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Spatiotemporal variability in stream chemistry in a high-elevation catchment affected by mine drainage

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Abstract

This study examined solute dynamics on both spatial and temporal (seasonal, 24 h) scales in a high-elevation stream affected by drainage from abandoned metal mines. Peru Creek is located along the Continental Divide in the US Rocky Mountains, and the hydrologic cycle is dominated by melting of snow. Spatially, tributary inflows produced order-of-magnitude concentration changes along Peru Creek; these were due to dilution and concentration, and also to precipitation of solids. Seasonally, the concentration of most solutes increased as snowmelt diminished. Concentrations of Al, Fe, Cu and Zn, at times affected by instream processes, increased the most, by factors of 2.1–12.8. Ca, Mg, and SO_4^{2-}, which approximated conservative behavior, increased by factors of 1.7–2.2. Si, Na and K, which were unaffected by mine drainage, increased less, by factors of 1.1–1.6. Concentrations of NO_3^- decreased slightly during the snowmelt season. Hydrologic, photochemical and biological processes were active on the 24 h timescale and produced daily concentration variations of up to 40%. Accurate predictions of solute concentrations, which rely on knowledge of processes that produce natural cycling, are crucial in developing models of toxicity and pollutant loading. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Acid mine drainage; Trace metals; Streams; Water quality; Hydrochemistry

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1. Introduction

Alpine catchments are especially sensitive to the effects of acid deposition (Unsworth and Fowler, 1988; Baron, 1992; Wolford et al., 1996), due to their rocky, shallow and poorly developed soils, and short growing seasons. The characteristics that make these high-elevation catchments susceptible to the effects of acidic deposition also make them sensitive to discharges from abandoned mines, which bring not only acidity, but also an influx of metals. Over 1200 miles of streams are affected by mine drainage in Colorado, USA (IMCC, 1992), and many of these streams are in high-elevation Rocky Mountain catchments.

In pristine high-elevation catchments, streams undergo characteristic chemical cycles. For example, on a seasonal timescale, an ionic pulse generally occurs during the initial melting of accumulated snow, as major solutes are preferentially eluted from the snowpack. The snowmelt runoff then becomes more dilute as the season progresses (Johannessen and Henriksen, 1978; Finley and Drever, 1992; Peters and Leavesley, 1995). On the other hand, solutes from

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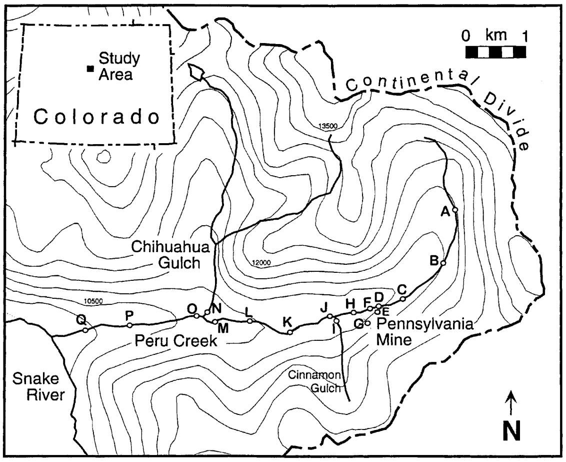

Fig. 1. Peru Creek is located in the United States Rocky Mountains in central Colorado. The location of sampling sites A through Q are noted on the map. Tributary sampling sites include Chihuahua Gulch (N), Cinnamon Gulch (I), the Pennsylvania Mine drainage (G) and a small unnamed tributary upstream of the Pennsylvania Mine (E). Elevations are in feet; the contour interval is 300 feet (approximately 91 m).

mineral weathering usually increase in concentration as snowmelt diminishes (Williams et al., 1993; Campbell et al., 1995b), since the soil water and the groundwater has longer contact time with primary minerals.

Understanding the dynamics of metals and other solutes from mine drainage in these unique streams is of great interest. Recognizing the processes that produce chemical cycles and variability is essential in planning remediation efforts and estimating pollutant loading and toxicity criteria. This study explored mechanisms that contributed to variation in solute concentrations, spatially and over seasonal and diel time-scales, in a high-elevation stream affected by mine drainage.

2. Site description

Peru Creek is a headwater stream of the Colorado River in central Colorado (Fig. 1) in the United States near the towns of Montezuma and Keystone. The watershed ranges in elevation from 3000 m to over 4200 m, and the Continental Divide defines the catchment to the north, east and southeast. Catchment geology consists of glacial debris, Tertiary intrusives and associated ores, and Precambrian gneisses and schists (Neuerburg and Botinelly, 1972). Much of the yearly precipitation falls as snow, and the annual hydrograph is characterized by a large pulse of snowmelt runoff, which generally peaks in mid-June before tapering off to baseflow, which persists from September to April (Fig. 2). In the years in which this work was completed, high flows during snowmelt exceeded base flow by a factor of greater than 10.

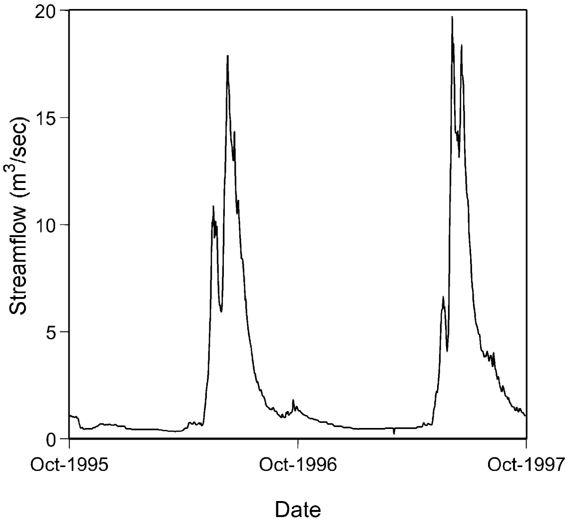

Fig. 2. Annual hydrographs for the 1995–1996 and 1996–1997 water years at the USGS station on the Snake River (#09047500).

