TECHNICAL ARTICLE



Effect of Ore Mineralogy and Bedrock Lithology on Metal Loading Rates and Acid-Mine Drainage: Bayhorse Creek, Idaho and the North Fork of the American Fork River, Utah

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Abstract

Metal contamination of the water in two streams was investigated at the Ramshorn Mine along Bayhorse Creek in Idaho, and the Pacific Mine along the North Fork of the American Fork River in Utah. The studies were conducted to determine what remediation measures should be implemented at each site to reduce metal loads in the streams. Discharge measurements and chemical analyses of filtered and unfiltered water samples allowed dissolved and total metal loads to be calculated. Copper, Fe, Mn, Pb, Zn, and As were found at both sites, and Cd also was present at the Utah site. Of these, Fe had the highest dissolved and total loading rates at the Ramshorn Mine, with Mn and Zn having intermediate rates; Fe and Zn had the highest loading rates at the Pacific Mine. Hydrous ferric oxides, particularly ferrihydrite, are abundant at both sites. Pyrite is the iron source at the Pacific Mine, while it is siderite at the Ramshorn Mine. The lack of sulfide at the latter site inhibits acid mine drainage (AMD) formation, and the presence of dolomite provides abundant alkalinity to neutralize any AMD that might be generated. PHREEQC was used to gain insight into the metal phases and oxidation states, to calculate saturation indices, and to perform surface sorption modeling. The results suggest that most of the metals at both sites are transported in the suspended rather than dissolved state, As occurs exclusively in the less toxic As⁵⁺ form, and several metals are likely sorbed to ferrihydrite. Based in part on the results of these studies, the US Forest Service removed the tailings at the Pacific Mine site, but only capped and regraded the tailings pile at the Ramshorn Mine.

Keywords Surface water · Groundwater · Mining

Introduction

Environmental regulatory agencies, such as the U.S. Environmental Protection Agency (EPA), recognize that waste from abandoned mines contaminates surface water, groundwater, soil, and air. The topic of mine remediation has been

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researched thoroughly (Alpers and Blowes 1994; Evangelou 1995; Evangelou and Zhang 1995; Gray 1996; Jambor and Blowes 1994, 1998; Keith and Vaughn 2000; Salomons 1995). Despite this work, effective remediation is yet to be implemented in many abandoned mines across the western U.S.

The EPA estimates that 40% of the headwaters in the U.S. have been degraded due to abandoned hard rock mining (USEPA 2000). Although the National Environmental Protection Act requires mining companies to create a clean-up plan for new mines during the project proposal stage, hundreds of mines in the western U.S. were abandoned before remediation plans were required (Tordo et al. 2000). The EPA has listed many abandoned mines under the Comprehensive Environmental Response, Compensation, and Liability Information System (CERCLIS), more commonly known as Superfund, which requires an analysis and assessment of the need for clean-up based on metal loading rates. The U.S. Forest Service (USFS) is responsible for



this analysis and assessment for abandoned mines located on Forest Service lands.

Although acid mine drainage (AMD) is a term commonly used to describe acidic water derived from mines, the Global Acid Rock Drainage (GARD) Guide (INAP 2009) encourages the use of the all-inclusive term Acid Rock Drainage (ARD). In addition to ARD, neutral mine drainage (NMD) is a term applied to mine drainage that has a pH of about six or greater (Plumlee et al. 1999). Pyrite (FeS₂) is by far the dominant mineral responsible for acid generation (Nordstrom and Alpers 1999; Stumm and Morgan 1996). However, ore deposits can contain other types of sulfide minerals, many of which do not generate acid when they are oxidized. Should these metals remain in solution, NMD will be generated. Metal concentrations in NMD tend to be lower due to the formation of secondary mineral phases and increased sorption of metals onto sorbents such as metal (oxy)hydroxides, clay minerals, and reactive particulate carbon (Smith 1999).

The USFS contracted with the authors and Utah State University (USU) to investigate the risk posed to human health and the environment by two abandoned mines; the Pacific Mine in Utah, and the Ramshorn Mine in the adjacent state of Idaho to the north (Fig. 1). However, the two studies were not conducted simultaneously; they were performed 9 years apart. The Pacific Mine was investigated first because the USFS deemed it a higher environmental and health risk than the Ramshorn Mine.

Burk (2004) conducted an investigation of metal contributions from groundwater to the North Fork of the American Fork River, which flows adjacent to the Pacific Mine. The results of this investigation (Lachmar et al. 2006) demonstrated that the dissolved loading rates for As, Cd, Cu, Fe, Mn, Pb, and Zn to the river from the tailings were sufficiently high to justify removing the tailings.

McDonough (2015) conducted the subsequent investigation at the Ramshorn Mine, which is adjacent to Bayhorse Creek. The two mine sites appeared very similar visually, with abundant hydrous ferric oxides (HFO) lining both the North Fork of the American Fork River and Bayhorse Creek. It was anticipated that groundwater flowing through the tailings could be contributing high dissolved metal loading rates to that creek, too. However, this did not prove to be the case. The reasons for the differences in metal loading rates at these two mine sites is the focus of this paper.

Pacific Mine

The Pacific Mine is an abandoned silver and lead mine. Historical accounts differ on when mining commenced. According to Keetch (1978), the Pacific Mining and Milling Company was incorporated on 24 February 1900. However, Crosland and Thompson (1994) assert that the claims were not acquired until 1904. The mill was

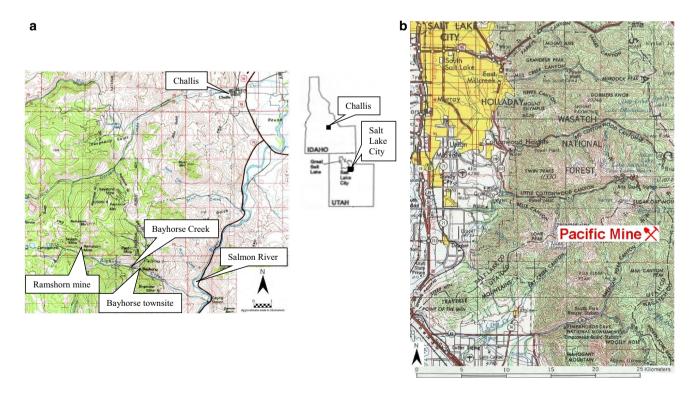


Fig. 1 Location of the Ramshorn (a) and Pacific (b) Mines relative to Challis, Idaho and Salt Lake City, Utah, respectively



permanently shut down in 1936 (Stauffer 1971), and the last shipment of ore from the mine was made in about 1953 (Johnson n.d.).

