

Prepared in cooperation with the Bureau of Land Management

Selenium in the Upper Blackfoot River Watershed, Southeastern Idaho, 2001–12

Scientific Investigations Report 2014–5203
Version 1.1, August 2015

U.S. Department of the Interior
U.S. Geological Survey

Front cover: Aerial view of the inactive Maybe Canyon Mines, Blackfoot River watershed. Photograph taken by Bruce Gordon at EcoFlight (www.EcoFlight.org), September 29, 2011. Used with permission.

Back cover: Streamgaging station 13063000, Blackfoot River above reservoir near Henry Idaho. Photograph taken by Marshall Williams, U.S. Geological Survey, July 25, 2014.

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By Christopher A. Mebane, Greg C. Mladenka, Lynn Van Every, Marshall L. Williams,
and Mark A. Hardy

With an appendix on selenium speciation analytical methods,
By John R. Garbarino

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Conversion Factors, Datums, and Abbreviations and Acronyms

[Note: the units used in this report are intended to follow common usage in the United States. As such, they are a blend of English and metric units, with flows, distances, and areas expressed in English units, and concentrations and values derived from concentrations expressed in metric units]

Multiply	By	To obtain
Length		
inch (in.)	2.54	centimeter (cm)
foot (ft)	0.3048	meter (m)
mile (mi)	1.609	kilometer (km)
meter (m)	3.281	foot (ft)
kilometer (km)	0.6215	mile (mi)
Area		
acre	0.4047	hectare (ha)
square mile (mi ²)	2.590	square kilometer (km ²)
Volume		
cubic foot (ft ³)	28.32	cubic decimeter (dm ³)
Flow rate		
cubic foot per second (ft ³ /s)	0.02832	cubic meter per second (m ³ /s)
cubic foot per second (ft ³ /s)	2,447	cubic meter per day (m ³ /d)
Concentration		
milligram per liter (mg/L)	1,000	micrograms per liter (µg/L)
milligram per liter (mg/L)	1	grams per cubic meter (g/m ³)
Mass		
pound, avoirdupois (lb)	0.4536	kilogram (kg)
kilogram (kg)	2.205	pound, avoirdupois (lb)
Pressure		
pound per square inch (lb/in ²)	6.895	kilopascal (kPa)

Conversion Factors, Datums, and Abbreviations and Acronyms

Temperature in degrees Celsius (°C) may be converted to degrees Fahrenheit (°F) as follows:

$$^{\circ}\text{F} = (1.8 \times ^{\circ}\text{C}) + 32.$$

Specific conductance is given in microsiemens per centimeter at 25 degrees Celsius ($\mu\text{S}/\text{cm}$ at 25 °C).

Concentrations of chemical constituents in water are given either in milligrams per liter (mg/L) or micrograms per liter ($\mu\text{g}/\text{L}$).

Datums

Vertical coordinate information is referenced to the North American Vertical Datum of 1929 (NAVD 29).

Horizontal coordinate information is referenced to the North American Datum of 1983 (NAD 83).

Elevation, as used in this report, refers to distance above the vertical datum.

Abbreviations and Acronyms

ADCP	acoustic Doppler current profiler
ANOVA	analysis of variance
d	day(s)
EDTA	ethylenediaminetetraacetic acid
EWI	equal-width increment
IDEQ	Idaho Department of Environmental Quality
MPV	most probable value
NWQL	National Water Quality Laboratory
RPD	relative percent difference
RSD	relative standard deviation
s	second(s)
Se	selenium
USGS	U.S. Geological Survey
WRTDS	weighted regressions on time, discharge, and season

Selenium in the Upper Blackfoot River Watershed, Southeastern Idaho, 2001–12

By Christopher A. Mebane¹, Greg C. Mladenka², Lynn Van Every², Marshall L. Williams¹, and Mark A. Hardy¹

Abstract

The upper Blackfoot River in southeastern Idaho receives runoff from 12 large phosphate mines. Waste shales that are removed to access the phosphate ore are highly enriched with selenium, resulting in elevated selenium in runoff from the mine waste dumps. In 2001, in cooperation with the Bureau of Land Management, the U.S. Geological Survey (USGS) began monitoring streamflow, selenium, and other water-quality parameters at a single location near the outlet of the upper Blackfoot River to the Blackfoot Reservoir. Water samples primarily were collected by a flow triggered, automated pump sampler, supplemented by manual point and equal-width integrated manual samples.

The approach to monitoring concentrations and streamflow over time at a fixed location is ideal for evaluating temporal trends, but provides no information about the relative source contributions from the mine waste dumps draining into various tributaries. In 2001, the Idaho Department of Environmental Quality (IDEQ) began an annual, mid-May, synoptic survey of selenium concentrations and streamflow at 21 locations along the main stem Blackfoot River and its tributaries. Individually, neither the intensive USGS sampling at the outlet nor the IDEQ annual synoptic sampling provides a comprehensive view of selenium runoff in the Blackfoot River watershed. Together, the efforts are complementary; therefore, in this report, results are presented from both sampling efforts.

The USGS collected time-series data from 2001 to 2012 at a fixed location, the Blackfoot River near the outlet of the reservoir, near Henry, Idaho (USGS streamgage 13063000). Dissolved selenium concentrations from 450 filtered samples collected at this site ranged from 0.5 to 11.4 micrograms per liter ($\mu\text{g/L}$). The State of Idaho chronic aquatic life criterion concentration of 5 $\mu\text{g/L}$ was exceeded in 31 percent of the samples, with most exceedances occurring during May of each year. No exceedances of the selenium criterion were recorded in months other than April, May, or June. Concentrations of selenium in unfiltered and filtered samples were similar, and concentrations from samples collected by depth and width

integrated methods were similar to those collected by grab (point) samples, indicating that the grab samples adequately represent selenium concentrations across the entire river cross section. In speciation analyses made during 2003 and 2004, the median percentage of total selenium as selenate was 81 percent, ranging from 17 to 98 percent, and the median percentage of total selenium as selenite was 19 percent, ranging from 2 to 83 percent of the total selenium. During the period of study, selenium concentrations had an upward trend during the low-flow season of August–October. Time trends were not obvious during other seasons. Selenium daily loads varied by more than a factor of 900 during the study period and ranged from 0.03 kilograms per day (kg/d) to more than 24 kg/d. Annual maximum daily loads of selenium varied over nearly a factor of 12, ranging from about 2 to 24 kg/d.

For the annual spring synoptic samples collected by the IDEQ along the main stem Blackfoot River and major tributaries, selenium concentrations ranged from less than 2 to 870 $\mu\text{g/L}$ in 176 samples. In most years, the synoptic sampling showed that the majority of the selenium loads passing the USGS streamgage at the outlet of the watershed could be attributed to a single tributary, East Mill Creek, which enters the Blackfoot River through Spring Creek. Selenium loads decreased by about half from East Mill Creek before reaching the Blackfoot River, suggesting that much selenium is at least temporarily removed from the water column by uptake by aquatic vegetation or by losses to sediment. Similar decreases in selenium loads occurred through the main stem Blackfoot River before reaching the outlet in low flow years, but not in high flow years.

Introduction

Phosphate has been mined and processed from the Permian Phosphoria Formation in southeastern Idaho for more than 100 years, with large scale production beginning in the 1950s (Lee, 2001). As of 2012, 18 large-scale phosphate mines were present in southeast Idaho, with 5 active and 13 inactive operations (U.S. Government Accountability Office, 2012). Twelve of these mines are in the upper Blackfoot River watershed. Selenium contamination associated with phosphate mining in

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the Blackfoot River watershed was only recognized in 1996 with livestock deaths near inactive mining operations (Hamilton and Buhl, 2004). Selenium concentrations in water and aquatic food webs in the study area were elevated to levels that in other settings have been determined to be harmful (Hamilton and Buhl, 2004; Presser and others, 2004a; Conley, 2012).

Although phosphate enriched rock occurs in the Montana, Wyoming, Idaho, and Colorado parts of the Permian Phosphoria Formation, mining activity has been concentrated in the Meade Peak geologic formation in southeastern Idaho (Jasinski and others, 2004). The Phosphoria Formation is notably enriched in several trace elements compared to most other black shales. Compared to the average world-shale composition, the Meade Peak waste rock is exceptionally enriched in silver, cadmium, chromium, selenium, uranium, and zinc (Herring and Grauch, 2004). Meade Peak waste rock is highly reactive with water and releases significant quantities of trace elements from finely ground-rock samples in periods as short as 1 hour. Furthermore, the rocks that are least altered and organic matter-rich, such as shales newly exposed by mining, release the greatest amounts of trace elements into solution (Herring, 2004).

Purpose and Scope

This report describes temporal and spatial patterns and trends in selenium concentrations and loads for the upper Blackfoot River watershed. Data described were collected by the U.S. Geological Survey (USGS) and the Idaho Department of Environmental Quality (IDEQ). USGS data collection included continuous streamflow measurement and water-quality samples. All data were collected from 2001 to 2012 at one location at the downstream end of the upper watershed. The effort was conducted in cooperation with the Bureau of Land Management. The IDEQ collected instantaneous streamflow measurements and manual water-quality samples at 21 tributary and main stem locations in the upper watershed from 2001 to 2012.

Description of Study Area

Hydrology and Geology

The Blackfoot River is a tributary to the Snake River in southeastern Idaho. The study area is in the upper part of the Blackfoot River watershed, upstream of Blackfoot Reservoir (fig. 1). The drainage area of the upper Blackfoot River watershed is about 345 mi², and ranges in elevation from about 6,100 ft at the watershed outlet, to 8,970 ft along its southern divide; the mean watershed elevation is about 7,000 ft. The USGS operates a streamgaging and water-quality monitoring station, (Blackfoot River above reservoir near Henry, Idaho, 13063000), about 4.9 mi upstream of the reservoir. The drainage area upstream of the streamgage is about 333 mi², represents 97 percent of the upper Blackfoot River watershed by area, and includes all major tributaries to the upper Blackfoot River (U.S. Geological Survey, 2012).

Sedimentary rock, including the Permian Phosphoria Formation, underlies the upper Blackfoot River watershed. Two phosphate ore zones occur within the formation, separated by a black-shale “waste zone.” The lower-ore zone is about 40 ft thick, the waste zone about 90 ft thick, and the upper-ore zone about 15 ft thick. These ore and waste zones maintain their thickness for more than 8,300 mi². The Phosphoria strata, including the ore zones that have been folded, form northwest and southeast trending ridges. Most mining occurs on the ridges because deep alluvium in the valleys makes the ore inaccessible to open pit or surface strip-mining (Petrun, 1999; Presser and others, 2004b). Selenium is greatly elevated in both the waste-shale and the ore zones, but is highest in the waste black shale, averaging about 65 milligrams per kilogram (mg/kg) and ranging as high as 1,040 mg/kg (Herring and Grauch, 2004). These concentrations are exceptionally high, compared to a worldwide average for shales of about 1 mg/kg, an average of about 4 mg/kg for coal, and compared to the average abundance of selenium in the Earth’s crust of about 0.05 mg/kg (Herring and Grauch, 2004; Plant and others, 2007).

Base flows in the Blackfoot River seem to be sustained by groundwater discharges from two hydrogeologic formations: alluvium and the Wells Formation. The Wells Formation underlies the Phosphoria Formation and is the primary regional aquifer in the Blackfoot River watershed. The Wells Formation with its lithology of dolomite, limestone, and sandstone is more permeable than the Phosphoria Formation with its less permeable shales (Ralston and Williams, 1979; Ralston and others, 1980; Myers, 2013). The low permeability of the Phosphoria Formation contributes to long and complex groundwater-flow systems, including interbasin groundwater-flow systems. For example, groundwater recharge occurring in the upper Dry Valley seems to travel beneath a ridge and discharge in the Slug Creek valley. Alluvial fans and valley-floor deposits are extensive, and test holes in the valley floor have penetrated 400 ft of unconsolidated material without entering bedrock (Ralston and Williams, 1979).

The phosphate mines in the Blackfoot River watershed are primarily situated in groundwater recharge areas on ridge tops or ridge flanks. Although this limits the extent of pit lake formation and the need for mine pit dewatering, this situation may influence the hydrology and chemistry of groundwater (Ralston and others, 1980). Selenium concentrations in groundwater within the Phosphoria Formation have been shown to be elevated relative to deep groundwater sampled within the underlying Wells Formation and to overlying shallow groundwater. In deep water collected from wells completed within bedrock and located upgradient from mining influences, dissolved selenium concentrations within the Phosphoria Formation ranged from 11 to 40 µg/L compared to less than 0.1 to 14 µg/L for samples collected from the Wells Formation. In shallow groundwater collected from wells completed within alluvial or colluvial aquifers and located upgradient to mining influences, dissolved selenium has ranged from less than 0.1 to 2 µg/L (Whetstone Associates, 2012).

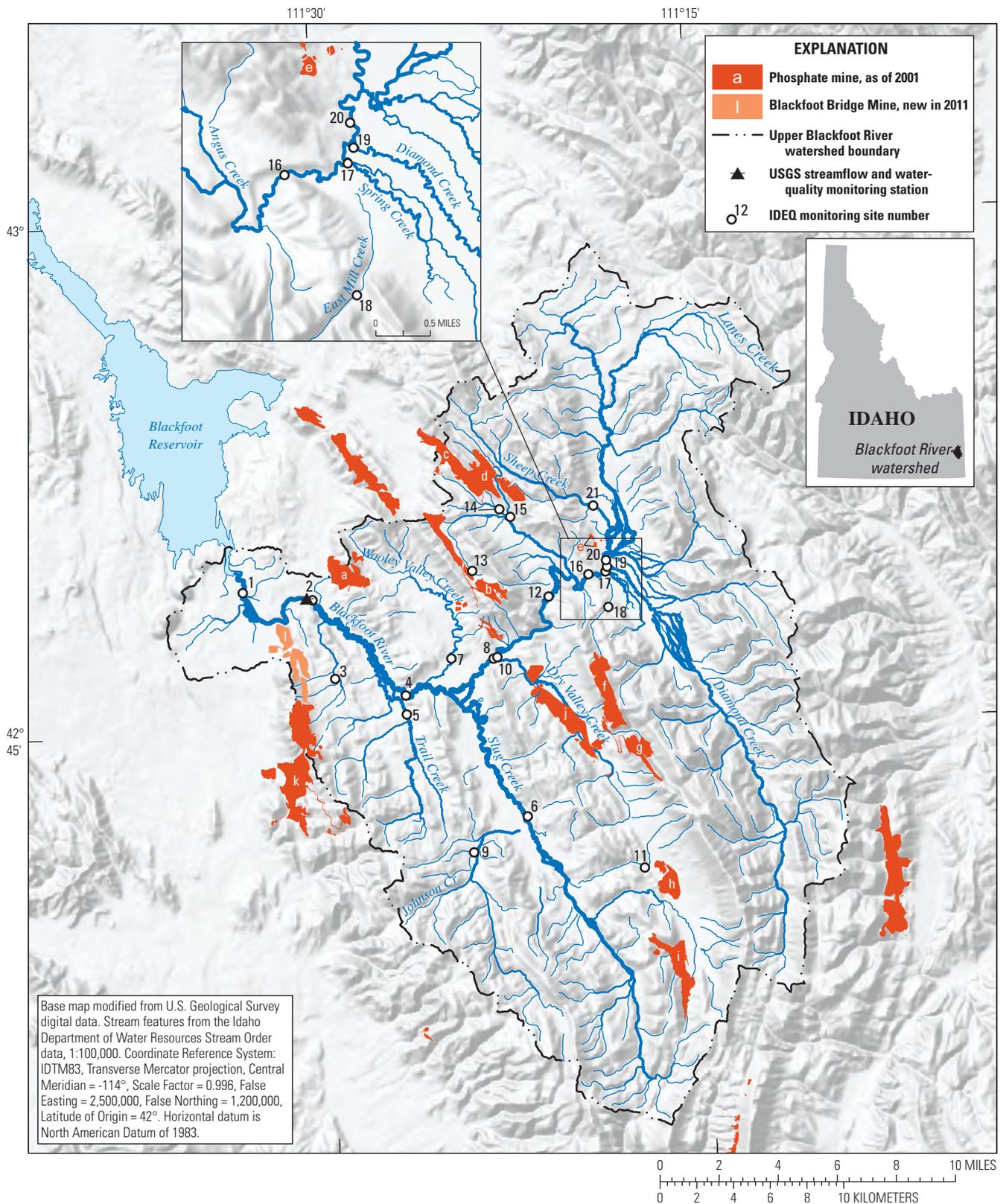


Figure 1. Phosphate mines and monitoring stations in the upper Blackfoot River watershed, southeastern Idaho, 2001–12. Phosphate mines upstream of the USGS streamgaging and water-quality monitoring station Blackfoot River above reservoir near Henry (13063000), include Ballard (a), Wooley Valley (b), Enoch Valley (c), Rasmussen Ridge (d), Lanes Creek (e), Maybe Canyon North (f), Maybe Canyon South (g), Champ (h), Mountain Fuel (i), Dry Valley (j), Conda (k), and Blackfoot Bridge (l). Locations of mines as of 2001 are from Moyle and Kayser (2006), and the location of the newer Blackfoot Bridge Mine was drawn from Bureau of Land Management (2011).

