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Diel cycles in dissolved metal concentrations in streams: Occurrence and possible causes

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[1] Substantial diel (24-hour) cycles in dissolved (0.1-μm filtration) metal concentrations were observed during low flow for 18 sampling episodes at 14 sites on 12 neutral and alkaline streams draining historical mining areas in Montana and Idaho. At some sites, concentrations of Cd, Mn, Ni, and Zn increased as much as 119, 306, 167, and 500%, respectively, from afternoon minimum values to maximum values shortly after sunrise. Arsenic concentrations exhibited the inverse temporal pattern with increases of up to 54%. Variations in Cu concentrations were small and inconsistent. Diel metal cycles are widespread and persistent, occur over a wide range of metal concentrations, and likely are caused primarily by instream geochemical processes. Adsorption is the only process that can explain the inverse temporal patterns of As and the divalent metals. Diel metal cycles have important implications for many types of water-quality studies and for understanding trace-metal mobility. *INDEX TERMS:* 1065 Geochemistry: Trace elements (3670); 1045 Geochemistry: Low-temperature geochemistry; 1871 Hydrology: Surface water quality; *KEYWORDS:* arsenic, cadmium, manganese, zinc, sorption, Montana

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1. Introduction

[2] Diel (24-hour) cycles in pH, dissolved oxygen, and water temperature commonly occur in rivers and streams in response to daily cycles of photosynthesis and respiration, as well as daily changes in weather. Diel changes in concentrations of trace metals, however, have been reported only rarely. Therefore scientists generally have not looked for diel concentration cycles in streams and historically have assumed that a properly collected water sample provides an accurate assessment of constituent concentrations on a given day, assuming stable hydrologic conditions. An increasing body of evidence, however, indicates that the concentration of many metals in streams with neutral to alkaline pH can change substantially during a 24-hour period irrespective of changes in streamflow and whether the ambient concentration of the metal is high or low. These diel cycles are robust and reproducible, and have been documented in streams in different geologic terranes. Diel concentration cycles have an important bearing on our understanding of the mobility of trace metals in watersheds, how we collect and interpret water-quality data, and how cyclical variation in metal concentrations may affect aquatic organisms.

[3] Diel cycles of metal concentrations in streams have been reported sporadically during the last 15 years. *McKnight et al.* [1988] and *Sullivan et al.* [1998] reported diel fluctuations of as much as 120% in dissolved Fe concentrations in small, acidic (pH less than 5.9) streams affected by mine drainage in Colorado. These cycles, driven by daytime photoreduction of hydrous Fe oxides, had the highest dissolved Fe concentrations in the afternoon. *Fuller and Davis* [1989] documented diel changes in dissolved As concentrations of about 40% at two sites on Whitewood Creek, an alkaline stream in South Dakota affected by inflow of metal-rich groundwater derived from fluvial tailings deposits. These As cycles were attributed to diel shifts in adsorption/desorption equilibria in response to photosynthesis-induced diel cycles in pH. *Nimick et al.* [1998] documented smaller diel cycles (changes of less than 20%) of naturally occurring As in the Madison and Missouri Rivers downstream from the geothermal As sources in Yellowstone National Park. The highest concentrations of dissolved As in Whitewood Creek and the Madison and Missouri Rivers generally occurred in the late afternoon, 1 to 3 hours after pH values had peaked. *Brick and Moore* [1996] and *Bourg and Bertin* [1996] were the first to document that divalent metals, such as Zn, that are toxic to aquatic life at low concentrations can exhibit diel cycles in streams with alkaline pH. Their work showed that concentrations of dissolved Mn and Zn in the Clark Fork at Deer Lodge, Montana, and dissolved Zn in the Lot River in southern France exhibited diel cycles, with highest concentrations in the early morning. More recently, *Scott et al* [2002] documented diel Mn cycles in Lake Fork Creek, Colorado.

[4] The purpose of this paper is twofold. First, we report on our investigations of the occurrence of diel cycles. Field data collected during 1994–2001 are presented to demon-

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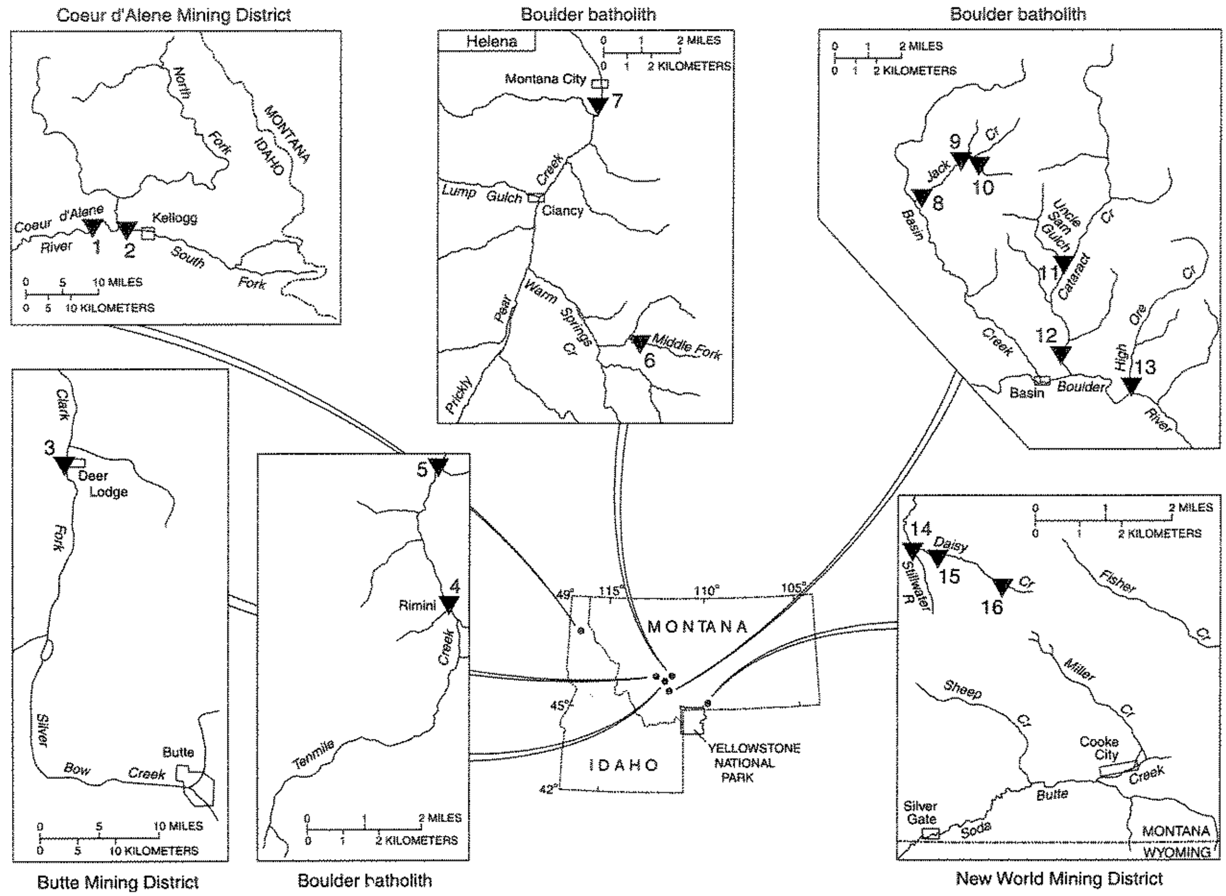

Figure 1. Location of diel sampling sites, Montana and Idaho.

strate that diel cycles of dissolved metal concentrations are much more common and widespread than previously recognized. Results are presented for As, Cd, Cu, Mn, Ni, and Zn for 20 diel sampling episodes at 16 sites on 13 streams draining historical mining areas in Montana and Idaho (Figure 1). Our second purpose is to outline and review possible causes of these diel metal cycles.

2. Study Areas

[5] Data describing diel metal cycles during low-flow conditions are presented for streams draining four historical mining areas in Montana and Idaho (Table 1). The South Fork and main stem of the Coeur d'Alene River in northern Idaho drain the Coeur d'Alene mining district, where Pb-Zn-Ag veins in Precambrian quartzite and argillite were mined for more than a century [*Fryklund*, 1964]. Site 2 is at the downstream end of the mining district at the mouth of the South Fork. Site 1 on the Coeur d'Alene River is about 9 river kilometers downstream from site 2. Zn is the metal of primary concern for aquatic toxicity in both rivers [*Paulson*, 1996].

[6] The Clark Fork of the Columbia River in southwestern Montana drains the Butte mining district, where porphyry Cu deposits have been mined since the mid-1800s. At the sampling site (site 3) near Deer Lodge, Cu is the metal of primary concern for aquatic toxicity, but Mn and Zn concentrations also are elevated [*Brick and Moore*, 1996]. Floodplain tailings deposits eroded from stream banks are the main source of the Cu in the Clark Fork [*Smith et al.*, 1998].

[7] Much of the data presented here are for streams (sites 4–13) draining the east and north sides of the Boulder batholith, which extends from Helena to Butte in southwestern Montana. Quartz veins were mined for Cu, Pb, Zn, Ag, and Au during the late 1800s [*Roby et al.*, 1960], and high concentrations of metals are found in these watersheds. These streams have similar chemistry, which is characterized by low hardness, neutral to alkaline pH, and concentrations of Cd, Cu, and Zn that are elevated relative to aquatic-life standards [*Klein et al.*, 2001; *Cleasby and Nimick*, 2002; *Farag et al.*, 2003].

[8] Daisy Creek and the Stillwater River in south-central Montana drain the New World mining district (Figure 1), where intrusion breccias as well as skarn and replacement deposits hosted in limestone were mined for Ag, Au, and Cu from the late 1800s to 1953 [*Elliot et al.*, 1992]. Acid-rock drainage from mine wastes and unmined pyritic rock causes low pH and elevated metal concentrations in upper Daisy Creek (site 16), but tributary inflow produces neutral pH and lower dissolved metal concentrations in lower Daisy Creek (site 15) and the Stillwater River (site 14). Cu is the trace metal with the highest concentrations, but concentrations of Cd, Mn, and Zn also are elevated [*Nimick and Cleasby*, 2001].

