SELENIUM IN WATER, SEDIMENT, PLANTS, INVERTEBRATES, AND FISH IN THE BLACKFOOT RIVER DRAINAGE

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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 was 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 was 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 eight sites (>5 μg/L), sediment at three sites (>2 μg/g), aquatic plants at four sites (>4 μg/g), aquatic invertebrates at five sites (>3 μg/g), and fish at seven sites (>4 μg/g in whole body). The 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.

Keywords: hazard assessment, Idaho, phosphate mining, Selenium

1. Introduction

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). Phosphorus is present in economically mineable quantities in organic-rich black shales of the Permian Phosphoria Formation, which constitutes the Western Phosphate Field. There are four active open-pit mines in southeastern Idaho Phosphate District that produce phosphate from the Meade Peak Phosphatic Shale Member, and 11 inactive mines 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

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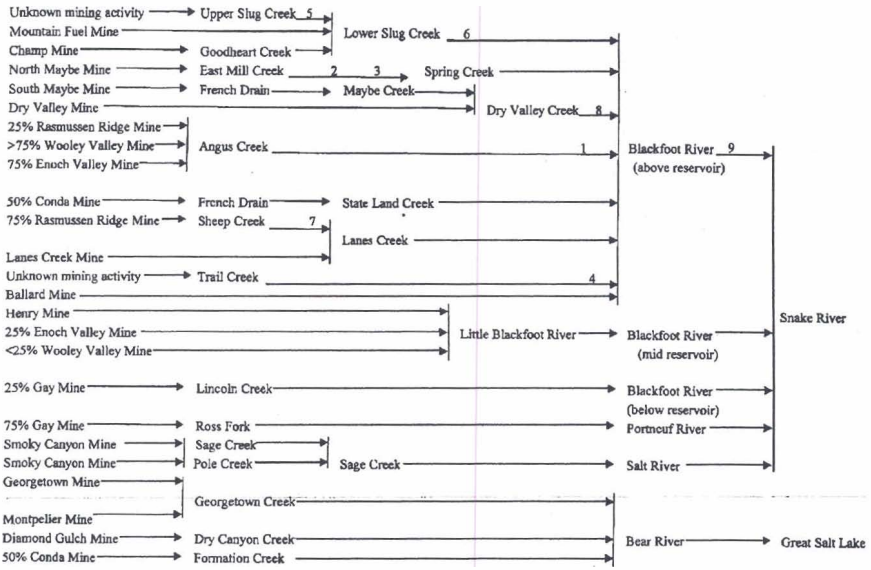

Figure 1. Diagram of surface water flow (generalized to 25% increments) from phosphate mines to drains, creeks, and rivers in southeastern Idaho. Numbers are sample locations: 1—Angus Creek, 2—upper East Mill Creek, 3—lower East Mill Creek, 4—Trail Creek, 5—upper Slug Creek, 6—lower Slug Creek, 7—Sheep Creek, 8—Dry Valley Creek, 9—lower Blackfoot River.

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.

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 Phosphoatic 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 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. In 2003, an additional 327 sheep died after eating high selenium vegetation on reclaimed mine land above the Conda Mine (Steele, 2003). 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 in water, surficial sediment, aquatic plants, aquatic invertebrates, and fish from streams in southeastern Idaho near phosphate mining operations. This information was used in a hazard assessment of the potential effects of selenium on aquatic resources in areas of the Blackfoot River watershed.

2. Materials and Methods

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 1 and 2). Sample collection occurred in September 2000 and was a joint effort of the USGS Water Resources Discipline (WRD), USGS Biological Resources Discipline, and the U.S. Forest Service (USFS). Latitude and longitude were measured at each site with a global positioning system (Rockwell International, type HNV-560C, Cedar Rapids, IA).

2.1. Site Description

The collection sites were as follows:

1. The Angus Creek near mouth (ACM, N42°49′42.24″, W111°20′15.04″) site was located at the crossing of the creek by Forest Route 095, and was approximately a half 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. Sample collection was primarily on the upstream side of the road crossing.
2. The upper East Mill Creek (UEMC, N42°48′26.74″, W111°18′38.82″) 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