The Pacific Mine consists of several tailings piles and a collapsed portal that has water discharging from it. The workings at the Pacific Mine are mainly in the Tintic Quartzite and the Ophir Shale. The main ore body is located in the Pacific fissure, which is a normal fault that strikes at about N 45°E and dips about 50°NW. Another ore body is the Copper fissure, which has a more easterly trend and steeper dip than the Pacific fissure. Mineralization in the Pacific fissure contains pyrite, galena (PbS), and locally abundant sphalerite (ZnS). Barite (BaSO₄) is found as a gangue mineral and tetrahedrite (Cu₁₂Sb₄S₁₃) is found in the Copper fissure (Calkins et al. 1943).

The water discharging from the collapsed portal contains HFO (Ludlow 2001) and high concentrations of As, Cd, Cu, Pb, and Zn (UDOGM 1993). Fitzgerald (2000) reported that in 1988, the USFS found the metal-contaminated water was having a detrimental impact on macroinvertebrates. Fish were sampled in 1998 and it was discovered that the brown trout (Salmo trutta) and cutthroat trout (Salmo clarkii) contained As, Cd, and Pb in their tissues at concentrations that would be hazardous to human health if consumed. The Utah Division of Oil, Gas and Mining (UDOGM) constructed a drainage channel to direct the portal effluent into a beaver pond wetland, which effectively removes suspended metals or those that have been sorbed onto HFO. Dissolved and total concentrations of As, Cu, and Pb in the effluent were significantly reduced after passing through the pond, but Cd and Zn concentrations were not (Ludlow 2001).

Ramshorn Mine

The Ramshorn Mine is an abandoned silver, lead, and copper mine. Mineralization was discovered in the Bayhorse mining district in 1872 (Wells 1983). The Ramshorn Mine property was discovered and purchased in August of 1877, and mining commenced soon thereafter. By 1959, the Umont Mining Company had leased the mine, but had lost interest by 1962. Inspiration Development Company leased the mine in 1979, but discontinued operations in 1980 (Mitchell 1999).

The mine originally consisted of 17 tunnels and intermediate levels (Ross 1937). According to the Idaho Dept. of Environmental Quality (IDEQ 2003), exploration activities by the Inspiration Development Corporation from 1979 to 1981 obliterated the surface expression of most of the early mine workings. Today, only three collapsed adits reach the surface. The lower workings of the mine include the three adits, a tailings pile, a pond on the tailings pile, a small decrepit portal shed, a tramway ore loading station, and a

tramway terminus ore shed. The upper workings include one collapsed adit.

The Cambrian Bayhorse Creek Dolomite hosts deposits of As, Cu, and Pb, and to a lesser extent Zn. However, the ore deposits in the overlying lower Ordovician Ramshorn Slate are more valuable. They form elongated lenses or ovoid pipe-like bodies as veinlets, disseminations, breccia fillings, and as massive or discontinuous replacements (Worl et al. 1989). Mineralization is thought to have occurred during the Cretaceous period (Seal and Rye 1992) when granites from the Idaho batholith intruded preexisting sedimentary rocks (Skipp 1987). The principal ore minerals are siderite (FeCO₃) and tetrahedrite, though galena was also mined; both are argentiferous. Pyrite, arsenopyrite (FeAsS), chalcopyrite (CuFeS₂), and sphalerite are also found in small traces, but siderite is the primary gangue mineral (IDEQ 2003).

The Ramshorn Mine was listed by the EPA on the CERC-LIS in 2003 due to metal contamination in Bayhorse Creek. Ecology and Environment, Inc. (2010), acting as the Superfund Technical and Response Team (START), used in-field X-ray fluorescence (XRF), pH, and electrical conductivity (EC) on soil, creek sediment, and surface water samples to determine the severity of metal contamination in and around the tailings pile at the Ramshorn Mine site. Other analyses, such as metals, hardness, nitrate/nitrite, and sulfate, were performed at GEL Laboratories, of Charleston, South Carolina. The START analyses had high concentrations of As and Pb throughout the soil, sediment, and water samples. As a result, the EPA proposed three possible site remediation actions, of which in-place capping was chosen and completed during the late summer of 2011.

Methods

Sample Locations

Discharge measurements and water samples were collected at the locations shown on Fig. 2 (Pacific Mine) and Fig. 3 (Ramshorn Mine). Location SW-8 was at the Bayhorse townsite (Fig. 1). A set of sediment, tailings, and rock samples was taken at the Ramshorn Mine site as well.

Both mines are remote and accessible only with a four-wheel drive vehicle. Additionally, both sites are at high elevations where the bulk of the precipitation falls as snow during the winter months (November through May). Consequently, both sites are only accessible from June through October. Furthermore, discharges are very low during the winter months when temperatures remain below freezing, and there is a large and dramatic increase when the snow melts in the spring, followed by a gradual decrease during the 5 months when the sites are accessible. There are no



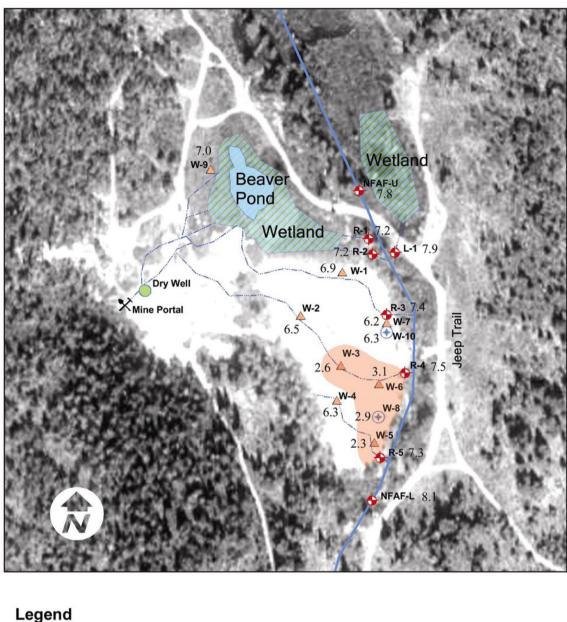




Fig. 2 Map of the Pacific Mine study area showing June 2002 well and surface water pH. The area where the tailings groundwater is very acidic has been highlighted (Lachmar et al. 2006; aerial photograph from; USGS 1995)

gaging stations on either the North Fork of the American Fork River or Bayhorse Creek. Consequently, the only discharge measurements available for either stream are the ones obtained for these two investigations.

