

WATER-RESOURCE SAMPLING IN AREAS OF OIL AND GAS DEVELOPMENT



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Montana Bureau of Mines and Geology

In collaboration with the Montana Department of Environmental Quality and the Montana Department of Natural Resources and Conservation



Cover photo by Elizabeth Meredith, MBMG. Oil production outside of Baker, Montana.

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INTRODUCTION

Project Purpose

To address requests from Montana citizens concerned about potential impacts from oil and gas development upon their water resources, the Montana Department of Environmental Quality (DEQ) and the Montana Bureau of Mines and Geology (MBMG) collected a series of surface-water and groundwater samples. The sample sites and analyses were chosen to establish the current condition of the water, thereby allowing for identification of possible future changes as well as potentially identifying existing impacts from development.

Oil and Gas Development in Montana

Oil and gas production in Montana has been ongoing since the early 20th century (chart embedded in fig. 1). Production cycles are driven by economics

and technology; since 1980, oil-related drilling rates have peaked and fallen twice [Montana Board of Oil and Gas Conservation (MBOGC), 2016]. The recent peak in oil production occurred in 2006 when production exceeded 36 million barrels; in 2013, production had dropped to 28.8 million barrels. In 2011, Montana produced 74.6 billion cubic feet of natural gas. Most of this is exported out of state. Almost all (92 percent) of Montana’s gas production comes from the north and northeast (MT DEQ, 2013b). Currently, oil and gas wells are present in nearly all eastern Montana counties (fig. 1).

Identification of Contamination from Oil and Gas Development

The introduction of hydraulic fracturing in its current form in 1997 (Turcotte and others, 2014), opened unconventional shale plays into economically viable targets. The new technology requires larger volumes

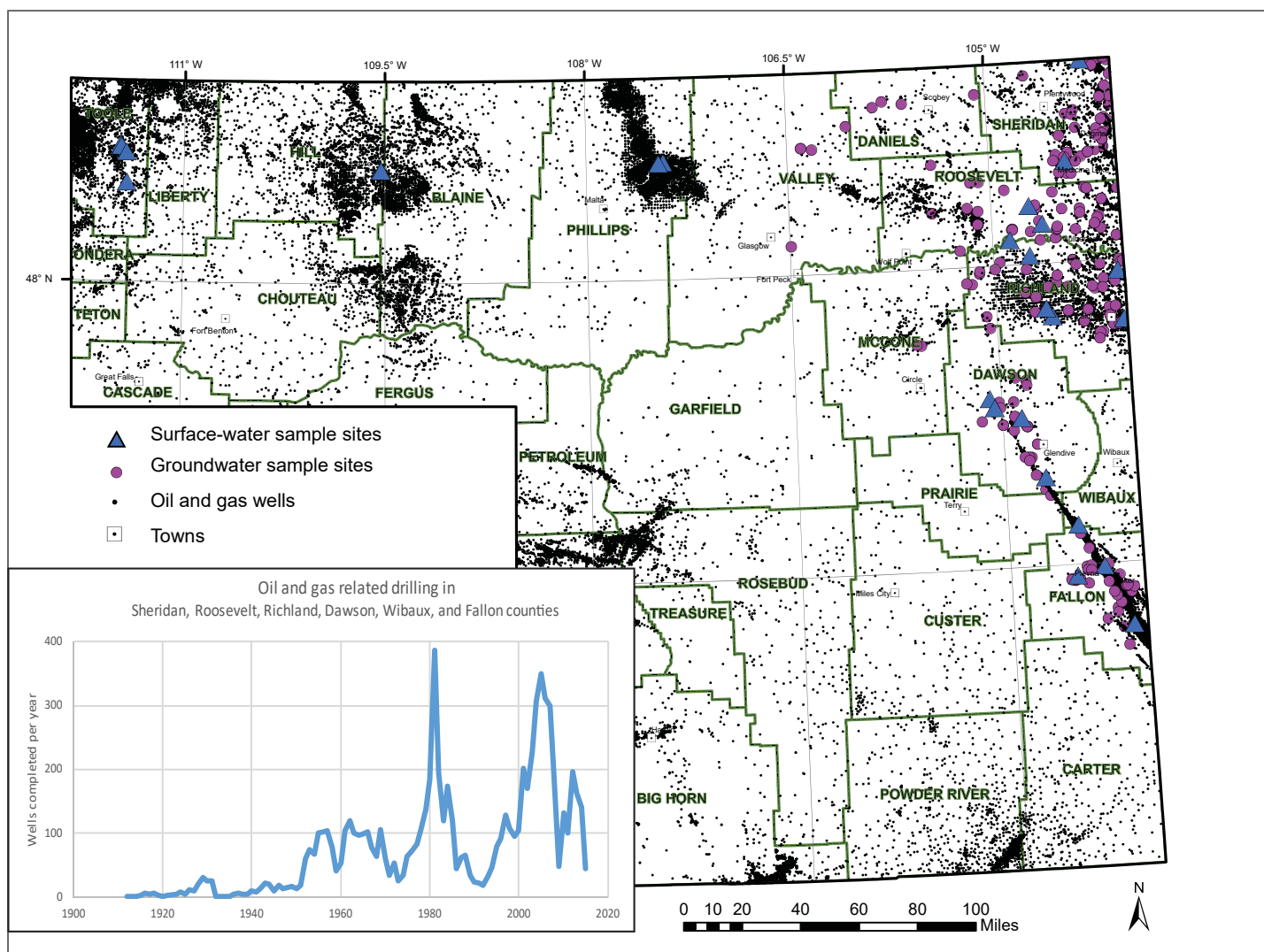


Figure 1. Map of oil and gas development in Montana and water-resource sample site locations. Inset chart data from Montana Board of Oil and Gas (2016).

