	3	0.3	<LOD	<LOD	8.4	2.6	5.6	<LOD
Chromium	8	0.8	<LOD	6.6	9.6	0.2	6.4	5.2 (2.1)
Copper	2	0.2	<LOD	<LOD	6.4	1.3	3.0	6.6 (0.7)
Iron	4	0.4	<LOD	6.5	1.0	8.1	9.0	3.5 (1.8)
Lead	10	0.2	<LOD	<LOD	1.6	<LOD	<LOD	<LOD
Magnesium	0.6	0.06	<LOD	2.3	0.7	2.1	2.2	4.4 (1.2)
Manganese	1	0.1	<LOD	3.5	1.1	0.1	10.8	10.6 (0.3)
Molybdenum	5	0.5	<LOD	<LOD	<LOD	12.6	13.8	<LOD
Nickel	5	0.5	<LOD	8.9	13.1	5.2	3.6	10.3 (3.7)
Strontium	0.3	0.03	<LOD	4.1	4.3	6.6	0.5	4.2 (0.2)
Vanadium	2	0.2	<LOD	<LOD	11.9	3.8	6.1	5.9 (1.3)
Zinc	5	0.5	<LOD	<LOD	11.8	1.2	4.4	5.2 (0.6)

Table 5. Continued.

	% Recovery of certified materials					% Recovery of digested spike				
Element	W[3]	S[4]	P[5]	I[5]	F[5]	W	S	P	I	F
Aluminum	92	88	81	105	86(0)	100	97	103	100	92(1)
Arsenic	106	95	95	92	88(1)	102	97	93	105	93(2)
Barium	95	109	NG	NG	NG	100	101	92	99	90(1)
Beryllium	79	NG	NG	NG	NG	<LOD	84	105	101	96(1)
Boron	90	NG[6]	NG	NG	NG	102	98	90	96	90(3)
Cadmium	97	103	90	90	85(0)	93	96	104	98	96(4)
Chromium	91	87	108	85	96(2)	90	97	103	106	97(1)
Copper	99	90	96	102	108(1)	95	102	88	97	98(5)
Iron	94	90	105	91	98(4)	99	94	98	102	95(4)
Lead	104	91	95	110	100(10)	93	94	103	102	92(4)
Magnesium	90	88	NG	NG	NG	98	104	101	105	86(4)
Manganese	106	91	105	101	96(4)	108	102	80	97	94(5)
Molybdenum	89	NG	NG	NG	NG	97	92	94	107	96(0)
Nickel	105	110	109	95	104(2)	103	92	93	103	94(3)
Strontium	94	NG	NG	NG	NG	96	96	98	92	94(0)
Vanadium	103	89	NG	NG	NG	101	105	94	105	91(4)
Zinc	90	97	103	95	100(1)	91	87	92	91	89(1)

[1]LOD: Limit of detection.
[2]%RSD: percent relative standard deviation for duplicate preparation and analysis.
[3]National Institute of Standards and Technology (NIST) standard reference material 1643d (water).
[4]NIST standard reference material 2704 (Buffalo River sediment).
[5]National Resource Council of Canada standard reference material DORM-2 (dogfish muscle).
[6]NG: not given.

Table 6. Quality assurance and quality control measures of analyses of inorganic elements in sediment collected at nine sites in the Blackfoot River watershed. Analyses at the GD lab, Denver, CO.

Element	LOD[1]	% RSD[2]	% spike recovery	% Recovery in reference material NIST 2704[3]	% Recovery in reference material GSD-3[4]	% Recovery in reference material PACS-2[5]
Mercury	NG[6]	NG	NG	88	82	102
Selenium	NG	NG	NG	107	108	109
Major elements						
Calcium	20	3.6	NG	100	104	101
Magnesium	0.3	2.0	NG	98	91	90
Phosphorus	8	3.9	NG	99	99	101
Potassium	20	3.3	NG	98	97	96
Sodium	6	2.5	NG	103	84	91
Trace elements						
Aluminum	8	0.6	NG	98	100	96
Antimony	0.02	24.7	NG	90	122	105
Arsenic	2	2.7	99	89	106	101
Barium	0.5	3.6	103	101	99	NG
Beryllium	0.001	0	100	NG	93	100
Bismuth	0.005	0	95	NG	98	NG
Cadmium	0.003	3.0	101	99	105	100
Cerium	0.5	0.2	NG	84	98	NG
Cesium	0.003	2.4	102	93	99	99
Chromium	0.2	5.0	113	104	100	97
Cobalt	0.1	5.8	100	95	96	97
Copper	0.5	2.6	96	93	99	93
Gallium	0.006	1.7	97	100	98	NG
Iron	50	6.1	NG	98	100	99
Lanthanum	0.3	3.5	NG	114	100	NG
Lead	0.2	9.4	98	88	108	88
Lithium	0.2	2.3	96	92	102	94
Manganese	0.2	5.4	NG	105	105	96
Molybdenum	0.1	4.8	NG	NG	99	96
Nickel	1	2.7	93	90	100	91
Niobium	2	1.1	NG	NG	100	NG
Rubidium	0.01	3.0	100	97	98	NG
Scandium	0.3	1.3	NG	101	96	NG
Silver	0.05	26.7	111	NG	76	75
Strontium	0.05	3.9	101	103	105	98
Thallium	0.003	1.7	NG	102	88	95
Thorium	0.03	2.2	NG	95	103	NG
Titanium	40	3.9	NG	72	84	119
Uranium	0.02	7.6	108	95	94	NG
Vanadium	0.4	5.1	103	97	98	100
Yttrium	0.3	3.7	NG	NG	69	NG
Zinc	5	4.8	101	97	109	96

Table 6. Continued.

[1]LOD: limit of detection.
[2]%RSD: percent relative standard deviation for duplicate sample preparation and analysis.
[3]NIST 2704: National Institute of Standards and Technology standard reference material 2704 (Buffalo River sediment).
[4]GSD-3: Chinese Stream sediment standard.
[5]PACS-2: National Research Council Canada marine sediment standard.
[6]NG: not given.

Table 7. Selenium concentrations (µg/L for water and µg/g dry weight for sediment, aquatic plants, and aquatic invertebrates; n=1; <: less than limit of detection) in water, sediment, aquatic plants, and aquatic invertebrates collected from nine sites in the Blackfoot River watershed. Analyses at ESTL, Rolla, MD.

	Location[1]									
Matrix	ACH	ACM	UEMC	LEMC	TC	USC	LSC	DVC	ShpC	LBR
Water	NS[2]	<0.5	29.9	14.9	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
Sediment	NS	1.0	32.5	45.8	0.8	0.8	1.7	5.2	0.5	2.1
Aquatic plant[3]	NS	0.9	30.2	74.1	0.8	1.1	1.5	3.8	0.6	4.5
Aquatic invertebrate[4]	186	7.2	35.7	NS	2.9	4.9	NS	19.5	2.6	5.4

[1]ACH: seep at head of Angus Creek; ACM: Angus Creek near mouth; UEMC: upper East Mill Creek; LEMC: lower East Mill Creek; TC: Trail Creek; USC; upper Slug Creek; LSC: lower Slug Creek; DVC: Dry Valley Creek: ShpC: Sheep Creek; LBR: lower Blackfoot River.
[2]NS: not sampled.
[3]Aquatic plant samples consisted of leaves of white-water buttercup *Ranunculus longirostris.*
[4]Aquatic invertebrate samples consisted of composites of several taxa, except only one taxon (Tipulidae) was collected from ACH.

Table 8. Inorganic element concentrations (µg/g dry weight; n=1; <: less than limit of detection) in water from nine sites in the Blackfoot River watershed. Analyses at ESTL, Rolla, MO.

	Location[1]								
Element	ACM	UEMC	LEMC	TC	USC	LSC	DVC	ShpC	LBR
Aluminum	46	54	26	42	50	20	89	63	98
Arsenic	14	13	11	11	16	12	13	11	11
Barium	37	24	26	56	67	39	42	60	54
Beryllium	<0.8	<0.8	<0.8	<0.8	<0.8	<0.8	<0.8	<0.8	<0.8
Boron	48	48	37	43	46	40	51	47	48
Cadmium	<3	<3	<3	<3	<3	<3	<3	<3	<3
Chromium	8	7	8	7	8	8	7	8	8
Copper	<2	<2	<2	<2	<2	<2	12	<2	<2
Iron	103	89	90	92	106	94	164	90	106
Lead	<10	<10	<10	<10	<10	<10	<10	<10	<10
Magnesium	12,900	14,000	13,200	11,200	13,000	13,000	17,300	12,700	16,600
Manganese	86	4	5	79	28	31	70	10	42
Molybdenum	<5	<5	<5	<5	<5	<5	<5	<5	<5
Nickel	12	9	9	9	9	18	13	9	9
Strontium	199	245	234	150	136	230	203	111	208
Vanadium	<2	<2	<2	<2	<2	<2	<2	<2	<2
Zinc	<5	<5	<5	<5	<5	<5	<5	<5	<5

[1]ACM: Angus Creek near mouth; UEMC: upper East Mill Creek; LEMC: lower East Mill Creek; TC: Trail Creek; USC; upper Slug Creek; LSC: lower Slug Creek; DVC: Dry Valley Creek: ShpC: Sheep Creek; LBR: lower Blackfoot River.

Table 9. Concentrations of mercury and selenium (µg/g dry weight; n=1; <: less than limit of detection) in sediment from nine sites in the Blackfoot River watershed. Analyses at the GD lab, Denver, CO.

	Location[1]								
Element	ACM	UEMC	LEMC	TC	USC	LSC	DVC	ShpC	LBR
Mercury	0.03	0.10	0.10	0.03	0.04	0.02	0.04	<0.02	0.02
Selenium	1.0	35	52	1.4	1.0	1.3	4.3	0.4	2.1

[1]ACM: Angus Creek mouth; UEMC: upper East Mill Creek; LEMC: lower East Mill Creek; TC: Trail Creek; USC; upper Slug Creek; LSC: lower Slug Creek; DVC: Dry Valley Creek: ShpC: Sheep Creek; LBR: lower Blackfoot River.

Table 10. Inorganic element concentrations (µg/g dry weight; n=1; <: less than limit of detection) in sediment from nine sites in the Blackfoot River watershed. Analyses at the GD lab, Denver, CO.

	Location[1]								
Element	ACM	UEMC	LEMC	TC	USC	LSC	DVC	ShpC	LBR
Major elements									
Calcium	16,200	31,200	36,600	37,000	16,000	47,600	16,900	20,200	82,100
Magnesium	6,500	7,630	7,500	6,360	4,960	2,400	6,280	5,680	7,070
Phosphorus	3,820	6,860	4,940	2,180	2,120	14,100	2,930	1,680	1,880
Potassium	14,800	16,500	17,100	12,900	17,300	7,550	16,500	15,500	14,100
Sodium	6,760	6,800	6,910	6,610	6,580	3,190	6,750	6,220	5,780
Trace elements									
Aluminum	47,700	46,500	48,800	39,200	43,200	20,000	52,200	39,200	39,100
Antimony	0.39	1.10	0.84	0.26	0.44	0.20	0.48	0.21	0.34
Arsenic	7.4	8.2	8.6	2.5	6.4	4.5	4.5	3.2	3.3
Barium	603	391	400	446	527	279	525	354	460
Beryllium	1.7	1.7	1.7	1.2	1.3	0.8	1.7	1.3	1.4
Bismuth	0.14	0.14	0.15	0.09	0.12	0.03	0.17	0.06	0.10
Cadmium	3.3	9.6	8.4	1.0	3.6	2.4	8.8	0.3	1.4
Cerium	66.0	56.3	51.4	49.4	53.7	42.1	58.4	50.9	46.6
Cesium	4.2	4.5	4.7	3.3	4.4	1.6	4.9	3.1	3.8
Chromium	93	329	343	114	78	124	128	40	54
Cobalt	13.3	8.8	8.1	5.8	7.0	3.9	9.8	6.7	6.8
Copper	15.3	33.6	30.9	12.6	14.6	5.9	22.3	8.9	12.8
Gallium	11.7	11.2	11.4	9.3	10.1	4.6	12.8	8.8	9.0
Iron	25,400	22,100	22,000	16,100	16,600	8,340	24,900	16,300	17,600
Lanthanum	39.3	47.0	39.0	32.4	34.6	49.8	36.9	30.2	27.0
Lead	17.2	14.3	13.4	10.8	14.6	7.5	15.6	11.4	12.2
Lithium	30.1	31.2	31.7	21.5	29.7	13.8	29.6	25.0	23.5
Manganese	5,740	1,990	1,290	1,120	676	363	1,970	348	1,110
Molybdenum	0.64	3.50	3.50	0.56	0.33	0.57	0.56	0.25	0.28
Nickel	28.9	67.9	64.5	19.0	19.5	11.6	75.2	15.7	17.6
Niobium	9.2	9.5	6.4	8.1	14	5.0	14	6.5	13

Table 10. Continued.

