

Quantification of Metal Loads by Tracer Injection and Synoptic Sampling in Daisy Creek and the Stillwater River, Park County, Montana, August 1999

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Abstract

A metal-loading study using tracer-injection and synoptic-sampling methods was conducted in Daisy Creek and a short reach of the Stillwater River during baseflow in August 1999 to quantify the metal inputs from acid rock drainage in the New World Mining District near Yellowstone National Park and to examine the downstream transport of these metals into the Stillwater River. Loads were calculated for many mainstem and inflow sites by combining streamflow determined using the tracer-injection method with concentrations of major ions and metals that were determined in synoptic water-quality samples.

Water quality and aquatic habitat in Daisy Creek have been affected adversely by drainage derived from waste rock and adit discharge at the McLaren Mine as well as from natural weathering of pyrite-rich mineralized rock that comprises and surrounds the ore zones. However, the specific sources and transport pathways are not well understood. Knowledge of the main sources and transport pathways of metals and acid can aid resource managers in planning and conducting effective and cost-efficient remediation activities.

The metals cadmium, copper, lead, and zinc occur at concentrations that are sufficiently elevated to be potentially lethal to aquatic life in Daisy Creek and to pose a toxicity risk in part of the Stillwater River. Copper is of most concern in Daisy Creek because it occurs at higher concentrations than the other metals. Acidic surface inflows had dissolved concentrations as high as 20.6 micrograms per liter ($\mu\text{g/L}$) cadmium, 26,900 $\mu\text{g/L}$ copper, 76.4 $\mu\text{g/L}$ lead, and 3,000 $\mu\text{g/L}$ zinc. These inflows resulted in maximum dissolved concentrations in Daisy Creek of 5.8 $\mu\text{g/L}$ cadmium, 5,790 $\mu\text{g/L}$ copper, 3.8 $\mu\text{g/L}$ lead, and 848 $\mu\text{g/L}$ zinc.

Significant copper loading to Daisy Creek occurred only in the upper half of the stream. Sources included subsurface inflow and right-bank (mined side) surface inflows. Copper loads in left-bank (unmined side) surface inflows were negligible. Most (71 percent) of the total copper loading in the study reach occurred along a 341-foot reach near the stream's headwaters. About 53 percent of the total copper load was contributed by five surface inflows that drain a manganese bog and the southern part of the McLaren Mine. Copper loading from subsurface inflow was substantial, contributing 46 percent of the total dissolved copper load to Daisy Creek. More than half of this subsurface copper loading occurred downstream from the reaches that

received significant surface loading.

Flow through the shallow subsurface appears to be the main copper-transport pathway from the McLaren Mine and surrounding altered and mineralized bedrock to Daisy Creek during base-flow conditions. Little is known about the source of acid and copper in this subsurface flow. However, possible sources include the mineralized rocks of Fisher Mountain upgradient of the McLaren Mine area, the surficial waste rock at the mine, and the underlying pyritic bedrock.

INTRODUCTION

Daisy Creek is a headwater tributary of the Stillwater River near Cooke City in south-central Montana (fig. 1) near the northeast corner of Yellowstone National Park. Water quality and aquatic habitat in Daisy Creek have been affected by acid rock drainage from the New World Mining District (Gurrieri, 1998), where mining started in 1869. The metals and acid in Daisy Creek are derived from waste rock and adit discharge at the McLaren Mine as well as from natural weathering of pyrite-rich mineralized rock that forms and surrounds the ore zones in the district.

Although the metals and acid in Daisy Creek are derived generally from the McLaren Mine area, the specific source areas and transport pathways are not well understood. In addition, the relative contributions of acid rock drainage from disturbed rock in mined areas and from mineralized rock that was not mined have not been quantified. Similarly, the relative importance of surface runoff and ground water (either shallow subsurface flow or deeper flow) as pathways for transporting metals to Daisy Creek is not well understood. Remediation activities are being planned for the McLaren Mine area by the U.S. Department of Agriculture-Forest Service (USDA-Forest Service) (Maxim Technologies, Inc., 1999) to improve water quality in Daisy Creek and the Stillwater River. Knowledge of the main sources and transport pathways of metals and acid can aid resource managers in planning and conducting effective and cost-efficient remediation activities.

Metal-loading studies have been useful in characterizing water quality in historical mining areas and identifying metal sources and pathways (Kimball, 1997; Kimball, Runkel, and others, 1999). In these studies, detailed profiles of metal loads along a stream are developed from streamflow data (obtained by tracer injection) and metal-concentration data (obtained by synoptic water-quality sampling) collected at many closely spaced sites. Downstream changes in metal loads in the stream then can be attributed to sources along the stream as well as to instream geochemical reactions. These sources can include visible surface inflows, such as discharge from mine adits or drainage from waste-rock and tailing piles, and ground water that enters the stream as subsurface inflow. Similarly, the relative contribution of metals from natural rock weathering in unmined areas can be investigated. Examples of this type of study are reported by Kimball and others (1994, 1998) for streams affected by acid rock drainage in Colorado and by Kimball, Nimick, and others (1999) for Fisher Creek (fig. 1), another stream draining the New World Mining District. The methods described in these reports were used during this study to quantify metal loads in Daisy Creek and a short reach of the Stillwater River.

Purpose and Scope

The purpose of this report is to quantify and identify the principal sources of metal loads to Daisy Creek and to examine the downstream transport of metals into the Stillwater River during August 24-27, 1999. Physical and chemical data were collected at 25 mainstem and 29 inflow sites. The study reach included almost the entire length of Daisy Creek and an 850-ft reach of the Stillwater River downstream from the confluence of Daisy Creek (fig. 2). The total length of the study reach was 12,410 ft. This study was conducted in cooperation with the USDA-Forest Service.

Metal loads in the mainstem were quantified from streamflow data determined by tracer injection and water-quality data obtained from analysis of synoptic samples. Loads contributed by surface inflows were determined from these data as well as from supplemental streamflow measurements made by conventional methods. Downstream profiles of metal loads provided the information needed to identify the principal sources of metals to Daisy Creek and the Stillwater River.

Description of Study Area

The headwaters of Daisy Creek originate in the Custer National Forest and the New World Mining District in south-central Montana at an altitude of about 9,400 ft. Daisy Creek is about 2.2 mi long and flows northwest into the Stillwater River at an altitude of 8,500 ft about 1 mi downstream from the river's headwaters. Daisy Creek can be divided into three reaches on the basis of topography and hydrology. The upstream reach, from 0 to 1,340 ft, (cover photograph) is in the bottom of a glacial cirque. The stream valley is relatively flat, and considerable ground water discharges to Daisy Creek. The streambed is composed of sand and small cobbles. In many places, the streambed is cemented with iron oxyhydroxide, forming ferricrete. One unusual feature in this reach is a manganese bog, formed where acidic ground water discharges, on the north side of Daisy Creek (fig. 2). Vegetation in this bog is coated with black manganese precipitates. The middle reach, from 1,340 to 9,925 ft, (fig. 3) is steeper than the upper and lower reaches and is incised in a narrow ravine within the broader valley. The streambed within this cascading reach is composed mostly of bedrock and large boulders. The downstream reach, from 9,925 to 11,549 ft, (fig. 4) has a lower gradient than the middle reach. The channel has a typical pool-and-riffle sequence, and the streambed is composed of cobbles. The Stillwater River downstream from Daisy Creek is similar in character to the lower reach of Daisy Creek, except that the channel is larger owing to the greater streamflow.

Water quality and biota in Daisy Creek have been affected adversely by acid rock drainage (Gurreri, 1998). Metal concentrations, which have been measured since the mid-1970s in Daisy Creek downstream from the McLaren Mine, ranged from 930 to 7,360 $\mu\text{g/L}$ dissolved copper and 130 to 1,200 $\mu\text{g/L}$ dissolved zinc in 1989-96; pH values ranged from 3.1 to 5.0 (URS Operating Services, Inc., 1998). Metals transported from Daisy Creek affect the Stillwater River for several miles downstream. In this reach of the Stillwater River, concentrations of total-recoverable copper are near the chronic aquatic-life standard established by the U.S. Environmental Protection Agency (U.S. Environmental Protection Agency, 1999), and copper concentrations in bed sediment are elevated at least 10-fold over background values for streams in nearby unmineralized basins (Gurreri, 1998). Fish and other

aquatic life typical of most mountain streams are absent from Daisy Creek owing to the acidic and metal-rich nature of the stream. In the Stillwater River downstream from Daisy Creek, biointegrity decreases sharply from levels in the river upstream of Daisy Creek; macroinvertebrate and periphyton communities are impoverished and dominated by metal-tolerant species (Gurrieri, 1998).