Phosphate Mining and Selenium

Industrial scale phosphate mining near the upper Blackfoot River watershed began at least by 1920 with the Conda Mine; mining greatly expanded after 1948 following development of open pit and surface strip-mining techniques (Mansfield and Girty, 1927; Jasinski and others, 2004). Of the 12 phosphate mine complexes in the upper Blackfoot River watershed, 4 were active as of 2012 (Blackfoot Bridge, Dry Valley, and two units of the Rasmussen Ridge complex) (fig. 1; U.S. Government Accountability Office, 2012).

The economic value of phosphates in southeastern Idaho was recognized by at least 1889, and in 1908, the Idaho Phosphate Reserve was established by executive order of the Secretary of the Interior James Rudolph Garfield, which was later enacted into legislation and expanded under Presidents Taft and Wilson (Richards and Mansfield, 1911; Lee, 2001). The purpose of the reserve was to withdraw public lands from private claim and to protect the western phosphate resources from foreign acquisition. At the time, the United States was primarily dependent on German phosphate suppliers, and the eastern phosphate deposits in Tennessee and the Carolinas were owned or controlled by European companies with most ore being exported for the use of European farmers. The establishment of the Phosphate Reserve in 1908 led to a system of federal mineral leasing in 1920 in lieu of private claims, a system which remains in effect to date (Lee, 2001; Jasinski and others, 2004). Extensive surveys by USGS geologists followed, starting with hand-dug trenches to expose fresh phosphate rock for sampling and analysis, and later, machine dug trenches, prospects, pits, tunnels, and drillholes. The surveys determined that the “Phosphoria Formation” as they named it, was widespread and relatively consistent in its phosphate content and quality (Mansfield and Girty, 1927; Lee, 2001).

Many of the early USGS trenching and other explorations of near surface phosphate rock in the 1900s can be linked directly to the later development of the major open-pit mines (years when the USGS exploration activities occurred are in parentheses). These mines include the Ballard (1912), Enoch Valley (1912, 1949), Rasmussen Ridge (1912), Maybe Canyon (1911, 1948), Champ (1911), Dry Valley (1910, 1948), in addition to the Smokey Canyon mine (1914, 1949), which is located just east of the Blackfoot River watershed divide (fig. 1; Mansfield and Girty, 1927; Lee, 2001). The duration of active mining operations at the larger mines often has been about 20 years, but has varied from as few as 5 years at the Champ Mine to more than 50 years at the Conda Mine (Lee, 2001).

By the 1970s, reclamation was required as mining was completed, which usually involved partial backfilling the pits with overburden and waste and contouring, amending soil, and reseeding (Chambers and others, 1994). Mine waste dump designs focused on stability, water passage, and surface erosion, with few mentions of water quality (Riker and others, 1978; Sidle and others, 1994). Concerns were

focused on potential or actual structural failures such as slope instabilities, mudflows, and siltation pond overflows such as those at the Wooley Valley complex and Maybe Canyon Mine South that “caused a great amount of anxiety on the part of the mine operator, the mine owner and government officials” (Lee, 2001; U.S. Forest Service, 2011). By the 1980s, mining operations sought to revegetate dump surfaces as they were built to reduce surface erosion, increase water losses from transpiration, and increase canopy interception of precipitation, which in turn increases evaporation of rain and snow (Sidle and others, 1994). Contemporary mine management reclamation plans include ongoing surface reclamation as mining proceeds, detailed water-management plans, extensive groundwater and surface-water monitoring and adaptive management plans, among other steps to minimize the ongoing and post-mining degradation of public lands (Bureau of Land Management, 2011).

Prior to 1996, water-quality concerns relating to the phosphate mines appear to have been focused on sediment loading to streams (Sidle and others, 1994). As late as 1995, a detailed geochemical report of elevated trace metals in mine dump influenced water in upper East Mill Creek did not mention selenium (Amacher and others, 1995), although subsequent work has shown extremely high selenium concentrations in this stream. Beginning with the 1996 selenium-poisoning deaths of four horses grazing in a pasture in Dry Valley, livestock deaths associated with grazing on grasses and other plants that accumulated selenium from shallow groundwater have been a major issue in the Blackfoot River watershed and vicinity. As of April 2012, more than 600 deaths of sheep, cattle, and horses had been reported (U.S. Government Accountability Office, 2012), and in October 2012, another 95 sheep died after grazing in a re-vegetated, inactive mine site (Miller, 2012). Selenium is accumulated in vegetation in mining disturbed areas, as well as in wetlands downgradient from mining disturbed areas (Mackowiak and others, 2004). For instance, in 2009, 16 yearling steer died after grazing for only a few days in a 500-acre pasture, 5 acres of which were a reclaimed mining disturbed area. The pasture had been previously used for nearly 20 years without problems. The cause of the deaths was linked to eating western aster, a selenium hyperaccumulating-plant species that accumulated selenium to more than 100 times higher than concentrations in grasses and other co-occurring plants (Davis and others, 2012). Restricting livestock from areas with high risks of selenium poisoning from selenium accumulating plants provides continuing challenges to both mine managers and range managers.

Elk and deer seem to be more tolerant of elevated selenium than are horses and other domestic livestock (Drew, 2014). Although elevated selenium in livers of hunter-killed elk was correlated with distance of the harvested elk from the nearest phosphate mine (Presser and others, 2004b), there have been fewer reports of selenium toxicity to elk than to livestock. In October 2013, the Idaho Department of Fish and Game investigated a case of suspected selenium toxicosis in

an elk with impaired neuromuscular coordination near the Lanes Creek Mine. Selenium poisoning was suspected owing to greatly elevated selenium concentrations in blood and liver relative to the ranges of usual values for elk, with 1.5 mg/L selenium in blood (usual range 0.1–0.3) and 12 mg/kg in liver (usual range 0.25–1.4) (Drew, 2014).

Ecology

When defined by ecoregional areas of general similarity, the Blackfoot River watershed has been classified within the Partly Forested Mountains and Cold Valley zones of the Middle Rockies ecoregion. The Partly Forested Mountains support open-canopied forests, shrublands, and grasslands; Douglas-fir, lodgepole pine, and aspen are most common on north-facing slopes and gently sloping uplands, whereas mountain big sagebrush and mountain brush dominate south facing slopes. Cold Valleys contain bottomlands, terraces, marshlands, alluvial fans, and foothills that are nestled below the Partly Forested Mountains. Potential natural vegetation in the Cold Valleys is mostly sagebrush steppe, and wet bottomlands support sedges, rushes, and willows. The growing season is too short for most crops, and agriculture is limited to pastureland, rangeland, and small grain production (McGrath and others, 2002). The valleys are at about 6,300 ft and the ridge tops generally are about 7,500–7,800 ft in elevation. From 2001 through 2012, annual precipitation ranged from 8 to 22 in. in the valley bottoms and from 20 to 45 in. in the wetter headwaters regions in the vicinity, as measured at the Dry Valley Mine and at the divide at the head of Slug Creek (fig. 1; Whetstone Associates, 2012). No towns are located in the watershed, and the primary economic activities are phosphate mining, ranching, and farming.

For the most part, the upper Blackfoot River is a low gradient, highly meandering stream, with abundant riparian vegetation. At its outlet, the upper Blackfoot River is a fifth-order stream (fig. 1). An unbranched perennial stream is defined as a first-order stream, where two first-order streams join is defined as a second-order stream, and so on. The native fish community in the upper Blackfoot River consists of cold- and cool-water adapted species, including Yellowstone Cutthroat Trout (*Oncorhynchus clarkii bouvieri*), Paiute Sculpin (*Cottus beldingii*), Mottled Sculpin (*Cottus bairdii*), Mountain Sucker (*Catostomus platyrhynchus*), Longnose Dace (*Rhinichthys cataractae*), Speckled Dace (*Rhinichthys osculus*), and Redside Shiner (*Richardsonius balteatus*) (Meyer and others, 2003; 2013). Brook Trout (*Salvelinus fontinalis*) also are established in the upper Blackfoot River watershed (Hamilton and Buhl, 2004). Aquatic plants (macrophytes) are abundant, and species in the Blackfoot River include aquatic buttercup, sago pondweed (*Stuckenia pectinata*), and Cladophora (Mebane and others, 2014). Phosphorus is more abundant than nitrogen in the upper Blackfoot River, relative to requirements for periphyton growth, and as result, periphyton growth seems to be limited by the availability of nitrogen (Marcarelli and others, 2009).

Numerous measurements have been made of selenium concentrations in aquatic ecosystem components including periphyton, macrophytes, macroinvertebrates, forage fish, sculpin, trout, and bird eggs. These collections and analyses showed that selenium was elevated throughout aquatic food webs in mining-influenced stream sites in the Blackfoot River watershed. Concentrations often were elevated above those considered potentially harmful to related species in review articles, studies from other settings, or population modeling (Hamilton and Buhl, 2004; Presser and others, 2004b; Van Kirk and Hill, 2007; Conley, 2012). For instance, as part of a randomized, probabilistic study of selenium, mercury, and arsenic in water and fish tissue in Idaho's major rivers, Essig (2010) collected Cutthroat Trout and Bridgelip Sucker from the Blackfoot River near the USGS monitoring station located near the outlet of the upper Blackfoot River (fig. 1). Mean selenium concentration of 14.7 mg/kg in muscle as a composite of fillets from 10 fish, was highly elevated relative to the statewide median of 1.0 mg/kg dry weight (dw) for Cutthroat Trout (n=10 sites). (All tissue concentrations mentioned in this report are as dry weight.) Bridgelip Sucker also had highly elevated selenium in muscle tissue, with 10.5 and 12.3 mg/kg in duplicate composite samples of 10 fish each, compared to a statewide family median concentration for all catostomids (suckers) sampled of 1.1 mg/kg dw, n=10 sites (Essig, 2010). However, although selenium concentrations in fish are greatly elevated in the Blackfoot River watershed relative to reference areas and exceed literature values linked to adverse effects, Conley (2012) cautioned that data were mostly insufficient to evaluate whether actual depression of fish populations was occurring, owing in part to the mobility of Yellowstone Cutthroat Trout in open systems, and the lack of well structured, quantitative population survey designs.

Importance of Selenium in Aquatic Ecosystems

Selenium is elevated through aquatic food webs in mining-influenced streams in the Blackfoot River watershed (Hamilton and Buhl, 2004; Conley, 2012). The risks of elevated selenium in aquatic ecosystems have been an area of intense research from the 1980s to date, and this research has produced a complex body of knowledge with many apparent conflicts of interpretation (Chapman, 2009; Janz and others, 2010). For instance, selenium is an essential micronutrient for all animals that have a nervous system, yet it is toxic at not much higher concentrations. With fish, selenium is essential for proper nutrition at dietary selenium concentrations of 0.1–0.5 mg/kg, with selenium toxicity risks developing at dietary selenium concentrations as low as 3 mg/kg (Janz and others, 2010). At optimal concentrations, selenium is an antioxidant nutrient with positive effects on the immune system in at least mammals and birds, yet oxidative stress seems to be the primary mechanism of toxicity in animals and may compromise immune function at higher concentrations (Burk, 2002; Palace and others, 2004; Miller and others, 2007;

Janz and others, 2010). The cell damage caused by oxidative stress can in turn lead to a cascade of symptoms that include edema in developing embryos; teratogenic deformities in offspring; spinal deformities; anemia; cataracts; popeye; pathological alterations in liver, kidney, heart, and ovary; reduced egg viability; and reduced growth of juveniles. Selenium has been called an insidious threat in waters where it is elevated, because adult fish may appear perfectly healthy, whereas severe effects may be occurring to early life stage fish but not be noticed in routine surveys until a large percentage of the age class structure is affected (Lemly, 2002). Oviparous (egg laying) vertebrates seem to be the most sensitive taxa to selenium toxicity (Lemly, 2002; Janz and others, 2010). Mammals appear to be less at risk, although livestock deaths resulting from acute dietary exposure through grazing on plants that had accumulated selenium from waste rock areas or from shallow groundwater is a major concern in the study area (Mackowiak and others, 2004). Human fatalities have resulted from consuming commercially available selenium dietary supplements in excess of nutritional needs (Chapman, 2009). Selenium also is closely linked with mercury bioaccumulation and toxicity, and has been reported to reduce accumulation and toxicity from methylmercury in fish and animals under some circumstances (Khan and Wang, 2009; Peterson and others, 2009).

Selenium Speciation and Solubility

The chemical form of selenium affects its bioaccumulation and mobility in aquatic ecosystems. Selenium is a nonmetal with chemistry similar to sulfur. Selenium can exist in the environment in four relatively stable oxidation states, 2^- , 0 , 4^+ , and 6^+ (Se(-II), Se(0), Se(IV), and Se(VI), respectively). Selenide (Se^{2-}) tends to occur in metal sulfide ores and is insoluble in water. Elemental selenium (Se^0) tends to be stable in reducing environments and insoluble in water. In oxic waters, selenium usually occurs in the 4^+ and 6^+ oxidation states as the anions selenite and selenate. In streams, selenium is usually detected in three forms, in order of usual abundance, selenate (SeO_4), selenite (SeO_3), and organic selenium (McNeal and Balistrieri, 1989; Maher and others, 2010). In laboratory settings, organic selenium and selenite have been shown to bioaccumulate more strongly than selenate (Besser and others, 1993; Franz and others, 2011). However, organisms within natural periphyton can reduce selenate to selenite, which may lead to selenium being readily bioavailable through the food web, regardless of initial oxidation state of inorganic selenium in the water column (Conley and others, 2013). Sulfate tends to compete with selenate for uptake by plants, and thus selenium bioaccumulation may be enhanced when sulfate concentrations are low, and vice versa (Bailey and others, 1995).

Solubility of selenium species is highest for selenate, and selenium mobility is mostly controlled by adsorption to iron oxides. Conditions that favor the mobility of selenium in the environment with respect to adsorption are alkaline pH, high selenium concentrations, oxidizing conditions, and high concentrations of additional anions that also adsorb to iron oxides. Anions in water that tend to increase selenium mobility and thus increase selenium concentrations in water include phosphate, sulfate, and carbonate (McNeal and Balistrieri, 1989; Balistrieri and Chao, 1990).

Selenium Toxicity to Aquatic Organisms

Risks of selenium toxicity to fish and waterbirds do not usually occur directly from exposure to selenium in water. Rather, in most environmental settings where selenium is elevated to moderate concentrations (1–20 $\mu\text{g/L}$), the risks of selenium poisoning are via trophic transfer through the food web, not from direct exposure to selenium in water (Janz and others, 2010; Presser and Luoma, 2010). In closed reservoir ecosystems, entire fish communities have collapsed once selenium concentrations reached 8–10 $\mu\text{g/L}$. However, what concentrations of selenium in water relate to aquatic risks varies because of differences in bioaccumulation in lotic (flowing) systems versus lentic systems (reservoir or lakes), differences in food webs among waters, the chemical form of selenium, the difficulties of detecting fish population effects in streams that are open to movements by fish, and other factors (Janz and others, 2010; Presser and Luoma, 2010; Stewart and others, 2010).

Although selenium concentrations in water do not usually relate directly to ecological risks, two water-based guidelines are germane. First, Swift (2002), Lemly and Skorupa (2007), and Presser and others (2004a and 2004b) suggested that across most aquatic ecosystems, if selenium concentrations in water are less than 2 $\mu\text{g/L}$, there will be low risk of trophic transfer to sensitive aquatic species, and little need for food web or fish tissue monitoring. Second, an older guideline with the force of law is the State of Idaho's chronic aquatic life criterion for selenium of 5 $\mu\text{g/L}$. This value in turn was based on the U.S. Environmental Protection Agency (EPA) (1987) analysis, which included interpretations of field studies of selenium contaminated Belews Lake, North Carolina. In Belews Lake, selenium concentrations in water reached about 10 $\mu\text{g/L}$ in the main body of the lake. Populations of several fish species collapsed following recruitment failure (that is, the failure to add juveniles to the population). In an upper arm of the reservoir that had limited circulation with the main body of the reservoir and where selenium in water was mostly less than the detection limit of 5 $\mu\text{g/L}$, the fish assemblage was mostly intact. Therefore, the chronic criterion was set at 5 $\mu\text{g/L}$, the selenium detection limit available during the studies (U.S. Environmental Protection Agency, 1987). Although this 5 $\mu\text{g/L}$ criterion followed from information available at the time, and was detectable using

methods routinely available at the time, subsequent studies that had access to lower detection limits for selenium found adverse effects in sensitive fish species in the upper arm of the reservoir that previously had been thought to be unaffected at selenium concentrations ranging from 0.2 to 4 $\mu\text{g/L}$ (U.S. Environmental Protection Agency, 1998). The EPA has proposed to replace their aquatic life criteria for selenium with a fish-tissue based water-quality criterion, but the final form and values of this proposal are unresolved as of the time of this writing (U.S. Environmental Protection Agency, 2014). The Idaho aquatic life criteria is formally expressed as a 4-day average concentration that is not to be exceeded more than once every 3 years, on the average (Idaho Department of Environmental Quality, variously dated). However, for simplicity, in this report we contrast selenium concentrations with the aquatic life criterion concentration of 5 $\mu\text{g/L}$, without regard to averaging periods.

