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JAMES R. HEIN

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Chapter 16

SELENIUM LOADING THROUGH THE BLACKFOOT RIVER WATERSHED: LINKING SOURCES TO ECOSYSTEMS

T.S. PRESSER, M. HARDY, M.A. HUEBNER and P.J. LAMOTHE

ABSTRACT

The upper Blackfoot River watershed in southeast Idaho receives drainage from 11 of 16 phosphate mines that have extracted ore from the Phosphoria Formation, three of which are presently active. Toxic effects from selenium (Se), including death of livestock and deformity in aquatic birds, were documented locally in areas where phosphatic shales are exposed (Piper et al., 2000; Presser et al., Chapter 11). Current drainage conditions are leading to Se bioaccumulation at concentrations that pose a risk to fish in the Blackfoot River and its tributaries (Hamilton et al., Chapter 18). A gaging station on the Blackfoot River was re-activated in April 2001 to assess hydrologic conditions and concentration, load, and speciation for Se discharges on a watershed scale. The gaging-station data are considered to represent regional drainage conditions in the upper Blackfoot River watershed because of its location near the outlet of the watershed and directly upstream of the Blackfoot Reservoir.

Watershed discharges for 2001 and 2002 were below minimum hydrologic conditions for the gage as documented by the historical record. Drought emergencies were declared in the area in both 2001 and 2002. Unmonitored diversions for irrigation that routinely take place during the snowmelt season also affected conditions downstream. Annual cycles in Se concentration, load, and selenate (Se^{6+}) reached maxima in the spring during the period of maximum flow at the gaging station. Thirty-seven to 44% of annual flow occurred during the three-month high-flow season (April through June) in 2001 and 56% of annual flow occurred during that time period in 2002. Extrapolation from historical hydrographs for average and wet years and a limited data set of regional Se concentrations for 2001 and 2002 indicated potential for a 3.6- to 7.4-fold increase in Se loading because of increased seasonal flows in the Blackfoot River watershed.

Supplementation data indicate that: (a) the difference between total Se and dissolved Se, as a measure of the contribution of particulate Se, was <10% except at the peak of concentration when total Se was 18% more than dissolved Se; (b) selenite (Se^{4+}) represented less than 10% of the dissolved species during all months of 2001; and (c) dissolved Se was approximately a 50:50 mixture of selenate and organic selenide (operationally defined Se^{2-}) during summer 2001 (June through August).

Ecological risk based on regional Se drainage occurred during both the high- and low-flow seasons. Seventy to 83% of the Se load occurred during the high-flow season. During early May of both years, dissolved-Se concentrations exceeded the criterion for the protection of aquatic life and the ecological threshold of 5 $\mu g L^{-1}$ Se at which substantive risk occurs. During the majority of the three-month high-flow season, dissolved-Se concentrations exceeded the 2 $\mu g L^{-1}$ Se concern level for aquatic biota. The Se concentration in suspended material during high flow in 2002 was within the range of marginal risk to aquatic life (2–4 $\mu g g^{-1}$ Se, dry weight). Selenate was the major species during peak flows, with both selenate and organic selenide being major species during relatively low-flow periods in summer. A change in speciation to reduced Se may indicate elevated biotic productivity during summer months and could result in enhanced Se uptake in food webs.

In addition to the magnitude of regional Se release in the Blackfoot River watershed, Se concentrations in individual source drains and waste-rock seeps, and those predicted by experimental column leaching of proposed mining overburden materials, also indicate that drainage options that currently meet existing demands for phosphate mining cause ecological risk thresholds to be exceeded. At times, the drinking-water Se standard (50 $\mu g L^{-1}$ Se) and the criterion for hazardous Se waste (1000 $\mu g L^{-1}$ Se) (US Department of the Interior, 1998; US Environmental Protection Agency, 1987) are also exceeded.

For water-years 2001 and 2002, seasonal increased input of water in the mining area resulted in increased Se transport, suggesting a mechanism of contamination that involves a significant Se reservoir. Hence, recognition and monitoring of Se loading to the environment on a mass balance basis (i.e. inputs, fluxes and storage within environmental media, and outputs) are essential to evaluating how to control Se concentrations within environmentally protective ranges (Presser and Piper, 1998). In areas where release of Se to aquatic systems is anticipated as a product of future expansion of phosphate mining, continuous monitoring of flow and development of seasonal Se loading patterns would help to model watersheds in terms of sources, flow periods, and environmental-Se concentrations that most influence bioavailability. These data, in turn, could be linked to Se-bioaccumulation models specific to food webs and vulnerable species of the impacted areas to accurately project ecological effects. Gaging at this site on the Blackfoot River is planned to continue in order to establish a long-term (>10 year) record of hydrologic conditions.

INTRODUCTION

Accurate forecasting of the environmental fate of Se is crucial because Se released from irrigation drainage, power production, refining, and mining has caused: (a) fish mortality and deformities in waterfowl; (b) posting of human health advisories for consumption of contaminated food; and (c) termination of grazing (Trelease and Beath, 1949; Presser, 1994; Skorupa, 1998; Hamilton, 1998; Lemly, 2002). Selenium is enriched in organic-rich marine shales that are source rocks for phosphorites and petroleum and is

secondarily enriched in soils and runoff derived from weathering of shales in many semi-arid regions of the western United States (Presser et al., 1994; Presser et al., Chapter 11).

Long-term assessment of Se discharges associated with the regional geology of Se-impacted areas quantifies reservoirs of Se and allows modeling of exposure and risk to fish and wildlife. In addition to traditional variables such as loads and water column concentrations, assessment of biological effects in ecosystems depends on understanding Se speciation, partitioning of Se in sediment and water, Se bioaccumulation in food webs, and trophic transfer of Se to higher predators (Luoma and Presser, 2000).

The upper Blackfoot River watershed, northeast of Soda Springs, has the highest density of phosphate leasing areas and areas for expansion of phosphate mining in southeast Idaho (US Department of Interior et al., 2000). The upper Blackfoot River watershed receives drainage from 11 existing mines (Ballard, Champ, Conda, Dry Valley, Enoch Valley, Henry, Lanes Creek, Maybe Canyon (North and South), Mountain Fuel, Rasmussen Ridge, and Wooley Valley) and their associated mining disturbances (e.g. open pit mines, overburden dumps, stockpiles, processing facilities). Dry Valley, Enoch Valley, and Rasmussen Ridge are the only active mines in the watershed. Areas of possible expansion in the Blackfoot River watershed by 2015 include: Rasmussen Ridge, Lanes Creek, Enoch Valley, Maybe Canyon, and Dry Valley (US Department of Interior et al., 2000). New mine sites, mine sites under environmental review, or under phosphate lease include the areas of Caldwell Canyon, south Rasmussen Ridge, Dairy Syncline, and Trail Creek. The total surface area of mining disturbance is estimated at 32.4 km^2 or 3.6% of approximately 910 km^2 in the watershed. In terms of volume, individual dumps contain 6–70 million tons (Mt) of waste rock that is contoured into hills or used to fill valleys (e.g. cross-valley fill) and pits.

Streams and drains issuing from mined waste rock and forage grown to stabilize waste rock provide pathways for dispersal of Se in the environment, which lead to toxic effects in livestock, aquatic birds, and fish (Piper et al., 2000; Presser et al., Chapter 11; Hamilton, Chapter 18; Mackowiak et al., Chapter 19). In addition, a risk assessment performed in 2002 showed that Se affected by far the greatest number of biological receptors throughout three evaluated watersheds (Idaho Department of Environmental Quality, 2002). Those watersheds were the Blackfoot River/Little Blackfoot River, the Salt River (drainage from Smokey Canyon Mine), and the Georgetown River (drainage from Georgetown Mine). Hazard was identified with potential ingestion by humans of fish from the Blackfoot River watershed. Twenty-seven percent of the stream segments in the Blackfoot River watershed were estimated as impacted by Se when assessed for human-health risk (Idaho Department of Environmental Quality, 2002). Ecological risk to both avian and mammalian terrestrial receptors was highest in the Blackfoot River/Little Blackfoot River watershed (Idaho Department of Environmental Quality, 2002). The extremely high hazard quotients (>2000; quotients > 1 are indicative of risk) for some terrestrial receptors indicated that there is a high probability of significant risk occurring in local areas. Aquatic receptors were not as extensively evaluated for risk (i.e. the potential risk to aquatic receptors could not be ruled out), but the average Se concentration for impacted area surface water was estimated at 67 $\mu g\,L^{-1}$ Se (Idaho Department of Environmental Quality, 2002).

This average exceeded the criterion for protection of aquatic life (5 $\mu g\,L^{-1}$ Se; US Environmental Protection Agency, 1987) by a factor of 13.4. A maximum concentration of Se in impacted surface water for the risk assessment was estimated at 1140 $\mu g\,L^{-1}$ Se, a level above the hazardous water-extracted Se waste criterion (1000 $\mu g\,L^{-1}$ Se, US Department of Health and Human Services, 1996). A maximum Se concentration reported for sediment (188 $\mu g\,g^{-1}$ Se, dry weight or dw) exceeds the hazardous Se waste criterion of 100 $\mu g\,g^{-1}$ Se, wet weight, for a solid waste if it is assumed the sediment contained 40% moisture and this criterion applied to mining waste (US Department of Health and Human Services, 1996). The risk assessment also used an average Se concentration of 19.7 $\mu g\,g^{-1}$ Se (dw) for impacted sediment (Idaho Department of Environmental Quality, 2002), which is approximately fivefold above the 4 $\mu g\,g^{-1}$ Se (dw) ecological substantive risk threshold concentration (US Department of Interior, 1998).

In terms of effects on the environment, a recent compilation of sampling results in the vicinity of phosphate mine sites in southeast Idaho showed, in general, "elevated levels of Se in virtually every media and species of wildlife tested." (Idaho Department of Environmental Quality, 2002). Areas of concern specifically noted were as follows.

