

Metal Concentrations and Sources in the Miller Creek Watershed, Park County, Montana, August 2000

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By Thomas E. Cleasby and David A. Nimick

Abstract

Miller Creek is a tributary of Soda Butte Creek in south-central Montana near the northeast corner of Yellowstone National Park. Surface-water and streambed-sediment samples were collected from streams and seeps throughout the Miller Creek watershed during low-flow conditions on August 28-31, 2000, to characterize metal concentrations and identify possible sources contributing metal to Miller Creek.

Most water in Miller Creek appears to be unaffected by mining disturbances or natural weathering of mineralized rocks, although such effects are common elsewhere in the New World Mining District. Values for pH were near neutral to basic. Total-recoverable copper, lead, and zinc concentrations were low, relative to State of Montana water-quality standards, with many concentrations less than the analytical minimum reporting levels. Metal concentrations in Miller Creek during this study ranged from 1 to 6 micrograms per liter ($\mu\text{g/L}$) for total-recoverable copper, <1 to 5 $\mu\text{g/L}$ for total-recoverable lead, and <1 to 26 $\mu\text{g/L}$ for total-recoverable zinc. Concentrations of cadmium, copper, lead, and zinc in all samples from Miller Creek were less than the chronic aquatic-life criteria, except for one total-recoverable lead value (5 $\mu\text{g/L}$) just downstream from the Black Warrior Mine inflow.

Leachable lead and zinc concentrations in streambed-sediment samples collected during this study were highest at the Black Warrior Mine inflow. Leachable concentrations at this site were about 20 times greater for lead and 11 times greater for zinc than concentrations in the streambed-sediment sample collected from Miller Creek upstream from this inflow. However, these elevated concentrations had little effect on the leachable metal concentrations in the streambed-sediment sample collected downstream from the Black Warrior Mine inflow.

Metal loading to Miller Creek during this low-flow study was relatively small. Three small left-bank inflows having elevated copper concentrations entered Miller Creek near the middle of the study reach and their combined total-recoverable copper load accounted for about 96 percent of the copper load in Miller Creek. Small loads of lead (about 2 micrograms per second) entered Miller Creek from the Black Warrior Mine inflow and a right bank inflow. None of the loads entering Miller Creek had an appreciable effect on mainstem metal concentrations. In addition, substantial differences between mining related areas and areas influenced by local geology could not be determined.

INTRODUCTION

Miller Creek is a tributary of Soda Butte Creek in south-central Montana (fig. 1) near the northeast corner of Yellowstone National Park. Miller, Fisher, and Daisy Creeks are the three primary streams (fig.

1) draining the highly mineralized New World Mining District. The New World Mining District extends about 10 miles north and about 5 miles east of the southwest corner at the intersection of the 45th parallel and the 110th meridian (Lovering, 1929). Mining for gold, copper, silver, lead, and zinc began in the late 1800s and continued through the early 1900s, resulting in mining wastes that have been sporadically distributed throughout the Miller Creek watershed. These metal-enriched wastes have the potential to degrade the water quality of Miller Creek.

Metal-loading studies have been a useful tool in characterizing water quality and identifying metal sources in historical mining areas (Kimball, 1997; Kimball and others, 1999; Cleasby and others, 2000; Nimick and Cleasby, 2001). In these studies, detailed profiles of metal loads (mass of metal transported over a given time) along a stream are developed. Metal loads are calculated at many closely spaced sites by multiplying streamflow and metal concentration. Metals can enter the stream from metal-rich surface inflows such as tributaries, discharge from mine adits, and runoff from waste-rock and tailings piles; or from ground-water discharge (subsurface inflow). In addition, intense rainstorms and snowmelt runoff can flush tailings into streams and cause short-term increases in total-recoverable concentration and load (John H. Lambing, U.S Geological Survey, written commun., 2001). Results from metal-loading studies conducted in the nearby Fisher and Daisy Creek watersheds document elevated metal concentrations and show that substantial metal loads enter both creeks from natural and mining-related sources (Kimball and others, 1999; Nimick and Cleasby, 2001).

Periodic water-quality samples collected in the Miller Creek watershed (URS Operating Services, Inc., 1998) indicate that metal concentrations are typically low and metal loads entering Miller Creek are small compared to the other two watersheds in the mining district. However, a detailed metal-loading study along Miller Creek, similar to those along Fisher and Daisy Creeks, was needed to obtain information to identify sources contributing metals to the stream. Potential metals sources in the Miller Creek watershed were thought to include abandoned mines or tailings piles, natural weathering of the pyrite-rich mineralized rock that surrounds the ore zones and occurs as regional alteration in intrusive rocks, or ground-water discharge from faults that cross the watershed. Identification of metal sources along Miller Creek will aid resource managers in planning and conducting effective remediation activities in this part of the New World Mining District.

Purpose and Scope

The purpose of this report is to characterize metal concentrations and identify possible sources contributing metals to Miller Creek during low flow. This study was conducted during August 28-31, 2000. Surface-water samples were collected at 55 mainstem and inflow sites along Miller Creek (fig. 2) and analyzed for pH, major ions, and metals. Streambed-sediment samples were collected at 16 sites and analyzed for metal concentrations. The study reach was about 15,000 ft in length (about 2.8 miles) and covered almost the entire length of Miller Creek. This study was conducted by the U.S. Geological Survey (USGS) in cooperation with the U.S. Department of Agriculture (USDA)-Forest Service.

Description of Study Area

The headwaters of Miller Creek originate in the Gallatin National Forest in south-central Montana (fig. 1). Miller Creek flows southeast from Bull of the Woods Pass (altitude about 9,700 ft) to Soda Butte Creek (altitude about 7,600 ft) just east of the town of Cooke City (fig. 2) and about 3.5 mi east of Yellowstone National Park. One small, unnamed tributary, commonly called and hereinafter referred to

as the East Fork Miller Creek, drains the area below Daisy Pass (altitude about 9,700 ft). The Miller Creek channel upstream from the East Fork, commonly called the West Fork (Maxim Technologies, Inc., 1995), is referred to as the mainstem of Miller Creek in this report. The confluence of the East Fork Miller Creek is about 0.6 mi downstream from the origin of Miller Creek (fig. 2).

