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ORIGINAL ARTICLE

Influence of diurnal cycles on metal concentrations and loads in streams draining abandoned mine lands: an example from High Ore Creek, Montana

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Abstract Diurnal water samples were collected simultaneously at four locations along High Ore Creek (Montana, USA), a small stream with near-neutral pH that contains elevated concentrations of Zn, Mn, Cd, and As from abandoned mines near its headwaters. During the same time period, two sets of synoptic samples were collected by workers moving in opposite directions along the stream. Large diurnal fluctuations in Zn concentration were found at three of the 24-h monitoring stations, but not at the outlet to a settling pond. Because the concentrations of Zn were dropping at most locations in the creek during the day (in response to the daily cycle of day-time attenuation and night-time release), the synoptic sampler who moved upstream obtained a data set that led to the conclusion that Zn load increased with distance downstream. The sampler who moved in a downstream direction obtained the opposite results. Thus, failure to take short-term diurnal cycling into account can lead to incorrect conclusions regarding spatial or temporal trends in water quality within a watershed.

Keywords Diel · Diurnal · Zinc · Arsenic · Geochemistry

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Introduction

The State of Montana, USA, has several hundred abandoned hard rock mine sites, most of which are located in remote mountainous regions, and many of which are discharging water of poor quality to local streams (Montana DEQ 1996). Because the majority of these abandoned mines have no corporate owner, government agencies are left with the burden of reclamation and long-term monitoring. Contaminants of concern include heavy metals (e.g., Cd, Cu, Mn, Ni, Pb, Zn), metalloids (As, Se), and acidity. These contaminants enter the watersheds by a number of different pathways, including adit discharges, leaching of solutes from waste rock or tailings piles located within a stream bed or floodplain, or discharge of contaminated groundwater to the stream. The State of Montana has prioritized the various abandoned mine sites for clean-up, with the severity of contamination and threat to human health being the two main criteria used to rank the sites (Montana DEQ 1996). Typically, the ongoing reclamation activities involve mitigation of surface features, such as removal of waste rock and tailings, diversion of surface water around mine dumps, revegetation, and construction of settling ponds or wetlands. Treatment of adit discharges is often not possible, given the high costs involved and the remoteness of many of the mines.

The success of a given reclamation project is often assessed by comparing the local surface water quality before and after the remedial work. Such efforts usually involve collection of water samples over a multiple-year period at a number of strategic locations within a watershed, and may involve seasonal or event (e.g., summer storm) sampling. However, the usefulness of this approach is compromised when concentrations of dissolved or total metals vary cyclically over a 24-h period. Such ‘‘diel’’ or ‘‘diurnal’’ cycles can be very large (e.g., up to a fivefold change in dissolved Zn concentration, Nimick et al. 2003), and are known to exist in many streams draining abandoned mine lands in the northern Rocky Mountains (Brick and Moore 1996; Nimick et al. 2003, 2005; Gammons et al. 2005), and elsewhere (e.g., Bourg and Bertin 1996). In some cases, the 24-h variations in metal concentration can be greater than the seasonal or long-term (e.g., pre- vs. post-reclamation) differences (Nimick et al. 2005). Monitoring programs that do not take these diurnal cycles into account may lead to erroneous conclusions regarding the effectiveness of the remediation work if samples are collected at different times of the day in subsequent years.

As well as complicating the comparison of metal concentrations collected at the same location in different years, diurnal cycling can also influence the results of synoptic investigations. Such studies involve collection of multiple, closely-spaced samples along a stream by teams of samplers working upstream or downstream (e.g., Kimball et al. 2002; Wayland et al. 2003). The results are used to draw conclusions regarding the location of point or non-point sources of contamination, and also whether a given solute is behaving conservatively or non-conservatively in a watershed. For example, a steady increase in load with distance downstream would most likely indicate a widespread, predominantly non-point source of contamination, with little if any chemical attenuation. In contrast, a steady decrease in load with distance would indicate that the contaminant of concern is being attenuated—for example, by chemical or biological reactions occurring in the water column or streambed. However, a synoptic sampling event may take many hours or days to complete. If solute concentrations at any given point along the stream are varying diurnally, then this can lead to incorrect conclusions regarding whether the metal concentration or load (concentration × streamflow) is increasing or decreasing with distance downstream.

The purpose of this paper is to discuss diurnal variations in the concentration of Zn in High Ore Creek, a small stream draining abandoned mine lands in southwest Montana. In order to get a better spatial understanding of Zn cycling in the watershed, four simultaneous diurnal samplings were conducted at four locations along the stream. In conjunction with the diurnal sampling, two sets of synoptic water samples were collected from the stream; one by a worker who was moving upstream and a second by a worker moving downstream. The implications of this study to water quality monitoring studies of other rivers and streams, particularly those near abandoned mine sites, are discussed.

Site description and previous work

High Ore Creek is a small watershed (22 km^2) located in southwest Montana approximately midway between the cities of Butte and Helena (Fig. 1). The local geology is dominated by granitic rock of the Cretaceous Boulder Batholith and coeval volcanic units. Elevations range from 1,580 to 2,410 m and the climate is characterized by cold, snowy winters and warm, dry summers occasionally interrupted by convective thunderstorms. Stream discharge varies seasonally, but averages 10–30 l/s during summer and fall baseflow periods. High Ore Creek flows into the Boulder River of the upper Missouri drainage basin. The High Ore Creek watershed is bounded to the west by Basin Creek and Cataract Creek (Fig. 1). The latter two streams, together with the upper Boulder River, comprise the Basin Mining Area which was recently included on the US Environmental Protection Agency’s National Priority List (NPL), more popularly known as ‘‘Superfund’’. The US Geological Survey (USGS) has published a compendium of monitoring and scientific studies addressing trace metal contamination in the Basin-Boulder mining district (Nimick et al. 2004). The present study was conducted independent of the work of the USGS, but complements and reinforces their earlier findings.

High Ore Creek has been severely impacted by pollution from the abandoned Comet Mine, located 7 km upstream of the confluence with the Boulder River (Gelinas and Tupling 2004). Most of the recorded production was between 1883 and 1941, during which over $20M of Ag–Pb–Zn sulfide ore was produced from large quartz-rhodochrosite veins cutting granite bedrock (Roby et al. 1960). Mill tailings and waste rock from the combined underground/open pit operation were discarded in the creek. Reclamation activities conducted between 1990 and 2001 included removal of mine waste from the streambed and floodplain and disposal in nearby repositories, stream re-construction and floodplain re-vegetation, and construction of two small settling ponds below the Comet Mine site (Gelinas and Tupling 2004).