Elk: "Elk surveys conducted by Idaho Fish & Game and Idaho Mining Association in 1999 show a direct correlation between elevated concentrations of Se in elk liver versus the distance of harvested elk from the nearest phosphate mine. Approximately 70% of the elk harvested within 2 miles of historic reclaimed mining areas exhibit elevated Se accumulations in their organs. These results also demonstrate upper range subpopulation elk-liver accumulations (~38 mg Se kg^{-1} dw) approaching referenced toxic threshold liver concentration ranges (20–60 mg Se kg^{-1} dw) for other large mammals in a limited number of the individual elk tested."

Birds: "... Over 10% of the 117 bird eggs collected in the mining areas exceeded 10 mg kg^{-1} (dw) egg-shell Se concentration even though the collection effort appears to have missed a significant portion of the higher impacted riparian zones. The mean egg Se (MES) effects threshold (EC10) for Se is reported to occur between 6 and 16 mg kg^{-1}, however, effects are universally accepted to be both site- and species-specific. ..."

Fish: "... Whole body fish samples collected by Idaho Department of Environmental Quality in impacted stream segments also ranged up to 33 mg kg^{-1} (dw) Se as compared to typical reported background levels of 1–4 mg kg^{-1}." Note that the substantive risk threshold for fish occurs at >6 mg kg^{-1} Se, whole-body, dw (US Department of Interior, 1998).

Small Mammals: "Small mammal whole body sample concentrations in impacted areas were up to 7 mg kg^{-1} (wet weight or ww) with reported background levels typically from 1–4 mg kg^{-1} (dw) ..."

Vegetation: "... The former practice of increasing forage productivity on reclaimed sites has inadvertently resulted in providing an enhanced pathway for wildlife exposure .... All reclaimed waste rock piles are exhibiting vegetation concentrations well in excess of the typical 5 mg kg^{-1} grazing recommendations ... The Agency (Idaho Department of Environmental Quality) considers continued livestock grazing losses of the magnitude observed in the past to be unacceptable. ..."

In this chapter, we present an analysis of field data for the Blackfoot River gaging station above the Blackfoot Reservoir to evaluate Se loading from the upper Blackfoot River watershed. This approach to assessing a regional source of Se in southeast Idaho addresses: (a) the geologic inventory of Se available as a source of influx; and (b) natural drainage as a source of efflux. How Se loads are delivered in terms of dissolved Se concentration, speciation, and Se concentrations in particulate materials are also assessed to help evaluate Se bioavailability for foodwebs. The watershed parameters are compared to: (a) past and current hydrographs for the Blackfoot River; (b) Se guidelines and ecological thresholds that represent risk to aquatic life; and (c) data compiled from environmental assessments. These provide perspective on the release potential of Se from phosphate mining waste rock and its ability to cause adverse environmental impacts. Loading scenarios, which are based on seasonal and climate-year type (wet, dry, or average) discharges, are developed in an effort to help define a comprehensive approach to control environmental-Se concentrations within environmentally protective ranges.

SITE LOCATION AND DESCRIPTION

In April 2001, the US Geological Survey (USGS) reactivated a gaging station on the Blackfoot River above the Blackfoot Reservoir (USGS gaging station #13063000, Fig. 16-1) to provide continuous-flow measurements. Operation of the gage is to continue to obtain a 10-year record of hydrologic conditions. Reports of *Water Resources Data for Idaho*, which now includes station #1306300, are published annually as part of the *USGS Water-Data Report Series* (e.g. O'Dell et al., 2001). Real-time data for the gaging station are available at http://idaho.usgs.gov.

The station records drainage from an area of approximately 910 km^2 in Caribou County. The gaging-station data are considered to represent regional-drainage conditions in the upper Blackfoot River watershed because of its location near the outlet of the upper watershed and directly upstream of the Blackfoot Reservoir. The drainage area is designated as the upper Blackfoot River watershed, hydrologic unit 17040207 (Fig. 16-1) (O'Dell et al., 2001). The upper watershed is shown differentiated from the lower Blackfoot River watershed and the Blackfoot Reservoir (Fig. 16-1). Both the Blackfoot River and Little Blackfoot River drain to the reservoir (Fig. 16-1). The Blackfoot River is the largest tributary to the Blackfoot Reservoir. The reservoir has a storage capacity of 509 million cubic meters (Mm^3). Storage in the reservoir began in the spring of 1910 and drainage from mining activities in the watershed began in 1920. The Blackfoot River is a tributary of the Snake River and the watershed ultimately drains to the Pacific Ocean through the Columbia River.

The gaging station is located downstream of ten mines in the upper Blackfoot River watershed (Ballard, Champ, Conda, Dry Valley, Enoch Valley, Lanes Creek, Maybe Canyon (North and South), Mountain Fuel, Rasmussen Ridge, and Wooley Valley) (Figs 16-1 and 16-2). The eleventh mine in the upper watershed (Henry Mine) drains downstream of the gaging station, as do parts of the Enoch Valley and Wooley Valley mines (Fig. 16-2). Other

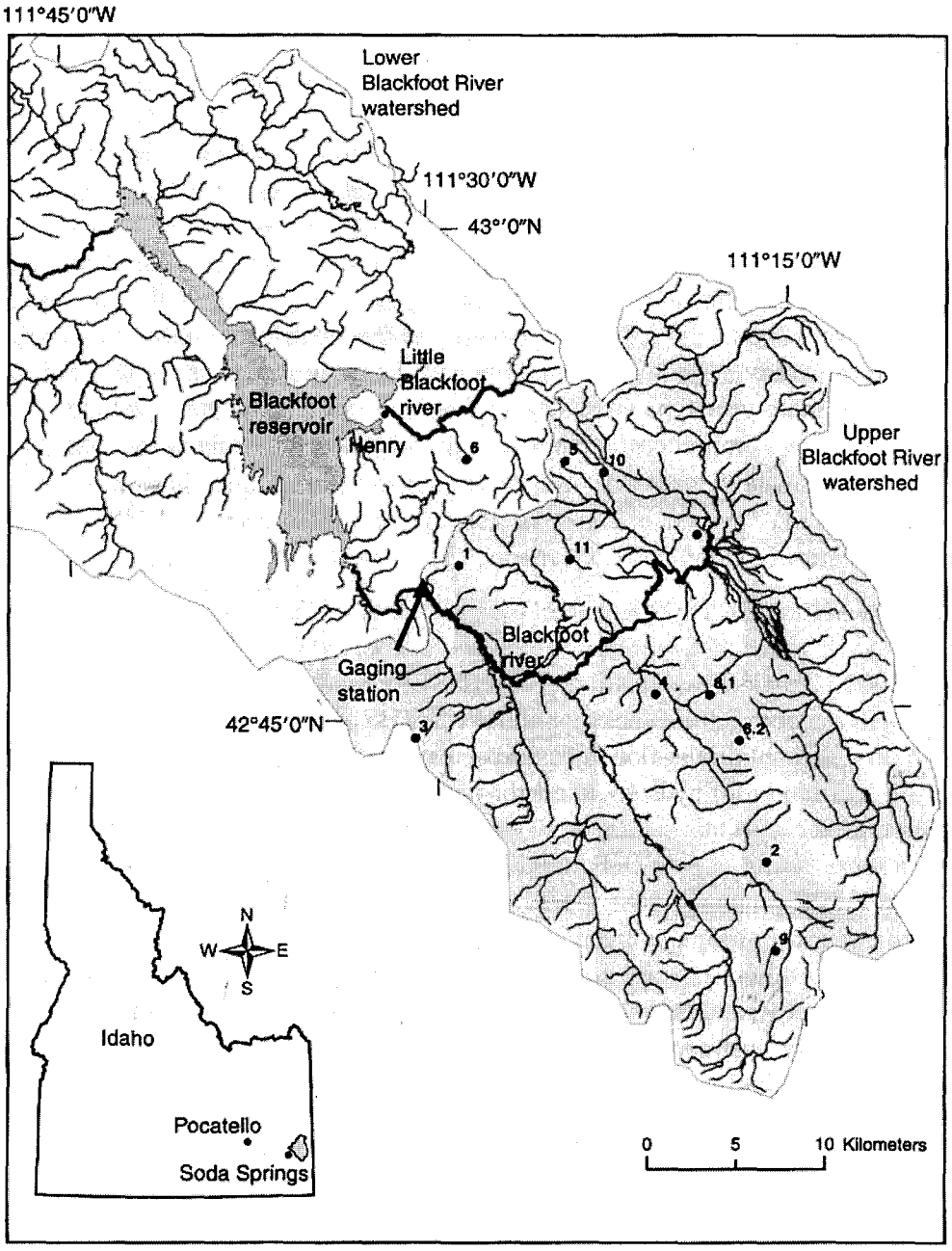


Fig. 16-1. The Blackfoot River watershed (upper and lower) and location of US Geological Survey Blackfoot River gaging station (#13063000). Generalized locations of 11 phosphate mines are shown: Ballard (1), Champ (2), Conda (3), Dry Valley (4), Enoch Valley (5), Henry (6), Lanes Creek (7), Maybe Canyon North (8.1), Maybe Canyon South (8.2), Mountain Fuel (9), Rasmussen Ridge (10), and Wooley Valley (11). The gaging station is located downstream of 10 mines.

