DEVELOPING A SULFATE-ISOTOPE FINGERPRINT OF ACID MINE DRAINAGE TO IDENTIFY UNDERGROUND CONTROLS ON GROUNDWATER FLOW PATHS

Chris Gammons[1] and Shawn Kuzara[2]

[1]Department of Geological Engineering, Montana Technological University

[2]Montana Bureau of Mines and Geology

MBMG
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November 2022

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EXECUTIVE SUMMARY

The main objective of this project was to test the hypothesis that stable S- and O-isotopes of dissolved sulfate (SO_4^{2-}) can be used as a tracer to evaluate whether acid mine drainage (AMD) associated with historic underground coal mines in central Montana has contaminated water wells in the underlying Madison Aquifer, a thick limestone aquifer that provides drinking water for many homes and municipalities in the area. Previous work (Gammons and others, 2013) has shown that the S-isotope ($\delta^{34}S$) and O-isotope ($\delta^{18}O$) values of sulfate in AMD are distinct from the $\delta^{34}S$ and $\delta^{18}O$ of sulfate in Madison Aquifer groundwater. Furthermore, the concentrations of dissolved sulfate in the mine waters are much higher than in the Madison wells. Therefore, even a relatively small amount of mine water in the aquifer should cause a measurable shift in the stable isotope composition of sulfate in the Madison groundwater.

A total of 84 water samples were collected in this study for isotopic analysis of dissolved sulfate. The samples were collected from domestic water wells, groundwater monitoring wells, acid mine drainage, unpolluted springs, and streams. Most of these samples were analyzed for a full suite of major and trace solutes, as well as the stable isotope composition ($\delta^{18}O$ and δD) of water. In addition, 26 samples were analyzed for $\delta^{13}C$ of dissolved inorganic carbon. The new chemical and isotopic data were combined with preexisting data to create a combined stable-isotope database for over 125 samples. An attempt was made to analyze a subset of groundwater wells by helium–tritium age dating to interpret groundwater residence time, but the results were inconclusive.

The results of this study confirm the hypothesis that AMD from the historic coal mines has locally infiltrated to the Madison Aquifer. On an isotope cross-plot ($\delta^{18}O$-sulfate vs. $\delta^{34}S$-sulfate), samples from wells in the Stockett–Sand Coulee area lie along a mixing line between background sulfate in the aquifer and sulfate from AMD, which is derived from oxidation of pyrite in the coal and associated rocks that were disturbed by mining. The latter end-member is well represented by samples of acidic mine drains as well as monitoring wells screened within the flooded mine pools. The majority of AMD-influenced wells are located in proximity to historic coal-mining centers. Many wells with the highest amount of AMD-sourced sulfate were drilled more than 50 years ago, when well-drilling and well-completion protocols were less strict than at present. However, a cluster of domestic water wells from a new subdivision located about 5 mi north and downgradient of the closest coal-mining center contain sulfate that appears to be derived, in part, from oxidation of pyrite from the coal. Additional monitoring wells along the inferred regional groundwater flow path are needed to say with certainty that the sulfate in domestic wells at the subdivision is mining-related or the result of natural weathering of unmined coal beds.

Despite sulfate-isotope evidence for the presence of AMD in aquifers, the vast majority of groundwater wells sampled in this study contain water that meets drinking water standards, based on Department of Environmental Quality guidelines (DEQ, 2021). In terms of water quality, indicators of AMD contamination include elevated sulfate concentration and slightly elevated concentrations of trace metals such as aluminum, manganese, cobalt, nickel, and zinc. None of the water wells had high dissolved iron concentrations. The isotopic composition of sulfate in the Madison Aquifer was not influenced by anaerobic processes, such as bacterial sulfate reduction. Overall, the absence of major water-quality problems in this study underscores the capacity of the Madison Aquifer to buffer groundwater chemistry to a range that is acceptable for human use.

Although they do not change the major conclusions outlined above, certain findings from this study make the interpretation of the stable isotope data more complicated. For example, instead of having a single "background" sulfate composition, the Madison Aquifer shows considerable variation in sulfate and other solute concentrations depending on the distance groundwater has travelled from its inferred area of recharge. This is because the Madison Group contains localized deposits of sedimentary gypsum/anhydrite, which are readily dissolved by groundwater as it travels downgradient (to the north and east) away from recharge areas (south of the field area). Because of contributions from these sulfate minerals, a high sulfate concentration, by itself, is

not necessarily an indicator of AMD contamination. Likewise, just because a water contains dissolved sulfate that is isotopically similar to AMD does not mean that the water must have inherited its sulfate from AMD. An example of this line of reasoning includes several water wells and springs sourced by the Jurassic Formation, which sits atop the Madison Group. This water contains sulfate with an isotopic composition similar to that of the coal-mine AMD, but has much lower sulfate concentration than the Madison samples, and therefore is unlikely to have been influenced by mine drainage.

The approach used in this study has a high transferability to other watersheds in which contamination from coal-mine drainage is known or suspected. Isotopic analyses are relatively inexpensive and samples are easy to collect. For isotope fingerprinting using dissolved sulfate to be successful, a strong contrast is needed between the isotopic composition of sulfate in the mine water vs. sulfate in the background surface and groundwater in the study area. Ideally, the field site should not show evidence of bacterial sulfate reduction, which can change the isotopic composition of sulfate after it is released into the water. This study also shows the importance of supporting water-chemistry data in stable isotope studies.

INTRODUCTION

Historic coal mines around Great Falls, Montana have been discharging highly acidic, metal-laden water for over 100 years. The mines have variable discharge rates and metal loads (Hydrometrics, 2012). The mined coal and associated rock contain pyrite (FeS$_2$) that oxidizes after exposure to air, forming sulfuric acid. Acidic mine drainage (AMD) infiltrates into the alluvial and bedrock aquifers, including the Madison Group, which is an important regional aquifer in central Montana. The limestone is faulted, fractured, and locally karstified; these qualities have greatly increased aquifer storage and transmissivity—but in an anisotropic, highly irregular fashion. The faulted and karstic limestone surface can allow quick infiltration and direct pathways for acid mine drainage to travel downgradient, potentially affecting groundwater quality at wells. However, because it is difficult to predict where preferential flow paths exist in the karstic limestone, it is difficult to identify areas in the aquifer impacted by acid mine drainage and to target remediation efforts. Preliminary findings published by Gammons and others (2013) illustrate the potential for using sulfur and oxygen isotopes of sulfate to fingerprint the AMD entering the local flow system. The Foothills Ranch subdivision is potentially located along the local flow path.

The presented work demonstrates the potential for using isotopic tracers of sulfur and oxygen of sulfate to inexpensively identify the presence and percent composition of acid mine drainage in downgradient wells, potentially identifying preferential flow paths in the limestone aquifer. The transferability of this technique to other locations impacted by acid mine drainage was evaluated by comparing two sources of acid mine drainage in Montana. The data associated with this work are publicly available through the Montana Bureau of Mines and Geology (MBMG) Groundwater Information Center database.

Mining History

Montana's coal deposits were first exploited in the 1860s. In the Stockett–Sand Coulee area, broad benches are incised by ephemeral stream valleys. Most of the coal mines were accessed from the valleys, where horizontal tunnels led into extensive (multiple mile) underground room-and-pillar galleries that followed the shallow dip of the coalbeds (fig. 1). Coal mines in the area are now abandoned (DEQ, 2011).

Geology and Hydrostratigraphy

Most of the waters sampled in this study are located southeast of Great Falls, Montana (fig. 2), at the western edge of the Great Falls Coal Field (Silverman and Harris, 1967). The Sand Coulee Basin is a subarea of the Great Falls Coal Field. The medium-grade bituminous coal is at the top of the Morrison Formation of the Cretaceous Period and is overlain by sandstone and shale of the Kootenai Formation (fig. 3). The coal is interbedded with layers of carbonaceous shale and clay and is roughly 8.5 ft thick in the Sand Coulee area. The coal layer has a nearly horizontal, undulating dip, and crops out in the deeper stream valleys of the area, but is buried roughly 230 to 310 ft below the surface of the flat-topped uplands.

Figure 1. Extensive mining occurred in the Stockett–Sand Coulee mines.

Figure 2. Location of the study area and sample sites. Map shows the outcrop area of the Madison Group (Mm, gray), and green shades of the Cretaceous and Jurassic Formations (modified from Vuke and others, 2002).

Figure 3. Stratigraphic column for the study area.

Kootenai Formation

Comprised of five distinct members composed of interlayered beds of siltstone, mudstone, and sandstone; two of these are relatively clean and thick sandstone water-bearing units.

The uppermost unit (Kk5) is predominantly red mudstone and sandstone, but according to the map is not present above mines in this study.

The Fourth member (Kk4) is predominantly thin-bedded layers of sandstone at the land surface overlying the mine and averages about 80 feet thick.

The Third member (Kk3) is a sandstone unit and is also referred to as the Sunburst Sandstone Member. This unit is about 45 feet thick near the Belt area and is composed of light-yellowish-brown, well-sorted, resistant, quartzose sandstone.

The Second member (Kk2) is about 110 feet thick at the mine and is predominantly red mudstone with limestone lenses.

The basal unit is the Cutbank Sandstone Member (Kk1). The Cutbank Sandstone is resistant quartz sandstone and is up to 100 ft thick (Vuke and others, 2002).

Morrison Formation

Morrison Formation is about 100 feet to 300 feet thick in this area. It is light greenish gray mudstone with lenses of yellowish-brown-weathering sandstone. A subbituminous coalbed as thick as 12 feet is located at or near the top of the Morrison Formation (Vuke and others, 2002).

Swift Formation

Swift Formation is predominantly sandstone that ranges from 50 to 120 feet thick in the area. The Swift weathers grayish orange and is composed of fine- to coarse-grained sandstone.

Big Snowy Formation

Rocks of the Big Snowy Group do not appear to underlie the Belt area. However, the unit is present towards the Little Belt Mountains (Vuke and others, 2002).

Mission Canyon Formation

An unconformity at the top of the Mission Canyon Formation created karst features. Mission Canyon Formation limestone is up to 800 feet thick in the area, and forms the upper unit of the Madison Group. The Madison Group is light gray to dark gray weathering, resistant, massive limestone (Vuke and others, 2002). Drill holes into the Mission Canyon Formation frequently encounter solution cavities. Sinkholes, caves, and other karst features are common in the Mission Canyon Formation.

Lodgepole Formation

Lodgepole Formation is light gray, brownish gray thin-bedded fossiliferous limestone that contains abundant black chert (Vuke and others, 2002).

The public water supply for Sand Coulee, the Foothills Ranch subdivision, and most other residents in the area is from wells completed in the Mississippian Madison Group, a limestone aquifer consisting of the Lodgepole and overlying Mission Canyon Formations. In central Montana, the Madison Aquifer feeds Giant Springs near Great Falls, one of the largest fresh-water springs in the U.S., which discharges ~300 cfs groundwater (Davis and others, 2001) near the banks of the Missouri River (fig. 2). The Madison Aquifer is recharged where it crops out on the flanks of structural and topographic uplifts, such as the Little Belt Mountains to the immediate south of the study area (Madison, 2016).

In the southern part of the study area, the Madison Group is overlain by marine sandstones and carbonates of the upper Mississippian Big Snowy Group that was eroded to the north and are completely absent near Great Falls. Jurassic sediments of the Swift Formation and overlying Morrison Formation unconformably overlie the Madison/Big Snowy strata (figs. 2, 3; Vuke and others, 2002). Sandstone beds of the Swift Formation are primary aquifers for the community of Stockett. Recharge for groundwater in the Swift Formation is more localized than that for the Madison Aquifer. In addition to the aquifers of the Swift Formation and the Madison Group, the Kootenai Formation makes up the third aquifer system in the study area. The lower Kootenai Formation contains two sandstone units (the Cutbank and Sunburst Members) that contain groundwater that is perched several hundred feet above the regional water table in the Madison and Swift Aquifers (Duaime and others, 2004; Reiten and others, 2006). This groundwater infiltrates into the abandoned coal mines, where it forms laterally extensive mine pools that discharge from adits or constructed horizontal drains. The drains direct groundwater to excavated channels or streams (figs. 4, 5, 6). The discharges are typically acidic with high concentrations of metals and, because there are no mitigation measures in place, this has led to local contamination of streams (Osborne and others, 1983a,b, 1987; Karper, 1998; Gammons and others, 2010).

The chemistry and stable isotope characteristics of the AMD waters in the western part of the Great Falls Coal Field were summarized previously (Karper, 1998; Gammons and others, 2010). Most of the AMD waters are strongly acidic (pH 2.5 to 4.5), with typical metal concentrations of (geometric means; all concentrations in mg/L): Al (215), As (0.008), Cd (0.027), Co (1.06), Cu (0.069), Fe (315), Mn (1.50), Ni (2.07), SO_4 (3600), and Zn (8.67) (Karper, 1998). With the exception of Mn, these solute concentrations are much higher than median concentrations from coal mine drainage in Pennsylvania (Cravotta, 2008). As shown by Gammons and others (2010), the isotopic composition of dissolved sulfate from the AMD drains is distinct from sulfate that occurs naturally within the Madison Aquifer. Thus, the isotopic composition of sulfate could potentially be used to test the extent to which AMD from the coal mines is draining into the underlying Madison Aquifer.

Figure 4. A ditch referred to locally as "Rusty Ditch" transports low-pH AMD through the town of Sand Coulee. The AMD completely infiltrates into the ground over about 1 mi.

Figure 5. Kate's Coulee AMD and unimpacted spring water mix together, which raises the pH, allowing aluminum to precipitate (white suspended sediment). Streambank is coated with iron oxide from a former time when pH was too low to precipitate aluminum.