The New World Mining District is underlain by lower Paleozoic sedimentary rocks that were subjected to Tertiary igneous activity, alteration, and mineralization. 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 brecciation and intrusion of stocks, laccoliths, sills, and dikes. Alteration and mineralization in the mining district were associated with this intrusive activity. The economic deposits contain gold, copper, and silver and are either skarn and replacement deposits hosted mainly by the Meagher Limestone, replacement and vein deposits along high-angle faults, or replacement deposits in limestone blocks within intrusion breccias. The ore bodies and surrounding altered rock are rich in sulfide minerals, including pyrite and chalcopyrite (Elliot, 1979; Elliot and others, 1992).

Erosion by the glacial ice cap that covered the Beartooth Plateau during the late Pleistocene exposed unweathered pyritic rocks in the New World Mining District. Oxidation of these pyritic rocks released acid and metals to surface and ground water. Ferricrete deposits in the three stream valleys draining the mining district document the existence of this natural acid rock drainage. Radiocarbon age dates for wood embedded in five ferricrete samples collected from the Daisy Creek drainage were more than 300 years old, pre-dating mining; four of five samples were more than 6,400 years old (Furniss and others, 1999).

Mining for gold, copper, and silver began in 1869 in the New World Mining District (Elliot and others, 1992). The principal mining-related feature in the Daisy Creek drainage is the McLaren Mine on the southern flank of Fisher Mountain (fig. 2). Several prospects are located in the drainage on the north side of Crown Butte. The McLaren Mine is an open-pit mine that was active from 1933 to 1953 (Elliot and others, 1992). The McLaren deposit was the most extensively mined ore body in the district. Several short adits were driven into Fisher Mountain, but most were later exhumed by the open pit mine. Only the upper portion of the McLaren deposit was mined. In 1987, Crown Butte Mines, Inc., began exploratory drilling and estimated that over two million tons of sulfide-rich ore remained in the McLaren deposit. In 1993, after deciding not to proceed with mining, the company began surface-restoration work to reclaim the historical open pit. The pit was recontoured to approximate pre-mining topography, and diversion ditches were constructed to prevent ponding of water and to reduce the amount of water that infiltrated through the pit and associated waste rock. Revegetation efforts in 1994 included liming, seeding, and fertilization (URS Operating Services, Inc., 1998).

Drainage from the McLaren Mine area flows to Daisy Creek through surface and subsurface (ground-water) pathways. Many small intermittent streams convey surface runoff from the mine area to Daisy Creek. In late summer, most of these streams are dry except near their confluence with Daisy Creek. The lower reaches of these streams are perennial, with surface flow derived

from ground-water discharge. Whether the surficial layer of glacial deposits or the underlying bedrock is the primary conduit for this subsurface flow is not known. In either circumstance, drainage from the McLaren Mine area is acidic and metal rich. Potential sources of the metals and acidity include the mineralized rocks of Fisher Mountain upgradient of the McLaren Mine area, the surficial waste rock at the mine, or the underlying bedrock, which hosts both the McLaren deposit and surrounding altered rock that is pyritic.

Average annual precipitation in the study area is about 60 in. The mean annual snowpack is between 300 and 500 in., with the thickest snowpack occurring in May. Peak streamflow occurs during snowmelt runoff in June and July. Base-flow conditions are approached in late summer and continue through the winter (URS Operating Services, Inc., 1998).

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METHODS OF DATA COLLECTION

This metal-loading study was designed to determine streamflow and chemical quality at many mainstem and surface-inflow sites in a short period of time in order to create a nearly instantaneous snapshot of the loading and downstream transport of metals in the study reach. Tracer-injection methods were used to determine streamflow, and synoptic-sampling methods were used to determine chemical quality of water. Supplemental streamflow data for surface inflows were collected using conventional measuring methods.

A reconnaissance of the study reach was conducted during August 19-20, 1999, a few days before the start of the metal-loading study. The study reach included most of Daisy Creek and the Stillwater River from the mouth of Daisy Creek to the road to Lake Abundance. Although no additional metal loading was expected in the Stillwater River, this reach was included to document the extent, if any, of metal attenuation. The metal-loading study was conducted during August 24-27, 1999. Field notes from the reconnaissance are listed in table 4 (at back of report). Right bank and left bank are terms used in the field notes and in this report to refer to the respective sides of the stream viewed while looking downstream.

The tracer-injection site (fig. 2) was about 150 ft downstream from the headwater springs of Daisy Creek and 74 ft upstream from the most upstream surface inflow of acidic water. The tracer-injection site was assumed to be upstream of any metal-rich inflows that might originate from the McLaren Mine area. Downstream, sites to be sampled synoptically were selected and marked with flagging, and their distances from the tracer-injection site were measured (table 4, at back of report). Sampling sites along Daisy Creek and the Stillwater River were selected

upstream and downstream from visible surface inflows. Although some streams affected by historical mining have tailings piles or other mining-related sources of metals located adjacent to the channel, these features did not exist along the study reach. Almost all visible surface inflows were selected for sampling. In some places, several inflows were channeled temporarily along the flood plain and combined into one inflow to facilitate field measurements. To detect possible subsurface inflow, additional mainstem sites were selected in longer subreaches that had no visible surface inflow. A base-flow condition absent of precipitation runoff was targeted to minimize complications of varying streamflow and short-term metal loading that might result from overland runoff from the McLaren Mine area.

Sampling sites for this study were either on the mainstem or near the mouths of surface inflows (table 4). Mainstem sites included those on Daisy Creek and the Stillwater River downstream from Daisy Creek. Inflow sites included tributaries to Daisy Creek, the Stillwater River upstream of Daisy Creek, and a tributary of the Stillwater River. Sampling-site numbers were designated according to the site's distance in feet downstream from the tracer-injection site (fig. 2). Many surface-water sites in the Daisy Creek drainage had been sampled during previous water-quality studies (summarized by URS Operating Services, Inc., 1998). The names of these sites are listed on figure 2b and in table 4 and are noted in the text of this report.

Tracer Injection

Streamflow can be determined by tracer injection in a gaining stream reach where dilution of the tracer concentration by surface or subsurface inflows can be translated to a quantifiable increase in flow. Streamflow cannot be determined in a losing stream reach because the tracer concentration remains constant even though flow decreases. No indications of losing mainstem reaches were observed during this study.

Before the start of the tracer injection, an ample volume of tracer solution was prepared in a polyethylene tank by mixing 325 pounds of sodium chloride (NaCl) with 175 gallons of stream water collected from site 0. This mixture ratio produced a chloride concentration much higher than ambient concentrations in the stream, but less than the concentration at which the solution would be saturated with respect to sodium chloride. The tracer solution was injected continuously into Daisy Creek at a rate of 160 mL/min for 47 hours. The injection was started at 1703 hours on August 24 using a positive-displacement pump system controlled and monitored by an electronic data logger. This pump system failed at 1205 hours on August 25. Starting at 1215 hours on August 25, the tracer solution was manually added to the stream for 10 minutes until a backup constant-head metering system with manual control and monitoring was started to continue injection of the tracer solution. The tracer injection was stopped at 1600 hours on August 26 after all synoptic water samples had been collected. Three samples of the tracer solution were collected periodically during the injection period to document the tracer concentration. The chloride concentration of each tracer-solution sample was determined by measuring the solution density with volumetric glassware and an analytical balance and then converting density to concentration using data in West and Astle (1981). The chloride concentration ranged from 128.4 g/L to 130.8 g/L; the average concentration (129.2 g/L) was used for calculating streamflow.

Water samples for chloride analysis were collected at four mainstem sites, referred to as tracer-monitoring sites (fig. 2), to document the downstream movement of the injected tracer. Each tracer-monitoring site was sampled prior to the arrival of the tracer to determine the natural pre-injection chloride concentration and sampled multiple times during and after the tracer injection. These samples were collected manually or with automatic pumping samplers at a single point near midstream and were filtered through 0.45- μm capsule filters.

Supplemental Streamflow Measurements

Streamflow in a surface inflow can be determined by tracer injection if synoptic-sampling sites are positioned on the mainstem just upstream and downstream from the inflow. The increase in streamflow between the two mainstem sites generally can then be assumed to equal the streamflow contributed by the inflow. However, if mainstem sampling sites are widely spaced, part of the downstream increase in streamflow could come from subsurface inflow. In this circumstance, flow cannot be apportioned between surface and subsurface contributions using data from the tracer injection. In this study, mainstem sites along Daisy Creek, particularly the reach upstream from mainstem site 1,340, were too widely spaced to individually bracket every surface inflow. Therefore, streamflow in most of the surface inflows to Daisy Creek was determined during the synoptic sampling on August 26 by the volumetric (bucket-and-stop-watch) method or by measurements of channel cross-sectional area and flow velocity. These streamflow data are in table 5 (at back of report). The magnitude of subsurface inflow between two mainstem sites was then calculated as the difference between the tracer-calculated increase in streamflow between mainstem sites and the sum of the measured surface inflows entering the reach between the mainstem sites.