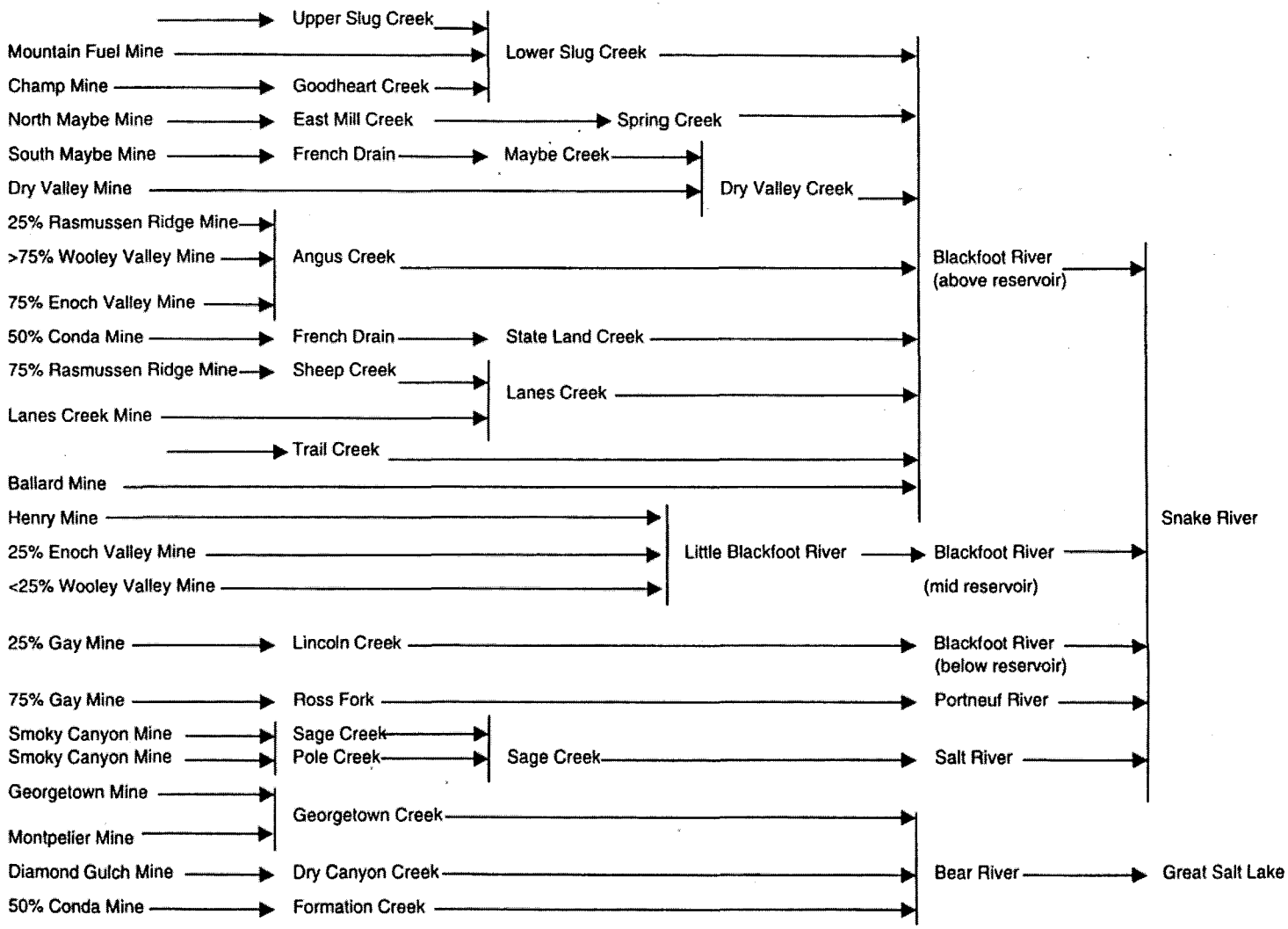


Fig. 16-2. A hierarchy of streams and the phosphate mines that affect drainage quality in southeast Idaho. The mining disturbance drained to each creek is generalized to 25% increments. The Blackfoot River, Little Blackfoot River, Salt River, and Portneuf River watersheds drain to the Snake River, while the Bear River drains to the Great Salt Lake.

watersheds impacted by phosphate mining in southeast Idaho are: Bear River, Portneuf River, and Salt River (Fig. 16-2). The Conda Mine drains both to the Blackfoot River and Bear River watersheds (Fig. 16-2). The Bear River ultimately drains to the Great Salt Lake, Utah, while the Portneuf River and Salt River drain to the Snake River (Fig. 16-2).

Previous periods of record for the gaging station were April 1914 to September 1925 (from 5.3 to 6.4 km downstream of the current site) and August 1967 to September 1982 (at the current site). No winter records are available for the period 1914–1925 except for 1915. The gaging station is located at latitude 42.816° and longitude 111.506°, at 1908 m above sea level. The gage is on the right bank 21 m upstream from the railroad bridge; immediately upstream from the Monsanto Chemical Company Haul Road; 8 km upstream from Blackfoot Reservoir flow line; 9.6 km south of Henry; and 17.7 km north of Soda Springs. Diversions for irrigation take place upstream of the gaging station. A 1966 survey showed irrigation of approximately 18.2 km^2 of land (O'Dell et al., 2001). The volume of diversions has not been estimated.

METHODS

Flow

River-stage measurements were made using a submersible pressure transducer. Data were logged every 15 min using a Sutron data-collection platform. Manual measurements of discharge (Rantz et al., 1982) were related to stage measurements to obtain a continuous record of discharge (Kennedy, 1983; Buchanan and Somers, 1984). Personnel visited the site approximately every six weeks, and more frequently during snowmelt, to service gage equipment and make manual measurements of stream discharge. The logged data are transmitted to US Geological Survey computers every 4 h via the Geo-stationary Operations Environmental Satellite (GOES) for posting as real-time data (http://idaho.usgs.gov).

Sample collection

Water

More frequent sampling occurred during snowmelt when the majority of discharge occurred. A combination of samples collected manually and with an automated sampler were used to document the water year, depending on access to the gage and snow conditions. Samples were collected by manual methods when crews were on site and by an automatic sampler at times when crews could not be on site often enough to document rapidly changing hydrologic conditions. Pairs of samples collected manually and with an automated sampler also served to document that the placement of the sampler intake was adequate for representing integrated samplings across the stream channel and that

contamination was not introduced by the sampling method. Field-equipment and field blanks were collected using USGS certified inorganic-free water (USGS Water Quality Field Supply Unit, Ocala, Florida) to determine the potential for contamination of samples by equipment and processing of manual and automatic samples. Duplicate manual samples were submitted to the laboratories to help define analytical precision.

Manual samples were collected using an equal-width-increment method to integrate sampling across the stream width and processed using a modified clean-sampling procedure, which includes further homogenization using a churn (Wilde et al., 1999). Analyses designated as "manual dissolved" were filtered onsite through 0.45 μm capsule filters that were certified free of trace-element contamination (USGS Water Quality Field Supply Unit, Ocala, Florida). Dissolved Se-species samples were preserved with high purity hydrochloric acid to a pH less than 2. Dissolved cation and trace-metal samples were preserved with high purity nitric acid to a pH less than 2. Anion samples were not acidified. At the time of sample collection, in-stream measurements of temperature, pH, dissolved oxygen, and specific conductance were made at the center of flow using calibrated electrometric meters. From October 2000 through September 2001, alkalinity measurements were made immediately after sample collection using a fixed-endpoint titration (Radtke et al., 1998). After September 2001, alkalinity measurements were made at the USGS National Water Quality Laboratory (Fishman and Friedman, 1989). Several samples collected manually during low flow were lost during shipment to laboratories.

An automatic sampler (ISCO Model 3700) was installed only during the April–October period when freezing conditions did not exist. The automatic sampler and the stream-discharge measurement equipment are co-located in the same housing. This sampler collected point samples through an intake located in flowing water near the north side of the stream. All components of the auto-sampling system were cleaned with detergent and acid solutions followed by flushing with deionized water prior to each installation. The sampler was programmed to collect frequent samples during snowmelt to help define water-quality changes in response to flow variations in the stream. Samples were retrieved from the sampler during routine crew visits, capped, and stored in darkness until the end of runoff. Selected samples based on timing and duration of hydrograph peaks were then processed and submitted for laboratory analyses. Total Se samples were preserved with high purity hydrochloric acid to a pH less than 2. Analyses designated as "automatic dissolved" were filtered at the time of selection through 0.45 μm capsule filters certified to be free of trace-element contamination (USGS Water Quality Field Supply Unit, Ocala, Florida). Preservation protocols used for dissolved species are the same as those described for manual sampling.

Sediment

Suspended-sediment samples were collected on April 10 and 17, 2002 at the gaging station for a preliminary assessment of sediment loading. Steam samples were pumped with a peristaltic pump through the automatic sampler intake into 19 L plastic carboys.

This method was used instead of the standard equal-width increment or equal-discharge increment integrated sampling methods (Horowitz et al., 1989) because of the relatively low amount of suspended material expected to be transported by the river at the gaging site during drought conditions and the relatively large quantity of suspended material needed for analysis. Pumping through the automatic sampler intake for a long period of time was necessary to obtain enough material for processing and analysis. Intensive sampling throughout the snowmelt period and depth-integrated cross-sectional samples would provide a more accurate assessment of suspended-sediment concentrations than that given here.

Analysis

Samples were analyzed for dissolved Se, total Se, dissolved Se speciation (selenate, selenite, and organic Se), quantity of sediment, and suspended-material Se. Other analyses included dissolved major cations and anions and dissolved trace elements. Only the results of the Se analyses are reported here.

Selenium in water samples was determined using inductively coupled plasma-mass spectrometry (ICP-MS) (Lamothe et al., 1999) and hydride generation atomic-adsorption spectrophotometry (AA-hydride) (Cutter, 1978, 1983). Determination of dissolved Se speciation was by differential digestion and AA-hydride (Cutter, 1978, 1983). Suspended-sediment samples were recovered using a high-speed centrifuge and decanted (Horowitz et al., 1989). Samples were air-dried for weighing. Selenium in sediment was analyzed by AA-hydride. (XRAL Laboratories, http://www.sgs.ca/xral/method/methods.html).

RESULTS

Quality assurance and quality control

Records for the Blackfoot River gaging station are rated as "good" (i.e. approximately 95% of daily discharges are within 5% of the true measurement) (Meyers, 1996; O'Dell et al., 2001). The stage–discharge relation or station rating relating the water-surface elevation (gage height or stage) in the river to the volume of water flowing in the channel per unit time is periodically updated (http://idaho.usgs.gov).