METHODS

Field Sampling

Inorganic Water-Quality Sampling

Water-quality samples were collected from 56 wells (31 Madison, 11 Kootenai, 9 Morrison, 4 Swift, 1 Alluvium), 3 springs (1 Kootenai, 1 Madison, 1 Swift), and 45 acid mine drains (appendix A). Samples referred to in this report as "mine pools" are collected through monitoring wells. MBMG standard sampling procedures (Gotkowitz, 2022) were followed. Groundwater samples were bottled after purging approximately three well-casing volumes and observation of stable field parameters (±10 percent of three readings within 15 min). Grab samples were collected from the springs and AMD sites. Field parameters included pH, temperature, and specific conductance. Nitric (1 percent) and sulfuric (0.5 percent) acids preserved the samples. A 0.45-mm filter was used for the filtered samples. Deionized water was used to rinse sampling equipment that was used at multiple sample sites. Nitrile powderless gloves were worn to prevent sample contamination. Water samples were analyzed by the Analytical Laboratory at the Montana Bureau of Mines and Geology in Butte, Montana for common ions and trace elements (Timmer, 2020).

Stable Isotope Analysis

Water Isotopes

The O- and H- isotope compositions of filtered and unacidified water samples were measured on a Picarro L1102-i cavity ring-down spectrometer (CRDS) at the Montana Bureau of Mines and Geology. The analyses were calibrated using USGS 47 ($\delta^{18}O$ = -19.8‰, δD = -150.2‰) and USGS 48 ($\delta^{18}O$ = -2.22‰; δD = -2.0‰) isotope standards. The results are reported in units of per mil (‰) in standard δ notation versus VSMOW for oxygen and hydrogen (Rozanski and others, 1993). The approximate analytical uncertainty is ±0.1‰ for $\delta^{18}O$-water and ±1‰ for δD-water.

Sulfate Isotopes

Samples for sulfate isotope analysis were prepared at the lab of C. Gammons at Montana Tech. Dissolved sulfate in each water sample was first precipitated as barite ($BaSO_4$), following the methods of Carmody and others (1998). A rough estimate of the sulfate concentration in each sample was obtained using a HACH colorimeter (Hach method 8051). Based on this result, a weighed mass of water sample (usually 50 to 200 g) was transferred to an Erlenmeyer flask where the pH was adjusted to <4 by addition of dilute HCl, after which the sample was stirred and heated to T >60ºC. A 3X excess of $BaCl_2$ was added to precipitate all of the dissolved sulfate as $BaSO_4$. The purpose of the pH adjustment was to avoid precipitation of $BaCO_3$ at this step. However, it is important not to drop the pH too low (<2), to avoid possible exchange of O-isotopes between SO_4 and H_2O. After cooling back to room temperature, the white precipitates were filtered, rinsed several times

Figure 6. At some locations the AMD flows from hillsides (A), and at other locations the contaminated water is piped from the adit to a point of release (B).

with deionized water, and placed in a drying oven at 60°C overnight. By weighing the filter paper and keeping track of masses, it was possible to accurately estimate the dissolved SO_4 concentration in the water samples (the concentration of SO_4 was also determined by ion chromatography). The barite precipitate was transferred to a small glass vial and sent to the University of Nevada–Reno (UNR) for isotope analysis.

All isotope analyses of sulfate were performed at The Nevada Stable Isotope Laboratory at the University of Nevada–Reno using a Eurovector elemental analyzer interfaced to a Micromass IsoPrime stable isotope ratio mass spectrometer (IRMS). The analyses followed the method of Giesemann and others (1994) for $\delta^{34}S$-sulfate, and Kornexl and others (1999) for $\delta^{18}O$-sulfate. The results are reported in units of per mil (‰) in the usual δ notation versus VSMOW for sulfate-O and VCDT for sulfate-S. Based on replicate analyses, the analytical uncertainties are ±0.2‰ for $\delta^{34}S$-sulfate and ±0.4‰ for $\delta^{18}O$-sulfate. All isotope results are in appendix B.

Dissolved Inorganic Carbon Isotopes

Thirty-two water samples (filtered in the field into 20-mL glass vials and unacidified) were analyzed at the MBMG lab at Montana Tech for the isotopic composition of dissolved inorganic carbon ($\delta^{13}C$-DIC) using an Aurora 1030W TIC/TOC analyzer interfaced with a Picarro G2131-i CRDS carbon isotope analyzer. The analyses were calibrated using USGS 40 (glutamic acid, $\delta^{13}C$ = -26.39‰), USGS 41 (enriched glutamic acid, $\delta^{13}C$ = +37.63‰), and NBS 18 (calcite, $\delta^{13}C$ = -5.01‰), as well as in-house standard reference materials (Li_2CO_3 and $NaHCO_3$). The results are reported in units of per mil (‰) in the usual δ notation versus VPDB and have an estimated uncertainty of ±0.1‰ for $\delta^{13}C$-DIC (appendix C).

RESULTS AND DISCUSSION

Madison Aquifer Groundwater System

The Madison Group consists of two separate formations dominated by limestone: the Lodgepole Formation and the overlying Mission Canyon Formation. In general, the depth to the Madison Group increases with distance away from the Little Belt Mountains. Faulting, fracturing, and karstification of limestone units have increased aquifer storage and transmissiv-

ity, but these features are not evenly distributed within the Madison Group.

Recharge sources include precipitation, stream loss, and leakage from overlying aquifers, such as in the Swift or basal Kootenai sandstones. Sinkholes also serve as pathways for recharge.

A cross section (fig. 7) illustrates a conceptual model of the Madison Aquifer, from recharge areas near the Little Belt Mountains to a known discharge point at Giant Springs. Precipitation infiltrates into the aquifer through bedding planes, faults, and fractures. Stream loss also recharges the aquifer where streams flow across outcrops.

The black dashed line in figure 7 represents a potentiometric surface mapped from water levels reported from well logs or measured in wells. Some wells may be completed in portions of the Madison Aquifer where fractured zones act as perched aquifers that are not hydraulically connected to the regionally saturated part of the formation (Ground-Water Information Center GWIC 276129; fig. 7).

Madison Aquifer water levels were monitored in the Great Falls and Little Belt Mountain area and are presented in figure 8. Monitoring well 276129 (black line) is located in a recharge area on the north side of the Little Belt Mountains (fig. 7). This well showed flashy water-level responses in 2018 and 2019 but not in previous years (fig. 8). The water-level response in the recharge area is a characteristic of fracture-flow environments with limited storage (Weight, 2008). Two Madison Aquifer wells completed in the regional water table show similar seasonal water-level responses, indicating greater transmissivity than at well 276129 (fig. 8, orange and blue lines).

Water Chemistry

All water-quality data for samples collected in this study are included in appendix A. Aspects of the analyses that have relevance to the influence of AMD on groundwater in the Madison Aquifer are discussed below.

General Trends

The average and standard deviation of pH and specific conductance (SC, $\mu S/cm$) values of all groundwater samples and springs in the Madison Aquifer were 7.37 ± 0.22 and 755 ± 318, respectively (figs. 9, 10).
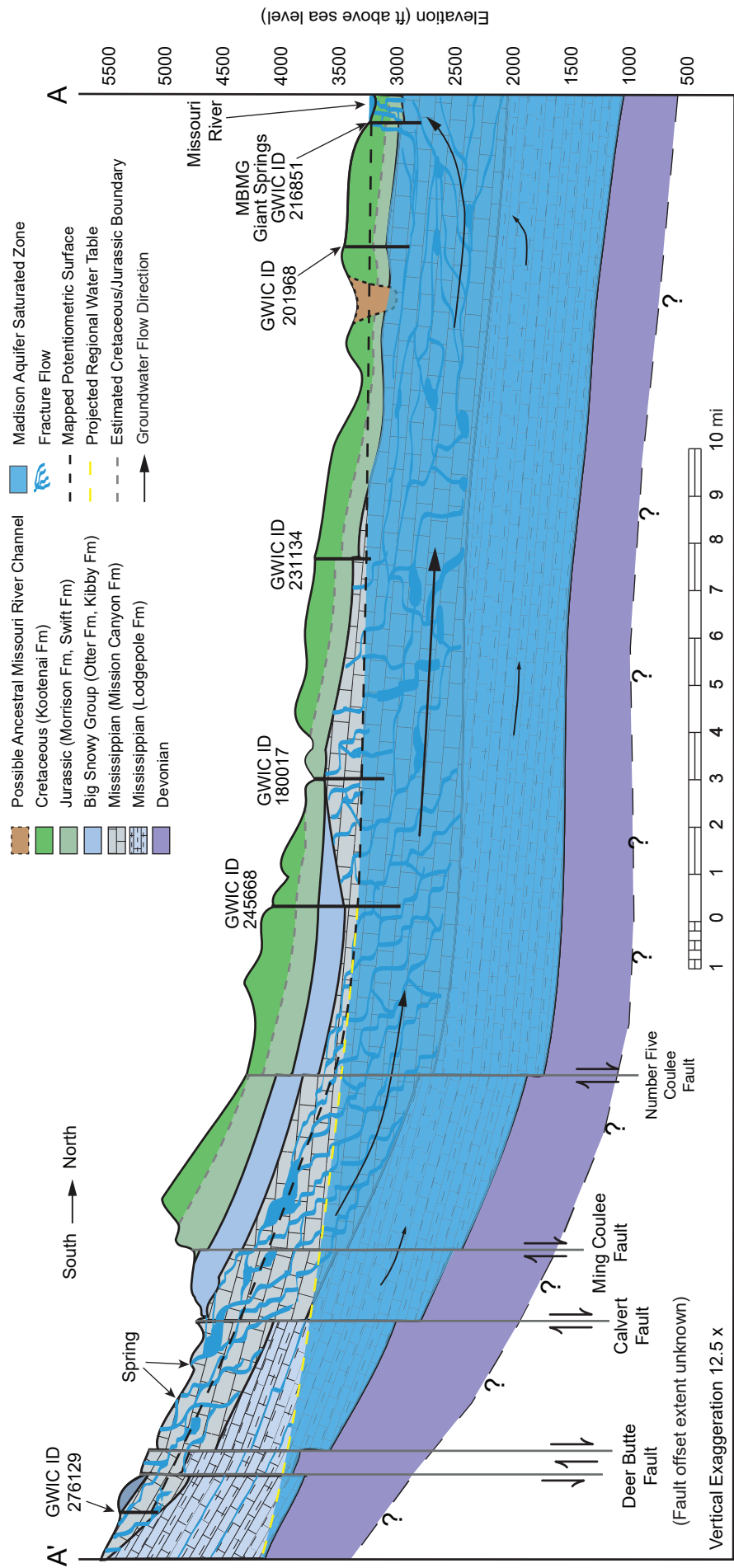
Figure 7. Generalized geologic cross-section showing major hydrostratigraphic units and structures in the study area. Wells completed in the Mission Canyon Formation were used for this cross-section. Study includes wells completed in the Cretaceous Kootenai and Jurassic Swift Formations, but they are not included in the cross-section.
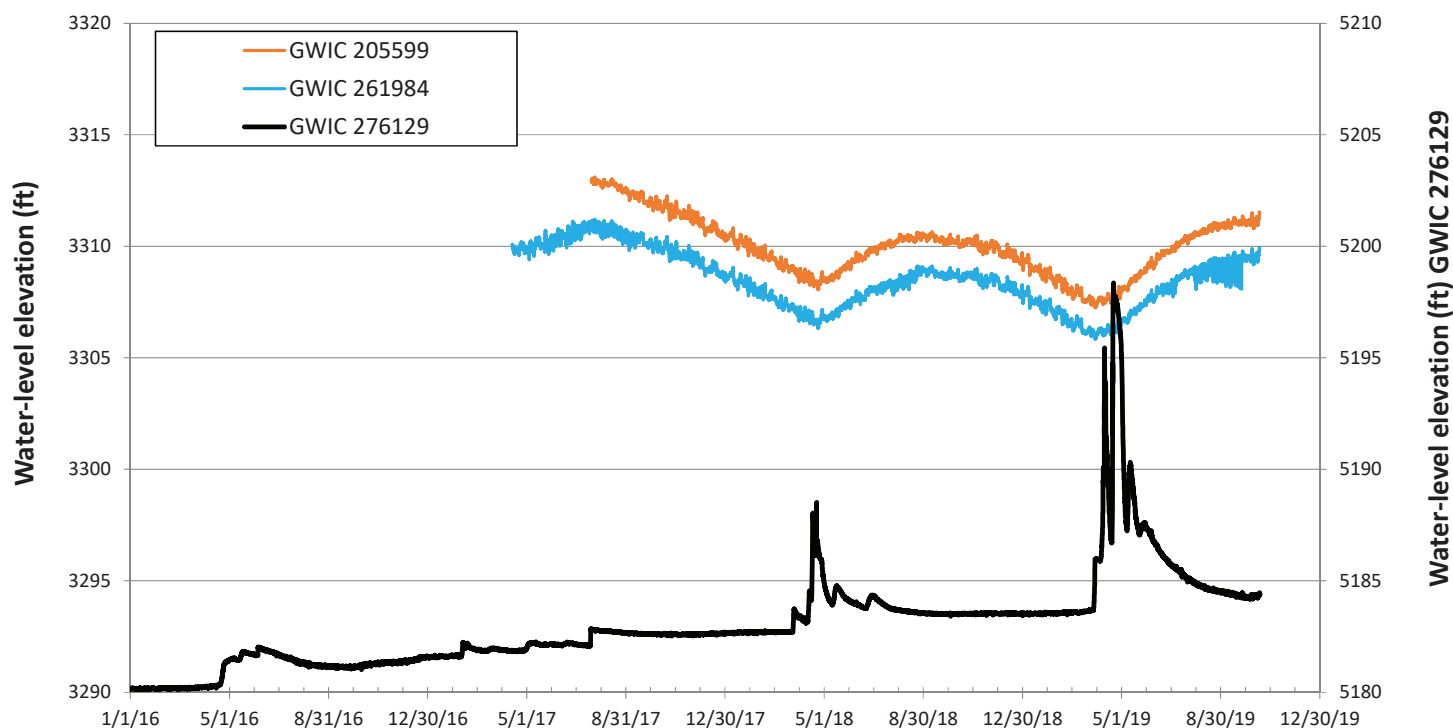
Figure 8. Wells located in the recharge area (well 276129) respond rapidly compared to wells located in the highly transmissive regional water table (205599 and 261984).

