



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:
September 2000.**

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Abstract

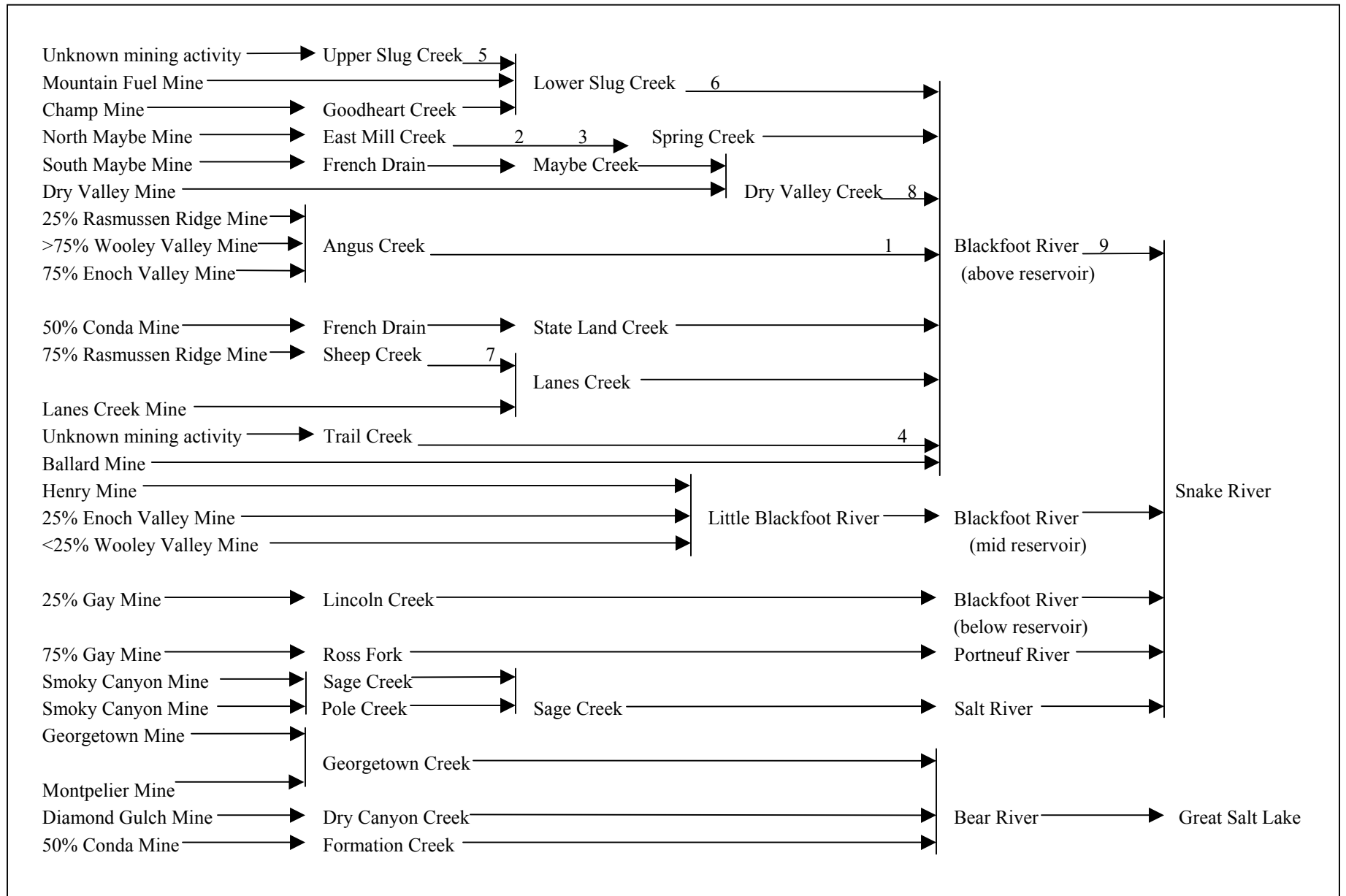
Nine stream sites in the Blackfoot River watershed in southeastern Idaho were sampled in September 2000 for water, surficial sediment, aquatic plants, aquatic invertebrates, and fish. Selenium and other inorganic elements were measured in these aquatic ecosystem components, and a hazard assessment was performed on the data. Water quality characteristics such as pH, hardness, and specific conductance were relatively uniform among the nine sites examined. Selenium and several inorganic elements were elevated in water, sediment, aquatic plants, aquatic invertebrates, and fish from several sites suggesting deposition in sediments and food web cycling through plants and invertebrates. Selenium was elevated to concentrations of concern in water at 8 sites (>5 microgram/liter, $\mu\text{g/L}$), sediment at 3 sites (>2 $\mu\text{g/g}$), aquatic plants at four sites (>4 $\mu\text{g/g}$), aquatic invertebrates at 5 sites (>3 $\mu\text{g/g}$), and fish at 7 sites (>4 $\mu\text{g/g}$ in whole body). A hazard assessment of selenium in the aquatic environment suggested low hazard at Sheep Creek, moderate hazard at Trail Creek, upper Slug Creek, lower Slug Creek, and lower Blackfoot River, and high hazard at Angus Creek, upper East Mill Creek, lower East Mill Creek, and Dry Valley Creek. The results of this study are consistent with results of a previous investigation and 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 (Dry Valley Mine, Smoky Canyon Mine, Enoch Valley Mine, Rasmussen Ridge Mine) in southeastern Idaho Phosphate District that produce phosphate from the Meade Peak Phosphatic Shale Member, and 11 inactive mines (Gay Mine, Lanes Creek Mine, Conda Mine, Henry Mine, Ballard Mine, Mountain Fuel Mine, Champ Mine, North Maybe Mine, South Maybe Mine, Georgetown Canyon Mine, Wooley Valley Mine) in the Southeast Idaho Phosphate Resource Area (MW 1999). Most mining of these phosphatic shales is by open-pit or contour strip surface mining, and waste materials are generally deposited 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-rock piles. These drainage systems transfer leachates from mining areas to surface waters, eventually draining into tributaries, and later, the Blackfoot River and Blackfoot Reservoir. Thus, water movement releases toxic inorganic elements to aquatic and terrestrial ecosystems.

The Blackfoot River watershed has several active and inactive phosphate mines that 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 were expressed (Platts and Martin 1978). Recent concerns about the potential impact on aquatic and terrestrial ecosystems from phosphate mining have been the subject of several reports (MW 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 Phosphatic Shale (e.g., Desborough et al. 1999, Herring et al. 2000a, 2000b). Other USGS investigations have reported inorganic element concentrations in aquatic bryophytes and terrestrial plants that were influenced by

Figure 1. Diagram of surface water flow (generalized to 25% increments) 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.



mining (Herring and Amacher 2001, Herring et al. 2001).

Release of toxic inorganic elements from phosphate mining in southeastern Idaho and accumulation in the food chain has resulted in adverse biological effects. In recent years, seven horses in the Dry Valley and Woddall areas were euthanized, and 60-80 sheep died in 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 inorganic elements have been reported in limited samples of fish fillets and aquatic invertebrates (MW 1999). Recent USGS reports suggest that selenium concentrations in fish and wildlife were sufficiently elevated to cause adverse effects in sensitive fish species (Piper et al. 2000, Hamilton et al. 2002).

The purpose of this study was to determine the concentrations of selenium and other inorganic elements in water, surficial sediment, aquatic plants, aquatic invertebrates, and fish from streams in southeastern Idaho near phosphate mining operations during the fall, low flow period. This information was used for comparison with samples from the spring, high flow period (Hamilton et al. 2002), and 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.

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). Sample collection occurred in September 2000 and was a joint effort of the USGS Water Resources Discipline (WRD), USGS Biological Resources Discipline (BRD), and the U.S. Forest Service (USFS).

Site description

The collection sites were as follows:

1. The Angus Creek near mouth (ACM) site was located at the crossing of the creek by Forest Route 095 (USFS map, Caribou National Forest, Montpelier and Soda Springs Districts, 1988), and was approximately a half kilometer (km) above the confluence with the Blackfoot River. The sampling site was below the active Rasmussen Ridge, inactive Wooley Valley, and active Enoch Valley mines. 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 (no grazing impacts noted). Sample collection was primarily on the upstream side of the road crossing.

2. The upper East Mill Creek (UEMC) 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 sampling site was below the inactive North Maybe Mine. The land was owned by the USFS and was composed of pine forest with some sagebrush in open areas. Sample collection was in a generally open area of forbs, grass, and sparse pine trees with very limited grazing (no grazing impacts noted).

3. The lower East Mill Creek (LEMC) site was located at the crossing of the creek by

Figure 2. Map of study area. Dots are general locations of sample sites. (Map source: modified from Herring et al. 2001).

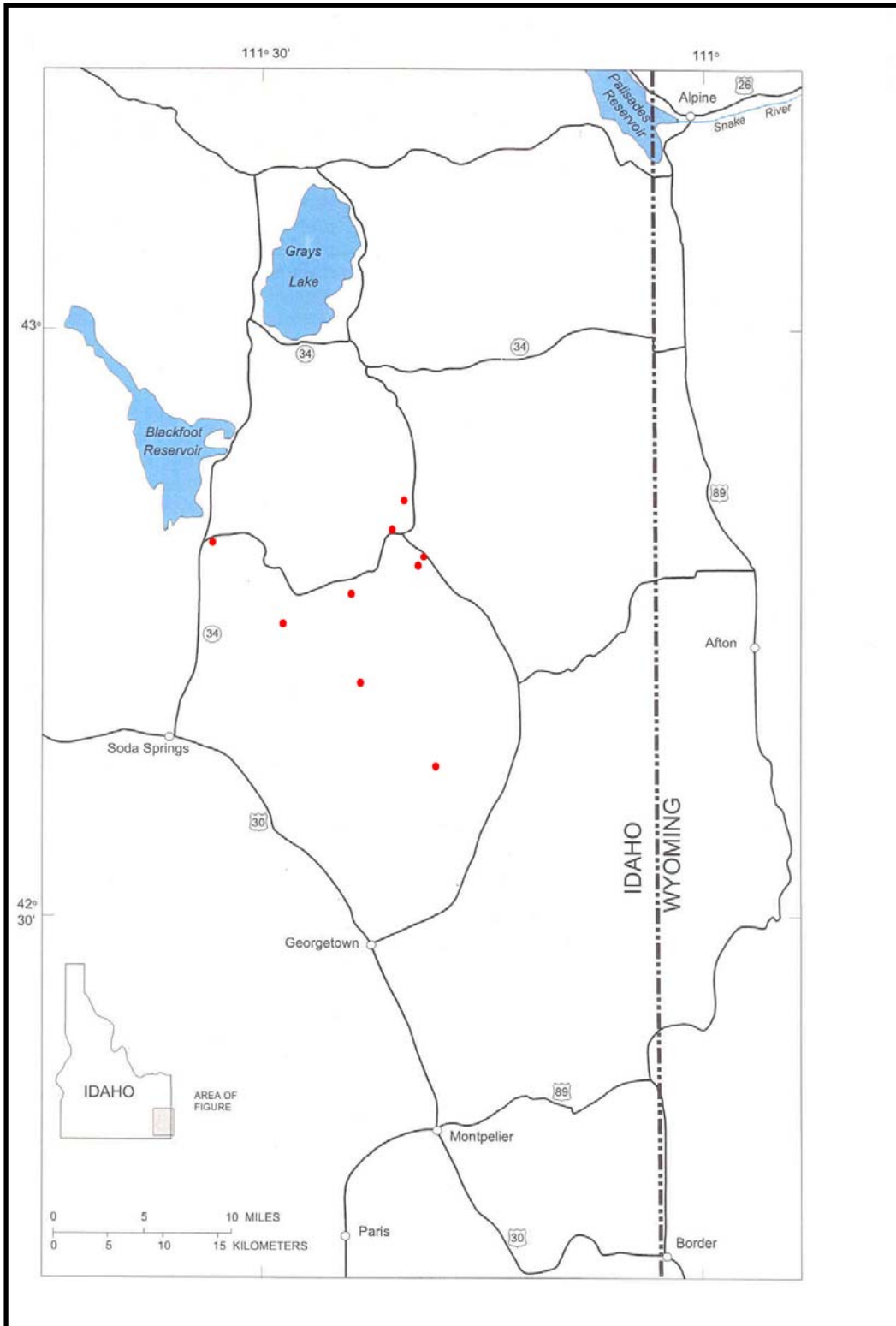


Figure 3. Map of sample sites: 1 Angus Creek, 2 upper East Mill Creek, 3 lower East Mill Creek, 4 Trail Creek, 5 upper Slug Creek, 6 lower Slug Creek, 7 Sheep Creek, 8 Dry Valley Creek, 9 lower Blackfoot River. (Map source: Bureau of Land Management, BLM/ID/GI-94/026+421A0 and BLM/GI-94/026+421A).