of water [median of 1.5 million gallons per well (U.S. EPA, 2016)] than traditional well development and requires the addition of proppants (e.g., sand) and chemical additives (e.g., gelling agents, surfactants, biocides, and corrosion inhibitors, for example Brantley and others, 2014). The hydraulic fracturing fluid is generally 90 percent water, 9.5 percent proppant, and 0.5 percent chemical additives (Fross and Lyle, 2013). The larger volumes of water for drilling and completion result in proportionately larger volumes of wastewater that must be properly handled at the surface. In Montana, the only currently approved method for wastewater disposal is through injection into disposal wells.

Widespread concern over the potential for migration of natural gases into water resources from modern hydraulic fracturing techniques has spurred large, dissolved-gas groundwater sampling programs in Pennsylvania, U.S. (Molofsky and others, 2013); Alberta, Canada (Humez and others, 2016); and Lower Saxony, Germany (Schloemer and others, 2016). All studies found a high frequency of naturally occurring methane and a smaller number of samples with ethane and propane. They concluded that in almost all cases, these gases did not migrate from deeper oil sources but occur naturally. Their work supported earlier findings that the ratio of methane to propane and ethane is an indication of the source: the closer to even proportion of the gases, the more likely the source of gas was from a deep, hydrocarbon target. Higher proportions of methane to the other gases indicated a shallow, biogenic source of gases.

Produced waters from Texas and Pennsylvania have salinities in excess of 20,000 mg/L and naturally occurring radioactive materials (226Radium, 228Radium, and 222Radon) up to 10,000 picocuries/L (pCi/L; Kharaka and others, 2013). The drinking water standard for radioactivity is 15 pCi/L (alpha radiation). The recommended secondary standard (for aesthetics) for salinity is 500 mg/L (TDS). Additionally, the produced water from shale gas wells can include organic constituents: polycyclic aromatic hydrocarbons (PAH), heterocyclic compounds, aliphatic alcohols, phenols, aromatic amines, other aromatics, phthalates, fatty acids, nonaromatic compounds, and total organic carbon (TOC) from 8 to 5,500 mg/L, with the higher TOC concentrations associated with the addition of hydraulic fracturing fluids (Orem and others, 2014).

Brantley and others (2014) found that understanding water resource impacts from development in Pennsylvania was hindered by the lack of publicly available water-quality data related to specific incidents, sparseness of available data on analytes of interest, and the presence of preexisting water impairments, among other factors. The majority of complaints of impacts from Pennsylvania oil and gas development included natural gas, brine salt, sediment, turbidity, and drill cuttings. The Pennsylvania regulator issued notices of violations to 0.24 percent of gas wells for methane migration. No cases of migration of hydraulic fracturing fluid were reported. Brine from Marcellus shale production water can be identified by high levels of chloride (15,600–146,000 mg/L), strontium (1,000–7,000 mg/L), barium (2,000–8,000 mg/L), and bromide (2–15 mmol/L). Brantley and others (2014) conclude that relatively few environmental impacts occurred compared to the size of the development, but assessing impacts is difficult due to the lack of publicly available data.

Work done by Drollette and others (2015) in Pennsylvania looked specifically for indications of migration of hydraulic fracturing fluid to the surface from the hydraulic fracturing target. Analyses of total purgeable and extractable hydrocarbon compounds (TPH and TEH) found low levels of volatile organic compounds, gasoline range (0–8 ppb) and diesel range (0–157 ppb) organic compounds [gasoline range organics (GRO) and diesel range organics (DRO)], and bis(2-ethylhexyl) phthalate (a disclosed additive to hydraulic fracturing fluids). It has been shown previously that shallow Pennsylvania groundwater has elevated chloride through slow, natural migration of deep groundwater (Warner and others, 2012) that makes distinguishing brine contamination through isotopic and inorganic analyses difficult. Through age dating techniques, noble gas composition, and a lack of inorganic markers such as bromide, they conclude that the presence of DRO in the groundwater was through accidental releases of production water at the surface, rather than migration from the subsurface (Drollette and others, 2015).

In response to the increased oil and gas production in Kansas, the Kansas Geologic Survey defined a set of analyses it recommended well owners complete (Fross and Lyle, 2013) based on indicators of brine contamination. The minimum recommended set of analytes include inorganic constituents: barium,

bromide, chloride, strontium, sodium, and sulfate in addition to pH and salinity. Additional tiers add organic components and more inorganic analytes (Fross and Lyle, 2013).

The U.S. Environmental Protection Agency (EPA) investigated the possibility of hydraulic-fracturing-related groundwater contamination after residents of Pavillion, Wyoming reported degraded taste and odor of their groundwater. Their investigation found high pH, elevated potassium and chloride, and detections of organic compounds in the groundwater, which were interpreted to indicate the presence of hydraulic fracturing fluids in the aquifer. The EPA's conclusions had extensive media coverage and attention from State and Federal agencies and industry. The multiple interpretations presented by these groups highlighted uncertainty in the conclusions. As a result, the Pavillion investigation has inspired improved stakeholder involvement and predevelopment guidelines (Stephens, 2015). To establish predevelopment groundwater conditions and to ensure viable data, Wyoming has adopted a sampling and analysis procedure for all oil and gas operators to follow (appendix K of WOGCC, 2013), which is similar to the groundwater monitoring program in place in Colorado (COGA, 2011). The procedure outlines an extensive set of inorganic and organic analytes, proper sampling and handling methods, and data review along with other necessary documentation (WOGCC, 2013).