Despite the abundance of sulfidic mine waste in its headwaters, High Ore Creek has always had a near-neutral to alkaline pH. However, concentrations of several contaminants exceed current Montana regulatory standards, including As, Zn, and Cd. Previous

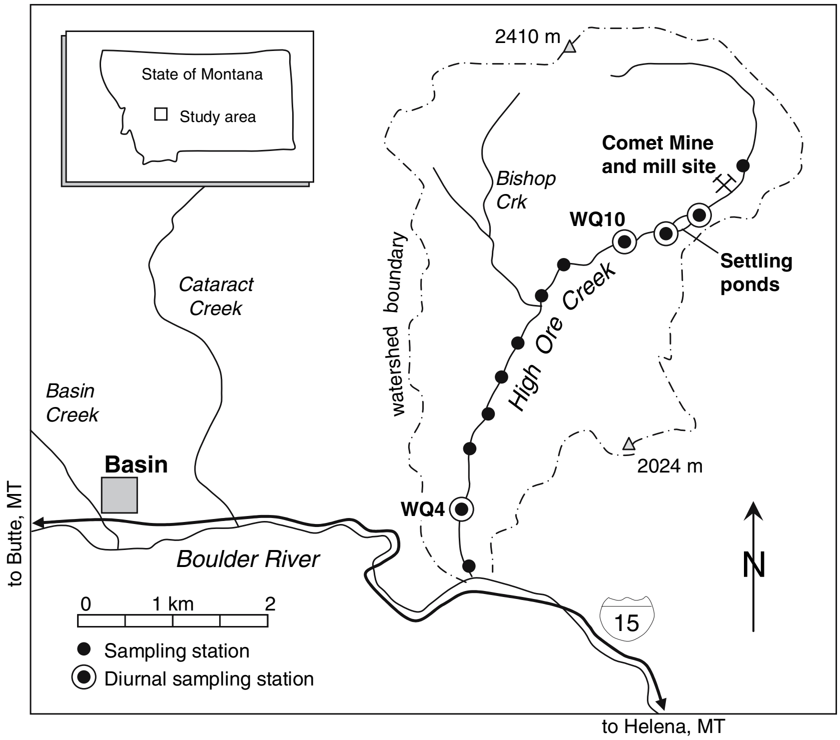

Fig. 1 Map of High Ore Creek, showing the location of diurnal and synoptic sampling stations used in this study. The boundary of the High Ore Creek watershed is shown by the *dot-dashed line*. The Boulder River flows from west to east across the map

studies by Nimick et al. (2003), Lambing et al. (2004), Shope et al. (2006), and Morris et al. (2005) have documented the existence of large and robust diurnal cycles in dissolved and total Zn and Cd concentrations in High Ore Creek. Zn and Cd concentrations typically reach a minimum in the late afternoon (when pH and water temperature are highest), and a maximum in the early morning (when pH and temperature are lowest). Although the concentrations of Zn in the stream have shown some improvement when comparing pre- versus post-reclamation data (Gelinas and Tupling 2004), the diurnal cycles in Zn concentration have persisted.

Methods

The field work described in this study was conducted during August 25–26, 2003. The weather during this period was warm, sunny, and dry.

Automated samplers were installed at three locations along High Ore Creek (Fig. 1), and were programmed to collect 0.5 l samples on hourly intervals. These locations included: (1) the inlet to the settling ponds; (2) monitoring station WQ-10, located approximately 0.5 km below the outlet from the ponds; and (3) monitoring station WQ-4, located approximately 1 km upstream of the mouth of High Ore Creek. All of the sample containers were acid-washed polyethylene bottles, and were thoroughly rinsed with de-ionized water prior to field sampling. During each hourly sampling event, the automated samplers flushed their nylon sampling tubes once with stream water before filling their respective bottles. The sample bottles were collected at the end of the diurnal period. Because of the possibility of back-reaction between dissolved and suspended solid while the water was stored in the sample bottles, no attempt was made to filter the stream samples to obtain dissolved metal concentrations. In the laboratory, 5 ml of concentrated Trace Metal grade HNO_3 was added to each bottle and the samples were digested for 1 week at room temperature. The total "acid available" concentrations of a suite of major and trace elements in each sample was then determined by Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES). A fourth set of diurnal water samples was collected manually at the outlet to the settling ponds (Fig. 1), following methods discussed below for the synoptic samples. A total of 12 samples were collected at this site over the 24-h period.

Field parameters (water temperature, specific conductance, and pH) were continuously monitored at sites WQ-4 and WQ-10 using Hydrolab Datasonde multimeters. The multimeter at WQ-10 also collected dissolved oxygen (DO). These units were calibrated according to the manufacturer's specifications, and were placed in ~30 cm of water with a velocity of >0.3 m/s. At the inlet and outlet to the settling ponds, field parameters were collected using a freshly calibrated, hand-held WTW 340i multimeter. At WQ-4, WQ-10, and the outlet to the settling ponds, streamflow was measured by Parshall Flumes that had been previously installed by the Montana Bureau of Mines and Geology (MBMG) or the USGS. The flumes at WQ-4 and WQ-10 both had a water level recorder in a stilling well that provided a continuous record of streamflow. At the pond outlet, the flume staff gage was read manually each time the station was visited, approximately every other hour. At the inlet to the settling ponds, stream discharge was determined by manual measurement using a Marsh-McBirney Flo-Mate velocity meter. A stage-discharge rating curve was established from four discharge measurements performed over a 36-h period, and a staff gage in the stream was read during each visit to the site.

On the afternoon of August 25, 2003, a set of 11 water samples was collected from upper High Ore Creek in the reclaimed meadow between the Comet Mill site and the inlet to the upper settling pond. The purpose of this exercise was to examine the loading of Zn and other contaminants through this gaining stream reach. Each sample location was separated by 150 m, and all samples were collected over a 30-min period, between 15:00 and 15:30. Stream pH and specific conductance (SC) were recorded, and all water samples were unfiltered.

