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Technical Article

Distribution of Metals in Water and Bed Sediment in a Mineral-Rich Watershed, Montana, USA

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Abstract. We sampled the Blackfoot River (Montana) and its major tributaries from the headwaters of the basin to near its confluence with the Clark Fork River over the course of 5 days in August 1998. We measured streamflow, collected fine-grained (<63 µm) streambed sediment, and sampled the dissolved (operationally defined as <0.2 µm) phase of the surface water using clean techniques. Water and sediment collected from near the historic Heddleston mining district contained the highest concentrations of most trace elements in the basin. Many solute trace metals were at their highest several kilometers downstream from the mining district, where the river flows through an unremediated marsh system that has collected mine wastes in the past. Downstream of the headwaters area, water and bed sediment metal concentrations declined sharply. Comparison of sediment samples with those collected by other workers in August 1989 and August 1995 do not show evidence of basin-scale long term changes, despite the onset of remediation efforts in 1993. The area of the proposed McDonald gold deposit near the confluence of the Landers Fork with the Blackfoot River was not contributing anomalous concentrations of naturally-occurring dissolved and bed-sediment metals into the basin.

Key Words: anthropogenic effects, Blackfoot River, environmental geochemistry, geochemical baselines, Montana, stream sediments, surface water quality, trace elements

Introduction

One of the current research priorities of the Mineral Resources Program of the U.S. Geological Survey (USGS) is to evaluate geochemical baselines in watersheds where mineral deposits erode naturally or are exposed by mining and mineral processing. Baseline characterization research is important for understanding how to differentiate between natural and human influences on the geochemistry of surface waters, soils, and sediments. Globally, there is almost no reliable pre-disturbance data on the solute geochemistry of rivers in watersheds that have been mined. In the past 2 decades, the recognition of the critical importance of using clean sampling methods (Horowitz et al. 1994) has essentially discredited the historical database for trace metal concentrations in surface waters. In order to set realistic remediation targets in contaminated areas and to better quantify potential environmental impacts of proposed mining projects, it is necessary to characterize the geochemical distribution of trace elements in both mining impacted and pristine streams and rivers.

The 215 km long Blackfoot River (BFR) in western Montana is a tributary to the Clark Fork River, which in turn flows into the Columbia River (Figure 1). It was chosen as a case study for the USGS's investigations on geochemical baselines because it contains both historic and proposed mines. The Heddleston mining district is located in the headwaters of the basin, and the area has been undergoing remediation since 1993. The proposed McDonald gold mine is located approximately 25 km downstream from the headwaters, and the ore body is approximately 5 km from the confluence of the BFR with Landers Fork. In the research presented here, we characterize the spatial distribution of the aqueous and bed sediment geochemistry in the BFR and many of its tributaries over a single, short (5 day) time period and make some comparisons with earlier bed sediment data.

The primary goal of the current study was to examine the downstream distribution of mining-related contaminants in the water and bed sediments of the BFR from the historical mining area in the headwaters. Bed sediment dispersion trains have been extensively used for prospecting purposes and for impact characterization of mining (Hawkes 1976; Helgen and Moore 1996). However, the relationship between dispersion trains in the water column and bed sediment trains have not been commonly evaluated, even though water is subject to human and aquatic health standards. Detecting levels of trace metals in water samples is typically more difficult

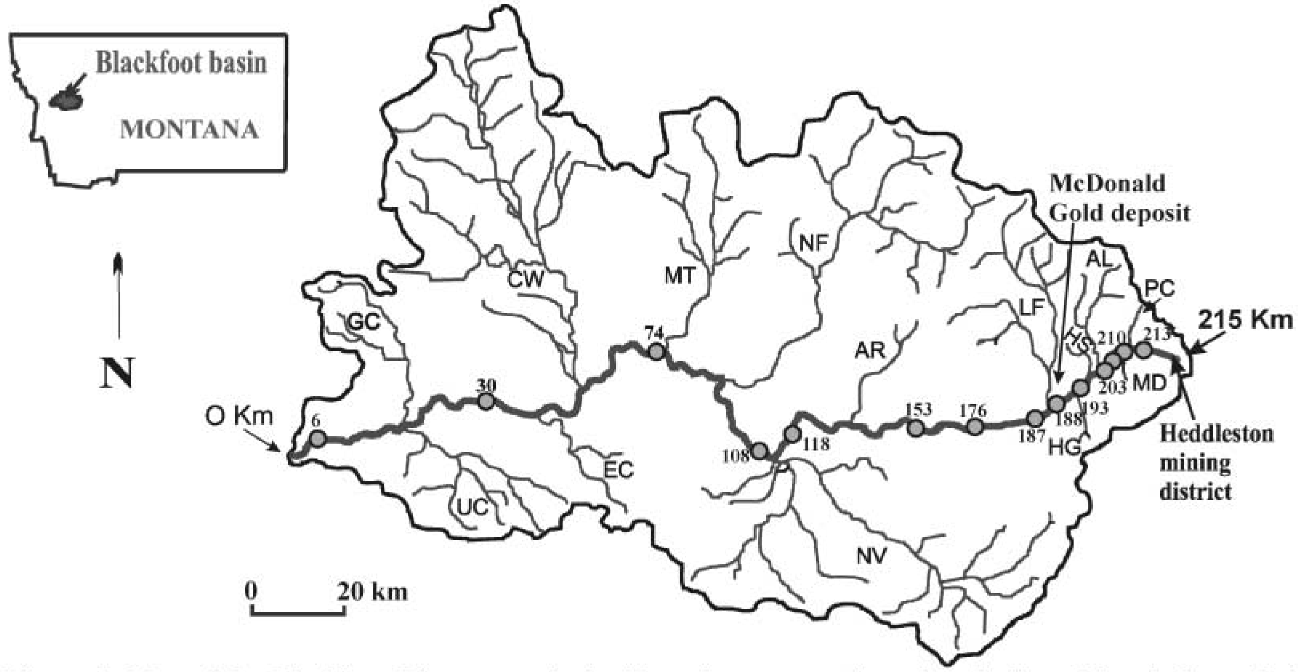

Figure 1. Map of the Blackfoot River watershed with mainstem sampling sites (indicated by circles and river km designations) and sampled tributaries (indicated by name abbreviations). Tributary abbreviations: PC=Pass Creek; MD=Meadow Creek; AL=Alice Creek; HS= Hardscrabble Creek; HG=Hogum Creek; LF= Landers Fork; AR= Arrastra Creek; NV= Nevada Creek; NF= Northfork; MT= Monture Creek; CW= Clearwater River; EC= Elk Creek; GC= Gold Creek; and UC= Union Creek

and labor-intensive than for bed sediments due to their shorter dispersion train lengths and lower concentrations. Within each type of dispersion train, it is of geochemical interest to observe how tributaries affect the mainstem concentrations and to identify the relative mobility of elements downstream from the source of contamination.

A second goal of the project was to compare the abundance and distribution of selected chemical elements in bed sediment in the basin to that determined in 1989 and 1995 by Moore et al. (1991) and Menges (1997), respectively. The 1989 sampling event occurred prior to the start of the remediation projects in the headwaters region in 1993. In 1995, Menges (1997) found few changes in the trace metal concentrations in the bed sediments in the basin other than in the immediate area of the remediation district. We wanted to determine if there had been further changes in the geochemistry of bed sediments in the three years since the Menges (1997) study.

The third purpose of this study was to bring the unmined McDonald Gold ore body area into the geochemical context of the BFR watershed. This tests whether or not there is a measurable input of trace metals from the mineralized yet unmined area to the waters and sediments of Landers Fork and BFR in the vicinity of the deposit. Based on research on the dispersion trains in water draining unmined yet mineralized areas, naturally elevated concentrations rarely extend more than a few hundred meters from the source (Hoffman and Fletcher 1972; Runnells et al. 1992; Schmitt et al. 1993; Leybourne et al. 1998). In bed sediments, natural dispersion trains typically do not extend for longer than 20 km from the mineral source (Helgen and Moore 1996).

Previous investigations of the solute geochemistry of the Blackfoot River on the basin-scale have not employed "clean" sampling protocols for surface water. Standard water quality sampling methods have likely caused some degree of contamination to samples taken from both unpolluted and polluted watersheds (Windom et al. 1991; Benoit 1994; Taylor and Shiller, 1995). The new clean methods to collect, process, and analyze trace element samples are replacing the problematic older methods (e.g., Horowitz et al. 1994; Hurley et al. 1996; Balogh et al. 1998). With the increasing number of watersheds being impacted by mining and other human activities, it is important to build a database of accurate surface water geochemical measurements in order to adequately monitor and regulate water quality into the future. As a result, an additional and final purpose of this project was to add to the growing database of water quality measurements that are as accurate and reliable as currently possible.

Basin description and mining history

The majority of the BFR basin is comprised of the Middle Proterozoic Belt Supergroup, and vast sections of the valley floor are covered by glacial sediments and alluvium (Tysdal et al. 1996). The Belt formation is a thick sequence of sedimentary rocks, mostly sandstones, mudstones, and limestones, that dominates the geology of most of northwestern Montana. Glacial and alluvial sediments cover many of the wider BFR valley floors, as the area was heavily glaciated during the Pleistocene ice ages. The Nevada Creek basin is anomalous in that it is consists of extensive Tertiary volcanic deposits. Smaller volcanic deposits are also present north and south of the BFR several miles east of Lincoln, in the area of the McDonald gold deposit. In the area of the headwaters of the BFR, ore bodies were created by Tertiary igneous intrusions into the Belt rocks.

