Applied Geochemistry 57 (2015) 35–44

Contents lists available at ScienceDirect

Applied Geochemistry

journal homepage: www.elsevier.com/locate/apgeochem

Review

Diel cycling of trace elements in streams draining mineralized areas—A review

Christopher H. Gammons[a], David A. Nimick[b,*], Stephen R. Parker[c]

[a] Department of Geological Engineering, Montana Tech of The University of Montana, Butte, MT 59701, USA
[b] U.S. Geological Survey, Helena, MT 59601, USA
[c] Department of Chemistry and Geochemistry, Montana Tech of The University of Montana, Butte, MT 59701, USA

ARTICLE INFO

Article history:
Available online 19 May 2014

ABSTRACT

Many trace elements exhibit persistent diel, or 24-h, concentration cycles in streams draining mineralized areas. These cycles can be caused by various physical and biogeochemical mechanisms including streamflow variation, photosynthesis and respiration, as well as reactions involving photochemistry, adsorption and desorption, mineral precipitation and dissolution, and plant assimilation. Iron is the primary trace element that exhibits diel cycling in acidic streams. In contrast, many cationic and anionic trace elements exhibit diel cycling in near-neutral and alkaline streams. Maximum reported changes in concentration for these diel cycles have been as much as a factor of 10 (988% change in Zn concentration over a 24-h period). Thus, monitoring and scientific studies must account for diel trace-element cycling to ensure that water-quality data collected in streams appropriately represent the conditions intended to be studied.

Contents

1. Introduction

Diel cycles are persistent patterns of measureable phenomena that follow a day-night, or 24-h, period. The words "diel" and "diurnal" are widely used in the literature, and in this article, they are treated as synonyms. Although diel cycles can occur in any type of water body, our focus is on streams, especially those that drain watersheds that have been actively mined or are being considered for mining activity, and therefore are of interest to mining companies or regulatory agencies. Collection of water-quality samples from such streams is critical at all stages of mining operations, including before mining (e.g., to establish baseline conditions, or as an exploration tool), during mining (e.g., to demonstrate minimal impacts to receiving water bodies), and after mining (e.g., to assess the degree of success of mine closure and reclamation activities). Important management decisions are often made based on water-quality data for streams. The main purpose of this chapter is to point out that in many (but not all) streams, the results obtained from water-quality sampling may depend on the time of day of sample collection. Thus, failure in a monitoring plan to recognize the existence of daily changes in physical and chemical properties could lead to data that are potentially biased, inconclusive, or misleading.

---

* Corresponding author. Tel.: +1 406 457 5918; fax: +1 406 457 5990.
E-mail address: dnimick@usgs.gov (D.A. Nimick).

http://dx.doi.org/10.1016/j.apgeochem.2014.05.008
0883-2927/Published by Elsevier Ltd.

This article begins with a discussion of some of the important physical and biogeochemical mechanisms that are responsible for diel cycling in all types of streams (see also Nimick et al., 2011). Next, selected results from our research group are presented to show examples of diel cycles in the concentration and speciation of trace elements in streams draining abandoned mine lands. Additional examples then are presented to show how diel cycles can confound the interpretation of data collected during otherwise routine monitoring or scientific field investigations. Finally, some suggestions are given for how to best collect water samples from streams that exhibit large diel cycles in solute concentration.

2. Diel mechanisms

Diel variations in water quality can result from any physical, biological, or chemical process that operates on a day-night cycle (Table 1). Changes in streamflow, for example, often follow a diel pattern and commonly are accompanied by changes in water chemistry. The two most common and widely recognized causes of diel streamflow patterns are daily changes in the rates of melting of snowpack and evapotranspiration by riparian vegetation (Lundquist and Cayan, 2002). Also, streams that are perched or losing water through the streambed may experience greater seepage loss during the afternoon (Constantz et al., 1994). More seepage occurs in the afternoon because the viscosity of water decreases as temperature increases during the day, and the lower viscosity increases the hydraulic conductivity of the streambed, thus making it easier for water to infiltrate into the streambed. Temperature-dependent viscosity changes could also change the rate of settling of fine mineral particles and organic matter, leading to night-time increases in suspended-sediment concentration. Nocturnal activity of macroinvertebrates and other benthic stream biota also can increase night-time suspended-sediment concentration, and in contaminated streams, the increase in suspended-sediment concentration correlates with an increase in particulate trace-element concentrations (e.g., Brick and Moore, 1996). Human activities, such as cyclic release of water from reservoirs or water-treatment plants, can also result in diel streamflow patterns. Finally, physical changes in aquatic vegetation may also, in rare cases, impart a diel signal in streams; for example, “macrophyte dams” may decrease streamflow during the day (Ovesen, 2001; Nimick et al., 2011).

Although any of the physical processes listed above could cause diel changes in the chemistry of a stream, the remainder of this discussion will concentrate on biogeochemical mechanisms that are direct, in-stream drivers of diel water-quality changes. The most important and ubiquitous of these processes is the diel cycle of photosynthesis and respiration by aquatic life. Simplified reactions can be written as follows:

$$\text{Photosynthesis}: \; CO_2 + H_2O + \text{sunlight} \rightarrow CH_2O(\text{org.}) + O_2 \qquad (1)$$

$$\text{Respiration}: \; CH_2O(\text{org.}) + O_2 \rightarrow CO_2 + H_2O \qquad (2)$$

Thus, photosynthesis creates organic compounds from inorganic carbon, whereas respiration does the reverse. Photosynthesis increases the concentration of dissolved O_2 and also results in an increase in pH. This pH effect is mainly due to the biological consumption of CO_2, a weak acid, which drives the following reaction to the left, lowering the activity of H^+:

$$CO_2(aq) + H_2O = HCO_3^- + H^+ \qquad (3)$$

Photosynthesis is mainly dependent on sunlight and typically peaks when the sun is directly overhead. Respiration consumes O_2 and releases CO_2 and nutrients to the water column, and usually is accompanied by a decrease in pH. Respiration takes place throughout the day and night, but because its rate is dependent on temperature, respiration is faster in warm versus cold water. On sunny days, the rate of photosynthesis is typically greater than respiration during the mid-day period, and the net result is an increase in dissolved oxygen (DO) concentration and pH (Odum, 1956). At night, the persistence of respiration in the absence of photosynthesis results in a decrease in DO and pH. A rather extreme example of this daily cycle is shown in Fig. 1. The stream in question was experiencing low flows and a heavy bloom of algae and aquatic macrophytes (Fig. 2a). Although diel pH cycles are common in most streams, in our experience, the amplitude of these cycles are usually <1 pH unit.

Changes in pH caused by aquatic photosynthesis and respiration can induce a change in the concentration of any solute whose mobility or chemical speciation is pH-dependent. For example, the solubilities of many minerals are pH-dependent, as represented by the following reaction for the dissolution of calcite:

$$CaCO_3(s) + H^+ = HCO_3^- + Ca^{2+} \qquad (4)$$

Thus, streams draining carbonate terrains, calcite-rich soils in arid environments, or treatment facilities where mine wastes are amended with lime may experience calcite precipitation in the afternoon when pH is higher and/or calcite dissolution at night when pH is lower (Spiro and Pentecost, 1991; Gammons et al., 2007a; de Montety et al., 2011). These reactions could cause a diel signal in alkalinity or Ca^{2+} concentration as well as in the concentration of any trace element that can partition into freshly formed calcite (e.g., Sr, Ba, Cd, Mn). However, the precipitation and dissolution of calcite (and most other minerals) are kinetically slow, making it unlikely that equilibrium could be maintained during parts of the 24-h period when pH and temperature of the water are changing rapidly.

Adsorption is another important chemical process that influences the mobility of trace elements in natural waters. Unlike mineral precipitation, most adsorption reactions are kinetically

Table 1
Summary of important processes that can cause diel cycles in streams.

