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Occurrence and Transport of Selected Constituents in Streams near the Stibnite Mining Area, Central Idaho, 2012–14

Scientific Investigations Report 2015–5166

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

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By Alexandra B. Etheridge

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Conversion Factors

Inch/Pound to International System of Units

Multiply	By	To obtain
Length		
inch (in.)	2.54	centimeter (cm)
inch (in.)	25.4	millimeter (mm)
foot (ft)	0.3048	meter (m)
mile (mi)	1.609	kilometer (km)
Area		
acre	4,047	square meter (m^2)
acre	0.004047	square kilometer (km^2)
square mile (mi^2)	2.590	square kilometer (km^2)
Volume		
cubic yard (yd^3)	0.7646	cubic meter (m^3)
Flow rate		
cubic foot per second (ft^3/s)	0.02832	cubic meter per second (m^3/s)
Mass		
pound per day (lb/d)	0.4536	kilogram per day (kg/d)
pound per year (lb/yr)	0.4536	kilogram per year (kg/yr)
ton per day (ton/d)	0.9072	metric ton per day
ton per year (ton/yr)	0.9072	metric ton per year

International System of Units to Inch/Pound

Multiply	By	To obtain
Length		
millimeter (mm)	0.03937	inch (in.)
meter (m)	3.281	foot (ft)
meter (m)	1.094	yard (yd)
Volume		
milliliter (mL)	0.033814	ounce, fluid (fl. oz)
liter (L)	0.2642	gallon (gal)

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

°F=(1.8×°C)+32.

Concentrations of chemical constituents in water are given either in milligrams per liter (mg/L) or micrograms per liter (µg/L).

Datums

Vertical coordinate information is referenced to the North American Vertical Datum of 1988 (NAVD 88).

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

Elevation, as used in this report, refers to feet above NAVD 88.

Abbreviations

AWQC	ambient water-quality criteria
BFI	base-flow index
CVO	Cascades Volcano Observatory
EFSFSR	East Fork of South Fork of the Salmon River
EPA	U.S. Environmental Protection Agency
FWC	streamflow-weighted concentration
IDEQ	Idaho Department of Environmental Quality
IBSP	Inorganic Blind Sample Project
IDEQ	Idaho Department of Environmental Quality
LOADEST	LOAD ESTimation program
LRL	laboratory reporting level
LT-MDL	long-term method detection level
MDAT	maximum daily average water temperature criterion for cold-water aquatic life
MDAT-SS	maximum daily average water temperature criterion for salmonid spawning
MDMT	maximum daily maximum water temperature (criterion for salmonid spawning)
MWMT	maximum weekly maximum water temperature criterion for bull trout habitat
MGI	Midas Gold, Inc.
MLE	maximum likelihood estimation method
NWIS	National Water Information System
NWQL	National Water Quality Laboratory
QA/QC	quality-assurance/quality-control
QC	quality-control
R^2	coefficient of determination
RMSE	root mean square error
RPD	relative percent difference
SVT	streamflow variability term
USFS	U.S. Forest Service
USGS	U.S. Geological Survey

Occurrence and Transport of Selected Constituents in Streams near the Stibnite Mining Area, Central Idaho, 2012–14

By Alexandra B. Etheridge

Abstract

Mining of stibnite (antimony sulfide), tungsten, gold, silver, and mercury near the town of Stibnite in central Idaho has left a legacy of trace element contamination in local streams. Water-quality and streamflow monitoring data from a network of five streamflow-gaging stations were used to estimate trace-element and suspended-sediment loads and flow-weighted concentrations in the Stibnite mining area between 2012 and 2014. Measured concentrations of arsenic exceeded human health-based water-quality criteria at each streamflow-gaging station, except for Meadow Creek (site 2), which was selected to represent background conditions in the study area. Measured concentrations of antimony exceeded human health-based water-quality criteria at sites 3, 4, and 5.

Regression models developed using the U.S. Geological Survey LOAD ESTimation (LOADEST) program showed that concentrated sources of arsenic and antimony are present in specific reaches along Meadow Creek and the East Fork of South Fork of the Salmon River (EFSFSR) between the EFSFSR at Stibnite (site 3) and the EFSFSR above Sugar Creek (site 4). Eighty percent of the arsenic and antimony loads were attributable to discrete reaches that accounted for 25 percent of the total streamflow in the study area. Streamflow was negatively correlated with arsenic and antimony concentrations, indicating groundwater sources. Continuously monitored specific conductance, alone or combined with continuously computed streamflow, was more significant than streamflow alone as a surrogate measure of dissolved arsenic and antimony concentrations. Surrogate regression models (with coefficients of determination ranging from 0.96 to 0.65) can be used to estimate arsenic and antimony concentrations in real time at all five streamflow-gaging stations.

LOADEST model simulation results indicated hysteresis in transport of suspended sediment and sediment-associated constituents. Predictor variables that account for streamflow variability reduced model bias and root mean square error when included in regression models used to estimate concentrations and loads of suspended sediment, total aluminum, total lead, and total mercury.

Ninety-eight percent of the estimated total mercury load transported downstream of the study area is attributable to Sugar Creek. A maximum concentration of 26 micrograms per liter was measured in Sugar Creek during May 2013 when snowmelt runoff occurred during a single peak in the hydrograph. Monitoring and modeling results indicate sediment and sediment-associated constituent concentrations and loads increase along Meadow Creek, likely because of the inflow of the East Fork of Meadow Creek, and decrease between sites 3 and 4 because the Glory Hole is trapping sediments. Sugar Creek (site 5) accounted for most of the sediment and sediment-associated constituent loading leaving the study area because loads from the East Fork of Meadow Creek remained trapped in the Glory Hole. Additionally, total mercury was detected at all five streamflow-gaging stations, and sampled mercury concentrations exceeded Idaho ambient water-quality criteria at all five streamflow-gaging stations.

Introduction

The Stibnite mining area (study area) is in the Boise and Payette National Forests along the East Fork of South Fork of the Salmon River (EFSFSR), 14 mi southeast of Yellow Pine, Idaho (fig. 1). Deposits of gold, silver, mercury, antimony, iron, arsenic, and tungsten occur in the study area. In 2009, Midas Gold, Inc. (MGI) began mineral exploration activities as part of the Golden Meadows Exploration Project to better define the potential of mineral deposits in the area. The exploration project defined a need to evaluate existing water-quality conditions in the study area and to identify potential source areas to target further reclamation efforts to be completed prior to or incorporated into plans for renewed mining activity. In cooperation with the Idaho Department of Lands and MGI, the U.S. Geological Survey (USGS) maintains and collects water-quality samples at five streamflow-gaging and waterquality monitoring -stations (herein referred to as monitoring sites) in the study area (fig. 1, table 1). The monitoring site at the EFSFSR at Stibnite, (site 3, table 1) was installed in 1928 and operated intermittently.
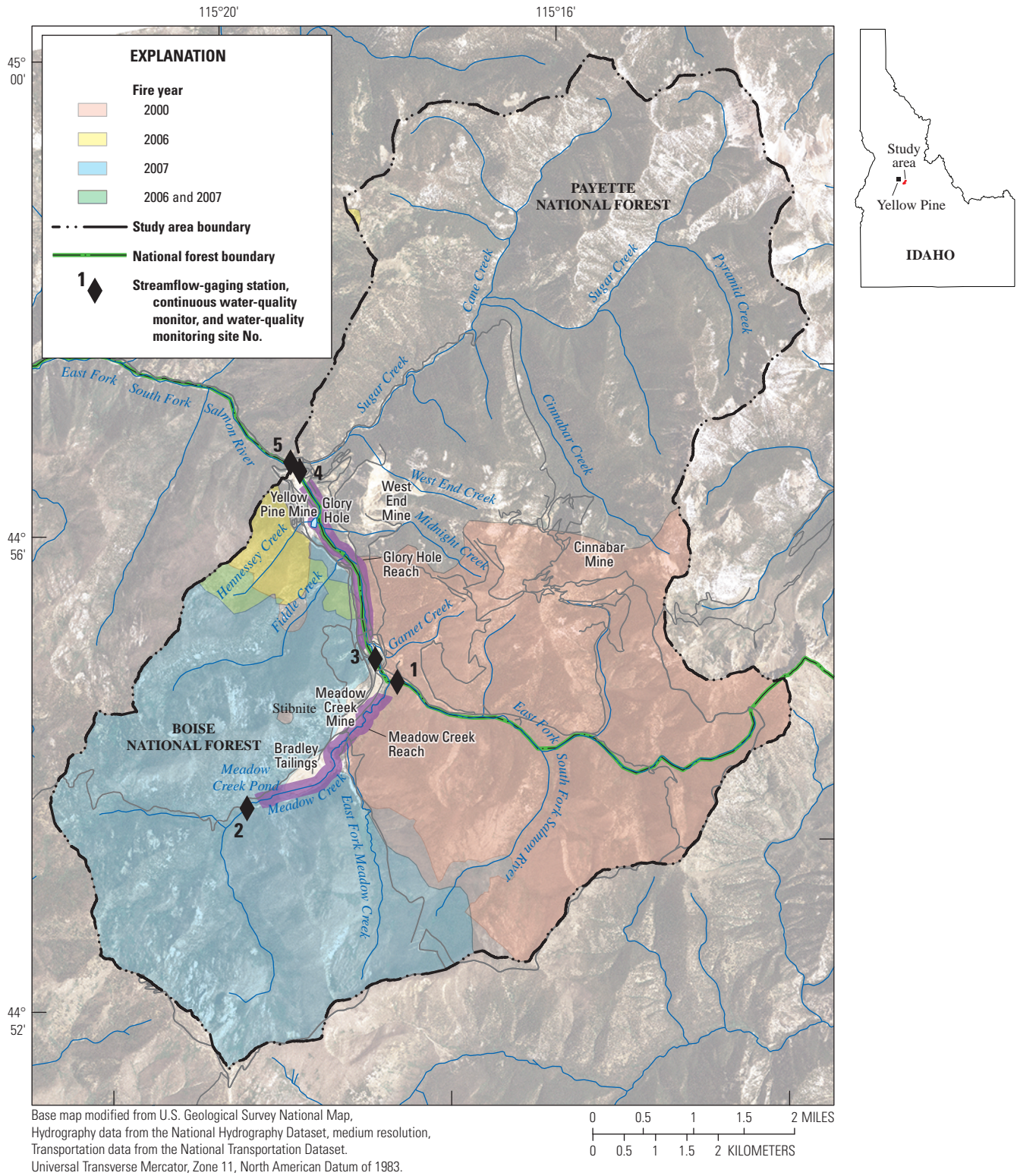
Figure 1.   Streamflow-gaging stations and water-quality monitoring sites near the Stibnite mining area, central Idaho, 2012–14.

Table 1.   Streamflow-gaging and water-quality monitoring stations near the Stibnite mining area, central Idaho, 2012–14.

Abbreviated site No.	Streamflow-gaging and water-quality monitoring station	Streamflow-gaging and water-quality monitoring station name	Continuous parameters collected	Number of water-quality samples
1	13310800	East Fork of South Fork Salmon River above Meadow Creek, near Stibnite, Idaho	Continuous stage-discharge; seasonally continuous water temperature, specific conductance, pH	20
2	13310850	Meadow Creek near Stibnite, Idaho	Continuous stage-discharge; seasonally continuous water temperature, specific conductance, pH	20
3	13311000	East Fork of South Fork Salmon River at Stibnite, Idaho	Continuous stage-discharge; seasonally continuous water temperature, specific conductance, pH	24
4	13311250	East Fork of South Fork Salmon River above Sugar Creek, near Stibnite, Idaho	Continuous stage-discharge; seasonally continuous water temperature, specific conductance, pH	22
5	13311450	Sugar Creek near Stibnite, Idaho	Continuous stage-discharge; seasonally continuous water temperature, specific conductance, pH	21

During October 2010 the site was reinstated on a continuous basis. The remaining monitoring sites were installed in September 2011 to support the analysis of trace element occurrence and transport in surface water. This report summarizes findings from hydrologic and water-quality monitoring in the network of five monitoring sites in the Stibnite mining area during water years[1] 2012–14.

Gold, antimony, mercury, and tungsten have been mined and processed in the study area since the early 1900s. During World War II, the Stibnite mining area produced 98 percent of the antimony and 60 percent of the tungsten for the Allied war effort. Mining operations took place at Meadow Creek Mine in the Meadow Creek valley between 1919 and 1938; at Yellow Pine Mine in the area surrounding the Glory Hole (a pit lake) between 1937 and 1952; and at West End Mine in areas near

West End Creek and Garnet Creek between 1982 and 1999 (fig. 1). Cinnabar Mine was operated intermittently between 1902 and 1966 in the Cinnabar Creek drainage, which is a tributary to Sugar Creek (fig. 1).

Historical mining-related activities altered stream configuration and habitat in the study area. Mill tailings, known as the Bradley tailings, were disposed in impoundments covering 100 acres of the Meadow Creek valley floor during active mining periods. The Meadow Creek stream channel was diverted around tailings and reconstructed several times to mitigate effects on water-quality from tailings. A dam constructed for mining operations in the East Fork of Meadow Creek failed in 1965, which resulted in tailings and debris deposits downstream. Waste rock dumps were generated upstream and downstream of the Glory Hole, and the EFSFSR was diverted around the Glory Hole as it was mined prior to 1955. After 1955, the Glory Hole was allowed to fill with water and remains part of the EFSFSR channel to date. An estimated 3,000 yd^3 of mercury-laden tailings deposited near the Cinnabar Mine on Cinnabar Creek act as a substantial source of mercury in Cinnabar and Sugar Creeks (Trainor, 2003).

[1]A water year is the period from October 1 of any given year to September 30 of the following year. Water year is used almost exclusively throughout this report. To reduce confusion between calendar years and water years, all reference to years and periods in this report is to water years unless specifically referred to as calendar year.

Mining-related activities also have affected surface-water quality in the study area. Water-quality monitoring efforts historically preceded periods of renewed mining exploration and followed the completion of various reclamation efforts. A water-quality trend study conducted from 1979 to 1985 showed large increases in turbidity and concentrations of arsenic, antimony, and iron after a renewed period of mining activity in 1982 (Klahr, 1987). Prior investigations monitoring water quality report concentrations of arsenic, free cyanide, lead, mercury, silver, and zinc exceeding chronic freshwater ambient water-quality criteria (AWQC) established for the protection of aquatic organisms in the study area (Trainor, 1993; URS Corporation, 2000).

Federal agencies implemented remediation efforts in mining-affected areas in the late 1990s. The U.S. Environmental Protection Agency (EPA) oversaw a reconstruction of the upper Meadow Creek stream channel that was completed in 1998 (URS Corporation, 2000). The U.S. Forest Service (USFS) reconstructed 4,300 ft of the lower Meadow Creek channel in 2005. The USFS and the EPA capped or removed mercury-contaminated tailings in the Cinnabar Mine area in 2003, and the EPA has shown renewed interest in remediating the Cinnabar Mine area.

The Federal Water Pollution Control Act (the "Clean Water Act", 33 U.S.C §§1251–1387; see http://www.epa.gov/oecaagct/lcwa.html) requires states to evaluate surface-water quality and periodically update a list of water bodies where beneficial uses are impaired as a result of poor water quality (the 303[d] list). The Idaho Department of Environmental Quality (IDEQ) determined that beneficial uses in the EFSFSR and Sugar Creek included cold-water salmonid spawning and primary-contact recreation. Additional beneficial uses in the EFSFSR include drinking-water supply for the town of Yellow Pine, and "special-resource water," a classification indicating the need for intensive protection to preserve unique characteristics (Idaho Department of Environmental Quality, 2002). Streams in the study area are critical habitat for Chinook salmon (*Oncorhynchus tshawytscha*), steelhead (*Oncorhynchus mykiss*), bull trout (*Salvelinus confluentus*), and westslope cutthroat trout (*Oncorhynchus clarki lewisi*), which are all threatened, endangered, or sensitive species (Idaho Department of Environmental Quality, 2002). The IDEQ listed the EFSFSR as impaired for contamination of metals and sediment in 1998, but removed the EFSFSR from the 303(d) list in 2002 (Idaho Department of Environmental Quality, 2002). In 2012, IDEQ listed the EFSFSR and Sugar Creek as water-quality impaired because of concentrations of arsenic and antimony that exceed human health criteria (Idaho Department of Environmental Quality, 2014). IDEQ also listed Sugar Creek as water-quality impaired because of concentrations of mercury that exceed the Idaho chronic AWQC.

Purpose and Scope

This report summarizes findings from a five-station water-quality and hydrologic monitoring network in the Stibnite mining area during 2012–14. Findings will provide a baseline understanding of surface-water-quality conditions and trace-metals transport in the study area prior to future mining activities. Water-quality models summarized in this report may be used to estimate constituent loads and concentrations with ongoing model validation using discrete samples. The monitoring network was designed to provide interpretable results that meet the following objectives:

- Identify and quantify contributions and transport of selected trace elements in discrete reaches between monitoring sites in the Stibnite mining area;

- Estimate the spatial and temporal variation in trace-metals and suspended-sediment loading and streamflow-weighted concentrations in the Stibnite mining area; and

- Evaluate continuous water-quality parameters and streamflow as surrogates to estimate concentrations of selected constituents.

Description of Study Area

Trace elements and sediment occurrence and transport were evaluated in the EFSFSR from the headwaters to the confluence with Sugar Creek and in the Sugar Creek watershed (fig. 1). The study area includes 42.9 mi^2 of steep mountain terrain ranging from 5,930 to 9,310 ft in elevation. Seventy-one percent of the study area slopes at a gradient greater than 30 percent (U.S. Geological Survey, 2012), resulting in occasional mass wasting and substantial surface erosion during periods of rainfall and snowmelt runoff. Mean annual precipitation is 31 in., falling mostly as snow between October and April. Peak snowmelt and streamflow typically occur between May and July and low flows occur from September to January (Kuzis, 1997). Most of the study area is comprised of USFS public land in the Payette and Boise National Forests. Mining-related activity occurs on both private and public lands. Wildfires in 2000, 2006, and 2007 burned about 40 percent of the forested land in the MGI-proposed exploration area (fig. 1). Recent wildfires likely resulted in increased soil erosion and solar loading to surface-water bodies (U.S. Forest Service, 2012). Streams in the study area are critical habitat for Chinook salmon, steelhead, bull trout, and westslope cutthroat trout, which are all either threatened, endangered, or sensitive species (Idaho Department of Environmental Quality, 2002).

Mineralization and mineral extraction influence hydrogeology and water quality in the study area. The granitic Idaho batholith intruded the region in the Cretaceous

period, leaving a roof of Neoproterozoic to Cambrian age metasedimentary rocks known as a roof pendant in the east side of the study area (Mitchell, 2000). Eocene mineralization occurred in a series of faults that cut through granitic and metasedimentary rocks, and Pleistocene glaciation deposited as much as 60 ft of alluvium in valley floors (Larsen and Livingston, 1920). During low flow conditions, streams in the study area generally gain streamflow from shallow groundwater, which is present in seeps and springs at the surface and ranges to depths of about 20 ft below the alluvial surface (URS Corporation, 2000). Depth to groundwater is deeper where mining waste materials have been placed. Groundwater also is present to a limited extent in fractured bedrock (Mitchell, 2000). Naturally occurring mineralized zones and mine tailings in contact with the water table act as sources of trace elements to both groundwater and surface water (Kuzis, 1997). Concentrations of dissolved metals are typically higher in groundwater than in surface water (Trainor, 1993; URS Corporation, 2000).

Water-quality conditions generally deteriorate in a downstream direction in the EFSFSR. In particular, concentrations of arsenic and antimony increase downstream of the confluence with Meadow Creek and between the confluences with Meadow and Sugar Creeks (URS Corporation, 2000). As streamflow increases in the EFSFSR, concentrations of sediment and sediment-associated metals including aluminum, iron, and mercury also increase. Suspended-sediment concentrations and total concentrations of some trace elements decrease as the EFSFSR flows past the Glory Hole, which acts as a sediment trap (Idaho Department of Environmental Quality, 2002). In May 2014, the Glory Hole was surveyed with a water surface elevation of 6,037.5 ft and a maximum depth of 35.2 ft (K. Fend, Midas Gold, written commun., 2014). Most surface-water-quality samples show similar concentrations of total and dissolved arsenic or antimony, indicating a groundwater source (URS Corporation, 2000). An negative correlation between streamflow and concentrations of arsenic and antimony also implicates groundwater as a source of arsenic and antimony in the study area. Concentrations of suspended sediment and sediment-associated metals such as aluminum and mercury are lower in filtered samples and higher in unfiltered samples, suggesting surface runoff as the largest contributing source. A positive correlation between streamflow and concentrations of suspended sediment, total aluminum, and total mercury also implicates surface runoff as a source of sediment, aluminum, and mercury in the study area. Sugar Creek is also a known source of mercury (Trainor, 1993; URS Corporation, 2000).

Water-quality samples and streamflow data from the five monitoring sites provided information necessary to evaluate the spatial and temporal transport of trace elements and suspended sediment (fig. 1, table 1). The EFSFSR monitoring site upstream of the confluence with Meadow Creek (site 1) quantifies constituent loads in the EFSFSR absent any loading from Meadow Creek. The monitoring site on Meadow Creek (site 2), upstream of the Bradley tailings

disposal area, provided data used to quantify background water-quality conditions. Site 3 is on the EFSFSR about 1,300 ft downstream of the confluence of Meadow Creek and the EFSFSR, and is used to quantify source contributions from the East Fork of Meadow Creek (also known as Blowout Creek) and the Bradley tailings disposal area. Site 4 is on the EFSFSR about 2,660 ft downstream of the Glory Hole and about 700 ft upstream of the confluence with Sugar Creek and is used to quantify loads from ungaged tributaries, groundwater exchange along this reach, and the Glory Hole. Site 5, near the mouth of Sugar Creek, quantifies constituent loading from the Sugar Creek watershed including Cinnabar Creek, a known source of mercury contamination. Combined, hydrologic and water-quality data from sites 4 and 5 provide information on trace elements transport to the EFSFSR from the entire study area.