	Location[1]								
Element	ACM	UEMC	LEMC	TC	USC	LSC	DVC	ShpC	LBR
Trace elements									
Rubidium	73.4	74.2	78.8	61.7	87.0	31.8	81.8	62.8	68.0
Scandium	7.8	8.7	8.5	6.2	5.8	3.5	8.3	6.0	6.8
Silver	0.34	1.30	1.40	0.27	0.28	0.36	0.30	0.24	0.28
Strontium	125	184	182	134	146	194	140	82	193
Thallium	0.60	0.78	0.75	0.45	0.56	0.27	0.81	0.41	0.48
Thorium	8.9	8.4	8.6	7.2	8.6	4.1	9.8	7.2	7.3
Titanium	1,740	2,110	1,620	1,820	2,360	839	2,280	1,510	2,370
Uranium	4.7	8.3	6.0	2.9	3.4	11.4	3.5	2.2	2.4
Vanadium	74	141	141	49	52	45	79	49	49
Yttrium	37.0	49.2	39.6	31.3	27.6	66.7	32.6	23.9	22.4
Zinc	121	316	326	86	119	48	904	54	87

[1]ACM: Angus Creek mouth; UEMC: upper East Mill Creek; LEMC: lower East Mill Creek; TC: Trail Creek; USC; upper Slug Creek; LSC: lower Slug Creek; DVC: Dry Valley Creek: ShpC: Sheep Creek; LBR: lower Blackfoot River.

Table 11. Inorganic element concentrations (µg/g dry weight; n=1; <: less than limit of detection) in sediment from nine sites in the Blackfoot River watershed. Analyses at ESTL, Rolla, MO.

	Location[1]								
Element	ACM	UEMC	LEMC	TC	USC	LSC	DVC	ShpC	LBR
Aluminum	1,650	1,020	1,320	1,160	1,010	1,090	1,330	944	1,240
Arsenic	7.7	6.6	8.0	6.5	3.9	7.5	4.5	6.3	2.0
Barium	131	7.8	9.4	11.2	85	10.4	10.9	7.8	108
Beryllium	0.8	0.7	0.7	0.6	<0.1	0.5	0.7	0.6	<0.1
Boron	12	9.0	13	9.4	7.3	8.7	8.3	9.0	9.0
Cadmium	2.8	5.2	4.4	0.6	1.9	1.4	5.5	0.4	0.8
Chromium	33	10.2	12	6.7	20	7.6	7.7	6.2	16
Copper	8.8	18	18	5.9	7.0	5.4	10.7	5.8	5.7
Iron	184	161	175	156	710	130	171	140	782
Lead	8.1	5.6	5.8	4.8	5.0	4.3	6.3	5.1	3.9
Magnesium	453	461	498	388	258	315	363	367	516
Manganese	280	117	107	91	51	173	142	29	99
Molybdenum	<0.5	1.9	1.9	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
Nickel	18	43	43	11	12	12	54	12	13
Strontium	70	78	69	40	29	94	34	20	73
Vanadium	39	58	62	15	16	21	24	15	16
Zinc	69	175	182	41	61	48	555	34	41

[1]ACM: Angus Creek near mouth; UEMC: upper East Mill Creek; LEMC: lower East Mill Creek; TC: Trail Creek; USC; upper Slug Creek; LSC: lower Slug Creek; DVC: Dry Valley Creek: ShpC: Sheep Creek; LBR: lower Blackfoot River.

to the other six sites. Other sites such as lower Slug Creek had elevated strontium compared to upper Slug Creek, and Angus Creek had elevated boron, manganese, strontium, vanadium, and zinc compared to upper Slug Creek, thus suggesting some contamination by inorganic elements.

There was close agreement for measured concentrations of some inorganic elements in surficial sediments reported by GD lab and ESTL (Tables 10-11). The Pearson correlation coefficients were r=>0.90 (P<0.001-0.003) for selenium, beryllium, cadmium, copper, nickel, vanadium, and zinc; r=0.60 to 0.89 (P=0.01-0.006) for barium, lead, magnesium, manganese, and strontium; and r<0.59 (P=0.26-0.76) for aluminum, arsenic, chromium, and iron (all n=9, except beryllium n=7) (Table 12). The difference in concentrations of some elements between the GD lab and ESTL were probably due to the four-acid digestion used at the GD lab and the single-acid digestion (USEPA procedure) at ESTL. The data from ESTL was used in comparisons with other ecosystem components.

Aquatic plants

Selenium concentrations in aquatic plants followed a similar pattern as in surficial sediments: low at five sites (0.6-1.5 µg/g, Sheep Creek, Trail Creek, Angus Creek, upper Slug Creek, lower Slug Creek), moderately elevated at the Dry Valley Creek and lower Blackfoot River (3.8-4.5 µg/g), and very elevated at the upper and lower East Mill Creek (30-74 µg/g) (Table 7). Sheep Creek and Trail Creek had the lowest selenium concentration in aquatic plants, which was consistent with selenium concentrations in surficial sediment. The Pearson correlation coefficient between selenium concentrations in sediment and those in aquatic plants was r=0.96 (P<0.0001, n=9). However, the correlations were probably dominated by the elevated selenium concentrations at the upper and lower East Mill Creek sites (Table 7).

Concentrations of inorganic elements in aquatic plants followed a similar pattern as selenium in surficial sediments (Table 13). Lower East Mill Creek tended to have the highest concentrations of aluminum, arsenic, cadmium, copper, iron, lead, magnesium, molybdenum, nickel, strontium, vanadium and zinc, whereas Dry Valley Creek had an intermediate amount of these elements relative to the other seven sites. In contrast, lower Slug Creek tended to have slightly higher concentrations of aluminum, arsenic, barium, boron, chromium, iron, and strontium than Dry Valley Creek. This relative elevation of inorganic elements in aquatic plants in lower Slug Creek compared to Dry Valley Creek was not present in sediment data. In general, aquatic plants from Sheep Creek and Trail Creek tended to have low inorganic element concentrations compared to the other sites, except for barium, which was elevated in aquatic plants from Trail Creek. Although upper Slug Creek was considered the reference site, it had higher concentrations of some inorganic elements in aquatic plants than in Sheep Creek.

There were strong correlations between inorganic element concentrations in aquatic plants and surficial sediments for nickel (r=0.74, P<0.02) and zinc (r=0.90, P<0.0009) and for cadmium, copper, strontium, and vanadium (r=0.60 to 0.64, P<0.10).

Aquatic invertebrates

The opportunistic sample of crane fly nymphs collected at the Angus Creek headwater contained 186 µg/g of selenium (Table 7). For the other sites, aquatic invertebrates collected from Sheep Creek and Trail Creek had low selenium concentrations (2.6 to 2.9 µg/g), upper Slug

Table 12. Significant (P<0.05) Pearson correlation coefficients for various aquatic ecosystem components.

	Ecosystem component				
Ecosystem component	Sediment (GD lab)	Sediment (ESTL)	Aquatic plant	Aquatic invertebrate	Fish
Sediment (GD lab)		Se 0.99	Se 0.97	Se 0.92	Se 0.95
				Al 0.85	
				As 0.92	
		Ba 0.69		Ba 0.92	
				Cr 0.90	
		Be 0.93			
		Cd 0.98	Cd 0.73		
		Cu 0.97		Cu 0.78	
				Fe 0.91	
		Pb 0.78			
		Mg 0.76			Mg -0.66
		Mn 0.83		Mn 0.87	
		Ni 0.99	Ni 0.71	Ni 0.79	
		Sr 0.80			
		V 0.96		V 0.93	
		Zn 0.99	Zn 0.91	Zn 0.83	
Sediment (ESTL)			Se 0.96	Se 0.94	Se 0.96
				Al 0.78	
				Cu 0.79	Cu 0.79
				Mn 0.87	
			Ni 0.74	Ni 0.84	
				V 0.92	V 0.81
			Zn 0.90	Zn 0.83	
Aquatic plant				Se 0.91	Se 0.95
				Cd 0.99	
				Mn 0.85	Mn 0.71
				Mo 0.83	
				Ni 0.98	
				Zn 0.84	
Aquatic invertebrate					Se 0.99
					Cu 0.84

Table 13. Inorganic element concentrations (µg/g dry weight; n=1; <: less than limit of detection) in aquatic plants from nine sites in the Blackfoot River watershed. Analyses at ESTL, Rolla, MO.

	Location[1]								
Element	ACM	UEMC	LEMC	TC	USC	LSC	DVC	ShpC	LBR
Aluminum	168	69	1,796	465	290	699	549	90	153
Arsenic	1.4	1.8	7.6	1.9	2.5	3.4	1.6	1.0	1.4
Barium	92	14	94	156	65	281	106	32	60
Beryllium	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Boron	12	10	28	14	12	38	17	10	14
Cadmium	2.3	22	13	0.6	3.2	1.1	1.9	1.7	3.2
Chromium	3.7	8.1	13.8	7.1	8.5	18	15	2.4	3.5
Copper	5.3	4.4	18	4.7	5.4	4.0	5.0	3.5	5.6
Iron	103	64	834	267	163	408	315	68	113
Lead	<2	<2	4.8	<2	<2	2.4	2.3	<2	<2
Magnesium	288	269	575	334	306	375	389	232	416
Manganese	888	85	75	749	544	266	419	242	442
Molybdenum	2.2	1.7	2.1	0.8	1.6	<0.5	1.4	0.5	0.8
Nickel	7.4	7.7	41	5.7	7.6	8.1	27	4.0	6.4
Strontium	64	53	99	39	36	61	53	21	45
Vanadium	3.8	3.6	79	8.1	6.0	15	14	2.1	4.0
Zinc	32	166	197	22	40	34	300	29	115

[1]ACM: Angus Creek near mouth; UEMC: upper East Mill Creek; LEMC: lower East Mill Creek; TC: Trail Creek; USC; upper Slug Creek; LSC: lower Slug Creek; DVC: Dry Valley Creek: ShpC: Sheep Creek; LBR: lower Blackfoot River.

Creek, lower Blackfoot River, and Angus Creek mouth had moderate concentrations (4.9 to 7.2 µg/g), and Dry Valley Creek and upper East Mill Creek had elevated concentrations (19 to 36 µg/g).

The Pearson correlation coefficient between selenium concentrations in aquatic invertebrates was significant with aquatic plants (r=0.91, P<0.004, n=7) and surficial sediment (r=0.94, P<0.002, n=7). Although the selenium concentrations in aquatic invertebrates were somewhat distributed between extremes, the correlations were probably dominated by elevated selenium concentrations in sediment and aquatic plants at the upper East Mill Creek and Dry Valley Creek sites (Table 7).

Crane fly larvae nymphs collected from the Angus Creek headwater contained elevated concentrations of chromium, iron, nickel strontium, and vanadium compared to invertebrates from the other nine sites (Table 14). Concentrations of inorganic elements in aquatic invertebrates from seven sites (none collected at lower East Miller Creek or lower Slug Creek) followed a similar pattern as found in surficial sediments and aquatic plants (Table 14). Low concentrations of inorganic elements occurred in aquatic invertebrates from Sheep Creek and Trail Creek, moderate concentrations in upper Slug Creek and lower Blackfoot River, and elevated concentrations in upper East Mill Creek, Angus Creek near mouth, and Dry Valley Creek. At the three sites with elevated concentrations, the elements that were generally elevated included aluminum, barium, boron, chromium, iron, vanadium, and zinc. At upper East Mill Creek other elevated elements included cadmium, copper, and nickel, whereas at Dry Valley Creek nickel and strontium were elevated.

There were strong correlations between inorganic element concentrations in aquatic invertebrates and surficial sediments for aluminum, copper, manganese, nickel, vanadium, and zinc (r=0.78 to 0.92, P<0.05, all n=7). There also were strong correlations for inorganic elements between aquatic invertebrates and aquatic plants for cadmium, manganese, molybdenum, nickel, and zinc (r=0.83 to 0.99, P<0.05, all n=7).

Fish

Six species were collected at eight sites, but no one fish species was collected at all eight sites. A substantial effort was made to collect fish from lower East Mill Creek by electrofishing, however, no fish were captured. Mottled sculpin (*Cottus bairdi*) were collected at six sites, and selenium in these fish followed the same pattern as present in the geometric mean of combined fish data (Table 15). Trout at upper East Mill Creek had the highest selenium concentrations. Speckled dace (*Rhinichthys osculus*) were collected at five sties, and had the second highest whole-body selenium concentrations of the species collected. Although redside shiner (*Richardsonius balteatus*) were collected from only four sites, they consistently had the lowest whole-body selenium concentrations of the species collected at each of those sites. Geometric mean selenium concentrations in fish were low from upper Slug Creek (4.0 µg/g), Trail Creek (5.1 µg/g), Sheep Creek (5.2 µg/g), and lower Slug Creek (5.3 µg/g), intermediate from Angus Creek near mouth (6.4 µg/g) and lower Blackfoot River (7.8 µg/g), and elevated from Dry Valley Creek (16.1 µg/g) and upper East Mill Creek (32.2 µg/g) (Table 15).