Physical processes	Biogeochemical processes
Changes in streamflow:	Photosynthesis and respiration
Snowmelt	Inorganic photochemical reactions:
Evapotranspiration	Photoreduction of Fe^{3+}
Reservoir or treatment-plant discharges	Mn redox reactions
Macrophyte dams	Reductive dissolution of hydrous metal oxides
Changes in hydraulic conductivity of streambed	pH- and T-dependent adsorption
Bioturbation (e.g., by macroinvertebrates)	pH- and T-dependent mineral solubility
Changes in rate of settling of particles	Biological assimilation (absorption)

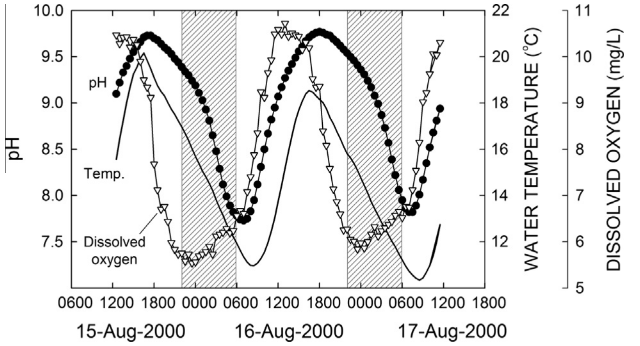

Fig. 1. Diel changes in pH, water temperature, and dissolved oxygen concentration in the Big Hole River, Montana, in August 2000 (Dickie Bridge site, Gammons et al., 2001). Shaded areas denote night-time hours.

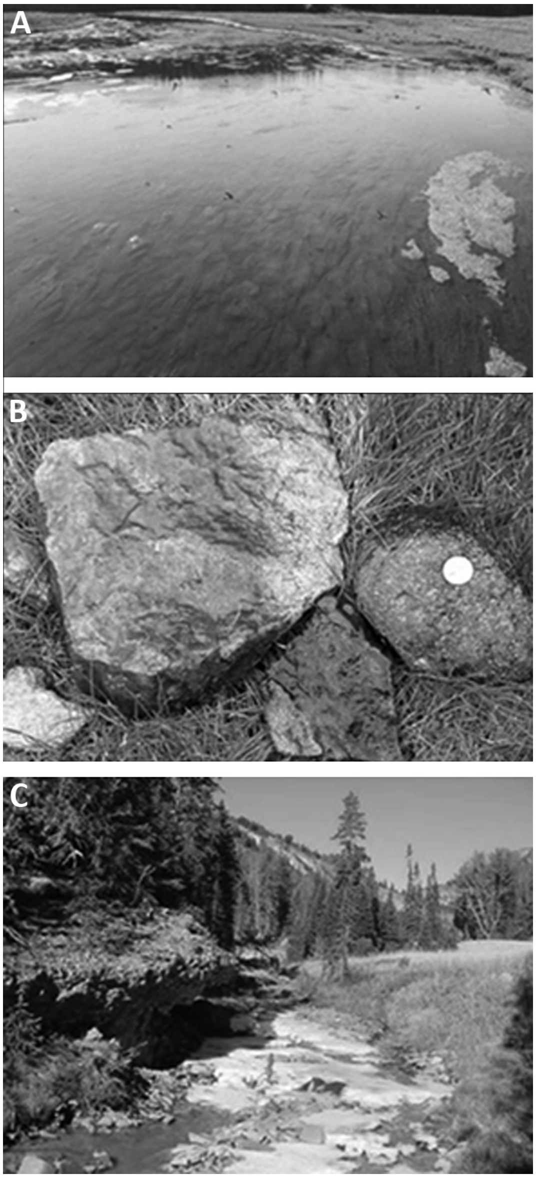

Fig. 2. Photographs of selected field sites: (A) upper Big Hole River, Montana, with heavy growth of macrophytes and algae (August 2000). The river is about 60-m wide at this location; (B) Top side (large rock at left) and bottom sides (two smaller rocks at right) of granitic boulders from High Ore Creek, Montana. The top sides of the boulders have a greenish-brown biofilm whereas the undersides are coated with a brownish-black crust of Zn-rich, hydrous Mn-oxide; (C) Fisher Creek, Montana, in spring (white is ice). The ledge at left is a pre-mining ferricrete deposit. The active channel is coated with freshly formed hydrous ferric oxide, which becomes increasingly rich in Cu and Zn with distance downstream.

fast. However, adsorption requires the existence of a suitable mineral or organic surface. Hydrous metal oxides (e.g., of Fe, Al, or Mn) are common secondary minerals formed during the weathering of mineral deposits. These solids commonly are very fine-grained and have high specific-surface areas, and furthermore have a strong chemical affinity to adsorb trace elements (Smith, 1999). Based on established surface-complexation models (e.g., Dzombak and Morel, 1990; Machesky, 1990), adsorption of positively charged species (e.g., Cu^{2+}, Mn^{2+}, Zn^{2+}) onto hydrous metal oxides is favored by an increase in pH (Fig. 3a) or an increase in temperature. Thus, concentrations of trace cationic species whose aqueous concentrations are limited by adsorption should decrease in the afternoon as pH and temperature increase in a stream. In contrast, adsorption of anions (e.g., $HAsO_4^{2-}$, HPO_4^{2-}, SO_4^{2-}) onto hydrous metal oxides is favored by a decrease in pH or temperature. The sorption behavior of certain metalloids, such as arsenic and selenium, is complicated by the existence of multiple possible redox states. In general, dissolved As(V) species adsorb more strongly onto hydrous Fe oxide compared to As(III) species, and also show a stronger pH dependence (Fig. 3b). In well-oxygenated surface waters, As(V) species should dominate over As(III) species.

One reason for the strong pH- and temperature-dependence of the above sorption reactions is that metal-oxide surfaces become more protonated (and therefore more positively charged) at lower pH and temperature and more de-protonated at higher pH and temperature. Opposite charges attract, and therefore a protonated surface would tend to attract an anion (such as $HAsO_4^{2-}$) and repel a cation (such as Zn^{2+}). Similar protonation/deprotonation reactions occur at the surfaces of organic matter such as bacteria or algal cell walls (Fein et al., 2001), making biofilms another important substrate for trace-element adsorption in streams (Fig. 2b). Because of the multitude of possible interactions between aqueous and solid compounds, accurate modeling of sorption reactions in natural or polluted environments is difficult, and requires knowledge of the concentrations of all possible sorbents and sorbates, along with information on how binding constants change as a function of pH and temperature (e.g., see Drever, 1997).

Besides photosynthesis, which requires living organisms, a number of inorganic reactions are catalyzed by sunlight. Most important to the present discussion is the photoreduction of oxidized forms of ferric iron (Fe^{3+}) to more soluble ferrous iron (Fe^{2+}) (McKnight et al., 1988). Both dissolved (e.g., Fe^{3+}, $Fe(OH)^{2+}$, $Fe(OH)_2^+$) and solid (e.g., $Fe(OH)_3$, hydrous ferric oxide) forms of Fe^{3+} can be photoreduced, as shown by the following reactions:

$$Fe(OH)^{2+} + \text{sunlight} \rightarrow Fe^{2+} + OH^{\cdot} \tag{5}$$

$$Fe(OH)_3(s) + 2H^+ + \text{sunlight} \rightarrow Fe^{2+} + OH^{\cdot} + 2H_2O \tag{6}$$

The $OH^{\cdot}$ radical formed on the right side of both reactions is unstable and goes on to react with other species, such as dissolved organic matter, in the water. Although Fe photoreduction is a ubiquitous process in all natural waters, it is most recognizable in mildly to strongly acidic streams that are shallow and clear (McKnight and Duren, 2004). Photoreduction is less obvious in pH-neutral or alkaline streams because the rate of re-oxidation of Fe^{2+} to Fe^{3+} compounds is much faster at high pH than at low pH (Stumm and Morgan, 1996). In addition, non-acidic streams typically have a much lower concentration of dissolved and particulate Fe^{3+} compared to acidic streams. In acidic streams, Fe^{3+} compounds are normally abundant (Fig. 2C), and photoreduction of Fe^{3+} is faster than re-oxidation of Fe^{2+}, resulting in an overall increase in dissolved Fe^{2+} concentration during the day (McKnight et al., 1988; McKnight and Duren, 2004). These diel changes in the concentration and redox speciation of Fe can set up diel variations in other trace elements that have an affinity for hydrous ferric oxide, as is shown in an example below.