Two sets of synoptic samples were collected on lower High Ore Creek on August 26, 2003. One sampler worked downstream beginning at the furthest upstream station (located above the Comet Mine, Fig. 1), whereas the other sampler worked upstream beginning at the furthest downstream station (near the mouth of High Ore Creek). Each sampler collected her first water sample at 8:00 in the morning, moved in opposite directions to the next station, and then collected each subsequent sample precisely on the hour, ending at 19:00 in the late afternoon. Streamflow was measured at 0.6 × total depth at each station with a Marsh McBirney current meter. At least eight water velocity measurements were made for each stream cross-section, which was sufficient given the small size of the stream (less than 1 m wide in most reaches). After measuring streamflow, a pair of water samples was collected, one filtered to 0.2 μm and the other non-filtered. The water samples were stored in 60 ml high density polyethylene (HDPE) bottles that had previously been acid-washed. Filtration was accomplished using a plastic syringe and 0.2 μm PES syringe filters. Field blank samples showed traces of Zn in the filtered samples, although the concentrations were low enough (<0.003 mg/l) to not affect the outcomes or conclusions of the study. Each sample was acidified with 0.6 ml of concentrated Trace Metal HNO_3 and stored in the refrigerator until analysis.

All samples were analyzed for a suite of 26 metals by ICP-AES at the Murdock Laboratory at the University of Montana, Missoula, MT. EPA Method 200.15 was used, which employs ultra-sonic nebulization. Continuing calibration verification standards, laboratory blanks, sample replicates, and spikes were run every 10 samples, and all quality control checks passed for all elements reported in this paper. Field duplicate samples ($n = 3$) agreed within 2% for all elements, with the exception of one Fe duplicate sample (25%).

Results

Metal loading above the settling ponds

Figure 2 summarizes results of the detailed synoptic sampling in the reclaimed meadow between the Comet Mine site and the settling ponds. Concentrations of total (non-filtered) trace metals in upper High Ore Creek were very low before entering the former area of the mine. However, as the creek passed through the meadow, concentrations of Zn and Mn rose steadily to values near 2 mg/l at the inlet to the settling ponds. These two metals were highly correlated with each other, as well as with SC. Other trace metals that showed a similar increase through this reach included Cd, Ni, and Pb. A number of prominent, red-stained springs are present in the floodplain below the Comet Mill. Mini-piezometers and shallow monitoring wells installed in the reclaimed meadow (Shope 2003; Sudbrink 2007), as well as detailed stream gaging and continuous tracer injection studies (Sudbrink 2007), indicate that this portion of the stream is gaining a significant amount of highly contaminated groundwater. Concentrations of Zn in the discharging shallow groundwater are very high, with most samples in excess of 10 mg/l and a few exceeding 100 mg/l Zn (Shope 2003; Sudbrink 2007).

As shown in Fig. 2, concentrations of total Fe and As initially rose in the upper portion of the reclaimed meadow, but then dropped through the lower reach. The latter observation is explained by oxidation of soluble Fe^{2+} (sourced from shallow groundwater) to hydrous ferric oxide (HFO), with simultaneous co-precipitation of As (Sherman and Randall 2003). Concentrations of total P also decreased steadily through the meadow, which could be due to a combination of uptake by algal biofilms as well as sorption or co-precipitation onto HFO (Tate et al. 1995).

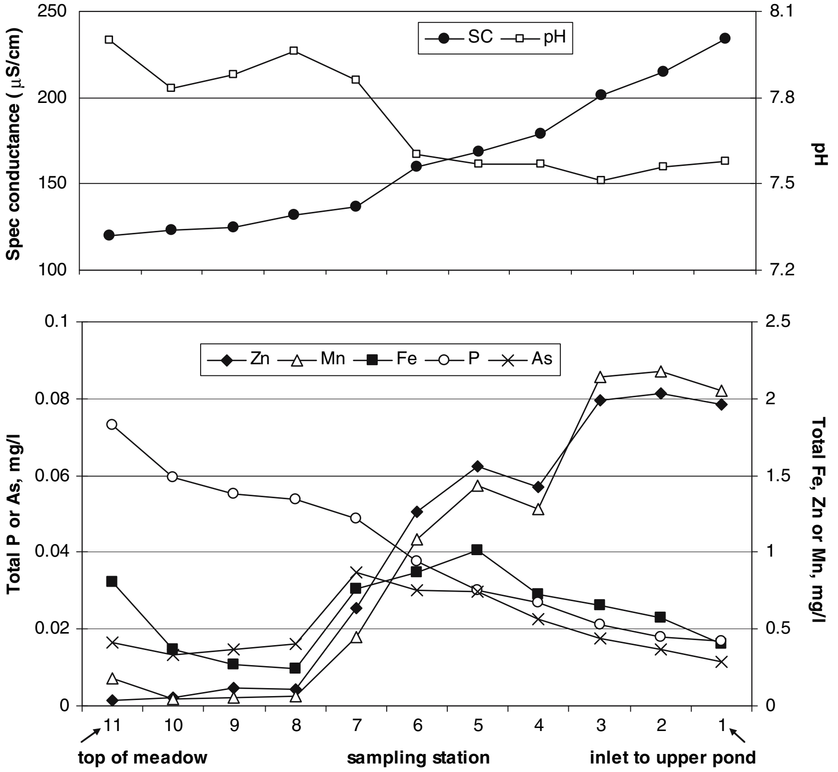

Fig. 2 Synoptic changes in pH and specific conductance (*top*) and total Fe, Zn, Mn, P, and As (*bottom*) in the reclaimed meadow between the Comet Mill site and the upper settling pond. All sample locations were separated by exactly 150 m, and were collected within a 30 min period between 15:00 and 15:30, August 26, 2003

Diurnal changes

Figure 3 shows diurnal changes in water temperature, pH, and streamflow recorded on August 25–26, 2003 at the inlet to the upper settling pond, the outlet to the lower settling pond, station WQ-10, and station WQ-4 (see Fig. 1 for locations). With the exception of the lower pond outlet, the pH at each diurnal station increased during the day, as is usually the case in pH-neutral to alkaline streams with moderate to high biological activity. The increase in pH was primarily due to consumption of dissolved CO_2 by aquatic plants and algae during the photic period when photosynthesis was the dominant biological process. The total 24-h range in pH was greatest at WQ-10, which is consistent with the abundance of periphyton at this location in the creek (Morris et al. 2005). The much smaller range in temperature and lack of a diurnal pH cycle at the outlet to the settling ponds was probably due to mixing of water in the pond.

Streamflow followed a diel cycle of increased flow during the night and decreased flow during the day at the inlet to the ponds, and also near the mouth of High Ore Creek at WQ-4 (Fig. 3). This pattern is typical of High Ore Creek in the summer, and is explained by day-time loss of shallow groundwater to evapotranspiration from riparian vegetation in the floodplain of the creek (Bond et al. 2002). Owing to the large residence time of water in the two settling ponds, no such diel cycle in streamflow was noted at the lower pond outlet. Instead, an overall decrease in flow was observed, which could have been due to drain-down of the ponds after a rain event that had occurred on August 22, 3 days before the diel sampling was conducted. Because of the short stream reach and lack of riparian vegetation between the pond outlet and WQ-10, the flows at these two stations were closely correlated (Fig. 3).

