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An empirical method for estimating instream pre-mining pH and dissolved Cu concentration in catchments with acidic drainage and ferricrete

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ABSTRACT

Methods for assessing natural background water quality of streams affected by historical mining are vigorously debated. An empirical method is proposed in which stream-specific estimation equations are generated from relationships between either pH or dissolved Cu concentration in stream water and the Fe/Cu concentration ratio in Fe-precipitates presently forming in the stream. The equations and Fe/Cu ratios for pre-mining deposits of alluvial ferricrete then were used to reconstruct estimated pre-mining longitudinal profiles for pH and dissolved Cu in three acidic streams in Montana, USA. Primary assumptions underlying the proposed method are that alluvial ferricretes and modern Fe-precipitates share a common origin, that the Cu content of Fe-precipitates remains constant during and after conversion to ferricrete, and that geochemical factors other than pH and dissolved Cu concentration play a lesser role in determining Fe/Cu ratios in Fe-precipitates. The method was evaluated by applying it in a fourth, naturally acidic stream unaffected by mining, where estimated pre-mining pH and Cu concentrations were similar to present-day values, and by demonstrating that inflows, particularly from unmined areas, had consistent effects on both the pre-mining and measured profiles of pH and Cu concentration. Using this method, it was estimated that mining has affected about 480 m of Daisy Creek, 1.8 km of Fisher Creek, and at least 1 km of Swift Gulch. Mean values of pH decreased by about 0.6 pH units to about 3.2 in Daisy Creek and by 1–1.5 pH units to about 3.5 in Fisher Creek. In Swift Gulch, mining appears to have decreased pH from about 5.5 to as low as 3.6. Dissolved Cu concentrations increased due to mining almost 40% in Daisy Creek to a mean of 11.7 mg/L and as much as 230% in Fisher Creek to 0.690 mg/L. Uncertainty in the fate of Cu during the conversion of Fe-precipitates to ferricrete translates to potential errors in pre-mining estimates of as much as 0.25 units for pH and 22% for dissolved Cu concentration. The method warrants further testing in other mined and unmined watersheds. Comparison of pre-mining water-quality estimates derived from the ferricrete and other methods in single watersheds would be particularly valuable. The method has potential for use in monitoring remedial efforts at mine sites with ferricrete deposits. A reasonable remediation objective might be realized when the downstream pattern of Fe/Cu ratios in modern streambed Fe-precipitates corresponds to the pattern in pre-mining alluvial ferricrete deposits along a stream valley.

1. Introduction

The question of pre-mining water quality is commonly encountered during remediation planning for catchments disturbed by hard rock mining because natural weathering of sulfide-bearing rock likely released acid and metals to streams prior to mining. Streams in many metal-mining districts do not meet water-quality standards and may not have prior to mining (Runnells et al., 1992). Thus, the pre-mining characteristics of streams and methods for assessing natural background water quality are vigorously debated (Runnells et al., 1992,1998; Miller and McHugh, 1994; Alpers and Nordstrom, 2000; Yager et al., 2000; Mast et al., 2007).

A variety of approaches have been reported for estimating pre-mining or natural background metal concentrations in areas affected by mining. These approaches include analysis of historical data (Mast et al., 1998, Maest et al., 2004), using other similarly mineralized areas as analogs (Rose et al., 1979; Davis et al., 2000; Bove et al., 2007), collecting stream sediment deposited prior to mining (Persaud et al., 1993; Church et al., 2000; Hren et al., 2001), using stable isotopes to distinguish mining-affected water (Verplanck et al., 2001; Nordstrom et al., 2007), geochemical modeling (Runnells et al., 1992; Walton-Day et al., 1999; Runkel et al., 2007), statistical analyses (Sinclair, 1976; Runnells et al., 1998), detailed synoptic water sampling (Kimball et al., 1999), and a combination of some of

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these methods (Mast et al., 2007). None of these approaches have proven to be satisfactory for estimating pre-mining conditions nor have any gained widespread acceptance by the regulatory community.

Holocene ferricrete deposits in metal-mining districts are recognized as indicators of ancient acid rock drainage (Bassett et al., 1992; Plumlee et al., 1995; Furniss et al., 1999; Yager et al., 2003; Wirt et al., 2007). Furniss (1999) took the idea that ferricrete provides geologic evidence of pre-mining acidic conditions a step farther and suggested that the difference in trace metal content between the Fe-precipitates currently forming on a streambed and the terrace deposits of ferricrete along the adjacent valley floor might provide an approach for distinguishing between natural acid rock drainage and anthropogenic acid mine drainage. The authors have developed such an approach and propose a method based on empirical trace-metal relationships between ancient ferricrete, modern Fe-precipitates, and stream water. The method uses the downstream spatial variation in geochemical characteristics of ferricrete and Fe-precipitates to estimate longitudinal profiles of pre-mining pH and dissolved Cu concentrations during base-flow conditions in acidic streams affected by mining. The method uses an empirical approach rather than a more rigorous geochemical modeling approach because the complexities involved with the latter are difficult given the incomplete understanding of the geochemical processes taking place (Walton-Day et al., 1999).

Ferricrete is a common geologic deposit in both mined and unmined mineralized areas (Lovering, 1929; Pardee and Schrader, 1933; Miller and McHugh, 1994; Logsdon et al., 1996; Yager et al., 2003; Verplanck et al., 2007). Ferricrete commonly forms when alluvial or colluvial material is cemented by Fe-precipitates that form as acidic water rich in Fe(III) is neutralized or as reduced water rich in Fe(II) is oxidized. These Fe-precipitates include Fe-oxyhydroxides such as ferrihydrite, Fe-oxyhydroxysulfates such as schwertmannite and jarosite, and Fe-oxides such as goethite. Trace metals adsorb to or co-precipitate with the Fe-precipitates as they form (Benjamin and Leckie, 1981; Drever, 1982; Salomons and Forstner, 1984). Once formed, crystalline and dehydrated Fe-precipitates such as goethite are chemically stable in most natural settings (Cornell and Schwertmann, 1996; Webster et al., 1998; Morris et al., 2000).

Government agencies are planning and implementing restoration efforts at abandoned mine sites in Montana, USA. For example, the USDA-Forest Service has embarked on a comprehensive restoration of the historical mining disturbances in the New World mining district (Fig. 1) to minimize effects of acid mine drainage on water quality. Previous researchers contend that natural sources in this mining district contribute a large percentage of the metal loads in Fisher and Daisy Creeks (Kimball et al., 1999; Hren et al., 2001; Nimick and Cleasby, 2001) and that eliminating all water-quality effects generated by mining activities probably would not result in achievement of water-quality standards. Similarly, the Bureau of Land Management and Montana Department of Environmental Quality have initiated restoration efforts at the Landusky mine in the Little Rocky Mountains mining district of northeastern Montana (Fig. 1). The study described in this paper was undertaken to determine if the ferricrete deposits in these mined areas could be used to estimate pre-mining, or natural background, water quality. The study also included Paymaster Creek (Fig. 1), a rare naturally acidic stream with ferricrete deposits in its catchment, as a control site.

2. Site descriptions

2.1. Daisy and Fisher Creeks

Daisy and Fisher Creeks are alpine streams that begin at altitudes near 2900 m in glacial valleys of the New World mining district, which is adjacent to the NE corner of Yellowstone National Park (Fig. 1). The catchments lie in the Beartooth uplift, a large fault block of uplifted Cambrian to Ordovician shales and limestones and Precambrian granitic gneiss (Elliot, 1979). Sulfide-ore zones associated with vertical hydrothermal breccia pipes and high-angle faults crop out in the headwaters of both streams (Elliot et al., 1992; Johnson and Meinert, 1994).

Historical mining has occurred in both the Fisher Creek and Daisy Creek catchments. Mining operations in the Fisher Creek catchment began in 1888 with small-scale Au and Ag mines. Large-scale development began in the early part of the twentieth century and continued sporadically until the 1950s (Elliot et al., 1992). The Glengarry adit was the largest source of acidic, metal-rich water to Fisher Creek (Kimball et al., 1999). During low-flow conditions, discharge from the Glengarry adit became the headwaters of Fisher Creek. Gold was produced on a large scale in the Daisy Creek headwaters during 1938–53 at the McLaren open-pit mine (Elliot et al., 1992). The headwaters of Daisy Creek begin at the McLaren mine from diffuse, acidic seeps (Nimick and Cleasby, 2001).

Prominent alluvial ferricrete deposits extend along the valley bottoms of Fisher and Daisy Creeks, and colluvial ferricrete deposits are found higher on the valley walls (Lovering, 1929; Furniss and Hinman, 1998). The ages of the ferricrete deposits were established using ^{14}C-dating of co-deposited wood fragments, which can be common in ferricrete deposits. Natural acidic drainage resulted in episodic ferricrete formation during the last 8.84 ka (Furniss and Hinman, 1998; Furniss et al., 1999; Hren et al., 2001). Alluvial ferricrete is exposed along Fisher and Daisy Creeks as 0.1–2-m thick lenses of Fe-cemented gravels as much as 2 m above the present-day stream channel. These ferricrete outcrops extend downstream along the first 1.2 km of Daisy Creek and the first 2 km of Fisher Creek (Fig. 1). Similar ferricretes are forming in the streambeds of present-day channels, suggesting that the ferricretes were formed at the level of paleo-stream channels and have been preserved as terraces by later stream incision. Logs, twigs, and volcanic ash from the eruption of Mount Mazama 6.845 ka BP are locally preserved within the ferricretes. The alluvial ferricrete generally is composed of reddish-brown, cemented, alluvial sediment. Deposits are stratified to weakly stratified and consist mostly of heterogeneous subrounded to subangular pebbles and cobbles with occasional boulder-size clasts in a Fe-cemented matrix of coarse sand- to pebble-size sediment. Clasts are imbricated and dip upstream.