The Pearson correlation coefficient between selenium concentrations in the combined fish data for six species was significant with sediment (r=0.96, P<0.0001, n=8), aquatic plants

Table 14. Inorganic element concentrations (µg/g dry weight; n=1; <: less than limit of detection) in composite samples of aquatic invertebrates from nine sites in the Blackfoot River watershed. Analyses at ESTL, Rolla, MO.

	Location[1]									
Element	ACH	ACM	UEMC	LEMC	TC	USC	LSC	DVC	ShpC	LBR
Aluminum	49	459	257	NS[2]	72	224	NS	381	59	213
Arsenic	2.6	3.0	3.6	NS	<2	3.0	NS	2.7	<2	2.5
Barium	14	215	30	NS	112	145	NS	140	22	30
Beryllium	<0.1	<0.1	<0.1	NS	<0.1	<0.1	NS	<0.1	<0.1	<0.1
Boron	4.3	8.9	9.5	NS	6.8	6.6	NS	8.2	3.7	7.1
Cadmium	12	2.7	31	NS	1.0	3.7	NS	1.7	0.6	0.5
Chromium	31	11	31	NS	2.7	14	NS	12	2.6	5.6
Copper	12	21	51	NS	11	29	NS	17	16	27
Iron	374	296	251	NS	68	174	NS	262	59	160
Lead	<2	<2	<2	NS	<2	<2	NS	<2	<2	<2
Magnesium	308	238	191	NS	135	175	NS	227	129	181
Manganese	168	434	29	NS	196	109	NS	198	21	68
Molybdenum	3.5	1.5	1.0	NS	0.6	0.7	NS	1.0	0.7	0.6
Nickel	46	16	12	NS	1.8	6.9	NS	50	2.2	6.3
Strontium	32	11	21	NS	8.2	47	NS	30	3.8	17
Vanadium	46	11	18	NS	1.7	5.7	NS	11	1.7	5.5
Zinc	326	330	595	NS	87	143	NS	659	138	127

[1]ACH: seep at the head of Angus Creek (only Tipulidae collected); ACM: Angus Creek near mouth; UEMC: upper East Mill Creek; LEMC: lower East Mill Creek; TC: Trail Creek; USC; upper Slug Creek; LSC: lower Slug Creek; DVC: Dry Valley Creek: ShpC: Sheep Creek; LBR: lower Blackfoot River.
[2]NS: not sampled.

Table 15. Selenium concentrations (µg/g dry weight; n=1; <: less than limit of detection) in whole-body fish from nine sites in the Blackfoot River watershed. Analyses at ESTL, Rolla, MO.

	Location[1]								
Species	ACM	UEMC	LEMC	TC	USC	LSC	DVC	ShpC	LBR
Brook trout	-[2]	42.7	-	-	2.4	-	-	-	-
Cutthroat trout	6.7	24.3	-	-	-	-	16.6	3.6	-
Mottled sculpin	7.1	-	-	4.4	3.7	-	15.6	5.6	6.7
Longnose dace	7.0	-	-	5.9	-	-	-	7.1	-
Speckled dace	-	-	-	6.3	7.2	5.8	16.1	-	6.7
									14.1
Redside shiner	5.3	-	-	4.0	-	4.9	-	-	5.8
Geometric mean	6.4	32.2	-	5.1	4.0	5.3	16.1	5.2	7.8

[1]ACM: Angus Creek near mouth; UEMC: upper East Mill Creek; LEMC: lower East Mill Creek; TC: Trail Creek; USC; upper Slug Creek; LSC: lower Slug Creek; DVC: Dry Valley Creek: ShpC: Sheep Creek; LBR: lower Blackfoot River.
[2]-: not collected.

(*r*=0.95, *P*<0.0003, n=8), and aquatic invertebrates (*r*=0.99, *P*<0.0001, n=7). For the two most commonly collected species, the significant correlations for selenium concentrations in mottled sculpin were with sediment (*r*=0.95, *P*<0.003, n=6), and invertebrates (*r*=0.96, *P*<0.002, n=6), and in speckled dace were with sediment (*r*=0.93, *P*<0.02, n=58), and invertebrates (*r*=0.99, *P*<0.005, n=4). Although the selenium concentrations in aquatic invertebrates and fish were somewhat distributed between extremes, the correlations were probably dominated by elevated selenium concentrations in sediment and aquatic plants at the upper East Mill Creek and Dry Valley Creek sites (Tables 7 and 15).

Few inorganic elements other than selenium were elevated in whole-body fish from the eight sites (Table 16). The few elements elevated in fish were primarily in speckled dace, whereas the lowest inorganic element concentrations tended to occur in redside shiner. The elements that tended to be elevated in speckled dace included aluminum, barium, copper, manganese, nickel, strontium, and zinc, but no site seemed to have fish with consistently elevated inorganic elements based on geometric means (Table 17). Upper Slug Creek, the reference site, had the highest geometric means for aluminum, barium, chromium, iron, and manganese. Upper East Mill Creek had the highest geometric mean copper concentrations in fish. Lower Slug Creek had the highest geometric mean strontium and zinc in fish.

There were few correlations between concentrations of inorganic elements in fish (using the geometric mean for all fish at each site) and either surficial sediment, aquatic plants, or aquatic invertebrates. For surficial sediment data there were two correlations: copper (*r*=0.79, *P*=0.02, n=8) and vanadium (*r*=0.81, *P*=0.03, n=7). For aquatic plant data there was one correlation: manganese (*r*=0.71, *P*=0.05, n=8). For aquatic invertebrate data there were two correlations: copper (*r*=0.84, *P*=0.02, n=7) and manganese (*r*=0.73 *P*=0.06, n=7). Copper and vanadium seemed to be the only two elements in surficial sediment or aquatic invertebrates that were consistently correlated with selenium concentrations in fish.

Discussion

Water

Upper and lower East Mill Creek had substantially elevated selenium concentrations in water, whereas the other seven sites had concentrations below the limit of detection (Table 7). Selenium in East Mill Creek was substantially higher than the current national water quality criterion for the protection of aquatic life of 5 µg/L (USEPA 1987).

A recent peer consultation workshop on selenium aquatic toxicity and bioaccumulation was held to discuss the technical issues underlying the freshwater aquatic life chronic criterion for selenium (USEPA 1998a). The current aquatic criterion for selenium was derived by the U.S. Environmental Protection Agency (USEPA) in 1987 (USEPA 1987). The workshop was guided by technical questions categorized into three areas: a water-based criterion, a tissue-based criterion, and a sediment-based criterion. Participants in the consultation workshop on selenium thought the water compartment was a poor choice for a criterion for selenium because of large variations in temporal selenium concentrations, types of organisms constituting the food chain, speciation and rates of transformation of selenium, and rates of exchange between water, sediment, and organisms (USEPA 1998a). Even though there has been a substantial number of papers calling for a water criterion of 2 µg/L (reviewed by Hamilton and Lemly, 1999), there was

Table 16. Inorganic element concentrations (µg/g dry weight; n=1; <: less than limit of detection) in whole-body fish from nine sites in the Blackfoot River watershed. Analyses at ESTL, Rolla, MO.

	Location[1] and Species[2]									
Element	ACM Cutthroat trout	ACM Mottled sculpin	ACM Longnose dace	ACM Redside Shiner	UEMC Cutthroat trout	LEMC	TC Mottled sculpin	TC Longnose dace	TC Speckled dace	TC Redside shiner
Aluminum	40	86	166	10	41	NF[3]	24	4	226	8
Arsenic	<2	<2	<2	<2	<2	NF	<2	<2	<2	<2
Barium	1.5	6.6	9.2	3.5	3.0	NF	4.2	11.1	14.9	4.1
Beryllium	<0.1	<0.1	<0.1	<0.1	<0.1	NF	<0.1	<0.1	<0.1	<0.1
Boron	2.1	2.2	2.3	2.0	2.1	NF	1.8	1.8	2.0	2.0
Cadmium	<0.3	<0.3	<0.3	<0.3	<0.3	NF	<0.3	<0.3	<0.3	<0.3
Chromium	1.2	1.6	1.9	1.3	1.6	NF	1.2	1.0	1.4	1.1
Copper	3.4	2.4	7.3	2.4	11	NF	2.9	3.8	8.3	3.5
Iron	20	36	30	20	19	NF	24	23	40	20
Lead	<2	<2	<2	<2	<2	NF	<2	<2	<2	<2
Magnesium	121	137	109	120	104	NF	124	135	147	128
Manganese	25	72	78	16	5.4	NF	27	17	56	11
Molybdenum	<0.5	<0.5	<0.5	<0.5	<0.5	NF	<0.5	<0.5	<0.5	<0.5
Nickel	1.7	4.6	2.7	2.3	1.6	NF	3.0	2.8	2.7	2.2
Strontium	10	29	24	20	4	NF	20	26	23	17
Vanadium	<0.2	2.1	0.8	<0.2	<0.2	NF	0.9	<0.2	0.7	<0.2
Zinc	81	64	98	142	62	NF	69	96	149	126

Table 16. Continued.

	Location[1] and Species[2]							
Element	USC Brook trout	USC Mottled sculpin	USC Speckled dace	LSC Speckled dace	LSC Redside shiner	DVC Cutthroat trout	DVC Mottled sculpin	DVC Speckled dace
Aluminum	518	194	162	213	16	49	112	160
Arsenic	<2	<2	<2	<2	<2	<2	<2	<2
Barium	5.6	7.6	22	11	5.1	6.5	3.3	5.9
Beryllium	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Boron	2.8	1.6	1.6	2.2	2.0	1.6	1.7	1.8
Cadmium	<0.3	<0.3	<0.3	<0.3	<0.3	<0.3	<0.3	<0.3
Chromium	5.9	1.4	1.4	1.8	1.3	1.3	1.4	1.5
Copper	2.9	2.2	6.3	7.2	2.8	2.2	2.0	2.2
Iron	34	27	42	38	22	18	23	29
Lead	<2	<2	<2	<2	<2	<2	<2	<2
Magnesium	121	96	132	151	132	123	113	125
Manganese	20	14	204	42	13	24	46	40
Molybdenum	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
Nickel	2.0	1.8	2.5	4.1	2.5	1.4	2.7	2.7
Strontium	14	10	19	38	30	9	16	20
Vanadium	2.0	0.8	0.7	0.8	<0.2	<0.2	1.3	0.7
Zinc	50	38	109	134	122	82	69	116

Table 16. Continued.

	Location[1] and Species[2]						
Element	ShpC Cutthroat trout	ShpC Mottled sculpin	ShpC Longnose dace	LBR Mottled sculpin	LBR Speckled dace	LBR Speckled dace	LBR Redside shiner
Aluminum	24	104	195	69	16	127	16
Arsenic	<2	<2	<2	<2	<2	<2	<2
Barium	1.5	3.7	8.8	2.9	8.3	6.3	2.7
Beryllium	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Boron	1.7	1.8	1.8	1.7	1.6	2.0	1.6
Cadmium	<0.3	<0.3	<0.3	<0.3	<0.3	<0.3	<0.3
Chromium	1.3	1.3	1.5	1.2	1.1	1.5	1.0
Copper	2.7	2.5	5.7	2.4	3.2	6.0	1.8
Iron	16	27	29	21	24	25	17
Lead	<2	<2	<2	<2	<2	<2	<2
Magnesium	104	113	102	112	131	112	102
Manganese	5	11	16	18	15	29	8
Molybdenum	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
Nickel	1.5	2.9	2.2	2.2	3.2	2.2	1.6
Strontium	4	13	24	17	32	20	18
Vanadium	<0.2	0.6	0.7	0.9	<0.2	0.6	0.3
Zinc	62	50	59	50	98	101	128

[1]ACM: Angus Creek near mouth; UEMC: upper East Mill Creek; LEMC: lower East Mill Creek; TC: Trail Creek; USC; upper Slug Creek; LSC: lower Slug Creek; DVC: Dry Valley Creek: ShpC: Sheep Creek; LBR: lower Blackfoot River.

[2]Cutthroat trout (*Oncorhynchus clarki*), brook trout (*Salvelinus fontinalis*), mottled sculpin (*Cottus bairdi*), longnose dace (*Rhinichthys cataractae*), speckled dace (*Rhinichthys osculus*), redside shiner (*Richardsonius balteatus*).

[3]NF: no fish found.

Table 17. Geometric mean of inorganic element concentrations (µg/g dry weight) in whole-body fish from nine sites in the Blackfoot River watershed. Analyses at ESTL, Rolla, MO.