Biological reactions other than photosynthesis/respiration also can directly influence the mobility of trace elements in streams. For example, assimilation of nutrients by aquatic plants can reduce the concentrations of dissolved N and P during the day, when photosynthesis is fastest (Scholefield et al., 2005). Less is known regarding the ability of plants or microbes to actively assimilate trace elements, and few studies have attempted to demonstrate whether or not such a process could impart a diel cycle in concentration of a toxic element. Morris et al. (2005) showed that biofilms growing in a small, alkaline stream preferentially sequestered Zn^{2+} during the day, both in the field and in controlled streamside experiments. However, it is not known whether this phenomenon was the result of a metabolic process (i.e., absorption) or a passive,

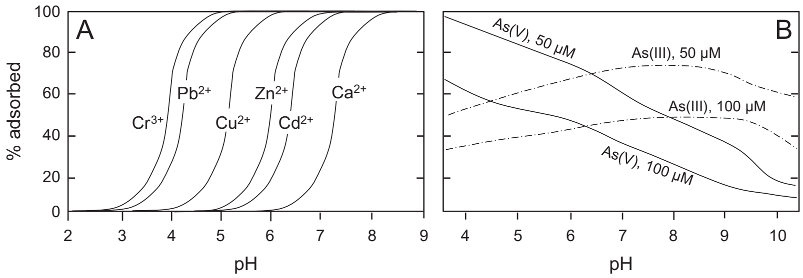

Fig. 3. Diagrams summarizing the pH dependence of adsorption of selected solutes onto hydrous Fe oxide (HFO). A) Sorption of divalent cations onto HFO for a system with a high HFO:cation ratio and an ionic strength of 1 molal (from Figs. 9–17 of Drever, 1997). (B) Sorption of As(V) (solid curves) and As(III) (dashed curves) onto HFO for total dissolved As = 50 or 100 μM, ionic strength = 0.01 molal, and HFO = 30 mg L^{-1} (from Fig. 3A of Dixit and Hering, 2003).

surface-controlled process (i.e., adsorption). Regardless, the chemical conditions within a biofilm may be very different from the chemical conditions of the bulk water in the stream (e.g., Hartley et al., 1996; Beck et al., 2009). For example, the pH within a biofilm may be 1–2 units higher (during the day) or lower (during the night) than the pH of the stream. The same is true of redox conditions. Thus, the internal portions of biofilms may become anoxic, especially during the night, even as the overlying water column contains measurable quantities of dissolved oxygen. Once conditions become anoxic in biofilm, a host of microbially catalyzed redox reactions are possible, including reductive dissolution of Fe or Mn hydrous oxides, as shown by the following reactions:

$$\mathrm{Fe(OH)_3(s)} + 1/4\mathrm{CH_2O(org)} + 2\mathrm{H^+} \rightarrow \mathrm{Fe^{2+}} + 1/4\mathrm{CO_2} + 2.75\mathrm{H_2O} \quad (7)$$

$$\mathrm{MnO_2(s)} + 1/2\mathrm{CH_2O(org)} + 2\mathrm{H^+} \rightarrow \mathrm{Mn^{2+}} + 1/2\mathrm{CO_2} + 1.5\mathrm{H_2O} \quad (8)$$

If these reactions occur, the liberated Fe^{2+} and Mn^{2+} will diffuse out of the biofilm into the overlying water column (Brick and Moore, 1996; Scott et al., 2002; Parker et al., 2007a). In the process, any trace elements (e.g., As, Cu, Zn) that are associated with the hydrous metal oxides may also be mobilized to the stream.

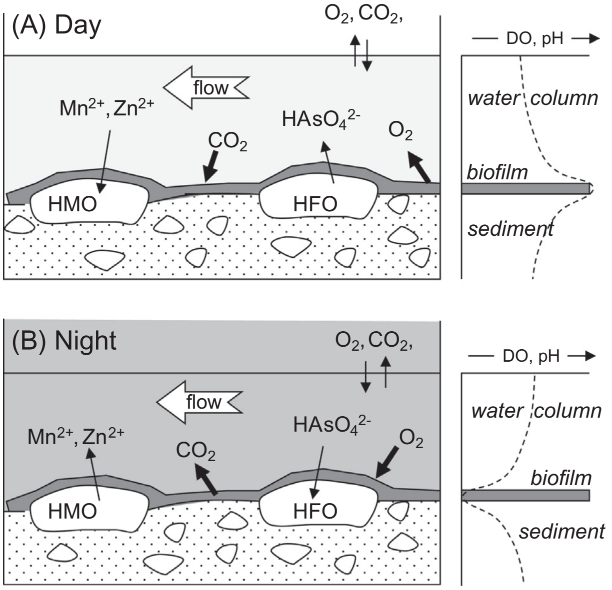

Fig. 4. Summary of diel processes occurring in a non-acidic stream (modified from Parker et al., 2007a). (A) During the day, biofilm (dark band) and plants create O_2 and raise pH by consuming CO_2, conditions that promote adsorption of cations, such as Zn^{2+}, and desorption of anions, such as $HAsO_4^{2-}$. (B) At night, these cycles reverse. Trace elements may preferentially adsorb onto biofilm surfaces or onto minerals, here exemplified by hydrous Mn oxide (HMO) and hydrous Fe oxide (HFO). Both panels show schematic changes in dissolved oxygen (DO) and pH with depth, and emphasize the steep geochemical gradients that can be set up within a biofilm.

All of the diel processes discussed above could potentially be happening simultaneously in a stream, and they may or may not be in phase. Thus, the shape and amplitude of any diel signal is usually the result of a combination of several input variables. Fig. 4 illustrates some of these complexities. In this example, different solutes adsorb onto or desorb from different mineral or organic substrates in response to changes in pH and temperature of the water column. These changes, which may be relatively subdued in the bulk water, may be more extreme near the surfaces of plants or biofilms that are actively photosynthesizing or respiring. Although any solid surface is a potential sorbent, there is a broad range of affinities of sorbates for various solid phases. Dissolved Zn, for example, has a strong affinity for hydrous manganese oxide (HMO), whereas dissolved As has a strong affinity for hydrous ferric oxide (HFO). Copper, on the other hand, forms strong complexes with organic carbon. Exchange of volatile compounds (e.g., O_2, CO_2, N_2) occurs day and night between air and water, and hyporheic exchange may occur between stream water and shallow groundwater. If conditions near the sediment–water interface become anoxic, then reductive dissolution of HFO and HMO may occur, releasing Fe^{2+}, Mn^{2+}, and other adsorbed trace elements to the water column. Finally, changes in streamflow can result in diel concentration cycles in dissolved or suspended trace elements. Often, the complexity of the field system makes it difficult to discern which chemical or physical mechanisms are primarily responsible for a given diel signal. Field experiments have been attempted where one or another variable is controlled, keeping the others constant. For example, stream mesocosms have been constructed on site to mimic the stream environment but without the confounding effects of advection, hyporheic exchange, and changes in streamflow (e.g., Jones et al., 2004; Parker et al., 2007b).

3. Examples of diel trace-element cycling in streams

The authors of this review article have performed several dozen diel investigations of rivers and streams that drain mined lands. A few representative case studies are presented here. Streams with alkaline versus acidic pH are discussed separately because of differences in the types of diel phenomena that are encountered. Additional examples of studies of diel trace-element cycles in alkaline and acidic streams are compiled in Tables 2 and 3.

3.1. Streams with near-neutral or alkaline pH

Many streams that drain abandoned mine lands are not acidic, but nonetheless contain elevated concentrations of one or more toxic elements, such as Zn, Cd, or As. High Ore Creek, located in

Table 2
Published studies of diel trace-element cycling in near-neutral or alkaline streams.

Stream	Trace element(s)	Reference(s)
Clark Fork River, Montana	Al, As, Cd, Fe, Mn, Zn	Brick and Moore (1996) and Parker et al. (2007a)
High Ore Creek, Montana	As, Cd, Mn, Zn	Nimick et al. (2003, 2007a), Morris et al. (2005), Shope et al. (2006) and Gammons et al. (2007b)
Prickly Pear Creek, Montana	As, Cd, Mn, Zn	Nimick et al. (2003, 2005) and Jones et al. (2004)
Dry Fork Belt Creek, Montana	Cd, Cu, Zn	Nimick et al. (2007a)
Daisy Creek and Stillwater River, Montana	Cd, Mn, Zn	Nimick et al. (2003)
Mary Ellen Gulch, Utah	Zn	Kimball and Runkel (2009)
S. Fork Coeur d'Alene River, Idaho	Cd, Mn, Ni, Zn	Nimick et al. (2003)
Wallkill River, New Jersey	Al, As, Fe, Mn, Zn	Barringer et al. (2007, 2008)
Lot River, France	Zn	Bourg and Bertin (1996)
Whitewood Creek, S. Dakota	As	Fuller and Davis (1989)
Silver Bow Creek, Montana	As, Cd, Mn, Zn, U	Gammons et al. (2007a) and Balistrieri et al. (2012)
Madison River, Montana	As, Hg	Nimick et al. (1998, 2007b)
Missouri River, Montana	As	Nimick et al. (1998)
Silver Creek, Montana	Hg	Nimick et al. (2007b)
Riou Mort, France	Cd, Cu, Pb	Beck et al. (2009), Tercier-Waeber et al. (2009)

Table 3
Published studies of diel trace-element cycling in acidic streams.