Study Methods

In October 2010 and September 2011, five monitoring sites were established as a network to provide information about trace elements and the occurrence and transport of suspended sediments in the study area (fig. 1). Hydrologic and water-quality data from each monitoring site were used in regression models to estimate constituent loads and concentrations. Estimated loads were compared between stations to identify source areas for trace elements and to quantify constituent loading in discrete reaches.

Hydrologic Monitoring

Streamflow at the five monitoring sites and water-quality sampling sites (fig. 1, table 1) was measured using standard USGS methods as described in Mueller and Wagner (2009) and Turnipseed and Sauer (2010). Continuous streamflow records were computed using methods described in Rantz and others (1982). Streamflow was computed using a continuous record of water stage calibrated to periodic streamflow measurements. Monitoring sites were operated year-round.

Continuous Water-Quality Monitoring

Water temperature, specific conductance, and pH were measured continuously at each of the monitoring sites. Continuous monitors were installed at sites 1–3 in September 2011 and at sites 4 and 5 in April 2012. Continuous monitors were operated and continuous water-quality data were reviewed in accordance with Wagner and others (2006). Continuous water-quality monitors were operated seasonally (April to late October) and removed during the winter because of limited access and to prevent damage during extreme cold conditions.

Water-Quality Sampling and Analysis

Discrete water-quality samples were routinely analyzed for total and dissolved concentrations of aluminum, antimony, arsenic, cadmium, chromium, copper, iron, lead, mercury, and zinc. Discrete water-quality samples were also routinely analyzed for acid neutralizing capacity (hardness) as calcium carbonate, and for major ions including dissolved calcium, magnesium, manganese, potassium, silica, sodium, chloride,

fluoride, and sulfate. Water-quality constituents collected in the field included water temperature, specific conductance, and pH.

Although the number of samples collected at each site varied, the approach at each site was designed to allocate samples over the full range of the station hydrograph to develop a robust relation between constituent concentration and streamflow. For example, samples collected at site 3 are plotted on the streamflow duration hydrograph to summarize hydrologic conditions during the sampling periods (fig. 2).
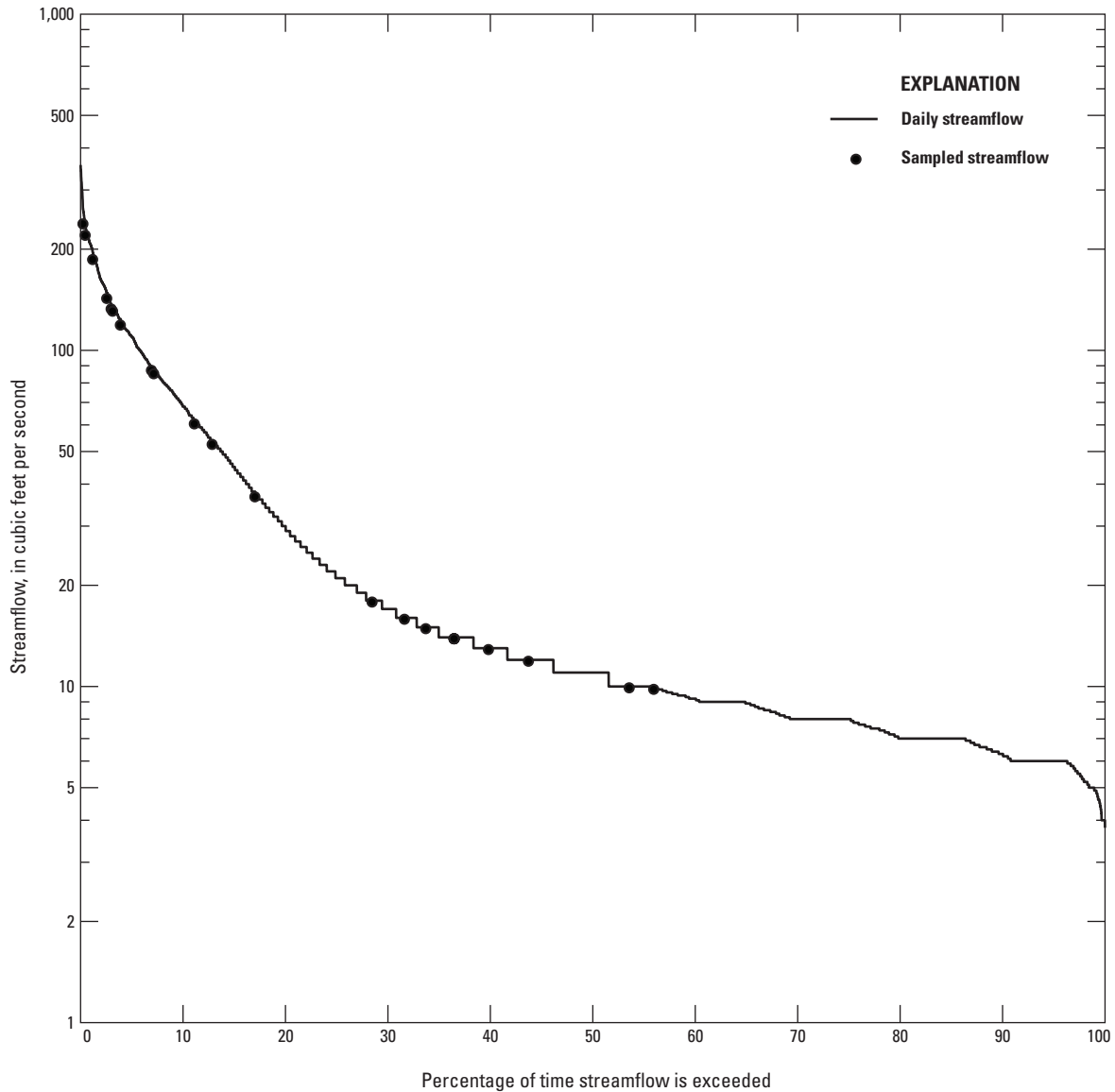
Figure 2.   Streamflow duration (1928–2014) and measured streamflow at East Fork of South Fork of the Salmon River at Stibnite, central Idaho, 2012–14.

Although the magnitude of measured streamflow differed among sites, the timing of sample collection over the streamflow hydrograph was similar at each site.

Water-quality samples at all sites were collected using nonmetallic samplers and cross-sectional, depth-integrated sampling procedures (U.S. Geological Survey, various dates). Most samples were collected isokinetically and in equal-width increments. However, low-streamflow conditions with shallow, slow moving water occasionally precluded isokinetic sample collection. Prior to installation of bank-operated cableways in October 2013, samples collected during high streamflow at sites 3 and 4 were collected non-isokinetically using multiple vertical transects. Minor variations in sample collection methods are documented in sample metadata stored in the USGS National Water Information System (U.S. Geological Survey, 2015). Sampling equipment was cleaned and samples were collected according to trace-metal protocols described in the USGS National Field Manual (U.S. Geological Survey, various dates). Samples for laboratory analyses were composited and subsampled using a polyethylene churn splitting device. Samples for whole-water recoverable (total) analyses were withdrawn directly from the splitting device. Samples for dissolved (smaller than 0.45-micrometer [µm] diameter) analyses were withdrawn directly from the churn splitter and filtered through a pre-rinsed, 0.45-µm pore size, disposable capsule filter. Samples to be analyzed for trace elements were preserved with 2 milliliters (mL) of Ultrex® nitric acid. Samples to be analyzed for mercury were preserved with 2 mL of Omni-Trace® hydrochloric acid. Samples were shipped in plastic coolers to the USGS National Water Quality Laboratory (NWQL) in Denver, Colorado.

All water-quality samples (excluding suspended sediment) were analyzed at the NWQL using established analytical techniques. Trace-element concentrations were determined at NWQL by atomic absorption spectrometry in conjunction with a graphite furnace and inductively coupled plasma-mass spectrometry (Fishman and Friedman, 1989; Fishman, 1993; Hoffman and others, 1996; Garbarino and Struzeski, 1998; Garbarino and others, 2005, 2006). Mercury concentrations were determined by atomic fluorescence spectrometry (Garbarino and Damrau, 2001). Suspended-sediment samples were analyzed for concentration and the weight percentage of particles less than 0.0625 mm by the USGS Cascades Volcano Observatory (CVO) Sediment Laboratory using methods described in Guy (1969) and the American Society for Testing and Materials (2002) method D3977-97. Quality-assurance/quality-control (QA/QC) procedures used at the NWQL were documented by Pritt and Raese (1995). The CVO Sediment Laboratory QA/QC procedures are described in Knott and others (1993). All the data collected as part of this study are publicly available from the USGS National Water Information System (U.S Geological Survey, 2015).

Data Quality Assurance and Quality Control

Water-quality sample results were reviewed after receipt of the laboratory analysis. Data validation included use of a relative percent difference (RPD) to evaluate the relation between dissolved concentrations and whole-water concentrations. RPDs were calculated using the absolute value of the difference between the result pair, divided by the mean of the result pair, multiplied by 100. Expressing precision relative to a mean concentration standardizes comparison of precision among individual constituents. Laboratory analyses were rerun and (or) verified when the dissolved fraction exceeded the whole-water fraction with an RPD greater than 10 percent. Suspended-sediment results were reviewed for anomalies in comparison with historical results at the same location.

Analytical data also were validated using results from quality-control (QC) programs in use at the NWQL. The NWQL monitors and evaluates quality of inorganic analytical results through the use of double-blind QC samples as part of the Inorganic Blind Sample Project (IBSP). A "double-blind sample" is a QC sample submitted for analysis for which the identity of the sample and the concentration of the individual constituents within the sample are not known to the analyst. The QC samples typically are not synthetic reference materials; rather, they are derived from snowmelt, surface-water, or groundwater sources (Woodworth and Connor, 2003). Analytical errors settle into two major categories: bias and variability. Bias is systematic error that causes consistently positive or negative deviation in the results relative to the median expected concentration in the reference sample. Variability is random error that affects the ability to reproduce results. Repeated measurements of the IBSP samples over time provide estimates of systematic bias and random variability in the analytical procedures at the laboratory.

Quality-control samples also were collected in the field to evaluate the quality of the analytical results, and were analyzed concurrently in the laboratory with routine samples. Split replicates were collected and submitted at a proportion equivalent to at least 10 percent of the total number of water samples, and one field blank sample was collected during every sampling event.

Replicate data can be obtained in different ways to provide an assessment of precision (reproducibility) of analytical results. All replicate samples collected as part of this study were split replicates representing a single composite sample collected in the field and split into two subsamples for separate analysis. Analyses of split replicates indicate the reproducibility of environmental data that are affected by the combined variability potentially introduced by field and laboratory processes. The precision of the analytical results was determined using the RPD between the split replicates. An RPD of less than 20 percent for chemical analytes was considered acceptable.

Blank samples identify the presence and magnitude of potential contamination that could bias analytical results. Field blanks are aliquots of deionized water that are certified as contaminant free and are processed through the sampling equipment used to collect stream samples. All blanks were collected as field blanks. Field blanks are subjected to the same processing (sample splitting, filtration, preservation, transportation, and laboratory handling) as environmental samples. Field blanks included all sources of contamination associated with source-solution blanks plus any contamination from ambient conditions at sample sites. Field blanks also included any contamination from shipping or delivering the blanks to the analytical laboratory and storing, processing, and analyzing the blanks at the laboratory. Blank samples were analyzed for the same constituents as the environmental samples.

Summarized quality-assurance data analysis (appendix A) shows that dissolved cadmium and lead results from this study should be used with caution. Both analytes commonly were not detected at concentrations greater than the long-term method detection level (LT-MDL). Less frequently, dissolved cadmium and lead were detected near the laboratory LT-MDL at concentrations that did not exceed hardness-based AWQC.

Model Development

Two types of regression models were developed to estimate trace-metal and suspended-sediment transport and occurrence. The USGS LOAD ESTimator (LOADEST) FORTRAN program (Runkel and others, 2004; Runkel, 2013) was used to estimate daily and monthly loads. Estimated annual loads and total annual streamflow were used to compute streamflow-weighted concentrations (FWCs) of selected water-quality constituents. Surrogate regression models were developed using continuously monitored water-quality parameters, and optionally, functions of time and streamflow to estimate 15-minute and daily trace metal concentrations and loads.

LOADEST Models for Estimating Constituent Loads

For this study, loads were estimated for selected constituents using LOADEST. The LOADEST modeling program is based on a rating-curve method (Cohn and others, 1989, 1992; Crawford, 1991) that uses regression to estimate constituent concentrations and loads in relation to several predictor variables related to streamflow and time. This type of model has been used to estimate constituent concentrations for periods when sample data were not available (Gilroy and others, 1990), and to estimate a basin flux of water-quality constituents (Goolsby and others, 1999). Additional predictor variables describing streamflow variability were tested for significance in LOADEST models according to methods described by Garrett (2012).

Streamflow variability terms (SVTs) were defined in one of two ways. The first type of SVT was defined as the difference between mean streamflow (Q) on day i and the mean streamflow of the previous k days, given as:

$$dQk = \sum_{j=i-k}^{i-1} \frac{\ln Qj}{k} \qquad (1)$$

This variability term (dQ) with a 1-day time step ($dQ1$) helps describe effects of hysteresis (Wang and Linker, 2008). Hysteresis occurs when the value of a physical property (constituent concentration) changes at a different rate than the effect assumed to be causing it (streamflow). Use of a streamflow variability term eliminates the need to develop a different regression between streamflow and load on the rising compared to the falling limb of the hydrograph. A term with a 30-day step ($dQ30$) helps describe effects of sequential events or prolonged event peaks. In some instances, the absolute value of $dQ1$ ($|dQ1|$) better describes loads in the regression model than $dQ1$, representing cases where the degree of flashiness of the event was the critical element, rather than hysteresis. In some instances, use of the untransformed streamflow also better describes loads in the regression model than the use of $\ln Q$.

The second type of SVT used the base-flow index (BFI) to explain streamflow variability. The BFI describes the amount of streamflow in a river derived from groundwater discharge using a simple ratio of estimated daily runoff to daily mean streamflow. Runoff was estimated using the local minimum method of hydrograph separation (Lim and others, 2005; Gustard and Demuth, 2009).

LOADEST was used for this study to develop regression models for estimating loads of arsenic, antimony, aluminum, manganese, lead, cadmium, zinc, mercury, and suspended sediment for each site. Because of the short duration of the study and to facilitate comparison among sites, predictor variables related to trends over time were not used. Data collected between September 2011 and October 2014 were used to calibrate the regression models, and constituent loads were estimated for 2012–14. The equation for the regression models is:

$$\ln L = I + a(\ln Q) + b(\ln Q^2) + c[\sin(2\pi T)] \qquad (2)$$
$$+ d[\cos(2\pi T)] + e(SVT) + \varepsilon$$

where

$\ln$	is the natural logarithm;
L	is the constituent load, in pounds per day;
I	is the regression intercept;
Q	is the centered streamflow, in cubic feet per second;
T	is the centered decimal time in years from the beginning of the calibration period;

$\sin(2\pi T)$ and
$\cos(2\pi T)$ are periodic time functions that describe seasonal variability;

SVT is the term describing streamflow variability ($dQ_k, \left|dQ_k\right|$, or BFI);

a, b, c, d, e are regression coefficients that remain constant over time; and

ε is the unaccounted error associated with the regression model.

For each model, time and streamflow predictor variables in the regression equation were selected on the basis of Akaike Information Criterion (Akaike, 1981; Judge and others, 1985). The criterion is designed to achieve a good compromise between using as many predictor variables as possible to explain the variance in load while minimizing the standard error of the resulting estimates. The streamflow variability predictor variable was selected based on its significance level. Estimates of the daily constituent load for each site were computed using the selected model and daily mean streamflow. Bias introduced by conversion of the logarithm of load into estimates of actual load was corrected using the Bradu-Mundlak method (Bradu and Mundlak, 1970; Cohn and others, 1989; Crawford, 1991).

Surrogate Regression Models for Estimating Constituent Concentrations

Multiple linear regression models were developed using continuously monitored water-quality parameters (surrogates) to estimate concentrations of dissolved arsenic, dissolved antimony, and total mercury at selected sites. Functions of time and discharge also were used as predictor variables in surrogate regression models if determined to be significant. Surrogate models were developed using stepwise linear regression analysis as described in Wood and Etheridge (2011) using the U.S. Geological Survey R statistical programming package "GSqwsr" (DeCicco and Corsi, 2014). The functional form of the surrogate models is:

$$C = I + a(SC) + b(\ln SC) + c(Q) + d(\ln Q)$$
$$+ e\left[\sin(2\pi T)\right] + f\left[\cos(2\pi T)\right] + g(\text{BFI}) \quad (3)$$

where

C is the constituent concentration, in micrograms per liter;

I is the y-intercept; and

a,c,...g are regression coefficients.

Surrogate models were calibrated using 15-minute values of continuously monitored streamflow and water-quality parameters in conjunction with laboratory analytical results for environmental samples.

Calculation of Streamflow-Weighted Concentrations using LOADEST Results

Interpretation of concentrations of trace elements in streams is improved by examining the mean FWC spanning a specified time period rather than individual concentrations or statistics based on a dataset of individual concentrations. An FWC is an estimate of the mean concentration in a total volume of water flowing past a site during a specific period, such as a year, or group of years. For this study, a mean FWC at each site was calculated using the LOADEST result for a constituent load during a given water year or water-year span divided by the total streamflow during that water year or water-year span. Loads and FWCs were estimated for each water year (2012–14) and as a mean for the 3-year study period.

Statistical Analysis of Sample Results

Summary statistics are provided for concentrations of all analyzed constituents and are compared with applicable ambient water-quality criteria (AWQC). Concentrations of total and dissolved mercury, cadmium, lead, and zinc, as well as dissolved manganese, were commonly lower than applicable LT-MDLs and LOADEST (which requires 7 detections to compute regression estimates); could not be used to estimate loads; and, thus, mean FWCs could not be determined for these constituents at all sites in the study area. The maximum likelihood estimation (MLE) method was used to estimate summary statistics on censored sample results. Logarithmic transformation was used with MLE as necessary to normalize the distribution of censored results (Helsel, 2012). Summary statistics were calculated from the data when less than 25 percent of the results were censored (Helsel and Hirsch, 2002).

Ambient Water-Quality Criteria

Streamflow-weighted concentrations and (or) summary statistics of constituent concentrations were compared to applicable AWQC. Comparisons of measured AWQC values for trace metals are complicated because criteria change as a function of water hardness. For this assessment, chronic freshwater AWQC concentrations were based on the applicable State of Idaho criteria for the protection of aquatic life (Idaho Department of Environmental Quality, various dates). Representative chronic criteria values were calculated using the minimum hardness value measured in samples collected from each site. The statewide cadmium criterion is from Mebane (2006) and the statewide zinc criterion is from U.S. Environmental Protection Agency (2002).

Streamflow and Water-Quality Monitoring

Monitoring sites in the study area were established in September 2011 except for site 3, operated from 1928–42, 1983–97, and 2011–14. Statistics for the 50th and 90th percentiles of streamflow over 32 years of record at site 3 show that peak snowmelt runoff occurred earlier in the water year during the study period (fig. 3). Sample-collection timing shown on the hydrograph for site 3 suggests that streamflows

at all sites likely included the 90th percentile of streamflow (figs. 2 and 3). Concentrations of suspended sediment and sediment-associated constituents generally were highest in the samples collected during peak streamflows in May 2013, possibly because snowmelt runoff in 2013 occurred as a single peak with higher capacity to mobilize, transport, and concentrate sediment near the peak of snowmelt runoff. Samples were collected after relatively short-duration rainfall runoff events in October 2011 and August 2014, but were not collected on the rising limb of the hydrograph for any rainfall runoff event.
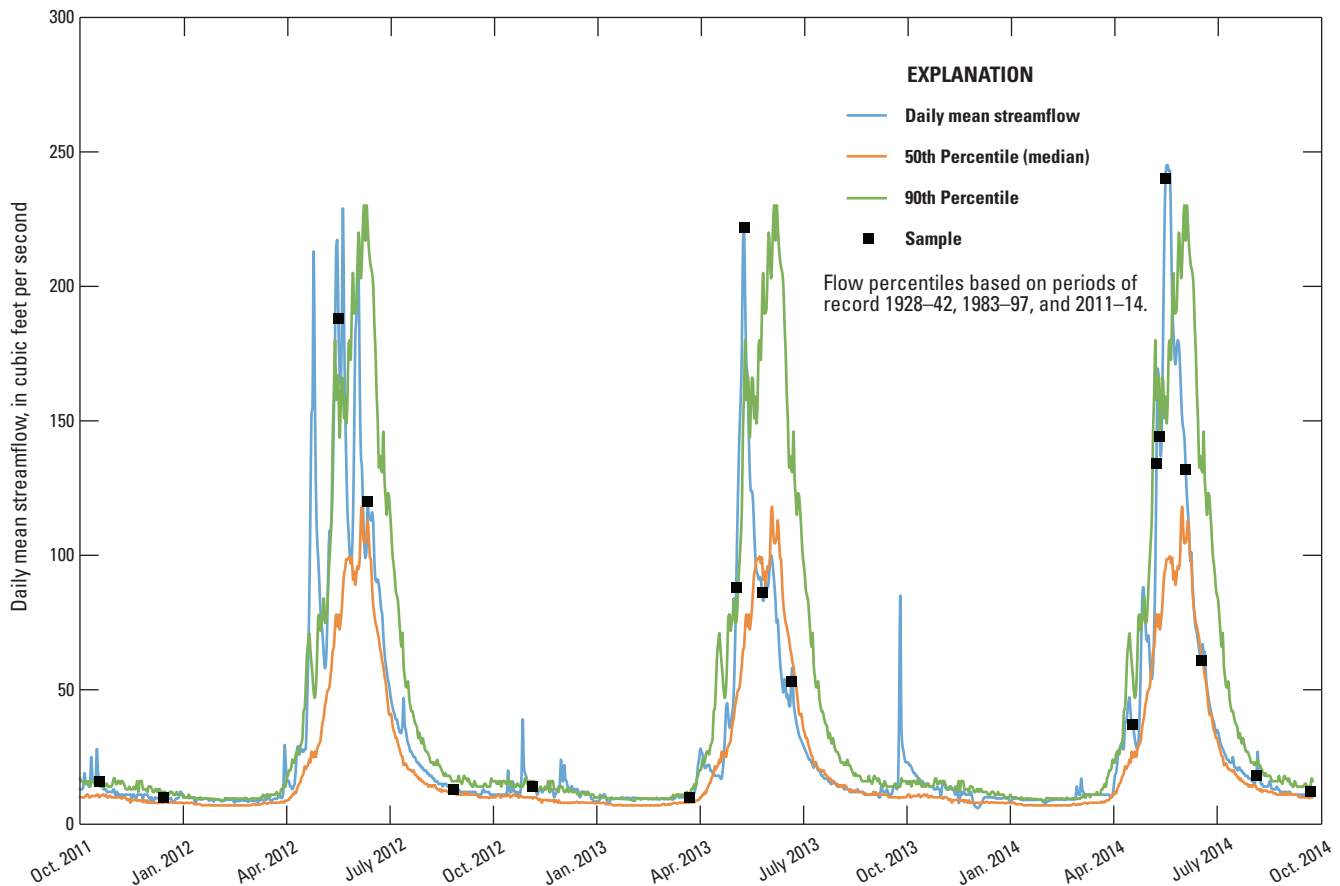
Figure 3. 50th and 90th streamflow percentiles for the periods of record, daily mean streamflow, and timing of water-quality sample collection at East Fork of South Fork of the Salmon River at Stibnite, central Idaho, 2012–14.