Table 1. Sampling Sites and Maximum Diel Range of Streamflow, pH, and Dissolved Metal Concentrations

Stream	Site Number (Figure 1)	Drainage Area, km^2	USGS Gaging Station Number	Sampling Dates	Time Between Samples, hours	Diel Range							
						Streamflow, m^3/s	pH	Temperature, °C	As, μg/L	Cd, μg/L	Cu, μg/L	Mn, μg/L	Zn, μg/L
						Coeur D'Alene Mining District , Idaho							
Coeur d'Alene River	1	3,170	12413500	11–12 Sept. 2001	1–3	7.69	7.15–7.27	14.1–15.3	–[a]	2.2–2.8	–	85.4–98.1	477–533
South Fork Coeur d'Alene River	2	774	12413470	11–12 Sept. 2001	1	2.21–2.38	6.88–7.33	11.6–17.4	–	5.3–9.2	–	461–661	1,250–1,970
						Butte Mining District, Montana							
Clark Fork[b]	3	2,370	12324200	21–23 July 1994	1	1.19–1.53	8.28–8.72	15.1–26.5	–	–	7.2–11	40.8–98.7	5.6–14.6
						Boulder Batholith, Montana							
Tenmile Creek near Rimini	4	80.9	06062500	13–14 Sept. 2000	2	0.010[c]	7.01–7.63	8.6–19.2	–	–	–	–	120–240
Tenmile Creek at Rimini	5	59.0	–	14–15 Sept. 2000	2	<0.008[c]	6.62–6.73	9.0–20.4	–	–	–	–	1,640–2,710
Middle Fork Warm Springs Creek	6	8.7	–	26–27 June 2001	1	0.031–0.034	7.76–7.97	10.6–16.7	25.5–29.2	0.54–0.75	–	–	145–231
Prickly Pear Creek	7	497	06061500	26–28 June 2000	1	0.350–0.400	8.26–9.05	10.4–21.9	4.6–7.1	–	–	19.6–49.5	11.8–70.8
Jack Creek at mouth	8	22.1	–	12–14 July 2000	1	–	7.63–7.79	10.0–18.1	–	2.0–2.8	–	51.8–63.2	205–327
Jack Creek below Bullion mine	9	5.5	–	2 Aug. 1999	1	0.043[c]	7.31–7.45	8.3–15.8	–	–	–	–	684–1,010
Bullion Mine tributary	10	3.1	–	2 Aug. 1999	1	0.007[c]	5.18–5.27	–	–	–	–	–	3,880–4,150
Uncle Sam Gulch	11	7.9	–	4 Aug. 1999	1–3	0.018[c]	7.3[c]	–	–	–	–	–	4,040–4,940
Cataract Creek	12	74.1	–	10–12 July 2000	1	0.138–0.194	7.82–8.07	11.0–20.2	–	3.9–6.8	16.0–17.5	28.2–36.9	263–401
High Ore Creek	13	22.9	–	1–2 Sept. 1995	2–5	–	–	9.5–17.9	21.1–26.5	–	–	–	580–1,930
High Ore Creek	13	22.9	–	26–27 Aug. 1997	2	–	–	10.8–18.5	13.1–16.8	3.2–7.0	2.3–2.8	890–1,500	509–2,570
High Ore Creek	13	22.9	–	2–4 Aug. 1999	1	0.016–0.023	8.12–8.34	11.5–21.0	22–33	1.4–3.0	3.0–4.3	36–142	214–634
High Ore Creek	13	22.9	–	24–25 July 2000	1	0.005–0.010	8.38–8.71	9.8–22.1	38.5–44.0	1.5–2.9	3.3–4.2	28.2–57.6	202–572
High Ore Creek	13	22.9	–	22–23 Aug. 2001	1	0.006–0.011	8.18–8.36	10.0–20.2	30.6–36.6	2.3–3.9	–	36.0–60.6	456–814
						New World Mining District, Montana							
Stillwater River	14	11.9	–	25–27 Aug. 1999	3–6	0.155–0.228	8.1[c]	–	–	–	17–24	60.2–92.7	2.2–9.5
Lower Daisy Creek	15	4.1	–	25–27 Aug. 1999	1–4	0.031–0.040	7.49–7.83	6.9–17.3	–	–	34.3–55.4	477–609	45–112
Upper Daisy Creek	16	0.73	–	25–26 Aug. 1999	1–14	0.010–0.012	3.53–3.69	–	–	–	34–55	–	501–543

[a] No data.

[b] Previously published by *Brick and Moore* [1996].

[c] Approximate value; diel data not available.

[9] All streams sampled had gravel beds and were typical of mountain headwater streams in the northern Rocky Mountains. Hydrous Mn and Fe oxide coatings were visible on streambed material at all sites. Concentrations of metals in streambed sediment at or near all sites were elevated owing to drainage from upstream historical mining areas [*Gurrieri*, 1998; *Fey et al.*, 1999; *Klein et al.*, 2001; *Beckwith*, 2002; *Dodge et al.*, 2002]. Riparian vegetation typically consisted of grasses and shrubs (such as willows). Streams varied in size. The smallest streams were Bullion Mine tributary (site 10) and upper Daisy Creek (site 16), where streamflow ranged from 0.007 to 0.012 m^3/s. These two streams were the only acidic (pH less than 5.4) streams sampled (Table 1). The largest stream was the Coeur d'Alene River (site 1), where streamflow during diel sampling was 7.69 m^3/s (Table 1). All streams (except High Ore Creek) were gaining streams, with shallow groundwater discharging to the stream. This assessment was based on previous synoptic-streamflow surveys as well as the topographic setting of each site within these mountain headwater areas. High Ore Creek for at least 1 km upstream from site 13 was a losing stream based on synoptic streamflow measurements and the downward head gradient measured in minipiezometers installed in the streambed.

3. Methods

[10] Methods of collection, processing, and analysis of water samples varied. Samples typically were collected hourly during each diel sampling episode, although samples were separated by as much as 2–14 hours at some sites. The duration of sampling episodes ranged from 12 to 58 hours, with 11 of the 20 sampling episodes lasting at least 36 hours.

[11] Procedures for samples collected from the Clark Fork (site 3) were described by *Brick and Moore* [1996]. Samples from High Ore Creek (site 13) were collected in 1995 and 1997 by the Montana Bureau of Mines and Geology (MBMG).

[12] The U.S. Geological Survey (USGS) collected samples at all sites sampled during 1999–2001 except sites 4 and 5 on Tenmile Creek, where samples were collected by Montana Fish, Wildlife and Parks. Automatic pumping samplers were used to collect samples during this period. All hoses and polyethylene collection bottles used with the automatic sampler were cleaned and acid rinsed between sample sites. Hoses and bottles were rinsed with stream water before sample collection. The intake for the automatic sampler was positioned 5–15 cm above the streambed in a riffle where the stream velocity was sufficient to ensure flushing of rinse water expelled by the sampler. Collection bottles were removed from the automatic sampler to a field laboratory, where they were filtered through 0.1-μm capsule or plate filters and acidified with ultrapure nitric acid.

[13] Water samples collected in 1995–97 from High Ore Creek (site 13) were analyzed by inductively coupled plasma-atomic emission spectroscopy (ICP-AES) by the MBMG Analytical Laboratory in Butte, Mont. Samples collected in 2000 from Tenmile Creek (sites 4 and 5) were analyzed by ICP-AES by the Montana Department of Public Health and Human Services in Helena, Mont. All other samples collected in 1999–2000 as well as samples collected in 2001 from Middle Fork Warm Springs Creek (site 6) were analyzed by inductively coupled plasma-mass spectroscopy (ICP-MS) [*Garbarino and Taylor*, 1996] by the USGS National Water Quality Laboratory in Denver, Colo. Samples collected in 2001 (except Middle Fork Warm Springs Creek samples) were analyzed for Cd, Mn, and Zn by ICP-AES, for As by hydride generation atomic absorption spectrometry, and for Ni by graphite furnace atomic absorption spectrometry by the USGS laboratory in Boulder, Colo. The analytical precision for Ni was poor because Ni concentrations were less than 3 times the detection limit.

[14] During sampling episodes, water samples remained in collection bottles inside the automatic sampler generally for less than 4 hours but never more than 6 hours. Quality-assurance samples were collected to determine if the time period between sample collection and sample processing had an effect on dissolved metal concentration. Concentrations of dissolved Fe changed dramatically, decreasing by as much as 64–98% between samples filtered immediately after collection and samples held in collection bottles for 5–8 hours before filtration. These decreases likely were caused by precipitation of hydrous Fe oxides. However, concentrations of As, Cd, Cu, Mn, and Zn generally did not change (within the precision of the analyses) and exhibited no consistent increase or decrease in concentration over these holding periods in the collection bottles. Iron concentrations were low (less than about 100 μg/L) at all diel sampling sites (except sites 10 and 16 where pH was less than 5.4). Therefore, in the case of this study, although a large portion of the dissolved Fe may have been removed while unfiltered water was stored in the collection bottles, the amount of Fe precipitates that formed likely was too small to noticeably decrease concentrations of other metals that might co-precipitate or adsorb to the newly formed hydrous oxides.

[15] Water temperature, specific conductance, and dissolved oxygen were measured hourly (or more frequently) with a multiparameter instrument submerged in the stream in an area of slow-moving water near the intake of the pumping sampler. Stream pH was measured either with the instream multiparameter instrument or with a laboratory pH meter using water samples that were manually collected from the stream and immediately analyzed. In some instances, both types of pH measurements were made to provide comparisons of results.

[16] Streamflow data were collected by periodic current-meter or Parshall flume measurements [*Rantz et al.*, 1982], by continuous tracer injection [*Kilpatrick and Cobb*, 1985], or from a nearby USGS gaging station. All diel data sets were collected during low flow in the summer after high flow associated with spring snowmelt runoff had subsided. Streamflow during each sampling episode was unaffected by rainfall-runoff and remained stable except for typical diel variations, which likely were caused by evapotranspiration from floodplain vegetation [*Troxell*, 1936; *Lundquist and Cayan*, 2002].

4. Results

4.1. Definition of Dissolved

[17] The term 'dissolved,' as used in this report, is defined as the concentration in 0.1-μm filtrates (1999–2001 data) or 0.45-μm filtrates (1994–1997 data). However, metals associated with colloids can pass through filters having these pore sizes; in these circumstances, concentrations in 0.45- or 0.1-μm filtrates may overstate the

concentration of dissolved metals. Ultrafiltration using a tangential-flow filtration apparatus with an effective pore size of 10,000 Daltons (about 0.001 μm) can be used to define concentrations of metals in the dissolved phase [*Kimball et al.*, 1995]. Ultrafiltration data for 16 samples collected periodically during 1996–2000 at five of the diel sites during low- to moderate-streamflow conditions were used to determine whether the 0.1-μm or 0.45-μm filtrates, as well as unfiltered samples, contained a substantial colloidal fraction. The percentage of colloidal material (determined as the difference in concentration between unfiltered and ultrafiltered aliquots) was quite large for Al and Fe (medians greater than 92%), intermediate for As and Cu (medians of about 55%), and much smaller for Cd, Mn, and Zn (medians of 6–14%).

