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Developing a sulfate-isotope fingerprint of acid mine drainage to identify underground controls on groundwater flow paths

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Abstract

Abandoned coal mines near Great Falls Montana have been discharging acid mine drainage (AMD) to the surrounding environment for over 100 years. Without mitigation, this metal-laden, acidic water has been mixing with streams and infiltrating into the soil and bedrock. The purpose of this study was to investigate the use of isotopic tracers of sulfur and oxygen of sulfate to identify the presence of acid mine drainage in domestic wells and to identify the regional extent of impact. The use of isotopes as tracers is not new to hydrogeologic studies; however, this setting is uniquely positioned to use isotopic tracers specific to AMD to identify flow paths and impacted aquifers.

The results of this study confirm that sulfur and oxygen of sulfate isotopes effectively fingerprint the presence of AMD in the Madison Aquifer in the Stockett–Sand Coulee area. Despite the influence of AMD on the aquifer, the limestone efficiently buffers the acidity and the water quality data show the groundwater meets US-EPA and Montana regulatory standards for pH and metals in drinking water. This isotope tracing technique will be successful in any setting that has a distinct sulfur and/or oxygen isotope signature in sulfates in AMD versus the unimpacted groundwater. However, this work has also shown the importance of using isotope tracers in conjunction with standard chemical analyses because of the mutability of these isotope tracers in the environment.

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Introduction

Historic coal mines around Great Falls, Montana have been discharging highly acidic, metal-laden water for over 100 years. Acidic mine drainage (AMD) infiltrates into the alluvial and bedrock aquifers, including the Madison Group limestone, which is an important regional aquifer in central Montana. The limestone is faulted, fractured, and 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 uniquely fingerprint the acid mine water entering the local flow system.

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 and reports resulting from this work will be made available to the public on the Montana Bureau of Mines and Geology (MBMG) database and library.

Mining History

Montana's coal deposits were first exploited in the 1860s. Initially primarily used for domestic purposes, industrial use of coal grew with the expansion of the railroad, which made large-scale shipping economically feasible. After rail was introduced, statewide coal production increased from 41,467 tons in 1888 to 363,301 tons in 1889. The development of the railroads' coal mine at Sand Coulee (Fig. 1) started in early 1888. Most of the coal produced between 1889 and 1902 went to the trans-continental line and branches of the Great Northern Railway. Other important consumers were the copper smelter at Anaconda, a silver-lead smelter in Great Falls, and several smaller smelters elsewhere in Montana. During its most active period, the Stockett–Sand Coulee mines accounted for over 55 percent of Montana's coal output: approximately 7 million tons. 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 coal beds. Coal mines in the area are now abandoned (DEQ, 2009).

Geology and Hydrostratigraphy

The study area is located southeast of the city of Great Falls, Montana (Fig. 1), at the western edge of the Great Falls Coal Field (Silverman and Harris, 1967). The Sand Coulee Basin is a sub-area of the Great Falls Coal Field. The medium-grade bituminous coal is at the top of the Morrison Formation of the Jurassic Period and is overlain by sandstone and shale of the Cretaceous Kootenai Fm. (Fig. 2). The

coal is interbedded with layers of carbonaceous shale, shale, and clay and is buried roughly 230 to 310 feet below ground surface. The coal bed in the Sand Coulee area averages 8.5 feet thick.

Except for public water supplies for the towns of Stockett and Sand Coulee, most residents in the area receive their drinking water from private wells completed in the Mississippian Madison Limestone aquifer. In central Montana, the Madison Aquifer feeds two very large natural springs: Giant Springs near Great Falls and Big Springs near Lewistown, Montana. Giant Springs, one of the largest freshwater springs in the U.S., discharges ~300 CFS groundwater (Davis and others, 2001) near the banks of the Missouri River in the city of Great Falls (Fig. 1). 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 field area, the Madison Group is overlain by marine sandstones and carbonates of the upper Mississippian Big Snowy Group that pinch out to the north and are completely absent near Great Falls. Jurassic sediments of the Swift Fm. and overlying Morrison Fm. unconformably overlie the Madison/Big Snowy strata (Fig. 2; Vuke and others, 2002). Sandstone beds of the Swift Fm. are primary aquifers for the community of Stockett. Recharge for groundwater in the Swift Fm. is more localized than that for the Madison Aquifer. In addition to the aquifers of the Swift Fm. and the Madison Group, the Kootenai Fm. makes up the third aquifer system in the study area. The lower Kootenai Fm. contains two sandstone units (the Cutbank and Sunburst Members) that contain groundwater that is perched several hundred feet above the regional groundwater table in the Madison and Swift aquifers (Duaime and others, 2004; Reiten and others, 2006). This groundwater infiltrates into the abandoned coal mines forming laterally extensive mine pools that discharge from adits or constructed horizontal drains. The drains direct groundwater to excavated channels or streams (Figs. 3, 4, 5). 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 et al., 1983a, 1987; Karper, 1998; Gammons et al., 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), SO₄ (3600), and Zn (8.67) (Karper, 1998). 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.

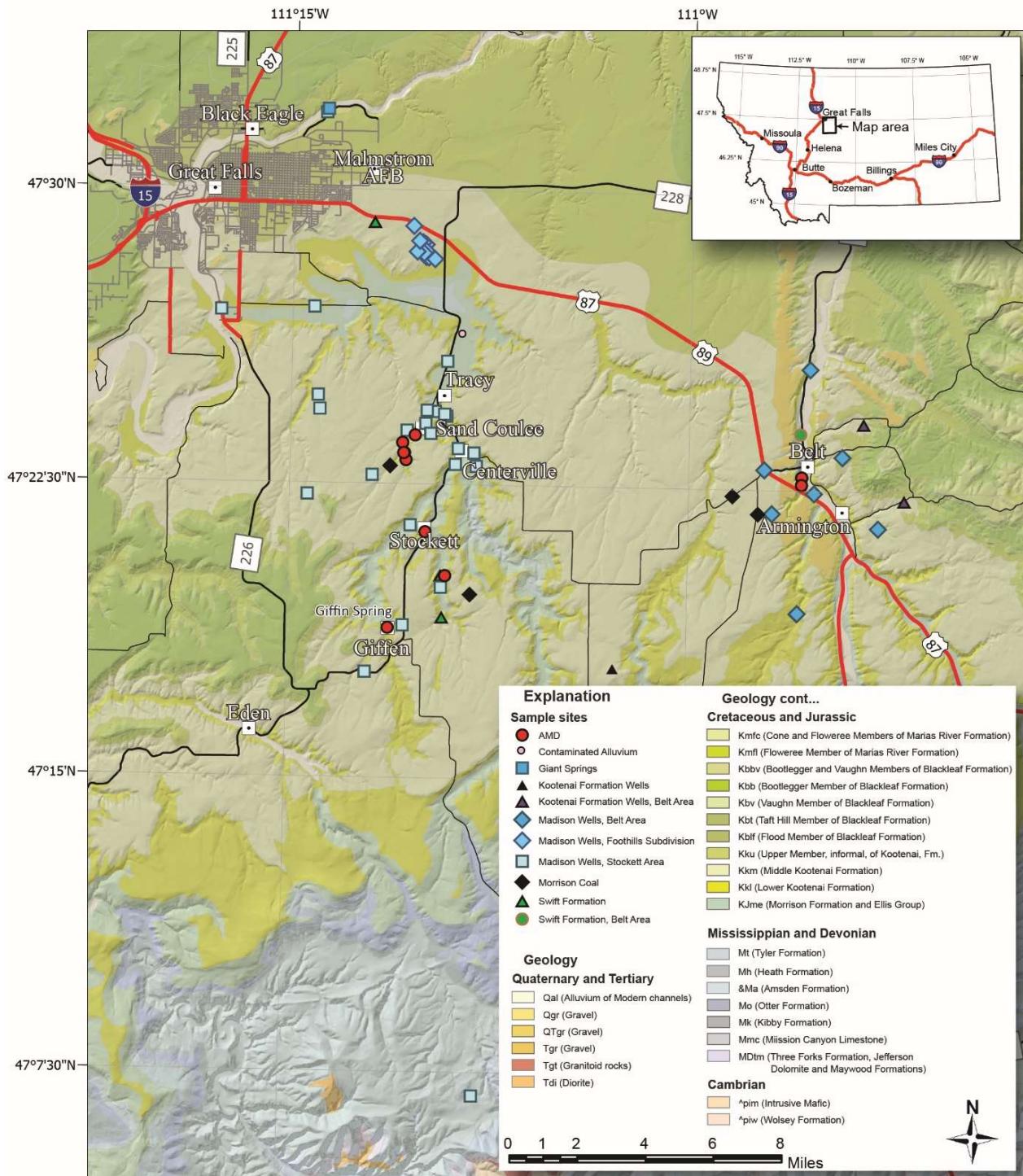


Figure 1. Location of the study area and sample sites. Map shows the outcrop area of the Madison Limestone (Mmc, gray), and green shades of the Cretaceous and Jurassic Formations (modified from Vuke and others, 2002).

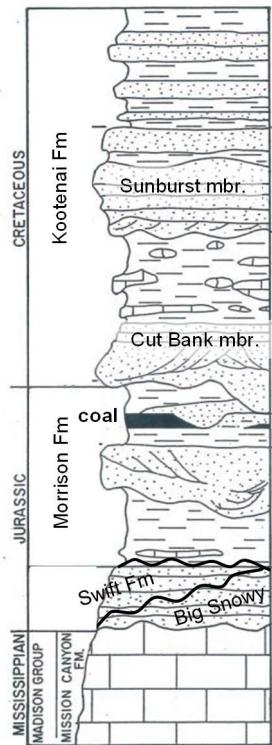


Figure 2. Stratigraphic column for the study area.



Figure 3. A ditch referred to locally as “Rusty Ditch” transports AMD through the town of Sand Coulee. The low pH water completely infiltrates into the ground over about 1 mile.



Figure 4. Kate's coulee AMD and unimpacted spring water mix together, which raises the pH, allowing aluminum to precipitate (white suspended sediment shown here).



Figure 5. At some locations the AMD flows from hillsides, and at other locations the contaminated water is piped from the adit to a point of release.

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 ($\delta^{34}\text{S}$) and O-isotope ($\delta^{18}\text{O}$) of sulfate in AMD are distinct from the $\delta^{34}\text{S}$ and $\delta^{18}\text{O}$ 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 samples were collected in this study for isotopic analysis of sulfate. These were a mixture of 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 ($\delta^{18}\text{O}$ and δD) of water. In addition, 26 samples were analyzed for $\delta^{13}\text{C}$ 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 get information on 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 ($\delta^{18}\text{O}$ -sulfate vs. $\delta^{34}\text{S}$ -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. 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 miles north and downgradient of the closest coal-mining center contains 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 US-EPA and Montana DEQ guidelines (<http://water.epa.gov/aboutow/ogwdw/creg.cfm>). 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 concentration, consistent with the elevated dissolved oxygen values measured during sample collection. This also means that 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 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). For this reason, 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 Pennsylvanian Swift 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. This study also shows the importance of supporting water-chemistry data in stable isotope studies.

Experimental

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. MBMG standard sampling procedures were followed. Groundwater samples were bottled after purging approximately three well-casing volumes and observation of stable field parameters of ± 10 percent of three readings of one another in 15 minutes. Grab samples were collected from the spring and AMD sites. Field parameters include pH, temperature, and specific conductance. Nitric (1 percent) and sulfuric (0.5 percent) acids preserved the samples. A 0.45-micron 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 ($\delta^{18}\text{O} = -19.8\text{\textperthousand}$, $\delta\text{D} = -150.2\text{\textperthousand}$) and USGS 48 ($\delta^{18}\text{O} = -2.22\text{\textperthousand}$; $\delta\text{D} = -2.0\text{\textperthousand}$) isotope standards. The results are reported in units of per mil (‰) in the usual δ notation versus VSMOW for oxygen and hydrogen (general isotope reference here). The approximate analytical uncertainty is $\pm 0.1\text{\textperthousand}$ for $\delta^{18}\text{O}$ -water and $\pm 1\text{\textperthousand}$ 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 $T > 60^\circ\text{C}$. 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 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 et al. (1994) for $\delta^{34}\text{S}$ -sulfate, and Kornexl et al. (1999) for $\delta^{18}\text{O}$ -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 $\pm 0.2\text{\textperthousand}$ for $\delta^{34}\text{S}$ -sulfate and $\pm 0.4\text{\textperthousand}$ for $\delta^{18}\text{O}$ -sulfate.

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 ($\delta^{13}\text{C}$ -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, $\delta^{13}\text{C} = -26.39\text{\textperthousand}$), USGS 41 (enriched glutamic acid, $\delta^{13}\text{C} = +37.63\text{\textperthousand}$), and NBS 18 (calcite, $\delta^{13}\text{C} = -5.01\text{\textperthousand}$), 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 $\pm 0.1\text{\textperthousand}$ for $\delta^{13}\text{C}$ -DIC.

Results and Discussion

Madison Aquifer Groundwater System

A cross section illustrates our conceptual model of a flow path within the Madison aquifer, from recharge areas near the Little Belt Mountains to a known discharge point at Giant Springs (Fig. 6). Along the flow path, precipitation infiltrates into the aquifer in the Madison Limestone through bedding planes, joints, fractures, and stream loss in the recharge areas. The black dashed line in Figure 6 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 that are perched above (not hydraulically connected) the regionally saturated part of the formation (e.g., Ground-Water Information Center GWIC 276129; Fig. 6).