Stream	Trace element(s)	Reference(s)
Fisher Creek, Montana	Al, Fe, Cu, Mn, Zn, REE	Gammons et al. (2005a, 2005b) and Parker et al. (2007b)
Odiel and Tinto Rivers, Spain	Fe	Gammons et al. (2008)
Rio Agrio, Argentina	As, Fe, REE	Parker et al. (2008)
St. Kevin Gulch, Colorado	Fe	McKnight et al. (1988), Kimball et al. (1992) and McKnight et al. (2001)
Peru Creek, Colorado	Fe, Mn, Zn	Sullivan et al. (1998)
Lambert Run, West Virginia	As, Co, Fe, Mn, Ni, REE	Vesper and Smilley (2010)
Middle Crow Creek, Wyoming	Fe	Borman et al. (2010)
Snake River, Colorado	Fe	McKnight and Bencala (1988)

southwestern Montana between the cities of Butte and Helena, is one, well-studied example. High Ore Creek is a small (baseflow <50 L/s), steep-gradient stream, whose streambed contains granitic cobbles and boulders coated with mixtures of biofilm, brownish HFO, and black HMO (Fig. 2b). Fig. 5 shows a set of hourly data collected over a 3-day period near the mouth of High Ore Creek in August 1999. Filtered Zn concentrations varied approximately 3-fold, between about 200 and 600 μg/L, with maximum concentrations in the early morning (~0600 to 0700 h) and minima in the late afternoon (~1600 to 1700 h). Filtered Mn and Cd, which were at lower concentration levels, followed a similar diel pattern to Zn, but had different amplitudes of diel variation. Manganese concentrations (35–142 μg/L) increased about 4-fold each night whereas Cd concentrations (1.4–3.0 μg/L) only increased about 2-fold. In contrast to these metals, filtered As concentrations (22–33 μg/L) followed the reverse diel pattern and had a smaller amplitude of variation. Night-time increases in Zn, Mn, and Cd concentrations and decreases in As concentration coincided with decreases in pH and temperature. Diel changes in streamflow were very poorly correlated with the changes in trace element concentration. Note, for instance, that when trace-element concentrations were changing rapidly between 1800 h and midnight, streamflow was constant.

The diel patterns of trace-element behavior shown in Fig. 5 for High Ore Creek have been observed at multiple locations along the stream and repeatedly during summer baseflow conditions over a 10-year period at one site near the mouth (Fig. 6) (Nimick et al., 2003, 2007a; Morris et al., 2005; Shope et al., 2006; Gammons et al., 2007b). A detailed investigation of seasonal diel cycling in Prickly Pear Creek, a stream located immediately to the north of High Ore Creek, showed that diel cycles in filtered trace-element concentrations can occur at all times of the year, during all types of flow regimes, and always with similar temporal patterns (Nimick et al., 2005). Diel concentration cycles similar to those found in High Ore Creek and Prickly Pear Creek have been documented from many other non-acidic streams (Table 2).

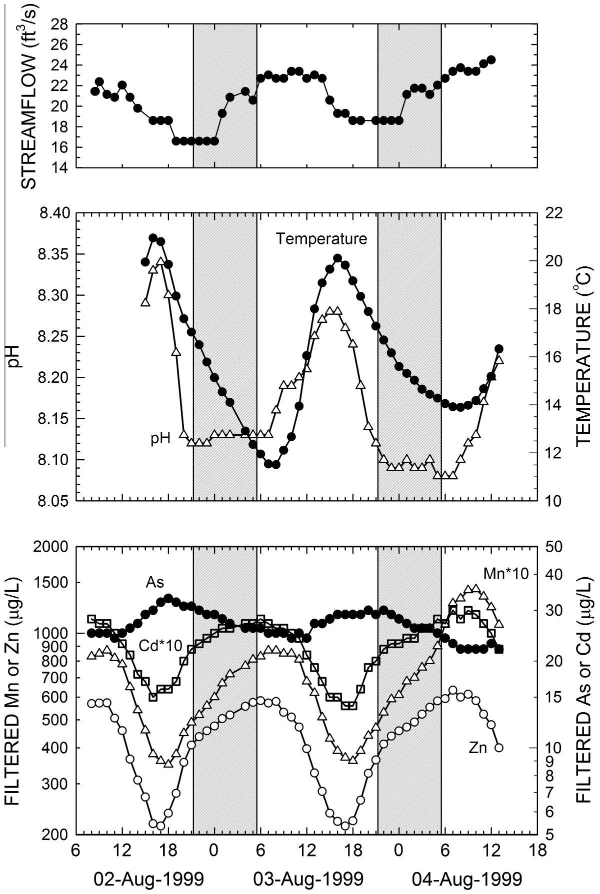

Fig. 5. Diel variation in streamflow, pH, temperature, and concentrations of filtered As, Cd, Mn, and Zn in High Ore Creek, Montana, August 2–4, 1999. Cross-hatched areas denote night-time hours. Data from Nimick et al. (2003).

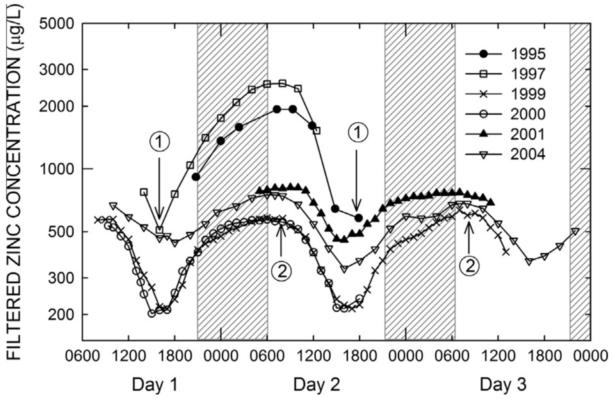

Fig. 6. Filtered Zn concentrations for diel sampling episodes conducted during summer, low-flow periods, 1995–2004. Remediation of an upstream abandoned mine site conducted between the 1997 and 1999 sampling episodes resulted in the overall lower, post-1997 Zn concentrations. Timing of minimum, pre-remediation concentrations labeled with a "1." Timing of approximate maximum, post-remediation concentrations labeled with a "2." Shaded areas denote approximate night-time hours. Data from Nimick et al. (2003, 2007a).

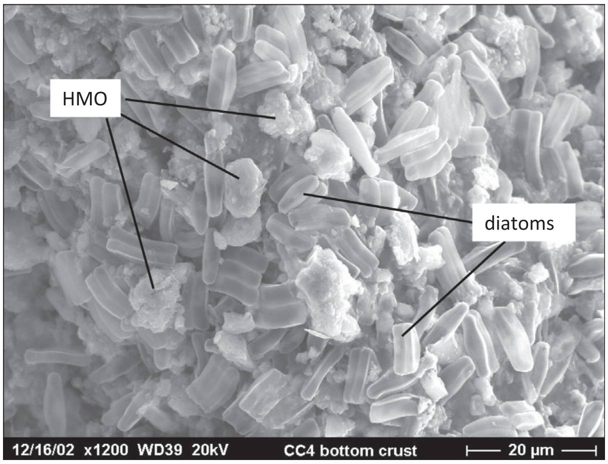

Fig. 7. SEM image of mixed biofilm/mineral crust on boulders from Cataract Creek, a small stream draining abandoned mine lands immediately west of High Ore Creek. Both the hydrous Mn oxide (HMO) mineral grains and the diatom frustules are highly enriched in Zn (see Shope et al., 2006).

Based on the antithetic relationship between the diel behavior of the cationic trace elements (Zn^{2+}, Mn^{2+}, Cd^{2+}) and the anionic trace element ($HAsO_4^{2-}$), Nimick et al. (2003) concluded that the diel cycles in High Ore Creek and other non-acidic streams are caused primarily by pH- and temperature-controlled sorption reactions. A similar conclusion was reached in the earlier study of Fuller and Davis (1989), which dealt only with diel cycling of As. Shope et al. (2006) conducted laboratory experiments of sorption of Zn and Mn onto HMO mineral crusts collected from High Ore Creek and found that the sorption reactions that control aqueous Zn and Mn concentrations are rapid, reversible, and sensitive to small changes in either pH or temperature. In a separate set of laboratory and field experiments, Morris et al. (2005) showed that biofilm in contact with High Ore Creek water preferentially sequestered Zn during the day, with little or no reaction at night. However, the form of Zn in the biofilm (e.g., adsorbed versus absorbed) was not determined. In all likelihood, adsorption of trace elements from the water column takes place on all available organic and inorganic surfaces on the streambed and within the stream (e.g., see Fig. 7). At a minimum, the biofilms are essential to set up the diel pH cycle that, in turn, helps drive the sorption/desorption reactions. In this way, biofilm may act like a "portal" to facilitate exchange of trace elements between mineral substrates and the bulk water column (Fig. 4; see also Morris et al., 2005; Nimick et al., 2011).