The streambed varies throughout the study reach (fig. 3). In the upper reach (from about site 0 to site 3,225), the streambed is composed of mostly gravel and cobbles. Near mid-basin (downstream from site 3,225 to about site 7,120), the Miller Creek streambed is mostly composed of large cobbles with some scattered boulders. In the lower reach (between sites 7,120 and site 14,505), the stream is mostly confined to a steep, narrow incised channel, and flow is mostly over exposed bedrock. Streamflow near the downstream end of the lower reach cascades through a series of small waterfalls. At the downstream end of the study reach, the channel once again becomes less constricted and the streambed is composed of cobbles, boulders, and woody debris (fig. 3). Many of the boulders found in the streambed probably represent a lag deposit from the erosion of glacial till on the valley floor.

Mining for gold began in 1870 in the Miller Creek watershed (Lovering, 1929). Adits, trenches, tailings piles, waste-rock dumps, and prospect pits are scattered throughout the watershed. Most of these mining features are relatively small but larger mines include the Daisy, Little Daisy, Black Warrior, and the Alice E. Mines. The Black Warrior Mine is the only mine that is close to the Miller Creek channel. Several other small waste-rock piles and prospect pits also are located along the creek. The Daisy, Little Daisy, and Alice E. Mines are uphill from Miller Creek, on the south slope of Henderson Mountain.

Paleozoic sedimentary rocks intruded by Tertiary igneous rocks and subjected to genetically related alteration and mineralization underlie the New World Mining District. The sedimentary rocks include the Cambrian Flathead Sandstone, Wolsey Shale, Meagher Limestone, Park Shale, Pilgrim Limestone, and Snowy Range Formation, and the Ordovician Bighorn Dolomite. Tertiary igneous activity included hydrothermal brecciation and intrusion of stocks, laccoliths, sills, and dikes. Alteration and mineralization in the mining district were associated with this intrusive activity. The larger, recently discovered mineral deposits are gold, copper, and silver-bearing skarn and replacement deposits hosted mainly by the Meagher Limestone, replacement deposits in limestone along high-angle faults, and replacement deposits hosted in limestone blocks within intrusion breccias. The Little Daisy Mine is located in an area of this latter style of mineralization, with mineralized blocks of Pilgrim Limestone within an intrusion breccia (Elliott and others, 1992).

The Black Warrior Mine is located in an area of vein and replacement mineralization developed in the Ordovician Bighorn Dolomite along a high-angle fault or fracture structure. The Black Warrior Mine contains lead and zinc mineralization typical of vein-type mineralization in the perimeter of the district where lower temperature hydrothermal fluids were telescoped out along faults and fractures (Allan R. Kirk, Maxim Technologies, Inc., Helena, Mont., written commun, 2001).

The Alice E. Mine complex is a small open-pit mine that recovered gold from stockwork fracture-controlled gold-pyrite mineralization in the Cambrian Flathead Sandstone. The intrusive complexes, ore bodies, and surrounding altered rocks are all rich in sulfide minerals, including pyrite and chalcopyrite (Elliott, 1979; Elliott and others, 1992).

Natural (non-mining related) acid drainage is evidenced by the presence of several ferricrete deposits in the Miller Creek watershed. Radiocarbon dating of wood embedded in one ferricrete deposit in the Miller Creek watershed resulted in an age estimate of more than 2,000 years old. This age estimate clearly predates mining and substantiates a natural source of acid drainage (Furniss and others, 1999).

Three main faults traverse the upper reaches of the Miller Creek watershed (fig. 2). The eastern fault trends north towards the Little Daisy adit, the middle fault correlates with the regionally extensive north-south trending Crown Butte fault, and the western fault extends into the Daisy Creek watershed (Elliot, 1979; Maxim Technologies, Inc., 1995). Each of these faults are splays of the Crown Butte Fault. The eastern and middle faults converge in the upper portion of the East Fork Miller Creek. The western fault parallels the upper portion of Miller Creek.

Previous Studies

Periodic water-quality data were collected during the late 1980s through 1996 at sites SW-2 (site 7,120) and SW-5 (downstream from the end of the study reach) (fig. 1) (Miller and others, 1997; Nimmo and others, 1998; and URS Operating Services, Inc., 1998). Generally, metal concentrations in water from Miller Creek were low to slightly elevated with respect to Montana water-quality standards. During low flow, dissolved copper concentrations ranged from 2 to 10 $\mu\text{g/L}$ and zinc concentrations ranged from 1 to 30 $\mu\text{g/L}$. During periods of higher streamflows (spring sampling periods), Nimmo and others (1998) determined that dissolved copper concentrations ranged from 8 to 11 $\mu\text{g/L}$ and were slightly higher than concentrations during low-flow periods.

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METHODS OF DATA COLLECTION

A reconnaissance of the area was conducted 3 weeks before the start of data collections. Sites were selected to provide a dense spatial resolution that bracketed all visible surface inflows to the mainstem of Miller Creek, including all tributaries and seeps, and bracketed any streamside mine waste. Sampling sites were selected and marked with flagging. Their locations were determined in the field using a global-positioning system. Field locations were verified in the office by plotting each site by latitude and longitude on a topographic map. Forty-nine sites were selected for sampling along the mainstem of Miller Creek. The most upstream site, the tracer-injection point, was located just upstream from the Black Warrior Mine, site 0 on figure 2. Site numbers were assigned on the basis of the distance of each site, in feet, downstream from the tracer-injection point. Site locations and descriptions are presented in table 1 (back of the report). Reference to the left or right bank in the site descriptions and throughout this report refers to the bank of Miller Creek viewed while looking downstream.

