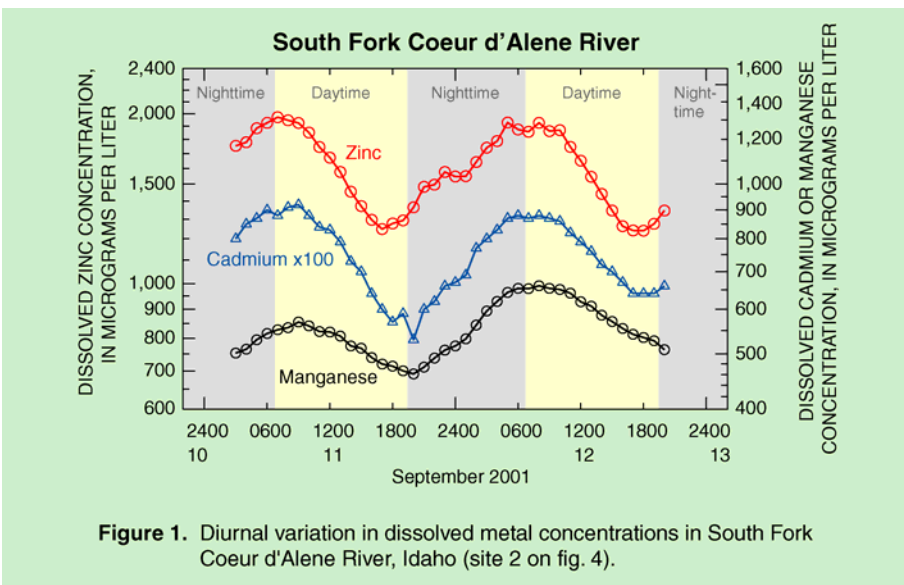


Diurnal Variation in Trace-Metal Concentrations in Streams

Assessing concentrations of trace metals in streams is found to be significantly more complex than previously thought. New research indicates that concentrations of metals dissolved in stream water vary by time of day.

Trace metals in streams can be toxic to fish and aquatic insects. Therefore, sampling streams for metals is an important aspect of water-quality monitoring. In the past, scientists assumed that a stream water sample collected at any time of the day would provide an accurate assessment of metal concentrations on that day assuming streamflow was relatively constant. Recent studies, however, have shown that dissolved concentrations of some trace metals exhibit substantial and consistent variation throughout the day (fig. 1). The magnitude and widespread occurrence of these diurnal (24-hour) concentration patterns, or cycles, was unexpected. This discovery of the consistent occurrence of diurnal metal cycles has significant implications for how we study and monitor the environment.



Scientists and government agencies will need to consider diurnal metal cycles to ensure accurate assessment of metal concentrations in streams.

DIURNAL METAL CYCLES

Daily variations in dissolved metal concentrations are shown in figure 1 for the South Fork Coeur d'Alene River in Idaho. These variations are examples of diurnal metal cycles. Two important characteristics of diurnal metal cycles are the time of day when the minimum and maximum concentrations occur and the magnitude of the change in metal concentration. In the South Fork, the timing of the diurnal cycles for cadmium, manganese, and zinc was similar. Concentrations of these metals increased during the night, reaching the highest values shortly after sunrise. Concentrations then decreased during the late morning and early afternoon, reaching the lowest values during mid to late afternoon.



South Fork Coeur d'Alene River, Idaho (site 2 on fig. 4)

