

GEOCHEMISTRY AND HYDROGEOLOGY OF ACID MINE DRAINAGE IN THE GREAT FALLS-LEWISTOWN COAL FIELD, MONTANA¹

Christopher H. Gammons², Terence E. Duaine, William S. Botsford,
Stephen R. Parker, and Tracy Grant

Abstract. The Great Falls–Lewistown Coal Field (GFLCF) in central Montana contains over 400 abandoned underground coal mines, many of which are discharging acidic mine water with serious environmental consequences. Completely submerged areas of the mines are not strongly acidic, whereas water quality quickly deteriorates in portions that are only partially flooded. In general, the pH of the GFLCF mine waters can decrease or increase after discharging to the surface, depending on the initial ratio of acidity, mainly as dissolved ferrous iron, to alkalinity, mainly as bicarbonate ion. Although the chemistry of many of the adit discharges is nearly constant with time, large diurnal and seasonal changes in the quality of down-gradient waters have been observed. Decreases in concentrations of dissolved Fe and Zn during the day at one location are explained by an increase in the rate of Fe²⁺ oxidation and precipitation of ferric hydroxide as the water warms. The precipitation of ferric hydroxide resulted in sorption of Zn²⁺, a reaction that was also thermodynamically favored by an increase in water temperature and pH during the afternoon. Historical efforts to passively treat acid mine drainage in the GFLCF using wetlands, limestone channels, and anoxic drains have been unsuccessful, due to the harsh climate, high metal concentrations, and acidity loads of the mine waters. Alternative mitigation concepts are currently being evaluated that focus on source control rather than treatment.

Additional Key Words: diel, diurnal, iron, zinc

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²C. H. Gammons, Professor, Dept. of Geological Engineering, Montana Tech of The University of Montana, Butte, MT 59701 (cgammons@mtech.edu); T.E. Duaine, Associate Research Hydrogeologist, Montana Bureau of Mines and Geology, Butte, MT 59701; W. S. Botsford, Abandoned Mines Reclamation Specialist, Montana Department of Environmental Quality, Helena, MT 59620; S. R. Parker, Assistant Professor, Dept. of Chemistry and Geochemistry, Montana Tech; T. Grant, Graduate Student, Dept. of Chemistry and Geochemistry, Montana Tech.

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Introduction

Central Montana, like other historic coal mining regions of the US, has serious acid mine drainage (AMD) problems. In the Great Falls-Lewistown Coal Field (GFLCF) these problems date to the late 1880s and early 1900s (Fisher, 1909; Silverman and Harris, 1967). The GFLCF stretches east from the city of Great Falls 150 km to Lewistown, Montana (Fig. 1). The region has over 400 abandoned coal mines, most of which were underground operations. Many of the mines are now generating AMD with the more extensively mined areas producing the worst water quality problems. Waters draining from abandoned underground workings near the small towns of Belt, Sand Coulee and Stockett are degrading the water quality of local streams and ground water. Because there is no active mining in the area, the environmental problems associated with AMD in the GFLCF are now the responsibility of the State of Montana. Past reclamation efforts led by the Montana Department of Environmental Quality – Mine Waste Cleanup Bureau have mainly focused on surface mine features such as removal of waste rock piles and sealing of adits. However, AMD water continues to be released from many abandoned mine adits, locally known as “drains”. The purpose of this paper is to provide background on the general characteristics of AMD in the western portion of the GFLCF, and to present three case studies that provide insight into the mechanisms that control the geochemistry of these waters.

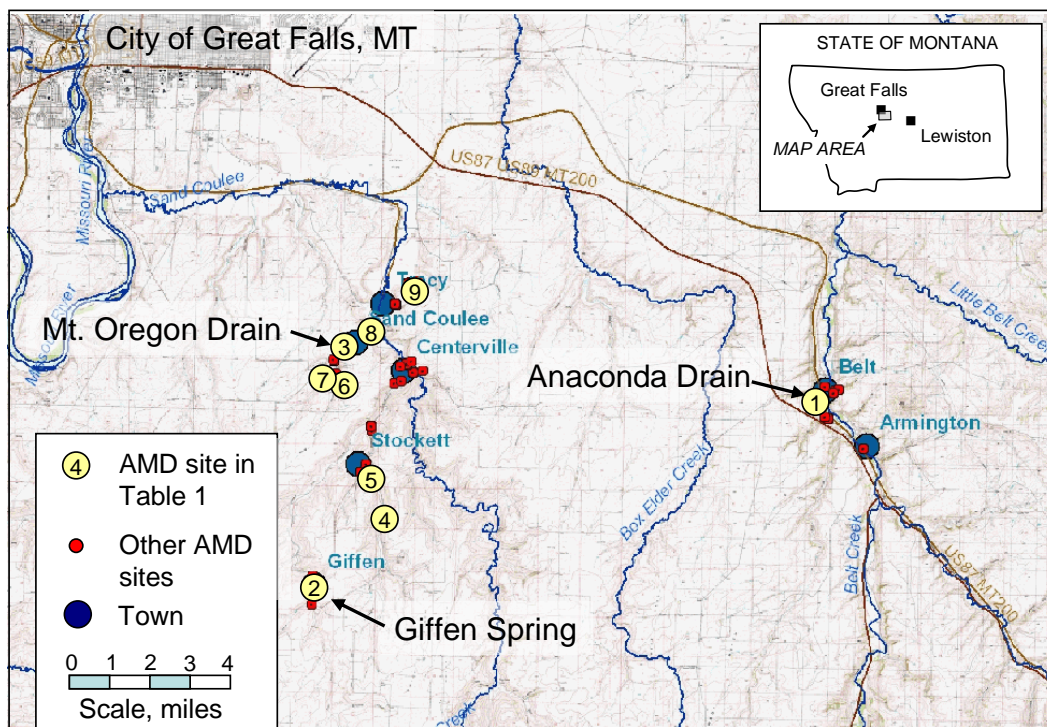


Figure 1. Location map of the western portion of the Great Falls-Lewistown Coal Field. Circled numbers in yellow refer to mine drains for which water quality data are summarized in Table 1.

Background

Geology and hydrogeology

The main coal seam mined in the GFLCF varies from 1 to 4 m in thickness, and is located at the top of the Jurassic Morrison Formation, the latter being predominantly shale and mudstone that weather easily. The GFLCF yielded sub-bituminous to bituminous coal with an average S content of 4%, locally as high as 11% (Silverman and Harris, 1967; Sholes and Daniel, 1992). The high S content of GFLCF coal is a major reason for the severity of its associated AMD. The coal is unconformably overlain by lower Cretaceous sandstone and shale of the Kootenai Formation. The sandstone units of the Kootenai are relatively resistant to erosion, and support broad, grassy upland areas between the valleys in which the coal beds outcrop. Beneath the Morrison and roughly 50 m below the coal is the Mississippian Madison Formation, a thick limestone unit that is an important regional source of groundwater. The Madison Aquifer feeds two very large and locally famous natural springs at either end of the coal field, i.e., Giant Springs in Great Falls and Big Spring in Lewiston. At this time there is no evidence that the Madison Aquifer has been contaminated from coal-derived AMD, although this is a concern that is being monitored.