[18] For Cd, Mn, and Zn, the differences between concentrations in 0.1- or 0.45-μm filtrates and concentrations in ultrafiltrates were small. The maximum difference was less than 16% for Cd, 9% for Mn, and 13% for Zn. The median differences were 7% or less. Because these differences are small in comparison to the diel range in concentrations of these metals, the data reported here for Cd, Mn, and Zn in 0.1- or 0.45-μm filtrates are considered representative of the dissolved fraction. The fraction of Cu associated with colloidal material in the 0.1- and 0.45-μm filtrates was larger than that for Cd, Mn, and Zn, with a median difference of 20%. Insufficient data were available for As and Ni in ultrafiltrates to assess the colloidal component in 0.1- or 0.45-μm filtrates.

4.2. Diel Variation of Zn

[19] Zn was studied at more sites than As, Cd, Cu, Mn, or Ni because it is a relatively mobile trace metal in oxygenated water [*Hem*, 1989] and concentrations of dissolved Zn in streams typically are higher than laboratory detection levels for extended distances downstream from trace-metal source areas. The magnitudes of diel concentration variations were computed by dividing the difference between the maximum and minimum concentrations for a 24-hr period by the minimum concentration. The results were multiplied by 100 and are reported as percent increases from the minimum diel value. Collection times for all sampling episodes are reported as Mountain Daylight Time.

4.2.1. Diel Variation of Zn in High Ore Creek

[20] Data for five sampling episodes during mid to late summer on High Ore Creek (site 13) are shown in Figure 2 to illustrate typical diel concentration patterns. During each episode, concentrations of dissolved Zn increased during the night, reaching maximum values shortly after sunrise (0600–0800 hours). Concentrations then decreased to minimum values during mid to late afternoon (1500–1700 hours). When diel sampling episodes lasted for more than 24 hours, concentration variations on successive days were consistent, displaying a distinct symmetry in both magnitude and timing during the daily rise and fall of concentrations. The differences between minimum and maximum Zn concentrations were similar on each day, with a gradual concentration increase during the night, followed by a more rapid concentration decrease during the day.

[21] The major source of metals to High Ore Creek was mill tailings at the Comet mine, which was active from 1880 to 1941. Fluvial tailings deposits along the 6-km reach between the mine area and site 13 were a smaller source of metals. Zn concentrations during diel sampling in 1995 and 1997 ranged from 509 to 2,570 μg/L (Table 1). Remediation efforts conducted during 1997–1999 appear to have reduced metal loading, and Zn concentrations were much lower (202–814 μg/L) during the 1999–2001 sampling episodes. The diel data for High Ore Creek (Figure 2) demonstrate that diel cycles in dissolved Zn concentration are persistent, even though metal loading and ambient Zn concentrations changed during the 6-year period.

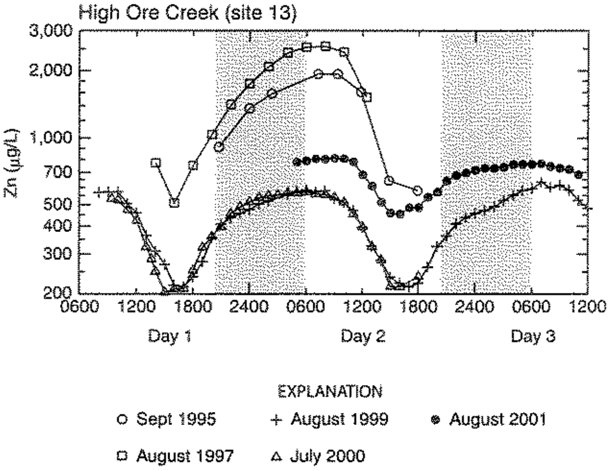

Figure 2. Diel variation in dissolved Zn concentration, High Ore Creek, 1995–2001. Shaded areas indicate nighttime hours.

4.2.2. Diel Variation of Zn in Other Boulder Batholith Streams

[22] In addition to High Ore Creek, diel Zn data were collected at nine sites on seven streams that drain the Boulder batholith (Figures 3 and 4). On Figure 3, the data for Jack Creek below Bullion mine (site 9), Bullion Mine tributary (site 10), and Uncle Sam Gulch (site 11) span only 12–13 hours because severe evening thunderstorms interrupted the sampling episodes and caused heavy runoff of metal-laden water from upstream mine and mill wastes. The runoff masked whatever diel concentration pattern would have been typical for base-flow conditions at these sites.

[23] Diel Zn cycles at Cataract and Tenmile Creeks (Figure 3) and Prickly Pear Creek and Jack Creek (Figure 4) had timing of concentration maxima and minima similar to those in High Ore Creek (Figure 2). Maximum and minimum concentrations generally were between 0600–0800 hours and 1500–1900 hours, respectively. Prickly Pear Creek had the longest period between the morning maximum (0600 hours) and afternoon minimum (1700–1900 hours), most likely because daylight lasted longer during this late June sampling episode than it did during the other sampling episodes. The diel peak at Uncle Sam Gulch (site 11, Figure 3) occurred 2–4 hours later than at other sites, with the maximum concentration at 0900 hours and the minimum at 1900 hours. A diel Zn cycle was not observed in Bullion Mine tributary (site 10), where concentrations varied less than 7% during the 12-hour sampling period (0600 to 1800 hours). The lack of a diel cycle at this site where pH during sampling was 5.2–5.3, is presumably due to the acidic conditions.

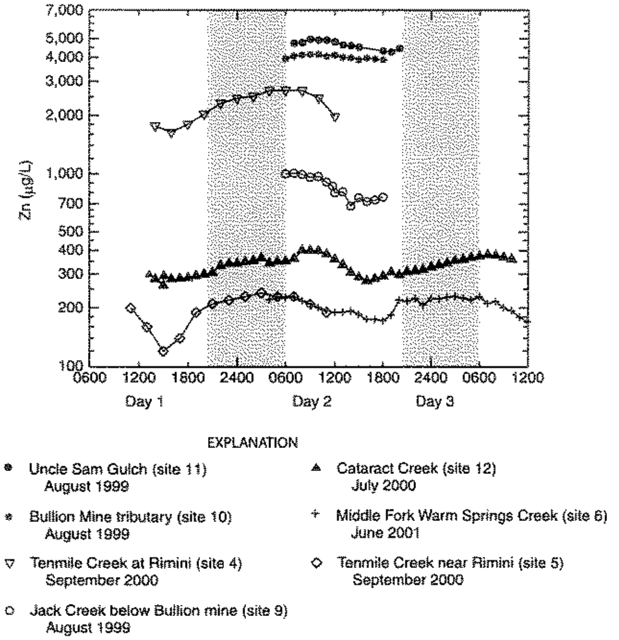

Figure 3. Diel variation in dissolved Zn concentration in Uncle Sam Gulch, Bullion Mine tributary, Tenmile Creek, Jack Creek, Cataract Creek, and Middle Fork Warm Springs Creek. Shaded areas indicate general nighttime hours.

[24] Diel Zn cycles occurred over a wide range of Zn concentrations in streams draining the Boulder batholith. Concentrations were greater than 1,000 µg/L in Uncle Sam Gulch and Tenmile Creek at Rimini; greater than 100 µg/L in Jack and Cataract Creeks as well as Tenmile Creek near Rimini; and less than 100 µg/L in Prickly Pear Creek (Figures 3 and 4). The diel change (500%) in dissolved Zn concentration in Prickly Pear Creek was the largest percentage change for any of the data sets and occurred for relatively low Zn concentrations (11.8–70.8 µg/L). A similar large change (405%) in Zn concentration in High Ore Creek in 1997, when Zn concentrations were very high (509–2,570 µg/L), indicate that proportionally large diel cycles can occur over a wide range of ambient concentrations.

4.2.3. Diel Variation of Zn in Streams in Other Areas

[25] Dissolved Zn concentrations in the Clark Fork (site 3) increased by 161%, with maximum and minimum concentrations at 0700 hours and 1800–1900 hours, respectively (Figure 5). Dissolved Zn concentrations in the South Fork Coeur d'Alene River (site 2) increased 58%, ranging from 1,250 to 1,970 µg/L, with maximum and minimum concentrations at 0500–0800 hours and 1700–1800 hours, respectively (Figure 6). The magnitude and timing of these cycles were similar to those in the Boulder batholith area.

[26] The magnitude and temporal pattern of Zn concentrations in the Coeur d'Alene River (site 1) deviated substantially from the magnitude and temporal pattern in all other streams with nonacidic pH. Dissolved Zn concentrations changed only 12%, varying from 477 to 533 µg/L, with maximum and minimum concentrations at 2300 hours and 1300–1400 hours, respectively (Figure 6). This subdued diel Zn cycle at site 1 appears to represent the diluted cyclic Zn input from the South Fork Coeur d'Alene River