Discharge Measurements

The discharges at two of the Pacific sites (NFAF-U and NFAF-L) and at six of the Ramshorn sites (SW-1, SW-5 through SW-8 and GW-3) were measured using the trapezoidal method (USGS 1980), in which the area of individual



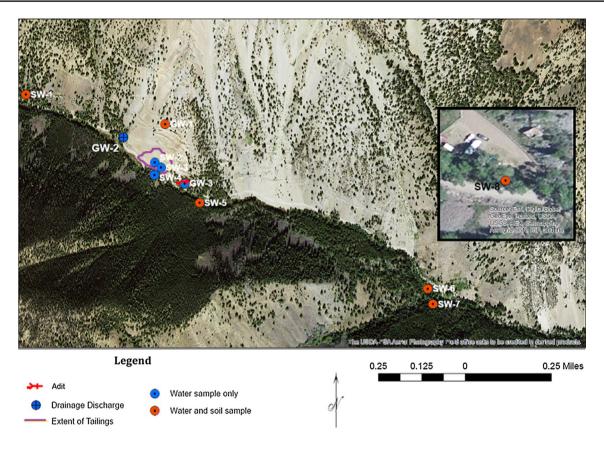


Fig. 3 Map of the Ramshorn Mine study area showing locations of discharge measurements, and water and sediment samples

trapezoids are multiplied by the average water velocity through each trapezoid, and then the individual discharges for each trapezoid are added together. The current velocity was measured in either 30 or 60 cm (1 or 2 ft) increments, depending on the width of the channel, using a Marsh McBirney current meter with a top-setting wading rod, and the 6/10-depth method for determining mean velocity (USGS 1980). The stream width was determined using a measuring tape strung above the channel from each bank, and the depth was measured with the wading rod.

The discharges at Pacific sites L-1 and R-1 through R-5, and at Ramshorn sites GW-1, GW-2, SW-2, and SW-3 were measured using the volumetric method (USGS 1980). A stopwatch was used to measure the time required to fill a 1400 or 2000 mL or 20 L (5 gal) container, depending on the discharge. Five measurements were made and the average (mean) time was used to calculate the discharge.

Water Sampling and Chemical Analyses

Samples to be analyzed for dissolved metals were filtered using a 0.45 μ m filter and then acidified to a pH \leq 2 with concentrated nitric acid. Unfiltered acidified samples to

be analyzed for total metals were only taken from NFAF-U, NFAF-L, L-1, and R-1 through R-5 at the Pacific Mine, and from SW-1, SW-5 through SW-8, and GW-3 at the Ramshorn Mine. Temperature, EC, pH, and alkalinity were all measured in the field prior to filtering and acidification. Temperature and EC were measured using a YSI 30 m, pH was measured using an Orion 230A m, and alkalinity was measured using a Hach field alkalinity kit. Dissolved oxygen (DO) was also measured in October for the Pacific Mine samples, and in August, September, and October for the Ramshorn Mine samples using a Hanna HI 9142 m.

All of the samples were analyzed using ICP-MS (inductively coupled plasma–mass spectrometry). The filtered samples were analyzed for Al, As, B, Ba, Ca, Cd, Co, Cr, Cu, Fe, K, Mg, Mn, Mo, Na, Ni, P, Pb, S, Si, Sr, and Zn by the Utah State University Analytical Laboratory (USUAL). Chloride concentrations were determined using a Lachat flow injector analyzer, which is an automated colorimeter. The unfiltered samples were analyzed at the Utah Water Research Laboratory (UWRL) and the Utah Veterinary Diagnostic Laboratory (UVDL) for the Pacific and Ramshorn samples, respectively.



Sediment Sampling and Analysis

Five stream sediment samples were collected once at four of the water sampling sites (SW-1 SS, SW-5 SS, SW-6 SS, and SW-8 SS) and the bedrock seep (GW-1 SS). These samples were collected with a shovel and placed in Ziploc[©] bags, and then were analyzed for metals using XRF. Because the samples were a heterogeneous mix of clast sizes, a representative sample was obtained from each Ziploc bag by sorting the sample into smaller proportionate piles using an aggregate soil sample splitter. Then the samples were oven dried and crushed for 1 min in a rock pulverizer, mixed with three to five drops of polypropylene film in a mortar and pestle, and transferred into an aluminum pellet cup and crushed using a force of 1000 kg in a manual press. The solid pellet was dried overnight and run on a Philips XRF for metal and oxide compounds. A sample of the Ramshorn Slate was also collected at the bedrock seep (GW-1 ROCK) and analyzed by XRF.

One tailings sample (SS-2) was collected at the Ramshorn Mine site and, along with three other samples (SW-1 SS, SW-5 SS, and GW-1 ROCK), analyzed by the UVDL using ICP-MS. The samples were weighed to 0.5 g and mixed with 5 mL of concentrated nitric acid. The mixture was heated at 120–130 °C for 14–16 h, and then hydrogen peroxide was added and the sample was diluted to 50 mL. The solution was further diluted by a 1:9 ratio for analysis of minor and trace elements (Soil & Plant Analysis Laboratory 2005).

Metal Loading Rates

Dissolved and total metal loading rates were calculated by multiplying the metal concentrations for the filtered and unfiltered samples, respectively, by the discharge. The values are reported in units of mg/sec. The net flux then was calculated for a segment of a stream, either between NFAF-U and NFAF-L for the North Fork of the American Fork River (Fig. 2), or between SW-1 and SW-5 (upper segment), SW-5 and SW-6 (middle segment), and SW-6 and SW-8 (lower segment) for Bayhorse Creek (Fig. 3). The net flux was calculated by subtracting the metal loading rates from the upper stream location plus any tributaries flowing into the stream between the upper and lower locations from the metal loading rates at the lower stream location. A positive net flux indicates that the dissolved and/or total metal load increases in that segment, and a negative net flux indicates that the load decreases. Only a positive net flux for the dissolved load is attributed to contaminated groundwater mixing with the stream, either the North Fork of the American Fork River or Bayhorse Creek. Suspended metal loads were calculated by subtracting the dissolved (filtered) load from the total (unfiltered) load.