3.2. Streams with acidic pH

Two case studies are presented here as examples of diel cycling in acidic streams. The first example is the Odiel River, one of several streams that receive acid drainage from massive sulfide deposits of the Iberian Pyrite Belt in southern Spain and Portugal. Gammons et al. (2008) examined diel changes in water chemistry in this river, as well as the nearby Tinto River (Rio Tinto). Fig. 8A summarizes results for the upper sampling site on the Odiel River. The pH of the stream was essentially invariant at 3.04 ± 0.04. Filtered Fe^{2+} concentration increased 10-fold during the day and at the same time that filtered Fe^{3+} concentration decreased. These trends were attributed to photoreduction of dissolved Fe^{3+} to Fe^{2+} during the day and re-oxidation of Fe^{2+} to Fe^{3+} at night (Gammons et al., 2008). Meanwhile, the concentration of total filtered Fe (i.e., sum of Fe^{2+} and Fe^{3+}) showed no diel trend. Although the streambed of the Odiel River was coated with reddish-brown precipitates, suspended particles of Fe were minimally present (Fig. 8A) owing to the stable weather and low-flow conditions during the study period. Concentrations of other metals (e.g., Cu, Zn) likewise showed no diel trends. This absence of a diel trend is consistent with the fact that adsorption of Cu and Zn onto HFO should be minimal at pH 3.

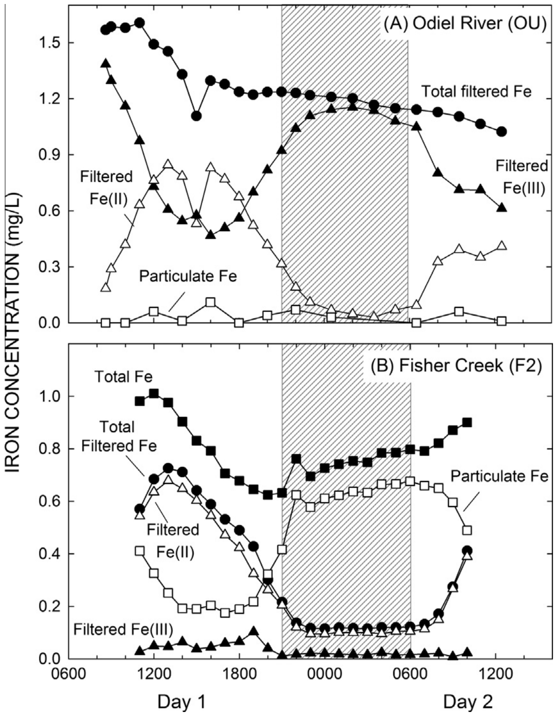

Fig. 8. Diel changes in the concentration and speciation of Fe in two acidic streams. (A) Odiel River, Spain, with mean pH = 3.04 (site OU of Gammons et al., 2008). (B) Fisher Creek, Montana, with mean pH = 5.46 (site F2 of Gammons et al., 2005a). Shaded area denotes approximate night-time hours.

The second case study is Fisher Creek, a small alpine stream near the northeast corner of Yellowstone National Park. One of the main differences between this stream and the Odiel River is that the pH of Fisher Creek steadily increases from its headwaters to its mouth. As a result, HFO and HAO (hydrous aluminum oxide) actively precipitate over extended reaches of the stream.

Gammons et al. (2005a) conducted simultaneous diel samplings along Fisher Creek at three locations where the mean pH values were 3.31 (site F1), 5.46 (site F2), and 6.80 (site F3). As was the case in the Odiel River study, the pH of Fisher Creek at each location showed minimal changes over a 24-h period. Fig. 8B shows diel Fe data for the middle (F2) site on Fisher Creek. Photoreduction resulted in a sharp increase in filtered Fe^{2+} concentration during the day. However, because the filtered Fe^{3+} concentration was extremely low at the pH of the F2 site, the main source of Fe^{3+} for photoreduction was freshly formed, suspended HFO particles. The formation of HFO particles is itself a temperature-dependent process, both kinetically and in terms of solubility. As daytime temperature increases, the solubility of the HFO decreases and the rate of formation of particles increases. Thus, an interesting pattern emerged at F2 wherein most of the total Fe load passing down the stream was in dissolved form during the day and in suspended particles at night. At pH 5.46, sorption of trace metals onto these HFO particles was still relatively weak. However, further downstream at F3, the highest pH (6.80) sample site, several trace elements, including Cu, Zn, and the rare earth elements (REE), had diel concentration cycles. Minimum concentrations for all of these elements occurred during the afternoon, which also was the time of day when the calculated rate of precipitation of fresh HFO between sites F2 and F3 passed through a maximum (Fig. 9). The higher rate of precipitation of HFO in the afternoon, in turn, was caused by oxidation of the pulse of Fe^{2+} formed by photoreduction in the upstream reaches as well as the increased rate of colloid formation and the lower solubility of HFO. As shown in Fig. 9, the magnitude of the diel cycle was greatest for Ce (a light REE), underscoring the very strong affinity of REE for freshly formed HFO. Likewise, the diel variation in Cu was greater than that for Zn due to the greater affinity of Cu to adsorb onto HFO at pH values between 6 and 7 (Fig. 3A).

3.3. Summary of conditions that promote diel cycling in streams

Sunlight is the primary driver of almost all diel cycles and therefore diel cycles can be larger on cloudless days and in streams that are not shaded. Sunny, cloudless conditions promote larger diel cycles in temperature and also greater rates of photosynthesis, which can lead to larger diel pH cycles. In near-neutral and alkaline streams, where diel trace-element cycling is thought to be driven primarily by adsorption/desorption reactions, larger amplitude cycles in pH, temperature, or both result in larger amplitude diel cycles in trace-element concentrations. In contrast, near-neutral and alkaline streams that are deep, turbid, or shaded typically have much smaller diel pH and temperature cycles and consequently little, if any, diel trace-element cycling (for an example, see data for the Coeur d'Alene River in Nimick et al., 2003). In acidic streams, diel trace-element cycling is driven primarily by Fe photoreduction, which is dependent on direct sunlight. Iron photoreduction likely occurs in all acidic streams draining mined areas but measureable diel cycles in Fe concentration or speciation may only occur where ambient Fe concentrations are low enough to not mask the concentration changes in the Fe participating in the redox cycling. A special case of diel concentration changes in near-neutral waters may occur when the sampling site is only a short distance downstream from a reach where hydrous metal oxides formed during pH-neutralization, as was the case for site F2 on Fisher Creek (Fig. 8B).

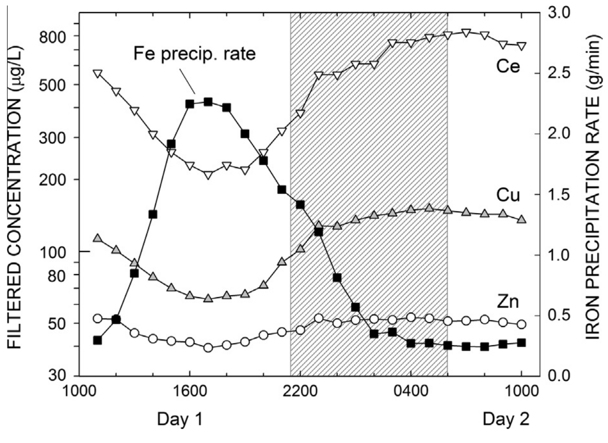

Fig. 9. Diel changes in the concentrations of selected trace metals in Fisher Creek at the downstream (F3) sampling site (Gammons et al., 2005a, 2005b). Also shown is the hourly change in the rate of precipitation of Fe, as calculated by changes in filtered Fe concentration between F2 and F3 divided by travel time. Shaded area denotes night-time hours.