Many abandoned silver mines remain along Peru Creek from a mining era that peaked in the late 1800's and early 1900's. The Pennsylvania Mine, developed on six levels in the mountainside, was the largest of these. The drainage from this mine discharges through a settling pond into Peru Creek. Some remediation of this drainage was attempted, but those endeavors were abandoned due in part to Clean Water Act liability issues. The macroinvertebrate community of Peru Creek is severely stressed (US Forest Service, 1989–1991). The water from Peru Creek eventually flows through the Snake River into Dillon Reservoir, a major drinking-water supply for the city of Denver. The Snake River is acidic and metal-rich from weathering of disseminated pyrite in the country rock, and has been the site of a number of geochemical studies (cf. Theobald et al., 1963;

Moran and Wentz, 1974; Bencala et al., 1987; McKnight and Bencala, 1988; Bencala et al., 1990).

3. Sampling and analytical methods

Synoptic samples from Peru Creek were collected at 17 sites (A–Q) on 31 July 1996 (Fig. 1), and most sites were resampled on 19 August 1997. Most sites were located along Peru Creek. Four sampling locations were on tributaries to Peru Creek. Site N was Chihuahua Gulch, site I was on Cinnamon Gulch, site G was the Pennsylvania Mine Drainage, and site E was on a small tributary upstream of the Pennsylvania Mine drainage. Diel samples were collected at site K on 1 July and 12–13 August 1996, and at site M on 27–28 June, 14–15 July and 13–14 September 1997. Access to the upper reaches of the watershed is difficult before late June, due to snowpack. For each sampling event, two-liter grab samples were collected. Temperature and pH were measured immediately on subsamples; the water was then filtered with a Millipore Minitan II tangential flow system using filter plates with 0.45 μm pore size. The samples collected in 1997 were first filtered through a 41μm screen filter, and then filtered with the 0.45 μm filter plates. Use of this pore size may have left some colloidal material in the filtrate. While the chemical composition of the 41 μm filtrate was also determined, this paper only uses results from the 0.45 μm filtered fraction. Samples were collected from both filtered fractions in plastic bottles that had been soaked in 5% nitric acid and rinsed 5 times with deionized water. Samples for cation analysis were acidified with ultrapure nitric acid. All samples were placed on ice after collection and stored in the laboratory at 4°C before analysis. Ambient levels of UV radiation (300–400 nm) were measured during the diel samplings at approximately 15 min intervals with a Spectronics Inc. solar radiometer.

Anions (SO_4^{2-}, Cl^-, F^-, NO_3^-, PO_4^{3-}) were analyzed with a Dionex System 14 Ion Chromatograph. Cations were analyzed with a Perkin Elmer 2380 Atomic Absorption Spectrophotometer (Na, K) and a Thermo-Jarrell Ash P 300 Inductively Coupled Plasma Spectrophotometer or Perkin-Elmer ICP-MS (Fe, Mn, Zn, Cu, Si, Al, Ca, Mg). Iron (0.45 μm filtered total, and 0.45 μm filtered Fe(II)) was also analyzed with a colorimetric method (Gibbs, 1979). Reagents for Fe(II) analysis were added in the field immediately after filtration, and samples were analyzed < 24 h after collection. Alkalinity was determined by potentiometric titration. The precision of most analyses was between 2 and 3%, except for sulfate analysis which had a precision of 0.2%; this information was obtained from five to ten analyses of the same sample, done during a number of the analytical runs. On occasion, duplicate samples were collected in the field, and the analytical error was determined to comprise most of the total error associated with sampling and analysis. Charge balance on samples was excellent; ninety-eight percent of charge-balance errors were $< 5\%$, and $> 90\%$ were $< 3\%$.

All hydrologic data were obtained from the USGS stream gage (#09047500) located on the Snake River, approximately 10 km downstream from site K. The Peru Creek catchment makes up approximately 27% of the total catchment area contributing flow to that gage.

4. Results and discussion

4.1. Spatial patterns in stream chemistry

Results from one synoptic sampling of Peru Creek are shown in Fig. 3. Abandoned mines and tailings piles occur in the headwaters upstream from the Pennsylvania Mine, but there, streamwater was characterized by relatively low concentrations of metals, positive alkalinities, and near-neutral pH values. This upstream reach of Peru Creek was sampled intensively by McKnight and Bencala (1990).

Acidic ($pH \sim 3$) Pennsylvania Mine drainage caused alkalinity of water in Peru Creek to decline to zero (or negative values), and most metals increased in concentration by at least 10×. Solutes affected by the Pennsylvania Mine drainage included H^+, Al, Fe, Mn, Zn, Cu, SO_4^{2-}, Ca, Mg and F^-. In addition to the metals presented in the figures, the mine drainage also contained high concentrations of Pb, Cd and Ni (0.92, 1.2 and 2.2 μm, respectively, on 31 July 1996). Despite its strong influence on Peru Creek chemistry, drainage from the Pennsylvania Mine contributed only about 5% of the flow in Peru