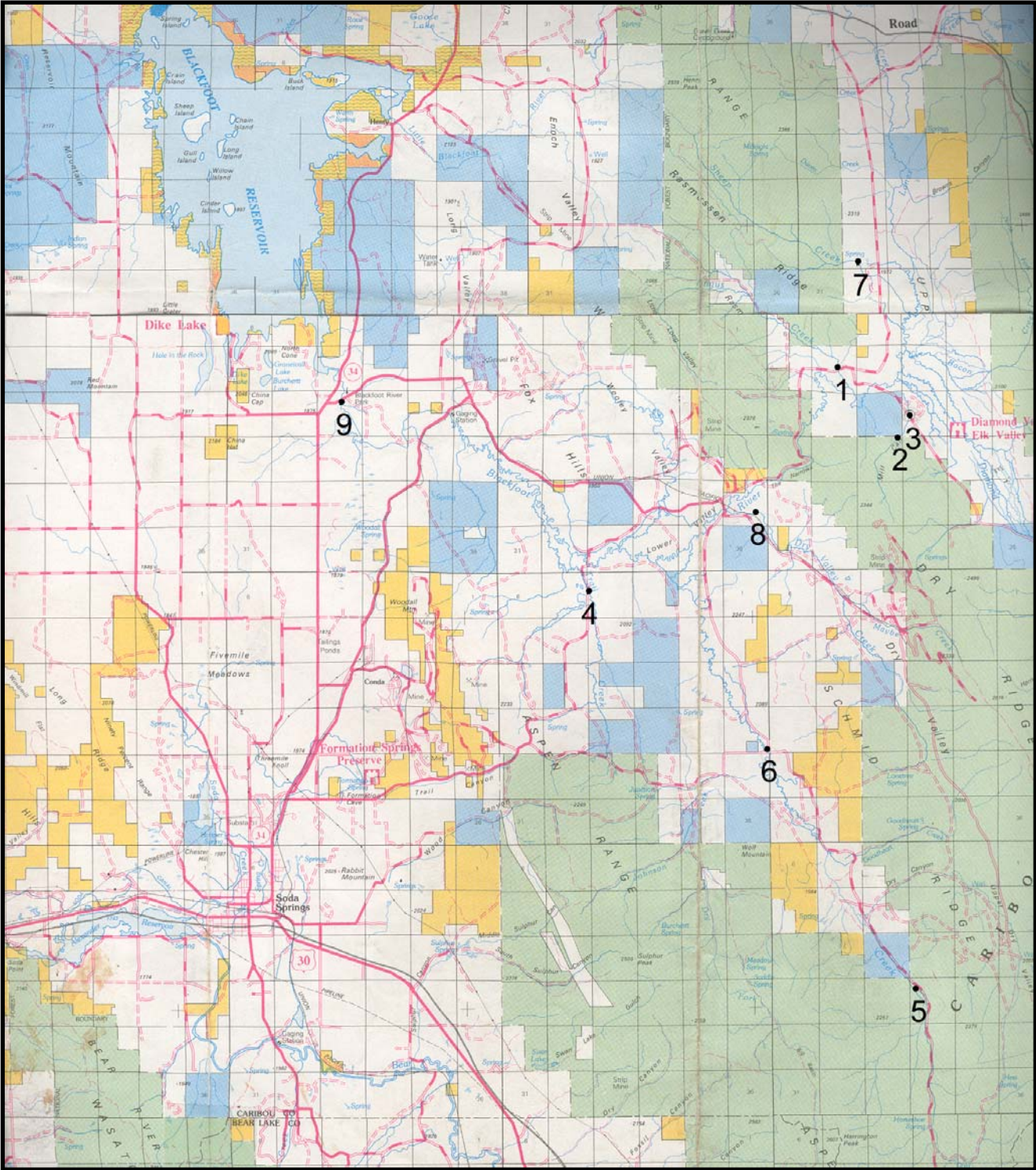


Table 1. Latitude and longitude of nine sites sampled in the Blackfoot River watershed.

Site name & ID	Site ¹
Angus Creek (ACM)	N42°49'42.24" ±11m W111°20'15.04"
Upper East Mill Creek (UEMC)	N42°48'26.74" ±14m W111°18'38.82"
Lower East Mill Creek (LEMC)	N42°48'53.56" ±11m W111°18'25.98"
Trail Creek (TC)	N42°45'29.82" ±8m W111°26'47.53"
Upper Slug Creek (USC)	N42°37'50.85" ±14m W111°18'20.51"
Lower Slug Creek (LSC)	N42°42'23.79" ±9m W111°22'03.89"
Sheep Creek (ShpC)	N42°51'46.92" ±18m W111°20'00.53"
Dry Valley Creek (DVC)	N42°46'58.71" ±14m W111°22'26.47"
Lower Blackfoot River (LBR)	N42°49'12.49" ±10m W111°33'09.33"

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

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 sampling site was below the inactive North Maybe Mine. 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 (some grazing impacts noted). Sample collection was about equally distributed upstream and downstream of the road crossing.

4. The Trail Creek (TC) 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 sampling site was not below any mining activity. The land on either side of the road was grazed grassland. Sample collection was primarily downstream of the crossing in an area with light grazing, whereas the upstream side of the crossing had moderate to heavy grazing.

5. The upper Slug Creek (USC) 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 and >20 km above the confluence with the Blackfoot River. The sampling site was not below any mining activity. The land was owned by the USFS. 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 moderate grazing (some grazing impacts noted). This site was considered the reference site.

6. The lower Slug Creek (LSC) 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 sampling site was below the inactive Mountain Fuel Mine. 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.

7. The Sheep Creek (ShpC) 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 sampling site was below the active Rasmussen Ridge Mine. 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.

8. The Dry Valley Creek (DVC) 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 sampling site was below the inactive South Maybe and active Dry Valley mines. 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.

9. The lower Blackfoot River (LBR) 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 sampling site was below all the other sampling sites and several active and inactive mines (Figure 1). 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.

Sample collection

Samples of water, surficial sediment, aquatic plants, aquatic invertebrates, and fish were collected at each of nine stream sites. Water sample bottles were conditioned by immersion in site water three times. Sample container conditioning and sample collection of water collected by WRD technicians followed procedures of the WRD (USGS 1998). Water samples were collected using width and depth-integrated sampling techniques. For each sample site, water was filtered through a 0.45 micrometer (μm) polycarbonate filter using standard sampling techniques of the WRD (USGS 1998). One water subsample was collected for measurement of major cations and anions, a second subsample of 200 milliliter (ml) sample of water was collected in an acid-cleaned polyethylene bottle for analysis of selenium concentrations, a third subsample collected for analysis of inorganic element concentrations, a fourth subsample for water quality measures by WRD, and a fifth subsample for water quality measurements by BRD. Water samples for selenium analysis were acidified with ultrapure hydrochloric acid (HCl) and those for inorganic elements were acidified with ultrapure nitric acid (HNO_3). A reagent blank was collected for analysis of selenium and inorganic element concentrations, and consisted of deionized water from a mobile laboratory combined with the acid preservative. All samples for selenium and other inorganic element analyses were stored frozen.

Two sediment samples were collected at each site using a plastic scoop to gently acquire surficial sediments including detritus, but not pebbles or plant material. The scoop and acid-cleaned 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 discarded and the sample stored frozen. One sample was used for analysis of selenium concentration, and a second sample used for analysis of inorganic element concentrations.

Submerged aquatic plants (white-water buttercup, *Ranunculus longirostris*) were collected from each site, except lower East Mill Creek, Trail Creek, and Dry Valley Creek. At lower East Mill Creek over 30 meters of stream were searched, but no white-water buttercup was found, so a filamentous green algae was collected. Similar search effort was accomplished at Trail Creek and Dry Valley Creek, but no white-water buttercup was found, so watermilfoil (*Myriophyllum*) was collected. Plants were collected by hand. The sample consisted of leaf whorls removed from stems using plastic or stainless steel forceps. Two plant samples were collected from each site, squeezed to remove excess water, weighed, bagged in Whirl-Pak bags, labeled, and stored frozen. One composite sample was analyzed for selenium concentration and the other sample analyzed for inorganic element concentrations.

Aquatic invertebrates were sieved from bed substrate materials collected either by D-frame kick nets or by 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. Invertebrate samples were separated by taxa group, and weighed by taxa group. One half of the weight of each taxa group was combined as a composite invertebrate sample. One composite sample was analyzed for selenium concentration and the other sample analyzed for inorganic element concentrations.

Fish were collected by electrofishing with a Coffelt Mark-10 electroshocker provided and operated by the USFS, Caribou National Forest, Soda Springs, ID. The anode and cathode wands were rinsed in ambient water for sufficient time to condition the equipment to ambient conditions. Fish samples were collected from each site, euthanized with MS-222 (tricaine methanesulfonate), identified to species, measured for total length and weight, bagged in Whirl-Pak bags, labeled with identification information, and stored frozen. When possible, one or more fish of each species from each site was analyzed for selenium concentrations in whole body and other fish of the same species from the same site analyzed for inorganic element concentrations in whole body. A specimen of some species was retained to confirm identification. Year class information was not collected on fish.

Water quality analyses and flow measurement

Water samples (~1L) at each site were collected by WRD technicians and analyzed for general water quality characteristics in a mobile laboratory according to standard methods (APHA et al. 1995). Site water was analyzed *in situ* for the following general water quality characteristics: conductivity, pH, temperature, dissolved oxygen, and percent saturation of dissolved oxygen concentration. Flow measurements were taken following WRD techniques (USGS 1998).

Immediately after arrival of the site water at the mobile laboratory, the following water quality characteristics were measured: conductivity, pH, alkalinity, hardness, calcium, magnesium, and temperature. A subsample of 200 ml water was collected and stored at 4°C with no preservative, and transported to the Columbia Environmental Research Center Field Research Station (FRS), Yankton, SD, for analysis of sulfate and chloride. A second subsample of 125 ml water was collected, acidified with 0.5 ml concentrated sulfuric acid (H₂SO₄), 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 by the mercuric nitrate titration method (Hach Company 1997).

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 oxygen saturation, and water temperature). This duplication of effort allowed the Yankton FRS to cross check measurement analyses of water quality characteristics collected in the field.