Numerous quality-control measures were conducted to ensure Se data quality. The close agreement of dissolved-Se analyses for pairs of samples collected manually and with an automated sampler documented that (a) the placement of the sampler intake was adequate for representing integrated samplings across the stream channel and (b) contamination was not introduced by the sampling method (Table 16-I). Duplicate samples within manual- and auto-sample categories showed that adequate analytical precision was achieved during sampling conditions (Table 16-I). Field-equipment blanks, automatic-sampler blanks, and atmosphere blanks were below detection limits for Se analysis

TABLE 16-I

Quality assurance and quality control for dissolved and suspended-sediment selenium analyses. Samples collected during 2001 and 2002 at the Blackfoot River gaging station, except as noted. Entries indicated water-dissolved Se ($\mu g\,L^{-1}$)

	Manual ICP-MS	Manual duplicate ICP-MS	Auto ICP-MS	Auto duplicate ICP-MS	Methodology duplicate AA-hydride	Independent analysis (ICP -hydride or AA-hydride
Water year 2001						
4/18/01	–	–	1.4	1.5	–	–
4/19/01	1.5	–	1.3	–	1.1	–
5/01/01	7.4	–	7.3	–	5.0	–
5/11/01	4.6	–	4.6	–	4.0	–
5/17/01	3.9	4.0	3.3	3.3	3.2/3.2	–
5/15–18/01	–	–	–	–	–	2.6[1]
5/21/01	3.6	–	3.4	–	2.2	–
5/31/01	2.5	–	2.8	–	1.8	–
6/07/01	2.6	–	2.4	–	1.8	–
6/12–16/01	–	–	–	–	–	2.3[1]
6/19/01	2.5	–	2.2	–	1.4	–
8/23/01	1.3	1.3	1.5	–	1.1/0.7	–
9/14/01	1.0	–	–	–	0.7	–
9/18–21/01	–	–	–	–	–	1.6[1]
Water year 2002						
12/21/01	–	–	–	–	0.6	–
2/21/02	1.8	1.7	–	–	0.4/0.4	–
4/10/02	2.0	–	2.0	–	0.6/0.6	–
4/17/02	3.1	–	3.4	3.3	0.7/0.9/1.3/0.7	–
5/8/02	7.4	–	7.2	–	0.7/1.5	–
5/10/02	–	–	7.6	–	2.0	–
5/11/02	–	–	–	–	–	7.0[2]
6/5/02	3.4	–	3.3	–	0.7/0.7	–

Suspended-sediment Se ($\mu g\,g^{-1}$, dry weight)

	Lab #1 AA-hydride	Lab #2 AA-hydride
4/10/02	3.2	2.6
4/17/02	3.2	2.2

[1]Independent verification: www.deq.state.id.us/news/may23_02.htm, sampling site on Blackfoot River, approximately 3.2 km upstream of gaging station (i.e. Blackfoot River upstream of Dry Valley Creek inflow).

[2]Independent verification: Montgomery Watson, 2002 at Blackfoot River gaging station.

methodologies. Standard reference materials used in the analysis of dissolved Se determined by ICP-MS were within 10% of expected (true) values.

Samples analyzed for Se analysis by ICP-MS for Se were also analyzed by AA-hydride (Table 16-I). During 2001, trends seen in the data produced by the two methods were similar. However, the maximum value determined by AA-hydride was 28% lower than that determined by ICP-MS. Lower values deviated less. Independent sampling as part of regional assessments by mining companies conducted at a site near the gaging station showed Se concentrations comparable to both methodologies used here during periods of concentration in the river below 3 $\mu g\,L^{-1}$ Se (Idaho Department of Environmental Quality, 2001; www.deq.state.id.us/news/may23_02.htm). During 2002, Se concentrations determined by AA-hydride were significantly lower than those determined by ICP-MS, although a peak during snowmelt was observed. Independent sampling as part of regional assessments by mining companies conducted at the Blackfoot River gaging site (Montgomery Watson, 2002) showed a Se concentration similar to the maximum concentration at the hydrograph peak determined by ICP-MS (7.0 $\mu g\,L^{-1}$ Se on May 11, 2002 vs 7.6 $\mu g\,L^{-1}$ Se on May 10, 2002). The data sets for dissolved Se for 2001 and 2002 determined by ICP-MS were used in the data assessment and interpretation that follow.

Data considered supplemental to the assessment of dissolved Se loading are speciation of Se (AA-hydride in 2001) and Se loading via particulate material (total Se in water in 2001 and suspended sediment Se in 2002). These collections and analyses were done to provide an estimate of parameters essential to understanding Se exposure through the watershed. These data sets are considered limited in number, scope, and quality checks. However, Se concentrations for suspended sediment were analyzed by two laboratories, both using AA-hydride during 2002 (Table 16-I). All values for solids are given in dry weight (dw), except as noted.

Regional water-discharge and selenium concentration, speciation, and loading

Hydrologic conditions

Drought conditions (i.e. low snow pack) in southeastern Idaho (www.idwr.state.id.us/about/issues/drought.htm) affected discharges based on comparison to the historical record for the gaging station (Table 16-II). Historical-record-years used for comparison are: minimum year, 1977 (US Geological Survey, 1977); average year, 1980 (US Geological Survey, 1980); maximum based on peak height, 1974 (US Geological Survey, 1974); and maximum based on total discharge, 1982 (Harper et al., 1982). Diversion of flows for irrigation upstream of the gaging site also occured from thaw to July 1 (O'Dell et al., 2001). Results for 15 months of data collection are shown based on water years (WYs), which begin October 1 (Figs 16-3–16-5).

Data from two snowmelt seasons (2001 and 2002) (Figs 16-3 and 16-4) are the focus of analysis because that is when the majority of runoff occurred. Analysis of data for flow and Se load was based on division of the WY into a three-month high-flow season (April through

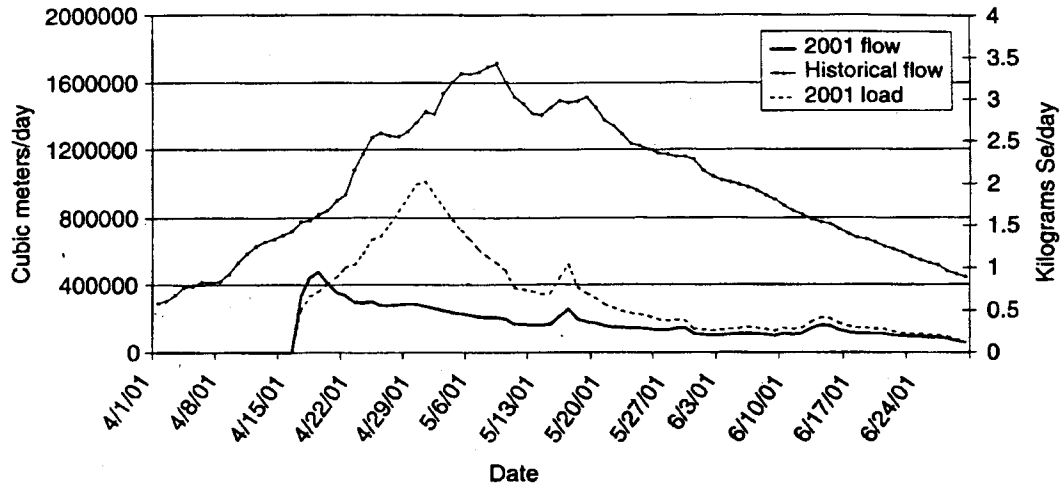


Fig. 16-3. Flow and Se load at the Blackfoot River gaging station from April 17 through June 30, 2001, defined as the three-month high-flow season. For comparison is the historical mean daily discharge based on 28 years of record (O'Dell et al., 2001; http://idaho.usgs.gov). Calculations of Se loads were made using mean daily flow and a linear extrapolation of Se concentrations between sampling points for the three-month high-flow season (see Fig. 16-6). See Table 16-II and *Results* section for details of calculations of Se loads.

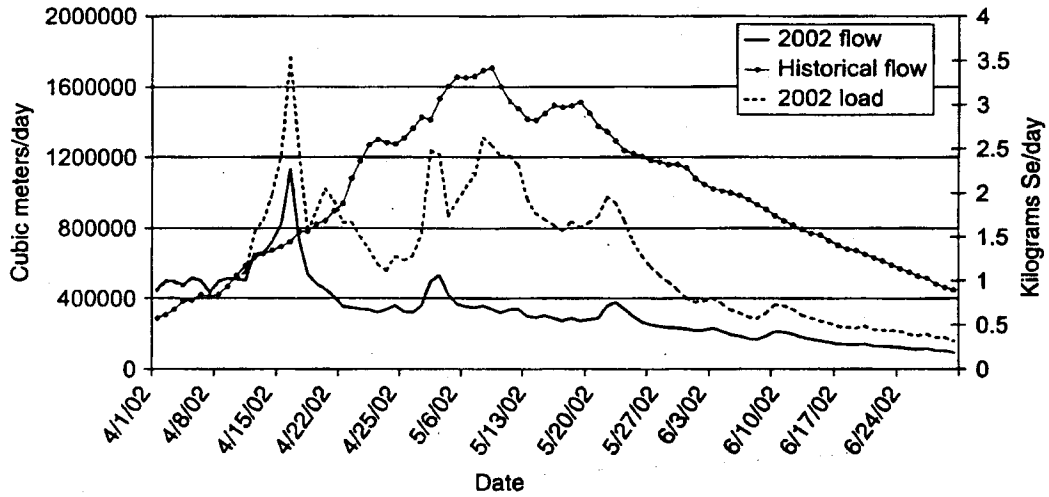


Fig. 16-4. Flow and Se load at the Blackfoot River gaging station from April 1 through June 30, 2002, defined as the three-month high-flow season. Given for comparison is the historical mean daily discharge based on 28 years of record (O'Dell et al., 2001; http://idaho.usgs.gov). Calculations of Se loads were made using mean daily flow and a linear extrapolation of Se concentrations between sampling points for the three-month high-flow season (see Fig. 16-6).