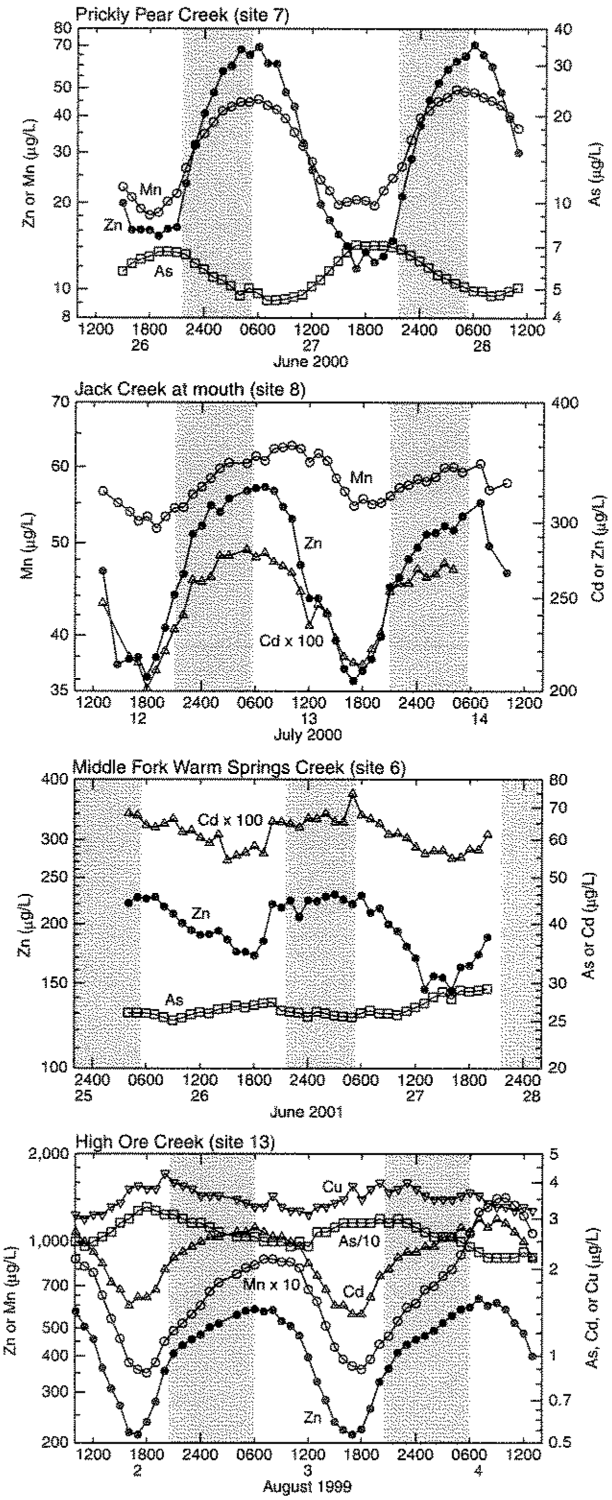

Figure 4. Diel variation in dissolved metal concentrations in Prickly Pear, Jack, Middle Fork Warm Springs, and High Ore Creeks. Shaded areas indicate nighttime hours. Concentrations that were multiplied or divided by 10 or 100 before plotting are indicated.

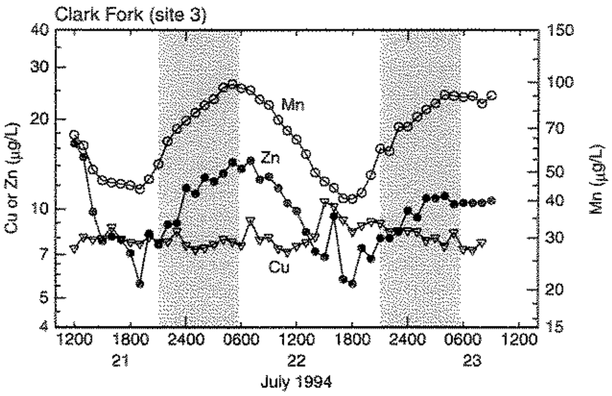

Figure 5. Diel variation in dissolved Cu, Mn, and Zn concentrations in the Clark Fork, July 21–23, 1994. Data are from *Brick and Moore* [1996]. Shaded areas indicate nighttime hours.

(site 2). The Zn concentration in the North Fork Coeur d'Alene River at its confluence with the South Fork (Figure 1) was less than 5 μg/L on 12 September 2001 (D.A. Nimick, U.S. Geological Survey, unpublished data, 2001), so essentially all of the Zn in the main stem (site 1) was contributed by the South Fork (site 2). Streamflow at site 1 was about 3.4 times greater than at site 2, while the median concentration at site 2 was 3.2 times greater than at site 1. Therefore dilution of South Fork water can explain the ambient concentration in the main stem at site 1. The maximum and minimum concentrations occurred 15–21 hours later at site 1 than at site 2. Assuming a 13-hr travel time between the sites (G. M. Clark, U.S. Geological Survey, personal communication, 2001), some temporal retardation of the zinc cycles apparently occurred as the diel Zn cycle of the South Fork was advected downstream. The lack of a diel Zn cycle at site 1 with timing similar to that at other sites may result from the negligible diel cycles in pH and temperature in the Coeur d'Alene River. The diel pH variation (0.12 units) at site 1 was among the smallest of any stream (Table 1), while the diel temperature variation (1.2 °C) was much less than for any other stream. Although the Coeur d'Alene River was the largest stream we sampled, the lack of diel metal cycles at site 1 probably is not related to the stream's size. *Nimick et al.* [1998] demonstrated that As has a diel cycle in the Madison and Missouri Rivers at sites with streamflow as much as 25 times greater than at site 1.

[27] Diel variations in dissolved Zn concentrations at three sites in the New World mining district (Figure 7) followed the patterns observed in the other study areas. A diel Zn cycle was not apparent at upper Daisy Creek (site 16), where the pH ranged from 3.53–3.69. The lack of a diel Zn cycle at upper Daisy Creek is consistent with other acidic streams such as Bullion Mine tributary (site 10) as well as streams reported by *McKnight et al.* [1988] and *Sullivan et al.* [1998]. Downstream, at lower Daisy Creek

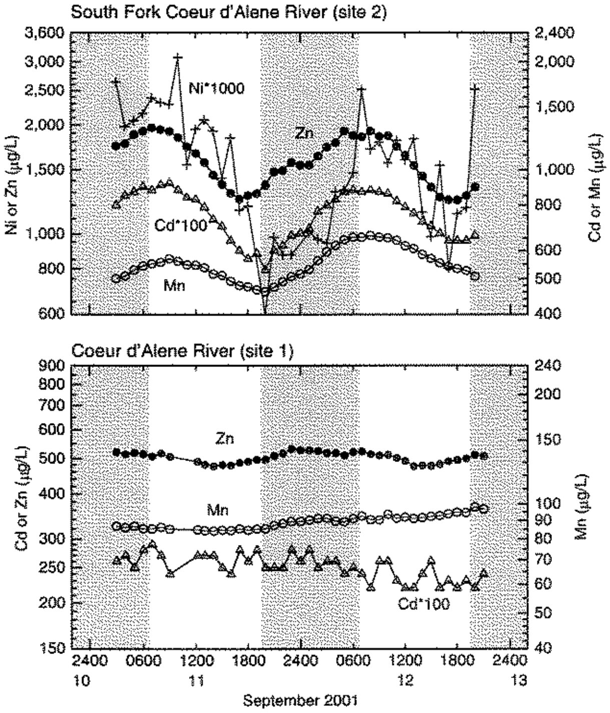

Figure 6. Diel variation in dissolved Cd, Mn, Ni, and Zn concentrations in the South Fork Coeur d'Alene and Coeur d'Alene Rivers, 11–12 September 2001. Shaded areas indicate nighttime hours. Cd and Ni concentrations were multiplied by 100 and 1,000, respectively, before plotting.

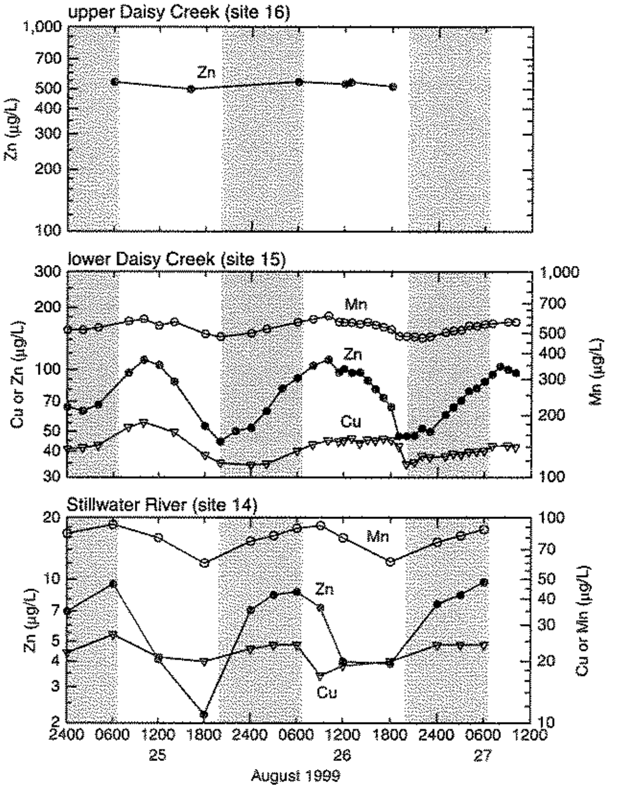

Figure 7. Diel variation in dissolved Cu, Mn, and Zn concentrations in Daisy Creek and the Stillwater River, 25–27 August 1999. Shaded areas indicate nighttime hours.

(site 15), where tributary inflows had increased stream pH to 7.49–7.83, a diel Zn cycle was apparent but its timing was delayed. Maximum and minimum concentrations occurred at 0800–1000 hours and 1900–2000 hours, respectively, 2–3 hours later than at most other sites. Although not as well defined because of the larger sampling intervals between samples, the diel Zn cycle in the Stillwater River (site 14) was substantial, with concentrations increasing 332% from 2.2 to 9.5 μg/L.

4.3. Diel Variation of Other Metals

[28] Metals other than Zn were examined during 15 of the 20 diel sampling episodes (Table 1). Diel cycles are illustrated in Figures 4–7 for 9 of these episodes to demonstrate the similarities and differences in magnitude and temporal patterns of the diel concentration variation for As, Cd, Cu, Mn, and Ni in comparison to Zn.

[29] The timing of diel cycles for Cd and Mn were very similar to those for Zn (Figures 4–7), but the range of Cd concentrations (0.54–9.2 μg/L, Table 1) was much smaller than for Zn. Diel increases in Cd concentrations in five streams ranged from 39% in Middle Fork Warm Springs Creek to as much as 119% in High Ore Creek. Mn concentrations (19.6–1,500 μg/L) ranged more widely. Diel increases in Mn concentrations in the eight streams ranged from 22% in Jack Creek to 294% in High Ore Creek.

[30] Concentrations of Cd and Mn had no diel cycle in the Coeur d'Alene River (Figure 6). Cd concentrations varied within a narrow range (2.2–2.9 μg/L) but generally decreased during the 42-hr sampling episode. Mn concentrations also varied within a narrow range (84.2–98.1 μg/L) but increased during the sampling episode. The lack of diel cycles for Cd and Mn was not unexpected because these metals typically had smaller diel concentration ranges than Zn at other sites, and Zn had a small diel concentration range at this site.

[31] Ni exhibited a diel cycle in the South Fork Coeur d'Alene River, the only site for which samples were analyzed for this metal. The temporal pattern of the Ni diel cycle broadly followed the Cd, Mn, and Zn cycles; however, the analytical imprecision in the Ni data precluded determination of the precise timing of minimum and maximum concentrations. The diel increase in Ni was about 167%, with concentrations ranging between about 0.9 and 2.4 μg/L.