	Location[1]								
Element	ACM	UEMC	LEMC	TC	USC	LSC	DVC	ShpC	LBR
Aluminum	49	41	NF[3]	20	253	58	96	79	39
Arsenic	<2	<2	NF	<2	<2	<2	<2	<2	<2
Barium	4.2	3.0	NF	7.3	9.8	7.5	5.0	3.7	4.5
Beryllium	<0.1	<0.1	NF	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Boron	2.1	2.1	NF	1.9	1.9	2.1	1.7	1.8	1.7
Cadmium	<0.3	<0.3	NF	<0.3	<0.3	<0.3	<0.3	<0.3	<0.3
Chromium	1.5	1.6	NF	1.2	2.3	1.5	1.4	1.4	1.2
Copper	3.5	11	NF	4.2	3.4	4.5	2.1	3.4	3.0
Iron	26	19	NF	26	34	29	23	23	22
Lead	<2	<2	NF	<2	<2	<2	<2	<2	<2
Magnesium	121	104	NF	133	115	141	120	106	114
Manganese	39	5.4	NF	23	39	23	35	10	16
Molybdenum	<0.5	<0.5	NF	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
Nickel	2.6	1.6	NF	2.7	2.1	3.2	2.2	2.1	2.2
Strontium	19	4	NF	21	14	34	14	11	21
Vanadium	1.3	<0.2	NF	0.8	1.0	0.8	1.0	0.6	0.5
Zinc	92	62	NF	106	59	128	87	57	89

[1]ACM: Angus Creek near mouth; UEMC: upper East Mill Creek; LEMC: lower East Mill Creek; TC: Trail Creek; USC; upper Slug Creek; LSC: lower Slug Creek; DVC: Dry Valley Creek: ShpC: Sheep Creek; LBR: lower Blackfoot River.
[2]NF: no fish found.

also a substantial number of examples of aquatic situations where waterborne selenium concentrations of 2-4 µg/L have allowed selenium accumulation in the food chain to approach concentrations near or above the proposed dietary toxic threshold. The logic in proposing a national criterion of 2 µg/L was based in part on the well established use of waterborne elemental or compound concentrations in setting a national water quality criterion (USEPA 1996, 1998b, 1999). However, the growing body of selenium literature, which emphasizes the toxicological importance of the dietary route of selenium exposure, requires a reassessment of the continued use of a water-based criterion.

We considered the upper Slug Creek as the reference site because it was not influenced by mining activities (Figure 3). In general, most of the other eight stream sites had similar inorganic element concentrations in water to those in upper Slug Creek, except for selenium (Table 8). Dry Valley Creek had slightly elevated concentrations of aluminum, copper, iron, magnesium, and manganese compared to upper Slug Creek. Upper and lower East Mill Creek, in addition to elevated selenium concentrations, also had slightly elevated strontium concentrations compared to upper Slug Creek.

Water concentrations of inorganic elements are generally the basis of water quality standards issued by the U.S. Environmental Protection Agency (USEPA 1998b, 1999). However, investigations have been reported that indicate that dietary routes of exposures of inorganic elements were important in discerning effects on biota (reviewed in Hamilton and Hoffman 2002). For example, Kiffney and Clements (1993) reported that monitoring concentrations of cadmium, copper, and zinc in aquatic invertebrates was a better indicator of element bioavailability in the Arkansas River of Colorado, which was impacted by acid mine drainage, than element concentrations in water.

Comparison to other Idaho data

The Idaho Mining Association Selenium Subcommittee (Selenium Subcommittee) investigated concentrations of selenium, cadmium, manganese, nickel, vanadium, and zinc in water from numerous sites in the Southeastern Idaho Phosphate Resource Area and concluded that selenium was the major contaminant of potential concern (Montgomery Watson 1999). In May 1998, selenium concentrations in water at 12 of 37 stream sites exceeded the USEPA criteria of 5 µg/L, whereas in September 1998 only one stream, East Mill Creek (32 µg/L), exceeded the criteria (Montgomery Watson 1999). In the May 1998 sampling, the stream sites exceeding the criterion included five on the Blackfoot River (5-12 µg/L), Trail Creek (8.7 µg/L), Dry Valley Creek (5.6 µg/L), and two on East Mill Creek (210 and 260 µg/L). The values reported by Montgomery Watson (1999) were higher than those measured in the current investigation.

Montgomery Watson (2000) continued measuring selenium concentrations in waters of the Blackfoot River in 1999. Concentrations in the lower Blackfoot River near our sampling site were 6.7 µg/L in May, 2.1 µg/L in June, 2.4 µg/L in July, and 1.5 µg/L in August, which shows the variability over time that can occur in the river. Montgomery Watson (2002) reported similar variability in Dry Valley Creek: 49 µg/L in May, 6.8 µg/L in June, 2.7 µg/L in July, and 1 µg/L in August. In May 1999 Dry Valley Creek (49 µg/L) and Spring Creek (46 µg/L) were major selenium contributors to the Blackfoot River. Above Spring Creek the Blackfoot River had <1 µg/L selenium, whereas below Spring Creek selenium concentrations ranged from 9.8 to 6.7 µg/L. Thus, substantial contamination of the Blackfoot River occurred during 1999. This contamination was evidenced in selenium concentrations in sediment, aquatic plants, aquatic invertebrates, and fish measured in the current study and as discussed in the following sections.

Montgomery Watson (2001a, 2001b) reported additional selenium concentrations in water sampled in September 1999 and May 2000. Most water samples in September 1999 to April 2000 contained <5 µg/L, except for Dry Valley Creek, which contained 12 µg/L above the Blackfoot River, 270 µg/L downstream of Maybe Creek, and 120 µg/L upstream of Maybe Creek, and East Mill Creek, which contained 19 µg/L (Montgomery Watson 2001a). In May 2000 selenium concentrations >5 µg/L were reported in the Blackfoot River (5.5-7.1 µg/L) and several creeks including State Land Creek (10 µg/L) and two tributaries (16 µg/L), North Fork Wooley Valley Creek (98 µg/L), lower Slug Creek (6.3 µg/L), Dry Valley Creek (8-87 µg/L), Angus Creek (6.5 µg/L), Spring Creek (28 µg/L), and East Mill Creek (400 µg/L) (Montgomery Watson 2001b). These data demonstrate continued selenium contamination of the Blackfoot River watershed. The data also demonstrate that selenium contamination occurs primarily during spring runoff.

Sediment

Selenium concentrations in surficial sediment from upper and lower Slug Creek, Sheep Creek, Trail Creek, and Angus Creek were 1.7 µg/g or less (Table 7), which was between the no hazard rating of <1 µg/g and the minimal hazard rating of 1-2 µg/g proposed by Lemly (1995), and below the no effect concentration of <2 µg/g proposed by Stephens et al. (1997). In contrast, Presser et al. (1994) and Moore et al. (1990) used 0.5 µg/g as a reasonable selenium concentration in sediment to represent the threshold between uncontaminated, background conditions and environments with elevated selenium concentrations.

Selenium in surficial sediment from the lower Blackfoot River site (2.1 µg/g) falls in the concentration of concern range of >2-4 µg/g of Stephens et al. (1997) and the moderate hazard of 2-4 µg/g of Lemly (1995). Selenium in surficial sediment from the Dry Valley Creek (5.2 µg/g) and upper and lower East Mill Creek (32.5 – 45.8 µg/g) sites were higher than the toxicity threshold of >4 µg/g proposed by Stephens et al. (1997) and the high hazard rating of >4 µg/g proposed by Lemly (1995). Similar no effect, level of concern, and toxicity thresholds of selenium in sediments were given in Engberg et al. (1998). Elevated selenium concentrations in surficial sediment at upper and lower East Mill Creek suggested a substantial contamination concern, as did the elevated selenium concentrations in Dry Valley Creek.

The selenium concentration in surficial sediment from East Mill Creek was in the same range as measured at North Pond in Walter Walker State Wildlife Area near Grand Junction, CO (geometric mean 25.1 µg/g in 1996 and 38.9 µg/g in 1997) (Hamilton et al. 2001a, 2001b). The sediment concentrations at North Pond were accumulated over a 20+ year period from groundwater upwelling derived from down slope movement from irrigated seleniferous farmlands in the Grand Valley. Elevated selenium in sediments at North Pond were associate with elevated selenium in the food chain, and increased mortality of larval endangered razorback sucker (*Xyrauchen texanus*) in two 30-day water and dietary exposures (Hamilton et al. 2001a, 2001b).

The peer consultation workshop on selenium aquatic toxicity and bioaccumulation (USEPA 1998a) discussed the possibility of a sediment-based criterion. However, the workshop participants concluded that the sediment compartment was a poor choice for a criterion because of spatial heterogeneity of selenium deposition, variable water retention time, variable volatilization rates, heterogeneity of the benthic periphyton community and benthic invertebrates, and variable feeding habitats of higher trophic organisms (USEPA 1998a).

The consideration of a possible sediment-based criterion was based on two papers that proposed the use of a sediment-based criterion expressed on a particulate basis, such as sediment selenium concentration or a measure of the organic content of sediment (Canton and Van Derveer 1997, Van Derveer and Canton 1997). In an example in their second paper, they present a sediment selenium model and used it to derive a site-specific chronic dissolved selenium waterborne standard of 31 µg/L, using a sediment selenium toxicity threshold of 2.5 µg/g and a site-specific mean sediment total organic carbon of 0.5%. This site-specific standard contrasts sharply with the current USEPA criterion of 5 µg/L. Hamilton and Lemly (1999) reviewed these two papers and pointed out how they incorrectly interpreted contaminant survey reports as being exposure-response studies, did not acknowledge the importance of the waterborne entry of selenium in aquatic food webs, overlooked key studies from the extensive body of selenium literature, and failed to consider the off-stream consequences of proposing high in-stream selenium standards. Hamilton and Lemly (1999) concluded that the two papers failed to provide an adequate argument for changing the selenium chronic criterion from a water basis to a particulate or sediment basis.

In the present study, the strong correlation for selenium concentrations between surficial sediments and aquatic plants (r=0.96), and between surficial sediment and aquatic invertebrates (r=0.94) (Table 12) suggested a ready movement of selenium among aquatic ecosystem components and accumulation in the food web. Similar movements of selenium through the food web were reported in two field studies of seleniferous areas of the upper Colorado River (Hamilton et al. 2001a, 2001b).

Surficial sediments from the upper and lower East Mill Creek sites tended to have the highest concentrations of antimony, cadmium, chromium, copper, molybdenum, nickel, silver, vanadium, and zinc of the nine sites examined (Tables 10 and 11). Concentrations of inorganic elements differed between East Mill Creek and nonimpacted upper Slug Creek site by factors of 1.8 to 3.9. Lower Slug Creek and Angus Creek also had several inorganic elements elevated relative to upper Slug Creek. In contrast, the magnitude of difference for selenium concentrations between upper and lower East Mill Creek and upper Slug Creek ranged from 41 to 57, thus suggesting a major disparity between selenium enrichment in the East Mill Creek compared to upper Slug Creek. Of all the elements measured, selenium was the most bioaccumulative in the food web, and the element of principal concern for effects in biota.

The sediment component in aquatic ecosystems is an important pathway of inorganic element movement through the food web (Seelye et al. 1982). Sediments represent the most concentrated pool of metals in aquatic environments, and many types of aquatic organisms ingest sediment during the foraging process (Luoma 1983). Fish can ingest inorganic elements from sediment and detritus (Kirby et al. 2001a, 2001b). For example, Campbell (1994) reported that inorganic element contaminated lakes and ponds, bottom feeding redear sunfish (*Lepomis microlophus*) had significant concentrations of cadmium, nickel, copper, lead, and zinc, whereas predatory largemouth bass (*Micropterus salmoides*) had significant accumulations of cadmium and zinc, and omnivorous bluegill (*Lepomis macrochirus*) had significant accumulation only of copper. Others have reported similar findings (Delisle et al. 1977, Van Hassel et al. 1980, Ney and Van Hassel 1983). Dallinger and Kautzky (1985) and Dallinger et al. (1987) concluded that sediments were an important link in the contamination of food webs by inorganic elements and resultant adverse effects in fish.

Specific to selenium, Woock (1984) demonstrated in a cage study with golden shiner (*Notemigonus crysoleucas*) that fish in cages with access to bottom sediments accumulated more selenium than fish held in cages suspended about 1.5 m above the sediments. This study revealed that effects in fish were linked to selenium exposure via sediment, benthic invertebrates, or detritus, or a combination of sediment components. A similar finding was presented by Barnhart (1957) who reported that "numerous species of game fish" lived at least 4 months when held in a livebox, which limited access to food organisms and sediment, but fish lived less than 2 months when released in selenium-contaminated Sweitzer Lake, CO. The highly toxic nature of benthic invertebrates from selenium-contaminated Belews Lake, NC, was reported by Finley (1985) in an experiment where bluegill fed Hexagenia nymphs died in 17 to 44 days.

<u>Comparison to other Idaho data</u>

Selenium concentrations in sediment from Maybe Creek, a tributary of Dry Valley Creek, near its mouth were 261 µg/g (TRC Environmental 1999), which suggested that much of the selenium loading in Dry Valley Creek comes from Maybe Creek. They reported other portions of Maybe Creek contained 12-77 µg/g of selenium in sediment.