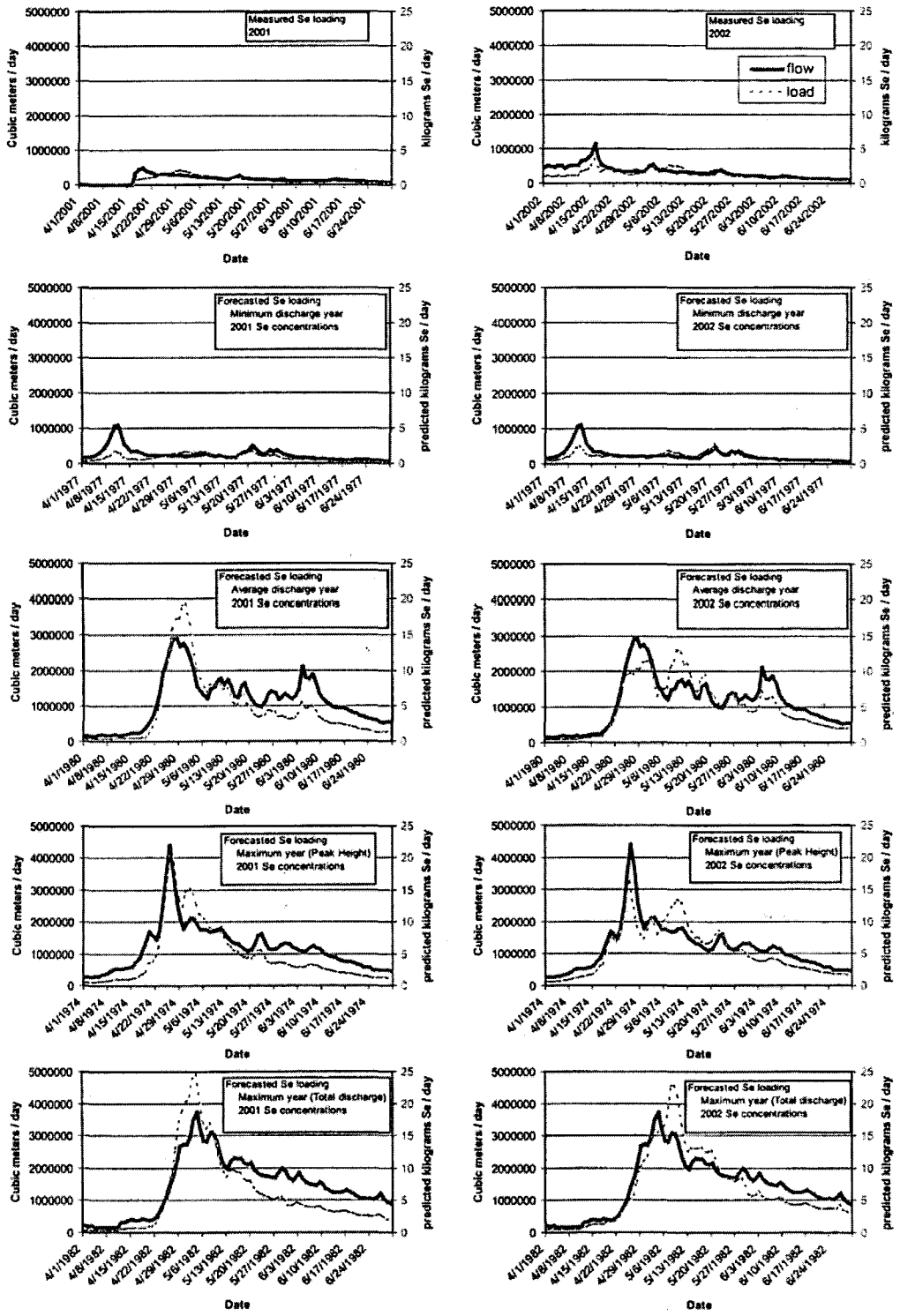
TABLE 16-II

Flow in million cubic meters (Mm^3) and Se loads [(kg), (kg day^{-1}), and (kg yr^{-1})] for designated three-month high-flow snowmelt period and nine-month low-flow period at the Blackfoot River gaging station. Historical-record-years used for comparison are: minimum (1977), average (1980), maximum based on peak height (1974), and maximum based on total discharge (1982). Calculations of Se loads were made using mean daily flow and a linear extrapolation of Se concentrations ($\mu g\, L^{-1}$ Se) between sampling points observed during 2001 and 2002 (see Fig. 16-6). Patterns of Se concentration observed in 2001 and 2002 were assigned to historical flows for 1977, 1980, 1974, and 1982 to show ranges of potential Se loading. See Results Section for data limitations

Water year (starts October 1)	Mm^3 (% annual flow)	$Mm^3\, d^{-1}$ (range)	kg Se[1] (% annual Se load)	kg d^{-1} Se (range)	Mm^3	$Mm^3\, d^{-1}$ (range)	kg Se[1] (at 1 $\mu g\, L^{-1}$)	kg Se d^{-1} (range)	$Mm^3\, y^{-1}$	kg y^{-1} Se
Se loads (water years 2001 and 2002)										
	Three month period (April through June)				Nine month period (July through March)				Annual	
2001[2]	13.7 (37%)	0.059–0.48	51 (68%)	0.14–2.05	23.4[3]	0.023–0.047	24	0.023–0.41	37.0	75
2001	18.1 (44%)	0.059–0.48	56 (70%)				24		41.4	80
2002[4]	29.8 (56%)	0.095–1.13	116 (83%)	0.32–3.55	23.4[3]	0.023–0.474	24	0.032–0.41	53.2	140
Se load forecast										
1977[7] min	23.0 (37%)	0.068–1.10	68[5] (56%)	0.14–1.67	38.8	0.057–0.122	39	0.045–0.14	61.9	107
	23.0 (37%)	0.068–1.10	88[6] (56%)	0.23–2.95	38.8	0.057–0.122	39	0.045–0.14	61.9	127

1980[8] avg	101.9 (67%)	0.15–2.91	405[5] (56%)	0.23–19.55	49.3	0.076–0.592	50	0.091–0.59	151.2	455
	101.9 (67%)	0.15–2.91	451[6] (56%)	0.32–13.18	49.3	0.076–0.592	50	0.091–0.59	151.2	501
1974[9] max (peak height)	108.9 (64%)	0.27–4.40	421[5] (56%)	0.41–21.8	62.2	0.083–0.490	62	0.091–0.50	170.9	483
	108.9 (64%)	0.27–4.40	479[6] (56%)	0.55–16.4	62.2	0.083–0.490	62	0.091–0.50	170.9	541
1982[10] max (peak discharge)	130.9 (66%)	0.16–3.74	525[5] (56%)	0.23–24.6	69.0	0.078–0.881	69	0.091–0.86	199.8	594
	130.9 (66%)	0.16–3.74	605[6] (56%)	0.32–22.7	69.0	0.078–0.881	69	0.091–0.86	199.8	674

[1] Se ($\mu g\ L^{-1}$) × volume (m^3) × (10^6) = load (kg Se).
[2] April–June only; O'Dell et al., 2001.
[3] July–December 2001 and January–March 2002.
[4] http://idaho.usgs.gov.
[5] Patterns of Se concentrations were applied from 2001.
[6] Patterns of Se concentrations were applied from 2002.
[7] Flow: US Geological Survey, 1977.
[8] Flow: US Geological Survey, 1980.
[9] Flow: US Geological Survey, 1974.
[10] Flow: Harper et al., 1982.


Measured Se loading 2001
Measured Se loading 2002
flow
load
Forecasted Se loading Minimum discharge year 2001 Se concentrations
Forecasted Se loading Minimum discharge year 2002 Se concentrations
Forecasted Se loading Average discharge year 2001 Se concentrations
Forecasted Se loading Average discharge year 2002 Se concentrations
Forecasted Se loading Maximum year (Peak Height) 2001 Se concentrations
Forecasted Se loading Maximum year (Peak Height) 2002 Se concentrations
Forecasted Se loading Maximum year (Total discharge) 2001 Se concentrations
Forecasted Se loading Maximum year (Total discharge) 2002 Se concentrations
Cubic meters / day
kilograms Se / day
predicted kilograms Se / day
Date

June) and a nine-month low-flow season (July through March) (Table 16-II). Several data limitations and assumptions occur in the data analysis. In 2001, data were available only from April 17, when gaging was reactivated. An additional flow total for WY 2001 is given, which includes estimated conditions in early April 2001 (O'Dell et al., 2001) (Table 16-II). Data are not included from a period when the gage registered ice (12/11/01–2/18/02). Flow data for the nine-month period of July 2001 through March 2002 were used for analysis of both WYs because only 15 months of data were available for analysis (Table 16-II).

Patterns of flow were similar in 2001 and 2002, with maximum flow occurring on April 19 in 2001 and April 16 in 2002. Annual total discharges (37.0–41.4 $Mm^3 yr^{-1}$ in WY 2001 and 53.2 $Mm^3 yr^{-1}$ in WY 2002) were below minimum hydrologic conditions defined by the historical record for the gage (61.9 $Mm^3 yr^{-1}$ in 1977) (Table 16-II). The three month high-flow season for 2001 and 2002 is compared to historical record hydrographs for the pre-2001 minimum year, the average year, and the two maxima years for the gaging station (Table 16-II and Fig. 16-5). Thirty-seven to 44% of annual flow occurred during the three-month high-flow season in 2001 and 56% of annual flow occurred during that time period in 2002 (Table 16-II). In general, daily mean discharges from April 2001 through June 2002 were well below the historical mean daily discharge based on 28 years of data (Figs 16-3 and 16-4) (O'Dell et al., 2001; http://idaho.usgs.gov).

Selenium concentrations

Selenium concentrations as measured at the gaging station (Fig. 16-6) reached maxima of 7.4 $\mu g L^{-1}$ Se in May 2001 and 7.6 $\mu g L^{-1}$ Se in 2002 in May, with a gradual decrease to an overall minimum of 1.0 $\mu g L^{-1}$ Se in September 2001. Levels of marginal (>2 $\mu g L^{-1}$ Se) and substantive risk (>5 $\mu g L^{-1}$ Se) to aquatic life also are shown on Fig. 16-6 (US Department of Interior, 1998). In detail, the peak of the hydrograph occurred first, followed by a peak in Se concentration 12 days later in 2001 and 24 days later in 2002 (Fig. 16-6). Selenium concentration maxima for 2001 and 2002 both occurred within the first 10 days of May.