Synoptic Sampling

After concentrations of the injected chloride achieved equilibrium throughout the study reach, synoptic water samples for chemical analyses were collected on August 26 in acid-washed 3-L polyethylene bottles at each sampling site. To reduce the effect of load changes caused by diel variation in streamflow, samples were collected and processed as rapidly as possible. At sampling sites where stream mixing was good, samples were collected at a single vertical near midstream. At all other sites, equal-width, depth-integrated sampling methods (Knapton, 1985; Ward and Harr, 1990) were used. Synoptic sampling was conducted by one sampling team traveling upstream. Sampling was started at 0905 hours at site 12,410 and was completed at 1513 hours at site 0.

Water-quality samples were transported to a central processing location near the middle of the study reach as soon after collection as possible. Field values of specific conductance and pH were determined on an unfiltered aliquot of each sample. A second unfiltered aliquot was drawn for analysis of total-recoverable metals. Samples for major ions and dissolved metals were filtered through a 0.1- μm plate filter. Sample processing, filtration, and preservation were performed according to procedures described by Knapton (1985), Ward and Harr (1990), and Horowitz and others (1994). Water samples were analyzed by the USGS National Water Quality Laboratory (NWQL) in Lakewood, Colo., using methods described by Fishman and Friedman (1989), Fishman (1993), Garbarino and Taylor (1996), Hoffman and others (1996), and

Garbarino and Struzeski (1998) . Water-quality data are reported in table 6 (at back of report). The procedure for determining the minimum reporting level was changed (Childress and others, 1999) during analysis of water samples collected for this study. Consequently, two different minimum reporting levels appear for chloride in table 6.

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 Knapton (1985), Edwards and Glysson (1988), Ward and Harr (1990), Knapton and Nimick (1991), and Horowitz and others (1994).

The quality of analytical results reported for water-quality samples can be evaluated with data from quality-control samples that were submitted from the field and analyzed concurrently in the laboratory with routine samples. These quality-control samples consisted of duplicates and blanks, which provide quantitative information on the precision and bias of the overall field and laboratory process. In addition to quality-control samples submitted from the field, internal quality-assurance practices at the NWQL were performed systematically to provide quality control of analytical procedures (Pritt and Raese, 1995). These internal practices included analyses of quality-control samples such as calibration standards, standard-reference-water samples, replicate samples, deionized-water blanks, or spiked samples at a proportion equivalent to at least 10 percent of the sample load.

Duplicate 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 duplicates is affected by many sources of variability within the field and laboratory environments, including sample collection, processing, and analysis. For this study, two duplicate samples were obtained in the field by splitting a single composite sample into two subsamples, which then were analyzed separately. Analytical results for field duplicates are presented in table 6. Precision of analytical results for any constituent can be determined from the relative percent difference (RPD) of the concentrations of the constituent in duplicate analyses. The RPD is calculated for a constituent by dividing the absolute value of the difference between the two concentrations by the mean of the two concentrations. RPD values for dissolved and total-recoverable metals were almost all less than 10 percent, with no systematic exceedance of this value, indicating good precision for analytical results.

Two field blanks were analyzed to identify the presence and magnitude of contamination that potentially could bias analytical results. A field blank is an aliquot of deionized water that is certified as essentially free of the measured trace elements and that is processed through the sampling equipment used to collect stream samples. The blank is then subjected to the same processing (filtration, preservation, transportation, and laboratory handling) as stream samples. Blank samples were analyzed for the same constituents as those of stream samples to identify whether any detectable concentrations existed. Analytical results for field blanks are presented in table 6. With the exception of dissolved aluminum and copper, concentrations of all metals were less than the minimum reporting level. Consequently, analytical results (except for dissolved

aluminum and copper) for the synoptic samples are assumed to be free of significant or systematic bias from contamination associated with sample collection and processing. Dissolved aluminum was detected at low concentrations (2-6 $\mu\text{g/L}$) in field blanks as well as in water samples from some surface inflows that otherwise had dissolved metal concentrations less than the minimum reporting level. These data suggest that all water samples may have been affected by low-level contamination from sampling and processing equipment, sample bottles, or the nitric acid used for sample preservation. Dissolved copper was detected in one of the two field blanks.

The dissolved copper concentration in this blank was 3.8 $\mu\text{g/L}$ while the total-recoverable concentration was $<1 \mu\text{g/L}$, likely indicating some cross contamination from the sample processed prior to the blank. This contamination probably resulted from incomplete rinsing of the filter-plate apparatus. On the basis of these data, the possibility exists that cross contamination affected the dissolved copper concentration in the few synoptic samples that had concentrations of dissolved copper that were low ($<5 \mu\text{g/L}$) but higher than the total-recoverable concentration. However, cross contamination was not evident in the other field blank or the majority of synoptic samples, particularly samples from surface inflows with low or undetectable copper concentrations.

TRACER-INJECTION RESULTS

A mass-loading profile for a stream can be developed using synoptic streamflow and water-quality data for many sites along a stream. Such a profile can reveal notable spatial differences in loads, identify the location of significant sources of constituents, and indicate where geochemical reactions affect instream concentrations and loads. Because load is the product of streamflow and concentration, good streamflow measurements are necessary for meaningful results. The tracer-injection method utilizes conservation-of-mass theory and represents an alternative to traditional current-meter methods for determining streamflow in high-gradient mountain streams, particularly where traditional methods are hampered by turbulent flow and irregular channel cross sections (Bencala and others, 1990). The tracer-injection method also accounts for the portion of streamflow, referred to as underflow or hyporheic flow, that moves through the gravels and cobbles comprising the bed of the stream. In mountain streams, hyporheic flow can represent a substantial portion of the total streamflow (Kimball, 1997). Hyporheic flow cannot be measured by current-meter methods; therefore, loads may be underestimated with streamflow values obtained by current-meter measurements. Another advantage of the tracer-injection method is that streamflow data can be obtained at many sites more quickly than with current-meter measurements, thus allowing a long study reach to be characterized in less time and minimizing the potential effect of temporal changes in streamflow that could complicate a synoptic profile of load.

Downstream Travel and Dilution

During continuous tracer injection, the downstream movement of the tracer solution is documented by sampling at a few key sites called tracer-monitoring sites. Four tracer-monitoring sites located along the study reach (fig. 2, table 4) were sampled during this study. The first

tracer-monitoring site (T-1) was at mainstem site 104 and was located as close to the tracer-injection site as possible to minimize the potential for subsurface inflow to increase streamflow between the sites, but far enough downstream to ensure complete mixing of the tracer solution. Additional tracer-monitoring sites were located at mainstem sites 1,340 (T-2) and 9,925 (T-3) on Daisy Creek. The fourth site (T-4) was on the Stillwater River at the end of the study reach (site 12,410).

Information on the movement of the chloride tracer was gained by constructing temporal concentration profiles that show the change in chloride concentration with time for each tracer-monitoring site (fig. 5). 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.

Once the tracer has reached equilibrium at a site, a generally stable plateau concentration ideally will exist until the tracer injection is terminated. As the tracer moves downstream during the plateau period, it becomes diluted by inflows. Therefore, in a gaining stream system, the magnitude of the plateau concentration decreases downstream as the instream flow increases. Data from the tracer-monitoring sites are used to determine whether a relatively stable plateau concentration was reached at each site prior to collection of the synoptic samples. Changes in chloride concentrations during the plateau period can be caused by natural streamflow variations or changes in the tracer-injection rate.

Plateau concentrations were determined for each tracer-monitoring site and used to calculate arrival times and travel times through the subreaches between tracer-monitoring sites (table 1). Arrival time is defined as the time it takes for the injected tracer to achieve half of the plateau concentration (Zellweger and others, 1988). At the upstream site (site T-1), a relatively stable plateau in tracer concentration was reached quickly (fig. 5). The calculated travel time from the tracer-injection site was 7 minutes.

At each of the three downstream sites (T-2, T-3, and T-4), a relatively stable plateau concentration was reached and maintained for 12 to 18 hours after the tracer arrival. Subsequently, natural changes in streamflow caused the tracer concentration to increase (see discussion below). For determination of arrival time at these three sites, the plateau concentrations were defined as the average concentration of all samples collected at each site within the time period from initial onset of the plateau concentration to the time when tracer concentrations increased. The calculated arrival times for tracer-monitoring sites T-3 and T-4 are not well defined because the sampling interval (every 2-4 hours) was too infrequent to adequately document the changes in concentration during the arrival periods. As a result, one-half the plateau concentration was achieved at site T-4 before site T-3. The arrival time for site T-4 thus was re-calculated using data for the departure of the tracer at sites T-3 and T-4 after termination of injection. These data indicated that the tracer departed site T-4 about 143 minutes after the departure at site T-3. Accordingly, the arrival time for site T-4 was assumed to occur 143 minutes after the arrival time for site T-3.

Chloride concentration remained fairly uniform during the injection period at the upstream tracer-monitoring site (T-1), particularly during the period when the tracer was injected into

Daisy Creek with a pump (fig. 5). After the pump failed at 1205 hours on August 25, the tracer-injection rate was more variable because the constant-head metering system could not be controlled as precisely as the pump system. This variability is reflected in the temporal profiles of chloride concentration and specific conductance.