The Montana Board of Oil and Gas Conservation held two public hearings in 2017 to discuss rule making for water monitoring around oil and gas development (MBOGC, 2018).

Project objectives

The lack of publicly available water-quality data in areas of Marcellus Shale development and elsewhere has left regulators struggling to understand the potential and real impacts of unconventional hydrocarbon resource development. The Montana DEQ began the process of addressing similar shortcomings in Montana by working with the MBMG to collect surface and groundwater samples from Montana counties undergoing oil and gas development (fig. 2). Funding for this work came through the Montana Department of Natural Resources and Conservation (DNRC), U.S. Bureau of Land Management, and the U.S. EPA Clean Water Act. The development of an extensive set of

water-quality samples protects water users by identifying contamination and prevents misattributing natural or historical water-quality issues to industry.

Specific objectives include:

1. Measure characteristics sufficient to establish the current condition of the surface and groundwater resources:
 - physical parameters
 - temperature, dissolved oxygen (DO), pH, specific conductance (SC), and flow rate
 - chemical parameters
 - inorganic analytes, total suspended solids (TSS), total dissolved solids (TDS), nutrients, and metals
2. Analyze samples for indications of oil and gas production contamination
 - organic constituents
 - methane concentrations and isotopes of methane
 - radiochemistry
3. Assess evidence of migration of contaminants from oil and gas activities, and define current conditions

Analyte Selection and Description

Analytes were chosen to characterize the current condition of the water with a specific emphasis on constituents related to human and fish health (MT DEQ 2012, 2013a). Additionally, major cations, major anions, and trace elements were included to differentiate aquifers and sources of salt that are generally derived from the surrounding geology. Organic constituents and radiochemistry were included to identify the presence of oil and gas related contamination. A list of analytes measured in surface and groundwater is presented in appendix A.

Inorganic constituents include those elements found on a periodic table and non-carbon-chain-based molecules. They include:

- Major cations: calcium, magnesium, sodium, and potassium, and to a lesser extent iron, manganese, and silica (SiO₂).