In addition to the mainstem and inflow sites sampled along Miller Creek, six sites were sampled upstream from the mouth of East Fork Miller Creek. East Fork sites were labeled with a prefix letter (E) to avoid confusion with mainstem sites (fig. 2). The most upstream site in the East Fork watershed, designated as site E0, was located about 50 ft downstream from a spring that flowed into the East Fork channel. Upstream from the spring the channel was dry. Sampling-site numbers for the East Fork

watershed were designated according to the site's distance, in feet, downstream from site E0. The mouth of the East Fork (site 3,205) was designated in the same manner as other inflows to Miller Creek, thus its site number was not prefixed with an E.

Streamflow Determination

Various techniques were used in the determination of streamflow during this study. Tracer-injection methods using changes in chloride concentrations to indicate flow volume changes described in Kimball (1997), Kimball and others (1999), Cleasby and others (2000), and Nimick and Cleasby (2001) were used for the mainstem sites. Equations used for calculating flow from downstream changes in tracer concentration are presented in Nimick and Cleasby (2001). Streamflow for all surface inflows to the mainstem, including sites in the East Fork watershed, plus selected mainstem sites were physically measured using either traditional current-meter methods (Rantz and others, 1982) or volumetrically using a calibrated collection container and stopwatch.

For the tracer-injection part of this study, an ample supply of tracer-injection solution was prepared by mixing about 96 kg of sodium chloride (NaCl) with about 643 L of streamwater from site 0. The tracer-injection solution was sampled seven times during the study. The mean chloride concentration (89.7 ± 0.95 g/L) was used in the determination of tracer-calculated streamflow. Tracer solution was injected continuously into Miller Creek just upstream from the Black Warrior Mine tributary at a rate of 206 ± 1.5 mL/min for about 47 hours using a positive-displacement pump system controlled and monitored by an electronic data logger. The injection began at 1330 hours on August 28 and ended at 1220 hours on August 30, 2000. Three tracer-monitoring sites (T-1, T-2, and T-3) were sampled prior to the arrival of the tracer solution to determine the natural chloride concentrations (fig. 2). During the tracer-injection study, these three "tracer" sites were sampled approximately hourly to document the concentration and downstream movement of the injected chloride tracer. Samples at tracer-monitoring sites (fig. 2) were either collected manually or with automatic pumping samplers at a single point near midstream where water was well mixed. Samples were filtered through a 0.45- μ m capsule filter.

Sample Collection and Analysis

Synoptic water samples were collected on August 30, 2000, at 49 mainstem and inflow sites along Miller Creek and on August 31, 2000, at 7 sites in the East Fork Miller Creek watershed (fig. 2). One site (3,205) at the mouth of East Fork Miller Creek was sampled twice—once during the mainstem synoptic and once during the East Fork sampling. The samples were analyzed for pH, selected major ions, and dissolved and total-recoverable metals (table 2). Owing to the shallow depths, samples during this study were collected using grab methods. Six sites (5,790; 9,735; 10,280; 14,160; E550; and E700) were very shallow and impossible to sample without introducing some streambed sediment into the sample. This additional sediment would have likely erroneously elevated the total-recoverable metal concentrations. Therefore, samples from these six sites were not analyzed for total-recoverable metal concentrations.

Samples were collected in acid-washed 4-L polyethylene bottles at each site. Water-quality samples were transported to a central processing location near the middle of each study reach as soon after collection as possible. Values of pH were determined on an unfiltered aliquot of each sample. A second unfiltered aliquot was drawn for analysis of total-recoverable metals. A third aliquot was filtered through a 0.45- μ m capsule filter for the analysis of dissolved major cations and metals. The latter two aliquots were acidified with ultra-pure nitric acid to a pH of less than 2. A fourth filtered aliquot was

drawn for the analysis of anions. Sample processing, filtration, and preservation were performed according to procedures described by Ward and Harr (1990), and Horowitz and others (1994).

The USGS National Water Quality Laboratory in Denver, Colo., analyzed water samples collected during this study. All concentrations of dissolved and total-recoverable metals, except for iron, were analyzed using inductively coupled plasma-mass spectrometry. Iron concentration was determined by inductively coupled plasma. Dissolved calcium and sodium concentrations were determined by inductively coupled plasma-atomic absorption spectrometry. Dissolved chloride and sulfate concentrations were determined by ion chromatography. The analytical methods used are described by Fishman and Friedman (1989), Fishman (1993), Garbarino and Taylor (1996), and Garbarino and Struzeski (1998).

Streambed-sediment samples were collected at 16 sites throughout the watershed (fig. 2). The streambed-sediment samples were analyzed for leachable metals (table 3). A composite sample was collected at each of the 16 sites by scooping sediment deposited in pools and in low-velocity areas. Using streamwater, the samples were wet-sieved onsite through a 10-mesh (2-mm) stainless-steel screen and collected into a plastic pan. After a sufficient amount of sediment was collected at each site (about 3 kg), samples were sealed in acid-washed plastic containers.

The USGS laboratory of the Geologic Discipline in Denver, Colo., analyzed streambed-sediment samples collected during this study. In the laboratory, streambed-sediment samples were dried in ovens at about 50°C and sieved to 100-mesh (<150 mm). Samples were partially digested using warm (50°C) 2 molar hydrochloric acid-1 percent hydrogen peroxide solution for 3 hours with continuous agitation. Partial digestion releases the leachable fraction of trace elements associated with hydrous amorphous iron- and manganese-oxide mineral coatings and colloidal particles on the surface of the sediment sample. The leachate from the digestion was analyzed for 35 elements using inductively coupled plasma-atomic emission spectrometry as described by Church and others (1997).