Mining from 1865 to 1953 in the Heddleston district in the headwaters of BFR has been linked to water and bed sediment contamination and declines in benthic organisms and fish populations (Spence 1975; Moore et al. 1991; Menges 1997). These impacts are not limited to the headwaters, but continue for tens of kilometers downstream. The district is a collection of numerous mines and prospects scattered within the watersheds of small tributaries that come together to form the BFR. The earliest operations consisted of gold placer mining, but later operations led to the building of an on-site smelter, and after the 1920s, activities were expanded to lode mining of Pb, Ag, Au, and Cu (Spence 1975). Ore and waste rock contain sulfide minerals such as pyrite (FeS_2), galena (PbS), and sphalerite (ZnS), tetrahedrite ($Cu_{12}Sb_4S_{13}$), bornite (Cu_5FeS_4), chalcopyrite ($CuFeS_2$), and arsenopyrite (FeAsS), as well as quartz (SiO_2) and rhodochrosite ($MnCO_3$) (Pardee and Schrader 1933). The tailings, waste rock, and acid mine drainage from adits have been the primary sources of contamination to the BFR. A particularly damaging event occurred in 1975, when a tailings dam broke and released approximately 100,000 tons of pyritic mine tailings into the river (Spence 1975). The recent remediation activities have focused on plugging adits, excavating, liming, and revegetating waste rock and tailings, and treating acid mine drainage by channeling it into an oxidation pond and a wetland treatment system.

Elsewhere in the basin, little mining has taken place other than some relatively small-scale operations in the Nevada, Elk, and Union Creek basins. Portions of the watershed are used extensively for grazing, irrigation, and logging, but there are no major urban areas or industries. Several of the major tributaries of the BFR (Landers Fork, Northfork, and Monture Creek) originate in wilderness areas and supply high quality water and clean sediment to the mainstem.

Current mining interests in the watershed are focused on the McDonald Gold Deposit, near the confluence of the Landers Fork and the BFR. The approximate location of the ore body is as close as about 1 km east of the Landers Fork and 1 km to the north of the BFR. The proposed mine targets a gold and silver-bearing ore body hosted almost entirely in a lithic-rich rhyolite tuff concealed at the surface by glacial till and alluvium (Schafer and Associates 1994; Tysdal et al. 1996). The proposed mine would be an open-pit operation with cyanide heap leaching and waste rock disposal situated between the ore body and the rivers. Other studies in the area have shown that the ground and surface water of the Landers Fork and BFR are closely connected hydrologically (Nagorski et al. 1998, 2001). Notably, sections of both rivers receive perennial inputs of groundwater where they flow adjacent to the ore deposit. Therefore, a major environmental concern is that mining would affect the physical dynamics and geochemical conditions in the adjacent rivers.

Methods

Sampling Design

We sampled 14 sites along the BFR and 14 tributaries from August 16-20, 1998 (Figure 1). We selected sites along the BFR so that the mainstem was sampled above and below the major tributaries. This design resulted in more closely spaced sampling intervals in the upper portion of the basin. We did not sample many of the numerous small headwater tributaries, many of which have been impacted by mining. The most upstream site sampled was below most of the remediated area at the headwaters of the BFR. Three more tributaries (Shave Gulch, Paymaster Gulch and Swamp Gulch) not sampled for this project join the BFR between the first and second sampling sites. Paymaster Gulch and Swamp Gulch were subject to remediation treatments in the early 1990s. These and other tributaries not included in this study were omitted because we estimated them to have relatively insignificant flow contributions to the mainstem. We sampled all the selected tributaries as close to their confluence to the BFR as possible; generally, this was within 1 km of the confluence.

We began sampling at the headwaters and progressed downstream, except that we did not sample two sites near the headwaters until the fifth day. Also on the final sampling day, we resampled an upper basin site to check for any changes in river chemistry compared to Day 1 (no measurable changes were found). Considering that the average measured water velocity was 0.5 m/s, the estimated travel time downstream from the headwaters (river km 215) to the confluence with the Clark Fork River (river km 0) was 5.2 days. Therefore, we roughly followed a parcel of water as it traveled down the basin. Such an approach presumably minimized possible complications from sampling water variably influenced over time by hydrologic, climatic, or chemical changes in subsections of the watershed. During the study period, weather conditions varied from sunny to partly cloudy, with only trace amounts of precipitation in the watershed (WRCDC 1999).

Streamflow measurement

We measured streamflow following standard USGS protocol, with the exception that for a few of the small headwater streams that were <2 m in width, we used only 6 instead of the recommended minimum of 10 sampling stations per transect (Rantz et al. 1982). The streamflow measured on the Northfork for this project compared well with the streamflow reported by the real-time USGS gauge data at the site (6.23 ± 0.08 vs. 6.40 ± 0.31 m^3/s, respectively) (USGS 1999). We determined our measurement precision by measuring discharge at some sites multiple times. Our measurement precision increased with higher streamflows. Accordingly, we assigned sites with <0.28 m^3/s, an error of ±0.003 m^3/s, 0.28-1.84 m^3/s, an error of ± 0.11 m^3/s, and >1.84 m^3/s, an error of ± 0.17 m^3/s. These represent the maximum discrepancies obtained.

Water sampling

At each site, we measured pH, dissolved oxygen, temperature, and conductivity in situ. At all sites, we collected the water samples by depth and width integration. At 12 of the sites, we collected a single water sample; at 13 of the sites we collected 4 samples; and at 3 sites we collected 10 samples. The purpose of collecting multiple samples per site was to define the spatial variability along the sampling transect. Four samples per site were deemed adequate for this estimation, based on previous studies in the upper part of the basin (Nagorski et al. 1998). However, at the 3 sites where we collected 10 samples, we did so to test whether 4 samples could adequately capture variability in different sized river sections. Results show insignificant improvement in the within-site variability estimate with the use of 10 versus 4 samples. Error bars on the data from sites with multiple samples represent the standard deviation of the mean concentration of the multiple samples. Error bars at sites with single samples were derived from the average percent relative standard deviation at all sites with multiple samples.

We collected, processed, and filtered samples using clean techniques. This required the exclusive use of materials that had undergone extensive acid-washing (2 hours in 50% HCl followed by 24 hours in 1% trace metal grade HNO_3, with a minimum of 3 rinses with Milli-Q deionized water before and after each acid treatment), double-bagging of sample bottles, and filtering of samples under a class 100 laminar flow hood wearing clean nitrile gloves. In the field, two people were required to obtain the water samples, and both wore nitrile gloves that were changed between each site. One person was designated as “dirty hands” and the other as “clean hands.” The former handled the outside bag, whereas only the latter could open the inner bag and take out the sample bottle. The clean hands person opened the sample bottle moments before sampling, emptied out the Milli-Q water which was stored in it, and rinsed the bottle and cap with river water. The sample was then taken by filling the 1-L low-density polyethylene (LDPE) Nalgene sample bottle to capacity. We were careful to always sample upstream of where we had physically disturbed the site by wading and to sample upstream of bridges. We then returned the sample bottle to its double bags and stored it on ice for transport to the University of Montana’s Laboratory.

At the laboratory, we filtered the samples under a laminar flow hood within 12 hours of collection. We used Gelman Sciences Serum Acrodisc GF filters (<0.2μm) and discarded the first 50 mL of filtrate in order to reduce the effective pore size of the filter and to rinse the filtration materials (Taylor and Shiller 1995). Next, we filtered 60 mL of sample into pre-cleaned but non-acid washed amber glass bottles for anion analysis. We then filtered another 125 mL into ultra-clean LDPE bottles for cation and arsenic analysis. We acidified each of these samples with 200 μL (to bring the pH to <2) of ultrapure, double distilled from quartz, Optima (Fisher Scientific) HCl. We stored the sample bottles in sealed plastic bags until analysis.

Bed sediment sampling

Following collection of the water samples, we took streambed sediment samples at each site. At half of the sites, we collected 4 samples, and at the other half, we collected 1 sample. At the single-sample sites, we integrated the sample over the same sized area that would have been divided into 4 sections had the site been selected for multiple samples. Error bars were determined the same way as described for water samples, in which the mean variability found at sites with multiple samples was applied to sites with single samples.

We sampled the sediment by scooping the top 1-2 cm of fine-grained bed sediment with a plastic spoon. Sediment availability varied among sites, and hence the area from which sediment was integrated per sample varied from approximately 30-100 m of streambank length. We strove to collect an equal amount of sample from each channel bank and sieved the sediment with ambient stream water through a 63μm mesh plastic screen set in a plastic funnel casing. After collecting the sieved sediment-water slurries in 250 mL acid washed bottles, we stored them on ice for transport to the laboratory.

Upon returning to the laboratory, we centrifuged the samples at 2000 rpm for 15 minutes, decanted the water, and dried the sediments at 70°C for one day. Next, we crushed each dried sample to a fine powder in the sample bottle with an acid-washed glass rod. We used a microwave aqua-regia digest procedure to prepare the samples for analysis. This method entailed adding 0.5 ml of Milli-Q water, 1.25 ml trace metal grade HNO_3, and 3.75 ml trace metal grade HCl to 0.5 g of sediment sample, microwaving the mixture for 6 minutes on high power (ca. 570 watts), and adding Milli-Q water to bring the cooled solution to 50 g. We centrifuged the completed digests for 5 minutes at 2500 rpm and transferred the clarified solutions to acid-washed polyethylene bottles for chemical analysis.

Laboratory analysis

We analyzed the trace element and major ion concentrations in the water using a Thermo Jarrell-Ash IRIS ICP-AES with ultrasonic nebulization (Cetac, U-5000AT+) according to EPA Method 200.15 (Martin et al. 1994). We used the ICP with pneumatic nebulization according to EPA Method 200.7 (EPA 1991) for the analysis of sediment digests. We measured anions on a Dionex ion chromatograph (IC) within 48 hours of sample collection according to EPA Method 300.0 (Pfaff 1993). We determined alkalinity on another subsample by titration with sulfuric acid to pH 4.5 within 1 day of sample collection.

Following Standard Method 303A, we measured total arsenic using atomic absorption spectroscopy with hydride generation (HGAAS) (Franson 1985). However, we modified the arsenic reduction method to follow a method developed at our laboratory (Mickey, written communication 1997). This method calls for the addition of KI and HCl to all standards and samples to achieve final concentrations of 2% KI and 1 M HCl. We made the additions at least 2 hours prior to analysis to allow for complete reduction of oxidized arsenic species. We ran solutions of 0.35% sodium borohydride (stabilized with 0.5% NaOH) and 6N HCl together with the samples through the hydride generator.