Inorganic element analysis

Water, surficial sediment, aquatic plants, aquatic invertebrates, and fish were analyzed for selenium concentrations by atomic absorption spectroscopy graphite furnace (AA-GF) at the Research Triangle Institute (RTI), Research Triangle Park, NC. 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, duplicate samples, certified reference materials, and spiked samples. Analysis of selenium concentrations was based on U.S. Environmental Protection Agency (USEPA) method 7740 (USEPA 1983). Results were reported on a dry weight basis for sediment, aquatic plants, aquatic invertebrates, and fish.

Water, surficial sediment, aquatic plant, aquatic invertebrate, and fish samples were analyzed for inorganic element concentrations (aluminum, arsenic, barium, beryllium, boron, cadmium, chromium, copper, iron, lead, magnesium, manganese, molybdenum, nickel, strontium, vanadium, and zinc) by inductively-coupled plasma (ICP) spectrophotometry. Analyses were conducted by the RTI and incorporated appropriate QA/QC described above. Analysis of inorganic elements by ICP was based on USEPA method 6020 (USEPA 1983), except arsenic analysis which was method 7060A (USEPA 1983). Results were reported on a dry weight basis for sediment, aquatic plant, aquatic invertebrate, and fish samples.

Statistical analyses

Data were analyzed (SAS 2002) to determine the relation among various measures made during the study. Pearson correlation analyses tested 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 nonparametric Freidman test (Conover 1980) ranked the streams from highest inorganic concentrations to lowest for each ecosystem component (water, sediment, plant, invertebrate, and fish). Significant differences ($P=0.05$) among streams were determined with Freidman's multiple comparison test.

Results

Water quality

Water quality characteristics measured by BRD are 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. Correlation coefficients for the two measures for pH were $r=0.98$ ($P<0.0001$, $n=9$), conductivity $r=0.99$ ($P<0.0001$, $n=9$), and alkalinity $r=0.96$ ($P<0.0001$, $n=9$).

In general, Dry Valley Creek had the highest conductivity, hardness, calcium, and sulfate concentrations of the nine sites examined. The other stream sites had similar water quality characteristics to each other, except that sulfate was greater at Angus Creek and lower at upper Slug Creek than most other sites. The nine sites were well oxygenated at the time of sampling.

Inorganic element analyses

The results of QA/QC sample analysis by AA-GF for selenium concentrations are given in Table 4. The QA/QC results were within acceptable ranges, except that the percent relative standard for aquatic invertebrate samples was 17%, which was higher than normal, i.e., ~10%. Analysis of the procedure blank indicated no contamination from reagents or sample handling; duplicate sample preparation and analysis indicated consistent sample handling during preparation, digestion, and analysis; recovery of certified material indicated the digestion and analysis procedure accurately measured selenium concentrations; and recovery of samples spiked before digestion indicated the digestion procedure did not alter the amount of spiked selenium in the sample, i.e., suggested no loss of selenium during digestion.

Table 2. Water quality characteristics measured by BRD in water 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.

Measure	Site ¹								
	ACM	UEMC	LEMC	TC	USC	LSC	ShpC	DVC	LBR
pH	8.6 [2]	8.3 [1]	8.4 [1]	8.7 [1]	8.3 [2]	8.1 [1]	8.3 [2]	8.1 [1]	8.0 [1]
Conductivity (µmhos/cm)	404 [1]	352 [1]	349 [1]	359 [1]	421 [1]	369 [1]	371 [1]	511 [1]	443 [1]
Hardness (mg/L as CaCO ₃)	205 [2]	178 [1]	178 [1]	180 [1]	212 [2]	177 [1]	192 [2]	262 [1]	231 [1]
Calcium (mg/L)	62 [2]	52 [1]	52 [1]	54 [1]	62 [2]	47 [1]	58 [2]	75 [1]	59 [1]
Magnesium (mg/L)	12 [2]	12 [1]	12 [1]	11 [1]	14 [2]	14 [1]	12 [2]	18 [1]	20 [1]
Alkalinity (mg/L as CaCO ₃)	178 [2]	177 [1]	176 [1]	176 [1]	217 [2]	168 [1]	192 [2]	212 [1]	222 [1]
Chloride (mg/L)	4.9 [1]	1.6 [1]	1.6 [1]	5.9 [1]	4.2 [2]	7.5 [1]	2.1 [2]	7.2 [1]	3.2 [1]
Sulfate (mg/L)	22.5 [1]	7.6 [1]	7.7 [1]	9.1 [1]	<6.0 [2]	12.6 [1]	7.1 [1]	52.5 [1]	12.6 [1]
Total ammonia (mg/L as N)	<0.01 [1]	<0.01 [1]	<0.01 [1]	<0.01 [1]	<0.01 [1]	<0.01 [1]	<0.01 [1]	<0.01 [1]	<0.01 [1]

¹ACM: Angus Creek, 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 by WRD in water from nine sites in the Blackfoot River watershed. n=1.

Measure	Site ¹								
	ACM	UEMC	LEMC	TC	USC	LSC	ShpC	DVC	LBR
pH	8.7	8.2	8.5	8.8	8.4	8.0	8.3	8.0	7.8
Conductivity (µmhos/cm)	394	347	344	343	413	357	366	504	440
Alkalinity (mg/L as CaCO ₃)	182	176	182	160	211	156	194	196	219
Bicarbonate (mg/L)	207	200	198	185	257	190	237	240	267
Carbonate (mg/L)	7.3	7.3	12.2	4.9	-	-	-	-	-
Dissolved oxygen (mg/L)	7.3	9.2	9.3	10.9	9.4	8.2	9.2	8.5	9.7
% Saturation dissolved oxygen	146	98	103	149	96	108	96	106	123
Water temperature (°C)	17.0	7.6	10.8	19.0	6.1	16.8	6.7	14.5	16.1
Discharge (cfs)	0.36	1.36	0.56	1.96	0.56	1.02	2.67	0.41	50

¹ACM: Angus Creek, 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 from nine sites in the Blackfoot River watershed. n=1 for water, sediment, plant, invertebrate; n=2 for fish (mean and standard error in parentheses).

Measure	Ecosystem component				
	Water	Sediment	Aquatic Plant	Aquatic Invertebrate	Fish
Limit of detection (LOD) ($\mu\text{g/L}$ or $\mu\text{g/g}$)	5	0.5	0.5	0.5	0.5
Procedural blank	<LOD	<LOD	<LOD	<LOD	<LOD
% RSD ¹	0.4	2	1	17	4 (4)
% Recovery of reference material	103 ²	101 ³	NG ^{4,5}	117 ⁶	90 (4) ⁶
% Recovery of digested spike	105	100	93	96	118 (5)

¹%RSD: percent relative standard deviation.

²Leeman Labs commercial standard solution (lot number 387201).

³National Institute of Standards and Technology (NIST) standard reference material 2709 (San Joaquin soil; 1.57 $\mu\text{g/g}$).

⁴NG: not given.

⁵NIST standard reference material 1547 (peach leaves, 0.12 $\mu\text{g/g}$).

⁶National Resource Council of Canada standard reference material TORT-2 (lobster hepatopancreas; 5.63 $\mu\text{g/g}$).

The results of QA/QC sample analyses by ICP for inorganic element concentrations 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 analyses. Percent relative standard deviations were elevated (i.e., >30%) in sediments for boron, in invertebrates for arsenic and vanadium, and in fish for chromium, nickel and vanadium (Table 5). Measurement of inorganic elements in reference materials (% recovery of reference material) was outside the normal range of recovery (i.e., ~80 to ~120%) in sediments for aluminum, barium, cadmium, lead, strontium and vanadium, in invertebrates for chromium and lead, and in fish for chromium (Table 5). Measurement of recovery of spiked elements in samples was outside the normal range of recovery (i.e., ~80% to ~120%) in plants for arsenic and boron, in invertebrates for copper, and in fish for lead and nickel (Table 5). There was no consistent pattern for percent relative standard deviations, percent recovery of reference material, or percent recovery of digested spikes. In general, concentrations of inorganic elements were relatively low, which may have contributed to the variability in the analysis of duplicate samples.

Water

The selenium concentration in water from the lower Blackfoot River was less than the LOD (<5 µg/L), relatively low (5-8 µg/L) at six other sites, but substantially elevated at upper and lower East Mill Creek (Table 6). Concentrations of inorganic elements in water were generally similar among the nine sites (Table 7). Although upper and lower East Mill Creek water contained elevated selenium concentrations, they were not among the highest in other inorganic element concentrations, except for strontium. Relative to the other sites, Dry Valley Creek water contained elevated lead, manganese, and zinc, Sheep Creek water contained elevated aluminum, iron, and zinc, Trail Creek water contained elevated vanadium, and Angus Creek water contained elevated boron and copper. However, based on the Friedman test, there was no significant difference among streams in the ranking of inorganic element concentrations in water (with selenium in dataset). In contrast, there were clear differences among streams based on selenium concentrations alone.

Sediment

Selenium concentrations in surficial sediment were relatively low at six sites (<2 µg/g), moderately elevated at Dry Valley Creek (3.0 µg/g), and very elevated at upper and lower East Mill Creek (32-39 µg/g) (Table 6). Angus Creek and Trail Creek sediment contained the lowest selenium concentrations in surficial sediment.

Concentrations of inorganic elements in surficial sediments followed a similar pattern as selenium in sediments (Table 8). Upper and lower East Mill Creek sediment contained the highest concentrations of chromium, copper, molybdenum, and vanadium, and second highest concentrations of cadmium, nickel, and zinc. Dry Valley Creek sediment contained the highest concentrations of barium, cadmium, manganese, nickel, and zinc, and the second highest concentrations of chromium, copper, iron, lead, and vanadium. Angus Creek sediment contained the highest concentrations of aluminum and iron, second highest manganese, and the third highest barium, lead, nickel, vanadium, and zinc, thus suggesting some contamination by inorganic elements. The remaining five sites contained relatively similar concentrations of inorganic elements.

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) from 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); all procedural blanks less than limit of detection.

Element	LOD ¹				% RSD ²				
	W (µg/L)	S (µg/g)	P (µg/g)	I & F (µg/g)	W	S	P	I	F
Aluminum	10	100	20	5	<LOD	12	20	23	15 (4)
Arsenic	5	1	0.5	1	0	10	5	57	8 (6)
Barium	1	1	0.2	0.5	0	2	4	28	6 (4)
Beryllium	1	0.2	0.2	0.1	<LOD	8	<LOD	<LOD	<LOD
Boron	10	1	1	2	<LOD	33	12	16	8 (-)
Cadmium	1	0.1	0.1	0.1	<LOD	1	3	25	6 (-)
Chromium	3	1	0.5	0.5	<LOD	13	0	21	39 (31)
Copper	6	1	0.5	0.5	<LOD	6	12	1	4 (1)
Iron	20	100	20	5	<LOD	5	14	22	14 (8)
Lead	7	1	0.5	0.5	0.4	8	17	<LOD	<LOD
Magnesium	50	50	20	5	0	9	2	<1	4 (2)
Manganese	5	2	2	0.5	<LOD	2	2	8	8 (7)
Molybdenum	2	0.5	0.5	0.5	<LOD	6	5	<LOD	<LOD
Nickel	6	0.5	0.5	0.5	<LOD	4	11	11	65 (44)
Strontium	5	0.5	0.5	0.5	0.4	4	1	11	7 (1)
Vanadium	5	0.5	0.3	0.5	0	9	6	34	36 (27)
Zinc	10	2	2	0.5	10	8	1	6	3 (0)

Table 5. Continued.