Fig. 16-5. Comparison of flow for 2001 and 2002 to historical record years (minimum year, 1977; average year, 1980; maximum based on peak height, 1974; and maximum based on total discharge, 1982) at the Blackfoot River gaging station. The period shown is defined as the three-month high-flow season. The range of Se loads for the snowmelt periods of 2001 and 2002 is also shown. Loads for 1977, 1980, 1974, and 1982 were forecast by applying the Se concentration patterns of 2001 and 2002 to historical hydrographs. The assumption of dry-year concentration patterns may not be applicable for high flow years. However, the forecasts are valuable in that they illustrate the timing and relative scale of potential seasonal loading in a system subjected to a snowmelt climatic regime, but do not necessarily indicate the exact magnitude for wet years.

Selenium speciation – supplemental data

In 2001, selenite (Se^{4+}) represented less than 10% of the dissolved species during all months. Selenate (Se^{6+}) increased to a maximum of 74% with increased flow during May 2001 (Fig. 16-7). During June through August 2001, dissolved Se was approximately

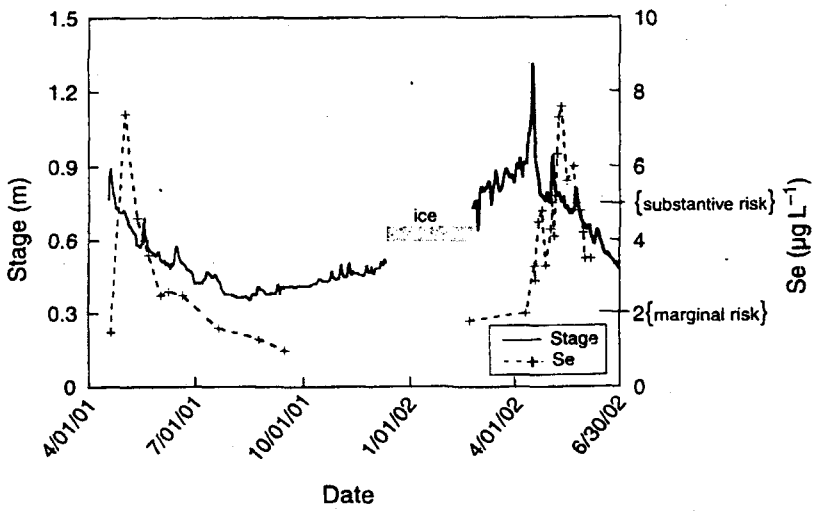


Fig. 16-6. Stage (m) and Se concentration ($\mu g\, L^{-1}$ Se) as measured at the Blackfoot River gaging station from April 17 (the day the gaging station was reactivated) through June 30, 2002 (15 months).

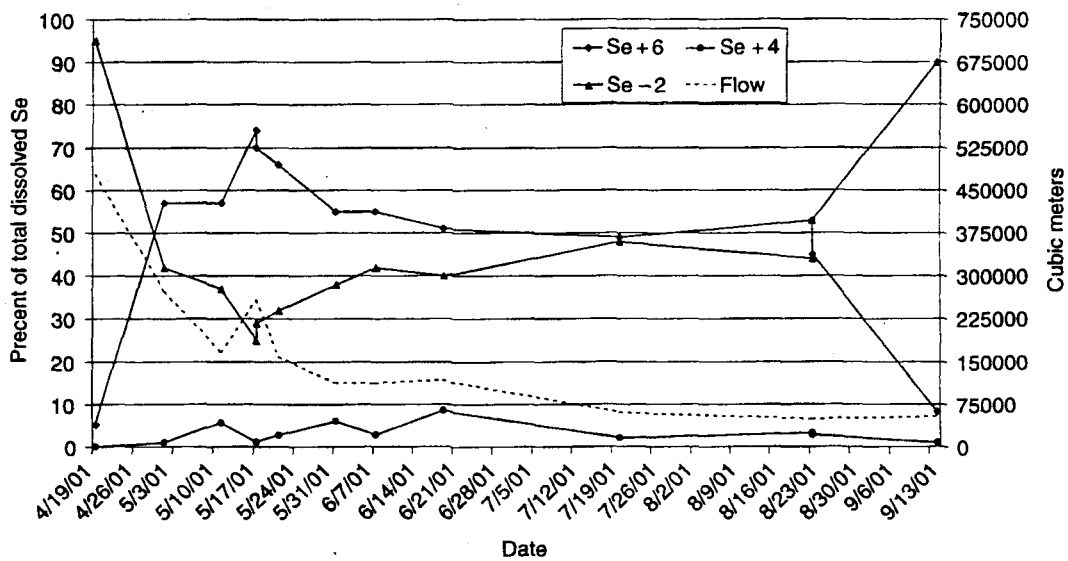


Fig. 16-7. Speciation (% of total dissolved Se) and flow ($m^3\ day^{-1}$) at the Blackfoot River gaging station from April through September 2001. Dissolved selenate (Se^{6+}), selenite (Se^{4+}), and organic Se (operationally defined, Se^{2-}) are shown.

a 50:50 mixture of selenate and organic selenide. In 2001, selenate peaked 16 days after the dissolved concentration maximum.

During relatively low-flow in September 2001 when Se concentration had decreased, the organic selenide (Se^{2-}, operationally defined) fraction of the dissolved species reached 90%. Both speciation of waterborne Se and partitioning of Se between water and organic material substantially affect the potential for bioaccumulation in diet and tissue. Reduced organic forms of Se and, by inference, elevated biotic productivity, as occurred in low-flow summer months, may indicate increased Se uptake in food webs (US Department of Interior, 1998; Luoma and Presser, 2000). Additional data for Se speciation are needed to verify seasonal trends and adequately assess variability.

Suspended sediment – supplemental data

Flow conditions during 2001 and 2002 were likely to minimize the amount of sediment and sediment-associated constituents that were transported in the Blackfoot River. Suspended-sediment concentration was approximately 100 mg L^{-1} during two sampling periods in April 2002. The difference between total Se and dissolved Se, as a measure of the contribution of particulate Se, was <10% except at the peak of concentration when total Se was 18% greater than dissolved Se. Concentrations in the suspended sediment were 3.4 $\mu g\, g^{-1}$ Se on April 10, 2002 and 3.2 $\mu g\, g^{-1}$ Se on April 17, 2002.

Concentrations for a suite of major and minor elements in the suspended-sediment samples (i.e. an example of regional eroded material) are compared to average concentrations for the Meade Peak Member at the Enoch Valley Mine (i.e. an example of source rock) (Table 16-III). Without additional monitoring of suspended material in the mining area, it is difficult to directly relate suspended-sediment concentrations at the gaging station to sources. However, the source-rock Se concentration (48 $\mu g\, g^{-1}$ Se) exceeds the substantive risk threshold to aquatic life from sediment (4 $\mu g\, g^{-1}$ Se) and the suspended sediment Se concentration remains within the range of concern for risk to aquatic life from sediment (2–4 $\mu g\, g^{-1}$ Se) (US Department of Interior, 1998). Additional data for Se loading via particulate material are needed to verify amounts and assess the adequacy of methodologies under snowmelt conditions.

Dissolved selenium load calculations

Calculation of Se loads was done through use of the generalized equation:

concentration × volume = load.

Specifically, calculation of daily Se loads (Table 16-II; Figs 16-3–16-5) during the three-month high-flow season were made using daily mean flow and a linear extrapolation of Se concentrations between sampling points observed during 2001 and 2002 (Fig. 16-6). For the nine month low-flow season, an assigned value of 1 $\mu g\, L^{-1}$ Se (i.e. the minimum

TABLE 16-III

Concentrations of major and minor elements in suspended sediment collected at Blackfoot River gaging station

	Se ($\mu g\,g^{-1}$)	OC[1] (%)	C (%)	S (%)	P[2] (%)	As ($\mu g\,g^{-1}$)	Sb ($\mu g\,g^{-1}$)	Mo ($\mu g\,g^{-1}$)	V ($\mu g\,g^{-1}$)
4/10/02	3.4	4.0	5.2	0.08	0.15	3.7	0.9	3	65
4/17/02	3.2	4.3	5.3	0.08	0.16	4.4	0.6	2	76
MPM[4]	48	2.8	3.9	0.38	5.2	32	2.0[3]	30	520

	Hg ($\mu g\,g^{-1}$)	Cd ($\mu g\,g^{-1}$)	Pb ($\mu g\,g^{-1}$)	Cr ($\mu g\,g^{-1}$)	Cu ($\mu g\,g^{-1}$)	Zn ($\mu g\,g^{-1}$)	Ni ($\mu g\,g^{-1}$)	Sr ($\mu g\,g^{-1}$)
4/10/02	0.045	<2	17	83	17	133	27	154
4/17/02	0.056	<2	20	95	23	161	33	139
MPM[4]	–	60	12	1194	96	1137	213	553

[1] OC, organic carbon.
[2] Converted concentrations: P_2O_5 = 0.34%, 0.37%, 11.8%, from top to bottom, respectively.
[3] Sb from Hot Springs Mine (Piper et al., 2000).
[4] Average concentration for the Meade Peak Member (MPM) at the Enoch Valley Mine for comparison (from Piper, 1999; Piper et al., 2000); – not analyzed.

concentration) was used because available concentration data for this period were equal to or nearly equal to the minimum concentration (Fig. 16-6). This concentration was applied to the total volume of drainage for the nine-month low-flow period.

Sixty-eight to 83% of the Se load occurred during the high-flow season (Table 16-II). Selenium loads for both years ranged from 0.14 to 3.6 kg day^{-1} during the three-month high-flow season and from 0.02 to 0.41 kg day^{-1} during the nine-month low-flow season (Table 16-II; Figs 16-3 and 16-4). The range of maximum Se loading was 2.0–3.6 kg day^{-1}. Annual loads for 2001 and 2002 were 80 and 140 kg Se, respectively. Both years defined new minimum flow levels, and by inference, minimum Se loads.

