

# **Short-Term Variation of Trace-Element Concentrations during Base Flow and Rainfall Runoff in Small Basins, August 1999**

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Chapter D7 of

**Integrated Investigations of Environmental Effects of Historical Mining in the Basin and Boulder Mining Districts, Boulder River Watershed, Jefferson County, Montana**

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CONVERSION FACTORS, VERTICAL DATUM, ABBREVIATED UNITS

| Multiply                      | By       | To obtain              |
|-------------------------------|----------|------------------------|
| cubic foot per second (ft³/s) | 0.028317 | cubic meter per second |

Temperature can be converted to degrees Celsius (°C) or degrees Fahrenheit (°F) by the following equations:

°C = 5/9 (°F – 32)  
°F = 9/5 °C + 32

Sea level: In this report, “sea level” refers to the National Geodetic Vertical Datum of 1929 (NGVD of 1929)—a geodetic datum derived from a general adjustment of the first-order level nets of both the United States and Canada, formerly called Sea Level Datum of 1929.

|           |                                                   |
|-----------|---------------------------------------------------|
| µg/L      | microgram per liter                               |
| µg/L/hour | microgram per liter per hour                      |
| µm        | micrometer                                        |
| µS/cm     | microsiemens per centimeter at 25 degrees Celsius |
| mg/L      | milligram per liter                               |

## ***Chapter D7***

# **Short-Term Variation of Trace-Element Concentrations during Base Flow and Rainfall Runoff in Small Basins, August 1999**

By John H. Lambing, David A. Nimick, and Thomas E. Cleasby

### **Abstract**

Water-quality data for the Boulder River watershed of southwest Montana indicated that dissolved zinc concentrations vary cyclically throughout the day during base flow. To provide insight into the pattern and magnitude of trace-element concentration changes during a 24-hour (diel) cycle, water samples were collected hourly in three small tributary basins of the Boulder River watershed that drain abandoned mine lands. Hourly zinc variations were examined at five sites in High Ore, Jack, and Cataract Creeks; arsenic, copper, and manganese also were analyzed at the High Ore Creek site. Dissolved zinc concentrations in High Ore Creek varied by about 400  $\mu\text{g/L}$  (micrograms per liter) during a 24-hour cycle, representing about a three-fold change in concentration. Another type of short-term variation in zinc concentrations was documented when rainstorms produced runoff over mine wastes during the sampling of base flow at four sites. Within 1 to 5 hours following the onset of intense rain, dissolved zinc concentrations increased rapidly at all four sites, ranging from a 670  $\mu\text{g/L}$  increase in Cataract Creek below Uncle Sam Gulch to a 6,200  $\mu\text{g/L}$  increase in a tributary below the Bullion mine. Short-term variations of trace-element concentrations caused by either diel cycles or rainfall runoff can potentially affect interpretation of trace-element sources, long-term trends, and biological risk.

### **Introduction**

Periodic sampling conducted during 1997–99 to describe water-quality conditions on a watershed scale (Nimick and Cleasby, this volume, Chapter D5) provided insufficient data to characterize two important phenomena: diel (24-hour) variation in trace-element concentrations during base flow and changes induced by short-duration rainstorm events. Diel cycles have been noted in other streams affected by metals (McKnight and others, 1988; Brick and Moore, 1996; Nimick

and Cleasby, 2001) and arsenic (Fuller and Davis, 1989) derived from mine wastes, as well as naturally occurring arsenic (Nimick and others, 1998). The specific mechanism causing diel concentration changes is not known, but the effect likely results from a combination of geochemical, biological, and physical processes that affect the partitioning of trace elements between the dissolved and solid phases. Such processes that occur regularly during the course of a 24-hour cycle could produce systematic temporal patterns in trace-element concentrations, thereby causing analytical results to vary depending on the time of day that samples are collected. Water-quality data collected for Cataract Creek (Cleasby and others, 2000) and High Ore Creek (Nimick and Cleasby, 2000) indicated that relatively large variations of dissolved zinc concentrations were occurring at different times of the day during base flow. This phenomenon warranted further investigation because diel concentration changes might affect synoptic load calculations and subsequent interpretation of trace-element sources, detection of long-term trends, and reliable evaluations of the effectiveness of remediation efforts. In addition, diel cycles in concentrations of potentially toxic constituents could affect assessment of biological exposure risks.

Short-term and potentially large variations in trace-element concentrations also can be caused by rainfall runoff that flushes trace elements from mine wastes into stream channels. This type of pulse event has been documented in mining areas where waste rock or mill tailings are exposed, or where historical floods have redistributed tailings along the flood plain (Lambing, 1991; Nimick and Moore, 1991; Smith and others, 1998). Because of the inherent difficulty in sampling short-lived and localized storm events, little quantitative information exists on the duration and magnitude of elevated trace-element concentrations that can occur in response to the overland flushing of mine waste. Tailings erosion and transport, however, can be an extremely important influence in mining-impacted watersheds, as this mechanism of metal delivery to the stream is presumed to be responsible for fishkills noted in other mining areas (Lambing, 1991; U.S. Environmental Protection Agency, 1999).