Element	% Recovery of reference material					% Recovery of digested spike				
	W ³	S ⁴	P ⁵	I ⁶	F ⁶	W	S	P	I	F
Aluminum	101	45	93	NG ⁷	NG	91	NG	NG	84	104 (6)
Arsenic	103	79	NG	108	109 (0)	97	96	149	108	112 (14)
Barium	102	40	85	NG	NG	102	114	97	88	95 (6)
Beryllium	104	NG	NG	NG	NG	104	108	121	90	91 (-)
Boron	96	NG	95	NG	NG	94	82	160	95	100 (2)
Cadmium	98	242	NG	94	88 (8)	105	105	77	86	92 (6)
Chromium	91	89	NG	287	238 (-)	99	109	77	85	88 (8)
Copper	94	94	102	99	99 (13)	99	104	79	63	98 (6)
Iron	100	101	95	85	81 (5)	102	NG	96	80	96 (4)
Lead	106	68	100	163	NG	104	107	90	87	74 (22)
Magnesium	103	109	101	NG	NG	102	NG	NG	74	106 (8)
Manganese	96	103	85	82	83 (2)	98	NG	NG	NG	92 (1)
Molybdenum	92	NG	NG	106	83 (6)	99	91	111	92	94 (2)
Nickel	101	94	123	107	92 (4)	98	110	90	91	75 (23)
Strontium	94	45	97	84	84 (2)	97	107	123	96	96 (2)
Vanadium	100	61	90	121	98 (8)	98	104	113	93	96 (3)
Zinc	97	90	108	96	90 (8)	96	115	95	82	94 (2)

¹LOD: Limit of detection.

²%RSD: percent relative standard deviation.

³Leeman Labs commercial standard solution (lot number 387201).

⁴National Institute of Standards and Technology (NIST) standard reference material 2709 (San Joaquin soil).

⁵NIST standard reference material 1547 (peach leaves).

⁶National Resource Council of Canada standard reference material TORT-2 (lobster hepatopancreas).

⁷NG: not given.

Table 6. Selenium concentrations ($\mu\text{g/L}$ for water and $\mu\text{g/g}$ dry weight for sediment, aquatic plants, and aquatic invertebrates) in water, sediment, aquatic plants, and aquatic invertebrates from nine sites in the Blackfoot River watershed. $n=1$; $<$: less than limit of detection.

Ecosystem component	Site ¹								
	ACM	UEMC	LEMC	TC	USC	LSC	ShpC	DVC	LBR
Water	6	24	24	5	7	6	8	8	<5
Sediment	1.0	32.2	38.9	1.2	1.8	1.7	1.5	3.0	1.8
Aquatic plant	2.0	30.3	25.7 ²	1.7 ³	1.6	1.7	1.2	4.4 ³	5.8
Aquatic invertebrate	6.7	26.9	75.2	<0.5	0.5	<0.5	1.9	12.8	7.7

¹ACM: Angus Creek; 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.

²Filamentous green algae.

³Watermilfoil (*Myriophyllum*).

Table 7. Inorganic element concentrations ($\mu\text{g/L}$) in water from nine sites in the Blackfoot River watershed. n=1; <: less than limit of detection.

Element	Site ¹								
	ACM	UEMC	LEMC	TC	USC	LSC	ShpC	DVC	LBR
Aluminum	<10	<10	<10	<10	<10	<10	239	11	<10
Arsenic	15	12	11	<5	17	11	14	10	<5
Barium	28	20	21	51	78	38	67	42	50
Beryllium	<1	<1	<1	<1	<1	<1	<1	<1	<1
Boron	39	26	<10	<10	30	<10	<10	<10	<10
Cadmium	<1	<1	<1	<1	<1	<1	<1	<1	<1
Chromium	<3	<3	<3	<3	<3	<3	<3	<3	<3
Copper	19	11	<6	<6	10	<6	<6	<6	<6
Iron	<20	<20	<20	23	<20	<20	55	<20	<20
Lead	10	18	10	14	19	20	8	26	12
Magnesium	12,200	11,800	11,400	11,400	14,700	14,600	12,700	15,200	20,800
Manganese	48	<5	<5	35	17	85	13	200	12
Molybdenum	<2	<2	<2	<2	<2	<2	<2	<2	<2
Nickel	<6	<6	<6	<6	<6	<6	<6	<6	<6
Strontium	190	239	235	143	150	226	113	160	224
Vanadium	6	5	5	14	8	7	6	8	9
Zinc	11	10	10	12	11	10	30	17	10

¹ACM: Angus Creek; 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 8. Inorganic element concentrations ($\mu\text{g/g}$ dry weight) in sediment from nine sites in the Blackfoot River watershed. n=1; <: less than limit of detection.

Element	Site ¹								
	ACM	UEMC	LEMC	TC	USC	LSC	ShpC	DVC	LBR
Aluminum	19,800	11,600	11,200	11,800	11,600	9,730	16,800	19,000	13,200
Arsenic	4.1	4.3	3.9	2.0	5.1	1.8	3.7	3.6	2.8
Barium	229	100	111	150	157	97	237	240	169
Beryllium	1.0	0.6	0.6	0.8	0.7	0.5	1.1	1.0	0.6
Boron	63	60	63	85	52	66	59	65	93
Cadmium	3.2	8.3	6.3	1.4	4.5	2.0	1.3	13.9	1.5
Chromium	30	67	61	19	28	21	23	41	20
Copper	16	25	22	11	14	8	16	18	11
Iron	25,400	15,800	15,700	15,400	14,400	10,890	20,600	25,100	17,800
Lead	16	10	9	11	12	10	18	17	13
Magnesium	6,150	4,900	4,630	4,160	3,480	3,250	6,000	5,330	6,010
Manganese	3,210	1,280	1,390	1,310	550	540	1,350	6,630	940
Molybdenum	0.6	3.0	2.3	0.9	0.5	<0.5	<0.5	0.7	0.6
Nickel	29	57	53	15	23	12	24	76	16
Strontium	51	99	80	53	44	133	42	44	115
Vanadium	34	68	58	18	21	17	26	41	20
Zinc	138	254	245	67	116	65	92	765	90

¹ACM: Angus Creek; 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.

Based on the Freidman test, the streams were ranked from highest inorganic element concentrations in sediment (with selenium in dataset) to lowest as follows (streams with lower case letters in common are not significantly different at $P=0.05$): DVC_a, ACM_{ab}, UEMC_{ab}, LEMC_{ab}, ShpC_{bc}, LBR_{bc}, USC_c, TC_{cd}, LSC_d. Based on selenium concentrations alone, the streams from highest concentration to lowest were: LEMC, UEMC, DVC, LBR, USC, LSC, ShpC, TC, ACM. Major disparities in order between the two approaches occurred for lower and upper East Mill Creek and Angus Creek.

Significant correlation coefficients were found between concentrations of inorganic elements in sediment and water for manganese, selenium, and strontium (Table 9).

Aquatic plants

Selenium concentrations in aquatic plants were low at Sheep Creek, upper and lower Slug Creek, Trail Creek, and Angus Creek (1.2-2.0 $\mu\text{g/g}$); moderately elevated at the Dry Valley Creek and lower Blackfoot River (4.4-5.8 $\mu\text{g/g}$); and very elevated at the upper and lower East Mill Creek (26-30 $\mu\text{g/g}$) (Table 6). Filamentous green algae collected at lower East Mill Creek contained 25.7 $\mu\text{g/g}$ selenium, which was similar to that in white-water buttercup collected at upper East Mill Creek (30.3 $\mu\text{g/g}$). The pattern of selenium concentrations in aquatic plants was consistent with selenium concentrations in surficial sediment and water, and resulted in significant correlation coefficients (Table 9).

Concentrations of inorganic elements in aquatic plants followed a somewhat similar pattern as selenium in surficial sediments (Table 10). East Mill Creek plants contained the highest concentrations of arsenic, barium, cadmium, chromium, copper, nickel, vanadium, and zinc, whereas Dry Valley Creek plants contained an intermediate amount of these elements relative to East Mill Creek and the other seven sites. In general, aquatic plants from Sheep Creek and Trail Creek contained low inorganic element concentrations compared to the other sites. Upper Slug Creek, the reference site, contained higher concentrations of aluminum, barium, cadmium, chromium, iron, lead, manganese, and zinc in aquatic plants than observed at Sheep Creek.

Based on the Freidman test, the streams were ranked from highest inorganic element concentrations in aquatic plants (with selenium in dataset) to lowest as follows (streams with lower case letters in common are not significantly different): LSC_a, DVC_a, UEMC_a, LEMC_a, LBR_a, USC_a, TC_{ab}, ACM_{ab}, ShpC_b. Based on selenium concentrations alone, the streams from highest concentration to lowest were: UEMC, LEMC, LBR, DVC, ACM, LSC, TC, USC, ShpC. The only major disparity in order between the two approaches was for lower Slug Creek.

Significant correlations were observed for inorganic element concentrations in aquatic plants and water for magnesium, and in aquatic plants and surficial sediments for chromium, manganese, nickel, and zinc (Table 9).

Aquatic invertebrates

Selenium concentrations in aquatic invertebrates followed a similar pattern as those in sediment: low at Trail Creek, upper and lower Slug Creek, and Sheep Creek (<0.5-1.9 $\mu\text{g/g}$), moderately elevated at Angus Creek, lower Blackfoot River, and Dry Valley Creek (6.7-12.8 $\mu\text{g/g}$), and highly elevated at upper and lower East Mill Creek (27-75 $\mu\text{g/g}$) (Table 6).

The correlation coefficient between selenium concentrations in aquatic invertebrates was

Table 9. Significant ($P < 0.05$) Pearson correlation coefficients for various aquatic ecosystem components and inorganic elements (standard symbols in table).

Ecosystem component	Inorganic element										
	As	Cd	Cr	Cu	Mg	Mn	Ni	Se	Sr	V	Zn
Water											
Sediment						0.85		0.99	0.82		
Aquatic plant					0.74			0.99			
Aquatic invertebrate								0.83			
Fish								0.91			-0.70
Sediment											
Aquatic plant			0.71			0.87	0.74	0.97			0.74
Aquatic invertebrate			0.84			0.78		0.89	0.80		
Fish								0.96			
Aquatic plant											
Aquatic invertebrate		0.97	0.80			0.87		0.78			0.76
Fish				0.88				0.87			
Aquatic invertebrate											
Fish	-0.84						0.90	0.98			

Table 10. Inorganic element concentrations ($\mu\text{g/g}$ dry weight) in aquatic plants from nine sites in the Blackfoot River watershed. n=1; <: less than limit of detection.

Element	Site ¹								
	ACM	UEMC	LEMC ²	TC ³	USC	LSC	ShpC	DVC ³	LBR
Aluminum	1,290	1,040	3,490	4,140	14,300	5,380	1,560	3,120	5,790
Arsenic	1	1	2	1	1	1	1	1	1
Barium	239	23	3,120	274	174	192	105	571	133
Beryllium	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2
Boron	12	12	5	12	15	17	6	18	15
Cadmium	2	40	11	1	4	1	1	4	2
Chromium	1	8	8	2	4	5	1	1	2
Copper	1	4	2	1	1	2	2	1	1
Iron	870	810	2,580	2,840	8,650	3,264	1,010	2,800	4,210
Lead	1	1	1	2	6	2	1	1	3
Magnesium	4,360	3,270	2,830	2,840	4,160	3,980	2,390	5,050	5,050
Manganese	12,400	990	250	6,890	5,850	8,690	860	26,100	6,400
Molybdenum	<0.5	1	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
Nickel	3	8	5	2	2	4	3	5	2
Strontium	181	60	30	104	48	113	81	58	68
Vanadium	1	4	4	3	3	4	2	3	2
Zinc	25	330	150	25	97	38	18	301	142

¹ACM: Angus Creek; 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.

²Filamentous green algae.

