

Geochemical response to variable streamflow conditions in contaminated and uncontaminated streams

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Received 11 February 2002; revised 10 September 2002; accepted 10 September 2002; published 28 February 2003.

[1] Seasonal variations in stream inorganic geochemistry are not well documented or understood. We sampled two mining-impacted and two relatively pristine streams in western Montana over a 12-month period, collecting samples every 4 weeks, with supplemental sampling (at least weekly) during spring runoff. We analyzed all samples for dissolved (operationally defined as $<0.2 \mu\text{m}$) and total recoverable concentrations. Generally, the trace elements (Al, As, Cu, Fe, Mn, and Zn) did not correlate linearly with streamflow, while the major elements (e.g., Ca, K, and Mg) did. Suspended sediment, total recoverable metals, and H^+ followed clockwise hysteresis rotations, driven by short-term flushing events during the very early stages of spring runoff. Mining-impacted sites had higher concentrations of many trace elements than did relatively pristine sites. One of the mining impacted sites exhibited strong geochemical responses to spring rain events in the basin. The results underscore the need to sample streams frequently during changing hydrologic and climatic conditions in order to accurately monitor surface water quality and to determine solute and particulate loads (both contaminant and noncontaminant). **INDEX TERMS:** 1806 Hydrology: Chemistry of fresh water; 1860 Hydrology: Runoff and streamflow; 1871 Hydrology: Surface water quality; 1803 Hydrology: Anthropogenic effects; 1065 Geochemistry: Trace elements (3670); **KEYWORDS:** hysteresis, runoff, trace metals, suspended sediment, water quality, spring flushing

Citation: Nagorski, S. A., J. N. Moore, T. E. McKinnon, and D. B. Smith, Geochemical response to variable streamflow conditions in contaminated and uncontaminated streams, *Water Resour. Res.*, 39(2), 1044, doi:10.1029/2001WR001247, 2003.

1. Introduction

[2] Designing effective management strategies for the regulation of pollution sources and the restoration of rivers requires a rigorous approach to water quality sampling. This not only includes an adherence to modern sampling and analytical techniques (i.e., “clean” or “ultraclean methods” as described by Horowitz *et al.* [1994] and Benoit [1994]) to minimize contamination, but also an understanding of spatial and temporal variability. Of the studies that have incorporated both spatial and temporal measurements of water quality [e.g., McKnight and Bencala, 1990; Carroll *et al.*, 1998; Clow and Mast, 1999; Meixner *et al.*, 2000; Holloway and Dahlgren, 2001], few have sampled for trace metals using ultraclean techniques. This approach is now recognized as being critical to the accurate assessment of trace element concentrations in both pristine and contaminated waters [Shiller and Boyle, 1987; Ahlers *et al.*, 1990; Windom *et al.*, 1991; Horowitz *et al.*, 1994; Benoit, 1994; Taylor and Shiller, 1995]. Of the published papers based on data generated using clean methods, many have looked at

either spatial patterns or temporal dynamics of aqueous geochemistry, but not both.

[3] There is also a particularly acute lack of understanding of how mining-impacted and relatively pristine watersheds respond to processes driving variability, from seasonal changes in runoff to short-term responses to storms and diel fluctuations. Understanding whether or not mining-impacted watersheds have more dynamic temporal variations than do their unmined counterparts has important implications for the design of monitoring studies and the determination of long-term effects of past, present and future mining operations on water quality. This is especially true for mountainous regions where winter snowpacks create large streamflow surges in the spring and where there are numerous streams contaminated by mining wastes.

[4] Runoff dilution is commonly thought to be a dominant control on much of the variability of the composition of surface waters. However, researchers are increasingly documenting complex hysteresis patterns, elemental concentrations along the rising limb of a hydrograph peak differing from those along the falling limb [Johnson and East, 1982; Williams, 1989; Campbell *et al.*, 1995; Evans and Davies, 1998]. For example, the initial stages of spring runoff may be characterized by a surge of the dissolved major ion concentrations. This phenomenon has been

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explained as a flushing of ions that have accumulated on snow crystals, in the soils, and in the groundwater over a relatively long winter residence period [Stottleyer and Toczydlowski, 1990; Harrington and Bales, 1998; Marsh and Pomeroy, 1999]. Such flushing events have been reported in several hysteresis studies from alpine regions [Williams et al., 1993; Campbell et al., 1995; Stottleyer et al., 1997]. These events cause clockwise hysteresis patterns, in which solute concentrations are higher along the rising limb than on the falling limb. Other research from similar regions has shown that some solutes can exhibit counter-clockwise hysteresis patterns as well [Stoddard, 1987; Bhangu and Whitfield, 1997]. These researchers have explained these trends by the volumetric dominance of dilute snowmelt over contributions from groundwater and soil water during the early stages of runoff. The identification of such hysteresis patterns in surface waters is important for designing monitoring studies, for making more informative comparisons among watersheds, and for evaluating the timing and nature of chemical sources to streams [Hooper et al., 1990; Droppo and Jaskot, 1995; Sokolov and Black, 1996].

[5] Most of the studies discussed above on seasonal variation have considered only major ions but not trace metals. From the limited research using ultraclean methods, the relationship between streamflow and trace element concentrations appears to be much more variable from site to site than that found for major ions. For example, Shafer et al. [1997] report 1- to 5-fold increases in filterable metal concentrations (and up to 17-fold increases in particulate metals) in two Wisconsin rivers during high flow events compared to base flow. Similarly, Sherrell and Ross [1999] found highly significant positive correlations between discharge and dissolved metals in four acidic New Jersey streams. In contrast, Sullivan and Drever [2001] report that most solute metals in Peru Creek, CO, were relatively low during maximum snowmelt, although their results were based on only a few sampling events. Finally, Shiller [1997] found that the dissolved metal concentrations in the Mississippi River do not correlate with discharge at all.

[6] This wide range in results shows that a much deeper understanding of stream response to seasonal fluctuations is needed to elucidate seasonal patterns in discharge versus trace metal relationships at the watershed scale. The purpose of this study is to document temporal variability in trace metal and major element geochemistry of both mining-impacted and uncontaminated streams and to evaluate the geochemical changes occurring during spring runoff. We show that major differences exist among study sites in both overall concentration values as well as in the seasonal timing of the concentration variations, and that detailed responses to flow events must be considered when planning any water quality monitoring program.

2. Methods

2.1. Sampling Design

2.1.1. Spatial Design

[7] We chose four sites in the Clark Fork watershed of western Montana (USA) for this study (Figure 1). Two sites are relatively small, moderately high elevation (1450 m) streams and the other two are lower elevation (1000 m and

1200 m) sites on much higher-order streams draining 20-times the land area of the smaller streams. One of the two sites from each size category drains a region impacted by mining contamination, while the other drains a relatively pristine area.

[8] The two low-order streams are in the upper Blackfoot River watershed. The Landers Fork (LF) is a major tributary to the upper basin, and the site along the Blackfoot River near Hogum Creek (BH) is 6 km upstream of the Blackfoot-Landers Fork confluence. The Landers Fork drains 350 km², and the Blackfoot at BH drains 254 km². Site BH is ca. 20 km downstream from the historic Heddleston mining district. Site LF is located 1 km upstream from the confluence with the Blackfoot and is immediately adjacent to the undisturbed McDonald gold deposit. The Landers Fork drains the mountainous Scapegoat Wilderness area, receives more snowmelt than does site BH, and its streamflow levels are typically several times larger than at BH.

[9] The two higher-order stream sites are on the lower Blackfoot River (near Bonner, site "BFB") and on the Clark Fork River (near Bearmouth and Drummond, site "CFBM"). They were selected due to the presence of USGS gaging stations (gaging station 12340000 at BFB and gaging station 12331800 at CFBM) as well as their similar discharges at base flow conditions. We acknowledge the potential lack of independence for site BFB due to its location downstream of BH and LF. However, BFB is 187 km downstream from the headwater sites, and its flow during the study period was on average 10 times larger than the headwaters streams combined. Studies on the geochemistry of the watershed [Spence, 1975; Moore et al., 1991; Nagorski et al., 2002] indicate that the impacts of the headwater mines are not detectable in the solute phase by about 20–30 km downstream of the headwaters. The major tributaries feeding the Blackfoot River between the upper basin sites and the lower basin site drain large portions of wilderness areas, and there are no large-scale industrial or urbanized areas.