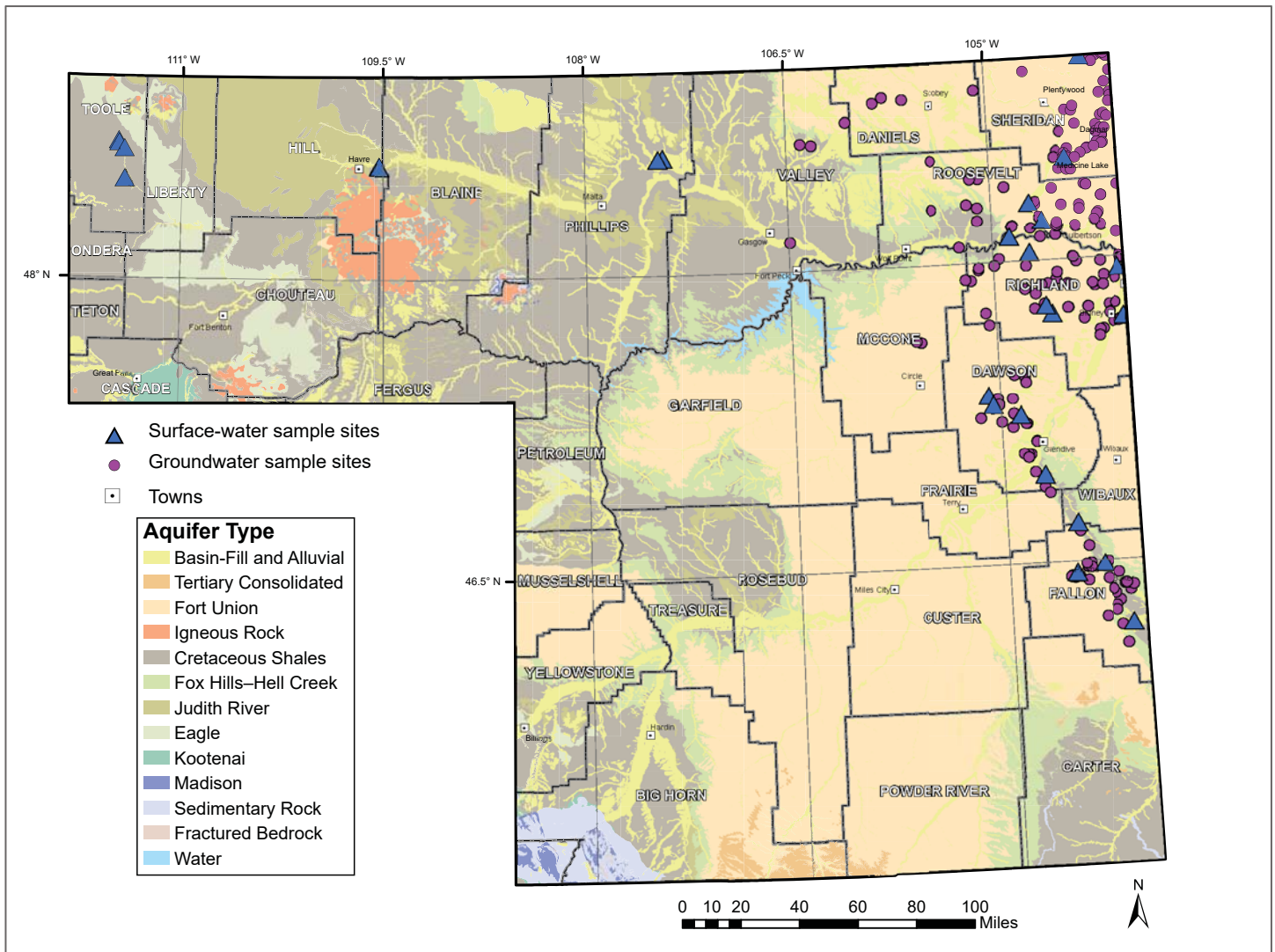


Figure 2. Montana aquifers and water-resource sample site locations. Principal aquifer map from Crowley and others (2017).

- **Major anions:** bicarbonate (HCO_3), sulfate (SO_4), and chloride, and to a lesser extent nitrate (NO_3) and fluoride.
- **Total dissolved solids:** the sum of all dissolved constituents but primarily made up of the sum of the major cations and anions. This is the measurement of the salinity of the water. It can be approximated through direct measurement of the SC of the water, which is the water’s ability to pass an electric current.
- **Total suspended solids:** the dried weight of the suspended particles that are $>0.45 \mu\text{m}$ in size.
- **Trace elements (trace metals):** includes elements that make up a much smaller proportion of the dissolved constituents but can be important for health (human, fish, and animals) such as aluminum, cadmium, lead,

arsenic, chromium, copper, mercury, selenium, uranium, and others. For example, the MBMG analytical laboratory currently reports 36 trace elements (37 if mercury is reported).

Organic constituents are carbon-chain-based compounds that occur in shallow and deep natural systems and may be derived from petroleum refining processes. The organic analytes measured during the surface- and groundwater-sampling program include:

- **Gasoline range organics and diesel range organics** are defined by the U.S. EPA. GRO is approximately $n\text{C}_6$ through $n\text{C}_{10}$ and DRO is approximately $n\text{C}_{10}$ through $n\text{C}_{28}$ (Drollette and others, 2015). It is important to note that these designations do not necessarily imply the measured organics are derived from gasoline or diesel, only that they have similar molecular weights. These organic classes can

occur naturally in the environment or through contamination.

- **Total purgeable hydrocarbons** include gasoline range, benzene, toluene, xylene, naphthalene, and light aliphatics and aromatics. This is not to be confused with total petroleum hydrocarbons, also abbreviated TPH. Total petroleum hydrocarbons as defined by EPA method 8015 (modified) reports the concentration of purgeable and extractable hydrocarbons, which are roughly equivalent to GRO and DRO, respectively.
- **Total extractable hydrocarbons** include DRO and heavy aliphatics and aromatics.
- **Aliphatics** are organic molecules structured as a chain with either single bonds (alkanes), double bonds (alkenes), or triple bonds (alkynes). Alkanes measured in this study include methane (CH_4), ethane (C_2H_4), and ethene (C_2H_6), and are measured as dissolved gases in water samples.
- **Aromatics** contain a stable, planar ring of carbon. An example aromatic measured in this study is benzene (C_6H_6).
- **BTEX** is an acronym for benzene (C_6H_6), toluene (C_7H_8), ethylbenzene (C_8H_{10}), and xylene (C_8H_{10}). There are three isomers of xylene based on the structure: ortho- (o-xylene), meta- (m-xylene), and para (p-xylene).

Radiochemistry measures the radioactivity of the water either through direct measurement of alpha and beta radioactive decay or by measurement of the radioactive elements (such as uranium species).

Isotopes of methane include carbon isotopes ($^{13}\text{C}/^{12}\text{C}$) and hydrogen isotopes ($^2\text{H}/^1\text{H}$). Biological processes that create methane, such as anaerobic respiration, preferentially use the more common isotope weights ^{12}C and ^1H . This preference causes the lighter isotopes to be concentrated in the methane byproduct. Alternatively, in thermocatalytic methane

generation, long chains of carbon-based molecules are broken through heat into smaller molecules (e.g., methane), and there is no preferential concentration of isotopes based on weight. The ratio of the heavy to light isotope can therefore indicate the source of the methane as from either biological or thermocatalytic processes.

METHODS

Site Selection Criteria

Surface water

The DEQ collected surface-water samples in areas where conventional and unconventional oil and natural gas development has occurred and will likely continue (table 1, fig. 3, and appendix B). The targeted stream sample sites were located where pollutants associated with oil and natural gas development are thought to have the highest probability of detection, if present. Additional sample sites were selected based on requests from local Conservation Districts and from the MBMG.

Table 1. Surface-water sample site summary. Site location is listed in appendix B.