Water temperatures ranged from 9.5 to 15°C. Although there are relatively few samples, pH and SC values for the Swift and Kootenai groundwaters are similar to those in the Madison. By contrast, most of the acid mine drainage sites had a pH between 2.5 and 3.5 and SC >2000 µS/cm (maximum of 9,860 µS/cm for the Nelson drain). One large-volume AMD discharge, the Giffen Spring, had a higher pH, near 6. As discussed by Gammons and others (2010), this spring drains a large underground coal mine that is mostly inundated with groundwater, thereby limiting the extent of oxidation of pyrite in the coal. In contrast, the other AMD sites drain mines that are not completely flooded or partially flooded, with easy ingress of air to promote pyrite oxidation.

The major element chemistry of all groundwater and AMD samples collected in this study, as well as in the previous studies of Gammons and others (2010, 2013), is summarized in a Piper diagram (fig. 11). As a whole, the groundwaters are Ca-Mg type in terms of cations, and HCO_3-SO_4 type in terms of anions. The anion makeup of the AMD samples is dominated by sulfate, consistent with pyrite oxidation. Although the AMD waters plot as Ca-Mg type for cations, this is somewhat misleading since most of the acidic seeps have higher concentrations of dissolved Fe and Al than the traditional major cations (see next section).

Samples of Madison Aquifer groundwater have a wide range of SO_4 concentrations. This may result from: (1) regionally, groundwater in the Madison Aquifer accumulates SO_4 as it flows north and east, away from its mountainous recharge areas due to dissolution of salts (gypsum, anhydrite) in the Paleozoic formations (Plummer and others, 1990); or (2) some areas within the Madison Aquifer may receive acidic water from abandoned coal mines and the SO_4 reflects mixing of groundwater with this contamination. The relative importance of these two mechanisms is evaluated after a presentation of the stable isotope results.

The water-quality results (fig. 11) indicate contaminated groundwater in the alluvium in a monitoring well downgradient of AMD areas. The shallow alluvium is not considered an aquifer in this area because it does not produce appreciable amounts of groundwater.

Acid Mine Drainage Chemistry

The water quality of most of the AMD seeps and springs discharging from abandoned coal mines in the Belt–Stockett–Sand Coulee area is extremely poor. Table 1 summarizes data for selected parameters, including most of the trace metals of interest. The data are also summarized in a plot of combined metal concentration (mmol/L of Al + Co + Cu + Fe + Mn + Ni
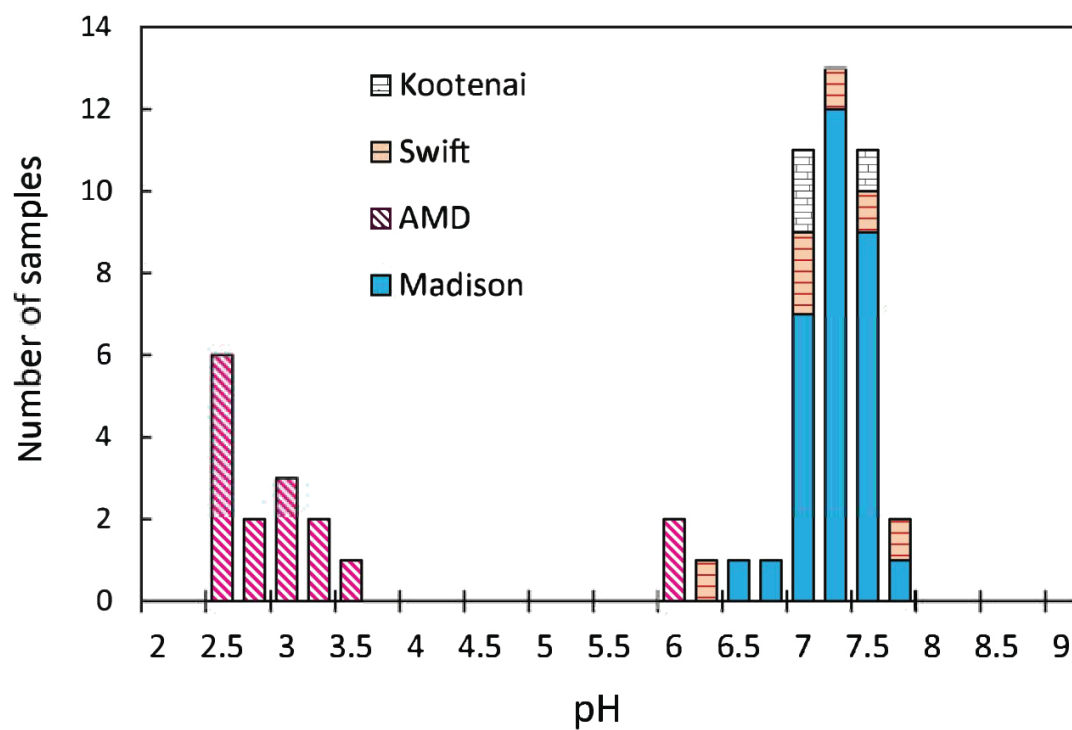
Figure 9. Histogram of pH values for samples collected in this study.
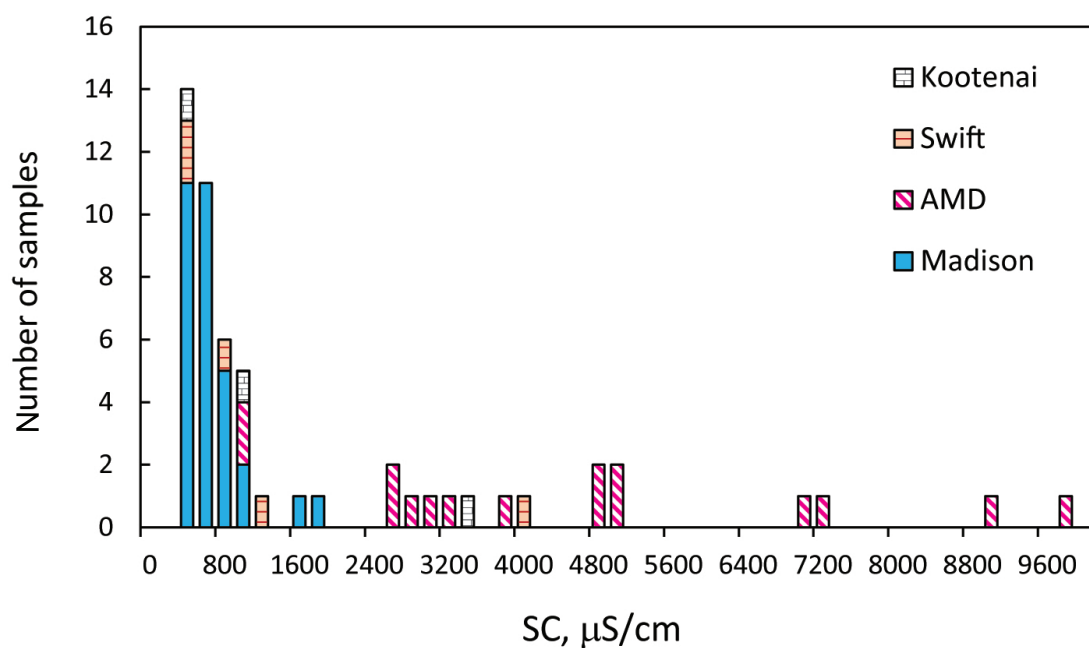

Figure 10. Histogram of specific conductance (SC) values for samples collected in this study.
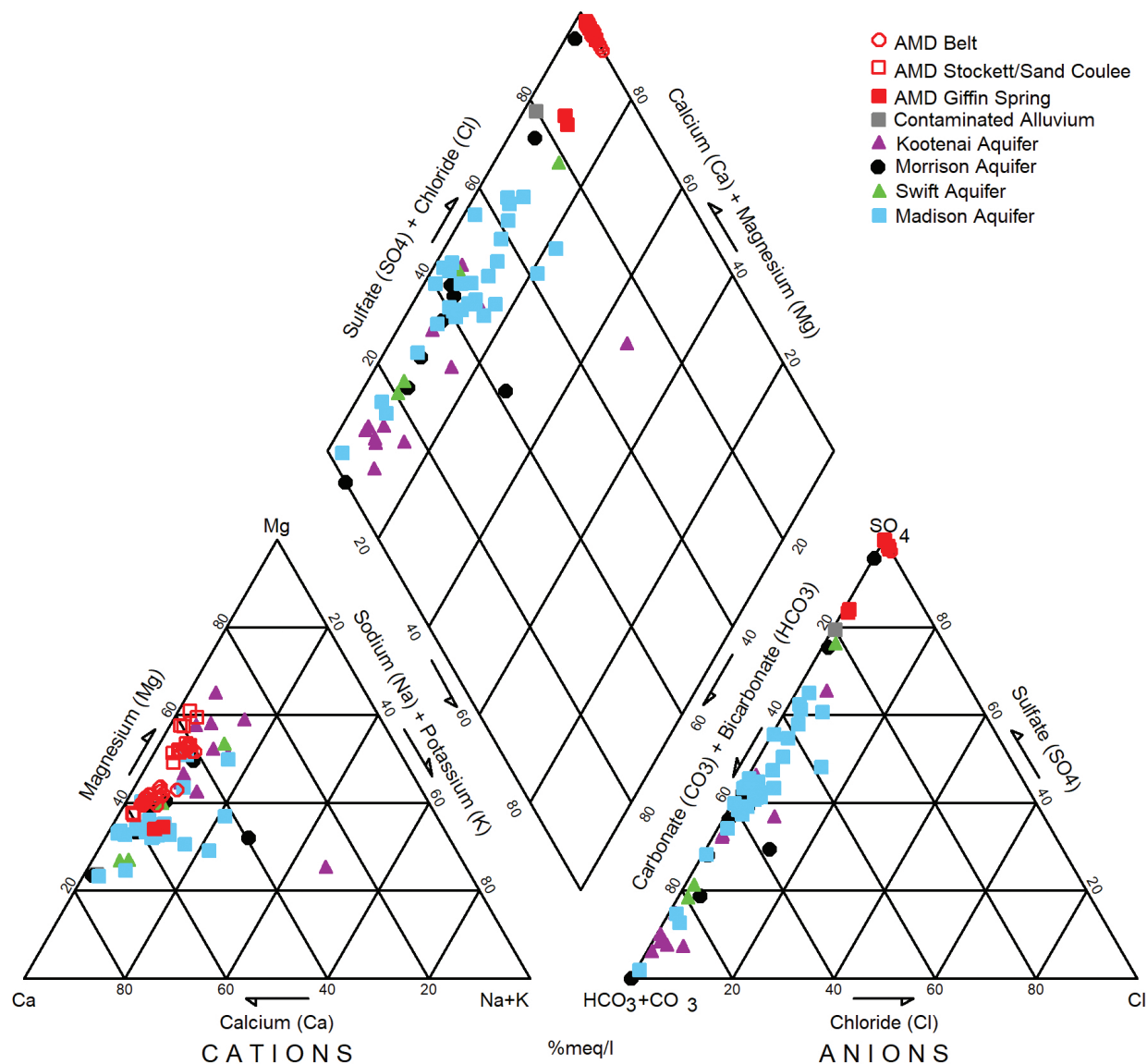
Figure 11. Piper diagram showing the major ion composition of all samples collected in this study.

+ Zn) vs. pH (fig. 12). As expected, the concentrations of metals are inversely related to pH. In general, the abundances (maximum values in parentheses) fall in the order of Fe (1,734 mg/L) > Al (1,166 mg/L) >> Zn (37 mg/L) > Ni, Mn (7 to 8 mg/L) > Co (4 mg/L) > Cu (1 mg/L) > Cd (0.08 mg/L) > Pb (0.025 mg/L). The discharge with the highest metal and sulfate concentrations is the Nelson Drain, whereas Mining Coulee had the lowest pH. As discussed by Gammons and others (2010), the pH of several of the mine drains in the study area decreases after emerging to the surface due to oxidation of Fe^{2+} to Fe^{3+} and precipitation of ferric minerals such as jarosite or goethite. For example, although the pH of the Mt. Oregon drain is near 4 at the sampling point where it emerges from the ground, the pH is closer to 2.5 hundreds of meters downstream where the AMD sinks into the alluvium of an ephem-

eral stream and disappears from sight (Gammons and others, 2010). Speciation of dissolved Fe between the +2 and +3 oxidation states was not done in this study. Based on a comparison with previous work (Gammons and others, 2010), most of the Fe is Fe^{2+} (ferrous) for samples with pH >3 and a mix of Fe^{2+} and Fe^{3+} (ferric) for samples with pH <3.

Several of the mine discharges had high concentrations of dissolved rare earth elements (REE) (see appendix A). Of the REEs, the MBMG lab routinely quantifies lanthanum (La), cerium (Ce), praseodymium (Pr), and neodymium (Nd). Some AMD samples had total concentrations of these four constituents >1 mg/L, with the Nelson drain (OSM-30) having the highest values (1.8 mg/L Ce, 0.65 mg/L La, 1.08 mg/L Nd, and 0.25 mg/L Pr). Although REEs are not known

Table 1. Concentrations of metals and pH values for acid mine drainage samples.