[10] In contrast, site CFBM is approximately 130 km downstream from Butte, the setting for one of the world's largest historical metal mining operations. Over a hundred years of mining and smelting in the upper Clark Fork basin have contaminated the river to the extent that the river's approximately 200 km stretch between Butte and Missoula is the largest Superfund complex in the USA. [Moore and Luoma, 1990]. Although CFBM is located far from the major mining contamination, it is chronically impacted by metal pollution from the tailings on the floodplain, elevated metals in the streambed sediments, and other nonpoint sources [Moore and Luoma, 1990; Nimick and Moore, 1991].

2.1.2. Temporal Design

[11] We sampled the sites on a monthly basis with supplemental high flow sampling during spring runoff. Robertson and Roerish [1999] found that such a design was highly effective for one-year studies aiming to estimate loads in small streams. Our monthly sampling started on a randomly chosen weekend in February 2000, followed by sampling at four-week intervals from then on, through January 2001. The four-week rule was given an allowance of ± 2 days in order to deal with adverse winter weather or other logistical inconveniences.

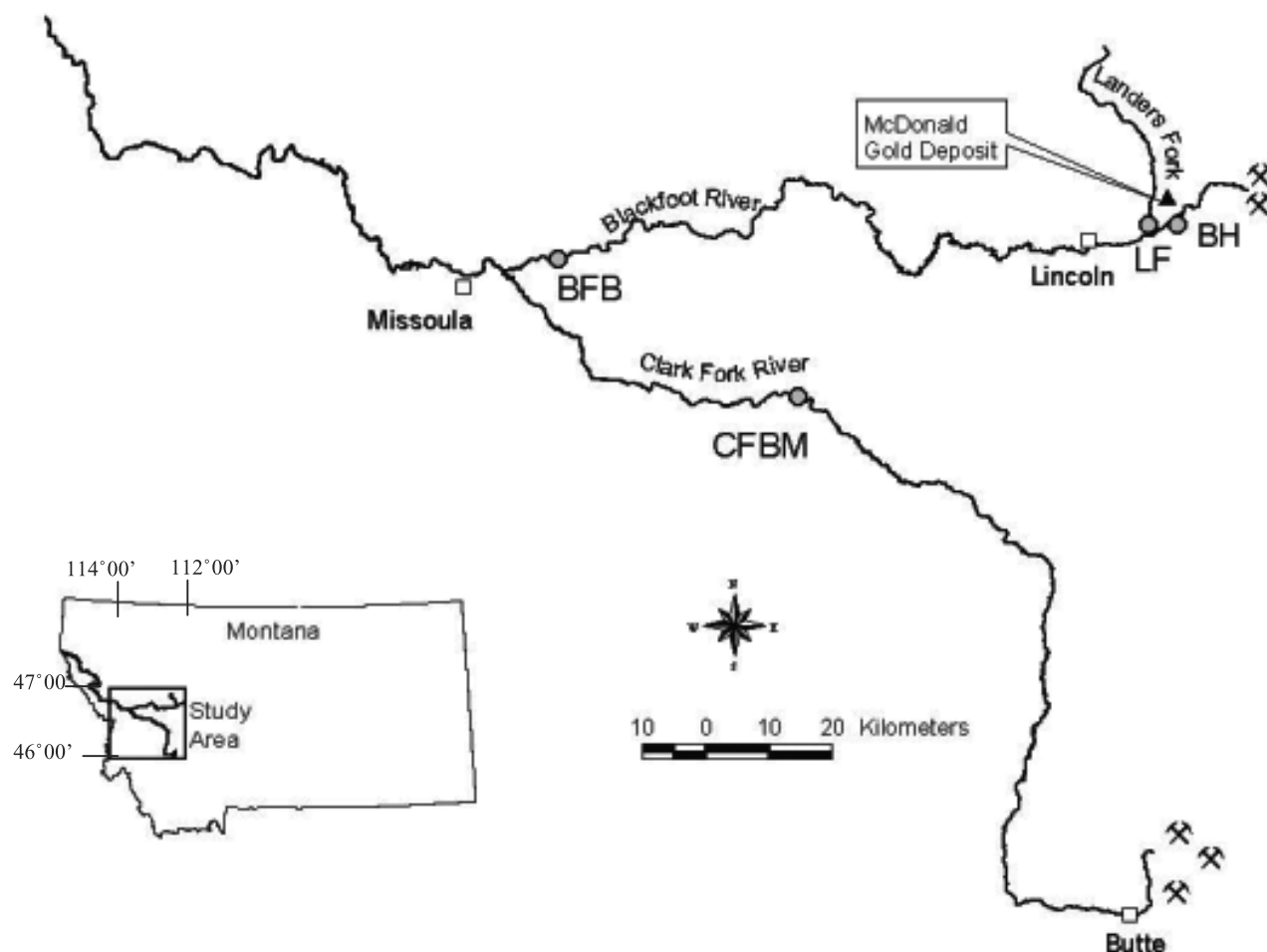


Figure 1. Site location map. Sites: BFB, Blackfoot River at Bonner; CFBM, Clark Fork River near Bearmouth; LF, Landers Fork; BH, Blackfoot River near Hogum Creek.

[12] During spring runoff from mid-April through mid-June, we collected samples once or twice per week in order to capture as much flow variability and as many spring rain events as possible. Frequent site visitation was particularly important for sites BH and LF, as real-time streamflow data were unavailable. We visited all 4 sites for each event, except for one supplemental sampling event (on 14 April 2000) when we sampled only at BFB and CFBM. As a result, BFB and CFBM had a total of 24 sampling events, while BH and LF had a total of 23. We sampled each site at approximately the same time of day in order to minimize confounding any seasonal trends with diel trends.

2.2. Streamflow Measurement

[13] We obtained streamflow (Q) values at BFB and CFBM from the USGS gaging stations at the sites. The estimated error of the Q measurements is 5% (M. White, USGS, personal communication, 2001). From the end of November through the end of the study period in January, Q measurements at BFB were unavailable due to ice at the site.

[14] We measured Q manually at BH and LF using a Price AA current meter or a pygmy meter, according to standard USGS protocol [Rantz, 1982]. Our reproducibility

of the Q measurements (determined by making multiple measurements per site visit) at site BH averaged 7%, but the highest error of 17% was made during the low flow period in December. At LF the mean measurement reproducibility was 3%, with the largest error at 7%.

[15] At LF, daily Q values were estimated from the nearest USGS gaging station on the Blackfoot River, 71 km downstream from LF. Despite the distance from LF, there was a good linear relationship between Q measurements we made at LF and the Q reported at the gaging station ($R^2 = 0.96$). Hence, we could monitor the approximate Q at site LF. Site BH did not correlate well with the USGS gaging station, and so we have no estimations of Q at BH on days between sampling events.

2.3. Sampling Protocol

[16] We precleaned all sample bottles (made of high- or low-density polyethylene) by washing them in a 6N HCl bath for 2 hours and a 1% trace-metal grade HNO_3 bath for 24 hours, with multiple Milli-Q deionized water rinses before and after each cleaning stage. Wearing clean, unpowdered nitrile gloves at all stages, we double-bagged all sample bottles in Class 100 laminar flow hoods and removed each bottle from its bags only moments before

sampling. We collected three width- and depth-integrated water chemistry samples from each site on each sampling event (however, site BFB was too deep to wade safely, so all BFB samples were collected from the northern half of the channel only). Immediately following collection, we sealed the samples back into their double bags and put them on ice, where they remained until filtration in the lab. The triplicate samples were never composited and were put through handling and analysis procedures independently. Following collection of the water chemistry samples, we took samples for total suspended sediment (TSS) and measured pH, dissolved oxygen (D.O.), and stream temperature in situ from the same areas from where we collected the water samples.

2.4. Laboratory Protocol

[17] All sample processing and analysis took place at the Murdock Environmental Biogeochemistry Laboratory at the University of Montana. Wearing clean nitrile gloves, we filtered all samples within 24 hours of sample collection under the Class 100 laminar flow hood. To check for possible chemical changes in the sample bottles prior to filtration, on one occasion we filtered samples from the Clark Fork River and Blackfoot River sites over a variety of time spans, from 2 hours to 100 hours postcollection. There were no detectable changes in chemical concentrations in the first 48 hours postcollection.