Except for arsenic, antimony, and mercury, concentrations of trace elements in streams in the EFSFSR (sites 1, 3, and 4), Meadow Creek (site 2), and Sugar Creek (site 5) did not exceed applicable AWQC or human-health criteria (appendix B, table 2). Arsenic concentrations exceeded the human-health-based criterion of 10 µg/L in all samples collected in the EFSFSR at stations 3 and 4 downstream of the confluence with Meadow Creek. Antimony concentrations exceeded the human-health based criterion of 5.6 µg/L in 87 percent of the samples collected from

site 3 and 100 percent of the samples collected from site 4. Every site had at least one exceedance of the 0.012-µg/L chronic AWQC for total mercury, and two samples from site 5 exceeded the 2.1-µg/L acute AWQC for total mercury (table 2, fig. 4, appendix A). Concentrations of regulated trace elements, including cadmium, copper, and zinc, were detected infrequently and did not exceed the AWQC. Water-quality sample results for chromium were not speciated, but dissolved and total chromium were not detected at concentrations higher than hardness-dependent AWQC for hexavalent chromium.

Table 2. Exceedances of water-quality criteria in samples collected from five streamflow and water-quality monitoring sites in the Stibnite mining area, central Idaho, 2012–14.

[Site names and locations are shown in table 1 and figure 1, respectively. **Applicable criteria:** Criteria shown are not hardness-dependent. MDAT, maximum daily average water-temperature criterion for coldwater aquatic life; MDAT-SS, maximum daily average water-temperature criterion for salmonid spawning; MDMT, maximum daily maximum water-temperature criterion for salmonid spawning; MWMT, maximum weekly maximum water-temperature criterion for bull trout habitat. **Criterion type:** HHB, human-health based criterion; CCC, criterion continuous concentration or "chronic" aquatic-life criterion; CMC, criterion maximum concentration or "acute" aquatic-life criterion; CW, coldwater; SS, salmonid spawning; BT, bull trout. **Abbreviations:** µg/L, microgram per liter; °C, degrees Celcius; <, less than; NA, not applicable]

Constituent	Applicable criteria	Criterion type	Site 1	Site 2	Site 3	Site 4	Site 5
			Frequency of exceedance, in percent				
Dissolved arsenic	Minimum: 10 µg/L	HHB	45	0	100	100	48
	Maximum: 150 µg/L	CCC	0	0	0	0	0
	Number of samples	NA	20	21	24	22	21
Dissolved antimony	Miniumum: 5.6 µg/L	HHB	0	0	87	100	30
	Maximum: NA	NA	NA	NA	NA	NA	NA
	Number of samples	NA	20	18	23	21	20
Total mercury	Miniumum: 0.012 µg/L	CCC	43	14	46	33	95
	Maximum: 2.1 µg/L	CMC	0	0	0	0	11
	Number of samples	NA	7	7	13	15	19
Water temperature[1]	MDAT: 19°C	CW	0	0	0	0	0
	MDAT-SS: 9°C	SS	29	32	37	47	47
	MDMT: 13°C	SS	< 1	< 1	9	9	4
	MWMT: 13°C	BT	0	0	0	1	11
	Number of 15-minute values assessed	NA	53,731	51,727	52,674	51,534	49,126

[1]Water-temperature data collected seasonally (April–October) every 15 minutes from each site were assessed with applicable criteria. A 7-day average was computed from 15-minute values and used to assess the MWMT. A daily average was computed from 15-minute values and used to assess the MDAT and MDAT-SS.
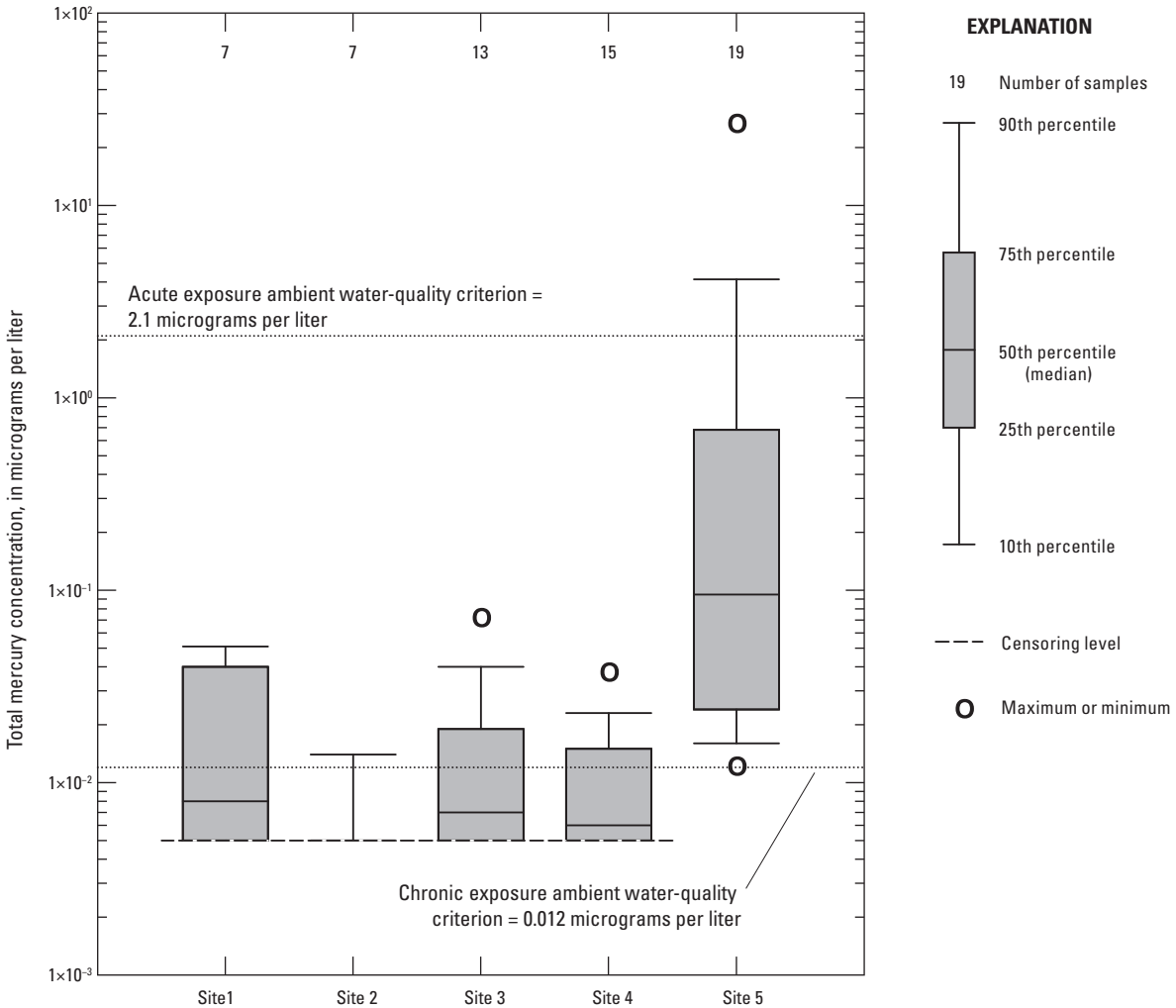
Figure 4.   Total mercury concentrations in five streamflow and water-quality monitoring sites in the Stibnite mining area, central Idaho, 2012–14. Site names and locations are shown in table 1 and figure 1, respectively.

Continuous measurements of stream temperature and pH showed few exceedances of applicable State-of-Idaho general water-quality criteria (Idaho Department of Environmental Quality, various dates). pH was greater than the general minimum criterion of 6.5 and less than the general maximum criterion of 9.0 at all of the sites.

Applicable salmonid spawning criteria in the South Fork of the Salmon River and its tributaries apply to seasonal periods between March 15 and July 1 for spring spawning salmonids (steelhead), and between August 15 and June 1 of the following year for autumn-spawning salmonids (Chinook salmon) (Idaho Department of Environmental Quality, 2012). Therefore, seasonal salmonid spawning criteria apply during a substantial part of the year because of the presence of both spring and autumn salmonid spawners. Continuous water-temperature data collected from late April to late October during 2012–14 showed that water temperature exceeded the 9 °C maximum daily average temperature criterion for salmonid spawning (MDAT-SS) at least 29 percent of the time at all sites (table 2, fig. 5). Water temperature at sites 3 and 4 in the EFSFSR and site 5 in Sugar Creek exceeded the 13 °C maximum daily maximum temperature (MDMT) criterion for salmonid spawning between 4 and 9 percent of the time (table 2, fig. 5).

Figure 5. Temperature exceedance for five streamflow and water-quality monitoring sites in the Stibnite mining area, central Idaho, 2012–14. Site names and locations are shown in table 1 and figure 1, respectively.

Occurrence, Transport, and Deposition of Selected Constituents

Occurrence and transport of trace elements and suspended sediment in the Stibnite mining area depend on constituent source. Groundwater sources seem to control concentrations and loading of dissolved and total arsenic, dissolved and total antimony, dissolved manganese, and dissolved iron, whereas erosion and overland runoff control concentrations and loading of suspended sediment and sediment-associated constituents including aluminum, lead, and mercury. Ratios of dissolved to total estimated FWCs of arsenic and antimony are close to 1 in the EFSFSR, indicating that they are primarily in the dissolved phase, and probably are derived from groundwater sources (table 3). Negative correlations between streamflow and concentrations of total and dissolved arsenic, total and dissolved antimony, dissolved manganese, and dissolved iron also suggest groundwater sources for these constituents in the Meadow Creek and (or) Glory Hole reaches (figs. 1 and 6). Ratios of dissolved to total estimated FWCs of lead and aluminum are relatively low, and concentrations of aluminum, lead, mercury, total iron, and suspended sediment are positively correlated with streamflow, indicating surface and stream channel erosion as sources (table 3, fig. 6). LOADEST models were not used to estimate annual loads or FWCs of cadmium, chromium, copper, and zinc because of a low rate of detection throughout the study area and the requirement of at least seven uncensored values to calibrate LOADEST models (appendix A). Laboratory analytical results for dissolved antimony often were slightly higher than for total antimony, resulting in ratios of greater than 1 for FWCs of dissolved to total antimony. When this occurred, ratios were rounded down to 1 in table 3. Total manganese was not analyzed in water-quality samples.

Estimated annual loads and FWCs for each site indicate that the Glory Hole reach between sites 3 and 4 (fig. 1) is the primary source of arsenic, antimony, and dissolved manganese in the study area (figs. 7–11, tables 4 and 5). On average, the Glory Hole reach contributed only 10 percent of the streamflow, but contributed 52 percent of total arsenic, 53 percent of total antimony, and 42 percent of the dissolved manganese loads attributable to streams in the study area (fig. 7). The Meadow Creek reach was the second largest source of arsenic, antimony, and dissolved manganese. On average, the Meadow Creek reach contributed only 15 percent of the streamflow, but 28 percent of total arsenic, 37 percent of total antimony, and 44 percent of the dissolved manganese

loads attributable to streams in the study area (fig. 7). Mean estimated FWCs exceed human-health criteria for arsenic at sites 3, 4 and 5 and antimony at sites 3 and 4. Based on incremental changes in the streamflow between sites and the loads of arsenic, antimony, and dissolved manganese between sites, a mean FWC of sources to the reach can be estimated. Estimated FWCs from the Glory Hole reach and the Meadow Creek reach indicate that those reaches have much higher concentrations compared to the monitoring sites immediately downstream (fig. 11). Water-quality samples were collected at numerous locations along the Meadow Creek reach between sites 2 and 3 on September 22, 2011, in an effort to identify sources of arsenic and antimony to Meadow Creek. Five samples collected at discrete sampling sites on September 22, 2011 (as opposed to regularly collected samples from monitoring sites) showed substantially higher concentrations and loads of arsenic or antimony relative to concentrations and loads measured at the adjacent upstream location (table 6, fig. 12). Results from all samples collected along Meadow Creek on September 22, 2011, are available from the USGS National Water Information System (U.S. Geological Survey, 2015).

Estimated annual loads and FWCs of suspended sediment, total aluminum, and total lead generally increased between sites 1 and 3 and decreased between sites 3 and 4, with the Glory Hole acting as a sediment trap (figs. 7, 13, 14, and 16; tables 4 and 5; appendix B). Although not sampled as part of this study, the East Fork Meadow Creek (fig. 1) likely is the source of suspended sediment and total aluminum load entering the Meadow Creek reach. The East Fork Meadow Creek is the only surface-water tributary to Meadow Creek capable of carrying a sediment (and sediment-associated constituent) load. The Meadow Creek reach contributed more sediment than Sugar Creek (site 5), but most of the sediment load discharged from the Meadow Creek reach was deposited in the Glory Hole (figs. 7 and 13). The FWCs of suspended sediment at sites 1 and 2 were less than 10 mg/L. However, the incremental gain between sites 1 and 2 downstream to site 3 indicates that the sources of suspended sediment to the Meadow Creek reach had a mean FWC of 78 mg/L (fig. 16C). The mean FWC of suspended sediment for 2012–14 at site 3 was nearly 4 times higher than the corresponding FWC of suspended sediment at site 4 (table 5). Load models show that about 90 percent of the coarse-grained sediment (>0.0625 mm in diameter) load at site 3 was deposited in the Glory Hole; however, about 82 percent of the fine-grained sediment (<0.0625 mm in diameter) load at site 3 was transported through the Glory Hole downstream to site 4 (table 4).

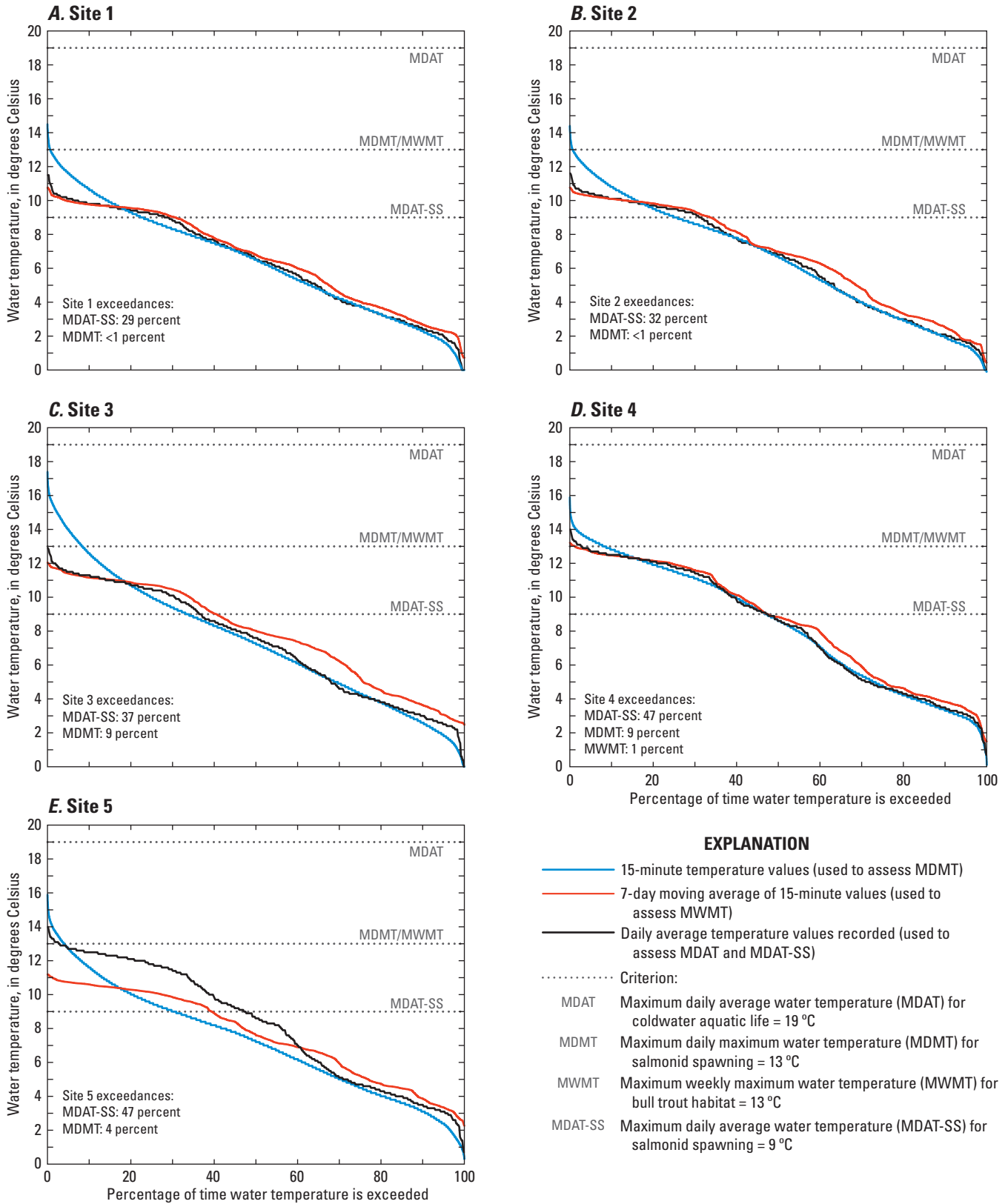**Table 3.** Ratio of dissolved to total mean streamflow-weighted concentrations for selected constituents at five streamflow and water-quality monitoring sites in the Stibnite mining area, central Idaho, 2012–14.

[Site names and locations are shown in table 1 and figure 1, respectively. Ratios are unitless. **Abbreviations:** FWC, streamflow-weighted concentration; NA, not applicable]

Constituent	Ratio of dissolved to total mean FWC 2012–14				
	Site 1	Site 2	Site 3	Site 4	Site 5
Arsenic	0.96	0.67	0.97	0.93	0.88
Antimony	1.00	1.00	0.97	1.00	1.00
Lead	NA	NA	0.11	0.30	0.20
Aluminum	0.23	0.12	0.08	0.13	0.08

EXPLANATION
- Site 1
- Site 2
- Site 3
- Site 4
- Site 5

No bar is shown for constituents not significantly correlated with streamflow.
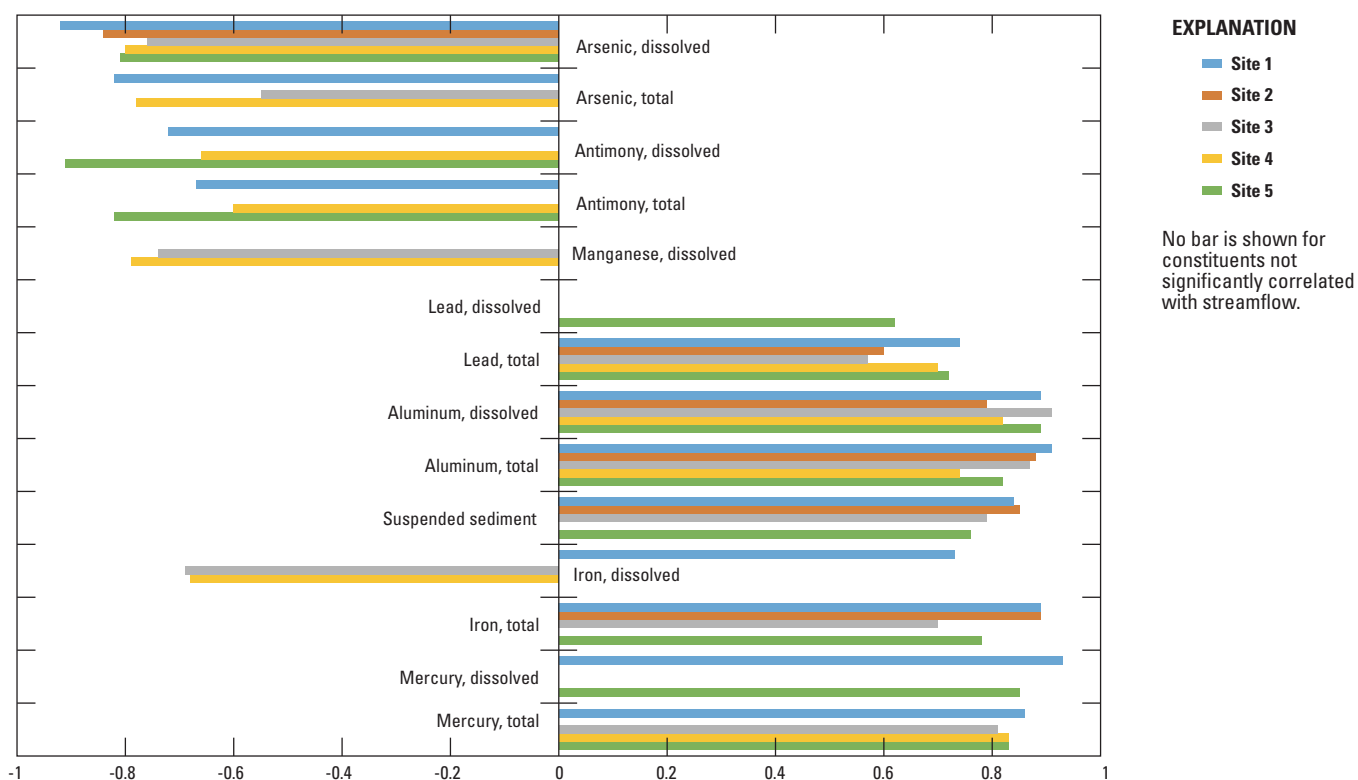
Statistically significant ($p < 0.01$) Spearman's *rho* correlation coefficients between streamflow and concentration, dimensionless