Stream	Station ID	Years Sampled
Bennie Peer Creek	Y23BENPC03	2013-2014
Big Muddy Creek	M50BMDYC11	2012-2016
	M50BMDYC12	2012
Cabin Creek	Y23CABNC08	2013-2016
Cedar Creek	Y23CEDRC04	2013-2016
Charlie Creek East	M51CHLYC04	2012-2016
Charlie Creek West	M51CHLYC05	2012-2016
Deer Creek Middle Fork	Y23DRMFC01	2014-2015
	Y23DEERC01	2014
	Y23DRSFC01	2014, 2016
Fourmile Creek	M51FORMC04	2013-2016
Fox Creek East Fork	Y23FXEFC01	2014
	Y23FXEFC02	2015-2016
Little Beaver Creek	Y27LBVRC13	2013-2016
Little Boxelder Creek	M42LBOXC05	2012-2016
Medicine Lake	M50MEDL01	2015-2016
Pennel Creek	Y22PENELC02	2013-2016
Sandstone Creek	Y22SNSTC04	2013-2016
Ueland Road Spring	M52ULDSP01	2015-2016
Whitewater Creek	M39WHTWC09	2012-2016
	M39WHTWC10	2012
Willow Creek	M17WILOC03	2013
	M17WILOC02	2012, 2014
	M17WILOC04	2014-2016

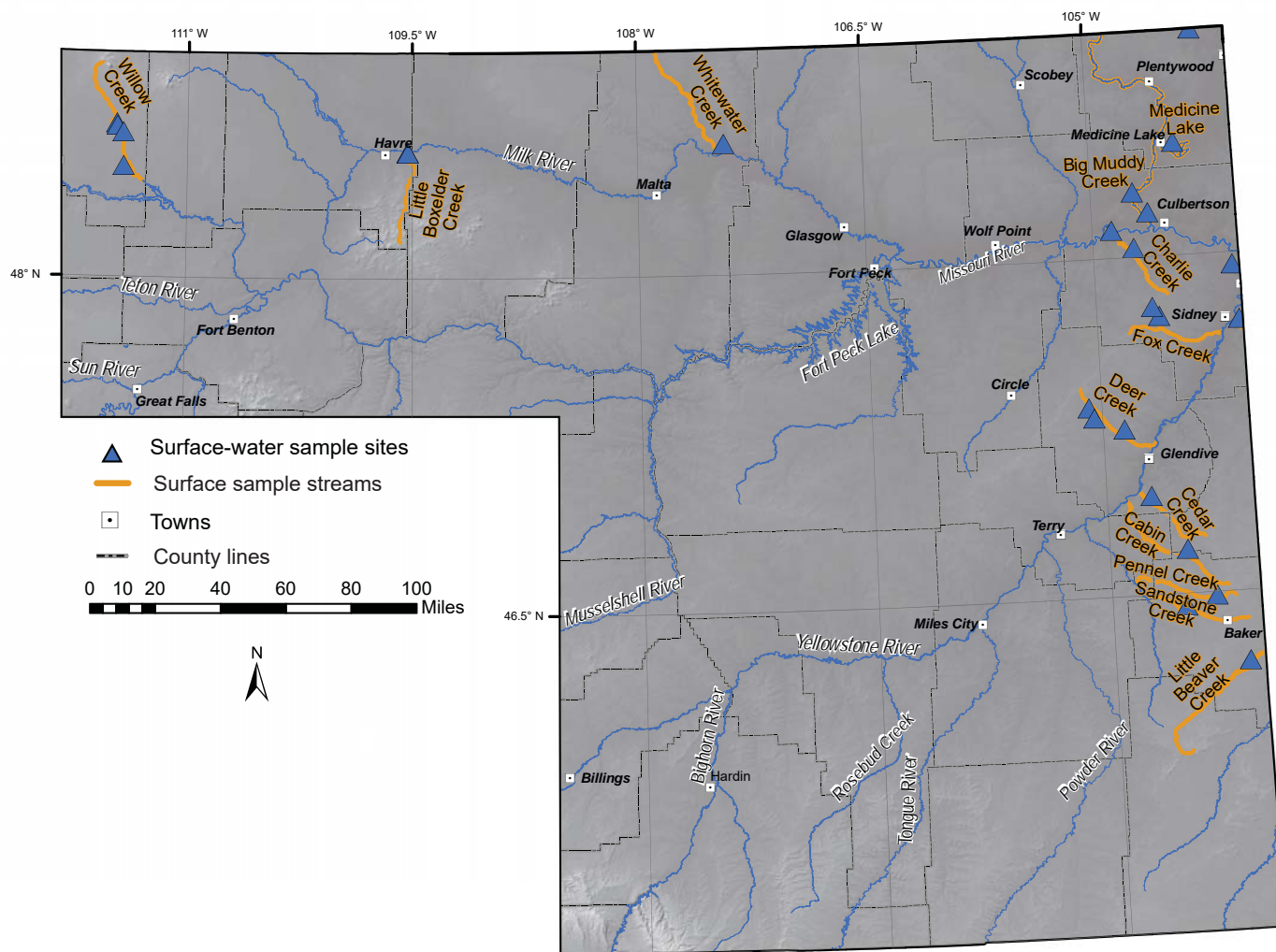


Figure 3. Surface-water sample site locations.