Dissolved oxygen concentrations at WQ-10 were between 95 and 105% of local atmospheric saturation at all times during the diel period (data not shown). Values above 100% were recorded between 11:00 and 16:00, corresponding to the mid-day hours of maximum photosynthesis.

Systematic diel fluctuations in total Zn concentration in High Ore Creek were observed at all of the sampling sites with the exception of the outlet to the settling ponds (Fig. 4). Minimum Zn concentrations occurred at 14:00 at the pond inlet, 16:00 at WQ-10, and 17:00 at WQ-4. At all three stations, Zn levels rose to a plateau during the night. The increase in total Zn concentration, defined here as the difference of the maximum and minimum concentrations divided by the minimum concentration, was 53% at the pond inlet, 109% at WQ-10, and 48% at WQ-4. In general, the magnitude of the diurnal fluctuations we observed in

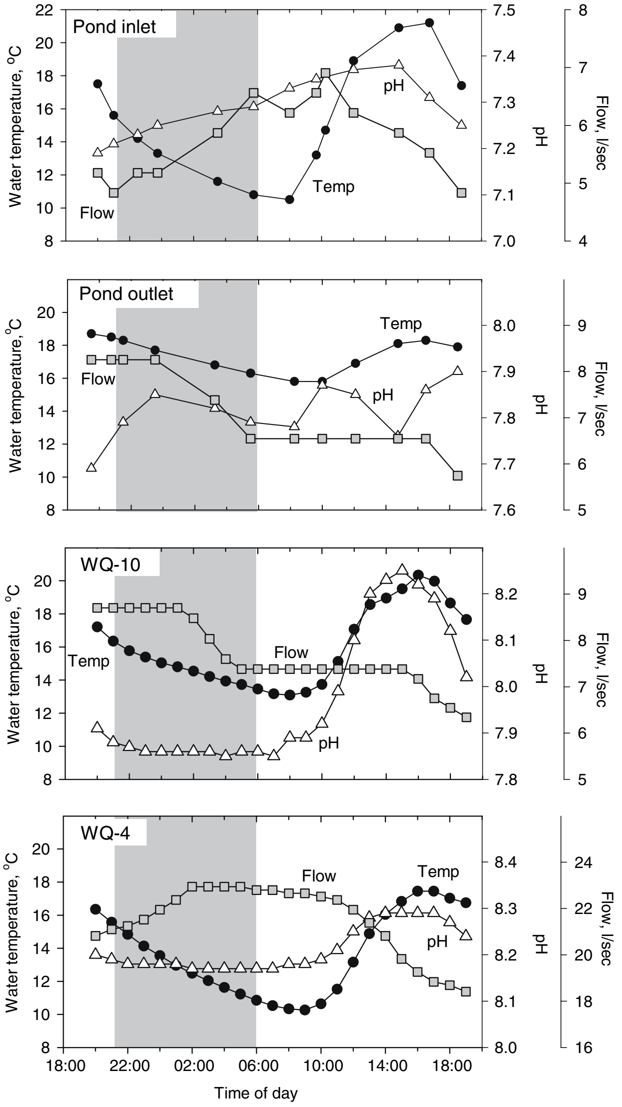

Fig. 3 24-hour changes in water temperature, pH, and streamflow at each diurnal monitoring station during August 25–26, 2003. The *shaded region* shows the approximate hours of nighttime

August 2003 were quite a bit less than what has been reported in previous studies of diurnal Zn cycling in High Ore Creek (e.g., Nimick et al. 2003; Lambing et al. 2004; Morris et al. 2005). The reasons for the more subdued cycles in this study are not known with confidence, but are tentatively attributed to the rain event that preceded our diurnal work by several days that may have flushed some of the Zn-rich organic or mineral substrates from the streambed. Although filtered samples were not collected at the diurnal stations, paired filtered and non-filtered samples collected by the synoptic samplers (see below) showed that Zn was predominantly (>80%) present in the dissolved phase.

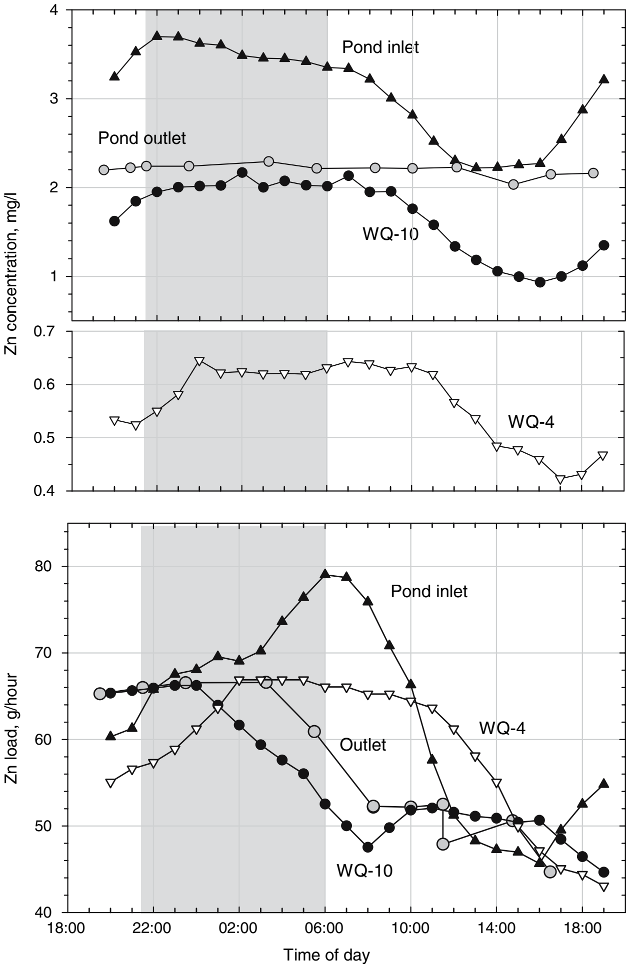

Fig. 4 Diurnal changes in total Zn concentration (*top*) and total Zn load (*bottom*) during August 25–26, 2003. The Zn concentration data were obtained by AAS. The *shaded region* shows the approximate hours of nighttime

Figure 5 summarizes diurnal changes in Zn concentration at the inlet to the settling ponds and at WQ-10 in relation to other selected elements of interest, including Fe, Mn, K, Cd, As, and P. At the ponds inlet, Zn and Cd followed a nearly identical diel pattern. Mn also followed a similar temporal pattern, but with a more subdued amplitude of variation. In contrast, As and P were both highly correlated with Fe, and were slightly out of phase with the peaks and valleys in the diel profiles for Zn, Cd, and Mn. At the range in pH of the pond inlet (~7 to 7.5) both As and P should have been dissolved predominantly as anions of a similar form (HAsO_4^{2-} and HPO_4^{2-}), both of which are known to adsorb strongly onto hydrous ferric oxide.