In the recharge area, where the regional water table is below the top of the Madison Limestone, the aquifer is generally unconfined. Recharge to the Madison aquifer occurs primarily from infiltration of precipitation in the outcrop areas and from stream loss across outcrops. The major recharge areas are in the uplifted areas of the Little Belt Mountains. Overlying aquifers, such as in the Swift or basal Kootenai sandstones, are also potential recharge sources. However, near Great Falls in the Giant Springs area, water levels in the Madison aquifer are higher than Swift or basal Kootenai aquifers, and therefore the Madison aquifer can potentially discharge to the stratigraphically higher aquifers.

Madison aquifer water levels were monitored in the Great Falls area and are presented in Figure 7. Monitoring well 276129 (black line) is located in the recharge area on the north side of the Little Belt Mountains (Fig. 7). In 2018 and 2019 the hydrograph shows a flashy response to late March snowmelt and early spring rain. The previous years did not have a strong recharge pulse. The dramatic water-level response in the recharge area is a characteristic of fracture-flow environments with limited storage (Weight, 2008)

Domestic monitoring wells show a damped seasonal water-level response indicating the well locations have no direct preferential pathways from limestone outcrops nearby (Fig. 7, orange and blue lines).

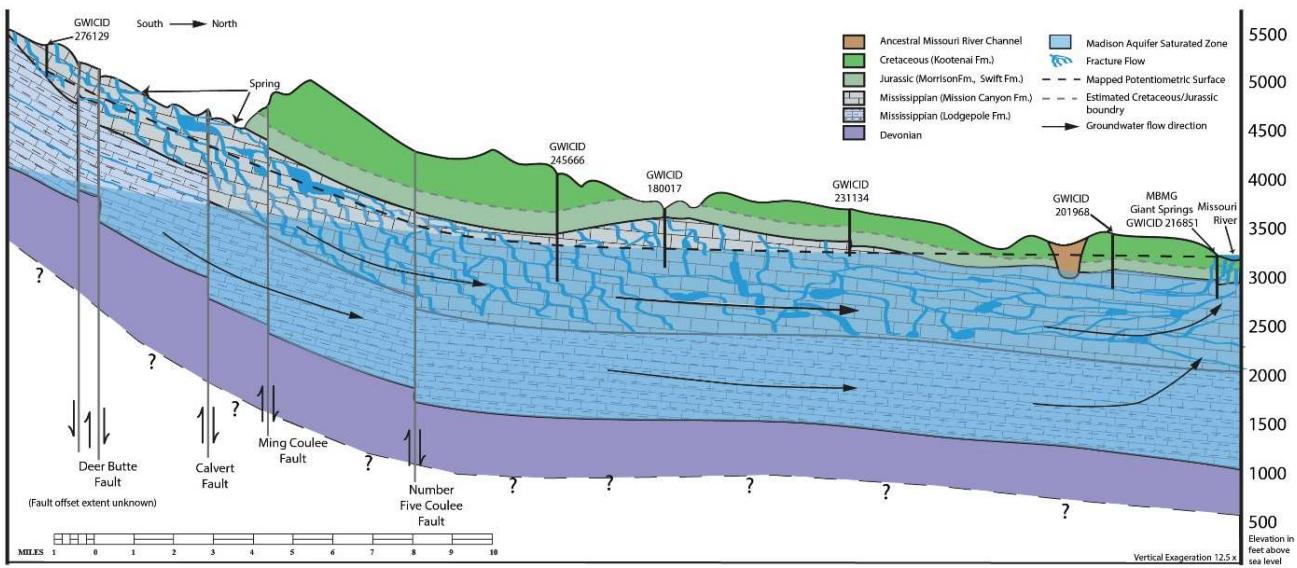


Figure 6. Generalized geologic cross-section showing major hydrostratigraphic units and structures in the study area. Wells completed in the Mission Canyon Formation were used for this cross-section. Study includes wells completed in the Cretaceous Kootenai and Jurassic Swift Fms. but they are not included in the cross-section.

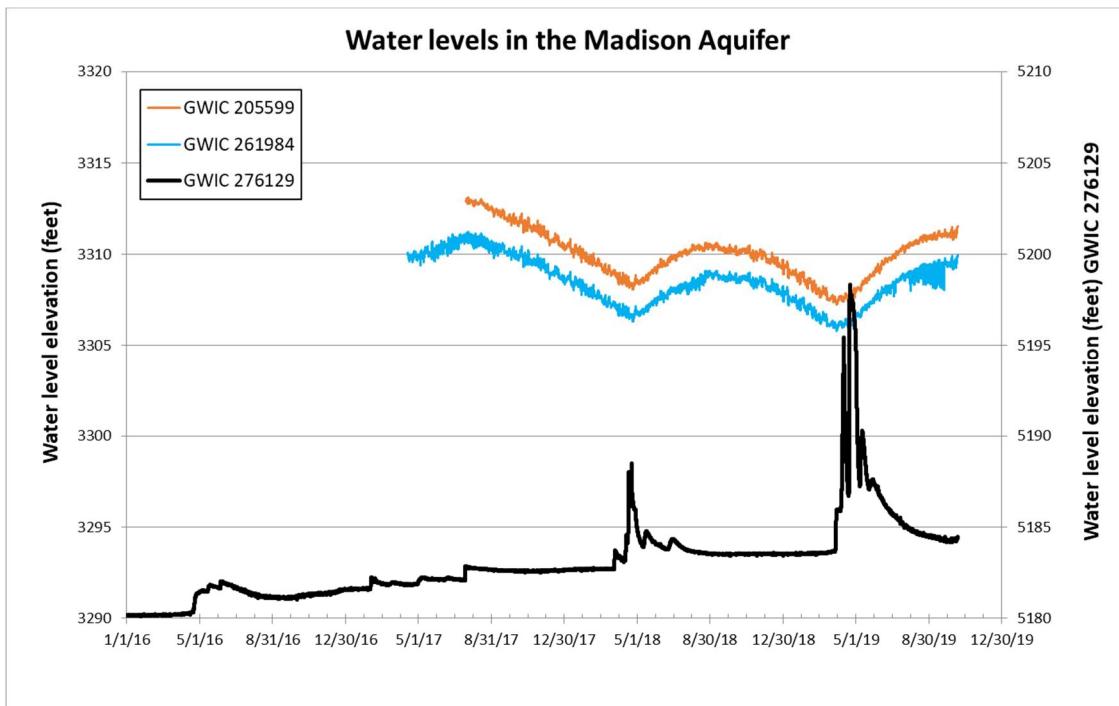


Figure 7. Wells located in the recharge area (well 276129) respond rapidly compared to wells located in the regional water table (205599 and 261984), which show a damped response.

Water Chemistry

All water-quality data for samples collected in this study are included as Appendix B. Aspects of the analyses that have relevance to the presence of acid mine drainage (AMD) in the Madison Aquifer are discussed below.

General trends

The average and standard deviation of pH and specific conductance (SC, $\mu\text{S}/\text{cm}$) values of groundwater and springs in the Madison aquifer were 7.37 ± 0.22 and 755 ± 318 , respectively (Figs. 8, 9). Water temperatures ranged from 9.5 to 15°C. With the exception of some of the AMD samples, all groundwaters contained measurable dissolved oxygen, indicating aerobic conditions within the Kootenai, Swift, and Madison Aquifers. 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 pH between 2.5 and 3.5 and SC $>2000 \mu\text{S}/\text{cm}$ (maximum of 9,860 $\mu\text{S}/\text{cm}$ for the Nelson drain). One large-volume AMD discharge, the Giffen Spring, had a higher pH, near 6. As discussed by Gammons et al. (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.

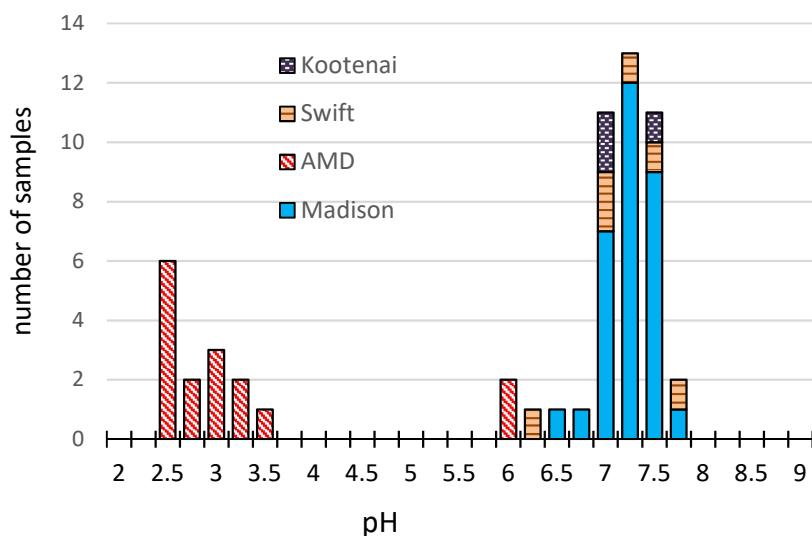


Figure 8. Histogram of pH values for samples collected in this study.

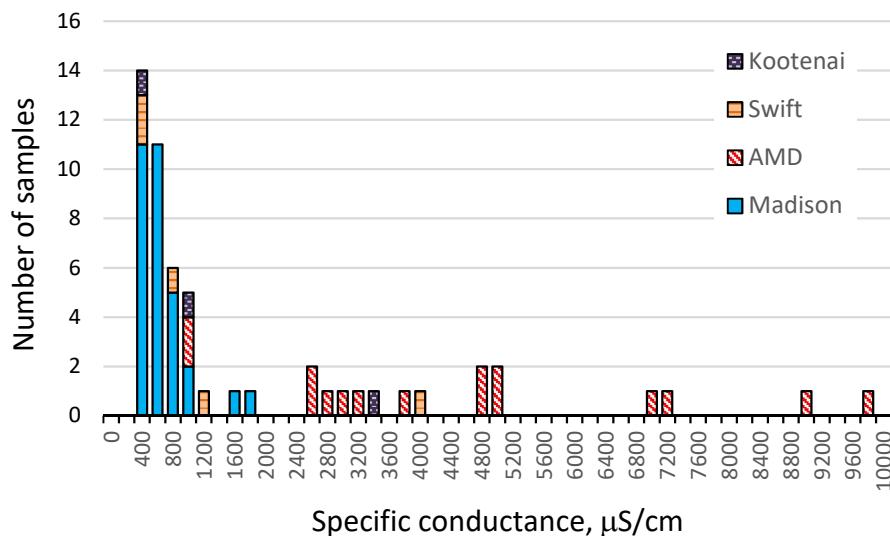


Figure 9. Histogram of specific conductance (SC) values for samples collected in this study.

The major element chemistry of all groundwater and AMD samples collected in this study is summarized in a Piper diagram (Fig. 10). 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 becomes enriched in 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 et al., 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. 10) 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.

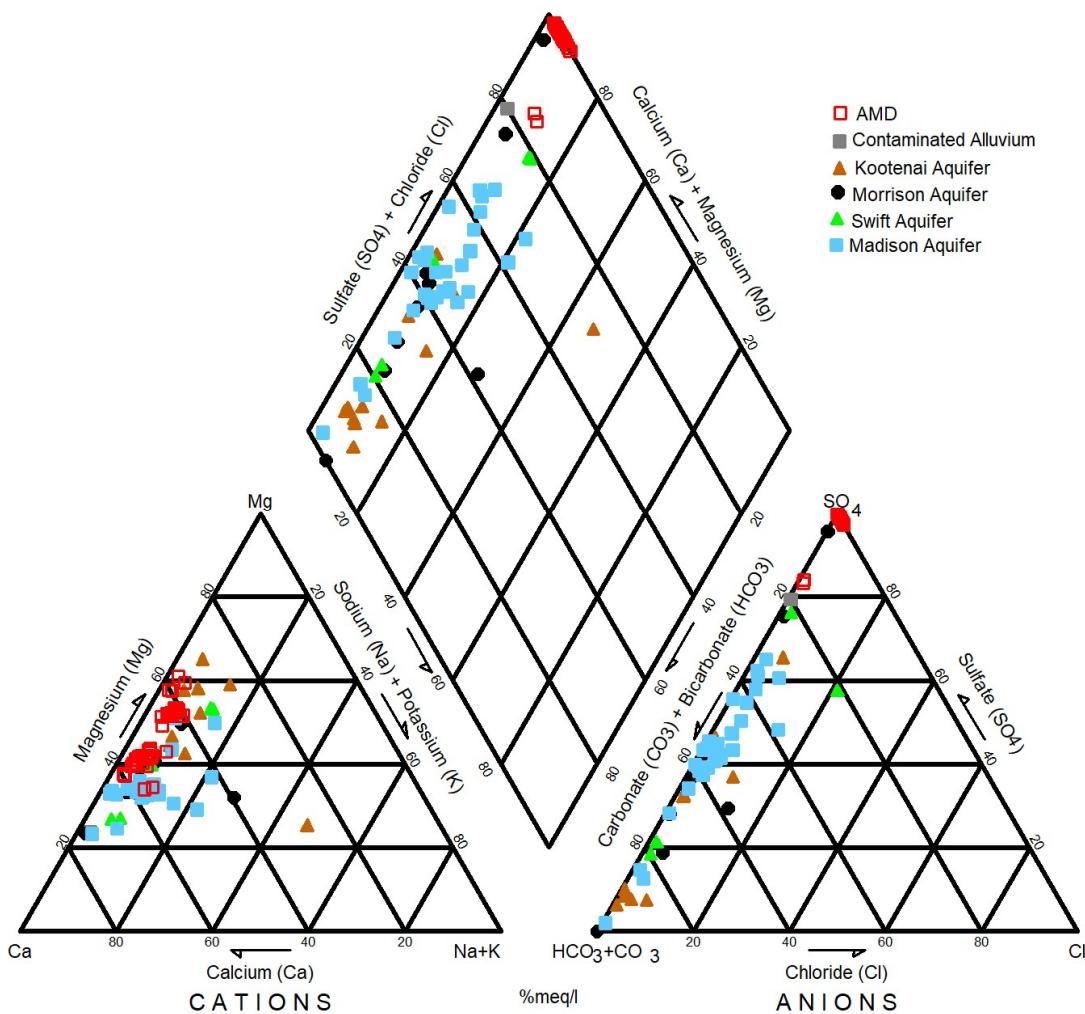


Figure 10. Piper diagram showing the major ion composition of all samples collected in this study.