Groundwater

The MBMG collected groundwater samples in 2015 and 2016. Targeted aquifers were those commonly used for domestic and stock water sources, which includes shallow unconsolidated aquifers (alluvium and glacial outwash, primarily), the Fort Union Formation, and the Fox Hills–Hell Creek Formation (table 2). In 2015, sample selection was a subset of priority wells identified by the DEQ based, in part, on proximity to old oil wells. Sample selection in 2016 had two priorities: (1) fill water-chemistry data gaps based on location and aquifer to further characterize general aquifer conditions, and (2) resample wells with previous samples to gauge changes with time (fig. 2, starred samples in appendix B). Detailed sample selection descriptions were set out in the Sampling and Analysis Plan authored by the MBMG, available online: <http://www.mbmgt.mtech.edu/energy/energy-oileval.html>.

Sampling Methods

Surface water

The DEQ sampling sites and sample analyses varied by year based on annual review of data and an adaptive project design (annual sampling and analyses plans are available from the DEQ). This generally included nutrients (e.g., total nitrogen, phosphorus, and nitrate), total suspended solids, total dissolved solids, metals (major cations and trace), a yearly sample of sediment minerals, radioactivity (alpha and beta), and pollutants associated with hydraulic fracturing fluids and industrial activities (e.g., BTEX, methane, methanol, and PAH). In addition to the analytical analyses, field parameters of DO, flow rate, pH, turbidity, temperature, and SC were measured at all sites. All surface-water information is stored in the national STORET database.

Table 2. Geologic description of sampled aquifers.

Stratigraphic unit	Geologic description	Aquifer properties
Quaternary Alluvium	Sand, silt, and gravel deposits.	Generally unconfined or semi-confined conditions.
Quaternary Glacial Outwash Deposits	Clean sand and gravel, found as lenses on glacial till. Can be terrace deposits or as semi-continuous meltwater channels.	Generally semi-confined or confined conditions.
Late Cretaceous–Tertiary Fort Union Formation	Interstratified grey clay, brown carbonaceous clay, lignite, tan siltstone, and grey and tan sandstone.	Unconfined to confined conditions.
Upper Cretaceous Fox Hills/Hell Creek Formation	Interstratified shale, siltstone, sandstone, and carbonaceous shale.	Generally confined conditions, wells may flow in low-lying areas.

Groundwater

Groundwater samples were analyzed for major ions, trace metals, and light stable isotopes of oxygen and hydrogen at the MBMG's analytical laboratory in Butte, Montana. Organic analyses of groundwater varied by year, but included methane (CH₄), ethane (C₂H₆), ethene (C₂H₄), radioactivity, and organics (GRO, TPH, DRO, and TEH). Energy Laboratories, in 2015, and Pace Analytical Laboratories, in 2016, performed the organic analyses. Measured field parameters include DO, pH, SC, temperature, and water level if accessible. A detailed description of sampling protocol, including quality assurance/quality control sampling, is presented in the MBMG's Sampling and Analysis Plan (<http://www.mbm.g.mtech.edu/energy/energy-oileval.html>). All groundwater information, including well location and depth, aquifer, and analytical results, is stored and available to the public on the MBMG database Groundwater Information Center (GWIC; MBMG, 2017).

Sites of Known Groundwater Contamination

The long history of Montana's oil and gas production (fig. 2, inset chart) has resulted in legacy environmental issues related to production practices now discontinued. Oil production began in eastern Sheridan County in the early 1960s (Rouse and others, 2013). Prior to the 1970s, produced brine water and drill cuttings were stored in unlined pits that allowed interaction of the associated salts, hydrocarbons, and other contaminants to interact with the shallow groundwater system. Known contaminated sites are found throughout the northeastern corner of Montana. A subset of

this larger northeastern Montana contamination site includes the Poplar Oil Field on the Fort Peck Indian Reservation. The USGS has estimated that between 15 and 37 billion gallons of groundwater at this site has been impacted by oil operations, including pipelines, storage tanks, production wells and brine disposal sites (Thamke and Smith, 2014).

The Williston Basin has numerous wetlands, which provide habitat for many species of migratory birds and waterfowl, and is also Montana's top oil-producing area. Produced water in the Williston Basin is highly saline; produced brines can exceed 380,000 mg/L TDS (Preston and others, 2012). In contrast, seawater is approximately 35,000 mg/L. Brine contamination was assessed at 87 wetlands, and 35 were determined contaminated; many of these were waterfowl production areas (Rouse and others, 2013).

Sites of known brine contamination in Sheridan County, including one near Medicine Lake Wildlife Refuge, were included in this study in order to understand the characteristics of brine contamination in the context of the chosen analytes. The MBMG, U.S. Geological Survey, U.S. Fish and Wildlife Service, and Sheridan County Conservation District instrumented these sites with monitoring wells and have sampled periodically for decades, providing an understanding of how contamination moves through the shallow, unconsolidated, glacial-outwash aquifers. The results from this monitoring work have been published regularly (e.g., Peterman and others, 2010; Preston and others, 2012; Reiten and Tischmak, 1993; Rouse and others, 2013; Thamke and Craig, 1997).

RESULTS AND DISCUSSION

Inorganic Constituents

Surface-water quality is controlled by the local geology over which the streams flow, the source(s) of groundwater baseflow, recent precipitation or snow-melt, evaporation, and human influences (e.g., agriculture, industry, septic/sewer). Groundwater chemistry reflects the water's interaction with soils, rocks, and other water sources. Changes in ion composition can provide information about groundwater flowpaths. Groundwater near recharge sources is usually low in overall salinity, and the chemistry is dominated by calcium, magnesium, and bicarbonate from the soils and weathered bedrock. Older water is generally higher in relative concentrations of sodium and bicarbonate due to sulfate reduction and ion exchange (Brinck and others, 2008).