Figure 6. Correlation between streamflow and constituent concentrations for trace elements and suspended sediment in streams in the Stibnite mining area, central Idaho, 2012–14. Site names and locations are shown in table 1 and figure 1, respectively.
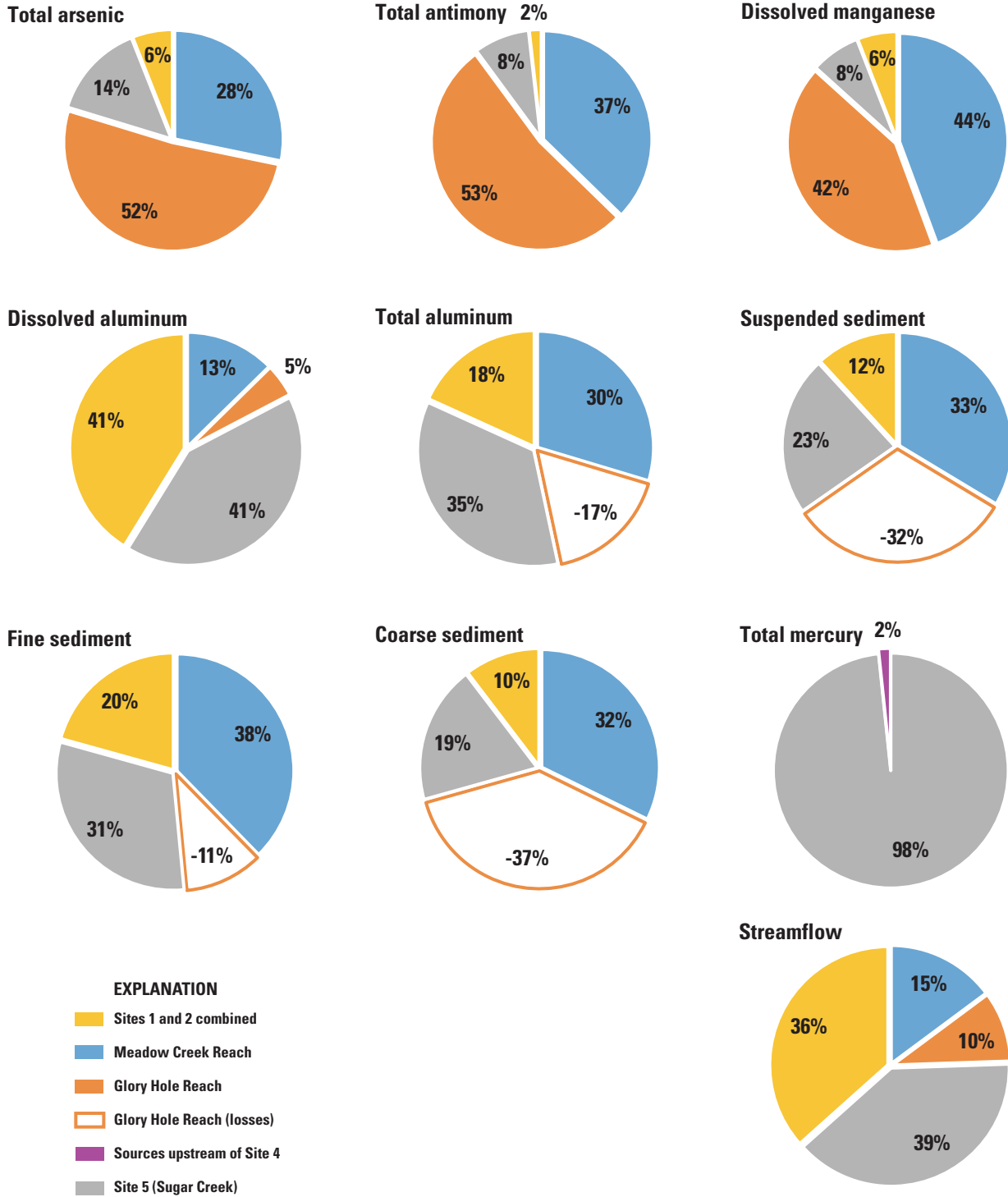
Figure 7.   Streamflow and load contributions from discrete reaches as a percentage of total estimated streamflow and loads attributable to streams in the Stibnite mining area, central Idaho, 2012–14.
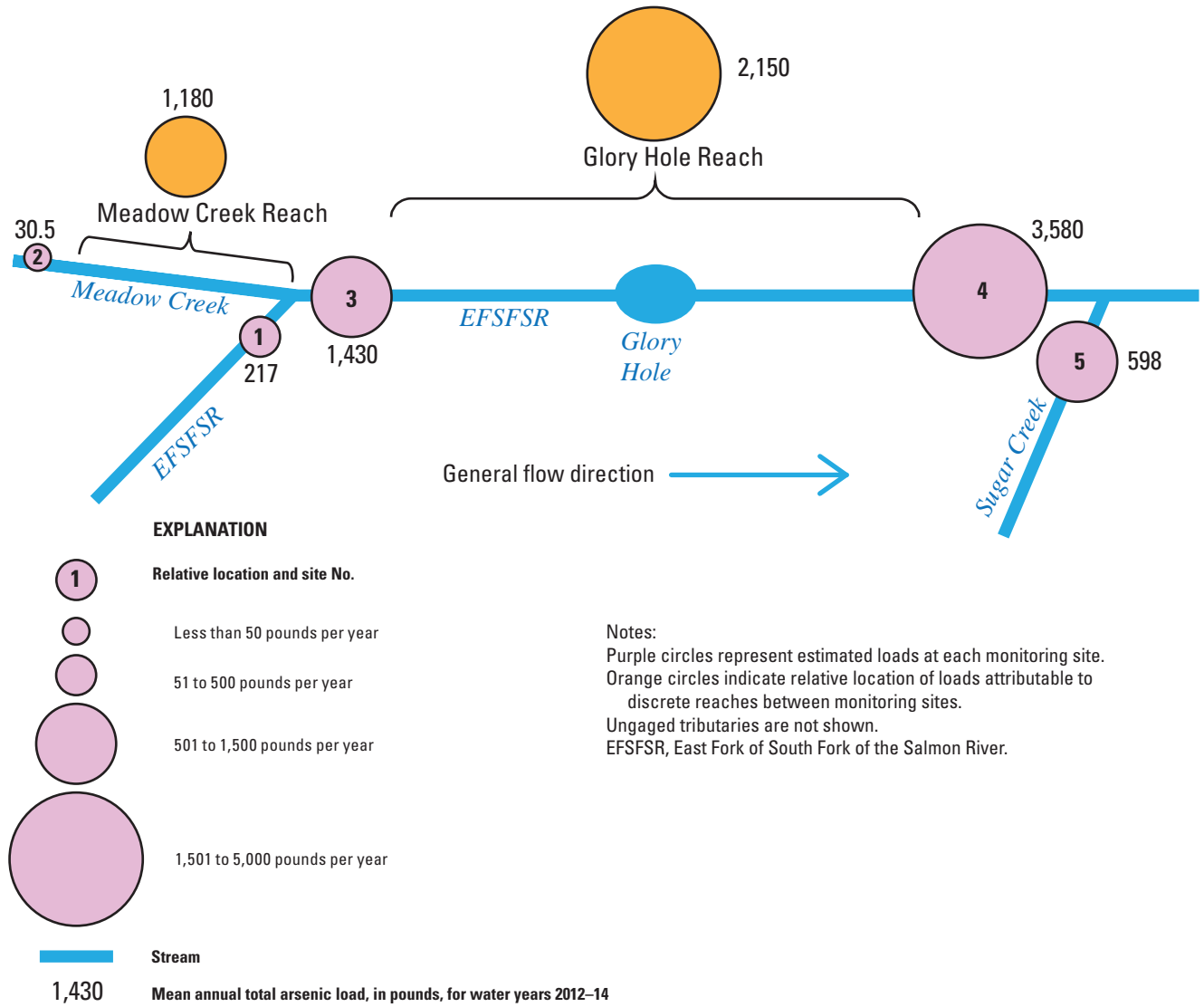
Figure 8. Estimated mean annual total arsenic loads in streams in the Stibnite mining area, central Idaho, 2012–14. Site names and locations are shown in table 1 and figure 1, respectively.

Figure 9.   Estimated mean annual total antimony loads in streams in the Stibnite mining area, central Idaho, 2012–14. Site names and locations are shown in table 1 and figure 1, respectively.

Figure 10. Estimated mean annual dissolved manganese loads in streams in the Stibnite mining area, central Idaho, 2012–14. Site names and locations are shown in table 1 and figure 1, respectively.

Table 4.   Estimated annual loads of selected trace elements and suspended sediment at five streamflow and water-quality monitoring sites in the Stibnite mining area, central Idaho, 2012–14.

[Site names and locations are shown in table 1 and figure 1, respectively. **Abbreviations:** L95, lower 95-percent confidence interval; U95, upper 95-percent confidence interval; lb/yr, pound per year; ton/yr, ton per year]

Constituent	Water year											
	2012			2013			2014			2012–14 mean		
	Annual load	L95	U95	Annual load	L95	U95	Annual load	L95	U95	Annual load	L95	U95
Site 1												
Arsenic, dissolved (lb/yr)	223	208	238	197	183	211	206	193	220	209	195	223
Arsenic, total (lb/yr)	233	215	253	203	187	220	214	198	232	217	200	235
Antimony, dissolved (lb/yr)	26.1	23.3	29.1	22.9	20.3	25.8	23.4	20.8	26.2	24.1	21.5	27.0
Antimony, total (lb/yr)	24.7	21.8	27.9	21.7	19.0	24.7	22.6	19.9	25.6	23.0	20.2	26.1
Manganese, dissolved (lb/yr)	43.7	29.5	62.4	34.8	23.6	49.7	39.6	26.4	57.2	39.4	26.5	56.5
Lead, dissolved (lb/yr)				no suitable LOADEST model								
Lead, total (lb/yr)				no suitable LOADEST model								
Aluminum, dissolved (ton/yr)	0.36	0.27	0.46	0.27	0.20	0.35	0.32	0.24	0.42	0.32	0.24	0.41
Aluminum, total (ton/yr)	1.54	1.19	1.97	1.28	0.95	1.68	1.37	1.02	1.81	1.40	1.05	1.82
Suspended sediment (ton/yr)	103	76.6	136	87.6	61.8	121	87.0	62.9	117	92.6	67.1	125
Fine sediment (ton/yr)	35.2	26.1	46.4	30.2	21.1	41.9	29.0	21.3	38.5	31.5	22.9	42.3
Coarse sediment (ton/yr)	68.9	41.7	107	58.6	32.2	98.3	58.1	33.4	94.5	61.9	35.8	100
Site 2												
Arsenic, dissolved (lb/yr)	21.2	20.3	22.2	18.2	17.4	19.0	21.9	21.0	23.0	20.5	19.6	21.4
Arsenic, total (lb/yr)	32.2	27.5	37.5	25.7	22.0	29.8	33.6	28.4	39.3	30.5	26.0	35.5
Antimony, dissolved (lb/yr)	8.69	7.78	9.68	7.28	6.45	8.18	8.96	8.00	10.0	8.31	7.41	9.29
Antimony, total (lb/yr)	8.46	7.11	9.98	6.74	5.71	7.90	8.65	7.28	10.21	7.95	6.70	9.36
Manganese, dissolved (lb/yr)	49.0	36.2	64.9	41.1	31.0	53.5	50.5	37.5	66.6	46.9	34.9	61.7
Lead, dissolved (lb/yr)				no suitable LOADEST model								
Lead, total (lb/yr)				no suitable LOADEST model								
Aluminum, dissolved (ton/yr)	0.32	0.27	0.39	0.25	0.21	0.30	0.33	0.27	0.39	0.30	0.25	0.36
Aluminum, total (ton/yr)	2.98	1.74	4.80	1.98	1.17	3.13	2.45	1.50	3.78	2.47	1.47	3.90
Suspended sediment (ton/yr)	162	84.0	285	83.1	49.7	131	120	65.2	204	122	66.3	206
Fine sediment (ton/yr)	75.1	32.1	150	37.3	19.4	65.3	54.0	24.0	105	55.5	25.2	107
Coarse sediment (ton/yr)	85.6	44.6	149	46.4	27.2	74.2	65.0	35.9	109	65.7	35.9	111
Site 3												
Arsenic, dissolved (lb/yr)	1,460	1,300	1,640	1,270	1,120	1,430	1,400	1,250	1,560	1,380	1,220	1,540
Arsenic, total (lb/yr)	1,540	1,350	1,760	1,280	1,110	1,450	1,460	1,280	1,670	1,430	1,250	1,630
Antimony, dissolved (lb/yr)	784	618	981	673	517	862	720	566	902	726	567	915
Antimony, total (lb/yr)	815	641	1020	682	524	873	743	586	929	747	584	941
Manganese, dissolved (lb/yr)	763	669	867	701	619	790	735	647	832	733	645	830
Lead, dissolved (lb/yr)	2.44	1.79	3.25	1.73	1.29	2.26	2.26	1.65	3.01	2.14	1.58	2.84
Lead, total (lb/yr)	23.2	2.15	97.3	20.0	1.63	87.7	11.7	3.17	31.0	18.3	2.32	72.0
Aluminum, dissolved (ton/yr)	0.95	0.77	1.16	0.57	0.47	0.69	0.89	0.71	1.09	0.80	0.65	0.98
Aluminum, total (ton/yr)	12.8	5.26	26.2	9.97	3.45	22.8	7.75	4.17	13.2	10.2	4.29	20.8
Suspended sediment (ton/yr)	1,100	342	2,670	545	222	1,130	835	347	1,700	825	304	1,830
Fine sediment (ton/yr)	339	120	767	174	76	343	223	103	422	245	100	511
Coarse sediment (ton/yr)	657	257	1,400	349	135	745	568	216	1,230	525	203	1,120

Table 4. Estimated annual loads of selected trace elements and suspended sediment at five streamflow and water-quality monitoring sites in the Stibnite mining area, central Idaho, 2012–14.—Continued

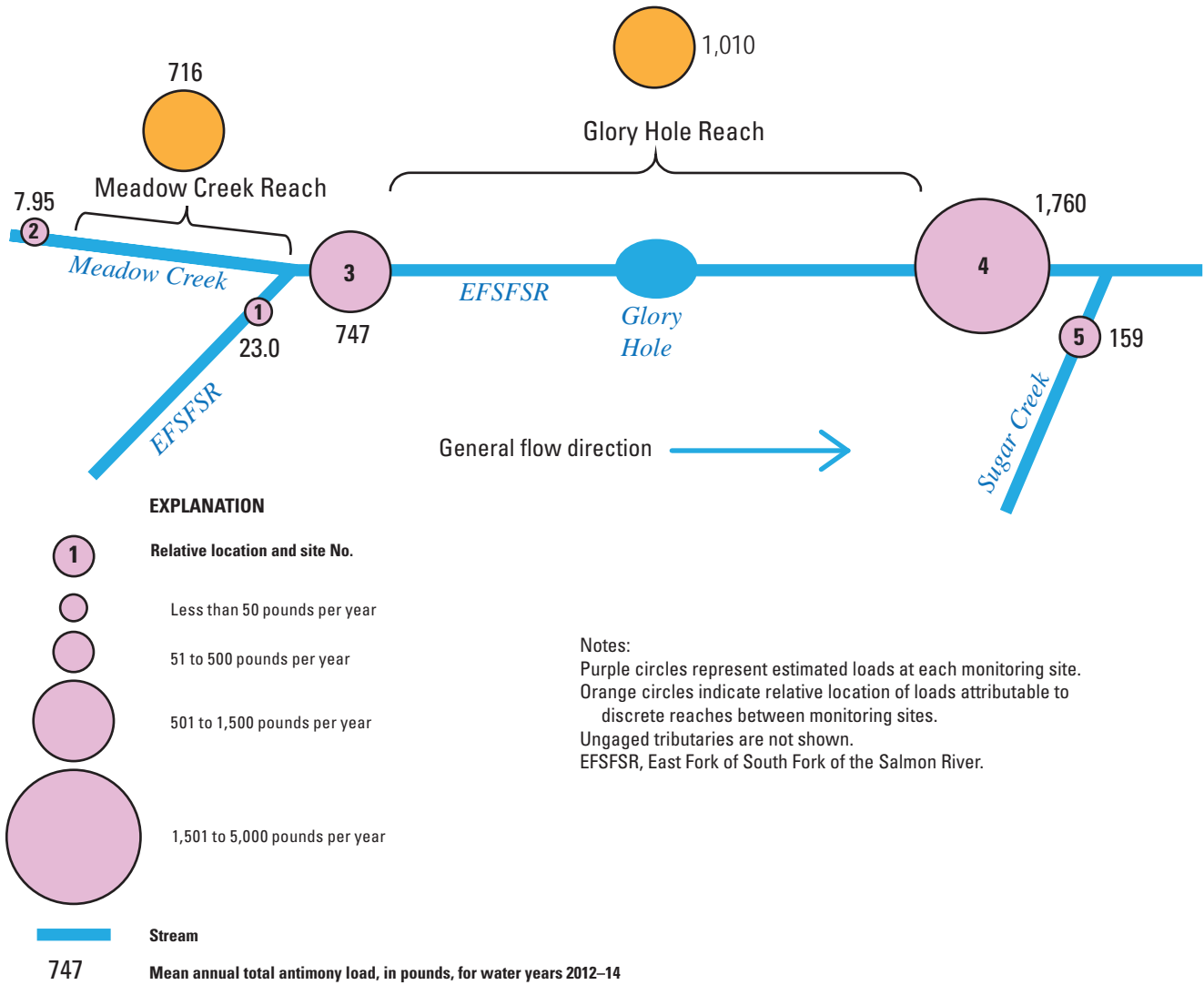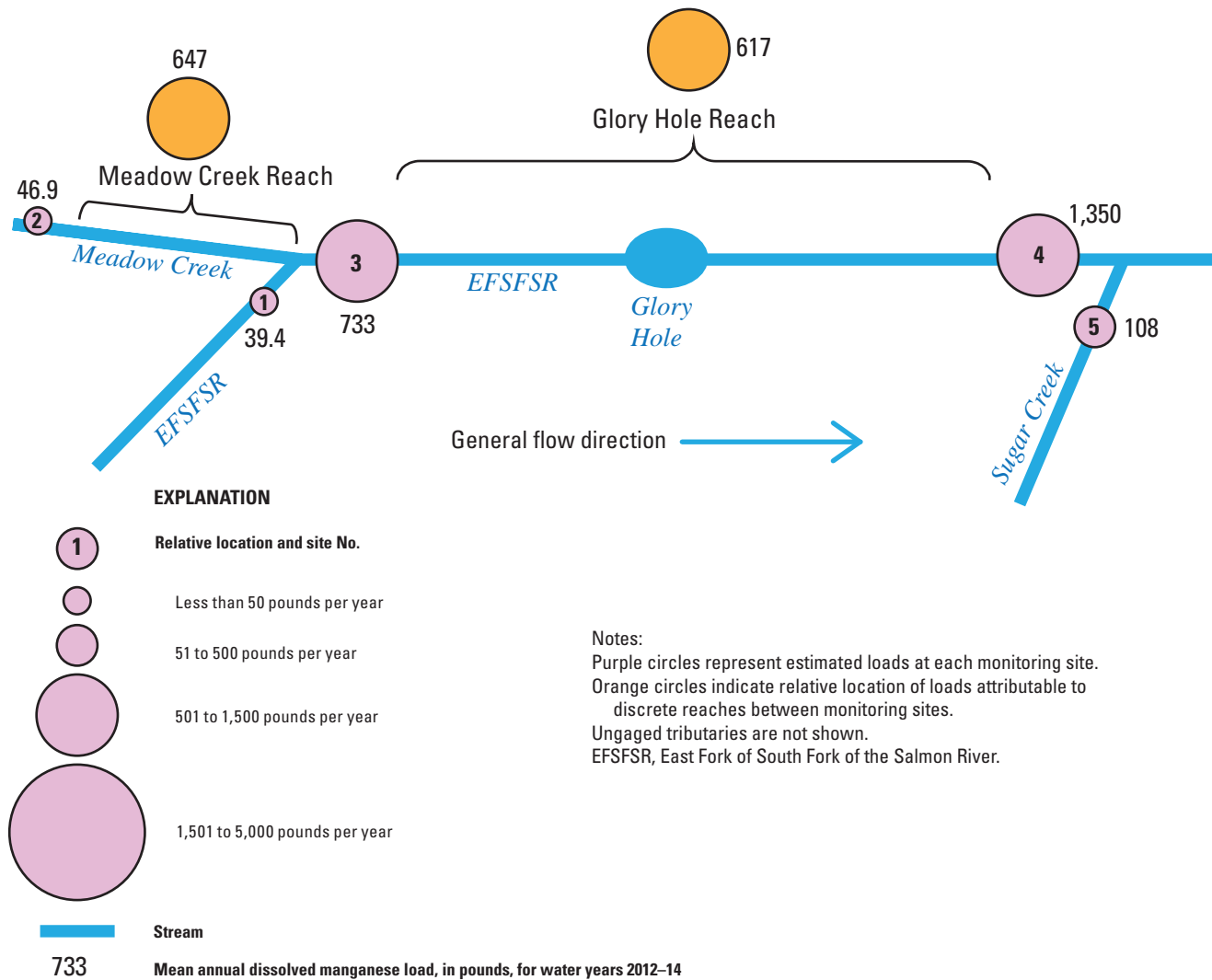[Site names and locations are shown in table 1 and figure 1, respectively. **Abbreviations:** L95, lower 95 percent confidence interval; U95, upper 95 percent confidence interval; lb/yr, pound per year; ton/yr, ton per year]