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 + Zn) vs. pH (Fig. 11). 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 et al. (2010), the pH of several of the mine drains in the study area decreases after emerging to the surface due to oxidation of Fe²⁺ to Fe³⁺ 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 ephemeral 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 $\text{pH} > 3$ and a mix of Fe^{2+} and Fe^{3+} (ferric) for samples with $\text{pH} < 3$.

Several of the mine discharges had high concentrations of dissolved rare earth elements (REE) (see Appendix B). 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 $> 1 \text{ mg/L}$, 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 for their toxicity to humans or aquatic organisms (reviewed by Pagano et al., 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 et al., 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 $24 \mu\text{g/L}$, respectively (Table 1). In addition, some of the mine waters had elevated concentrations of uranium (up to $365 \mu\text{g/L}$) and vanadium (up to $406 \mu\text{g/L}$) (see Appendix B).

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

Site	ID	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

n.d. = not detected

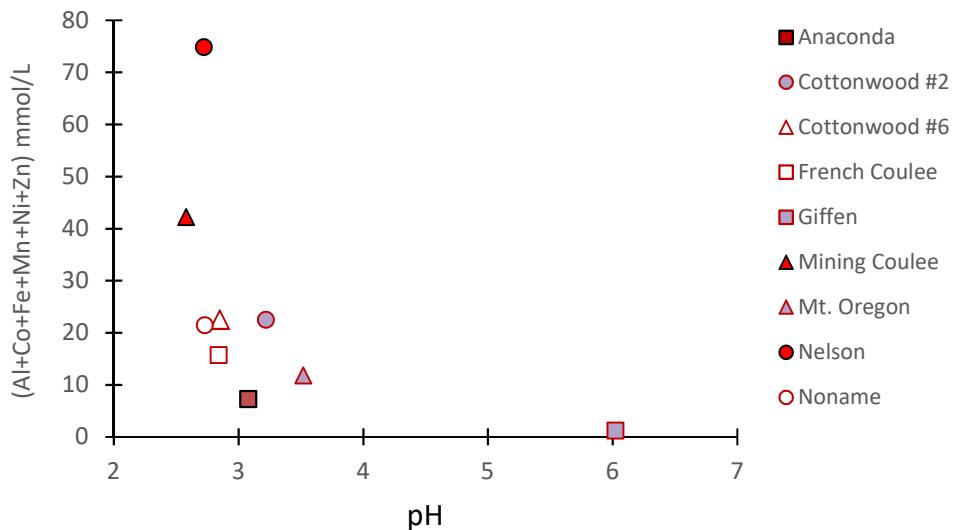


Figure 11. Plot of cumulative dissolved metal concentration (sum of Al, Co, Fe, Mn, Ni, Zn) vs. pH for the mine drainages listed in Table 1.

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 Subdivision with higher SC and dissolved sulfate concentration also showed slightly elevated concentrations of metals. Reports of new water wells being drilled in the subdivision that were producing acidic water with high sulfate and aluminum provided the impetus for collecting a set of samples in this study. Although none of the Foothills 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 µg/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 Limestone in the Sand Coulee–Stockett area (OSM-23 and OSM-26) had anomalously high nitrate concentrations (9.6 and 6.6 mg/L NO₃-N, respectively), suggesting localized contamination of the aquifer. However, neither of these wells had high SO₄ or trace metal concentrations. In fact, none of the Madison wells in the vicinity of the AMD sources in Sand Coulee–Stockett showed convincing evidence of elevated trace metal concentrations, despite there being several wells with anomalously high sulfate that has an AMD signature (see below). This underscores the ability of the Madison Aquifer to buffer pH and preventing the degradation of the drinking water.

Stable Isotopes of Water

The stable isotope compositions of all water samples collected in this study are summarized in Figure 12. The global meteoric water line (MWL) of Craig (1961) and the Butte meteoric water line of Gammons et al. (2006) are shown for reference. Groundwater samples that plot to more negative values of δD and $\delta^{18}\text{O}$ were recharged at colder temperatures and/or at higher elevations compared to samples with less negative values. As discussed by Gammons et al. (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 the Stockett–Sand Coulee–Belt area: $\delta D = 5.0 * \delta^{18}\text{O} - 51.5$. 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. 13). Overall, Madison Aquifer samples from the Stockett–Sand Coulee area have similar isotopic compositions to samples from the Foothills 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.

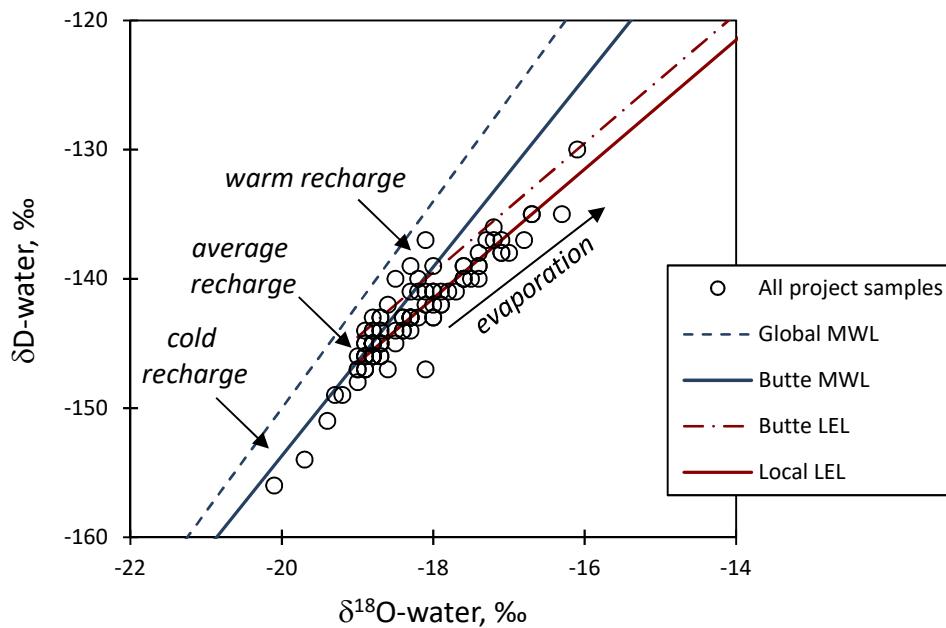


Figure 12. Summary of all water isotope data collected in the project. Global MWL = meteoric water line of Craig (1969); Butte MWL and Butte LEL = meteoric water line and evaporation line for Butte, MT (Gammons et al., 2006). Local LEL = local evaporation line (this study). The intersection of the local meteoric water line and the local evaporation line gives the isotopic composition of average groundwater recharge.

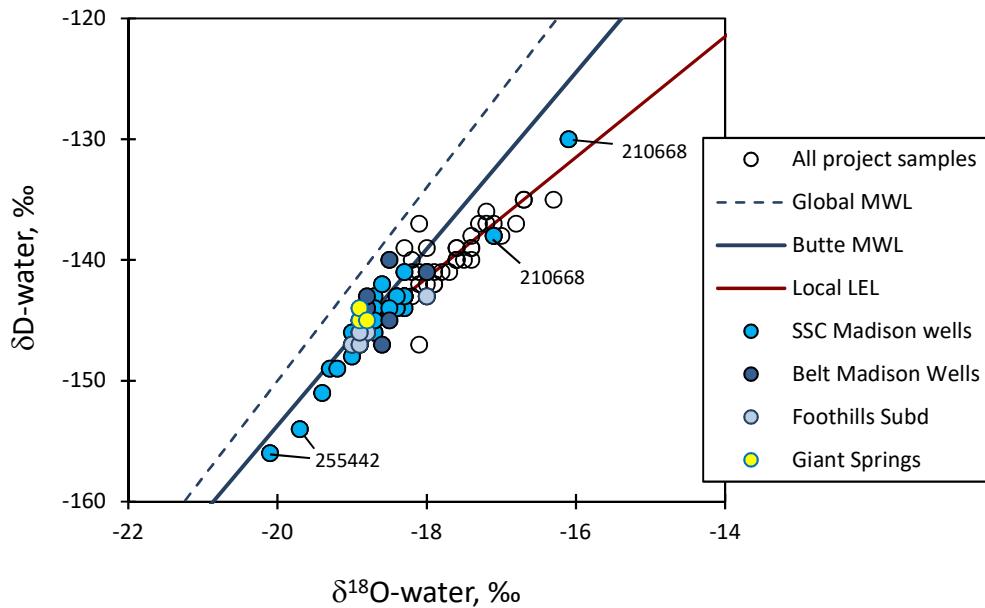


Figure 13. Water isotope data for wells and springs in the Madison Aquifer. Anomalous samples are labeled with GWIC ID numbers. SSC = Stockett–Sand Coulee.

Groundwater wells completed in the Swift and Kootenai Formations contain water that is shifted slightly along the evaporation line (Fig. 14), and that may have been recharged at higher temperature or lower elevation compared to the Madison wells. This makes sense, especially for the Kootenai Fm., which lies stratigraphically above the Morrison Fm. coal beds and does not crop out in the Little Belt Mountains. In some areas impermeable shale units create perched groundwater in the Kootenai Fm. Evidence with isotopes show the Kootenai Fm. was derived locally, by rain and snowmelt falling on treeless plateaus in the Stockett–Sand Coulee area. One Swift well (GWIC 236507) had an anomalous isotopic composition for reasons that are not known.

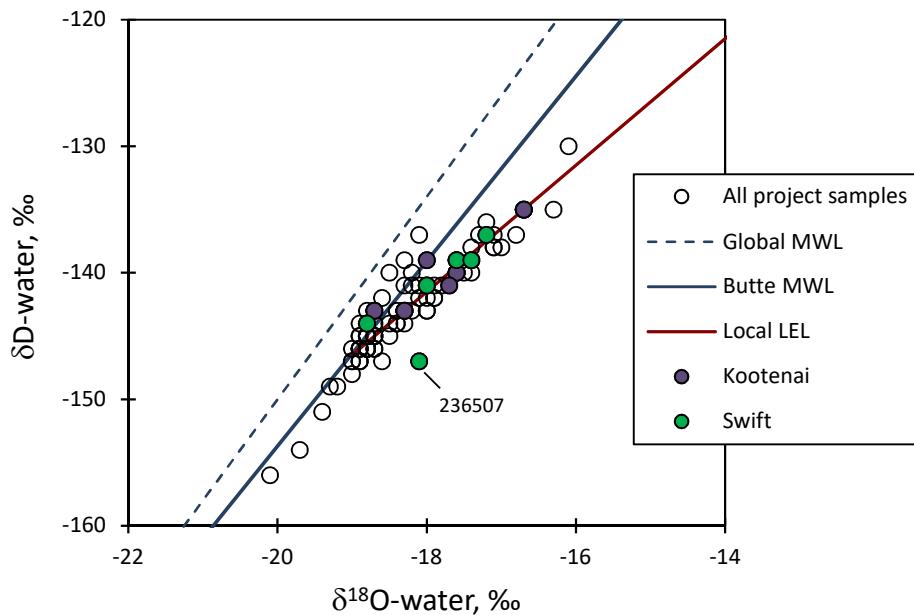


Figure 14. Water isotope data for wells in the Kootenai Fm. and Swift Fm. aquifers. One anomalous sample is labeled with its GWIC 236507.

Samples of acid mine drainage in the Stockett–Sand Coulee and Belt areas (Fig. 15) have water-isotope compositions that are similar to the Kootenai and Swift samples. This is also true for water in the Anaconda mine pool at Belt. 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 mine-pool water and acidic drains are perched and are recharged by downwards percolation of rain and snowmelt falling on the surrounding foothills.

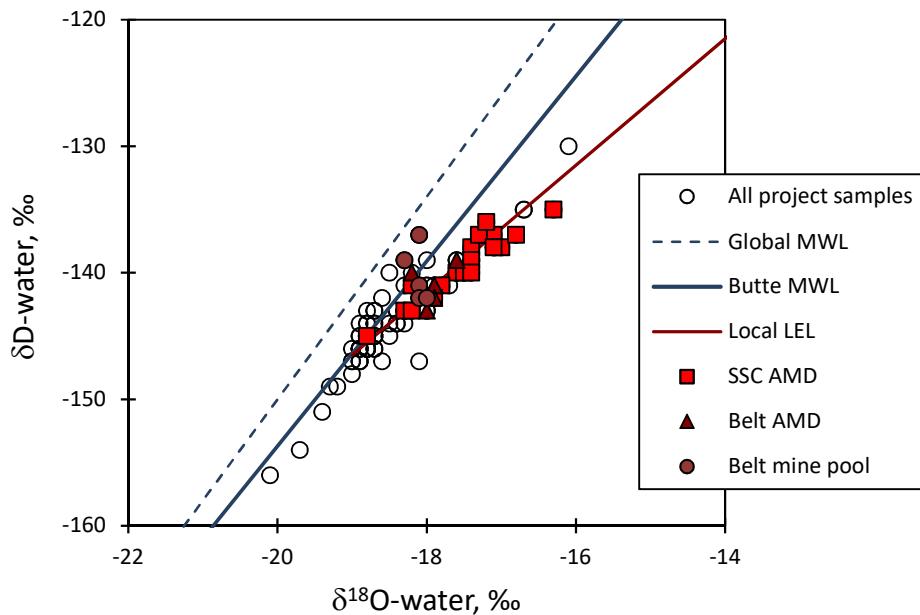


Figure 15. Water isotope data for acid mine drainage (AMD) in the Stockett–Sand Coulee (SSC) area and the Belt Mine area, as well as water samples taken from the flooded mine pool at the Belt Mine.