[18] Before collecting a filtered sample (at $<0.2\ \mu\text{m}$, operationally defined as the “dissolved” phase), we purged the syringe, filter (Gelman Sciences Serum Acrodiscs), and bottle with 50 mL of sample in order to reduce the filters’ effective pore size [Taylor and Shiller, 1995; Horowitz *et al.*, 1996]. Following filtration and acidification of the sample with ultra-pure HCl to $\text{pH} < 2$, we decanted 100 mL for alkalinity measurement. Then we preserved the remaining unfiltered sample with 3 mL of 6N trace metal grade HNO_3 per liter of sample for total recoverable element analysis. Total recoverable digests were performed within 2 months of sample collection according to EPA Method 200.2 [U.S. Environmental Protection Agency, 1991]. Samples were digested under laminar flow hoods and in molded plastic digestion vessels cleaned in the same manner as the sample bottles. The resulting concentrations in the digested samples are called “total” concentrations in this report.

[19] We quantified the TSS within 1 week, but usually within 1 day, of sample collection by weighing the mass of particulates retained on a $0.2\ \mu\text{m}$ filter following a vacuum-driven filtration of at least 300 mL (mean = 1.5 liters) of sample. We measured dissolved inorganic carbon (DIC) using a Shimadzu Carbon Analyzer within two weeks and determined alkalinity by titration with sulfuric acid to pH 4.5 within 3 days of sample collection. We measured As concentrations on a HGAAS and all other elements using ultrasonic nebulization with an ICP (Jarrel-Ash ICAPES-IRIS) according to EPA Method 200.15 [Martin *et al.*, 1994].

2.5. Laboratory QA/QC

[20] On the ICP we ran acidified blanks, fortified blanks, USGS Standards T143 and T145, sample analysis duplicates, and sample spikes at regular intervals so that

Table 1. Practical Quantifiable Limits (PQLs)

Element	PQL
Al	0.37 μM
As	0.003 μM
Ba	0.004 μM
Be	0.01 μM
Ca	0.002 mM
Cd ^a	0.01 μM
Co ^a	0.05 μM
Cu	0.05 μM
Fe	0.090 μM
K	0.005 mM
Li	0.29 μM
Mg	0.004 mM
Mn	0.009 μM
Mo	0.03 μM
Na	0.008 mM
Ni	0.02 μM
P	0.32 μM
Pb ^a	0.10 μM
S	0.22 μM
Si	0.71 mM
Sn ^a	0.02 μM
Sr	0.006 μM
Ti	0.10 μM
V ^a	0.10 μM
Zn	0.015 μM

^aThese elements were detectable in no samples.

40–60% of the total analysis consisted of QA/QC evaluations. On the HGAAS, we analyzed at least one sample spike, one sample analysis duplicate, one checks of the USGS standards, a blank, and all 5 calibration standards with each set of 10 samples. When analyzing DIC, we again had at least one sample duplicate, one blank, and all 3 calibration standards with each set of 10 samples. Practical Quantifiable Limits (PQLs) are provided in Table 1.

[21] Both lab-constructed and filtered field blanks had rare and insignificant concentrations of measured elements. An exception is that one field blank had 0.73 μM Fe, which was substantially above its PQL of 0.09 μM . Sodium’s maximum field blank concentration of 0.03 mM likely accounts for some of the noise in Na concentrations at sites LF, BFB, and BH, where Na concentrations were typically less than 0.17 mM; Na data at these sites were therefore excluded. Processing blanks through the digestion procedure resulted in some significant contamination for Cr, Ni, and Zn, and so these elements were discarded from the total recoverable data set.

[22] Mean concentrations of all analytes in laboratory standards were within 8% (most within 5%) of the constructed value on all instruments. Mean concentrations of all elements (except Si, which was about 12% low) in unaltered and digested USGS standards T-143 and T-145 analyzed on the ICP and HGAAS fell within the reported acceptable ranges. The mean percent difference between samples measured twice on all instruments was $<6\%$ for all elements. The only exception was for the TSS samples, for which the mean percent difference between samples was 26%. The mean percent difference between digest duplicates was $<6\%$ as well, except for Al, As, Fe, and P (average % differences = 11%, 8%, 7%, and 11%,

respectively). Mean spike recoveries on all detectable elements were between 97% and 111%, except for Li, whose mean recovery was 84%.

2.6. Data Analysis

[23] Due to the nonnormality of the concentration data, the presence of outliers for numerous parameters, heterogeneity of the sample variances, and the failure of data transformations to correct these problems, nonparametric statistical methods were used to analyze the data in SPSS. Kruskal-Wallis tests were done using SPSS to compare geochemical distributions among sites. (The Kruskal-Wallis test compares the distributions of the data sets, not the concentration values themselves, because the test is based on ranked data). Calculations of nonparametric multiple comparisons by simultaneous test procedures (STP) were done manually according to *Sokal and Rohlf* [1995].

3. Results and Discussion

3.1. Streamflow Variation

[24] Late spring-early summer peak runoff occurred at sites BFB, LF, and BH (Figures 2a, 2c, and 2d). At BFB and LF, runoff lasted between April and July. At BH, runoff peaked early relative to BFB and LF. There was a highly unusual runoff pattern at CFBM during the study year (Figure 2b). Instead of being characterized by the typical snowmelt runoff peak, discharge decreased from April through August. As a result, the hydrograph was approximately inverted. Streamflow averages for March through August were the lowest in the 8-year site record, and 31 July 2000 marked the lowest Q (2180 L/s) ever recorded at the site. The low discharge was caused by below normal snowpack and precipitation levels in the region, and by an unknown amount of irrigation withdrawal in the Clark Fork valley.

3.2. Geochemical Comparisons Among Sites

[25] Comparisons among sites (using the Kruskal-Wallis test) showed that pH, water temperature, and D.O. concentration were the only parameters whose distributions were not significantly different among the 4 study sites. All sites had pH values between 7.8–8.5; water temperature between 0.0–18.1°C, and D.O. values of 72–121% saturation. Nonparametric multiple comparisons by STP identified the significant ($p < 0.05$) differences between sites for the rest of measured parameters, as listed in Table 2. Not included in the analysis were elements that were entirely or mostly below detection at all four sites.

[26] The concentration distributions of most measured parameters (alkalinity, DIC, and dissolved (d) and total (t) As, Ca, Cu, K, Li, Mg, Mn, Mo, P, S, Si, and Sr) were highest at site CFBM. Site CFBM was lowest only for Ba_d and Ba_t . The high-order stream sites (CFBM and BFB) had higher TSS, Al_t , As_d , and Li_t concentration distributions and lower Ba_d and Ba_t concentration distributions than the low-order sites (LF and BH). The mining-impacted sites (CFBM and BH) had higher distributions of Fe_d , Mn_d , S_d , S_t , Si_d , Si_t , Sr_d , and Sr_t concentrations than the relatively pristine sites (BFB and

LF). While BFB and BH had similar distributions of alkalinity, DIC, Ca_d , Ca_t , K_d , K_t , Fe_t , Mg_d , Mn_t , and P_t concentrations, CFBM and LF had heterogeneous concentration distributions for all elements. This indicates that these two sites with the largest differences in land use and size also had the least in common in terms of geochemical concentrations.

3.3. Relationships Between TSS and Total Recoverable Concentrations

[27] Pearson's correlations of TSS against the total recoverable elemental concentrations reveal that total Al, Fe, and Mn are strongly correlated ($r \geq 0.88$, $p < 0.01$) with TSS at each site (except for Fe and Mn at LF, where they are below the PQL and so correlations could not be calculated) (Table 3). Total Cu was also positively correlated ($r = 0.95$, $p < 0.01$) with TSS at CFBM, while it was below the PQL at the other 3 sites. Strong correlations indicate that the total recoverable concentrations of the aforementioned metals could be reasonably well estimated using TSS at all these sites. While it would be necessary to periodically check the validity of the relationship at each site, this recognition could spare much money, time, and effort because TSS is far easier and less expensive to measure than total recoverable metal concentrations.

[28] Not all elements correlated uniformly with TSS across the sites. For example, As_t was poorly correlated with TSS ($r = 0.38$, $p = 0.07$; and -0.30 , $p = 0.16$) at the two minimally contaminated sites (BFB and LF), but it correlated reasonably well ($r = 0.78$, $p < 0.01$; and 0.81 , $p < 0.01$) at the two mining-impacted sites (CFBM and BH). That is, when there were higher particulate levels at CFBM and BH, the As_t concentrations increased accordingly, perhaps indicating a more uniformly available source of As at the mining-impacted sites. In contrast, the lack of a relationship between TSS and As at BFB and LF suggests that changes in As concentrations at the uncontaminated sites occurred independently of TSS fluctuations.