Quality assurance/quality control

We conducted all laboratory analysis under a strict quality control program. At the start of each day's analysis, we calibrated all instruments and checked, and corrected (if needed), the calibration at intervals of approximately every 10 samples. The detection limits used, called the Practical Quantifiable Limits (PQL), were defined as the concentrations at which elements could be reproduced within a variability range of approximately 30%.

For water samples, the mean difference between duplicate runs of samples on all instruments was less than 8.5%. Spike recoveries for all detectable elements were between 92-115%. On the ICP, USGS water standards T-143 and T-145 run with water sample analysis fell within the reported acceptable range for all elements except for Ba in T-143 and T-145 and Sr in T-145, which were slightly low. Analyses of external standards run on the HGAAS and IC also fell within the reported ranges. Accuracy was checked on the HGAAS, Shimadzu, and the IC by running in-house standards; the mean differences between the standards and the measured concentrations were less than 10%. Lab blanks were below the detection limits on all instruments. Field blanks were mostly below detection, with the exception that Ca (0.02 mg/L), Mg (0.01 mg/L), and Na (0.23 mg/L) were detected in most of the blanks. These levels are low enough not to interfere with concentrations found in environmental samples.

During ICP analysis of the sediment digests, the mean percent difference between duplicate runs of samples was less than 10%. Mean percent recoveries for spikes of all analytes were between 89-105%. As with the water samples, USGS standards T-143 and T-145 were analyzed using ICP during sediment analysis. All elements fell within the reported range, with the exception of mean Ca in T-143, which was 2% higher than the reported acceptable limit. All lab blanks were below detection limits, as were digest blanks, with the exception of insignificant amounts of Ca, Cr, Fe, Mg, Na, Si, and Ti.

Dissolved load calculations

Loads were calculated by multiplying the discharge (m^3/s) at each site with the concentration (mg/L or µg/L) of the solute of interest. The propagated error associated with each load calculation was found using the formula:

Load error $= \sqrt{B^2 \Delta A^2 + A^2 \Delta B^2}$ (Taylor 1982),

where B = discharge; ΔB = discharge error; A = concentration of solute; and ΔA = concentration error (within-site variability). Loads could not be quantified at sites where solute concentrations were below the specific element's PQL.

Average tributary concentrations:

The chemical concentrations in the water and bed sediments of the mainstem were compared with the average concentrations in the water and bed sediments of the BFR tributaries. However, Meadow Creek was not included in the calculations of average tributary concentrations because it was sampled where it flows through a metals-contaminated marsh system (a series of 3 marshes extending from km 211.6 to 196.6) near the headwaters. Many tributaries had some metal concentrations below the PQL. In these cases, we assigned a value of one-half the PQL to the undetectable concentration and calculated the averages using these assigned values.

Results

Mainstem water chemistry:

Dissolved (<0.2 µm) Al, Cd, Co, Cu, Mn, Ni, S, Zn, and sulfate peaked in the headwaters area, below the historic mining district, and then declined sharply downstream as cleaner tributaries joined the mainstem (Table 1). Discharge values increased with distance from the headwaters (Figure 2a). Mainstem Al, Cd, Co, Cu, Fe, Mn, and Ni concentrations dropped to average tributary concentrations or fell below detection at distances of 9-19 km from the most upstream site (Figure 2b). Zinc and sulfate were more mobile, remaining elevated above average tributary concentrations for 25 and 37 km, respectively (Figure 2c, d). Zinc may have been elevated over the average tributary levels for even longer distances, but this cannot be determined due to its drop below its PQL at 25 km downstream from the headwaters and its below-PQL values in most of the tributaries. Samples from the uppermost 3 km of the mainstem had concentrations of Al, Co, Cu, Mn, Ni, S, and sulfate that were at least 3 times greater than the mean tributary concentrations. Manganese and Zn were enriched by at least 2 orders of magnitude (exact enrichment factors cannot be calculated due to the undetectable levels lower in the basin).

Aluminum, Co, Cu, Mn, Ni, S, Zn, and sulfate were at their highest levels not at the site closest to the mining district, but at the second site, 2.5 km downstream (Figures 2b, c, d). This second site is located in the contaminated marsh system and is downstream of Pass Creek, Paymaster Creek, and Swamp Gulch. Conductivity, Fe, K, Li, Na, and Si were also higher at the second site, and pH was lower (7.3 compared to 7.7) (Figure 2e).

Other elements did not follow the pattern of declining downstream from a peak at the uppermost couple of sites. For example, Fe did not peak until river km 203.3 (BFR-above Alice Creek), where the BFR emerges from the second of three marshes downstream from the mining district (Figure 2e). Arsenic was below detection (<0.2 µg/L) at the uppermost site, but its concentration gradually increased to peak at 2.3 µg/L at river km 108.5, below the confluence with Nevada Creek, which had the highest As concentration (7.9 µg/L) in the basin (Figure 2f). Calcium concentrations almost doubled between the headwaters and river km 153 (Figure 2g). Mainstem Ba, K, Li, Mg, Na, Si, and Sr concentrations fluctuated little downstream, even though tributary concentrations of these elements varied far more widely.

Tributary water chemistry

Most tributaries were below detection levels for dissolved Al, Cd, Co, Cu, Mn, Ni, and Zn (Table 1). Tributaries with exceptionally high concentrations (relative to the mainstem) of measured solutes include: Hogum Creek, with the highest Fe and Sr detected in all the samples; Meadow and Elk Creeks, which were the only tributaries with detectable Al

Table 1. Geochemistry of filtered water samples. Mean concentrations are given in mg/L for most elements discussed in text. Samples were below practical quantifiable limits for nitrite (<0.05 mg/L), nitrate (<0.05 mg/L), phosphate (<0.05 mg/L), F (<0.05 mg/L), Cl (<2 mg/L), Ag (<1 µg/L), Be (<0.05 µg/L), Cr (<1 µg/L), Mo (<1 µg/L), Pb (<6 µg/L), and V (<1 µg/L). Al was only detectable (>5 mg/L) at km 210.0 (10 mg/L), 209.8 (10 mg/L), Meadow Cr. and Elk Cr. (6 mg/L). Co and Ni were only detectable (>0.5 and 2 mg/L, respectively) at km 210.0 (0.9mg/L and 3 mg/L), 209.8 (0.7 mg/L and 2 mg/L) and Meadow Cr. (0.6 mg/L and 2 mg/L)

	Q	pH	D.O.	Alk.	SO_4^{2-}	As	Ba	Ca	Cd	Cu	Fe	K	Li	Mg	Mn	Na	S	Si	Sr	Zn
PQL				1.0	2.00	0.2	1	0.01	0.5	0.8	5	0.10	0.5	0.01	0.3	0.15	0.02	0.02	2	0.2
BFR(km)																				
212.5	0.10	7.69	8.1	86	48.2	0.2	143	25.1	2.6	3.6	5	0.6	1.3	14.4	157	2.4	14.2	3.7	73	535
210.0	0.16	7.27	8.7	46	88.8	(<0.2)	103	26.8	2.1	4.0	27	0.9	2.1	14.1	245	4.1	25.9	6.8	76	762
209.8	0.21	7.51	8.7	51	87.4	(<0.2)	103	26.0	1.8	3.9	20	0.9	2.0	13.5	210	3.7	24.3	6.6	73	681
203.3	0.44	7.86	8.5	78	44.3	0.2	198	25.5	0.6	0.9	37	0.7	1.3	12.6	82	2.0	13.1	6.0	74	84
193.2	0.93	8.18	9.4	104	13.3	0.4	228	26.5	(<0.5)	(<0.8)	21	0.8	2.2	11.4	2.5	2.0	4.0	6.5	110	1.6
187.7	1.09	8.27	9.7	104	12.8	0.4	213	26.0	(<0.5)	(<0.8)	16	0.8	2.6	10.8	1.0	2.3	3.7	6.8	140	0.6
186.6	3.09	8.25	9.8	131	6.6	0.5	232	30.7	(<0.5)	(<0.8)	7	0.6	2.4	11.4	0.5	1.4	1.9	5.0	89	(<0.2)
175.9	1.53	8.11	7.8	120	6.6	0.5	232	35.6	(<0.5)	(<0.8)	(<5)	0.6	2.4	11.5	1.2	1.2	2.0	5.0	91	(<0.2)
153.3	5.87	8.31	9.6	170	5.7	1.1	228	42.8	(<0.5)	(<0.8)	11	0.8	3.4	12.3	3.3	1.7	1.8	5.8	110	(<0.2)
117.6	6.78	8.38	10.0	144	5.5	1.5	224	41.5	(<0.5)	(<0.8)	18	0.9	3.5	12.6	7.6	1.8	1.7	6.2	110	(<0.2)
108.5	7.43	8.46	9.8	143	9.3	2.3	203	41.0	(<0.5)	(<0.8)	14	1.3	4.9	12.2	8.6	3.9	2.7	7.2	142	(<0.2)
74.4	17.77	8.35	10.0	130	6.6	1.3	209	33.3	(<0.5)	(<0.8)	6	0.9	3.6	12.5	1.6	2.5	1.9	4.5	99	(<0.2)
30.3	25.60	8.74	11.3	121	6.0	1.2	199	30.6	(<0.5)	(<0.8)	6	0.9	3.9	11.8	1.5	2.6	1.7	4.4	90	(<0.2)
6.0	20.59	8.77	10.3	123	6.0	1.1	198	31.5	(<0.5)	(<0.8)	5	0.9	3.9	11.8	1.6	2.7	1.7	4.2	89	(<0.2)
Tributary																				
PC	0.01	7.90	8.5	80	4.3	0.9	215	18.5	(<0.5)	(<0.8)	5	0.4	0.8	7.4	3.2	2.0	1.3	5.1	55	0.4
MD	0.05	7.53	8.2	45	85.6	0.1	98	26.0	1.9	3.7	18	0.9	2.0	13.5	192	3.8	24.6	6.5	74	671
AL	0.43	8.17	8.4	110	2.8	0.4	281	27.4	0.5	(<0.8)	19	0.7	2.3	11.2	2.3	1.6	0.8	5.4	73	(<0.2)
HS	0.03	8.40	8.5	155	1.6	1.0	385	39.3	(<0.5)	(<0.8)	32	1.7	6.4	14.6	1.6	3.3	0.5	9.8	130	(<0.2)
HG	0.08	7.80	8.7	80	4.9	1.1	138	18.9	(<0.5)	(<0.8)	168	0.9	4.4	6.2	10.9	4.6	1.4	9.6	416	(<0.2)
LF	2.04	8.31	9.7	132	2.9	0.5	245	33.4	(<0.5)	(<0.8)	(<5)	0.5	2.2	11.7	(<0.3)	0.9	0.9	3.8	55	(<0.2)
AR	0.66	8.27	10.5	90	2.7	0.4	100	24.5	(<0.5)	(<0.8)	(<5)	0.4	2.0	9.8	0.7	1.3	0.8	4.7	73	(<0.2)
NV	1.19	8.50	9.4	158	28.0	7.9	121	42.9	(<0.5)	(<0.8)	18	3.2	11.7	11.0	18.2	13.4	8.2	12.6	293	(<0.2)
NF	6.23	8.37	10.3	135	4.0	0.7	229	31.0	(<0.5)	(<0.8)	(<5)	0.5	2.0	13.9	0.6	1.0	1.2	3.9	65	(<0.2)
MT	1.84	8.65	10.5	91	3.8	0.8	245	21.3	(<0.5)	(<0.8)	15	0.6	2.5	9.3	2.8	1.3	1.1	3.5	60	(<0.2)
CW	1.81	8.65	9.6	68	1.8	0.4	102	17.0	(<0.5)	(<0.8)	6	0.4	1.1	5.4	2.6	1.1	0.5	3.1	30	(<0.2)
EC	0.13	8.55	10.0	149	10.6	1.0	32	46.0	(<0.5)	(<0.8)	21	2.6	14.2	9.4	5.5	6.2	3.0	10.8	118	(<0.2)
GC	0.87	8.66	9.7	109	2.1	0.4	89	30.2	(<0.5)	(<0.8)	(<5)	0.4	1.1	8.0	0.6	1.4	0.6	4.5	35	(<0.2)
UC	0.34	8.47	9.7	195	7.1	1.4	95	40.0	(<0.5)	1.1	8	1.8	2.4	18.3	29.9	3.7	1.8	7.8	92	(<0.2)
Avg.trib*		8.36	9.5	119	5.91	1.29	175	30.0	(<0.5)	(<0.8)	23	1.1	4.1	10.5	6.1	3.2	1.7	6.5	115	(<0.2)