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 Limestone, 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 occur. The Swift Fm. unconformably overlies the Madison (Fig. 6), and hydrogeologists often lump the two formations into the same aquifer system. However, the Swift does not crop out in the Little Belts, but rather comes to the surface immediately south of the study area. Therefore, groundwater in the Swift is partly recharged by local precipitation and partly by mixing with the regional flow of groundwater in the Madison Limestone. The third aquifer system includes perched groundwater that sits in the coal beds at the top of the Morrison Formation, as well as sandstone lenses in the overlying Kootenai Fm. 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 Fm. 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 ($\delta^{18}\text{O}$ vs. $\delta^{34}\text{S}$) for dissolved sulfate in samples from the Stockett–Sand Coulee area (Fig. 16) shows a linear trend, with AMD samples clustered at strongly negative values near -10 to -15‰, 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 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).

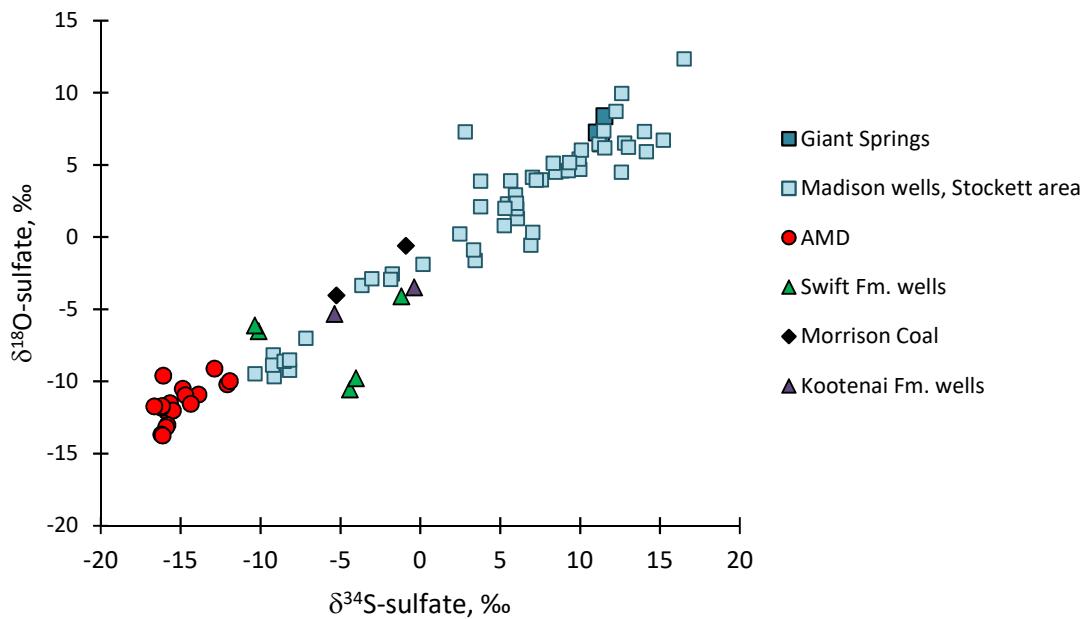


Figure 16. O- vs. S-isotope composition of dissolved sulfate for samples collected in the Stockett–Sand Coulee area. (Data for Giant Springs are added for comparison).

Figure 17 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 Subdivision, near Great Falls. The Foothills 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 samples appears to be shifted to lower $\delta^{18}\text{O}$ and/or higher $\delta^{34}\text{S}$ values. Acidic mine drains in the vicinity of Belt, Montana have $\delta^{18}\text{O}$ values similar to AMD from Stockett–Sand Coulee, but with more positive values of $\delta^{34}\text{S}$ (Fig. 18).

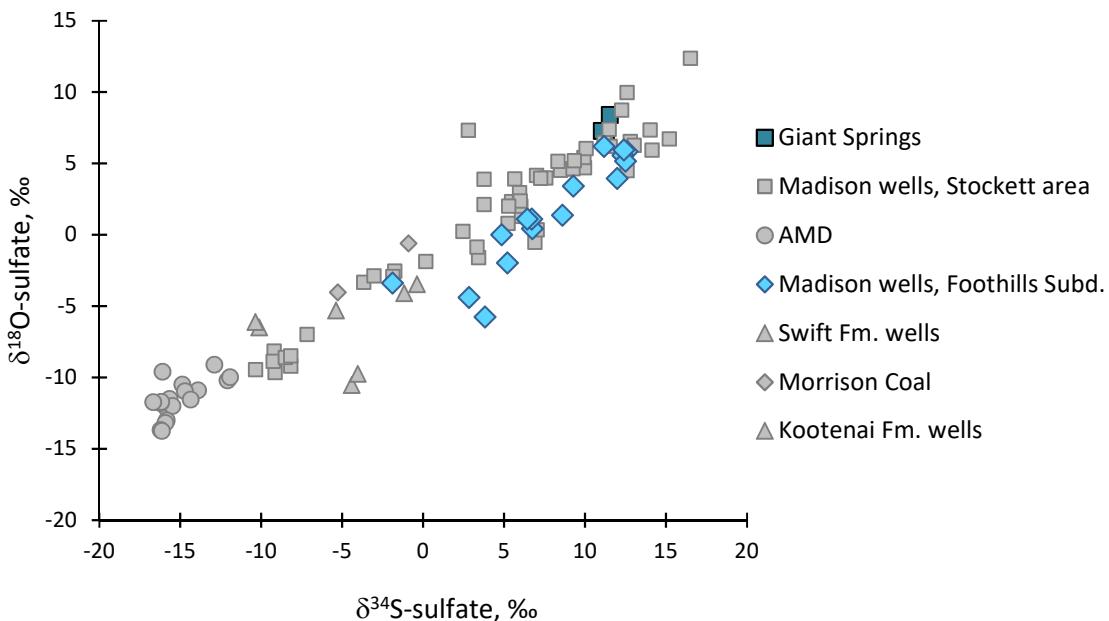


Figure 17. O- vs. S-isotope composition of dissolved sulfate for samples collected in the Foothills Subdivision area (blue symbols). Data from Stockett–Sand Coulee are shown in gray for comparison.

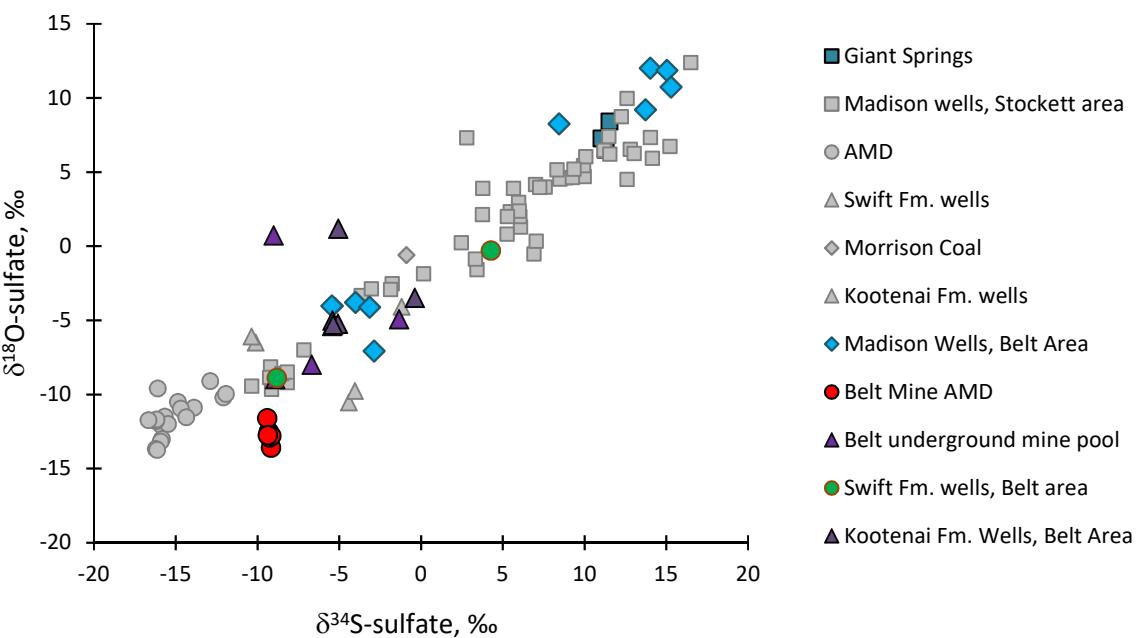


Figure 18. O- vs. S-isotope composition of dissolved sulfate for samples collected in the Belt area (colored symbols). Data from Stockett–Sand Coulee area are shown in gray for comparison.

Mixing of AMD with Belt Creek

Belt Creek is a clear mountain stream that begins in the Little Belt Mountains roughly 30 miles south of the field areas of this study. The upper and middle reaches of the watershed include extensive outcrops of Madison Limestone. Visual observations show after it leaves the mountains, Belt Creek loses some water to irrigation diversions and also 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 et al., 2006).

Figure 19 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 yards downstream (at a bridge in the center of town) has an isotopic composition that 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.

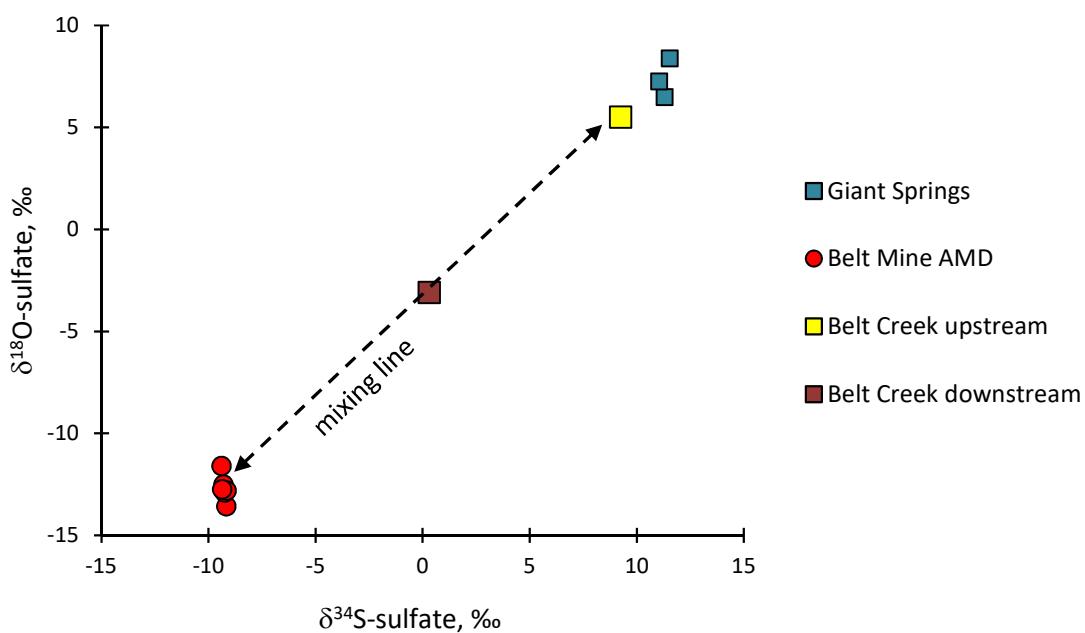


Figure 19. O- vs. S-isotope composition of dissolved sulfate for samples from Belt Creek collected above and below its confluence with AMD discharge from the Belt Mine. Based on the position of the downstream sample along the mixing line, it can be concluded that roughly half of the total dissolved sulfate in the downstream sample came from AMD, the other half being background sulfate in Belt Creek.

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 20 summarizes data for these locations. In most cases, the $\delta^{18}\text{O}$ and $\delta^{34}\text{S}$ 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 $\pm 0.7\text{\textperthousand}$ for $\delta^{34}\text{S}$ and $\pm 0.8\text{\textperthousand}$ for $\delta^{18}\text{O}$. These variations are greater than the analytical uncertainty in the isotope analysis ($\pm 0.2\text{\textperthousand}$ for $\delta^{34}\text{S}$ and $\pm 0.4\text{\textperthousand}$ for $\delta^{18}\text{O}$), 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.