Of import to the AMD problem is the moderate to low permeability of the overlying Kootenai Formation, resulting in a locally perched water table that is a source for slow but steady infiltration of shallow groundwater into the coal mines. The coal-bearing strata dip generally to the north at a low angle (Fisher, 1909), but folds and structural domes result in local exceptions to this trend. The undulating bedding plane surface typically has an amplitude of about 5 m in a period of about 500 m. In places, more pronounced folding has occurred near faults, anticline-syncline pairs, and small igneous intrusions. The topography in the region is characterized by rolling, grassy uplands incised by ephemeral drainages that follow local fault planes. The total relief in the area is on the order of 100 m, and the coal seams are exposed along the incised walls of the drainages. The practice of early coal miners was to mine the coal “up-dip”, generally in a southward direction, thereby providing gravity drainage of mine water. However, the gently folded nature of the beds resulted in large portions of the interior of the mine workings being flooded.

Today, extensive areas of each underground mine complex are completely flooded, whereas other areas are partially flooded or completely dewatered (Fig. 2). In many of the mine workings, the potentiometric surface is controlled by the elevation of high points in the floor of the undulating coal seams which act as spill-over points. Mine water crossing these spill-over points flows as subterranean runoff to the nearest adit or drainpipe, from which point the water discharges to the ground surface. The majority of the drains in the GFLCF discharge into ephemeral streams, and in the dry months AMD provides the only surface runoff in these valleys. In most cases the AMD soaks back into the dry streambed or evaporates within 1 or 2 km of discharging to the surface. The Anaconda drain near the town of Belt is an exception, as it discharges directly to Belt Creek, a sizeable stream whose headwaters are popular for trout-fishing and other recreational uses.

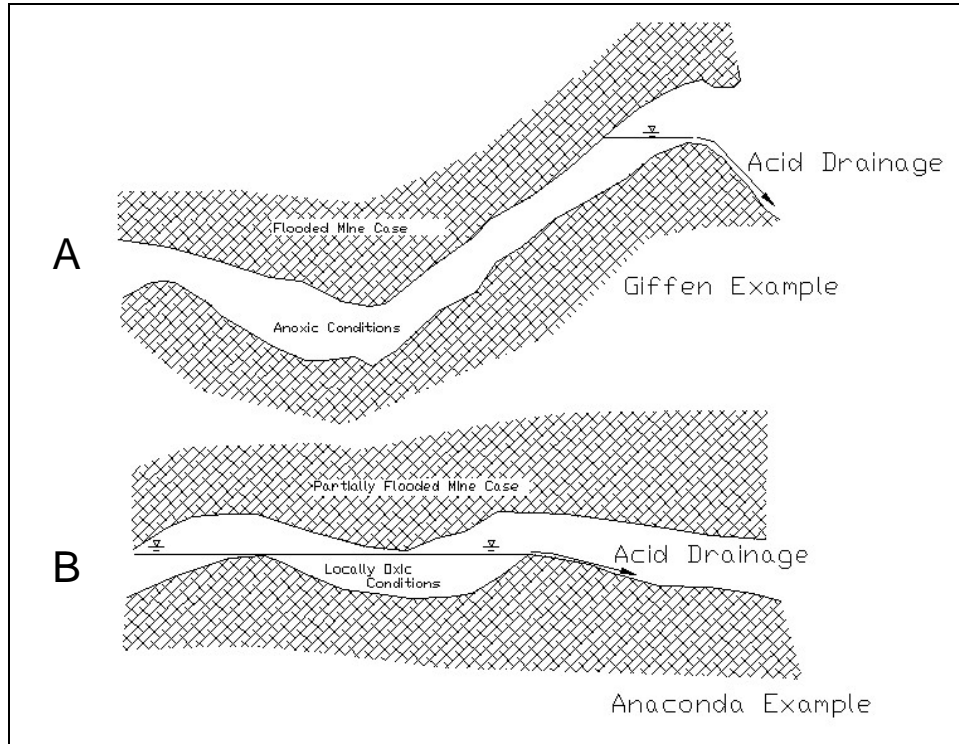


Figure 2. Schematic drawing of completely flooded vs. partially flooded mine workings.

General Characteristics of the GFLCF Acid Mine Drainage

Water quality and hydrogeological data were collected in the 1980s by the Montana Bureau of Mines and Geology (MBMG) for several of the abandoned mines in the Sand Coulee-Stockett area of the GFLCF (Osborne et al., 1983, 1987). These authors, along with Doornbos (1989), attributed major differences in the characteristics of the AMD to whether the underground workings were completely flooded or partially flooded. The basic concept is simple, and is illustrated in Figure 2. If the subterranean passageways are completely flooded (Fig. 2A), then this severely limits the amount of oxygen that contacts un-mined pyrite, resulting in minimal pyrite oxidation and relatively benign mine water chemistry. In contrast, a partially flooded condition (Fig. 2B) allows free ingress of air, and therefore the rate of pyrite oxidation is greatly accelerated. Of the two scenarios, the partially flooded example would be expected to generate more severe AMD.

From 1994 to 1996, the U.S. Geological Survey (USGS) conducted a detailed survey of the water-quality of mine discharges and down-gradient ephemeral streams and wetlands in the GFLCF (Karper, 1998). Each site was visited approximately once a month for two successive years. Table 1 summarizes selected data from Karper (1998) for nine of the more important mine discharges. The majority of the drains had pH in the 2.5 to 3.1 range, with extremely high concentrations of dissolved solids including sulfate (up to 16 g l^{-1}), Fe (up to 2000 mg l^{-1}), and Al (up to 1600 mg l^{-1}). Only two mine discharges – Giffen Spring and the Mt. Oregon Drain – had average pH values > 4 . Although the metal concentrations in Table 1 vary from mine to mine, the relative concentrations of the main constituents are remarkably consistent, and fall in the general order $\text{Fe} > \text{Al} \gg \text{Zn} > \text{Ni} > \text{Mn}, \text{Co} > \text{Cu} > \text{Cd} > \text{As} > \text{Pb}$ (not shown).

Table 1. Selected water quality parameters for AMD in the Great Falls-Lewiston Coal Field, Montana. All solute concentrations are for filtered (0.45 μm) samples. Values in blue (non-italicized) are averages of monthly measurements collected by the USGS during the period July 1994 to September 1996. All data are from Karper (1998) except the Eh and $\text{Fe}^{+2}/\text{Fe}^{+3}$ ratios, which are from this study and are based on single measurements.