The geochemical modeling program PHREEQC (Parkhurst and Appelo 2000) with the MINTEQA2 (Allison et al. 1990) thermodynamic database was used to gain insight into speciation distributions, calculate saturation indices, and perform surface sorption modeling. HFO, specifically ferrihydrite, was assumed as a surface for metal sorption. Surface complexation parameters were obtained from Dzombak and Morel (1990). The default parameters used were $600 \text{ m}^2/\text{g}$ for the specific surface area, 0.005 mol/mol Fe for the strong site density, and 0.2 mol/mol Fe for the weak site density. The default input parameter was pe = 4.0 as the redox potential. The input parameters were the temperature, pH, alkalinity, DO, and composition of the waters.

Results and Discussion—Pacific Mine

Discharge Measurements

Discharge measurements and water samples both were collected at the locations shown on Fig. 2 on June 12, July 10, August 19, September 14, and October 15 of 2002. The winter of 2001–2002 was a relatively normal one, with precipitation in Salt Lake City, Utah being 98% of the historical average.

Discharges at the Pacific Mine site were measured at eight locations (NFAF-U, NFAF-L, L-1, and R-1 through R-5; see Fig. 2) in all 5 months, except for R-5 from July through October and R-4 from August through October. The NFAF-U and NFAF-L locations are on the North Fork of the American Fork River immediately above and below the mine site, respectively. The L-1 location is on a tributary on the opposite side of the river from the mine site, and the R-1 through R-5 locations are tributaries that enter the river from the mine site itself.

Discharge measurements at the Pacific Mine are shown in Table 1. The discharge measurements made at NFAF-U, L-1, and R-1 through R-5 have been added together and shown as the "Sum." Then this cumulative discharge has been subtracted from NFAF-L to determine the amount of water either gained from or lost to the groundwater system. According to the data presented in this table, the North Fork of the American Fork River was a gaining stream in July, August and October. It was a losing stream in June, during the annual peak spring runoff period, and again in September, due to an early fall rainstorm that occurred shortly before the date when the discharges were measured. While there undoubtedly is uncertainty associated with the discharge measurements, it would be difficult, if not impossible, to quantify accurately. However, the relatively large differences in the values measured at different locations and



Table 1 Summary of discharge calculations, groundwater discharge or recharge rates, and stream type identification (all units in L/s) for the North Fork of the American Fork River (Lachmar et al. 2006)

	6/12/02	7/10/02	8/19/02	9/14/02	10/15/02
NFAF-U	1926	148	85	129	88
L-1	9.91	3.68	5.10	2.83	5.10
R-1	57.2	11.0	2.83	3.96	0.85
R-2	13.0	1.13	1.13	2.27	6.51
R-3	15.3	3.68	1.42	1.98	0.57
R-4	2.27	0.28	0	0	0
R-5	0.28	0	0	0	0
Sum	2024	168	95	140	101
NFAF-L	1820	294	119	96	134
Net gain/loss	-204	126	24	-44	33
Stream type	Losing	Gaining	Gaining	Losing	Gaining

at different times suggest that the conclusions of whether the North Fork of the American Fork River was a gaining or losing stream probably are correct.

Water Chemistry

Water samples were collected at all eight discharge measurement locations at the Pacific Mine site (Fig. 2) in June, but R-5 had dried up by July and R-4 had dried up by August. Water samples were also collected from 10 wells (W-1 through W-10) in June, and from four wells (W-2, W-7, W-8, and W-10) in October, as the other six wells were dry.

The field pH values at the Pacific Mine site (Fig. 2) ranged from 2.3 at W-5 to 8.1 at NFAF-L (Burk 2004). Both values were measured in June. The field DO contents at the Pacific Mine ranged from 2.91 mg/L at W-10 to 9.41 mg/L at NFAF-L (Burk 2004). The DO was only measured for the October samples.

All of the stream samples from the Pacific Mine were Ca-Mg-HCO₃ waters (Burk 2004). Five of the well samples (W-1, W-2, W-4, W-7, and W-10) were Ca-HCO₃ waters, too, while four (W-3, W-5, W-6, and W-8) were Ca-SO₄ waters. The tenth well sample (W-9) was a Na-Cl water. Sulfate obviously replaces bicarbonate as the dominant anion in the acidic portion of the tailings due to pyrite oxidation, as the pH values in W-3, W-5, W-6, and W-8 ranged from 2.3 to 3.1 in June. The lowest pH measured at the other sampling locations in June was 6.2 at W-7 (Fig. 2).

Metal Loading Rates

Arsenic, Cd, Cu, Fe, Mn, Pb, and Zn were all detected in the samples at the Pacific Mine site. The dissolved and total loading rates for these seven cations at each discharge measurement location are presented in Burk (2004). The dissolved and total net fluxes between NFAF-U and NFAF-L for each of the 5 months of the field season are shown in Table 2. Iron and Zn, and to a lesser extent Mn, had the highest values for both the dissolved and total net fluxes.

All seven cations had positive dissolved net fluxes throughout the study period except for As and Cu in June, As, Cd, Pb, and Zn in September, and Cd and Zn in October (Table 2). However, only the dissolved net fluxes for Fe and Zn in June, Fe, Mn, and Zn in July, Fe and Zn in August, and Fe in October were large enough to imply that the river was actually gaining these metals from the groundwater system, and were not simply the product of uncertainties in the discharge measurements, as mentioned above, and the chemical analyses.