In contrast to the other stations, the outlet to the settling ponds showed no significant diel change in the concentration of Zn (Fig. 4), nor any other solute (data not shown). This result is consistent with the pH data

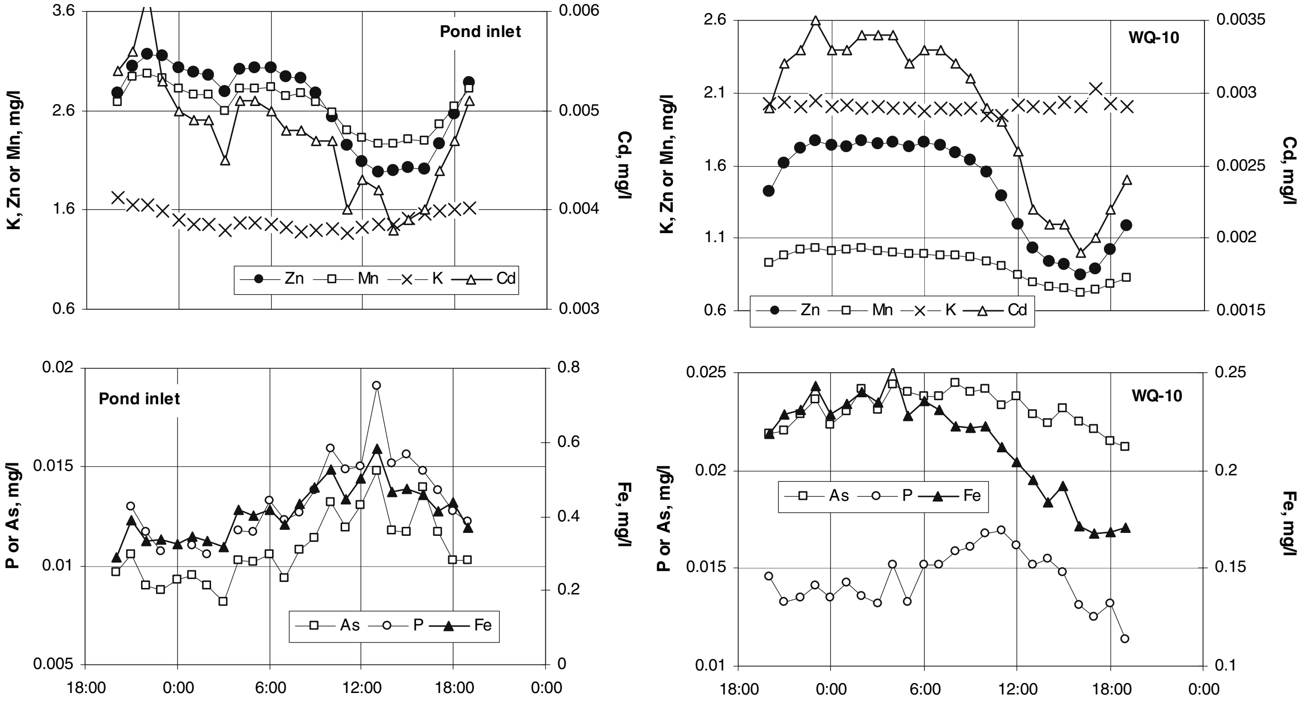

Fig. 5 Diurnal changes in the total concentration of selected elements of interest at the inlet to the settling ponds (*left*) and at WQ-10 (*right*). The *top pair* of diagrams show data for K, Cd, Mn, and Zn. The *bottom pair* show data for Fe, As, and P. All data were obtained by ICP-AES

summarized above, and suggests that the ponds act as mixing tanks that tend to even out any diurnal cycle in chemistry of the upstream influent waters. The fact that a strong diel cycle in Zn concentration was established in the relatively short stream reach (~0.6 km) between the pond outlet and WQ-10 is highly significant. This phenomenon was first noted by Morris et al. (2005), who attributed the diel Zn fluctuations at WQ-10 to in-stream micro-biological processes that were highly sensitive to the presence or absence of sunlight.

As shown in Fig. 4, the concentrations of Zn in High Ore Creek at each diurnal station generally decreased with distance downstream. However, when redrawn in terms of Zn load (Fig. 4b) the spatial and temporal trends are less clear. At all four stations, the Zn loads (g/h) peaked during the night of August 25 and decreased during the following day. However, the shapes of the diel patterns in Zn load and the timing of the maxima and minima varied considerably from site to site. The complex behavior in Zn load with respect to space and time is most likely due to the interference between the diel streamflow patterns at each site and the diel bio-geochemical reactions that are influencing the in-stream Zn concentrations. The implications of these changes are discussed in more detail below.

Table 1 summarizes the total loads (kg/day) of Zn, Mn, As, and Fe transported down High Ore Creek at each of the four diurnal stations between 20:00 on August 25 and 19:00 on the following day. There was a 10% decrease in total Zn load between the inlet and outlet to the settling ponds, and a further 18% decrease in Zn load between the pond outlet and station WQ-10. Manganese showed similar decreases in the upper stream reaches. The decrease in Zn and Mn load through the settling ponds was probably due in part to physical settling of metalliferous particles within the ponds, but also to chemical attenuation in response to a slight increase in pH as water passed through the ponds (see below). The sharp decrease in Zn and Mn load in the short stream reach between the pond outlet and

Table 1 Integrated 24-h loads (g/day) of total Zn, total Mn, total As, and total Fe at each of the four diurnal sampling stations

Location	24-h metal load (g/day) and % change from upstream station							
	Zn	ΔZn (%)	Mn	ΔMn (%)	As	ΔAs (%)	Fe	ΔFe (%)
Pond inlet	1,320		1,310		5		206	
Pond outlet	1,180	–10	939	–28	19	250	229	11
WQ-10	974	–18	613	–35	15	–19	143	–37
WQ-4	956	–2	171	–72	58	280	408	185

The Δ columns represent the percentage change in load between a given station and the preceding upstream station

WQ-10 was likely due to biological attenuation (Morris et al. 2005) and/or precipitation of hydrous Mn–Zn oxides that form a coating between surface biofilms and underlying cobbles and gravels of predominantly granitic composition (Shope et al. 2006). In the long stream reach between WQ-10 and WQ-4 there was no further change in total Zn load, implying that this metal was behaving conservatively in lower High Ore Creek when averaged over 24 h. In contrast, Mn load continued to decrease between WQ-10 and WQ-4, most likely in response to the slow oxidation of dissolved Mn^{2+} to hydrous Mn(III, IV) oxides.