Site	1	2	3	4	5	6	7	8	9
pH, s.u.	2.9	4.9	4.2	2.6	2.5	2.6	3.1	2.6	2.9
<i>max</i>	3	5.8	4.7	2.8	2.8	3	3.4	3	3.1
<i>min</i>	2.8	3.7	4.0	2.5	2.2	2.4	2.9	2.3	2.4
flow ^a	6.2	13.9	1.98	1.42	0.57	0.57	0.85	0.85	2.55
<i>max</i>	8.2	15.6	5.10	4.25	2.83	1.13	3.12	2.27	17.3
<i>min</i>	4.2	10.8	0.57	0.57	0.03	0.28	0.00	0.25	0.85
temp, °C	12.3	9.2	11.4	9.6	11.7	9.6	11.1	11.6	10.7
<i>max</i>	18.5	11	15	11.5	26	14.5	23	17.5	11.5
<i>min</i>	6.5	8.5	10	6	0	7.5	7.5	5.5	8.5
sp. cond. ^b	2.38	1.16	2.83	5.79	8.92	7.31	3.29	7.80	1.62
<i>max</i>	2.46	1.4	3.01	6.02	10.8	7.62	3.48	8.98	2.36
<i>min</i>	2.28	0.982	2.69	5.57	6.47	6.68	3.1	6.81	1.41
acidity ^c	1.1	0.22	1.5	4.1	10.0	7.5	2.1	8.4	0.30
<i>max</i>	1.3	0.48	1.7	4.4	13.5	8.0	2.2	10.0	0.65
<i>min</i>	0.9	0.03	1.4	3.7	5.0	7.0	1.8	7.0	0.21
acidity load ^d	560	258	257	502	490	367	151	617	65
<i>max</i>	880	640	727	1597	3304	783	592	1958	970
<i>min</i>	330	28	66	181	12	171	0	154	15
SO ₄ , g l ⁻¹	1.96	0.73	2.7	6.0	13	9.9	3.0	10.9	0.83
Fe, mg l ⁻¹	169	72	296	774	1380	1060	349	1390	6.8
Al, mg l ⁻¹	106	11.8	164	401	1180	893	229	889	32
Zn, mg l ⁻¹	3.4	1.5	6.1	50.5	63	34	10.3	17.6	1.05
Ni, mg l ⁻¹	0.78	0.37	1.5	10.8	12.6	7.8	2.4	4.8	0.35
Mn, mg l ⁻¹	0.42	0.38	1.2	2.4	8.5	3.4	1.3	8.6	0.58
Co, mg l ⁻¹	0.35	0.25	0.65	6.2	8.0	4.1	1.3	2.5	0.19
Cu, $\mu\text{g l}^{-1}$	27	17	n.d.	113	450	90	n.d.	369	15
Cd, $\mu\text{g l}^{-1}$	9	7	8	84	306	84	30	106	8
As, $\mu\text{g l}^{-1}$	1	n.d.	14	n.d.	2	3	5	53	n.d.
Eh, mV	650	328	397	653	n.a.	n.a.	n.a.	638	n.a.
Fe(II)/Fe(III)	9.2	∞^e	∞^e	3.7	n.a.	n.a.	n.a.	7.6	n.a.

^aFlow in L sec⁻¹; ^bSpecific conductance in mS cm⁻¹; ^cAcidity in g CaCO_{3,eq} l⁻¹. ^dAcidity load in kg CaCO₃ day⁻¹. ^eAll detectable Fe was Fe(II). Site descriptions: 1 - Anaconda drain; 2 - Giffen Spring; 3 - Mt. Oregon drain; 4 - Cottonwood Mine No. 6 drain; 5 - Cottonwood Mine No. 2 drain; 6 - unnamed drain in Mining Coulee; 7 - unnamed drain in Sand Coulee; 8 - Nelson Mine drain; 9 - Pipe Spring at Tracy. n.d. = non detected. n.a. = not analyzed.

Although the report of Karper (1998) contained no information for Eh or dissolved Fe speciation, results for selected AMD waters collected by our group in 2004 and 2005 are included at the bottom of Table 1. As is typical of iron-rich AMD waters, the Eh values are controlled by the $\text{Fe}^{+2}/\text{Fe}^{+3}$ redox couple, and show the usual inverse relationship with pH. The

limited data in hand indicates that the $\text{Fe}^{+2}/\text{Fe}^{+3}$ ratio varies quite a bit from mine to mine. At Giffen Spring and the Mt. Oregon drain, no Fe^{+3} could be detected using the Ferrozine method (To et al. 1999) on samples analyzed in the field. In contrast, a considerable amount of dissolved Fe(III) was present in water draining the Anaconda, Cottonwood No. 6, and Nelson mines. This indicates more oxidized conditions within the latter three mine workings, which is consistent with their lower pH values.

Average annual discharges of the mine drains based on the Karper (1998) study ranged from 0.5 to 14 l s^{-1} (Table 1). Whereas most of the drains showed seasonal variations in flow, others – such as the Anaconda drain – were more constant. In many cases, increases in mine discharge corresponded to seasonal patterns of snowmelt and extended precipitation events. The average acidity load (calculated as the product of the acidity x discharge) for the various mine drains ranged from 65 to 617 kg CaCO_3 per day. Most AMD sites showed large seasonal variability in acidity load, whereas others – such as the Anaconda Drain – were more constant.

Case Studies

The Anaconda Mine, Belt

This mine – known originally as the Castner Coal Mine – was started by John C. Castner in 1877 and was the first mine developed in the area. The Anaconda Mining Company bought the mine in 1894 and operated it until 1912. The Anaconda Mine was the largest producer of coal in this region, producing over 7.5 million tons in 25 years of production (Silverman and Harris, 1967). The mine extends several km west of the town of Belt towards the Box Elder Creek drainage (Fig. 3).

Water quality sampling of the Anaconda drain (Fig. 4A) conducted by the USGS and the MBMG from 1994 through 2003 has demonstrated the very consistent flow rates (averaging 7.9 liter s^{-1}), low pH, and elevated SO_4^{-2} , Al, Fe, and Zn concentrations in this water (Karper, 1998; Botsford and Duaine, 2003; Duaine et al., 2004). The surface discharge from the Anaconda drain is joined by additional AMD from the French Coulee drain, and then flows through a meadow before entering Belt Creek (Fig. 4B) immediately upstream of the town of Belt. During periods of low flow, the mine discharge can become a significant proportion of the total stream flow in Belt Creek (Fig. 4B). This is partly because the flow of Belt Creek, which is sizeable year-round in the mountainous headwaters, decreases abruptly upstream of Belt due to infiltration into the underlying alluvial sediments. This decrease in flow exacerbates the problem of metals contamination of Belt Creek from the coal mine waters.

In addition to the two AMD discharges from the Anaconda Mine, a number of monitoring wells within and adjacent to the mine workings have been sampled and monitored. Table 2 includes representative water-quality results for the various monitoring stations in the vicinity of the Anaconda Mine (locations for these sites are shown in Fig. 3). While waters from the mine drains are characterized by low pH and highly elevated metal concentrations, samples of groundwater from two sandstone aquifers that overlie the mine within the Kootenai Fm. have a neutral pH and low sulfate concentrations, with trace metal concentrations near or below the instrument detection limits. Groundwater from the *flooded* portion of the coal mine (Well 4B) is very similar to that of the overlying alluvial aquifers, with the exception of sulfate which is higher by an order of magnitude. However, the sulfate concentration is still an order of magnitude less than that of the mine drains. In contrast, mine water from *non-flooded* portions