(*excluding Meadow Cr)

(>5 µg/L); and Nevada Creek, with the highest dissolved As, K, Li, Na, and Si of all basin-wide samples. Meadow Creek, sampled where it flows through the contaminated marshes, had the highest tributary concentrations of Cd, Co, Cu, Mn, Ni, S, and Zn, and it was very similar chemically to the BFR River sites immediately above and below their confluence.

In the Landers Fork, concentrations of Cd, Co, Cu, Fe, Mn, Ni, and Zn were all below detection. It was the only site in the basin with Mn at levels below detection (<0.3 µg/L) and was one of only three sites with Fe below detection (<5 µg/L). Most of the detectable solutes (sulfate, As, K, Li, Na, S, Si, and Sr) were lower than the mean tributary concentrations, while alkalinity, Ba, Ca, and Mg were higher than the mean. All of these detectable elements fell within one standard deviation of the mean concentrations in the watershed tributaries, indicating that the Landers Fork was not geochemically anomalous in the basin.

Reactive solutes

Reactivity of the solutes in the BFR was evaluated by examining whether a drop in solute concentrations occurred between two mainstem sites after accounting for tributary contributions and measurement errors. A loss in solute concentrations along losing or steady-streamflow reaches (determined by the streamflow measurements) was assumed to be a product of solutes transferring to the solid phase. Results of this evaluation indicated that SO_4^{2-}, Fe, Mn, S, and Zn were dropping out of solution along several reaches of the river. Iron, Mn,

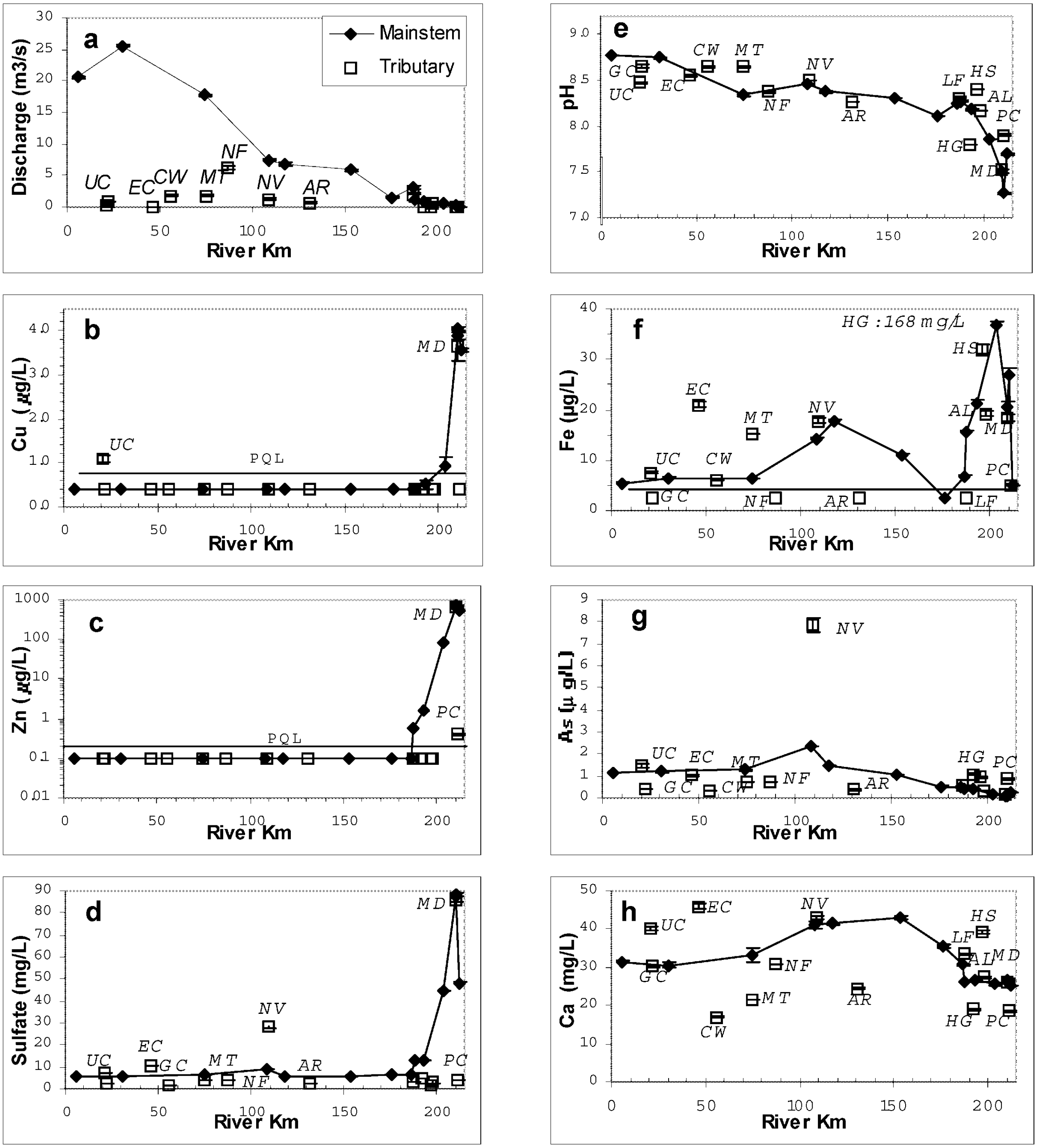

Figure 2. River kilometer vs. surface water a) discharge, b) Cu, c) Zn (note log scale), d) sulfate, e) pH, f) Fe, g) As, and h) Ca. Solid, connected diamonds represent the mainstem samples; the squares represent tributary samples. Tributaries are defined by their abbreviations listed in Figure 1.

and Zn were reactive between river kms 210.0 and 209.8; between kms 203.3 and 193.2; and between kms 193.2 and 187.7. Iron and Mn also were reactive along the reach above and below Nevada Creek's input (river kms 117.6 to 108.5). Sulfate and total S were reactive between river kms 203.3 and 193.2. Additionally, alkalinity (as mg/L $CaCO_3$) and Ba were found to be reactive between the uppermost site (river km 212.5) and the second site (river km 210.0).

Gaining reaches were more difficult to evaluate for reactivity, because a decrease in concentration may have occurred due to dilution by the gained water or by chemical reactions. Hence, for the most part, reactivity could not be determined along gaining reaches because groundwater entering the reach was not sampled. However, if the concentration at the downstream site was still lower than predicted assuming the extreme case that the gained water had zero dissolved elements, then we could determine that solutes were coming out of solution along the stretch of the river. According to this evaluation, Cd, Cu, Mn, and Zn were reactive along the gaining reach between river km 209.8 and km 203.3, and Fe and Mn were reactive along the gaining reach between river kms 108.5 and 74.4.

Evaluation of the tributary load contributions to the BFR

There was generally a positive, approximately linear relationship between the solute loads of alkalinity, sulfate, As, Ba, Ca, Fe, K, Li, Mg, Na, Si, and Sr in tributaries of the BFR and the tributary sizes (expressed as discharge) (e.g., Ca, Figure 3a). Manganese loads had no clear pattern; its load contributions from tributaries could not be predicted from discharge (Figure 3c). No more than two tributaries contained above-detection limit levels of Al, Cd, Co, Cr, Cu, Ni, and Zn, and therefore no conclusions can be made about the relationship between loads of those metals and tributary size. Considering the detectable elements, the Landers Fork was not an unusually large source of solute loads, because its solute loads fall in line with most other tributaries (Figure 3a and 3d). Because the amount by which it increased the mainstem load of solutes was unquantifiably low (Figure 3b and 3c) or not unusually high for its size, a geochemical signal of the McDonald ore body in the area was not discernable in the solute phase.