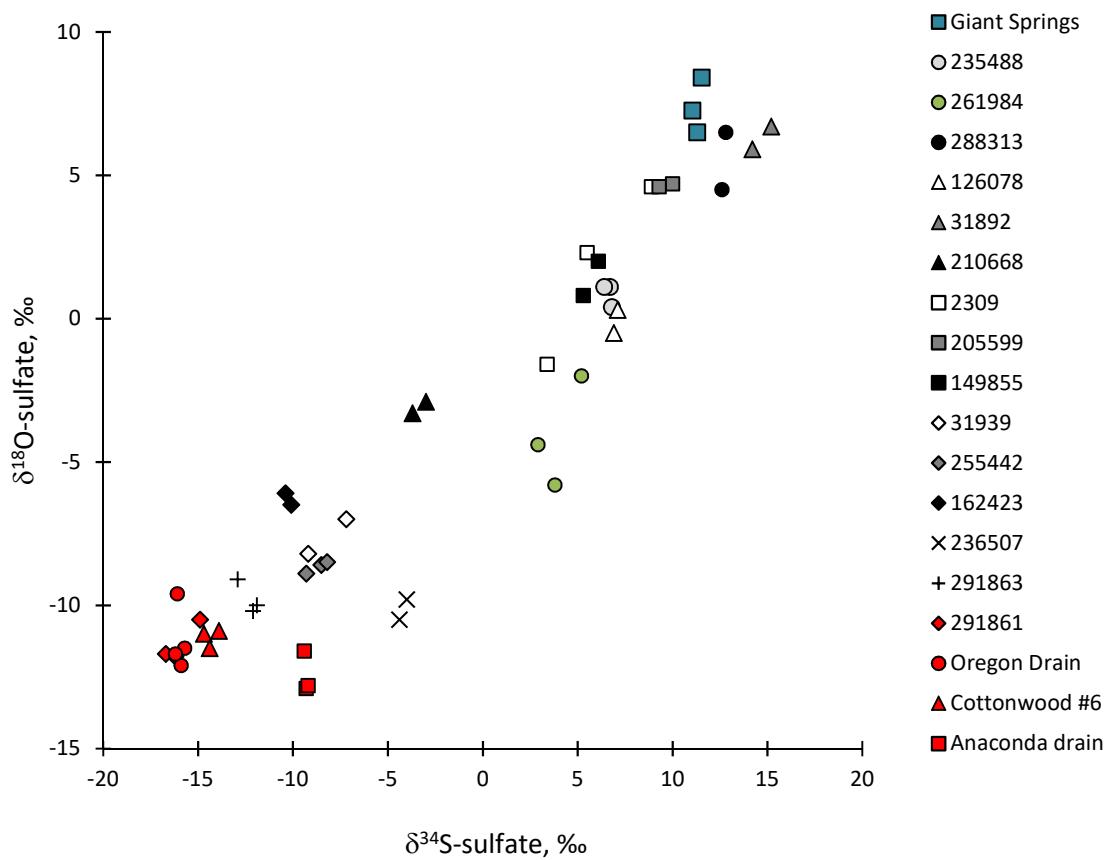


Figure 20. Comparison of the stable isotope composition of sulfate for locations that were sampled in more than one season (in most cases, different years). Numbers in legend are GWIC ID numbers for wells. The average standard deviation for locations sampled multiple times was $\pm 0.7\text{\textperthousand}$ for $\delta^{34}\text{S}$ and $\pm 0.8\text{\textperthousand}$ for $\delta^{18}\text{O}$.

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 ($\delta^{13}\text{C-DIC}$). The data are summarized in Appendix B and Figure 21. 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, $\text{H}_2\text{CO}_3(\text{aq})$ is the only significant DIC species present. However, for most of the groundwater samples with near-neutral pH, DIC will be a mix of $\text{H}_2\text{CO}_3(\text{aq})$ and HCO_3^- , with traces of CO_3^{2-} .

As shown in Figure 21, 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 ($\delta^{13}\text{C} = -6.5\text{\textperthousand}$ to $-8\text{\textperthousand}$). 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 $\delta^{13}\text{C}$ 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 in these formations was recharged locally on fields that are mostly used to grow hay and alfalfa.

Group III (Fig. 21) includes most of the water samples from the Madison Aquifer, including Giant Springs and all of the Foothills Subdivision wells. These waters have $\delta^{13}\text{C}$ -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 Limestone. However, the average $\delta^{13}\text{C}$ of carbonate minerals in the Madison Group is $+3.1 \pm 1.2\text{\textperthousand}$ (Plummer et al., 1990). If C-isotope exchange was occurring between the carbonate rock and the groundwater, then the range in $\delta^{13}\text{C}$ -DIC should be heavier, approaching 0 to +3‰. In their regional study of the Madison Aquifer, Plummer et al. (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 Limestone is focused along high-conductivity fractures and cave/karst features.

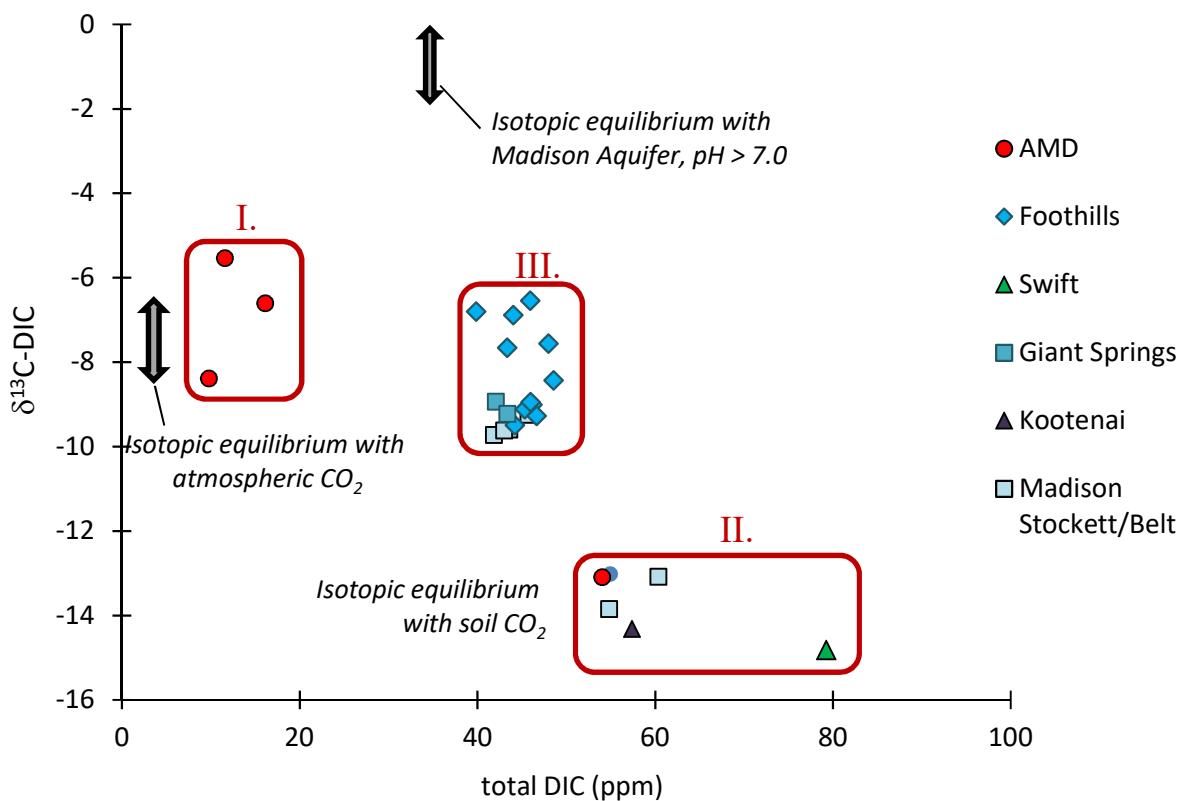


Figure 21. Sampled water sources fall into three groups based upon the primary source of DIC. Groundwater residence times are likely on the order of hundreds of years or less because no samples have been in contact with the Madison Limestone long enough to incorporate its average $\delta^{13}\text{C}$ of approximately +3‰.

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 22 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 et al. (1990) documented an evolution in groundwater type from Ca-Mg-HCO₃ near the recharge sites, to Ca-SO₄ 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. 23). As discussed by Plummer et al. (1990), these chemical changes are due to dissolution of ancient evaporite minerals in the Madison Group. Dissolution of gypsum explains the initial evolution towards Ca-SO₄ water, and this is followed by dissolution of halite and sylvite to form Na-K-Cl water (Fig. 23).

As shown by Figure 22, 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 et al., 1990). The presence of dissolved oxygen in all of the Madison wells sampled in this study indicates that dissolved sulfate concentrations and isotopic compositions should not be influenced by anaerobic reactions, such as bacterial sulfate reduction.

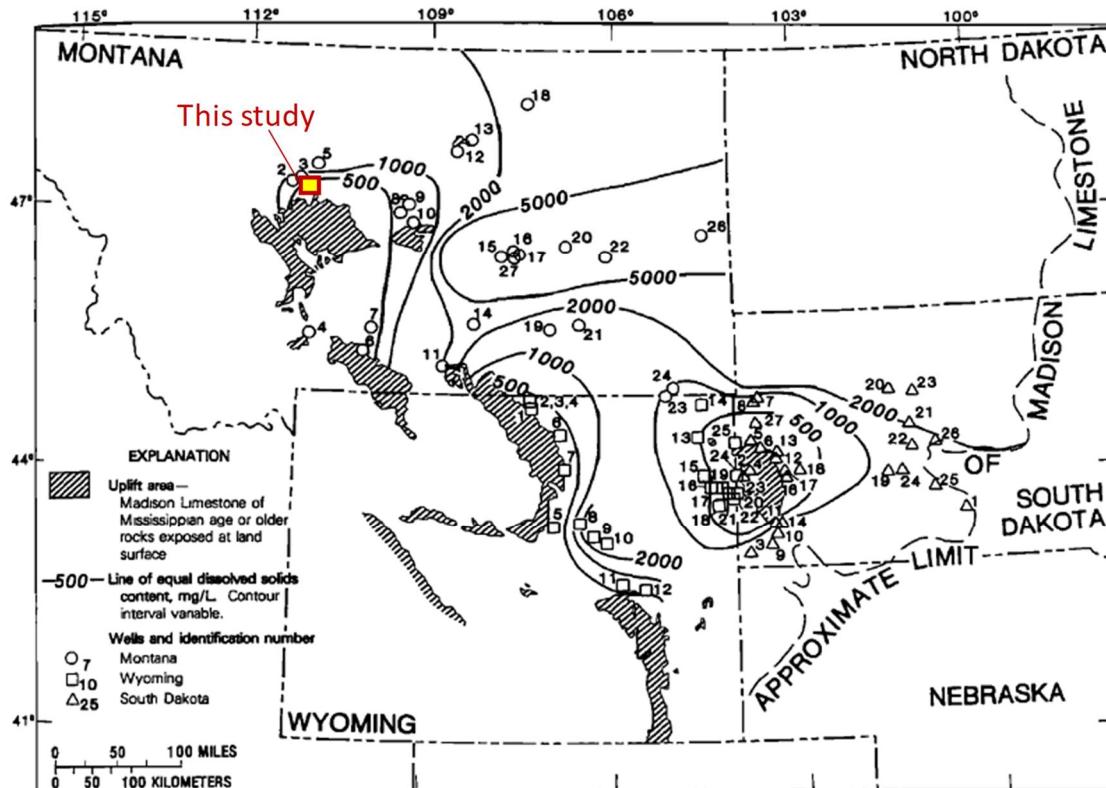


Figure 22. Map showing regional variation in total dissolved solids (TDS) of groundwater in the Madison Aquifer (taken from Plummer et al., 1990). The study area lies in an area where the TDS is changing quickly due to dissolution of sedimentary gypsum. The general flow of groundwater across the map is northward and eastward.

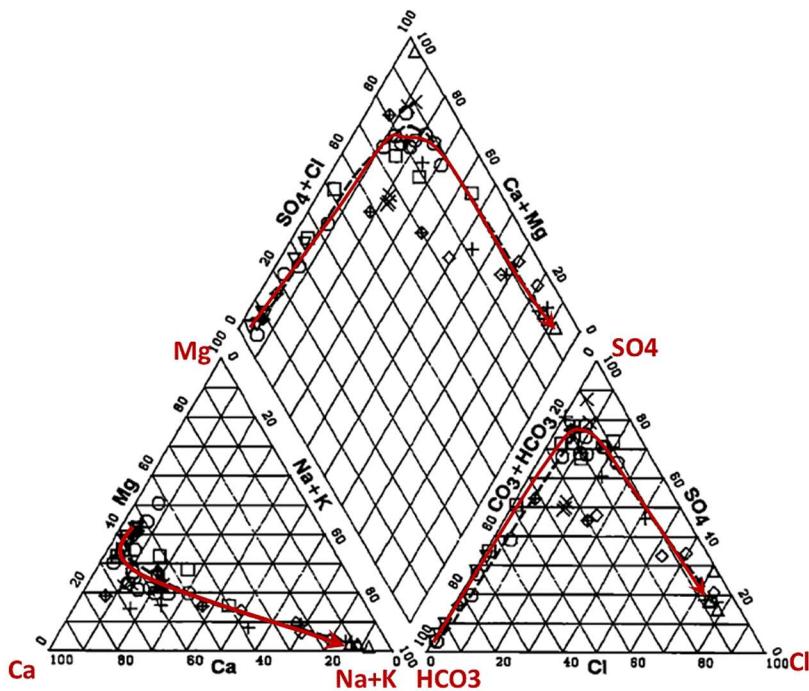


Figure 23. Piper diagram summarizing the chemical evolution of groundwater in the Madison Aquifer at a regional scale (modified from Plummer et al., 1990).

In their regional study, Plummer et al. (1990) included data on the S-isotope composition of dissolved sulfate in Madison groundwater. Data for samples from central Montana are summarized in Figure 24, along with results for the water samples of this study. The data of Plummer et al. (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 $\delta^{34}\text{S} > +20\text{\textperthousand}$. A heavy $\delta^{34}\text{S}$ 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 $\delta^{34}\text{S}$ -sulfate vs. sulfate concentration for the Madison Aquifer.

Groundwater Path B in Figure 24 is the pathway of most relevance to this study. In this case, recharge water for the Madison Aquifer follows Path A for a while, picking up some evaporite sulfate as it flows northward away from the Little Belt Mountains. However, when the water gets to 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 24 applies to some of the shallower aquifer systems, e.g., the Kootenai, Morrison coal, and Swift Fms. 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 Fm. and is the main source of water for the flooded coal mines at the top of the Morrison Fm. Once 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.