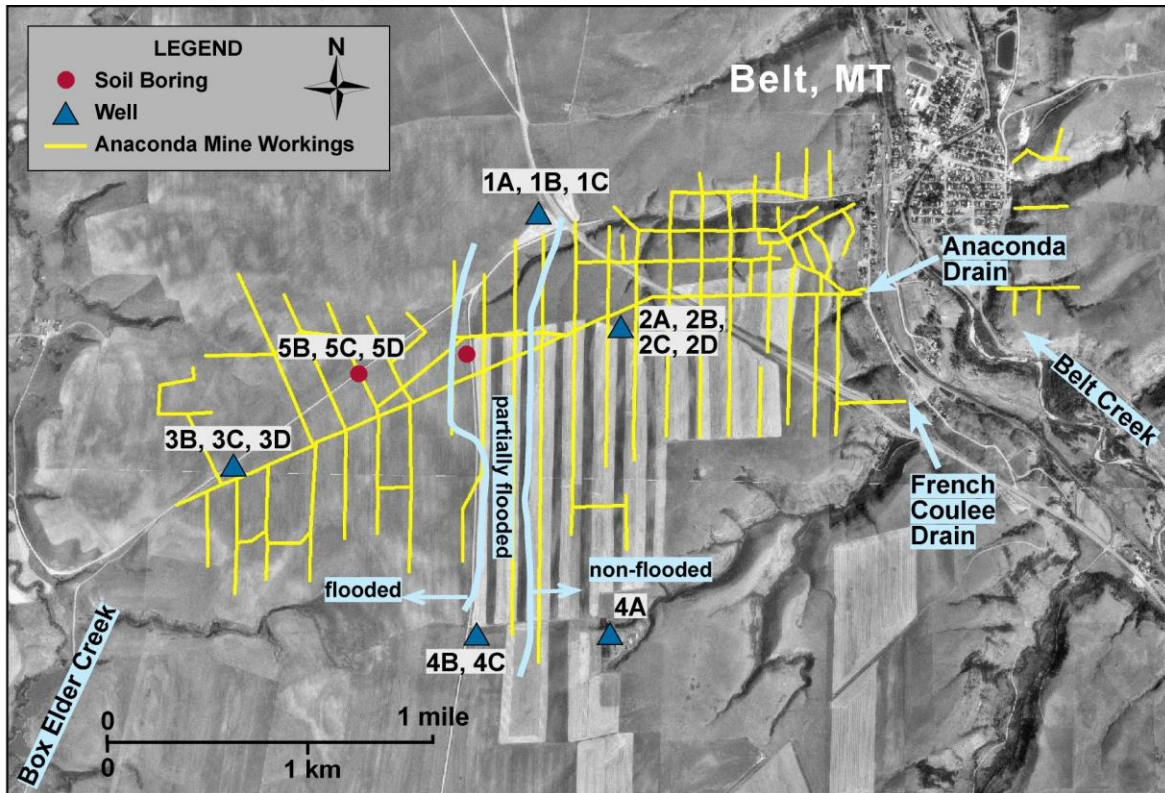


Figure 3. Aerial photo showing the extent of the underground workings (yellow) of the Anaconda Mine. The light blue lines separate portions of the workings that are completely flooded, partially flooded, and non-flooded. The general flow of groundwater in the mine is from WSW to ENE. Also shown are the location of sampling sites and monitoring wells.



Figure 4. Photographs of the Anaconda Drain. A – View of the Anaconda drainpipe and flume (white) for gaging flow; B – Confluence of Belt Creek (foreground) with the combined AMD from the Anaconda and French Coulee drains (upper arrow). View is looking downstream. The white precipitates in the foreground are hydrous aluminum oxides forming where pH 4.5 groundwater is entering Belt Creek from the left (lower arrow). [Photo by C. J. Fisk, Nov., 2005].

Table 2. Selected water quality data for drains and groundwater wells in the vicinity of the Anaconda Mine, Belt. Metal analyses were performed on filtered (0.45 µm) samples. n.a. = not analyzed. All data from GWIC (2005).

		pH	SC (µS/cm)	Temp (°C)	Fe (mg l ⁻¹)	HCO ₃ (mg l ⁻¹)	SO ₄ (mg l ⁻¹)	
Anaconda drain	Adit Seep	2.7	2,300	10.4	164	0	1,900	
French Coulee drain	Adit Seep	2.3	6,315	9	1,230	0	7,760	
Well 3C	Kootenai	7.2	560	14.7	0.45	413	29	
Well 2D	Kootenai	7.5	495	10.9	0.01	303	15	
Well 2B	Coal (void)	1.9	9,500	10.0	n.a.	0	n.a.	
Well 4B	Coal (flooded)	7.0	750	10.5	0.10	400	184	
Well 1A	Madison	7.4	535	10.8	0.01	203	188	
Well 4A	Madison	7.3	885	11.3	0.08	273	325	
		Al (µg l ⁻¹)	As (µg l ⁻¹)	Cd (µg l ⁻¹)	Co (µg l ⁻¹)	Cu (µg l ⁻¹)	Mn (µg l ⁻¹)	Zn (µg l ⁻¹)
Anaconda drain		95,000	<5	5.8	240	<10	400	2,710
French Coulee drain		560,000	49	10	362	25	1020	4,570
Well 3C		<10	8	<1	<2	<2	100	20
Well 2D		<10	1	<1	<2	<2	10	38
Well 2B		n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
Well 4B		<30	4	<1	3.1	<2	580	23
Well 1A		<10	<1	<1	<2	<2	<10	22
Well 4A		57	2	<1	<2	<2	70	11

of the mine (Well 2B) has poor quality (pH 2.2). Because of the small amount of water in Well 2B, it has not yet been possible to pump out a groundwater sample. However, judging from the very high specific conductance (SC) and low pH of water moving across the bottom surface of the mine void, it most likely has an overall chemistry that is similar to the drains. This underscores the importance of oxygen ingress into the mine passageways as a prerequisite for rapid oxidation of pyrite and dissolved Fe(II), and generation of mine water with strongly acidic pH.

Based upon the information collected to date at this site, two important facts are apparent: 1) water quality in the flooded portion of the mine is good; the high pyrite concentrations in the coal seam do not have an adverse affect on water quality conditions provided the coal is completely saturated; and 2) water quality degrades very quickly once it reaches the non-flooded portion of the mine.

Mt. Oregon Drain/Kate's Coulee

The Mt. Oregon drain is located near the town of Sand Coulee, in an ephemeral side drainage known as Kate's Coulee. As shown in Table 1, the pH of this adit discharge is typically in the range of 4.0 to 4.7, and the water contains several hundred mg/L of dissolved Fe and Al. Kate's Coulee was visited for intensive sampling on June 16, 2004. The purpose of this exercise was to see what chemical changes occurred to the mine water after it discharged to the surface. After emerging from a collapsed adit (Fig. 5A), the mine water flows down Kate's Coulee in an impressive series of iron-stained terraces (Fig. 5B) before joining the larger – usually dry – streambed of Sand Coulee. The red-stained water then passes through the community of Sand Coulee before soaking back into the ground. Filtered (0.2 µm) and non-filtered samples were

collected at a number of locations along the surface flow of the drain. Fe^{2+} and total Fe concentrations were determined on filtered samples in the field using the Ferrozine method (To et al., 1999). In addition, hourly samples were collected between 0800 and 1600 hours at a midpoint location to examine possible diurnal effects. The changes in chemistry with time were found to be minor, and are not discussed further in this report.



Figure 5. Photographs of the Mt. Oregon drain, taken in June, 2004. A – Upstream sampling location at collapsed adit. B – Iron-stained terraces in Kate's Coulee approximately 200 m downstream from the adit seep.