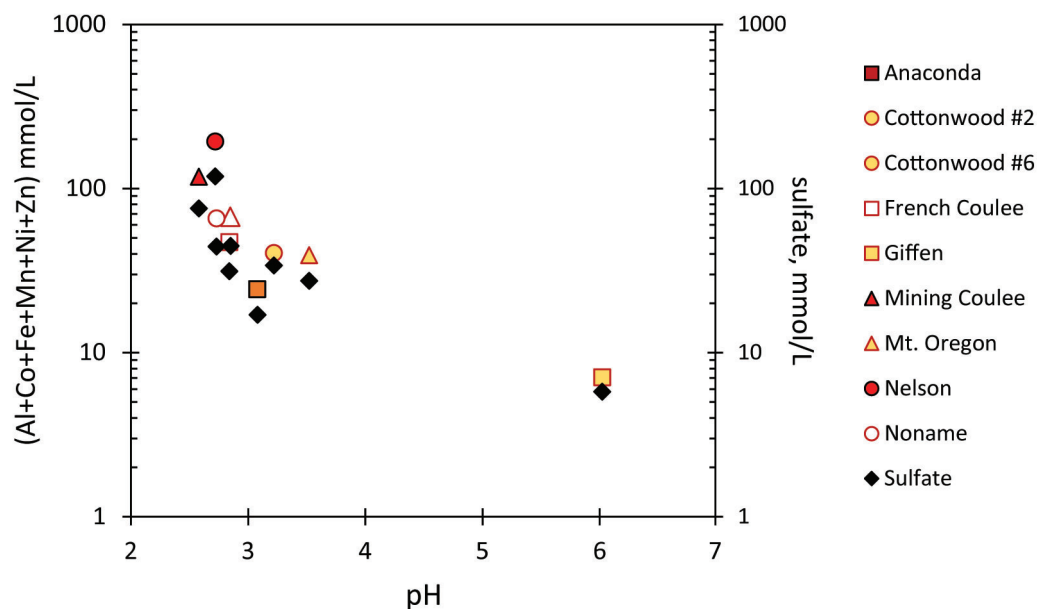| Site	ID	Lab pH	Dissolved Concentration (mg/L)													
			Al	As	Be	Cd	Co	Cr	Cu	Fe	Mn	Ni	Pb	Se	SO4	Zn
Anaconda drain	OSM-7	3.08	111	0.002	0.011	0.01	0.34	0.030	0.01	170	0.4	0.78	n.d.	0.004	1634	3.75
Cottonwood # 6	OSM-31	2.85	283	<.001	0.097	0.03	3.95	0.022	0.24	625	2.3	7.59	0.007	0.010	4280	37.0
Cottonwood # 2	OSM-58	3.22	161	<.005	0.014	0.04	0.85	0.009	0.11	24.4	0.7	1.47	0.004	0.003	3260	6.58
French Coulee	OSM-6	2.84	224	0.013	0.017	0.01	0.19	0.061	0.02	414	0.4	0.46	0.003	0.006	3006	2.29
Giffen	OSM-20	6.02	1.0	0.002	0.002	n.d.	0.09	<.001	0.02	68.2	0.4	0.18	0.003	<.001	555	0.65
Mining Coulee	OSM-33	2.58	726	0.003	0.047	0.08	2.05	0.220	0.82	829	2.1	4.68	0.007	0.019	7250	23.3
Mt. Oregon	OSM-21	3.52	185	0.020	0.026	0.01	0.66	0.023	0.10	267	1.2	1.48	0.011	0.006	2630	6.17
Nelson	OSM-30	2.72	1166	0.030	0.127	n.d.	2.40	0.343	1.09	1734	8.6	5.29	0.025	0.024	11400	20.2
No-Name	OSM-32	2.73	364	<.001	0.032	0.04	1.34	0.100	0.24	427	1.6	2.71	0.013	0.012	4250	14.7

Note. n.d. not detected.

Figure 12. Plot of cumulative dissolved metal concentration (sum of Al, Co, Fe, Mn, Ni, Zn) and sulfate (black diamonds, second y-axis) vs. pH for the mine drainages listed in table 1.

for their toxicity to humans or aquatic organisms (reviewed by Pagano and others, 2015), they have value, and it is interesting to speculate whether REEs could be recovered if a water treatment plant were ever built in the field area (e.g., see Ziemkiewicz and others, 2018).

Other trace metals and metalloids with detectable concentrations in many of the AMD waters include arsenic (As), beryllium (Be), chromium (Cr), and selenium (Se). Maximum concentrations for these four elements were 30, 127, 343, and 24 µg/L, respectively (table 1). In addition, some of the mine waters had elevated concentrations of uranium (up to 365 µg/L) and vanadium (up to 406 µg/L; see appendix A).

Chemical Evidence for the Presence of AMD in the Madison Aquifer

As stated above, all of the Madison wells had near-neutral pH water, regardless of their proximity to sources of acidic coal-mine drainage. This is not surprising, considering limestone's ability to neutralize acidity. Some wells in the Foothills Ranch subdivision near Great Falls (fig. 2) with higher SC and dissolved sulfate concentration also showed slightly elevated concentrations of metals. Although none of the Foothills Ranch wells investigated in this study were acidic (all were completed in the Madison Aquifer), the well with the highest sulfate content (407 mg/L) also had elevated concentrations of dissolved Al (44 µg/L), Co (20 µg/L), Mn (362 mg/L), Ni (95 µg/L), and Zn (133 µg/L). This set of trace elements could be sourced from coal-mine drainage, given the high concentrations of the same elements in the coal AMD (table 1). This particular well had dissolved Fe levels below detection, indicating that, if sourced from AMD, the Fe precipitated out as ferric compounds as the groundwater migrated downgradient.

Two wells completed in the Madison Group in the Sand Coulee–Stockett area (OSM-23 and OSM-26) had anomalously high nitrate concentrations (9.6 and 6.6 mg/L NO_3-N, respectively), suggesting localized contamination of the aquifer. However, neither of these wells had high SO_4 or trace metal concentrations. In fact, none of the Madison wells in the vicinity of the AMD sources in Sand Coulee–Stockett showed consistent evidence of elevated trace metal concentrations, despite several wells with anomalously high sulfate that have an AMD signature (see below). This

underscores the capacity of the Madison Aquifer to buffer pH and thereby minimize the degradation of the drinking water by dissolved metals.

Stable Isotopes of Water

The stable isotope compositions of all water samples collected in this study are summarized in figure 13 and appendix B. The global meteoric water line (MWL) of Craig (1961) and the Butte MWL of Gammons and others (2006) are shown for reference. Groundwater samples that plot to more negative values of δD and δ¹⁸O were recharged at colder temperatures and/or at higher elevations compared to samples with less negative values. As discussed by Gammons and others (2006; see also Clark and Fritz, 1997), the intersection of the local MWL and local evaporation line (LEL) gives the isotopic composition of average groundwater recharge for the region. The local evaporation line for Butte, MT did not fit the field data very well, and consequently a new LEL was developed for this study of the Stockett–Sand Coulee– Belt area: δD = 5.0*δ¹⁸O – 51.5. Groundwater or surface-water samples that plot further along the LEL experienced a greater degree of evaporation.

Groundwater samples from wells completed in the Madison Aquifer, as well as waters flowing to the surface at Giant Springs, show little or no evidence of evaporation (fig. 14). Overall, Madison Aquifer samples from the Stockett–Sand Coulee area have similar isotopic compositions to samples from the Foothills Ranch subdivision and the Belt area. This implies a common source of recharge for Madison groundwater in these three areas. The only exception to this rule was well 210668, which showed signs of evaporation for both sampling visits. Also, well 255442 was isotopically lighter compared to the majority of the Madison samples. The reasons for these two anomalous wells are not known at this time.

Wells completed in the Swift and Kootenai Formations contain water that is shifted slightly along the evaporation line (fig. 15), and that may have been recharged at a higher temperature or lower elevation compared to the Madison wells. This makes sense, especially for the Kootenai Formation, which lies stratigraphically above the Morrison Formation coalbeds. In some areas low conductivity shale units create perched groundwater in the Kootenai Formation. Isotopic evidence suggests the groundwater in the Koote-
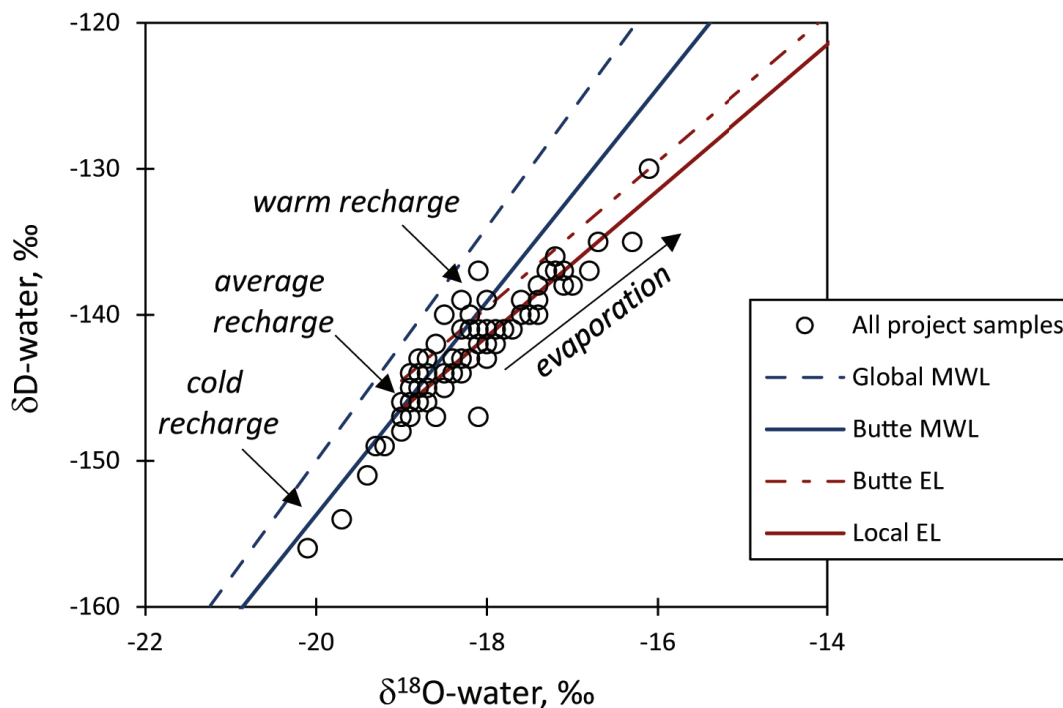
Figure 13. Summary of all water isotope data collected in the project. Global MWL, meteoric water line of Craig (1969); Butte MWL and Butte EL, meteoric water line and evaporation line for Butte, MT (Gammons and others, 2006). Local EL, local evaporation line (this study). The intersection of the local meteoric water line and the local evaporation line gives the isotopic composition of average groundwater recharge.
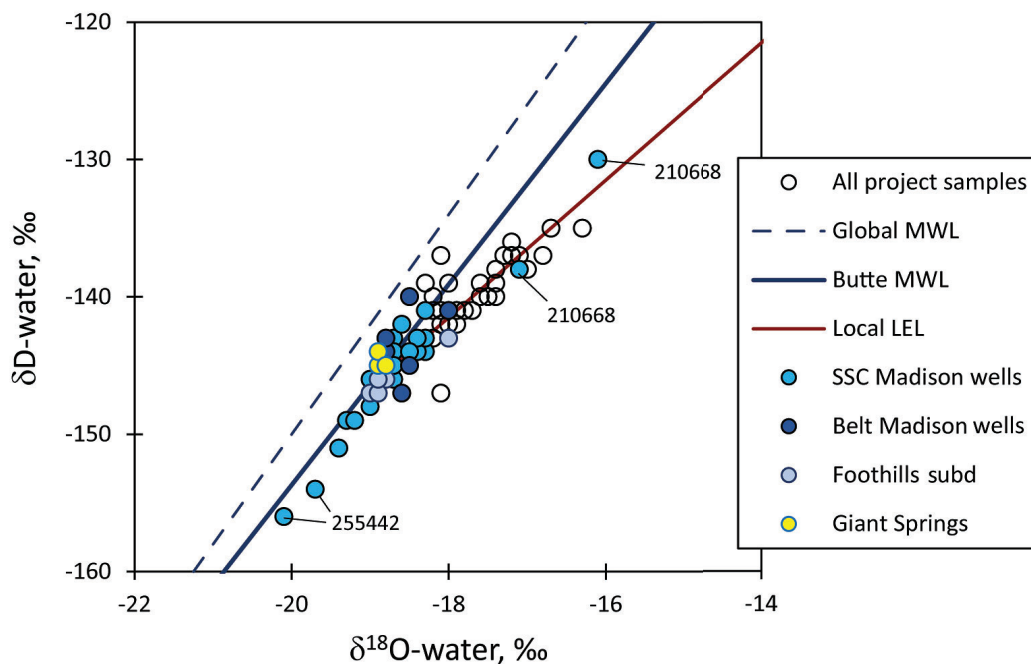

Figure 14. Water isotope data for wells and springs in the Madison Aquifer. Anomalous Stockett–Sand Coulee (SSC) Madison samples deviating from Butte MWL are labeled with GWIC ID numbers.

nai Formation was derived locally by rain and snow-melt falling in the Stockett–Sand Coulee–Belt area. One Swift well (GWIC 236507) had an anomalous isotopic composition for reasons that are not known.

Samples of AMD in the Stockett–Sand Coulee and Belt areas (fig. 16) have water-isotope compositions that are similar to the groundwater sampled from Kootenai and Swift Formations. This is also true for water in the Anaconda underground mine pool at Belt. The mine pool water is accessed through wells completed in the mine void. These waters tend to cluster along the local evaporation line, and have inferred recharge water that is isotopically heavier than the Madison wells. Like the Kootenai wells discussed above, the underground mine-pool water and acidic drains are perched and are recharged by downwards percolation of rain and snowmelt falling on the surrounding foothills.