Chloride concentrations were more variable at the three downstream tracer-injection sites (fig. 5). The variation in concentration at each site exhibited an apparent 24-hour (diel) cycle. This diel variation is assumed to be caused by changes in the amount of ground water discharging to the stream system in response to diel cycles of evapotranspiration. At tracer-monitoring site T-2 (mainstem site 1,340), chloride concentrations increased both days beginning at about noon, indicating a decrease in streamflow. Evapotranspiration, particularly from the surrounding valley floor in the relatively low-gradient reach upstream of site T-2, likely reduced the amount of ground water that discharged to the stream system. At tracer-monitoring site T-3 (mainstem site 9,925), the sharp daily increase in chloride concentration occurred approximately 9 hours after the similar increase at site T-2. This time interval is close to the calculated travel time, and therefore, the change in streamflow at site T-3 is attributed to the diel variations in ground-water discharge carried down from the upper low-gradient reach. At tracer-monitoring site T-4, the daily increase in chloride concentration occurred a few hours after the increase at site T-3, which corresponds fairly well with the approximate 2.5-hr travel time through the subreach. However, whether this increase at site T-4 reflects the downstream movement of the concentration pattern from site T-3 or is related to hydrologic phenomena in the Stillwater River upstream from Daisy Creek is not clear. Similarly, the sporadic spikes in chloride concentration at site T-4 may either be actual concentration fluctuations or represent sampling or analytical imprecision.

Collection of synoptic samples began about 40 hours after the start of the tracer injection to allow the tracer to travel to the most downstream site and have adequate time to mix and achieve equilibrium. The synoptic-sampling period (shown as the shaded area on fig. 5) at tracer-monitoring sites T-1, T-3, and T-4 coincided with periods of relatively constant chloride concentration, indicating that synoptic samples were collected during a period of generally stable streamflow. However, the synoptic-sampling period at site T-2 coincided with the daily period of decreasing streamflow (increasing chloride concentration). This pattern of decreasing streamflow probably affected synoptic-sampling sites for a few thousand feet downstream from site T-2 and a few hundred feet upstream. For these sampling sites, streamflow was decreasing as the sampling team moved upstream. The effect of decreased ground water, or subsurface, inflow to the stream is difficult to assess. The subsurface inflow derived from the left-bank side of the stream presumably is relatively metal-free, whereas the subsurface inflow from the right-bank side is metal rich. In terms of metal loading, the amount of subsurface inflow from the left bank is unimportant because this subsurface inflow presumably contributes almost no metal load. Hence, the instream flow and metal concentrations might change, but the metal load will not. On the right bank, decreased subsurface inflow could result in decreased metal loading to Daisy Creek. Therefore, the metal loads attributed to subsurface inflow in this reach are less well defined compared to subsurface loads in other reaches.

Determination of Streamflow

Streamflow can be calculated at any mainstem site in the study reach using the instream tracer (chloride) concentration and the concentration and injection rate of the tracer solution. The instream tracer concentration used in these calculations was the chloride concentration in the synoptic samples collected during the plateau phase.

Using the assumption that chloride is chemically conservative, the mass of the injected tracer was presumed to remain in solution as it traveled downstream. Any decrease in chloride concentration in the mainstem was assumed to be the result of dilution from inflows. For this study, the tracer solution was injected at a rate of 2.67 mL/s, and the average concentration of the tracer solution was 129.2 g/L Cl. Thus, the chloride injection rate was 345 mg/s. Streamflow at the first site downstream from the tracer-injection site was calculated using equation 1:

$$Q_a = \frac{Q_{inj}(C_{inj} - C_o)}{(C_a - C_o)} \quad (1)$$

where

Q_a is the streamflow at the first site downstream from the injection, in L/s;

Q_{inj} is the injection rate of the tracer solution, in L/s;

C_{inj} is the concentration of the tracer solution, in mg/L;

C_o is the background concentration of the tracer upstream from the injection site, in mg/L; and

C_a is the tracer concentration, in mg/L, at the first downstream site.

The calculated streamflow (Q_a) and ambient instream concentration (C_a) for the first site downstream from the tracer-injection site then were used to calculate streamflow at the next downstream mainstem sampling site and each subsequent sampling site by using equation 2:

$$Q_b = \frac{Q_a(C_a - C_i)}{(C_b - C_i)} \quad (2)$$

where

Q_b is the streamflow at the downstream site (site b), in L/s;

Q_a is the streamflow at the upstream site (site a), in L/s;

C_a is the chloride concentration at the upstream site, in mg/L;

C_i is the chloride concentration in the inflow water entering the stream between the two sites, in mg/L; and

C_b is the chloride concentration, in mg/L, at the downstream site.

The chloride concentration (C_i) in water entering the stream was determined in one of several ways. If the mainstem sites were closely spaced to bracket a single surface inflow, then C_i was assumed equal to the chloride concentration in that surface inflow. If no surface-inflow sites were between the mainstem sites, C_i was assumed equal to the median chloride concentration (0.18 mg/L) for all inflows sampled in the entire study reach. If multiple surface inflows were sampled between mainstem sites, C_i was assumed equal to the average chloride concentration in these surface inflows.

The magnitude of each surface inflow was determined in one of several ways. If the mainstem sites were closely spaced to bracket a single surface inflow, then the streamflow in the surface inflow was assumed equal to the difference in streamflow between the mainstem sites immediately downstream and upstream from the inflow. Streamflow in surface inflows at sites 5,519, 5,671, and 7,529 were determined by this method. Streamflow in surface inflows at sites 11,560 and 11,644, which were bracketed by the same upstream and downstream sites, was estimated by assuming 60 percent of the increase in mainstem streamflow was from inflow site 11,560 and the remainder from inflow site 11,644. This apportionment was based on visual estimates made in the field on August 20, 1999. Subsurface inflow was assumed to be zero in the mainstem reaches bracketing these five surface inflows because the distances between the upstream and downstream synoptic sites were small (178-505 ft).

In parts of the study reach (particularly the low-gradient reach upstream from mainstem site 1,340), closely spaced surface inflows and subsurface inflows contributed streamflow to Daisy Creek. Subsurface inflow occurred almost continuously along the channel. Mainstem sampling sites were not located directly upstream and downstream from each surface inflow, which would have been necessary to apportion Daisy Creek streamflow gains between surface and subsurface

inflows using just the tracer-calculated streamflow values. Therefore, all surface inflows in the middle and upper reaches of Daisy Creek were measured independently using standard volumetric or current-meter methods. The magnitude of subsurface inflow then was calculated by subtracting the sum of the measured surface inflows between mainstem sites from the gain in flow between the mainstem sites. These calculated subsurface inflows are presented in table 5.

Using the instream chloride concentration from synoptic samples collected on August 26 and the equations listed above, instantaneous streamflow was determined at the 25 mainstem sites (table 5). Streamflow increased in Daisy Creek from 1.49 L/s at the tracer-injection site (site 0) to 32.65 L/s at the mouth (site 11,549), representing an increase of 31.16 L/s (fig. 6). Surface inflows accounted for 20.6 L/s (66 percent) of this increase, leaving 10.5 L/s (34 percent) of the increase attributable to subsurface inflow.

Streamflow was measured in the Stillwater River (site 12,410) on August 20, six days before the synoptic samples were collected. This measurement was 131 L/s, whereas the tracer-calculated streamflow measurement was 178 L/s. Comparing the two values is assumed to be a reasonable basis for assessing differences in the two methods for determining streamflow because this study was done during near base-flow conditions, and the discharge in the study reach appeared to be relatively stable or possibly slowly decreasing. Because hyporheic flow is included in the streamflow value obtained when using the tracer-injection method, the tracer-calculated streamflow was expected to be greater than the streamflow measured with the current-meter method, which does not measure flow through the streambed. Comparing the two streamflow values indicates that about 26 percent (or possibly less if streamflow decreased between August 20 and 26) of the total streamflow was hyporheic flow. This difference is similar to values reported by other similar studies (Kimball, 1997; Kimball and others, 1998; Kimball, Nimick, and others, 1999).

SYNOPTIC-SAMPLING RESULTS

Accurate concentration data are equally as important as representative streamflow values for compiling a meaningful profile of constituent loads transported in a stream. The synoptic samples collected at each of the 25 mainstem sites and 29 inflow sites were analyzed for pH, concentrations of major ions, and concentrations of dissolved and total-recoverable metals (table 6, at back of report).

pH and Major-Ion Concentrations

Values of pH in Daisy Creek and the Stillwater River changed markedly through the study reach (fig. 7, table 6). At the upstream end of Daisy Creek (site 0), the pH (7.28) was slightly basic. Immediately downstream, the pH in Daisy Creek decreased as inflows on the right bank (mined side) contributed acidic water. Two right-bank inflows (sites 114 and 161) near the injection site had pH values of 4.57 and 4.17, respectively, and caused the pH in Daisy Creek to decrease to 7.03 at site 270. Four right-bank inflows between mainstem sites 270 and 611 had pH values ranging from 2.70 to 2.96, resulting in substantial decreases of pH values in Daisy Creek to a minimum value of 3.37 at mainstem site 611. These inflows drain the manganese bog (inflow sites 292, 348, and 401) and the southern part of the McLaren Mine area (inflow site 481).