Constituent	Water year											
	2012			2013			2014			2012–14 mean		
	Annual load	L95	U95	Annual load	L95	U95	Annual load	L95	U95	Annual load	L95	U95
Site 4												
Arsenic, dissolved (lb/yr)	3,520	3,150	3,910	3,070	2,740	3,430	3,380	3,030	3,760	3,320	2,970	3,700
Arsenic, total (lb/yr)	3,800	3,340	4,310	3,280	2,870	3,740	3,650	3,200	4,140	3,580	3,140	4,060
Antimony, dissolved (lb/yr)	2,050	1,690	2,460	1,750	1,410	2,150	1,940	1,600	2,330	1,910	1,570	2,310
Antimony, total (lb/yr)	1,910	1,600	2,270	1,560	1,300	1,850	1,810	1,510	2,150	1,760	1,470	2,090
Manganese, dissolved (lb/yr)	1,410	1,260	1,570	1,280	1,140	1,430	1,370	1,220	1,520	1,350	1,210	1,510
Lead, dissolved (lb/yr)	3.11	2.11	4.44	2.25	1.55	3.15	2.89	1.96	4.12	2.75	1.87	3.90
Lead, total (lb/yr)	11.0	6.77	16.9	6.52	4.09	9.90	10.4	6.16	16.5	9.30	5.67	14.4
Aluminum, dissolved (ton/yr)	1.03	0.76	1.36	0.64	0.48	0.84	0.96	0.70	1.28	0.88	0.65	1.16
Aluminum, total (ton/yr)	7.75	3.93	13.8	4.70	2.44	8.21	7.22	3.56	13.1	6.55	3.31	11.7
Suspended sediment (ton/yr)	284	162	463	175	103	277	292	152	508	250	139	416
Fine sediment (ton/yr)	229	121	397	140	76	235	231	111	426	200	103	353
Coarse sediment (ton/yr)	61.9	32.9	106	36.0	21.7	56.4	58.5	33.1	96.0	52.1	29.2	86.2
Mercury, total (lb/yr)	0.85	0.59	1.19	0.51	0.36	0.70	0.87	0.58	1.25	0.74	0.51	1.05
Site 5												
Arsenic, dissolved (lb/yr)	568	511	629	477	425	534	545	492	602	530	476	588
Arsenic, total (lb/yr)	597	469	753	552	481	630	644	564	732	598	505	705
Antimony, dissolved (lb/yr)	176	143	214	158	126	195	169	138	205	168	136	205
Antimony, total (lb/yr)	166	109	244	150	121	185	162	133	196	159	121	208
Manganese, dissolved (lb/yr)	112	69.8	171	88.5	56.0	133	123	69.3	202	108	65.0	169
Lead, dissolved (lb/yr)	2.30	1.84	2.84	1.68	1.34	2.09	2.25	1.77	2.82	2.08	1.65	2.58
Lead, total (lb/yr)	8.60	2.35	22.7	8.33	2.16	22.5	14.1	4.50	33.8	10.3	3.00	26.3
Aluminum, dissolved (ton/yr)	0.69	0.48	0.95	0.45	0.31	0.62	0.73	0.50	1.02	0.62	0.43	0.86
Aluminum, total (ton/yr)	7.47	2.88	16.0	4.61	1.51	10.9	10.3	3.12	25.5	7.46	2.50	17.5
Suspended sediment (ton/yr)	379	204	644	255	118	485	612	267	1208	415	197	779
Fine sediment (ton/yr)	92.0	43.6	174	129	49.6	277	168	84.6	299	129	59.2	250
Coarse sediment (ton/yr)	223	105	416	187	58	456	290	114	616	233	92	496
Mercury, total (lb/yr)	28.7	8.37	72.5	62.0	10.1	209	41.6	10.1	116	44.1	9.51	133

Table 5.   Estimated streamflow-weighted concentrations of selected constituents at five streamflow and water-quality monitoring sites in the Stibnite mining area, central Idaho, 2012–14.

[Site names and locations are shown in table 1 and figure 1, respectively. **Abbreviations:** FWC, streamflow-weighted concentration; L95, lower 95-percent confidence interval; U95, upper 95-percent confidence interval; µg/L, microgram per liter; mg/L, milligram per liter]

Constituent	Water years											
	2012			2013			2014			2012–14 mean		
	FWC	L95	U95	FWC	L95	U95	FWC	L95	U95	FWC	L95	U95
Site 1												
Arsenic, dissolved (µg/L)	8.11	7.58	8.66	8.59	8.01	9.20	8.25	7.71	8.83	8.32	7.77	8.90
Arsenic, total (µg/L)	8.48	7.82	9.19	8.82	8.12	9.57	8.58	7.90	9.29	8.63	7.95	9.35
Antimony, dissolved (µg/L)	0.95	0.85	1.06	1.00	0.88	1.12	0.94	0.83	1.05	0.96	0.85	1.08
Antimony, total (µg/L)	0.90	0.79	1.01	0.94	0.83	1.07	0.90	0.80	1.02	0.92	0.80	1.04
Manganese, dissolved (µg/L)	1.59	1.07	2.27	1.52	1.03	2.16	1.59	1.06	2.29	1.56	1.05	2.24
Lead, dissolved (µg/L)				no suitable LOADEST model								
Lead, total (µg/L)				no suitable LOADEST model								
Aluminum, dissolved (µg/L)	25.9	19.8	33.3	23.5	17.7	30.6	25.7	19.3	33.5	25.0	18.9	32.5
Aluminum, total (µg/L)	112	86.4	143	111	82.9	147	110	81.8	145	111	83.7	145
Suspended sediment (mg/L)	7.51	5.57	9.91	7.63	5.38	10.51	6.96	5.04	9.39	7.37	5.33	9.93
Fine sediment (mg/L)	2.56	1.90	3.37	2.63	1.84	3.65	2.32	1.70	3.08	2.50	1.81	3.37
Coarse sediment (mg/L)	5.01	3.03	7.80	5.10	2.80	8.56	4.65	2.67	7.56	4.92	2.83	7.97
Site 2												
Arsenic, dissolved (µg/L)	0.92	0.88	0.96	0.96	0.92	1.00	0.92	0.88	0.96	0.93	0.89	0.97
Arsenic, total (µg/L)	1.39	1.19	1.62	1.35	1.16	1.57	1.41	1.20	1.65	1.38	1.18	1.61
Antimony, dissolved (µg/L)	0.38	0.34	0.42	0.38	0.34	0.43	0.38	0.34	0.42	0.38	0.34	0.42
Antimony, total (µg/L)	0.36	0.31	0.43	0.35	0.30	0.42	0.36	0.31	0.43	0.36	0.30	0.43
Manganese, dissolved (µg/L)	2.11	1.56	2.80	2.16	1.63	2.81	2.12	1.57	2.80	2.13	1.59	2.80
Lead, dissolved (µg/L)				no suitable LOADEST model								
Lead, total (µg/L)				no suitable LOADEST model								
Aluminum, dissolved (µg/L)	27.9	23.1	33.4	26.3	21.9	31.4	27.6	22.8	33.0	27.2	22.6	32.6
Aluminum, total (µg/L)	258	150	414	208	124	329	206	126	318	224	133	354
Suspended sediment (mg/L)	11.8	6.10	20.7	7.23	4.33	11.4	9.64	5.22	16.3	9.55	5.22	16.1
Fine sediment (mg/L)	5.45	2.34	10.91	3.25	1.69	5.68	4.32	1.92	8.43	4.34	1.98	8.34
Coarse sediment (mg/L)	6.22	3.24	10.86	4.04	2.37	6.46	5.20	2.87	8.69	5.15	2.83	8.67
Site 3												
Arsenic, dissolved (µg/L)	21.0	18.7	23.4	23.7	20.9	26.9	21.4	19.1	24.0	22.1	19.6	24.8
Arsenic, total (µg/L)	22.1	19.3	25.3	23.9	20.9	27.2	22.4	19.6	25.6	22.8	19.9	26.0
Antimony, dissolved (µg/L)	11.2	8.85	14.1	12.6	9.68	16.1	11.0	8.68	13.8	11.6	9.07	14.7
Antimony, total (µg/L)	11.7	9.19	14.6	12.8	9.81	16.4	11.4	8.98	14.2	11.9	9.33	15.1
Manganese, dissolved (µg/L)	10.9	9.6	12.4	13.1	11.6	14.8	11.3	9.9	12.8	11.8	10.4	13.3
Lead, dissolved (µg/L)	0.03	0.03	0.05	0.03	0.02	0.04	0.03	0.03	0.05	0.03	0.03	0.05
Lead, total (µg/L)	0.33	0.03	1.39	0.38	0.03	1.64	0.18	0.05	0.48	0.30	0.04	1.17
Aluminum, dissolved (µg/L)	27.3	22.2	33.3	21.4	17.7	25.7	27.2	21.9	33.5	25.3	20.6	30.8
Aluminum, total (µg/L)	366	151	750	373	129	856	238	128	405	326	136	670
Suspended sediment (mg/L)	31.4	9.80	76.4	20.4	8.32	42.2	25.6	10.65	52.2	25.8	9.59	56.9
Fine sediment (mg/L)	9.72	3.44	22.0	6.50	2.83	12.9	6.83	3.17	13.0	7.69	3.15	15.9
Coarse sediment (mg/L)	18.8	7.37	39.9	13.1	5.06	27.9	17.4	6.62	37.7	16.4	6.35	35.2

Table 5. Estimated streamflow-weighted concentrations of selected constituents at five streamflow and water-quality monitoring sites in the Stibnite mining area, central Idaho, 2012–14.—Continued

[Site names and locations are shown in table 1 and figure 1, respectively. **Abbreviations:** FWC, streamflow-weighted concentration; L95, lower 95-percent confidence interval; U95, upper 95-percent confidence interval; μg/L, microgram per liter; mg/L, milligram per liter]

| Constituent | Water years | | | | | | | | | | | |
| | 2012 | | | 2013 | | | 2014 | | | 2012–14 mean | | |
	FWC	L95	U95	FWC	L95	U95	FWC	L95	U95	FWC	L95	U95
Site 4												
Arsenic, dissolved (μg/L)	42.0	37.6	46.7	48.6	43.3	54.3	43.2	38.7	48.1	44.6	39.9	49.7
Arsenic, total (μg/L)	45.4	39.9	51.5	51.9	45.3	59.1	46.6	40.9	52.9	48.0	42.1	54.5
Antimony, dissolved (μg/L)	24.5	20.2	29.4	27.7	22.3	34.0	24.8	20.4	29.7	25.6	21.0	31.0
Antimony, total (μg/L)	22.8	19.1	27.1	24.6	20.6	29.3	23.1	19.3	27.4	23.5	19.7	27.9
Manganese, dissolved (μg/L)	16.8	15.1	18.7	20.3	18.1	22.7	17.5	15.6	19.5	18.2	16.3	20.3
Lead, dissolved (μg/L)	0.04	0.03	0.05	0.04	0.02	0.05	0.04	0.02	0.05	0.04	0.02	0.05
Lead, total (μg/L)	0.13	0.08	0.20	0.10	0.06	0.16	0.13	0.08	0.21	0.12	0.07	0.19
Aluminum, dissolved (μg/L)	24.6	18.1	32.6	20.4	15.3	26.6	24.4	17.8	32.7	23.1	17.1	30.6
Aluminum, total (μg/L)	185	93.8	329	149	77.4	260	184	90.9	335	173	87.4	308
Suspended sediment (mg/L)	6.78	3.86	11.1	5.53	3.27	8.77	7.45	3.89	13.0	6.59	3.67	10.9
Fine sediment (mg/L)	5.48	2.89	9.49	4.42	2.42	7.43	5.89	2.84	10.9	5.26	2.71	9.27
Coarse sediment (mg/L)	1.48	0.79	2.54	1.14	0.69	1.79	1.49	0.85	2.45	1.37	0.77	2.26
Mercury (total) (μg/L)	0.010	0.007	0.014	0.008	0.006	0.011	0.011	0.007	0.016	0.010	0.007	0.014
Site 5												
Arsenic, dissolved (μg/L)	11.2	10.1	12.4	12.1	10.8	13.5	10.9	9.9	12.1	11.4	10.2	12.7
Arsenic, total (μg/L)	11.8	9.27	14.9	14.0	12.2	16.0	12.9	11.3	14.7	12.9	10.9	15.2
Antimony, dissolved (μg/L)	3.48	2.83	4.23	4.00	3.20	4.95	3.38	2.76	4.11	3.62	2.93	4.43
Antimony, total (μg/L)	3.27	2.16	4.82	3.80	3.05	4.68	3.26	2.67	3.94	3.45	2.63	4.48
Manganese, dissolved (μg/L)	2.21	1.38	3.37	2.24	1.42	3.37	2.47	1.39	4.06	2.31	1.40	3.60
Lead, dissolved (μg/L)	0.05	0.04	0.06	0.04	0.03	0.05	0.05	0.04	0.06	0.04	0.04	0.06
Lead, total (μg/L)	0.17	0.05	0.45	0.21	0.05	0.57	0.28	0.09	0.68	0.22	0.06	0.57
Aluminum, dissolved (μg/L)	16.5	11.6	22.7	14.2	9.91	19.7	18.6	12.8	26.1	16.4	11.4	22.8
Aluminum, total (μg/L)	179	68.7	383	146	47.8	346	263	79.7	651	196	65.4	460
Suspended sediment (mg/L)	15.0	8.07	25.4	12.9	5.98	24.6	24.6	10.7	48.5	17.5	8.26	32.8
Fine sediment (mg/L)	3.63	1.72	6.85	6.53	2.51	14.0	6.72	3.40	12.0	5.63	2.54	11.0
Coarse sediment (mg/L)	8.80	4.16	16.4	9.49	2.96	23.1	11.6	4.55	24.7	9.98	3.89	21.4
Mercury (total) (μg/L)	0.57	0.17	1.43	1.57	0.26	5.30	0.83	0.20	2.33	0.99	0.21	3.02
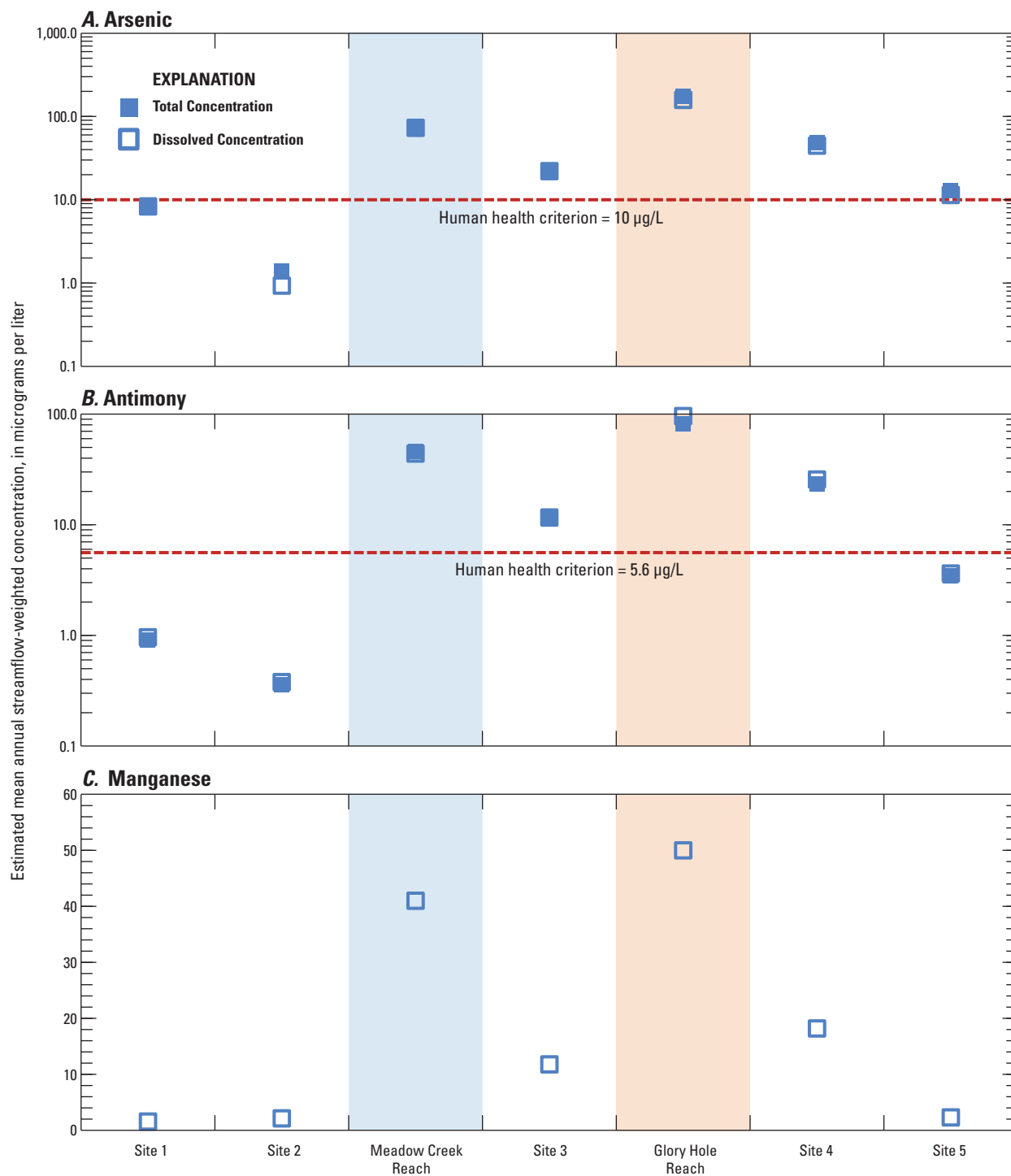
Figure 11.   Estimated mean annual streamflow-weighted concentrations of (*A*) arsenic, (*B*) antimony, and (*C*) manganese in streams in the Stibnite mining area, central Idaho, 2012–14. Site names and locations are shown in table 1 and figure 1, respectively.

Table 6. Substantial sources of arsenic and antimony identified at selected sites along Meadow Creek, Stibnite mining area, central Idaho, September 22, 2011.

[Site locations are shown in figure 12. Blowout Creek is officially named East Fork Meadow Creek in figure 1. **Abbreviations:** µg/L, microgram per liter; lb/d, pound per day; m, meter]

Site No.	Site name	Streamflow	Dissolved antimony		
			Concentration (µg/L)	Instantaneous load (lb/d)	Increase in load relative to adjacent upstream site (percent)
4453251152046	Meadow Creek inflow, 280 m upstream of bend in road	0.095	173	8.86E-2	390
4453261152043	Meadow Creek inflow, 240 m upstream of bend in road	0.142	26.1	2.00E-2	36
4453391152029	Meadow Creek inflow, below extent of cascading section	0.105	3.45	1.95E-3	2.4
4453441152021	Blowout Creek at Meadow Creek	1.94	1.30	1.36E-2	13
4453461152017	Meadow Creek inflow, near runway entrance	0.054	269	7.84E-2	57