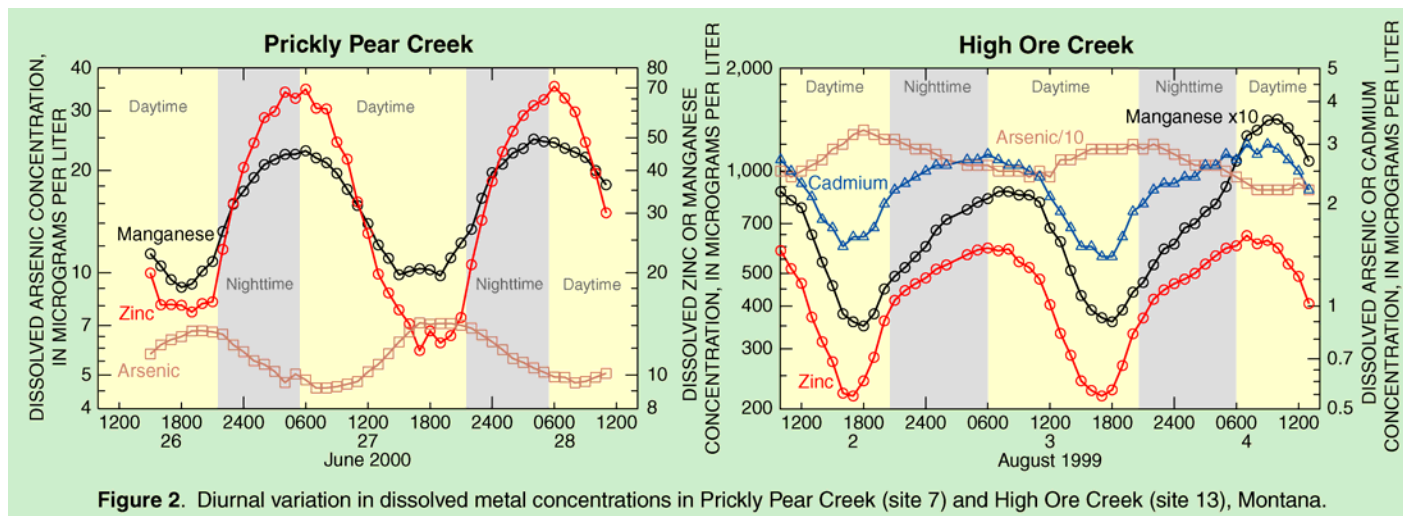


Figure 2. Diurnal variation in dissolved metal concentrations in Prickly Pear Creek (site 7) and High Ore Creek (site 13), Montana.

Diurnal metal cycles for Prickly Pear and High Ore Creeks in Montana are shown in figure 2. Note that the timing of diurnal cadmium, manganese, and zinc cycles in these streams was similar to the cycles for these metals in the South Fork Coeur d'Alene River (fig. 1). However, the timing of diurnal arsenic cycles was the opposite, with maximum concentrations in the late afternoon and minimum concentrations in the early morning.

The potential magnitude of diurnal metal cycles is shown by the data for Prickly Pear and High Ore Creeks (fig. 2). Diurnal cycles for zinc were the largest, with concentrations changing as much as 500 percent in Prickly Pear Creek. Cadmium and manganese cycles were intermediate, with changes as much as 120 and 290 percent, respectively, in High Ore Creek. Diurnal variations in arsenic concentrations (as much as 54 percent in Prickly Pear Creek) were proportionally much less than the variations for cadmium, manganese, and zinc.

Diurnal metal cycles occur over a wide range of concentration levels. For instance, diurnal zinc cycles were found at concentrations greater than 1,000 $\mu\text{g/L}$ in the South Fork Coeur d'Alene River (fig. 1)

and at concentrations less than 80 $\mu\text{g/L}$ in Prickly Pear Creek (fig. 2). Units of micrograms per liter ($\mu\text{g/L}$) are equivalent to parts per billion.

Trace-metal concentrations in streams exhibit diurnal cycles routinely and regularly. For example, during diurnal sampling episodes in 1995 and 1997 on High Ore Creek, dissolved zinc concentrations were relatively high (fig. 3). Cleanup efforts conducted upstream at an historical mine site after the 1997 sampling reduced the amount of zinc entering the stream, and zinc concentrations were lower during samplings in 1999-2001. These data show that the diurnal zinc cycle persisted and that the timing remained the same, even though the general concentration level changed substantially during the 6-year period.

Data on diurnal metal cycles for 13 streams in Montana and northern Idaho (fig. 4) are presented by Nimick and others (2003). The data document and confirm the widespread occurrence of diurnal metal cycles. The streams had gravel beds and were typical of mountain headwater streams in the northern Rocky Mountains. The streams varied in size, with the smallest having streamflow of about 0.5 cubic feet per second (ft^3/s) and the largest having streamflow of 270 ft^3/s at the time of sampling. One aspect common to diurnal metal cycles is that they occur in streams that have neutral to slightly alkaline pH, which is typical of most streams in the Nation. These types of diurnal metal cycles have not been observed in acidic streams more directly affected by mine drainage.