Inflows on the left bank through this reach were slightly basic. Between sites 611 and 2,334, the pH in Daisy Creek increased slightly, from 3.37 to 3.87. The pH values for most right-bank inflows in this reach were low (3.28 to 4.23), but not as acidic as in the right-bank inflows in the reach immediately upstream. These right-bank inflows drain the northern part of the McLaren Mine (inflow site 691) or intercept acidic shallow ground water flowing from the mine area (inflow sites 761, 804, 1,189, and 1,700). Inflow site 1,700 was the most downstream inflow with acidic water (pH of 3.98); right-bank inflows at sites 1,865 and 1,915 had near neutral pH values (6.87 and 6.94). Between mainstem sites 2,334 and 5,475, pH in Daisy Creek increased only slightly to 4.14 because little inflow entered this reach. However, relatively large inflows at sites 5,519 and 5,671 provided enough alkaline water to increase the pH in Daisy Creek markedly from 4.14 to 6.21 between mainstem sites 5,475 and 5,839. Farther downstream, pH values changed little until the small inflow at site 7,529 caused another increase in pH to 7.72 at mainstem site 7,829. Downstream from this point, pH remained slightly basic to the mouth of Daisy Creek and in the Stillwater River.

Downstream profiles of selected major-ion concentrations are shown on figure 8. Calcium, magnesium, and sulfate concentrations in Daisy Creek increased downstream from site 0 to site 611 in response to the high concentrations of these constituents in the acidic right-bank inflows. Sulfate concentrations were particularly affected, increasing from 46.3 to 405 mg/L between site 0 and site 611. Sulfate is liberated by oxidation of sulfide minerals in the altered and mineralized bedrock in the watershed. This geochemical reaction is accelerated after the sulfide-rich rocks are disturbed and exposed to the atmosphere by mining. Just downstream from mainstem site 611, concentrations of calcium, magnesium, and sulfate decreased in response to dilution from left-bank inflows. Farther downstream, concentrations of these major ions remained stable except where the large inflows at sites 5,519, 5,671 and 11,560 (the Stillwater River) provided dilution.

Metal Concentrations

The metals cadmium, copper, lead, and zinc have concentrations sufficiently elevated to be potentially lethal to aquatic life in Daisy Creek and to pose a toxicity risk in part of the Stillwater River (URS Operating Services, Inc., 1998). Copper is clearly the most important of these toxic metals, with maximum dissolved concentrations in Daisy Creek during this study of nearly 5,800 µg/L, compared to maximum concentrations of 848 µg/L for zinc and about 4 to 6 µg/L for cadmium and lead (table 6). These concentrations greatly exceed chronic aquatic-life standards and, except for lead, acute aquatic-life standards (U.S. Environmental Protection Agency, 1999). These metals, as well as aluminum, iron, and manganese, which potentially could control some geochemical reactions in these streams, were selected for analysis in the synoptic water samples collected on August 26.

Downstream concentration profiles are similar for cadmium, copper, and zinc (fig. 9). Concentrations were near minimum reporting levels at site 0 and increased sharply, reaching the highest levels measured in Daisy Creek at site 611. Acidic, right-bank inflows in this reach had dissolved concentrations as high as 20.6 µg/L cadmium, 26,900 µg/L copper, and 3,000 µg/L zinc. These inflows resulted in dissolved concentrations in Daisy Creek at site 611 of 5.8 µg/L cadmium, 5,790 µg/L copper, and 848 µg/L zinc. Left-bank inflows in this upstream reach

consistently had low concentrations (<1 µg/L cadmium, <21 µg/L copper, and <4 µg/L zinc), similar to the values at site 0. Downstream from site 611, concentrations of these metals decreased to the end of the study reach. The large inflows at sites 5,519, 5,671, 11,644, and 11,560 (the Stillwater River), in particular, caused large decreases in concentrations.

Dissolved and total-recoverable concentrations were nearly the same for cadmium, copper, and zinc in the upper half of the study reach between mainstem sites 425 and 5,475. These data indicate that these metals were entirely dissolved, which would be expected based on likely solubility controls for water having pH values less than about 4.5. Downstream from inflow sites 5,519 and 5,671, the higher pH in Daisy Creek resulted in changes in the partitioning of these metals between the dissolved and colloidal phases. The total-recoverable concentrations remained high (or unchanged), whereas the dissolved concentrations decreased (fig. 9), indicating an increase in colloidal concentrations. This pattern was most pronounced for copper and less so for cadmium and zinc, which is to be expected on the basis of the relative reactivity of these metals (Benjamin and Leckie, 1981). Amacher and others (1995) observed a similar pattern in metal partitioning in Daisy Creek and suggested that dissolved copper concentrations in Daisy Creek are controlled by dilution in reaches where pH is less than 4.5 and by sorption to iron oxyhydroxides where pH is higher than 4.5. Analysis of sequential extractions of sediment collected from Daisy Creek showed that copper concentrations in sediment were higher in those reaches of Daisy Creek where copper sorption was predicted (Amacher and others, 1995). A similar result was found in Fisher Creek and noted by Kimball, Nimick, and others (1999).

Lead concentrations were relatively low (<5.5 µg/L) throughout the study reach (fig. 9). Dissolved lead concentrations generally were between 2 and 4 µg/L in the reach between mainstem sites 611 and 5,661, where pH values were less than 5. Downstream from mainstem site 5,661, pH values were higher than 5, and the dissolved lead from upstream was converted to colloidal lead and transported downstream. Total-recoverable lead concentrations remained in the 1 to 5 µg/L range downstream to the Stillwater River. All left-bank surface inflows had lead concentrations less than the minimum reporting level (1 µg/L). Many of the right-bank inflows contributed lead to Daisy Creek, with dissolved concentrations generally between 1 and 12 µg/L. The dissolved lead concentration (76.4 µg/L) in surface-inflow site 1,700 was almost seven times higher than in any other inflow. The reason for this relatively high concentration is not known.

Some metals exhibit diel (24-hr) variation in dissolved concentration in streams affected by mine drainage (Brick and Moore, 1996; T.E. Cleasby and D.A. Nimick, unpubl. data). These studies indicate that, during mid-summer in Montana, maximum concentrations of dissolved manganese and zinc occur in the morning and that minimum concentrations occur in late afternoon or evening. These diel variations in concentration can have the potential to affect the results of metal-loading studies. Therefore, some of the samples collected for chloride analysis at tracer-monitoring sites T-2, T-3, and T-4 were analyzed for selected dissolved metals to determine if diel concentration variations occurred in Daisy Creek and the Stillwater River. Data for sites T-3 and T-4 are shown in figure 10.

Data for site T-3 show that dissolved copper, manganese, and zinc concentrations exhibit a diel variation in concentration, with maximum values occurring between 0800 and 1000 hours and minimum values between 1900 and 2200 hours. The magnitude of variation was different for

these metals, with copper and manganese varying proportionally much less than zinc. Dissolved copper concentrations varied between 34.3 and 55.4 $\mu\text{g/L}$, an increase of about 62 percent from the minimum value. Dissolved manganese concentrations varied between 477 and 609 $\mu\text{g/L}$, an increase of about 28 percent from the minimum value. Dissolved zinc concentrations ranged from 44.8 to 112 $\mu\text{g/L}$, an increase of about 150 percent from the minimum value. These variations do not correlate with stream-flow and corresponding dilution effects interpreted from the chloride data (fig. 5). Rather, the variations are thought to be related to diel cycles in other stream-water characteristics, such as pH or temperature, that can affect the partitioning of metals between the dissolved and adsorbed phases. Upstream from main-stem site 5,475, similar diel variations in concentration are not expected to occur because the low pH (<4.14) does not favor sorption of metals to colloids and the streambed. This hypothesis was supported by five samples collected at site T-2 over a 36-hr period on August 25-26. Zinc concentrations in these samples ranged from 501 to 543 $\mu\text{g/L}$ but displayed no diel pattern.

Data for site T-4 show diel variations similar to those at site T-3. Concentrations generally were higher in the morning and lower in the afternoon. The sampling interval (3-6 hr) was too long to precisely determine the timing of the minimum and maximum concentrations. The magnitude of variation for each metal at site T-4 was somewhat different from the variations at site T-3.

Dissolved copper concentrations

varied between 17 and 27 $\mu\text{g/L}$, an increase of about 59 percent from the minimum value.

Dissolved manganese concentrations varied between 60 and 93 $\mu\text{g/L}$, an increase of about 55 percent from the minimum value. Dissolved zinc concentrations ranged from 2.2 to 9.7 $\mu\text{g/L}$, an increase of about 340 percent from the minimum value.