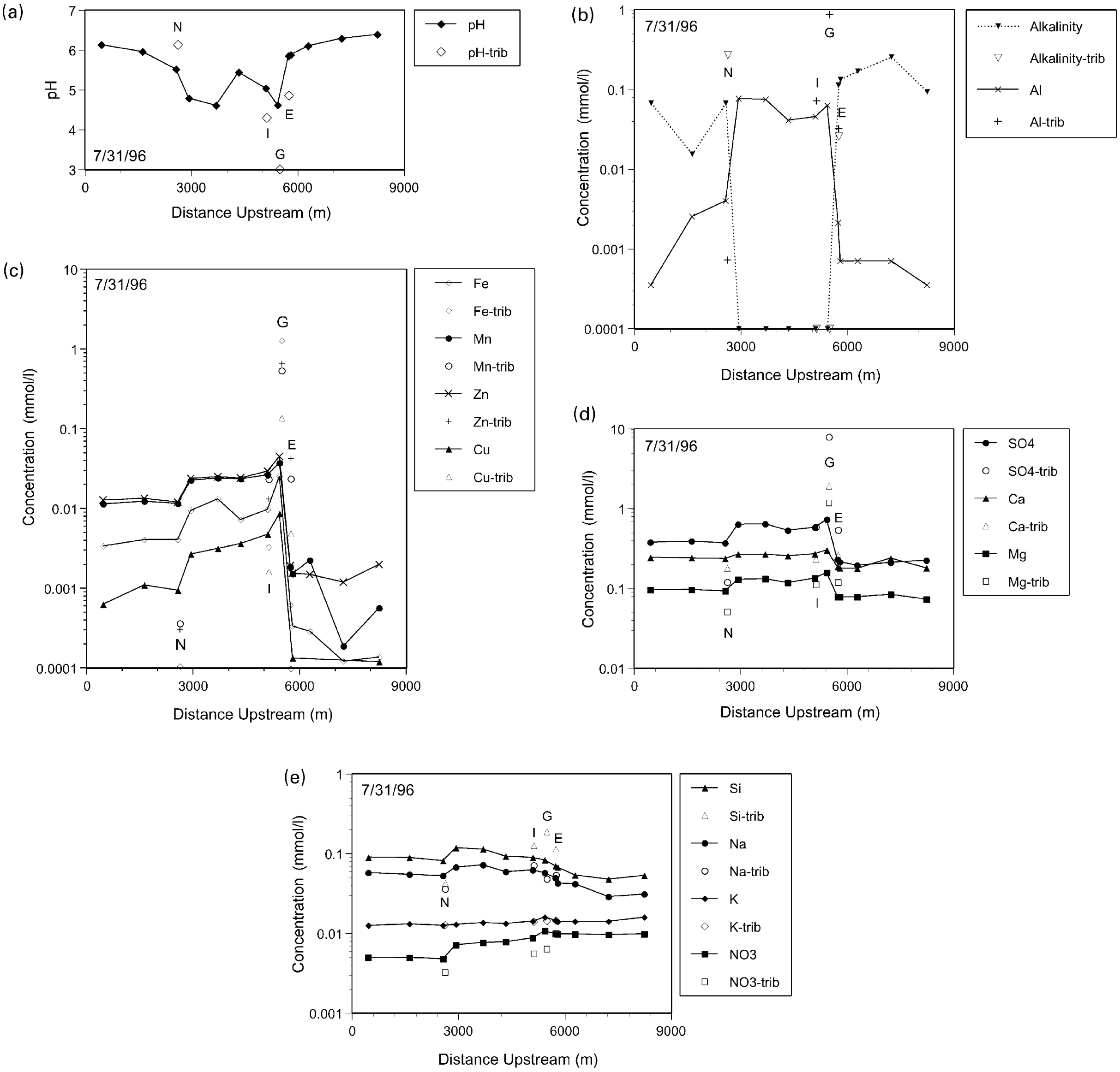

Fig. 3. (a–e) Results of one synoptic sampling event along Peru Creek (31 July 1996). Connected solid points are concentrations in Peru Creek; single open points are from tributaries. The tributary sampling locations (sites N, I, G, E) are noted. Negative alkalinities are plotted as zero. The zero point on the distance scale is the confluence of Peru Creek with the Snake River.

Creek at low flow based on conservative mixing calculations (Sullivan, 1999).

Another major chemical change in Peru Creek occurred at the influx of Chihuahua Gulch. Chihuahua Gulch is within a subcatchment with few ore bodies (Neuerburg and Botinelly, 1972) and has good water quality and low metal concentrations. The flow in Chihuahua Gulch is large: it contributes about 43% of the downstream flow in Peru Creek at low flow conditions based on conservative mixing calculations (Sullivan, 1999). After the influx of Chihuahua Gulch, the concentrations of many solutes decreased. The water quality in Peru Creek remained relatively constant further downstream.

The profound chemical changes that occurred in Peru Creek at the influx of the Pennsylvania Mine drainage and Chihuahua Gulch are the result of more than hydrologic mixing. Precipitation of solid-phase material from the waters also occurred; this was calculated using natural conservative tracers (Sullivan and Drever, in press). These nonconservative processes especially affected the concentrations of Fe and Al, and as a result much of the streambed was coated with orange (Fe) and/or white (Al) precipitates. Some Fe and Al also was transported downstream in the solid-phase in association with suspended aluminosilicate particles. In addition to Fe and Al, and depending on the conservative tracer used, Cu, Mn, Zn, SO_4^{2-}, and Ca were predicted to be nonconservative in some parts of Peru Creek (Sullivan and Drever, in press). The changes in metal concentrations and water quality at tributary junctions, accompanied by precipitation of solid phase material are often seen in flowing waters affected by acidic drainage (Chapman et al., 1983; Filipek et al., 1987). In addition to the dramatic chemical changes observed at tributary inflows, solute concentrations and pH changed in other stretches of Peru Creek as well. Some of these chemical changes could be due to precipitation of solid phases along Peru Creek. Also, although many of the mines in the Peru Creek valley have point-source inflows and drainages, diffuse inputs of metals from groundwater sources could contribute to the observed chemical changes along Peru Creek.