4. Implications of diel cycling to water-quality monitoring

Water-quality data collected to characterize trace-element concentrations in streams commonly are used to establish baseline environmental conditions, determine the locations of important contaminant sources, plan and evaluate cleanup of contaminated sites, detect long-term trends in constituent concentrations, and evaluate potential risks to fish and other aquatic organisms. However, if diel variability in concentrations is substantial and persistent, such evaluations may be less certain than previously thought, or even potentially wrong. In these circumstances, traditional sampling protocols may need to be revised. This section presents several examples that demonstrate the potential to reach incorrect conclusions and then provides suggestions for sampling strategies that can help account for diel cycling.

The first example of how incorrect conclusions could be reached if diel variability is not considered relates to monitoring to determine year-to-year trends in water quality. An approach traditionally used to evaluate long-term changes in trace-element concentrations in a stream undergoing remediation would be to sample during similar seasons and streamflow conditions over a period of many years. The potential problem with this type of sampling strategy for a stream where diel trace-element cycles are relatively large is shown for High Ore Creek in Fig. 6. When hourly samples are collected over 24 h, it is clear that filtered Zn concentrations were substantially lower after remediation. However, if the approach had been to collect only single samples and if these samples had been collected in the afternoon during the pre-remediation years of 1995 and 1997 (labeled "1" in Fig. 6) and during the early morning during post-remediation years from 1999 to 2004 (labeled "2" in Fig. 6), the conclusion would have been that remediation had produced essentially no change in Zn concentration.

The second example of how diel trace-element cycles might confound interpretation of water-quality data deals with comparison of concentration data to aquatic standards. Diel Zn cycles in Prickly Pear Creek were known to be large, with filtered concentrations having as much as a 6-fold daily variation (Nimick et al., 2005). Analysis of multiple diel data sets for this stream showed that during mid- to late-spring, daily maximum and minimum concentrations occurred at about 0600 h and 1630 h, respectively. Samples were collected at these times over a 5-week period that encompassed streamflow conditions affected by spring rain in the first part of the period and by annual peak flows (produced by melting of the high-elevation snowpack) in the later part of the period (Fig. 10). Filtered samples were analyzed for Zn as well as for hardness so that the aquatic-life standard could be calculated for each sample. On virtually every sampling day, the filtered Zn

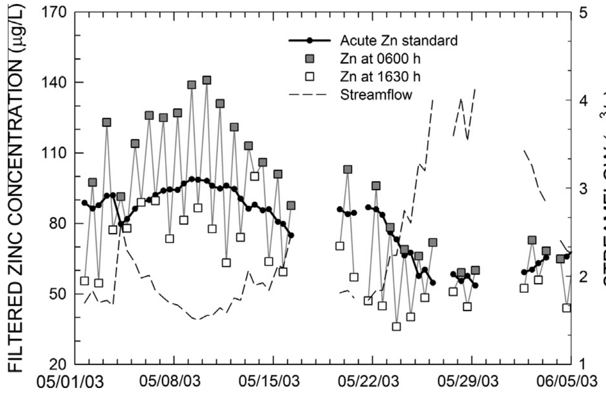

Fig. 10. Filtered zinc concentration at 0600 h (solid squares) and 1630 h (open squares) in Prickly Pear Creek near Helena, Montana (U.S. Geological Survey gaging station 06061500), May 1 to June 5, 2003. Solid circles indicate the State of Montana hardness-dependent acute aquatic-life standard for surface water (Montana Department of Environmental Quality, 2010) for each zinc sample. Dashed line indicates streamflow. Graph combines data from Nimick et al. (2005) and unpublished data for additional samples collected as described by Nimick et al. (2005).

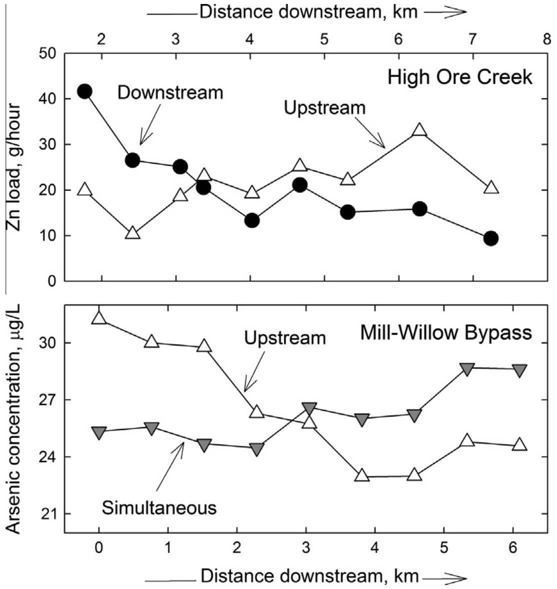

Fig. 11. Examples showing the influence of diel cycles on synoptic data: (A) synoptic changes in Zn load in High Ore Creek, Montana, as measured by sampling conducted in the downstream and upstream directions (data from Gammons et al., 2007b); (B) synoptic changes in filtered As concentration in the Mill-Willow Bypass, Montana, as measured by sampling conducted in the upstream direction or at all stations simultaneously (C. Gammons, unpublished data).

concentration in Prickly Pear Creek exceeded the acute aquatic-life standard each morning but did not exceed the standard in the afternoon. The regulatory standard, itself a function of water hardness, showed large seasonal changes but minimal diel changes (Fig. 10).

The final examples of how diel variability can confound interpretation of water-quality data deal with mass-loading studies that were conducted to identify and quantify sources and sinks of trace elements. Synoptic sampling is commonly used to track changes in trace-element concentrations and loads in watersheds that drain active or abandoned mine lands. Two popular approaches to synoptic sampling are the "upstream" and "Lagrangian" methods. In the former method, the sampling team moves upstream during the day, thereby preventing any contamination to samples from disturbances caused by walking in the stream. Lagrangian sampling involves following a parcel of water as it moves down the stream, collecting samples at specified locations along the way. Another possible synoptic-sampling method would be to spread out a number of samplers at multiple locations along a stream to collect samples simultaneously at a pre-determined time. As the following discussion illustrates, for all of these synoptic-sampling methods, diel cycling can have a major influence on the character of the data collected as well as the interpretations drawn from the data.

Gammons et al. (2007b) performed two simultaneous synoptic samplings of High Ore Creek downstream from the historical Comet mine. This stream was previously known to exhibit large diel cycles in Zn concentration, with maxima in the early morning and minima in the afternoon (Nimick et al., 2003). One student began sampling at 0800 h at the mouth of High Ore Creek and worked in an upstream direction, finishing late in the afternoon. The other student sampled the same stations in a downstream direction in a manner that was approximately Lagrangian. Both students collected filtered water samples and measured streamflow at each station. Fig. 11A summarizes results for Zn load (concentration times streamflow). According to the downstream sample set, Zn load decreased by about a factor of 4 over the 5.5-km reach. By itself, this result would lead to the conclusion that Zn from the Comet mine site is naturally attenuated in High Ore Creek. In contrast, the upstream sample set shows an *increase* in Zn load with distance downstream, especially if the last data point at km 7.4 is removed as an outlier. This result would lead to the opposite conclusion, i.e., that there are additional sources of Zn loading to High Ore Creek along the studied reach of the stream. Neither sampling method accurately represented Zn loading in the stream. The best way to estimate changes in Zn load between the upstream and downstream ends of this reach would be to collect and composite hourly or bi-hourly samples for 24 h at each site and then compare the 24-h loads. Sampling using this method demonstrated that there was no measureable change in daily Zn load between the upstream and downstream ends of the study reach (Gammons et al., 2007b).

In the second example of mass-loading studies affected by diel cycling, a group of students conducted two sets of synoptic samplings of the Mill-Willow Bypass, a small, reconstructed stream that meanders past a large lime-treatment facility near the town of Warm Springs, Montana. The Mill-Willow Bypass was known from previous studies (Gammons et al., 2007a) to exhibit robust diel cycles in As concentration, with daily maxima in the afternoon and minima in the early morning. On the first day, a team of samplers worked in an upstream direction, collecting filtered samples and measuring streamflow. On the second day, students spaced along the stream collected a filtered sample at precisely 1330 h at the same locations that were sampled on the previous day. The weather on both days was warm and clear, with no precipitation. Fig. 11B compares the results. Predictably, the upstream sample set shows a downstream decrease in As concentrations. In contrast, the synchronous sampling shows a slight downstream increase in As concentrations. Again, to accurately compare changes in As concentration and load between the upstream and downstream ends, collection of 24-h composite samples would be necessary. Sampling using this method in a previous year (Gammons et al., 2007a) demonstrated that 24-h mean As concentrations remained unchanged through the study reach, whereas the daily mean As load effectively doubled. The increase in As load was attributed to upwelling of a substantial amount of groundwater that had an As concentration similar to that of the stream.