Hourly sampling was conducted at five sites in three tributary basins of the Boulder River watershed during August 1999 (fig. 1) to quantify short-term variation in trace-element concentrations associated with diel cycles. Dissolved zinc was chosen as the primary trace element for analysis because it typically is present at detectable concentrations in the tributary basins, is known to display diel cycles (Brick and Moore, 1996), and can be toxic to aquatic life. Although the study was not originally designed to sample rainstorm runoff, rainstorms over two of the three basins produced runoff during sampling that provided a unique opportunity to characterize an important hydrologic condition that occurs irregularly, is short-lived, and is logistically difficult to sample.

## Purpose and Scope

The original purpose of this investigation was to collect data on diel changes in trace-element concentrations during base flow at five sites in three small basins—Jack, Cataract, and High Ore Creeks—that drain abandoned mine lands in the Boulder River watershed study area (fig. 1). The intent was to utilize these data to define temporal patterns and quantify magnitudes of trace-element concentration changes. This information could help to resolve whether load variations determined from synoptic sampling represented source inputs or sampling artifacts. Samples were collected hourly over 1.5- to 2-day periods to document the changes in dissolved zinc concentrations during base-flow conditions. Samples from the High Ore Creek site also were analyzed for dissolved arsenic, copper, and manganese to examine if concentrations of other trace elements exhibited diel cycles. In addition, field parameters known to exhibit diel cycles in aquatic environments (streamflow, pH, dissolved oxygen, specific conductance, and water temperature) were measured hourly to identify associations with zinc concentrations that could be potentially useful for understanding the process or processes controlling diel variations.

During the collection of hourly samples in the Jack and Cataract Creek basins, localized rainstorms produced runoff that interrupted base flow. However, the hourly samples of runoff collected during and following these rainstorms provided data characterizing the variations of dissolved zinc concentrations in response to a short-duration storm. The investigation was thus effectively expanded to include an assessment of rainfall runoff over mine wastes. Consequently, this report documents short-term changes in zinc concentrations and related parameters resulting from two distinct processes.

## Methods

Automated pumping samplers were used to collect water-quality samples at hourly intervals at each site. The intake of each sampler was placed in a riffle near midstream where the stream was well mixed. Samples were processed within 4 hours of collection according to procedures described by Wilde and others (1998). Samples were filtered through a 0.1- $\mu\text{m}$  (micrometer) plate filter and acidified using ultrapure nitric acid. Field measurements of pH, dissolved oxygen, specific conductance, and water temperature were recorded hourly at each site with a multiparameter meter according to procedures described in Wagner and others (2000). At each site, the meter was submerged in the stream near the intake of the pumping sampler.

Several different methods were used for the measurement of streamflow during this study. Streamflow was determined hourly in High Ore Creek by tracer dilution methods using procedures described by Kimball (1997). Samples for trace-element analyses from High Ore Creek were collected

**Figure 1.** Location of study area and sampling sites. Site numbers are those assigned by Nimick and Cleasby (this volume). Altitude shown in feet.

upstream from the tracer-injection point and were unaffected by the chloride solution. At the other four sites, streamflow values were determined periodically either by current-meter measurements (Cataract and Jack Creek sites) or with a Parshall flume (Uncle Sam Gulch and Bullion Mine tributary sites).

Most samples were analyzed for dissolved zinc by the U.S. Geological Survey (USGS) National Water Quality Laboratory in Denver, Colo. Most samples from the High Ore Creek site also were analyzed by the USGS for other selected trace elements (arsenic, cadmium, copper, and manganese) and for chloride (to calculate hourly streamflow values). Dissolved trace elements were determined by inductively coupled plasma–mass spectrometry, and dissolved chloride was determined by ion chromatography. Analytical procedures are described in Garbarino and Taylor (1996) and Fishman (1993).

## Diel Variation of Trace-Element Concentrations during Base Flow

During sampling in the Jack and Cataract Creek basins, rainfall runoff prevented full characterization of diel cycles under base-flow conditions. No significant rainfall or overland runoff was observed during sampling in the High Ore Creek basin; consequently, data for this site represent the most complete description of the base-flow diel cycle of trace-element concentrations. Hourly data for High Ore Creek were examined to determine temporal patterns and the magnitude of dissolved trace-element concentration changes, with zinc being the primary element evaluated.

### High Ore Creek

The diel variation of dissolved zinc concentrations in High Ore Creek (site 56, fig. 1) over a 53-hour period during August 2–4, 1999, is shown at the bottom of figure 2. The variation over the approximately 2-day period was relatively consistent, displaying a distinct symmetry in both magnitude and timing during the daily rise and fall of concentrations. The difference between the minimum and maximum zinc concentrations was about 400  $\mu\text{g/L}$  during the period of sampling. The minimum concentrations were about 210  $\mu\text{g/L}$  and occurred in the early evening at about 1700 hours. The maximum concentrations also were similar on both days, ranging from about 580 to 630  $\mu\text{g/L}$ . The maximum concentrations represented about a three-fold increase over the minimum and lasted about 2 hours in the early morning shortly after sunrise (from about 0600 to 0800 hours). Concentrations increased relatively gradually on the rising limb, followed by a more rapid concentration decrease on the falling limb. The average rate of concentration change during the falling limb (about 45  $\mu\text{g/L/hour}$ ) was slightly greater than that during the rising limb (about 30  $\mu\text{g/L/hour}$ ).

**Figure 2.** Diel variation of dissolved (0.1- $\mu\text{m}$  filtration) arsenic, copper, manganese, and zinc concentrations in High Ore Creek (site 56), August 2–4, 1999.