In Peru Creek, Si, Na, K and NO_3^-, were relatively unaffected by the influx of the Pennsylvania Mine drainage (Fig. 3e). Si, Na, and K were derived from the weathering of bedrock minerals throughout the catchment. Si and Na concentrations increased in Peru Creek downstream of the Pennsylvania Mine, and were slightly diluted by Chihuahua Gulch. Concentrations of K remained relatively constant in Peru Creek.

Unlike the other solutes, NO_3^- decreased consistently in concentration with distance downstream. The primary source of nitrogen in catchments similar to Peru Creek is from melting snow. Many Rocky Mountain catchments are becoming N-saturated due to fixed nitrogen in precipitation (Williams et al., 1996). Turk et al. (1992) found that concentrations of NO_3^- and SO_4^{2-} in the snowpack along the Continental Divide in northern Colorado were twice the regional background level. The decrease in nitrate concentrations at lower elevations may be due to the uptake of nitrogen by plants. Although vegetation is sparse in the upper reaches of the Peru Creek catchment, it is densely forested at lower elevations.

4.2. Seasonal patterns in stream chemistry

Seasonal trends in metal concentrations were different in the Pennsylvania Mine and Peru Creek. In the mine drainage, concentrations of metals were highest and pH values were lowest during maximum snowmelt (Boulder Innovative Technologies, 1993–1994), and concentrations of most measured metals were lowest during baseflow. The high concentrations during snowmelt were probably due to the flushing of accumulated weathering products from the upper levels of the Pennsylvania Mine workings.

Peru Creek showed a different seasonal cycle. During maximum snowmelt, most solutes were at low concentration and pH values were relatively high. Metal concentrations increased and the pH values declined during the summer (Table 1). In Peru Creek, the concentrations of Al, Fe, Cu, Zn, and Mn showed the greatest and most variable seasonal increases, from 2.1 to 12.8 times their concentration at high flow. Several interacting processes may have contributed to these concentration increases. One potential factor was the change in the proportion of dilute snowmelt versus mine drainage that occurred seasonally. During snowpack melting, dilute snowmelt contributes the high flows in Peru Creek, while at baseflow, there is no snowpack left to contribute to streamflow. Some of the changes, especially for Fe and Al, were due to nonconservative instream processes, such as precipitation of solid-phase materials onto the streambed. The importance of these latter processes varies seasonally, since changes in pH and concentrations would affect mineral saturation indices.

Aluminum showed particularly large seasonal concentration increases. The solubility of $Al(OH)_3$ phases is extremely sensitive to pH (Nordstrom and Ball, 1986), and Al concentrations in Peru Creek change markedly near pH 5 (Fig. 4). At high flow, the pH in Peru Creek was > 5, and Al concentrations would be controlled by the solid phase. As the pH

Table 1
Seasonal changes in solute concentrations at site K in 1996 and at site M in 1997. In parentheses is the concentration normalized to the concentration measured during high flow for that year; a solute whose concentration remained constant would stay at 1.0. To remove the effect of the diel variation in solute concentration observed for most solutes, each concentration is an average of 18–26 samples collected over 24 h periods. Concentrations are in mg/l

	1996		1997		
	1 July	12–13 August	27–28 June	14–15 July	13–14 September
NO_3^-	0.65	0.59 (0.9)	0.56	0.45 (0.8)	0.46 (0.8)
K	0.54	0.60 (1.1)	0.51	0.54 (1.1)	0.69 (1.4)
Na	1.04	1.37 (1.3)	1.08	1.31(1.2)	1.71 (1.6)
Si	6.21	9.12 (1.5)	6.72	7.97 (1.2)	10.2 (1.5)
Ca	7.03	12.0 (1.7)	7.28	9.23 (1.3)	13.4 (1.8)
Mg	1.83	3.34 (1.8)	1.96	2.54 (1.3)	3.92 (2.0)
SO_4^{2-}	29.6	57.7 (1.9)	33.2	44.0 (1.3)	73.0 (2.2)
Mn	0.42	1.37 (3.3)	0.52	0.91 (1.8)	1.52 (2.9)
Zn	0.55	1.89 (3.4)	0.72	1.33 (1.8)	1.53 (2.1)
Cu	0.05	0.22 (4.4)	0.07	0.12 (1.7)	0.15 (2.1)
Fe	0.08	0.44 (5.5)	0.18	0.32 (1.8)	0.50 (2.8)
Al	0.10	1.22 (12.2)	0.53	1.14 (2.2)	2.77 (5.2)
Flow (at gage on Snake River, m^3/s)	9.32	1.48	11.76	5.15	1.29
pH	5.9	5.0	5.2	4.9	4.7

values approach or drop below pH 5, most Al would be in the dissolved phase. This change from nonconservative to conservative behavior could explain the relatively large increase in dissolved Al over the snowmelt season at both sites. The proportions of Al and Fe carried downstream with suspended particles also changed through the season; more of both metals were found in the particulate fraction during periods of high flow (Sullivan and Drever, in press).

Concentrations of Ca, Mg and SO_4^{2-} in Peru Creek also were also affected by the inflow of the Pennsylvania Mine drainage, but these solutes had lower, and more consistent concentration increases, with factors ranging from 1.7 to 2.2. Sulfate approximates conservative behavior in Peru Creek (Sullivan and Drever, in press), and its concentration at both sites (Fig. 5) could be predicted using a simple mixing model (Gunnerson, 1967; Hall, 1970; Hall, 1971; Edwards, 1973). This model takes the form:

$$C = aQ^{-1/n}$$

where C is the concentration of the solute, Q the discharge, n the constant, and a is a constant loading from the mine ($Q_{\mathrm{mine}}C_{\mathrm{mine}}$).