Methods

Water-Quality Monitoring

For this study, the USGS measured streamflow and concentrations of selenium and other water-quality parameters at one location at the downstream end of the upper watershed. The sampling site is co-located with the streamgage, Blackfoot River near Henry, Idaho (13063000). The Blackfoot River sampling site at the outlet of the upper Blackfoot River captures flow and solutes for the watershed and integrates upstream watershed processes. This approach to monitoring concentrations and streamflow over time at a fixed location is ideal for evaluating temporal trends. However, when many possible sources of loading occur in a catchment, a spatially detailed approach that extends upstream from the outlet is needed to allow comparison among the various sources (Kimball and Runkel, 2009).

To examine different source contributions and spatial distribution of selenium concentrations and loads in the Blackfoot River watershed, in 2001, the IDEQ began an annual, mid-May, synoptic survey of selenium concentrations and streamflow at 21 locations along the main stem Blackfoot River and its tributaries. Individually, neither the USGS time-series outlet sampling nor the IDEQ annual spatial sampling provides a comprehensive view of selenium runoff in the Blackfoot River watershed. Together, the efforts are complementary and therefore results are presented from both sampling efforts.

USGS Sampling Methods

Continuous streamflow was measured by the USGS at the Blackfoot River near Henry, Idaho streamgage from 2001 to 2012 using the methods described by Sauer and Turnipseed (2010) and Turnipseed and Sauer (2010). The streamgage

was operated year-round in 2001–05; and subsequently the streamgage has been operated seasonally, from late March or early April through mid-September to late October, the time period that the automatic sampler is operated.

Because the site is somewhat remote and frequent sampling was required, an automatic sampler (ISCO model 3700) was installed to collect water samples that were later selected for laboratory analysis. The sampler was operated only from late March through mid-September when freezing conditions did not exist. The data-collection platform was programmed to trigger the automatic sampler based on the volume of water passing the site (generally one sample per every 2.67 million cubic feet passing the streamgage). Therefore, sampling frequency varied as streamflow changed, so that streamflow peaks were covered by higher-frequency sampling than lower streamflows were. All sample-contact components of the automatic sampler were cleaned with Liquinox[®] detergent, soaked in a 5 percent hydrochloric acid solution, and rinsed with deionized-water prior to installation. During site visits, field crews retrieved the samples once every 2–3 weeks. Samples were stored in the dark at room temperature for as much as about 90 days at the USGS Idaho Falls Field Office until selections were made for laboratory analyses. The selections were generally based on the timing and duration of the hydrograph peaks and specific conductance of the samples. Samples selected for laboratory analyses were filtered through a 0.45-micrometer (μm) pore-size disposable capsule filter and preserved with nitric acid as described by Wilde and others (2004). Samples were analyzed for major ions, selenium, and selected other trace elements.

Autosamplers are presently the only practical means of collecting samples that represent the range of hydrologically variable conditions at a remote site and at inconvenient times (such as at night, on weekends, or under hazardous conditions). Despite these advantages, autosamplers are subject to mechanical malfunction and have additional data quality considerations beyond conventional discrete samples. The quality-control issues include: the degree to which measurements or samples collected at one location in the stream by the autosampler represent conditions throughout the stream cross section, the possibility of carryover contamination because the purge and rinse cycles of the autosampler between sample collection might not completely clean the tubing, and exceeding prescribed sample holding times or temperatures in autosamplers. For instance, water-quality samples are recommended to be processed (for example, filtered and stabilized by chilling, freezing, or acidification) shortly after sampling to avoid losses from microbiological activity, adsorption to container, precipitation, photodegradation, or other causes.

With selenium, these quality-control factors are more important for samples intended for speciation analyses than for total selenium analyses. Gómez-Ariza and others (1999) reported that for unacidified (pH 8) seawater samples stored in polyethylene containers at 25 °C, significant losses of selenite started after 15 days and significant reductions in selenate

concentration occurred after 6 months. Temperature, ionic strength, and sample volume affect the stability of selenium in water samples, with increasing stability at increasing selenium concentrations, lower temperatures, higher ionic strength, and larger samples volumes (Gómez-Ariza and others, 2000). Wang (1994) reported that for losses of selenium in water samples with low ambient selenium concentrations (approximately 0.06 µg/L), losses were lower in natural water samples with higher ionic content than in low ionic strength river water, snowmelt, or in purified water. No selenium was lost from selenate dominated groundwater samples during 13 months stored at room temperature; however, selenite was lost from river water after only 3 days at room temperature. Selenium losses during holding were concentration dependent, with 28 percent loss after 125 days from selenate samples with a starting concentration of 0.09 µg/L that were stored at neutral pH and at room temperature, whereas no losses were observed under the same conditions with selenate samples with a starting concentration of 1 µg/L (Wang, 1994).

Although this previous literature suggests that for the mostly selenate dominated and high ionic strength Blackfoot River waters, losses of selenium prior to analysis likely would be small enough to not confound interpretations, the need for quality-control sampling and analysis is clearly indicated. Thus manual stream samples also were collected and processed onsite as described in Wilde (2006) and Wilde and others (2004). At the time that manual samples were collected, in-stream measurements of water temperature, pH, specific conductance, and dissolved oxygen were routinely made using a calibrated multi-parameter meter (Wilde, variously dated).

The Idaho Department of Environmental Quality (variously dated) chronic aquatic life criterion of 5 µg/L selenium is expressed as a total recoverable (whole water) concentration. However, for most samples, 0.45 µm filtered (“dissolved”) samples were analyzed for selenium instead of analyzing total selenium from unfiltered samples. The reasons for focusing on filtered samples were concerns regarding (1) accurate representation of particulates in the stream cross section using a single-point automatic sampler; (2) homogenization of the small-volume whole-water samples collected by the automatic sampler; and (3) demonstration that past dissolved selenium data typically represented greater than 90 percent of total selenium measured in the Blackfoot River. Only at peak concentrations were the dissolved fractions of selenium less, but fractions were always greater than 80 percent of the total selenium samples (Presser and others, 2004a). Other data collected from the study area indicated that dissolved selenium was indistinguishable from total selenium concentrations during both low- and high-flow conditions. From two high-flow sampling periods on East Mill Creek, Spring Creek, and Blackfoot River, dissolved selenium values averaged 99 percent of the total selenium values (95 percent confidence limits, 97–101 percent, range 83 to 110 percent, n=41) (Ecology and Environment, 2012; 2013). In sampling of Dry Valley Creek near IDEQ site 10 during low- and high-flow

conditions, dissolved selenium values averaged 99 percent of the total selenium values (95 percent confidence limits, 94–105 percent, range 75 to 113 percent, n=15) (Whetstone Associates, 2012). Henceforth, in this report dissolved and total selenium concentrations are treated interchangeably.

Laboratory analyses were done by the USGS National Water Quality Laboratory (USGS NWQL) in Denver, Colorado. Selenium analyses were done from 2001 through 2005 by inductively coupled plasma-mass spectrometry, with a method detection limit of about 0.1 µg/L as described by Garbarino (1999). From 2006 through 2012, selenium analyses were completed by collision/reaction cell inductively coupled plasma-mass spectrometry, with a method detection limit of about 0.03 µg/L, following methods described in Garbarino and others (2006). Analyses of major anions and cations used methods described in Fishman (1993).

During 2003–04, the inorganic selenium species selenite and selenate were measured in samples as described in [appendix B](#). Organic selenium was operationally defined as the difference between total selenium minus selenite and selenate. Samples for this inorganic speciation method were preserved by adding ethylenediaminetetraacetic acid (EDTA). To prevent species changes in samples held in the automatic sampler, EDTA was added to sample bottles intended for speciation analyses before they were placed in the automatic sampler.

Data Quality Evaluations

The quality of the water-chemistry data was evaluated in several ways, including evaluating the intrinsic uncertainty of the laboratory results, evaluating the potential for contamination of the samples collected through unattended automated pumping, and evaluating the representativeness and repeatability of the autosampler collections. Five types of project-specific quality-control data were used during the USGS sampling to evaluate the quality of selenium data collected by the automatic sampler. First, because the autosampler sits inside a galvanized steel gage house, and the sample bottles sit inside the autosampler case, open to the atmosphere for about 30 days, ambient blanks were used with all sample periods. Ambient blank samples were bottles of deionized water incubated with caps off in the automatic sampler for as many as 60 days to measure the potential for contamination from particles or dust in the sampler case. Second, equipment blanks, consisting of deionized water pumped manually through the autosampler were analyzed. Third, grab samples were collected at the location of the automatic-sampler intake to determine if samples might be significantly affected by the sampler pumping system. Fourth, replicate analyses were made on grab samples to determine if laboratory results were consistent. Finally, samples collected by depth and width integrated methods (EWI samples, see Wilde and others [2004]) were collected to determine how well samples collected by the automatic sampler intake tube represented the entire river cross section.

In addition to the project-specific quality-control samples, the USGS NWQL performance over time was examined with USGS standard reference samples. The USGS standard reference samples differ from other laboratory-fortified samples that are routinely used by chemical laboratories to evaluate their performance (standard reference samples are spiked into natural river waters, rather than spiked into laboratory reagent blanks). From 2001 to 2012, between about 100 and 150 USGS and non-USGS laboratories across the United States participated in a twice-annual round-robin sampling. The median values returned from the round-robin sampling define the most probable values for the sample (Woodworth and Connor, 2003). Multiple standard reference samples are submitted to the NWQL throughout each year as blind samples. For this report, the values obtained by the USGS NWQL for each of the standard reference samples were compared to the most probable values of standard reference samples to evaluate the uncertainty and potential bias associated with the sample results.

Watershed-Wide Sampling Methods

Idaho Department of Environmental Quality personnel sampled twenty-one main stem and tributary sites in the upper Blackfoot River watershed annually during May high-flow

conditions (table 1). The sampling hierarchy in the watershed (that is, which streams flow into which, and which mines are located within the drainages of each stream site), are shown in figure 2. Appendix A provides a high resolution, interactive view of the sampling sites.

Field teams followed USGS sampling protocols (Wilde and others, 2004; Wilde, 2006). Water samples were collected using a depth-integrated sampler. A bridgeboard winch platform or a long rod was used at sites where wading was not feasible. Samples were placed in polyethylene containers and preserved with nitric acid prior to analysis. Because the Idaho chronic selenium standard is expressed as a 4-day average concentration, samples were collected over 4-day periods for each site. During each targeted 4-day period, three samples were collected on the first, last, and on one other day. For economy, samples collected over the 4-day periods were composited at IDEQ's Pocatello office, by measuring equal volumes in a graduated cylinder. Glassware used for compositing was washed with Alconox® detergent, triple rinsed with deionized water, and rinsed with sample water between samples. From 2001 to 2008, samples were analyzed by ACZ Laboratories, Steamboat Springs, Colorado, and from 2009 to 2012, samples were analyzed by SVL Laboratories, Kellogg, Idaho, for total selenium analysis. Both laboratories used Standard Method 3114B, hydride generation, and atomic absorption (Eaton and others, 2005).

Table 1. Sites from Idaho Department of Environmental Quality synoptic sampling, Blackfoot River, southeastern Idaho, 2001–12.

[Locations of sites are shown in figure 1. Sites are listed downstream (site 1) to upstream]

Site No.	Name	Latitude (decimal degrees)	Longitude (decimal degrees)	Number of samples	Year(s) sampled
1	Blackfoot River at China Hat	42.820019	-111.553545	9	2004–2012
2	Blackfoot River at USGS streamgage 13063000	42.815541	-111.507253	9	2004–09, 2011–12
3	State Land Creek	42.776570	-111.493881	7	2001–2004, 2006–2008, 2011
4	Blackfoot River at Trail Creek Road	42.767308	-111.447211	9	2004–2012
5	Trail Creek	42.758152	-111.447033	8	2001, 2006–2012
6	Slug Creek	42.706277	-111.368497	8	2004, 2006–2012
7	Wooley Valley Creek	42.784806	-111.416222	8	2001, 2006–2012
8	Blackfoot River at Slug Creek Road	42.784243	-111.387956	12	2001–2012
9	Johnson Creek	42.689414	-111.404973	3	2008, 2011, 2012
10	Dry Valley Creek	42.784845	-111.385456	3	2004, 2006, 2008
11	Goodheart Creek	42.679389	-111.291889	9	2004, 2007–2012
12	Blackfoot River above Narrows	42.813696	-111.350299	12	2001–2012
13	Angus Creek	42.827583	-111.400389	11	2001, 2004–2010
14	Rasmussen Creek	42.857332	-111.381155	10	2001, 2004–2012
15	No Name Creek	42.853056	-111.3735	3	2001, 2010–2011
16	Blackfoot River at upper bridge	42.824076	-111.323242	12	2001–2012
17	Spring Creek	42.825307	-111.311674	12	2001–2012
18	East Mill Creek	42.807934	-111.310923	11	2001, 2003–2012
19	Diamond Creek above confluence with Lanes Creek	42.82741	-111.3106	3	2007, 2011, 2012
20	Lanes Creek above confluence with Diamond Creek	42.830729	-111.311123	9	2004–2012
21	Sheep Creek	42.857000	-111.318617	8	2001, 2006–2012

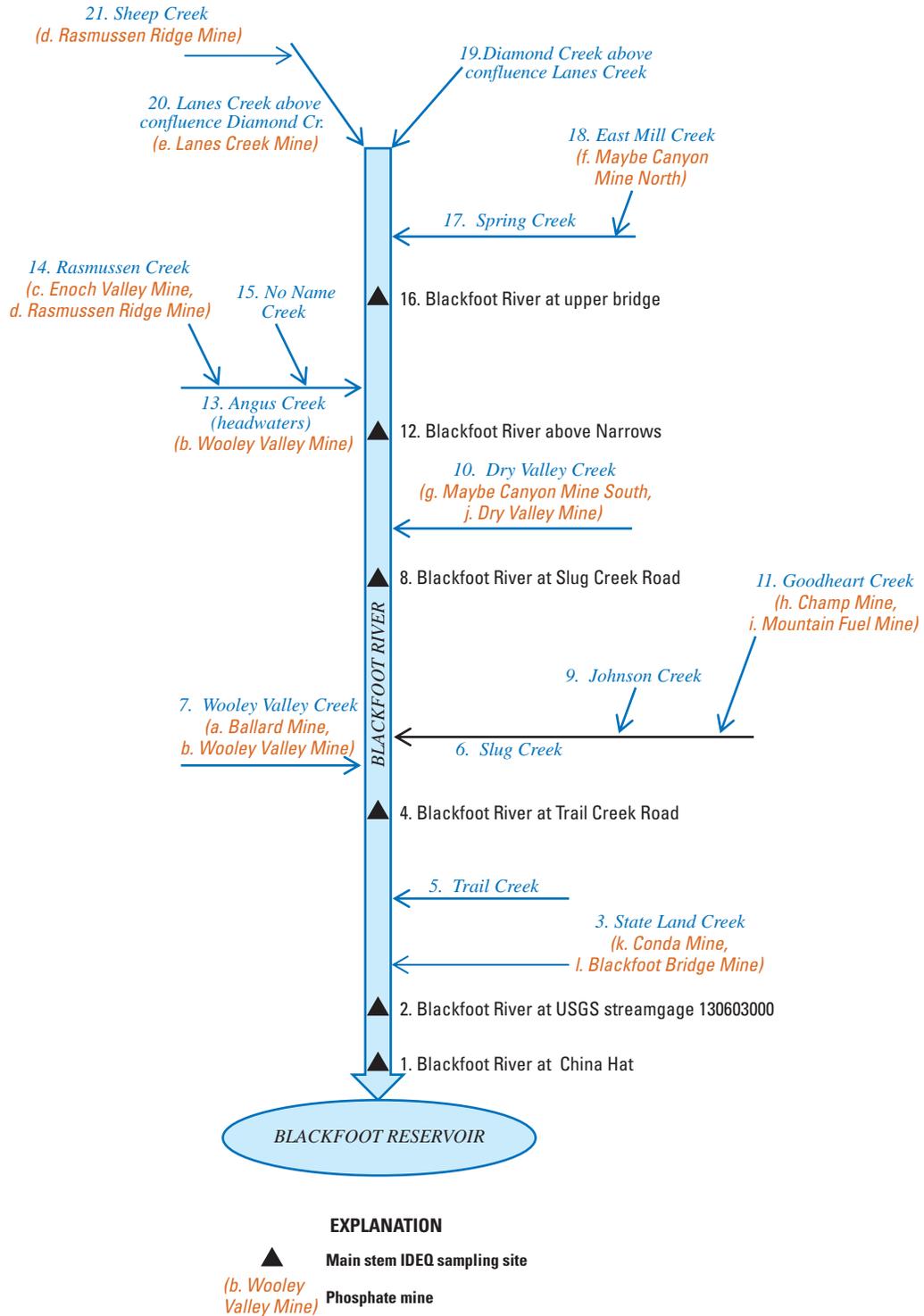


Figure 2. Hierarchy of tributaries and phosphate mines in relation to Idaho Department of Environmental Quality (IDEQ) sampling stations on the main stem upper Blackfoot River (triangles) and tributaries, Idaho. Phosphate mines located within the drainage basins of different tributaries are given in parentheses; letter and site numbers are shown in [figure 1](#) and [table 1](#).