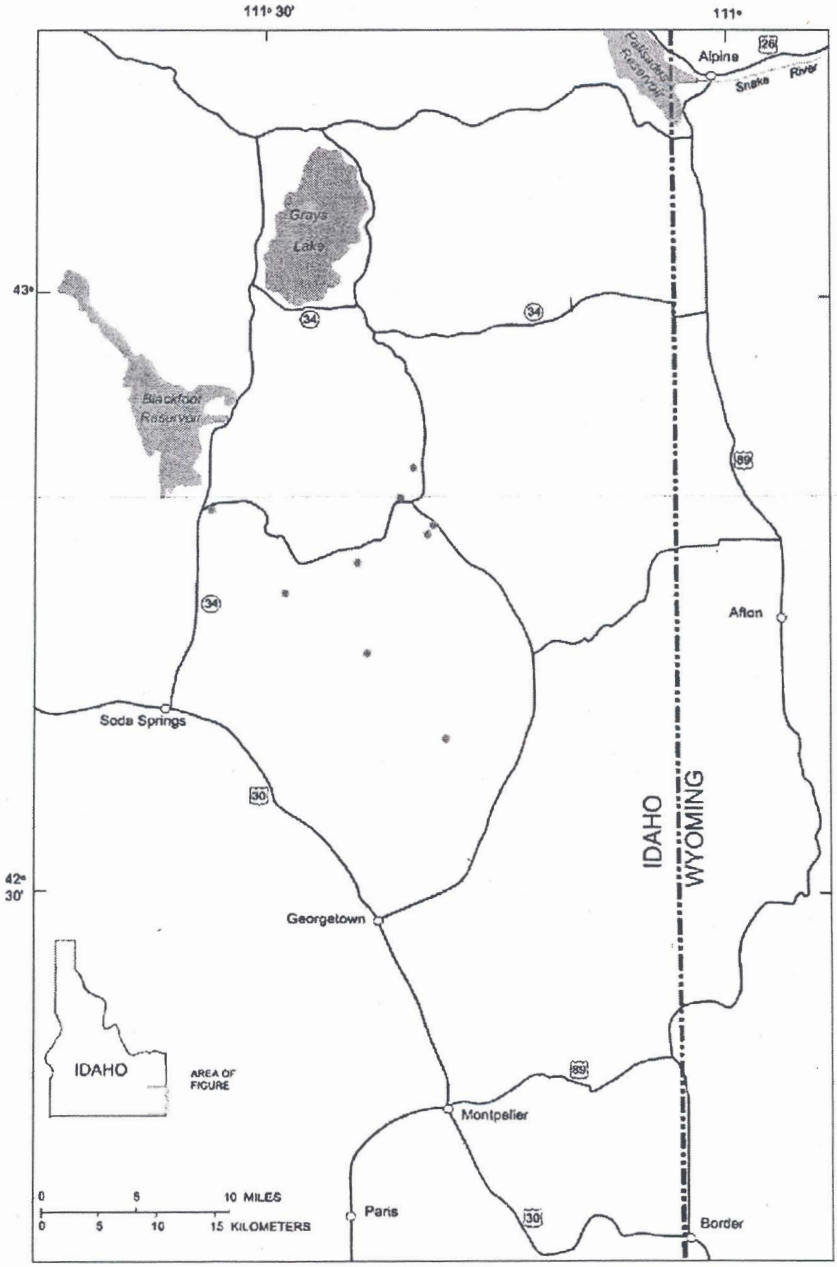

Figure 2. Map of study area. Dots are general locations of sample sites. (Map source: modified from Herring *et al.*, 2001).

was in a generally open area of forbs, grass, and spare pine trees with very limited grazing.

3. The lower East Mill Creek (LEMC, N42°48′53.56″, W111°18′25.98″) site was located at the crossing of the creek by Forest Route 102. The site was located approximately 4 km below the upper East Mill Creek site and about 4 km above the confluence with the Blackfoot River. The sampling site was below the inactive North Maybe Mine. The land on either side of the road was composed of grass and sagebrush and had moderate grazing. Sample collection was about equally distributed upstream and downstream of the road crossing.
4. The Trail Creek (TC, N42°45′29.82″, W111°26′47.53″) 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 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, N42°37′50.85″, W111°18′20.51″) 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 reference site was located above the influence of mining and >20 km above the confluence with the Blackfoot River. The sampling site was on land 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.
6. The lower Slug Creek (LSC, N42°42′23.79″, W111°22′03.89″) 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, N42°51′46.92″, W111°20′00.53″) 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 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, N42°46′58.71″, W111°22′26.47″) 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 along the stream was primarily grassland with some shrubs nearby and moderate grazing.
9. The lower Blackfoot River (LBR, N42°49′12.49″, W111°33′09.33″) 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. The land along the river was primarily riparian with some grass and light camping.