4.1. Sampling strategies

A variety of sampling strategies exist for monitoring trace elements in streams that have, or may have, diel trace-element cycles.

The choice of sampling plan can depend on whether the trace element of interest is likely to have a diel cycle given the attributes of the specific stream, the objective(s) of the intended monitoring, and the resources available to conduct the monitoring.

The trace elements that typically have diel cycles are different in acidic versus near-neutral and alkaline streams. Iron is the main trace element that typically exhibits diel cycling in acidic streams. In contrast, many trace elements undergo diel cycles in near-neutral to alkaline streams. The amplitude of these cycles can be very large, with maximum reported daily increases of 830% for REE (Gammons et al., 2005b); 988% for Zn (Balistrieri et al., 2012); 306%, 167%, and 119% for Mn, Ni, and Cd, respectively (Nimick et al., 2003); and 54% for As (Gammons et al., 2007a). Some common metals, however, do not consistently display diel concentration cycles. To our knowledge, no diel cycles of dissolved Pb concentration have been reported. Copper typically does not display distinct diel concentration cycles (Nimick et al., 2003; Tercier-Waeber et al., 2009). Copper has a strong affinity for dissolved organic C, and, if bound with DOC, is unlikely to have the same sorption behavior as other divalent cations such as Zn. Large diel Cu cycles were reported by Gammons et al. (2005a) for the downstream site (F3) of Fisher Creek (Fig. 8). The diel behavior of Cu in this stream probably was caused by a combination of the pH (∼6.8) being near the adsorption edge for Cu and the diel variation in the rate of precipitation of fresh hydrous ferric oxides (faster during the day and slower at night).

Sampling strategies utilized in monitoring or scientific programs need to be aligned with the objectives of the specific program but must also recognize the possibility of diel concentration cycles. How diel variation is accounted for depends on these objectives, as the following examples illustrate.

Comparison of trace-element concentrations to acute aquatic-life standards. Acute aquatic-life standards typically apply to instantaneous concentration values. Therefore, to determine the maximum daily concentration in streams with diel trace-element cycling, samples for cationic trace elements such as Cd and Zn would have to be collected shortly after dawn, and samples for anionic trace elements such as As would have to be collected in the afternoon.

Comparison of trace-element concentrations to chronic aquatic-life standards. Chronic aquatic-life standards typically apply to 4-day mean concentrations. Mean concentration data for a site could be obtained by collecting a series of samples at equal time intervals (e.g., every 1 or 2 h), analyzing each sample, and then determining the mean concentration. Alternatively, the same series of samples could be collected, composited, and then analyzed as one sample. The former method has the advantage of providing site-specific information that would describe diel variability, provide a dataset that could be used for assessing acute aquatic-life standards, and be useful for modifying the sampling program. The latter method is advantageous because of its lower cost.

Characterization of trace-element concentrations throughout a watershed or evaluation of temporal trends in water quality. Watershed characterization and trend analysis are most helpful when environmental conditions, such as streamflow or time of year, are similar within the sample population. The same applies for the time of day that samples are collected. If diel cycling exists, similarities or differences among sites or through time or space may be a function of short-term temporal variability. To minimize bias due to diel variability, all samples could be collected at approximately the same time of day, or 24-h values could be determined using one of the methods listed in the previous paragraph.

Comparison of trace-element loads temporally or spatially. The mass load of a constituent is dependent on concentration and streamflow, and both of these properties can exhibit diel cycles. Therefore, integrated data are needed to describe the flow-weighted, daily mean load. These data could be obtained over a 24-period from hourly water samples and streamflow measurements. Alternatively, a 24-h sample could be composited from hourly samples, each of whose volume was proportional to the streamflow at the time the sample was collected.

As described in the preceding paragraphs, accounting for diel variability in water-quality studies introduces additional complexity and increases the resources needed to accomplish the project goals. There is no easy way to account for diel variability, but several approaches offer ways to more efficiently obtain the needed samples and information. Automated samplers are useful for collecting hourly or composite water samples, but additional studies of the effects of leaving samples for multi-hour periods inside an automatic sampler are needed to supplement existing information, which is scarce and contradictory (Nimick et al., 2003; Grosbois et al., 2009). For sites where long-term monitoring is being considered, preliminary investigation of diel cycling could indicate whether there are periods or seasons of the year when the magnitude of diel cycles was relatively small or perhaps non-existent. Such an investigation could start with monitoring pH, temperature, and specific conductance, which are easily measured, and then expanding the monitoring to the constituents of interest if the initial data indicated that other constituents might have diel cycles. Determination of which constituents need special consideration in a sampling plan can be assessed seasonally and spatially before a sampling plan is finalized (Taylor and Hamilton, 1994).

References

Balistrieri, L.S., Nimick, D.A., Mebane, C.A., 2012. Assessing time-integrated dissolved concentrations and predicting toxicity of metals during diel cycling in streams. Sci. Total Environ. 425, 155–168.

Barringer, J.L., Bonin, J.L., Deluca, M.J., Romagna, T., Cenno, K., Alebus, M., Kratzer, T., Hirst, B., 2007. Sources and temporal dynamics of arsenic in a New Jersey watershed, USA. Sci. Total Environ. 379, 56–74.

Barringer, J.L., Wilson, T.P., Szabo, Z., Bonin, J.L., Fischer, J.M., Smith, N.P., 2008. Diurnal variations in, and influences on, concentrations of particulate and dissolved arsenic and metals in the mildly alkaline Wallkill River, New Jersey, USA. Environ. Geol. 53, 1183–1199.

Beck, A.J., Janssen, F., Polerecky, L., Herlory, O., De Beer, D., 2009. Phototropic biofilm activity and dynamics of diurnal Cd cycling in a freshwater stream. Environ. Sci. Technol. 43, 7245–7251.

Borman, C.J., Sullivan, B.P., Eggleston, C.M., Colberg, P.J.S., 2010. Is iron redox cycling in a high altitude watershed photocemically or thermally driven? Chem. Geol. 269, 33–39.

Bourg, A.C.M., Bertin, C., 1996. Diurnal variations in the water chemistry of a river contaminated by heavy metals: natural biological cycling and anthropic influence. Water Air Soil Pollut. 86, 101–116.

Brick, C.M., Moore, J.N., 1996. Diel variations in the upper Clark Fork River, Montana. Environ. Sci. Technol. 30, 1953–1960.

Constantz, J., Thomas, C.L., Zellweger, G., 1994. Influence of diurnal variations in stream temperature on streamflow loss and groundwater recharge. Water Resour. Res. 30, 3253–3264.

de Montety, V., Martin, J.B., Cohen, M.J., Foster, C., Kurz, M.J., 2011. Influence of diel biogeochemical cycles on carbonate equilibrium in a karszt river. Chem. Geol. 283, 31–43.

Dixit, S., Hering, J.G., 2003. Comparison of arsenic (V) and arsenic (III) sorption onto iron oxide minerals: implications for arsenic mobility. Environ. Sci. Technol. 37, 4182–4189.

Drever, J.I., 1997. The Geochemistry of Natural Waters, third ed. Prentice Hall, Upper Saddle River, New Jersey.

Dzombak, D.A., Morel, F.M.M., 1990. Surface Complexation Modeling – Hydrous Ferric Oxide. John Wiley and Sons, New York.

Fein, J.B., Martin, A.M., Wightman, P.G., 2001. Metal adsorption onto bacterial surfaces: development of a predictive approach. Geochim. Cosmochim. Acta 65, 4267–4273.

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

Gammons, C.H., Ridenour, R., Wenz, A., 2001, Diurnal and longitudinal variations in water quality along the Big Hole River and tributaries during the drought of August, 2000. Montana Bureau of Mines and Geology, Open-File Report 424.

Gammons, C.H., Nimick, D.A., Parker, S.R., Cleasby, T.E., McCleskey, R.B., 2005a. Diel behavior of Fe and other heavy metals in a mountain stream with acidic to neutral pH: Fisher Creek, Montana, USA. Geochim. et Cosmochim. Acta 69, 2505–2516.

Gammons, C.H., Wood, S.A., Nimick, D.A., 2005b. Diel behavior of rare earth elements in a mountain stream with acidic to neutral pH. Geochim. Cosmochim. Acta 69, 3747–3758.