The total net fluxes were negative for all seven cations in every month except for As and Pb in July, As, Mn and Pb in August, and Mn in October (Table 2). Furthermore, the negative total net fluxes were greater than the positive dissolved net fluxes, except for Mn in July. This suggests

Table 2 Net flux values (in mg/sec) for the North Fork of the American Fork River (Lachmar et al. 2006)

6/13/02	d-As	t-As	d-Cd	t-Cd	d-Cu	t-Cu	d-Fe	t-Fe	d-Mn	t-Mn	d-Pb	t-Pb	d-Zn	t-Zn
Net flux	- 0.156	- 0.394	0.046	- 2.65	- 2.39	- 35.9	12.5	- 305	0.905	- 14.6	0.238	- 14.9	26.9	- 5810
7/10/02	d-As	t-As	d-Cd	t-Cd	d-Cu	t-Cu	d-Fe	t-Fe	d-Mn	t-Mn	d-Pb	t-Pb	d-Zn	t-Zn
Net flux	0.165	0.173	0.281	- 0.670	0.441	- 1.27	4.96	- 19.7	3.28	- 0.146	0.744	2.29	24.8	- 524
8/19/02	d-As	t-As	d-Cd	t-Cd	d-Cu	t-Cu	d-Fe	t-Fe	d-Mn	t-Mn	d-Pb	t-Pb	d-Zn	t-Zn
Net flux	0.046	0.021	0.050	- 0.075	0.108	- 1.55	2.37	- 2.66	0.765	0.194	0.150	0.054	5.78	- 75.8
9/14/02	d-As	t-As	d-Cd	t-Cd	d-Cu	t-Cu	d-Fe	t-Fe	d-Mn	t-Mn	d-Pb	t-Pb	d-Zn	t-Zn
Net flux	0.000	- 0.154	- 0.024	- 0.390	0.064	- 0.486	0.626	- 5.86	0.145	- 0.768	- 0.037	- 0.119	- 1.547	- 374
10/15/02	d-As	t-As	d-Cd	t-Cd	d-Cu	t-Cu	d-Fe	t-Fe	d-Mn	t-Mn	d-Pb	t-Pb	d-Zn	t-Zn
Net flux	0.040	- 0.136	- 0.024	- 0.254	0.046	- 1.41	1.32	- 12.4	1.04	0.634	0.025	- 0.560	- 2.18	- 245



that much of the suspended load was being deposited on the streambed sorbed to HFO. The amounts of deposited Fe and Zn greatly exceeded the amounts of the other five cations.

Geochemical Modeling

PHREEQC (Parkhurst and Appelo 2000) was used to calculate saturation indexes, speciation distributions, and HFO surface complex distributions for each water sample collected in June and October at the Pacific Mine site. The pH values measured at the sampling locations during these 2 months were used for the geochemical modeling. For the most part, the pH was neutral to slightly alkaline (between 7 and 8). In general, the pH of the North Fork was slightly higher than that of the tributaries, except for L-1. However, the tributary input was not enough to alter the pH of the North Fork substantially. Because no DO measurements were obtained in June due to a faulty meter, the lowest measurement in October (5.2 mg/L at R-2) was used for the June samples. The surface water in June most likely was oxygenated, so using the lowest October value should maximize the proportion of the reduced species relative to the oxidized species for the speciation distribution calculations. This would provide a worst-case scenario for As, since As⁵⁺ is about 60 times less toxic than As³⁺ (Ferguson and Gavis 1972).

The saturation index (SI) results indicate that ferrihydrite (FeOH₃) was supersaturated in all surface water bodies at the Pacific Mine site throughout the study period. Other ironbearing oxide minerals had positive SI values, but since sorption only occurs onto ferrihydrite in the PHREEQC model, it was the only iron precipitate considered.

The speciation distribution calculations at the Pacific Mine site in June and October indicate that Fe occurred as Fe³⁺ in all of the surface water bodies, and that it was always complexed with hydroxide. The form for As was As⁵⁺, either as $HAsO_4^{2-} (\geq 77\%)$ or $H_2AsO_4^{-} (\leq 23\%)$. The dominant copper complex at NFAF-U, NFAF-L and L-1 was $Cu(OH)_2$, but it was $CuCO_3$ in the tributaries that flowed through the mine site, except for R-1 in October. The dominant form of both Cd, Mn, and Zn was in the free ionic state $(Cd^{2+}, Mn^{2+}, and Zn^{2+})$. Lead was complexed with carbonate (Burk 2004).

The PHREEQC results for the North Fork of the American Fork River suggest that the most important reaction is the precipitation of ferrihydrite, because sorption of the other six cations onto ferrihydrite is the dominant chemical process that removes them from the water column. The metals that travel in the surface waters as suspended solids, as determined by subtracting the dissolved loads from the total loads, are Cu, Fe, Pb, and Zn, whereas Cd and Mn travel as dissolved species (Table 3). Arsenic appears to travel both as a suspended solid and in the dissolved state (Lachmar et al. 2006).



Results and Discussion—Ramshorn Mine

Discharge Measurements

Discharge measurements and water samples were collected at the locations shown on Fig. 3 on July 8, August 5, September 1, and October 1 of 2011. Although precipitation in Challis, Idaho during the winter of 2010–2011 was 95% of the historical average, snow accumulations in the neighboring mountains were observed to be well above average. This was apparent during the first attempt to collect field data in June of 2011, when the unpaved access road to the mine site was washed out due to the high discharge of Bayhorse Creek.

Discharges at the Ramshorn Mine site were measured at all but one (SW-4, the tailings pond) of the 11 locations shown on Fig. 3 in July. Discharges were only measured at eight locations for the next 3 months. The eight locations included five surface water (SW-1 and SW-5 through SW-8) and three groundwater (GW-1 through GW-3) sites. The SW-1 site is upstream of the tailings pile and represents the uncontaminated surface water. SW-5 is located just below the confluence with an adit drainage. SW-6 is located just above the confluence with Juliette Creek, the only perennial tributary, and SW-7 is Juliette Creek. SW-8 is located at the Bayhorse townsite (Fig. 1) just downstream of the tailings pile. The GW-1 site is located where water is seeping out of the Ramshorn Slate just above the mine workings. GW-2 is a flowing well, and GW-3 is the adit drainage. SW-2 and SW-3 were ephemeral seeps from the toe of the tailings pile.