Quality Assurance

Data-collection and analytical procedures used in this study incorporated practices designed to control, verify, and assess the quality of sample data. Methods and associated quality control for collection and field processing of water-quality samples are described by Ward and Harr (1990), and Horowitz and others (1994).

Replicate samples were obtained in the field to provide data on precision (reproducibility) for samples exposed to all sources of variability. Precision of analytical results for field replicates is affected by many sources of variability within the field and laboratory environments, including sample collection, processing, and analysis. Replicates were collected by splitting a single composite sample into two subsamples. Each subsample was then processed and analyzed separately.

The differences between replicates can be used to estimate the precision of analytical results for a constituent by calculating a standard deviation according to the following equations (Taylor, 1987):

$$s = \sqrt{\frac{\sum d^2}{2k}}$$

where

- S = standard deviation of the difference
in concentration between replicate analyses,
- d = difference in concentration between each pair of replicate analyses, and
- k = number of pairs of replicate analyses.

Precision also can be expressed as a relative standard deviation (RSD), in percent, which is computed from the standard deviation and the mean concentration for all the replicate analyses. Expressing precision relative to a mean concentration standardizes comparison of precision among individual constituents. The RSD, in percent, is calculated according to the following equation (Taylor, 1987):

$$RSD = \frac{S}{\bar{x}} \times 100$$

where

- RSD = relative standard deviation,
- S = standard deviation, and
- x = mean of all replicate concentrations.

Three replicate water-quality samples and two replicate streambed-sediment samples were collected. Paired analyses along with the calculated RSD for each constituent are presented in table 4 for water-quality samples and table 5 for streambed-sediment samples (back of the report). RSDs were calculated using values that were rounded to standard reporting levels for the particular constituent and its analytical method. The RSD for constituents analyzed in water samples were all less than 20 percent (table 4). RSDs for total-recoverable metals were consistently greater than for dissolved metals. This difference was possibly caused by splitting of suspended sediment in the whole-water composite sample into two subsamples. Variability in the distribution of sediment among the subsamples could have resulted in unequal quantities of particulate-bound metal. The RSD for constituents analyzed in the streambed-sediment replicates were 12 percent or less, except for copper, which was 22 percent (table 5).

Two field-blank samples of deionized water certified to be free of detectable concentrations of trace elements were processed during this study. Blanks were processed through the same sampling equipment used in the collection of stream samples. Blank samples were subjected to the same processing (sample splitting, filtration, preservation, transportation, and laboratory handling) as stream samples. Each blank was analyzed for the same constituents as those of stream samples. All constituent concentrations in the blanks samples were less than the minimum reporting level for the analytical methods used during this study (table 4), indicating that the collection, field processing, and laboratory analyses were free of significant contamination that could bias results.

STREAMFLOW

Streamflow is an important component to determine for surface-water-quality studies because it gives insight to hydrologic processes that influence geochemical reactions and is necessary to accurately quantify the transport of constituent loads through the watershed. Tracer-injection methods, which use the principle of conservation of mass to calculate streamflow at synoptic sampling sites, represent an alternative to traditional current-meter methods for determining streamflow in mountain streams, particularly where traditional methods are hampered by irregular channel cross sections and turbulent

flow (Kimball, 1997). Tracer-injection methods also account for the portion of flow that moves through the gravels and cobbles (hyporheic flow). This hyporheic flow cannot be measured by current-meter methods; therefore, loads would be underestimated using streamflow values obtained by current-meter measuring techniques if hyporheic flow were a substantial portion of the total streamflow. Another advantage of the tracer-injection method is that synoptic samples for determination of streamflow can be collected at numerous sites more quickly than streamflow can be measured with a current-meter. Thus, streamflow can be characterized at many sites in a stream reach in less time using the tracer-injection method, thereby minimizing the potential effect of temporal changes in streamflow that could complicate comparisons of concentrations or loads between sites.

Chloride is a commonly used constituent for tracer studies because it is chemically conservative, inexpensive, and relatively benign to aquatic biota. Information on the movement of the chloride tracer was gained by constructing temporal concentration profiles that show the change in chloride concentration with time at each tracer-monitoring site (fig. 4). Ideal temporal concentration profiles of an injected tracer have three distinct regions that show the arrival, plateau (or equilibrium) conditions, and departure of the tracer. If equilibrium has been established, then a steady-state plateau will be evident at each tracer-monitoring site. When the stream is at equilibrium with the injected tracer, synoptic samples are collected at many points along the stream resulting from inflows. If equilibrium has been achieved, downstream changes in chloride concentration will be due to changes in streamflow.

The first tracer-monitoring site (T-1) was at site 190 (fig. 2), just downstream from the tracer injection. Chloride concentrations rapidly increased at T-1 as the injected tracer arrived and most likely established equilibrium with streamflow shortly after the injection began. The chloride concentrations at T-1 increased during the day (0900 to 1700 hours) as streamflow decreased, presumably due to evapotranspiration along the valley floor. Chloride concentrations then decreased through the evening to the following morning (1700 to 0800). After 0800 on August 30, chloride concentrations were generally stable for several hours, which corresponded to the period of synoptic sampling in the upper reach.

The second tracer-monitoring site (T-2) was located at site 7,120 (or historical site SW-2, fig. 2) near the middle of the study reach. Arrival of the tracer at T-2 was not evident until about 10 hours after the tracer was started (fig. 4). After the tracer reached T-2 on August 29, chloride concentrations increased for about 16 hours from 0000 to 1600 hours. Around 1600 hours the tracer concentrations at T-2 started to decrease slightly. This decrease coincided with the decrease at T-1 and was likely caused by an increase in streamflow associated with a diel cycle. Tracer concentrations at T-2 did not decrease as sharply as at T-1, likely because the tracer had not reached plateau conditions and concentrations were still increasing from the injection. From about 0100 to 0800 on August 30, tracer concentrations again increased at T-2, indicating that the tracer concentration at T-2 had not reached equilibrium. At around 0800 hours on August 30, a plateau apparently was established at T-2, and tracer concentrations were relatively stable during the entire synoptic sampling period, from 0835 to 1400 hours. Shortly after the synoptic sampling was completed, the tracer concentrations at T-2 significantly increased at about 1800 hours. This increase may possibly be due to a decrease in streamflow during the warm part of the day, but the magnitude of the increase may also be anomalously large.