The detection limit reported by both laboratories was usually 2 µg/L, ranging from 1 to 5 µg/L. Discharge was measured using a portable electromagnetic flow meter (Marsh-McBirney model 2000) in conjunction with a top-setting wading rod. An acoustic Doppler current profiler (ADCP; Teledyne-RD Instruments StreamPro) was used to measure streamflow on larger tributary and Blackfoot River sites. Mean streamflow was calculated from measurements taken on days 1 and 4 of the 4-day sampling periods. Flow was measured at all sites except for sites with low flows (estimated at < 0.25 ft³/s). Quality-control samples included analysis of rinsate collected from clean sampling equipment (equipment blanks) and split replicate samples.

Statistical Interpretations

Concentrations Versus Loads

Chemical concentrations and loads can inform different questions. Selenium concentration patterns and trends are important for evaluating risks to aquatic life and compliance with concentration-based regulatory standards (for example, Presser and Luoma, 2010; U.S. Environmental Protection Agency, 2014). Selenium loads, also called fluxes, are not directly relevant to risks to aquatic life. Rather, flow-normalized loads provide managers information on the progress of managing chemical sources in the watershed. Load histories also are important for understanding how water-quality affects downstream waters.

Selenium loads (mass per unit time) in the Blackfoot River at site 2, which is the same as USGS 130603000) were calculated as an amalgam of point-in-time concentrations and daily average streamflows. The selenium concentrations were determined from water samples, which were collected over a few seconds or a few minutes for the autosampled point samples or the EWI samples, respectively. The streamflows were continuously measured and were computed as daily average flows. To calculate daily loads, the point-in-time concentrations were assumed to be representative of that entire day, and loads were then calculated as mass per day. Daily selenium loads may be estimated as:

$$\text{Load (kg/d)} = Q \times C \times 2.447 \quad (1)$$

where

Q	is streamflow, in cubic feet per second,
C	is concentration, in milligrams per liter, and
2.447	is a unit conversion constant.

This equation is a simplification of

$$\text{Load (kg/d)} = Q \text{ (ft}^3\text{/s)} \times C \text{ (g/m}^3\text{)} \times 86,400 \text{ (s/d)} \\ \times 0.02832 \text{ (m}^3\text{/ft}^3\text{)} \times 0.001 \text{ (kg/g)} \quad (2)$$

where

s/d	is seconds and days.
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Statistical Methods

Statistical methods used to analyze data include descriptive statistics, univariate, and multivariate techniques. Assuming that water quality changes over time will occur, the analytical approach for temporal data emphasized describing the nature and magnitude of change. Thus, exploratory and descriptive analyses are emphasized with the time-series data. Further, the analysis of water-quality time series are complicated by data features such as non-normal distributions, seasonality, flow relatedness, missing values, and serial correlation (Hirsch and others, 1982). Thus, in addition to data graphing, analytical approaches for dampening the influence of seasonal or flow variability on selenium concentrations in the Blackfoot River to evaluate longer-term patterns included locally weighted (loess) regression with seasonally grouped datasets (Cleveland and Devlin, 1988). The nonparametric seasonal Kendall test was used to statistically evaluate whether seasonal selenium concentrations had increasing or decreasing trends over time. Calculations were made using Systat statistical software, version 12 (Wilkinson, 2010).

A multivariate technique, weighted regressions on time, discharge, and season (WRTDS; Hirsch and others, 2010), also was used with the time-series data. These techniques were developed for evaluating large datasets collected over time from fixed monitoring sites (sites with more than 10 years of record and greater than 100 samples). Generally, the techniques are intended to describe the evolving behavior of the watershed upstream of a site, without mathematically straightjacketing the analyses by assumed distributions or model structure. The procedures estimate both concentrations and loads (flux) as well as trends. The procedures are quantitative but also exploratory, with a focus on description and understanding, not on statistical significance. The data and a highly flexible smoothing model are used in WRTDS to compute an estimate of concentration and an estimate of flux for every day in the study period. The smoothing model expresses the behavior as a combination of influences of (1) time trend, (2) discharge, (3) seasonal cycle, and (4) a random component (Hirsch and others, 2010).

For data collected annually by IDEQ from throughout the upper Blackfoot River watershed, univariate techniques for statistically comparing concentrations from different locations were useful. Although water-quality datasets commonly are log-normally distributed, likely because the IDEQ samples were always collected during May each year, the data did not severely depart from assumptions of normality implicit in classical parametric techniques, including analysis of variance (ANOVA) and pairwise comparisons of groups. The non-parametric Kruskal-Wallis test, which is based on relative ranks rather than absolute values, also was used to test the probability of whether differences in selenium concentrations from different data groups likely could be attributed to chance (Helsel and Hirsch, 2002). These include comparisons between USGS and IDEQ data collected at the same site over similar time frames, and comparisons of data

collected from different locations on the mainstem Blackfoot River. In tests requiring judgment of “statistical significance,” if the probability of a result was solely due to chance was greater than 10 percent (P-values of >0.1), the test was considered “insignificant.”

Selenium in the Upper Blackfoot River Watershed

Although the water quality analyses conducted through this study have included several trace elements and major ions, this report focuses on selenium results. Trace elements other than selenium and major ions in the study area are presented in [appendix E](#).

Data Quality

Low-level selenium contamination ($0.03 \mu\text{g/L}$) in ambient blank samples exposed within the autosampler was detected in 1 of 21 ambient blank sample exposures. This very low level of potential contamination is more than 150 times lower than the current $5 \mu\text{g/L}$ aquatic life criterion for selenium and does not affect the presentation or interpretation of the environmental data.

Variability in matched replicate samples collected by the automated sampler, grab samples from a single point in the stream channel, or EWI samples was evaluated by comparing the relative standard deviation (RSD), also known as the coefficient of variability, and is defined as the standard deviation of all replicates values, divided by the average, expressed as a percentage. Twenty matched sets of automatically collected, grab, and EWI selenium samples were evaluated. These matched sets were collected at least once annually, and in most years twice annually, once during low flows and once during higher but still wadeable flows. Of these, 90 percent of the RSD comparisons were 8.3 percent or less, and the median RSD was 2.5 percent, indicating low sampling and laboratory variability. Details of these comparisons are presented in [appendix C](#).

For the vast majority of the selenium samples, the similar results between grab samples and automatically collected samples indicate that the sampler pumping system did not significantly affect samples. Likewise, the similarity between most grab and EWI collected samples indicates that the automatic sampler represented dissolved selenium well in the stream cross section.

Laboratory Results Compared With Most Probable Values From Standard Reference Samples

Underlying the variability in the comparisons among the field sampling methods is the intrinsic measurement uncertainty of the laboratory analyses. Thus, we considered the measurement uncertainty of the laboratory analyses by evaluating the accuracy and bias of selenium results obtained for blind, standard reference samples. Over the period of the study, 2001–12, the USGS National Water Quality Laboratory analyzed 1,608 blind standard reference samples (filtered river water samples that had been spiked with selenium and other inorganics). These results were matched with the most probable values (MPVs) obtained from round-robin sampling. Details of these evaluations are presented in [appendix C](#).

The results of these evaluations were indicated that over the range of selenium concentrations tested through the standard reference samples (approximately $0.7\text{--}8 \mu\text{g/L}$), the inherent measurement uncertainty of any given reported laboratory selenium value had about a 90 percent probability of being within a range of about 15 percent greater than or 27 percent less than the “true” selenium concentration. From about 2003 through 2012, laboratory analyses of filtered selenium tended to have a slight low bias, ranging from -10 to -1 percent.

Quality-Control Evaluations of the IDEQ Data

In the two to three equipment blanks sampled per year by IDEQ from 2004 through 2012, no selenium was detected in any sample, with the detection limit ranging from 1 to $3 \mu\text{g/L}$. Variability in the IDEQ data was examined through relative percent differences (RPDs). Relative percent difference is a similar statistic to the RSD, except that for duplicate samples, instead of using the standard deviation, the absolute value of the percent difference between the two samples defines the RPD. That is, $\text{RPD} = |A-B|/((A+B)/2)$, where A and B are the concentration values. The median RPD from the IDEQ samples was 11 percent, ranging from 0 to 59 percent ([appendix C](#), table C2).

Comparability of USGS and IDEQ Selenium Data

To evaluate the comparability of the USGS and IDEQ data, selenium concentrations collected by the two agencies at site 2, which is the same location as the USGS site, Blackfoot River above reservoir near Henry, Idaho (13063000).

The IDEQ results, consisting of 4-day composite whole water samples collected annually between May 20 and June 4 from 2004 to 2012, resulted in an average selenium concentration of 5.5 $\mu\text{g/L}$ (standard deviation 2.3, range 2–8.6 $\mu\text{g/L}$, $n=8$). The USGS 0.45 μm filtered samples, constrained to the same annual time frame from 2004 to 2008, had an average dissolved selenium concentration of 5.9 $\mu\text{g/L}$, standard deviation 2.1, range 1.2 to 11.6 $\mu\text{g/L}$, $n=66$). The probability that these differences were simply due to chance was about 60 percent ($P=0.61$, parametric t-test). For the purposes of this study, these results indicate that the two data sets are comparable.

Selenium Speciation

In the selenium speciation analyses, selenate and selenite dominated selenium speciation (fig. 3). The median percentage of total selenium as selenate was 81 percent, ranging from 17 to 98 percent, and the median percentage of total selenium as selenite was 19 percent, ranging from 2 to 83 percent of the total selenium. Organic selenium was negligible in all samples. In both years, selenate was more abundant during the spring runoff, and selenite occasionally was dominant during the late summer low flows.

Because selenate is favored in alkaline and well-oxidized environments, and because Blackfoot River water tended to be slightly alkaline during the speciation study (average pH during 2004 was 8.4, ranging from 7.2 to 8.9, $n=34$), the dominance of selenate was expected. However, selenite tended to be dominant during June to August in 2003 and 2004 (fig. 3). This suggests dissolution of sediment-bound selenium into the water column for several reasons. Selenium in surface sediments in a Blackfoot River tributary has been shown to be primarily present as selenite (Oram and others, 2010). Although selenite is much less soluble than selenate, studies of sediment-water interchange of selenium in low-energy, vegetated lake or wetland environments, showed that dissolved selenite was released to porewaters in the near-surface sediments resulting in the diffusive transport of these species into the water column (Martin and others, 2011). Selenium can substitute for sulfur and form selenium-substituted pyrite (McNeal and Balistrieri, 1989). Because the oxidation and dissolution of pyrite is an important process in circumneutral natural waters, Oram and others (2008) suggested that the dissolution of Se-substituted pyrite in Blackfoot River sediments might be a continuous, long-term source of dissolved selenium into the water column.

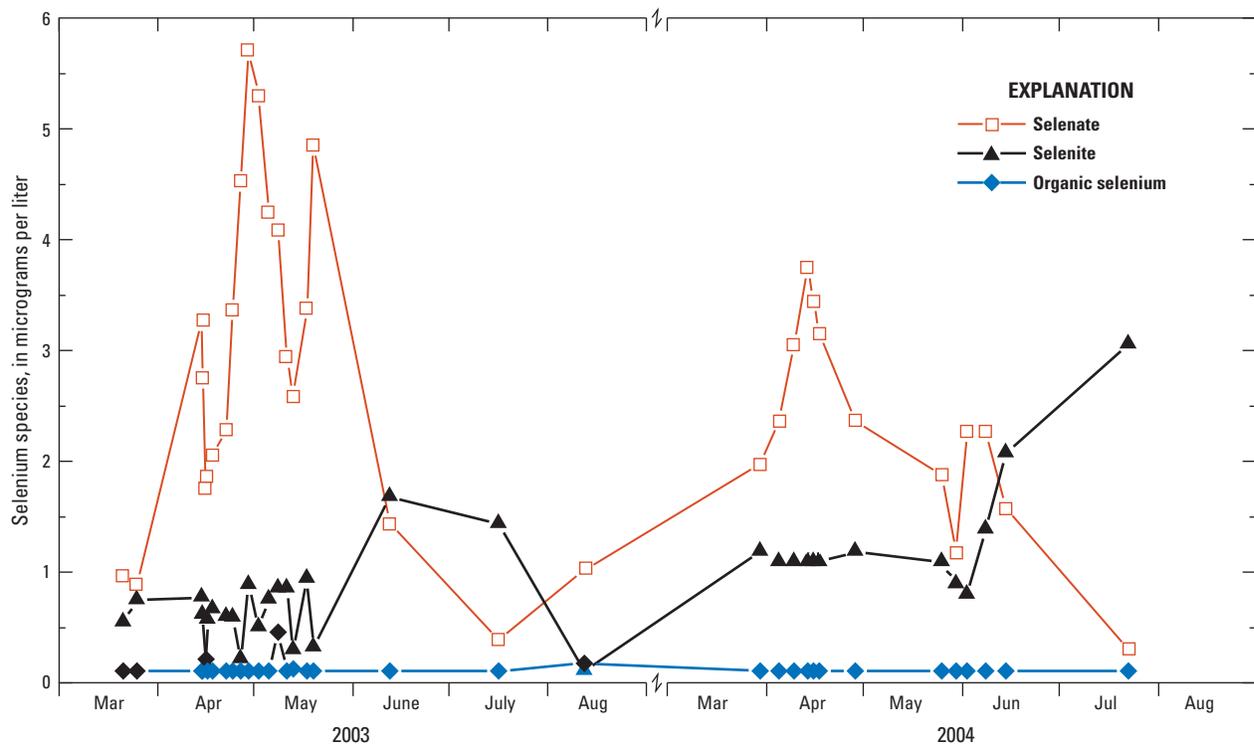


Figure 3. Selenium-species composition in the Blackfoot River above reservoir near Henry, Idaho (13063000), 2003 and 2004.

Temporal Patterns and Trends in Selenium Concentrations and Loads

Descriptive Patterns

Dissolved selenium concentrations in water samples collected by the USGS from 2001 through 2012 at the Blackfoot River near Henry (site 2) ranged from a minimum of 0.5 µg/L to a maximum of 11.4 µg/L with a median concentration of 3 µg/L (table 2, fig. 4). Concentrations tended to be elevated during the period of snowmelt runoff in April and May and decreased substantially during the recession of the runoff hydrograph and during base flow conditions throughout the remainder of the year. During base flow conditions, dissolved selenium concentrations consistently ranged from 1 to 3 µg/L. In contrast, the median total selenium concentration from a statewide, randomized survey of 55 rivers in Idaho was 0.14 µg/L, ranging from less than 0.09 to 1.75 µg/L (Essig, 2010).

The State of Idaho aquatic-life criterion concentration for selenium (5 µg/L) was equaled or exceeded in 142 of the 450 (31 percent) discrete water samples collected from 2001 to 2012. Of the criterion exceedances, 80 percent occurred during the month of May. No exceedances of the selenium criterion occurred other than during April, May, or June.