Gammons, C.H., Grant, T.M., Nimick, D.A., Parker, S.R., DeGrandpre, M.D., 2007a. Diel changes in water chemistry in an arsenic-rich stream and treatment-pond system. Sci. Total Environ. 384, 433–451.

Gammons, C.H., Milodragovich, L., Belanger-Woods, J., 2007b. Influence of diurnal cycles on monitoring of metal concentrations and loads in streams draining abandoned mine lands: an example from High Ore Creek, Montana. Environ. Geol. 53, 611–622.

Gammons, C.H., Nimick, D.A., Parker, S.R., Snyder, D.M., McCleskey, R.B., Amils, R., Poulson, S.R., 2008. Photoreduction fuels biogeochemical cycling of iron in Spain's acid rivers. Chem. Geol. 252, 202–213.

Grosbois, C., Schäfer, J., Bril, H., Blanc, G., Bossy, A., 2009. Deconvolution of trace element (As, Cr, Mo, Th, U) sources and pathways to surface waters of a gold mining-influenced watershed. Sci. Total Environ. 407, 2063–2076.

Hartley, A.M., House, W.A., Leadbeater, B.S.C., Callow, M.E., 1996. The use of microelectrodes to study precipitation of calcite upon algal biofilms. J. Colloid Interf. Sci. 183, 498–505.

Jones, C.A., Nimick, D.A., McCleskey, R.B., 2004. Relative effect of temperature and pH on diel cycling of dissolved trace elements in Prickly Pear Creek, Montana. Water Air Soil Pollut. 153, 95–113.

Kimball, B.A., Runkel, R.L., 2009. Spatially detailed quantification of metal loading for decision making: metal mass loading to American Fork and Mary Ellen Gulch, Utah. Mine Water Environ. 28, 251–317.

Kimball, B.A., McKnight, D.M., Wetherbee, G.A., Harnish, R.A., 1992. Mechanisms of iron photoreduction in a metal-rich, acidic stream (St. Kevin Gulch, Colorado, USA). Chem. Geol. 96, 227–239.

Lundquist, J.D., Cayan, D., 2002. Seasonal and spatial patterns in diurnal cycles in streamflow in the Western United States. J. Hydrometeorol. 3, 591–603.

Machesky, M.L., 1990. Influence of temperature on ion adsorption by hydrous metal oxides. In: Melchior, D.C., Bassett, R.L. (Eds.), Chemical Modeling of Aqueous Systems II, American Chemical Society Symposium Series, vol. 416, pp. 282–292.

McKnight, D.M., Bencala, K.E., 1988. Diel variations in iron chemistry in an acidic stream in the Colorado Rocky Mountains, USA. Arct. Alp. Res. 20, 492–500.

McKnight, D.M., Duren, S.M., 2004. Biogeochemical processes controlling midday ferrous iron maxima in stream waters affected by acid rock drainage. Appl. Geochem. 19, 1075–1084.

McKnight, D.M., Kimball, B.A., Bencala, K.E., 1988. Iron photoreduction and oxidation in an acidic mountain stream. Science 240, 637–640.

McKnight, D.M., Kimball, B.A., Runkel, R.L., 2001. PH dependence of iron photoreduction in a rocky mountain stream affected by acid mine drainage. Hydrol. Process. 15, 1979–1992.

Montana Department of Environmental Quality, 2010. Montana numeric water quality standards. Montana Department of Environmental Quality Circular DEQ-7, Helena, Mont.

Morris, J.M., Nimick, D.A., Farag, A.M., Meyer, J.S., 2005. Does biofilm contribute to diel cycling of Zn in High Ore Creek, Montana? Biogeochemistry 76, 233–259.

Nimick, D.A., Moore, J.N., Dalby, C.E., Savka, M.W., 1998. The fate of geothermal arsenic in the Madison and Missouri Rivers, Montana and Wyoming. Water Resour. Res. 34, 3051–3067.

Nimick, D.A., Gammons, C.H., Cleasby, T.E., Madison, J.M., Skaar, D., Brick, C.M., 2003. Diel cycles in dissolved metal concentrations in streams: occurrence and possible causes. Water Resour. Res. 39, 1247. http://dx.doi.org/10.1029/WR001571.

Nimick, D.A., Cleasby, T.E., McCleskey, R.B., 2005. Seasonality of diel cycles of dissolved trace-metal concentrations in a Rocky Mountain stream. Environ. Geol. 47, 603–614.

Nimick, D.A., Harper, D.D., Farag, A.M., Cleasby, T.E., MacConnell, E., Skaar, D., 2007a. Influence of in-stream diel concentration cycles of dissolved trace metals on acute toxicity to one-year-old cutthroat trout (*Oncorhynchus clarki lewisi*). Environ. Toxicol. Chem. 26, 2667–2678.

Nimick, D.A., McCleskey, R.B., Gammons, C.H., Cleasby, T.E., Parker, S.R., 2007b. Diel mercury concentrations cycles in streams affected by mining and geothermal discharge. Sci. Total Environ. 373, 344–355.

Nimick, D.A., Gammons, C.H., Parker, S.R., 2011. Diel biogeochemical processes and their affect on the aqueous chemistry of streams: a review. Chem. Geol. 283, 3–17.

Odum, H.T., 1956. Primary production in flowing waters. Limnol. Oceanogr. 2, 85–97.

Ovesen, N.B., 2001. Diurnal fluctuation in stage and discharge induced by aquatic plants in a Danish lowland stream. Verhandlungen der Internationalen Vereinigung fur Theoretische und Angewandte Limnologie 27, 3729–3732.

Parker, S.R., Gammons, C.H., Poulson, S.R., DeGrandpre, M.D., 2007a. Diel variations in stream chemistry and isotopic composition of dissolved inorganic carbon, upper Clark Fork River, Montana, USA. Appl. Geochem. 22, 1329–1343.

Parker, S.R., Gammons, C.H., Jones, C.A., Nimick, D.A., 2007b. Role of hydrous iron and aluminum oxide formation in attenuation and diel cycling of dissolved trace metals in an ARD-affected stream. Water Air Soil Pollut. 181, 247–263.

Parker, S.R., Gammons, C.H., Pedrozo, F., Wood, S.A., 2008. Diel changes in metal concentrations in a geogenically acidic river: Rio Agrio, Argentina. J. Volcanol. Geoth. Res. 178, 213–223.

Scholefield, D., Le Goff, T., Braven, J., Ebdon, L., Long, T., Butler, M., 2005. Concerted diurnal patterns in riverine nutrient concentrations and physical conditions. Sci. Total Environ. 344, 201–210.

Scott, D.T., McKnight, D.M., Voelker, B.M., Hrncir, D.C., 2002. Redox processes controlling manganese fate and transport in a mountain stream. Environ. Sci. Technol. 36, 453–459.

Shope, C.L., Xie, Y., Gammons, C.H., 2006. The influence of hydrous Mn–Zn oxides on diel cycling of Zn in an alkaline stream draining abandoned mine lands. Appl. Geochem. 21, 476–491.

Smith, K.S., 1999. Metal sorption on mineral surfaces: an overview with examples relating to mineral deposits. In: Plumlee, G.S., Logsdon, M.J. (Eds.), The Environmental Geochemistry of Mineral Deposits, Part A: Processes, Techniques, and Health Issues, Reviews in Economic Geology, Society of Economic Geologists, Lakewood, Colo., pp. 161–182.

Spiro, B., Pentecost, A., 1991. One day in the life of a stream – a diurnal inorganic carbon mass balance for a travertine-depositing stream (Waterfall Beck, Yorkshire). Geomicrobiol J. 9, 1–11.

Stumm, W., Morgan, J.J., 1996. Aquatic Chemistry, third ed. Wiley Interscience, New York.

Sullivan, A.B., Drever, J.I., McKnight, D.M., 1998. Diel variation in element concentrations, Peru Creek, Summit County, Colorado. J. f Geochem. Explor. 64, 141–145.

Taylor, B.R., Hamilton, H.R., 1994. Comparison of methods for determination of total solutes in flowing waters. J. Hydrol. 154, 291–300.

Tercier-Waeber, M.-L., Hezard, T., Masson, M., Schäfer, J., 2009. In situ monitoring of the diurnal cycling of dynamic metal species in a stream under contrasting photobenthic biofilm activity and hydrological conditions. Environ. Sci. Technol. 43, 7237–7244.

Vesper, D.J., Smilley, M.J., 2010. Attenuation and diel cycling of coal-mine drainage constituents in a passive treatment wetland: a case study from Lambert Run, West Virginia, USA. Appl. Geochem. 25, 795–808.