³Watermilfoil (Myriophyllum).

significant with water, surficial sediment, and aquatic plants (Table 9). Selenium concentrations in aquatic invertebrates were distributed somewhat evenly across sites, whereas selenium concentrations in sediments and aquatic plants were not (5-6 low values and 2 high values), thus the correlations were probably dominated by elevated selenium concentrations in sediment and aquatic plants at the upper and lower East Mill Creek and Dry Valley Creek sites (Table 6).

Concentrations of inorganic elements in aquatic invertebrates from the nine sites followed a similar pattern as found in surficial sediments and aquatic plants (Table 11). Low concentrations of inorganic elements occurred in aquatic invertebrates from Sheep Creek and Trail Creek, moderate concentrations in Angus Creek, upper and lower Slug Creek, and lower Blackfoot River, and elevated concentrations in upper and lower East Mill Creek and Dry Valley Creek. East Mill Creek invertebrates contained the highest concentrations of aluminum, boron, cadmium, chromium, iron, vanadium, and zinc. Dry Valley Creek invertebrates contained the highest concentrations of manganese, molybdenum, nickel, and zinc.

Based on the Friedman test, the streams were ranked from highest inorganic element concentrations in aquatic invertebrates (with selenium in dataset) to lowest as follows (streams with lower case letters in common are not significantly different): DVC_a, ACM_a, UEMC_a, LBR_a, LEMC_a, LSC_a, USC_a, TC_{bc}, ShpC_c. Based on selenium concentrations alone, the streams from highest concentration to lowest were: LEMC, UEMC, DVC, LBR, ACM, ShpC, USC, TC, LSC. The disparities in order between the two approaches occurred for Angus Creek, lower East Mill Creek, and Sheep Creek.

Significant correlations were observed for inorganic element concentrations in aquatic invertebrates and surficial sediments for chromium, manganese, and vanadium (Table 9). There also were significant correlations for inorganic elements between aquatic invertebrates and aquatic plants for cadmium, chromium, manganese, and zinc (Table 9).

Fish

Fish collected included cutthroat trout (*Oncorhynchus clarki*), brook trout (*Salvelinus fontinalis*), mottled sculpin (*Cottus bairdi*), longnose dace (*Rhinichthys cutaractae*), speckled dace (*Rhinichthys osculus*), and redbreast shiner (*Richardsonius balteatus*) (Table 12). No one fish species was collected at all nine sites. Mottled sculpin were collected at seven sites, speckled dace at six sites, and cutthroat trout at five sites (Table 12). Trout at upper East Mill Creek contained the highest whole-body selenium concentrations, and speckled dace contained the second highest whole-body selenium concentrations of the species collected (Table 13). Redbreast shiner were collected from only four sites, and contained the lowest whole-body selenium concentrations of the species collected, except at lower Slug Creek. Geometric mean selenium concentrations in fish ranged from 2.7 µg/g at Sheep Creek to 52.3 µg/g at lower East Mill Creek (Table 13).

Significant correlation coefficient were observed for selenium concentrations in the combined fish data for six species with water, sediment, aquatic plants, and aquatic invertebrates (Table 9).

Few inorganic elements other than selenium were elevated in whole-body fish from the nine sites (Table 14). The few elements elevated in fish were primarily in speckled dace, whereas the lowest inorganic element concentrations tended to occur in redbreast shiner. No site seemed to have fish with consistently elevated inorganic elements based on geometric means (Table 15).

Table 11. Inorganic element concentrations ($\mu\text{g/g}$ dry weight) in aquatic invertebrates from nine sites in the Blackfoot River watershed. $n=1$; <: less than limit of detection.

Element	Site ¹								
	ACM	UEMC	LEMC	TC	USC	LSC	ShpC	DVC	LBR
Aluminum	975	1,460	710	400	590	320	380	750	840
Arsenic	1	1	1	1	2	5	0	1	1
Barium	56	14	17	32	196	112	14	60	25
Beryllium	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Boron	5	6	2	3	1	2	1	2	2
Cadmium	4	16	4	1	1	1	0	1	0
Chromium	3	6	10	1	2	2	2	2	2
Copper	47	16	31	39	92	176	52	32	50
Iron	802	1,220	581	308	377	251	320	670	750
Lead	1	1	<0.5	<0.5	<0.5	1	<0.5	<0.5	1
Magnesium	1,420	1,680	1,280	1,040	2,280	1,880	1,470	1,610	1,730
Manganese	1,190	125	188	543	195	392	180	1,530	1,030
Molybdenum	<0.5	<0.5	1	<0.5	<0.5	<0.5	<0.5	2	1
Nickel	7	2	7	4	5	8	3	18	5
Strontium	8	15	6	9	147	260	3	50	9
Vanadium	3	3	4	1	1	2	2	3	2
Zinc	175	315	196	80	76	68	170	210	190

¹ACM: Angus Creek; 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 12. Fish species collected during June (●) and September (○) 2000 from nine sites in the Blackfoot River watershed.

Site ¹	Fish species					
	Cutthroat trout	Brook trout	Mottled sculpin	Longnose dace	Speckled dace	Redside shiner
ACM	● ○		● ○	●	○	● ○
UEMC	● ○	●				
LEMC	○					
TC			● ○	● ○	● ○	● ○
USC		● ○	● ○		● ○	
LSC			○		● ○	● ○
ShpC	● ○		● ○		●	
DVC	● ○	○	● ○		● ○	
LBR			● ○	○	● ○	● ○

¹ACM: Angus Creek, 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 13. Selenium concentrations ($\mu\text{g/g}$ dry weight) in whole-body fish from nine sites in the Blackfoot River watershed. n=1.

Species	Site ¹								
	ACM	UEMC	LEMC	TC	USC	LSC	ShpC	DVC	LBR
Brook trout	- ²	-	-	-	2.4	-	-	8.0	-
Cutthroat trout	6.3	27.0	52.3	-	-	-	1.8	10.2	-
Mottled sculpin	8.3	-	-	10.5	5.3	6.0	4.1	8.8	5.2
Longnose dace	-	-	-	6.2	-	-	-	-	6.2
Speckled dace	8.5	-	-	6.1	6.9	2.6	-	7.5	5.6
Redside shiner	6.0	-	-	2.2	-	3.8	-	-	2.7
Geometric mean	7.2	27.0	52.3	5.5	4.5	3.9	2.7	8.6	4.7

¹ACM: Angus Creek; 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.

Table 14. Inorganic element concentrations ($\mu\text{g/g}$ dry weight) in whole-body fish from nine sites in the Blackfoot River watershed. n=1; <: less than limit of detection.

Element	Site ¹ and Species									
	ACM Cutthroat trout	ACM Mottled sculpin	ACM Speckled dace	ACM Redside shiner	UEMC Cutthroat trout	LEMC Cutthroat trout	TC Mottled sculpin	TC Longnose dace	TC Speckled dace	TC Redside shiner
Aluminum	51	105	17	130	83	55	87	17	54	29
Arsenic	3	4	3	4	3	3	4	5	3	<1
Barium	5	10	6	6	1	3	6	19	15	7
Beryllium	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Boron	<2	<2	<2	<2	<2	<2	<2	<2	<2	<2
Cadmium	<0.1	0.2	<0.1	0.3	1.0	0.1	0.4	<0.1	0.1	0.5
Chromium	5	4	1	24	2	6	4	7	5	8
Copper	4	3	3	5	26	5	4	5	7	3
Iron	160	150	53	260	94	110	130	110	130	125
Lead	<0.5	1	<0.5	1	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
Magnesium	1,570	1,610	1,350	1,560	1,010	1,310	1,330	1,220	1,460	1,500
Manganese	24	130	17	63	6	13	31	21	30	26
Molybdenum	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
Nickel	1	4	<0.5	3	2	1	1	2	1	1
Strontium	20	37	35	33	16	20	31	24	26	25
Vanadium	1	5	1	1	1	1	1	1	1	<0.5
Zinc	200	140	140	260	98	180	120	140	190	180

Table 14. Continued.

Element	Site ¹ and Species									
	USC Brook trout	USC Mottled sculpin	USC Speckled dace	LSC Mottled sculpin	LSC Speckled dace	LSC Redside shiner	ShpC Cutthroat trout	ShpC Mottled sculpin	DVC Brook trout	DVC Cutthroat trout
Aluminum	104	340	28	130	33	119	26	67	37	38
Arsenic	3	5	4	5	<1	<1	<1	<1	<1	<1
Barium	3	14	15	13	4	11	2	7	3	2
Beryllium	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Boron	<2	<2	<2	<2	<2	<2	<2	<2	<2	<2
Cadmium	<0.1	<0.1	<0.1	0.2	0.7	0.8	0.5	0.5	0.5	0.5
Chromium	9	7	6	19	6	7	3	1	26	49
Copper	3	4	7	6	3	6	5	3	4	6
Iron	120	290	100	160	110	200	96	97	210	350
Lead	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
Magnesium	890	1,500	1,540	1,380	1,330	1,690	1,220	1,440	1,360	1,500
Manganese	11	21	12	99	38	22	8	15	34	33
Molybdenum	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	0.8
Nickel	3	1	2	12	2	2	<0.5	<0.5	10	12
Strontium	8	24	<0.5	40	33	40	6	15	15	12
Vanadium	1	2	1	3	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
Zinc	170	97	170	110	180	160	77	54	110	87

Table 14. Continued.

Element	Site ¹ and Species					
	DVC Mottled sculpin	DVC Speckled dace	LBR Mottled sculpin	LBR Longnose dace	LBR Speckled dace	LBR Redside shiner
Aluminum	43	3	14	8	41	16
Arsenic	<1	<1	<1	<1	<1	<1
Barium	4	4	5	5	7	4
Beryllium	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Boron	<2	<2	<2	<2	<2	<2
Cadmium	0.7	0.6	0.5	0.6	0.6	0.5
Chromium	8	<0.5	17	<0.5	7	<0.5
Copper	3	4	4	7	5	3
Iron	160	61	160	41	130	60
Lead	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
Magnesium	1,520	1,410	1,540	1,360	1,320	1,520
Manganese	48	12	24	14	21	6
Molybdenum	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
Nickel	2	<0.5	5	<0.5	2	<0.5
Strontium	31	22	35	33	29	41
Vanadium	1	<0.5	1	<0.5	<0.5	<0.5
Zinc	100	160	110	91	130	140

¹ACM: Angus Creek; 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 15. Geometric mean of inorganic element concentrations ($\mu\text{g/g}$ dry weight) in whole-body fish from nine sites in the Blackfoot River watershed.

Element	Site ¹								
	ACM	UEMC	LEMC	TC	USC	LSC	ShpC	DVC	LBR
Aluminum	59	83	55	39	99	80	42	21	17
Arsenic	4	3	3	4	4	1	<1	<1	<1
Barium	6	1	3	11	9	8	3	3	5
Beryllium	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Boron	<2	<2	<2	<2	<2	<2	<2	<2	<2
Cadmium	0.2	1.0	0.1	0.3	<0.1	0.5	0.5	0.6	0.5
Chromium	5	2	6	6	7	9	1	22	11
Copper	3	26	5	5	4	5	4	4	5
Iron	130	94	110	120	150	150	97	160	83
Lead	1	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
Magnesium	1,520	1,010	1,310	1,370	1,270	1,460	1,330	1,450	1,420
Manganese	44	6	13	27	14	44	11	29	14
Molybdenum	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	0.8	<0.5
Nickel	2	2	1	1	2	3	1	7	3
Strontium	31	16	20	26	14	38	9	19	34
Vanadium	1	1	1	1	1	3	<0.5	<0.5	1
Zinc	180	98	180	160	140	150	64	110	120

¹ACM: Angus Creek; 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.