[29] Another way of evaluating whether or not the mining-impacted sites had higher metal concentrations than the relatively pristine sites is to compare the total recoverable geochemistry. If rivers with similar TSS concentrations drain areas with similar physical and geochemical characteristics, the rivers should also have similar total recoverable metal concentrations. The median TSS distributions at the two high-order stream sites (BFB with 5.5 mg/L and CFBM with 6.8 mg/L) were not statistically different (Wilcoxon Signed Rank Test, $p < 0.05$); nor were the median TSS distributions different at the two low-order stream sites (BH with 1.3 mg/L and LF with 1.7 mg/L). Therefore one would expect that the concentrations of the total recoverable elements at the 2 high-order stream sites and the 2 low-order stream sites to be similar as well.

[30] However, total recoverable concentrations differed between the mining-impacted and unmined sites in each stream size category. Whereas Al_t , which is commonly used as a correction factor for grain size variations, had statistically identical median concentrations and concentration distributions at CFBM and BFB, median As_t , Fe_t ,

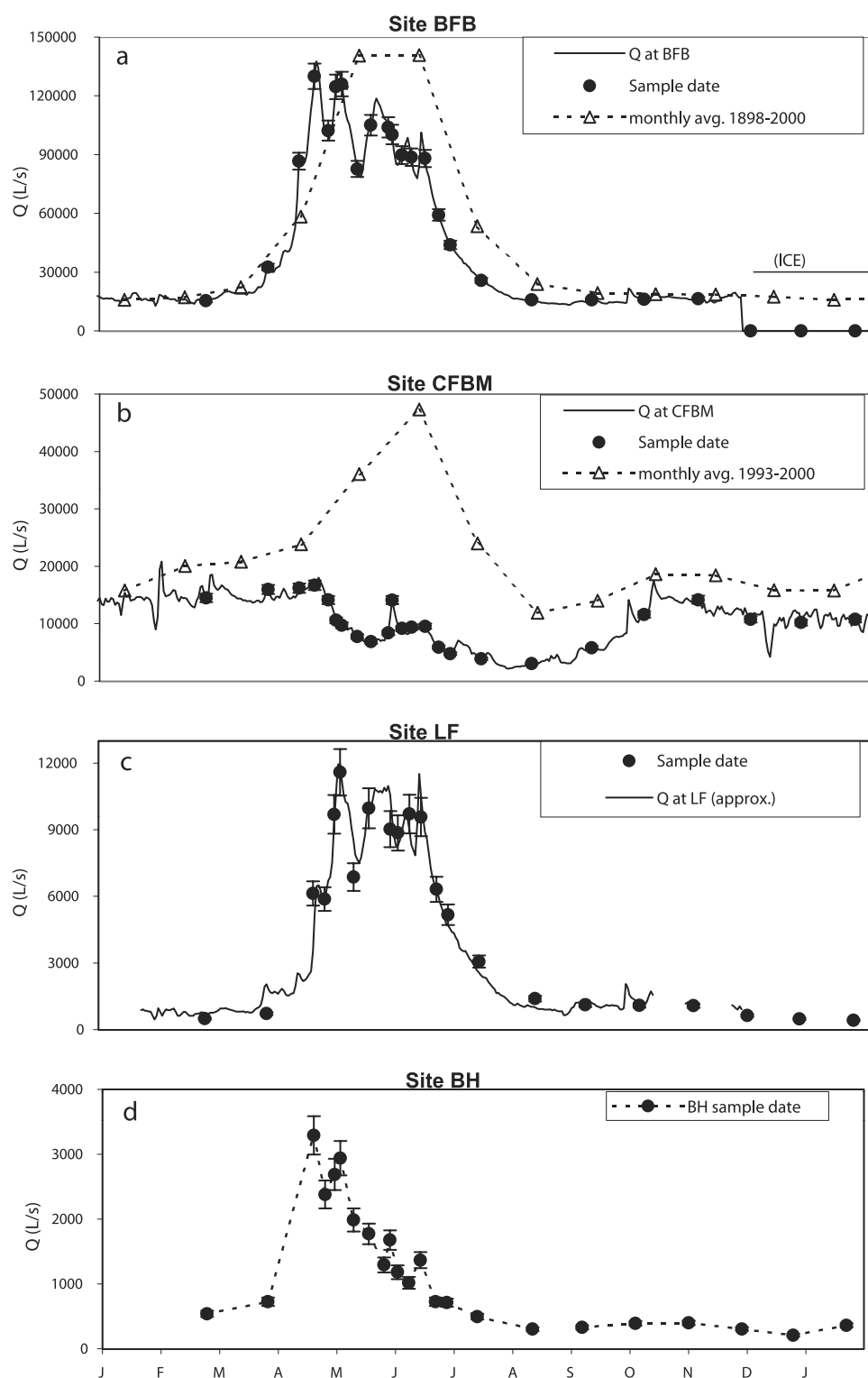


Figure 2. Hydrographs for the four study sites: (a) BFB (from USGS station 12340000), (b) CFBM (from USGS station 12331800), (c) LF, and (d) BH. The approximated hydrograph at LF is derived from data at a downstream gaging station on the Blackfoot River (USGS Station 12335100) where Q was strongly correlated ($R^2 = 0.96$) with Q measurements at LF. Sample dates are those when water quality samples were taken.

and Mn_t concentrations were 13, 1.6, and 4.7, times higher, respectively, at CFBM than at BFB. Total Cu was at least 4.3 times higher at CFBM than at BFB (exact enrichment factors can not be calculated because

Cu_t was below detection at BFB). Although median Al_t was twice as high at LF than at BH, median Fe_t and Mn_t were 2.8, and 4.8 times higher, respectively, at BH than at LF. Therefore both mining-impacted rivers were

Table 2. Summary of Results of Nonparametric Multiple Comparison Among Sites^a

Parameter	Order
Q	BFB > CFBM > LF > BH
TSS, Al _t	BFB = CFBM > LF = BH
Alk, Ca _t	CFBM > BFB = BH; BFB = LF, CFBM > LF, LF > BH
DIC, Ca _d , (Cu _d), (Cu _t), Li _d , Mg _t , (Mo _d), Mo _t , P _d	CFBM > BFB = LF = BH
As _d	CFBM > BFB > LF > BH
Ba _d , Ba _t	LF = BH > BFB > CFBM
Fe _d	CFBM = BH > BFB > LF
K _d , K _t , Mn _t , Na _d , Na _t	CFBM > BFB = BH > LF
Mg _d	CFBM > BH > BFB; BFB = LF, CFBM > LF, BH = LF
Mn _d , S _d , S _t , Si _d , Si _t , Sr _d , Sr _t	CFBM > BH > BFB > LF
As _t	CFBM > BFB = LF > BH
Fe _t	BFB = CFBM > LF; BFB = BH, CFBM > BH, BH = LF
Li _t	CFBM > BFB > LF = BH
P _t	CFBM > BFB = BH; BFB > LF, CFBM > LF, BH = LF

^aSites: BFB, Blackfoot River at Bonner; CFBM, Clark Fork River near Bearmouth; LF, Landers Fork; BH, Blackfoot River near Hogum Cr. Elements that were above the PQL only at site CFBM are in parentheses.

enriched in some total-recoverable elements over their unmined counterparts.

3.4. Was Streamflow A Predictor of Geochemical Concentrations?

[31] Streamflow had strong, significant, and inverse correlations (Pearson's $r < -0.80$; $p < 0.01$) with dissolved and total Ca, Mg, and Sr at all four sites (Table 4). On a site-specific basis, strong inverse correlations ($r < -0.80$; $p < 0.01$) with Q were present also for alkalinity, DIC, As_d, Ba_d, Ba_t, Li_d, and Li_t at BFB; for Li_d and Li_t at CFBM; for alkalinity, DIC, As_d, Ba_d, Ba_t, K_t, S_t, Si_d, and Si_t at LF; and for alkalinity, DIC, Ba_d, Ba_t, and Li_t at BH. Statistically significant positive correlations with Q were present only for TSS, Mn_d, Mn_t, Fe_t, Zn_d at site BH.