In contrast to Zn and Mn, the total As load increased dramatically as water passed through the settling ponds. This large increase in As load may have been caused by bacterial reduction of As(V) to more mobile As(III), or perhaps by reductive dissolution of As-rich hydrous ferric oxide near the pond sediment–water interface. Below the ponds, As load decreased slightly to WQ-10, and then increased substantially in the lower reaches of High Ore Creek. Because this lower portion of the creek is perched or losing (Shope 2003), the increases in load imply a residual source of As contamination within the streambed. Trends in total Fe load followed more or less the same patterns as As, but were generally more subdued.

Synoptic changes

Figures 6 and 7 summarize pertinent results of the synoptic sampling of High Ore Creek conducted on August 26, 2003. The data labeled ‘‘downstream’’ were collected by a sampler moving down the creek, from the near-pristine waters above the Comet Mine to the confluence with the Boulder River. The data labeled ‘‘upstream’’ were collected by a sampler moving in the reverse direction. Data in Fig. 6 are presented as instantaneous Zn concentrations in mg/l; data in Fig. 7 are presented as instantaneous metal loads of Zn, Mn, and As, computed from the product of the total metal concentration and the measured streamflow at each station. The results of streamflow measurements collected by the downstream sampler are given in Fig. 6 for reference.

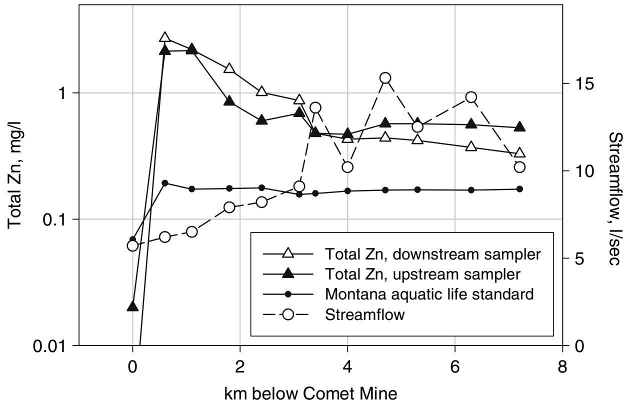

Fig. 6 Synoptic changes in the concentration of total Zn for the High Ore Creek drainage on August 26, 2003. Separate data are shown for the upstream and downstream samplers. Also shown for reference are the current aquatic life standards for Zn (Montana DEQ 2006) and the streamflow as measured by the downstream sampler

The trends in total Zn concentration (Fig. 6) and Zn load (Fig. 7a) show that virtually all of the Zn in the drainage enters High Ore Creek between the Comet Mill site and the upper settling pond. As discussed above, most of this Zn (as well as Mn and Cd) presumably comes from groundwater baseflow or surface seeps. From just below the mine site to the mouth of High Ore Creek, the concentrations of total Zn in the water column were well above the current regulatory standards based on aquatic health (Montana DEQ 2006). Because the regulatory standard for Zn depends on stream hardness, the standard changes slightly from station to station (Fig. 6). Based on a comparison of filtered and non-filtered samples, Zn was predominantly present in the dissolved phase at all sampling stations. The percentage of Zn as particles >0.2 μm in diameter increased with distance downstream, but nowhere exceeded 20% of the total Zn concentration.

The concentrations and loads of Zn and other metals exiting the lower settling pond were the same for both the upstream and downstream samplers, reflecting the nearly constant chemistry at the pond outlet. However, below the ponds, different synoptic trends in Zn concentration and Zn load were obtained, depending on whether the sampler started at the mouth of High Ore Creek in the morning and worked upstream, or the reverse. The upstream sampler found a general trend of increasing Zn load from the WQ-10 station to the mouth of the creek (Fig. 7a). In contrast, the downstream sampler found a general decrease in Zn load with distance downstream. This interesting result is a direct consequence of the previously documented short-term temporal variation in Zn concentrations in High Ore Creek during summer base-flow conditions.

Total As load more or less steadily increased along the entire drainage, whereas Mn load decreased (Fig. 7b, c). Below the settling ponds, concentrations of As in High Ore Creek were two to three times higher than the recently lowered Human Health Standard of 10 μg/l (Montana DEQ 2006). The percentage of total As present as filterable particles in each water sample ranged from 8 to 48% (average of 18%), and tended to

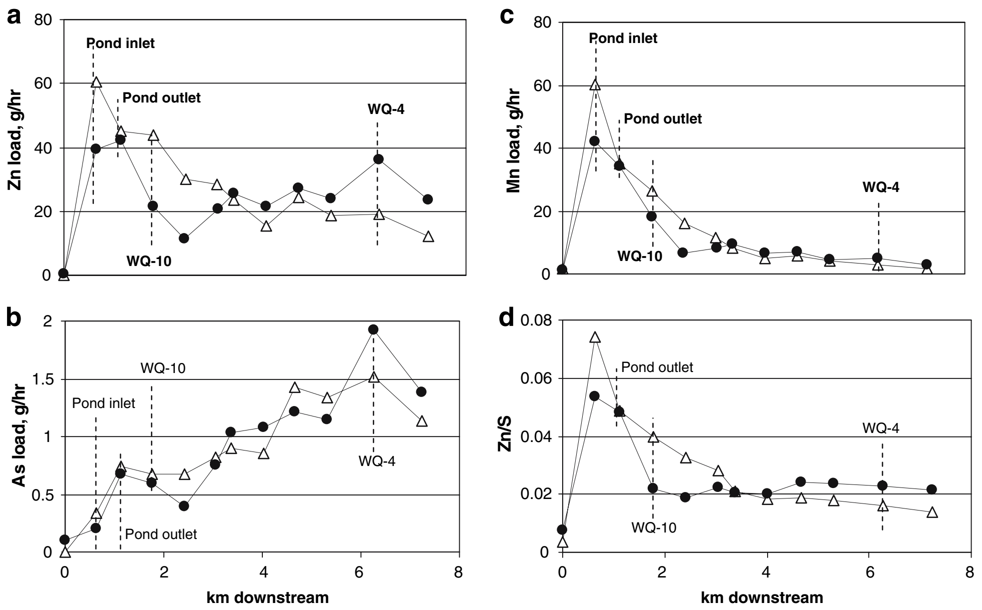

Fig. 7 Synoptic changes in the total load of Zn, Mn, and As, as well as the Zn/S ratio, for the High Ore Creek drainage on August 26, 2003. Data points shown by *open triangles* were obtained from a sampler who was moving downstream, whereas data shown by the *closed circles* were obtained by a sampler moving upstream. The Zn/S ratio diagram may be used to get a better idea of the conservative vs. non-conservative nature of Zn transport through different portions of the watershed (see text)