[32] The diel temporal pattern for As was the opposite of the pattern for Cd, Mn, and Zn (Figure 4), with maximum concentrations in the late afternoon and minimum concentrations generally in the morning. Concentrations of As at the three sites with diel data ranged from 4.6 to 44.0 μg/L (Table 1). Variations in diel As concentrations were proportionally much less than the variations for Cd, Mn, and Zn. Maximum diel increases in As concentrations in Middle Fork Warm Springs, High Ore, and Prickly Pear Creeks were 15, 50, and 54%, respectively, compared to maximum increases in Zn concentrations of 59, 196, and 500%, respectively. The magnitude and timing of these diel As cycles are similar to those previously reported by *Fuller and Davis* [1989] and *Nimick et al.* [1998]. In Prickly Pear Creek, the timing of the As cycle was the opposite of the Zn cycle, with minimum As concentrations closely coinciding with maximum Zn concentrations in the morning and maximum As concentrations coinciding with minimum Zn concentrations in the afternoon. However, the extremes of the diel As cycle in High Ore Creek generally were less well defined because the change in As concentration between hourly samples was small. The difference in timing of the diel cycles for As relative to Cd, Mn, and Zn indicates either that different mechanisms are driving the concentration changes for the two sets of metals or that one mechanism can produce the opposite responses.

[33] Cu concentrations varied widely among the five sites sampled for Cu. The highest Cu concentrations were in lower Daisy Creek (34.3–55.4 μg/L) and the Stillwater River (17–24 μg/L). These streams, as well as the Clark Fork (7.2–11 μg/L) (Figure 5), drain mining areas where Cu is the metal of primary concern. Cu concentrations in High Ore Creek were lower (2.3–4.3 μg/L). The temporal concentration patterns also were quite different in the five streams. The temporal pattern for Cu in lower Daisy Creek and the Stillwater River was the same as the pattern for Mn and Zn (Figure 7). In contrast, the timing of the Cu cycle during three sampling episodes in High Ore Creek was different from the Mn and Zn cycles. Instead, the temporal pattern for Cu was similar to As (Figure 4). In the Clark Fork and Cataract Creek, a diel Cu cycle was not evident. These differences in apparent behavior of Cu may be related to the stronger affinity of Cu (compared to Cd, Mn, and Zn) for organic matter and colloidal material (such as hydrous Al and Fe oxides), which can pass through the 0.1-μm filters used to define dissolved concentrations in this study. On the basis of the ultrafiltration data collected during this study, 20 to 55%, on average, of the Cu was associated with colloidal material. Therefore the observed diel patterns for Cu may result from a combination of factors, including processes affecting either dissolved or colloidal concentrations in the stream as well as variable effects introduced by filtration.

5. Correlation of Zn Concentrations and Field Parameters

[34] Field parameters such as streamflow, pH, dissolved oxygen (DO), specific conductance, and water temperature are easily measured, known to exhibit diel cycles, and might be associated with instream factors controlling diel metal cycles. Identification of strong temporal correlations between field parameters and dissolved Zn concentrations could be a first step in understanding the cause of diel metal cycles. Although these field parameters exhibit some correlations (Table 2) because each exhibits diel cycles, the analysis presented here is intended to show which field parameter(s) correlate consistently and strongly with Zn (Table 3). Data for three streams of different sizes (Prickly Pear Creek, the South Fork Coeur d'Alene River, and High Ore Creek) were used in this analysis (Figures 8 and 9). These three streams are representative of the correlation results for all sites with diel metal cycles. Similarly, the results for other metals (Table 3) generally correspond to those presented for Zn.

5.1. Streamflow

[35] The magnitude of diel variation in streamflow (Figures 8 and 9) varied in the three streams. The maximum change during a 24-hour period was 44% (0.016–0.023 m^3/s) in High Ore Creek, 14% (0.350–0.400 m^3/s) in Prickly Pear Creek, and 7.7% (2.21–2.38 m^3/s) in the South Fork

Table 2. Statistical Relations Between Field Parameters[a]

Stream	Site Number	Coefficient of Determination[b]						
		pH-T	pH-Q	pH-DO	pH-SC	T-Q	T-DO	T-SC
High Ore Creek (August 1999)	12	0.49 (<0.001)	0.02 (0.384)	0.21 (0.001)	0.33 (<0.001)	0.34 (<0.001)	0.88 (<0.001)	0.31 (<0.001)
Prickly Pear Creek	7	0.70 (<0.001)	0.17 (0.005)	0.05 (0.142)	0.74 (<0.001)	<0.01 (0.814)	0.42 (<0.001)	0.38 (<0.001)
South Fork Coeur d'Alene River	2	0.40 (<0.001)	0.38 (<0.001)	0.83 (<0.001)	0.002 (0.784)	0.19 (0.004)	0.10 (0.046)	0.25 (0.001)

[a] T is temperature, Q is streamflow, DO is dissolved oxygen, and SC is specific conductance.

[b] The p value for Pearson correlation coefficient is given in parentheses.

Coeur d'Alene River. Streamflow exhibited a well-defined diel cycle in High Ore and Prickly Pear Creeks, presumably caused by evapotranspiration. The diel cycle in the South Fork was very small. The relation between streamflow and dissolved Zn concentration (Table 3) was not significant in Prickly Pear Creek ($p > 0.05$) and weak in High Ore Creek ($R^2 = 0.30$) and the South Fork Coeur d'Alene ($R^2 = 0.32$). In some streams, variations in flow commonly are associated with variations in solute concentrations, with increased flow resulting in decreased concentration owing to dilution. However, the relative timing of the diel streamflow and Zn variations do not support a dilution effect, especially in High Ore and Prickly Pear Creeks. Although diel Zn cycles had similar temporal patterns in the three streams, diel streamflow cycles did not. Minimum flows occurred during the night between 2000 to 2400 hours in High Ore Creek and between about 2000 to 0200 hours in Prickly Pear Creek, but generally during the afternoon in the South Fork Coeur d'Alene River. Thus peak dissolved Zn concentrations (0500 to 0800 hours) were not synchronous with either minimum or maximum flows. If diel Zn cycles were caused by streamflow variations, the timing of diel Zn and streamflow cycles would be similar.

5.2. pH

[36] The relation between pH and Zn concentrations was similar in the three streams. Minimum pH values generally were reached a few hours after sunset and before midnight. Unlike streamflow, however, pH remained relatively constant throughout the night. Near sunrise, pH began to rise, reaching a maximum around mid-afternoon. These pH cycles were consistent with other studies that attributed pH cycles to photosynthesis [e.g., *Wright and Mills*, 1967; *Fuller and Davis*, 1989]. The increase in pH from the nighttime minimum was relatively minor in High Ore Creek, representing only about two tenths of a pH unit (range of 8.12 to 8.34), and much greater in Prickly Pear Creek (range of 8.26 to 9.05). Values of pH in the South Fork Coeur d'Alene River were intermediate, ranging from 6.88 to 7.33. The maximum pH value at each site was maintained only for 1–2 hours, unlike the nighttime minimum, which was maintained for 6–10 hours. Although the minimum pH was maintained for an extended time rather than continuing to decrease, the time interval spanning these minimum pH values coincided fairly well with the interval of increasing Zn concentrations. The relation between pH and Zn concentration was stronger ($p < 0.001$ and R^2 values of 0.62, 0.64, and 0.80, Table 3) than that for streamflow. In all instances, the slope was negative indicating that Zn concentrations increased as pH decreased. The relatively strong but variable relation between Zn and pH could indicate that pH may partially control Zn concentrations.

5.3. Dissolved Oxygen

[37] Diel DO cycles ranged from being synchronous to being out of phase with diel Zn cycles. DO cycles are caused primarily by diel cycles in photosynthesis and respiration. High Ore Creek had the smallest range of DO concentrations (6.7 to about 8.4 mg/L), which is reasonable because of its general lack of macrophytes. The timing of the DO and Zn concentration maxima and minima were within 1–2 hours of each other and exhibited generally similar patterns of symmetry. DO concentrations likely were responding primarily to water temperature in High Ore Creek because concentrations began decreasing in midmorning as the water warmed and oxygen solubility decreased. This DO pattern is generally the opposite of biologically productive streams, such as Prickly Pear Creek and the South Fork Coeur d'Alene River, with substantial photosynthetic activity. DO concentrations ranged more

Table 3. Statistical Relations Between Dissolved Metal Concentrations and Field Parameters

Stream	Site Number	Metal	Coefficient of Determination[a]				
			Streamflow	pH	Dissolved Oxygen	Specific Conductance	Water Temperature
High Ore Creek (August 1999)	12	As	0.84 (<0.001)	0.14 (0.010)	0.41 (<0.001)	0.54 (<0.001)	0.50 (<0.001)
High Ore Creek (August 1999)	12	Cd	0.31 (<0.001)	0.60 (<0.001)	0.66 (<0.001)	0.61 (<0.001)	0.85 (<0.001)
High Ore Creek (August 1999)	12	Mn	0.62 (<0.001)	0.23 (0.001)	0.38 (<0.001)	0.81 (<0.001)	0.50 (<0.001)
High Ore Creek (August 1999)	12	Zn	0.30 (<0.001)	0.62 (<0.001)	0.70 (<0.001)	0.57 (<0.001)	0.89 (<0.001)
Prickly Pear Creek	7	As	0.10 (0.037)	0.42 (<0.001)	0.74 (<0.001)	0.15 (0.008)	0.81 (<0.001)
Prickly Pear Creek	7	Mn	0.08 (0.056)	0.89 (<0.001)	0.17 (0.004)	0.70 (<0.001)	0.84 (<0.001)
Prickly Pear Creek	7	Zn	0.02 (0.328)	0.80 (<0.001)	0.21 (<0.001)	0.52 (<0.001)	0.83 (<0.001)
South Fork Coeur d'Alene River	2	Cd	0.15 (0.013)	0.32 (<0.001)	0.08 (0.078)	0.37 (<0.001)	0.94 (<0.001)
South Fork Coeur d'Alene River	2	Mn	0.05 (0.144)	0.11 (0.031)	0.02 (0.386)	0.62 (<0.001)	0.43 (<0.001)
South Fork Coeur d'Alene River	2	Zn	0.32 (<0.001)	0.64 (<0.001)	0.29 (<0.001)	0.15 (0.011)	0.91 (<0.001)

[a] The p value for Pearson correlation coefficient is given in parentheses.