Site No.	Site name	Dissolved arsenic		
		Concentration (µg/L)	Instantaneous load (lb/d)	Increase in load relative to adjacent upstream site (percent)
4453251152046	Meadow Creek inflow, 280 m upstream of bend in road	1,340	6.87E-1	257
4453261152043	Meadow Creek inflow, 240 m upstream of bend in road	21.4	1.64E-2	2.7
4453391152029	Meadow Creek inflow, below extent of cascading section	526	2.98E-1	36
4453441152021	Blowout Creek at Meadow Creek	7.32	7.66E-2	7.0
4453461152017	Meadow Creek inflow, near runway entrance	1,300	3.79E-1	29
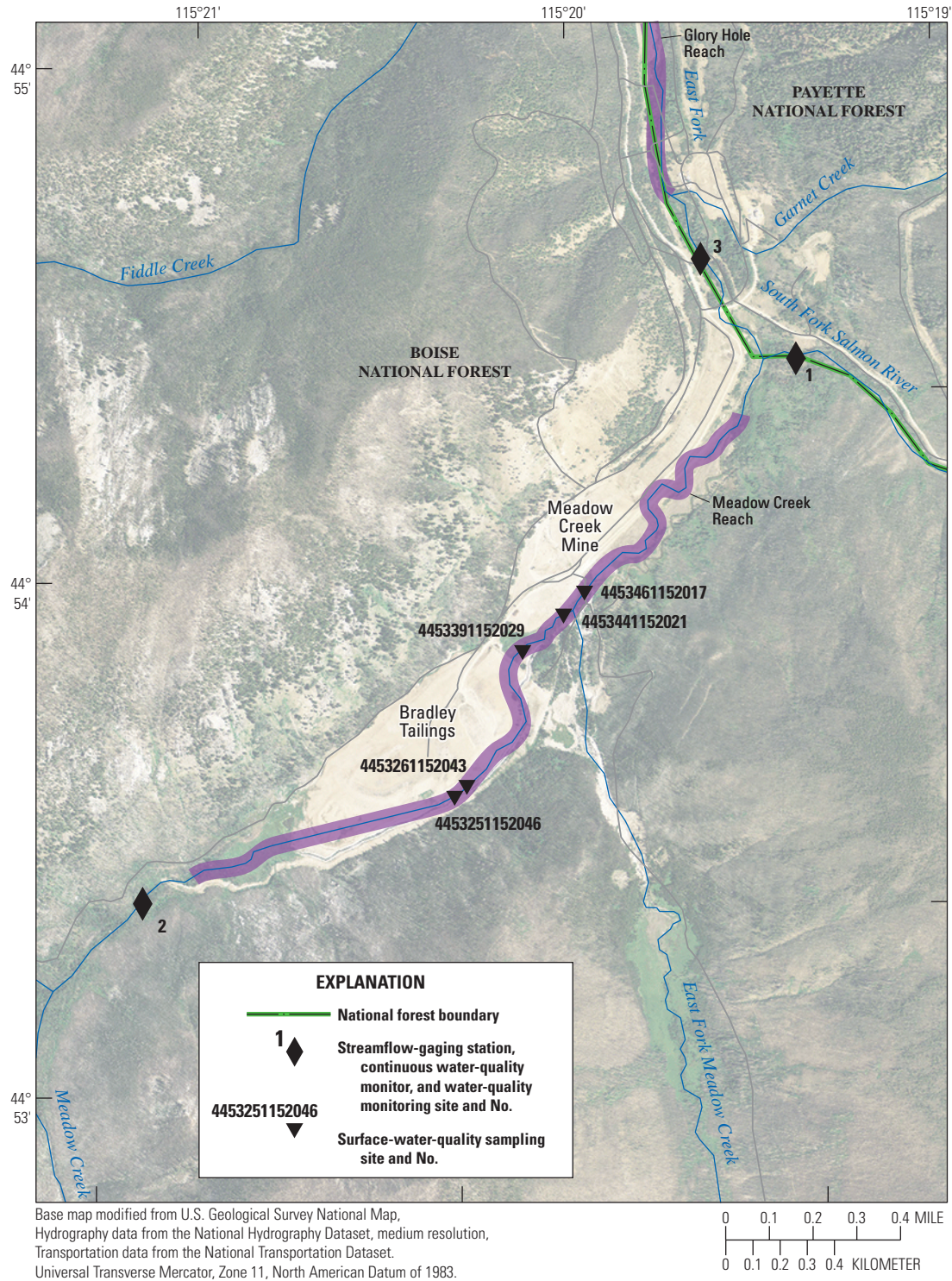
Figure 12. Locations of substantial sources of arsenic and antimony identified along Meadow Creek, Stibnite mining area, central Idaho, September 22, 2011.
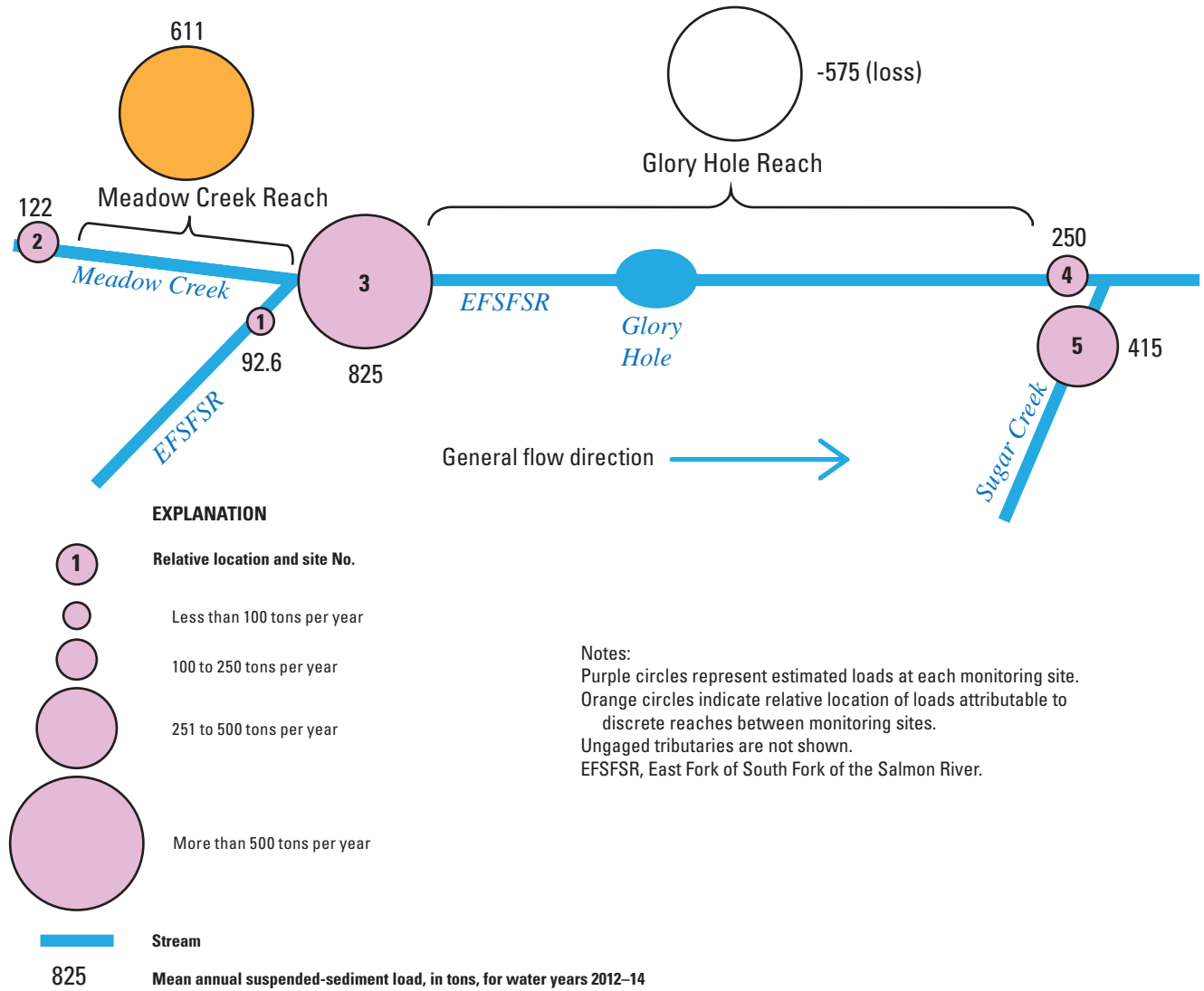
Figure 13.   Estimated mean annual suspended sediment loads at monitoring sites in the Stibnite mining area, central Idaho, 2012–14. Site names and locations are shown in table 1 and figure 1, respectively.
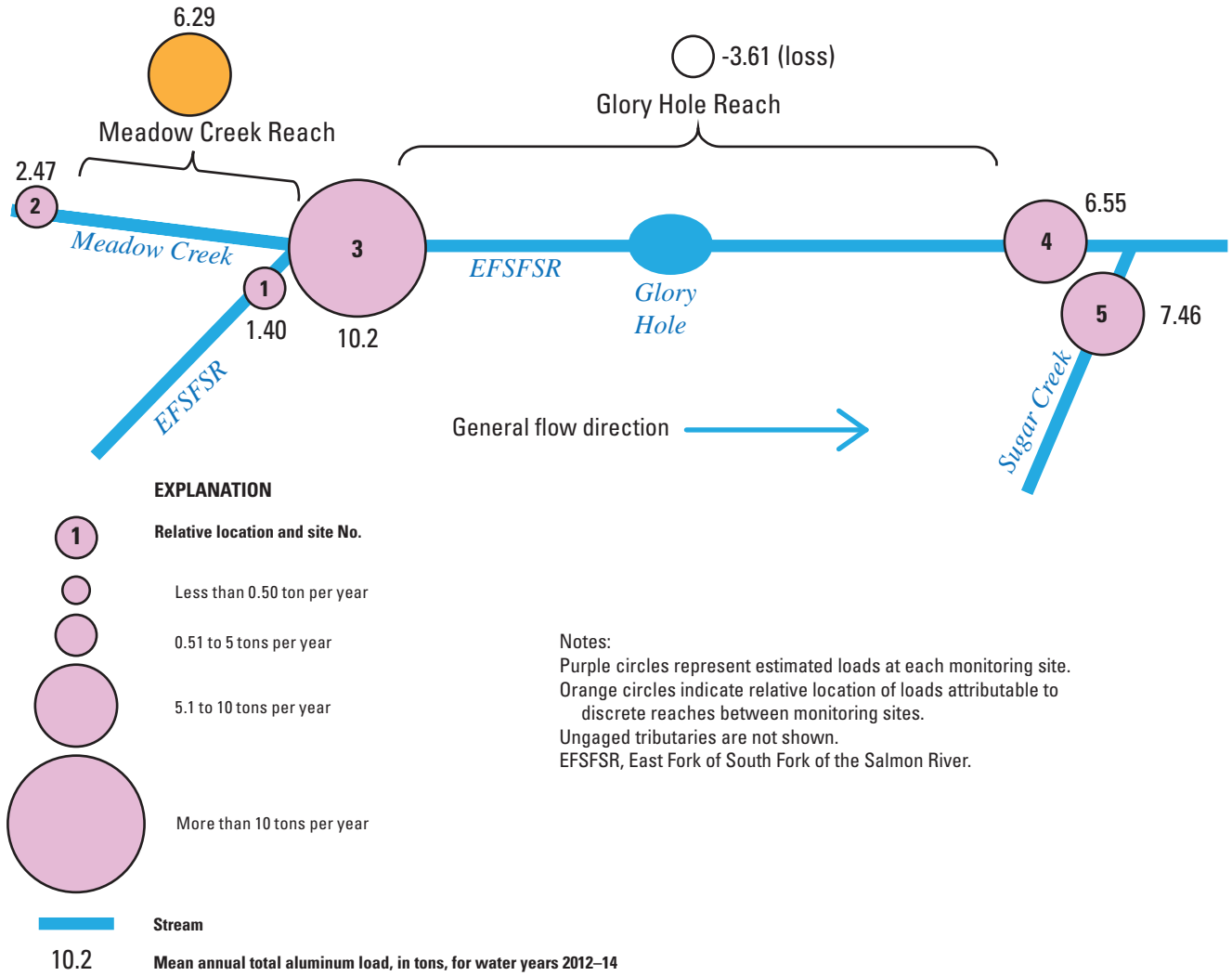
Figure 14. Estimated mean annual total aluminum loads at monitoring sites in the Stibnite mining area, central Idaho, 2012–14. Site names and locations are shown in table 1 and figure 1, respectively.
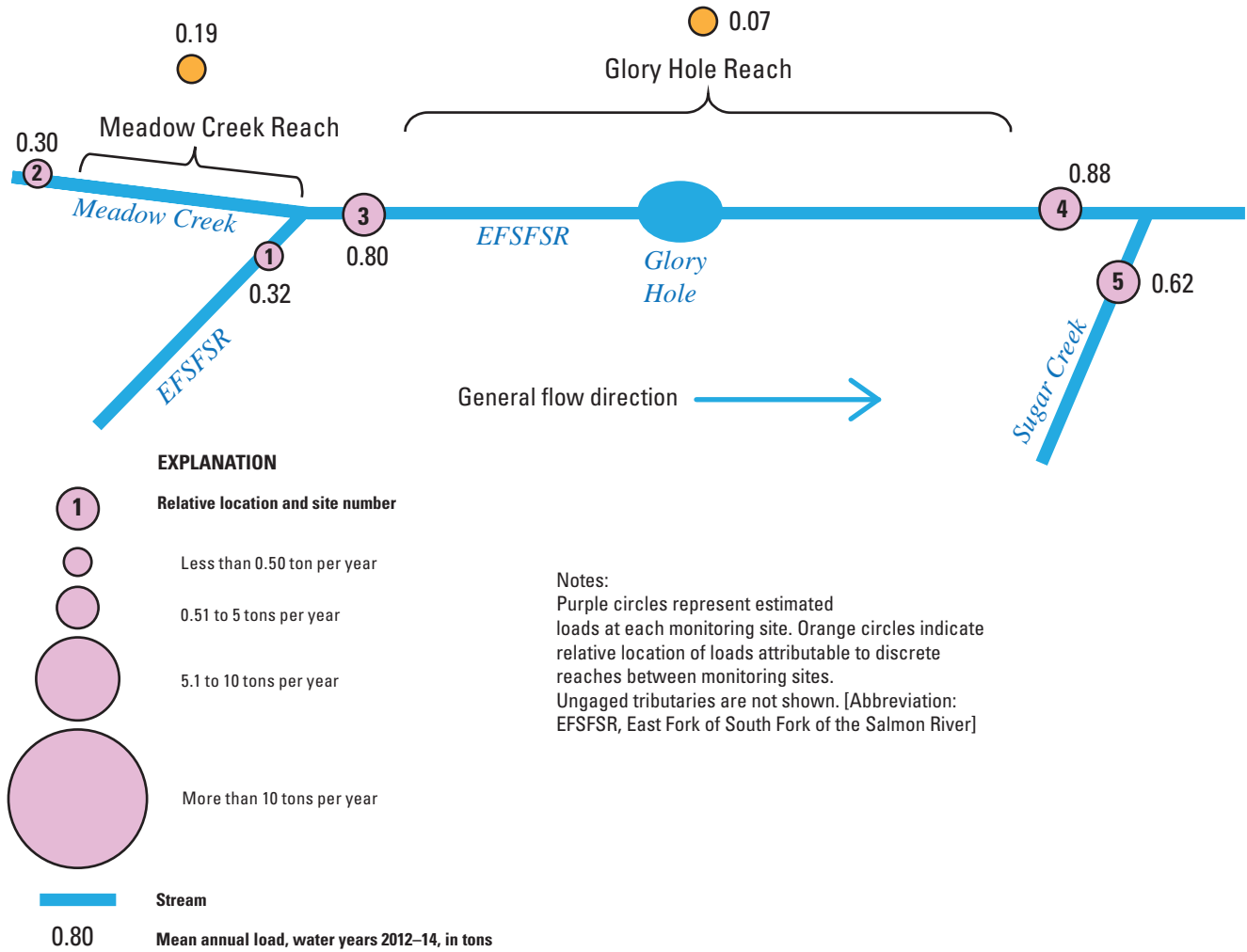
Figure 15. Estimated mean annual dissolved aluminum loads at monitoring sites in the Stibnite mining area, central Idaho, 2012–14. Site names and locations are shown in table 1 and figure 1, respectively.

Figure 16.   Estimated mean annual streamflow-weighted concentrations of (*A*) aluminum, (*B*) lead, and (*C*) suspended sediment at monitoring sites in the Stibnite mining area, central Idaho, 2012–14. Site names and locations are shown in table 1 and figure 1, respectively.

Loading and transport of total aluminum and total lead were similar to the loading and transport of suspended sediment. On average, the estimated annual total aluminum load in Sugar Creek (site 5) was about 1 ton higher than the annual total aluminum load discharged from the Meadow Creek reach. As compared to the EFSFSR at site 4, Sugar Creek (site 5) accounted for a slightly larger amount of the total aluminum load transported downstream of the study area (fig. 14). The estimated mean annual FWC of total aluminum in sources to the Meadow Creek reach was 4 times as high as the mean annual FWC of total aluminum in Sugar Creek at site 5, suggesting that the East Fork Meadow Creek is a concentrated source of total aluminum (fig. 16). With the exception of the East Fork Meadow Creek, total aluminum was not measured in the inflows shown in table 6 during intensive sampling in the Meadow Creek reach on September 22, 2011. However, the total aluminum concentration in the East Fork Meadow Creek was 53 µg/L, compared to an average concentration of 21 µg/L measured in Meadow Creek upstream of East Fork Meadow Creek on September 22, 2011. The total aluminum load in Meadow Creek doubled as a result of the total aluminum source from East Fork Meadow Creek and did not substantially increase in any additional samples collected downstream of East Fork Meadow Creek on September 22, 2011. Results from all samples collected along Meadow Creek on September 22, 2011, are available from the USGS National Water Information System (U.S. Geological Survey, 2015).

Because detections of total and dissolved lead were infrequent at sites 1 and 2, loads for lead upstream of site 3 were not estimated. About one-half of the total lead and one third of the total aluminum loads at site 3 were deposited in the Glory Hole (table 4, fig. 14). FWCs of total lead and total aluminum at site 3 were twice as high as those at site 4 because of losses of total lead and total aluminum loads in the Glory Hole (fig. 16). The mean annual load of total lead for 2012–14 at site 4 was 9.30 lb/yr compared to 10.3 lb/yr at site 5 (Sugar Creek), suggesting that Sugar Creek contributes more than one-half of the total lead transported downstream of the study area in the EFSFSR (table 4). Dissolved FWCs of lead and aluminum changed little from upstream to downstream, with the largest sources attributable to background loads at sites 1, 2, and 5 (tables 4 and 5; figs. 7, 15, and 16).

A limited number of samples and (or) detections of total mercury prevented the use of load models to estimate annual FWCs and loads of total mercury at sites 1–3. Total mercury load models for sites 4 and 5 indicate that 98 percent of the mercury load transported downstream of the study area is attributable to Sugar Creek (fig. 7, table 4). Estimated annual FWCs of total mercury were 0.010 µg/L at site 4 on the EFSFWR, which is close to the State of Idaho 0.012-µg/L chronic exposure AWQC. However, the mean annual FWC

estimated for total mercury at site 5 on Sugar Creek was 0.99 µg/L, nearly two orders of magnitude higher than the FWC at site 4 (table 5).

LOAD ESTimation (LOADEST) Model Results

Significant correlations (p <0.01) between streamflow and concentrations of modeled constituents generally resulted in favorable LOADEST models (fig. 6, table 7). Ninety-five percent confidence intervals around estimated mean annual loads and FWCs quantify uncertainty around estimates and generally were larger for constituents with greater variability in measured loads (tables 4 and 5). Recent research has shown that LOADEST models can produce biased estimates of long-term average constituent loads (Stenback and others, 2011; Garrett, 2012; Hirsch, 2014), and LOADEST has since been modified to facilitate residual analysis and bias identification (Runkel, 2013). Long-term bias in model estimates was less of a concern because the modeling period was only 3 years and predictor variables describing trends in time were not used. High model bias often indicated hysteresis in transport of sediment and sediment-associated constituents in the study area. Bias diagnostics described by Runkel (2013) were used as an indication that an additional predictor variable may be necessary to account for hysteresis in constituent transport. Use of a predictor variable describing variation in streamflow frequently resulted in large reductions in overall model bias where hysteresis in constituent transport was evident.

Streamflow Variability and Hysteresis in Particulate Constituent Transport

Various stream basin characteristics may have affected the significance of a particular streamflow variability term at each site. Moving averages of the previous 1, 3, 7, and 30 days were compared to daily mean streamflow and tested for significance as predictor variables describing particulate constituent transport. The ratio of estimated daily surface runoff in cubic feet per second to daily mean streamflow in cubic feet per second (the base flow index [BFI]) also was tested as a predictor variable to account for hysteresis. A streamflow variability term with a longer daily time-step helps describe the effects of sequential events or prolonged peaks, whereas absolute values of variability terms help describe the degree of flashiness of increased streamflow events (Wang and Linker, 2008). Snowmelt runoff controls particulate constituent transport in the study area, and most samples used to calibrate LOADEST models were collected during snowmelt runoff (fig. 3).

Table 7.   Regression coefficients and coefficients of determination (R²) for models used to estimate loads of selected constituents at monitoring sites in the Stibnite mining area, central Idaho, 2012–14.

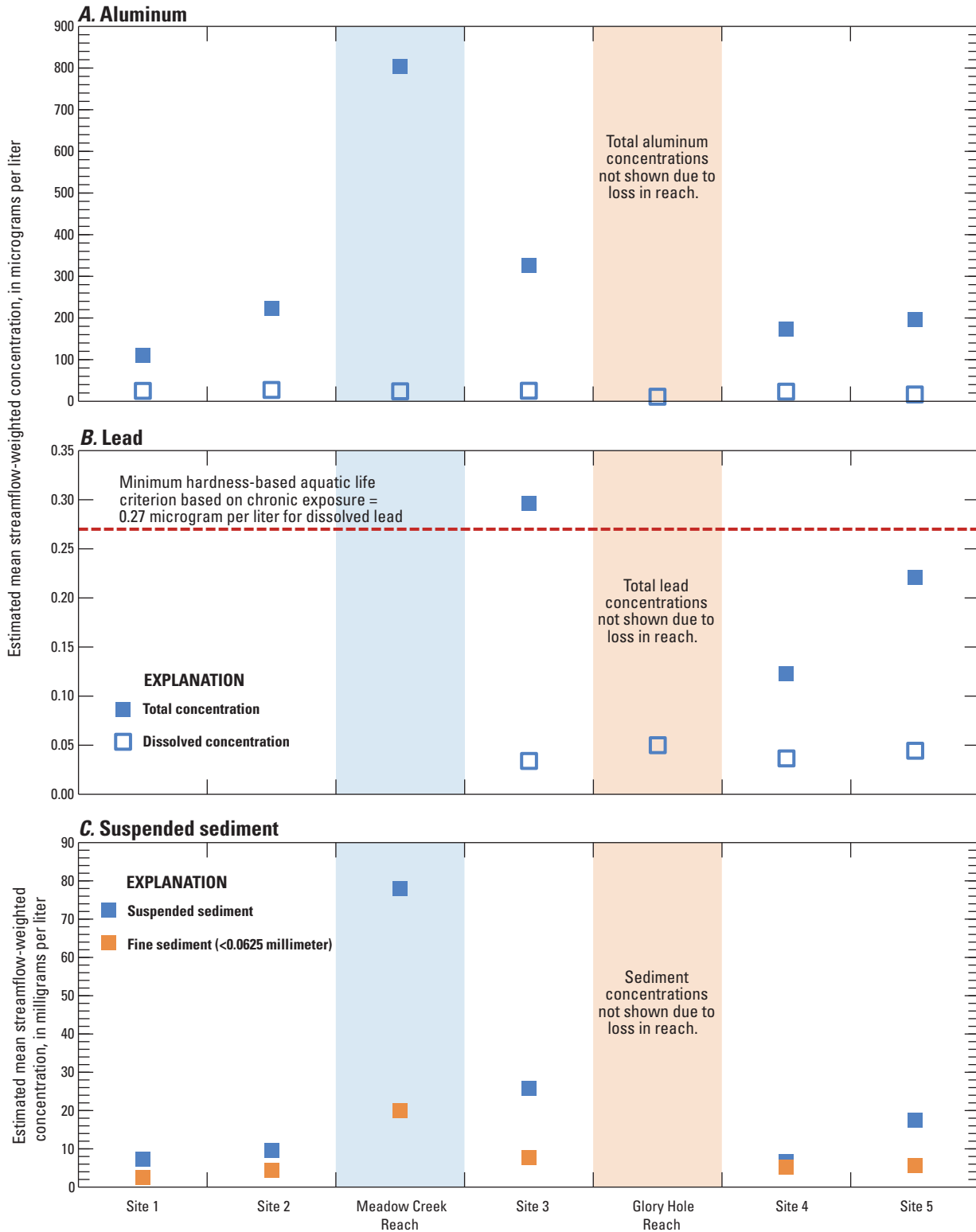[Site names and locations are shown in table 1 and figure 1, respectively. Each regression model was calibrated using the available data collected at each station for water years 2012–14. The regression equation is $\ln L = I + a\,(\ln Q) + b\,(\ln Q^2) + c\,[\sin(2\pi T)] + d\,[\cos(2\pi T)] + e\,(SVT) + \varepsilon$, where ln is the natural logarithm; L is the constituent load, in pounds per day; I is the regression intercept; Q is the centered streamflow, in cubic feet per second; T is the centered decimal time in years from the beginning of the calibration period; sin $(2\pi T)$ and cos $(2\pi T)$ are periodic time functions that describe seasonal variability; SVT is the term describing streamflow variability; a, b, c, d, and e are regression coefficients that remain constant over time; and ε is the unaccounted error associated with the regression model. R^2 (coefficient of determination) represents the amount of variance explained by the model. **Abbreviations:** RMSE, root mean square error; lb/d, pound per day; –, no regression coefficient]