2.2. Swift Gulch

Swift Gulch is in the Little Rocky Mountains mining district, 220 km east of Great Falls, Montana (Fig. 1). The stream borders a Au-bearing mineralized area (Emmons, 1908) where underground and placer mining occurred in the late 1880s and first half of the twentieth century and open-pit mining occurred from 1979–1997 (Gabelman et al., 2005). Swift Gulch is ephemeral in its headwaters and perennial in its middle and lower reaches. During base flow, reaches of the stream are acidic and contain elevated trace-metal concentrations. Ferricrete deposits crop out in the headwaters and intermittently along both sides of the stream for about 1.6 km. The most downstream outcrop of ferricrete at Swift Gulch was dated using ^{14}C at 10.36 ± 0.06 ka BP (Gabelman et al., 2005). Acidic springs on the south side of Swift Gulch discharge along the short reach where the Landusky mine is closest to the stream (Fig. 1).

2.3. Paymaster Creek

Paymaster Creek is in the Heddleston mining district, 100 km SW of Great Falls, Montana (Fig. 1). The surrounding area was

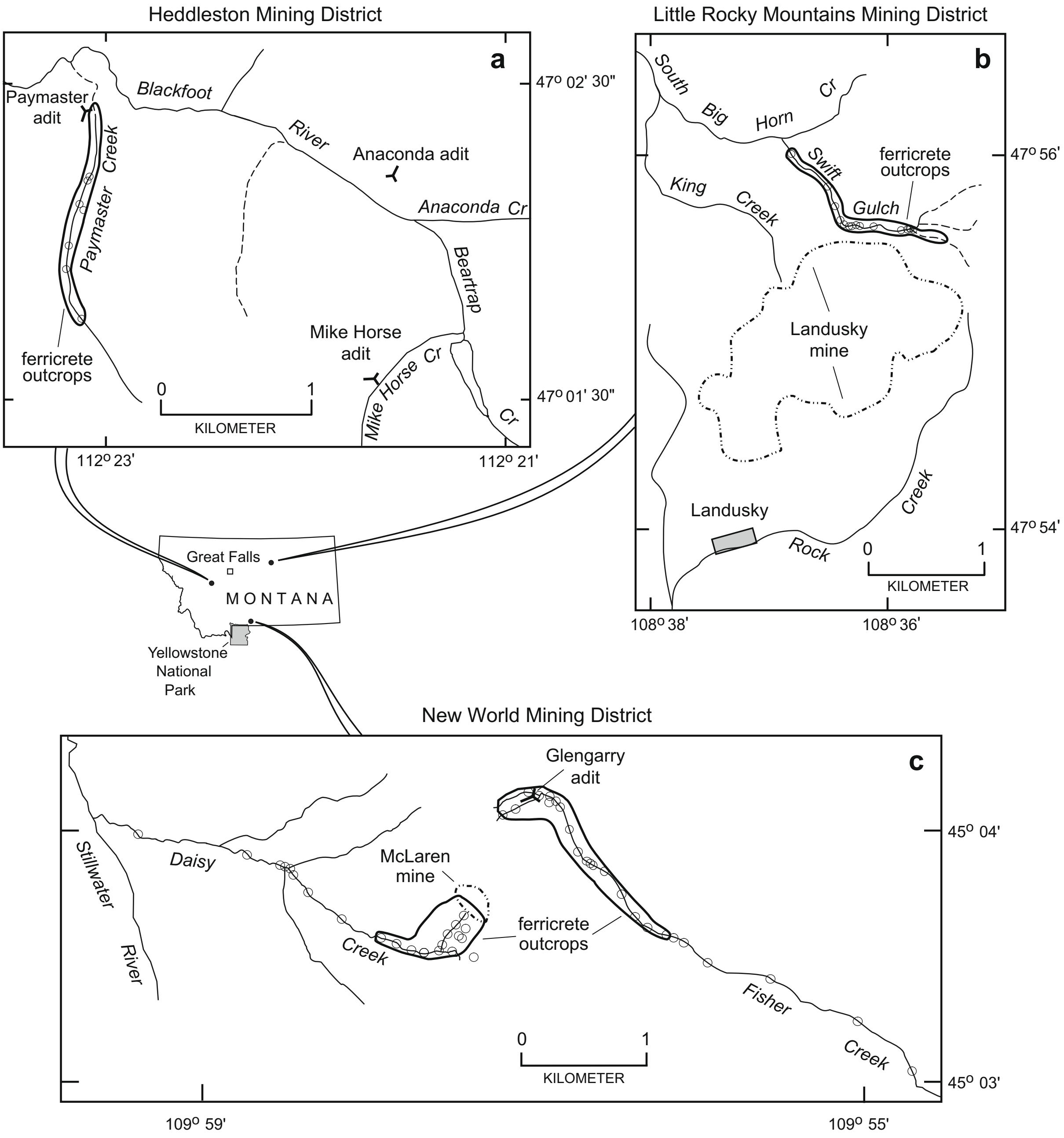

Fig. 1. Maps showing study reaches and locations of sampling sites (open circles) in (a) Heddleston, (b) Little Rocky Mountains, and (c) New World mining districts. Streams flow generally from SE to NW in panel a. Ephemeral stream reaches shown as dashed lines.

intermittently mined from 1889 to the 1950s, and mineral exploration continued intermittently through the 1980s (Pardee and Schrader, 1933; Montana Department of Environmental Quality, 2003); however, the reach of Paymaster Creek used as a control was not disturbed by these activities. During base flow, the stream is acidic and contains elevated trace-metal concentrations. The ferricrete at Paymaster Creek ranges in age from 0.06 to 7.3 ka BP (Furniss, 1998; Sjostrom et al., 2004) and extends across the entire valley floor. Paymaster Creek is a low-energy stream that produces fine-grained ferricrete lacking in pebbles or larger clasts. As Fe-precipitates form, they mix with organic debris to form dams creating a terraced architecture similar in appearance to carbonate hot-spring terraces. The ferricrete deposits show no signs of recent stream incision.

3. Methods

3.1. Proposed pre-mining water-quality estimation method

The proposed method for estimating pre-mining pH or dissolved Cu concentration for a stream is as follows: (1) Collect samples of water, modern streambed Fe-precipitate, and alluvial ferricrete at locations along the stream and valley floor. Collect additional water and Fe-precipitate samples downstream from the most downstream ferricrete deposit so that the suite of water and Fe-precipitate samples includes the full spectrum of pH and dissolved Cu concentrations found in the stream. Collect the water and Fe-precipitate samples during base flow because ferricrete that is preserved in the geologic record is thought to be deposited primarily during this hydrologic condition. This timing of ferricrete deposition has been inferred from isotopic studies that showed that $\delta^{18}O$ values for goethite in modern Fe-precipitates are in isotopic equilibrium with fall and winter stream water (Poage et al, 2000; Sjostrom et al., 2004). Collect primarily samples of alluvial ferricrete; some samples of colluvial ferricrete and ferricrete from Fe-rich springs may provide additional data. To the extent possible, collect dateable materials (e.g., wood) that can be used to bracket the age of ferricrete deposition and use younger, pre-mining samples of ferricrete. Analyze solid samples for Fe and Cu concentrations. Analyze water samples for pH and dissolved Cu concentration. (2) Generate equations using least-squares regression analysis to describe the relationships between the Fe/Cu concentration ratio in Fe-precipitates and either stream-water pH or dissolved Cu concentration for the stream. (3) Estimate pre-mining values of pH and dissolved Cu for each alluvial ferricrete sampling location by substituting the ferricrete Fe/Cu concentration ratio into the equation developed from Fe-precipitate data. (4) Construct and compare longitudinal profiles of measured and estimated pre-mining stream-water composition.

Copper is used in the proposed method because it is a common trace metal in areas with acid-generating sulfide mineralization and is found at moderate to high concentrations in Fe-precipitates across a wide range of stream pH. Copper is an appropriate metal to use for modeling pre-mining conditions because (1) adsorption of Cu onto Fe-minerals such as ferrihydrite, schwertmannite, and goethite occurs over a pH range from 3 to 6 (Webster et al., 1998), precisely the range typically encountered in catchments with acid rock drainage, and (2) Cu can be incorporated into the crystal lattice of Fe-precipitates such as goethite (Cornell and Schwertmann, 1996). In addition, adsorption-edge experiments from Webster et al. (1998) illustrate why Cu is a more reliable model parameter than Zn or other metals found in acidic drainages. In these experiments, the percent of metal adsorbed onto Fe-precipitates at a given pH decreased as the metal concentration increased. That is, the adsorption edges were displaced to higher pH. The Cu adsorption edge exhibited the smallest shift among the metals tested, amounting for about 0.5 pH units for a 10-fold increase in Cu concentration (0.5–5.0 mg/kg). Even with this displacement, 90% of the Cu was adsorbed at pH <6.

The Fe/Cu concentration ratio is used in the proposed method to minimize the potential dilution effect that any non-Fe minerals in the sample might have on the Cu concentration of the sample. This normalization is included because it is assumed that most of the Cu in solid samples is associated with Fe minerals (goethite in ferricrete; ferrihydrite, schwertmannite, and goethite in Fe-precipitates), and not with other minerals (e.g., silicates) or lithophile elements (e.g., Ca, Si, etc.). This normalization does not account for any Al-precipitates contained in samples. Although abundant in some waters affected by acid drainage from sulfidic rocks, Al-precipitates adsorb Cu less strongly than do Fe-precipitates (Kinniburgh et al., 1976; Karthikeyan et al., 1997; Schemel et al., 2007).

3.2. Sampling and analytical procedures

Along each stream, distances were determined to provide the spatial scale for constructing pH- and Cu-concentration profiles. For Paymaster Creek and Swift Gulch, distances were measured downstream from the uppermost sampling site using a GPS instrument. Distances along Fisher Creek had been measured previously by Kimball et al. (1999), and these distances, which started with zero in the southern headwater tributary (see Fig. 1), were used. Distances along Daisy Creek were initially those measured by Nimick and Cleasby (2001). However, the trace of uppermost Daisy Creek used for this study diverged from the Nimick and Cleasby (2001) trace at 481 m. At this location, the present study reach followed a tributary that headed almost due north to the base of the McLaren mine. The uppermost sampling site in Daisy Creek was assigned 0 m, and consequently, sites along the Nimick and Cleasby (2001) trace downstream from 481 m had 295 m added to their distance.