decrease with distance downstream. Although Montana has no primary drinking water or aquatic health standards for manganese, a secondary maximum contaminant level of 50 µg/l has been established (Montana DEQ 2006). Concentrations of total Mn in High Ore Creek below the mine site were well above this secondary MCL, although the concentrations decreased in the lower reaches and approached the MCL value of 50 µg/l near the mouth (Table 2). Particulate forms of Mn comprised 0–71% (average of 31%) of the total Mn concentration, and unlike As increased steadily with distance downstream. The small differences in synoptic trends for these metals based on whether sampling was conducted upstream or downstream are consistent with the fact that diurnal changes in the concentration of As and Mn were smaller than for Zn at all four of the diel sampling stations. Thus, in contrast to Zn, the overall conclusions based on the synoptic load analyses for As and Mn in High Ore Creek are not changed when one takes diel cycling into account.

There is considerable scatter in the Zn load trends (Fig. 7a), due mainly to error in streamflow measurement (Fig. 6). Accurate measurement of streamflow in small, steep, and rocky creeks is difficult at best, and the error is increased by the fact that a particular flow measurement only captures water that flows across the surface of the streambed, and does not allow for shallow, hyporheic water that may be moving down the drainage in the bouldery subsurface of the streambed. To eliminate error due to streamflow measurement, the data for Zn were normalized to sulfate. Here it was

Table 2 Selected data collected by synoptic samplers working downstream or upstream in High Ore Creek on August 25, 2003

Location (km)		Downstream sampler						Upstream sampler				
		Time	pH	Q	Zn	Mn	As	Time	Q	Zn	Mn	As
Above mine	0.0	8:00	8.15	5.7	0.00	0.00	0.020	19:00	4.8	0.02	0.07	0.006
Pond inlet	0.6	9:00	7.28	6.2	2.71	2.69	0.011	18:00	5.1	2.14	2.65	0.010
Pond outlet	1.1	10:00	8.15	6.5	2.21	2.69	0.015	17:00	6.2	2.16	2.29	0.011
WQ-10	1.8	11:00	8.06	7.9	1.54	0.93	0.024	16:00	7.1	0.85	0.70	0.023
WQ-9B	2.4	12:00	8.05	8.2	1.01	0.54	0.023	15:00	5.2	0.60	0.34	0.021
WQ-9	3.1	13:00	8.11	9.1	0.87	0.36	0.025	14:00	8.3	0.69	0.28	0.025
WQ-7	3.4	14:00	8.25	13.6	0.48	0.17	0.018	13:00	15.0	0.48	0.17	0.019
WQ-5	4.0	15:00	8.24	10.2	0.43	0.14	0.023	12:00	12.7	0.47	0.15	0.024
WQ-4C	4.7	16:00	8.18	15.3	0.44	0.11	0.026	11:00	13.3	0.57	0.14	0.026
WQ-4B	5.3	17:00	8.16	12.5	0.42	0.10	0.030	10:00	11.8	0.57	0.11	0.027
WQ-4	6.3	18:00	8.31	14.2	0.37	0.06	0.030	9:00	18.0	0.56	0.08	0.030
WQ-3	7.2	19:00	8.33	10.2	0.33	0.05	0.031	8:00	12.4	0.53	0.07	0.031

Q is streamflow in l/s. Total metal concentrations are mg/l assumed that sulfate behaves conservatively in High Ore Creek. This is a reasonable assumption, since sulfate is an anion that does not adsorb strongly at alkaline pH, and since the creek water is nowhere near saturation with any sulfate minerals. The results (Fig. 7d) once again show contrary patterns in Zn/S loading with distance downstream, depending on whether sampling was conducted in an upstream versus downstream direction. However, the data in Fig. 7d are much smoother than in Fig. 7a.

Discussion

Causes of diurnal Zn cycles

A number of mechanisms have been proposed to explain the diurnal Zn cycles in High Ore Creek. Nimick et al. (2003) and Shope et al. (2006) argued that the concentration fluctuations were caused by pH- and temperature-dependent adsorption of Zn^{2+} onto hydrous metal oxides on the creek bed. Boulders in High Ore Creek are typically coated with a dark brown to black layer of poorly crystalline, hydrous Mn oxide that is extremely rich in Zn (up to 20 wt %) (Shope et al. 2006). In contrast, Morris et al. (2005) argued that surface biofilms in the creek bed play a critical role in Zn cycling. As discussed by Morris et al. (2005) and Shope et al. (2006), biofilms recovered from High Ore Creek are enriched in Zn (up to 10% dry weight). Whether this Zn exists as organically-bound metal or as trapped mineral particles is not known.

The above hypotheses help to explain why some locations in High Ore Creek showed larger fluctuations in Zn concentration than others. The two sites with the largest Zn cycles were located in reaches of the stream with particularly abundant biofilm and thick (several mm) mineral coatings of hydrous Mn–Zn oxide. At the downstream WQ-4 station, both biofilm and hydrous metal oxide coatings were present, but were much less obvious. Although the relative importance of the organic versus inorganic material to the cycling of Zn is not known with confidence, it is likely that they work in concert. For example, algal biofilms are known to create large temporal and spatial gradients in pH and redox conditions in streams, due to their daily cycle of photosynthesis and respiration (Hartley et al. 1996; Haack and Warren 2003; Harrison et al. 2005). During the day, dissolved CO_2 is consumed (causing pH to increase) and O_2 is produced (causing Eh to increase). At night, these processes reverse. The combination of higher pH, higher temperature, and higher Eh promotes precipitation of hydrous Mn and Fe oxides during the day, and enhances the rate of sorption of metal cations (such as Zn^{2+}) onto these surfaces. It is also possible that Zn^{2+} ions are bonding directly to organic material in the biofilms, as suggested by Morris et al. (2005).