The third tracer-monitoring site (T-3) at site 14,930 was at the downstream end of the study reach (fig. 2). Arrival of the tracer at T-3 was not evident until about 22 hours after the tracer was started (fig. 4). After the 22-hour time lag, tracer concentrations at T-3 steadily increased for the remainder of the study, indicating that equilibrium at T-3 was not reached during the synoptic-sampling period. Since equilibrium was not established at T-3, streamflow could not be calculated using tracer-injection methods between T-2 and T-3. However, streamflow on the mainstem was physically measured at T-2 and at two

sites downstream from T-2 (table 2, fig. 5). In addition, inflows throughout the study reach were measured using either traditional current-meter methods or volumetrically. Streamflow values calculated by the tracer-injection method from site 0 to 7,120 (T-2) are shown in figure 5 and presented in table 2. Surface inflows to Miller Creek were assumed to be equal to the difference in tracer-calculated streamflow between the mainstem sites immediately downstream and upstream from the inflow.

Where both methods were used, tracer-calculated flows were greater than the physically measured flows at each surface-inflow site, except for site 4,680. The differences between these values may represent the amount of subsurface (hyporheic) flow that is moving through the streambed substrate and, therefore, is not measurable by traditional current-meter methods. However, some differences, particularly the large differences at sites 3,205 and 3,915, may represent the uncertainty of streamflow calculated by the tracer-injection method in the reach between tracer-monitoring sites T-1 and T-2.

In the lower part of the study reach, current-meter measurements were conducted at two stream sites during the tracer injection (fig. 5). Because streamflow was determined using both methods at site 7,120, the relative difference in results can serve as an estimate of hyporheic flow at the lower two sites. Comparing the two values at site 7,120 indicates that about 20 percent of the total streamflow may be hyporheic flow. This difference is comparable in magnitude to values reported in similar studies (Kimball, 1997; Kimball and others, 1999; and Cleasby and others, 2000). By comparing the results for this and other tracer-injection studies, the total streamflow (surface plus hyporheic) at mainstem sites 13,165 and 14,930 (also measured using current meters) was likely in the range of 20 percent greater than the current-meter measurement values shown on figure 5.

Streamflow values in the East Fork watershed were measured by current meter or volumetrically (table 2). Water from a spring entered the East Fork about 1,100 upstream from its confluence with Miller Creek (site E0, table 1). Upstream from the spring the channel was dry. An increase in streamflow of about 2.8 L/s was measured from site E0 (immediately below the spring) to the mouth of East Fork Miller Creek, site 3,205.

METAL CONCENTRATIONS

Analytical results for surface-water and streambed-sediment samples were examined to characterize the magnitude and spatial pattern of metal concentrations in the Miller Creek watershed. The data can indicate locations where concentrations exceed environmental standards or guidelines, and can be utilized to identify potential sources of metals.

Water

Water-quality data collected during this study indicate that metal concentrations (except for iron) were mostly low, with many values below the analytical minimum reporting levels (table 2). Values for pH were all nearly neutral to slightly basic (range from 7.1 to 8.5). These results indicate the water in the Miller Creek watershed is mostly unaffected by mining disturbances or natural weathering of the mineralized rocks common elsewhere in the mining district.

Profiles of copper, lead, and zinc concentrations in the mainstem sites are shown on figure 6. To evaluate the potential biological exposure risks from these metals, the State of Montana aquatic-life criteria for chronic and acute toxicity (Montana Department of Environmental Quality, 1999) also are

shown on this figure. Based on historical samples collected at SW-2 and SW-5 (URS Operating Services, Inc., 1998), a hardness of 100 mg/L CaCO₃ was used to calculate these hardness-dependent criteria. Except for the total-recoverable lead concentration in Miller Creek (site 190) just downstream from the Black Warrior Mine inflow, all mainstem concentrations of copper, lead, and zinc in Miller Creek were less than the chronic aquatic-life criteria. Water at site 190 had the highest mainstem concentration of total-recoverable lead (5 µg/L) and zinc (26 µg/L). These slightly elevated lead and zinc values, relative to site 0, presumably result from the Black Warrior Mine inflow (site 25), which had the highest total-recoverable lead (15 µg/L) and zinc (140 µg/L) values measured during this study.

In the upper part of Miller Creek (upstream from site 6,450), total-recoverable copper concentrations ranged from 1 to 3 mg/L. Three left-bank inflows (sites 5,945, 6,465, and 6,750) near site 6,450 had elevated copper concentrations (29 to 63 mg/L) that slightly increased concentrations in Miller Creek. From site 6,450 to the downstream end of the study reach, total-recoverable copper concentrations in Miller Creek ranged from 3 to 6 mg/L. These slightly elevated copper concentrations in the mainstem were less than the chronic aquatic-life criterion of 9.3 mg/L.

Similarly, metal concentrations in East Fork Miller Creek were mostly less than the minimum reporting level (table 2). At the six sites sampled upstream from the mouth of the East Fork (site 3,205), all copper, lead, and zinc concentrations were equal to or less than 1 µg/L, except for one dissolved copper value of 5 µg/L at site E700 and one total-recoverable zinc value of 2 µg/L at site E280. Both of these values were from surface inflows to East Fork.