On the date sampled, the drain water had a pH of 4.2, a flow of 0.8 l s^{-1} , and a dissolved Fe concentration of 275 mg l^{-1} , essentially all of which was in the reduced ferrous state at the adit mouth. With distance downstream of the drain, a number of changes in water quality were observed (Fig. 6), including: 1) an increase in water temperature; 2) an increase in specific conductance; 3) a steady drop in pH from 4.2 to 2.6; 4) a decrease in total dissolved Fe concentration; 5) an increase in the $\text{Fe}^{+3}/\text{Fe}^{+2}$ ratio; and 6) an increase in Eh. Judging from downstream trends in the major cations and anions, the 20% increase in SC was probably a result of evapo-concentration. The sampling day was hot (high temperatures above 30°C) and the mine water was moving very slowly through Kate's Coulee, pooling up in each of the iron-stained terraces (Fig. 5B). Based on an SC tracer test using a slug of NaCl, the water took over 2 hours to travel the 150 m length of lower Kate's Coulee; the flow would have been even slower in the shallower gradient of Sand Coulee.

The changes in pH, Eh, Fe concentration and $\text{Fe}^{+3}/\text{Fe}^{+2}$ ratio (Fig. 6) were due mainly to oxidation of Fe^{+2} to Fe^{+3} , followed by precipitation of ferric hydroxide. The reactions of interest are summarized as follows:



Thus, although the initial oxidation of Fe^{2+} to Fe^{3+} consumed protons, this effect was overwhelmed by the acid that was released during the precipitation of ferric hydroxide¹. The

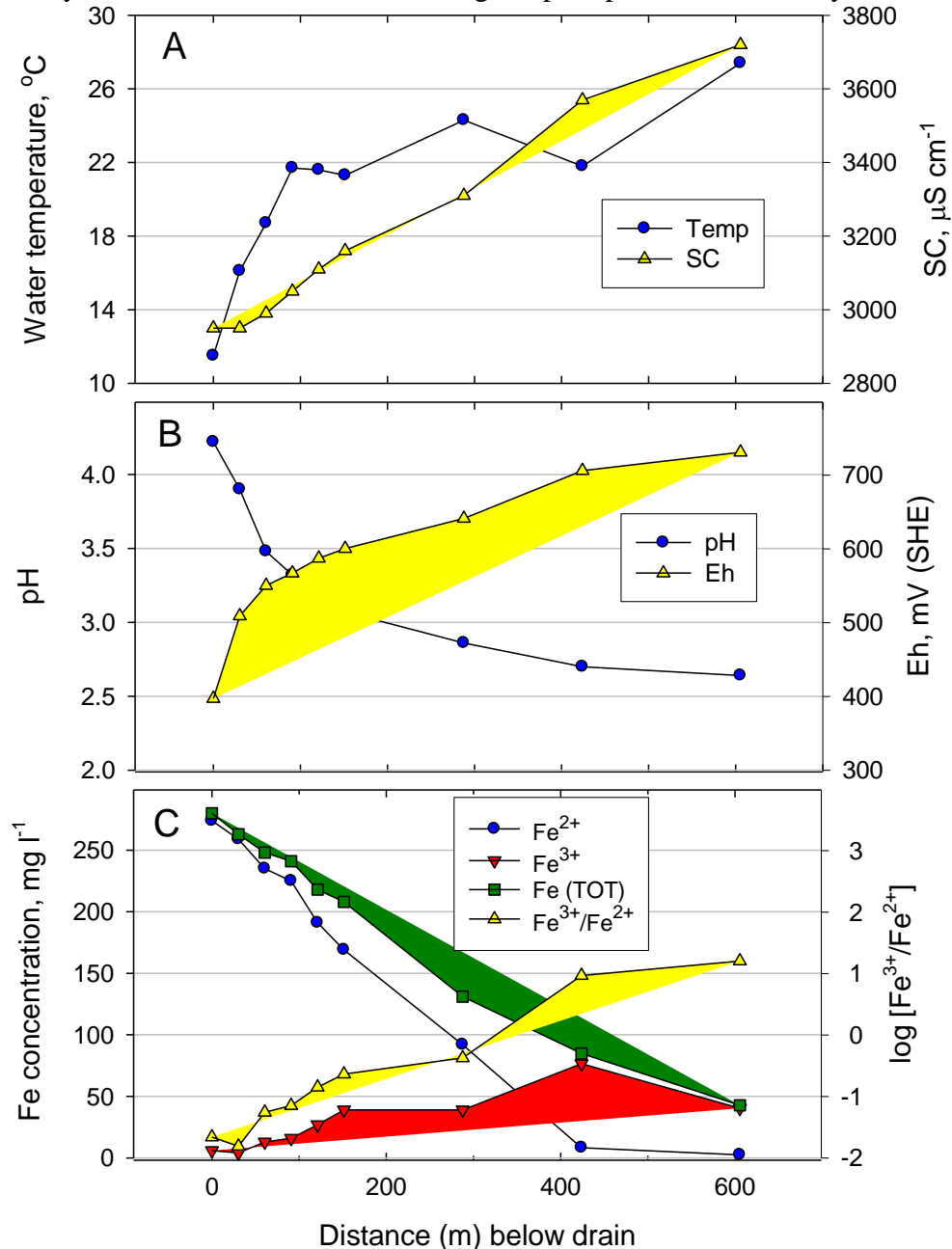


Figure 6. Changes in chemistry of the Mt. Oregon Drain waters with distance below the collapsed adit discharge point. A – changes in water temperature and specific conductance (SC); B- changes

¹ Mineralogical analysis of the iron precipitates was not performed. Although other phases such as schwertmannite or jarosite may have been present, no downstream decrease in dissolved sulfate was noted on the day of sampling.

in pH and Eh; C – changes in Fe^{+2} , Fe^{+3} , total dissolved Fe, and $\text{Fe}^{+3}/\text{Fe}^{+2}$ ratio.

overall reaction (3) shows that 2 moles of H^+ are formed for each mole of Fe^{+2} . Since the Mt. Oregon drain contained 5 mmol of Fe^{+2} ($\sim 280 \text{ mg l}^{-1}$) roughly 10 mmol of H^+ would have been released after precipitation of all of this Fe, explaining the fact that pH readings dropped well below 3 (a pH of 3 corresponds to roughly 1 mmol H^+). As shown in Fig. 6, over 80% of the initial dissolved Fe precipitated by the time the water soaked into the ground, 700 m downstream of the drain. The drop in pH was further amplified by evapo-concentration, which would have increased H^+ concentrations an additional 20%. Trace metals (such as Zn, Cu, Co, and Ni) showed conservative behavior, meaning that they did not partition into the Fe^{+3} precipitates at the low pH's of the mine water, but rather remained in solution, being evapo-concentrated slightly with distance downstream. Concentrations of dissolved As were below the analytical detection limit of $10 \mu\text{g l}^{-1}$ and could not be quantified.