The close fit of the data to this mixing model strongly suggests that hydrologic dilution is important in determining SO_4^{2-} concentration in Peru Creek. Interestingly, data collected over 24 h time periods and data collected through the snowmelt season both show the same trend. If the effect of nonconservative processes (such as precipitation, adsorption, dissolution) were removed, many of the other solutes probably could be modeled with this equation, as well.

Solutes that seemed to be unaffected by the mine drainage included Si, Na and K. The concentrations of all of these solutes increased less, through the season, than solutes derived from the mine drainage. At low flow, Si, Na and K had increased from 1.1 to 1.6 times the concentration measured at the high flow sampling. While these factors are not large, these solutes related to weathering of catchment bedrock would be expected to increase in concentration as snowmelt diminishes, since the soil water and groundwater has longer contact time with primary minerals (Williams et al., 1993; Campbell et al., 1995b).

The concentration increases for these weathering products were smaller than the change in flow, which decreased 6- to 9-fold for the range of dates

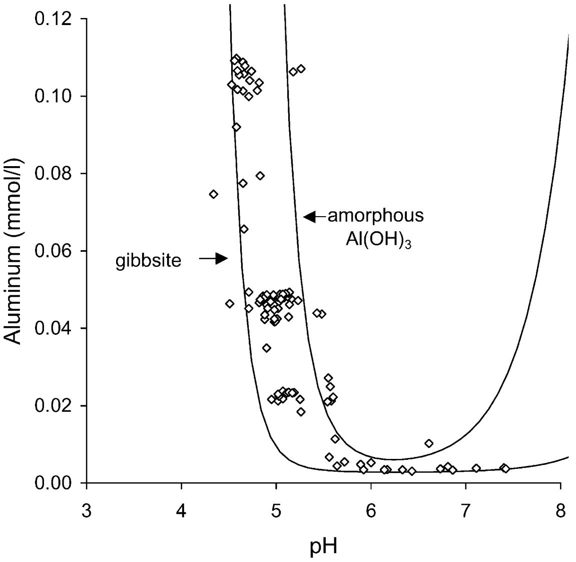

Fig. 4. Aluminum concentrations in Peru Creek and major tributaries, compared to solubility lines for microcrystalline gibbsite (log $K = 9.35$) and amorphous $Al(OH)_3$ (log $K = 10.8$).

sampled. This observation is similar to those reported by others. Campbell et al. (1995b), for example, found that ions from weathering or other soil processes changed by smaller factors (1.5 and 3) compared to the discharge factor (50) for another high-elevation stream in Colorado. Mixing of 'old' and 'new' groundwater can explain this moderation of concentrations. Much of the snowmelt is routed to the stream via piston-type displacement of shallow groundwater. One implication of this process is that while the groundwater system might not affect short-term fluctuations in flow, it could strongly influence the concentrations of chemicals in the stream. Many investigators have noted that this type of subsurface flow to streams is important during snowmelt (Caine, 1989; Kobayashi et al. 1993; Sueker, 1995; Campbell et al., 1995b).

The only solute that decreased in concentration in Peru Creek during the sampling period was NO_3^-. Part of the decrease in NO_3^- concentrations may be due to the ionic pulse effect, for a large portion of NO_3^- in the snowpack is released in early melt (Cameron, 1996; Campbell et al., 1995a). The lower NO_3^- concentrations also correspond to the growing season, and the lowered concentrations may also be due to biological uptake (Arheimer et al., 1996).

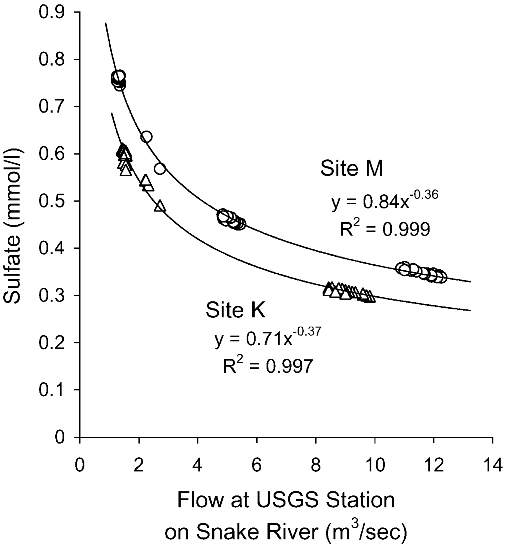

Fig. 5. Sulfate versus flow at sites M and K in Peru Creek during the falling limb of the hydrograph. Each site includes data collected in both 1996 and 1997. Groups of samples that cluster closely together were collected over 24 h periods.

The snowmelt season and low flow conditions constitute two very different geochemical regimes in Peru Creek and most other high-elevation stream systems. Total loads of metals exported from the catchment are greatest during periods of high flow associated with snowmelt, but water quality conditions are best during that time, too. During low-flow conditions, water quality conditions worsen and become detrimental to biota within Peru Creek: the adverse conditions included increased metal concentrations and a lower pH. The US Forest Service (1989–1991) found that invertebrate populations were at their best condition during the early summer, and become stressed by mid-summer to fall. The low-flow conditions persist in the stream for 8–9 months of each year.