[32] According to these results, the general pattern emerges that the major elements, Ba, and Sr were moderately well and inversely correlated with Q, while TSS and many of the trace elements were poorly or positively correlated with Q. Hence, the processes controlling the major element concentrations in these streams were different from those controlling the occurrence of trace metals. A

probable explanation for the behavior of the major elements is that in general, they were chemically conservative and were simply diluted by snowmelt during runoff [Whitfield and Clark, 1982; Bencala et al., 1987; Bhangu and Whitfield, 1997].

[33] In contrast, the temporal controls of trace element concentrations are likely chemical, as suggested by the lack

Table 4. Pearson's Correlations Between Q and TSS, Dissolved (d) Elements, and Total Recoverable (t) Elements at All Sites^a

	Site BFB	Site CFBM	Site LF	Site BH
Q versus TSS	0.67 ^b	0.64 ^b	0.66 ^b	0.85 ^b
Q versus alkalinity	-0.96 ^b	-0.77 ^b	-0.91 ^b	-0.95 ^b
Q versus DIC	-0.95 ^b	-0.55 ^b	-0.96 ^b	-0.93 ^b
Q versus Al _t	0.48 ^c	0.70 ^b	0.58 ^b	0.66 ^b
Q versus As _d	-0.82 ^b	-0.40 ^c	-0.81 ^b	-0.48 ^c
Q versus As _t	-0.27	0.37	-0.68 ^b	0.56 ^b
Q versus Ba _d	-0.91 ^b	-0.48 ^c	-0.96 ^b	-0.95 ^b
Q versus Ba _t	-0.94 ^b	-0.21	-0.95 ^b	-0.96 ^b
Q versus Ca _d	-0.96 ^b	-0.89 ^b	-0.94 ^b	-0.95 ^b
Q versus Ca _t	-0.96 ^b	-0.82 ^b	-0.93 ^b	-0.95 ^b
Q versus Cu _t	BPQL	0.66 ^b	BPQL	BPQL
Q versus Fe _d	0.01	0.58 ^b	-0.25	0.01
Q versus Fe _t	0.52 ^b	0.68 ^b	0.55 ^c	0.88 ^b
Q versus K _d	-0.71 ^b	-0.69 ^b	-0.95 ^b	-0.70 ^b
Q versus K _t	-0.59 ^b	-0.66 ^b	-0.85 ^b	-0.62 ^b
Q versus Li _d	-0.92 ^b	-0.89 ^b	-0.69 ^b	-0.75 ^b
Q versus Li _t	-0.85 ^b	-0.91 ^b	-0.75 ^b	-0.81 ^b
Q versus Mg _d	-0.94 ^b	-0.80 ^b	-0.94 ^b	-0.94 ^b
Q versus Mg _t	-0.96 ^b	-0.80 ^b	-0.93 ^b	-0.96 ^b
Q versus Mn _d	0.14	0.25	0.45 ^c	0.88 ^b
Q versus Mn _t	0.56 ^b	0.39 ^c	0.65 ^b	0.85 ^b
Q versus Na _d	-0.84 ^b	-0.68 ^b	-0.79 ^b	-0.77 ^b
Q versus Na _t	-0.86 ^b	-0.74 ^b	-0.89 ^b	-0.90 ^b
Q versus S _d	-0.75 ^b	-0.73 ^b	-0.68 ^b	0.39
Q versus S _t	-0.75 ^b	-0.78 ^b	-0.41	0.34
Q versus Si _d	-0.70 ^b	-0.38	-0.94 ^b	-0.70 ^b
Q versus Si _t	-0.28	-0.15	-0.91 ^b	-0.66 ^b
Q versus Sr _d	-0.94 ^b	-0.93 ^b	-0.97 ^b	-0.92 ^b
Q versus Sr _t	-0.93 ^b	-0.90 ^b	-0.96 ^b	-0.93 ^b
Q versus Ti _t	0.26	0.71 ^b	BPQL	
Q versus Zn _d	-0.30	0.10	BPQL	0.91 ^b

^aUnlisted elements lacked strong and significant correlations with Q at any site. Here $n = 23$ at LF and BH; $n = 24$ at CFBM; and $n = 21$ at BFB. (On 3 dates BFB had no Q measurements due to ice at gage.) BPQL is below practical quantifiable limit.

^bCorrelation is significant at the 0.01 level (2-tailed).

^cCorrelation is significant at the 0.05 level (2-tailed).

Table 3. Pearson's Correlations of TSS Versus Total Metal Concentrations

TSS Versus	BFB	CFBM	LF	BH
Al _t	0.89 ^a	0.97 ^a	0.99 ^a	0.88 ^a
As _t	0.38	0.78 ^a	-0.30	0.81 ^a
Ba _t	-0.67 ^a	0.31	-0.70 ^a	-0.76 ^a
Be _t	(BPQL)	0.83 ^a	(BPQL)	(BPQL)
Ca _t	-0.64 ^a	-0.50 ^b	-0.66 ^a	-0.77 ^a
Cu _t	(BPQL)	0.95 ^a	(BPQL)	(BPQL)
Fe _t	0.91 ^a	0.95 ^a	0.95 ^a	0.98 ^a
K _t	0.03	-0.60	-0.33	-0.22
Li _t	-0.45 ^b	-0.53 ^a	-0.53 ^a	-0.64 ^a
Mg _t	-0.67 ^a	-0.45 ^b	-0.70 ^a	-0.77 ^a
Mn _t	0.92 ^a	0.88 ^a	0.99 ^a	0.98 ^a
Na _t	-0.39	-0.37	-0.54 ^a	-0.67 ^a
P _t	0.78 ^a	0.89 ^a	0.05	0.35
S _t	-0.24	-0.58 ^a	-0.11	0.35
Si _t	0.38	0.26	-0.50 ^b	-0.29
Sr _t	-0.55 ^a	-0.48 ^b	-0.69 ^a	-0.71 ^a
Ti _t	0.81 ^a	0.97 ^a	(BPQL)	(BPQL)

^aCorrelation is significant at the 0.01 level (2-tailed).

^bCorrelation is significant at the 0.05 level (2-tailed).

of predictability of their concentrations by Q , the most dominant physical factor. Natural weathering and dissolution of minerals in the soils, alluvium, bedrock, and mine wastes (if present) likely play dominant roles in the timing and magnitude of trace element releases into the dissolved phase of the stream water. The reactive nature of the trace elements makes them more sensitive to changing pH, redox, and temperature conditions, biological activity, and varying availability of complexing agents in the basin source areas and in the channel [Förstner and Wittmann, 1979; Cossa et al., 1990; Shiller, 1997]. The lack of correlation between Q and dissolved trace elements at most sites is in general agreement with the highly scattered Q concentration relationships found in the Mississippi River by Shiller [1997], who speculated that seasonal variations in dissolved metals were most likely controlled by redox processes in the basin source areas and in the river itself.

[34] The poor association between Q and dissolved trace elements such as As, Cu, Fe, Mn, Zn was most pronounced at site CFBM. The major sources for the dissolved trace elements in the Clark Fork are the mining and smelting contaminated floodplain soils and streambed sediments along most of the river corridor [Nimick and Moore, 1991; Axtmann and Luoma, 1991]. For example, trace metals that were immobilized in reducing zones such as sulfide mineral complexes in the floodplain or in stagnant water areas may have become oxidized and displaced into the water column at higher flows, where they temporarily remained out of equilibrium with Fe- or Mn-oxides/oxyhydroxides [Shotyk, 1998; Wetherbee and Kimball, 1991; Shiller, 1997]. They also may have been released into the river by the transport of reduced bed sediments, from hydrologic flushing of the hyporheic zone [Nagorski and Moore, 1999], or surface runoff that washed metal-rich salts off the floodplain [Lucy, 1996].

[35] Additionally, the lack of trends in the dissolved trace metal concentrations over time may be a product of interference by colloids. Because colloids can pass through 0.2 μm filters [Horowitz et al., 1996; Ross and Sherrell, 1999], our samples may not represent the truly dissolved portion in the first place, if such a phase actually exists. Hence, any relationships between truly dissolved concentrations and Q may be obscured by varying colloidal contributions to the measured filtered geochemistry [Schemel et al., 2000]. For example, at site BH, where 2 “dissolved” metals (Mn and Zn) correlated strongly and positively with Q , it is not possible to know from our data whether these metals were truly present at higher dissolved concentrations during higher flows, whether they were transported by colloids that were abundant during high flows and passed through the filters, or a combination of both. Noting that both dissolved and total recoverable Mn and Zn concentrations had positive, approximately linear relationships with Q at BH, it appears more likely that the “dissolved” concentrations in fact included colloids as well.