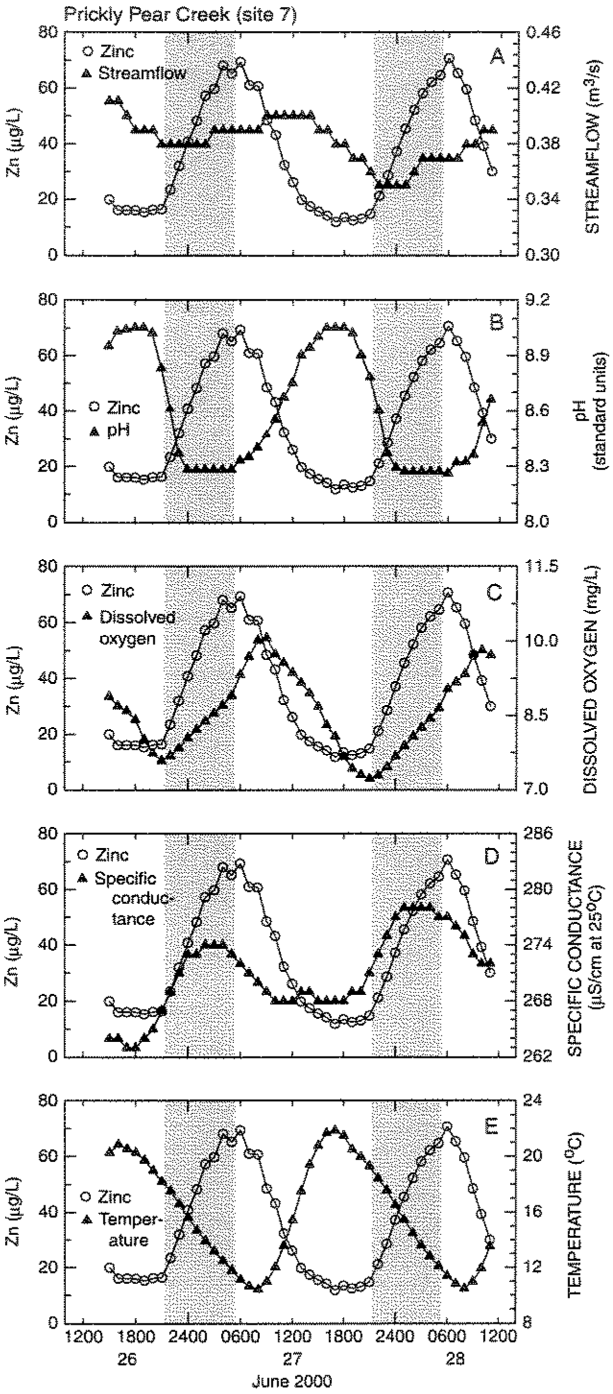

Figure 8. Concurrent diel variation of dissolved Zn concentrations in Prickly Pear Creek, 26–28 June 2000, and field parameters: (a) streamflow, (b) pH, (c) dissolved oxygen, (d) specific conductance, and (e) water temperature. Shaded areas indicate nighttime hours.

widely in the two other streams (7.2 to 10.1 mg/L in Prickly Pear Creek and 6.5 to 11.0 mg/L in the South Fork). Timing of the DO cycles in these streams was offset from the diel Zn cycles by several hours. Although the relation between DO and Zn concentrations (Table 3) was significant ($p < 0.001$) in each stream, the correlation was stronger in High Ore Creek ($R^2 = 0.70$) than in Prickly Pear Creek ($R^2 = 0.21$) and South Fork Coeur d'Alene River ($R^2 = 0.29$). The lack of consistent relations between DO and Zn concentrations in these three streams probably indicates that DO is not a controlling factor of diel metal cycles.

5.4. Specific Conductance

[38] Specific conductance commonly correlates well with major-ion concentrations. However, the relation between specific conductance and Zn concentrations in High Ore and Prickly Pear Creeks (Table 3) was moderate ($p < 0.001$ and R^2 values of 0.55 and 0.52, respectively), while the correlation was not significant in the South Fork ($p = 0.011$ and $R^2 = 0.15$). Although specific conductance values generally increased through the night, roughly corresponding to the temporal pattern observed for Zn, the correlation was not consistently strong, indicating that different processes likely controlled major-ion and trace-metal concentrations. Further indication that major-ion and metal concentrations are not related is suggested by the unusual specific conductance variations in the South Fork Coeur d'Alene River during the middle of the sampling episode (a large decrease) and in High Ore Creek at the end of the sampling episode (a large increase), which had no corresponding deviation in the diel Zn cycles (Figure 9).

5.5. Water Temperature

[39] The relation between water temperature and Zn concentration in each stream was consistently strong ($p < 0.001$ and R^2 values ranging from 0.83 to 0.91, Table 3) and was substantially stronger than for any other field parameter. This strong correlation suggests that temperature plays an important role in controlling diel Zn concentrations. In addition, the temperature maxima and Zn minima generally occurred at the same time. Temperatures were highest in late afternoon (about 1600–1800 hours), coinciding closely with the timing of minimum dissolved Zn concentrations (1700–1900 hours). In contrast, temperatures were lowest in mid-morning (0800–0900 hours), lagging the maximum dissolved Zn concentrations (0600–0700 hours) by 1–2 hours.

6. Mechanisms Influencing Diel Cycles

[40] A number of physical, geochemical, and biological mechanisms potentially can explain diel dissolved-metal cycles. This section provides a review of plausible explanations of the diel data presented above.

6.1. Variable Input From Source

[41] Diel variation in the flux from an upstream source of metals could explain diel metal cycles in streams. For example, diel Mn cycles in Lake Fork Creek in Colorado were caused primarily by diel Mn variation in the acidic outflow from a wetland affected by acid mine drainage [*Scott et al.*, 2002]. No diel data on metal fluxes from individual sources upstream from our sampling sites are available. However, considering the differences in travel time between an upstream source and various downstream reaches of a stream, this process likely would not produce the nearly synchronous diel concentration patterns that have been observed at multiple sites within the same watershed. In addition, the likelihood that similar upstream sources of

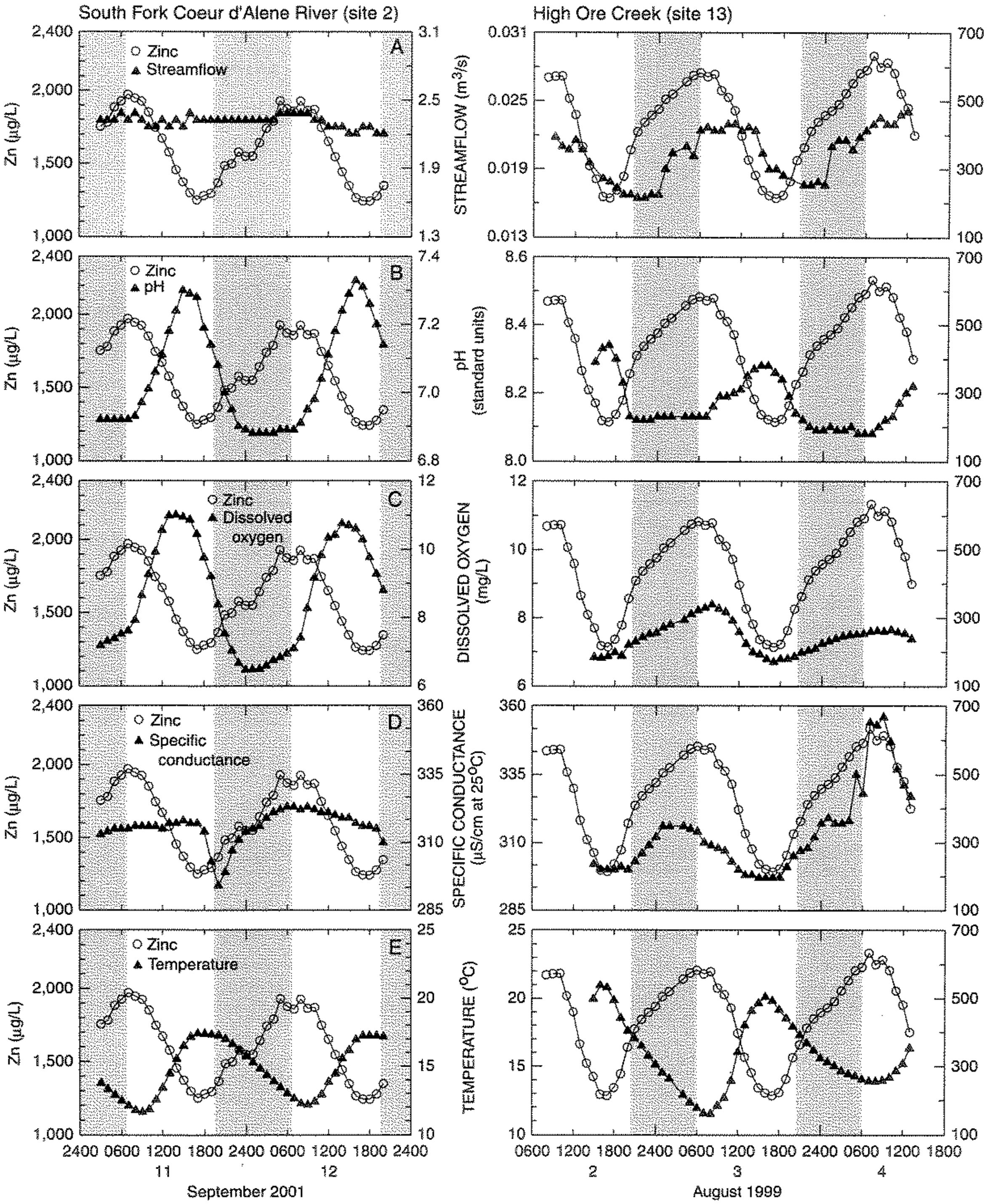

Figure 9. Concurrent diel variation of dissolved Zn concentrations in South Fork Coeur d'Alene River, 11–12 September 2001 (left) and High Ore Creek, 2–4 August 1999 (right), and field parameters: (a) streamflow, (b) pH, (c) dissolved oxygen, (d) specific conductance, and (e) water temperature. Shaded areas indicate nighttime hours.

metals would exist in 13 different streams and produce the same diel cycles is small.

6.2. Diel Streamflow Cycles

[42] Diel variation in streamflow is a plausible mechanism to explain diel metal cycles because the varying amount of flow would either dilute or augment metal concentrations in the stream. For example, pulses of runoff caused by daytime snowmelt can cause diel fluctuations in solute concentrations in mountain streams [*Sullivan et al.*, 1998]. However, a large time lag typically exists between melting of the headwater snowpack and the arrival of peak flows at a downstream monitoring point. Therefore, if diel metal cycles were controlled by snowmelt, then concentration minima and maxima would occur at different times of the day among various sites. In addition, snowmelt cannot explain most of the data sets in this paper because essentially no snow remained in the watersheds during the mid- and late summer sampling periods.