The Selenium Subcommittee investigated concentrations of selenium, cadmium, manganese, nickel, vanadium, and zinc in sediment from numerous sites in the Southeastern Idaho Phosphate Resource Area in September 1998 (Montgomery Watson 1999). Out of 54 sites investigated, 11 had selenium concentrations in sediment of 2-4 µg/g, thus placing them in the concentration of concern range proposed by Stephens et al. (1997) and the moderate hazard range of Lemly (1995). These sites included Slug Creek, Dry Valley Creek, Rasmussen Creek (tributary to Angus Creek), and East Mill Creek. Three sites had sediment values greater than 4 µg/g (State Land Creek, Sage Creek below Smoky Canyon Mine, North Fork Sage Creek below Pole Creek), which places them above the toxicity threshold of Stephens et al. (1997) and the high hazard of Lemly (1995). The selenium concentrations in sediment reported by Montgomery Watson (1999) in East Mill Creek (2.9 µg/g) were substantially lower than those in the present investigation (35-52 µg/g), whereas their values for Dry Valley Creek (3.3 µg/g) were slightly lower than our values (4.3-5.2 µg/g). Other sediment values reported by Montgomery Watson (1999) for similar sites were similar to those in the present study.

Montgomery Watson (2001a) reported elevated selenium concentrations in sediment collected in September 1999 from State Land Creek (2.1 µg/g), Pedro Creek (3.1 µg/g), Dry Valley Creek (3.9 µg/g), Rasmussen Creek (2.2 µg/g), and the Blackfoot River (2.1-3.0 µg/g), which were in the concentration of concern range of Stephens et al. (1997) and the moderate hazard of Lemly (1995). They reported high selenium concentrations in sediment from Dry Valley Creek (6.2 µg/g), Angus Creek (5.1 µg/g), and East Mill Creek (5.0 µg/g), which were in the toxicity threshold range of Stephens et al. (1997) and the high hazard of Lemly (1995).

Overall, the elevated concentrations of selenium and other inorganic elements in sediments from several streams in the Blackfoot River watershed that were reported by TRC Environmental (1999), Montgomery Watson (1999, 2001a), and in the present study suggest wide spread contamination of the aquatic environment by phosphate mining activities.

Aquatic plants

No guidelines were found that propose toxicity threshold concentrations for selenium in aquatic plants that might be considered hazardous to aquatic organisms. However, most domestic animals exhibit signs of selenium toxicity on terrestrial vegetative diets containing ≥3-5 µg/g natural selenium (NRC 1980, Eisler 1985, Olson 1986). Selenium concentrations in aquatic plants from upper Slug Creek, Trail Creek, Sheep Creek, Angus Creek, and lower Slug Creek were all 1.5 µg/g or less (Table 7). This concentration might be considered near background for the Blackfoot River watershed. By comparison, selenium concentrations at Dry Valley Creek (3.8 µg/g) and lower Blackfoot River (4.5 µg/g) were elevated, and those at upper and lower East Mill Creek (30-74 µg/g) were substantially elevated. All selenium concentrations in aquatic plants closely matched those in surficial sediments (Pearson correlation coefficient r=0.96) thus demonstrating their interconnectedness (Table 12).

Substantial accumulation of selenium has been reported in aquatic macrophytes by Saiki (1986), Schuler et al. (1990), Gutenmann et al. (1976), and Barnum and Gilmer (1988) in selenium-contaminated environments. Submerged macrophytes provide a substrate upon which periphyton and some macroinvertebrates colonize, and which benthic invertebrates and some aquatic and semi-aquatic birds and mammals feed.

Although fish typically do not feed on macrophytes, when macrophytes die, they become an important contributor to the detrital food chain. Detritus has been reported to contain highly elevated selenium concentrations in selenium-contaminated environments (Saiki 1986, 9.8-440 µg/g; Saiki et al. 1993, 7-22 µg/g; Saiki and Lowe 1987, 36-307 µg/g), whereas references areas had 1 µg/g or less (Saiki and Lowe 1987). Benthic invertebrates readily accumulate selenium from detritus (Alaimo et al. 1994), which in turn is bioaccumulated by predators such as fish. Saiki et al. (1993) concluded that high concentrations of selenium in aquatic invertebrates and fish in selenium-contaminated areas of central California were the result of food-chain transfer from selenium-enriched detritus rather than other pathways. Thus, the elevated selenium concentrations in aquatic plants from four of the streams sites in the Blackfoot River watershed were probably contributing to the selenium transfer in the aquatic food web.

Inorganic elements accumulate in aquatic plants both from water column uptake (Bryson et al. 1984, Devi et al. 1996) and sediment uptake (Cherry and Guthrie 1977, Dallinger and Kautzky 1985, Dallinger et al. 1987). The significant Pearson correlation coefficients for several inorganic elements (cadmium, copper, nickel, strontium, vanadium, zinc; r=0.59-0.91) between surficial sediments and aquatic plants suggested a strong interconnectedness in element cycles. Although few herbivores feed on aquatic plants directly, when rooted aquatic plants die, greater than 90% of their biomass enters the detrital food chain, whereas the remaining 10% is from algal detritus and animal detritus (Teal 1962, Mann 1972). Much of the nutritional content in detritus comes from microbe enrichment and metabolic products, which add proteins and amino acids to detritus (Odum and de la Cruz 1967, Foda et al. 1983). Although not sampled in the present study, periphyton (composed of diatoms, green algae, and cyanobacteria) are another source of nutrients for grazing aquatic invertebrates and to the detrital food web (Allan 1995). Uptake of inorganic elements by periphyton could have also contributed to elevated elements in sediments and aquatic invertebrates, especially in western streams where aquatic macrophytes might be limited. Plant litter and other coarse debris that enter a stream are a major source of energy that fuels higher trophic levels (Allan 1995). Thus, uptake of inorganic elements by aquatic plants by themselves might seem unimportant; however, inorganic elements in dead plant material can play an important role in the movement of elements and energy through the detrital food web to aquatic invertebrates and fish.

Comparison to other Idaho data

A native bryophyte that was collected from a seep at the base of the Wooley Valley phosphate mine Unit 4 waste pile in the headwater area of Angus Creek contained very elevated concentrations of several inorganic elements including cadmium (160 µg/g), cobalt (180 µg/g), chromium (210 µg/g), manganese (33,000 µg/g), nickel (2,000 µg/g), vanadium (1,000µg/g), zinc (11,000 µg/g), and selenium (750 µg/g) (Herring et al. 2001). This site and others on Angus Creek were monitored for inorganic element accumulation in late spring and late summer 1999 using an introduced bryophyte, *Hygrohypnum ochraceum* (Herring et al. 2001). The same elements as present in the native bryophyte accumulated in the introduced bryophyte, but selenium was the most enriched of the elements measured.

Elevated selenium concentrations have been reported in grasses (mean 64 µg/g), forbs (78 µg/g), and shrubs (11 µg/g) in Maybe Creek (TRC Environmental 1999), a tributary of Dry Valley Creek.

Montgomery Watson (2001a) reported selenium concentrations in periphyton collected from artificial substrates placed in streams between September and October 1999. Elevated selenium concentrations were found in the Blackfoot River (3.0 µg/g), Angus Creek (3.3-9.2 µg/g), Spring Creek (4.2-7.5 µg/g), and very high values in East Mill Creek (12-25 µg/g). Montgomery Watson (2001b) reported selenium concentrations in periphyton collected from artificial substrates placed in streams between May and June 2000, but fewer streams than investigated in Montgomery Watson (2001a). Elevated selenium concentrations were found in the Blackfoot River (4.3 µg/g) and Angus Creek (6.0 µg/g).

Plankton samples (combined phytoplankton and zooplankton) collected from various sites in Blackfoot Reservoir contained selenium concentrations of ≤1.5 µg/g in September 1999 (Montgomery Watson 2001a). However, in the May 2000 sampling, 9 of 12 samples contained a geometric mean selenium concentration of 3.3 µg/g (Montgomery Watson 2001b).

Submerged macrophytes were collected in September 1999 from numerous stream sites in the Blackfoot River watershed and analyzed for selenium concentrations (Montgomery Watson 2001a). They reported several samples with elevated concentrations ranged from 3.2 to 4.8 µg/g, 10 samples with high concentrations ranged from 5.1 to 8.8 µg/g, and one site, East Mill Creek, with very high concentrations ranging from 31 to 46 µg/g. Submerged macrophytes collected in May 2000 contained similar selenium concentrations as in the September 1999 collection (Montgomery Watson 2001b).

Taking the periphyton, plankton, and submerged macrophyte data together, the elevated selenium concentrations demonstrated that aquatic plants were accumulating selenium from water and sedimentary sources. Montgomery Watson (2001a, 2001b) acknowledged that submerged aquatic plants were efficient accumulators of selenium. Their values were similar to data in the present report. Aquatic plants, i.e., periphyton, plankton, submerged macrophytes, are the foundation of the food web including detritus. As such, they are the first link in the bioaccumulation of selenium to higher trophic consumers such as aquatic invertebrates and fish.

Aquatic invertebrates

Selenium concentrations in aquatic invertebrates from Sheep Creek and Trail Creek (2.6-2.9 µg/g) were the lowest of the sites investigated (Table 7), but were close to the proposed dietary selenium threshold of 3 µg/g (Lemly 1993, 1996b, Hamilton 2002a). Selenium concentrations of 4.6 µg/g in zooplankton caused nearly complete mortality of razorback sucker in about 10-13 days (Hamilton et al. 2001a, 2001b). Several other studies summarized in Hamilton (2002a) have reported that dietary selenium concentrations of 4 to 6 µg/g have caused adverse effects in larval fish. Consequently, the moderate dietary selenium concentrations in upper Slug Creek, lower Blackfoot River, and Angus Creek (4.9 to 7.2 µg/g), and the elevated concentrations in Dry Valley Creek and upper East Mill Creek (19 to 36 µg/g) were of concern to the health of fishery resources.

The high selenium concentration in crane fly nymphs (186 µg/g) collected from the headwaters of Angus Creek at the base of Wooley Valley phosphate mine Unit 4 waste pile probably poses an acute toxicity dietary hazard to predators that might feed on them. The dietary toxicity threshold for nonbreeding birds is 10-15 µg/g and for domestic livestock is 3-5 µg/g (USDOI 1998). Consequently, the cranefly nymphs had 12 to 19 times more selenium than the threshold for nonbreeding birds and 37 to 62 times more than the threshold for domestic livestock. Sandhill cranes (*Grus canadensis*) have been observed feeding in the marshy area within a few meters of the location where the nymphs were collected (L. Stillings, USGS, personal communication). The bryophyte sample with elevated concentrations of selenium and other inorganic elements discussed above (Herring et al. 2001) was collected within a few meters of the crane fly nymphs.

In the hazard assessment protocol proposed by Lemly (1995), selenium concentrations in benthic invertebrates of >5 µg/g represent a high hazard. Using these values suggests that selenium concentrations in invertebrates at lower Blackfoot River, Angus Creek, Dry Valley Creek, and upper East Mill Creek probably were adversely affecting sensitive larval fish, but not necessarily older life stages such as subadults or adults.

Although upper Slug Creek was the reference site and contained relatively low selenium concentrations in water, surficial sediments, and aquatic plants, selenium concentrations in aquatic invertebrates were elevated. Benthic invertebrates can be efficient accumulators of selenium and can retain elevated concentrations over long time periods. For example, Maier et al. (1998) reported that aquatic invertebrates contained selenium concentrations of 1.7 µg/g at pretreatment of watershed with selenium fertilizer, and elevated concentrations during post-treatment monitoring: 4.7 µg/g at 11 days, 4.0 µg/g at 2 months, 5.0 µg/g at 4 months, 4.2 µg/g at 6 months, 4.3 µg/g at 8 months, and 4.5 µg/g at 11 months.

Much of the selenium concentrations in invertebrates came from the food web transfer from detritus, which have been documented as the primary route of uptake by aquatic invertebrates and fish (Maier and Knight 1994, Lemly 1993, 1996b). Two investigators have reported high correlations between selenium concentrations in sediment and benthic invertebrates (r=0.94, Zhang and Moore 1996; r=0.90, ERG 1998), which suggested that selenium concentrations invertebrates were linked with sedimentary selenium. Recently, Peters et al. (1999) reported that two benthic organisms, a eunicid polychaete and a bivalve mollusk, accumulated selenium directly from spiked sediments. This linkage between selenium concentrations in invertebrates and sediment and detritus, i.e., dead plant material, was supported by the strong Pearson correlation coefficients between aquatic invertebrates and surficial sediments (r=0.94) and between aquatic invertebrates and aquatic plants (r=0.91). Selenium concentrations in invertebrates bioaccumulate through the food web to higher trophic organisms such as fish have been reported by several investigators (Sandholm et al. 1973, Finley 1985, Bennett et al. 1986, Dobbs et al. 1996, Hamilton et al. 2001a, 2001b).

Several inorganic elements (aluminum, barium, boron , cadmium, chromium, copper, iron, nickel, strontium, vanadium, and zinc) were elevated in aquatic invertebrates from upper East Mill Creek, Angus Creek near mouth, and Dry Valley Creek (Table 13). Several of these elements were also elevated in surficial sediments and aquatic plants, and apparently were linked with concentrations in aquatic invertebrates (surficial sediment r=0.78-0.93; aquatic plants r=0.83-0.99). Investigators have reported enrichment of aquatic invertebrates with inorganic elements in contaminated aquatic environments (Cherry and Guthrie 1977, Patrick and Loutit 1978, Furr et al. 1979, Dallinger and Kautzky 1985, Dallinger et al. 1987), and adverse effects on fish (Woodward et al. 1995, Farag et al. 1998, 1999). Kiffney and Clements (1993) reported that benthic invertebrates readily accumulated cadmium, copper, and zinc in a stream impacted by acid mine drainage, and the accumulation was strongly linked with element concentrations in *aufwuchs* (defined as biotic and abiotic materials accumulating on submerged surfaces).