Ferricrete and Fe-precipitate samples were collected along all four streams (Tables 1–3). Ferricrete samples were collected from outcrops along the present-day stream channels in 2002–03 (Daisy, Fisher and Paymaster Creeks) or 2004 (Swift Gulch). The deposits selected for sampling were thought to represent alluvial ferricrete deposited by streams. The Fe-precipitate cement was separated from gravel and finer clasts in the ferricrete samples and then air dried at room temperature and sieved to minus 200 mesh (0.075 mm). Iron-precipitates were sampled during late summer in 2004 by collecting rocks from the stream bottom. The rocks were placed in plastic bags with stream water and then agitated to detach the Fe-precipitate coatings. In headwater areas, a few samples also were collected adjacent to Fe-rich springs or in metal-rich fens near the base of steep slopes. The Fe-precipitate samples were air dried at room temperature and sieved to minus 200 mesh. All solid samples were analyzed for metals by Energy Laboratories, Inc. (Billings, Montana) using USEPA Method 3050 (US Environmental Protection Agency, 1987). This method involves digestion with HNO_3 and HCl followed by analysis by inductively coupled plasma–atomic emission spectroscopy (ICP–AES).

Table 1
Chemical data for ferricrete samples collected in 2002–03 from Daisy Creek, Fisher Creek, and Paymaster Creek, Montana.

Site name	Distance (m)	Fe (g/kg)	Cu (mg/kg)	Fe/Cu
New World mining district-Daisy Creek				
Dpit	0	519	1830	284
D1A	213	304	1600	190
D1	213	246	446	552
D2	417	214	702	305
DC ledge	444	377	802	470
D3	481	576	839	687
D3 replicate	–[a]	506	970	522
D3A	545	446	3390	132
D4	703	418	2320	180
D4A	905	303	1870	162
D5	1105	424	2600	163
New World mining district-Fisher Creek				
F1	0	535	362	1478
F1 replicate	–	535	391	1368
FCT-12	0	479	615	779
Glengarry adit	263	358	854	419
F2	567	366	5070	72
F1A	570	405	5970	68
F3	666	373	1880	198
F3 replicate	–	211	1040	203
F2B	681	311	2030	153
F4	810	207	1870	111
F4 replicate	–	232	2050	113
SW3 weir	955	368	3130	118
F4A	1072	228	2660	86
F5	1103	269	3190	84
F5A	1133	198	1910	104
F6	1267	290	1390	209
F6A	1412	221	1010	219
F6C	1768	321	2410	133
F6D	1920	315	2960	106
F7	2042	290	3750	77
Heddleston mining district-Paymaster Creek				
12	0	362	80	4525
10	335	512	176	2909
9	496	530	36	14,722
5	697	518	19	27,263
2	896	549	11	49,909
2fen	914	468	25	18,720

[a] No data.

Table 2
Chemical data for ferricrete, Fe-precipitate, and water samples collected in August and September 2004 from Swift Gulch, Montana.

Site name	Distance (m)	Ferricrete			Fe-precipitate			Water	
		Fe (g/kg)	Cu (mg/kg)	Fe/Cu	Fe (g/kg)	Cu (mg/kg)	Fe/Cu	Dissolved Cu (mg/L)	pH
Little Rocky Mountains mining district-Swift Gulch									
F1	30	330	904	365	–[a]	–	–	–	–
F3	61	445	250	1780	–	–	–	–	–
F4	76	260	297	875	–	–	–	–	–
F5	91	338	131	2580	–	–	–	–	–
F6	122	370	167	2216	–	–	–	–	–
F7	427	295	131	2252	–	–	–	–	–
M1	518	–	–	–	315	191	1649	0.001	6.6
M2	579	–	–	–	410	111	3694	0.005	6.0
F8/M3	610	388	44.4	8739	426	37	11,514	0.006	5.1
F9/M4	671	191	141	1355	430	35	12,286	0.011	3.6
F10/M5	747	389	33.5	11,612	418	25	16,720	0.005	4.0
F12/M6	823	338	97.1	3481	412	22	18,727	0.006	3.9
M7	945	–	–	–	432	35	12,343	0.007	3.7
F13/M8	1128	302	77.2	3912	436	34	12,824	0.010	3.6
F15/M9	1585	226	77.6	2912	286	180	1589	0.010	4.2

[a] No data.

Water samples were processed, filtered, and preserved according to procedures described by Ward and Harr (1990) and Horowitz et al. (1994). Sample pH was measured onsite with a field meter after calibration with buffers bracketing the sample pH. For Daisy, Fisher and Paymaster Creeks, water samples (Table 3) were filtered through 0.1-μm filters and analyzed for metals and cations by ICP–AES, Fe speciation by the Ferrozine method, anions by ion chromatography, and alkalinity by titration at a US Geological Survey laboratory in Boulder, Colorado, using instrumental and quality-assurance methods described or referenced by McCleskey et al. (2004). For Swift Gulch, water samples (Table 2) were filtered through 0.45-μm filters and analyzed for dissolved Cu by ICP–AES at Energy Laboratories, Inc. (Billings, Montana).

The quality of the analytical data was assessed by analyses of blank and replicate samples collected in the field (Tables 1 and 3). For dissolved Cu in water, the concentration was less than detection in the two blank samples, and the relative standard deviation (RSD) for the three replicate samples was <2%. For Cu and Fe in ferricrete and Fe-precipitates, the RSD was $\leqslant$10% for four of the five replicate samples. The fifth replicate had RSD values for Cu and Fe of ∼40%; however, this poor replication of the concentration data did not extend to the Fe/Cu ratios, which had a RSD of <2%.

4. Results

4.1. Composition of water, Fe-precipitate, and ferricrete

Chemical data for samples collected during this study are listed in Tables 1–3. The data needed for the proposed pre-mining water-quality estimation method include pH and dissolved Cu concentration for water as well as Cu and Fe concentrations for Fe-precipitates and ferricrete. Figs. 2–5 show the downstream profiles for Fe/Cu concentration ratio in Fe-precipitates and ferricrete and for measured pH and dissolved Cu concentration in water.

Values of pH exhibited a wide range in each of the streams except Paymaster Creek. In Daisy and Fisher Creeks (Figs. 2 and 3b, Table 3), pH was low (<∼4) in the headwaters and increased downstream to values near or greater than 7. The change from acidic to near-neutral pH occurred over a short reach where inflows from tributaries draining carbonate rocks provided neutralization. In Daisy Creek, the most acidic water (pH = 3.01 at 417 m) was in the upper reach (0–703 m) that drains the McLaren mine. In upper Fisher Creek (0–666 m), the pH decreased from 4.16 upstream from the Glengarry adit to 3.49 downstream from the adit. The upstream value reflects natural acid rock drainage from an area essentially undisturbed by mining; the downstream value reflects the input from the adit, which is the most upstream mining-affected inflow along Fisher Creek. In Swift Gulch (Fig. 4b), pH was near neutral (6.6) at the upstream end of the perennial reach, decreased over a short distance to 3.6 owing to inflow from acidic springs on the mining-affected south side of the drainage, and then increased slightly to 4.2 at the downstream end of the study reach. The pH in Paymaster Creek was acidic and decreased slightly from 4.04 upstream to 3.44 downstream (Fig. 5b).

Dissolved Cu concentrations in Daisy Creek ranged from 3.54 to 15.6 mg/L in the upper reach and decreased to <0.2 mg/L downstream from 2054 m (Fig. 2c). Dissolved Cu concentrations in Fisher Creek ranged from 0.558 to 0.690 mg/L in the upper reach (0–666 m) and decreased to about 0.3 mg/L at 1768 m and <0.1 mg/L downstream from 3537 m (Fig. 3c). In Swift Gulch, dissolved Cu concentrations ranged from 0.001 to 0.011 mg/L (Table 2) with no discernable downstream pattern. In Paymaster Creek, dissolved Cu concentrations ranged from <0.003 to 0.008 mg/L (Fig. 5c) with no discernable downstream pattern.

Copper is an abundant trace metal in ferricrete and Fe-precipitates and occurred in relatively large concentration ranges in the ferricrete and Fe-precipitate sample sets for each stream (Tables 1–3). At Daisy Creek, Cu concentrations were 446–3390 mg/kg in ferricrete and 41.0–17,100 mg/kg in Fe-precipitates. At Fisher Creek, Cu concentrations were 362–5970 mg/kg in ferricrete and 284–10,600 mg/kg in Fe-precipitates. At Swift Gulch, Cu concentrations were 33.5–904 mg/kg in ferricrete and 22–191 mg/kg in Fe-precipitate. At Paymaster Creek, Cu concentrations were 11–176 mg/kg in ferricrete and 37.4–129 mg/kg in Fe-precipitates.

Iron/Cu concentration ratios in ferricretes and Fe-precipitates for each stream generally decreased downstream (Figs. 2–5). This decrease was most clearly displayed in Daisy and Fisher Creeks, and both have a large mineralized zone in their headwaters. In Swift Gulch, the Fe/Cu ratio was lower upstream, increased through the mineralized or mining-affected area, and then decreased (Fe-precipitates) or displayed no overall trend (ferricrete) downstream. In Paymaster Creek, the range of Fe/Cu ratios in ferricretes and Fe-precipitates was smaller than in the other streams, and ratios generally increased downstream.

4.2. pH model

Bivariate plots of pH in water and Fe/Cu ratios in modern Fe-precipitates are presented for each stream in Fig. 2d, Fig. 3d, Fig. 4c and Fig. 5d. Power functions were used for each data set

Table 3

Chemical data for water and Fe-precipitate samples from Paymaster Creek, Fisher Creek, and Daisy Creek, Montana. Concentrations for water are from filtered (0.1 μm) samples.