2.2. Sample collection

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 μm polycarbonate filter using standard sampling techniques (USGS, 1998). One water subsample of 200 mL was collected in an acid-cleaned polyethylene bottle for analysis of selenium concentrations, and a second subsample collected for water quality measurements. Water samples for selenium analysis were acidified with ultrapure hydrochloric acid (HCl). A reagent blank was collected for analysis of selenium concentrations, and consisted of deionized water from a mobile laboratory combined with the acid preservative. All samples for selenium analyses were stored frozen.

One sediment sample was 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, the sample stored frozen, and the sample used for analysis of selenium concentration.

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 no white-water buttercup was found after a substantial search, 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. One composite plant sample was collected from each site, squeezed to remove excess water, weighed, bagged in Whirl-Pak bags, labeled, stored frozen, and analyzed for selenium concentration.

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 and analyzed for selenium concentration.

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. A specimen of some species was retained to confirm identification.

2.3. Water Quality Analyses and Flow Measurement

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). Water samples (~1 L) at each site were collected and analyzed for general water quality characteristics in a mobile laboratory according to standard methods (APHA *et al.*, 1995). Immediately after bringing 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, 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 (H_2SO_4), and transported to Yankton for analysis of ammonia concentrations. All water quality characteristics were measured according to standard methods (APHA *et al.*, 1995), except ammonia and chloride. Ammonia was measured using ion-selective electrodes and following the procedures for low concentration measurements of the electrode manufacturer (Orion Research, 1990, 1991; ATI Orion, 1994). Chloride was measured by the mercuric nitrate titration method (Hach Company, 1997).

2.4. Selenium 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.

2.5. 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 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 selenium concentration to lowest using ecosystem components (sediment, plant, invertebrate, and fish). Significant differences ($p = 0.05$) among streams were determined with Freidman's multiple comparison test.

3. Results

3.1. Selenium analyses

The results of QA/QC sample analysis by AA-GF for selenium concentrations are given in Table I. The QA/QC results were within acceptable ranges, except that the percent relative standard deviation 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 I

Quality assurance and quality control measures of selenium analysis of water, sediment, aquatic plants, aquatic invertebrates, and fish ($n = 1$ for water, sediment, plant, invertebrate; $n = 2$ for fish [mean and standard error in parentheses])

	Ecosystem component				
Measure	Water	Sediment	Aquatic plant	Aquatic invertebrate	Fish
Limit of detection (LOD) (μg/L or μg/g)	5	0.5	0.5	0.5	0.5
Procedural blank	<LOD	<LOD	<LOD	<LOD	<LOD
Percentage RSD[a]	0.4	2	1	17	4 (4)
Percentage Recovery of reference material	103[b]	101[c]	NG[d,e]	117[f]	90 (4)[f]
Percentage Recovery of digested spike	105	100	93	96	118 (5)

[a]%RSD: percent relative standard deviation.
[b]Leeman Labs commercial standard solution (lot number 387201).
[c]National Institute of Standards and Technology (NIST) standard reference material 2709 (San Joaquin soil; 1.57 μg/g).
[d]NG: not given.
[e]NIST standard reference material 1547 (peach leaves, 0.12 μg/g).
[f]National Resource Council of Canada standard reference material TORT-2 (lobster hepatopancreas; 5.63 μg/g).

3.2. Water Quality

Water quality characteristics are given in Table II. 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.

3.3. Water

The selenium concentrations in water from the lower Blackfoot River was less than the LOD (<5 μg/L), moderately elevated (5–8 μg/L) at six other sites, and substantially elevated at upper and lower East Mill Creek (Table III).

3.4. 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 III). A significant

TABLE II

Water quality characteristics (number of samples (n) in brackets; if $n > 1$, water quality measure is the mean; <: indicates below limit of measurement)

	Site[a]								
Measure	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)
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
Discharge (cfs)	0.36	1.36	0.56	1.96	0.56	1.02	2.67	0.41	50

[a]ACM: 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 III

Selenium concentrations (μg/L for water and μg/g dry weight for sediment, aquatic plants, and aquatic invertebrates) in water, sediment, aquatic plants, and aquatic invertebrates ($n = 1$; <: less than limit of detection)

	Site[a]								
Ecosystem component	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[b]	1.7[c]	1.6	1.7	1.2	4.4[c]	5.8
Aquatic invertebrate	6.7	26.9	75.2	<0.5	0.5	<0.5	1.9	12.8	7.7

[a]ACM: 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.
[b]Filamentous green algae.
[c]Watermilfoil (Myriophyllum).

correlation coefficient was found between concentrations of selenium in sediment and water ($r = 0.99$).