The relation between streamflow and selenium concentration is complex. Concentrations generally tend to be positively correlated with streamflow and large concentrations tended to occur in years with large streamflows (figs. 5 and 6); however, this is not always the case. In 2007, the annual maximum streamflow was 350 ft³/s and the corresponding maximum selenium concentration that year was 9.4 µg/L (figs. 6 and 7). Conversely, the maximum annual streamflows in 2006 and 2008 were substantially larger than 350 ft³/s, but the corresponding maximum selenium concentrations were less than 9.4 µg/L, the maximum concentration in 2007 (figs. 6 and 7). Similar disparities in the positive correlation between streamflow and selenium concentration were noted throughout the period of record. This finding indicates that streamflow magnitude, as measured at the outlet of the upper watershed, is not the only controlling factor for selenium concentrations at the same location.

The relation between streamflow and selenium concentration is further complicated because annual patterns in selenium concentrations and streamflow tended to show one or more peak, with the peak selenium concentrations always lagging the peak streamflow. The lag time between peak streamflows and peak selenium concentrations was shorter during high flow years. The median lag time between peak streamflows and peak selenium concentrations was 14 days, ranging from 2 days in 2006 and 2011 to 36 days in 2004 (fig. 7, table 3). Generally, for each spring runoff

Table 2. Summary statistics of dissolved selenium concentrations from U.S. Geological Survey data collected from streamgauge Blackfoot River above reservoir near Henry, Idaho (13063000), 2001–12.

[Raw data, including more recent data, are available for download at <http://waterdata.usgs.gov/nwis>, accessed April 1, 2014. µg/L, microgram per liter]

Statistic	Selenium, dissolved (µg/L)	
	Counts	Percent of group
Maximum	11.4	
Minimum	0.5	
Average	3.7	
Lower quartile (25th percentile)	2.0	
Median	3.0	
Upper quartile (75th percentile)	5.2	
Number of samples (n)	450	
Number of samples exceeding the Idaho aquatic life criterion of 5 µg/L	142	31
Number of April samples greater than 5 µg/L	24	17
Number of May samples greater than 5 µg/L	113	80
Number of June samples greater than 5 µg/L	4	8

period, there have been one to two streamflow peaks and one to two dissolved selenium concentration peaks. The lags between annual streamflow peaks and selenium-concentration peaks in table 3 were highly correlated (Pearson's $r = -0.80$; coefficient of determination (R^2), 0.64, $P = 0.003$, excluding uncertain 2001 values). The shortest time lags occurred during high-flow years; longer lags occurred during low-flow years.

Conceptually, the time lags between the peak streamflow and peak selenium concentrations indicate that the cross-valley fill mine dumps are the primary selenium contributors, rather than diffuse surface runoff or shallow groundwater plumes. Cross-valley fill mine dumps act as reservoirs with porous dams that attenuate and delay the through flow of infiltrated water, compared to natural channels (Amacher and others, 1995; Mars and Crowley, 2003). The mine waste rock dumps are constructed with French drains of coarse durable rock (chert), over which the less durable black-shale waste spoils are placed. The coarse rock in the French drains readily pass water, but with a more tortuous path and longer travel times than a natural stream channel (Sidle and others, 1994).

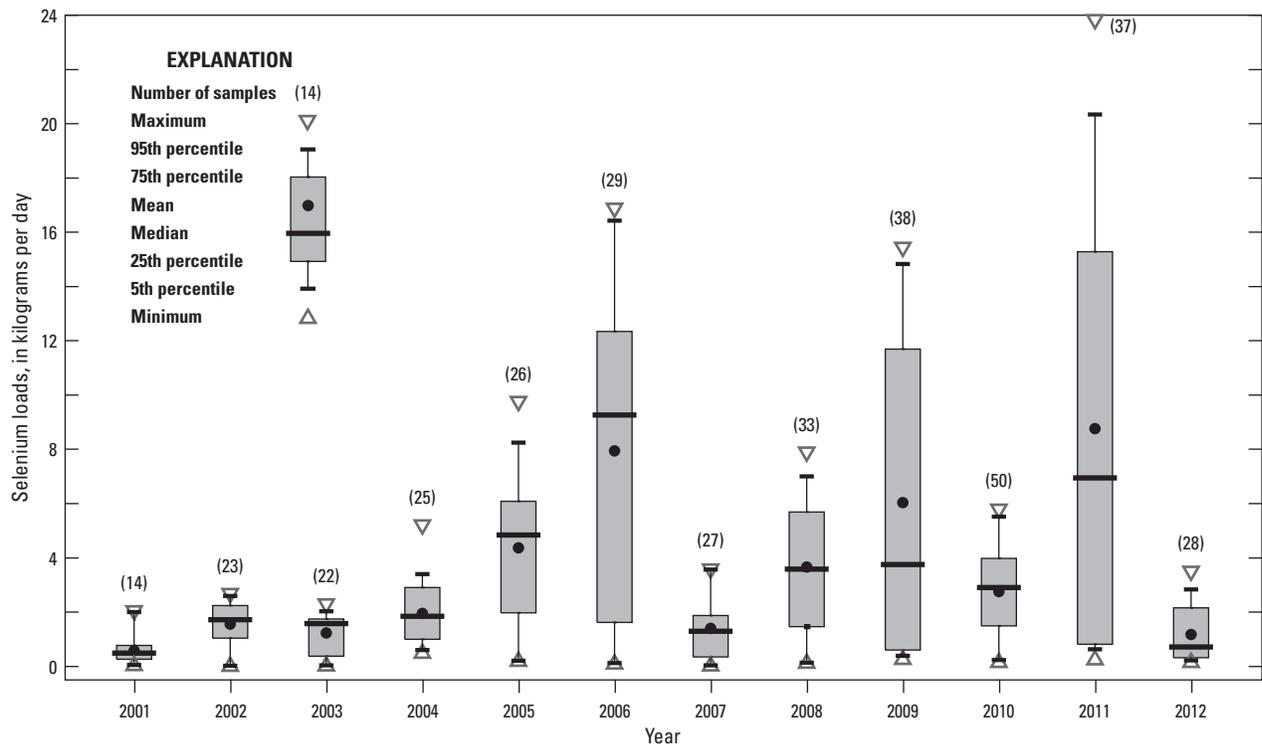
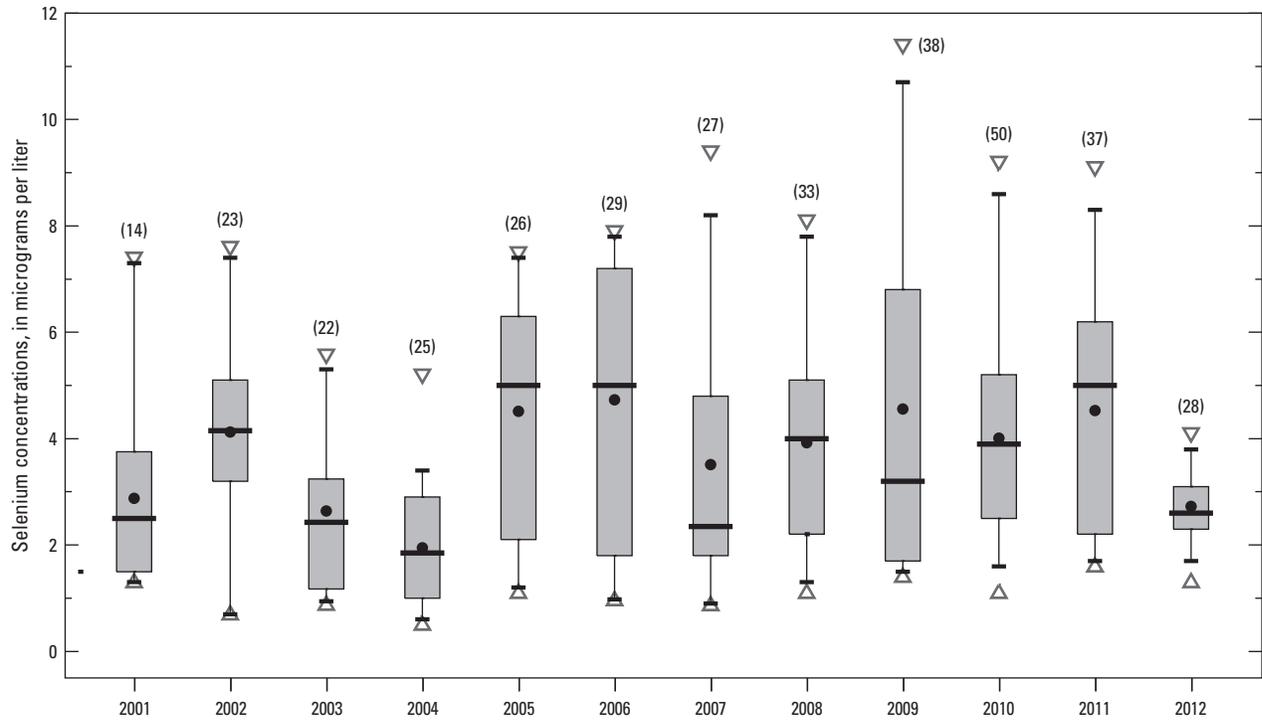


Figure 4. Dissolved selenium concentrations and daily loads at the Blackfoot River above reservoir near Henry, Idaho (13063000), 2001–12.

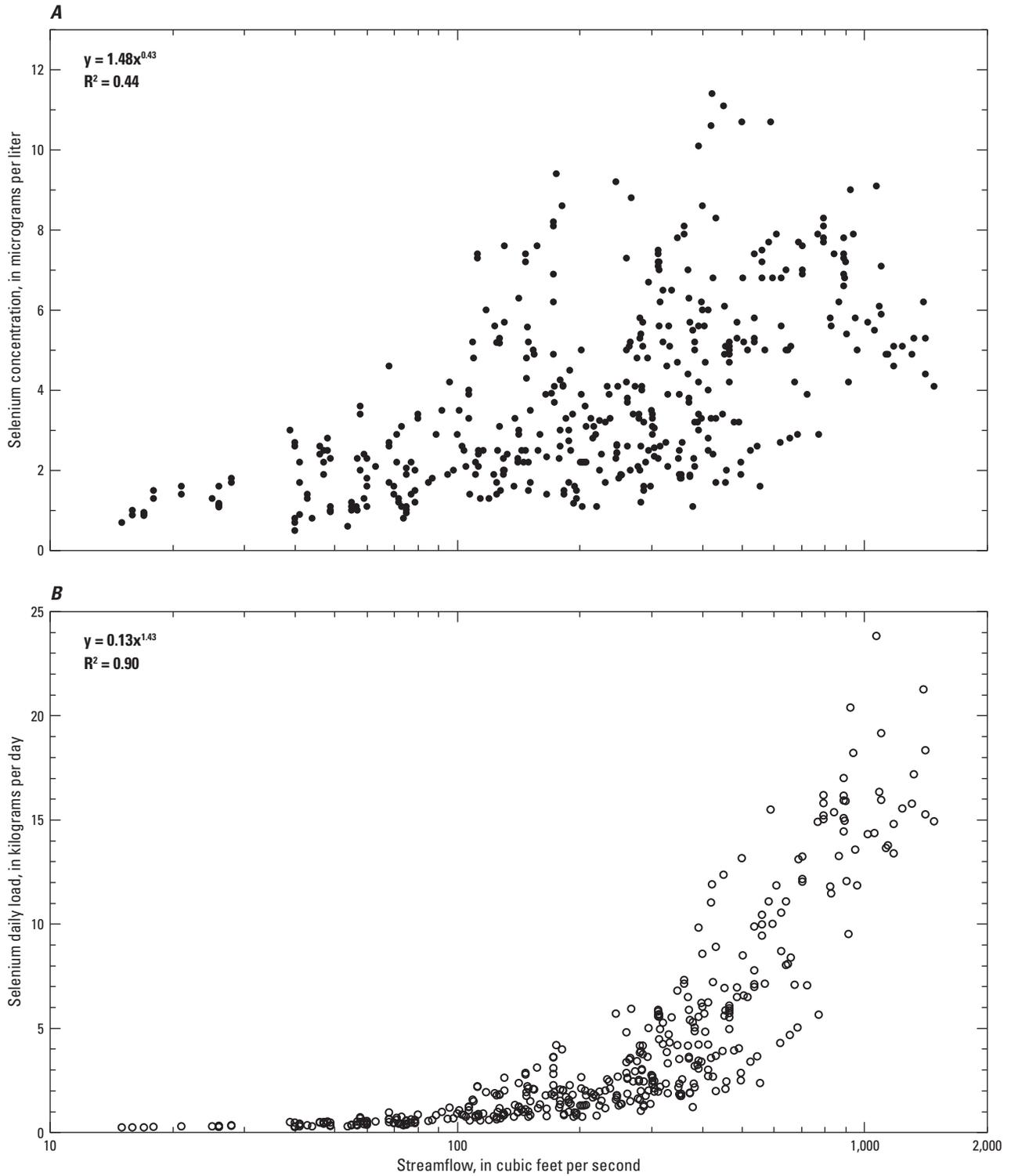


Figure 5. Streamflow dependence of selenium (A) concentrations and (B) daily load, for data collected at the Blackfoot River above reservoir near Henry, Idaho (13063000), 2001–12.

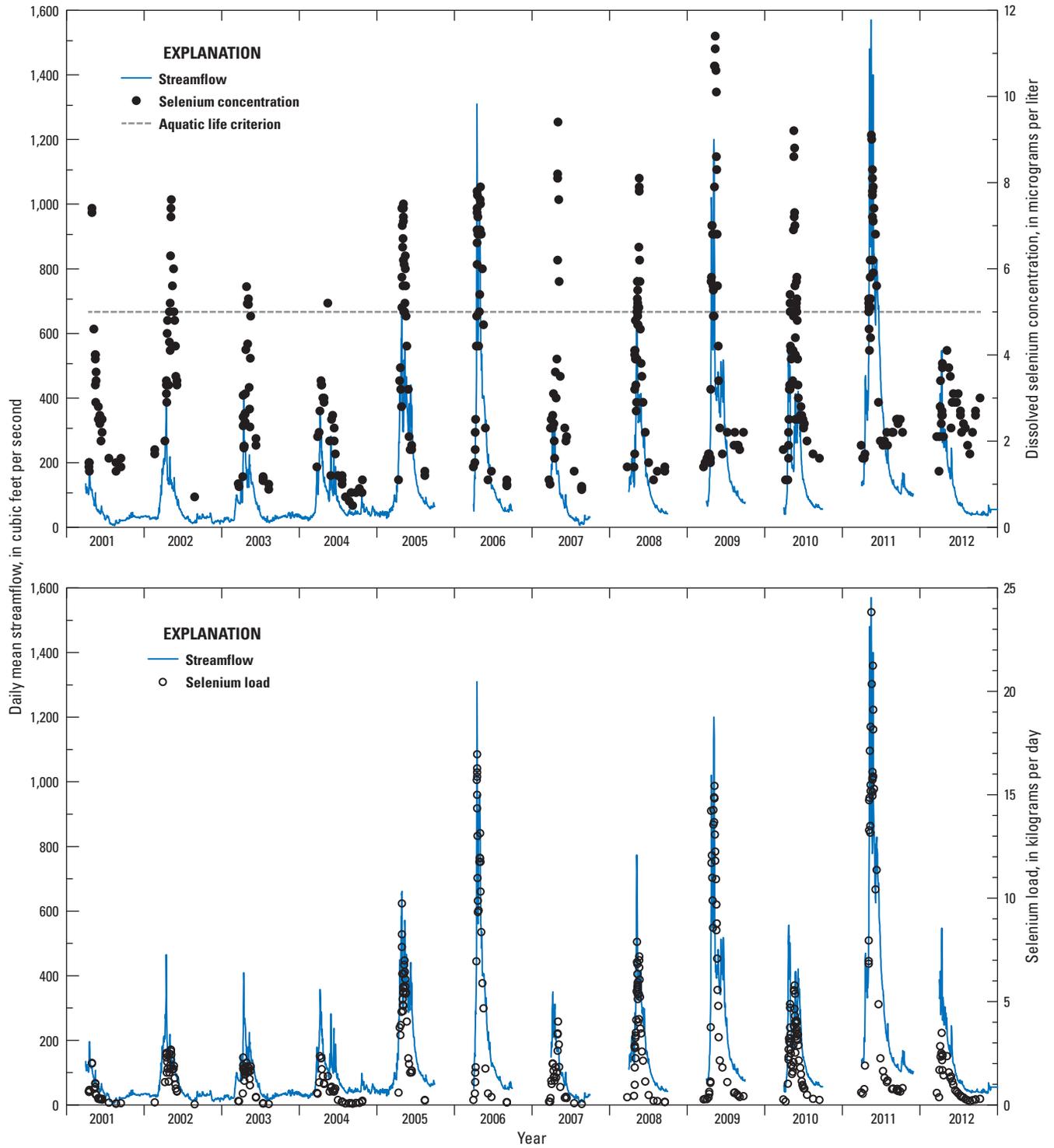


Figure 6. Long-term patterns of daily mean streamflow and (A) dissolved selenium concentrations and (B) selenium loads at the Blackfoot River above reservoir near Henry, Idaho (13063000), 2001–12.