Streambed Sediment

Streambed sediment can be used to identify metal sources on the basis of downstream patterns in concentration and locations of abrupt increases. Particulate-bound metals commonly occur where enriched hydrous amorphous iron- and manganese-oxide mineral coatings and colloidal particles have been deposited on the streambed. Although streambed-sediment samples were analyzed for a full suite of metals (table 3), this discussion focuses on four metals (cadmium, copper, lead, and zinc) that are commonly found to have elevated concentration in some surface water and streambed sediment in the mining district. Concentrations of these metals in streambed sediments typically are several orders of magnitude greater than in stream water. When these sediments are flushed from the streambed during high flow, they can contribute to the total-recoverable concentration. When these metals are weakly bound to sediments, they can become a source of waterborne-metal contamination that can be detrimental to aquatic biota. The partial-digestion method used to analyze sediment samples for this study extracts the weakly bound (leachable) metals from the sediment and provides an estimate of metal concentrations that could be solubilized under reducing conditions or if ingested and thus potentially affect aquatic organisms.

Leachable-cadmium concentrations in streambed sediment samples generally were 3 ppm or less (table 3). One notable exception (17 ppm) occurred at the Black Warrior Mine inflow (site 25), which was over 5 times higher than the cadmium concentration at site 0. In addition, copper, lead, and zinc concentrations were substantially higher at site 25 than site 0.

Leachable-concentration profiles of copper, lead, and zinc determined from streambed-sediment samples are shown in figure 7. Lead and zinc profiles were similar, with the greatest mainstem concentrations just downstream from the Black Warrior Mine inflow (site 190). Leachable-metal concentrations in the streambed-sediment sample collected directly from the Black Warrior Mine inflow

(site 25) were more than 5 times greater for cadmium, 20 times greater for lead, and 11 times greater for zinc than in the streambed-sediment samples collected upstream at site 0. Although leachable-metal concentrations were elevated at site 25, lead and zinc concentrations at site 190, just downstream from the Black Warrior Mine inflow, were only slightly higher than at site 0 (fig. 7). Downstream from site 190, both leachable lead and zinc concentrations in the streambed sediment decreased to concentrations less than site 0. The streambed-sediment sample collected at site 3,205 (East Fork Miller Creek) had about the same leachable lead concentration as nearby mainstem site 3,225 and slightly lower zinc concentration. Leachable lead and zinc concentrations showed little change from site 1,170 to site 2,225 where Miller Creek dumps 1 and 2 are located (figs. 2 and 7).

The leachable-concentration profile for copper was substantially different from that for lead and zinc (fig. 7). Leachable-copper concentrations in streambed sediment steadily increased from site 190 to site 7,120 (SW-2). Leachable-copper concentrations peaked at site 7,120 (about 500 ppm) and remained elevated at a similar concentration throughout the rest of the study reach. This increase in leachable-copper concentration occurred in the reach downgradient from an area in the vicinity and northwest of adit M-25 (fig. 2), where anomalies of as much as 400 ppm of copper in soils overlying intrusive rocks of Henderson Mountain Stock were identified (Allan R. Kirk, Maxim Technologies, Inc., written commun., 2001). The sample collected at the Black Warrior Mine inflow (site 25) had moderately elevated leachable copper concentration (330 ppm), but no apparent effect on the mainstem site immediately downstream. The East Fork Miller Creek (site 3,205) had a similarly elevated leachable-copper concentration (320 ppm) in streambed sediment but this value was only slightly higher than the concentrations at adjacent mainstem sites.

At the neutral pH of Miller Creek, the metals that are associated with the iron- and manganese-oxide coatings on the sediments do not tend to dissolve; however, when ingested by an aquatic organism and subject to the acidic digestive tract, the weakly bound metals associated with these coatings can be liberated and become incorporated into the tissue of the organism. Bioaccumulation of metal, over time, can detrimentally affect the biota in a stream system, either directly or through the food chain. Currently (2001), the State of Montana has no guidelines to assess the potential toxicity to aquatic biota from the leachable-metal concentrations in streambed sediment. Therefore, leachable concentrations measured during this study were compared to two guidelines established by the Canadian Council of Ministers of the Environment (1998) for the protection of aquatic life. The lower guideline is the interim sediment quality guideline (ISQG). Leachable concentrations less than the ISQG are not expected to have adverse effects on the aquatic biota. Leachable concentrations exceeding the upper guideline, the probable effect level (PEL), are expected to adversely affect aquatic biota. Values between the two levels are associated with occasional adverse effects to aquatic biota. These guidelines typically are used as references for concentrations of elements in bulk sediment, whereas the results from this study are associated with the sieved fraction finer than 2 mm. Higher metal concentrations typically are associated with the smaller size fraction analyzed in this study, and comparison to bulk sediment guidelines is intended only to provide a general reference to the exposure risk from the streambed sediment in Miller Creek.

Both ISQG and PEL guidelines are shown on figure 7 for copper, lead, and zinc. Upstream from East Fork Miller Creek (site 3,205), leachable-copper concentrations in the streambed sediment at all sites were between the ISQG (35.7 ppm) and PEL (197 ppm) guidelines. Downstream from East Fork Miller Creek, all leachable-copper concentrations exceeded the PEL. Leachable concentrations of lead in all streambed-sediment samples collected during this study exceeded the ISQG (35.0 ppm) and the PEL (91.3 ppm). Upstream from East Fork Miller Creek (site 3,205), leachable concentrations of zinc in streambed sediment either exceeded or were near the PEL (315 ppm). Downstream from East Fork,

leachable-zinc concentrations were between the ISQG (123 ppm) and the PEL. Leachable-cadmium concentrations in Miller Creek (table 3) ranged from 2 to 3 ppm, which were between the ISQG (0.6 ppm) and the PEL (3.5 ppm) guidelines. Based on these comparisons to the available bulk sediment guidelines, risks to aquatic biota might be associated with exposure to the streambed sediment of Miller Creek. These risks are basin-wide and appear to be influenced more by the local geology than a specific source.