[43] Streamflow also may fluctuate in response to floodplain evapotranspiration during the day. For a losing stream, this floodplain evapotranspiration should not result in any change in solute concentration. However, for a stream that gains flow from groundwater, diel changes in the groundwater flux could induce diel variations in instream concentrations of any metal, assuming that the concentration of the metal is substantially different (higher or lower) in groundwater compared to stream water. *Brick and Moore* [1996] concluded that this process was one plausible explanation for the diel variations in dissolved Mn and Zn concentrations in the Clark Fork. However, diel variation in groundwater inflow likely is not the dominant mechanism for most of the data presented in this paper because, as noted in section 5.1, the timing of the diel streamflow cycle does not correspond to the timing of the diel metal cycle. In addition, groundwater inflow cannot explain diel metal cycles in losing streams such as High Ore Creek. The importance of diel variation in groundwater exchange could be tested in more detail by collecting groundwater level and quality data and by sampling streams during the winter when effects of floodplain evapotranspiration on groundwater exchange would be negligible.

6.3. Mn Redox Reactions

[44] Oxidation and reduction reactions involving Mn occur in many streams and cause active diel geochemical Mn cycling [*Scott et al.*, 2002]. These reactions involving Mn can substantially affect the concentrations of other trace metals. Oxidation of dissolved Mn leads to removal of aqueous Mn (and other trace metals) by precipitation of Mn oxides [*Fuller and Harvey*, 2000]. This reaction is microbially mediated, and the oxidation rate increases with increased pH and solar radiation [*Stumm and Morgan*, 1996]. Conversely, Mn oxides can be reductively dissolved, releasing Mn to the water column. Dissolution rates are higher during the night when DO concentrations decline, especially at periphyton surfaces [*Revsbech et al.*, 1983; *Christensen et al.*, 1989] owing to cessation of photosynthesis. Concentrations of dissolved Mn and other divalent metals in the stream therefore could be controlled by the relative importance of oxidation and reduction reactions during a 24-hr period. Reductive dissolution of hydrous Mn oxides and release of associated metals from the hyporheic zone was suggested by *Brick and Moore* [1996] as a possible explanation of the diel cycles in dissolved Mn and Zn concentrations in the Clark Fork (Figure 5). *Scott et al.* [2002] attributed the diel variation in dissolved Mn in Lake Fork Creek in Colorado to diel changes in the relative rates of Mn oxidation and reduction reactions occurring simultaneously in the stream and upstream wetland.

[45] Mn redox reactionss are a plausible explanation for most of our data because these reactions are tied to the diel solar and biological stream cycles and because diel Mn cycles are in phase with the diel Cd and Zn cycles. Mn oxidation should predominate over Mn dissolution during the day, causing decreases in concentrations of dissolved Mn and other divalent metals. During the night, Mn dissolution should predominate and divalent metal concentrations should increase. However, these cycles of Mn oxidation and reduction cannot explain the inverse temporal patterns in concentrations of As. In addition, other issues exist concerning the ability of this mechanism to produce the consistent and widespread diel variations documented in this study. For example, the ratio of Mn and Zn concentrations (Table 1) is not consistent among the streams we studied, ranging from as high as 27 (Stillwater River, site 14) to about 1 (Prickly Pear Creek, site 7), to less than 0.1 (Cataract and High Ore Creeks, sites 12 and 13). For streams where the dissolved Mn/Zn ratio is much less than 1, as in High Ore Creek, cyclic dissolution and precipitation of Mn oxides cannot explain the observed diel variations in both metals, due to mass balance constraints. Additional data on the metal concentrations in the hyporheic zone, as collected by *Brick and Moore* [1996] for the Clark Fork and *Fuller and Harvey* [2000] at Pinal Creek, as well as solid-phase data for hydrous metal oxides from stream substrates would be useful to determine the potential importance of Mn redox reactions.

6.4. Iron Photoreduction

[46] Diel cycles in dissolved Fe concentrations caused by photoreduction have been reported in alpine streams with moderately low pH [*McKnight et al.*, 1988; *Sullivan et al.*, 1998; *Sullivan and Drever*, 2001]. In these streams, solar radiation induces reductive dissolution of hydrous ferric oxide (HFO), resulting in an increase in both Fe^{2+} and total dissolved Fe during the day. Presumably, dissolution of HFO would also release any ions adsorbed on the HFO surfaces and result in increases in dissolved metal concentrations during the day. Clearly, photoreduction of HFO cannot explain the observed daytime decreases in Cd, Mn, and Zn concentrations documented in our study. However, this process could be a contributing factor in the daytime increases of As concentrations in streams. In addition, photoreduction of HFO has been described mainly for acidic streams. At higher pH, the greater insolubility of HFO, coupled with the much faster rate of reoxidation of Fe^{2+} to Fe^{3+}, renders this mechanism less important. Data on diel changes in total dissolved Fe concentration or Fe^{2+}/Fe^{3+} ratios would be useful to fully evaluate whether HFO photoreduction controls As concentrations in the neutral to alkaline streams of this study.

6.5. Biological Absorption

[47] Many streams have an abundant macrophyte community and most exposed mineral surfaces in streams are

coated with a thin layer of biofilms. Because of their large capacity to store metals [*Farag et al.*, 1998], macrophytes and biofilm also may play an important role in controlling metal concentrations in streams through absorption (metabolic uptake). Little information exists to evaluate the importance of diel uptake of metals by biofilm or periphyton [*Sloof et al.*, 1995]. Although this mechanism certainly is plausible for the divalent metals, it does not explain the concentration pattern for As.

6.6. Precipitation/Dissolution Reactions

[48] Diel changes in temperature and pH in streams could result in cyclic precipitation and dissolution of amorphous hydrous oxides, carbonates, or other minerals containing metals. Given that diel concentration cycles occur in streams with widely differing metal concentrations but similar pH values, precipitation and dissolution of a single mineral, such as a pure zinc phase, likely cannot explain the observed trends. However, specific metal phases could play a role in certain streams.

[49] Cyclic precipitation and dissolution of calcite could conceivably result in a diel cycle for Zn, Cd, and Mn, all of which partition strongly into calcite [*Lorens*, 1981; *Zachara et al.*, 1991; *Tesoriero and Pankow*, 1995]. Some of the alkaline streams we sampled likely have diel calcite cycles, with supersaturation during daylight hours because calcite solubility decreases as either pH or temperature increase during the day and undersaturation at night when pH and temperature decrease. In addition, even if the bulk stream water does not produce cyclic calcite precipitation, the process may occur on biofilm or periphyton surfaces, where water chemistry can be very different from the bulk water owing to steep gradients in CO_2 induced by photosynthesis or respiration. For example, *Hartley et al.* [1996] demonstrated that the pH of water near the surface of algal biofilms exposed to light was 1.05 to 1.57 pH units higher than that of the bulk water, and that the higher pH resulted in selective precipitation of calcite onto the biofilm. Although *Cicerone et al.* [1999] documented a diel cycle of calcite precipitation and dissolution in a eutrophic lake, similar studies have not been conducted for streams. Cyclic calcite precipitation cannot explain diel cycling of As, because As occurs as a large oxyanion molecule that would not easily substitute in a carbonate crystal lattice.

6.7. Adsorption

[50] Temperature- and pH-dependent adsorption reactions could affect dissolved metal concentrations in streams because temperature and pH have diel cycles in most streams. Water temperature varies in response to changing air temperature and incident solar radiation. Photosynthesis and respiration of biofilm and periphyton create the diel pH cycle. The individual effect of either temperature or pH on sorption reactions can explain the general diel concentration patterns. Cation adsorption should increase while anion adsorption should decrease whenever either pH or temperature increases in neutral to alkaline water. Therefore adsorption, unlike any of the other processes discussed here, can explain the opposite cycles exhibited by Cd, Mn, and Zn, which are cations and have a positive charge as compared to As, which occurs as an anion and has a negative charge. Furthermore, sorption is a plausible cause of diel metal cycles because adsorption and desorption, at least to external surface sites, are fast and reversible reactions [*Fuller et al.*, 1993; *Fowle and Fein*, 2000; *Trivedi and Axe*, 2000] which can respond effectively to the continual instream changes in temperature and pH. Inorganic substrates such as hydrous metal oxides as well as organic substrates such as biofilm undoubtedly play important roles in the adsorption processes and are abundant in the sampled streams. These substrates can be in suspension (colloids), on the streambed, or in the streambed (hyporheic zone). Lastly, several studies that specifically examined the effect of diel pH variation on metal concentrations in streams indicate the plausibility of this mechanism. Laboratory experimental data for Whitewood Creek in South Dakota [*Fuller and Davis*, 1989] support the hypothesis that diel changes in pH can produce cyclic variation in adsorption and desorption of arsenate anions onto inorganic stream substrates. Similarly, pH-controlled laboratory experiments using water, biofilm, and bed sediment from High Ore Creek (site 13) have shown that dissolved Zn concentrations are sensitive to small changes in pH and that the experimental variations in pH and Zn concentrations are similar to the diel variations in the stream [*Xie*, 2002].

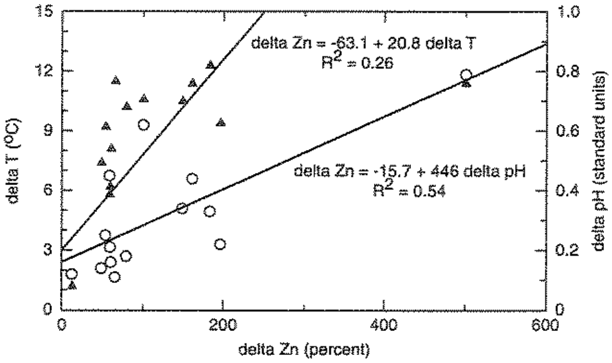

Figure 10. Relation of maximum diel change in Zn concentration to maximum diel change in pH (triangles) and water temperature (circles) at diel sampling sites.