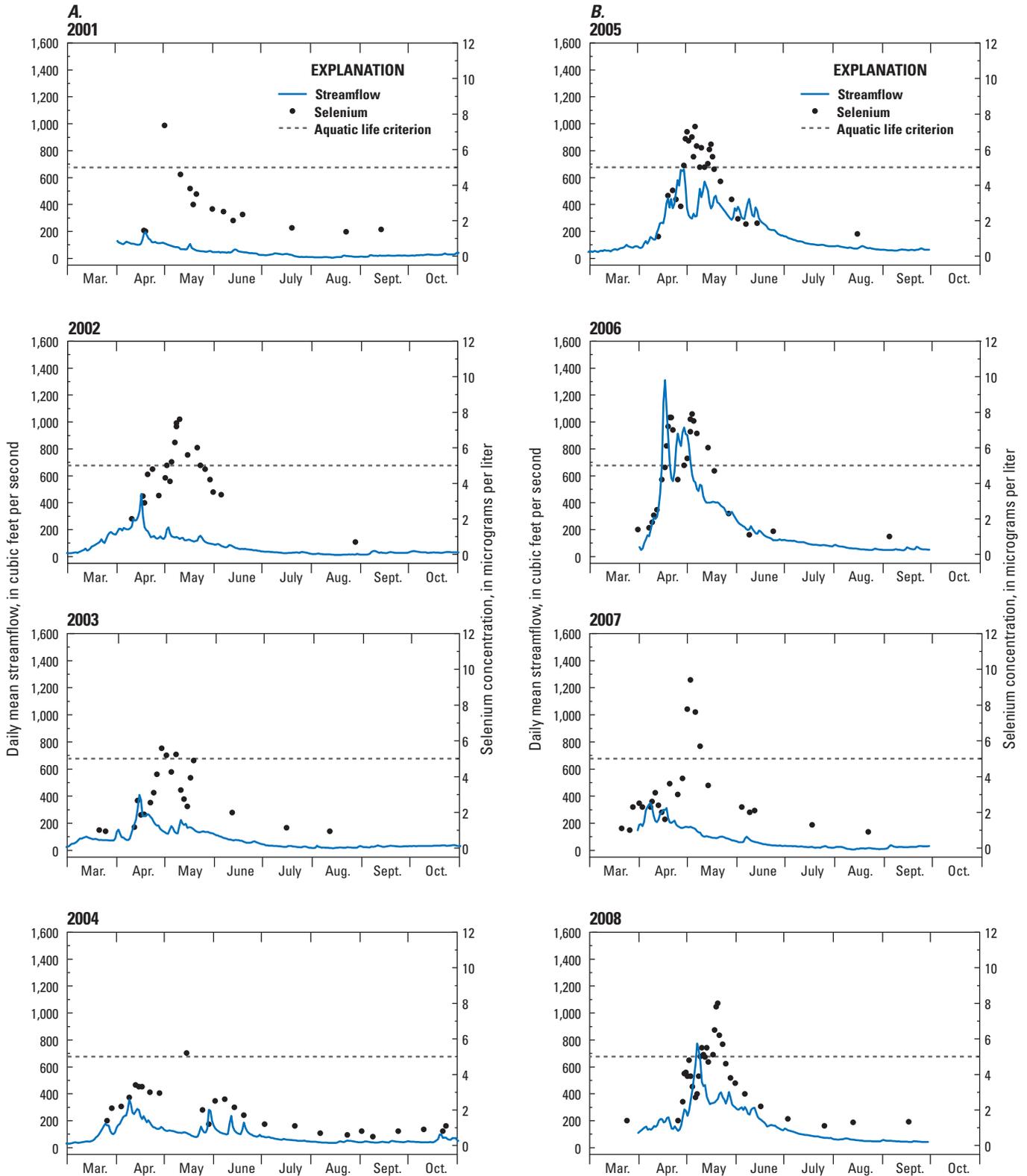


Figure 7. Annual patterns of dissolved selenium concentrations and daily mean streamflow in the Blackfoot River above reservoir near Henry, Idaho (13063000). (A) 2001–04, (B) 2005–08, and (C) 2009–12.

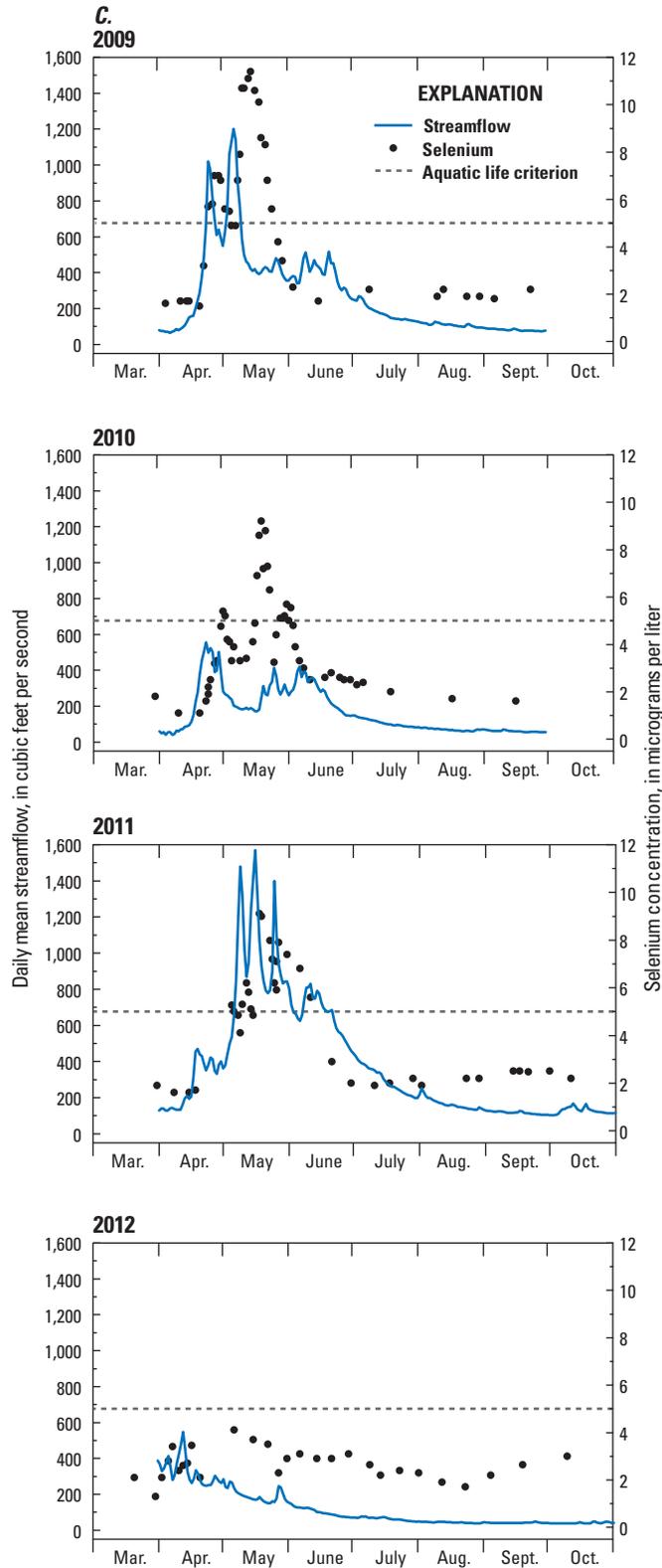


Figure 7.—Continued

Table 3. Lag times between peak selenium concentrations, peak streamflow, and ranges of dissolved selenium concentrations and streamflows measured when selenium samples were collected at the Blackfoot River above reservoir near Henry, Idaho, (13063000), 2001–12.

[Data collected by U.S. Geological Survey. **Number of selenium samples:** Includes quality-control samples. $\mu\text{g/L}$, microgram per liter; ft^3/s , cubic foot per second]

Year	Selenium ($\mu\text{g/L}$)		Number of selenium samples	Streamflow (ft^3/s)		Lag time between peak streamflows and peak selenium concentrations
	Minimum	Maximum		Minimum	Maximum	Days
2001	1.3	7.4	28	22	¹ 220	¹ 12
2002	0.7	7.6	29	16	284	23
2003	0.9	5.6	33	29	471	13
2004	0.5	5.2	34	38	353	36
2005	1.1	7.5	35	72	688	3
2006	1.0	7.9	35	48	1,360	2
2007	0.9	9.4	32	17	349	30
2008	1.1	8.1	45	42	684	20
2009	1.4	11.4	47	77	1,347	7
2010	1.1	9.2	60	60	556	26
2011	1.6	9.1	49	105	1,540	2
2012	1.3	4.1	35	39	558	24

¹Questionable values; peak flows may have occurred prior to the start of monitoring.

Geochemically, during the dry periods of the year, highly soluble selenium might be detected in easily hydrolyzed salts, be adsorbed to mineral surfaces of the waste rock, or both. Following percolation of new water into the dumps from snowmelt, high concentrations of selenium would be pushed out of the waste dumps into the stream headwaters, which lead to peak selenium concentration after the basin-wide streamflows. This concept is supported by the slow rates for selenium enriched waste shale to pass infiltrated water, on the order of 32–145 ft/yr (Riker and others, 1978; Sidle and others, 1994), and by experiments by Stillings and Amacher (2010). The kinetics of selenium release from waste rock from a cross-valley fill in Wooley Valley Mine (mine “b” in [fig. 1](#)) was evaluated by Stillings and Amacher (2010) in laboratory tests using packed bed reactors and in field tests. In every experiment, selenium concentrations in outlet flows were initially high, and then decreased to a much lower, steady-state concentration. Additionally, when flow was resumed after a period of drying, selenium in the reactor outlets would peak before beginning another exponential decrease. Field samples of selenium from the waste dump seeps showed a decrease from 3,600 $\mu\text{g/L}$ in the initial snowmelt driven discharge, to 10 $\mu\text{g/L}$ by September (Stillings and Amacher, 2010). The seasonal time-course of decreases in selenium concentrations recorded in waste dumps from the Wooley Valley Mine are congruent with seasonal decreases in selenium concentrations measured in East Mill Creek (site 18) downstream of the North Maybe Canyon Mine ([table 4](#); [fig. 1](#)).

Together, these hydrological and geochemical factors are congruent with the consistent lags in the timing of streamflow and selenium peaks, and indicate that the cross-valley waste-rock dumps are persistent sources of selenium in the upper Blackfoot River.

Statistical Trends

Time-series data that monotonically increase or decrease can be analyzed as a correlation using Kendall’s nonparametric tau statistic treating time as one of the variables (the Mann-Kendall test). Water-quality data and any time-series data with a non-monotonic, seasonal, or any other repetitive cyclical variation require modification of the Mann-Kendall test, such as monthly “seasons” for data collected monthly over years (Hirsch and others, 1982). August through October was defined as the low-flow season as streamflow was usually low and uniform during this period. The timing of annual peaks in selenium concentration varied, but often occurred during the month of May ([fig. 7](#)), and so the month of May was considered to be the high-flow “season.”

These seasonally constrained comparisons show that during the period of study, selenium has tended to increase during the low-flow conditions, with the median selenium concentrations roughly doubled from a low in 2004 to a high in 2012. Although the Kendall tau statistic was “significant” for an upward trend with the May samples, the concentrations were more variable over time and lower in 2012 ([fig. 8](#)).

Table 4. Attenuation of selenium loads in five synoptic surveys from the headwaters of East Mill Creek to the mouth of Spring Creek, upper Blackfoot River watershed, southeastern Idaho, 2010–12.

[Using dissolved (0.45 μm filtered) concentrations for consistency with other loads reported in this report. Total selenium also was measured in these surveys and was always similar to the filtered concentrations, which indicated that essentially all selenium was present as dissolved selenium. Data from Millennium Science & Engineering (2011); Ecology and Environment (2012; 2013). **Abbreviations:** $\mu\text{g/L}$, microgram per liter; kg/d , kilogram per day]

Synoptic survey	Selenium concentrations ($\mu\text{g/L}$)		Selenium loads (kg/d)		Load reductions (percent)
	Upper East Mill Creek	Near mouth of Spring Creek	Upper East Mill Creek	Lower Spring Creek	
High flow, May 10, 2010	2,790	23	2.85	1.04	64
High flow, June 7, 2010	2,480	16	6.67	2.92	56
High flow, June 2, 2011	3,100	24	20.2	6.1	70
High flow, May 2, 2012	2,400	31	2.7	2.2	17
Low flow, September 27, 2012	1,700	2.5	0.18	0.06	68

Trends in the low flow data were further examined using flow normalized annual average concentrations through weighted regressions of time, discharge, and season (Hirsch and others, 2010). Flow-normalization allows reducing the influence of the year-to-year variation in discharge, while retaining the natural seasonal variation in discharge. The procedure computes the estimated concentration, the flow-normalized concentration, the estimated load (flow times concentration), and the flow-normalized flux (by integrating flux over the frequency distribution of flow) for every day. Flow-normalization statistically removes the influence of the temporal pattern of discharge by viewing the discharge on any given day as a random sample of the discharges that might have taken place on that day. The flow-normalized concentration and load estimates are summarized into time series of monthly averages, which, in turn, are summarized into annual, seasonal averages. The flow-normalized, selenium concentrations for the August–October season show a generally increasing trend from 2001 through 2012, increasing about 8 percent per year on average (fig. 9). The resulting flow-normalized annual concentration histories are smooth temporally (fig. 9) because they eliminate the variation that is due to the random variation in streamflow. Because these flow-normalized records are not driven by random variations in streamflow and because they are much more stable than the

actual recorded water quality data, they are appropriate to use when computing changes over time.

The temporal variability in daily loads of selenium at the Blackfoot River near Henry (site 2) was also estimated using WRTDS (fig. 10). Because concentrations tended to be higher during high flow periods (figs. 5–7), and because loads were calculated as concentration times flow, the loads at the Blackfoot River at Henry are driven by streamflow. Therefore, the highest loads were measured during the high-flow years (2006, 2009, and 2011), and lower peak loads were measured during low-flow years.

The likely mechanisms related to the increasing selenium concentrations during low streamflow are not obvious. Conceptually, the long and complex groundwater-flow paths could be related to increasing selenium concentrations in the Blackfoot River, independent from surface runoff from the mine dumps. Groundwater selenium concentrations in the vicinity of the North Maybe Canyon mine were noted to be generally increasing as of 2012, even though mining had ended by 1993 (Lee, 2001; Ecology and Environment, 2013). Groundwater fluxes to the Blackfoot River were estimated to require as many as 80 years to approach steady state, based on a conceptual model of groundwater transport of selenium (Myers, 2013).

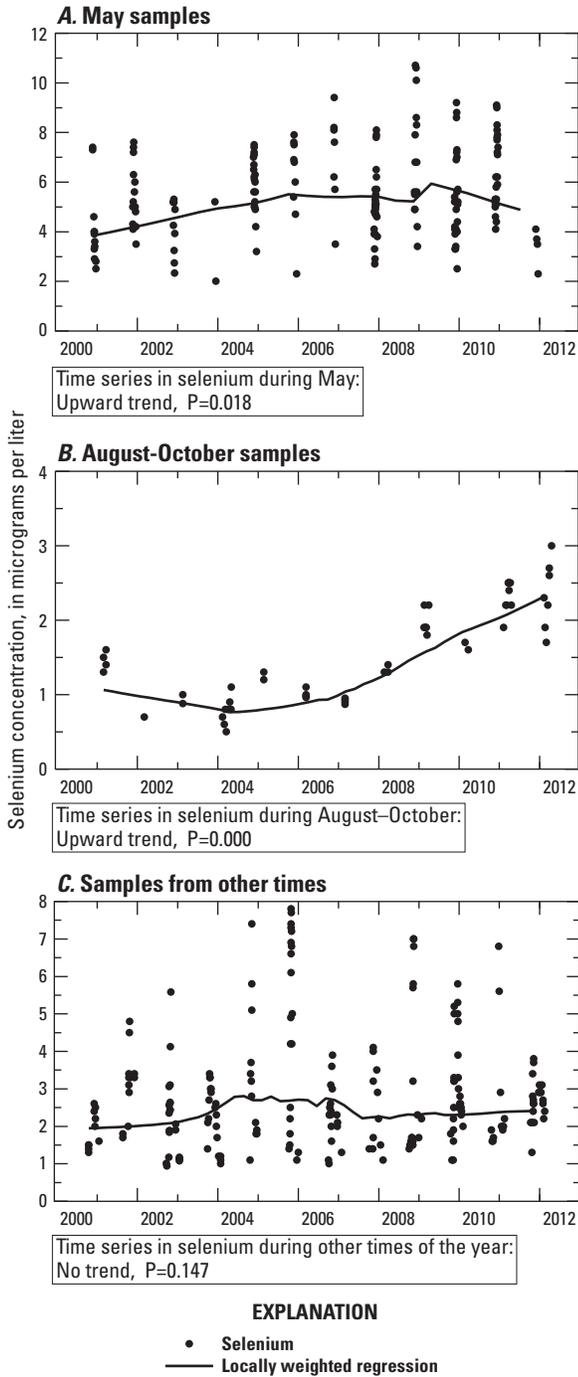


Figure 8. Seasonal time-series graphs showing dissolved selenium in the Blackfoot River above reservoir near Henry, Idaho (13063000). The probabilities of upward, downward, or no trend over time in the seasonal groups are from the Mann-Kendall test, where P, probability values, greater than 0.10 are considered not significant. Note differences in scale of the vertical axis.