METAL SOURCES

Metal loads in a mineralized area can enter a stream from various natural and mining-related sources that could include surface waters flowing through mines or mine wastes, natural acid rock drainage from altered pyritic outcrops, or other metal-rich surface or ground-water inflow (fig. 8). Sources of metal entering a stream commonly are identified by the incremental downstream changes in metal load determined by synoptic sampling and streambed quantification at multiple locations. Instantaneous loads used in synoptic-load studies are calculated as the product of the metal concentration and streamflow at the time of sampling. For typical loading studies, load profiles can illustrate how the magnitude of loads varies, and thereby, indicate the specific reach or inflow where metal loads substantially increase or decrease. However, for this study, metal-load profiles were not developed because the metal concentrations in Miller Creek generally were uniform and near the analytical minimum reporting level, and the chloride tracer used to determine streamflow did not come to full equilibrium in the lower reaches of the stream. Given the low concentrations throughout the study reach, loads entering Miller Creek can generally be assumed to be small.

The few sources contributing metal load to Miller Creek can be directly inferred from concentration profiles (fig. 6). The metal concentration data indicate that inflow from the Black Warrior Mine causes minor increases of lead and zinc concentrations for a limited distance along the mainstem. Several mid-basin inflows (sites 5,945, 6,465, and 6,750) having moderately elevated copper concentrations also cause minor increases of copper concentrations in the mainstem. Substantial concentration increases in Miller Creek were not observed in the upper reach where faults traverse the watershed, near ferricrete deposits, or near the Miller Creek dumps 1 and 2.

Although complete load profiles were not constructed, selected inflow loads were calculated to indicate the magnitude of load input relative to the mainstem load at the inflow site. Three left-bank surface inflows (sites 5,945, 6,465, and 6,750) upstream from site 7,120 (SW-2) were likely the only substantial sources of copper to Miller Creek (fig. 6). The combined total-recoverable copper load from the three inflows was about 123 $\mu\text{g/s}$. The total-recoverable copper load in Miller Creek at site 7,120 was about 128 $\mu\text{g/s}$. Thus, these three inflows collectively accounted for about 96 percent of the mainstem load at site 7,120. This instantaneous rate of transport is equivalent to about 0.02 pound of copper discharged per day by Miller Creek. This load is relatively minor with respect to the mainstem water volume, as can be seen by the minor effect on mainstem copper concentrations (fig. 6; increase in mainstem from 1 to 5 $\mu\text{g/L}$). The total-recoverable copper load in Miller Creek is negligible when compared with the maximum total-recoverable loads of other streams in the district. For example, copper loads determined during metal loading studies were about 70,000 $\mu\text{g/s}$ in Fisher Creek (Kimball and others, 1999) and about 48,800 $\mu\text{g/s}$ in Daisy Creek (Nimick and Cleasby, 2001).

The three surface inflows (sites 5,945, 6,465, and 6,750) where copper concentrations were moderately elevated had calcium concentrations ranging from 4.8 to 6.2 mg/L. These calcium

concentrations were substantially lower than in the majority of the other samples collected in the Miller Creek watershed. Concentrations in other samples typically were higher than 30 mg/L (table 2). The lower calcium concentrations probably indicate that the three inflows flow through different geologic units or originate from a different source than the rest of the water draining to Miller Creek. These inflows may represent diffuse drainage from an area where anomalous copper concentrations were identified in soil samples. This area is in the vicinity of and to the northwest of adit M-25 (fig. 2). Adit M-25 on Henderson Mountain (fig. 2), developed in the Henderson Mountain rhyodacite porphyry upgradient from the inflows, is another possible source of the elevated copper concentrations detected in these inflows. One sample collected at site M-25 in August 1990 had a similar calcium concentration (4 mg/L) as the three inflows. Water from the adit at site M-25 also had an elevated copper concentration (560 µg/L; URS Operating Service Inc., 1998). The load from the adit at the time the sample was collected was about 210 µg/s.

Elevated concentrations of total-recoverable lead in the Black Warrior Mine inflow (site 25; 15 µg/L) and a right bank seep downstream from the Miller Creek dumps 1 and 2 (site 2,645; 6 µg/L) were the only notable sources of lead identified during this study. The combined loading from both sources was about 2 µg/s. Total-recoverable lead concentrations in Miller Creek were above the minimum reporting level at only three sites, with the highest mainstem concentration (5 µg/L) occurring at site 190 just downstream from the Black Warrior Mine inflow. The lead load at site 190 was only about 3.4 µg/s, or 0.0006 pound of lead per day.

The Black Warrior Mine inflow (site 25), a right-bank inflow (site 2,645), and the same three left-bank inflows that had elevated copper concentrations (sites 5,945, 6,465, and 6,750), contributed small loads of dissolved and total-recoverable zinc (combined load of about 40 µg/s) to Miller Creek (fig. 6). The small load from the Black Warrior Mine inflow slightly increased zinc concentrations in Miller Creek (from 8 to 26 µg/L) only because streamflow in Miller Creek downstream from the Black Warrior Mine inflow was not large enough to dilute zinc from this source. Total-recoverable zinc loads that entered Miller Creek downstream from this site were not large enough to substantially change zinc concentrations in Miller Creek. Downstream from East Fork Miller Creek (site 3,205), dissolved and total-recoverable zinc values in Miller Creek did not exceed 3 µg/L, indicating that no significant sources of zinc from this area were affecting concentrations in Miller Creek during this study. The three left-bank inflows (which contributed about 28 µg/s of zinc) had little effect on zinc concentrations in the creek because the streamflow in Miller Creek near these inflows was large enough to dilute the small zinc loads.

From the concentration profiles and selected inflow loads, it appears metal loading to Miller Creek during this low-flow study was sufficiently small to not cause any sharp increases in mainstem metal concentrations. In addition, substantial differences between mining-affected areas and areas influenced by the local geology could not be readily determined.