In addition to zinc, diel variations of dissolved arsenic, copper, and manganese concentrations are shown in figure 2 to allow comparison of temporal patterns and magnitude of change. These data for base-flow conditions in High Ore Creek indicate that diel cycles exist to varying degrees for each of the four trace elements shown. In general, two patterns are evident: manganese and zinc display similar timing of concentration changes during the day, while arsenic and copper have nearly the opposite timing of concentration maxima and minima relative to zinc. Manganese is the most similar to zinc in the proportional magnitude of its diel

cycle. For example, the diel range of zinc concentrations was approximately three-fold (about 200 to 600  $\mu\text{g/L}$ ) and the maximum and minimum concentrations generally occurred at about 0700 and 1700 hours, respectively. Similarly, the diel range for manganese concentrations (35 to 87  $\mu\text{g/L}$  for the first-day cycle) was about 2.5-fold for most of the sampling period, although an anomalous increase in manganese concentrations during the last few hours of the second day may not be representative of the typical diel pattern. The maximum and minimum dissolved manganese concentrations occurred at about 0800 and 1800 hours, respectively. In contrast, the diel range for arsenic and copper concentrations was somewhat less than for manganese or zinc, varying only about 1.5-fold between the minimum and maximum concentrations. Concentrations of arsenic and copper also were substantially lower, with arsenic ranging from 22 to 33  $\mu\text{g/L}$  and copper ranging from about 3 to 4  $\mu\text{g/L}$ . The differences in timing of the diel concentration cycles for arsenic and copper relative to those for manganese and zinc indicate that either different processes are driving the concentration changes, or that the instream supply of arsenic and copper, possibly attached to colloids or metal-hydroxide coatings on streambed sediment, is more limited and cannot support a large shift in partitioning between the dissolved and particulate phases under the ambient physical and chemical conditions in the stream.

## Other Streams

Base-flow conditions at the other four sites (sites 17, 19, 43, and 44, fig. 1) lasted only for about the first 10 to 12 hours of hourly sampling before the onset of rainfall runoff (between about 1600 and 1800 hours on August 2 and 4). Zinc concentration data for these short pre-rainfall sampling periods generally follow the same pattern observed at High Ore Creek: maximum values occurred in early morning, followed by decreasing values through late morning and afternoon. The magnitude of the variations, however, was minor compared to that for High Ore Creek.

In the Jack Creek basin, the differences between the minimum and maximum zinc concentrations during the pre-rainfall period (about 0600 to 1800 hours on August 2) were about 250 to 300  $\mu\text{g/L}$  at both the Bullion Mine tributary (from 3,900 to 4,150  $\mu\text{g/L}$ ) and Jack Creek mainstem (from 722 to 1,010  $\mu\text{g/L}$ ). Although the magnitude of variation was similar at both sites, the pre-rainfall concentration difference represented only about a 6 percent change at the Bullion Mine tributary, but more than a 40 percent change at the Jack Creek site. The limited variability in diel zinc concentrations at the Bullion Mine tributary may be due to the low ambient pH (about 5.2 during base flow), which could prevent geochemical partitioning between the dissolved and particulate phases.

In the Cataract Creek basin, differences between the minimum and maximum concentrations during the pre-rainfall period (about 0700 to 1800 hours on August 4) were 660  $\mu\text{g/L}$  (from 4,330 to 4,990  $\mu\text{g/L}$ ) in Uncle Sam

Gulch and about 100  $\mu\text{g/L}$  (from 628 to 731  $\mu\text{g/L}$ ) in Cataract Creek. These concentration differences represent about a 15 percent variation at both sites.

Because the pre-rainfall data for the Jack and Cataract Creek basins span the period from about 0600 to 1800 hours, the full range of the zinc diel cycle likely was encompassed because that general time interval included the diel minimum and maximum values at High Ore Creek. If this assumption is correct, then the diel changes in zinc concentrations in the Jack and Cataract Creek basins are proportionally much less than the 3-fold change observed for High Ore Creek.

## Correlation of Zinc Concentrations with Field Parameters

The correlation of diel variations of dissolved zinc concentrations and selected field parameters in High Ore Creek (fig. 3) was examined to provide insight into possible causes of the diel zinc cycles. Field parameters such as streamflow, pH, dissolved oxygen, specific conductance, and water temperature are easily measured, are known to exhibit diel cycles, and might be associated with geochemical processes that control the diel zinc cycle. In addition, identification of strong correlations between field parameters and zinc concentrations could provide a basis for developing either mathematical methods or sampling strategies to minimize the effect of diel variations on data sets used to interpret trace-element sources, long-term trends, and biological risk.

The strength of relations was evaluated by the coefficient of determination ( $R^2$ ), which expresses the proportion of total variation in the dependent variable (Y) that is explained by regression with the independent variable (X). Also, the closeness in patterns of change and timing of maximum and minimum values was considered indicative of whether diel fluctuations in zinc concentrations have a strong likelihood of a direct geochemical association with the field parameter.

## Streamflow

Concurrent diel variations in streamflow and dissolved zinc concentration in High Ore Creek are shown in figure 3A. Streamflow during the 2-day period showed a nearly 1.5-fold diel variation, ranging from about 0.6 to 0.9  $\text{ft}^3/\text{s}$  (cubic feet per second). In many streams, flow increases commonly are associated with dilution and decreasing solute concentrations, but the timing of the diel streamflow variations in High Ore Creek relative to those of dissolved zinc concentrations does not support a dilution effect. Rather, the timing of peak dissolved zinc concentrations (around 0600 to 0800 hours) coincides with the rising limb of the diel flow increase.