[36] Finally, the mobilization of TSS and some total recoverable trace metals during higher flows, as indicated by the positive association between TSS, Mn_t , and Fe_t with Q at site BH, may be due to simple physical processes. Physical mobilization of sediments from the streambed and floodplain may occur with high Q events because the higher stage and velocity of the river can entrain more bottom

sediments and access broader areas of the floodplain [Bradley, 1984; Whitfield and Clark, 1982; Droppo and Jaskot, 1995]. Yet, the chemical characteristics and availability of different sized sediments can vary substantially as well [Bradley and Lewin, 1982; Bird, 1987; Hatch et al., 1999]. Therefore the size of the flow event may not necessarily correlate with the sediment and associated metal concentrations, as was the case at BFB, CFBM, and LF.

3.5. Streamflow-Concentration Patterns at BFB, LF, and BH

3.5.1. Hysteresis

[37] At BFB, LF, and BH, water temperature was the only parameter that followed counter-clockwise hysteresis, meaning that it was lower along the rising limb of the hydrograph than on the falling limb (Figure 3a). This pattern charts the transition from the period of cooler air temperatures and the abundance of fresh snowmelt earlier in the spring to the increasing influences of warmer air temperature, rain, and contributions from warmer soil water and groundwater in the receding portion of spring runoff.

[38] Rotating in the other direction, H^+ , dissolved oxygen, TSS, Al_t , As_t , K_d , K_t , Fe_t , Mn_t , S_d , S_t , and Sr_t followed clockwise hysteresis patterns at sites BFB, LF, and BH (Figures 3b–3f). The clockwise rotation of H^+ concentration indicates that earlier runoff was more acidic than later runoff, which presumably had more opportunity to become buffered by soils and saturated zone materials in the watershed en route to the water channel. Acidic “flushes” at the start of snowmelt have long been identified by numerous researchers, who have attributed these events both to the dilution of buffering compounds by meltwater [Stoddard, 1987] and to the early, preferential release of atmospherically derived acidic anions from the snowpack [Davies et al., 1982; Tsiouris et al., 1985; Tranter et al., 1988].

[39] Clockwise hysteresis rotations for dissolved elements may be explained by snowmelt-driven displacement into the stream channel of relatively highly concentrated soil water and/or by ionic flushing from the early snowmelt itself [Stottlemeyer and Troendle, 1992; Williams et al., 1993; Marsh and Pomeroy, 1999]. Clockwise rotations for TSS and total recoverable elements have been reported by many other researchers, who attribute the pattern to a physical washing out and subsequent depletion of sediments and other particulate matter in the channel and floodplain at the onset of high flow conditions [Williams, 1989; Droppo and Jaskot, 1995; Sokolov and Black, 1996; Moog and Whiting, 1998; Pierson et al., 2001].

[40] At BFB, dissolved and total As, K, Li, Mn, S, Si, and Sr surged in concentration on 29 March 2000 at BFB, when Q was at the very early stages of increasing spring runoff (Figures 4a and 4b). These early runoff increases are largely responsible for creating the clockwise-rotating hysteresis loops seen for many of these parameters on the seasonal scale. Of these elements, As_t , and total and dissolved K, S, and Si were higher on 29 March 2000 than on any other date during the study. The unusually high value for S on this one date in the early spring opened a clockwise loop in what would otherwise have been a linear relationship between Q and S concentration (Figure 3f). Total Al, Fe, Mn, and Ti, all of which showed clockwise hysteresis, generally followed TSS patterns by peaking in concentration on 14 April

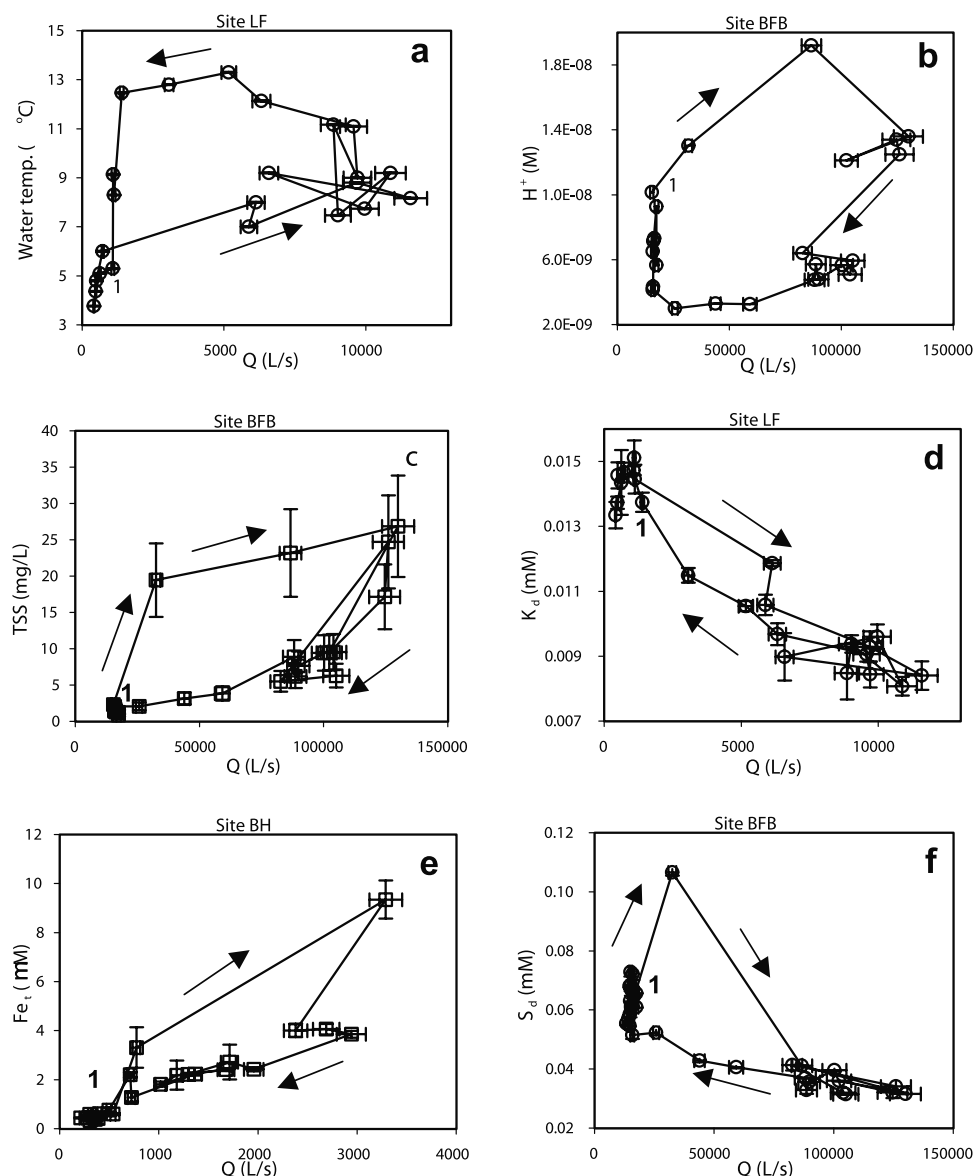


Figure 3. Streamflow (Q) versus (a) water temperature at LF, (b) H^+ at BFB, (c) TSS at BFB, (d) dissolved K at LF, (e) total recoverable Fe at BH, and (f) dissolved S at BFB, all showing hysteresis rotation. Data points are connected in chronological order, as directed by arrows. The number “1” indicates the first sampling date, for reference. Error bars represent the 95% confidence interval of the mean value of the triplicate samples taken on each sampling event.

2000, following the sharpest hydrograph rise of the spring runoff event (Figures 4c and 4d). Similarly, at site LF there were two main early-runoff peaks for TSS, Al_t , Fe_t , Mn_t , and Mn_d that controlled the formation of their clockwise hysteresis loops (Figure 5).