SUMMARY

Miller Creek is a tributary of Soda Butte Creek east of Cooke City in south-central Montana near the northeast corner of Yellowstone National Park. Mining for gold, copper, and silver began in the late 1800s and continued through the early 1900s, resulting in prospects and mining wastes that are sporadically distributed throughout the watershed. Metal-loading studies have been a useful tool in characterizing water quality in historical mining areas. Thus, a study was conducted during August 28-31, 2000 to characterize metal concentrations and identify possible sources contributing metal to Miller

Creek during low flow. Water-quality samples were collected at 55 sites throughout the watershed and streambed-sediment samples were collected at 16 sites. The study reach was about 15,000 ft in length, which comprised almost the entire length of Miller Creek.

Water-quality data collected during this study indicate that the water in Miller Creek is not substantially affected by mining disturbances or the weathering of naturally occurring mineralized rocks. Values for pH were near neutral to slightly basic in all samples and metal concentrations were mostly low, with many concentrations below the analytical minimum reporting level. In Miller Creek, total-recoverable concentrations of copper, lead, and zinc were less than the State of Montana chronic aquatic-life criteria in all samples, with the exception of one lead value that exceeded this criteria. This site, just downstream from the Black Warrior Mine inflow, also had the highest zinc concentration measured in Miller Creek. These slightly elevated concentrations in the mainstem originated from the Black Warrior Mine inflow, which had the highest total-recoverable lead (15 µg/L) and zinc (140 µg/L) values measured during this study.

In the upper part of Miller Creek, total-recoverable copper concentrations ranged from <1 to 3 µg/L. Three left-bank inflows had elevated total-recoverable copper concentrations (29 to 63 µg/L) that slightly increased concentrations in Miller Creek. From site 6,450 to the downstream end of the study reach, total-recoverable copper concentrations in Miller Creek ranged from 3 to 6 µg/L, which were less than the chronic aquatic-life criterion of 9.3 µg/L.

Similarly, metal concentrations in East Fork Miller Creek were typically less than the analytical minimum reporting level. At the seven sites sampled in the East Fork drainage, all copper, lead, and zinc concentrations were equal to or less than 1 µg/L, except for one dissolved copper value of 5 µg/L and one total-recoverable zinc value of 2 µg/L. Both of these values were from surface inflows to East Fork.

Leachable lead and zinc concentrations (4,500 and 4,200 ppm, respectively) in the streambed-sediment sample collected from the Black Warrior Mine inflow were the highest measured during this study and were about 20 times greater for lead and 11 times greater for zinc than the streambed-sediment samples collected in Miller Creek immediately upstream from this inflow. Although leachable metal concentrations were elevated in the streambed sediment at the Black Warrior Mine inflow, lead and zinc concentrations at the mainstem site just downstream from this inflow were only slightly elevated compared to the concentrations in the mainstem upstream from this inflow. The streambed-sediment sample collected at the mouth of East Fork Miller Creek had about the same leachable lead concentration and slightly lower zinc concentration compared to adjacent mainstem sites.

Leachable-copper concentrations in streambed-sediment samples from the mainstem peaked near mid-basin at site 7,120 and remained elevated at similar concentrations throughout the rest of the study reach. The sample collected at the mouth of the Black Warrior Mine inflow had moderately elevated leachable copper concentration (330 ppm), but no apparent effect on copper concentration in the mainstem immediately below. East Fork Miller Creek had leachable-copper concentrations in the streambed sediment (320 ppm) similar to the Black Warrior Mine inflow, but this value was only slightly higher than the concentrations at adjacent mainstem sites.

Compared to guidelines established by the Canadian Council of Ministers of the Environment, risks to aquatic biota associated with the leachable-metal concentrations found in the streambed sediments appear to be basin-wide rather than related to a particular source. Exceedances of the lower interim sediment quality guidelines for copper and zinc were observed in every sample collected during this study, with several values above the upper guideline, the probable effect level. Leachable-lead

concentrations in all streambed-sediments samples exceeded the upper probable effect level. According to the guidelines, values exceeding the upper guidelines are expected to adversely affect the aquatic biota and values between the lower and upper guidelines are associated with occasional adverse effects. The guidelines typically are used as references for concentrations of elements in bulk sediment, whereas the results from this study are associated with the sieved fraction finer than 2mm. Higher metal concentrations typically are associated with the smaller size fraction and comparison to bulk sediment guidelines is intended only to provide a general reference to the exposure risk from the streambed sediment in Miller Creek.

Substantial load increases in Miller Creek were not observed near faults that traverse the watershed, near ferricrete deposits, or near the Miller Creek dumps 1 and 2. The small loads entering Miller Creek during this study were delivered primarily from the Black Warrior Mine inflow, a right-bank inflow just downstream from Miller Creek dumps 1 and 2, and three left-bank inflows near mid-basin. The three left-bank surface inflows near mid-basin were the only substantial sources of copper loading to Miller Creek. The combined total-recoverable copper load from the three inflows was about 123 $\mu\text{g/s}$, which accounted for about 96 percent of the total-recoverable copper load (128 $\mu\text{g/s}$) in Miller Creek at site 7,120. The Black Warrior Mine inflow, a right-bank inflow, and the same three left-bank inflows that had elevated copper concentrations, contributed small loads of dissolved and total-recoverable zinc to Miller Creek. The Black Warrior Mine inflow and a right-bank seep downstream from Miller Creek dumps 1 and 2 were the only sources of lead identified during this study. The combined loading from both sources was small, being just over 2 $\mu\text{g/s}$. Total-recoverable lead concentrations in Miller Creek were above the minimum detection level at only three mainstem sites, with the highest mainstem concentration (5 $\mu\text{g/L}$) occurring at site 190 just downstream from the Black Warrior Mine inflow.

Metal loading to Miller Creek during this low-flow study was relatively small and had minor effect on metal concentrations in the mainstem. Substantial differences between mining-related areas and areas influenced by local geology could not be readily determined.

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