Table 3 summarizes the linear regression correlation coefficients (r^2) between total Zn and streamflow, pH, and temperature for diurnal data collected at the inlet to the ponds, WQ-10, and WQ-4. Similar data are not shown for the pond outlet, due to the very small range in Zn concentration at this site. Correlations for Zn versus pH and Zn versus temperature were consistently negative, with $r^2 > 0.6$. These negative correlations are in broad agreement with previous field and laboratory studies (Nimick et al. 2003, 2005; Shope et al. 2006) that have shown that dissolved Zn concentrations in High Ore Creek decrease rapidly in response to relatively small increases in pH and temperature. Although a strong positive correlation was found between Zn and streamflow at WQ-4 ($r^2 = 0.86$), the correlations were poor for this pair of parameters at WQ-10 ($r^2 = 0.36$) and the inlet to the ponds ($r^2 = 0.05$). Previous work has shown that diel metal cycles in pH-neutral to alkaline streams of Southwest Montana are largely independent of diurnal streamflow patterns (Nimick et al. 2003, 2005). Furthermore, the laboratory experiments of Shope et al. (2006) and Morris et al. (2005) have shown that it is possible to induce large fluctuations in Zn in bench-scale tanks containing High Ore Creek water, boulders, and biofilm, simply by shining light on and off the

Table 3 Correlations between Zn concentration and water temperature, pH, and streamflow

	Diurnal range in parameter			Linear regression correlation (r^2)		
	T (°C)	pH	Flow (l/s)	Zn vs. T	Zn vs. pH	Zn vs. flow
Pond inlet	10.5–21.2	7.19–7.38	4.8–6.9	0.68 (neg)	0.61(neg)	0.05 (neg)
Pond outlet	15.8–18.7	7.79–7.87	5.7–8.2	–	–	–
WQ-10	13.1–20.3	7.85–8.25	6.9–8.5	0.85 (neg)	0.96 (neg)	0.36 (pos)
WQ-4	10.3–17.5	8.17–8.29	18–23	0.87 (neg)	0.62 (neg)	0.86 (pos)

The parentheses indicate whether a correlation was positive (pos) or negative (neg) tanks. For this reason, we are confident that the diel metal cycles are caused by in-stream phenomena, not by diurnal cycles in the flow regime, such as exchange of surface water and groundwater.

Implications to stream monitoring

An important finding of this study was the way in which diel metal cycling can influence the results of synoptic sampling. In the case of High Ore Creek, different conclusions were drawn regarding downstream trends in Zn load depending on whether the synoptic samplers started near the mouth of the stream and worked uphill, or started near the top of the stream and moved downhill. Because Zn concentrations at any one location in the stream were higher in the early morning, the downstream sampler would have concluded based on her synoptic results that Zn load decreased steadily with distance downstream. Taken alone, this data set would suggest that natural attenuation processes were serving to ‘‘clean up the creek’’. However, during the same time period, the upstream sampler would have come to the opposite conclusion. Because Zn load apparently increased with distance downstream, this would imply that residual sources of Zn contamination exist in the lower reaches of the stream. It is only when the samples at a given location are averaged over 24 h that a meaningful comparison of loads can be made for different locations in the stream. In the present example, based on the 24-h average Zn loads in Table 1, it was concluded that no significant change in Zn load occurred in the lower 5 km of High Ore Creek for the sampling period in question.

Another potentially common problem involving synoptic sampling is when a team of workers is collecting samples within a larger watershed that is split for convenience into multiple reaches. In this case, all of the samplers may be working in the same direction (e.g., upstream) in such a way that the last sample collected at the end of the day by one worker is at the same location as the first sample collected at the beginning of the day by the next sampler working upstream. In such a case, a ‘‘disconnect’’ may occur where the two sample sets overlap. A good example of this sort of problem is shown in Fig. 20 of Cleasby and Nimick (2002), who presented results of a detailed synoptic loading study of Zn in the Tenmile Creek watershed of Montana. Because they were well aware of the diurnal cycling phenomenon, Cleasby and Nimick (2002) attributed the disconnect in their Zn load diagram to diel fluctuations in Zn concentration.

In light of the questions we have raised, one is left with the problem of how best to monitor water quality in streams and rivers in which diurnal cycling occurs. A detailed discussion of this topic is beyond the scope of the present paper. However, the following are a few suggestions that may have merit. To begin with, it is stressed that not all rivers display large diurnal cycles in chemistry. Work in progress by several research groups on a large number of sites throughout the northern Rockies has shown that some streams are much more prone to diurnal cycling than others, and that certain reaches of a given stream (such as High Ore Creek) may be much more prone to cycling than other reaches. Secondly, this study has shown that certain contaminants of concern may show stronger cycles than others, and that the cycles may be out of phase with each other. Clearly, in such a situation the best solution would be to collect a diurnal set of 12 or 24 samples covering a complete day–night period and to analyze each sample separately for a complete set of constituents. However, when the cost of such a procedure is prohibitive, a reasonable compromise would be to collect the samples, but then to homogenize them to a single composite sample that is sent to the laboratory. Such a composite sample could be flow-weighted, to take into account short-term variations in streamflow. Finally, in cases where it is only possible to collect a single, instantaneous sample from a given site, effort should be made to collect the sample from approximately the same time of day in the event that the analytical results will be compared to data obtained from other seasons or calendar years. The time of day that a particular sample is collected should always be reported in the spreadsheet or appendix of data that accompanies the final report for a particular project. In our experience, although the date of sample collection is usually specified, the time of day is often omitted from such reports or theses.

Conclusions

The results of our detailed 24-h investigation of High Ore Creek have revealed several important points:

1. The contaminants of concern in this relatively small drainage behave very differently from one another. Whereas Mn load decreased with distance downstream of the primary source of heavy metal contamination, the load of As increased. When averaged over 24-h, the daily load of Zn decreased sharply in the first kilometer below the main source of Zn contamination, but then was approximately constant over the remainder of the stream.
2. Large diel fluctuations in trace metal concentrations were noted at three locations along the creek, all of which had at least 0.5 km of free-flowing

drainage upstream of the sampling site. A fourth site near the outlet to a small settling pond showed no diel Zn fluctuations.

3. Greater diel variations in Zn concentration were noted in stream reaches that had abundant biofilm and surface mineral crusts of hydrous Mn–Zn oxide.
4. Because of the short-term temporal fluctuations in Zn concentration, different conclusions regarding trends in Zn load with distance downstream were obtained by workers who collected samples in opposite directions.

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