Because the synoptic samples were collected sequentially in the upstream direction from early morning to mid-afternoon, concentrations of copper, manganese, and zinc would have decreased during the sampling period. Concentrations in the samples collected near the downstream end of the study reach (at the beginning of the day) would have had higher concentrations relative to the samples taken upstream at a later time. However, because dissolved concentrations of these metals were higher upstream in the mainstem owing to metal-enriched inflows, the diel effect appears to be somewhat offset by the effect of inflows.

Concentrations of aluminum and iron (fig. 11) increased sharply between sites 0 and 611, where maximum total-recoverable concentrations were 18,400 $\mu\text{g/L}$ and 23,900 $\mu\text{g/L}$, respectively. Total-recoverable concentrations decreased gradually throughout the rest of the study reach, whereas dissolved concentrations decreased sharply downstream from site 5,475. Partitioning of aluminum and iron between dissolved and colloidal phases is controlled by pH. Upstream of site 481, where pH in Daisy Creek varied from near neutral to 4.5 (fig. 7), concentrations of total-recoverable aluminum were higher than dissolved concentrations (fig. 11). The dissolved aluminum contributed by acidic right-bank inflows was converted to colloidal aluminum, which coated the streambed (fig. 12). Downstream from site 481, the pH of Daisy Creek decreased to less than 4.5, and most aluminum was dissolved. The pH in Daisy Creek was low downstream to sites 5,519 and 5,671, the first large inflows downstream from the reach of Daisy Creek affected by drainage from the McLaren Mine area. Neutralization provided by these slightly basic inflows resulted in massive precipitation of aluminum, which thickly coated the streambed and caused a sharp decrease in dissolved aluminum concentrations.

Iron partitioning followed the same pattern as aluminum (fig. 11). However, the pH value below which iron was entirely dissolved was 3.5. Water this acidic was found in the short reach of Daisy Creek that extends from mainstem site 819 upstream to at least mainstem site 611 and probably as far upstream as inflow site 481. Left-bank inflows downstream from site 819 caused a sufficient increase in pH in Daisy Creek to allow formation of iron-oxyhydroxide colloids. Field observations indicated a visible change in the water in Daisy Creek from clear at site 761 to cloudy at site 1,082 (table 4). Stream water remained cloudy with iron and aluminum colloids from this point downstream to the end of the study reach.

Concentrations of manganese (fig. 11) increased sharply between sites 0 and 611, similar to aluminum and iron. Downstream from site 611, concentrations decreased. However, unlike aluminum and iron, dissolved concentrations were the same as total-recoverable concentrations, indicating that manganese-oxyhydroxide colloids did not form.

QUANTIFICATION OF LOADS

Load is the mass of a constituent transported downstream. For chemically conservative constituents, loads are additive as inflows contribute their load to the load in the receiving stream. The effect of loads on instream concentrations is dependent on the volume of water transporting the mass. For comparative purposes, loads are commonly expressed as a rate of transport in terms of mass per unit time (for example, mg/s for an instantaneous load; kilograms/year for an annual load). Instantaneous load, as used in this synoptic study, is calculated as the product of concentration and streamflow at the time of sampling. Instantaneous loads were calculated for the 25 mainstem and 31 surface-inflow sites for calcium, magnesium, sodium, and sulfate as well as for dissolved and total recoverable aluminum, cadmium, copper, iron, lead, manganese, and zinc (table 7, at back of report).

Downstream load profiles graphically illustrate the spatial distribution of loads at many locations along the mainstem and can be used to identify locations of important sources and sinks that affect the constituent load. Stream segments where constituent loads are added to or removed from the water column can be identified by comparing three different loading profiles: the instream load in the mainstem, the cumulative surface-inflow load, and the cumulative instream load.

The profile of instream load represents the instantaneous loads (table 7) measured at each mainstem sampling site. Instream loads were calculated by multiplying streamflow by constituent concentration. Downstream changes in instream loads are the net result of inputs from the sampled surface inflows and any unsampled subsurface inflow, as well as any loss of load caused by streamflow loss, formation of colloids and subsequent deposition on the streambed, or other geochemical reactions (Broshears and others, 1995; Kimball and others, 1994). The instream load profile is important because it defines the net effect of all inputs to the stream and losses in the stream. Partitioning of metals between the dissolved and colloidal phases can be assessed by comparing the dissolved and total-recoverable instream loads. If these loads are equal, then the load is entirely dissolved. Subtracting the dissolved load from the total-recoverable load gives the instream particulate load, which is assumed to be primarily colloidal.

The cumulative surface-inflow load at a site is the sum of all surface-inflow loads downstream to that point and is determined by summing surface-inflow loads in the downstream direction. The profile of cumulative surface-inflow load does not include loads contributed by subsurface inflows, which are calculated as the difference between instream loads and surface-inflow loads. Surface-inflow loads were calculated from the streamflow data in table 5 and the concentration data in table 6. The inflow load for a constituent was assumed to be zero if the constituent concentration was less than the minimum reporting level.

A third load profile that is useful for load analysis is the cumulative instream load. This load is calculated for each mainstem site by adding all individual increases in load between successive upstream mainstem sites. The profile of cumulative instream load indicates the entire load that entered the stream from surface and subsurface sources, disregarding any downstream loss from chemical or physical processes. The amount of subsurface loading to the mainstem can be estimated by subtracting the cumulative surface-inflow load from the cumulative instream load. The amount of dissolved load that has been converted to colloidal load in the mainstem can be calculated by subtracting the instream dissolved load from the cumulative instream dissolved load.

Major Ions

Load profiles for calcium and sulfate are shown in figure 13. The shapes of the load profiles are different because the sources of these elements are different, with calcium derived by weathering of the rocks prevalent in much of the watershed while sulfate is produced by weathering of the altered and mineralized rocks rich in sulfide minerals. Calcium concentrations varied relatively little (24.5-60.6 mg/L, table 6) in the mainstem, especially compared to the range in concentrations of metals, and therefore, instream calcium loads reflect, to a large extent, the streamflow profile (fig. 6). Large increases in calcium load occurred at the large tributaries (inflow sites 5,519, 5,671, 11,560, and 11,644). The difference between the instream load profile and the cumulative surface-inflow load profile indicates the magnitude of calcium loading from subsurface inflow (fig. 13). At the end of the study reach (mainstem site 12,410), surface inflows contributed 74 percent of the calcium load while subsurface inflow contributed 26 percent of the load.

In contrast to calcium, the instream load profile for sulfate (fig. 13) was dominated by load increases upstream of mainstem site 5,475, where surface and subsurface drainage from the McLaren Mine area enters Daisy Creek. Upstream of mainstem site 611, about 65 percent of the sulfate load came from surface inflows and about 35 percent came from subsurface inflows. Because almost all of the sulfate load in surface inflows along Daisy Creek came from right-bank inflows, the subsurface inflow also is assumed to have come mostly from the right bank. Between mainstem sites 611 and 5,475, the increase in instream sulfate load was derived almost entirely from subsurface inflow, as indicated by a nearly flat profile for cumulative surface-inflow load. Downstream from mainstem site 5,839, the instream sulfate load increased at about the same rate as calcium, primarily from inflow of ground water from unaltered and unmineralized areas. At the end of the study reach, surface inflows contributed only 51 percent of the sulfate load.

Metals

Metal-load profiles display the net effect of metal inputs from surface and subsurface sources as well as load changes resulting from geochemical reactions in the mainstem. Load profiles for aluminum, cadmium, copper, and zinc exhibit many of the same patterns, while profiles for iron and lead each display different patterns. Aluminum and iron loads are discussed first because of the importance of these metals, as well as pH, in controlling partitioning of the other metals.

Load profiles for aluminum and iron are shown in figure 14. For both metals, loading to Daisy Creek was negligible between sites 0 and 270. The instream loads increased substantially between sites 270 and 611. At site 611, surface inflows accounted for 62 to 77 percent of the dissolved and total-recoverable instream loads, whereas 23 to 38 percent came from subsurface inflow. Right-bank inflow sites 401, 411, and 481 contributed 59 to 73 percent of the instream load. Left-bank inflows contributed little aluminum or iron.

Downstream from site 611, the instream load profiles for aluminum and iron differ, particularly for the dissolved loads. These differences reflect the important role pH plays in partitioning these metals between dissolved and colloidal phases in streams affected by acid rock drainage. Between sites 611 and 4,283, instream dissolved-aluminum loads continued to increase downstream, essentially in step with total-recoverable loads. This increase was derived primarily from subsurface inflow, as indicated by a flat profile for cumulative surface-inflow load. Downstream from mainstem site 5,475, the instream dissolved-aluminum load decreased by almost two orders of magnitude, from 161 to 2.52 mg/s in less than 400 ft (between mainstem sites 5,475 and 5,839). In this short reach, the pH in Daisy Creek increased from 4.14 to 6.21 (table 6) owing to tributary inflow, resulting in rapid conversion of dissolved aluminum to colloidal aluminum. The total-recoverable aluminum load decreased through much of the rest of the study reach as this colloidal material settled to the streambed in the lower-gradient reaches of Daisy Creek, especially downstream from site 7,324 and in the Stillwater River.