Discharge results are shown in Table 4. Bayhorse Creek was divided into three segments: the upper segment, between SW-1 and SW-5; the middle segment, between SW-5 and SW-6; and the lower segment, between SW-6 and SW-8. For the upper segment, the sum of the discharges measured at SW-1 and GW-3 was subtracted from the discharge measured at SW-5. Similarly, for the lower segment, the sum of the discharges at SW-6 and SW-7 was subtracted from the discharge at SW-8. The SW-5 discharge simply was subtracted from the SW-6 discharge for the middle segment. As Table 4 shows, Bayhorse Creek was a gaining stream along its entire length during all 4 months except for the segment between SW-1 and SW-5 in July, September, and October. Thus, August is the only month during the 4-month field season in which contaminated groundwater from the tailings could possibly have entered the creek.

Water Chemistry

Water samples were collected at the Ramshorn Mine site at all 11 locations shown on Fig. 3 in July and at the eight

Table 3 Percentages of metals in the North Fork of the American Fork River in the form of suspended solids (Lachmar et al. 2006)

6/13/02	NFAF-U (%)	NFAF-L (%)	L-1 (%)	R-1 (%)	R-2 (%)	R-3 (%)	R-4 (%)	R-5 (%)
As	32	46	17	82	95	87	85	99
Cd	89	32	69	14	21	13	10	11
Cu	88	70	93	78	89	82	66	92
Fe	93	87	90	95	96	96	96	99
Mn	58	29	35	0	7	31	41	57
Pb	96	92	95	98	99	97	97	97
Zn	100	79	98	50	58	57	24	36
7/10/02	NFAF-U (%)	NFAF-L (%)	L-1 (%	(b) R	-1 (%)	R-2 (%)	R-3 (%)	R-4 (%)
As	0	12	2	7:	5	30	32	0
Cd	92	26	56	38	8	35	31	34
Cu	96	62	97	93	3	93	73	46
Fe	97	89	72	98	8	88	82	5
Mn	70	4	10	5.	3	28	22	20
Pb	85	78	47	7	7	82	76	68
Zn	99	63	97	4	4	64	61	45
8/19/02	NFAF-U (%)	NFAF-L (%)	L-1 (%)	R-	1 (%)	R-2 (%)	R-3 (%)
As	12	0		9	79		28	21
Cd	67	22		44	42		10	45
Cu	94	72		91	86		92	80
Fe	92	79		92	92		93	75
Mn	59	23		42	17		20	24
Pb	54	42		42	58		49	62
Zn	96	67		94	50		23	74
9/14/02	NFAF-U (%)	NFAF-L (%)	L-1 (%)	R-	1 (%)	R-2 (%)	R-3 (%)
As	60	25		43	76		79	50
Cd	83	22		77	34		40	36
Cu	95	86		100	94		96	53
Fe	97	94		95	97		96	84
Mn	58	23		35	20)	12	6
Pb	79	79		77	30)	78	90
Zn	99	70		99	59		72	56
10/15/02	NFAF-U (%)	NFAF-L	(%)	L-1 (%)	R	-1 (%)	R-2 (%)	R-3 (%)
As	81	55		60	84	1	77	68
Cd	86	40		54	28	3	17	23
Cu	99	89		95	90)	91	86
Fe	99	90		95	96	5	91	93
Mn	55	17		31	16	5	0	23
Pb	95	77		85	69)	66	97
Zn	98	80		93	64	1	64	67

locations where discharge measurements were made for the other three months. None of the unfiltered samples collected in September from the Ramshorn Mine were analyzed because of the similarity of the analytical results for the filtered samples taken in August, September, and October. Additionally, the filtered Ramshorn samples for SW-1, SW-2, and GW-3 collected on July 8, 2011, and for SW-1, GW-2, and GW-3 collected on August 5 were reanalyzed by the UVDL using ICP-MS.

The field pH at the Ramshorn Mine site ranged from 6.73 at GW-1 to 9.17 at SW-3 (McDonough 2015). Both of these extremes were measured in July. These pH values



Table 4 Summary of discharge calculations, groundwater discharge or recharge rates, and stream type identification (all units in L/s) for Bayhorse Creek

	7/8/11	8/5/11	9/1/11	10/1/11
GW-1	0.79	0.58	0.39	0.28
GW-2	0.06	0.06	0.06	0.06
GW-3	25.1	20.0	15.5	18.2
SW-1	235	73.9	26.3	17.9
SW-5	245	94.4	33.1	29.2
SW-6	379	138	60	50.2
SW-7	512	230	92.1	61.0
SW-8	1102	404	200	160
Upper segment	- 15.1	0.50	- 8.7	- 6.9
Middle segment	134	43.6	26.9	21
Lower segment	211	36	47.9	48.8
Net gain/loss	330	80.1	66.1	62.9
Stream type	Gaining	Gaining	Gaining	Gaining

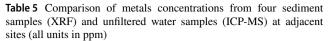
reflect the lack of acidity despite the abundance of HFO. The field DO contents for the 3 monthly samples (DO was not measured in July) collected at the eight sampling locations at the Ramshorn Mine ranged from 6.8 to 13.3 mg/L (McDonough 2015). Both of these values were measured in October when the discharges were lowest. Furthermore, the adit drainage (GW-3) had the lowest DO and the bedrock seep (GW-1) had the highest in all 3 months.

The samples at the Ramshorn Mine were Ca-Mg-HCO₃ waters except for GW-3, which was a Mg-HCO₃ water (McDonough 2015). In addition to Mg, GW-3 also had the most SO₄. The high HCO₃ and low SO₄ concentrations were consistent with the high pH, again in line with the lack of acidic water and/or sulfide minerals.

Sediment Sample Analyses

The concentrations of Cu, Fe, Mn, and Zn in SW-1 SS, SW-5 SS, SW-6 SS, SW-8 SS, GW-1 SS, and GW-1 ROCK detected by XRF analysis are shown in Table 5. Arsenic and Pb are not listed because they cannot be analyzed on the Philips XRF. As shown in Table 5, SW-5 SS has elevated Cu (1730 ppm), and SW-8 SS has elevated Zn (2230 ppm). As with the unfiltered water samples, which also have been included in Table 5 for comparison, Fe has the highest concentration in the sediment samples. The sediment samples have lower concentrations of Mn, even lower concentrations of Zn, and Cu has the lowest concentrations. The concentrations of these four cations increase from SW-1 to SW-5, decrease from SW-5 to SW-6, and then increase again from SW-6 to SW-8.