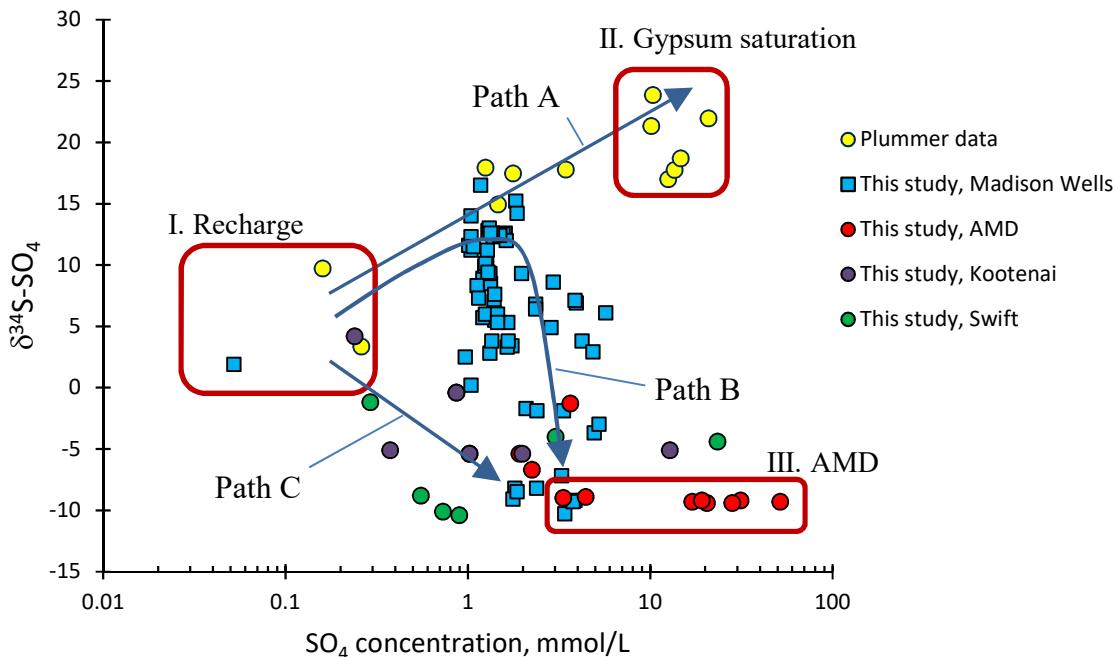


Figure 24. Plot of $\delta^{34}\text{S}$ -sulfate vs. sulfate concentration comparing the data from Plummer et al. (1990) for Madison water samples from Montana vs. waters investigated in this study. See text for explanation of the boxes and flow paths.

The data shown in Figure 24 are replotted vs. reciprocal sulfate concentration in Figures 25 and 26. 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 25 (e.g., Foothills Subdivision, Giant Springs, etc.). Figure 26 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 Subdivision wells, being further north than the other Madison water samples in this study, appear to have dissolved more of the end member (Box II) evaporite sulfate in addition to potentially receiving acid drainage from the coal beds. Some of the Madison wells that fall closer to Path C in Figure 26 are located further south, and may not have dissolved much gypsum before receiving sulfate from oxidation of pyrite in the coal beds.

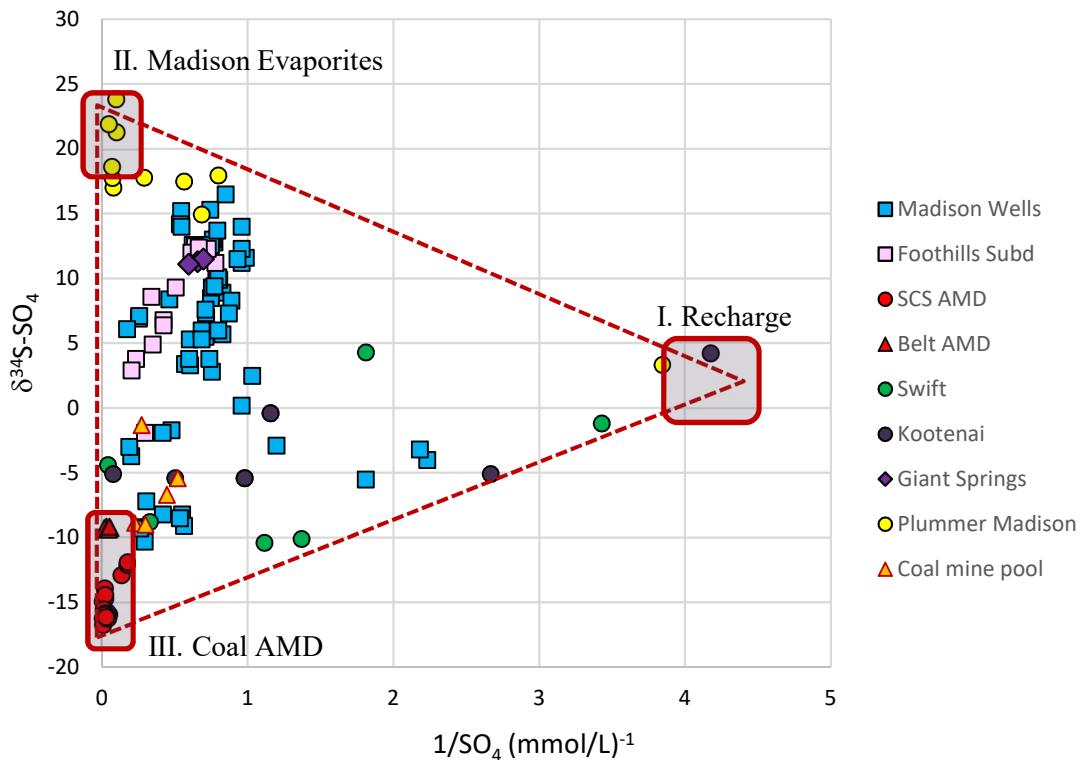


Figure 25. Plot of $\delta^{34}\text{S}$ -sulfate vs. reciprocal sulfate concentration for waters investigated in this study as well as data from Plummer et al. (1990) for Madison Aquifer samples from Montana.

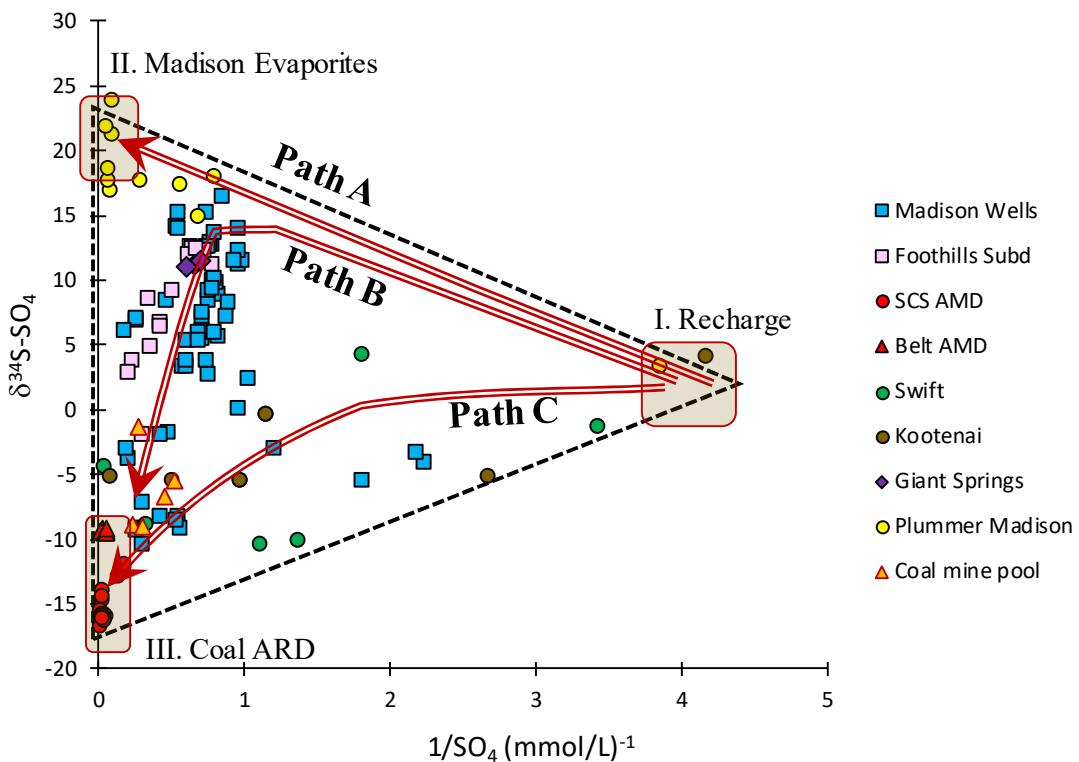


Figure 26. Plot of $\delta^{34}\text{S}$ -sulfate vs. reciprocal sulfate concentration showing groundwater evolution paths A, B, C (paths shown here are similar to Figure 24).

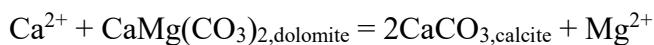
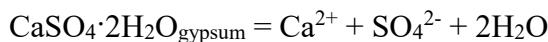
A final point that needs to be made with regards to the Foothills Subdivision wells is that just because many of the wells appear to have inherited sulfate from oxidation of pyrite in the Morrison coal beds (Path B of Fig. 26), this doesn't necessarily mean that this occurred from leakage of AMD from 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 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 (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}):

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

The results showed that all of the Madison groundwater samples are close to equilibrium with calcite (CaCO_3), dolomite ($\text{CaMg}(\text{CO}_3)_2$), 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 ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) 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 et al. (1990) demonstrated a link between gypsum dissolution and “de-dolomitization” in the Madison Aquifer according to the following reactions:



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 that 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, $\text{KAl}_3(\text{SO}_4)_2(\text{OH})_6$ or jurbanite, $\text{AlSO}_4(\text{OH})$). 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 ($\text{KFe}_3(\text{SO}_4)_2(\text{OH})_6$) 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 sizeable deposit of unconsolidated ferrihydrite/goethite “muck,” which is actually dangerous since a person or animal could sink up to their hips with a misstep. 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 Subdivision, near Great Falls, and 2) the town of Belt and its surrounding area.

In the case of the Foothills 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 Subdivision is roughly 5 miles 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 Fm. coal beds 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 18, 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 suggests significant mixing with AMD. However, the two wells that show mixing are located upgradient from mining activities.

Many papers published in the last 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 et al., 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 $\delta^{34}\text{S}$ - 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 $\delta^{34}\text{S}$ - SO_4 and $\delta^{18}\text{O}$ - 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 coal beds or underlying Madison Limestone. 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 $\delta^{34}\text{S}$ and $\delta^{18}\text{O}$ of the sulfate molecule, or if one isotope analysis (e.g., $\delta^{34}\text{S}$) is sufficient. Many academic and commercial labs can analyze $\delta^{34}\text{S}$ of sulfate, but $\delta^{18}\text{O}$ -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 $\delta^{34}\text{S}$ -sulfate and based on $\delta^{18}\text{O}$ -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, $\delta^{34}\text{S}$ -sulfate would be useless from a fingerprinting point of view, whereas $\delta^{18}\text{O}$ -sulfate would be an excellent tracer to sleuth out contributions from AMD vs. background sources. Overall, it is recommended that future studies employ both $\delta^{18}\text{O}$ and $\delta^{34}\text{S}$.

Conclusion

The following are four of the most important conclusions of this project:

- Stable S- and O-isotopes confirm that dissolved sulfate from abandoned coal mines in central Montana is present in the Madison limestone aquifer.
- Our data suggest that AMD may have migrated downgradient at least 5 miles 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 coal beds 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.

Some 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.

- Future investigation in this region should address the potential for wells constructed in the early 1900s to provide conduits for shallow groundwater in the coal mines to drain by gravity to the deeper, regional water table in the Madison aquifer.

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Appendices

Appendix A. Summary of all stable isotope data for dissolved sulfate and water.

Identifier	GWIC ID	Sample date	Aquifer	Dissolved Sulfate			Water Isotopes	
				$\delta^{34}\text{S}$, ‰	$\delta^{18}\text{O}$, ‰	SO_4 , mg/l	$\delta^{18}\text{O}$, ‰	δD , ‰
Foothills Subdivision								
OSM-01	235488	4/14/17	MDSN	6.8	0.4	226	-19.0	-147
OSM-152	235488	8/14/18	MDSN	6.7	1.1	n.a.	n.a.	n.a.
OSM-201	235488	7/17/19	MDSN	6.4	1.1	226	-18.8	-146
OSM-03	291365	4/13/17	MDSN	9.3	3.4	189	-18.9	-146
OSM-04	261984	4/13/17	MDSN	3.8	-5.8	407	-18.8	-146
OSM-153	261984	8/14/18	MDSN	5.2	-2.0	n.a.	n.a.	n.a.
OSM-202	261984	7/18/19	MDSN	2.9	-4.4	466	n.a.	n.a.
OSM-05	235689	4/14/17	MDSN	-1.9	-3.4	322	-18.8	-146
OSM-08	281405	6/21/17	MDSN	4.9	0.0	274	-18.9	-147
OSM-10	252467	6/20/17	MDSN	11.2	6.2	123	-18.8	-146
OSM-11	239236	6/21/17	MDSN	12.6	5.8	154	-18.0	-143
OSM-12	248664	6/20/17	MDSN	12.3	5.6	132	-18.8	-146
OSM-13	242151	6/20/17	MDSN	8.6	1.4	282	-18.9	-147
OSM-15	279108	6/21/17	MDSN	12.5	5.2	150	-18.9	-146
OSM-16	242153	6/20/17	MDSN	12.0	4.0	156	-18.9	-146
OSM-151	279137	8/14/18	MDSN	12.4	5.9	144	n.a.	n.a.