The relation between streamflow and dissolved zinc concentration in High Ore Creek was weak ( $R^2 = 0.29$ ) and had a positive slope, indicating that dissolved zinc concentrations increase as flow increases. Dissolved metal concentrations that increase with flow have been observed in other streams

**Figure 3.** Diel variation and correlation of dissolved (0.1- $\mu\text{m}$  filtration) zinc concentrations in High Ore Creek (site 56), August 2–4, 1999, with selected field parameters. *A*, streamflow; *B*, pH; *C*, dissolved oxygen; *D*, specific conductance; *E*, water temperature.

that are contaminated with mine and mill wastes (J.H. Lambing, unpub. data, 2000). Such increases in dissolved zinc concentration may result from entrainment of zinc-enriched tailings during runoff, followed by dissolution of weakly sorbed particulate zinc to a soluble form. The diel sampling in High Ore Creek, however, was conducted during base flow. In

the absence of overland runoff to entrain zinc-enriched tailings, an instream source of zinc is more likely to be causing the diel cycle.

A possible flow-related explanation for a zinc diel cycle is associated with the ground water residing in the alluvium below and adjacent to the stream channel. If ground water

was enriched in dissolved zinc, then an instream zinc diel cycle could result as diel variations in evapotranspiration from the flood plain change the amount of ground water discharging to the stream throughout the day. For example, if ground-water discharge to the stream is greater at night because less ground water is discharged to the atmosphere by evaporation and transpiration, then the instream flow and concentration of dissolved zinc could simultaneously increase. The concurrent increase in streamflow and zinc concentration during an approximately 6-hour period from about midnight to 0600 hours (fig. 3A) may support this concept. However, the temporal patterns of streamflow and concentration are not sufficiently in unison to assume that ground-water inflow could be solely responsible for the zinc diel cycle. Also, the ground water was not sampled; therefore, the potential for zinc enrichment by ground water is only speculated.

## pH

Concurrent diel variations in pH and dissolved zinc concentration in High Ore Creek are shown in figure 3B. The minimum pH values generally are reached within a few hours after sunset (about 2000 hours), similar to when minimum values for streamflow are observed. Unlike streamflow, however, pH is maintained at a relatively constant value throughout the night. Near sunrise (about 0600 hours), pH begins to rise, almost simultaneously as zinc concentrations begin to fall. Values of pH reach a maximum around mid-afternoon, which corresponds well with minimum zinc concentrations. The increase in pH from the nighttime minimum was relatively minor in High Ore Creek, representing less than 0.3 of a pH unit (range of 8.08 to 8.34). The maximum pH value was maintained only for about 2–4 hours, unlike the nighttime minimum that was maintained for about 10–12 hours. Although the pH minimum was maintained as an extended plateau rather than continuing to decline, the time interval spanning the minimum pH values coincided fairly well with the interval of increasing zinc concentrations.

The relation between pH and dissolved zinc concentration was slightly stronger ( $R^2 = 0.45$ ) than that for streamflow and dissolved zinc, with a negative slope indicating that dissolved zinc concentrations increase as pH decreases. This inverse correlation is typical of the solubility exhibited by many metals. The lower pH during the night possibly could solubilize particulate zinc from the instream colloidal fraction or streambed sediment to achieve a cyclical nighttime increase. If this is the case, however, the increased zinc solubility is occurring over a very narrow range of pH values.

## Dissolved Oxygen

Concurrent diel variations in dissolved oxygen and dissolved zinc concentrations in High Ore Creek are shown in figure 3C. Dissolved oxygen concentrations varied by less than 2 mg/L (milligrams per liter), ranging from about 6.7

to 8.4 mg/L. The maximum dissolved oxygen concentration occurred around 0800 hours, while the minimum occurred near 1700 hours. The dissolved oxygen concentrations likely were responding primarily to water temperature because concentrations began dropping in mid-morning as the water warmed and oxygen solubility decreased. This pattern of decreasing dissolved oxygen concentrations during the day generally is the opposite of biologically productive streams with substantial photosynthetic activity. Metal concentrations in the stream probably inhibit aquatic plant growth, thereby suppressing photosynthetic oxygen production. The temporal patterns of dissolved oxygen and zinc concentrations had generally similar symmetry and their maximum and minimum concentrations coincided within 1 hour of each other.

The relation between dissolved oxygen and dissolved zinc concentrations in High Ore Creek was fairly strong ( $R^2 = 0.67$ ) and displayed a positive slope, indicating that dissolved zinc concentrations increase as dissolved oxygen concentrations increase. The strength of the relation and the relatively close match in diel variation indicate that dissolved oxygen concentration might be a useful surrogate for estimating diel cycles in zinc concentrations. However, the relation might have been merely coincidental because the oxygen variations were responding almost entirely to water temperature. In addition, the multiple biological and physical factors influencing dissolved oxygen concentrations may complicate straightforward interpretation of diel effects.