Overall, the water-isotope data obtained in this study support the conceptual model for how groundwater in the three aquifer systems is recharged. The regional water table lies in the Madison Group, and is recharged where this formation crops out on the north side of the Little Belt Mountains where infiltration of precipitation in the outcrop areas and from stream loss across outcrops occurs. The Swift Formation unconformably overlies the Madison (fig. 3) in the Belt

vicinity and is recharged by local precipitation and leakage from overlying aquifers. The third aquifer system includes perched groundwater that sits in the coalbeds at the top of the Morrison Formation, as well as sandstone lenses in the overlying Kootenai Formation. This is the water that seeps into the abandoned coal mines, eventually discharging as acidic drains. This groundwater is exclusively recharged by local precipitation (rain and snowmelt) falling on the grassy plateaus in the Stockett–Sand Coulee–Belt area. Based on observed isotopic shifts away from the LEL, this water was partly evaporated, possibly when it was stored in the soil zone prior to infiltrating to the perched aquifer in the basal Kootenai Formation. Some of this ground is planted with hay, alfalfa, and wheat. However, loss of water by plant transpiration does not fractionate water isotopes (Clark and Fritz, 1997).

Stable Isotopes of Dissolved Sulfate

An isotope cross plot ($\delta^{18}O$ vs. $\delta^{34}S$) for dissolved sulfate in samples from the Stockett–Sand Coulee area (fig. 17) shows a positive linear trend, with AMD samples clustered at strongly negative values near -10 to -15‰ for both $\delta^{18}O$ and $\delta^{34}S$, and background wells and springs in the Madison Aquifer extending to strongly positive values near +10 to +15‰. A number of domestic wells completed in the Madison contain sulfate with an isotopic composition more similar
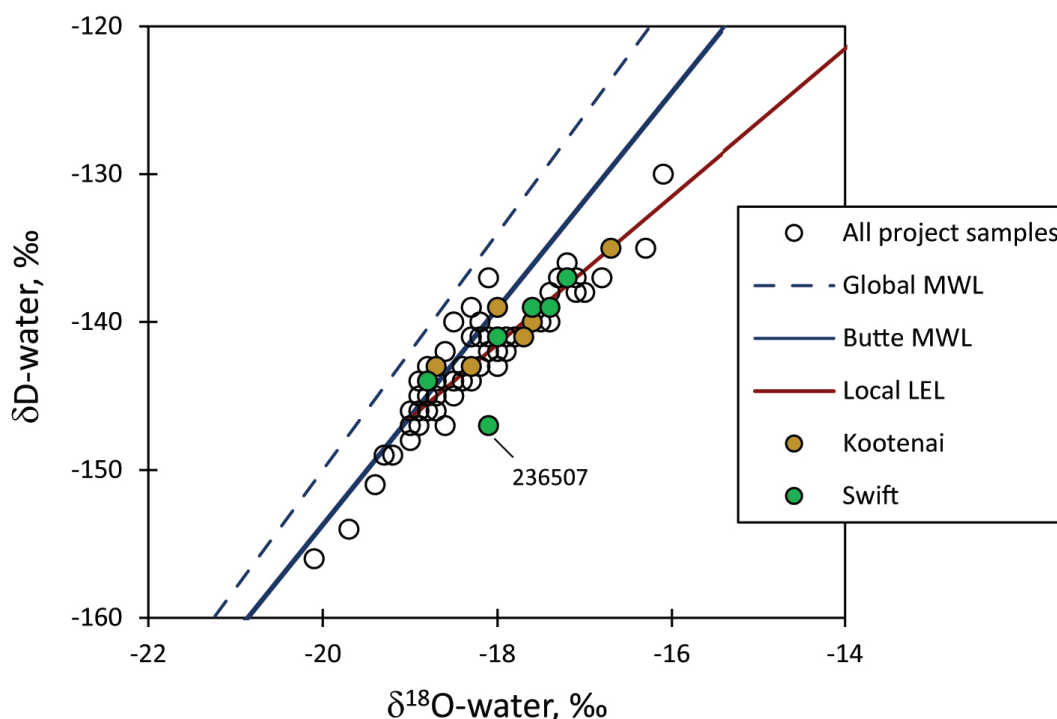

Figure 15. Water isotope data for wells in the Kootenai Formation and Swift Formation aquifers. One anomalous Swift Formation sample is labeled with its GWIC ID, 236507.
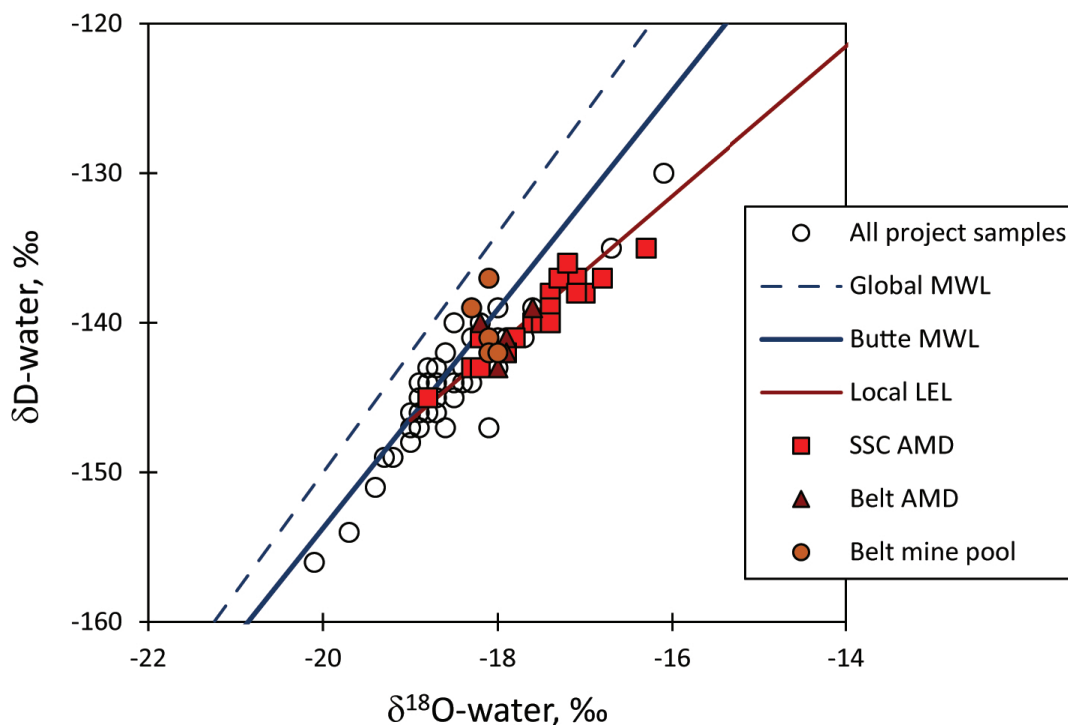
Figure 16. Water isotope data for acid mine drainage (AMD) in the Stockett–Sand Coulee (SSC) area and the Belt Mine area, as well as water samples taken from the flooded mine pool at the Belt Mine.

to the AMD source than the end-member Madison source. These wells, many of which also have anomalously high dissolved sulfate concentrations, most likely have a component of sulfate from AMD. Although several groundwater samples from the Swift, Kootenai, and Morrison Coal units also plot along the apparent mixing line, their sulfate may have a different origin (see below).

Figure 18 compares the isotopic composition of sulfate from Madison Aquifer wells in the Stockett–Sand Coulee with domestic wells drilled into the Madison Aquifer in the Foothills Ranch subdivision, near Great Falls. The Foothills Ranch samples also plot on an apparent mixing trend, but with a steeper slope than that for the Stockett–Sand Coulee samples. The mixing endmember for the Foothills Ranch samples appears to be shifted to lower $\delta^{18}O$ and/or higher $\delta^{34}S$
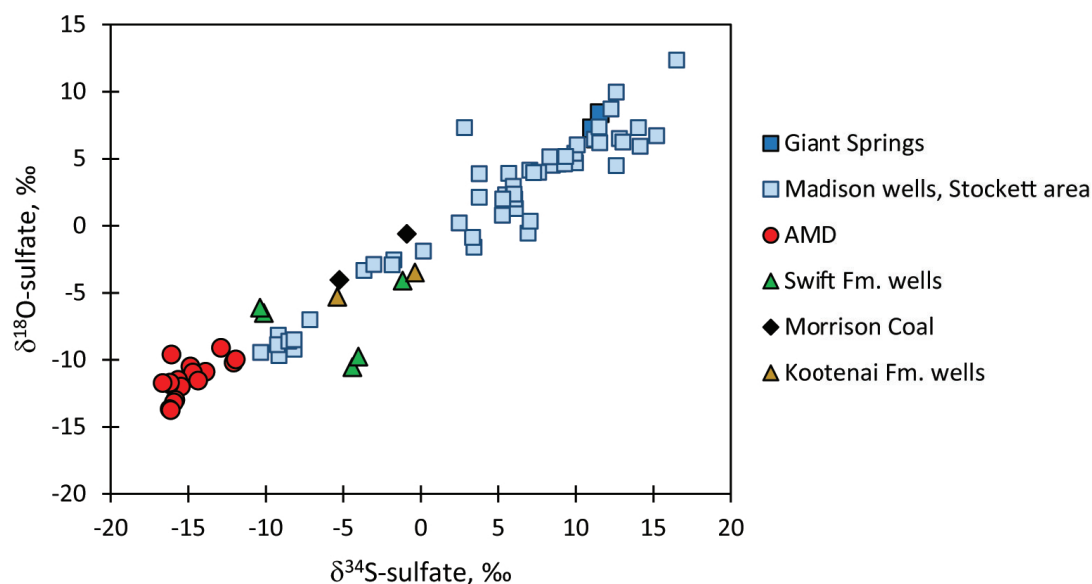

Figure 17. O- vs. S-isotope composition of dissolved sulfate for samples collected in the Stockett–Sand Coulee area. (Data for Giant Springs are added for comparison).

values. For comparison, samples collected in the Belt area are plotted on figure 19. Acidic mine drains in the vicinity of Belt have $\delta^{18}O$ values similar to AMD from Stockett–Sand Coulee, but with more positive values of $\delta^{34}S$ (fig. 19).

Mixing of AMD with Belt Creek

Belt Creek is a clear mountain stream that begins in the Little Belt Mountains roughly 30 mi south of the field areas of this study. The upper and middle reaches of the watershed include extensive outcrops of the Madison Group. Visual observations show that after it leaves the mountains, Belt Creek loses some water to leakage to alluvium. As a result, the flow of

lower Belt Creek can drop to very low levels in summer. Immediately upstream of the town of Belt, AMD from abandoned coal mines is discharged directly to the creek with no treatment. This degrades the quality of the creek, especially in summer's low-flow periods (Reiten and others, 2006).

Figure 20 summarizes the isotopic composition of dissolved sulfate in Belt Creek above and below the AMD discharges and the AMD. The upstream creek sample has a sulfate-isotope composition that is similar to background Madison Aquifer sulfate, as represented by Giant Springs. In contrast, sulfate in Belt Creek sampled 500 yd downstream (at a bridge in the center of town) has an isotopic composition that
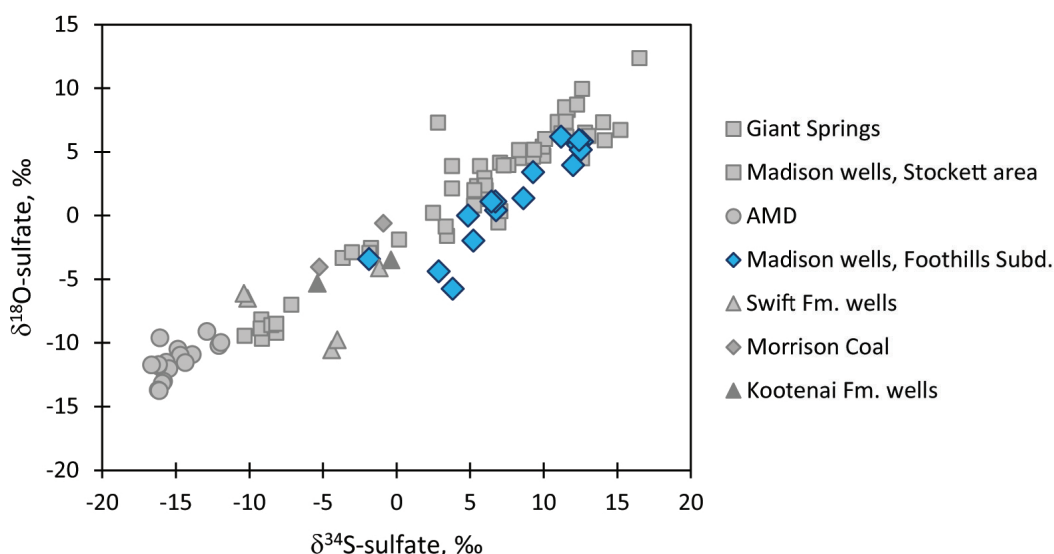

Figure 18. O- vs. S-isotope composition of dissolved sulfate for samples collected in the Foothills Ranch subdivision area (blue symbols). Data from Stockett–Sand Coulee are shown in gray for comparison.
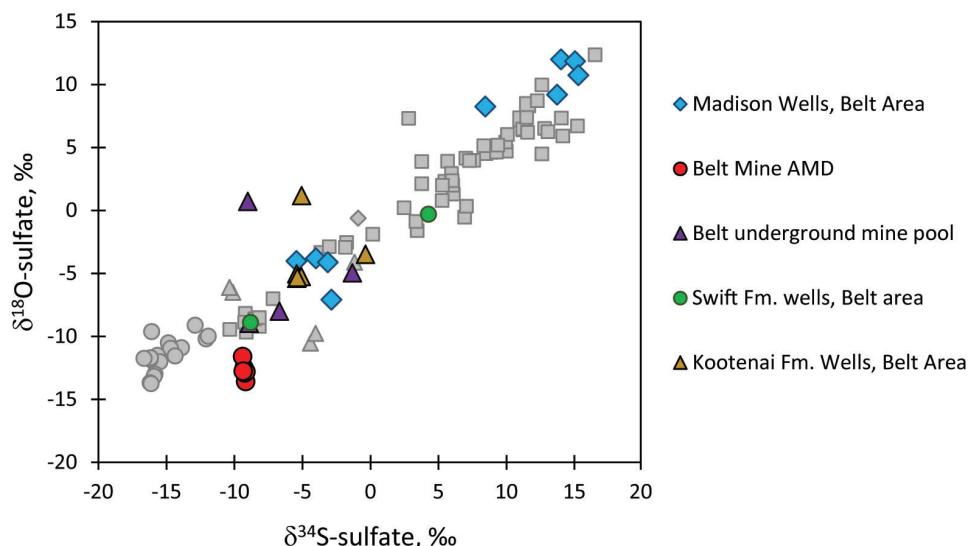

Figure 19. O- vs. S-isotope composition of dissolved sulfate for samples collected in the Belt area (colored symbols). Data from Stockett–Sand Coulee area are shown in gray for comparison.

is approximately midway on the mixing line between the upstream and AMD end members. This means that roughly half of the dissolved sulfate in the downstream sample was derived from AMD. Thus, despite its relatively small flow, the fact that the AMD is highly concentrated in sulfate and other solutes means that the contributions from AMD are sufficient to degrade the water quality of Belt Creek.