Trilinear, or Piper, diagrams are commonly used to show water types by plotting the relative percent concentration of major cations and anions in lower triangles and combining the two characteristics into a central diamond. The combined diamond plot defines general water types expressed as "major cation–major anion." Occasionally, more than one cation or anion will dominate the chemistry, in which case both will be noted in the water type. Piper diagrams are useful for displaying and comparing multiple water samples because they graphically illustrate water populations by water type and can show mixing or contamination.

Another graphical method to compare data sets, such as the chemistry from multiple streams or aquifers, is through box plots. In these plots, the boxes represent all data between the 25th and 75th percentiles, lines within the box are the average, the x marks the median, whiskers represent the 10th to 90th percentile, and dots represent outliers. These plots also identify outliers, which can indicate when the results from a water sample are potentially outside of normal variability.

Surface-water quality

Surface-water quality is controlled, in part, by surficial geology and groundwater baseflow. The main surficial geologic units the streams cross consist of alluvium terrace deposits, glacial deposits, and Tertiary and Cretaceous Formations (table 2). The Tertiary and Cretaceous Formations are composed of alternating

sandstone, shale, and, in some locations, coal layers. For detailed geologic descriptions, visit the MBMG Geologic State Map site (<http://mbmg.mtech.edu/gmr/gmr-statemap.asp>).

The stream sample sites consist of small creeks in north-central, north-eastern, and eastern Montana (fig. 2). The sample date range was from spring 2012 to fall 2016. The collection date and frequency of the samples was variable between sites (appendix C). Piper diagrams were created to display water chemistry for 15 creeks, 1 lake, and 1 spring. In general, the creek samples in the eastern counties have sodium–sulfate type water with the exception of Deer Creek and Fox Creek sites, which have magnesium–sulfate type water (figs. 4–7).

Ueland Road Spring (fig. 7) has a higher percent chloride than the other sampled sites. These high levels of chloride are uncommon in natural waters in this area and may indicate contamination from brines. The three creeks sampled in north-central Montana display unique water chemistry relative to each other (fig. 8). Willow Creek is sodium/magnesium–sulfate type water, while Whitewater Creek is sodium–bicarbonate/sulfate. Little Boxelder Creek has no dominant cation and bicarbonate type water.

Specific conductance was measured on all creek sites throughout the duration of this project (appendix C). There is a large variation in SC values between each creek site (fig. 9). The 25th to 75th percentile (the boxes on fig. 9) ranged between 2,000 and 7,000 $\mu\text{S}/\text{cm}$ for most sites. Pennel Creek is the most variable, with measured SC values between 1,214 and 15,060 $\mu\text{S}/\text{cm}$. Little Boxelder Creek had the lowest SC, ranging between 397 and 1,033 $\mu\text{S}/\text{cm}$.

Ueland Road Spring (221010), located west of Westby, has very high measured salinity. Historical data from May 18, 1989 show the SC was 72,060 $\mu\text{S}/\text{cm}$ (fig. 10; Reiten and Tischmak, 1993). The DEQ sampled this spring four times from April 2015 to August 2016 and the salinity values ranged from 19,690 to 42,440 $\mu\text{S}/\text{cm}$ (fig. 10). The spring is located near post-glacial ice-meltout 'kettle lakes' (Witkind, 1959). The lakes are almost exclusively groundwater fed and display an extreme range in natural salinity (Donovan and Rose, 1993). Ueland Road Spring's high salinity, combined with high levels of chloride, which is uncommon in the area's natural waters, indicate brine