Four samples (SS-2a, a duplicate of the tailings sample, SW-1 SS, SW-5 SS and GW-1 ROCK) were analyzed from



	Cu	Fe	Mn	Zn
GW-1 ROCK	10	36,500	350	68
GW-1 SS	73	65,800	680	129
GW-1 (Aug)	< 0.008	0.03	0.001	0.01
SW-1 SS	16	34,600	520	68
SW-1 (Aug)	0.004	0.25	0.01	0.014
SW-5 SS	1730	58,200	3060	256
SW-5 (Aug)	0.005	0.148	0.028	0.021
SW-6 SS	40	46,800	1100	133
SW-6 (Aug)	0.004	0.099	0.009	0.015
SW-8 SS	257	67,200	2690	2230
SW-8 (Aug)	0.002	0.12	0.003	0.012

the upper portion of the study area near the tailings pile, which is the most likely source of contamination. The Fe concentrations were highest, with lesser concentrations of Mn (Table 6). Predictably, As, Cu, Pb, and Zn occur in high concentrations in SS-2a and SW-5 SS, but not in SW-1 SS or GW-1 ROCK.

Metal Loading Rates

The dissolved and total loading rates for As, Cu, Fe, Mn, Pb, and Zn at the Ramshorn Mine site are presented in McDonough (2015). The dissolved and total net fluxes for each of these six cations along Bayhorse Creek for the upper (SW-1 to SW-5), middle (SW-5 to SW-6), and lower (SW-6 to SW-8) segments in July, August, and October are shown in Table 7. The highest net fluxes are in July. Iron had the highest net fluxes, with Mn and Zn having intermediate fluxes, and As, Cu, and Pb having low net fluxes.

The dissolved and total loads of Fe and Mn increased along the upper segment in July, but both Zn loads decreased. The dissolved Fe load decreased along the middle segment, but the total Fe load increased. Presumably, the dissolved Fe is precipitating as HFO and being transported in suspension. The dissolved Zn and total Zn and Mn loads increased along the middle segment in July. Both the dissolved and total Fe loads decreased along the lower segment. Along the middle segment, the dissolved Fe is probably precipitating as HFO, and the suspended Fe was settling out on the streambed. Both the dissolved and total Mn and Zn loads increased along the lower segment.

Both the dissolved and total Fe loads decrease along the upper segment in August, while both loads increase for Mn and Zn (Table 7). The dissolved Fe load increases along the middle segment, but the total load decreases slightly. Both the dissolved and total Mn loads, as well as the dissolved Zn



Table 6 ICP-MS analysis of sediment and rock samples (all units in mg/L)

	As	Cu	Fe	Mn	Pb	Zn
SS-2a	2870	328	64,300	4230	1380	510
SW-1 SS	13.0	11.0	19,500	300	18.0	46.7
SW-5 SS	714	1900	38,800	2470	278	228
GW-1 ROCK	3.27	8.83	24,300	220	2.09	42.9

Table 7 Net flux values (in mg/sec) for filtered (d=dissolved) and unfiltered (t=total) samples between sites SW-1 and SW-5, SW-5 and SW-6, and SW-6 and SW-8; net flux is the loading rate that enters (+) or leaves (-) Bayhorse Creek

7/08/11	d-As	t-As	d-Cu	t-Cu	d-Fe	t-Fe	d-Mn	t-Mn	d-Pb	t-Pb	d-Zn	t-Zn
Upper segment	0.99	0.99	- 0.43	- 0.43	107	70.9	2.21	4.71	- 0.11	0.50	- 9.02	- 1.26
7/08/11	d-As	t-As	d-Cu	t-Cu	d-Fe	t-Fe	d-Mn	t-Mn	d-Pb	t-Pb	d-Zn	t-Zn
Middle segment	0.68	0.68	0.54	0.92	- 60.8	80.4	- 0.08	1.85	0.07	0.41	2.16	2.78
7/08/11	d-As	t-As	d-Cu	t-Cu	d-Fe	t-Fe	d-Mn	t-Mn	d-Pb	t-Pb	d-Zn	t-Zn
Lower segment	1.05	- 0.64	0.84	2.67	- 48.3	- 53.5	1.11	2.15	0.10	0.63	1.89	6.30
8/05/11	d-As	t-As	d-Cu	t-Cu	d-Fe	t-Fe	d-Mn	t-Mn	d-Pb	t-Pb	d-Zn	t-Zn
Upper segment	0.40	0.31	0.31	0.17	- 2.11	- 4.50	1.25	1.90	0.01	- 0.06	2.97	0.95
8/05/11	d-As	t-As	d-Cu	t-Cu	d-Fe	t-Fe	d-Mn	t-Mn	d-Pb	t-Pb	d-Zn	t-Zn
Middle segment	0.22	0.17	0.17	0.08	4.73	- 0.27	- 0.83	- 1.39	0.02	0.05	- 1.47	0.10
8/05/11	d-As	t-As	d-Cu	t-Cu	d-Fe	t-Fe	d-Mn	t-Mn	d-Pb	t-Pb	d-Zn	t-Zn
Lower segment	0.18	- 0.43	0.15	- 1.81	1.51	6.49	0.27	- 1.88	0.01	- 0.20	- 0.67	- 2.52
10/01/11	d-As	t-As	d-Cu	t-Cu	d-Fe	t-Fe	d-Mn	t-Mn	d-Pb	t-Pb	d-Zn	t-Zn
Upper segment	0.06	0.28	0.05	0.15	- 0.33	7.84	0.04	3.10	0.00	0.13	0.31	0.09
10/01/11	d-As	t-As	d-Cu	t-Cu	d-Fe	t-Fe	d-Mn	t-Mn	d-Pb	t-Pb	d-Zn	t-Zn
Middle segment	0.10	- 0.02	0.08	- 0.05	0.38	- 5.81	- 0.05	- 3.08	0.02	- 0.07	0.13	0.56
10/01/11	d-As	t-As	d-Cu	t-Cu	d-Fe	t-Fe	d-Mn	t-Mn	d-Pb	t-Pb	d-Zn	t-Zn
Lower segment	0.24	0.06	0.20	0.27	- 0.27	8.35	0.20	0.71	0.02	0.32	1.62	1.75

load, decrease along the middle segment. Both the dissolved and total Fe loads increase along the lower segment, but the dissolved and total Zn and total Mn loads all decrease.