## Specific Conductance

Concurrent diel variations in specific conductance and dissolved zinc concentrations in High Ore Creek are shown in figure 3D. Specific conductance, which commonly correlates well with major-ion concentrations, was examined to indicate if a correlation also existed for trace concentrations typical of most metals. The maximum specific conductance values generally occurred within several hours of the maximum zinc concentrations, thereby indicating that major-ion solutes may respond to the same physical or geochemical process influencing zinc concentrations. The relation between specific conductance and dissolved zinc concentrations in High Ore Creek was moderately strong ( $R^2 = 0.55$ ) and had a positive slope, indicating that zinc concentrations increase as conductance increases. Specific conductance values generally increased through the night, which corresponds to the pattern observed for dissolved zinc concentrations and, to a lesser extent, for streamflow. However, the diel patterns for specific conductance, streamflow, and dissolved zinc concentrations in High Ore Creek are not sufficiently in unison to support the concept that constituent-enriched ground water flowing to the stream is primarily responsible for driving the diel concentration cycle.

An abrupt increase in specific conductance occurred during the second day of the sampling period from about 0500 to 0900 on August 4, followed by a rapid decrease for the next 4 hours until the end of sampling. These values appear to be anomalous relative to the preceding diel patterns. If

the values for the last 9 hours of sampling are omitted, the  $R^2$  for the regression relation between specific conductance and dissolved zinc concentrations increases to 0.75. Although this stronger correlation may indicate a more direct link between processes driving diel cycles in both major ions and dissolved zinc, the several-hour lag between conductance and zinc minima and maxima implies that other mechanisms may be exerting primary control over the diel zinc concentration cycle. Of note regarding the anomalously high conductance values during the last 9 hours of sampling is that a nearly identical pattern was observed for dissolved manganese (fig. 2). Other trace elements and field parameters did not display this anomalous pattern.

## Water Temperature

Concurrent diel variations in water temperature and dissolved zinc concentration in High Ore Creek are shown in figure 3E. The relation between water temperature and dissolved zinc concentrations in High Ore Creek was very strong ( $R^2 = 0.86$ ) and substantially better than the relation between zinc and any of the other field parameters. The negative slope of the relation indicates that dissolved zinc concentrations increase as water temperatures decrease. The timing of temperature maxima and zinc minima is nearly concurrent, which would be expected based on the strong inverse correlation. Maximum temperatures occurred in late afternoon, which closely matched the timing of minimum dissolved zinc concentrations (about 1700 hours). Similarly, minimum temperatures occurred in early morning within an hour or so of the maximum dissolved zinc concentrations (about 0700 hours).

A possible temperature-related explanation for a zinc diel cycle is geochemical adsorption-desorption reactions acting on zinc-enriched colloids or streambed sediments. Studies of solution equilibria using thermodynamic principles (Machesky, 1990; Barrow, 1992; Trivedi and Axe, 2000) indicate that cation adsorption onto particulate material increases as temperature increases, and decreases as the temperature decreases. Thus, during the night and early morning when water temperatures decrease, adsorption of divalent metals such as zinc would decrease, thereby resulting in higher dissolved zinc concentrations as the water cools. This pattern of increasing zinc concentration was observed in High Ore Creek throughout the night until shortly after sunrise: dissolved zinc concentrations reached a maximum in the early morning (0600 to 0800 hours) within an hour or so of the minimum water temperature (0700 to 0800 hours). As water temperature increased throughout the morning and afternoon, adsorption onto colloids or streambed sediment would increase and progressively remove zinc from solution, thereby causing a corresponding decrease in dissolved zinc concentration during the afternoon. This conceptual process was consistent with observed data, whereby dissolved zinc concentrations reached a minimum coincident with maximum water temperatures.

## Variation of Zinc Concentrations during Rainfall Runoff

Localized rainstorms over parts of the Boulder River watershed on August 2 and 4, 1999, created short-term overland runoff that affected streamflow conditions during the diel sampling investigation. As a result of increased flows, the base-flow diel cycle for dissolved zinc concentrations was obscured by both dilution effects and the inputs of additional zinc via runoff over wastes from inactive mines. Data from the hourly samples provide a temporally intensive characterization of changes in zinc concentrations over an approximately 1.5-day period in the Jack and Cataract Creek basins. The magnitude and duration of zinc concentration changes during rainfall runoff also may indicate how other metals associated with mine wastes or tailings might respond during short-term flushing events.

Rainfall volumes, intensity, and duration were not measured during the storms. However, changes in streamflow were periodically documented during the sampling period by stage readings and current-meter flow measurements. Because of the short period of runoff and the relatively minor increases in streamflow, the zinc loads derived from rainfall runoff were presumed to be small relative to loads transported by the much larger and sustained runoff during spring snowmelt. However, because instream dilution is minimal during low-flow conditions, increases in trace-element concentrations during rainfall runoff may be greater than those during either spring snowmelt runoff or base-flow diel cycles. Data from such a hydrologic condition, therefore, provide a valuable reference to short-term changes in biological exposure risks.

## Jack Creek Basin

In the Jack Creek basin, streamflows in Bullion Mine tributary and Jack Creek below Bullion Mine tributary (sites 17 and 19, fig. 1) were affected by rainfall runoff during the diel sampling period. Variations in dissolved zinc concentrations at both sites over a 36-hour period during August 2–3, 1999, are shown in figure 4.