Instream dissolved-iron loads decreased sharply downstream from site 611 (fig. 14), and most of the instream iron load was colloidal, as indicated by the much larger total-recoverable instream load. The decrease in dissolved load was most rapid between sites 611 and 1,082, where pH in Daisy Creek increased from 3.37 to 3.81 (table 6). The dissolved load decreased at a more gradual rate to virtually nothing at mainstem site 7,829. Unlike aluminum, the instream dissolved-iron load decreased gradually between sites 1,082 and 7,829, perhaps because photoreduction of iron oxyhydroxides maintained the dissolved-ferrous iron concentration in the stream (McKnight and others, 1988). Total-recoverable instream loads for iron decreased steadily downstream from site 7,324 through the rest of the study reach, similar to aluminum, suggesting that colloids settled on the streambed.

Load profiles for copper (fig. 15) follow a downstream pattern similar to that for aluminum. The instream load started near zero at site 0 and increased substantially between sites 270 and 611 in response to surface and subsurface inflows. Dissolved and total-recoverable copper loads continued to increase at a more gradual rate from site 611 downstream to site 4,283. The gradual increase in instream load was derived from subsurface inflow because surface-inflow loads were negligible in this reach, as indicated by the flat cumulative surface-inflow load profile. From site

0 downstream to site 5,475, almost all of the instream copper load was dissolved as opposed to colloidal. However, this pattern changed abruptly downstream from site 5,661 as dissolved copper was removed in response to increased pH, which caused dissolved copper to sorb to aluminum and iron colloids. The decrease in instream dissolved-copper load was more gradual than for aluminum (fig. 14), but almost all dissolved copper was converted to the colloidal phase upstream from the mouth of Daisy Creek.

The load profiles for cadmium (fig. 15) and zinc (fig. 16) follow a pattern generally similar to that for copper (fig. 15). Instream loads increased dramatically between sites 270 and 611 and more gradually between sites 611 and 4,283. The loads were almost entirely dissolved in these two reaches. Downstream from mainstem site 5,475, the decreases in dissolved cadmium and zinc instream loads were not as sharp as for dissolved aluminum or copper. Rather, the decreases were more gradual, and a substantial dissolved load persisted to the mouth of Daisy Creek and into the Stillwater River. Similar to copper and aluminum, total-recoverable instream loads for cadmium and zinc decreased in the downstream half of Daisy Creek, as the colloidal load settled on the streambed.

The load profiles for lead (fig. 16) are similar to those for aluminum (fig. 14) except for two unusual features, both of which are not well understood. First, lead is the only metal that exhibited any significant increase in cumulative surface-inflow load downstream from mainstem site 611 [at inflow site 1,700 (table 7)]. The dissolved lead concentration (76.4 $\mu\text{g/L}$) is anomalously high, and the source of the lead is unknown. Historical water-quality data for samples collected during 1994-98 at sites DCT-10 and DCT-14, which are in the same drainage and upstream from site 1,700, had dissolved lead concentrations near or less than the minimum reporting level (2-3 $\mu\text{g/L}$) (Michael Cormier, Maxim Technologies, Inc., written commun., 1999). The second unusual feature of the lead profiles is the large increase in total-recoverable instream load between mainstem sites 5,475 and 7,324. Increases in total-recoverable loads for iron and aluminum were also noted in this reach, but were not proportionally as large as that for lead. The cause of the sharp increase and the subsequent large decrease in total-recoverable load between sites 7,324 and 7,829 is not apparent. The increase in instream total-recoverable lead load downstream from mainstem site 5,475 corresponds to the concurrent sharp decrease in instream dissolved-lead load. However, these shifts may be relatively unimportant because the total-recoverable lead concentrations through this entire reach are relatively low (2.3-5.4 $\mu\text{g/L}$, table 6) in comparison to copper and zinc concentrations.

METAL SOURCES

Copper is the metal of most concern in Daisy Creek because it occurs at higher concentrations than other metals and can be toxic to aquatic life. Therefore, sources of copper loading are discussed in this section. The sources of the other metals in Daisy Creek, with the occasional exception of lead, are thought to be the same as copper. The magnitude and source of copper loads contributed to subreaches of Daisy Creek from surface and subsurface inflows are presented in table 2.

Copper loading to Daisy Creek was substantial in the reach upstream of mainstem site 5,475 (fig. 15). This reach can be divided into five subreaches on the basis of the different source areas that

contribute copper to Daisy Creek (table 2). Dissolved copper loads are discussed here because, in this reach, almost all of the copper load is dissolved. Sources of copper included right-bank surface inflows and subsurface inflow. Left-bank inflows contributed less than 0.02 percent of the entire copper load in this reach.

The upstream subreach (between sites 0 and 270) flows past a small, right-bank hill composed of landslide or glacial-moraine deposits. This subreach had minor copper loading (461 $\mu\text{g/s}$) from an inflow on the south side of the hill (inflow site 74) and from streamside seeps at its base (inflow sites 114 and 161). Subsurface inflow also contributed a small copper load (151 $\mu\text{g/s}$) to Daisy Creek (table 2).

The second subreach (between sites 270 and 460) received a substantial copper load (10,100 $\mu\text{g/s}$). Most of this load came from the four right-bank surface inflows (sites 292, 348, 401, and 411) that originate in the manganese bog adjacent to Daisy Creek. Copper loading from subsurface inflow was small (251 $\mu\text{g/s}$).

In the third subreach (between sites 460 and 611), one right-bank inflow (site 481), enters Daisy Creek and contributed more copper (16,400 $\mu\text{g/s}$) to Daisy Creek than all other surface inflows combined (table 7). This inflow drains the southern part of the McLaren Mine (fig. 2), where much of the mine wastes are stockpiled and where substantial unmined mineralized rock remains. Unlike the two upstream subreaches, copper loading from subsurface inflow (8,900 $\mu\text{g/s}$) in this part of Daisy Creek was substantial.

In the fourth subreach (between mainstem site 611 and inflow site 1,700), subsurface inflow contributed almost all the copper loading (7,040 $\mu\text{g/s}$). The most prominent right-bank inflows (sites 691 and 1,700, which drain the northern part of the McLaren Mine) contributed only 143 $\mu\text{g/s}$ (table 7). The copper loading from these two sites and the other four right-bank inflows was only 245 $\mu\text{g/s}$. Although inflow site 1,700 was not a significant source of copper to Daisy Creek, the inflow did contribute a relatively large load of dissolved lead (6.11 $\mu\text{g/s}$), almost as high as the load contributed by inflow site 481 (7.45 $\mu\text{g/s}$, table 7).

The fifth, and most downstream, subreach (between sites 1,700 and 5,475) is the longest of the five subreaches. Surface inflows to this subreach do not drain the McLaren Mine. Copper loading from surface inflows was negligible (2 $\mu\text{g/s}$) while subsurface loading (6,210 $\mu\text{g/s}$) was relatively large, although smaller than in the two previous upstream subreaches.

In summary, the most substantial copper loading to Daisy Creek (71 percent of the total copper load contributed to the entire study reach) occurred between sites 270 and 611, where right-bank inflows originate in the manganese bog and the southern part of the McLaren Mine. About 53 percent of the total load in the study reach was contributed by the five right-bank inflows in this 341-ft reach, with inflow site 481 (33 percent of the total) being the most important. Copper loading to Daisy Creek from all surface inflows downstream from mainstem site 611, including the surface inflows that drain the northern part of the McLaren Mine, was not significant, at least during the low-flow conditions that existed during this study. While surface inflows contributed the most copper to Daisy Creek upstream of site 611, subsurface loading was the only important source of copper for the longer downstream reach between sites 611 and 5,475. Subsurface

loading in this reach contributed over half of the total subsurface loading to Daisy Creek and 27 percent of the total load to Daisy Creek.

Although the subsurface inflow to Daisy Creek was not sampled, copper concentrations in the subsurface inflow (table 3) can be calculated from the subsurface inflow rates and copper loads contributed by subsurface inflow. These calculations assumed that one-half of the subsurface inflow came from the right bank and was metal rich; the subsurface inflow from the left bank was assumed to contribute no copper load to Daisy Creek. For the reach between sites 460 and 611, the calculated dissolved copper concentration (26,200 $\mu\text{g/L}$) in subsurface inflow from the right bank is similar to the concentration in some of the nearby right-bank inflows (for example, sites 292, 348, and 401), indicating that the subsurface pathway feeds both the right-bank surface and subsurface inflows. Calculated copper concentrations for subsurface inflow between sites 611 and 5,475 were lower, but substantially higher than concentrations in surface inflows in that reach. The pH and copper concentrations in the subsurface flow vary spatially, most likely in response to the varying amounts of alteration and buffering capacity in the rocks along different subsurface flow paths, as well as to dilution provided by any deeper ground water flowing from areas of unaltered bedrock.