Sample ID	Distance (m)	Date	Water														Fe-precipitate		
			pH	Al (mg/L)	Ca (mg/L)	Cu (mg/L)	Fe(T) (mg/L)	Fe(II) (mg/L)	K (mg/L)	Mg (mg/L)	Mn (mg/L)	Na (mg/L)	Zn (mg/L)	Cl (mg/L)	SO_4 (mg/L)	Alkalinity (mg/L as HCO_3)	Fe (g/kg)	Cu (mg/kg)	Fe/Cu
Heddleston mining district-Paymaster Creek																			
12	0	26-Oct-04	4.04	1.46	5.00	0.004	1.04	1.03	0.939	3.23	0.147	1.29	0.070	0.464	42.8	nd[c]	322	77.7	4144
10	335	26-Oct-04	3.83	2.35	4.51	0.008	2.48	1.89	1.42	3.73	0.324	1.44	0.086	0.541	53.9	nd	368	61.3	6003
9	496	26-Oct-04	3.80	2.09	4.56	0.007	2.32	1.52	1.45	3.71	0.326	1.48	0.078	0.531	52.4	nd	349	49.4	7065
5trib[a]	–[b]	26-Oct-04	4.28	0.531	2.33	0.013	1.78	1.60	0.696	1.39	0.075	1.57	0.022	0.931	23.4	nd	243	129	1884
5	697	26-Oct-04	3.85	1.55	4.44	0.005	2.66	2.06	1.52	3.59	0.331	1.51	0.058	0.533	48.8	nd	358	50.5	7089
2	896	26-Oct-04	3.63	1.75	4.43	0.008	2.90	1.82	1.70	3.69	0.344	1.61	0.061	0.511	53.1	nd	362	62.9	5755
2fen	914	26-Oct-04	3.44	2.45	3.70	<0.003	8.65	7.85	2.30	3.62	0.357	1.64	0.066	0.525	72.2	nd	373	37.4	9973
2fen replicate	–	26-Oct-04	–	2.48	3.75	<0.003	8.61	7.78	2.34	3.70	0.361	1.61	0.068	0.533	72.6	nd	–	–	–
field blank	–	26-Oct-04	–	<0.08	<0.4	<0.003	0.002	0.001	0.081	<0.04	<0.002	<0.06	<0.004	0.323	<0.8	nd	–	–	–
New World mining district-Fisher Creek																			
FCT-12 up[a]	–	9-Sep-04	4.12	2.23	2.13	1.13	0.271	0.227	0.827	0.49	0.108	3.48	0.043	0.947	31.7	nd	70.8	549	129
FCT-11 lower[a]	–	9-Sep-04	3.52	4.18	6.11	0.188	3.76	2.05	1.08	1.43	0.569	2.73	0.094	1.07	68.3	nd	244	318	767
FCT-12	0	9-Sep-04	4.16	1.41	3.24	0.558	0.142	0.102	0.796	0.591	0.185	3.24	0.046	0.996	30.1	nd	–	–	–
Glengarry	263	9-Sep-04	3.49	4.98	62.9	0.673	27.7	23.3	3.15	18.0	3.37	4.96	0.331	1.14	331	nd	404	284	1423
F3	666	9-Sep-04	3.54	3.10	33.1	0.690	10.1	8.38	2.13	9.47	1.49	3.78	0.205	1.02	180	nd	373	287	1300
F3 replicate	–	9-Sep-04	–	3.09	33.3	0.687	10.1	8.32	2.21	9.53	1.49	3.72	0.214	1.10	183	nd	–	–	–
F5	1103	9-Sep-04	3.52	2.22	23.0	0.576	4.65	3.65	1.62	6.61	0.996	3.48	0.138	1.00	118	nd	–	–	–
F6	1267	8-Sep-04	3.73	1.57	17.5	0.410	3.18	2.58	1.24	4.80	0.676	2.63	0.099	1.16	85.1	nd	346	449	771
F6C	1768	9-Sep-04	4.13	1.08	17.7	0.301	1.48	1.23	0.984	4.88	0.472	2.40	0.076	1.21	77.8	nd	–	–	–
F6D	1920	9-Sep-04	4.70	0.986	18.9	0.278	1.22	1.05	0.984	5.36	0.445	2.45	0.073	1.08	80.6	nd	81.7	525	156
F7	2042	9-Sep-04	5.02	0.906	19.2	0.270	1.02	0.902	0.933	5.41	0.415	2.51	0.065	0.633	83.2	<1	96.2	832	116
F7 replicate	–	9-Sep-04	–	0.924	20.4	0.276	1.00	0.879	0.995	5.82	0.429	2.58	0.069	1.08	77.8	n.d.	–	–	–
F7A	2088	9-Sep-04	6.28	<0.08	21.7	0.199	0.794	0.700	0.957	5.62	0.360	2.26	0.060	0.608	77.6	4.28	60.4	3510	17.2
F7AA	2134	9-Sep-04	6.05	<0.08	21.5	0.201	0.817	0.716	0.869	5.58	0.351	2.25	0.058	0.505	77.6	4.27	55.9	6480	8.6
F8	2355	9-Sep-04	6.33	<0.08	20.9	0.179	0.692	0.596	0.907	5.46	0.342	2.22	0.057	0.590	76.5	4.33	79.3	8760	9.1
FC5	3008	8-Sep-04	6.60	<0.08	19.3	0.121	0.305	0.269	0.891	4.83	0.290	2.08	0.049	0.598	70.4	4.40	92.0	8280	11.1
FC6	3537	8-Sep-04	6.79	<0.08	17.8	0.050	0.033	0.028	0.811	4.61	0.159	1.94	0.048	0.544	58.8	9.43	75.4	8840	8.5
SW4	4065	8-Sep-04	7.00	<0.08	17.3	0.024	0.008	0.006	0.721	4.45	0.123	1.97	0.036	0.509	58.0	9.74	79.6	10,600	7.5
New World mining district-Daisy Creek																			
DCSW-104ab[a]	–	10-Sep-04	4.65	13.6	151	3.80	3.60	0.407	3.54	29.1	5.85	4.08	1.67	5.47	571	nd	37.4	339	110
270 (USGS-0)[a]	–	10-Sep-04	7.30	<0.08	56.6	0.237	0.047	0.031	2.07	7.66	0.632	1.77	0.218	2.28	139	49.9	33.3	17,400	1.91
Pit underdrain	112	10-Sep-04	3.03	28.5	35.3	14.7	131	104	1.67	12.6	3.82	2.58	1.97	1.20	602	nd	–	–	–
Apron sp 2[a]	265	10-Sep-04	2.62	80.2	200	27.5	107	28.3	2.14	60.6	12.3	4.95	3.23	4.03	1640	nd	40.3	86	469
Apron spring[a]	271	10-Sep-04	3.45	30.5	217	13.4	15.0	6.46	3.71	30.1	6.50	9.06	1.75	17.9	883	nd	–	–	–
D2	417	10-Sep-04	3.01	41.8	93.4	15.6	97.6	12.4	2.69	27.7	6.11	4.20	2.19	4.69	865	nd	35.0	41	854
D3	481	10-Sep-04	3.44	17.7	68.4	4.66	15.7	8.75	2.39	15.6	2.87	2.81	0.742	3.24	367	nd	–	–	–
D4	703	10-Sep-04	4.32	13.3	62.6	3.54	7.07	6.08	2.11	16.1	2.06	2.48	0.601	2.76	302	nd	52.0	126	413
D6	1600	9-Sep-04	4.78	9.47	61.6	2.81	4.56	3.87	2.11	14.1	1.75	2.29	0.517	2.60	269	nd	56.7	479	118
4879	1782	9-Sep-04	4.78	–	–	–	–	–	–	–	–	–	–	–	–	–	155	801	194
5475	1964	9-Sep-04	4.77	8.37	61.9	2.54	3.24	2.81	1.96	14.2	1.64	2.33	0.496	2.58	266	nd	106	691	153
5661	2020	9-Sep-04	5.46	1.33	54.0	1.84	2.41	2.07	1.57	13.6	1.24	2.02	0.377	1.69	207	<1	37.8	2540	14.9
5770	2054	9-Sep-04	7.03	<0.08	47.2	0.149	0.193	–	1.10	11.1	0.772	1.55	0.185	1.25	149	21.3	97.2	10,300	9.44
D7	2075	9-Sep-04	7.16	<0.08	49.2	0.165	0.125	0.104	1.14	11.5	0.781	1.56	0.195	1.27	152	25.1	77.1	5090	15.1
7324	2527	9-Sep-04	7.65	<0.08	48.3	0.023	0.013	0.003	1.11	11.3	0.732	1.51	0.072	1.30	157	22.2	–	–	–
D8 (DC 5)	3320	9-Sep-04	7.51	<0.08	49.5	0.019	0.017	0.007	1.05	10.8	0.587	1.53	0.050	1.55	151	26.0	88.9	17,100	5.2
D8 replicate	–	9-Sep-04	–	–	–	–	–	–	–	–	–	–	–	–	–	–	91.0	15,900	5.7
Field blank	–	10-Sep-04	–	<0.08	<0.4	<0.003	0.005	<0.001	<0.02	<0.04	<0.002	<0.06	<0.004	0.388	<0.8	2.03	–	–	–

[a] Site on tributary; data used to develop relation between Fe/Cu concentration ratio in Fe-precipitates and pH and dissolved Cu concentration in water.

[b] No data.

[c] Not determined (lab pH < 4.5).