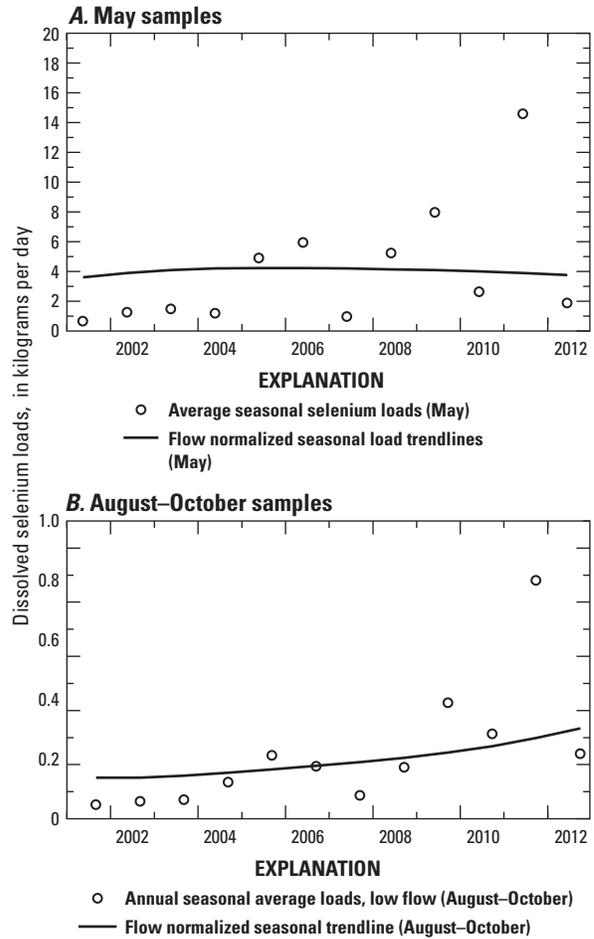


Figure 9. Average annual selenium loads by season, with flow normalized seasonal average loads at the Blackfoot River above reservoir near Henry, Idaho (13063000), 2001–12. The season was alternately defined as (A) May of each year to reflect annual high-flow periods or (B) August–October to reflect annual low-flow periods.

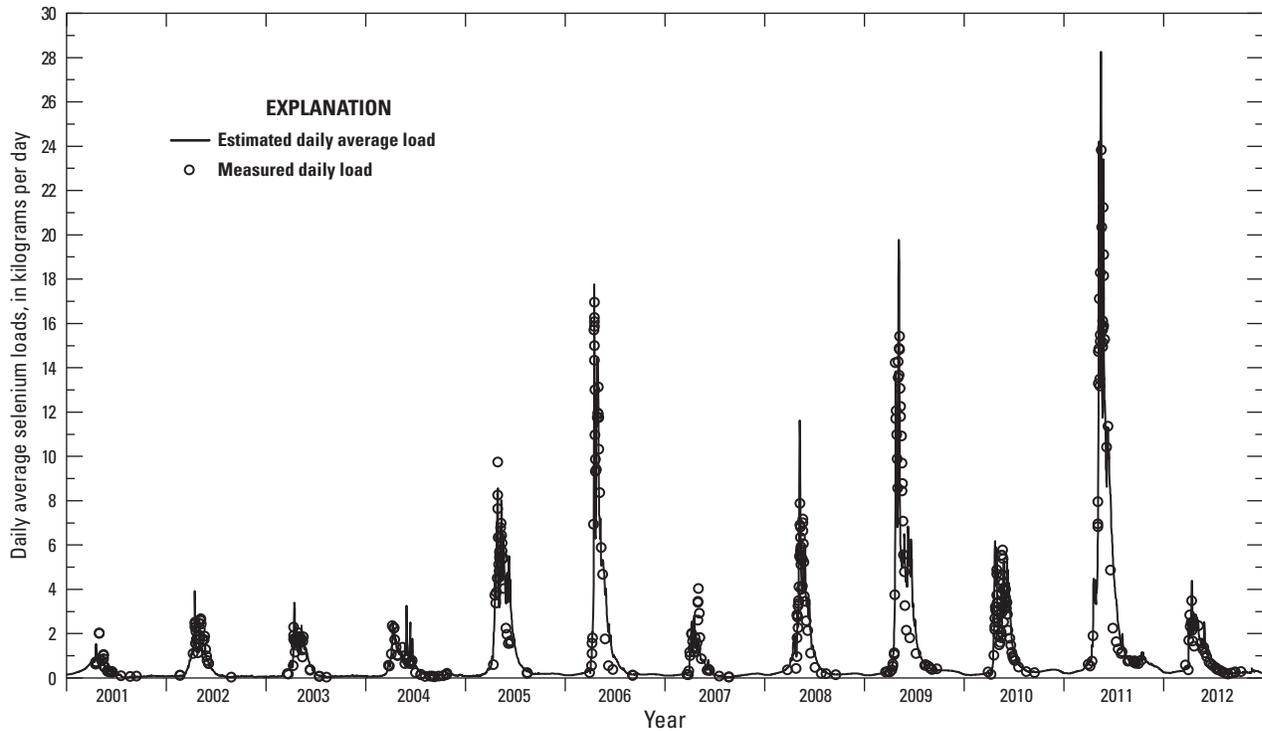


Figure 10. Variability in daily average dissolved selenium loads at the Blackfoot River above reservoir near Henry, Idaho (13063000), 2001–12.

Spatial Patterns in Selenium Concentrations and Loads

Selenium Concentrations

Complementing the USGS sampling and temporal patterns and trends in selenium concentrations and loads at the outlet of the upper Blackfoot River watershed is the IDEQ data collected at multiple main stem and tributary sites. This IDEQ watershed-wide dataset allows for an analysis of spatial patterns and trends in selenium concentration and loads throughout the upper watershed. The spatial analysis is presented to identify the relative selenium contributions from potential source areas. Six of the 21 IDEQ sampling locations are on the main stem Blackfoot River, and the remainder are distributed among the tributaries (figs. 1 and 2; appendix A).

Selenium concentrations in the main stem and tributaries of the upper Blackfoot River watershed were in a relatively consistent pattern from 2001–12 (fig. 11). Concentrations exceeded the State of Idaho selenium criterion (5 $\mu\text{g/L}$) in

about 50 percent of all samples collected at all main stem sites. Selenium concentrations in the sampled tributaries ranged from less than 2 to 870 $\mu\text{g/L}$, and concentrations in 8 of the 15 sampled tributaries typically exceeded the State of Idaho criterion (fig. 11). The mapped start of the “Blackfoot River” is the confluence of Lanes and Diamond Creeks, and selenium concentrations in these tributaries, sampled just upstream of their confluences, were uniformly low at less than 2 $\mu\text{g/L}$ (fig. 11).

Dry Valley Creek (site 10) was successfully sampled by the IDEQ crews only three times (2004, 2006, and 2008), with selenium concentrations ranging from 6.2 to 8.2 $\mu\text{g/L}$ (appendix D). However, Whetstone Associates (2012) obtained 11 samples from lower Dry Valley Creek during spring runoff over the same period as the IDEQ sampling (2001–12). This larger dataset shows a much larger range of concentrations (1.3–119 $\mu\text{g/L}$) than the IDEQ data, and thus the more complete Whetstone Associates dataset is shown in the box plots in figures 11 and 12 instead of the smaller IDEQ dataset.

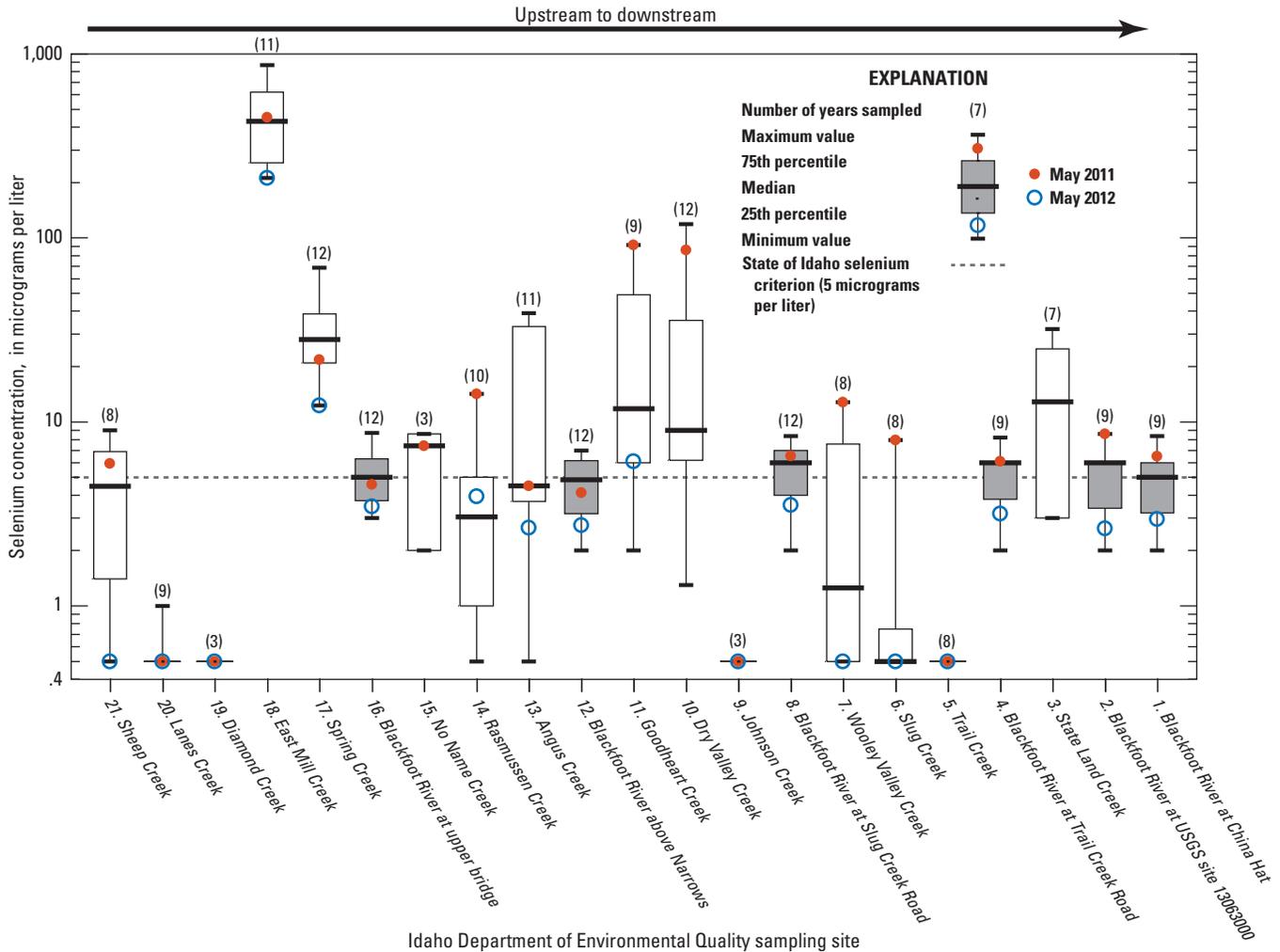


Figure 11. Selenium concentrations (whole water) in annual Idaho Department of Environmental Quality May sampling of main stem Blackfoot River (gray-shaded boxes) and tributaries, Idaho, 2001–12. Recent data points from years with larger (May 2011) and smaller (May 2012) snowmelt runoff are shown. For plotting concentrations and calculating loads, non-detected selenium concentrations (<2 micrograms per liter [$\mu\text{g/L}$]) were set at 0.5 $\mu\text{g/L}$, which was the lowest concentration in the USGS sampling at the Blackfoot River above reservoir near Henry (13063000). Data for site 10 are from Whetstone Associates (2012).

Spring Creek joins the Blackfoot River 0.6 km downstream of its origin at the confluence of Lanes and Diamond Creeks, which increases median selenium concentrations in the Blackfoot River by about a factor of 10. Although moderately elevated selenium concentrations were detected in various other mining influenced tributaries, Spring Creek had the highest median selenium concentration (28 $\mu\text{g/L}$) of the tributaries that flow directly into the Blackfoot River (figs. 2 and 11). The elevated concentrations in Spring Creek originate from East Mill Creek, which had a median selenium concentration of 435 $\mu\text{g/L}$ and a concentration range of 212 to 870 $\mu\text{g/L}$ during the study period.

The median selenium concentrations in the main stem Blackfoot River changed little from the confluence of Spring Creek to its outlet (fig. 11). Both the median and average concentrations at all six main stem sites ranged from 5 to 6 $\mu\text{g/L}$, with the total range of data from 2 to 8.6 $\mu\text{g/L}$ ($n=9$ to 12 per site). The concentrations at these six sites were not statistically different when tested either by analysis of variance ($P=0.94$) or by the non-parametric Kruskal-Wallis test ($P=0.92$). The P values greater than 0.9 suggest that there is greater than 90 percent probability that the differences in selenium concentrations between main stem Blackfoot River sites were solely due to chance and main stem selenium concentrations are statistically similar.

Selenium Loads

The largest discrete tributary loads of selenium to the Blackfoot River were usually from East Mill Creek, via Spring Creek. In contrast to selenium concentrations, which decreased by almost a factor of 100 from East Mill Creek to Spring Creek to the Blackfoot River, selenium loads decreased by less than a factor of 2 over the same reach (fig. 12). If concentrations decrease but loads remain similar, that indicates that the decrease in selenium concentrations was from simple dilution rather than losses. The reduction in loads from East Mill Creek to Spring Creek (fig. 12, sites 17 and 18) suggests losses of selenium from the water column by mechanisms

such as to plant uptake, adsorption to sediments, or biological volatilization (Lamothe and Herring, 2001; Lin and Terry, 2003; Stillings and Amacher, 2004; Oram and others, 2010).

These results and the attenuation of loads from East Mill Creek before reaching the Blackfoot River are supported by results of independent synoptic surveys from the East Mill Dump source areas to the confluence of Spring Creek and the Blackfoot River (fig. 1, table 4). In four high-flow synoptic surveys and one low-flow synoptic survey, the median attenuation of selenium loads from the source areas in upper East Mill Creek to the mouth of Spring Creek was 64 percent, with a range of 17 to 70 percent (table 4).