[41] At BH, spring flushing of K and S created clockwise hysteresis loops for these elements (Figure 6). Dissolved K concentrations increased by 10% on 29 March 2000 compared with 26 February 2000, even though discharge had also increased (from 540 to 770 L/s). Concentrations remained high through the end of April, after which they began to drop with decreases in Q. Potassium has been identified as being particularly mobile and easily leachable from organic materials; hence, flushing of K_d may have occurred due to a disproportionate amount of K being

transported out of adjacent soils at the early stages of snowmelt [Stottlemeyer and Toczydlowski, 1990; Stottlemeyer and Troendle, 1999]. Similarly, S_d dropped sharply after rising with Q though 22 April 2000. It remained at relatively low levels during much of the summer, when most other major ions were at their highest. Its largest concentration peak was in early November for unknown reasons. Interestingly, spring flushing of S was also observed at the same site in 1998 by Nagorski *et al.* [2001]. Although S flushing has been widely reported in the literature as occurring in watersheds draining snowpacks with atmospherically-derived S [Schemenauer *et al.*, 1985; Campbell *et al.*, 1991], S flushing was observed at BH and not at nearby LF in both study years. This indicates that the upstream sulfur-rich mining sources, and not atmospheric inputs, in

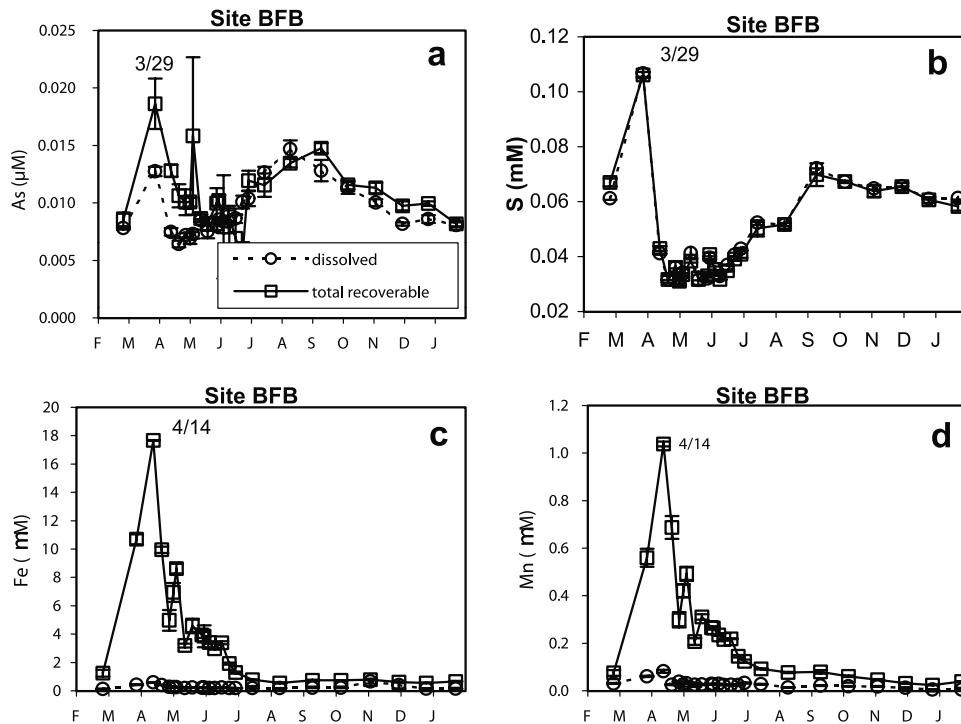


Figure 4. Date versus (a) As, (b) S, (c) Fe, and (d) Mn at BFB, with peak concentrations specified by date.

the Blackfoot River basin were likely driving the S surges during high flow events.

3.5.2. No Hysteresis

[42] Alkalinity, Ba_d , Ba_t , Ca_d , Ca_t , Mg_d , Mg_t , and Sr_d generally lacked open hysteresis loops at the sites. This lack means that the rising and falling limb concentrations were not distinct from one another or that there were cross-over patterns. Linear relationships without hysteresis loops indicate that concentration variations are simply in phase with Q variations. Such relationships can form when the different geochemical sources (e.g., soil water, groundwater and overland-flow water) mixing with base flow contributions have indistinguishable chemical signatures, or when the same sources are regulating the solute chemistry in similar proportions on both the falling and rising limbs of the hydrograph [Evans and Davies, 1998]. Cross-over patterns are formed by a few data points disrupting an otherwise open loop pattern by residing

with the opposite set of rising limb or falling limb data points.

[43] A lack of clear hysteresis patterns for some elements at site BFB is explained by one or two data points from the early stages of runoff that defy otherwise discernable patterns. Specifically, As_d , Ca_d , Ca_t , Mg_d , Mg_t , and Sr_d at site BFB would have had open counter-clockwise hysteresis loops if a single early event data point is not considered (Figure 7). These samples, which are characterized by a disproportionately large increase in concentration with the initial rise in Q are evidence of spring flushing. They probably indicate that significant portions of the meltwater did not enter the stream unaltered, but were first routed through mineral-rich soil zones, which presumably were especially concentrated following the winter months [Williams and Melack, 1991; Campbell et al., 1995; Stottlemyer et al., 1997; Stottlemyer and Troendle, 1999]. It is important to note that these elements had good overall linear correla-

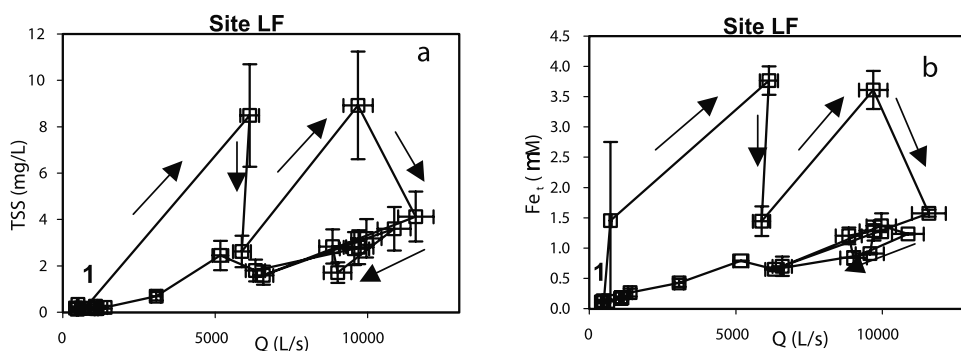


Figure 5. Streamflow (Q) versus (a) TSS and (b) total recoverable Fe at LF. Data points are connected in chronological order, as directed by arrows.

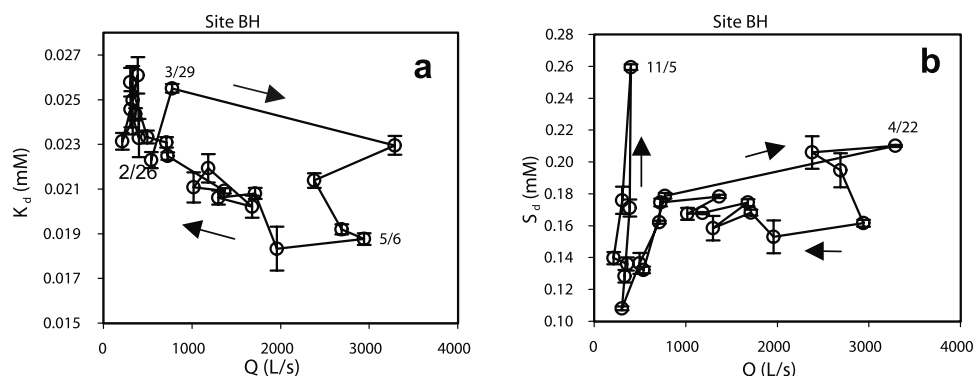


Figure 6. Streamflow (Q) versus dissolved (a) K and (b) S at site BH. Data points are connected in chronological order, as directed by arrows.

tions ($r < -0.80$, $p < 0.01$) with Q, but closer examination of the chronological sequence of these relationships revealed the presence of these single-event concentration spikes.

3.5.3. Hysteresis Differences Among Sites

[44] Several elements did not have consistent trends among sites BFB, LF, and BH. For example, although DIC and Ba_d had no hysteresis loops at the low-order stream sites (LF and BH), they had counter-clockwise hysteresis at BFB. Dissolved Fe was below the PQL at LF and had no discernable pattern at BH, but had a clockwise pattern at BFB. Dissolved As had clockwise rotation at LF, no hysteresis at BH, and had counterclockwise hysteresis at BFB if one discounts a single early season data point. These variations prove that some elements may have entirely different seasonal patterns in distinct portions of the same watershed.