Selenium load forecasts for average and wet years – supplemental data

Future monitoring during average and wet years in the Blackfoot River watershed will give additional information on regional Se loading under a range of hydrologic conditions. However, the limited data set of Se concentrations for dry and drought conditions of 2001 and 2002 can be applied to historical hydrographs for average and wet years to give an indication of the magnitude of potential Se loading due to increased flow in the Blackfoot River watershed. These forecasts help provide a range of possible Se loads for the watershed to

assess whether likely combinations of concentrations, load, hydrology, climate, Se reactivity, and Se bioavailability pose significant ecological risks in the Blackfoot River watershed.

Applying Se concentration patterns of 2001 and 2002 (both years ranged from 1 to ~7.5 $\mu g L^{-1}$ Se) to historical dry-, average-, and wet-year hydrographs for the gaging station (Table 16-II and Fig. 16-5) showed annual potential Se loadings of: (a) 107–127 kg for a minimum year; (b) 455–501 kg for an average year; (c) 483–541 kg for a maximum year based on peak height; and (d) 594–674 kg for a maximum year based on total discharge. The extrapolation for a historical dry-year load shows a 29% increase over the 2001 load of 80 kg Se and a 10% decrease over the 2002 load of 140 kg Se. For average and wet years, these extrapolations indicate potentials for a 3.6–7.4-fold increase in Se loading because of increased seasonal flows in the Blackfoot River watershed, if Se concentrations remain the same as in 2001 and 2002.

In general, the forecasts for wetter years are valuable in that they illustrate the timing and relative scale of potential seasonal loading in a system subjected to a snowmelt climatic regime, but not necessarily the exact magnitude for wet years. The use of 2001 and 2002 concentration patterns to forecast average- and wet-year Se loads may not be valid for higher flow years, given that with more flow, Se concentrations increase. Additionally, only two years of snowmelt were observed. Both years in which Se concentrations were measured were atypical in that drought emergencies had been declared in southeast Idaho. The range of Se concentrations and timing of Se concentration maxima for both years were similar however, leading to an approximate 10% difference within average and wet year forecast categories (Table 16-II). In terms of potential daily Se loading, the ranges are, dry: 0.04–3.0 kg day^{-1}; average, 0.09–19.5 kg day^{-1}; wet based on peak discharge, 0.09–21.8 kg day^{-1}; and wet based on net discharge, 0.09–24.6 kg day^{-1} (Table 16-II; Fig. 16-5). Thus the forecasted maximum daily Se loads during the snowmelt period of a normal to wet year are approximately 20–25 kg day^{-1}. These daily loads are in contrast to maximum daily measured Se loads of 2–3.6 kg day^{-1} during the snowmelt period for 2001 and 2002, representing the high-flow period of critical or dry years.

REGIONAL SELENIUM RESERVOIR

Geohydrologic balance

Seasonal high flow in the mining area resulted in increased Se concentrations and loads as measured at the gaging station (Figs 16-3, 16-4, and 16-6). This approximately three-month temporal trend appears to exceed that expected from a short-duration spring flush of evaporative salts that occurs after dry periods (King, 1995). Increase in both concentrations and loads with increasing flows suggests a regional reservoir of Se that is a function of the geohydrologic balance of Se between the primary geologic inventory of Se (as the source of influx) and drainage (as the source of efflux). The similarity in this mobility trend in an area of mine-waste drainage to trends occurring in Se-impacted areas in California, where subsurface drains have been installed (Luoma and Presser, 2000; Presser et al., Chapter 11), suggests significant Se storage in the mining area of southeast Idaho that is now subject to transport.

Selenium sources and source drainage

Regional Se drainage, as measured at the gaging station, is linked to release of Se through mining activities associated with the Phosphoria Formation. Streams, seeps, and drains with elevated Se concentrations issue from phosphate mining waste-rock that has been contoured into hills, used to fill valleys, or used as backfill for mine pits. Studies related to Se drainage have shown the following:

- Waste rock is generated at a rate of 2.5–5 times that of mined ore and individual dumps contain 6–70 Mt of waste rock (US Department of Interior and US Department of Agriculture, 1977).
- Prior to the knowledge of Se release and impacts, waste rock was used as a construction material for under-drains for valley fill (US Department of Interior and US Department of Agriculture, 1977) and was considered suitable as a growth medium for reclamation (i.e. vegetation of slopes for stability and grazing) (Maxim Technologies Inc., 2002).
- The Meade Peak Member contains up to 1200 $\mu g\,g^{-1}$ Se (dw) (Bloomington Canyon, McKelvey et al., 1986), a value exceeding a solid Se hazardous waste (100 $mg\,g^{-1}$ Se, ww; or 111 $mg\,g^{-1}$ Se, dw at 10% moisture), if this criterion was applied to mining waste (McKelvey et al., 1986; US Department of Health and Human Services, 1996). The highest Se concentrations occur in the waste shales (Perkins and Piper, Chapter 4; Perkins and Foster, Chapter 10).
- Average concentrations of Se in the Meade Peak Member at different mine locations are: Enoch Valley, 51 $\mu g\,g^{-1}$ Se (range 1–410 $\mu g\,g^{-1}$ Se); Hot Springs, 70 $\mu g\,g^{-1}$ Se (range 6–240 $\mu g\,g^{-1}$ Se), and Lakeridge, 48 $\mu g\,g^{-1}$ Se (0.5–380 $\mu g\,g^{-1}$ Se) (Piper, 1999; Piper et al., 2000). More recent data from a channel section of the uppermost part of the Meade Peak Member show a maximum of 425 $\mu g\,g^{-1}$ Se (Grauch et al., Chapter 8).
- Selenium concentrations in tributary streams draining both active and inactive mines in the Blackfoot River watershed contained up to 400 $\mu g\,L^{-1}$ Se (Piper et al., 2000; Montgomery Watson, 2001a,b), which exceeds the guideline for protection of aquatic life by 50-fold (5 $\mu g\,L^{-1}$ Se, US Environmental Protection Agency, 1987).
- Selenium concentrations in source drains and waste-rock seeps can exceed the criterion for a water-extracted hazardous waste of 1000 $\mu g\,L^{-1}$ Se (US Department of Health and Human Services, 1996; TRC Environmental Corporation, 1999; Piper et al., 2000; US Department of Interior, 2002).

Besides these field data, recent data from controlled leaching of mine waste in laboratory column tests also relate to the overall magnitude of the source reservoir of Se available for release on a regional basis (Table 16-IV) (US Department of Interior and US Department of Agriculture, 2002). This testing was conducted as part of environmental documentation for expansion of mining in southeast Idaho (US Department of Interior and US Department of Agriculture, 2002). Mining of the Meade Peak Member will be the major source of phosphate and waste rock in the mining expansion areas. However, this set

TABLE 16-IV

Selenium concentrations in mine waste leachate as exemplified by column tests of proposed overburden for mining expansion and in seeps and springs (adapted from US Department of Interior and US Department of Agriculture, 2002)

	Weighted *run-of-mine* (average)	Hanging-wall mudst.	Hanging-wall phosphatic shale	Center-waste shale, altered	Center-waste shale, reduced	Run-of-mine, surface (Panel A)	Chert mudst.	Footwall
Column tests[1] ($\mu g L^{-1}$ Se)								
Overburden[2] (%)	100	24.4	7.2	30.3 (altered + reduced)		0	33.3	4.8
1st pore volume	149–181	232	273	205–404	117–134	951	6	109
2nd pore volume	58–64	47	101	131–141	66–126	459	3	62
3rd pore volume	38–47	30	61	60–124	49–53	230	2	75
1st, 2nd, 3rd (average)	81	103	145	132–223	77–104	547	4	82
5th pore volume	47	26	56	52–129	52–59	195	2	62
7th pore volume	47	25	95	45–117	58–68	220	<2	52
9th pore volume	41	22	52	47–111	52–68	39	2	40
10th pore volume	44	20	57	51–120	59–78	141	2	42
1–10 (average)	55	57	99	84–164	65–84	334	3	63
Overburden seeps and springs[3]		($\mu g L^{-1}$ Se)						
Regional, range		5-1,617						
Regional, average/median		252/114						
Panel D[4] seeps, grab		280						
Panel E[4] seeps, grab		240						
Panel D seeps, avg. (1999 through June 2001)		716						
Panel E seeps, avg. (1999 through June 2001)		310						

Continued

TABLE 16-IV *Continued*

Predicted seepage based on column tests[1]	($\mu g\ L^{-1}$ Se)
<100 years	81 (average of pore volumes 1–3)
>100 years	55 (average of pore volumes 1–10)

[1]All leaching solutions were filtered (Maxim, 2002).
[2]A weighted average *run-of-mine* reflects percentages in proposed overburden (Maxim, 2002).
[3]Seepage quality throughout southeast Idaho Phosphate District based on 23-sample data set (US Department of Interior and US Department of Agriculture, 2002) for comparison.
[4]Local overburden panels in area of mining expansion (US Department of Interior and US Department of Agriculture, 2002).

of column test results (Table 16-IV) serves as only one example that may be specific to proposed local overburden (i.e. waste-rock). Further column testing of overburden from other mine sites is needed to define limits of Se concentrations in seepage from mine waste and the predictive utility of column tests (e.g. Herring, Chapter 13).

A compilation of data from 23 seeps was provided as part of the environmental documentation to evaluate predictions from column testing concerning groundwater quality in areas of expansion (US Department of Interior and US Department of Agriculture, 2002; Maxim Technologies Inc., 2002) (Table 16-IV). Two local seeps specific to existing overburden in the area of mining expansion averaged 310 and 716 $\mu g\,L^{-1}$ Se, with the range of Se concentrations in source drainage from 5 to 1617 $\mu g\,L^{-1}$ Se (Table 16-IV). This data set was considered representative of seepage quality through the phosphate-mining area of southeast Idaho, but also was thought limited when applied to systems as complex as those involved in mine expansion (US Department of Interior and US Department of Agriculture, 2002).