Constituent	Number of samples	Regression coefficient						R²	RMSE (lb/d)	Load bias (percent)
		I	a	b	c	d	e			
Site 1										
Arsenic, dissolved	20	-0.140	0.696	–	–	–	–	97	1.15	0.04
Arsenic, total	20	-0.091	0.788	–	–	–	–	96	1.19	1.68
Antimony, dissolved	20	-2.132	0.748	-0.090	0.279	0.312	–	95	1.24	-1.08
Antimony, total	20	-2.357	0.752	–	0.253	0.135	–	94	1.28	-0.16
Manganese, dissolved	15	-2.084	1.356	–	–	–	–	89	1.70	-2.31
Lead, dissolved	19			no suitable LOADEST model						
Lead, total	20			no suitable LOADEST model						
Aluminum, dissolved	20	0.642	1.855	-0.166	–	–	–	97	1.51	0.11
Aluminum, total	19	-3.789	1.842	–	0.521	0.136	[1]0.018	98	1.40	-3.15
Suspended sediment	19	0.895	1.767	–	0.448	0.508	[1]0.030	97	1.49	-1.00
Fine sediment	19	0.606	1.504	–	0.395	0.339	[1]0.047	97	1.52	1.79
Coarse sediment	19	-0.104	1.943	–	0.484	0.710	[1]0.024	95	1.82	2.03
Site 2										
Arsenic, dissolved	21	-2.677	0.821	0.037	–	–	–	99	1.10	-0.40
Arsenic, total	21	-2.641	1.019	0.180	–	–	–	96	1.35	-8.20
Antimony, dissolved	18	-3.377	1.133	–	0.221	0.557	–	98	1.22	-0.18
Antimony, total	21	-3.749	1.112	–	–	–	–	96	1.38	-2.61
Manganese, dissolved	16	-1.977	0.923	–	–	–	–	88	1.60	-5.76
Lead, dissolved				no suitable LOADEST model						
Lead, total				no suitable LOADEST model						
Aluminum, dissolved	21	0.551	1.341	–	0.123	0.315	–	97	1.38	1.47
Aluminum, total	19	-2.587	1.742	–	-0.048	0.546	[2]0.043	95	1.81	-15.0
Suspended sediment	20	1.749	1.424	–	–	–	[1]0.101	95	1.83	-8.23
Fine sediment	20	1.243	1.284	–	–	–	[1]0.116	92	2.03	-15.6
Coarse sediment	20	0.929	1.540	–	0.333	0.290	[1]0.082	95	1.88	-3.06
Site 3										
Arsenic, dissolved	23	1.557	0.589	–	0.210	-0.150	–	94	1.26	-0.50
Arsenic, total	23	1.695	0.798	–	–	–	–	91	1.35	0.07
Antimony, dissolved	22	1.327	0.874	-0.271	0.625	0.542	–	92	1.50	-4.71
Antimony, total	22	1.266	0.914	-0.188	0.603	0.550	–	92	1.50	-3.87
Manganese, dissolved	17	0.417	–	–	–	–	[3]0.338	87	1.27	-1.63
Lead, dissolved	20	-4.945	1.207	–	–	–	–	80	1.66	3.10
Lead, total	23	-5.710	1.400	–	–	–	[4]-4.512	71	3.36	15.5
Aluminum, dissolved	23	1.370	1.691	–	–	–	–	97	1.39	-0.72
Aluminum, total	22	-0.939	1.772	–	–	–	[4]-3.224	92	2.05	17.4
Suspended sediment	20	-0.620	2.245	–	0.433	1.201	[5]0.0215	91	2.41	-5.93
Fine sediment	20	1.052	1.418	–	0.448	0.362	[2]0.022	91	2.21	-1.45
Coarse sediment	20	7.424	2.506	–	0.421	1.411	–	90	2.63	-6.82

Table 7. Regression coefficients and coefficients of determination (R^2) for models used to estimate loads of selected constituents at monitoring sites in the Stibnite mining area, central Idaho, 2012–14.—Continued

[Site names and locations are shown in table 1 and figure 1, respectively. Each regression model was calibrated using the available data collected at each station for water years 2012–14. The regression equation is $\ln L = I + a\,(\ln Q) + b\,(\ln Q^2) + c\,[\sin(2\pi T)] + d\,[\cos(2\pi T)] + e\,(SVT) + \varepsilon$, where ln is the natural logarithm; L is the constituent load, in pounds per day; I is the regression intercept; Q is the centered streamflow, in cubic feet per second; T is the centered decimal time in years from the beginning of the calibration period; $\sin(2\pi T)$ and $\cos(2\pi T)$ are periodic time functions that describe seasonal variability; SVT is the term describing streamflow variability; a, b, c, d, and e are regression coefficients that remain constant over time; and ε is the unaccounted error associated with the regression model. R^2 (coefficient of determination) represents the amount of variance explained by the model. **Abbreviations:** RMSE, root mean square error; lb/d, pound per day; –, no regression coefficient]

Constituent	Number of samples	Regression coefficient I	a	b	c	d	e	R²	RMSE (lb/d)	Load bias (percent)
					Site 4					
Arsenic, dissolved	22	2.514	0.575	–	–	–	–	89	1.27	0.49
Arsenic, total	22	2.587	0.614	–	–	–	–	87	1.33	0.53
Antimony, dissolved	21	1.888	0.611	–	0.327	0.050	–	88	1.42	-0.93
Antimony, total	21	1.868	0.787	–	–	–	–	87	1.45	-0.25
Manganese, dissolved	16	1.717	0.467	-0.133	–	–	–	88	1.24	0.61
Lead, dissolved	19	-4.762	1.126	–	–	–	–	65	1.89	4.46
Lead, total	21	-3.541	2.000	–	-0.545	0.620	–	88	1.94	-6.36
Aluminum, dissolved	22	1.473	1.578	–	–	–	–	94	1.62	2.50
Aluminum, total	21	3.124	1.709	–	–	–	–	84	2.44	6.45
Suspended sediment	20	6.370	1.358	0.522	–	–	–	84	2.14	3.78
Fine sediment	20	6.198	1.424	0.430	–	–	–	82	2.31	3.08
Coarse sediment	20	4.211	1.125	0.822	–	–	[6]0.020	89	1.90	5.49
Mercury, total	15	-6.777	1.521	0.411	–	–	–	90	1.64	3.06
					Site 5					
Arsenic, dissolved	21	0.862	0.796	–	0.021	0.367	–	95	1.23	0.26
Arsenic, total	20	-0.915	0.377	–	–	–	[7]0.015	94	1.31	4.52
Antimony, dissolved	20	-0.358	0.587	–	-0.031	0.579	–	72	1.38	1.72
Antimony, total	19	-2.288	0.483	–	0.004	0.561	[7]0.007	84	1.37	-1.30
Manganese, dissolved	15	-1.710	0.928	0.455	–	–	–	76	1.95	-7.03
Lead, dissolved	20	-9.042	1.069	–	–	–	[8]0.018	88	1.04	10.0
Lead, total	20	-11.347	1.776	–	–	–	[7]0.019	84	2.60	10.0
Aluminum, dissolved	21	0.815	1.780	–	0.409	-0.030	–	96	1.68	3.86
Aluminum, total	21	2.146	2.339	0.333	–	–	–	89	2.81	9.77
Suspended sediment	20	6.140	1.979	0.724	–	–	–	92	2.12	-6.41
Fine sediment	19	4.841	1.226	0.439	–	–	[7]1.756	95	1.83	-3.95
Coarse sediment	20	4.802	1.860	0.827	–	–	[6]5.341	95	1.90	-3.51
Mercury, total	19	1.868	1.685	0.223	–	–	[4]-7.106	91	2.71	-0.79

[1]Moving average of streamflow for the previous 3 days compared to each daily streamflow.

[2]Moving average of streamflow for the previous 7 days compared to each daily streamflow.

[3]Absolute value of the moving average of streamflow for the previous 7 days compared to each daily streamflow.

[4]Ratio of estimated daily mean runoff to daily mean streamflow in cubic feet per second (known as the base flow index [BFI]).

[5]Moving average of streamflow for the previous 1 day compared to each daily streamflow.

[6]Absolute value of the moving average of streamflow for the previous 1 day compared to each daily streamflow.

[7]Absolute value of the moving average of streamflow for the previous 30 days compared to each daily streamflow.

[8]Absolute value of the moving average of streamflow for the previous 7 days compared to each daily streamflow.

The shape of the hydrograph may affect the significance of streamflow terms in the LOADEST models. Sample results from Sugar Creek (site 5) show that the way the snowpack melts affects particulate constituent transport (fig. 3, fig. 17). Snowmelt runoff was similar in 2012 and 2014, with numerous spring increases in the hydrograph as the snowpack melted. In contrast, most of the snowpack melted in one event in 2013, which also produced the highest concentration

of mercury in Sugar Creek (site 5) at 26 µg/L. Although a sample from Sugar Creek was collected at the peak-of-record streamflow in May 2014, the total mercury concentration was only 2.8 µg/L, likely because several smaller-magnitude snowmelt events prior to the 2014 peak had already transported much of the sediment that had accumulated during the winter months of 2013–14 (fig. 17).
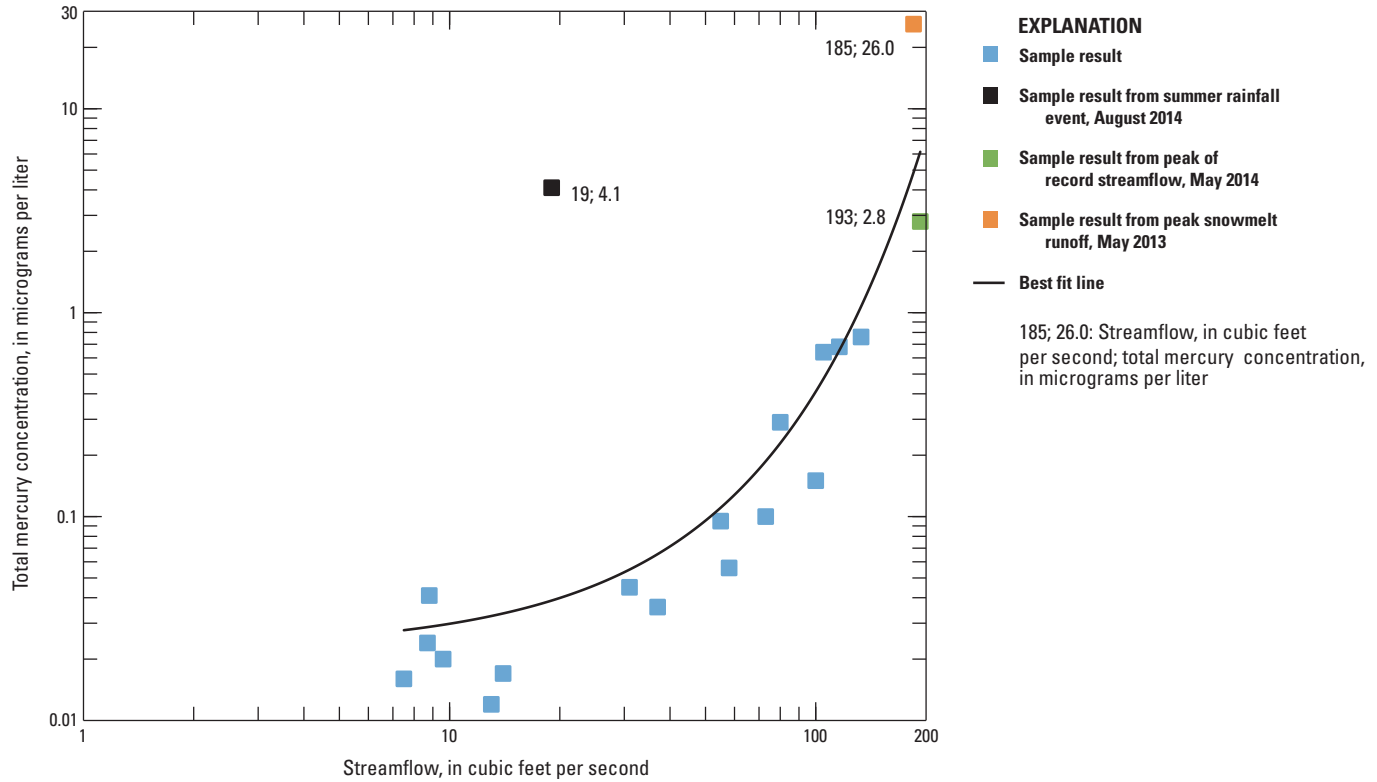

Figure 17.   Sampled streamflow and total mercury concentrations in Sugar Creek near Stibnite, central Idaho, 2012–14.

Runoff and interflow (lateral flow in the unsaturated zone) associated with the first flow-inducing event of the snowmelt season tend to pick up unconsolidated, fine sediment that has accumulated on or just below the land surface and in the stream channel of the watershed (Wang and others, 2010). Because snowpack and snowmelt runoff vary from year to year, simple linear or periodic time functions probably do not adequately characterize hysteresis in constituent transport. Changes in particle-size distribution during prolonged streamflow events also have contributed to hysteresis in sediment and sediment-associated constituent transport (Landers and Sturm, 2013). Changes in sediment source during snowmelt runoff may be affected by antecedent conditions, including air temperature, soil moisture, and ground temperature. Forest fires burned much of the study area in 2000, 2006, and 2007 (fig. 1), and sediment transport in the study area may change as areas become re-vegetated and the sediment sources vary.

Rainfall runoff events occurred each autumn in the study area, and samples were collected during one late-summer rainfall event in August 2014 (fig. 3). Changes in sediment source during rainfall runoff events may be affected by antecedent conditions and also can result from localized mass wasting. The relation between total mercury concentration and streamflow in the sample collected from Sugar Creek in August 2014 was substantially different as compared to all the other samples collected from Sugar Creek (fig. 17), likely because of conditions preceding the August rainfall event. The suspended-sediment concentration in the August 2014 sample was 13 mg/L and the streamflow was 19 ft^3/s. The suspended-sediment concentration in the August 2014 sample was in the range of suspended-sediment concentrations from other samples collected at streamflows between 80 and 133 ft^3/s on the rising or falling limb of the hydrograph during periods of sustained snowmelt runoff. The relatively high sediment and mercury concentration associated with a relatively low flow in August 2014 shows that sediment (and mercury) transport during a rainfall event preceded by a dry period is greater relative to sediment and mercury transport during a period of sustained high flows.

In general, use of the untransformed streamflow (rather than ln$Q$) to generate the streamflow variability term in load models resulted in greater significance of SVT as a predictor variable. Except for site 3, a specific streamflow variability term typically was more significant than other streamflow variability terms tested for significance in load models at a given site (table 7). At sites 1 and 2, which represent the headwaters of EFSFSR and Meadow Creek, a moving average of the previous 3 days compared to the daily mean streamflow generally was most significant as a term to account for hysteresis in constituent transport (table 7). Streamflow variability terms generally were insignificant in load models

developed for site 4 (downstream of the Glory Hole), likely because most sediment and sediment-associated constituents were captured in the Glory Hole. A moving average of the previous 30 days compared to the daily mean streamflow generally was most significant as a term to account for hysteresis in constituent transport at site 5 (table 7). Mean slope in the watershed upstream of each monitoring site was similar (37–38 percent) at sites 1–4, but was 50 percent at site 5 (U.S. Geological Survey, 2012). Each monitoring site, with the exception of site 5, also showed a diurnal variation in streamflow during snowmelt runoff periods. A more detailed analysis of watershed characteristics that control sediment sources and transport is beyond the scope of this study.

Surrogate Regression Modeling of Constituent Concentrations

Results of surrogate regression modeling indicate the value of continuously measured specific conductance for estimating constituent concentrations. Specific conductance was used as a predictor variable in surrogate models developed to estimate concentrations of dissolved arsenic and antimony at all five monitoring sites (table 8). Continuous specific conductance was a more significant predictor than streamflow in four of five surrogate regression models for dissolved arsenic concentrations, and two of five surrogate regression models for dissolved antimony concentrations (table 8). Streamflow and specific conductance were both significant in models of dissolved arsenic and antimony concentrations at the remaining sites.

Unlike LOADEST regression models, which were used to estimate and evaluate constituent transport in the study area on annual time scales, surrogate regression models were developed for the purpose of using real-time data from monitoring sites to generate a 15-minute time-series record of estimated constituent concentrations. LOADEST models also output estimated daily concentrations in addition to loads, and estimated LOADEST concentrations were compared to estimated daily concentrations from surrogate regression models. Surrogate regression models generally explained more variability in measured arsenic and antimony concentrations than LOADEST models, but specific conductance was not used as a predictor variable in the LOADEST models (tables 7 and 8). Results of surrogate regression modeling show that continuous water-quality and streamflow data at each study-area monitoring site can be used to estimate concentrations of dissolved arsenic and antimony in real time. Further, in conjunction with real-time streamflow data, the estimated concentrations can be used to calculate loads in real time.

Specific conductance was not a significant predictor for estimating real-time concentrations of total mercury (table 8). Surrogate regression model results show that streamflow and the BFI calculated from the local minimum method of hydrograph separation (Lim and others, 2005) can be used to estimate concentrations and loads of total mercury in real time at sites 4 and 5. Additional total mercury samples are necessary to develop regression estimates of total mercury concentrations and loads at the remaining study sites. Sample results for total mercury from site 5 (Sugar Creek) suggest that summer storms can generate high concentrations of mercury at moderate streamflow (fig. 17). Substantial variance in sample results for total mercury at site 5 resulted in a large root mean square error for the surrogate regression model estimating total mercury concentrations at site 5. Additional samples collected during summer storms would provide valuable information towards understanding how mercury is transported to streams in the Stibnite area and would help to calibrate models for estimating mercury concentration and loading.

Table 8.   Regression coefficients and model diagnostics for surrogate models used to estimate concentrations of selected constituents at monitoring sites in the Stibnite mining area, central Idaho, 2012–14.

[Site names and locations are shown in table 1 and figure 1, respectively. Each regression model was calibrated using the available data collected at each station for water years 2012–14. The regression equation is $\ln C = I + a\,(SC) + b\,(\ln SC) + c\,(Q) + d\,(\ln Q) + e\,[\sin(2\pi T)] + f\,[\cos(2\pi T)] + g(BFI)$, where C is the constituent concentration, in micrograms per liter; I is the regression intercept; Q is the centered streamflow, in cubic feet per second; $\sin(2\pi T)$ and $\cos(2\pi T)$ are periodic time functions that describe seasonal variability; BFI is the term describing streamflow variability; ln is the natural logarithm transformation; and a, b, c, d, e, f, and g are regression coefficients that remain constant over time. R^2 (coefficient of determination), represents the amount of variance explained by the model in percent. **Abbreviations:** BCF, bias correction factor; RMSE, root mean square error; –, no regression coefficient]

Constituent				Regression coefficient						BCF	RMSE (percent)	Surrogate concentration model R^2	LOADEST concentration model R^2
	N	I	a	b	c	d	e	f	g				
Site 1													
Arsenic, dissolved	20	0.614	0.025	–	–	–	0.107	0.007	–	1.003	8.34	96	86
Antimony, dissolved	20	-5.359	–	1.313	–	–	0.314	0.175	–	1.009	15.2	86	72
Site 2													
Arsenic, dissolved	21	-0.758	0.014	–	–	–	–	–	–	1.004	9.65	87	89
Antimony, dissolved	18	14.457	–	2.920	–	0.816	0.375	0.583	–	1.012	18.1	72	62
Site 3													
Arsenic, dissolved	23	2.273	–	1.126	–	–	0.127	-0.106	–	1.020	20.8	76	58
Antimony, dissolved	22	-9.525	–	2.377	–	0.503	0.532	0.303	–	1.055	37.3	65	54
Site 4													
Arsenic, dissolved	21	-3.072	–	1.561	–	–	-0.044	-0.180	–	1.007	13.6	95	72
Antimony, dissolved	21	-11.776	–	2.888	–	0.615	0.182	0.156	–	1.010	16.1	91	32
Mercury, total	15	-3.957	–	–	0.003	–	–	–	-1.755	1.030	35.0	85	76
Site 5													
Arsenic, dissolved	21	1.407	0.011	–	–	–	0.119	0.274	–	1.013	18.2	86	77
Antimony, dissolved	20	-0.867	0.021	–	–	–	0.151	0.410	–	1.032	29.1	90	75
Mercury, total	19	3.045	–	–	0.010	–	-0.369	-1.194	-7.644	1.367	109	87	82

Areas of Further Study

Additional samples collected on the rising and falling limbs of the streamflow hydrograph during summer storms would help validate all regression models presented in this report. Given the remote location of the study area and the flashiness of storm events, obtaining storm samples may require installation of auto-samplers. However, because concentrations of sediment and sediment-associated constituents may not be evenly distributed in the stream cross section, auto-samplers, which are point samplers, may not provide an adequate representation of stream concentrations. A continuous physical measure of sediment in the water column, or a surrogate such as turbidity, is not appropriate for the study area because most sediment transported is coarse (>0.0625 mm in diameter) and does not necessarily cause increases in turbidity. Acoustic backscatter may or may not be a significant predictor of sediment concentration at study-area sites and would require further investigation of feasibility. The steep gradient in the study area may contribute to bedload transport of coarse sediment and sediment-associated metals. Bedloads are not well characterized by surrogate measures of sediment concentrations in the water column.