[45] In summary, the hysteresis loops for DIC, Ba, K, Si, and Sr were wider (i.e. the differences between rising and falling limb concentration were greater) at BFB than at sites LF and BH. This result is similar to those reported by Whitfield and Schreier [1981] and Whitfield and Clark [1982], who found wider hysteresis loops at sites further downstream than near the headwaters in several British Columbia streams. They hypothesized that wider hysteresis loops may be produced by the more numerous and chemically diverse sources available for contribution to a stream at sites further downstream in a basin than at sites closer to the headwaters and draining smaller areas. Areas where water is being contributed by tributaries draining areas of variable lithologic, land use, and climatic characteristics likely will have a greater availability of diverse chemical signatures throughout the water year than will smaller areas with relatively homogeneous characteristics.

3.6. Discharge-Concentration Relationships at CFBM

[46] At CFBM, where there was an absence of a spring snowmelt peak, there was also a complete absence of hysteresis patterns for all parameters measured. The Q-concentration plots for CFBM show overall disorder for most elements. However, a prominent feature of CFBM's data set is that TSS and total Al, As, Cu, Fe, Mn, P, and Ti were most highly concentrated on 1 June 2000 and second most highly concentrated on 22 April 2000 (Figure 8). On 1 June 2000, the Montana Aquatic Life Standards for chronic and acute Cu (adjusted for hardness) were exceeded. Acute Cu violations also occurred on 22 April 2000, while chronic

violations occurred on 29 March 2000, 14 April 2000, 22 April 2000, and 1 June 2000. The acute values are defined as those that should never be exceeded, and chronic values are not to be exceeded for longer than four days [Montana Department of Environmental Quality, 1998].

[47] The 1 June 2000 sampling event captured the peak of a several-day long surge in Q caused by a large rain event the previous day (Figure 2b). On this day (31 May 2000), 2.8 cm of precipitation was recorded in the nearby town of Drummond, and this was the second largest single-day rain event of the year (Western Regional Climate Center (WRCC), <http://www.wrcc.dri.edu/wrccmssn.html>, 2001). Streamflow on 1 June 2000 was double that of the week before. Other researchers have also reported the flushing of suspended sediment and metals in industrialized watersheds at the onset of increasing Q levels [Bradley and Lewin, 1982; Bird, 1987; Sanden et al., 1997].

[48] The sampling on 22 April 2000 followed 1–2 weeks of intermittent rainfall that was also accompanied by fluctuations in the hydrograph, although these Q variations were not nearly as dramatic as on 1 June 2000 (Figure 2b). Considering the 5% error on the Q values, the Q on 22 April 2000 was no different from those on both 29 March 2000 and 4 April 2000, when TSS and metal concentrations were substantially lower. Therefore the surge in TSS and associated total recoverable elements occurred due to processes in the basin that supplied the river with sediment and its associated elements without significantly changing the

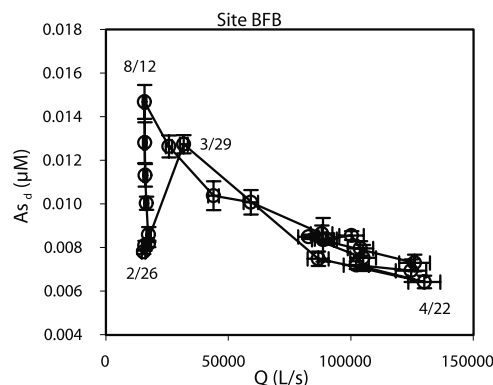


Figure 7. Streamflow (Q) versus dissolved As at BFB. Data points are connected in chronological order.

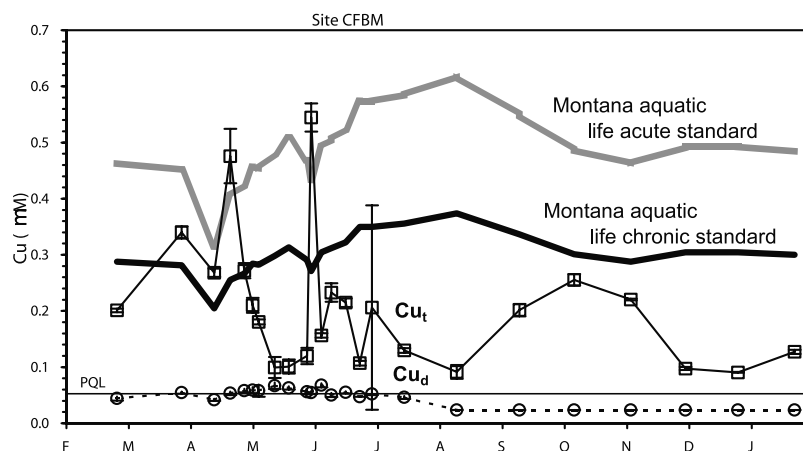


Figure 8. Date versus dissolved and total recoverable Cu at CFBM over the study period (February 2000 to January 2001). Also shown are Montana aquatic life acute and chronic standards, which vary depending on hardness.

Q values. One possible mechanism for this could be that early spring rains saturated the soils, resulting in a larger proportion of overland flow carrying floodplain soils and sediments into the water channel. Potential sources of metals-enriched sediments are abundant along the Clark Fork River floodplain due to the mining and smelting wastes in the watershed [Nimick and Moore, 1991].

[49] It is important to note that had we not increased our sampling intensity during spring runoff, half of these events when water quality violations occurred would have been missed. That these extremely short-lived toxic water conditions were captured in this study shows the merits of sampling frequently during the spring, when snowmelt runoff and rainstorms occur in mountainous regions such as in our study area. These results emphasize the importance of adapting a sampling plan to account for short-term dynamics in climatic and hydrologic conditions.

4. Summary and Conclusions

[50] Using clean sampling and analytical techniques, we have documented large seasonal variations in several mining-impacted and pristine streams in western Montana. Our results indicate that frequent monitoring over variable climatic and hydrologic conditions is necessary for the characterization of trace element geochemical trends in these streams. Many of the more extreme geochemical measurements were short-lived and would not have been captured in a study designed around monthly sampling alone. Some elements had different types of relationships with Q at each of the study sites, indicating that watershed-specific processes regulate the timing of their geochemical variations.

[51] A comparison of the contaminated and uncontaminated streams revealed that CFBM, the high-order mining-impacted stream site that lacked the typical spring runoff peak, had higher concentrations of most elements than the 3 other sites over the 12 month study period. The two mining-impacted sites (CFBM and BH) had higher concentrations of Fe, Mn, S, Si, and Sr than the relatively pristine sites (BFB and LF). Suspended sediments at the contaminated sites were also enriched in some trace elements (As, Cu, Fe, and Mn) compared with sediments at the pristine sites. At CFBM, several incidents of acute and chronic water quality

standard violations for Cu were found during the spring, particularly following a large rain event. Additionally, a S pulse in early snowmelt was identified at the mining-impacted site BH but not at nearby LF, the pristine site.

[52] At all sites, Q was correlated inversely with many of the major elements but was correlated poorly with trace elements. As a result, predicting the geochemistry of many trace solutes and particulates in these streams cannot be accurately done using Q alone. The major elements were conservatively diluted by snowmelt (generally by 40–70%) during spring runoff and most lacked open hysteresis loops. In contrast, few dissolved trace elements followed any patterns at all and appeared to be regulated by unidentifiable chemical dynamics in the watershed. Several total recoverable trace elements (Al, Cu, Fe, and Mn) were strongly correlated with TSS concentrations, which had clockwise hysteresis rotations at BFB, LF, and BH. This rotation direction is likely due to higher flows acting in early runoff to physically wash out sediments in the watershed that had built up over low-flow winter conditions. Several dissolved elements at BFB and BH also appeared to be flushed out early in the spring. These early spring surges in concentrations are thought to be produced by snowmelt water infiltrating into the ground, flushing out the soil and groundwater zones, which have built up weathering products over the long winter period, and transporting the solutes into the stream channel. At all sites, H^+ levels followed orderly clockwise hysteresis patterns, possibly due to early runoff acidic flushes from the snowpack itself.

[53] **Acknowledgments.** Many thanks to Justin Harris, Beth Nichols, Nate Stevens, and Amanda Yakos for assistance with laboratory work. We are grateful to B. Kimball, J. Holloway, D. Tallmon, and an anonymous reviewer for very helpful comments on the manuscript. Any use of trade, firm, or product names is for descriptive purposes only and does not imply endorsement by the U.S. Government.

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