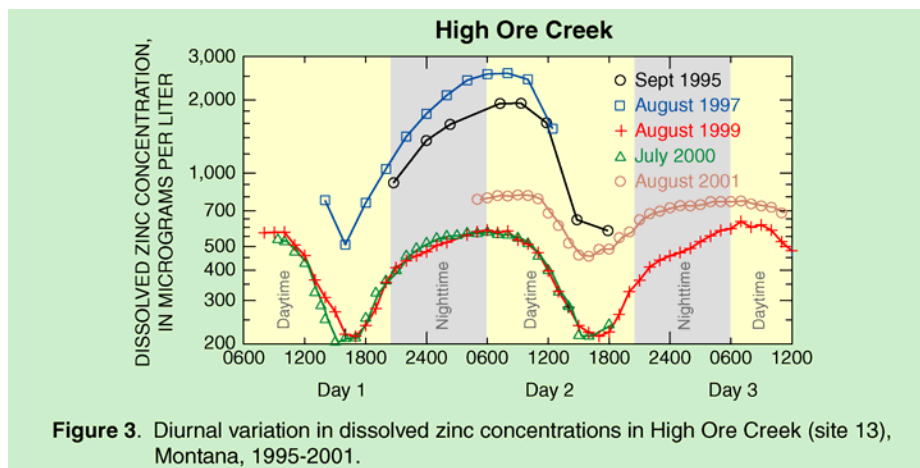


Figure 3. Diurnal variation in dissolved zinc concentrations in High Ore Creek (site 13), Montana, 1995-2001.

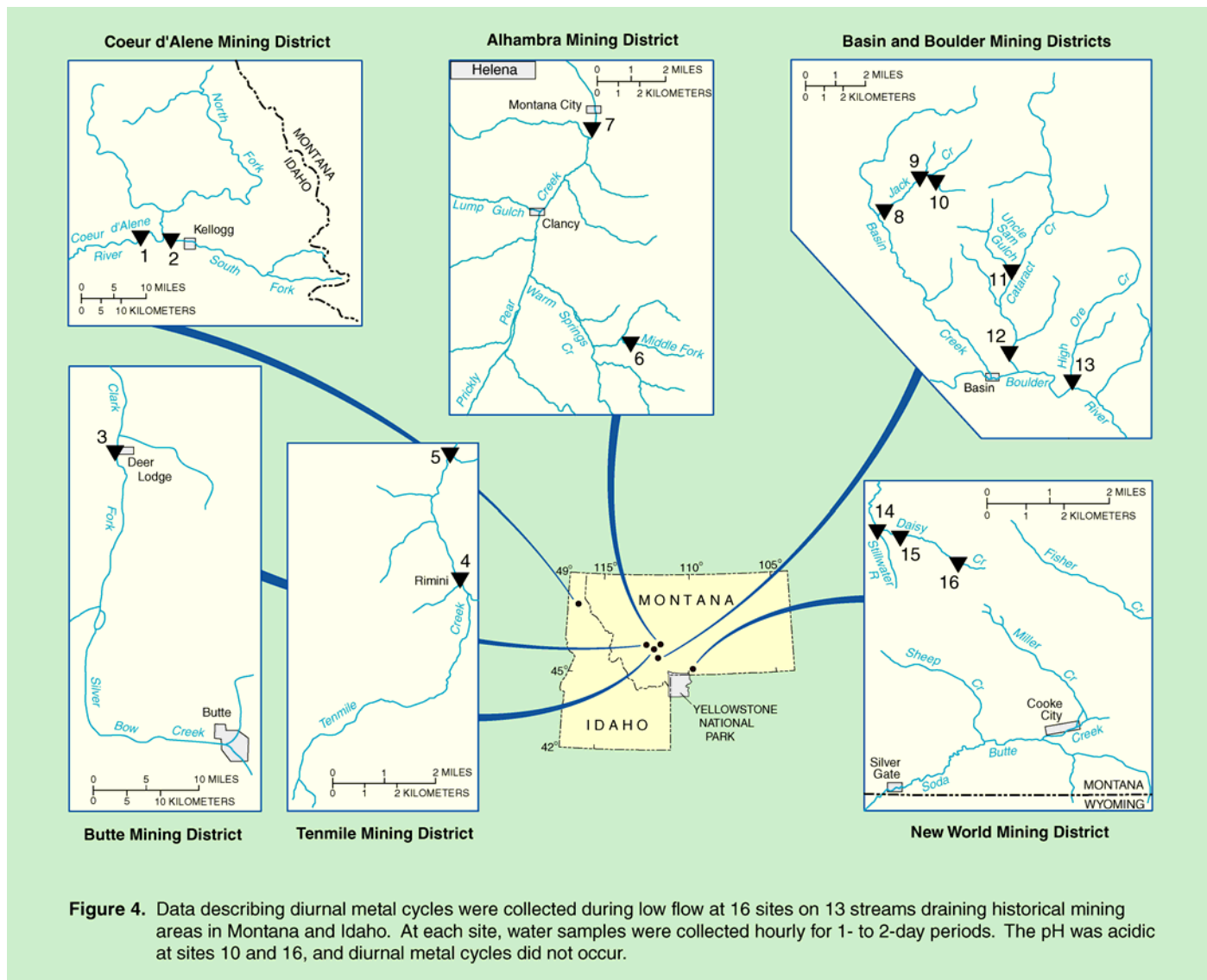


Figure 4. Data describing diurnal metal cycles were collected during low flow at 16 sites on 13 streams draining historical mining areas in Montana and Idaho. At each site, water samples were collected hourly for 1- to 2-day periods. The pH was acidic at sites 10 and 16, and diurnal metal cycles did not occur.