Mainstem bed sediment chemistry

A sharp downstream decline in concentrations of Al, As, Cd, Co, Cu, Fe, Mn, Ni, Pb, S, Si, V, and Zn is seen in the mainstem sediments (Figure 4a-d). Bed sediment collected immediately below the mining district (river km 212.5) contained the highest concentrations of As, Cd, Co, Cu, Fe, Mn, Ni, Pb, S, and Zn of all the mainstem and tributary samples. These elements were elevated over average tributary concentrations by up to 3 orders of magnitude. The furthest downstream site in the basin, at river km 6.0, contained the lowest concentrations of Al, As, Co, Cr, Cu, Fe, K, Mn, Ni, Pb, and Zn in the mainstem (Figures 4a-e).

Arsenic, Co, Cu, Fe, Pb, V, and Zn reached average tributary concentrations at river km 117.6, almost 100 km downstream from the mines. Aluminum, Ba, Be, Cd, Mn, Ni, and S reached average tributary concentrations by river km 186.6 (below input of the Landers Fork), about 30 km downstream of the headwaters (Figures 4c, d). Yet not all elements were at a maximum in the headwaters. The sample taken below the mining district contained the lowest concentrations of Li, Na, P, and Ti in the BFR mainstem and the lowest Ba in all the basin samples. Barium, Ca, Cr, K (Figure 4e), Li, Mg, Na, P, Sr, and Ti do not show clear downstream spatial trends below the mining district. Calcium (Figure 4f) and Mg are at their lowest between river kms 210.0 and 186.6. Chromium, K, P, Sr, and Ti exhibit relatively little fluctuation; their maximum concentrations in the mainstem are no more than twice their minimum concentrations.

Tributary bed sediment chemistry

Downstream from the Heddleston mining district, the influence of tributaries with atypical bed sediment concentrations of some elements is seen on the mainstem. For example, Sr concentrations increase below the input of Hogum Creek (river km 187.7) and Nevada Creek (river km 108.5), which have anomalously high Sr concentrations. A 2- to 4-fold increase in Mg and Ca in the BFR mainstem occurs below the confluence with the Landers Fork (river km 186.6), which contained the highest Mg and Ca (Figure 4f) concentrations of the tributaries sampled.

Meadow Creek, which joins the BFR several km downstream from most of the mines in the Heddleston district, contained the highest Al, As, Cd, Co, Cu, Fe, Mn, Ni, Pb, S, Si, and Zn of all of the tributaries that were sampled. As noted earlier, Meadow Creek was sampled where it flows through the contaminated marsh, and as a result, its high concentrations of solute and sediment metals are likely due to the influence of the contaminated marsh itself. Monture Creek had the lowest concentrations of Al, As, Cr, Cu, Fe, K, Mg, Na, Ni, Si, Ti, V, and Zn of all the basin samples. The Hardscrabble Creek sample had the highest Ba and the lowest Co and Li of the tributaries. Hogum Creek contained the highest Cr, P, and Sr of all the basin samples. Arrastra Creek had the highest V and the lowest Mn of all the tributaries. The highest Na concentration was found in the Nevada Creek sample, and the sample from Elk Creek had the highest K of both mainstem and tributary samples. The Clearwater River, Monture Creek, and Elk Creek were the only sites with As concentrations below detection (<6.5 ppm).

The Landers Fork was anomalous in that it had the highest Mg and lowest Ba concentrations of all the tributaries, and the highest Ca and lowest S concentrations of all samples in the basin. Still, elemental concentrations in the sediments from the

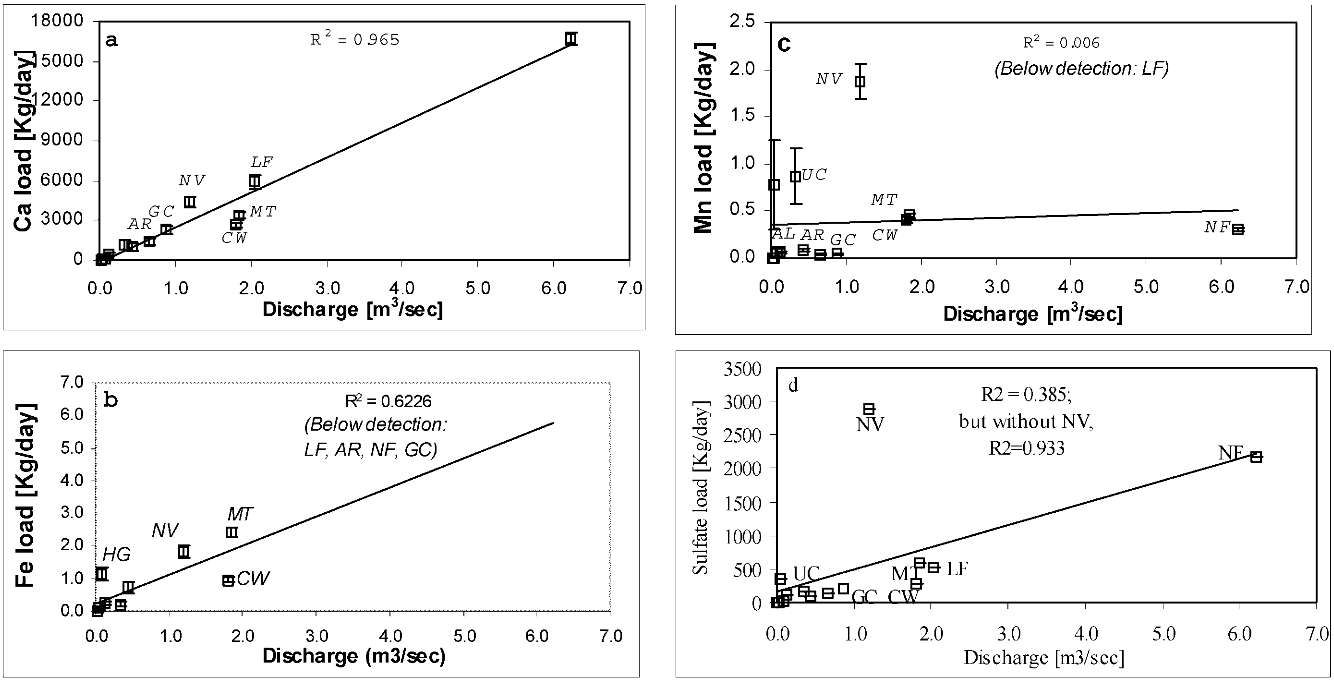

Figure 3. Tributary discharge vs a) tributary Ca load, b) tributary Fe load, c) tributary Mn load, and d) tributary sulfate load.

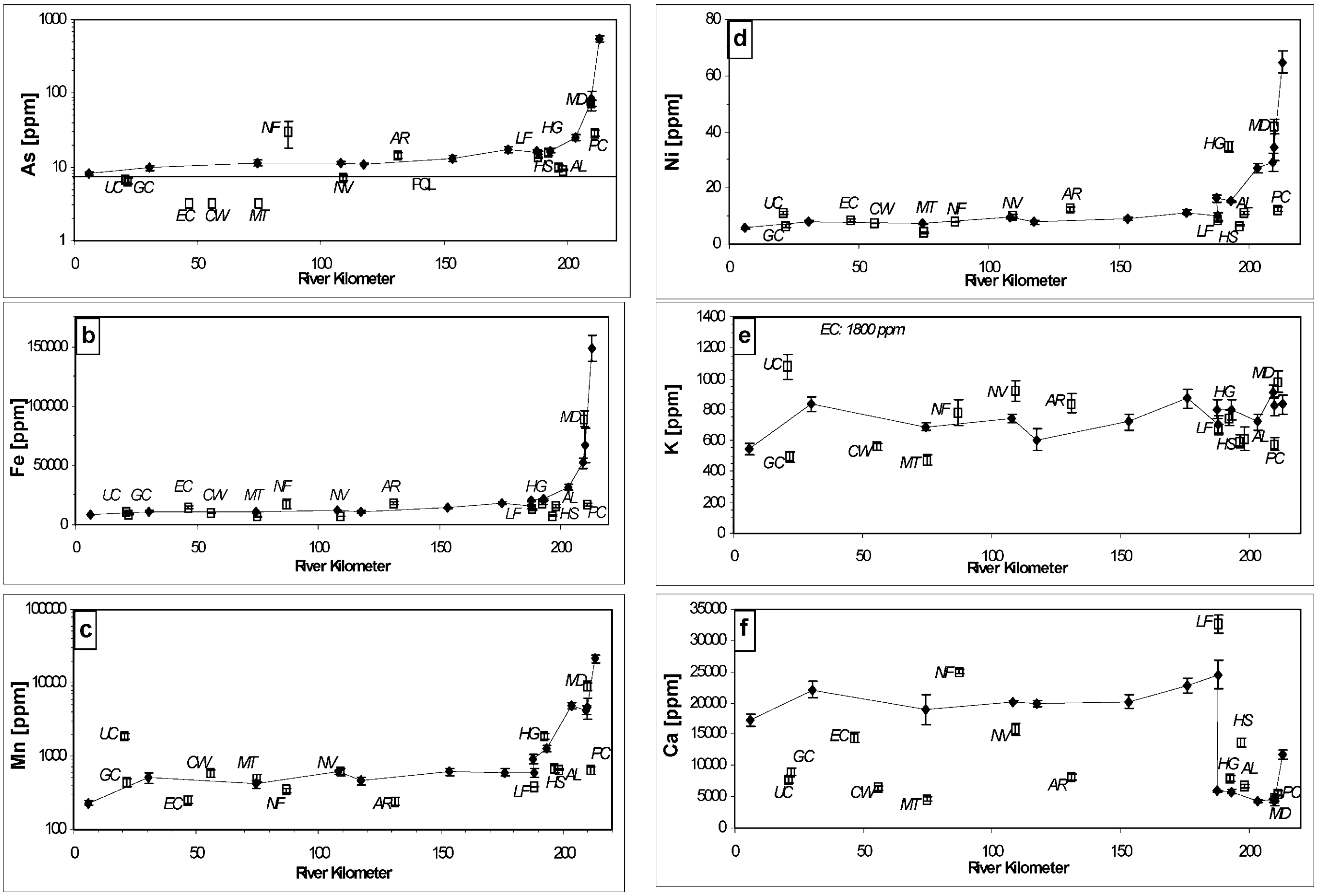

Figure 4. River kilometer vs. bed sediment concentrations of a) As, b) Fe, c) Mn, d) Ni, e) K, and f) Ca

Landers Fork fell within one standard deviation of the mean concentrations of the basin tributaries, with the exception that its Ca and Mg concentrations were higher and its P and S concentrations were lower than the mean ±1 standard deviation. This result implies that the Landers Fork did not contain geochemically anomalous bed sediments, despite its close proximity to the McDonald ore body.