The results of the synoptic sampling of Kate's Coulee are interesting because they illustrate the ability of the Fe-rich mine waters, although not strongly acidic in the subsurface, to generate copious quantities of acid upon contact with the atmosphere. In the preceding case study of the Anaconda drain the iron oxidation process happened in the interior of the mine complex, implying partially flooded conditions. However, in the case of the Mt. Oregon drain the more moderate pH and reduced nature of the waters emanating from the drain (as evidenced by the low Eh and absence of dissolved ferric iron) suggests that the Mt. Oregon mine workings are completely flooded. Only after discharging to the surface did these waters become strongly acidic with $\text{pH} < 3$.

Giffen Spring/Coulee No. 5

The third case study in this report is Giffen Spring, a large man-made spring near the headwaters of Coulee No. 5, an ephemeral tributary of Sand Coulee (Fig. 1). Of the various mine waters in Table 1, Giffen Spring typically has the highest discharge, the highest pH, and the lowest heavy metal concentrations. These conditions, along with information on the orientation of the underground workings with respect to the land surface, have prompted previous workers to hypothesize that the mine workings which Giffen Spring drains are completely flooded (Doornbos, 1989), thus limiting the availability of oxygen and curtailing the rate of oxidation of pyrite or dissolved Fe^{+2} (Fig. 2). Despite the relatively benign pH values, the total acidity loading as dissolved Fe^{+2} from this spring is considerable (Table 1), and the coulee drainage below Giffen Spring is heavily laden with Fe^{+3} precipitates.

The Giffen Spring/Coulee No. 5 site was visited for intensive sampling during June 14 to 15 of 2004. Similar to the preceding example, the purpose of this study was to examine the downstream changes in mine water chemistry and to collect a full 24-h set of hourly samples at three locations (see below) to look for short-term temporal changes in water chemistry. On the two days of sampling, Giffen Spring had a constant pH of 5.7, a constant discharge of roughly 4 l s^{-1} , and a constant dissolved Fe concentration of 62 mg l^{-1} . During our 2004 visit the main flow at Giffen Spring issued from a PVC drainpipe (Fig. 7A) and was joined by a small amount ($< 1 \text{ l s}^{-1}$) of natural groundwater seepage at the head of a natural wetland (Fig. 7B) dominated by cattails and sedges. At this time Giffen Spring and the smaller adjacent groundwater seeps

constituted the only contribution of surface water in Coulee No. 5. This water soaked back into the ground roughly 1.5 km below the headwater springs.

One of the most interesting aspects of the Giffen Spring drain was that the pH of the water *increased* with distance downstream (Fig. 8A), a result that is in contrast to the situation for Kate's Coulee. The main reason for this pH increase is the fact that Giffen Spring water – unlike most of the strongly acidic waters of the GFLCF – contains appreciable alkalinity. The alkalinity of the combined flow from Giffen Spring and the adjacent seeps as measured in the field by titration was approximately 1.5 meq l^{-1} ($75 \text{ mg l}^{-1} \text{ CaCO}_{3,\text{eq}}$). The acidity of this water was not



Figure 7. Photographs of Giffen Spring taken in June 2004. A – View of the spring. The main mine discharge issues from the PVC pipe, and is joined by additional natural seepage from the left (south) before bending right (north) and entering a natural wetland. B – Fe-rich precipitates in the wetland below Giffen Spring.

measured in the field, but was approximated from the dissolved Fe^{+2} concentration assuming that each mole of Fe^{+2} would release two moles of H^{+} (eqn. 3). The acidity of the combined headwater discharge calculated in this way was 1.8 meq l^{-1} . Thus, despite its moderately low pH, the alkalinity and acidity of Giffen Spring were nearly balanced, with a slight (0.3 meq l^{-1}) excess of acidity. The fact that the downgradient waters did not become acidic after near total precipitation of dissolved Fe implies some minor additional inputs of alkalinity, for example from discharging fresh groundwater within the wetland, or via biological reactions within the wetland.

As shown in Fig. 8A, the alkalinity of the surface water below Giffen Spring steadily decreased with distance downstream. This is explained by the consumption of HCO_3^{-} by the acid released during the oxidation and hydrolysis of Fe^{+2} , as shown by the following overall reaction:



The synoptic data (Fig. 8B) show that essentially all of the dissolved Fe in Coulee No. 5 was removed by the time the water soaked back into the ground, 1.5 km below the spring. Ferrozine measurements performed in the field showed that all of the dissolved Fe was present as Fe^{+2} at all locations and at all times. This means that the rate of hydrolysis and precipitation of Fe^{+3} as $\text{Fe}(\text{OH})_3(\text{s})$ must have been faster than the rate of oxidation of Fe^{+2} to Fe^{+3} , a result that is

consistent with the elevated pH of the waters of concern. The difference between dissolved (filtered to 0.2 μm) and total Fe concentrations in the lower reaches of the surface flow (Fig. 8B) indicates the presence of suspended particles of ferric hydroxide, which are notoriously slow to settle out of water.

Paradoxically, as the alkalinity of the water in Coulee No. 5 decreased with distance downstream, the pH of the water *increased* (Fig. 8A). The reason for this unusual behavior is that the water discharging at Giffen Spring had a very high concentration of dissolved CO_2 (i.e., H_2CO_3) and, therefore, a very high partial pressure of CO_2 gas. An estimate of the $p\text{CO}_2$ was made using the program Visual MINTEQ based on the measured pH, temperature, and alkalinity of the Giffen Spring water. The calculated $p\text{CO}_2$ was 0.12 bars, which compares with an