Comparison to other Idaho data

Elevated selenium concentrations have been reported in benthic invertebrates collected from ponds (110-390 µg/g) and a lotic area (14 µg/g) of Maybe Creek, a tributary of Dry Valley Creek (TRC Environmental 1999). These selenium concentrations in invertebrates in ponds were substantially higher than those measured in benthic invertebrates from Dry Valley Creek in the present study, but were similar to lotic areas in the present study.

Benthic invertebrate samples collected from various sites in Blackfoot Reservoir contained ≤2 µg/g in September 1999, except for three samples, which contained selenium concentrations of 3.8, 4.6, and 10 µg/g (Montgomery Watson 2001a). However, in the May 2000 sampling, 8 of 12 samples from Blackfoot Reservoir contained a geometric mean selenium concentration of 7.8 µg/g (range 5.3 to 12 µg/g; Montgomery Watson 2001b).

Benthic invertebrates collected in September 1999 from numerous stream sites in the Blackfoot River watershed had moderately elevated selenium concentrations in 5 of 26 samples (3.0 to 4.6 µg/g), elevated concentrations in 5 samples (5.0 to 15 µg/g), and very elevated concentrations at East Mill Creek (72 µg/g) (Montgomery Watson 2001a). In the May 2000 sampling, moderately elevated selenium concentrations occurred in 11 of 42 samples (3.0 to 4.9 µg/g), 17 samples had elevated concentrations (5.0 to 37µg/g), and East Mill Creek had 100, 120 and 170 µg/g (Montgomery Watson 2001b).

Selenium concentrations reported by Montgomery Watson (2001a, 2001b) tended to be higher than those in the present study for similar collection sites. The large number of samples with substantial selenium concentrations far above the proposed toxic threshold of 3 µg/g (Lemly 1993, 1996b) suggested that benthic invertebrate populations were highly contaminated with selenium. Similar to aquatic plants, benthic invertebrates also demonstrated that selenium accumulation was occurring. Aquatic invertebrates are an important link in the food web, and as such, they allow higher trophic consumers like predatory aquatic invertebrates and fish to bioaccumulate selenium.

Fish

Selenium concentrations in fish from the eight sites, based on geometric mean values, followed the same pattern of accumulation as in surficial sediments, aquatic plants, and aquatic invertebrates. The similarity in selenium accumulation between aquatic ecosystem components also paralleled the significant correlations between selenium concentrations in fish and sediments, aquatic plants, and aquatic invertebrates, which demonstrated the interconnectedness of the aquatic ecosystem components (Table 12). This accumulation pattern was supported by the selenium literature, which states that fish bioaccumulate selenium primarily from the dietary route of exposure (Maier and Knight 1994, Lemly 1993, 1996b).

In the present study, there were consistent differences in selenium concentrations between fish species within a site. For example, trout had the highest selenium concentrations and speckled dace had the second highest selenium concentrations, whereas redside shiner had the lowest selenium concentrations. Brook trout (*Salvelinus fontinalis*) and cutthroat trout (*Oncorhynchus clarki*) are insectivores. Speckled dace are a bottom browser that feeds on invertebrates and plant material (Lee et al. 1980), possibly detritus, and thus seemed to accumulate elevated inorganic elements similar to bottom-feeding redear sunfish reported by Campbell (1994). Redside shiner are omnivores (Lee et al. 1980), and thus seemed to accumulate low organic element concentrations similar to omnivorous bluegill reported by Campbell (1994). We concluded that feeding niche differences (benthic versus water column and plant versus animal diet) resulted in different dietary exposures, and more importantly, different selenium bioaccumulation in fish collected in the present study.

The conclusion that a fishes' feeding niche can influence the residues accumulated seems to be supported by studies of inorganic element accumulation. For example, Campbell (1994) reported that bottom feeding redear sunfish had accumulated the most inorganic elements (cadmium, copper, lead, nickel, zinc), piscvorous largemouth bass had the second most accumulation of inorganic elements (cadmium, zinc), and omnivorous bluegill had the least accumulation of inorganic elements (copper). Ney and Van Hassel (1983) reported that the benthic species fantail darter (*Etheostoma flabellare*) and blacknose dace (*Rhinichthys atratulus*) had the highest accumulation of cadmium, lead, nickel, and zinc, bottom-dwelling northern hog sucker (*Hypentelium nigricans*) and white sucker (*Catostomus commersoni*) had intermediate accumulations, and water-column dwelling redbreast sunfish (*Lepomis auritus*) and rock bass (*Ambloplites rupestris*) had the least accumulations. Similar differences in bioaccumulation of inorganic elements among fish species due to trophic niche has been reported by Murphy et al. (1978). However, others have reported that inorganic element residues can vary between fish species, but the variation was not conclusively related to food habits and trophic status (summarized in Wiener and Giesy 1979). In contrast, Besser et al. (1996) studied selenium concentrations in fish in waters with the fly ash disposal ponds and concluded that differences in habitat preference was probably the dominant factor in accumulation because limnetic species generally contained greater selenium concentrations than benthic species.

In contrast to selenium concentrations in fish, concentrations of inorganic elements in fish were highest in upper Slug Creek (aluminum, barium, chromium, manganese), which was the reference site (Tables 16 and 17). Only elevated copper occurred in fish from upper East Mill Creek, which had the highest selenium concentrations in fish and other aquatic ecosystem components compared to the other sites. There seemed to be no parallel bioaccumulation of inorganic elements in fish from the eight sites in the same pattern as selenium.

This scenario of selenium dominating contaminant concerns with inorganic elements in the Blackfoot River watershed has occurred in other contaminant investigations. For example, Furr et al. (1979) examined contaminated food chains in coal ash settling basins and reported that aluminum, cobalt, europium, iron, lanthanum, lutetium, samarium, selenium, and titanium were elevated in biota, but concluded that only selenium was of concern to biota. Sorensen (1988) stated that "Fish kills [at Belews Lake, NC, and Martin Lake, TX] were considered a direct result of selenium release into the main basin of the lakes because several hundred analyses for metals, metalloids, physiochemical parameters, and pesticides provided essentially negative results except for sufficiently high levels of selenium in the water (about 5 µg/L) to warrant concern." Lemly (1985) reviewed information in 10 studies of potential causes for the cause of fishery problems at Belews Lake (16 species eliminated, 2 species present as adults only, 1 species recolonized, and 1 species unaffected), and of the 16 inorganic elements of concern, concluded that only selenium was present at elevated concentrations in water and fish. Saiki and Lowe (1987) measured several inorganic and organic chemicals in water and biota collected from Kesterson Reservoir area, CA, and concluded only selenium was elevated sufficiently to be of concern to fisheries resources. Nakamoto and Hassler (1992) measured 20 trace elements in fish from the Merced River and Salt Slough, San Joaquin Valley, CA, which was primarily irrigation return flows, and concluded only selenium was present at toxic concentrations. Gillespie and Baumann (1986) concluded that selenium was the element causing the deformities and reduced survival of bluegill larvae and not other elements (arsenic, cadmium, copper, lead, mercury, zinc) present in females from Hyco Reservoir, NC. Bryson et al. (1984) concluded that selenium was the only element elevated sufficiently in zooplankton collected from Hyco Reservoir, NC, and not other elements present in food organisms (arsenic, cadmium, copper, mercury, or zinc) to cause 97% mortality of juvenile bluegill after 1 week of dietary exposure. Montgomery Watson (1999) concluded that selenium was the major element of concern associated with phosphate mining activities in the Blackfoot River watershed of southeastern Idaho and not other elements (cadmium, manganese, nickel, vanadium, and zinc). In the two reproduction studies with endangered razorback sucker, several inorganic elements (aluminum, antimony, arsenic, barium, beryllium, bismuth, boron, cadmium, chromium, cobalt, copper, iron, lead, lithium, magnesium, manganese, molybdenum, nickel, silicon, silver, strontium, thallium, tin, titanium, vanadium, zinc) were elevated in water, zooplankton, sediment, and fish eggs, but only selenium was elevated to concentrations reported to cause adverse effects in fish (Hamilton et al. 2001a, 2001b).

A peer consultation workshop on selenium aquatic toxicity and bioaccumulation concluded that the tissue-based criterion might be the best approach for a criterion because tissue residues accounted for selenium's biogeochemical pathways by integrating the route, duration, and magnitude of exposure, chemical form, metabolic transformations, and modifying biotic and abiotic factors (USEPA 1998a). A recent paper gave the rationale for a tissue-based criterion for selenium in fish (Hamilton 2002a). That paper proposed a national criterion of 4 µg/g in whole body based on the review of several laboratory and field studies. This value was the same as the toxicity threshold for fish proposed earlier by Lemly (1993, 1996b) and similar to the threshold of 4.5 µg/g proposed by Maier and Knight (1994). Recent papers have proposed selenium toxicity thresholds of 6 µg/g for coldwater anadromous fish and 9 µg/g for warm water fish (DeForest et al. 1999, Brix et al. 2000). The approach, information, and conclusions presented in DeForest et al. (1999) and Brix et al. (2000) have been reviewed and problems in their interpretation and conclusions have been discussed in Hamilton (2002b).

Based on the toxicity threshold of 4 µg/g proposed by Lemly (1993, 1996b) and Hamilton (2002a) and 4.5 µg/g proposed by Maier and Knight (1994), the geometric mean selenium concentrations in fish from upper Slug Creek, lower Slug Creek, Trail Creek, and

Sheep Creek (range 4.0-5.2 µg/g) would probably have some effects on early life stages of sensitive species. Fish in Angus Creek near the mouth (6.4 µg/g) and lower Blackfoot River (7.8 µg/g) had selenium concentrations above the 4-4.5 µg/g threshold value, thus suggesting possible effects in sensitive fish species in these streams. Elevated whole-body residues of selenium in fish from Dry Valley Creek (16.1 µg/g) and East Mill Creek (32.2 µg/g) suggested sensitive and moderately sensitive fish are probably being adversely affected by selenium exposure.

<u>Comparison to other Idaho data</u>

Rich and Associates (1999) reported concentrations of inorganic elements in cutthroat trout, rainbow trout (*Oncorhynchus mykiss*), brook trout, sculpin species, dace species, and redside shiner collected from Dry Valley Creek immediately upstream of the Blackfoot River, and Dry Valley Creek directly below Maybe Creek. In general, their concentrations were higher than in the present study for cadmium, chromium, copper, vanadium, and zinc, but lower for selenium. They concluded that selenium and other elements (cadmium, copper, lead, vanadium, and zinc) were probably causing stress in fish populations in Dry Valley Creek. In the present study selenium was the only element in fish elevated at Dry Valley Creek.

Montgomery Watson (1999) reported salmonid fillets collected in 1998 contained selenium concentrations of 6 µg/g wet weight (maximum 7.9 µg/g) from East Mill Creek, whereas fish from two other sites (Blackfoot River above Wooley Range Ridge Creek and South Fork Sage Creek) had 1.2-1.3 µg/g. Converting these values to a dry weight basis (dry weight = wet weight × 4; assuming 75% moisture) results in 24 µg/g in fish fillets from East Mill Creek and 4.8-5.2 µg/g in fish fillets from the reference sites.

Selenium concentrations in fillets reported by Montgomery Watson (1999) underestimate the concentrations in whole-body fish, which is the dominant matrix of selenium residues in fish reported in the literature. Muscle contains less selenium than whole-body due to the relatively high amounts of selenium found in spleen, liver, kidney, heart, and other tissues, especially mature ovaries (Adams 1976, Sato et al. 1980, Lemly 1982, Hilton et al. 1982, Hilton and Hodson 1983, Kleinow and Brooks 1986, Hermanutz et al. 1992). Consequently, the actual whole-body selenium concentrations in trout would be about 40 µg/g in fish from East Mill Creek and 8-8.7 µg/g in fish from the Blackfoot River and South Fork Sage Creek (based on a conversion factor of 1.667 × muscle concentration = whole body concentration, Lemly and Smith 1987). Other conversion factors reported in the literature were 2.355 based on data from Adams (1976) for rainbow trout, and 1.745 from Lemly (1982) for bluegill and largemouth bass, both of which would have increased the converted values for trout in Montgomery Watson (1999). In the present study, the selenium concentrations in whole-body brook trout (42.7 µg/g) and cutthroat trout (24.3 µg/g) from East Mill Creek were similar to those reported by Montgomery Watson (1999) after conversion to dry weight and whole-body (40 µg/g).