MGI-directed sample collection at various surface-water sites within the study area in addition to the five USGS monitoring sites operated and sampled during this study. Measured discrete loads at additional sites in the study area could be compared to load estimates in the Meadow Creek reach and the Glory Hole reach that are summarized in this report. Such comparisons may identify more specific source areas and validate LOADEST modeling results.

Tracer-injection methods also can be used to validate findings in this report and to identify more specific sources of contaminants. Tracer injection in discrete reaches of interest (such as the Glory Hole reach) can provide reliable streamflow measurements on a watershed scale in addition to spatially detailed concentration information when combined with synoptic sampling. Streamflow and concentration data then can be used to develop mass-loading profiles for metals of interest. Streamflow and loading profiles identify the primary sources in spatial detail and demonstrate the importance of unsampled, dispersed subsurface inflows and attenuation (Kimball and others, 2004). Longitudinal loading profiles generated from tracer injection studies, therefore, are useful for targeting remediation efforts.

With continued operation of continuous stream stage and specific conductance sensors at monitoring sites, real time estimates of arsenic, antimony, and mercury concentrations can be made publicly available on the USGS National Water Information System (U.S. Geological Survey, 2015). Changes in land use associated with mining activities may be detected with subsequent evaluation of regression model coefficients and inclusion of a predictor variable that accounts for trends.

Summary

Water-quality and streamflow monitoring during 2012–2014 showed that concentrations of trace elements, except for mercury, generally do not exceed ambient water-quality criteria applicable in streams in the Stibnite mining area of central Idaho. Total mercury was detected at concentrations greater than the State of Idaho 0.012-microgram per liter (µg/L) chronic exposure limit for freshwater aquatic life at five monitoring sites used for the study. Arsenic and antimony concentrations exceeded human-health based water-quality criteria in Sugar Creek (site 5) and both monitoring sites located on the East Fork of the South Fork of the Salmon River (EFSFSR) downstream of the confluence with Meadow Creek. Arsenic concentrations exceeded the 10-µg/L human-health-based standard about one-half the time in the EFSFSR upstream of the confluence with Meadow Creek (site 1), but did not exceed 10 µg/L at Meadow Creek (site 2). Site 2 was selected to represent background conditions, and the median total arsenic concentration in samples collected from site 2 was 1.3 µg/L. Water temperature exceeded the 9 °C maximum daily average temperature criterion for salmonid spawning at least 29 percent of the time at each site. Water temperature at sites 3 and 4 in the EFSFSR and site 5 in Sugar Creek exceeded the 13 °C maximum daily maximum temperature criterion for salmonid spawning between 4 and 9 percent of the time.

Two distinct constituent sources are present in the study area. Significant positive correlations between streamflow and concentrations of suspended sediment and sediment-associated constituents (total aluminum, total lead, and total mercury) indicate that surface runoff and stream-channel erosion deliver these constituents to streams during rainfall or snowmelt runoff. Significant negative correlations between streamflow and concentrations of arsenic, antimony, and dissolved iron and magnesium indicate that groundwater is the source for these constituents. Significant correlation between constituent concentrations and streamflow also showed that the U.S. Geological Survey LOAD ESTimation (LOADEST) program is a useful tool for estimating mean annual loads and streamflow-weighted concentrations (FWCs) of selected constituents in streams in the study area.

Mass balance estimates show that concentrated sources of arsenic, antimony, and dissolved manganese are present in discrete reaches along Meadow Creek and between sites 3 and 4 along the EFSFSR. Although they accounted for only 25 percent of the total streamflow, the reaches along Meadow Creek (the Meadow Creek reach) and between sites 3 and 4 (the Glory Hole reach) accounted for 80 percent of the total arsenic and antimony loads and 86 percent of the dissolved manganese load transported downstream of the study area. Estimated FWCs exceeded human-health based water-quality criteria for arsenic and antimony at sites 3 and 4 in the EFSFSR and for arsenic at site 5 in Sugar Creek.

Continuously monitored specific conductance was statistically significant as a predictor (surrogate) for concentrations of dissolved arsenic and antimony at all study-area sites. Surrogate regression models using continuous stage and specific conductance, and, in some cases, functions of streamflow and time, can be used to estimate concentrations and loads of dissolved arsenic and antimony at all five study-area sites.

The East Fork of Meadow Creek was not monitored as part of this study, but LOADEST model results indicate that the East Fork Meadow Creek, the only tributary stream in the Meadow Creek reach, likely accounts for most of the suspended sediment loading in the study area. Sediment and sediment-associated constituent loads from the East Fork of Meadow Creek are trapped in the Glory Hole between sites 3 and 4. FWCs of suspended sediment, total aluminum, and total lead decrease in the Glory Hole reach between sites 3 and 4. The Meadow Creek reach was the largest contributor of suspended sediment and the second largest contributor of total aluminum in the study area. The East Fork Meadow Creek in the Meadow Creek reach was not sampled, but likely contributes most of the sediment and aluminum attributed to the Meadow Creek reach. Because sediment and sediment-associated constituents from sources upstream of the Glory Hole are trapped in the Glory Hole, Sugar Creek accounts for most of the sediment and sediment-associated constituent loading transported downstream of the study area. Sugar Creek (site 5) is the second largest contributor of suspended sediment and the largest contributor of total aluminum in the study area. Sugar Creek accounted for 98 percent of the total mercury load transported downstream of the study area.

LOADEST model results indicated hysteresis in transport of suspended sediment and sediment-associated constituents within the study area. Biases in estimated loads were reduced using an additional predictor variable to describe streamflow variability relative to an n-day average streamflow. The ratio of estimated surface runoff to streamflow, known as the base-flow index, was tested for significance as another predictor variable to account for streamflow variability. Different streamflow variability terms were significant as predictor variables in different sub-watersheds, indicating that watershed characteristics and (or) conditions preceding erosional events may influence sediment transport in the study area. Results from samples collected during a summer storm in August 2014 showed that LOADEST and surrogate regression models may not produce reliable estimates of sediment and sediment-associated constituent concentrations and loads during rainfall runoff events. Regression models using streamflow and the base-flow index as predictor variables accounted for at least 80 percent of the variability in sampled concentrations of total mercury at sites 4 (EFSFSR above Sugar Creek) and 5 (Sugar Creek). With continued operation of continuous stage sensors, concentrations and loads of total mercury can be estimated in real time at sites 4 and 5.

Additional sample results are necessary to evaluate LOADEST and surrogate models for total mercury concentrations and loads at remaining study area sites and during summer storms at sites 4 and 5.

Acknowledgments

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Appendix A. Analysis of Quality-Assurance and Quality-Control Data from Field Samples in Streams in the Stibnite Mining Area, Central Idaho, and Laboratory Samples from the National Water-Quality Laboratory, 2012–14

Results from the National Water Quality Laboratory's (NWQL) inorganic blind sampling project (IBSP) showed a positive bias for dissolved analyses of cadmium and lead. Wilcoxon signed-rank tests were used to assess bias relative to the median expected concentration in the reference sample (Woodworth and Connor, 2003; T. Struzenski, U.S. Geological Survey, written commun., 2013). Positive biases in dissolved cadmium and lead results were known to occur starting in October 2011 and January 2012, respectively, and were corrected by the end of water year 2013. Positive bias in dissolved cadmium results ranged from 13 to less than 6 percent, and positive bias in dissolved lead results ranged from 7.4 to 5.8 percent (T. Struzenski, U.S. Geological Survey, written commun., 2013).

Positive bias in dissolved concentrations of cadmium and lead affected the quality of analytical results. Uncensored dissolved concentrations were greater than whole-water concentrations in 86 percent of cadmium results and 24 percent of lead results (table A1). Consistent positive or negative bias in dissolved or whole-water results for zinc, copper, antimony, and arsenic was not documented. However, dissolved concentrations of zinc, copper, antimony, and arsenic also commonly exceeded concentrations from whole-water samples (table A1. Dissolved antimony concentrations that were commonly higher than total antimony concentrations resulted in model results with larger loads and streamflow-weighted concentrations for dissolved antimony than total antimony in some cases. However, this did not affect the interpretive results in the report because analytical data indicate that most of the antimony on site is dissolved. Numerous dissolved results were flagged in the National Water Information System (NWIS) database based on:

1. The known positive bias shown in IBSP analytical results for dissolved cadmium and lead,

2. The relative percent difference (RPD) between uncensored dissolved concentrations and censored or uncensored whole-water concentrations, and

3. The 2014 long-term method detection level (LT-MDL) for the dissolved constituent. The LT-MDL is determined based on the standard deviation of a minimum of 24 method-detection-limit spike sample measurements over an extended period of time (Oblinger Childress and others, 1999).

The NWQL collects quality-control data on a continuous basis to assess variations in LT–MDLs and to determine or revise LT–MDLs from year to year. Several LT-MDLs changed during the study period (table A1). Dissolved concentrations were flagged as "estimated" in the NWIS database if they were reported as uncensored at a concentration lower than the latest LT-MDL regardless of the RPD compared to the whole-water concentration in the same sample. Uncensored dissolved constituents detected at higher concentrations than whole-water constituents were flagged as "reviewed and rejected" in the NWIS database if the RPD compared to the censored or uncensored whole-water concentration in the same sample was greater than 20 percent. In most of these cases, repeated laboratory analysis for dissolved and total constituents confirmed original results. Analysis of the quality-control dataset collected for this study includes rejected results, but they are not otherwise used, interpreted, or provided to the public. Estimated results are used, interpreted, and provided to the public.

During water years 2012–14, 11 split replicate samples were collected on a rotating basis between the five study sites. Split-replicate RPDs greater than 20 percent for individual sets of samples generally occurred with rarely detected trace elements or trace elements detected near the applicable LT-MDL. Relatively large RPDs also occurred with concentrations of total iron, total aluminum, and suspended sediment in split-replicates collected at site 3 near the peak runoff event in May 2012 (table A2).

Results from the field blanks indicate overall acceptable quality (table A2). Four field blanks collected between May 17 and June 23, 2012, contained 29 out of a total of 41 detections (table A3). Field equipment cleaning practices between May and June of 2012 may have been ineffective in removing residual contamination, which may have resulted in positive bias to sample results, but other sources of bias also were present during the period. Forty-eight percent of the field blank detections between May and June 2012 were associated with cadmium, lead, and manganese. Positive laboratory bias in dissolved cadmium and lead was confirmed in laboratory quality-assurance testing (T. Struzenski, U.S. Geological Survey, written commun., 2013). Eight detections of dissolved manganese out of 15 blanks probably resulted from bias introduced during filtration (S. Skrobialowski, U.S. Geological Survey, written commun., 2015).

Table A1.   Quality-assurance summary for selected constituent analyses from streams in the Stibnite mining area, central Idaho, 2012–14.

[**Abbreviations:** QA, quality assurance; QC quality control; RPD, relative percent difference; >, greater than; µg/L, micrograms per liter; NWIS, National Water Information System; LT-MDL, long-term method detection limit. Dissolved concentrations are determined from filtered samples and whole-water concentrations are determined from unfiltered samples]

	Cadmium	Copper	Lead	Zinc	Antimony	Arsenic
Number of environmental samples (including split replicate QA/QC samples)	118	115	118	118	115	118
Number of uncensored dissloved results	36	17	68	11	115	118
Number of uncensored dissolved concentrations > whole-water concentrations (censored or uncensored)	31	8	16	4	64	32
Percentage of uncensored dissolved concentrations > whole-water concentrations (censored or uncensored)	86	47	24	36	56	27
Average RPD between uncensored dissolved concentrations > whole-water concentrations (censored or uncensored)	91.1	42.3	32.9	63.2	8.15	5.58
Number of dissolved results flagged as "rejected" in the NWIS database	22	6	10	0	3	0
Long-term method detection limit October 1, 2011 to September 30, 2013, µg/L (dissolved; whole-water)	0.016; 0.016	0.80; 0.70	0.025; 0.04	1.4; 3.0	0.027; 0.18	[1]0.04; 0.28
Long-term method detection limit as of October 1, 2013, µg/L (dissolved; whole-water)	0.03; 0.03	0.80; 0.80	0.04; 0.04	2.0; 2.0	0.027; 0.18	0.10; 0.20
Number of dissolved results flagged as "estimated" because of increased LT-MDL	6	0	0	0	0	0

[1]The LT-MDL for dissolved arsenic was 0.03 µg/L from October 1, 2011 to September 30, 2012 and increased to 0.04 µg/L until September 30, 2013.

Blank sample detections did not indicate consistent positive bias from sampling equipment cleaning procedures or ambient conditions during sample processing, but did indicate occasional contamination bias from the source blank solution, shipping, storing, or analytical procedures. Blank detections that exceeded the minimum detections in environmental samples from the same trip are further summarized in table A3. In some cases, the blank detection exceeded the maximum detected concentration in environmental samples collected during the same trip, ruling out contamination bias from ambient processing conditions or equipment. In other cases, the dissolved constituent was detected and the total constituent was not detected in the same blank sample, suggesting positive bias in analytical procedures for the dissolved constituent. One detection each of dissolved cadmium, total lead, and total aluminum were within the range of detections for the same analyte during the same sampling trip, suggesting possible field equipment contamination.

Overall, split replicate, field blank, and IBSP quality-assurance sample results indicate that detections of dissolved cadmium and lead in environmental sample results should be used with caution. Blank results also suggest possible positive laboratory bias in dissolved chromium during May 2012. Manganese concentrations in environmental samples collected with potentially contaminated capsule filters were compared with environmental samples collected at similar streamflows at each site using uncontaminated capsule filters. The comparison showed that dissolved manganese introduced during sample filtration and quantified in blank results did not consistently bias environmental sample results for dissolved manganese.

Table A2. Results from quality-control samples collected in the Stibnite mining area, central Idaho, 2012–14.

[Bold type indicates a relative percent difference of greater than 20 percent. Shaded cells indicate that the maximum field blank detection was higher than the minimum detection for an analyte in environmental samples. **Abbreviations:** CaCO$_3$, carbonate; RPD, relative percent difference; mg/L, milligrams per liter; µg/L, micrograms per liter; (f), filtered; (unf), unfiltered; >, greater than; <, less than; mm, millimeter; NA, not applicable; N, no; Y, yes; 2×LT-MDL long-term method detection level multiplied by 2 (also known as the laboratory reporting level or LRL)]

Constituent	Number of field blank samples	Number of field blank detections	Number of field blank detections > 2×LT-MDL	Median detected field blank concentration (µg/L)	Maximum detected field blank concentration (µg/L)	Minimum detected concentration in environmental samples (µg/L)	Number of split replicate pairs	Split replicate minimum RPD	Split replicate 75th percentile RPD	Split replicate maximum RPD
Hardness as CaCO$_3$, mg/L	15	0	0	NA	NA	13.5	9	0.00	1.66	6.67
Calcium (f), mg/L	15	2	0	NA	0.034	4.2	9	0.52	1.73	6.78
Magnesium, (f), mg/L	15	0	0	NA	NA	0.72	9	0.00	1.95	7.55
Magnesium, (unf), mg/L	20	1	0	NA	0.009	0.72	11	0.37	5.00	8.40
Sodium, (f), mg/L	15	0	0	NA	NA	1.25	9	0.00	4.46	7.96
Potassium, (f), mg/L	15	1	0	NA	0.008	0.46	9	0.30	4.15	**29.1**
Chloride, (f), mg/L	15	1	1	NA	6.07	0.10	9	0.00	3.07	3.82
Sulfate, (f), mg/L	15	1	1	NA	0.10	0.93	9	0.00	2.02	**35.3**
Fluoride, (f), mg/L	15	0	0	NA	NA	0.03	8	0.00	5.17	**22.2**
Silica, (f), mg/L	15	2	0	NA	0.07	8.45	9	0.00	3.23	4.08
Arsenic, (f), µg/L	20	3	0	0.05	0.06	0.61	11	0.50	4.55	8.00
Arsenic, (unf), µg/L	20	0	0	NA	NA	0.81	11	0.00	6.63	8.70
Cadmium, (f), µg/L	20	5	4	0.303	1.22	0.033	11	0.00	**36.1**	**63.6**
Cadmium, (unf), µg/L	20	4	1	0.036	0.101	0.016	11	0.00	**30.3**	**119**
Chromium, (f), µg/L	20	2	0	NA	0.09	0.052	11	0.00	16.7	**57.8**
Chromium, (unf), µg/L	20	0	0	NA	NA	0.05	11	0.00	0.00	18.2
Copper, (f), µg/L	20	1	1	NA	2.00	0.117	11	0.00	0.00	**40.0**
Copper, (unf), µg/L	20	0	0	NA	NA	0.30	11	0.00	0.00	**117**
Iron, (f), µg/L	20	1	0	NA	6.00	4.1	11	0.81	16.4	**23.4**
Iron, (unf), µg/L	20	0	0	NA	NA	11.2	10	0.00	16.0	**54.7**
Lead, (f), µg/L	20	4	0	0.046	0.069	0.008	10	0.00	**72.6**	**93.0**
Lead, (unf), µg/L	20	1	0	NA	0.06	0.01	11	0.00	18.2	**76.9**
Manganese, (f), µg/L	15	8	1	0.21	0.59	0.36	9	1.28	**23.5**	**54.8**
Zinc, (f), µg/L	20	1	0	NA	3.30	1.4	10	0.00	0.00	**38.2**
Zinc, (unf), µg/L	20	1	1	NA	4.50	2.1	11	0.00	0.00	**158**
Antimony, (f), µg/L	20	1	0	NA	0.027	0.23	11	0.00	3.74	4.34
Antimony, (unf), µg/L	20	0	0	NA	NA	0.21	11	0.00	4.58	7.23
Aluminum, (f), µg/L	20	0	0	NA	NA	2.9	11	1.16	18.4	**66.7**
Aluminum, (unf), µg/L	20	1	1	NA	8.20	4.7	10	0.87	13.9	**45.9**
Suspended sediment, percent fines (<0.0625 mm)	0	0	0	NA	NA	11	6	1.40	**41.6**	**63.4**
Mercury, (f), µg/L	8	0	0	NA	NA	0.005	2	13.3	NA	18.2
Mercury, (unf), µg/L	11	0	0	NA	NA	0.005	2	7.41	NA	**22.2**
Suspended sediment concentration, mg/L	0	0	0	NA	NA	1	6	0.00	**65.6**	**66.7**
Sum	549	41	11	NA	NA	NA	310	NA	NA	NA

Table A3.   Blank sample detections exceeding minimum detections in environmental samples collected in the Stibnite mining area, central Idaho, 2012–14.

[**Likely source of contamination:** Handling, likely contamination bias from any of the following sources—source blank solution, shipping, storing, or analytical procedures; Equipment, contamination bias from sampling equipment; Filter, likely contamination bias from a capsule filter. **Abbreviations:** mg/L, milligrams per liter; µg/L, micrograms per liter; (f), filtered; (unf), unfiltered; <, less than; NA, not applicable]

Constituent	Blank detection date	Blank	Detected in dissolved and total results?	Environmental range during sampling event	Likely source of contamination
Chloride (f), mg/L	05-23-12	6.07	NA	0.23–0.38	Handling
Aluminum (unf), µg/L	06-13-12	8.2	No	58.2–199	Equipment
Cadmium (f), µg/L	05-17-12	0.434	Yes	0.088–0.371	Handling
Cadmium (f), µg/L	05-18-12	1.22	Yes	0.088–0.371	Handling
Cadmium (f), µg/L	05-23-12	0.251	Yes	0.088–0.371	Handling
Cadmium (f), µg/L	11-06-12	0.017	No	<0.016–0.056	Handling
Cadmium (f), µg/L	10-01-14	0.303	No	<0.030–0.194	Handling
Cadmium (unf), µg/L	05-17-12	0.025	Yes	0.017–0.037	Equipment
Cadmium (unf), µg/L	05-18-12	0.046	Yes	0.017–0.037	Handling
Cadmium (unf), µg/L	05-23-12	0.101	Yes	0.017–0.037	Handling
Cadmium (unf), µg/L	06-13-12	0.021	No	<0.016–0.156	Handling
Chromium (f), µg/L	05-17-12	0.09	No	0.17–0.36	Handling
Chromium (f), µg/L	05-18-12	0.09	No	0.17–0.36	Handling
Copper (f), µg/L	05-23-12	2.00	No	<0.80	Handling
Iron (f), µg/L	05-23-12	6.00	No	18.0–33.6	Handling
Lead (f), µg/L	05-18-12	0.029	No	0.027–0.063	Handling
Lead (f), µg/L	05-23-12	0.069	No	0.027–0.063	Handling
Lead (f), µg/L	06-14-12	0.027	No	0.027–0.105	Handling
Lead (f), µg/L	05-19-14	0.062	No	<0.040–0.048	Handling
Lead (unf), µg/L	06-13-12	0.06	No	0.04–0.10	Equipment
Manganese (f), µg/L	05-17-12	0.38	NA	1.16–6.29	Filter
Manganese (f), µg/L	05-18-12	0.59	NA	1.16–6.29	Filter
Manganese (f), µg/L	05-23-12	0.17	NA	1.16–6.29	Filter
Manganese (f), µg/L	06-13-12	0.14	NA	1.28–9.08	Filter
Manganese (f), µg/L	11-06-12	0.17	NA	0.57–37.5	Filter
Manganese (f), µg/L	03-26-13	0.25	NA	1.56–28.8	Filter
Manganese (f), µg/L	06-25-13	0.17	NA	0.83–18.5	Filter
Manganese (f), µg/L	04-25-14	0.29	NA	0.77–20.5	Filter
Zinc (f), µg/L	05-23-12	3.3	No	<1.4–1.5	Handling
Zinc (unf), µg/L	08-28-12	4.5	No	<3.0	Handling

Appendix B. Statistical Summary of Constituent Concentrations in Water-Quality Samples Collected at Streamflow-Gaging Stations in the Stibnite Mining Area, Central Idaho, 2012–14

Appendix B is a Microsoft Excel® file and is available for download at http://dx.doi.org/10.3133/sir20155166.

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