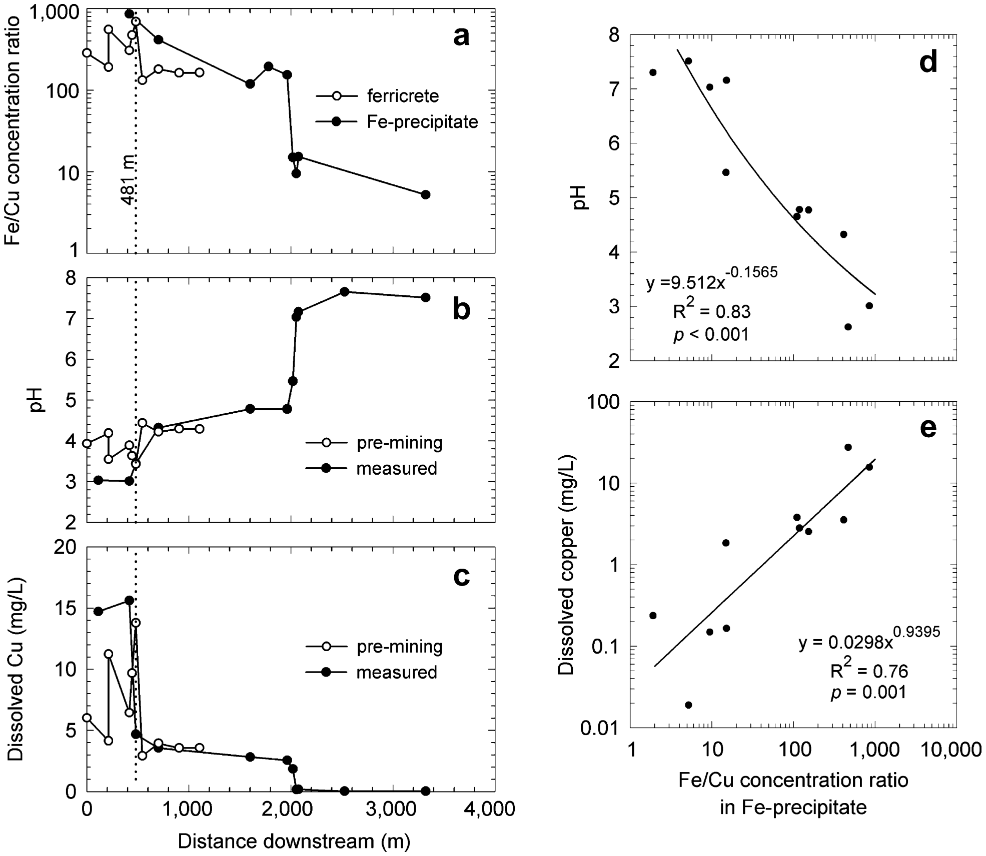

Fig. 2. Downstream profiles of (a) Fe/Cu concentration ratio in ferricrete and Fe-precipitates, (b) estimated pre-mining and measured pH, and (c) estimated pre-mining and measured dissolved Cu concentration. Estimation models for (d) pre-mining pH based on relationship of measured pH and Fe/Cu ratio in Fe-precipitates, and (e) pre-mining dissolved Cu concentration based on relationship of measured dissolved Cu concentration and Fe/Cu ratio in Fe-precipitates for Daisy Creek.

to obtain the best fit (R^2 values of 0.43–0.96) and are asymptotic to both the *x* and *y* axes thereby avoiding negative values. These regression equations then were used to estimate the pre-mining stream pH for each ferricrete sampling location.

The profile of estimated pre-mining pH for Daisy Creek (Fig. 2b) shows headwater values with a mean of 3.8 (range = 3.4–4.2 from 0 to 481 m). Measured pH in this reach was lower (mean = 3.16; range = 3.01–3.44). The pre-mining and measured pH profiles merge downstream from 481 m and maintain essentially the same value to the end of the ferricrete deposits at 1105 m. The estimated pre-mining pH values were 4.2–4.4 between 545 and 1105 m, similar to the one measured pH value (4.32) in this reach.

The profile of estimated pre-mining pH for Fisher Creek (Fig. 3b) shows that in the headwaters upstream from the Glengarry adit, pre-mining pH (3.5–3.8 at 0 m) was similar to the pre-mining pH in Daisy Creek (mean = 3.8) and more acidic than the measured pH (4.16). Downstream through the reach affected by inflow from the Glengarry adit, the pre-mining and measured pH values diverge, with the pre-mining pH increasing to 5.1 at 567 m and the measured pH decreasing to 3.54 at 666 m. Between 666 and the end of the ferricrete deposits at 2042 m, pre-mining pH was fairly constant (mean = 4.8; range 4.4–5.0). Measured pH through the upper part of this reach (666–1103 m) was about 3.5, about 1–1.5 pH units lower than the pre-mining values. Between 1103 and 2042 m, measured pH gradually increased to 5.02, which is the same as the estimated pre-mining value at 2042 m (Fig. 3b).

The profile of estimated pre-mining pH for Swift Gulch (Fig. 4b) is fairly uniform, with a pH range of 4.9–6.1 except for the most upstream site (pH = 7.0) and for two locations (at 610 and 747 m in the zone of acidic springs) with lower pH (4.3 and 4.1, respectively). Measured pH was 6.6 upstream from the zone of acidic springs at 518 m and decreased through the zone of acidic springs to 3.6 at 671 m. Measured pH remained low (3.6–4.2) through the rest of Swift Gulch to the end of the ferricrete deposits. Unlike the other streams, the ferricrete deposits in Swift Gulch extend farther upstream through a reach where the stream is ephemeral (Fig. 1). Therefore, water samples could not be collected upstream from 518 m, and estimated pre-mining and measured pH could not be compared.

For Paymaster Creek, the profile of paleo pH estimated from the ferricrete deposits (Fig. 5b) shows a small range of paleo pH (3.0–4.1), with a mean of 3.5. These values are similar to the measured values (mean = 3.77; range = 3.44–4.04).

4.3. Dissolved Cu model

Bivariate plots of dissolved Cu concentration in water and Fe/Cu ratios in modern Fe-precipitates are presented for Daisy, Fisher and Paymaster Creeks in Figs. 2, 3 and 5e. Power functions were fitted to each data set by regression analysis (R^2 values of 0.47–0.76) and used to estimate the pre-mining Cu concentration for each ferricrete sampling location. Pre-mining Cu concentrations were not estimated for Swift Gulch because the relationship between dissolved Cu concentration and the Fe/Cu ratio in Fe-precipitates was not significant ($p = 0.22$). The small range of Cu concentrations in Paymaster Creek limits the utility of the equation for Paymaster Creek. The reason the slope of the Cu equation for Paymaster Creek is opposite that of the Cu equations for Daisy and Fisher Creek is not clear. The Cu content of Fe-precipitates in Daisy and Fisher Creek likely is controlled by pH, which varies considerably in each

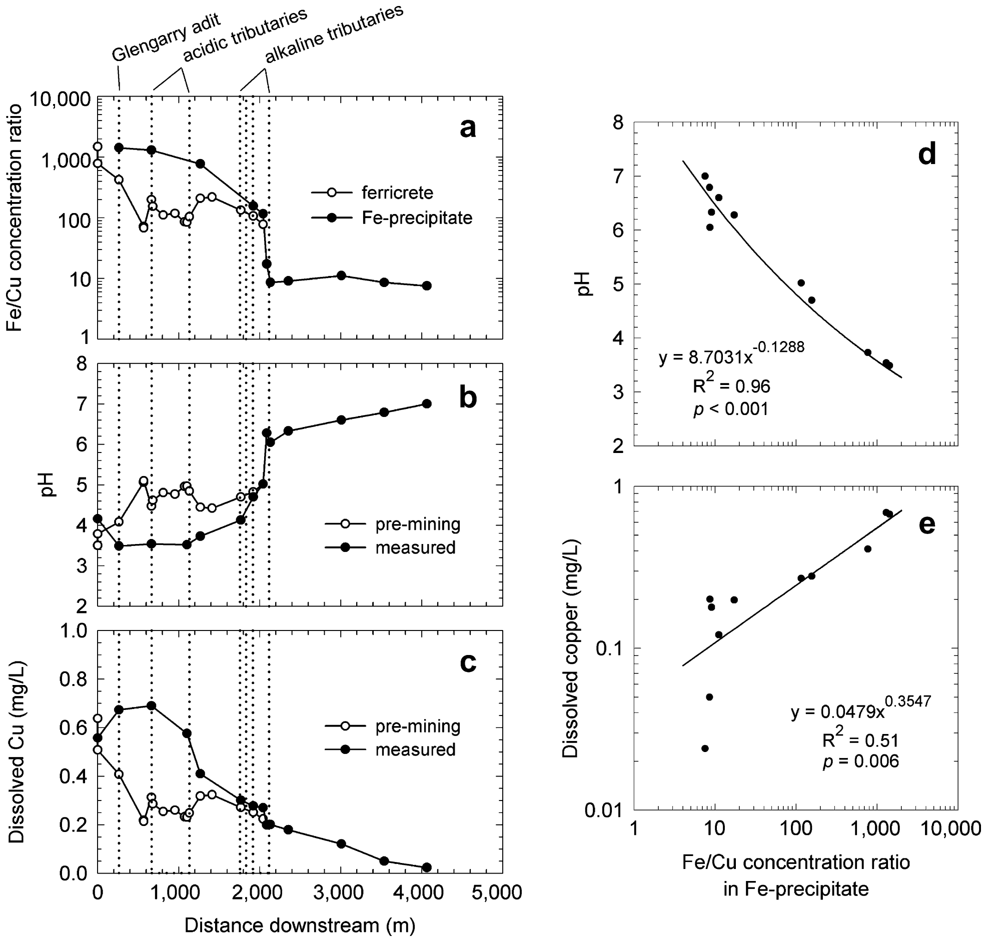

Fig. 3. Downstream profiles of (a) Fe/Cu concentration ratio in ferricrete and Fe-precipitates, (b) estimated pre-mining and measured pH, and (c) estimated pre-mining and measured dissolved Cu concentration. Estimation models for (d) pre-mining pH based on relationship of measured pH and Fe/Cu ratio in Fe-precipitates, and (e) pre-mining dissolved Cu concentration based on relationship of measured dissolved Cu concentration and Fe/Cu ratio in Fe-precipitates for Fisher Creek. Inflows noted in panels a–c were identified by the detailed synoptic sampling of Kimball et al. (1999).