At about 1800 hours on August 2, heavy rain began falling in the Jack Creek basin and lasted for about 4 hours. Within an hour after the start of the rainstorm, overland runoff was observed. The largest measured streamflow in Jack Creek during the sampling period was 2.22 ft<sup>3</sup>/s, but streamflow was estimated by stage readings to have increased 5-fold from about 1 to 5 ft<sup>3</sup>/s. Although flows were not measured during runoff in Bullion Mine tributary, overland runoff also was observed at this nearby site, presumably increasing flow in a manner similar to that of Jack Creek. The initial effect of this runoff was a rapid decrease of about 1,000 µg/L in dissolved zinc concentrations in Bullion Mine tributary during the first 2–3 hours of heavy rain (fig. 4). The zinc concentration also decreased rapidly by about 400 µg/L in Jack Creek,

**Figure 4.** Variation of dissolved (0.1- $\mu\text{m}$  filtration) zinc concentrations during rainfall runoff in Bullion Mine tributary (site 17) and Jack Creek below Bullion Mine tributary (site 19), August 2–3, 1999. Heavy rain began falling at about 1800 hours on August 2.

beginning about an hour after the decline began in the Bullion Mine tributary and continuing during the 2–3 hour period of initial rainfall runoff. The decreases in dissolved zinc concentrations at both sites were likely the result of dilution from overland runoff draining from upland headwater areas containing relatively few sources of waste rock or tailings.

After the initial 2–3 hours of runoff and concentration decreases at both sites, dissolved zinc concentrations increased rapidly over the following 1–2 hours, presumably resulting from dissolution of soluble zinc sulfate salts such as goslarite (Fey and Desborough, this volume, Chapter D4, fig. 3) from waste rock and tailings at the Bullion mine. At the Bullion Mine tributary, zinc concentrations increased by about 6,200  $\mu\text{g/L}$  (from 2,880 to 9,100  $\mu\text{g/L}$ ) during a 2-hour period. At Jack Creek, zinc concentrations increased by nearly 1,000  $\mu\text{g/L}$  (from 346  $\mu\text{g/L}$  to 1,320  $\mu\text{g/L}$ ) during a 1-hour period. Because the timing of both concentration peaks was nearly identical (fig. 4), inflow from the Bullion Mine tributary likely contributed most of the zinc to Jack Creek during this rainfall event. It is not known how far downstream the peak concentrations measured in the Jack Creek mainstem below Bullion Mine tributary were maintained until dilution from other tributaries or overland runoff from non-mined areas caused concentrations to decrease.

Dissolved zinc concentrations at both sites decreased from their peaks as sharply as they had risen. The temporal pattern of declining zinc concentrations was very similar at both sites, with concentrations decreasing for the next 4 hours to values similar to those observed during the initial periods of runoff (fig. 4). After reaching a post-peak minimum concentration at both sites at about 0300 hours on August 3, zinc concentrations gradually began increasing over the next several hours before stabilizing at near pre-rainfall values.

## Cataract Creek Basin

In the Cataract Creek basin, streamflows in Uncle Sam Gulch and Cataract Creek below Uncle Sam Gulch (sites 43 and 44, fig. 1) also were affected by rainfall runoff during the diel sampling period. Variations in dissolved zinc concentrations at both sites over a 35-hour period during August 4–5, 1999, are shown in figure 5.

Beginning at about 1800 hours on August 4, a gradual but steady increase in dissolved zinc concentrations began in Cataract Creek and lasted for about 6 hours. A light rain was falling at the time. During this same period, zinc concentrations increased and decreased irregularly in Uncle Sam Gulch, possibly indicating sporadic runoff volumes and accompanying dilution effects, or variable quality of runoff from different parts of the basin. A relatively large increase in dissolved zinc concentration occurred in Cataract Creek between 2400 and 0100 hours on August 5, but only a small increase occurred in Uncle Sam Gulch during this time. The concentration increases in Cataract Creek likely originated from sources upstream from Uncle Sam Gulch, such as the Morning Glory mine or Cataract mine and tailings (fig. 1).

Shortly after the onset of heavy rain during the night, zinc concentrations increased irregularly between about 2400 and 0500 hours at both sites on Uncle Sam Gulch and Cataract Creek. The sharpest increase occurred between 0300 and 0500 hours in Uncle Sam Gulch. Zinc concentrations during the 5-hour period increased by about 3,100  $\mu\text{g/L}$  (from 4,040 to 7,130  $\mu\text{g/L}$ ) in Uncle Sam Gulch and about 670  $\mu\text{g/L}$  (from 779 to 1,450  $\mu\text{g/L}$ ) in Cataract Creek, with concentrations at both sites peaking at the same time and at nearly identical proportions (nearly a 2-fold increase). The uniformity in timing and proportionality of concentration increases at the two sites strongly indicates that Uncle Sam Gulch was the primary source of zinc input to Cataract Creek during this runoff event.

**Figure 5.** Variation of dissolved (0.1- $\mu$ m filtration) zinc concentrations during rainfall runoff in Uncle Sam Gulch (site 43) and Cataract Creek below Uncle Sam Gulch (site 44), August 4–5, 1999. Rain began falling about 1800 hours on August 4.

It is not known how far downstream the peak concentration of dissolved zinc in Cataract Creek was maintained.

Dissolved zinc concentrations at both sites decreased from their peak concentrations as rapidly as they had risen. Within 3 hours of their peaks, concentrations in Cataract Creek and Uncle Sam Gulch decreased to levels similar to those measured during the pre-rainfall period. Concentrations continued to gradually decrease at both sites for several hours, eventually stabilizing within about 8–10 hours after the peak.