Comparisons with 1989 and 1995 bed sediment data

In August 1989, Moore and others (1991) collected bed sediment samples at many of the same sites sampled in this study. In August, 1995, Menges (1997) revisited many of these sites for bed sediment collection, and digested and analyzed both the 1989 and 1995 samples using the same method used in this study. Hence, direct comparisons among the sets of data can be made.

Generally, the downstream trends of metal concentrations are the same for each of the datasets. In all, there is a steep downstream decline in such elements as Al, As, Cd, Co, Cu, Fe, Mn, Ni, Pb, and Zn, which are typically at least one order of magnitude higher in the headwaters than in most of the mainstem (Figure 5). Although there are some site-specific changes, a basin-wide systematic decline in metal concentrations through time is not apparent, as indicated by the overlapping trends of metal concentrations with distance (Figure 5). These nearly identical chemical trends occurred despite potential complications from natural variables (e.g., spring runoff intensity differences, weathering rate variations) that could have influenced the relative source contributions and chemical nature of the sediments over the course of the study period.

Despite the overall lack of change in the basin, examination of the trends on a site-specific basis reveals some among-year variation. The strongest case was at the uppermost site, immediately downstream of the bulk of the mining district and remediation operations (river km 212.5 in 1998 and river km 211.8 in 1989 and 1995). Data indicate a decrease in mean concentrations of Al, Cu, Na, and P over the three study years. However, although As, Cd, Co, Fe, K, Mn, Ni, Sr, and Zn also decreased in 1995 compared to 1989, their concentrations in 1998 were higher than in one or both of the previous study years. Furthermore, both Ca and Pb show marked increases over the three study years (10-fold increase in Ca and doubling of Pb in 1998 compared to 1989). The increase in Ca, the largest change evident from the data sets, may be explained by the use of lime in the remediation treatments. It is unknown why the Pb concentrations increased, although one possibility is that $PbCO_3$ complexes formed as a by-product of the liming in the area.

Examination of the other end of the basin, at the furthest downstream site which was sampled in all three study years (river km 74.4; BFR-below Monture Creek), reveals some of the largest changes in the lower basin (Figure 5). Mean Al, As, Ca, Co, Cu, Fe, K, Mg, Na, Ni, Pb, Sr, Ti, and Zn appear to have decreased over the three study periods at the site (mostly by about 10%, but 30% for As and Fe and 50% for Ca and Pb). Also, Mn and P showed little change between 1995 and 1998, but in both years, concentrations were higher than in 1989. These apparent differences are likely explained by the fact that this site is situated immediately downstream of the confluence of a major tributary (Monture Creek) with the BFR mainstem. (Other sites were located at greater distances downstream from tributary inputs.) Because of the short distance below the confluence (approximately 300 m), bed sediments were probably not fully mixed on both banks. It is unknown from the Moore et al. (1991) dataset whether the sole 1989 sediment sample came from one or both banks, while Menges (1997) collected all three of her samples from the bank on the side of Monture Creek's input. The 4 samples collected for this project were split between the two banks. As a result, the apparent changes over time at this site are inconclusive.

In sum, site-scale variations may be complex and a more refined temporal sampling scale and a consistent sampling design is recommended to elucidate specific changes in localized areas. Nonetheless, considering the bed sediment samples from the entire basin dataset, there appears to have been no detectable systematic decline in trace element concentrations over time.

Discussion

Water chemistry

Much of the sharp decline in the solute trace element concentrations may be explained by simple dilution by cleaner tributaries. Yet not all elements exhibited the same proportional declines in trace elements at each stage downstream. The longer distance (from the mining complex) over which above-average tributary concentrations of Zn and sulfate concentrations persisted compared to other solutes can be explained by a higher degree of conservative behavior. Although the load data indicate that both

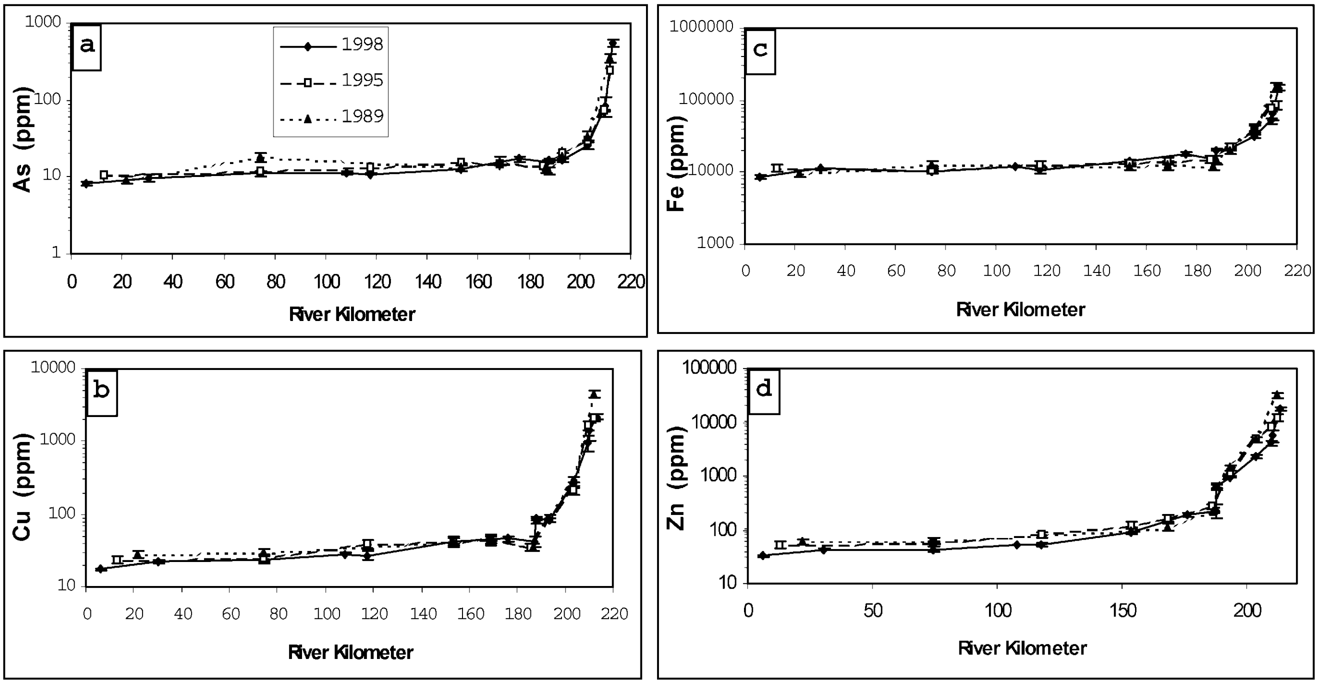

Figure 5. River kilometer vs. bed sediment a) As, b) Cu, c) Fe, and d) Zn in 1989 (Moore et al. 1991), 1995 (Menges 1997), and 1998 (this study)

sulfate and Zn were reactive in the upper basin, they were less reactive than elements such as Al, Cu, and Fe. Zinc is generally believed to be more mobile than other trace metals in aqueous systems. Its sorption onto amorphous Fe oxyhydroxides is favored at higher pH levels than for many other trace metals, (Benjamin and Leckie 1981; Filipek et al. 1987; Rampe and Runnells 1989). Therefore, it would be expected to remain in the dissolved phase for a greater distance downstream from an acidic source than would other metals that are more reactive under such conditions. Other researchers have also identified sulfate as a nearly or fully conservative ion in surface water (e.g., Bencala et al. 1987; Kimball et al. 1994; Schemel et al. 2000).

The reactivity of many of the trace metals and sulfate in the upper basin is expected in oxygenated, near-neutral pH surface waters. Presumably the metals are being lost from the water column by microbially-mediated precipitation and sorption reactions involving the formation of Fe and Mn oxides and the co-precipitation of other trace metals, metal sulfate formation, and scavenging by organic matter in the river. Such processes have been documented in many other streams impacted by mining contamination (e.g. Rampe and Runnells 1989; McKnight and Bencala 1990; Schemel et al. 2000). Additionally, our results are largely consistent with the geochemical patterns observed by Moore et al. (1991).

The increase in concentrations of several dissolved metals and sulfate and the drop in pH at the second mainstem site in a system of marshes a couple of kilometers below the mining district are likely related to the impacts from the mining. The marshes have collected wastes from past mine operations, including those released during a tailings dam break in 1975 (Spence 1975; Moore et al. 1991.) The site is also downstream of Paymaster Creek and Swamp Gulch, which are small, mining-impacted tributaries that were not sampled in this study. Although these creeks have undergone remediation, it remains possible that they supplied the metals and acidity measured in the samples at river km 210.0.