Selenium concentrations in whole-body salmonids collected in September 1999 from Blackfoot Reservoir and the mainstem and tributaries of the Blackfoot River were elevated in 21 of 50 samples (4.2 to 9.7 µg/g) and high in 7 samples (12 to 31 µg/g) (converted to dry weight using the appropriate percent moisture from Montgomery Watson 2001a, and whole-body using a factor of 1.667, Lemly and Smith 1987). For salmonids collected in May 2000 from various locations in the Blackfoot River, selenium concentrations in whole-body were elevated in 13 of 27 samples (5.2 to 9.2 µg/g) and high in 12 samples (10 to 48 µg/g) (converted to dry weight using the appropriate percent moisture from Montgomery Watson 2001b, and whole-body using a factor of 1.667, Lemly and Smith 1987).

These selenium residues in salmonids were substantially above background concentrations in fish from laboratory and field investigations. Background selenium concentrations in fish are typically 1-2 µg/g (Maier and Knight 1994; Hamilton et al. 2000). More importantly, the selenium residues were above those reported to cause adverse effects in early life stages of fish, including salmonids (4-5 µg/g; Hamilton et al. 2000). In particular, selenium residues of 5.2 µg/g in rainbow trout were associated with reduced survival (Hunn et al. 1987), and 3.8-4.9 µg/g in chinook salmon (*Oncorhynchus tshawytscha*) were associated with reduced survival and growth (Hamilton et al. 1986, Hamilton and Wiedmeyer 1990). Older life stages typically are more tolerant of contaminant stresses than are early life stages (Rand and Petrocelli 1985). Consequently, effects in adults may not be as readily apparent as effects in early life stages.

Based on the above discussion, selenium contamination of the Blackfoot River and its tributaries are most likely adversely affecting aquatic resources, especially in early life stages of fish. Thurow et al. (1981) reported that 13 fish species used the Blackfoot River and its tributaries, and that the indigenous cutthroat trout was the dominant species. They noted that cutthroat trout used several tributaries, as well as the main stem river and the Blackfoot Reservoir during their life cycle. Thurow et al. (1981) noted the potential for mining activities to cause negative effects on trout and others species, primarily from erosion, sedimentation, and nutrient loading from phosphorous, but did not specially mention impacts from inorganic elements.

Montgomery Watson (2000) reported that eggs from cutthroat trout in 1999 containing selenium concentrations of 4.4 and 6.7 µg/g dry weight in two ripe females from the Blackfoot River, 4.0 µg/g in two partially spawned females from the Blackfoot River, and 1.4 µg/g in females from the reference site Henry's Lake. These data demonstrated that trout were accumulating selenium and depositing it in their eggs. However, the selenium concentrations in eggs were less than the toxic effects threshold of 10 µg/g proposed by Lemly (1993, 1996b). The low number of egg samples in Montgomery Watson (2000) precludes further speculation on the extent of selenium contamination of fish eggs.

Selenium concentrations in forage fish reported by Montgomery Watson (2001a, 2001b) were similar to those in the present study. Forage fish samples collected in September 1999 from various sites in Blackfoot River watershed contained selenium concentrations ≥4 µg/g (Montgomery Watson 2001a), which was above the generally accepted toxic threshold of 4 µg/g (Lemly 1993, 1996b, Maier and Knight 1994, Hamilton 2002a). Nine of 13 samples had elevated selenium concentrations in fish (5.2 to 8.3 µg/g, after conversion to dry weight using the percent moisture given for each sample), and two samples had high selenium concentrations of 10 and 12.9 µg/g (Montgomery Watson 2001a). For forage fish collected from various sites in the Blackfoot River watershed in May 2000, 13 of 36 samples contained selenium concentrations of 5.0 to 9.4 µg/g, and 13 samples had concentrations of 10 to 37 µg/g (Montgomery Watson 2001b).

The large number of samples with substantial selenium concentrations above the proposed toxic whole-body threshold of 4 µg/g suggested that fish populations have accumulated elevated selenium concentrations similar to aquatic plants and benthic invertebrates. Thus, forage fish and salmonids probably pose a hazard of selenium toxicity to predatory fish and fish-eating wildlife.

Other considerations

One concern that might be raised was the presence of elevated selenium residues in fish without readily apparent biological effects. In addressing this concern, the first consideration that should be mentioned is that the data in the current study and studies by others (Rich and Associates 1999, Montgomery Watson 1999, 2000, 2001a, 2001b) were contaminant surveys and not biological effects studies. No biological effects such as survival, growth, reproduction, diversity, population structure, community structure, or other biological effects were measured.

The second consideration was that residues measured in fish were for adults or subadults. This life stage is generally not sensitive to the effects of environmental contaminants (Rand and Petrocelli 1985). Rather, early life stages are generally considered the most sensitive life stage.

The third consideration was the movement of fish in the Blackfoot River watershed or in any open river system. Adverse effects on a demographically open fish population in a section of the river with contaminant impacts would be very difficult to detect and must be confirmed with detailed biological studies because of immigration of individuals from the portion of the population in non-affected river reaches or tributary streams that could occur. The review by Skorupa (1998) addresses this concern succinctly and states, "It is common for instream studies to report the counterintuitive combination of abnormally elevated levels of selenium in fish tissue associated with what is viewed as a normally abundant and diverse fish fauna." Papers that seem to have reached this unproven conclusion include Canton and Van Derveer (1997), Van Derveer and Canton (1997), and Kennedy et al. (2000). These papers tended to conclude that the toxic thresholds for selenium derived from laboratory studies or field studies in closed basins, i.e., demographically closed populations, do not apply to stream studies. Effects of selenium on species or populations of fish in the lake and reservoir studies were substantiated with appropriate biological tests, whereas stream or river investigations typically have not incorporated appropriate biological tests. Problems in the interpretation of information in Canton and Van Derveer (1997), Van Derveer and Canton (1997) were given in Hamilton and Lemly (1999), and problems in Kennedy et al. (2000) were given in Hamilton and Palace (2001).

Monitoring of fish populations in rivers is an insensitive measure of contaminant effects unless substantial effort is made to assess the health of the fish community. This assertion was addressed by the USEPA in their guidelines for deriving water quality criteria. Stephan et al. (1985) stated that, "The insensitivity of most monitoring programs [for number of taxa or individuals] greatly limits their usefulness for studying the validity of [water quality] criteria because unacceptable changes can occur and not be detected. Therefore, although limited field studies can sometimes demonstrate that criteria are under protective, only high quality field studies can reliably demonstrate that criteria are not under protective [i.e., overprotective]."

Claim of no biological effects in stream or river studies cannot often be confirmed without appropriate biological effects tests. Statements of no biological effects in streams or rivers without appropriate testing fall into the null fallacy trap: (1) There is no evidence for adverse effects, versus (2) There is evidence for no adverse effects (J. Skorupa, USFWS, personal communication). The null fallacy occurs when statement 1 (a null finding) is given equal weight as statement 2 (a positive finding). What often is overlooked is that a null finding usually implies a lack of positive evidence in both directions -- for effects or for absence of effects. The null fallacy is just one of several errors in logic found in scientific dialogues (Sagan 1996).

Montgomery Watson (2001b) acknowledged that higher than expected selenium concentrations in forage fish from a reference site on Spring Creek above influences of East Mill Creek were probably due to the mobility of fish. Forage fish in the upper Spring Creek contained selenium concentrations of 10, 12, and 22 µg/g. However, in spite of high selenium residues in whole-body forage fish collected in May 2000, Montgomery Watson (2001b) stated that, "There is no evidence of forage fish in the Blackfoot Reservoir being impacted by either selenium or cadmium at either time of year." Likewise, Montgomery Watson (2001a) reported elevated selenium concentrations in forage fish collected in September 1999, yet stated that, "Evaluation of forage fish data show no evidence that this medium is impacted in the reservoir." Because no biological effects were assessed in fish collections in September 1999 or May 2000, their statements were unsupported by their data and the selenium literature.

Hazard assessment

Lemly (1995) presented a protocol for aquatic hazard assessment of selenium, which was formulated primarily in terms of the potential for food-chain bioaccumulation and reproductive impairment in fish and aquatic birds. The protocol incorporated five ecosystem components including water, sediment, benthic invertebrates, fish eggs, and bird eggs. Each component was given a numeric score based on the degree of hazard: 1, no identifiable hazard; 2, minimal hazard; 3, low hazard; 4, moderate hazard; 5, high hazard. The final hazard characterization was determined by adding the individual scores and comparing the total to the following evaluation criteria. Lemly (1996a) modified his protocol for use with four ecosystem components due to the difficulty in collecting residue information for all five components in an assessment. He adjusted the final ecosystem-level hazard assessment to the following four-component evaluation criteria: 4, no hazard; 5-7, minimal hazard; 8-10, low hazard; 11-14, moderate hazard; 15-20, high hazard.

Lemly (1995) defined five categories of hazards as follows: (1) high hazard denotes an imminent, persistent toxic threat sufficient to cause complete reproductive failure in most species of fish and aquatic birds; (2) moderate hazard indicates a persistent toxic threat of sufficient magnitude to substantially impair but not eliminate reproductive success; some species will be severely affected whereas others will be relatively unaffected; (3) low hazard denotes a periodic or ephemeral toxic threat that could marginally affect the reproductive success of some sensitive species, but most species will be unaffected; (4) minimal hazard indicates that no toxic threat identified but concentrations of selenium are slightly elevated in one or more ecosystem components (water, sediment, invertebrates, fish eggs, bird eggs) compared to uncontaminated reference sites; (5) no hazard denotes that no toxic threat is identified and selenium concentrations are not elevated in any ecosystem component. Table 18 gives the hazard term and corresponding selenium concentration range for each of the four ecosystem components in the four-component model (Lemly 1996a).

These protocols have been used to assess the selenium hazard to aquatic ecosystems at Ouray NWR, UT (Lemly 1995, 1996a), the Animas, LaPlata, and Mancos rivers in the San Juan River basin (Lemly 1997), three Wildlife Management Areas in Nevada (Lemly 1996a), and three sites near Grand Junction, CO (Hamilton et al. 2001a, 2001b). Although the original protocol was published in 1995, apparently no critiques have been published pointing out any deficiencies in the protocol (D. Lemly, USFS, personal communication).

The selenium hazard protocols give equal weigh to each component (Lemly 1995, 1996a). However, a critique of the protocol by selenium expert Harry Ohlendorf pointed out the need to give more weight to the biological components: benthic invertebrates, fish eggs, and bird eggs (written communication, H. Ohlendorf, 1996). Ohlendorf suggested a multiplication factor of two for benthic invertebrate information and a factor of three for fish eggs and bird eggs. Similar concerns have been raised by a USGS scientist (written communication, M. Sylvester, Menlo Park, CA, 2002), and by a USFWS Environmental Contaminant Specialist (written communication, B. Osmundson, Grand Junction, CO, 2001). The weighting of the three biological components seems justified based on the repeated expression of their importance in the selenium literature (reviews by Lemly 1985, 1993, Maier and Knight 1994, Presser et al. 1994, Hamilton and Lemly 1999, Hamilton 2002a, 2002b).

Incorporating these factors into the protocol using the offset summation approach used by Lemly (Lemly 1995, 1996a) results in modified final hazard characterizations for the four-component protocol of 7, no hazard; 8-13, minimal hazard; 14-20, low hazard; 21-27, moderate hazard, and 28-35, high hazard (Table 18). The offset summation is explained as follows: for the low hazard column, Lemly (1996a) gives a score of 3 for each of the four components being evaluated (water, sediment, benthic invertebrate, and fish eggs), which results in a summed score of 12 (Table 18). However, if in an environmental situation all measured selenium concentrations of the four components fell into the “low” column, the additive effect of the combined low exposures would most likely result in a “moderate” final hazard to biota. Thus, Lemly (1996a) set the final hazard range for a “low” final hazard at 8-10, instead of closer to the summed total of 12. This offsetting of the final hazard total seems biologically reasonable and is referred to here as the offset summation approach. Similar offsets for other final hazards are given in Table 18. For the five-component protocol, the modified final hazard characterization would be 10, no hazard; 11-19, minimal hazard; 20-28, low hazard; 29-38, moderate hazard, and 39-50, high hazard.

In the present study, fish eggs were not collected. In the hazard assessment, we converted the geometric mean whole-body concentrations of selenium in fish to fish eggs concentrations using the conversion factor: based on Lemly (1995, 1996a), who reported: whole-body × 3.3 = fish egg. The hazard assessment for the eight sites is given in Table 19.

The two sites with low selenium concentrations in most aquatic ecosystem components had low overall hazard rating: Trail Creek and Sheep Creek. Although selenium concentrations were none or low in water and sediment at upper Slug Creek and lower Slug Creek, they were

Table 18. Aquatic ecosystem components and the concentrations posing various hazards based on Lemly (1996a).

	Hazard														
	None			Minimal			Low			Moderate			High		
Ecosystem component	Conc.	Lemly[1] score	Current score	Conc.	Lemly[1] score	Current score	Conc.	Lemly[1] score	Current score	Conc.	Lemly[1] score	Current score	Conc.	Lemly[1] score	Current score
Water (µg/L)	<1	1	1	1-2	2	2	2-3	3	3	3-5	4	4	>5	5	5
Sediment (µg/g)	<1	1	1	1-2	2	2	2-3	3	3	3-4	4	4	>4	5	5
Benthic invertebrate (µg/g)	<2	1	2	2-3	2	4	3-4	3	6	4-5	4	8	>5	5	10
Fish eggs (µg/g)	<3	1	3	3-5	2	6	5-10	3	9	10-20	4	12	>20	5	15
Sum		4	7		8	14		12	21		16	28		20	35
Final hazard (Lemly[1])		4			5-7			8-10			11-14			15-20	
Final hazard (Current)			7			8-13			14-20			21-27			28-35

[1]Lemly 1996a.