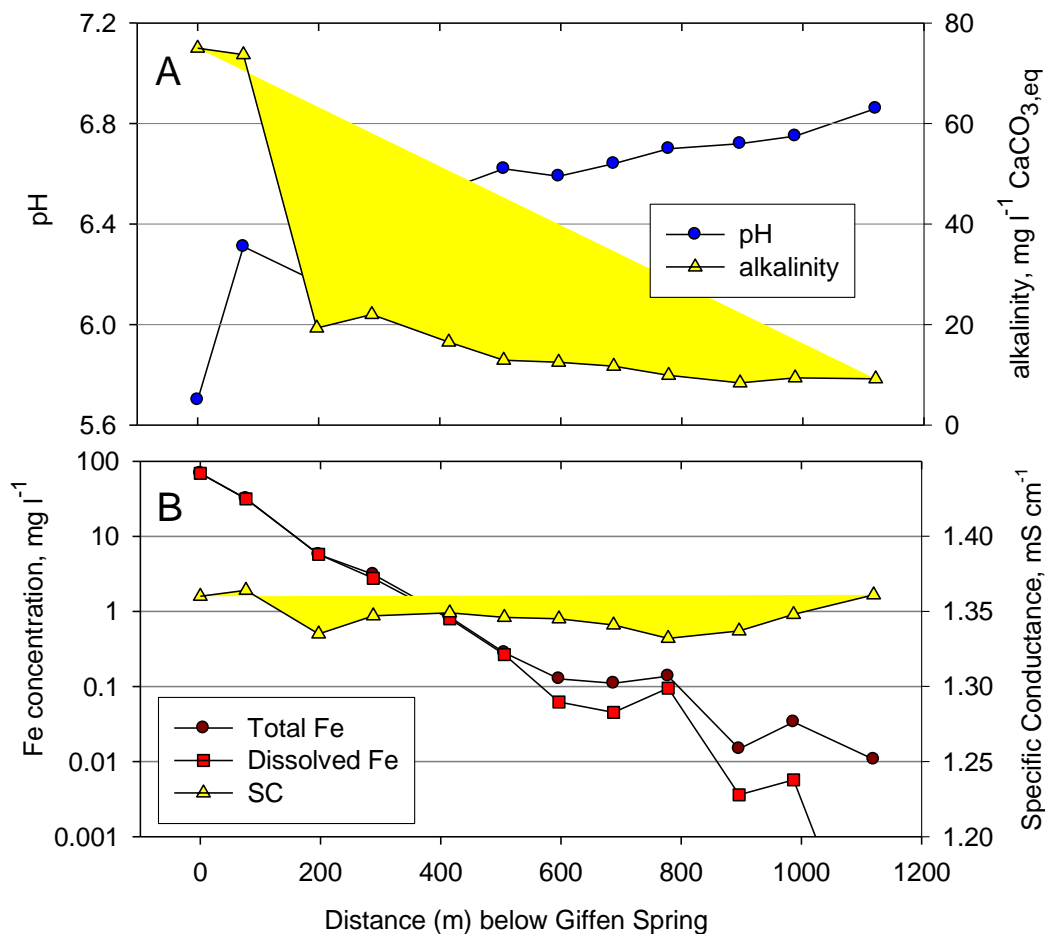


Figure 8. Changes in water chemistry with distance downstream of Giffen Spring. A – pH and alkalinity; B – dissolved and total Fe concentration and specific conductance (SC).

equilibrium $p\text{CO}_2$ of roughly 0.0003 bars for air-saturated water at 1000 m elevation. Therefore, after reaching the land surface, the dissolved CO_2 would have diffused quickly back into the atmosphere. The fact that the pH of the waters increased with distance implies that the rate of loss of CO_2 due to gas-water exchange must have been greater than the rate of consumption of

HCO_3^- from iron oxidation (equation 4), resulting in an overall increase in the $\text{HCO}_3^-/\text{H}_2\text{CO}_3$ ratio, this being the main control on the pH of the water.

Fig. 9 and 10 show some of the diurnal behavior that we observed at two of the monitoring stations in Coulee No. 5. Fig. 9 summarizes diel changes in Fe and Zn concentration at a site located below the natural wetland, roughly 500 m downstream of Giffen Spring (Station 3 of Karper et al., 1998). The pH at this station averaged 6.5 ± 0.15 over the 24-h period, and showed no clear diel trend. Levels of dissolved Fe^{2+} increased roughly an order of magnitude during the night (Fig. 9). This type of behavior is the opposite of what is normally observed in acidic Fe-rich streams, where photo-reduction results in an increase in Fe^{+2} during the day (McKnight et al., 1988). Instead, the night-time increases in Fe^{+2} concentration in the

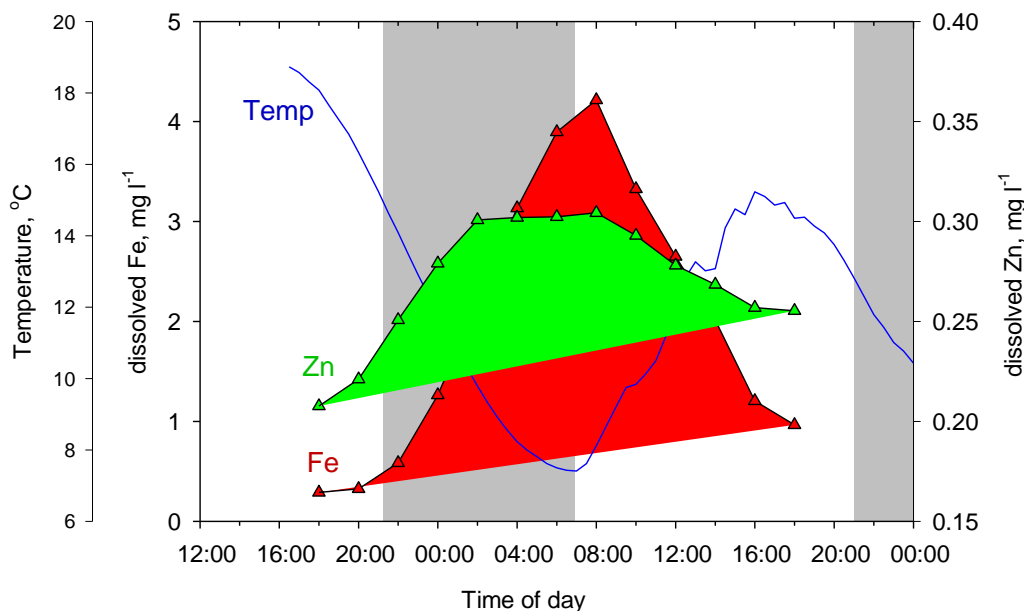


Figure 9. Diurnal changes in water temperature, Fe^{2+} concentration, and dissolved Zn concentration in Coulee No. 5 at a point roughly 500 m downstream of Giffen Spring. Shaded regions denote night-time hours.

more pH-neutral waters of Coulee No. 5 were probably related to the slower kinetics of oxidation and hydrolysis of Fe^{+2} in cold vs. warm water. In other words, the slower rates of reaction during the colder night-time hours would have allowed more Fe^{+2} to advect downstream from the headwater springs. A similar explanation was recently offered by Gammons et al. (2005) to explain diel trends in $\text{Fe}^{+2}/\text{Fe}^{+3}$ in Fisher Creek, another Montana stream impacted by mining.

Fig. 9 shows a robust diel cycle for dissolved Zn concentrations as well, which more or less followed the trend for Fe. The most likely cause of this pattern is cyclic adsorption of Zn^{+2} (and possibly Fe^{+2}) onto freshly formed ferric hydroxide particles. Because the Fe^{+2} was oxidizing and precipitating at a faster rate during the warmer day-time hours, this provided additional fresh metal hydroxide surfaces for the Zn^{+2} to adsorb to during the day (see also Gammons et al., 2005). As well, the thermodynamic driving force for metal cations to adsorb onto hydrous metal oxide surfaces increases with increase in temperature (Nimick et al., 2003), which would tend to reinforce the pattern shown in Fig. 9 of lower dissolved Zn concentrations during the day.