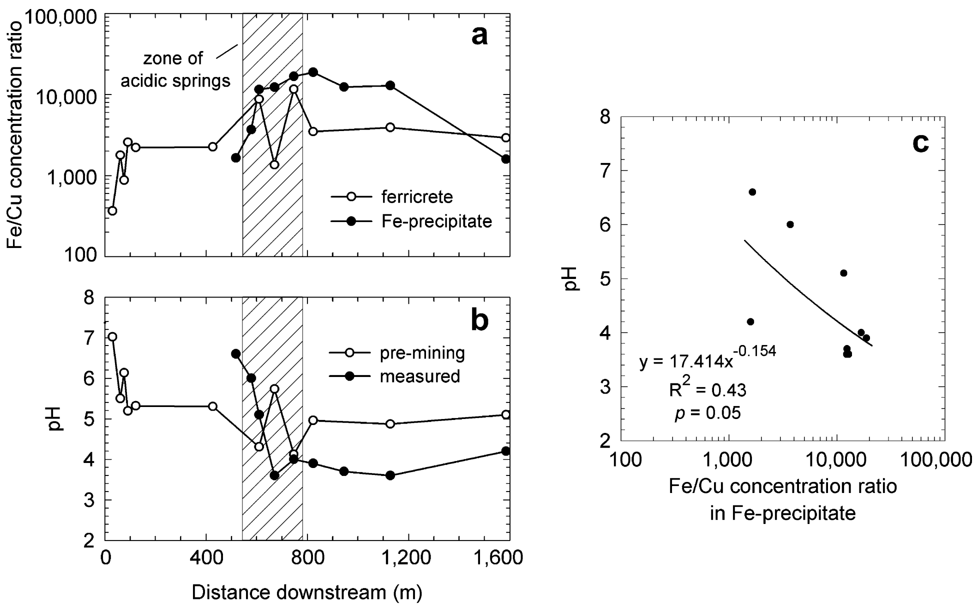

Fig. 4. Downstream profiles of (a) Fe/Cu concentration ratio in ferricrete and Fe-precipitates and (b) estimated pre-mining and measured pH. (c) Estimation model for pre-mining pH based on relationship of measured pH and Fe/Cu ratio in Fe-precipitates for Swift Gulch.

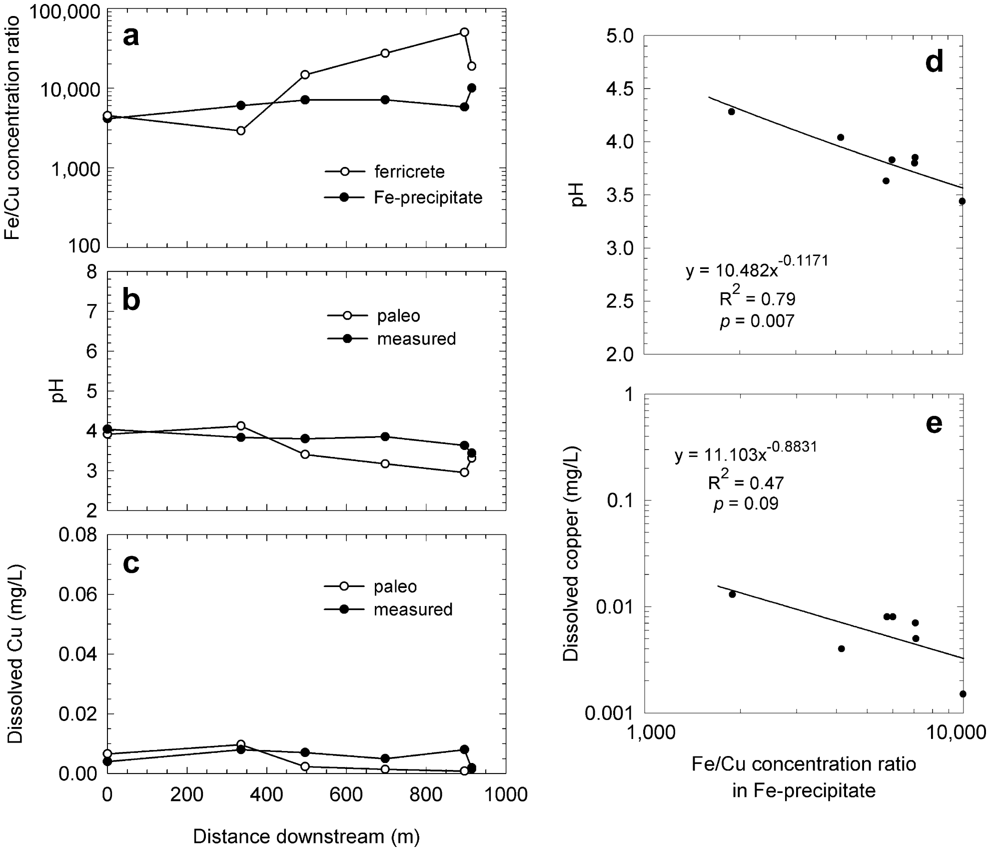

Fig. 5. Downstream profiles of (a) Fe/Cu concentration ratio in ferricrete and Fe-precipitates, (b) estimated paleo and measured pH, and (c) estimated paleo and measured dissolved Cu concentration. Estimation models for (d) paleo pH based on relationship of measured pH and Fe/Cu ratio in Fe-precipitates, and (e) paleo dissolved Cu concentration based on relationship of measured dissolved Cu concentration and Fe/Cu ratio in Fe-precipitates for Paymaster Creek. Measured Cu concentration of <0.003 mg/L at 914 m is plotted as 0.0015 mg/L in panels c and e.

stream. In contrast, the Cu content of Fe-precipitates in Paymaster Creek probably is not controlled by pH, which varies little in this stream, but instead by a concentration-based relationship in which the Cu content of the Fe-precipitates (Table 3) is directly proportional to the aqueous Cu concentration.

The profile of estimated pre-mining Cu concentrations for Daisy Creek (Fig. 2c) shows that the highest concentrations (mean = 8.5 mg/L; range = 4.1–14 mg/L) were just downstream from the McLaren mine in an area where an extensive ferricrete apron formed over glacial till between 0 and 481 m. The measured concentrations in this reach (mean = 11.7 mg/L; range = 4.66–15.6 mg/L) were, on average, almost 40% higher than the estimated pre-mining values. Further downstream, the neutral ground-water inflows currently near the toe of the ferricrete apron likely existed in the past and, as occurs today, caused a decrease in Cu concentration downstream from 481 m. The pre-mining concentrations then remained at nearly the same level (2.9–3.9 mg/L) for the remaining part of the ferricrete deposits (545–1105 m), and closely matched the measured concentrations of 3.54 at 703 m and 2.81 downstream from the ferricrete reach at 1600 m.

The profile of estimated pre-mining Cu concentrations for Fisher Creek (Fig. 3c) shows conditions without the influence of the inflow from the Glengarry adit (263 m), which was the primary mining-related source of metals to the stream (Kimball et al., 1999). Upstream from the Glengarry adit (at 0 m), estimated pre-mining Cu concentrations (0.51–0.64 mg/L) were similar to the measured concentration (0.558 mg/L), indicating that the measured Cu concentration likely represents natural background conditions. Between 0 and 570 m, the pre-mining concentration decreased to 0.21 mg/L while the measured concentration increased to 0.690 mg/L (at 666 m) owing primarily to the inflow from the adit at 263 m. The pre-mining concentration decrease in this reach suggests that Cu was either being diluted by inflows or being precipitated. Between 666 and 1412 m (Fig. 3c), the estimated pre-mining Cu concentrations (0.23–0.33 mg/L) were constant to slightly increasing. Streamflow presumably was increasing in this reach as it does today (Kimball et al., 1999) indicating that inflows were adding Cu to the stream. The increase at 666 and 681 m (Fig. 3c) coincides with the location of a tributary (FC-2 in Fig. 1 of Kimball et al., 1999) that contributed acid and Cu. Similarly, the pre-mining increase at 1267 and 1412 m likely was caused by the same acidic tributary (FCT-14 at 1134 m) and diffuse ground-water inflows identified by the detailed synoptic sampling of Kimball et al. (1999) in this unmined reach. These results indicate that locations of metal-rich ground-water discharge to the stream may be the same today as they were thousands of years ago. Near the downstream end of the ferricrete deposits (1768–2042 m), the estimated pre-mining concentrations (0.22–0.27 mg/L) were almost the same as the measured concentrations (0.270–0.301 mg/L).

For Paymaster Creek, the profile of paleo Cu concentrations estimated from the ferricrete deposits (Fig. 5c) ranged from 0.0008 to 0.010 mg/L. These values are very similar to measured Cu concentrations (<0.003–0.008 mg/L), as would be expected for an unmined catchment.

5. Discussion

The widespread applicability of the proposed method relies on the similarity in geochemical constituents and reactions that occur in catchments affected by acid drainage from sulfidic rocks. The abundance of pyrite as a source of acid and Fe and the dominance of pH-dependent Fe geochemistry ensure similar geochemical processes in all streams as pH increases downstream from the primary source areas where stream water is most acidic. The general sequence has Fe-minerals precipitating abundantly from solution as pH rises above ~3.5 and Al-mineral precipitation predominating further downstream where pH is higher than ~5 (Lee et al., 2002). Less abundant trace metals also have a downstream, pH-dependant pattern, with Pb tending to co-precipitate or sorb first, then Cu, and Zn at near neutral pH (Webster et al., 1998; Kimball et al., 1999; Munk et al., 2002). The downstream pattern of the Fe/Cu ratio is related to stream pH, which is a primary determinant on the mineral-solubility and adsorption-desorption reactions that control partitioning of metals between solid and aqueous phases (Drever, 1982). This sequence of reactions is the cause for the downstream decrease in Fe/Cu ratios in both ferricrete and Fe-precipitates in the mining-affected streams that were studied. However, the decrease in the Fe/Cu ratios for Fe-precipitates occurs farther downstream in the mining-affected streams than the decrease for ferricrete. Note that Fe/Cu ratios are higher in Fe-precipitates than in ferricrete upstream from 703 m in Daisy Creek (Fig. 2a), between the Glengarry adit and 2042 m in Fisher Creek (Fig. 3a), and between the acidic springs and 1128 m in Swift Gulch (Fig. 4a). This downstream displacement of higher Fe/Cu ratios in Fe-precipitates is the main factor that indicates that mining-related acid drainage has decreased instream pH and increased Cu concentrations from pre-mining levels.