Streams

Based on the Freidman test, the streams were ranked from highest geometric mean inorganic element concentrations in fish (with selenium in dataset) to lowest as follows (streams with lower case letters in common are not significantly different): LSC_a, ACM_{ab}, DVC_{ab}, TC_{ab}, USC_{ab}, LBR_{ab}, LEMC_b, UEMC_b, ShpC_c. Based on selenium concentrations alone, the streams from highest concentration to lowest were: LEMC, UEMC, DVC, ACM, TC, LBR, USC, LSC, ShpC. There was a major disparity in order between the two approaches for lower and upper East Mill Creek and lower Slug Creek.

There were few significant correlations observed for concentrations of inorganic elements in fish (using the geometric mean for all fish at each site) and water (zinc), surficial sediment (none), aquatic plant (copper), and aquatic invertebrates (arsenic and nickel) (Table 9).

There was no significant difference among streams based on inorganic element concentrations including selenium in water, sediment, aquatic plant, aquatic invertebrate, and fish using the individual Freidman test ranks. In contrast, there were significant differences among streams based on selenium concentrations using the individual ranks for the five matrices. Streams were ranked from highest selenium concentration to lowest as follows (streams with lower case letters in common are not significantly different): LEMC_a, UEMC_a, DVC_{ab}, LBR_{bc}, ACM_c, USC_c, ShpC_c, LSC_c, TC_c.

Discussion

Water

Upper and lower East Mill Creek water contained substantially elevated selenium concentrations in water compared to the seven other sites. Selenium concentrations in water from East Mill Creek collected in June 2000 (15-30 µg/L, Hamilton et al. 2002) were similar to those in the present study. Selenium in East Mill Creek was substantially higher in both June and September 2000 than the current national water quality criterion for the protection of aquatic life of 5 µg/L (USEPA 1987).

The upper Slug Creek site was used as the reference site because it was not influenced by mining (Figure 1). In general, most of the other eight stream sites contained similar inorganic element concentrations in water to those in upper Slug Creek, except for selenium. Upper and lower East Mill Creek, in addition to elevated selenium concentrations, also contained elevated strontium concentrations compared to upper Slug Creek, which was similar to the June collection (Hamilton et al. 2002).

A recent workshop on selenium aquatic toxicity and bioaccumulation was held to discuss the technical issues underlying the federal freshwater aquatic life chronic criterion for selenium (USEPA 1998a) and concluded that water was a poor choice for a criterion for selenium. 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 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 of 3 µg/g for fish (Lemly 1993, 1996b, Hamilton 2002). This latter scenario seems to be occurring at several sites in the present study.

Water concentrations of inorganic elements are generally the basis of water quality standards issued by the USEPA (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 water 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 (MW 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 USEPA criteria (MW 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 MW (1999) for East Mill Creek were higher than those measured in the present study, but were similar for Trail Creek and Dry Valley Creek.

MW (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. MW (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. Thus, substantial contamination of the Blackfoot River occurred during 1999.

MW (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, and East Mill Creek, which contained 19 µg/L (MW 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 lower Slug Creek (6.3 µg/L), Dry Valley Creek (8-87 µg/L), Angus Creek (6.5 µg/L), and East Mill Creek (400 µg/L) (MW 2001b). These data and those from Hamilton et al. (2002) demonstrate continued selenium contamination of the Blackfoot River watershed. The data also demonstrate that selenium contamination occurs primarily during spring runoff. This contamination was evidenced in selenium concentrations in sediment, aquatic plants, aquatic invertebrates, and fish measured in the current study and as discussed below.

Sediment

Selenium concentrations in surficial sediment from upper and lower Slug Creek, Sheep Creek, Trail Creek, Angus Creek, and the lower Blackfoot River were 1.0 to 1.8 µg/g, which was above the value that 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 Dry Valley Creek and upper and lower East Mill Creek were elevated and suggested a substantial contamination concern. Selenium concentrations in surficial sediments in the present study were similar to those in the June 2000 collection from the same nine sites (Hamilton et al. 2002).

Selenium concentrations in surficial sediment from East Mill Creek were in the same range as measured in North Pond at Walter Walker State Wildlife Area near Grand Junction, CO (25.1 $\mu\text{g/g}$ in 1996 and 38.9 $\mu\text{g/g}$ in 1997) where elevated selenium in sediments were associated with elevated selenium in the food chain, and mortality of endangered razorback sucker larvae (*Xyrauchen texanus*) in two 30-day studies with water and dietary exposure (Hamilton et al. 2001a, 2001b).

Elevated selenium in sediments is an important consideration in assessing the health of aquatic ecosystems and has been considered as a federal criterion for selenium in a workshop (USEPA 1998a). However, the workshop participants concluded that the sediment compartment was a poor choice (USEPA 1998a). Two papers have proposed the use of a sediment-based criterion for selenium 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). 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.

In the present study, the significant correlation of selenium concentrations in surficial sediment and water ($r=0.99$), sediments and aquatic plants ($r=0.97$), and sediment and aquatic invertebrates ($r=0.89$) suggested that selenium moves easily among aquatic ecosystem components and accumulates in the food web. Similar movements of selenium through the food web were reported in two field studies conducted in seleniferous areas of the upper Colorado River (Hamilton et al. 2001a, 2001b).

Surficial sediment concentrations of cadmium, chromium, copper, molybdenum, nickel, vanadium, and zinc in upper and lower East Mill Creek were 1.4 to 6 times higher than nonimpacted upper Slug Creek. In contrast, selenium concentrations were 18 to 22 times higher in upper and lower East Mill Creek compared to upper Slug Creek, thus suggesting a major disparity between selenium enrichment in the East Mill Creek compared to upper Slug Creek. These findings were similar to those observed in the June 2000 sampling of sediment from the same nine sites (Hamilton et al. 2002).

The sediment component of 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 inorganic elements 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 in lakes and ponds contaminated by inorganic elements, bottom feeding redear sunfish (*Lepomis microlophus*) accumulated significant concentrations of cadmium, nickel, copper, lead, and zinc, whereas predatory largemouth bass (*Micropterus salmoides*) significantly accumulated cadmium and zinc, and omnivorous bluegill (*Lepomis macrochirus*) significantly accumulated 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 with inorganic elements and in the 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. That 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 died in 17 to 44 days after being fed *Hexagenia* nymphs containing 13.6 µg/g wet weight selenium.

Comparison to other Idaho sediment data

The Selenium Subcommittee investigated concentrations of inorganic elements in sediment from numerous sites in the Southeastern Idaho Phosphate Resource Area in September 1998 (MW 1999). Out of 54 sites investigated, 11 contained selenium concentrations of 2-4 µg/g in sediment including Slug Creek, Dry Valley Creek, Rasmussen Creek (tributary to Angus Creek), and East Mill Creek. The selenium concentrations in sediment reported by MW (1999) in East Mill Creek (2.9 µg/g) were substantially lower than those in the present investigation (32-39 µg/g), whereas their value for Dry Valley Creek (3.3 µg/g) was similar to our value (3.0 µg/g). MW (2001a) reported elevated selenium concentrations in sediment collected in September 1999 from Dry Valley Creek upstream of Maybe Creek (3.9 µg/g), Dry Valley Creek downstream of Maybe Creek (6.2 µg/g), Angus Creek (5.1 µg/g), East Mill Creek (5.0 µg/g), and Blackfoot River (2.1-3.0 µg/g).

Much of the selenium loading in Dry Valley Creek comes from Maybe Creek where selenium concentrations were 261 µg/g in sediment from Maybe Creek near its mouth (TRC Environmental 1999). Other portions of Maybe Creek contained 12-77 µg/g of selenium in sediment (TRC Environmental 1999).

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), MW (1999, 2001a), Hamilton et al. (2002), and in the present study suggest widespread selenium contamination of the aquatic environment by phosphate mining.

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 and lower Slug Creek, Trail Creek, Sheep Creek, and Angus Creek were 2.0 µg/g or less, and thus, this concentration might be considered near background for the Blackfoot River watershed. By comparison, selenium concentrations in aquatic plants at Dry Valley Creek (4.4 µg/g) and lower Blackfoot River (5.8 µg/g) were elevated, and those at upper and lower East Mill Creek (26-30 µg/g) were substantially elevated. Selenium concentrations in aquatic plants in the present study were similar to those in the previous study (Hamilton et al. 2002). Selenium concentrations in watermilfoil collected at Trail Creek (1.7 µg/g) and Dry Valley Creek (4.4 µg/g) in the present study were similar to concentrations in white-water buttercup collected at these two sites in June 2000 (0.8 and 3.8 µg/g, respectively; Hamilton et al. 2002). Selenium concentrations in aquatic plants were significantly correlated with those in water ($r=0.99$) and in surficial sediments ($r=0.97$), thus demonstrating that selenium was easily

transferred among these aquatic components.

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.

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 (9.8-440 µg/g, Saiki 1986; 7-22 µg/g, Saiki et al. 1993; 36-307 µg/g, Saiki and Lowe 1987), whereas reference areas contained 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 and waterbirds. 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, plant-based detritus rather than other pathways. Thus, aquatic plants with elevated selenium concentrations from four of the stream sites in the Blackfoot River watershed (upper and lower East Mill Creek, Dry Valley Creek, lower Blackfoot River) were probably contributing to 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 correlation coefficients between surficial sediments and aquatic plants for several inorganic elements (chromium, manganese, nickel, zinc; $r=0.71-0.87$) suggested a strong interconnectedness in some element cycles. In the June 2000 study, significant correlations between aquatic plants and sediments were reported for cadmium, nickel, and zinc ($r=0.71-0.91$; Hamilton et al. 2002).

Uptake of inorganic elements by aquatic plants alone 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 in the Blackfoot River watershed similar to selenium. When rooted aquatic plants die, their biomass constitutes greater than 90% of 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 and inorganic elements for grazing aquatic invertebrates and contributes 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).

Comparison to other Idaho aquatic plant data

A native bryophyte that was collected in 2000 from a seep at the base of the Wooley Valley Phosphate Mine Unit 4 waste-rock 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 (1,000 µg/g), zinc (11,000 µg/g), and selenium (750 µg/g) (Herring et al. 2001). This site and

others on Angus Creek were previously 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 that were present in the native bryophyte also accumulated in the introduced bryophyte, but selenium was the most enriched of the elements measured.

Elevated mean selenium concentrations have been reported in grasses (64 µg/g), forbs (78 µg/g), and shrubs (11 µg/g) in Maybe Creek (TRC Environmental 1999), a tributary of Dry Valley Creek. These concentrations were higher than those in Dry Valley Creek in the present study (4.4 µg/g) and the previous study (3.8 µg/g; Hamilton et al. 2002).

MW (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), and very high values in East Mill Creek (12-25 µg/g). MW (2001b) reported elevated selenium concentrations in periphyton collected from artificial substrates placed in the Blackfoot River (4.3 µg/g) and Angus Creek (6.0 µg/g) between May and June 2000.

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

Submerged macrophytes were collected in September 1999 from numerous stream sites in the Blackfoot River watershed and analyzed for selenium concentrations (MW 2001a). They reported several samples with elevated concentrations ranging from 3.2 to 4.8 µg/g, 10 samples with high concentrations ranging 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. These concentrations were similar to those in the present study measured at East Mill Creek (26-30 µg/g) and the previous study (30-74 µg/g; Hamilton et al. 2002). Submerged macrophytes collected by MW (2001b) in May 2000 contained similar selenium concentrations as in the September 1999 collection.