## Implications of Short-Term Variation in Trace-Element Concentrations

Efforts to characterize trace-element concentrations in streams draining abandoned mine lands typically rely upon data collected at widely dispersed locations and over a broad range of hydrologic conditions. These data are used to establish baseline conditions, indicate the locations of major sources of trace-element inputs, detect long-term trends for evaluating remediation effectiveness, evaluate potential risks to aquatic biota, and provide information on how streamflow conditions and season influence concentrations. But if short-term variability of metal or other constituent concentrations is substantial and persistent, interpretations of source inputs, trends, or biological exposure risks may be susceptible to error due to inadequate characterization by routine sampling strategies where samples are widely spaced in time. Large diel cycles in trace-element concentrations, and rapid concentration increases caused by rainfall runoff, pose difficulties in assessments of trace-element sources or long-term trends, and thereby produce uncertainty for resource managers attempting to prioritize areas for cleanup, design remedial treatments, or evaluate remediation effectiveness. The information obtained during these short-term sampling episodes in the Boulder

River watershed may not quantitatively relate to other similar sites, but the patterns of variation observed can provide an awareness of potential factors to consider when studies to characterize streams draining abandoned mine lands are being planned.

Diel cycles of zinc or other trace-element concentrations can complicate comparison of loads determined during synoptic sampling because of the difficulty in resolving whether load differences between successive sites are the result of actual inputs or simply an artifact of sampling time. Synoptic sampling to identify spatially discrete source areas (for example, Kimball and others, this volume, Chapter D6) commonly is conducted during base flow when a steady-state input of constituent loads is assumed. However, if the steady-state assumption is not met and concentrations at a site vary widely during the course of a day, then comparisons of load differences between sites may under- or over-estimate actual inputs if successive sites are sampled many hours apart and at different phases of a diel concentration cycle. Under this condition, interpretations of some trace-element sources could be invalidated. In High Ore Creek, the diel variation (fig. 2) was small for copper (about 1  $\mu$ g/L) and moderate for arsenic (about 10  $\mu$ g/L). Consequently, the effect on synoptic load calculations and source interpretations for these elements is relatively small. The larger diel variations for manganese (about 80  $\mu$ g/L) and zinc (about 400  $\mu$ g/L) could affect interpretations of synoptic loads and inputs along stream reaches. Therefore, unless the diel effect is accounted for by either design of a synoptic sampling schedule that minimizes time differences between successive sites, or by mathematical normalization of analytical results, the only stream reaches that can reliably be considered as a source of trace-element input are those where between-site concentration differences exceed the diel rate of change.

Similar to the effect on synoptic load determinations, evaluations of long-term trends at a site could be complicated

in streams having large diel variations if samples collected periodically over multiple years were obtained at different times of the day. The variable sampling times would result in different phases of the diel cycle being sampled and a potentially wide range of concentrations representing base-flow conditions. The wide range of time-dependent concentrations caused by the natural variability of diel concentration cycles could obscure the presence of an actual trend, or mistakenly indicate a trend where none exists.

If same-time sampling over multiple years is not practical, a possible approach to facilitate interpretation of diel variation is to develop a means to mathematically normalize ambient concentrations. Although water temperature may not be the sole, or even predominant, control on diel cycling of dissolved zinc concentrations, its strong correlation with dissolved zinc concentrations makes it a potentially good surrogate to normalize sample concentrations to an equivalent concentration at a standard reference temperature. Because concentrations of zinc can vary widely from site to site, a diel-adjustment method needs to be independent of the magnitude of concentration. Presumably, such a method would be based on a proportional rate of change of concentration relative to temperature or other surrogate parameters. With further study, mathematical-adjustment methods might be developed that are process-based and applicable to a wide range of stream conditions.

In terms of biological exposure, diel cycles of trace-element concentrations could have sustained but difficult-to-detect impacts on aquatic biota. A chronic stress conceivably could be imposed on aquatic biota if trace-element concentrations regularly exceeded aquatic-life standards, even if only for portions of each day. Characterization of short-lived exceedances may be difficult, however, using data obtained from routine sampling strategies that assume a discrete value measured in a sample represents a consistent level of exposure throughout the day.

A hypothetical example of the effect of diel zinc loading from High Ore Creek on dissolved zinc concentrations in the Boulder River during base flow is illustrated in figure 6. In this example, estimated diel variations of dissolved zinc concentrations in the Boulder River resulting solely from the inflow of High Ore Creek have been constructed from mass-balance calculations using the diel variations in zinc load from High Ore Creek and the instream flow and background zinc concentration in the Boulder River (Nimick and Cleasby, 2000). This estimate of the diel loading effect indicates a maximum increase of about 20  $\mu\text{g/L}$  (from about 10 to 30  $\mu\text{g/L}$ ) of dissolved zinc in the Boulder River resulting from the inflow of this one tributary. Although this level of increase is not sufficient to cause exceedances of aquatic-life criteria for zinc, similar diel effects from loading of other trace elements, cumulative diel effects from multiple tributaries draining abandoned mine lands, or more substantial loading effects from storm runoff during low flow could cause receiving streams and their biota to be adversely impacted on short-term time scales that are difficult to document.