Stockett–Sand Coulee, Madison Wells								
DEQ100	P-13	2011	MDSN	14.0	7.3	100	n.a.	n.a.
DEQ110	C7	2011	MDSN	11.2	6.5	100	-18.3	-143
DEQ103	C5	2011	MDSN	11.6	6.2	97	-18.7	-143
OSM-35	288313	9/13/17	MDSN	12.6	4.5	131	-18.8	-145
OSM-203	288313	7/18/19	MDSN	12.8	6.5	124	-18.7	-145
OSM-37	126078	10/19/17	MDSN	6.9	-0.5	377	-18.8	-146
OSM-204	126078	7/18/19	MDSN	7.1	0.3	371	-18.9	-147
OSM-38	31892	10/19/17	MDSN	15.2	6.7	176	-18.9	-147
OSM-205	31892	7/18/19	MDSN	14.2	5.9	179	-18.8	-146
OSM-39	139022	10/19/17	MDSN	12.3	8.7	100	-18.7	-145
OSM-40	245668	10/19/17	MDSN	16.5	12.4	113	-18.7	-144
OSM-206	245668	7/16/19	MDSN	n.a.	n.a.	n.a.	-18.8	-145
OSM-43	141006	10/20/17	MDSN	2.8	7.3	127	-18.9	-146

Identifier	GWIC ID	Sample Date	Aquifer	Dissolved Sulfate			Water Isotopes	
				$\delta^{34}\text{S}$, ‰	$\delta^{18}\text{O}$, ‰	SO_4 , mg/l	$\delta^{18}\text{O}$, ‰	δD , ‰
Stockett–Sand Coulee, Madison Wells (Cont.)								
OSM-26	276129	7/18/17	MDSN	1.9	n.a.	5	-18.6	-142
OSM-68	210668	6/20/18	MDSN	-3.7	-3.3	474	-16.1	-130
OSM-207	210668	7/18/19	MDSN	-3.0	-2.9	504	-17.1	-138
OSM-71	149852	6/21/18	MDSN	6.1	1.3	547	-19.0	-148
OSM-155	294553	8/14/18	MDSN	13.0	6.3	126	n.a.	n.a.
MT1	2309	8/28/09	MDSN	3.4	-1.6	168	-18.4	-143
OSM-27	2309	7/19/17	MDSN	8.9	4.6	116	-18.8	-145
OSM-208	2309	7/17/19	MDSN	5.5	2.3	135	-18.8	-146
MT2	2308	8/28/09	MDSN	3.3	-0.9	158	-18.7	-146
MT3	167881	8/28/09	MDSN	12.6	10.0	128	-19.0	-146
MT4	205599	8/29/09	MDSN	8.5	4.5	128	-18.8	-145
OSM-25	205599	7/19/17	MDSN	10.0	4.7	122	-18.7	-145
	205599	7/17/19	MDSN	9.3	4.6	127	-18.8	-146
MT5	2249	8/29/09	MDSN	7.0	4.2	134	-18.8	-145
MT6		8/29/09	MDSN	9.9	5.4	119	-18.7	-146
MT8	2295	8/29/09	MDSN	10.1	6.0	120	-18.8	-145
MT9	158293	9/19/09	MDSN	7.6	4.0	135	-18.8	-146
MT11	122947	9/19/09	MDSN	5.7	3.9	116	-18.7	-145
MT12	165613	9/19/09	MDSN	9.4	5.2	124	-18.7	-145
MT15	210883	9/11/10	MDSN	11.5	7.4	103	-18.9	-146
MT16	130732	9/11/10	MDSN	8.3	5.1	108	-18.8	-145
MT18	230156	10/23/10	MDSN	0.2	-1.9	100	-18.3	-144
MT19	254474	10/23/10	MDSN	2.5	0.2	93	-19.0	-147
MT21	149855	10/23/10	MDSN	6.1	2.0	134	-18.9	-145
OSM-24	149855	7/19/17	MDSN	5.3	0.8	159	-18.8	-145
DEQ101		2011	MDSN	-1.7	-2.5	200	n.a.	n.a.
DEQ102		2011	MDSN	-1.9	-2.9	230	n.a.	n.a.
DEQ104		2011	MDSN	3.8	2.1	130	-18.7	-144
DEQ105		2011	MDSN	7.3	4.0	110	-18.4	-144
DEQ106		2011	MDSN	6.0	2.9	120	-18.7	-145
DEQ107		2011	MDSN	6.0	2.4	140	-18.4	-144
DEQ108		2011	MDSN	5.3	2.0	140	-18.3	-143
DEQ109		2011	MDSN	3.8	3.9	160	-18.3	-143

Identifier	GWIC ID	Sample Date	Aquifer	Dissolved Sulfate			Water Isotopes	
				$\delta^{34}\text{S}$, ‰	$\delta^{18}\text{O}$, ‰	SO_4 , mg/l	$\delta^{18}\text{O}$, ‰	δD , ‰
Stockett–Sand Coulee, Madison Wells (cont.)								
MT17		10/23/10	MDSN	-10.3	-9.5	326	-18.3	-141
MT20		10/23/10	MDSN	-8.2	-9.2	174	-19.3	-149
MT7	2305	8/29/09	MDSN	-9.1	-9.7	170	-19.4	-151
MT10	31939	9/19/09	MDSN	-9.2	-8.2	372	-18.4	-143
OSM-29	31939	7/19/17	MDSN	-7.2	-7.0	314	-18.5	-144
MT13	255442	9/11/10	MDSN	-9.3	-8.9	363	-19.2	-149
OSM-23	255442	7/19/17	MDSN	-8.5	-8.6	179	-20.1	-156
OSM-209	255442	7/18/19	MDSN	-8.2	-8.5	229	-19.7	-154
Stockett–Sand Coulee, Swift Fm. Aquifer								
MT14	162423	2009/10	SWIFT	-10.1	-6.5	70	-17.6	-139
OSM-41	162423	10/20/17	SWIFT	-10.4	-6.1	86	-17.4	-139
OSM-42	2174	10/20/17	SWIFT	-1.2	-4.1	28	-17.2	-137
OSM-02	236507	4/14/17	SWIFT	-4.4	-10.5	2246	-18.1	-147
OSM-154	236507	8/14/18	SWIFT	-4.0	-9.8	n.a.	n.a.	n.a.
Stockett–Sand Coulee, Kootenai Fm. Aquifer								
OSM-44		10/18/17	KOOT	-0.4	-3.5	83	-16.7	-135
OSM-45		10/12/17	KOOT	-5.4	-5.3	98	-17.6	-140
OSM-19	30542	8/3/17	KOOT	4.2	n.a.	23	-18.0	-139
Stockett–Sand Coulee, Contaminated Alluvium								
OSM-69	2441	6/21/18	ALVM	-13.0	-8.7	1061	-18.3	-143
Stockett–Sand Coulee, Morrison Fm. Coal								
OSM-146	152258	5/4/2018	MRSN	-0.9	-0.6	169	n.a.	n.a.
OSM-147	146929	5/4/2018	MRSN	-5.3	-4.0	77	n.a.	n.a.

Identifier	GWIC ID	Sample Date	Aquifer	Dissolved Sulfate			Water Isotopes	
				$\delta^{34}\text{S}$, ‰	$\delta^{18}\text{O}$, ‰	SO_4 , mg/l	$\delta^{18}\text{O}$, ‰	δD , ‰
Giant Springs, City of Great Falls								
OSM-28	2528	7/21/17	MDSN	11.3	6.5	146	-18.9	-145
		11/18/05	MDSN	11.5	8.4	138	-18.9	-144
OSM-18	2526	6/20/17	MDSN	11.1	7.3	161	-18.8	-145
Coal Mine Discharges, Stockett–Sand Coulee Area								
Giffen	291863	11/18/05	AMD	-12.9	-9.1	721	-18.2	-141
OSM-20	291863	7/20/17	AMD	-12.1	-10.2	555	-18.3	-143
OSM-60	291863	5/22/18	AMD	-11.9	-10.0	549	-18.2	-143
Nelson	291861	11/18/05	AMD	-14.9	-10.5	12100	-17.1	-137
OSM-30	291861	7/20/17	AMD	-16.2	-11.8	11366	-17.0	-138
OSM-56	291861	5/22/18	AMD	-16.7	-11.7	10214	-16.8	-137
Oregon		11/18/05	AMD	-16.1	-9.6	2550	-17.6	-140
Oregon	MT-22	1/1/09	AMD	-15.9	-12.1	1920	-17.4	-138
OSM-21	291858	7/20/17	AMD	-15.7	-11.5	2628	-18.8	-145
OSM-55	291858	5/22/18	AMD	-16.2	-11.7	2822	-17.5	-140
C-wood 6	291859	11/18/05	AMD	-13.9	-10.9	4710	-17.3	-137
OSM-31	291859	7/20/17	AMD	-14.7	-11.0	4277	-17.2	-136
OSM-59	291859	5/22/18	AMD	-14.4	-11.5	4325	-16.3	-135
OSM-33	2276	7/20/17	AMD	-15.5	-12.0	7253	-17.1	-138
OSM-32	2262	7/20/17	AMD	-15.8	-13.0	4254	-17.4	-139
OSM-70	2262	5/22/18	AMD	-15.9	-13.2	4301	-17.4	-140
OSM-57	291865	5/22/18	AMD	-16.2	-13.7	2231	-17.8	-141
OSM-58	291865	5/22/18	AMD	-16.1	-13.7	3260	-17.9	-142

Identifier	GWIC ID	Sample Date	Aquifer	$\delta^{34}\text{S}$, ‰	$\delta^{18}\text{O}$, ‰	SO_4 , mg/l	Water Isotopes	
							$\delta^{18}\text{O}$, ‰	δD , ‰
Belt Area, Madison Wells								
OSM-09	196148	6/22/17	MDSN	-4.0	-3.8	43	-18.5	-145
Reddish	196148	11/1/07	MDSN	-5.5	-4.0	53	n.a.	n.a.
OSM-210	196148	7/19/19	MDSN	-3.2	-4.1	44	-18.6	-147
OSM-17	32069	6/22/17	MDSN	-2.9	-7.1	80	-18.0	-141
Belt-1A	217046	8/3/05	MDSN	14.0	12.0	175	-18.5	-140
Belt	188537	11/1/07	MDSN	15.0	11.9	n.a.	n.a.	n.a.
OSM-211	188537	7/17/19	MDSN	15.3	10.7	129	-18.8	-144
OSM-64	32009	6/20/18	MDSN	8.4	8.3	207	-18.8	-144
OSM-67	32000	6/20/18	MDSN	13.7	9.2	121	-18.8	-143
Belt Coal Mine, Mine Pool Water								
Belt-3B	217052	8/5/05	AMD	-8.9	-9.0	425	-18.1	-141
Belt-4B	215048	8/5/05	AMD	-5.4	-5.4	184	-18.3	-139
Belt-4A	217055	8/5/05	AMD	-9.0	0.7	320	-18.1	-137
OSM-34	999030	9/14/17	AMD	-6.7	-8.0	215	-18.1	-142
OSM-36	999030	9/12/17	AMD	-1.3	-4.9	350	-18.0	-142
Belt Mine, AMD Discharges								
OSM-06	217524	4/13/17	AMD	-9.2	-13.6	3006	-17.9	-141
Fr. Coul	217524	11/18/05	AMD	-9.3	-12.5	4950	-17.9	-141
OSM-62	217524	5/22/18	AMD	-9.4	-12.7	2700	-17.6	-139
OSM-07	200616	4/13/17	AMD	-9.3	-12.9	1634	-17.9	-142
Anaconda	200616	11/18/05	AMD	-9.4	-11.6	1960	-18.2	-140
OSM-61	200616	5/22/18	AMD	-9.2	-12.8	1844	-18.0	-143
Belt Area, Swift Aquifer								
OSM-14	31965	6/22/17	SWIFT	-8.8	-8.9	291	-18.0	-141
OSM-65	145604	6/20/18	SWIFT	4.3	-0.3	53	-18.8	-144
Belt Area, Kootenai Aquifer								
OSM-66	212233	6/20/18	KOOT	-5.4	-5.0	191	-18.7	-143
OSM-63	296888	5/23/18	KOOT	-5.1	-5.2	36	-18.3	-143
OSM-44	MW-102K	10/18/17	KOOT	-0.4	-3.5	83	-16.7	-135
OSM-45	MW-103K	10/12/17	KOOT	-5.4	-5.3	98	-17.6	-140
OSM-212	277205	7/18/19	KOOT	-5.1	1.2	1231	-17.7	-141
Belt Creek Mixing Samples								
OSM-148	8/14/18	Belt Bridge		0.3	-3.1		-18.1	-141
OSM-149	8/14/18	Belt Creek Upstream		9.2	5.5		-18.2	-142
OSM-150	8/14/18	Belt Creek Downstream		1.6	-1.7		-18.2	-141

Appendix B: Stable isotopes of dissolved inorganic carbon (DIC).