4.3. Diel patterns in stream chemistry

Imprinted upon the seasonal trends in water quality were significant daily chemical cycles. In Peru Creek, processes that produced daily cycles at site K (Fig. 1) could be classified into three groups: hydrological, photochemical, and biological (Sullivan et al.,

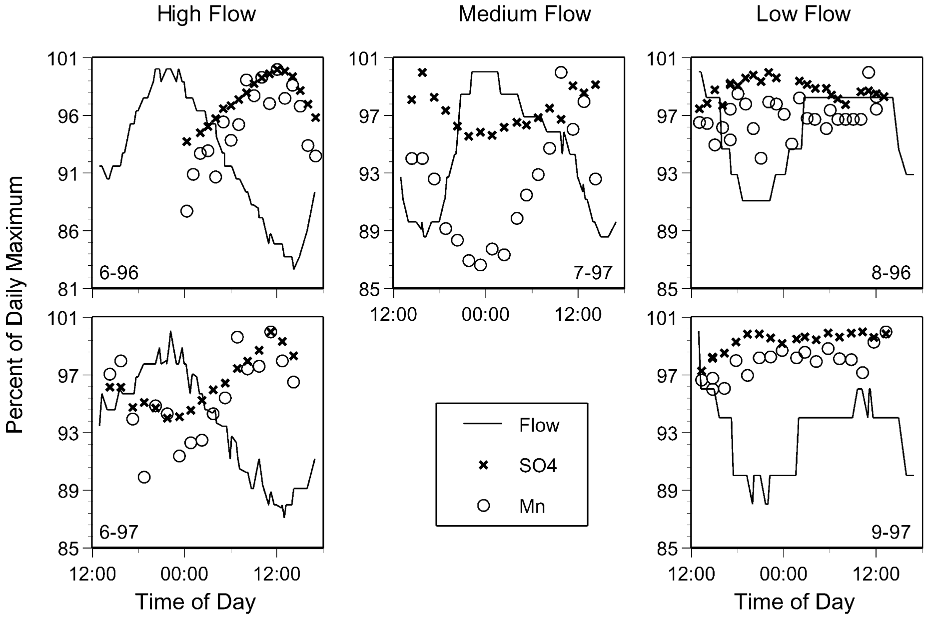

Fig. 6. Diel variation in flow and concentration of SO_4^{2-} and Mn, during high, medium and low flow conditions, shown as a percent of the daily maximum.

1998). Many of the same processes were found to occur at site M through the snowmelt season.

Streamflow produced 24 h concentration cycles at sites K and M through the season, with concentration maxima corresponding to flow minima. Solutes showing evidence of hydrologic control on 24 h concentration cycles included SO_4^{2-}, Mn, Zn, Si, Mg, and Ca. The concentrations of these constituents varied daily from 3 to 15% of their daily maximum concentrations, depending on the solute and time of year; cycles for two solutes (SO_4^{2-}, Mn) are shown in Fig. 6. Some data for Zn was also shown in Sullivan et al. (1998). Al and Cu showed hydrologic control during some sampling periods, but not during others. Presumably, this was because Al and Cu could behave either conservatively or nonconservatively, depending on chemical conditions in the stream. Although pH in Peru Creek changed over the season, there was no discernable 24 h pH cycle during any sampling.

Two major processes probably created the daily streamflow cycles. The first was snowmelt. The amount of snowmelt varies from day to night driven by large changes in air temperature. The flow maxima allows for dilution of solutes by melted snow, and produced concentration minima for many of the solutes. A progressive shift was evident in the timing of the flow minimum (and corresponding concentration maximum) from 12 p.m. in mid-June, to 3 p.m. in early July, to 8 p.m. in early September (Fig. 7). This shift can be used to predict the time of concentration maxima for the solutes under hydrologic control. In some other catchments, the daily peak flows shift to earlier times as the season progresses (Jordan, 1983; Caine, 1992; Peters and Leavesley, 1995). In smaller catchments, reduction in snow depth results in a faster hydrologic response. In the larger Snake River-Peru Creek catchment, the increased hydrologic response time probably is due to the fact that the remaining snow is left at increasingly higher elevations. Asymmetry of the diel flow curves during snowmelt (20 May 1997–3 August 1997) results in an average 8.1 h ($\sigma = 1.4$) time difference between flow maximum and minimum.

The second hydrologic process that likely produced diel chemical cycles was temperature-controlled changes in streamflow gain or loss. This cycle only becomes evident after snowpack has melted. In the years of these samplings, snowpack was gone by mid-August, and diel flow curves at this time of

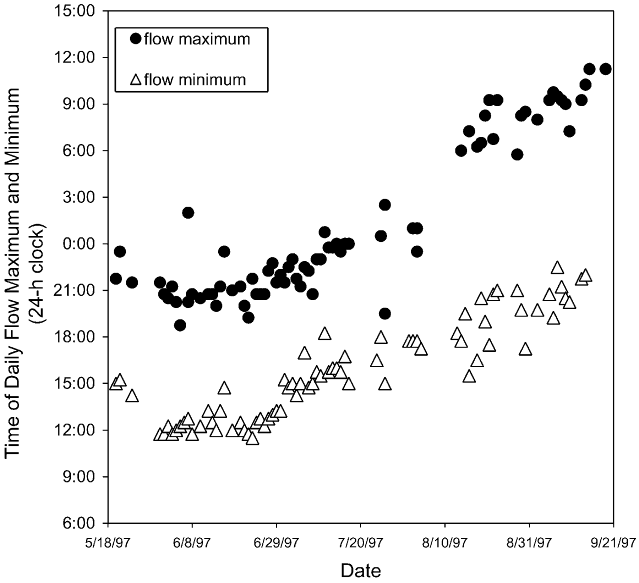

Fig. 7. Shift in the timing of the daily maximum and minimum flow. Fifteen-minute flow data was obtained from USGS stream gage #09047500 on the Snake River. Days with significant precipitation were not plotted.

year (14 August 1997–15 September 1997) were more symmetrical, and the flow maximum and minimum differed by an average of 12.7 h ($\sigma = 1.9$). Diel flow cycles caused by streamflow losses or gains have been studied in other catchments (Constantz et al., 1994; Constantz, 1998), and are a possible explanation for the flow cycles observed here. Those investigators found streambed hydraulic conductivity varied in response to large daily temperature changes. In losing reaches, warmer temperatures allowed relatively more streamflow loss and resulted in lower flows. In Peru Creek, stream temperature varied significantly over 24 h cycles, and daily changes of 10–15°C were common (Fig. 8). The time lag between flow and temperature maxima and minima is thought to be due to the time required to cool or heat the controlling streambed layer (Constantz, 1998). Evapotranspiration by riparian vegetation also can produce diel flow cycles at baseflow (Kobayashi et al., 1990; Bren, 1997) and is another possible explanation for the flow cycles observed in Peru Creek after the disappearance of snowpack.