Streams were ranked from highest selenium concentrations in sediment to lowest as follows: LEMC, UEMC, DVC, LBR, USC, LSC, ShpC, TC, ACM.

3.5. 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 μg/g); moderately elevated at the Dry Valley Creek and lower Blackfoot River (4.4–5.8 μg/g); and very elevated at the upper and lower East Mill Creek (26–30 μg/g) (Table III). Filamentous green algae collected at lower East Mill contained 25.7 μg/g selenium, which was similar to that in white-water buttercup collected at upper East Mill Creek (30.3 μg/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 with sediment ($r = 0.97$) and water ($r = 0.99$).

Streams were ranked from highest selenium concentrations in aquatic plants to lowest as follows: UEMC, LEMC, LBR, DVC, ACM, LSC, TC, USC, ShpC.

3.6. 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 μg/g), moderately elevated at Angus Creek, lower Blackfoot River, and

Dry Valley Creek (6.7–12.8 μg/g), and highly elevated at upper- and lower-East Mill Creek (27–75 μg/g) (Table III).

The correlation coefficient between selenium concentrations in aquatic invertebrates was significant with water ($r = 0.83$), surficial sediment ($r = 0.89$), and aquatic plants ($r = 0.78$). 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.

Streams were ranked from highest selenium concentrations in aquatic invertebrates to lowest as follows: LEMC, UEMC, DVC, LBR, ACM, ShpC, USC, TC, LSC.

3.7. 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 redside shiner (*Richardsonius balteatus*) (Table IV). 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. 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 IV). Redside shiner were collected from only four sites, and contained the lowest whole-body selenium

TABLE IV

Selenium concentrations (μg/g dry weight) in whole-body fish ($n = 1$)

	Site[a]								
Species	ACM	UEMC	LEMC	TC	USC	LSC	ShpC	DVC	LBR
Brook trout	–[b]	–	–	–	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

[a]ACM: 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.

[b]–: not collected.

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 IV). Significant correlation coefficient were observed for selenium concentrations in the combined fish data for six species with water ($r = 0.91$), sediment ($r = 0.96$), aquatic plants ($r = 0.87$), and aquatic invertebrates ($r = 0.98$).

Streams were ranked from highest geometric mean selenium concentrations in fish to lowest as follows: LEMC, UEMC, DVC, ACM, TC, LBR, USC, LSC, ShpC.

3.8. Streams

There were significant differences among streams on the basis of selenium concentrations using the individual ranks for the five matrices in the Freidman test. 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.

4. Discussion

4.1. 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. In general, most of the nine stream sites contained similar inorganic element concentrations in water to those in upper Slug Creek, except for selenium (Hamilton and Buhl, 2003). 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).

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.

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). Data from MW (1999, 2000, 2001a, 2001b, 2002) and Hamilton *et al.* (2002) reported selenium contamination of the Blackfoot River watershed during 1998 to 2000.

4.2. 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 μg/g in 1996 and 38.9 μg/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).

In the present study, the significant correlation of selenium concentrations in surficial sediment and water, sediment and aquatic plants, and sediment and aquatic invertebrates suggested that selenium moves 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 (Hamilton and Buhl, 2003). 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 selenium movement through the food web. Woock (1984) demonstrated in a cage study with golden shiner (*Notemigonus crysoleucas*) that fish in cages with access to bottom sediments (sediment, benthic invertebrates, and detritus) accumulated more selenium than fish held in cages suspended about 1.5 m above the sediments. 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 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 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.

4.3. 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 and in surficial sediments 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 on 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 of selenium 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). 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.

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 (33000 μg/g), nickel (2000 μg/g), vanadium (1000 μg/g), zinc (11000 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 elevated selenium concentrations in periphyton collected from artificial substrates placed in streams between September and October 1999 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.

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 and submerged macrophyte data together, the elevated selenium concentrations demonstrated that aquatic plants were accumulating selenium. Aquatic plants are the foundation of the food web including detritus. As such, they are an important link in the bioaccumulation of selenium to higher trophic consumers such as aquatic invertebrates and fish.

4.4. 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.

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 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 and between aquatic invertebrates and aquatic plants. 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).

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.

4.5. 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 redside shiner contained the lowest selenium concentrations. 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. Redside shiner are omnivores (Lee *et al.*, 1980), and thus seemed to accumulate low inorganic element concentrations. 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 (Murphy *et al.*, 1978; Ney and Van Hassel, 1983; Campbell, 1994; Besser *et al.*, 1996). 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).