The mining-contaminated marshes may have been the source for the higher metals at the second site due to geochemical processes in the fine-grained, organic-rich marsh sediments. Geochemical partitioning within saturated sediments is strongly controlled by pH and reduction-oxidation reactions, and other studies have suggested that marshes, wetlands, hyporheic sediments, and reservoir sediments can therefore influence the geochemistry of receiving waters (Shotyk 1988; Moore 1994; Shiller 1997; Nagorski and Moore 1999). In reduced zones, many metals preferentially reside in the solute phase over the particulate phase, largely due to the instability of Fe- and Mn-oxides and hydroxides, which in turn can release co-precipitated metals when dissolved (Stumm and Morgan 1996). Although no ground water was sampled in this study, it is reasonable to speculate that groundwater had higher metal concentration than did the oxygenated overlying surface waters. Hence, the increase in filterable metals in the surface water may be a result of hydrologic flushing of the more highly concentrated marsh ground water into the stream channel.

Bed sediment

The high concentrations of metals in the bed sediments at the uppermost sites indicate that the headwater mining district is still the major source of contaminants to the sediments of the BFR. The relatively low concentrations of metals in the sediment in upper-basin tributaries explain the sharp downstream decline in metal concentrations in the upper basin. Because Pass Creek, Alice Creek, Hardscrabble Creek, and the Landers Fork contain many-fold lower concentrations of elements such as As, Cd, Cu, Fe, Mn, Ni, Pb, S, and Zn, the mixing of their sediments with those in the mainstem lead to the observed declines in metal concentrations. (Table 2 and Figure 5).

In her 1995 samples, Menges (1997) calculated that the bed sediment concentrations of Al, As, Cd, Fe, Mn, Ni, and Pb reached average tributary levels or fell below detection at 25 km from the headwaters, and that Cu and Zn reached average tributary concentrations at 80 and 140 km from the headwaters, respectively. Results from this project are somewhat different, with As, Fe, and Pb persisting over average tributary values for longer distances, up to 97 km downstream from the mining district. However, these discrepancies are most likely a product of differences in the amount and type of data used to calculate the average tributary values in the two studies. Our study included a larger number of tributaries than did the study by Menges (1997). Although both projects compared mainstem concentrations to average concentrations in uncontaminated tributaries, the use of additional data in our calculation lowered the levels for the sediment concentrations. Importantly, Monture Creek was not sampled by Menges (1997), while we found this tributary to contain the lowest basin-wide concentrations of Al, As, Cr, Cu, Fe, K, Mg, Na, Ni, Si, Ti, V, and Zn. These results underscore the importance of having large sample sizes, using consistent sampling designs, and employing consistent sample preparation and analytical protocols in long-term observational studies.

Differences between trends in water and sediment dispersion trains

Although, in general, the metal concentrations in both the water and bed sediment were highest in the headwaters region, their patterns did not correspond exactly. While the bed sediment metal concentrations exhibited predictable, exponentially declining dispersion curves in accordance with sediment dilution models (Hawkes 1976; Helgen and Moore 1996), the solute trends were more complicated. Their pattern irregularities were likely due to their higher sensitivity to tributary contributions, in-stream chemical reactions, ground water inputs, and other physical and chemical factors in the watershed.

An example of these differences is illustrated by arsenic in the sediment and water. Although the lowest solute As concentrations in the basin were in the headwaters, sediment concentrations of As were highest there, indicating strong partitioning into the solid phase for As or major differences in As sources (Figures 2d and 4a). Additionally, solute Fe was relatively low at the headwater sites and peaked at river km 203, while sediment Fe was highest at the top of the basin and declined by over an order of magnitude downstream (Figures 2c and 4b). Comparison of sediment with solute distributions of other metals also show that one or two sites downstream of the mines offset many solute peaks. This trend may indicate that some solutes near the remediated mining district were being precipitated out of the water column, and the downstream marshes or unsampled tributaries resupplied the solute phase with some trace elements.

Summary and conclusions

Bed sediment and water analyses of samples taken from the BFR and its major tributaries show a downstream decline in trace metal concentrations from the general vicinity of the historic Heddleston mining district. Most solute contaminants extended for 20 km downstream of the mining complex, while elevated metal concentrations in sediments extended for up to 100 km below the headwaters.

Sediment metal concentrations follow patterns predicted by simple dilution models (Helgen and Moore, 1996), while solute trends were more complicated. Solute sulfate, Cd, Cu, Fe, Mn, and Zn were identified as behaving non-conservatively along portions of the river, mostly in the headwaters area. Comparing the trends in water and sediment dispersion trains reveals that many solute peaks

Table 2. Geochemistry of bed sediment (<63µm) samples. Mean concentrations in ppm per site are given for most elements discussed in the text.