Taking the periphyton, plankton, and submerged macrophyte data together, the elevated selenium concentrations demonstrated that aquatic plants were accumulating selenium from both water and sedimentary sources. MW (2001a, 2001b) acknowledged that submerged aquatic plants were efficient accumulators of selenium. Their values for several locations in the Blackfoot River watershed were similar to data in the present study and the previous investigation (Hamilton et al. 2002). 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, Trail Creek, and upper and lower Slug Creek (<0.5 - 1.9 µg/g) were less than the proposed dietary selenium threshold of 3 µg/g for fish (Lemly 1993, 1996b, Hamilton 2002). Selenium concentrations of 4.6 µg/g in zooplankton caused nearly complete mortality of razorback sucker larvae in about 10-13 days (Hamilton et al. 2001a, 2001b). Several other studies summarized in Hamilton (2002) 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 lower Blackfoot River and Angus Creek (6.7 to 7.7 µg/g), and the elevated concentrations in Dry Valley Creek (12.8 µg/g) and upper and lower East Mill Creek (27 to 75 µg/g) were of concern

to the health of fishery resources and species that use these resources. A very similar pattern of selenium concentrations in aquatic invertebrates was reported in the June 2000 study (Hamilton et al. 2002).

Although selenium concentrations in invertebrates from upper Slug Creek were low in the present study (0.5 µg/g), they were elevated in the previous study (4.9 µg/g) in spite of low selenium concentrations in water, sediments, and aquatic plants (Hamilton et al. 2002). The difference in selenium concentrations between these two studies may be due to a shift in the composition of taxa in the composite samples. In the June study the composite sample contained 0.6 g Gammaridae, 1.9 g caddisfly larvae, and 0.5 g mayfly larvae (Hamilton et al. 2002), whereas in the present study, the composite sample contained 4.0 g Gammaridae, 0.3 g caddisfly larvae, and 0.2 g mayfly larvae (Appendix 2).

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 a 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 in invertebrates likely 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). Three investigations have reported high correlations between selenium concentrations in sediment and benthic invertebrates ($r=0.94$, Zhang and Moore 1996; $r=0.87$, Malloy et al. 1999 and Hamilton et al. 2001b), which suggested that selenium concentrations in 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. In our study, the linkage between selenium concentrations in invertebrates, sediment, and plants, was supported by the significant correlation between aquatic invertebrates and surficial sediments ($r=0.89$) and between aquatic invertebrates and aquatic plants ($r=0.78$). Similar significant correlations between sediments and aquatic plants or aquatic invertebrates were reported in the previous study of these nine sites (Hamilton et al. 2002). Several investigators have reported that selenium concentrations in invertebrates bioaccumulate through the food web to higher trophic organisms such as fish (Sandholm et al. 1973, Finley 1985, Bennett et al. 1986, Dobbs et al. 1996, Hamilton et al. 2001a, 2001b).

Several inorganic elements (aluminum, boron, cadmium, chromium, iron, manganese, nickel, vanadium, and zinc) were elevated in aquatic invertebrates collected from East Mill Creek and Dry Valley Creek. Several of these elements were also elevated in surficial sediments and aquatic plants, and significantly correlated with concentrations in aquatic invertebrates. Similar to the present study, 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 aquatic invertebrate 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 mining-impacted 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 (MW 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; MW 2001b).

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

Selenium concentrations in aquatic invertebrates reported by MW (2001a, 2001b) tended to be higher than those in the present study and previous study (Hamilton et al. 2002) for similar collection sites. The large number of samples with substantial selenium concentrations above the proposed dietary toxic threshold of 3 µg/g for fish suggested that benthic invertebrate populations were highly contaminated with selenium. 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 nine 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 water, sediments, aquatic plants, and aquatic invertebrates, which demonstrated the interconnectedness of the aquatic ecosystem components. This accumulation pattern was also observed in the previous investigation in June 2000 at the same nine sites (Hamilton et al. 2002) and is supported in reviews of the selenium literature (Maier and Knight 1994, Lemly 1993, 1996b).

There were consistent differences in whole-body selenium concentrations among fish species within a site in the present study. For example, trout and speckled dace contained the highest selenium concentrations, and reidside shiner contained the lowest selenium concentrations. This pattern was similar to the findings in the June 2000 investigation (Hamilton et al. 2002). Brook trout and cutthroat trout are insectivores and accordingly seemed to accumulate elevated concentrations of inorganic elements. Speckled dace are bottom browsers that feed 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 fish's 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 accumulated the most inorganic elements (cadmium, copper, lead, nickel, zinc), piscivorous largemouth bass contained the second most accumulation of inorganic elements (cadmium, zinc), and omnivorous bluegill contained 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*) contained the highest accumulation of cadmium, lead, nickel, and zinc, bottom-dwelling northern hog sucker (*Hypentelium nigricans*) and white sucker (*Catostomus commersoni*) contained intermediate accumulations, and water-column dwelling redbreast sunfish (*Lepomis auritus*) and rock bass (*Ambloplites rupestris*) contained 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 among 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 not consistently elevated in one stream, but rather the highest inorganic element concentrations were distributed among streams: Angus Creek and Dry Valley Creek fish contained the highest concentrations (or tied for highest concentrations) of four elements each, and East Mill Creek, Trail Creek, and upper and lower Slug Creek fish contained the highest concentrations of two elements each. Neither Sheep Creek nor lower Blackfoot River fish contained a "highest" concentration of the elements measured. There seemed to be no parallel bioaccumulation of inorganic elements in fish from the nine sites in the same pattern as selenium. This lack of a dominant stream with numerous elevated inorganic elements was similar to findings in the June 2000 study (Hamilton et al. 2002).

This scenario of selenium being a more important contaminant than other 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 only selenium was of concern to biota. Other investigations reaching similar conclusions were reported by Sorensen (1988), Lemly (1985), Saiki and Lowe (1987), Nakamoto and Hassler (1992), Gillespie and Baumann (1986), Bryson et al. (1984), MW (1999), and Hamilton et al. (2001a, 2001b).

A workshop on selenium aquatic toxicity and bioaccumulation concluded that the tissue-based national 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 2002). 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 whole-body 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). Other 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 (2003). DeForest et al. (1999) and Brix et al. (2000) used selective data to propose high toxicity thresholds for selenium in whole-body and diet of fish, cited older selenium literature containing errors, excluded data from publications based on minor justifications, and overlooked key studies from the extensive selenium literature.

Based on a whole-body toxicity threshold of 4-5 µg/g, the geometric mean selenium concentrations in fish from upper and lower Slug Creek, Trail Creek, and lower Blackfoot River would probably have some effects on early life stages of sensitive species. Fish in Angus Creek and Dry Valley Creek contained 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 East Mill Creek suggested sensitive and moderately sensitive fish are probably being adversely affected by selenium exposure (e.g., reduced recruitment).

Comparison to other Idaho fish data

Rich and Associates (1999) reported concentrations of inorganic elements in cutthroat trout, rainbow trout (*Oncorhynchus mykiss*), brook trout, sculpin species, dace species, and redbreast 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 elevated in fish from Dry Valley Creek.

MW (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 reference sites (Blackfoot River above Wooley Range Ridge Creek and South Fork Sage Creek) contained 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 MW (1999) may 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 $1.667 \times \text{muscle concentration} = \text{whole body concentration}$ (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 MW (1999). The converted selenium concentration in MW (1999; 40 µg/g) is similar to the selenium concentrations in whole-body trout in East Mill Creek in the present study (27-52 µg/g) and the previous study (24-43 µg/g; Hamilton et al. 2002).

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 $\mu\text{g/g}$) and high in 7 samples (12 to 31 $\mu\text{g/g}$) (converted to dry weight using the appropriate percent moisture from MW 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 $\mu\text{g/g}$) and high in 12 samples (10 to 48 $\mu\text{g/g}$) (converted to dry weight using the appropriate percent moisture from MW 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, which are typically 1-2 $\mu\text{g/g}$ (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 $\mu\text{g/g}$; Hamilton et al. 2000). In particular, selenium residues of 5.2 $\mu\text{g/g}$ in rainbow trout were associated with reduced survival (Hunn et al. 1987), and 3.8-4.9 $\mu\text{g/g}$ 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), thus effects in adults such as mortality and growth may not be as readily apparent as effects in early life stages. However, effects on adults could occur through reduced reproductive success.

Based on the above discussion, selenium contamination of the Blackfoot River and its tributaries is most likely adversely affecting aquatic resources, especially 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 specifically mention impacts from inorganic elements.

MW (2000) reported that eggs from cutthroat trout in 1999 contained selenium concentrations of 4.4 and 6.7 $\mu\text{g/g}$ dry weight in two ripe females from the Blackfoot River, 4.0 $\mu\text{g/g}$ in two partially spawned females from the Blackfoot River, and 1.4 $\mu\text{g/g}$ 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 $\mu\text{g/g}$ proposed by Lemly (1993, 1996b). The low number of egg samples in MW (2000) precludes further speculation on the extent of selenium contamination of fish eggs.

Selenium concentrations in forage fish reported by MW (2001a, 2001b) were similar to those in the present study and the previous study (Hamilton et al. 2002). Forage fish samples collected in September 1999 from various sites in Blackfoot River watershed contained selenium concentrations ≥ 4 $\mu\text{g/g}$ (MW 2001a), which was above the generally accepted toxic threshold of 4 $\mu\text{g/g}$ (Lemly 1993, 1996b, Maier and Knight 1994, Hamilton 2002). Nine of 13 samples contained elevated selenium concentrations in fish (5.2 to 8.3 $\mu\text{g/g}$, after conversion to dry weight using the percent moisture given for each sample), and two samples contained high selenium concentrations of 10 and 12.9 $\mu\text{g/g}$ (MW 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 $\mu\text{g/g}$, and 13 samples contained concentrations of 10 to 37 $\mu\text{g/g}$ (MW 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 aquatic invertebrates. Thus, forage fish and salmonids probably pose a hazard from dietary selenium toxicity to predatory fish and fish-eating wildlife.

Other considerations

One concern may be the presence of elevated selenium residues in fish without readily apparent biological effects. However, data in the current study and studies by others (Rich and Associates 1999, MW 1999, 2000, 2001a, 2001b) were results from contaminant surveys and not biological effects studies. No biological or behavioral effects such as survival, growth, reproduction, diversity, population structure, community structure, predator/prey relationships, or other biological effects were measured. Secondly, residues measured in fish were for adults or subadults. This life stage is generally less sensitive to the effects of environmental contaminants than are early life stages (Rand and Petrocelli 1985). 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 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. The review by Skorupa (1998) addresses this concern succinctly and stated, "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 (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).

MW (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 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, MW (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, MW (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.

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 (no toxic threat is identified and selenium concentrations are not elevated in any ecosystem component); 2, minimal hazard (no toxic threat identified but concentrations of selenium are slightly elevated in one or more ecosystem components [water, sediment, benthic invertebrates, fish eggs, bird eggs] compared to uncontaminated reference sites); 3, low hazard (a periodic or ephemeral toxic threat that could marginally affect the reproductive success of some sensitive species, but most species will be unaffected); 4, moderate hazard (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); 5, high hazard (an imminent, persistent toxic threat sufficient to cause complete reproductive failure in most species of fish and aquatic birds). The final hazard characterization was determined by adding the individual scores and comparing the total to the following evaluation criteria: 5, no hazard; 6-8, minimal hazard; 9-11, low hazard; 12-15, moderate hazard; 16-25, high hazard.

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, and 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. Table 16 gives the hazard term and corresponding selenium concentration range for each

Table 16. Aquatic ecosystem components and selenium concentrations posing various hazards based on Lemly (1996a).

Ecosystem component	Hazard														
	None			Minimal			Low			Moderate			High		
	Conc.	Lemly ¹ score	Modified score	Conc.	Lemly ¹ score	Modified score	Conc.	Lemly ¹ score	Modified score	Conc.	Lemly ¹ score	Modified score	Conc.	Lemly ¹ score	Modified 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 (Modified)			7			8-13			14-20			21-27			28-35

¹Lemly 1996a.