Hamilton and Buhl (2003) concluded that selenium was a more important contaminant than other inorganic elements in the Blackfoot River watershed. This scenario 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 Bryson *et al.* (1984), Lemly (1985), Gillespie and Baumann (1986), Saiki and Lowe (1987), Sorensen (1988), Nakamoto and Hassler (1992), MW (1999), and Hamilton *et al.* (2001a, 2001b).

A recent paper gave the rationale for a tissue-based criterion for selenium in fish and proposed a national criterion of 4 μg/g in whole body based on the review of several laboratory and field studies (Hamilton, 2002). 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 4–5 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).

Rich and Associates (1999) measured concentrations of inorganic elements in several fish species collected from Dry Valley Creek immediately upstream of the Blackfoot River and concluded that selenium and other elements (cadmium, copper, lead, vanadium, and zinc) were probably causing stress in fish populations. MW (1999) reported salmonid fillets collected from East Mill Creek in 1998 contained selenium concentrations of 6 μg/g wet weight (maximum 7.9 μg/g), whereas fish from two reference sites contained 1.2–1.3 μg/g. Converting these values to a dry weight basis (dry weight = wet weight $\times$ 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; Hilton *et al.*, 1982; Lemly, 1982; 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 reference sites based on a conversion factor of 1.667 × muscle concentration = whole body concentration (Lemly and Smith, 1987). The converted selenium concentration in East Mill Creek (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 were also elevated in whole-body salmonids collected in September 1999 and May 2000 from Blackfoot Reservoir and the mainstem and tributaries of the Blackfoot River (MW, 2001a, 2001b). These selenium residues in salmonids were substantially above background concentrations in fish from laboratory and field investigations, which are typically 1–2 μg/g (Maier and Knight, 1994; Hamilton *et al.*, 2000). More importantly, these selenium residues were above those reported to cause adverse effects in early life stage salmonids (4–5 μg/g; Hamilton *et al.*, 1986; Hunn *et al.*, 1987; Hamilton and Wiedmeyer, 1990; Hamilton *et al.*, 2000).

Selenium concentrations in non-salmonid 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 $\geq$4 μg/g (MW, 2001a), which was above the generally accepted toxic threshold of 4 μg/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 μg/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 μg/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 μg/g, and 13 samples contained concentrations of 10 to 37 μg/g (MW, 2001b).

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.

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. Another concern was that

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). A third concern 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."

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]."

4.6. 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 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 V gives the hazard term and corresponding selenium concentration range for each of the four ecosystem components in the four-component model (Lemly, 1996a).

These protocols have been used to assess the selenium hazard to aquatic ecosystems at Ouray NWR, UT (Lemly, 1995, 1996a), the Animas, LaPlata, and Mancos rivers in the San Juan River basin (Lemly, 1997), three Wildlife Management Areas in Nevada (Lemly, 1996a), and three sites near Grand Junction, CO (Hamilton *et al.*, 2001a, 2001b). 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, Ohlendorf, 1996). Ohlendorf suggested a multiplication factor of 2 for the score for benthic invertebrate information and a factor of 3 for the score for fish eggs and bird eggs. Similar concerns have been raised by a USGS scientist (written communication, Sylvester, Menlo Park, CA, 2002), and a USFWS Environmental Contaminant Specialist (written communication, Osmundson, Grand Junction, CO, 2001). The weighting of the three biological components seems justified on the basis of 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 V). 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 V). 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 V. 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).

TABLE V

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

	Hazard														
	None			Minimal			Low			Moderate			High		
Ecosystem component	Conc.	Lemly[a] score	Modified score	Conc.	Lemly[a] score	Modified score	Conc.	Lemly[a] score	Modified score	Conc.	Lemly[a] score	Modified score	Conc.	Lemly[a] 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[a])		4			5–7			8–10			11–14			15–20	
Final hazard (Modified)			7			8–13			14–20			21–27			28–35

[a]Lemly (1996a).

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

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 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, 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).

On the basis of 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 in five ecosystem components: $LEMC_a$, $UEMC_a$, 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 by MW 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

TABLE VI

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

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

(*Continued on next page*)

TABLE VI
(*Continued*)

Site[a] and ecosystem component	Selenium concentration[b]	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[c]	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		

[a]ACM: 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.
[b]Selenium concentrations in μg/L for water, μg/g for sediment, benthic invertebrates, and fish eggs.
[c]Fish eggs: Fish egg values converted from whole-body residues using: whole-body $\times$ 3.3 = fish egg (Lemly, 1995, 1996a).

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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