Much of the metal-rich subsurface inflow to Daisy Creek probably was acidic. Although pH was not measured in subsurface flow, this hypothesis is supported by the presence of dissolved aluminum in the subsurface inflow. Aluminum is only likely to be dissolved where the pH is less than about 4.5 (Stumm and Morgan, 1996, p. 273).

The copper load entering Daisy Creek between sites 270 and 1,700 as surface and subsurface inflow is derived from the McLaren Mine area. Although this copper load has been divided between surface and subsurface inflows (table 2), in reality virtually none of this load comes directly from the McLaren Mine to Daisy Creek as surface flow. Almost all of the right-bank channels (except site 1,700) were dry from the McLaren Mine area to within a short distance of Daisy Creek. Flow in these short reaches near Daisy Creek was maintained by subsurface inflow. Determining the source of the subsurface inflow to Daisy Creek and inflow channels is difficult because several possible sources exist within the McLaren Mine area. These sources include the mineralized rocks of Fisher Mountain upgradient of the McLaren Mine area, the surficial waste rock at the mine, and the underlying bedrock, which hosts both the McLaren ore deposit and the surrounding altered rock that is pyritic. More detailed hydrogeologic information would be needed to determine the importance of each of these sources.

The occurrence of metal-rich subsurface inflow to Daisy Creek upstream and downstream from the tributaries that drain the McLaren Mine area indicates that bedrock to the south and north of the McLaren Mine area apparently is a source of acid rock drainage not related to mining. The small subsurface metal load that discharges to Daisy Creek upstream of site 104 may be derived from the Chimney Rock area (fig. 1). The larger subsurface metal load that discharges to Daisy Creek downstream from site 1,700 may be derived from Fisher Mountain. The ferricrete deposits mapped by Furniss and others (1999) near site 2,334 and dated as 6,490 radiocarbon years before present support the hypothesis that unmined bedrock is one of the current sources of metals to Daisy Creek. However, this subsurface flow has not been directly measured. Monitoring well MW-3 (fig. 2) presumably should intercept this subsurface flow, but water-quality data for

samples collected from the well do not support this hypothesis. This shallow well is completed in unconsolidated surficial material and the Wolsey Shale with a screen that extends from 16 to 46 ft below ground surface (Hydrometrics, Inc., 1990). Five samples collected during 1989-90 had pH values greater than 7 and low dissolved-metal concentrations. Cadmium, copper, and lead concentrations were at or less than minimum reporting levels (Michael Cormier, Maxim Technologies, Inc., written commun., 1999). Manganese (230-380 $\mu\text{g/L}$) and zinc (10-100 $\mu\text{g/L}$) concentrations were higher than minimum reporting levels but much lower than would be expected if ground water at this site were affected by acid rock drainage.

Cleanup activities that reduce metal and acid loading from the McLaren Mine area will result in improvements in water quality in Daisy Creek and the Stillwater River. Metal concentrations likely would decrease, and pH values in reaches that are currently acidic likely would increase. However, potential reductions in metal and acid loading and changes in pH and metal concentrations are difficult to predict because the ultimate source of the metals and acid are not well defined. In addition, decreasing copper concentrations during baseflow conditions to values less than the aquatic-life standards may be impossible because of natural sources of copper in unmined mineralized and altered bedrock. If the assumptions are made that all copper loading upstream of site 1,700 comes from sources at the McLaren Mine and that these sources can be removed or isolated, the copper load (6,210 $\mu\text{g/s}$, table 2) contributed by subsurface inflow derived from bedrock away from the mine between sites 1,700 and 5,475 would result in a copper concentration in Daisy Creek of about 450 $\mu\text{g/L}$ at site 5,475 compared to the 3,570 $\mu\text{g/L}$ measured in this study (table 6). Because the assumed cleanup activities likely would substantially reduce acid loading, thereby resulting in higher pH values, iron and aluminum colloids would be present and some copper likely would be adsorbed to this material. Therefore, this calculated copper concentration represents a total-recoverable concentration; the dissolved copper concentration would be lower. Downstream, at the mouth of Daisy Creek (site 11,549), the estimated total-recoverable copper concentration would be about 190 $\mu\text{g/L}$ under base-flow conditions compared to the 1,200 $\mu\text{g/L}$ measured during this study. Both calculated copper concentrations are higher than the acute aquatic-life standard of 13 $\mu\text{g/L}$ (assuming a hardness of 100 mg/L , U.S. Environmental Protection Agency, 1999). Farther downstream, the maximum total-recoverable copper concentration in the Stillwater River at the end of the study reach (site 12,410) would be about 35 $\mu\text{g/L}$ compared to the 176 $\mu\text{g/L}$ measured in this study. These calculated copper concentrations are based on the copper loading and streamflow conditions that existed during the short period during which this study was conducted. Concentrations would vary to an unknown degree as hydrologic conditions in the drainage basin changed.

The toxicity of copper (and other metals) is dependent on the hardness of the water. If the metals load in Daisy Creek were reduced, hardness values also would be lower because the right-bank and subsurface inflows contributing metals also contribute calcium and magnesium. Therefore, in considering post-cleanup hardness values to use to compute aquatic-life standards, the values in left-bank inflows (generally less than 100 mg/L) or the Stillwater River (58 mg/L) may represent potential post-cleanup values.

SUMMARY AND CONCLUSIONS

A metal-loading study was conducted during August 24-27, 1999, to quantify and identify the principal sources of metal loads to Daisy Creek and to examine the downstream transport of these metals into the Stillwater River. Water-quality and aquatic conditions in Daisy Creek have been affected by acid rock drainage derived from waste rock and adit discharge at the McLaren Mine as well as from natural weathering of pyrite-rich altered and mineralized rock that makes up and surrounds the ore zones in the New World Mining District. Knowledge of the main sources and transport pathways of metals and acid can aid resource managers in planning and conducting effective and cost-efficient remediation activities.

The study reach included virtually all of Daisy Creek and a 850-ft reach of the Stillwater River downstream from the confluence of Daisy Creek. Metal loads in the mainstem were quantified from streamflow data determined by tracer injection and water-quality data determined from synoptic samples. Loads contributed by surface inflows were determined from these data as well as supplemental streamflow measurements made using conventional methods. Downstream changes in metal loads in the stream then were attributed to sources along the stream as well as to instream geochemical reactions. These sources included visible surface inflows and diffuse subsurface inflows.

The metals cadmium, copper, lead, and zinc have concentrations sufficiently elevated to be of concern for aquatic life in Daisy Creek and the Stillwater River. Copper is the most important of these toxic metals, with a maximum dissolved concentration of nearly 5,800 mg/L measured in Daisy Creek during this study. Metal concentrations increased sharply in the short reach between the tracer-injection site and a site 611 ft downstream, where the highest concentrations measured in Daisy Creek occurred. Acidic, right-bank (mined side) inflows in this reach had dissolved concentrations as high as 20.6 µg/L cadmium, 26,900 µg/L copper, 76.4 µg/L lead, and 3,000 µg/L zinc. These inflows resulted in maximum dissolved concentrations in Daisy Creek of 5.8 µg/L cadmium, 5,790 µg/L copper, 3.8 µg/L lead, and 848 µg/L zinc. Left-bank inflows in this upstream reach consistently had low concentrations (<1 µg/L cadmium, <21 µg/L copper, <1 lead, and <4 µg/L zinc), similar to the values in Daisy Creek at the tracer-injection site. Downstream from mainstem site 611, concentrations of metals decreased to the end of the study reach.

Significant copper loading to Daisy Creek only occurred in the reach upstream of mainstem site 5,475. Sources included right-bank surface inflows and subsurface inflow; copper loads in left-bank surface inflows were virtually nonexistent. The most significant metal loading (71 percent of the total copper loading in the study reach) occurred between mainstem sites 270 and 611. About 53 percent of the total load was contributed by the five right-bank inflows in this reach. Four of these inflows drain the manganese bog that is on the right bank between mainstem sites 270 and 460. Just downstream, inflow site 481, which heads in the southern part of the McLaren Mine, contributed the single largest amount of copper, or about 33 percent of the total copper load in the study reach.

Copper loading from subsurface inflow is substantial, contributing 46 percent of the total dissolved copper load to Daisy Creek. Most of this subsurface copper loading occurred in the reach of Daisy Creek downstream from the reach that received surface loading.

Flow through the shallow subsurface is an important copper-transport pathway from the McLaren Mine and surrounding altered and mineralized bedrock to Daisy Creek during base-flow conditions. The pH and metal concentrations in the subsurface flow probably varied in response to the varying amounts of alteration and buffering capacity in the rocks along different subsurface flow paths. Unfortunately, little is known about the source of acid and copper in this subsurface flow. Possible sources include the mineralized rocks of Fisher Mountain upgradient of the McLaren Mine area, the surficial waste rock at the mine, and the underlying bedrock, which hosts both the McLaren ore deposit and the surrounding altered rock.

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