Sample ID	GWIC ID#	Aquifer	Modifier	Date Sampled	DIC, mg/L as C	$\delta^{13}\text{C}$ -DIC, ‰
OSM-1	235488	Madison	Foothills Subd.	4/14/17	44.0	-6.9
OSM-3	291365	Madison	Foothills Subd.	4/13/17	43.3	-7.7
OSM-4	261984	Madison	Foothills Subd.	4/13/17	45.9	-6.5
OSM-5	235689	Madison	Foothills Subd.	4/14/17	39.8	-6.8
OSM-8	281405	Madison	Foothills Subd.	6/21/17	48.0	-7.6
OSM-9	196148	Madison		6/22/17	55.0	-13.0
OSM-10	252467	Madison	Foothills Subd.	6/20/17	44.2	-9.5
OSM-11	239236	Madison	Foothills Subd.	6/21/17	46.2	-9.0
OSM-12	248664	Madison	Foothills Subd.	6/20/17	45.3	-9.1
OSM-13	242151	Madison	Foothills Subd.	6/20/17	48.6	-8.4
OSM-14	31965	Swift		6/22/17	79.2	-14.8
OSM-15	279108	Madison	Foothills Subd.	6/21/17	46.7	-9.3
OSM-16	242153	Madison	Foothills Subd.	6/20/17	46.0	-9.0
OSM-18	2526	Madison	Giant Springs	6/20/17	42.1	-8.9
OSM-19	30542	Kootenai		8/3/17	57.4	-14.3
OSM-21	291858	AMD	Mt. Oregon Drain	7/20/17	16.1	-6.6
OSM-22	999030	AMD	Giffen Spring	7/20/17	54.0	-13.1
OSM-23	255442	Madison		7/19/17	60.4	-13.1
OSM-24	149855	Madison		7/19/17	45.7	-9.3
OSM-25	205599	Madison		7/19/17	43.6	-9.6
OSM-26	276129	Madison		7/18/17	54.8	-13.8
OSM-27	2309	Madison		7/19/17	41.9	-9.7
OSM-28	2528	Madison	Giant Springs	7/21/17	43.4	-9.2
OSM-29	31939	Madison		7/19/17	43.0	-9.6
OSM-31	291859	AMD	Cottonwood #6	7/20/17	11.6	-5.5
OSM-32	2262	AMD	No-name creek	7/20/17	9.8	-8.4

Appendix C: Helium Tritium

Fourteen groundwater samples collected from Madison aquifer were sent to the University of Utah Nobel Gas Lab for helium-tritium age dating. The copper tube method (https://noblegaslab.utah.edu/_resources/documents/services-pricing/cu_tube_sampling.pdf) was used to collect the dissolved gas. Results were inconclusive and are not discussed further in this report (Appendix C).

Appendix C. Helium
Tritium data

Sample I.D.	Utah Database ID	Dissolved Gas Collection Date	Dissolved Gas run ID	Tritium Collection Date	Tritium run ID	CO2 total (ccSTP/g)	CH4 total (ccSTP/g)	Ar total (ccSTP/g)	Ne total (ccSTP/g)
Measured Dissolved Gas(ccSTP/g)									
196148	20-0100	08/17/19	12131901	08/17/19	Trit02032004.prc		4.23E-04	2.41E-07	
245668	20-0101	08/18/19	12121902	08/18/19	Trit11221902.prc		4.01E-04	2.10E-07	
31892	20-0102	08/18/19	12121903	08/18/19	Trit01272008.prc		3.93E-04	2.21E-07	
126078	20-0103	08/18/19	12121905	08/18/19	Trit01242007.prc		5.73E-04	4.73E-07	
205599	20-0104	08/19/19	12111904	08/19/19	Trit01242003.prc		3.95E-04	2.14E-07	
255442	20-0105	08/19/19	12131906	08/19/19	Trit01232004.prc		3.80E-04	2.40E-07	
2309	20-0106	08/19/19	12161904	08/19/19	Trit01272005.prc		4.18E-04	2.15E-07	
294553	20-0107	08/19/19	12141903	08/19/19	Trit12121906.prc		3.67E-04	2.22E-07	
210668	20-0108	08/19/19	12111903	08/19/19	Trit01282007.prc		4.40E-04	2.57E-07	
288313	20-0109	08/20/19	12171902	08/20/19	Trit01232008.prc		4.02E-04	2.18E-07	
261984	20-0110	08/20/19	12131904	08/20/19	Trit12031908.prc		3.96E-04	2.24E-07	
235488	20-0111	08/20/19	12141901	08/20/19	Trit01242004.prc		3.89E-04	2.31E-07	
188537	20-0112	08/20/19	12161903	08/20/19	Trit01172008.prc		4.28E-04	2.40E-07	
2528 Giant Springs	20-0229	10/18/19	12131903	10/18/18	Trit01232005.prc		3.89E-04	2.27E-07	
2262 - TU Only	20-0097			07/16/19	Trit01242006.prc				
200616 - TU Only	20-0098			07/18/19	Trit12031907.prc				
277205 - TU Only	20-0099	This sample needed to be analysed again, will be done in April.							

Appendix C. Helium
Tritium data

Sample I.D.	He4 (ccSTP/g)	R/Ra	TU	1-sigma error +/-	Ne only model	Ne only (1-sigma error +/-)	EA model	EA model (1-sigma error +/-)	Tritoogenic He3 - Gas Ne only model (TU)	Gas Fractionatio n (F) (%)
	Measured Tritium (TU)									
196148	5.6E-08	1.176	2.20	0.13	18.5	3.8	22.9	2.3	3.98	0.6
245668	6.8E-08	1.256	5.73	0.36	26.8	1.4	26.6	1.3	19.74	0.0
31892	4.0E-05	0.075	3.47	0.23	Appears mixed		Appears mixed		1191.74	0.0
126078	3.8E-05	0.078	2.06	0.09	Appears mixed		Appears mixed		1149.76	0.2
205599	9.3E-06	0.086	4.75	0.19	Appears mixed		Appears mixed		308.30	0.0
255442	2.7E-07	0.317	3.34	0.11	Appears mixed		Appears mixed		12.73	0.0
2309	3.4E-06	0.087	4.46	0.29	Appears mixed		Appears mixed		95.46	0.7
294553	1.2E-05	0.084	4.68	0.16	Appears mixed		Appears mixed		405.30	0.0
210668	2.0E-05	0.079	3.65	0.12	Appears mixed		Appears mixed		623.22	0.5
288313	1.4E-05	0.082	4.25	0.14	Appears mixed		Appears mixed		441.86	0.7
261984	1.8E-05	0.082	3.45	0.46	Appears mixed		Appears mixed		569.51	0.6
235488	2.8E-05	0.079	3.28	0.13	Appears mixed		Appears mixed		871.13	0.6
188537	7.9E-08	1.503	5.59	0.21	Appears mixed		Appears mixed		33.27	0.6
2528 Giant Springs	7.5E-06	0.091	4.82	0.16	Appears mixed		Appears mixed		264.97	0.6
2262 - TU Only			9.23	0.70						
200616 - TU Only			5.31	0.95						
277205 - TU Only										

Appendix C. Helium
Tritium data

Sample I.D.	Excess Air (ccSTP/g)	Lab O2 (mg/l)	Chi^2	ΔNe (%)	Tot Dis Gas (atm)	Recharge Elevation (m)
196148	0.04	0.00	1.6	42.4	0.925	1647
245668	0.00	0.00	14.2	23.7	1.038	1674
31892	0.00	0.00	5.2	28.2	1.197	1647
126078	0.03	0.00	0.1	171.5	1.911	1647
205599	0.00	0.00	5.5	24.6	1.086	1674
255442	0.00	0.00	1.4	42.7	0.811	1674
2309	0.05	0.00	12.0	30.0	1.086	1674
294553	0.00	0.00	3.2	31.1	1.034	1674
210668	0.03	0.00	11.9	52.8	1.078	1674
288313	0.02	0.00	5.8	28.6	1.235	1674
261984	0.02	0.00	2.7	33.0	0.805	1674
235488	0.02	0.00	1.0	38.6	0.955	1674
188537	0.04	0.00	3.5	42.4	1.235	1674
2528 Giant Springs	0.02	0.00	1.6	34.3	1.111	1674
2262 - TU Only						
200616 - TU Only						
277205 - TU Only						

Appendix C. Helium
Tritium data

Sample I.D.	Water Temp (°C)	Water Salinity (‰)	Recharge Salinity (‰)	Field O2 (mg/l)	R-terrigenic	NOTES
196148	9.3		0.0	0.0	0.0	Model fits well,
245668	11.6		0.0	0.0	0.0	Model fit is ok, but there seems to be excess He. R/Ra indicates elevated radiogenic He but TU concentration is close to modern. It's likely the sample is a mixture of differing ages.
31892	15.9		0.0	0.0	0.0	Large He excess that seems to be radiogenic. Given the presence of tritium this sample is likely a mixture.
126078	15.7		0.0	0.0	0.0	Model fits well. He excess of apparent radiogenic origin. Likely a mixture.
205599	13.7		0.0	0.0	0.0	Model fits well. He excess of apparent radiogenic origin. Likely a mixture.
255442	11.0		0.0	0.0	0.0	Model fits well. He excess of apparent radiogenic origin. Likely a mixture.
2309	12.1		0.0	0.0	0.0	Model fits well. He excess of apparent radiogenic origin. Likely a mixture.
294553	13.4		0.0	0.0	0.0	Model fits well. He excess of apparent radiogenic origin. Likely a mixture.
210668	11.2		0.0	0.0	0.0	Model fits well. He excess of apparent radiogenic origin. Likely a mixture.
288313	15.3		0.0	0.0	0.0	Model fits well. He excess of apparent radiogenic origin. Likely a mixture.
261984	13.7		0.0	0.0	0.0	Model fits well. He excess of apparent radiogenic origin. Likely a mixture.
235488	13.9		0.0	0.0	0.0	Model fits well. He excess of apparent radiogenic origin. Likely a mixture.
188537	10.3		0.0	0.0	0.0	Model fits well. He excess of apparent radiogenic origin. Likely a mixture.
2528 Giant Springs	11.4		0.0	0.0	0.0	Model fits well. He excess of apparent radiogenic origin. Likely a mixture.
2262 - TU Only						
200616 - TU Only						
277205 - TU Only						

gwicid	no3_no2_n_mgl	oh_mgl	dissolved_organic_mgl	dissolved_inorga_mgl	total_dissolved_mgl	sum_dissolved_c	sar	procedure_type
214914	0			3562.392	3562.392	602.7236	0	0.4076 DISSOLVED
214915	0		25.4	4101.627	4101.627	812.5885	0	0.3053 DISSOLVED
214915	0		28.1	4184.784	4184.784	895.7027	0	0.2908 DISSOLVED
214915	0			3732.117	3732.117	794.6656	0	0.3241 DISSOLVED
214915	0			3605.491	3605.491	720.0905	0	0.3081 DISSOLVED
200616	0		8.04	2796.911	2796.911	758.0277	0	0.1897 DISSOLVED
200616	0		15.1	2565.087	2565.087	729.2188	0	0.2095 DISSOLVED
200616	0		11.5	2672.814	2672.814	724.8116	0	0.1778 DISSOLVED
200616	0		11.5	2440.234	2440.234	719.0869	0	0.1623 DISSOLVED
200616	0			2217.711	2217.711	623.2767	0	0.1743 DISSOLVED
200616	0		15.6	2454.375	2454.375	706.0377	0	0.1801 DISSOLVED
200616	0		12.9	2525.015	2525.015	749.057	0	0.159 DISSOLVED
200616	0		16.8	2474.4	2474.4	731.1492	0	0.177 DISSOLVED
200616	0			2033.212	2033.212	650.4899	0	0.1877 DISSOLVED
200616	0			2242.753	2242.753	699.9937	0	0.1645 DISSOLVED
200616	0			2387.068	2387.068	704.1997	0	0.1804 DISSOLVED
217524	0		0.11	5947.942	5947.942	928.9879	0	0.257 DISSOLVED
217524	0		1.11	4393.696	4393.696	697.8399	0	0.5106 DISSOLVED
217524	0		11.2	3931.798	3931.798	631.8715	0	0.2423 DISSOLVED
217524	0		11.1	4871.893	4871.893	741.7124	0	0.2876 DISSOLVED
217524	0			4541.83	4541.83	806.8043	0	0.3983 DISSOLVED
217524	0		11.1	3676.693	3676.693	779.558	0	0.3429 DISSOLVED
217524	0		10.6	4996.822	4996.822	676.4077	0	0.251 DISSOLVED
217524	0		19.7	4797.852	4797.852	691.4847	0	0.2648 DISSOLVED
217524	0			4349.984	4349.984	860.9871	0	0.3262 DISSOLVED
217524	0			4031.925	4031.925	722.7262	0	0.3399 DISSOLVED
217524	0			4872.721	4872.721	707.0554	0	0.2455 DISSOLVED
291863 <0.200 U	0		29.1	898.4628	963.916	484.6465	105.8021	0.4151 DISSOLVED
291863 <0.200 U	0		44.1	900.5284	963.952	489.5892	102.5214	0.354 DISSOLVED
291858 <0.200 U	0		28.2	3688.456	3688.456	981.9761	0	0.3888 DISSOLVED
291858 <0.200 U	0		25.3	3479.299	3479.299	1004.2649	0	0.3295 DISSOLVED
291861	1.53	0	1.3	13308.389	13308.389	1580.83	0	0.3721 DISSOLVED
291861	1.5	0	3.81	15032.851	15032.851	1820.683	0	0.2039 DISSOLVED
296887	1.2	0	1.53	4967.562	4967.562	1135.6187	0	0.3228 DISSOLVED
291865	0.22	0	1.94	2820.991	2820.991	1004.0016	0	0.2884 DISSOLVED
291865 <0.200 U	0		2.5	3870.83	3870.83	1039.6389	0	0.2969 DISSOLVED
291859	0.2	0	15.5	5806.189	5806.189	1295.544	0	0.1693 DISSOLVED
291859	0.35	0	14.3	5812.658	5812.658	1368.8096	0	0.1647 DISSOLVED
2262	0.6	0	2.45	5500.594	5500.594	1021.7415	0	0.2995 DISSOLVED
2276	1.86	0	1.37	9758.822	9758.822	1415.1668	0	0.2198 DISSOLVED
2262	0.47	0	13	5495.789	5495.789	1017.8784	0	0.2455 DISSOLVED
2276	1.81	0	4.96	9403.643	9403.643	1392.9138	0	0.1632 DISSOLVED