Seasonal and Year-To-Year Variations in Sulfate Isotopes

Many of the water wells and AMD seeps in this study were sampled on more than one visit. Figure 21 summarizes data for these locations. In most cases, the $\delta^{18}O$ and $\delta^{34}S$ values were similar between visits, some of which were separated by several months, and others by several years. The average standard deviation between repeat visit samples was ± 0.7‰ for $\delta^{34}S$ and ± 0.8‰ for $\delta^{18}O$. These variations are greater than the analytical uncertainty in the isotope analysis (± 0.2‰ for $\delta^{34}S$ and ± 0.4‰ for $\delta^{18}O$), but are still relatively small, which implies that seasonal or year-to-year variations in isotopic composition of dissolved sulfate are of secondary importance compared to the total spread in the data.

Stable Isotopes of Dissolved Inorganic Carbon

A total of 32 water samples collected in this study were analyzed for the concentration of dissolved inorganic carbon (DIC) as well as the DIC-isotope composition ($\delta^{13}C$-DIC). The data are summarized in appendix C and figure 22. The parameter "DIC" is the sum of dissolved CO_2 (H_2CO_3), bicarbonate ion (HCO_3^-), and carbonate ion (CO_3^{2-}). For the acidic AMD drains, H_2CO_3(aq) is the only significant DIC species present. However, for most of the groundwater samples with near-neutral pH, DIC will be a mix of H_2CO_3(aq) and HCO_3^-, with traces of CO_3^{2-}.

As shown in figure 22, the C-isotope data fall into three groups. Group I includes three of the more acidic AMD drains. These low-pH waters have low DIC concentrations (<20 ppm) and isotopic compositions consistent with derivation of DIC from atmospheric CO_2 ($\delta^{13}C$ = -6.5‰ to -8‰). Group II includes water well samples from the Swift and Kootenai Formations, as well as two Madison samples and one mine-drain sample (Giffen Spring) that had a higher pH value of 5.4. The Group II waters have higher DIC concentrations (50 to 80 ppm) and lighter $\delta^{13}C$ values (-12‰ to -15‰). It is possible that the Group II water samples obtained much of their DIC from the soil zone. As discussed by Clark and Fritz (1997), DIC in soil water and shallow groundwater is a mixture of isotopically light CO_2 produced by the decay of organic matter, and heavier CO_2 derived from the atmosphere or by dissolution of carbonate minerals. In the case of the Swift and Kootenai samples, incorporation of soil-derived DIC makes sense given the fact that groundwater

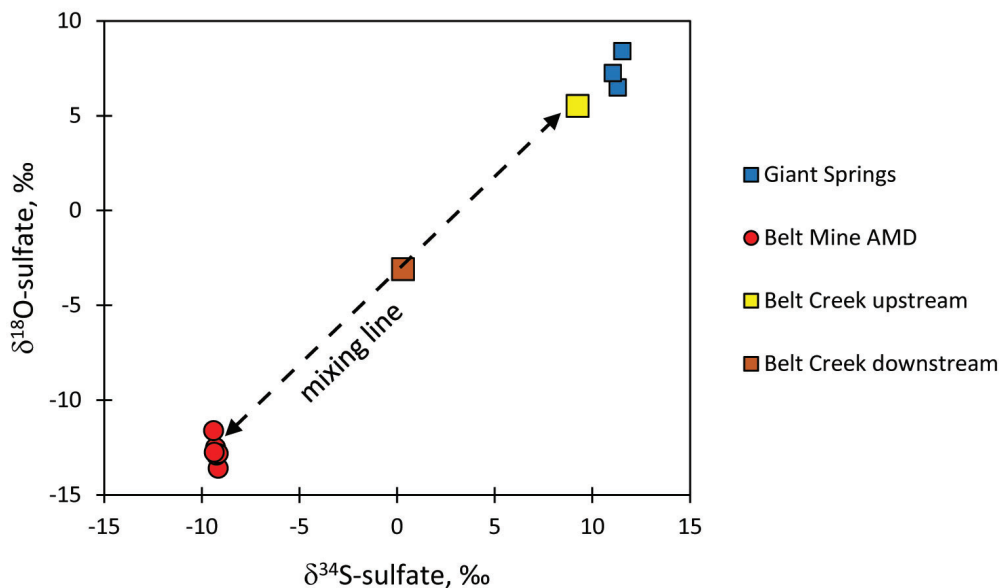Figure 20. O- vs. S-isotope composition of dissolved sulfate for samples from Belt Creek collected above and below its confluence with AMD discharge from the Belt Mine. Based on the position of the downstream sample along the mixing line, it can be concluded that roughly half of the total dissolved sulfate in the downstream sample came from AMD, the other half being background sulfate in Belt Creek.

Figure 21. Concentrations and C-isotope compositions of dissolved inorganic carbon (DIC) in groundwater samples in this study. The data cluster into three groups, indicating differences in the sources of DIC. Numbers in legend are GWIC ID numbers for wells. The average standard deviation for locations sampled multiple times was ±0.7‰ for $\delta^{34}S$ and ±0.8‰ for $\delta^{18}O$.

Figure 22. Sampled water sources fall into three groups based upon the primary source of DIC ($\delta^{13}C$ of approximately +3‰).

in these formations was recharged locally on fields that are mostly used to grow hay and alfalfa.

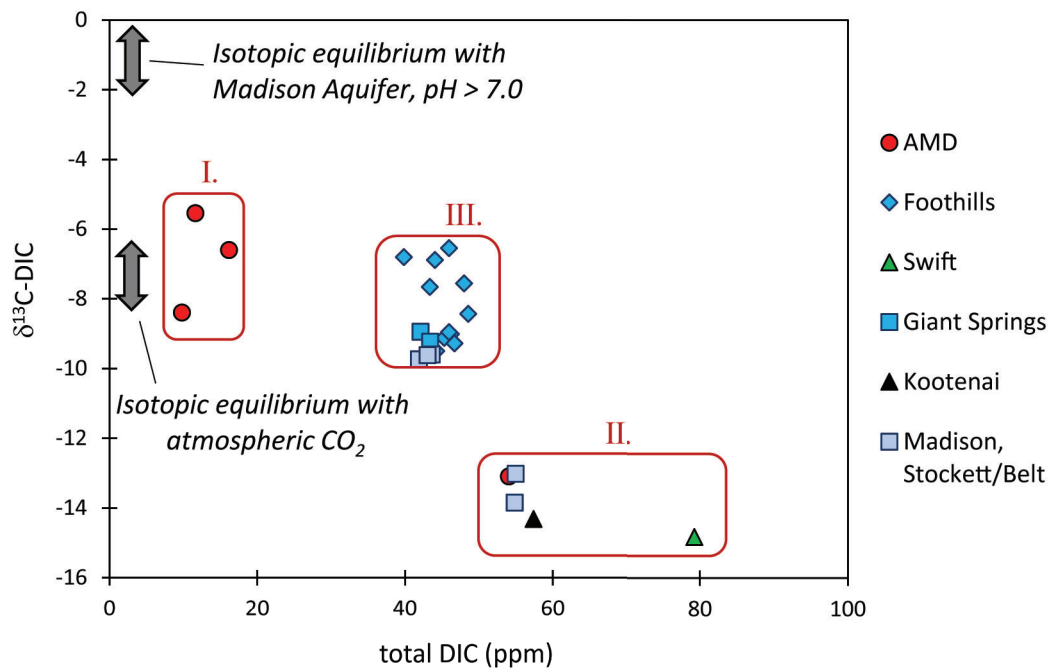Group III (fig. 22) includes most of the water samples from the Madison Aquifer, including Giant Springs and all of the Foothills Ranch subdivision wells. These waters have δ^{13}C-DIC values in the range of -6‰ to -10‰, and moderate DIC concentrations around 40 to 50 ppm. Given the long flow paths of groundwater in the Madison Aquifer, it is tempting to assume that the DIC in this groundwater would have equilibrated its carbon isotopes with the Madison Group. However, the average δ^{13}C of carbonate minerals in the Madison Group is +3.1 ± 1.2‰ (Plummer and others, 1990). If C-isotope exchange was occurring between the carbonate rock and the groundwater, then the range in δ^{13}C-DIC should be heavier, approaching 0 to +3‰. In their regional study of the Madison Aquifer, Plummer and others (1990) concluded that C-isotope exchange was minimal on the time scale of the groundwater flow paths investigated. This is consistent with the study of Gonfiantini and Zuppi (2003), who showed that C-isotope exchange between DIC and limestone can take thousands of years. The fact that C-isotope disequilibrium is widespread in the Madison groundwater suggests that the residence time of water in the aquifer is likely on the order of tens or hundreds of years, not thousands of years. This is consistent with the idea that groundwater flow in the Madison Group is focused along high-conductivity fractures and cave/karst features.

Regional Sulfate Trends in the Madison Aquifer

Plummer and others (1990) conducted a regional study of the chemistry and isotopic composition of groundwater in the Madison Aquifer, and it is useful to consider some of their findings to help interpret the results of this study. Figure 23 shows changes in the concentration of total dissolved solids (TDS) of Madison groundwater in Montana and bordering states. The general pattern is an evolution from low TDS at high-elevation recharge areas to high TDS in downgradient wells to the north and east. Coincident with the rise in TDS, Plummer and others (1990) documented an evolution in groundwater type from Ca-Mg-HCO$_3$ near the recharge sites, to Ca-SO$_4$ at middle flow-path distances and intermediate TDS values, and to Na-K-Cl type at longer flow paths and the highest TDS values (fig. 24). As discussed by Plummer and others

(1990), these chemical changes are due to dissolution of ancient evaporite minerals in the Madison Group. Dissolution of gypsum explains the initial evolution toward Ca-SO$_4$ water, and this is followed by dissolution of halite and sylvite to form Na-K-Cl water (fig. 24).

As shown by figure 23, the present study area is located in a part of the Madison Aquifer where there is a steep increase in TDS from a recharge area to the south (Little Belt Mountains). In this region of the aquifer, the increase in TDS is mainly attributed to dissolution of gypsum (Plummer and others, 1990).

In their regional study, Plummer and others (1990) included data on the S-isotope composition of dissolved sulfate in Madison groundwater. Data for samples from central Montana are summarized in figure 25, along with results for the water samples of this study. The data of Plummer and others (1990; yellow circles) follow a trend labeled "Path A." This path connects water with very low sulfate concentration in the recharge area of the Madison Aquifer (Box I) with high-TDS groundwater that is saturated with gypsum (Box II). Note that SO$_4$ in Box II is isotopically heavy, with δ^{34}S > +20‰. A heavy δ^{34}S value is typical of gypsum formed by evaporation of seawater. From the standpoint of the present study, Path A represents the regional "background" trend in evolution of δ^{34}S-sulfate vs. sulfate concentration for the Madison Aquifer.

Groundwater Path B in figure 25 is the pathway of most relevance to this study. In this case, recharge water for the Madison Aquifer evolves along Path A, picking up some evaporite sulfate as it flows northward away from the Little Belt Mountains. However, when this groundwater reaches the Sand Coulee–Stockett–Belt area, it mixes with sulfate-rich AMD. This causes the trajectory of Path B to bend sharply towards an isotopic composition corresponding to AMD (Box III). The more contaminated the well, the closer it plots to Box III.