Table 19. Hazard assessment of selenium at eight sites in southeastern Idaho.

Site[1] and ecosystem component	Selenium concentrations[2]	Evaluation by component		Totals for the site	
		Hazard	Score	Score	Hazard
ACM					
Water	<0.5	None	1		
Sediment	1.0	Minimal	2	28	High
Benthic invertebrate	7.2	High	10		
Fish eggs[3]	21.1	High	15		
UEMC					
Water	29.9	High	5		
Sediment	32.5	High	5	35	High
Benthic invertebrate	35.7	High	10		
Fish eggs	106.3	High	15		
LEMC					
Water	14.9	High	5		
Sediment	45.8	High	5	10	High[5]
Benthic invertebrate	NS[5]	-	-		
Fish eggs	NS	-	-		
TC					
Water	<0.5	None	1		
Sediment	0.8	None	1	18	Low
Benthic invertebrate	2.9	Minimal	4		
Fish eggs	16.9	Moderate	12		
USC					
Water	<0.5	None	1		
Sediment	0.8	None	1	22	Moderate
Benthic invertebrate	4.9	Moderate	8		
Fish eggs	13.2	Moderate	12		
LSC					
Water	<0.5	None	1		
Sediment	1.7	Minimal	2	14	Moderate[5]
Benthic invertebrate	NS	-	-		
Fish eggs	17.5	Moderate	12		
DVC					
Water	<0.5	None	1		
Sediment	5.2	High	5	31	High
Benthic invertebrate	19.5	High	10		
Fish eggs	53.1	High	15		
ShpC					
Water	<0.5	None	1		
Sediment	0.5	None	1	18	Low
Benthic invertebrate	2.6	Minimal	4		
Fish eggs	17.2	Moderate	12		

Table 19. Continued.

Site[1] and ecosystem component	Selenium concentrations[2]	Evaluation by component		Totals for the site	
		Hazard	Score	Score	Hazard
LBR					
Water	<0.5	None	1		
Sediment	2.1	Low	3	29	High
Benthic invertebrate	5.4	High	10		
Fish eggs	25.7	High	15		

[1]ACM: Angus Creek near mouth, UEMC: upper East Mill Creek, LEMC: lower East Mill Creek, TC: Trail Creek, USC: upper Slug Creek, LSC: lower Slug Creek, DVC: Dry Valley Creek, ShpC: Sheep Creek, LBR: lower Blackfoot River.

[2]Selenium concentrations in µg/L for water, µg/g for sediment, benthic invertebrates, and fish eggs.

[3]Fish eggs: fish egg values converted from whole-body residues using: whole-body × 3.3 = fish egg (Lemly 1995, 1996a).

[4]NS: not sampled.

[5]Based on available aquatic ecosystem components.

elevated in benthic invertebrates or whole body residues converted to fish egg concentrations or both, resulting in a moderate overall hazard rating. Selenium concentrations in water or sediment were in the none, minimal, or low categories at Angus Creek near mouth and the lower Blackfoot River, but high in benthic invertebrates and whole-body residues. Thus these two sites receive high final hazards using the multiplication factor of two for benthic invertebrates and three for fish eggs. Using the original Lemly (1996a) approach, these two sites would have received moderate final hazards in spite of the high score for benthic invertebrates and fish eggs (converted from whole-body residues). The use of the multiplication factor for benthic invertebrate and fish eggs seems justified in light of the importance of elevated selenium residues and degraded ecosystem health (Lemly 1985, 1993, Maier and Knight 1994, Presser et al. 1994, Hamilton and Lemly 1999, Hamilton et al. 2002a, 2002b). Upper East Mill Creek and Dry Valley Creek consistently had elevated selenium concentrations in sediment, invertebrates, or whole-body residues, thus resulting in high overall hazard rating. The overall hazard rating at lower East Mill Creek was considered high because of the elevated selenium concentrations in water and sediment, which probably would have resulted in high concentrations in invertebrates and fish if they had been collected.

Reports by Montgomery Watson (1999, 2000, 2001a, 2001b) do not present hazard assessments. However, the general wording in the data evaluations of the various aquatic ecosystem components for water, sediment, submerged macrophytes, benthic invertebrates, forage fish and salmonid fillets, tends to suggest no major impacts from selenium and other elements, with the exception of creeks influenced directly by phosphate mining activities.

A preliminary assessment of selenium hazard in the Caribou National Forest was conducted using selenium residue data in water and fish collected from 1997-1998 (Lemly 1999). Lemly (1999) concluded that there was a high potential for toxic impacts to fish and wildlife associated with the Blackfoot River, its tributaries, and Blackfoot Reservoir. The results of the present study add substantially more support to the premise that selenium concentrations in several aquatic ecosystem components were sufficiently elevated to cause adverse effects to aquatic resources in the Blackfoot River watershed.

Acknowledgement: The authors thank the following personnel for assistance in this study: Bill Janowski, Jeff Jones, and Larry Michelson, U.S. Forest Service; Jay Bateman, Don Cole, Mark Hardy, Jim Herring, Mark Huebner, Phil Moyle, and Theresa Presser, U.S. Geological Survey; Peter Oberlindacher, U.S. Bureau of Land Management; and Jim Mende, Idaho Department of Fish and Game. The authors thank John Besser and Marc Sylvester for reviewing the report, and Theresa Presser for drafting Figure 1.

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Appendix 1. Wet weight (g) of aquatic plant (white-water buttercup *Ranunculus longirostris*) collected at nine sites in the Blackfoot River watershed, and submitted for either selenium (Se) analysis by atomic absorption or elemental analysis by inductively coupled plasma-mass spectroscopy (ICP-MS) [1].

	Analysis	
Location[2]	Se	ICP-MS
ACM	7.82	7.46
UEMC	9.03	8.44
LEMC	5.29	5.40
TC	4.36	6.00
USC	10.38	7.83
LSC	8.25	14.32
DVC	8.84	11.20
ShpC	6.62	12.14
LBR	12.51	10.16

[1]ICP-MS elements: Aluminum, arsenic, barium, beryllium, boron, cadmium, chromium, copper, iron, lead, magnesium, manganese, mercury, molybdenum, nickel, strontium, vanadium, zinc.

[2]ACM: Angus Creek near mouth, UEMC: upper East Mill Creek, LEMC: lower East Mill Creek, TC: Trail Creek, USC: upper Slug Creek, LSC: lower Slug Creek, DVC: Dry Valley Creek, ShpC: Sheep Creek, LBR: lower Blackfoot River.

Appendix 2. Wet weight (g) of aquatic invertebrates collected from nine sites in the Blackfoot River watershed and submitted for either selenium (Se) analysis by atomic absorption or elemental analysis by inductively coupled plasma-mass spectroscopy (ICP-MS)[1].

			Aquatic invertebrate type							
Location[2]	Chemical analysis	Composite weight	Gammaridae	Caddisfly	Mayfly	Damselfly	Beetle larvae	Stonefly	Leech	Cranefly
ACH	Se	2.10	-	-	-	-	-	-	-	2.10
	ICP-MS	2.18	-	-	-	-	-	-	-	2.18
ACM	Se	4.42	-	3.44	0.04	-	0.16	-	-	0.78
	ICP-MS	5.76	-	4.11	0.04	-	0.23	-	-	1.38
UEMC	Se	3.39	-	0.14	2.56	-	-	-	0.69	-
	ICP-MS	4.00	-	0.27	2.94	-	-	-	0.79	-
LEMC	Se	NC[3]	-	-	-	-	-	-	-	-
	ICP-MS	NC	-	-	-	-	-	-	-	-
TC	Se	4.19	0.07	2.00	-	2.12	-	-	-	-
	ICP-MS	5.41	0.10	2.66	-	2.65	-	-	-	-
USC	Se	2.98	0.57	1.90	0.51	-	-	-	-	-
	ICP-MS	3.40	0.79	2.00	0.61	-	-	-	-	-
LSC	Se	NC	-	-	-	-	-	-	-	-
	ICP-MS	NC	-	-	-	-	-	-	-	-

DVC	Se	4.37	0.56	3.40	0.09	-	0.32	-	-	-
	ICP-MS	9.10	0.67	7.61	0.11	-	0.71	-	-	-

Appendix 2. Continued.

Location[2]	Chemical analysis	Composite weight	Aquatic invertebrate type							
			Gammaridae	Caddisfly	Mayfly	Damselfly	Beetle larvae	Stonefly	Leech	Cranefly
ShpC	Se	6.30	-	3.07	1.23	-	-	2.00	-	-
	ICP-MS	9.94	-	5.89	1.48	-	-	2.57	-	-
LBR	Se	12.87	-	1.35	0.14	-	-	9.55	-	1.83
	ICP-MS	13.46	-	1.43	0.23	-	-	9.57	-	2.23

[1]ICP-MS elements: Aluminum, arsenic, barium, beryllium, boron, cadmium, chromium, copper, iron, lead, magnesium, manganese, mercury, molybdenum, nickel, strontium, vanadium, zinc.
[2]ACH: seep at head of Angus Creek; ACM: Angus Creek near mouth, UEMC: upper East Mill Creek, LEMC: lower East Mill Creek, TC: Trail Creek, USC: upper Slug Creek, LSC: lower Slug Creek, DVC: Dry Valley Creek, ShpC: Sheep Creek, LBR: lower Blackfoot River.
[3]NC: not collected.

Appendix 3. Total length (mm) and weight (g) of fish collected at nine sites in the Blackfoot River watershed.

Location[1]	Species[2]	Total length	Weight
ACM	Cutthroat trout	119	15.62
		103	10.08
		109	11.28
	Mottled sculpin	55	2.05
		75	5.57
		107	15.88
		54	1.90
	Longnose dace	83	6.38
		72	3.88
		63	2.65
	Redside shiner	83	5.96
		68	3.65
		66	2.39
UEMC	Cutthroat trout	93	7.62
		116	15.84
	Brook trout	200	74.52
LEMC	(no fish found)	-	-
TC	Mottled sculpin	115	25.84
		114	25.33
		63	3.54
		71	4.71
	Longnose dace	80	5.02
		92	7.13
	Speckled dace	71	3.89
		79	5.62
		71	4.22
		73	4.53
		71	3.72
		66	2.74
		60	2.55
		64	2.80
		59	1.94

Appendix 3. Continued.

Location[1]	Species[2]	Total length	Weight
TC	Speckled dace	74	4.68
		64	2.94
		60	2.33
		66	2.86
		153	42.17
	Redside shiner	81	4.77
		78	4.38
		96	8.84
		71	3.86
		77	4.62
USC	Brook trout	193	77.71
		108	13.79
		134	26.67
		115	16.88
	Mottled sculpin	58	2.38
		52	1.78
		48	1.26
	Speckled dace	74	5.63
		62	2.36
		78	5.82
		57	2.27
		58	1.86
LSC	Speckled dace	70	4.07
		59	2.31
		65	2.88
		64	2.64
		53	1.93
		57	1.98
		61	2.47
		64	2.65
		55	2.05
		55	1.74
	Redside shiner	105	12.16
		92	8.12
		80	5.88
		94	10.25
		83	6.10
		83	5.62
		72	4.04

Appendix 3. Continued.

Location[1]	Species[2]	Total length	Weight
LSC	Redside shiner	71	3.33
		61	2.42
DVC	Cutthroat trout	81	5.16
		67	2.89
		60	1.97
	Mottled sculpin	81	7.78
		75	3.31
		50	1.65
	Speckled dace	72	4.33
		73	5.00
		81	5.69
ShpC	Cutthroat trout	86	6.32
		86	7.06
		82	5.22
		97	9.44
	Longnose dace	88	6.60
		95	9.47
LBR	Mottled sculpin	79	7.45
		76	6.06
		73	5.49
	Speckled dace	84	6.05
		71	3.35
		67	3.11
		65	2.87
		71	4.75
	Speckled dace	63	2.64
		56	1.93
		69	3.80
		60	2.18
		53	1.18
		65	3.14
	Redside shiner	56	1.73
		53	1.16
		42	0.68

Appendix 3. Continued.

[1]ACM: Angus Creek near mouth, UEMC: upper East Mill Creek, LEMC: lower East

Mill Creek, TC: Trail Creek, USC: upper Slug Creek, LSC: lower Slug Creek, DVC: Dry Valley Creek, ShpC: Sheep Creek, LBR: lower Blackfoot River.

[2]Cutthroat trout (*Oncorhynchus clarki*), brook trout (*Salvelinus fontinalis*), mottled sculpin (*Cottus bairdi*), longnose dace (*Rhinichthys cataractae*), speckled dace (*Rhinichthys osculus*), redside shiner (*Richardsonius balteatu)*.