The controlled leach data analysis was based on a run-of-mine (i.e. ore as it is mined in its natural, unprocessed state) weighted average reflecting percentages in proposed overburden (US Department of Interior and US Department of Agriculture, 2002; Maxim Technologies Inc., 2002). In order to assess a weighted average of run-of-mine, the overburden was estimated to contain 24.4% hanging-wall mudstone; 7.2% hanging-wall phosphatic shale; 30.3% center-waste shale (altered and reduced); 33.3% chert; and 4.8% footwall mudstone (Table 16-IV). The fine-grained characteristics of leached material led to what was considered a high-reaction rate. In addition, Se concentrations obtained from leaching of strongly weathered surface overburden were considered probable maxima for this series of tests (Maxim Technologies Inc., 2002).

In the column tests, the results of the first pore volume were considered not in equilibrium with reduced phases (Table 16-IV). The average of the first three pore volumes calculated as a run-of-mine weighted average was considered as the near-term leaching condition (<100 years, 81 $\mu g\,L^{-1}$ Se) (Table 16-IV). Use of all pore-volume data (1 through 10), calculated as a run-of-mine weighted average, was considered representative of long-term leaching (>100 years, 55 $\mu g\,L^{-1}$ Se) that would eventually produce a source depletion (Table 16-IV). Specifically, field-weathered run-of-mine surface overburden showed the highest rate of Se release (951 and 141 $\mu g\,L^{-1}$ Se, first pore volume and tenth pore volume Se concentration, respectively) followed by the altered (i.e. weathered) center-waste shale and the hanging-wall phosphatic shale (273 and 57 $\mu g\,L^{-1}$ Se). The unaltered (i.e. reduced) shale showed less release of Se than the altered shale. Chert showed the lowest release (6 and 2 $\mu g\,L^{-1}$ Se).

CONCLUSIONS

Data presented here suggest a significant Se reservoir that is now subject to mobility in the mining area of southeast Idaho. Ecological impacts in the Blackfoot River watershed are linked to the magnitude of regional Se release. Both source and watershed data help assess

whether likely combinations of hydrology, climate, Se loading, and Se bioavailability pose significant risks to fish and wildlife. Mine-drainage options that currently meet existing demands for phosphate mining cause ecological risk thresholds to be exceeded.

Annual cycles in Se concentration, load, and the Se-species selenate reached maxima in the spring, during the period of maximum flow at a gaging station on the Blackfoot River (Figs 16-3–16-7). During peak periods of flow during May, dissolved-Se concentrations exceeded the criterion for protection aquatic life and the ecological threshold at which substantive risk occurs (5 $\mu g\,L^{-1}$ Se) (US Environmental Protection Agency, 1987). During the majority of the three-month high-flow period, dissolved Se concentrations exceeded the 2 $\mu g\,L^{-1}$ concern level for aquatic biota (US Department of Interior, 1998). Suspended-material Se concentration during high flow in 2002 was within the range of marginal risk to aquatic life (Table 16-III). Both selenate and organic selenide (operationally defined Se^{2-}) were major species during relatively low-flow periods in summer. A change in speciation to reduced Se may indicate elevated biotic productivity during summer months and could result in enhanced Se uptake in food webs (US Department of Interior, 1998; Luoma and Presser, 2000).

Determination of a Se budget throughout the watershed is crucial because sources of Se are changing as a result of climate and mining management and expansion. Extrapolation from historical hydrographs for average and wet years and a limited data set of regional Se concentrations for 2001 and 2002 indicated potential for a 3.6- to 7.4-fold increase in Se loading because of increased seasonal flows in the Blackfoot River watershed.

A site just below the Blackfoot River gaging station showed a high hazard based on Se concentrations in water, sediment, macroinvertebrates, and fish in June 2000 (Hamilton et al., Chapter 18). Sites documented above the gaging station nearer source drainages showed moderate to high hazards (Hamilton et al., Chapter 18). For the Blackfoot River site, the geometric mean Se concentration in invertebrates was 5.4 $\mu g\,g^{-1}$ Se, dw (composite sample of several taxa) and in fish was 7.8 $\mu g\,g^{-1}$ Se, whole-body, dw (range 5.8–14.1 $\mu g\,g^{-1}$ Se) (Hamilton et al., Chapter 18).

Regional Se drainage, as measured at the gaging station, is linked to release of Se through mining activities associated with the Meade Peak Member. Selenium concentrations in source rocks can exceed the criterion for a solid waste (100 $\mu g\,g^{-1}$ Se, ww) and Se concentrations in individual source drains and waste-rock seeps associated with phosphate mining can exceed the criterion for a water-extracted hazardous waste (1000 $\mu g\,L^{-1}$ Se) (US Department of Health and Human Services, 1996). An example given in environmental documentation of expected Se release in source seepage from mining expansion in SE Idaho, based on column leaching of proposed overburden (Table 16-IV) (Maxim Technologies Inc., 2002; US Department of Interior and US Department of Agriculture, 2002), predicted Se concentrations source seepage of 81 $\mu g\,L^{-1}$ Se in the near term (within 100 years) with decreasing concentrations to 55 $\mu g\,L^{-1}$ Se over the longer term (>100 years). These predicted Se concentrations are site-specific, but give some perspective for comparison of Se concentrations derived from leaching of source rocks to Se concentrations in regional drainage. Both of the predicted concentrations are above the drinking-water

standard for Se (50 $\mu g L^{-1}$ Se, US Department of Health and Human Services, 1996) and 11- to 16-fold above the Se criterion for protection of aquatic life (5 $\mu g L^{-1}$ Se, US Environmental Protection Agency, 1987). Column leaching of specific shale zones of the Meade Peak Member showed higher concentrations (up to 404 $\mu g L^{-1}$ Se), as did leaching of weathered overburden (up to 951 $\mu g L^{-1}$ Se) (Table 16-IV).

Determination of a Se mass balance for the watershed and Se cycling through the components of the watershed's ecosystems are also crucial because of Se bioaccumulation (Presser and Piper, 1998). A comprehensive linked approach would include all considerations that cause systems to respond differently to Se contamination. Both speciation and partitioning of Se between water and particulate material substantially affect the potential for bioaccumulation in diet and tissue of predators. Even though Se concentrations decrease during low-flow months, risk may increase due to increased biotic productivity and longer residence times during summer. Risk during the high-flow season may be associated with increased Se loading and concentrations in streams.

As management and remediation plans for Se are proposed, the kind of analysis done in this chapter would help in modeling the Blackfoot River and tributary watersheds to accurately project ecological effects based on sources, flow periods, and environmental Se concentrations that most influence Se reactivity and bioavailability in food webs. This kind of analysis provides inputs into Se-pathway bioaccumulation models based on site-specific food webs to define Se exposures to sensitive higher-level predators. Regulatory approaches that emphasize source load quantification and reduction could work towards an overall load target determined by vulnerable food webs. A Se mass balance approach through the Blackfoot River watershed would provide a comprehensive understanding of the physical, chemical, and biological processes that underlie Se exposure and offer opportunities to identify resolutions of phosphate-mining management and expansion questions that may arise.

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Appendix 2

Quality Assurance Check

To receive the utmost reliability and accuracy from your Digibar Pro, it is recommended that a quality assurance check be performed periodically. This is a simple task that and will not take long to complete, but will give the user a high level of confidence in the data collected.

You will need a bucket of water, the calibration certificate at the back of your Digibar Pro Operation Manual, a reliable thermometer and the Digibar Pro. The use of a calibrated laboratory thermometer is recommended, but is not necessary. Fill the bucket with fresh water. Choose the water temperature between 4°C and 30°C. Obtain a copy of the Digibar Pro Calibration Certificate.

Immerse the Digibar Pro Sound Velocity Probe in the bucket containing the water of room temperature. Acquire a sound velocity reading. Measure the temperature of the water. Find the temperature on the Digibar Pro Calibration Certificate and read the value under the "RES-VEL" column. Compare the reading to the actual value on the Digibar Pro. It should be within ± 1 meter/sec of the "RES-VAL" on the certificate. It may be necessary to allow the transducer to become acclimated to the different water temperature, so allow two to three minutes for the velocity value to settle. The following is an example of a Digibar Pro Calibration Certificate.

03/01/2002					STANDARD DEL GROSSO H2O				SERIAL# 98XXX
TEMP	VELOCITY	MEASURED FREQUENCY	RES VEL	OBS-CAL	TEMP	VELOCITY	MEASURED FREQUENCY	RES VEL	OBS-CAL
4.0	1421.62		1421.4		17.5	1474.38		1474.6	
4.5	1423.90		1423.7		18.0	1476.01		1476.2	
5.0	1426.15		1426.0		18.5	1477.62		1477.9	
5.5	1428.38		1428.3		19.0	1479.21		1479.4	
6.0	1430.58		1430.5		19.5	1480.77		1481.0	
6.5	1432.75		1432.7		20.0	1482.32		1482.6	
7.0	1434.90		1434.9		20.5	1483.84		1484.1	
7.5	1437.02		1437.0		21.0	1485.35		1485.6	
8.0	1439.12		1439.1		21.5	1486.83		1487.0	
8.5	1441.19		1441.2		22.0	1488.29		1488.5	
9.0	1443.23		1443.2		22.5	1489.74		1490.0	
9.5	1445.25		1445.3		23.0	1491.16		1491.4	
10.0	1447.25		1447.3		23.5	1492.56		1492.7	
10.5	1449.22		1449.3		24.0	1493.95		1494.1	
11.0	1451.17		1451.3		24.5	1495.32		1495.4	
11.5	1453.09		1453.2		25.0	1496.66		1496.8	
12.0	1454.99		1455.1		25.5	1497.99		1498.1	
12.5	1456.87		1457.0		26.0	1499.30		1499.3	
13.0	1458.72		1458.9		26.5	1500.59		1500.6	
13.5	1460.55		1460.7		27.0	1501.86		1501.8	
14.0	1462.36		1462.6		27.5	1503.11		1503.1	
14.5	1464.14		1464.3		28.0	1504.35		1504.2	
15.0	1465.91		1466.1		28.5	1505.56		1505.4	
15.5	1467.65		1467.9		29.0	1506.76		1506.6	
16.0	1469.36		1469.6		29.5	1507.94		1507.8	
16.5	1471.06		1471.3		30.0	1509.10		1508.9	
17.0	1472.73		1472.9						