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). Stephens et al. (1997) and Engberg et al. (1998) has reported hazard classification schemes that were similar to Lemly (1995, 1996a).

The selenium hazard protocols give equal weight to each component (Lemly 1995, 1996a). However, there may be 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 the score for benthic invertebrate information and a factor of three for the score for fish eggs and bird eggs. Similar concerns have been raised by a USGS scientist (written communication, M. Sylvester, Menlo Park, CA, 2002), and 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 2002, 2003).

Incorporating these factors into the protocol using the offset summation approach 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 16). 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 16). 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 16. 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. This modified hazard assessment was used in a previous investigation in the Blackfoot River watershed (Hamilton et al. 2002).

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 egg concentrations using the conversion factor based on Lemly (1995, 1996a), who reported: whole-body $\times 3.3 =$ fish egg. The hazard assessment for the nine sites is given in Table 17.

The site with low selenium concentrations in most aquatic ecosystem components had a low overall hazard rating was Sheep Creek. Using the original Lemly (1996a) approach, this site would have received a moderate final hazard in spite of the low score for benthic invertebrates and fish eggs (converted from whole-body residues). This final hazard rating is the only one that was changed by the use of the multiplication factors for benthic invertebrates or whole-body residues.

Selenium concentrations were high in water at upper Slug Creek, lower Slug Creek, and

Table 17. Hazard assessment of selenium at nine sites in the Blackfoot River watershed using modified scores.

Site ¹ and ecosystem component	Selenium concentration ²	Evaluation by component		Total for the site	
		Hazard	Score	Score	Hazard
ACM					
Water	6	High	5	32	High
Sediment	1.0	Minimal	2		
Benthic invertebrate	6.7	High	10		
Fish eggs ³	24	High	15		
UEMC					
Water	24	High	5	35	High
Sediment	32	High	5		
Benthic invertebrate	27	High	10		
Fish eggs	89	High	15		
LEMC					
Water	24	High	5	35	High
Sediment	39	High	5		
Benthic invertebrate	75	High	10		
Fish eggs	173	High	15		
TC					
Water	5	High	5	21	Moderate
Sediment	1.2	Minimal	2		
Benthic invertebrate	<0.5	None	2		
Fish eggs	18	Moderate	12		
USC					
Water	7	High	5	21	Moderate
Sediment	1.8	Minimal	2		
Benthic invertebrate	0.5	None	2		
Fish eggs	15	Moderate	12		
LSC					
Water	6	High	5	21	Moderate
Sediment	1.7	Minimal	2		
Benthic invertebrate	<0.5	None	2		
Fish eggs	13	Moderate	12		
ShpC					
Water	8	High	5	18	Low
Sediment	1.5	Minimal	2		
Benthic invertebrate	1.9	None	2		
Fish eggs	9	Low	9		

Table 17. Continued.

Site ¹ and ecosystem component	Selenium concentration ²	Evaluation by component		Total for the site	
		Hazard	Score	Score	Hazard
DVC					
Water	8	High	5		
Sediment	3.0	Low	3	33	High
Benthic invertebrate	13	High	10		
Fish eggs	28	High	15		
LBR					
Water	<5	None	1		
Sediment	1.8	Minimal	2	25	Moderate
Benthic invertebrate	7.7	High	10		
Fish eggs	16	Moderate	12		

¹ACM: Angus Creek, 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.

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

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

Trail Creek, but low in sediments and benthic invertebrates, and moderate in whole body residues converted to fish egg concentrations, thus resulting in moderate overall hazard ratings. Selenium concentrations in water and sediment were in the none or minimal categories at the lower Blackfoot River, but high in benthic invertebrates and moderate in whole-body residues, thus this site received a moderate final hazard. Upper and lower East Mill Creek, Dry Valley Creek, and Angus Creek consistently contained elevated selenium concentrations in sediment, invertebrates, or whole-body residues (which were converted to fish eggs), thus resulting in high overall hazard rating. These hazard ratings were similar to those derived in the June 2000 investigation of the same nine sites (Hamilton et al. 2002).

Based on the final hazard score the streams can be listed from highest environmental selenium hazard to lowest as follows: LEMC, UEMC, DVC, ACM, LBR, USC, LSC, TC, ShpC. This ranking is nearly identical to the results of the Freidman test using the ranked selenium concentrations: LEMC_a, UEMC_a, DVC_{ab}, LBR_{bc}, ACM_c, USC_c, ShpC_c, LSC_c, TC_c. Only slight differences in the position of lower Blackfoot River and Sheep Creek sites occurred when comparing the two approaches. Thus, the selenium hazard protocol seems to be a useful tool in assessing the differences among sites due to the comparable outcome of a statistical approach such as the Freidman test.

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

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 occurring in fish and wildlife associated with the Blackfoot River, its tributaries, and Blackfoot Reservoir. The results of the present study and the previous study (Hamilton et al. 2002) 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 and terrestrial species that utilize these resources in the Blackfoot River watershed.

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Appendix 1. Wet weight (g) of aquatic plant (white-water buttercup *Ranunculus longirostris*) from nine sites in the Blackfoot River watershed submitted for either selenium analysis (Se) or inorganic element analysis (ICP).

Analysis

Site ¹	Se	ICP
ACM	15.73	16.24
UEMC	17.96	18.34
LEMC ²	6.72	6.56
TC ³	6.12	7.25
USC	4.75	5.00
LSC	6.32	5.60
ShpC	5.60	5.40
DVC ³	7.30	7.35
LBR	7.59	7.18

¹ACM: Angus Creek, 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.

²Filamentous green algae.

³Watermilfoil (Myriophyllum).

Appendix 2. Wet weight (g) of aquatic invertebrates from nine sites in the Blackfoot River watershed submitted for either selenium analysis (Se) or inorganic element analysis (ICP).

Site ¹	Chemical analysis	Composite weight	Aquatic invertebrate type								
			Gammaridae	Caddisfly	Mayfly	Damselfly	Beetle larvae	Stonefly	Diptera	Dragonfly	Tendipedidae midge
ACM	Se	3.94	-	0.36	0.46	0.29	0.22	1.32	0.11	1.18	-
	ICP	3.29	-	0.42	0.44	0.28	0.22	1.12	0.13	0.90	-
UEMC	Se	3.34	-	0.22	3.08	-	0.04	-	-	-	-
	ICP	4.17	-	0.14	4.01	-	0.02	-	-	-	-
LEMC	Se	6.85	-	4.47	1.48	-	-	-	-	-	0.90
	ICP	7.68	-	5.08	1.80	-	-	-	-	-	0.80
TC	Se	7.52	0.84	1.31	-	4.09	-	-	-	1.28	-
	ICP	8.41	0.69	1.66	-	4.59	-	-	-	1.47	-
USC	Se	4.45	3.98	0.26	0.21	-	-	-	-	-	-
	ICP	4.79	4.26	0.27	0.26	-	-	-	-	-	-
LSC	Se	12.55	9.11	-	0.33	3.11	-	-	-	-	-
	ICP	13.14	10.21	-	0.25	2.68	-	-	-	-	-
ShpC	Se	9.59	-	4.99	0.05	-	-	4.55	-	-	-
	ICP	9.36	-	4.85	0.03	-	-	4.48	-	-	-
DVC	Se	15.74	4.50	8.93	1.88	-	0.43	-	-	-	-
	ICP	15.24	5.01	7.94	1.80	-	0.49	-	-	-	-
LBR	Se	6.28	-	1.08	-	-	-	5.20	-	-	-
	ICP	8.11	-	1.11	-	-	-	7.00	-	-	-

¹ACM: Angus Creek, 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 3. Total length (mm), weight (g), and use (selenium analysis [Se], inorganic element analysis [ICP], or archive [A]) of fish from nine sites in the Blackfoot River watershed.

Site ¹	Species	Total length	Weight	Use
ACM	Cutthroat trout	69	2.74	ICP
		67	2.44	ICP
		90	6.39	Se
	Mottled sculpin	70	3.77	ICP
		64	2.83	ICP
		91	8.25	Se
	Speckled dace	74	4.18	Se
		68	2.98	Se
		72	3.96	ICP
		40	0.65	ICP
		69	3.45	A
	Redside shiner	73	3.90	Se
		73	4.44	Se
		67	3.25	ICP
		81	5.19	ICP
UEMC	Cutthroat trout	149	29.52	Se
		145	30.18	ICP
LEMC	Cutthroat trout	64	1.82	ICP
		60	1.72	ICP
		71	2.87	Se
TC	Mottled sculpin	86	8.46	Se
		66	3.80	Se
		93	10.63	ICP
	Longnose dace	88	6.58	Se
		68	3.20	Se
		110	14.82	ICP
	Speckled dace	68	3.34	Se
		70	3.58	Se
		69	2.79	Se
		60	2.47	ICP
		55	1.89	ICP
		71	3.74	ICP
62		2.74	A	
71	3.42	A		

Appendix 3. Continued.

Site ¹	Species	Total length	Weight	Use	
TC	Redside shiner	95	8.94	Se	
		90	7.11	Se	
		99	10.34	ICP	
USC	Brook trout	147	30.29	Se	
		130	19.03	Se	
		144	27.74	ICP	
		137	21.57	ICP	
	Mottled sculpin	86	8.18	Se	
		75	4.86	Se	
		85	7.99	ICP	
		84	6.94	ICP	
	Speckled dace	72	3.90	Se	
		57	1.96	Se	
		67	3.29	ICP	
		65	2.71	ICP	
		71	3.65	A	
	LSC	Mottled sculpin	95	9.62	Se
			83	6.89	ICP
		Speckled dace	66	3.31	Se
66			3.35	Se	
72			4.05	Se	
54			1.66	Se	
81			6.13	ICP	
64			3.04	ICP	
45			0.89	ICP	
48			1.18	ICP	
90			8.46	A	
75			4.97	A	
73			4.17	A	
69			3.56	A	
57			1.56	A	
50			1.34	A	
48	1.08	A			
48	1.24	A			

Appendix 3. Continued.

Site ¹	Species	Total length	Weight	Use
LSC	Redside shiner	62	1.96	Se
		57	1.60	Se
		53	1.34	Se
		52	1.24	Se
		60	1.89	ICP
		62	2.22	ICP
		56	1.50	ICP
		56	1.51	ICP
		89	7.41	A
		52	1.31	A
		53	1.33	A
		34	0.35	A
		ShpC	Cutthroat trout	146
123	17.71			Se
Mottled sculpin	64		2.79	ICP
	59		2.09	ICP
	100		13.10	Se
DVC	Cutthroat trout		151	32.15
		107	11.21	Se
		168	39.44	ICP
	Brook trout	117	16.96	Se
		63	2.30	Se
		113	13.68	ICP
		84	5.29	ICP
		255	160.46	A
	Mottled sculpin	84	8.37	Se
		85	7.98	Se
		108	17.66	ICP
		85	7.98	ICP
	Speckled dace	52	1.25	Se
		48	1.05	Se
		62	2.25	ICP
LBR	Mottled sculpin	83	6.64	Se
		58	2.03	Se
		103	16.01	ICP

Appendix 3. Continued.

Site ¹	Species	Total length	Weight	Use
LBR	Longnose dace	54	1.40	Se
		39	0.55	Se
		51	1.28	ICP
		47	0.95	ICP
	Speckled dace	73	4.00	Se
		68	3.35	Se
		61	2.21	Se
		72	3.86	ICP
		69	3.08	ICP
	Redside shiner	57	1.57	Se
		46	0.89	Se
		45	0.82	Se
		64	2.27	ICP
		45	0.67	ICP
		38	0.47	ICP

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