[51] The strong similarity in the symmetry of plots of concentration, temperature, and pH, and the nearly simultaneous timing of the maxima and minima (Figures 8 and 9) point to the potential importance of temperature- and pH-dependent adsorption in controlling diel metal cycles. Another factor that suggests the importance of temperature- and pH-dependent adsorption is the relation between the amplitude of the concentration cycles and the amplitude of the pH and temperature cycles. As shown in Figure 10, the percent change in diel Zn concentration generally is proportional to the magnitude of the diel pH ($p = 0.003$) and temperature ($p = 0.061$) variations at a large number of sites, suggesting the importance of these two factors in widely varying stream environments. The data and correlations also suggest that pH has a more substantial effect than temperature.

[52] The effect of temperature on adsorption is not widely recognized but, as stressed by *Machesky* [1990], the effect of temperature on adsorption equilibria is large enough to have a significant effect on metal concentrations in natural aqueous systems. A number of experimental studies have

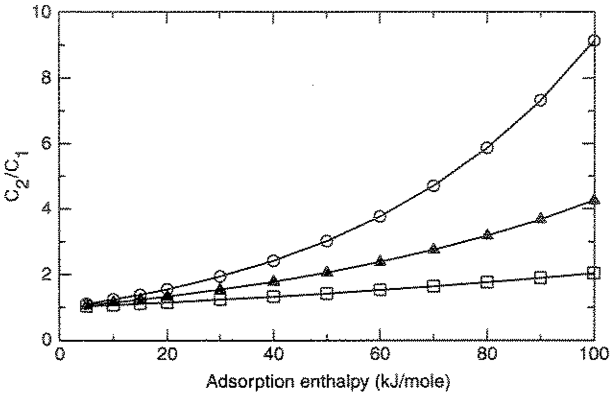

Figure 11. Influence of temperature on cation adsorption. C_2/C_1 is the ratio of the concentration of a given metal at two temperatures of interest. Curves are shown for T_1 = 20°C and T_2 = 5°C (squares), 10°C (triangles), and 15°C (circles).

documented the temperature dependence of adsorption of ions onto hydrous metal oxide surfaces [*Hodgson et al.*, 1964; *Foda et al.*, 1982; *Johnson*, 1990; *Machesky*, 1990; *Barrow*, 1992; *Rodda et al.*, 1996; *Angove et al.*, 1998; *Almås et al.*, 1999; *Trivedi and Axe*, 2000; *Scheckel and Sparks*, 2001]. These studies show that adsorption of metal cations is endothermic and therefore is favored by an increase in temperature. Conversely, adsorption of anions is exothermic and decreases with an increase in temperature. In addition, the surface charge on sorption substrates is temperature dependent, and this effect also increases cation adsorption as temperature increases [*Barrow*, 1992].

[53] *Machesky* [1990] illustrated that the ratio of the dissolved concentration of a given metal at two temperatures in a system in which adsorption is the limiting control on metal mobility can be determined using the Clausius-Clapyron equation:

$$\Delta H_{ads} = [2.303R \log(C_2/C_1)]/(1/T_2 - 1/T_1) \quad (1)$$

where ΔH_{ads} is the adsorption enthalpy (J mol^{-1}), R is the gas constant (8.3144J K^{-1} mol^{-1}), C is dissolved metal concentration, and T is temperature in degrees Kelvin. This equation can be rearranged to solve for the ratio C_2/C_1.

$$\frac{C_2}{C_1} = \exp\left[\frac{\Delta H_{ads}}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)\right] \quad (2)$$

[54] The solution to this equation is plotted in Figure 11 for T_1 = 20°C and T_2 = 15°C, 10°C, and 5°C. The results show that a doubling in aqueous concentration could occur for a 5°C, 10°C, or 15°C decrease in temperature, given an adsorption enthalpy of roughly +100 kJ/mol, +50 kJ/mol, or +30 kJ/mol, respectively. The latter values are well within the range of experimentally determined enthalpy values for adsorption of divalent metals onto hydrous oxide surfaces. For example, *Trivedi and Axe* [2000] reported adsorption enthalpies of +67 to +105 kJ/mol for adsorption of Cd and Zn onto hydrous oxides of Al, Fe, and Mn, with the highest enthalpies corresponding to adsorption of Zn onto hydrous Mn oxide. Because the absolute values of adsorption enthalpies fall in the order $Zn^{2+} > Cd^{2+}, Mn^{2+} > Cu^{2+}$ [*Machesky*, 1990; *Trivedi and Axe*, 2000, 2001], the magnitude of the concentration change during temperature-induced diel cycles should be largest for Zn, intermediate for Cd and Mn, and smallest for Cu. This progression of relative effect matches that observed in our field studies. In summary, the trends shown in Figure 11 provide a theoretical basis for proposing a causative relationship between temperature and dissolved metal concentrations at the field sites in mining-affected streams investigated in this study. In addition to this direct geochemical effect, temperature also can have an indirect effect on diel metal cycles because photosynthesis increases as temperature increases, causing increased pH and thus greater cation adsorption. However, the effect of these temperature-induced reactions likely is less important than the effect of pH-dependent adsorption in controlling diel metal cycles.

[55] The effect of pH on adsorption reactions is well established, with increasing pH producing increased cation adsorption and decreased anion adsorption [*Benjamin and Leckie*, 1981; *Dzombak and Morel*, 1990]. This effect is largely due to the decrease in protonation of hydrous metal-oxide surfaces as pH increases, resulting in a shift from a positive to negative surface charge [*Dzombak and Morel*, 1990]. Aqueous metal concentrations are especially sensitive to pH changes when the ambient pH is near the adsorption edge of a particular solute onto a given sorbent. For example, the amount of a dissolved metal adsorbed to a pure oxide, such as ferrihydrite, can change from near 0% to close to 100% as pH changes by 1 unit [*Stumm and Morgan*, 1996].

[56] The relative importance of mineral and organic substrates in metal adsorption reactions in neutral to alkaline streams is unknown. Geochemists traditionally have focused on the importance of hydrous metal oxides in the adsorption of metals from polluted waters, and clearly these oxides are key sorption substrates in mining-affected streams. However, relatively little attention has been paid to the importance of algal or bacterial biofilms as sorption substrates. Nonetheless, an increasing body of literature clearly demonstrates that microbiological substrates have a large capacity to adsorb metals [*Gray and Hill*, 1995; *Hill et al.*, 2000; *Fein et al.*, 2001; *Wilson et al.*, 2001]. Biofilm may be an especially dynamic sorption substrate in streams, because the diel range of pH at biofilm surfaces can be much greater than that of the bulk water column [*Hartley et al.*, 1996]. Experimental work to determine sorption equilibrium constants for components of biofilm is in its infancy [*Yee and Fein*, 2001]. We are not aware of any data that could be used to predict the temperature dependence of adsorption for these substrates.

7. Implications

[57] Efforts to characterize metal concentrations in streams 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 metal sources, plan and evaluate remediation, detect long-term trends for evaluating remediation effectiveness, evaluate potential risks to aquatic biota, and provide resolution on how streamflow conditions and

season influence concentrations. However, if diel 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.

[58] Diel variation of metal concentrations can complicate comparison of loads determined during synoptic sampling because of the difficulty in resolving whether load differences between sites are the result of actual inputs or simply an artifact of sampling time. If concentrations at a sampling site vary widely during the course of a day, then comparisons of load differences between sites may underestimate or overestimate actual inputs if successive sites are sampled many hours apart and at different phases in a diel concentration cycle. Unless the diel effect is accounted for by either design of the synoptic sampling schedule or by mathematical normalization of analytical results, only those between-site concentration differences that exceed the diel rate of change can be considered real.

[59] Similar to the effect on load determinations, long-term trend analysis could be complicated in streams having large diel variations if periodically collected samples over multiple years were obtained at different times of the day. The time-dependent concentrations could result in a wide range of concentrations for a given hydrologic condition (up to about 500% for some streams). Therefore the natural variability of diel concentration cycles could either obscure actual trends or indicate trends where none exist. Such effects on trend detection could produce misleading conclusions as to the effectiveness of remediation.

[60] In terms of potential risks to aquatic biota, diel variation of metal concentrations could have sustained effects that may be difficult to detect. A chronic stress conceivably could be imposed on aquatic biota if metal concentrations regularly exceeded chronic aquatic-life standards, even if only for parts of each day. However, characterization of short-lived exceedances may be difficult 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 and night.

[61] The occurrence of large diel concentration cycles likely will require changes in traditional sampling protocols used to monitor water quality in streams. For instance, the U.S. Environmental Protection Agency acute freshwater aquatic-life standards for metals apply to the 24-hr average concentration. Therefore adequate monitoring for regulatory compliance might require time- and volume-weighted composite samples collected for multihour periods. By combining the multihour samples into a single composite, the number of analyses would be no different than for a single discrete sample. Automatic samplers could facilitate this type of sampling, but the effects of compositing samples for multihour periods inside an automatic sampler would require further testing. For comparing metal concentrations among streams, a 24-hr average concentration may suffice. However, collecting one sample that would be representative of the 24-hr average concentration would be difficult because the ambient concentration in a stream will equal the average concentration of the diel cycle only during brief periods (less than an hour) at about noon and again about midnight. Furthermore, the timing of this brief period would not be known without prior detailed diel sampling during a period with nearly identical conditions of weather, streamflow, pH, temperature, day length, and other stream-specific factors that are not yet well understood.

8. Conclusions

[62] Diel cycles in dissolved As, Cd, Mn, and Zn concentrations are widespread during low-flow conditions, and occur irrespective of the ambient concentration in streams with neutral and alkaline pH. These diel metal cycles are synchronous with diel cycles in pH and water temperature but not with diel cycles in streamflow, DO, or specific conductance. Diel Zn cycles were the largest (up to 500%), Cd, Mn, and Ni cycles were intermediate (up to 119, 294, and 167%, respectively), and As cycles were the smallest (up to 54%). Cu did not exhibit consistent diel concentration patterns, but our data may have been affected by colloidal material with adsorbed Cu. Diel Zn cycles were not observed in the two acidic streams sampled.

[63] Our data suggest that one or more instream geochemical processes probably control diel metal cycles in most streams. Some mechanisms, such as groundwater exchange and Mn redox reactions, likely could be locally or perhaps universally important for specific metals. Adsorption is the only mechanism that potentially can explain cycling of both As and divalent metals. If adsorption does not control diel metal cycles, then multiple processes must be active to produce the inverse temporal patterns of the As and divalent metal cycles.

[64] Further study is needed to better understand the extent and causes of diel cycling of metals in fluvial systems. Field studies are needed to investigate the occurrence of diel metal cycles at additional sites, during different seasons and flow regimes, and in areas not affected by historical mining. Carefully designed instream and laboratory studies are needed to more definitively evaluate the relative importance of the plausible hydrological and geochemical mechanisms.

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