5.1. Method assumptions

The proposed method relies on several critical assumptions. First, it must be assumed that pre-mining alluvial ferricretes and modern Fe-precipitates share a common origin—colloidal precipitates that form in streams with acidic drainage. Ferricretes have many similarities in terms of morphology, mineralogy and trace-metal composition to the Fe-precipitate coatings that form in present-day streams, and both occur as laminated deposits within streambed sediment (Furniss, 1998; Furniss and Hinman, 1998; Verplanck et al., 2007; Wirt et al., 2007). Ferricrete cements from Daisy, Fisher and Paymaster Creeks contain primarily goethite (Morris et al., 2000; Poage et al., 2000; Sjostrom et al., 2004). Modern streambed precipitates in these streams also contain Fe-precipitate minerals (e.g., ferrihydrite, schwertmannite) that are goethite precursors and that transition to goethite during initial stages of preservation (Morris et al., 2000).

Second, in circumstances where samples were collected from ferricretes deposited a long time prior to mining (e.g., more than 0.5–1 ka), it is assumed that the hydrogeochemical system producing the ferricretes was stable through time and therefore produced ferricretes with constant trace metal content prior to mining. This assumption appears to be valid for this study because ferricretes that differed in age by thousands of years and that were sampled from different stratigraphic levels at single sites along Fisher, Daisy and Paymaster Creeks were consistent in trace metal concentration (Hinman et al., 2000).

A third assumption concerns the longitudinal difference in mechanisms of Fe-precipitate formation. In the upper stream reaches where pH is lower and stream gradient is higher, Fe-precipitates grow as a hard coating directly onto the stream substrate. In the lower reaches, Fe-precipitates form in the water column, drift downstream for some distance, and eventually settle and accumulate on the streambed as thick, gelatinous masses (Gammons et al., 2005). This downstream transport should not present a problem for the proposed estimation method because the hydromorphic mechanisms occurring today are the same as those that would have occurred during ferricrete formation, and probably more importantly, because the settled Fe-precipitates presumably are at chemical equilibrium with the water column.

Fourth, it is assumed that the Cu content of Fe-precipitates remains constant during conversion to ferricrete and that Cu is not then leached from or added to the ferricrete through time. This assumption is important because the conversion of Fe-precipitates to ferricrete typically involves the transformation of amorphous and less thermodynamically stable minerals such as ferrihydrite and schwertmannite in Fe-precipitates to more crystalline and stable minerals such as goethite in ferricrete. This difference in mineralogy has been demonstrated for Daisy, Fisher, and Paymaster Creeks by Morris et al. (2000), who analyzed three or four ferricrete samples from each of these streams and single Fe-precipitate samples from Fisher and Paymaster Creeks using X-ray diffraction (XRD) and transmission Mossbauer spectra. Goethite was the only Fe phase identified in the ferricrete samples, whereas the Fe-precipitate samples contained primarily schwertmannite with some goethite (Morris et al., 2000). Single Fe-precipitate samples collected from Daisy and Fisher Creeks (Poage et al., 2000) and from Paymaster Creek (Sjostrom et al., 2004) had goethite as the only Fe phase identifiable by XRD.

Laboratory studies of the transformation from jarosite, schwertmannite and ferrihydrite to more stable Fe-oxide solid phases such as goethite support the assumption that large changes in Cu concentration do not occur during these phase transformations in the field. Martínez and McBride (1998) monitored solid-phase transformation and metal solubility after co-precipitation of Cu with ferrihydrite formed by slow (to simulate natural conditions) titration at pH 6. The Fe/Cu concentration ratio in the initial ferrihydrite was ~440, a value within the range for ferricrete and Fe-precipitate from the study areas. The uptake and release of co-precipitated Cu were monitored during aging at room temperature for 200 days and then at 70 °C for 60 days. The solid phase had lost a minor amount (5%) of the co-precipitated Cu after 100 days, and no further loss was measured during the last 160 days. Welch et al. (2007) showed that most transition metals (including Cu) were retained in the solid phase during experimental dissolution of jarosite because metals released during dissolution were adsorbed or co-precipitated by (unidentified) Fe-precipitate phases that formed during the dissolution. Kumpulainen et al. (2007) found that trace-metal/Fe ratios in oxalate total extractions of schwertmannite, ferrihydrite, and goethite were similar, suggesting that during the phase transformation of schwertmannite or ferrihydrite to goethite, trace metals bound to the precursor Fe phase would be bound in the transformation product. Experiments by Acero et al. (2006) showed that a substantial (~80%) amount of Cu is retained during the schwertmannite-to-goethite transformation. The apparent retention of Cu during the transformation of ferrihydrite and schwertmannite to more crystalline Fe oxides likely happens because trace metals do not occupy binding sites solely on Fe-oxyhydroxide surfaces but can become incorporated into the oxide through active precipitation of the oxide or diffusion into the oxide (Webster et al., 1998). When present as aqueous species during the formation of initial amorphous Fe phases, metals are adsorbed and incorporated throughout the Fe aggregate. During subsequent transformation to and growth of Fe-oxides, these metals, which were buried in the aggregate, are protected from going into solution. The opposite would be true for metals bound to the surface, which is where metals would be expected to be if the initial Fe phases formed and then were introduced to metal-rich solution. In addition, Cu can be incorporated directly into the crystal structure of Fe oxides via isomorphous substitution (Cornell and Schwertmann, 1996). To the authors' knowledge, only one study has suggested that a substantial amount of Cu would be lost during these transformations. Schroth and Parnell (2005) examined samples of precipitates collected from acid mine drainage and hypothesized a 56% loss of Cu during the schwertmannite-to-goethite transformation, but they compared schwertmannite and goethite samples that were precipitated from different waters; therefore, their results are not as applicable as the previously cited laboratory studies.

If some Cu is lost during the transformation of schwertmannite or ferrihydrite to goethite, the effect on the estimated values of pre-mining pH and dissolved Cu concentration would be relatively small. For example, assuming only 80% retention of Cu during the transformation (Acero et al., 2006), estimated pre-mining (or paleo) pH would be $\leqslant 0.16$ pH unit higher in Daisy and Fisher Creeks, $\leqslant 0.25$ pH unit higher in Swift Gulch, and $\leqslant 0.11$ pH unit higher in Paymaster Creek than the values shown in Figs. 2, 3, 4 and 5b, respectively. For dissolved Cu, estimated pre-mining values would be $\leqslant 19\%$ lower in Daisy Creek, $\leqslant 10\%$ lower in Fisher Creek, and $\leqslant 22\%$ higher in Paymaster Creek than the values shown in Figs. 2, 3 and 5c, respectively.

Finally, it is assumed that Fe/Cu ratios in Fe-precipitates directly reflect the pH and dissolved Cu concentration of the stream even though sorption of Cu to Fe-precipitates can be affected by other geochemical factors including complexation with SO_4 and dissolved organic C (DOC), competitive adsorption with other metals, sorbate/sorbent ratio, and specific surface area. As described below, the effects of these other factors generally are small but would cause the potential error in the estimated values of pre-mining pH and dissolved Cu concentration to be greater than that attributed above to loss of Cu during mineral transformation. Further testing could help quantify this potential error.

The adsorption of Cu by ferrihydrite, schwertmannite, and goethite increases with increased SO_4 concentration, with laboratory studies showing increases of <5% at a Fe/Cu ratio of 33 and as much as 25% at a Fe/Cu ratio of 530 as SO_4 concentration was increased from 0 to 2000 mg/L (Swedlund and Webster, 2001). The actual effect of SO_4 on Cu adsorption in the study areas would be less than these values because the variation in SO_4 concentration (Table 3) generally was much less than 2000 mg/L. Similarly, Cu adsorption can increase when pH is low and DOC concentration is high. Laboratory studies have shown that Cu adsorption to goethite did not increase as DOC concentration was increased from 0 to 28 mg/L but did increase at 56 mg/L (Jönsson et al., 2006). Similarly, Ali and Dzombak (1996) documented enhanced Cu adsorption to goethite in the presence of phthalic acid at a DOC concentration of 21 mg/L. Although not measured in the study streams, DOC likely occurred at concentrations that were lower than 28 mg/L and in forms that were less reactive than phthalic acid. In addition, Webster et al. (1998) concluded that organic C did not enhance Cu adsorption to schwertmannite, and Munk et al. (2002) concluded that humic substances enhance cation sorption only at low pH and low SO_4 concentration. Competitive adsorption with other metals could be a factor, but the difference in the pH ranges for the adsorption edge of Cu relative to the adsorption edges of other metals lessens the potential effect of this factor.

The amount of sorbate relative to either sorbent or the specific surface area of the sorbent are important controls on adsorption as many studies have demonstrated higher adsorption with increased sorbent or specific surface area. This demonstrates the interdependence of pH, Cu concentration, and the amount and specific surface area of Fe-precipitate in controlling the amount of Cu that adsorbs to Fe-precipitates. In general, sorption of Cu^{2+} to a surface (S) can be written as a proton exchange in which Cu^{2+} and H^+ compete for the same sorption sites:

$$\mathrm{SOH} + \mathrm{Cu}^{2+} - \mathrm{H}^{+} = \mathrm{SO} \cdot \mathrm{Cu}^{+} \tag{1}$$

The relationship between Fe/Cu ratio [represented by $(SOH)/(SO{\cdot}Cu^+)$], Cu concentration, pH, and an equilibrium constant (K) can be written as

$$\frac{(\mathrm{SOH})}{(\mathrm{SO} \cdot \mathrm{Cu}^{+})} = K \times \frac{(\mathrm{H}^{+})}{(\mathrm{Cu}^{2+})} \tag{2}$$

Eq. (2) does not have a unique solution. For example, the same Fe/Cu ratio would result if H^+ concentration was doubled (equivalent to a decrease in pH of 0.3 units) and Cu concentration was doubled, assuming a fixed amount of Fe-precipitate. However, assuming that mining just accelerates the weathering processes that already were producing the Cu, acid and Fe input to a stream prior to mining, the relationships between Fe/Cu ratio and either Cu concentration or pH should not change substantially after mining.