	Al	As	Ca	Cd	Co	Cr	Cu	Fe	K	Mg	Mn	Ni	Pb	S	Si	Sr	Zn
PQL	10	6.5	1	1	1	0.5	0.5	1.5	50	0.5	0.5	2	6	7	2	1	0.5
BFR (Km)																	
212.5	$5.8\cdot10^{3}$	$5.5\cdot10^{2}$	$1.2\cdot10^{4}$	115	63	5.6	$2.2\cdot10^{3}$	$1.5\cdot10^{5}$	$8.3\cdot10^{2}$	$6.73\cdot10^{3}$	$2.13\cdot10^{4}$	65	$8.7\cdot10^{3}$	$3.8\cdot10^{4}$	$4.0\cdot10^{3}$	25	$1.7\cdot10^{4}$
210.0	$1.9\cdot10^{4}$	$8.3\cdot10^{1}$	$4.3\cdot10^{3}$	32	40	8.7	$1.4\cdot10^{3}$	$6.7\cdot10^{4}$	$8.2\cdot10^{2}$	$3.25\cdot10^{3}$	$4.61\cdot10^{3}$	34	$1.3\cdot10^{3}$	$3.5\cdot10^{3}$	$4.6\cdot10^{3}$	19	$5.7\cdot10^{3}$
209.8	$1.7\cdot10^{4}$	$7.3\cdot10^{1}$	$4.5\cdot10^{3}$	26	39	9.3	$9.9\cdot10^{2}$	$5.2\cdot10^{4}$	$9.1\cdot10^{2}$	$3.52\cdot10^{3}$	$4.27\cdot10^{3}$	29	$1.1\cdot10^{3}$	$3.5\cdot10^{3}$	$2.0\cdot10^{3}$	19	$4.1\cdot10^{3}$
203.3	$1.0\cdot10^{4}$	$2.6\cdot10^{1}$	$4.3\cdot10^{3}$	10	38	9.0	$2.6\cdot10^{2}$	$3.2\cdot10^{4}$	$7.2\cdot10^{2}$	$3.45\cdot10^{3}$	$4.90\cdot10^{3}$	27	$1.5\cdot10^{2}$	$4.3\cdot10^{2}$	$6.5\cdot10^{2}$	16	$2.3\cdot10^{3}$
193.2	$6.3\cdot10^{3}$	$1.7\cdot10^{1}$	$5.9\cdot10^{3}$	3	13	9.9	$8.1\cdot10^{1}$	$2.2\cdot10^{4}$	$8.0\cdot10^{2}$	$3.28\cdot10^{3}$	$1.27\cdot10^{3}$	15	$4.3\cdot10^{1}$	$4.3\cdot10^{2}$	$4.9\cdot10^{2}$	25	$9.6\cdot10^{2}$
187.7	$6.8\cdot10^{3}$	$1.7\cdot10^{1}$	$6.0\cdot10^{3}$	3	13	10.7	$8.6\cdot10^{1}$	$2.0\cdot10^{4}$	$8.0\cdot10^{2}$	$3.30\cdot10^{3}$	$9.01\cdot10^{2}$	16	$3.8\cdot10^{1}$	$4.7\cdot10^{2}$	$4.3\cdot10^{2}$	30	$6.6\cdot10^{2}$
186.6	$5.2\cdot10^{3}$	$1.6\cdot10^{1}$	$2.5\cdot10^{4}$	(<1)	8	7.0	$4.3\cdot10^{1}$	$1.5\cdot10^{4}$	$7.0\cdot10^{2}$	$6.97\cdot10^{3}$	$5.91\cdot10^{2}$	9.9	$2.1\cdot10^{1}$	$2.7\cdot10^{2}$	$3.3\cdot10^{2}$	24	$2.3\cdot10^{2}$
175.9	$6.5\cdot10^{3}$	$1.7\cdot10^{1}$	$2.3\cdot10^{4}$	(<1)	8	8.5	$4.6\cdot10^{1}$	$1.8\cdot10^{4}$	$8.7\cdot10^{2}$	$9.11\cdot10^{3}$	$6.00\cdot10^{2}$	11	$2.0\cdot10^{1}$	$2.5\cdot10^{2}$	$2.9\cdot10^{2}$	23	$1.9\cdot10^{2}$
153.3	$5.6\cdot10^{3}$	$1.3\cdot10^{1}$	$2.0\cdot10^{4}$	(<1)	7	6.7	$4.2\cdot10^{1}$	$1.4\cdot10^{4}$	$7.2\cdot10^{2}$	$6.87\cdot10^{3}$	$6.20\cdot10^{2}$	9.1	$1.8\cdot10^{1}$	$2.7\cdot10^{2}$	$2.8\cdot10^{2}$	21	$9.3\cdot10^{1}$
117.6	$4.3\cdot10^{3}$	$1.1\cdot10^{1}$	$2.0\cdot0^{4}$	(<1)	5	5.9	$2.7\cdot10^{1}$	$1.1\cdot10^{4}$	$6.0\cdot10^{2}$	$6.65\cdot10^{3}$	$4.57\cdot10^{2}$	7.7	$1.3\cdot10^{1}$	$2.7\cdot10^{2}$	$2.4\cdot10^{2}$	22	$5.3\cdot10^{1}$
108.5	$5.3\cdot10^{3}$	$1.1\cdot10^{1}$	$2.0\cdot10^{4}$	(<1)	6	7.5	$2.9\cdot10^{1}$	$1.2\cdot10^{4}$	$7.5\cdot10^{2}$	$6.33\cdot10^{3}$	$6.11\cdot10^{2}$	9.3	$1.3\cdot10^{1}$	$3.9\cdot10^{2}$	$2.5\cdot10^{2}$	31	$5.4\cdot10^{1}$
74.4	$4.2\cdot10^{3}$	$1.1\cdot10^{1}$	$1.9\cdot10^{4}$	(<1)	5	5.8	$2.3\cdot10^{1}$	$1.0\cdot10^{4}$	$6.9\cdot10^{2}$	$5.58\cdot10^{3}$	$4.17\cdot10^{2}$	7.3	$1.2\cdot10^{1}$	$5.6\cdot10^{2}$	$1.9\cdot10^{2}$	23	$4.1\cdot10^{1}$
30.3	$5.4\cdot10^{3}$	$9.7\cdot10^{0}$	$2.2\cdot10^{4}$	(<1)	6	7.3	$2.2\cdot10^{1}$	$1.1\cdot10^{4}$	$8.4\cdot10^{2}$	$6.19\cdot10^{3}$	$5.17\cdot10^{2}$	8.2	$1.1\cdot10^{1}$	$7.3\cdot10^{2}$	$2.1\cdot10^{2}$	28	$4.3\cdot10^{1}$
6.0	$3.4\cdot10^{3}$	$8.2\cdot10^{0}$	$1.7\cdot10^{4}$	(<1)	4	5.0	$1.7\cdot10^{1}$	$8.4\cdot10^{3}$	$5.5\cdot10^{2}$	$5.19\cdot10^{3}$	$2.30\cdot10^{2}$	5.6	$8.6\cdot10^{0}$	$4.3\cdot10^{2}$	$2.0\cdot10^{2}$	20	$3.3\cdot10^{1}$
Tributary																	
PC	$1.1\cdot10^{4}$	$2.9\cdot10^{1}$	$5.6\cdot10^{3}$	1	11	10.3	$5.8\cdot10^{1}$	$1.7\cdot10^{4}$	$9.8\cdot10^{2}$	$4.90\cdot10^{3}$	$6.42\cdot10^{2}$	12	$5.7\cdot10^{1}$	$6.5\cdot10^{2}$	$2.3\cdot10^{2}$	18	$1.9\cdot10^{2}$
MD	$2.1\cdot10^{4}$	$7.2\cdot10^{1}$	$4.7\cdot10^{3}$	42	60	8.7	$1.9\cdot10^{3}$	$8.9\cdot10^{4}$	$5.8\cdot10^{2}$	$2.80\cdot10^{3}$	$8.90\cdot10^{3}$	42	$2.0\cdot10^{3}$	$5.0\cdot10^{3}$	$6.8\cdot10^{3}$	19	$8.1\cdot10^{3}$
AL	$4.2\cdot10^{3}$	$9.1\cdot10^{0}$	$6.8\cdot10^{3}$	(<1)	9	8.4	$5.1\cdot10^{1}$	$1.6\cdot10^{4}$	$6.1\cdot10^{2}$	$3.48\cdot10^{3}$	$6.65\cdot10^{2}$	11	$1.4\cdot10^{1}$	$2.3\cdot10^{2}$	$3.4\cdot10^{2}$	14	$4.2\cdot10^{1}$
HS	$5.6\cdot10^{3}$	$9.9\cdot10^{0}$	$1.4\cdot10^{4}$	(<1)	3	10.4	$4.3\cdot10^{1}$	$7.8\cdot10^{3}$	$5.9\cdot10^{2}$	$2.77\cdot10^{3}$	$6.74\cdot10^{2}$	6.6	$9.5\cdot10^{0}$	$1.3\cdot10^{3}$	$2.7\cdot10^{2}$	44	$4.8\cdot10^{1}$
HG	$7.9\cdot10^{3}$	$1.6\cdot10^{1}$	$7.9\cdot10^{3}$	(<1)	13	21.9	$2.3\cdot10^{1}$	$1.8\cdot10^{4}$	$7.4\cdot10^{2}$	$3.82\cdot10^{3}$	$1.88\cdot10^{3}$	35	$1.7\cdot10^{1}$	$4.5\cdot10^{2}$	$4.5\cdot10^{2}$	156	$5.9\cdot10^{1}$
LF	$4.9\cdot10^{3}$	$1.3\cdot10^{1}$	$3.3\cdot10^{4}$	(<1)	6	7.9	$2.7\cdot10^{1}$	$1.3\cdot10^{4}$	$6.7\cdot10^{2}$	$8.64\cdot10^{3}$	$3.85\cdot10^{2}$	8.3	$1.5\cdot10^{1}$	$1.9\cdot10^{2}$	$2.8\cdot10^{2}$	23	$3.9\cdot10^{1}$
AR	$1.1\cdot10^{4}$	$1.4\cdot10^{1}$	$8.2\cdot10^{3}$	(<1)	9	21.0	$7.9\cdot10^{1}$	$1.9\cdot10^{4}$	$8.4\cdot10^{2}$	$5.78\cdot10^{3}$	$2.41\cdot10^{2}$	13	$1.2\cdot10^{1}$	$7.0\cdot10^{2}$	$2.9\cdot10^{2}$	26	$6.8\cdot10^{1}$
NV	$4.7\cdot10^{3}$	$7.2\cdot10^{0}$	$1.6\cdot10^{4}$	(<1)	5	7.9	$1.7\cdot10^{1}$	$7.3\cdot10^{3}$	$9.2\cdot10^{2}$	$4.06\cdot10^{3}$	$6.14\cdot10^{2}$	10	$8.0\cdot10^{0}$	$7.9\cdot10^{2}$	$2.0\cdot10^{2}$	76	$3.0\cdot10^{1}$
NF	$6.2\cdot10^{3}$	$3.0\cdot10^{1}$	$2.5\cdot10^{4}$	(<1)	6	7.8	$3.5\cdot10^{1}$	$1.8\cdot10^{4}$	$7.8\cdot10^{2}$	$8.52\cdot10^{3}$	$3.41\cdot10^{2}$	8.0	$1.4\cdot10^{1}$	$5.0\cdot10^{2}$	$4.5\cdot10^{2}$	20	$4.0\cdot10^{1}$
MT	$3.1\cdot10^{3}$	(<6.5)	$4.7\cdot10^{3}$	(<1)	3	4.1	$1.3\cdot10^{1}$	$6.9\cdot10^{3}$	$4.7\cdot10^{2}$	$2.39\cdot10^{3}$	$4.97\cdot10^{2}$	4.1	$7.3\cdot10^{0}$	$5.2\cdot10^{2}$	$1.7\cdot10^{2}$	12	$2.2\cdot10^{1}$
CW	$7.2\cdot10^{3}$	(<6.5)	$6.4\cdot10^{3}$	(<1)	4	7.5	$1.4\cdot10^{1}$	$1.0\cdot10^{4}$	$5.6\cdot10^{2}$	$3.52\cdot10^{3}$	$5.87\cdot10^{2}$	7.4	$1.0\cdot10^{1}$	$1.2\cdot10^{3}$	$2.3\cdot10^{2}$	11	$2.9\cdot10^{1}$
EC	$1.0\cdot10^{4}$	(<6.5)	$1.4\cdot10^{4}$	(<1)	6	15.8	$1.7\cdot10^{1}$	$1.5\cdot10^{4}$	$1.8\cdot10^{2}$	$8.30\cdot10^{3}$	$2.52\cdot10^{2}$	8.6	(<6)	$4.1\cdot10^{2}$	$6.1\cdot10^{2}$	31	$3.7\cdot10^{1}$
GC	$7.2\cdot10^{3}$	(<6.5)	$9.0\cdot10^{3}$	(<1)	5	6.6	$1.5\cdot10^{1}$	$8.7\cdot10^{3}$	$4.9\cdot10^{2}$	$3.60\cdot10^{3}$	$4.42\cdot10^{2}$	6.5	(<6)	$8.4\cdot10^{2}$	$2.0\cdot10^{2}$	11	$2.4\cdot10^{1}$
UC	$8.5\cdot10^{3}$	$6.7\cdot10^{0}$	$7.7\cdot10^{3}$	(<1)	8	7.8	$2.9\cdot10^{1}$	$1.1\cdot10^{4}$	$1.1\cdot10^{2}$	$3.76\cdot10^{3}$	$1.88\cdot10^{3}$	11	$1.7\cdot10^{1}$	$7.4\cdot10^{2}$	$2.3\cdot10^{2}$	20	$6.7\cdot10^{1}$
Avg. *	$7.0\cdot10^{3}$	$1.1\cdot10^{1}$	$1.2\cdot10^{4}$	(<1)	7	10.6	$3.2\cdot10^{1}$	$1.3\cdot10^{4}$	$8.1\cdot10^{2}$	$4.89\cdot10^{3}$	$7.00\cdot10^{2}$	11	$1.4\cdot10^{1}$	$6.5\cdot10^{2}$	$3.0\cdot10^{2}$	36	$5.3\cdot10^{1}$

*without MD

occurred one or two sites further downstream from the headwaters than the sediment samples, which showed peak concentrations mostly at the furthest upstream site. This indicates that solute concentrations near the remediated mining district might have been partially transferred to the solid phase, and that the contaminated marshes or unsampled tributaries resupplied the dissolved phase with some trace metals.

Comparisons to samples collected in 1989 and 1995 indicate that remediation efforts begun in 1993 have had no effect on lowering the sediment-metal concentrations in the basin. Aluminum, As, Cd, Co, Cu, Fe, Mn, Ni, Pb, and Zn were still at least an order of magnitude higher in the headwaters than in most of the mainstem. For most metals analyzed, the downstream dispersion trends were almost identical for each of the three study years.

Compared with other tributaries in the BFR watershed, the Landers Fork had no anomalously high solute concentrations or loads, at least for the detectable elements. It had only a few anomalously high sediment concentrations (i.e. for Ca and Mg) despite its close proximity to an unmined ore body. These results suggest that the undisturbed ore body is not a detectable natural source of trace elements to the watershed.

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