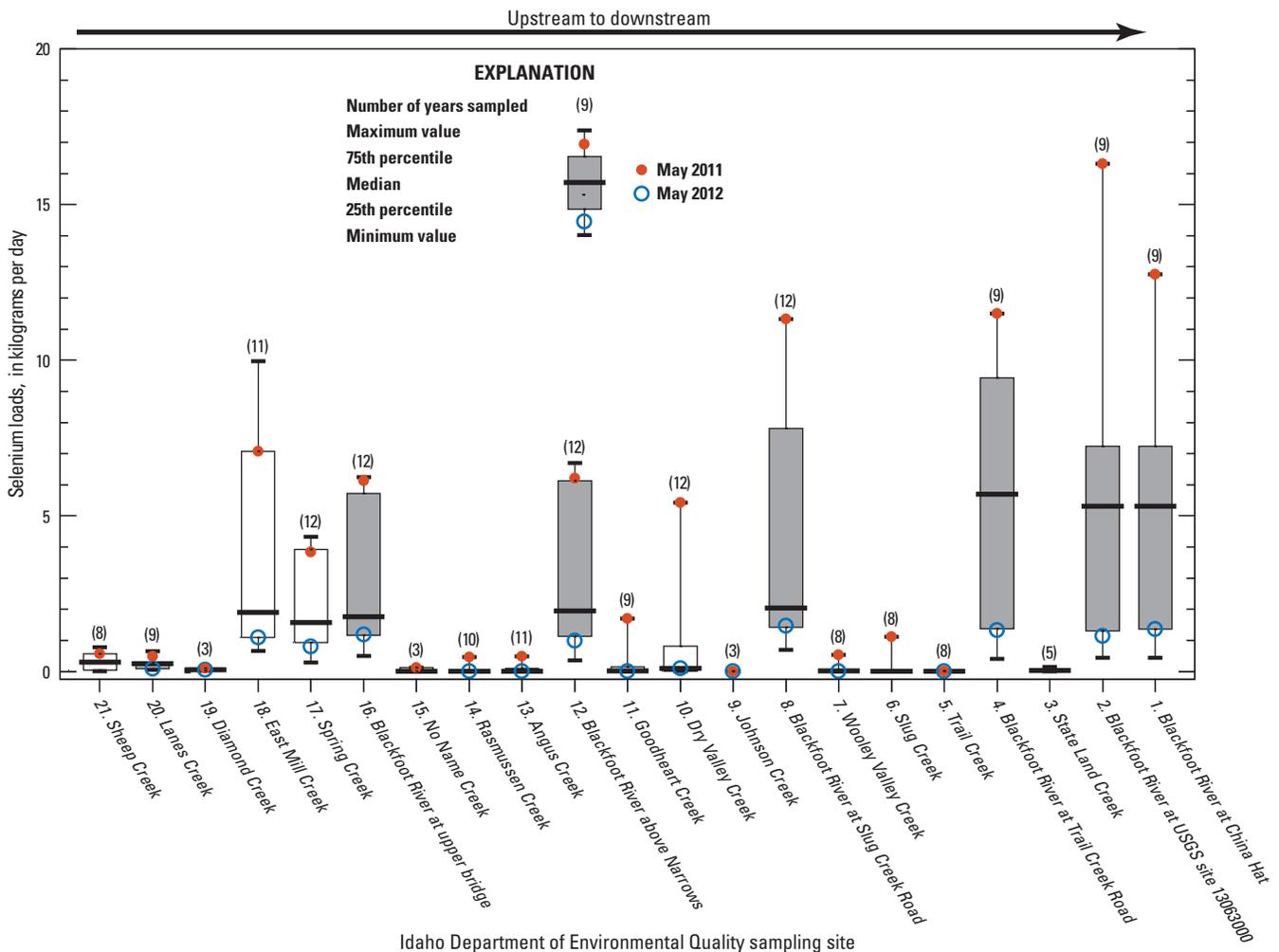


Figure 12. Selenium daily loads from annual Idaho Department of Environmental Quality May sampling of main stem Blackfoot River (gray-shaded boxes) and tributaries, 2001–12. Recent high-flow (May 2011) and low-flow (May 2012) data points are overlain on the box plots. Data for site 10 are from Whetstone Associates (2012).

Measured loads usually were low on all other tributaries to the Blackfoot River. However, on one occasion, May 2011, loads from Dry Valley Creek (site 10) exceeded those from Spring Creek (fig. 12). Despite these low tributary measurements, the annual synoptic data show that in most years selenium loads increased longitudinally in the Blackfoot River between sites 16 and 8, that is, between the Blackfoot River at the upper bridge and the Blackfoot River at the Slug Creek Road (appendix D). These load increases are unexplained by the data presented in this report, but suggest that additional investigations are needed to identify potential unmeasured tributary contributions, or instream sources such as remobilization of sediment-sorbed selenium. Thus, selenium measured in major tributary surface waters may not necessarily reflect all important sources of selenium to the Blackfoot River.

The patterns observed with the markedly different selenium concentrations and loads in tributaries are consistent with the conceptual approach advanced by Mars and Crowley (2003), in which the severity of selenium contamination in Blackfoot River watershed tributaries is related more to the characteristics of the waste rock dumps and stream channels, rather than the open pit mines directly. Watersheds with the most severe selenium contamination are associated with mine dumps that have large catchment areas, high stream gradients, a paucity of downstream wetlands, and cross-valley dump designs that tend to obstruct streamflow. Watersheds associated with low concentrations of selenium have mine dumps with small watershed areas, low stream gradients, abundant wetlands vegetation, and less obstructing dump morphologies (Mars and Crowley, 2003).

Instream increases or decreases in selenium loads along the upper Blackfoot River also can be visualized as a relative function of the loads at the outlet of the watershed (fig. 13). In this comparison, for each sampling period, the downstream selenium load near the outlet is set at 100 percent and the loads at the mainstem Blackfoot River stations upstream of the outlet are calculated relative to the loads near the outlet. Data collected by IDEQ at the Blackfoot River at Henry (13063000, site 2) is used as the “outlet” station instead of data collected from the Blackfoot River at China Hat (site 1), because the streamflow data were incomplete at the latter site. Data are from the IDEQ synoptic surveys except for the 2010 selenium value for the USGS Blackfoot River at Henry (13063000), which is from USGS sampling, and streamflow data at the same “outlet” site.

From 2006 to 2012 (the years with the most complete data), during years with lower spring runoffs, selenium loads tended to peak in the middle reaches of the upper Blackfoot River near the Slug Creek Road (site 8), and decrease downstream toward the outlet (site 2). In contrast, during the high-flow years, selenium concentrations tended to peak at or near the outlet, located downstream of all sources. For the high-flow years, this suggests the river channel was simply acting as a transport reach, passing the selenium loads

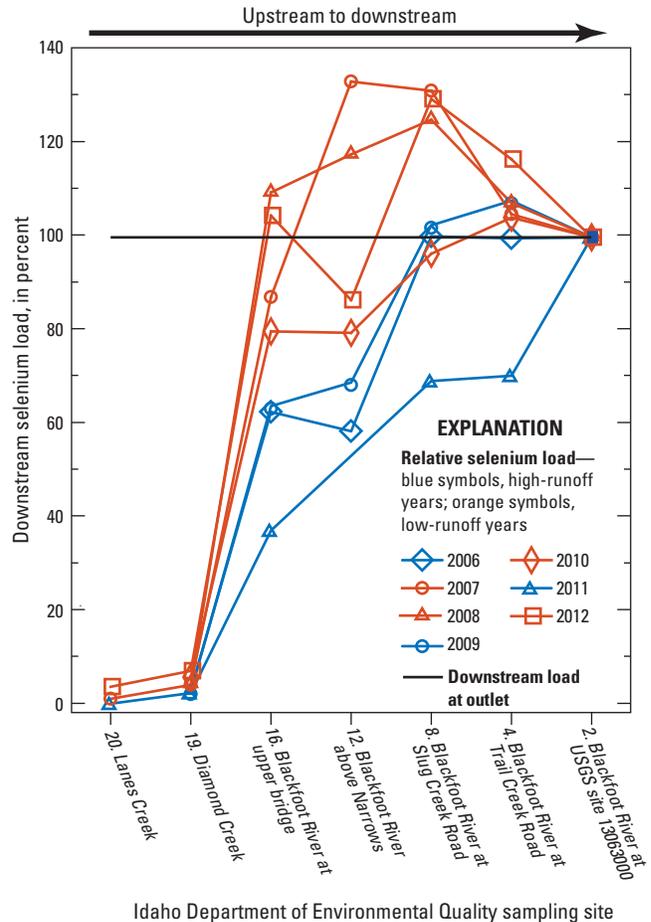


Figure 13. Selenium loads in the main stem Blackfoot River, relative to the loads near the outlet of the upper Blackfoot River, downstream of most known selenium sources, southeastern Idaho.

downstream without much instream processing and removal. For the low-flow years, the patterns suggest more complex interactions, which includes possible additional tributary loading in the middle reaches followed by removal from plant uptake, or losses to sediment. This interpretation is consistent with the correlation between peak streamflows and the time lags between the occurrences of peak streamflows and peak selenium concentrations (table 3). If the bulk of the selenium loading measured at the USGS streamgage (13063000) originated from East Mill Creek in most years, the longer lag times between the peak streamflows and peak selenium concentrations during low-flow years is consistent for longer travel times for selenium-laden waters compared to the overall watershed flows. The longer travel times indicate increased transient storage of stream water. Transient storage is the process in which water is stored in either stream channel dead zones (side pools, eddies) or exchanges through the hyporheic zone. Transient storage influences stream biogeochemical cycling by increasing the residence time of stream solutes,

such as selenium, nitrogen, or phosphorous, and the opportunity for contact time with microbial communities (Gooseff and others, 2007; Martin and others, 2011).

The decrease in relative loads in the lower Blackfoot River reaches suggests attenuation by uptake from aquatic and riparian plants, or reduction in sediments to less soluble selenite. The lower Blackfoot River upstream of the USGS streamgage include slow moving, meandering segments with fringing wetlands and abundant riparian and aquatic vegetation. Support for the role of aquatic plants that remove selenium from the water column in this environment includes experimental plant translocations and field studies. Aquatic plants (bryophytes) collected in low selenium environments and then translocated to the headwaters of Angus Creek (a tributary to the Blackfoot River [fig. 1 inset]), just downstream of a waste rock seep, were enriched with selenium 100-fold after 10-days, and selenium was enriched 1,000-fold in indigenous plants relative to reference samples. Selenium in Angus Creek was additionally attenuated after flowing through a beaver pond complex. In Angus Creek only 1-km from the waste rock seep but downstream of the beaver ponds, selenium concentrations in the aquatic plants were no higher than concentrations from reference sites (Herring and others, 2001). Stillings and Amacher (2004) investigated the removal of selenium from surface waters in a wetland located at the base of a waste-rock dump located in the Wooley Valley Creek watershed (fig 1). Selenium was quickly attenuated from surface water as it flowed from the seeps through the wetland, and concentrations dropped from a range of 11 to 520 µg/L at the main seep site to less than 5 µg/L within 50 m of the seeps. Conservative ion analyses showed that dilution could not account for the decreased selenium concentrations in surface water, as compared to seep water, and Stillings and Amacher (2004) concluded that adsorption and or coprecipitation with non-crystalline iron oxides and plant uptake were responsible for selenium attenuation from the surface water. (Stillings and Amacher, 2004).

While it is clear that selenium is removed from surface water by aquatic plants and sediments in Blackfoot River watershed, the ultimate fate of selenium removed from the stream water by instream vegetation or riparian wetlands is uncertain. Selenium taken up by plants might be biologically volatilized and actually removed from the aquatic environment (Hansen and others, 1998; Lamothe and Herring, 2001; Lin and Terry, 2003), and selenium might be sequestered from the water column by adsorption to iron oxides in sediments and in the hyporheic zone of streams (Stillings and Amacher, 2004; Oram and others, 2010). However, seasonal losses to sediment and periphyton and plant uptake may be transient, and sediments can act as a long-term reservoir of selenium and be an important source of internal loading. Hydrological and biogeochemical processes may delay the responses of streams and rivers to a decrease in chemical inputs, potentially for decades. This transient storage phenomenon has been particularly well documented with integrated surface and groundwater studies of nitrate behavior (Gooseff and others,

2007; Hamilton, 2012), which are instructive here because of the similar high solubility of nitrate and selenate.

These hydrological and biogeochemical factors suggest important questions regarding the ultimate fate of selenium in the Blackfoot River watershed:

- Are losses of selenium from the water column through mechanisms, such as uptake from aquatic and riparian plants and losses to sediments persistent or transient?
- Would much of the removed selenium be cycled back into the water column as plants senesced and as sediments if later mobilized by flow disturbance, bioturbation, or redox changes?
- Are the aquatic plants and riparian wetlands vulnerable to accumulating selenium to the point of harming fish, waterbirds, or browsing mammals?

These would be important questions to resolve before relying heavily on natural or enhanced riparian wetland attenuation to mitigate selenium risks in the upper Blackfoot River drainage.

Summary and Conclusions

The analyses in this report support the following conclusions and observations for the study period, 2001–12:

1. The State of Idaho aquatic-life criterion concentration for selenium (5 µg/L) was equaled or exceeded in 142 of the 450 (31 percent) discrete water samples collected from 2001 to 2012. Of the criterion exceedances, 80 percent occurred during the month of May. No exceedances of the selenium criterion occurred other than during April, May, or June.
2. Selenium concentrations in the upper Blackfoot River, measured through flow-weighted sampling at the Blackfoot River near Henry streamgaging site, always had one or two clearly defined annual peaks. The timing of the peak selenium concentrations always lagged the peak streamflows. From the information reviewed, the most plausible reasons for these patterns between the timing of peak selenium concentrations and streamflow relate to the longer and more complex flow paths of water through mine cross-valley fill waste rock dumps, compared to natural stream channels.
3. During the annual lower flow August–October season, selenium concentrations have trended upward over the 2001–12 period of record. During other times of the year, changes over time were inconsistent.
4. Among tributary surface water sources of selenium to the main stem Blackfoot River, East Mill Creek was usually the largest source except for May 2011, when the largest tributary loads were measured in lower Dry Valley Creek.

- Using synoptic data, the selenium loading analyses showed that in 11 of 12 years, loads increased in the Blackfoot River between stations 12 and 8, which are located upstream and downstream of the Dry Valley Creek confluence ([appendix D](#)).

The analyses presented in this report gave insight on the strengths and limitations of the monitoring and assessment of water quality in the upper Blackfoot River watershed. These include:

- The present USGS “integrator site” sampling approach used to date is well suited for quantifying annual loading and the temporal changes in load for the watershed as a whole. When complemented with the IDEQ annual, spring synoptic sampling of different main stem and tributary sites, the sampling efforts seem to provide a good synopsis of status and changes in selenium concentrations and loading in the upper Blackfoot River watershed.
- Systematic continuous streamflow measurement would be valuable for interpreting changes in selenium loading to and within the Blackfoot River. The selenium loading patterns in tributaries and loading changes along the main stem Blackfoot River suggest a rough priority for continuous streamflow measurement: lower East Mill Creek, Spring Creek, Dry Valley Creek, Slug Creek, and a second main stem Blackfoot River site near Idaho Department of Environmental Quality (IDEQ) sites Blackfoot River at upper bridge (site 16) or Blackfoot River above Narrows (site 12).
- On smaller watersheds, such as East Mill Creek, developing surrogate relations for selenium in water, such as done with conductivity and selenium on Wooley Valley Creek likely would be successful. This would allow selenium loading to be estimated from continuous monitoring of conductivity at a streamgage, and reported in real time with streamflow and other measurements. The IDEQ data suggest increased selenium loading to the Blackfoot River downstream of Dry Valley Creek and downstream of Slug Creek or Trail Creek. Although measured loads in these streams were low, the apparent increase in loads along the Blackfoot River suggests additional streamgaging on the Blackfoot River and major tributaries would be useful. A more spatially detailed round of synoptic sampling during high- and low-flow conditions could provide insight into the sources of apparent load increases in the Blackfoot River that could not be attributed to measured tributary inputs.
- Selenium sampling should not be excessively focused on periods of high flow. Base flow selenium concentrations are also needed. A “seepage run” at low flows with collection of selenium samples would likely contribute valuable information as to the sources of apparent increases in selenium concentrations during low flows at the outlet monitoring site.
- The risks of selenium in the aquatic environment are related to bioaccumulation and food web transfer. The strong seasonal differences in selenium concentrations in the Blackfoot River raise important questions about relative seasonal risks. Are the long-term (10–11 months per year) exposures to selenium concentrations in the range of 1.5 to 3 $\mu\text{g/L}$ during low-flow periods more or less influential to selenium concentrations in biota than the shorter-term (1 to 2 months per year) exposures to selenium in the range of 4 to 6 $\mu\text{g/L}$ per year? This question has implications for management strategies, which might differ for different hydrologic scenarios and cannot be answered from the available data or literature reviewed. Twice annual collections in June and October of low mobility aquatic species, such as periphyton, aquatic insects, and sculpin could provide valuable information on relative seasonal risks from selenium in the Blackfoot River.
- Extensive data collections have been made in the southeast Idaho phosphate area associated with individual mines, and unpublished agency collections. Most of this unpublished information is not easily available to environmental managers or the public at large. An area-wide compilation and synthesis of existing surface water and groundwater chemistry, fish tissue, and intermediate food web components such as periphyton, insects, and non-migratory fish such as sculpin likely would be a valuable undertaking.

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Appendixes

Appendixes A–E are available for download at <http://pubs.usgs.gov/sir/2014/5203>.

Appendix A. Interactive Map of Sampling Sites and Landscape Settings

Map is in the Keyhole Markup Language (kml) format, viewable with 3D Virtual Globe Programs such as the National Aeronautic and Space Administration (NASA) World Wind, Google Earth™, or ESRI ArcGIS Explorer™.

Appendix B. Analytical Method for the Speciation of Dissolved Inorganic Selenium in Natural Water

Appendix C. Data Quality-Control Results

Appendix D. Summary of Streamflow Measurements and Selenium Concentration Data Obtained by the Idaho Department of Environmental Quality in the Upper Blackfoot River Watershed, southeastern Idaho, 2001–12

Appendix E. Trace Metals and Ionic Composition in the Blackfoot River

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