Groundwater Path C in figure 25 applies to some of the shallower aquifer systems, e.g., the Kootenai, Morrison Coal, and Swift Formations. Path C begins with recharge water falling on the low-elevation plateaus surrounding and to the immediate south of the study area. This water infiltrates into the Kootenai Formation and is the main source of water for the flooded coal mines at the top of the Morrison Formation. Once
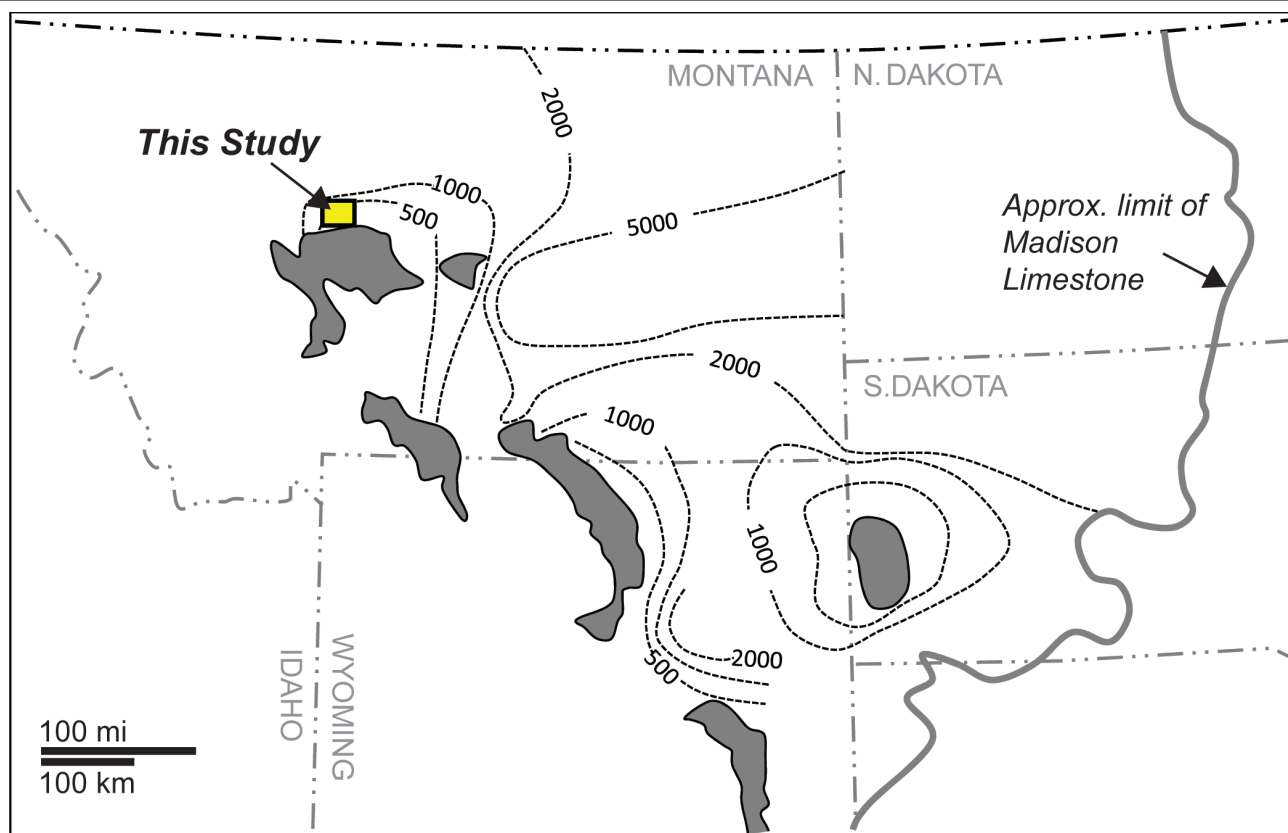
Figure 23. Map showing regional variation in total dissolved solids (TDS, mg/L) of groundwater in the Madison Aquifer (taken from Plummer and others, 1990). Shaded regions show areas of basement uplift where the Madison Group and older rocks are exposed. The study area lies in an area where the TDS is changing quickly due to dissolution of sedimentary gypsum. The general flow of groundwater across the map is northward and eastward (from low to high TDS).

in contact with the abandoned mines, the water picks up isotopically light sulfate from the oxidation of pyrite in the coal and the isotopes evolve towards Type III (AMD). Some of this water may also penetrate deeper into the Swift Formation, which lies above the Madison.

The data shown in figure 25 are replotted vs. _reciprocal_ sulfate concentration in figures 26 and 27. The reason for doing this is that the end members for isotope mixing (Boxes I, II, and III) can be defined more accurately. Also, some of the subcategories in the data are separated out better in figure 26 (e.g., Foothills Ranch subdivision, Giant Springs, etc.). Figure 27 shows the same evolution pathways A, B, and C, where Path A is the regional path for the Madison Aquifer, Path C corresponds to the shallower aquifers (Kootenai, Morrison, Swift), and Path B shows the evolution of Madison groundwater as it mixes with AMD. Instead of following a single mixing line, the data for Paths B and C show a continuum of mixing lines. This is caused by differences in the relative proportion of mixing of the three sulfate end members

(recharge, Madison gypsum, and AMD). For example, the Foothills Ranch subdivision wells, being further north than the other Madison water samples in this study (fig. 2), appear to have dissolved more of the end member (Box II) evaporite sulfate in addition to potentially receiving acid drainage from the coalbeds. Some of the Madison wells that fall closer to Path C in figure 27 are located further south, and may not have dissolved much gypsum before receiving sulfate from oxidation of pyrite in the coalbeds.

A final point that needs to be made with regards to the Foothills Ranch subdivision wells is that just because many of the wells appear to have inherited sulfate from oxidation of pyrite in the Morrison coalbeds (Path B of fig. 27), this doesn't necessarily mean that this occurred from leakage of AMD from abandoned mines in the Sand Coulee–Stockett area. It is also possible that oxidation of pyrite in the coal occurred as a consequence of natural weathering. Several of the well logs in the subdivision mention drilling through coal before reaching the Madison Aquifer. However, considering that natural oxidation of unmined coal is
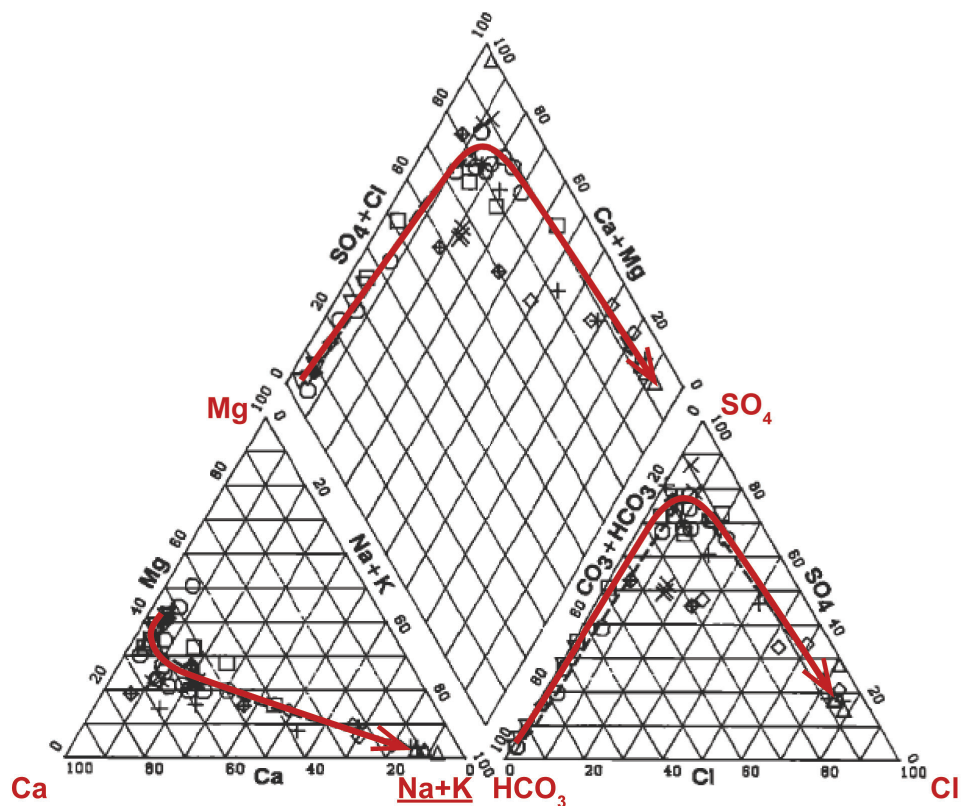
Figure 24. Piper diagram summarizing the chemical evolution of groundwater in the Madison Aquifer at a regional scale with data points from Plummer and others (1990). Data from the current study are plotted similarly in figure 11.
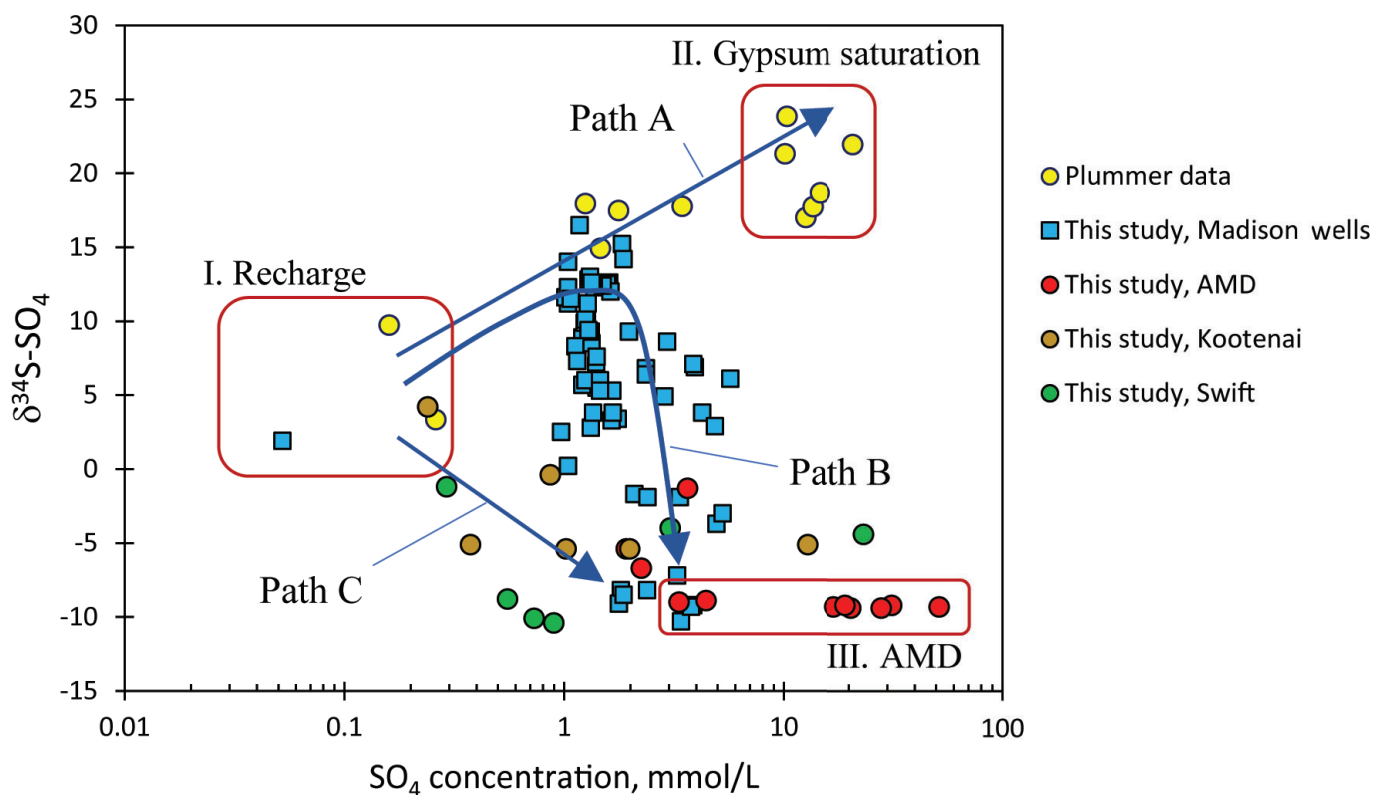