Data from the sampling of rainfall runoff provide clear evidence that runoff from waste rock or tailings into streams can result in rapid and large increases of dissolved zinc concentrations that are sufficient to greatly increase biological risk in the vicinity of source areas. The sharp increases noted for dissolved zinc presumably could occur for other trace elements that are prevalent in mine wastes of the Boulder River watershed. This local increase is likely maintained for some distance downstream, although the magnitude and spatial extent have not been quantified. Sampling such episodes of trace-element input to quantify the magnitude, spatial extent, and duration of biological risk can be very difficult logistically due to the short-lived and localized nature of storm runoff. Opportunistic sampling such as occurred in this study, or the use of automated pumping samplers triggered by a continuously monitored surrogate, may be the only feasible means to

**Figure 6.** Hypothetical diel variation of dissolved (0.1- $\mu\text{m}$  filtration) zinc concentrations in Boulder River resulting from inflow of High Ore Creek.

characterize the site-specific responses to the flushing of trace elements from abandoned mine lands into streams.

Whether the cause of short-term variation in trace-element concentrations is a diel cycle or localized rainfall runoff, the downstream cumulative effect is of concern. Depending on the magnitude of loads delivered and the dilution capacity of the receiving stream, cyclical diel peak loads in tributaries or the flushing of waste rock and tailings by rainfall runoff may sufficiently impact the chemistry of both local and more distant stream reaches to temporarily exceed thresholds for biological impairment. The short-term variation of zinc concentrations may not have much practical consequence for evaluating biological risk in those tributaries where aquatic-life criteria for acute toxicity are consistently exceeded. But inflows from such impacted tributaries may have pronounced effects downstream in Basin Creek or the Boulder River mainstem, both of which support a trout fishery (Farag and others, this volume). Biological risks, including possible lethality, would be especially pronounced for the pulse of trace elements delivered by rainfall runoff during low flows when concentrations increase to a greater extent and more rapidly than from the diel cycle.

## Summary

Variations in trace-element concentrations on a 24-hour (diel) basis in streams draining historical mining areas can, if sufficiently large and persistent, affect interpretations of trace-element sources, long-term trends, and biological risk. In this study, hourly samples were collected at five sites in August 1999 to quantify short-term variation of dissolved trace-element concentrations associated with base-flow diel cycles in three small basins that drain abandoned mine lands in the Boulder River watershed. The zinc diel cycle in High Ore Creek over a 53-hour period during base flow was relatively consistent, with zinc concentrations varying by about 400  $\mu\text{g/L}$  between the maximum and minimum. Maximum concentrations (about 580 to 630  $\mu\text{g/L}$ ) occurred shortly after sunrise (between 0600 to 0800 hours) and represented about a three-fold increase over the minimum concentration (about 210  $\mu\text{g/L}$ ), which occurred in the early evening at about 1700 hours. The maximum rate of zinc concentration change was about 45  $\mu\text{g/L/hour}$  on the falling limb of the diel cycle. At High Ore Creek, samples also were analyzed for dissolved arsenic, copper, and manganese, all of which exhibited diel cycles to varying degrees. The manganese cycle was the most similar to zinc in both symmetry and proportionality of concentration differences (about a 2.5-fold range in concentration). The diel cycles for arsenic and copper were proportionally smaller (about a 1.5-fold range in concentration), and the timings of concentration minima and maxima were nearly opposite to those for zinc and manganese.

Selected field parameters (streamflow, pH, dissolved oxygen, specific conductance, and water temperature) also

were measured hourly to identify correlations that might provide insight into possible geochemical associations with the zinc diel cycle. Zinc concentrations generally increased as streamflow increased; therefore, dilution was not indicated to be the cause of the diel cycle. An inverse correlation between pH and dissolved zinc concentrations exhibited fairly good concurrence in the timing of maxima and minima, possibly indicating a geochemical association. The correlation between water temperature and dissolved zinc concentration was stronger than that observed for any of the other field parameters; dissolved zinc concentrations increased as water temperatures decreased. The inverse symmetry of diel variations for dissolved zinc concentrations and water temperature coincided closely in time. This observation corresponds well to solution equilibria using thermodynamic principles, which indicates that zinc can undergo adsorption-desorption reactions with particulate material (colloids and streambed sediment) as water temperature changes. With further study, it might be possible to utilize one or more field parameters as surrogates to normalize zinc concentrations to minimize the effect of diel variation on data sets used to interpret trace-element sources, long-term trends, and biological risk.

During the diel sampling period, rainstorms over the Jack and Cataract Creek basins produced runoff that obscured the base-flow diel cycles but provided a unique opportunity to document zinc variations during rainfall runoff. Rapid increases in dissolved zinc concentrations over 1–5 hour intervals ranged from about 670  $\mu\text{g/L}$  in Cataract Creek below Uncle Sam Gulch to about 6,200  $\mu\text{g/L}$  in Bullion Mine tributary of the Jack Creek basin. Data from this sampling provide clear evidence that runoff from waste rock or tailings into streams can result in rapid and large increases of dissolved trace-element concentrations that are sufficient to increase the potential for biological risk in the vicinity of source areas.

Whether the cause of short-term variation of instream trace-element concentrations is a diel cycle or localized rainfall runoff, data reported herein show that the cumulative effect of trace-element loading from mining-affected tributaries on downstream reaches is of concern. Depending on the magnitude of loads delivered and the dilution capacity of receiving streams, impacts to water quality may be sufficient to exceed thresholds for biological impairment or lethality, both locally and for extended distances downstream from the trace-element source.

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