In October, the total Fe and Mn loads both increased along the upper segment. The dissolved Fe and Mn fluxes, as well as both the dissolved and total Zn fluxes, were small. The total loads for both Fe and Mn decreased along the middle segment, while the dissolved Fe and Mn fluxes and both the dissolved and total Zn fluxes were small. Along the lower segment, the total Fe load as well as both the dissolved and total Zn loads, increased. The dissolved Fe and both the dissolved and total Mn fluxes were small.

Geochemical Modeling

A mixing model was created for the upper segment in August. This segment was used because it flows adjacent to the tailings, and August was the only month during which this segment was a gaining stream. The mixing model was created based on the measured discharges and chemical concentrations at the three sampling locations along the stream. Mix 1 represents a mix of 99% SW-1 and 1% GW-2, as these reflect the relative discharges of surface and ground water inflow, respectively, into Bayhorse Creek. Mix 2 represents a mix of 79% Mix 1 and 21% GW-3, based on the contribution of the adit to the discharge of the creek. The August pH values of SW-1, GW-2, and GW-3, of 8.29, 8.86, and 7.15, respectively, were used in the mixing model.

As expected, Mix 1 was nearly identical chemically to SW-1, and Mix 2 was very similar to Mix 1. The PHREEQC SI results suggest that Fe and Mn are the most likely to precipitate. Specifically, both Mix 1 and Mix 2 have large positive SIs for the iron oxides, hydroxides, and oxyhydroxides, cupric ferrite (CuFe₂O₄), hematite (Fe₂O₃), maghemite



 (Fe_2O_3) , magnesioferrite (Fe_2MgO_4) , and magnetite (Fe_3O_4) . The manganese oxides with large positive SIs in both mixes consist of birnessite (MnO_2) , bixbyite (Mn_2O_3) , hausmannite (Mn_3O_4) , nsutite (MnO_2) , and pyrolusite (MnO_2) . Manganite (MnOOH) also has a high SI in Mix 2 (McDonough 2015).

In addition, Fe and Mn travel primarily as suspended solids, whereas Zn travels primarily in the dissolved form (Table 8). Based on the results of the speciation distribution calculations, As occurs exclusively as As⁵⁺. The results also show that Fe occurs as Fe³⁺, and that Mn and Zn only occur in the +2 oxidation state. Surface sorption modeling suggests that As and Zn are the cations that are most likely to sorb onto ferrihydrite (McDonough 2015).

Conclusions

Both the North Fork of the American Fork River and Bayhorse Creek are located at relatively high elevations near the headwaters of drainage basins that receive most of their precipitation as snow during the winter months, which extend from November through May. As a result, there is a dramatic increase in the discharges of these two streams at the beginning of the snowmelt season immediately following the winter months. Obviously, this increase in discharge produces relatively large dissolved and total metal loads at both the Pacific and Ramshorn Mines during the five nonwinter months, unlike many other areas affected by AMD where precipitation falls mainly as rain during the winter and spring.

Water flowing through the tailings was the source of the AMD at the Pacific Mine. The pyrite in the tailings was responsible for the acidity. In turn, the portion of the tailings in which acidic groundwater was generated (see Fig. 2) was the primary source of the dissolved As, Cd, Cu, Fe, Mn, Pb, and Zn. The fate and transport of Fe and Zn are of primary concern because of their high loading rates in the surface and ground waters. However, the PHREEQC results suggest that both Fe and Zn, and also the Cu and Pb, are largely removed from the water at the site due to the precipitation of ferrihydrite and the subsequent sorption of Cu, Pb, and Zn. Only Cd and Mn appear to travel primarily in the dissolved state, while As seems to travel both as a suspended solid and in the dissolved state.

The PHREEQC results also suggest that the suspended As sorbs onto ferrihydrite (Lachmar et al. 2006).

While the tailings at the Ramshorn Mine site are the main contaminant source to Bayhorse Creek, the tailings pile at the Bayhorse townsite downstream also contributes contaminants to the stream, as demonstrated by the increase in Cu, Fe, Mn, and Zn in the sediments at SW-8 compared to SW-6 (see Table 5). These four metals, as well as Pb and the metalloid As, comprise the full suite of contaminants at this site. Of these, Fe had the highest concentrations and loads, Mn and Zn had intermediate concentrations and loads, and As, Cu and Pb had very low concentrations and loads (McDonough 2015). The latter two may have been largely removed by mining.

Unlike the Pacific Mine site, no acidic water persists at the Ramshorn Mine, either because so little is generated due to the lack of pyrite or because the acid water is neutralized by the dolomite bedrock. Furthermore, it appears that Fe and Mn travel primarily as suspended solids. The PHREEQC results suggest that the Fe is largely removed by precipitation of ferrihydrite. The Mn probably precipitates out of solution in the stream and is deposited onto the streambed sediments. Only Zn travels primarily in the dissolved form, but the PHREEQC results suggest that this metal, as well as As, are sorbed onto ferrihydrite. According to the PHREEQC results, As occurs exclusively in the less toxic As⁵⁺ form (McDonough 2015).

The USFS removed the tailings from the Pacific Mine site during the summer and fall of 2003, eliminating the generation of acidic groundwater, which led to the dissolution of the seven cations that were found to be contaminating the North Fork of the American Fork River. At the Ramshorn Mine site, the USFS provided oversight for the capping and regrading of the tailings pile, which was performed during the late summer of 2011. However, the level of contamination found during the present investigation did not indicate any acidic surface or groundwater, due to siderite being the primary iron-bearing gangue mineral and the Cambrian Bayhorse Creek Dolomite being the main host rock for the ore. Furthermore, Fe was the only contaminant found at relatively high concentrations and loads, and this metal appears to be removed from Bayhorse Creek by ferrihydrite precipitation.

Table 8 Percentages of metals in Bayhorse Creek in the form of suspended solids (As, Cu, and Pb were not measured in high enough concentrations to calculate)

8/5/11	SW-1 (%)	GW-3 (%)	SW-5 (%)	SW-6 (%)	SW-7 (%)	SW-8 (%)
Fe	82	71	91	57	90	79
Mn	80	0	47	54	86	10
Zn	21	0	0	0	51	13



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