Iron concentrations in Peru Creek varied by 25–40% (relative to daily maximum) over 24 h periods throughout the season at both sites (Fig. 9), with maximum concentrations near noon. Photochemistry appears to be the dominant process producing these cycles; this process also has been documented in the nearby Snake River (McKnight and Bencala, 1988). Photochemical reduction of Fe(III) solids produces dissolved Fe(II) species, resulting in the increase of both total dissolved Fe and Fe(II) during daylight hours (Fig. 10). In Peru Creek, there was also an upstream source of Fe(II) (most likely the Pennsylvania Mine), and the background levels of both Fe(II) and total Fe increased through the season. The difference between total dissolved Fe and Fe(II) is presumed to be Fe(III); this species was at its highest concentration during low flow.

Photochemistry accounts for much of the Fe diel cycles, but other processes clearly are involved as well. For example, while the most rapid increase and decrease of Fe(II) and total Fe occur in concert with UV light intensity, during medium and low flow, Fe(II) concentrations begin to rise immediately after sunset when conditions are dark. This phenomenon has been observed previously by McKnight and Bencala (1988), who speculated that the predawn increase in Fe(II) may be due either to abiotic oxidation of streambed pyrite, or to microbiological reduction of Fe(III).

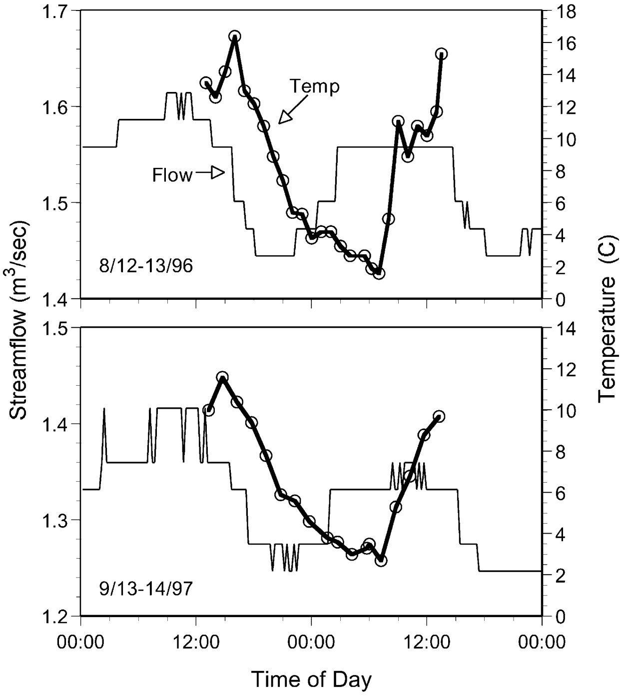

Fig. 8. Stream temperature during the low flow diel samplings at site K in 1996 and site M in 1997 plotted with streamflow.

However, during high-flow conditions in June, the Fe(II) concentrations did not increase immediately after sunset. It is also possible that flow had some control on Fe concentrations during peak snowmelt. During this time of year, strong hydrologic cycles produced similar concentration patterns with maxima also near noon. However, iron concentrations during high flow did show a larger daily percent variation (~40%) than other solutes whose concentrations were controlled purely by hydrology. More work is

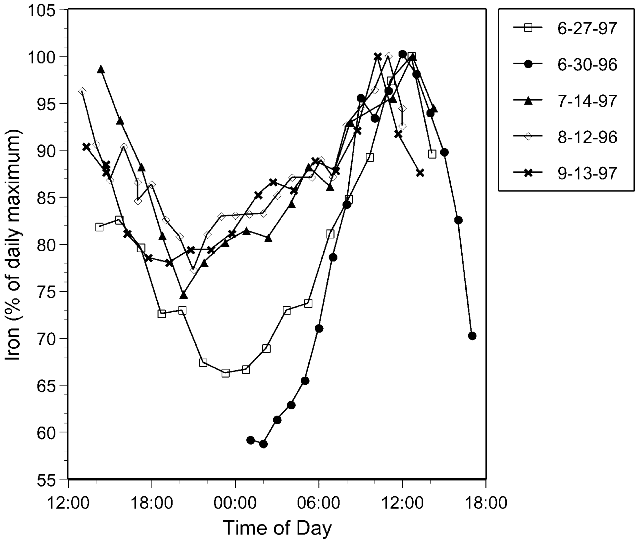

Fig. 9. Diel variation in iron concentration shown as a percent of the daily maximum concentration.