Figure 25. Plot of δ^{34}S-sulfate vs. sulfate concentration comparing the data from Plummer and others (1990) for Madison water samples from Montana (yellow solid circles) vs. waters investigated in this study. See text for explanation of the boxes and flow paths.
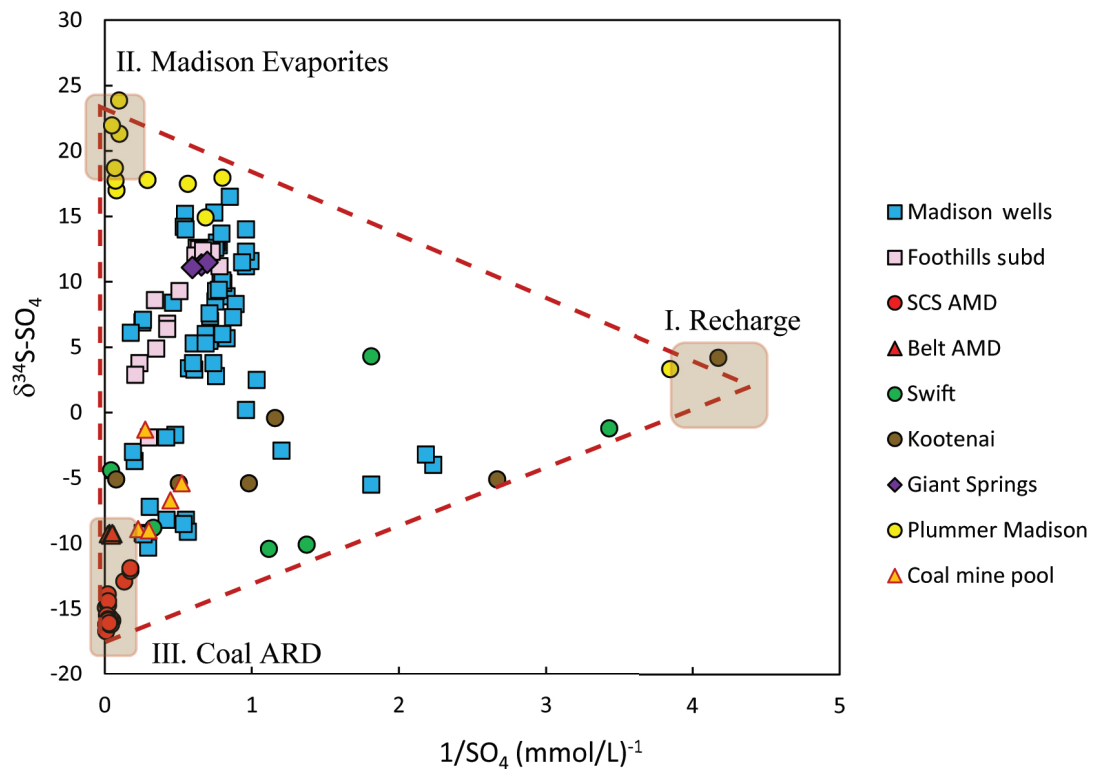
Figure 26. Plot of δ^{34}S-sulfate vs. reciprocal sulfate concentration for waters investigated in this study as well as data from Plummer and others (1990) for Madison Aquifer samples from Montana.
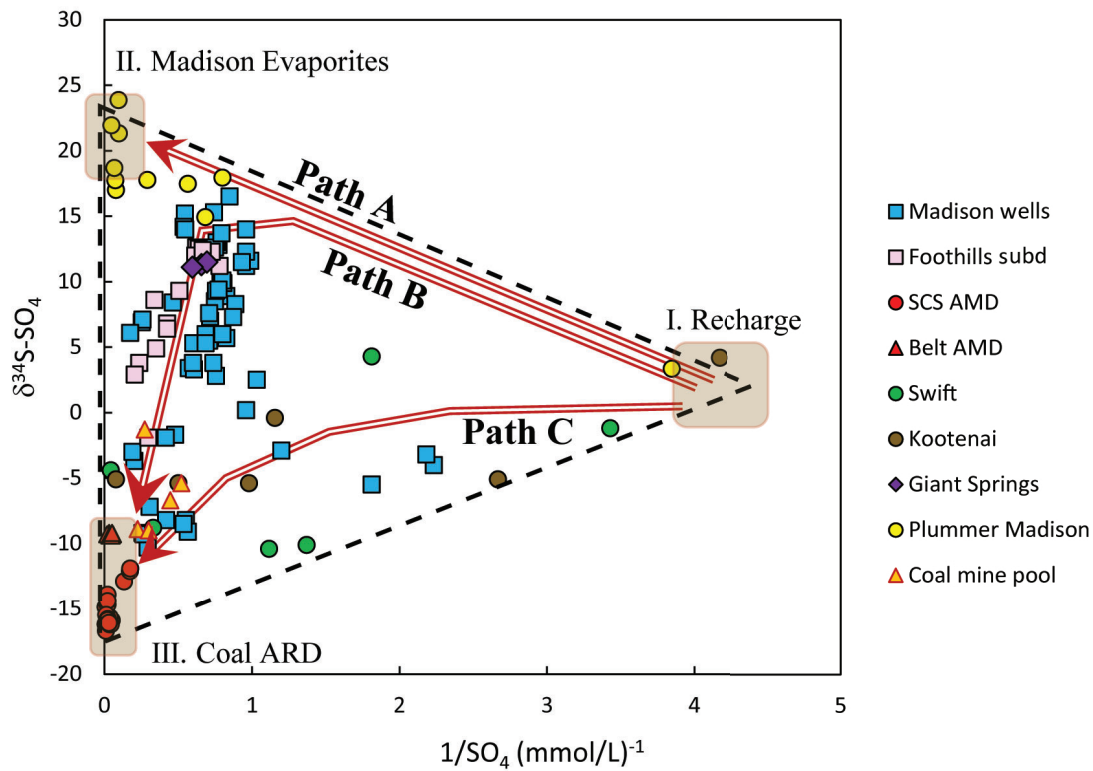

Figure 27. Plot of δ^{34}S-sulfate vs. reciprocal sulfate concentration showing groundwater evolution paths A, B, C (paths shown here are similar to figure 25).

likely to be a slow process taking thousands or even millions of years, it is unclear how much sulfate could be added to the Madison Aquifer by this mechanism. This question could possibly be addressed by installation of additional groundwater-monitoring wells in the Madison between the northern edge of the coal mines and the subdivisions on the outskirts of Great Falls.
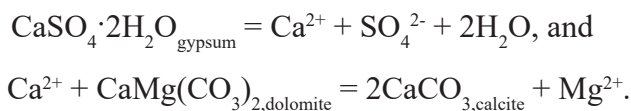
Geochemical Modeling of AMD Mixing with Madison Aquifer Groundwater

Chemical data for all of the Madison Aquifer samples and most of the AMD drains were input into the geochemical modeling program Visual Minteq (Gustafsson, 2020) v. 3.1, a modification of the original Minteq program of Allison and others (1991). The main purpose of this exercise was to evaluate the saturation state of the waters with minerals that may be buffering the water chemistry. Saturation indices (S.I.) were computed as the logarithm of the ratio of the ion activity quotient (Q) divided by the equilibrium constant (K_{eq}):

$$S.I. = \log (Q/K_{eq}).$$

The results showed that all of the Madison groundwater samples are close to equilibrium with calcite ($CaCO_3$), dolomite ($CaMg(CO_3)_2$), and chalcedony (fine-grained quartz), with S.I. values typically within ±0.2 log units of 0.0 (equilibrium). Most of the Madison waters are also near equilibrium with barite ($BaSO_4$), and an inverse relationship was noted between dissolved Ba^{2+} and SO_4^{2-} concentrations. However, because Ba is a trace element and SO_4 is a major ion, the precipitation of small amounts of barite in the aquifer would have a minimal effect on overall SO_4^{2-} concentrations. Gypsum ($CaSO_4 \cdot 2H_2O$) is likely to have a greater influence on dissolved sulfate. Most of the Madison samples were about an order of magnitude undersaturated with gypsum, which means that the waters have the capacity to dissolve any gypsum/anhydrite that could be present along the flow path.

Plummer and others (1990) demonstrated a link between gypsum dissolution and "de-dolomitization" in the Madison Aquifer according to the following reactions:

$$CaSO_4 \cdot 2H_2O_{gypsum} = Ca^{2+} + SO_4^{2-} + 2H_2O, \text{ and}$$

$$Ca^{2+} + CaMg(CO_3)_{2,dolomite} = 2CaCO_{3,calcite} + Mg^{2+}.$$

However, no chemical evidence for de-dolomitization was seen in the samples collected in this study. This is likely due to the lower saturation state with respect to gypsum compared to the waters examined by Plummer's group, which were collected further north and east of the study area.

Geochemical modeling of the AMD waters shows the majority of samples were near-equilibrium saturation with amorphous silica and an aluminum phase [usually alunite, $KAl_3(SO_4)_2(OH)_6$, or jurbanite, $AlSO_4(OH)$]. Modeling of iron minerals was hampered by a lack of data on the speciation of dissolved Fe between the +2 and +3 oxidation states. The strongly acidic and Fe-rich mine drains were likely precipitating a ferric oxide of some sort after emerging from the ground. In the pH range of 2.5 to 3.5, precipitation of K-jarosite ($KFe_3(SO_4)_2(OH)_6$) is likely, and could explain the complete lack of detectable K^+ in the most acidic waters. In a wetland below the Giffen Spring, rapid oxidation of Fe^{2+} at near-neutral pH has formed a sizable deposit of unconsolidated ferrihydrite/goethite "muck." Similar precipitates are actively forming in Belt Creek below the confluence of the Anaconda drain, but are swept away each spring during high flow.

Transferability of the Current Project to Other Locations

To evaluate the transferability of the dual-isotopes of sulfate method to other basins impacted by AMD drainage, nearby watersheds and evidence from the scientific literature were evaluated. The field sites that were selected were: (1) the Foothills Ranch subdivision, near Great Falls, and (2) the town of Belt and its surrounding area.

In the case of the Foothills Ranch subdivision, a number of wells drilled into the Madison Aquifer were shown to have elevated SO_4 concentration with an isotopic signature that is consistent with AMD. The Foothills Ranch subdivision is roughly 5 mi north and downgradient of the coal mining centers of Stockett and Sand Coulee. However, as discussed above, it is theoretically possible that some of the SO_4 in the subdivision wells came from natural oxidation of pyrite in the overlying Morrison Formation coalbeds by rainwater and snowmelt that slowly infiltrated to the regional water table. Without more hydrological, chemical, and isotopic data, it is not possible to say with certainty that the elevated sulfate levels in the subdivision wells came from the abandoned coal mines.

The situation is also ambiguous for the Belt area wells. As shown in figure 19, wells drilled into the Madison Aquifer near Belt fall into two categories: a group of wells that show no presence of AMD, and another that suggest significant mixing with AMD. However, the two wells that show mixing are located upgradient from mining activities.

Many papers published in the past 12 years have used stable isotopes to track contamination of groundwater and surface water from coal AMD. The majority of these studies were done in China, including Bottrell (2007), Lang and others (2011), Li and others (2010, 2018), Sun and others (2017, 2019), Zang and others (2015), Zhang and others (2009, 2015), and Zhou and others (2018). Denimal and others (2002) and Migaszewski and others (2018) performed similar studies in France and Poland, respectively. The only previous study in the U.S. (aside from the work in the Belt–Stockett–Sand Coulee area by Gammons and others, 2010, 2013) is that of Vengosh and others (2013), who demonstrated that S-isotopes of dissolved sulfate in a West Virginia watershed could be used as a tracer of contamination from mountaintop mining of coal.

Overall, the transferability of the SO_4-isotope approach to other coal mine areas in the U.S. and around the world should be very high. For any isotope-fingerprinting study, the only requirement to make the method work is a strong contrast between the stable isotope signature of sulfate in AMD and sulfate in background waters. Coal typically has isotopically light pyrite, and the majority of previous studies cited above reported AMD with negative values of $\delta^{34}S$-SO_4, as is the case for the AMD waters of this study. Interpretation can be complicated by "background" sulfate in a field area that is also isotopically light. For example, the Swift Aquifer of this study has $\delta^{34}S$-SO_4 and $\delta^{18}O$-SO_4 values that are indistinguishable from the AMD drains. However, the SO_4 *concentrations* in the Swift are low, much lower than water in the overlying coalbeds or underlying Madison Group. Thus, although isotopes are useful, they should be used in conjunction with supporting chemical analyses.

A relevant question to ask with regard to future studies using sulfate isotopes is whether or not it is necessary to analyze both $\delta^{34}S$ and $\delta^{18}O$ of the sulfate molecule, or if one isotope analysis (e.g., $\delta^{34}S$) is sufficient. Many academic and commercial labs can analyze $\delta^{34}S$ of sulfate, but $\delta^{18}O$-sulfate is less commonly performed: it is a separate analysis that approximately doubles the cost per sample. However, for most projects the added value by using the dual-isotope approach should justify the additional costs, which likely will be a small fraction of the total project budget. In the present study, stable isotope mixing calculations based on $\delta^{34}S$-sulfate and based on $\delta^{18}O$-sulfate gave similar results, and served as independent checks on each other. At other sites, it might well be the case that the S-isotope composition of AMD sulfate and background sulfate are similar, whereas the O-isotope compositions are distinct. In this scenario, $\delta^{34}S$-sulfate would be useless from a fingerprinting point of view, whereas $\delta^{18}O$-sulfate would be an excellent tracer to sleuth out contributions from AMD vs. background sources. Overall, it is recommended that future studies employ both $\delta^{18}O$ and $\delta^{34}S$.

CONCLUSIONS

Four important conclusions of this project include:

- Stable S- and O-isotopes confirm that dissolved sulfate from abandoned coal mines in central Montana is present in the Madison Aquifer.

- Our data suggest that AMD may have migrated downgradient at least 5 mi to the vicinity of a new subdivision in the outskirts of the city of Great Falls. However, it is also possible that sulfate infiltrates to the Madison Aquifer by natural weathering of unmined coalbeds in the Great Falls area.

- Despite isotopic evidence for the presence of AMD in the Madison Aquifer, the vast majority of the affected groundwater wells contain water that meets all U.S. EPA and Montana regulatory standards for drinking water. This underscores the ability of the Madison Aquifer to buffer groundwater chemistry to acceptable levels.

- The sulfate "dual-isotope" approach used in this study is easily transferable to other sites where groundwater and/or surface water is known or suspected of being contaminated by coal mine drainage.

Additional findings include the following:

- Collection of samples on multiple visits showed that seasonal changes in isotopic composition of

sulfate in individual wells are relatively small, and are much smaller than the total spread in isotopic data between wells.

- Background sulfate concentrations in the Madison Aquifer increase as groundwater moves downgradient (northward) away from recharge zones. This is due to dissolution of evaporative salts (gypsum, anhydrite) in the formation. This "sliding scale" added a level of complexity to the interpretation of stable-isotope mixing diagrams.

- Water isotopes (δD and $\delta^{18}O$) support the conceptual model of regional hydrogeology, which includes recharge of the Madison Aquifer by higher-elevation snowmelt and rain as opposed to the overlying Swift and Kootenai Aquifers, which are recharged by local precipitation falling directly on the grassy foothills in the vicinity of the abandoned coal mines.

- Geochemical modeling showed that groundwater in the Madison Aquifer is in chemical equilibrium with calcite and dolomite, but undersaturated with gypsum/anhydrite. Most of the AMD waters are near-equilibrium with an aluminous phase (e.g., jurbanite or alunite) and one or more Fe-bearing phases (e.g., jarosite, schwertmannite, ferrihydrite).

- Stable isotopes of dissolved inorganic carbon ($\delta^{13}C$-DIC) showed that Madison Aquifer groundwaters are in isotopic disequilibrium with their limestone host rock. This is explained by the slow kinetics of C-isotope exchange between water and rock at low temperature. This result also implies that the residence time of groundwater in the aquifer is probably on the order of tens or hundreds of years, not thousands of years, consistent with the idea that groundwater flow in the Madison is focused along fractures and open cavities.

ACKNOWLEDGMENTS

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