Finally, Fig. 10 shows diurnal changes in selected water quality indicators at our furthest downstream monitoring station, located 1200 m below Giffen Spring. By the time the surface runoff reached this point the pH had increased to 6.85 and the water no longer contained any detectable dissolved Fe. However, the concentrations of dissolved Zn were still elevated. At the downstream station, filtered Zn concentrations again increased during the night from a low of 0.08 mg l^{-1} to a high of 0.14 mg l^{-1} . This nightly increase in Zn is similar to what was noted further upstream (Fig. 9). However, in contrast to the upstream site, the downstream site had a diurnal trend in pH, with slightly higher values in the day and lower values at night. This type of diurnal pH trend is typical of streams in Montana with near-neutral or alkaline pH, and is due to day-time consumption of dissolved CO_2 by photosynthetic plants and bacteria and night-time

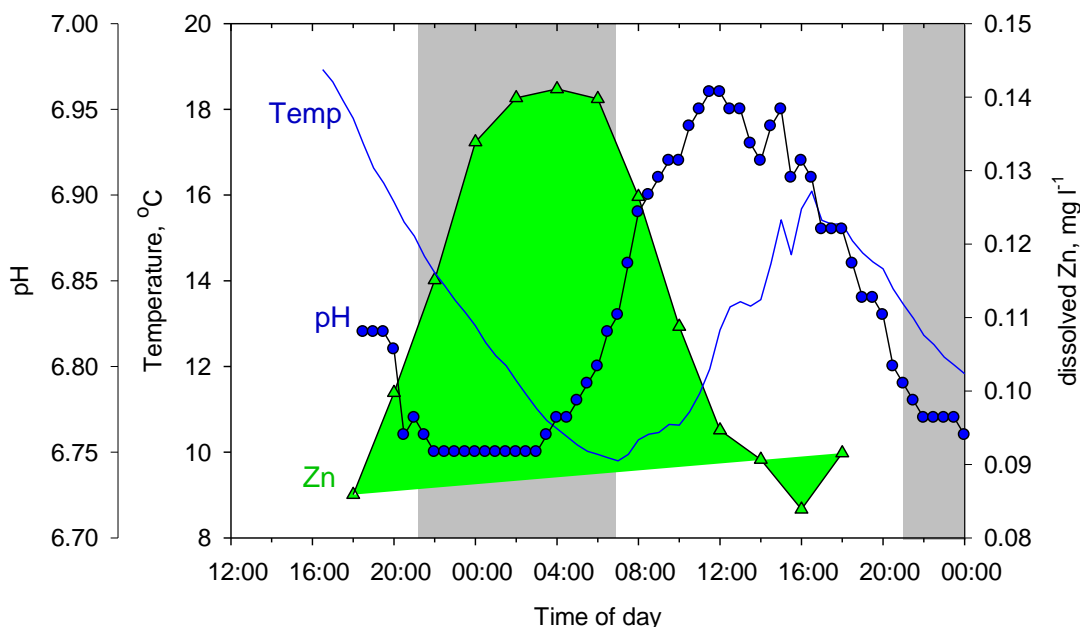


Figure 10. Diurnal changes in pH, temperature, and dissolved Zn concentration in Coulee No. 5 at a site located 1200 m below Giffen Spring. The shaded regions denote night-time hours.

production of CO_2 via respiration. Diurnal changes in Zn^{+2} concentration have been reported from mining-impacted streams with near-neutral pH throughout Montana and northern Idaho (Brick and Moore, 1996; Nimick et al., 2003; Gammons et al., 2005). The Zn cycles are thought to be caused by preferential adsorption of Zn^{+2} onto hydrous metal oxide surfaces during the day, when both the pH and temperature of the waters are higher. Adsorption of Zn^{+2} onto hydrous metal oxide is strongly pH dependent and is also endothermic, meaning that sorption is stronger in warm vs. cold water (Nimick et al., 2003). As shown in Fig. 10, the minimum Zn concentrations occurred in the late afternoon, when both pH and temperature were highest.

AMD Treatment and Control

Many of the AMD waters in the GFLCF pass through populated areas such as the towns of Belt, Stockett, and Sand Coulee, and are easily accessible by animals and humans. Because AMD has been occurring since at least the early 1900s (Shurick, 1909), time alone will not solve

the problem for many centuries. Despite the longevity and severity of this AMD, relatively little reclamation has been done to date, mainly because there is no long-term source of funding to operate and maintain AMD treatment facilities. Treatment has been attempted at a modest scale using passive methods, only to end in disappointing results. Technologies that were tested but failed include aerobic and anaerobic constructed wetlands, limestone channels, and anoxic limestone drains (McArthur, 1970; McCurley and Koerth, 1994). In most cases, the treatment designs failed due to the very high concentrations and loads of acidity, metals and sulfate of the AMD waters. Another negative factor is Montana's harsh winter. Copious quantities of metal-rich precipitate accumulate in the winter months when vegetation is frozen, and these metalliferous precipitates inhibit regrowth of wetland vegetation during the next summer.

Construction and long-term operation of water treatment plants would be very costly and at present exceeds the financial ability of the State of Montana. In lieu of passive or chemical treatment, the most promising mitigation approach involves some form of AMD source control. Due to the large extent of the mine workings (approximately 13 km² for the Anaconda Mine at Belt, approximately 46 km² for the complex of mines at Stockett and Sand Coulee), solutions such as grouting of fractures to reduce the migration of water into the underground workings are impractical. A short-term pilot program in the mid-1980's to reduce the infiltration of meteoric water from the overlying crop lands to the mine workings showed some potential but could not be sustained due to the lack of the necessary funding and administrative infrastructure. An alternative idea (described by Osborne et al., 1987) is to install a series of drain wells into the Kootenai Formation which would route the shallow, clean groundwater overlying the coal-bearing strata by gravity into the underlying Madison Aquifer. If successful, this could cut off the primary source of recharge into the coal beds with a resultant decrease in adit seepage. In some cases it may be more practical to take the opposite approach and completely flood the mine workings by plugging the existing adit drains or installing grout curtains in portions of the interior of the mines. Although this would not prevent mine drainage entirely, the quality of the water exiting the subsurface would likely improve due to reduction of oxygen infiltration rates into the coal-bearing strata. The relative merits of these various alternatives are still being evaluated.

Conclusions

The Great Falls-Lewiston Coal Field contains serious AMD problems which are likely to persist for the foreseeable future. This paper has reviewed some of the existing literature on the state of the problem, and also has presented new data dealing with synoptic and diel changes in chemistry of the mine drain waters after they discharge to the surface. The following is a list of some of the more important conclusions that we feel have relevance to AMD research:

- 1) Portions of each mine complex that are completely flooded (such as Well 4B at the Anaconda Mine, Table 2) have relatively benign water quality, whereas other portions that are partly submerged or completely open to air (such as Well 2B, Table 2) have very poor mine water quality. This underscores the importance of subsurface oxygen ingress in the generation of the acidic waters.
- 2) Although most of the mine drains in the GFLCF are strongly acidic (pH < 3), two of the drains discussed in this report have more moderate pH. In one case (Mt. Oregon drain), the pH of the mine water decreased to values < 3 after discharge to the surface, whereas in the other case (Giffen Spring) the pH of the mine water increased to values > 6 after discharge.

The reason for this contrasting behavior lies in the balance of acidity and alkalinity in the discharge waters. In the case of Giffen Spring, these two quantities were nearly equal at the point of discharge: small additional inputs of alkalinity downstream kept the water from going acidic.

- 3) Although the chemical composition of the drain waters are constant over time periods of several days, diurnal changes in chemistry may occur downstream of the point of discharge. For example, in the lower reaches of the Giffen Spring drainage (pH 6.3 to 7.0), concentrations of dissolved Fe and Zn increased dramatically at night, and decreased during the day. These changes are believed to be linked to the temperature-dependence of the rate of oxidation and hydrolysis of Fe^{+2} to $\text{Fe}(\text{OH})_3(\text{s})$, as well as the temperature and pH-dependence of adsorption of trace metals (such as Zn) onto metal hydroxide surfaces. Similar diel patterns likely occur in rivers and streams draining coal-mining regions elsewhere in the world, such as the Appalachian coal belt of the eastern US.

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