Diurnal metal cycles have previously been reported in a few instances. Diurnal cycles in dissolved arsenic concentrations were measured in Whitewood Creek, South Dakota (Fuller and Davis, 1989), and in the Madison and Missouri Rivers, Montana (Nimick and others, 1998). Bourg and Bertin (1996) and Brick and Moore (1996) were the first to document diurnal zinc cycles.

IMPLICATIONS

Water-quality data commonly are collected to characterize metal concentrations in streams. These data are used to establish baseline environmental conditions, indicate

the locations of important metal sources, plan and evaluate cleanup of contaminated sites, detect long-term trends in metal concentrations, and evaluate potential risks to fish and other aquatic organisms. However, if diurnal variability of metal concentrations is substantial and persistent, such evaluations likely are, at least, much less certain than previously thought and, at worst, potentially misleading or wrong. In the future, the implications of diurnal metal cycles will be an important consideration when designing plans for water-quality sampling and evaluating historical data on metal concentrations.



Collecting water-quality samples in Prickly Pear Creek, Montana (near site 7 on fig. 4)

What Causes Diurnal Metal Cycles?

A number of physical, chemical, and biological mechanisms potentially can explain diurnal cycles in dissolved metal concentrations. These mechanisms include:

- Diurnal cycles of sorption of metals to the surfaces of streambed material
- Diurnal cycles of formation and dissolution of minerals containing metals
- Diurnal cycles of uptake of metals by growing aquatic plants
- Diurnal variation of the input of metals from an upstream source
- Diurnal changes of geochemical conditions within the streambed
- Diurnal variation of streamflow

Sorption best explains diurnal metal cycles for two reasons. First, it explains the concurrent timing of the high and low dissolved metal concentrations found daily in streams (fig. 1). Second, it is the only mechanism that explains the opposite timing of the arsenic concentration cycles relative to the concentration cycles of the other metals (fig. 2).

Sorption is a chemical reaction in which metals are transferred between stream water and the surfaces of streambed materials, such as rocks and aquatic plants. During desorption, metals are detached from streambed materials and added to stream water, thereby increasing dissolved metal concentrations in stream water. During adsorption, metals are transferred from stream water to streambed materials, thereby decreasing dissolved metal concentrations.

Sorption is affected by the temperature and pH of stream water. Water temperature and pH commonly increase in streams during the day and decrease during the night in response to the daily cycles of daylight and darkness. These changes in temperature and pH are key factors in determining the amount of each metal that is adsorbed or desorbed.

Sorption of a specific metal ion is affected by its charge. Arsenic ions are negatively charged whereas cadmium, manganese, and zinc ions are positively charged. Therefore, arsenic desorbs when the other metals adsorb. This opposite behavior explains the opposite timing of the diurnal arsenic cycles relative to cadmium, manganese, and zinc cycles (fig. 2).

This Fact Sheet was prepared by David A. Nimick and is based on the journal article:

Nimick, D.A., Gammons, C.H., Cleasby, T.E., Madison, J.P., Skaar, Don, and Brick, C.M., 2003, Diel cycles in dissolved metal concentrations in streams—Occurrence and possible causes: *Water Resources Research*, v. 39, no. 9, 1247, doi:10.1029/2002WR001571.

Suggestions for Additional Information:

Bourg, A.C.M., and Bertin, Clotilde, 1996, Diurnal variations in the water chemistry of a river contaminated by heavy metals—Natural biological cycling and anthropic influence: *Water, Air, and Soil Pollution*, v. 86, p. 101-116.

Brick, C.M., and Moore, J.N., 1996, Diel variation of trace metals in the upper Clark Fork River, Montana: *Environmental Science and Technology*, v. 30, p. 1953-1960.

Fuller, C.C., and Davis, J.A., 1989, Influence of coupling of sorption and photosynthetic processes on trace element cycles in natural waters: *Nature*, v. 340, p. 52-54.

Nimick, D.A., Moore, J.N., Dalby, C.E., and Savka, M.W., 1998, The fate of geothermal arsenic in the Madison and Missouri Rivers, Montana and Wyoming: *Water Resources Research*, v. 34, p. 3051-3067.

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