5.2. Method evaluation

The validity and overall reasonableness of the method were evaluated in two ways. The first was by comparing measured and estimated paleo pH and Cu concentration data for a control stream (Paymaster Creek) that was unaffected by mining. In this catchment, sulfide mineralization produces naturally acidic waters with elevated Cu concentrations. It was assumed that the water chemistry and geochemical processes involved in Fe-precipitate formation operating today should be unchanged from those processes operating in the past, and therefore, measured stream water chemistry should be the same as the water chemistry estimated from ferricrete. Although limited by a small range of spatial variability, the pH and Cu models (Fig 5b and c) produce longitudinal profiles that are essentially the same as they are today, thus suggesting that the method works. Nevertheless, further evaluation of the method is warranted in other unmined watersheds where stream pH and Cu concentration have larger ranges than in Paymaster Creek.

A second check on the validity of the method was to determine whether inflows, particularly from areas where hydrologic or other effects of mining are absent, had a consistent effect on both the pre-mining and measured profiles of pH and Cu concentration. These inflows could contribute either acidic and metal-rich water that would decrease pH and increase Cu concentration in the stream or alkaline water that would cause neutralization and loss of aqueous Cu. Perhaps the most noteworthy example of this effect of inflows is the convergence of pre-mining and measured pH and Cu concentration at the downstream end of the ferricrete deposits. For both Daisy Creek and Fisher Creek, the pre-mining and measured values converge to essentially the same value in these reaches. It is noteworthy that this convergence occurs even though the values at the downstream end of the ferricrete deposits were quite different in Daisy Creek ($\mathrm{pH} \cong 4.3$; $\mathrm{Cu} \cong 3.6$ mg/L) than in Fisher Creek ($\mathrm{pH} \cong 5.0$; $\mathrm{Cu} \cong 0.3$ mg/L). For Daisy Creek, alkaline inflows near 704 m (identified by Nimick and Cleasby, 2001) provide some neutralization (Fig. 2b). For Fisher Creek, Ca-rich inflows between 1756 and 2116 m (identified by Kimball et al., 1999) cause the rapid neutralization of pH indicated in the middle of the measured pH profile (Fig. 3b). These inflows, which drain carbonate terrain unaffected by mining, almost certainly existed prior to mining. Pre-mining and measured pH did not converge at the downstream end of the ferricrete deposits in Swift Gulch because no neutralizing inflows are present.

Other examples of the effect of inflows include acidic tributaries as shown in the pre-mining and measured profiles for Fisher Creek (Fig. 3b and c) at 666 and 1134 m. The pre-mining profile shows decreased pH and increased Cu concentration where these tributaries enter Fisher Creek. Similar effects (decreased pH and increased Cu concentration) are not as evident in the measured record at these locations because the composition of the tributary water was similar to that in Fisher Creek, which was being degraded by the inflow from the upstream Glengarry adit. Similarly, the location of acidic springs along Swift Gulch (shown in Fig. 4a,b) are the same as they were before mining, but the amount of acid contributed by present-day inflows is apparently much greater. The inflows coincide with a shear zone that extends southward into the mined area (Gabelman et al., 2005). The shear zone presumably served as a conduit for ground water affected by pre-mining acid rock drainage, and more recently, by acid mine drainage as well.

5.3. Assessment of mining effect and implications for restoration efforts

Mining appears to have adversely affected at least the upper 481 m of Daisy Creek. Dissolved Cu concentrations were increased almost 40%, from a mean estimated pre-mining value of 8.5 mg/L to a mean measured value of 11.7 mg/L, and pH was decreased by about 0.6 pH units from a mean estimated pre-mining value of 3.8 (range = 3.4–4.2) to a mean measured value of 3.16 (range = 3.0–3.4) upstream from 481 m. Although conditions were not as acidic or metal rich before mining, pH was low and Cu concentrations were high prior to mining.

Mining appears to have adversely affected about 1.8 km of Fisher Creek between the Glengarry adit at 263 m downstream to 2042 m. Dissolved Cu concentrations increased as much as 230%, from the estimated pre-mining value of 0.21–0.690 mg/L in the reach between 570 and 666 m, and pH decreased by a pH unit or more after mining between 570 and 1103 m. Thus, mining appears to have decreased pH and increased Cu concentration to a greater degree in Fisher Creek than in Daisy Creek.

In Fisher Creek upstream from the Glengarry adit, the estimated pre-mining pH (3.5–3.8) is slightly lower than the measured value (4.16), indicating that the pre-mining condition was worse than the measured condition. This unique situation could have two possible explanations. The first is that sulfide oxidation may have lessened after the sampled ferricrete was deposited and resulted in improved water quality in Fisher Creek. The pre-mining pH for Fisher Creek upstream from the Glengarry adit is based on very old ferricrete (the one sample that has been dated from this upstream area is 5.650 ± 0.050 ka old; unpublished data, G. Furniss). Thus, the difference in pH over this long time period could be reasonable because fresh surfaces of the abundant sulfidic rock that crops out in this headwater area (Elliot et al., 1992) presumably would have been exposed after the retreat of the late Pleistocene mountain ice cap. Weathering of these surface materials may have produced more acid and Cu during the earlier millennia of the Holocene than during later millennia, causing pH to increase slightly during the entire period. This possibility emphasizes the importance of using samples of relatively young ferricretes. A second explanation is that mining activity caused the increase in pH. A raise extending vertically from the Glengarry adit to land surface daylights into and drains the sulfidic rock that crops out in this headwater area. Prior to mining, drainage from the sulfidic rocks likely would have flowed into headwater tributaries of Fisher Creek. After construction of the raise, the acid and metal load in this drainage water no longer would have flowed to upper Fisher Creek.

Mining appears to have adversely affected the lower 1 km of the Swift Gulch study reach, and these effects may extend farther downstream. Almost the entire study reach, including the part that was dry in September 2004, was estimated to be at least mildly acidic ($\text{pH} \leqslant 6.1$) before mining. Mining appears to have decreased pH to 4.2 or less downstream from 671 m, and in some places, by almost two pH units to 3.6.

The ferricrete deposits in Daisy Creek, Fisher Creek, and Swift Gulch indicate that pre-mining conditions were mildly to strongly acidic owing to natural weathering of sulfidic rocks in each catchment. Therefore, although restoration efforts focused on eliminating mining-related sources of acid and metals could produce some improvements in water quality, these improvements likely would not be sufficient in affected reaches such that pH would be > 6.5 to meet the State of Montana surface water-quality standards and Cu concentrations would be < 0.014 mg/L (assuming 100 mg/L hardness) to meet the State of Montana acute aquatic-life standard (Montana Department of Environmental Quality, 2006). In addition, restoration efforts may have a limited effect in improving water quality in Daisy and Fisher Creeks in the reaches downstream from the ferricrete deposits because the measured pH and Cu concentration already are similar to the estimated pre-mining values.

6. Conclusions

A method for estimating pre-mining pH and dissolved Cu concentrations in streams with acidic drainage is presented. The method can be employed with relative ease and generates reasonable results. Differences in Fe/Cu concentration ratios are identified between the terrace deposits of alluvial ferricrete dated from middle Holocene to present-day and the Fe-precipitates presently forming in the streams to distinguish current (2002–04) conditions from natural background. Empirical relationships are determined between Fe/Cu ratios for Fe-precipitates and stream-water pH or Cu concentration. These relationships then are used to estimate pre-mining stream pH and dissolved Cu concentration from the Fe/Cu ratios in ferricrete. The reliability of this method is demonstrated by (1) the similarity in estimated paleo and measured profiles for pH and Cu concentration in Paymaster Creek, a stream undisturbed by mining and exhibiting naturally acidic conditions, and (2) the consistent effect of alkaline and acidic inflows on both pre-mining and measured profiles. However, additional testing of the method is warranted, particularly by further evaluation of the method assumptions, by applying the method in other unmined watersheds to determine if estimated pre-mining values match measured values, and by comparing results of several pre-mining water-quality estimation methods in single watersheds.

The estimated pre-mining pH in the headwaters of Daisy and Fisher Creeks generally was between 3.5 and 4 and Cu concentrations ranged from 4.1–14 mg/L in Daisy Creek and 0.51–0.64 mg/L in Fisher Creek. In Swift Gulch, estimated pre-mining pH for almost the entire study reach was 4.9–6.1. Within each catchment, high Cu concentrations in Fe-precipitates extend further downstream than high Cu concentrations in ferricrete deposits. The downstream spatial extension of high Cu concentration in Fe-precipitates is a result of the mining-induced lowering of stream pH and the resulting downstream transport of metals in solution before neutralization caused precipitation or sorption of the metals.

The pre-mining water-quality estimation method presented here has the potential for use in monitoring the progress of remedial efforts at mine sites where ferricrete deposits are present. Once longitudinal profiles of Fe/Cu ratios are established for the ferricrete deposits, monitoring of Fe and Cu concentrations in Fe-precipitates before, during, and after remedial actions provides a method for documenting the stream's response to remediation. A reasonable remediation objective might be realized when the downstream pattern of Fe/Cu ratios in the Fe-precipitates corresponds to the pattern found in the stream's pre-mining ferricrete deposits. As conditions improve, the downstream pattern of Fe/Cu ratios in Fe-precipitates likely would begin to migrate upstream to more closely resemble the pattern in the ferricrete. Although it may not be possible to mitigate all effects of mining or meet water-quality standards, a lack of substantial change in the downstream pattern of Fe/Cu ratios might suggest that additional remediation activities would be needed to improve water quality. Developing a more thorough understanding of ferricrete deposits and their relationship to natural acid rock drainage in mining-affected catchments might be an important step in planning cost-effective mine reclamation.

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