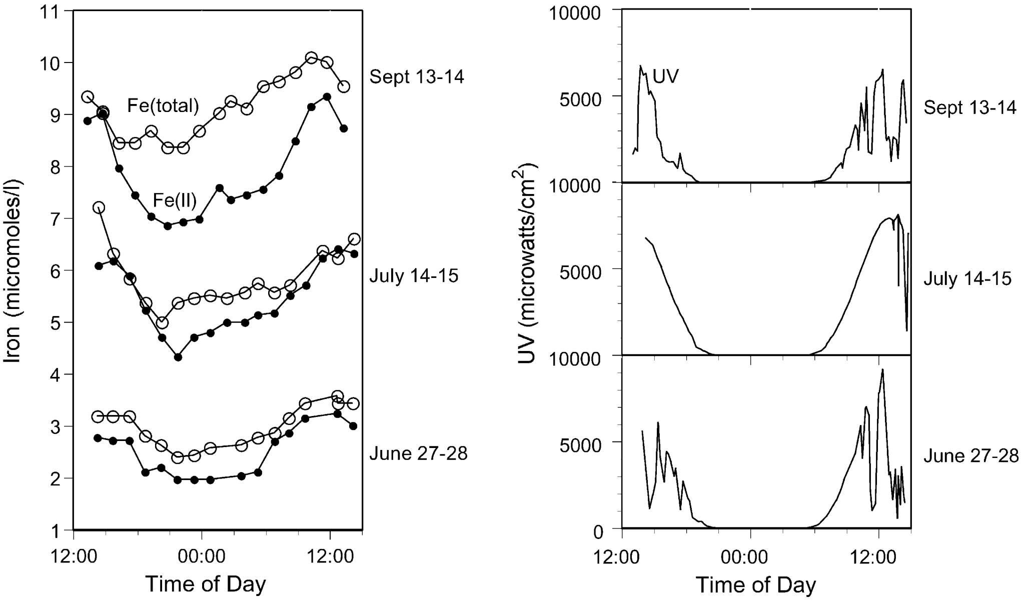

Fig. 10. Total iron and ferrous iron concentrations (both are 0.45 μm filtered), and ambient UV radiation (300–400 nm) for high (June), medium (July) and low flow (September).

needed to better understand the changes in diel iron cycling through the snowmelt season.

One solute, NO_3^-, showed concentration maxima in the early morning and minima during the afternoon (Fig. 11). The percent daily variation in NO_3^- concentrations at site K was approximately 15–25%. The timing of these cycles were similar to diel NO_3^- cycles observed by others in flowing waters (Mulholland, 1992; Brick and Moore, 1996); those cycles were attributed to its uptake as a nutrient, possibly by stream autotrophs. No NO_3^- cycle was observed at site M.

Other studies have examined diel solute cycles, and there are additional controlling processes that can occur in stream environments besides the three discussed above. These sources of diel variation include: instream photosynthesis and respiration,

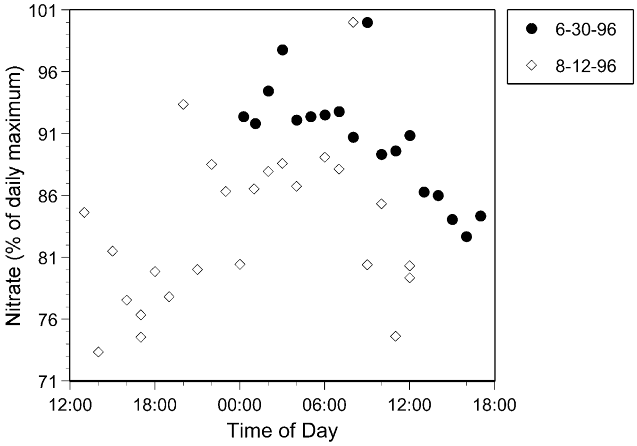

Fig. 11. Nitrate cycles at site K, shown as a percent of the maximum daily concentration. No nitrate cycles were observed at site M.

which can produce cycles in pH and dissolved oxygen (Fuller and Davis, 1989; Bourg and Bertin, 1996; Cicerone et al., 1999), redox processes at the sediment-water interface (Brick and Moore, 1996), and bacterial processes (Wieder, 1994). Brick and Moore (1996) demonstrated that diel cycles can cause toxicity criteria to be exceeded for only certain portions of the day. The great diversity in the controlling processes and the significant chemical variation that these processes can cause indicate that they should be considered carefully in the context of pollutant loadings.

5. Conclusions

Spatial changes and temporal cycles in stream water-quality parameters were significant in this high-elevation watershed affected by mine drainage. Spatial variation along Peru Creek was caused largely by the influx of water from tributaries. Conservative mixing and nonconservative processes collectively produced order-of-magnitude changes in the concentrations of some solutes.

Temporal variation in solute concentrations on the seasonal scale also was large. Solutes from the mine drainage had the largest seasonal increases in concentration. For metals having the biggest seasonal changes (i.e. Al, Fe, Cu, Zn, and Mn), changes from nonconservative to conservative behavior through the season were important. Solutes that were unaffected by the mine drainage either increased less (i.e. Na, K, Si) or decreased (NO_3^-) through the season. The latter solutes seemed to have controlling processes more typical of those that dominate in pristine mountain watersheds.

Temporal variation was also significant on the 24 h timescale. Diel cycles in several of the solutes were produced by hydrology, photochemistry and biology. Changes in the magnitude and timing of these short-term cycles occurred through the season. Most solutes showed similar diel concentration cycles at both sites, but cycling of nitrate was evident only at one of the sites.

The spatial and seasonal variations were large, causing order-of-magnitude changes in solute concentration. The temporal variations on the shorter, 24 h, timescale were smaller, but still accounted for concentration changes up to 40% of the daily maximum concentrations. The concentrations of some solutes were particularly variable, and appeared to be controlled by a number of processes. Iron, for example, showed great spatial variability due to tributary influxes and nonconservative instream processes. The concentration of Fe on the seasonal timescale was controlled both by hydrology and instream processes. On the 24 h timescale, the major control on Fe was photochemistry, with other contributing processes. In contrast, other solutes, such as K, scarcely varied in concentration, either spatially or temporally.

Knowledge of the controlling processes is essential in making useful predictions about pollutant loads and ambient toxicity. High variability for some solutes, spatially and on multiple timescales, show that timing and location of sampling is crucial to understand the natural chemical cycles in these streams.

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