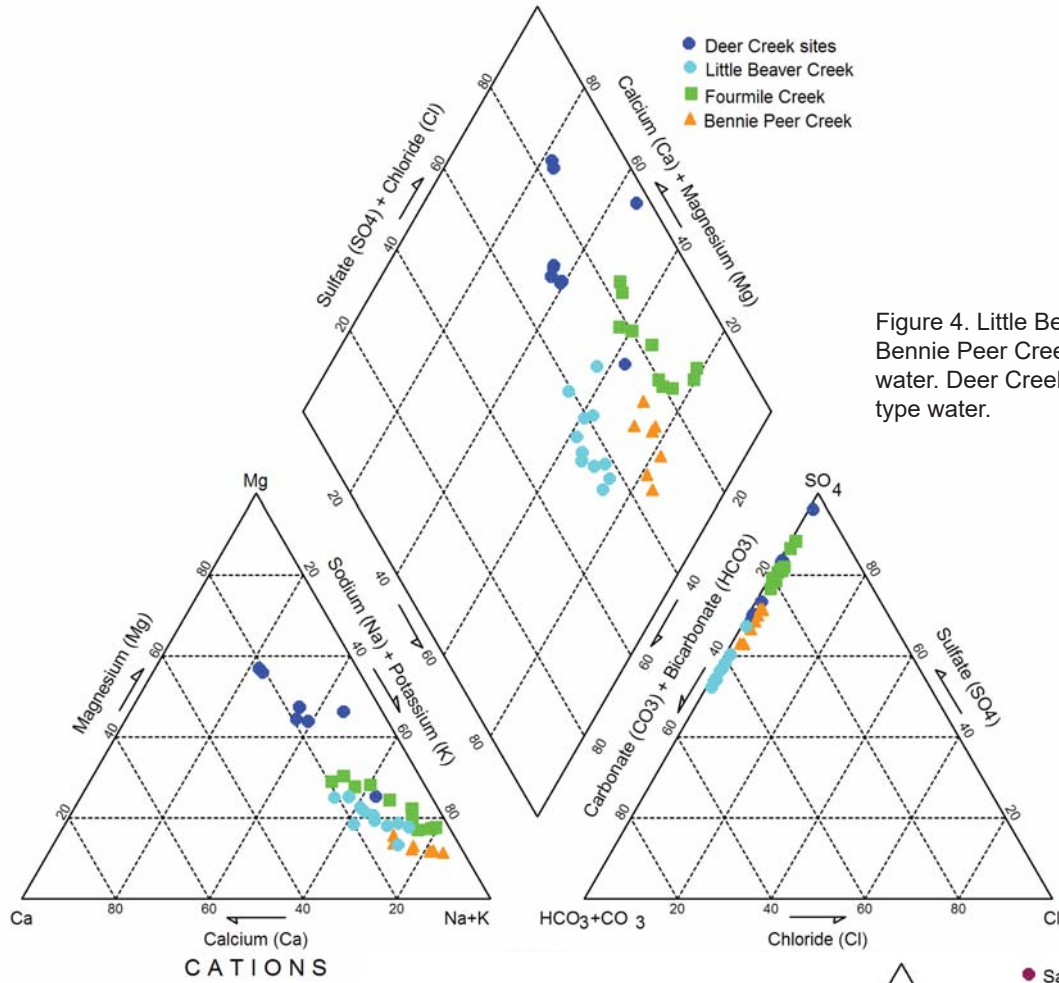
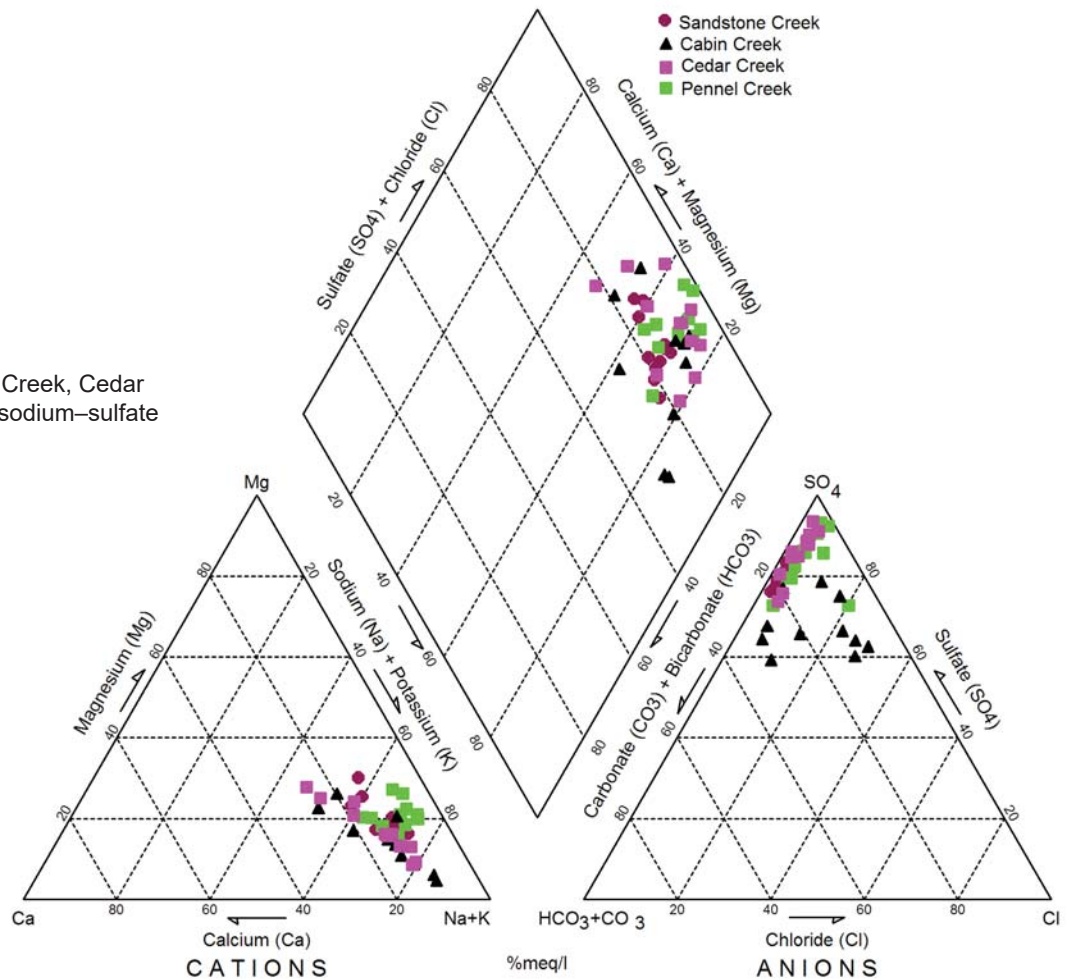


Figure 4. Little Beaver Creek, Fourmile Creek, and Bennie Peer Creek all have sodium–sulfate type water. Deer Creek has magnesium/sodium–sulfate type water.

Figure 5. Sandstone Creek, Cabin Creek, Cedar Creek, and Pennel Creek all have sodium–sulfate type water.



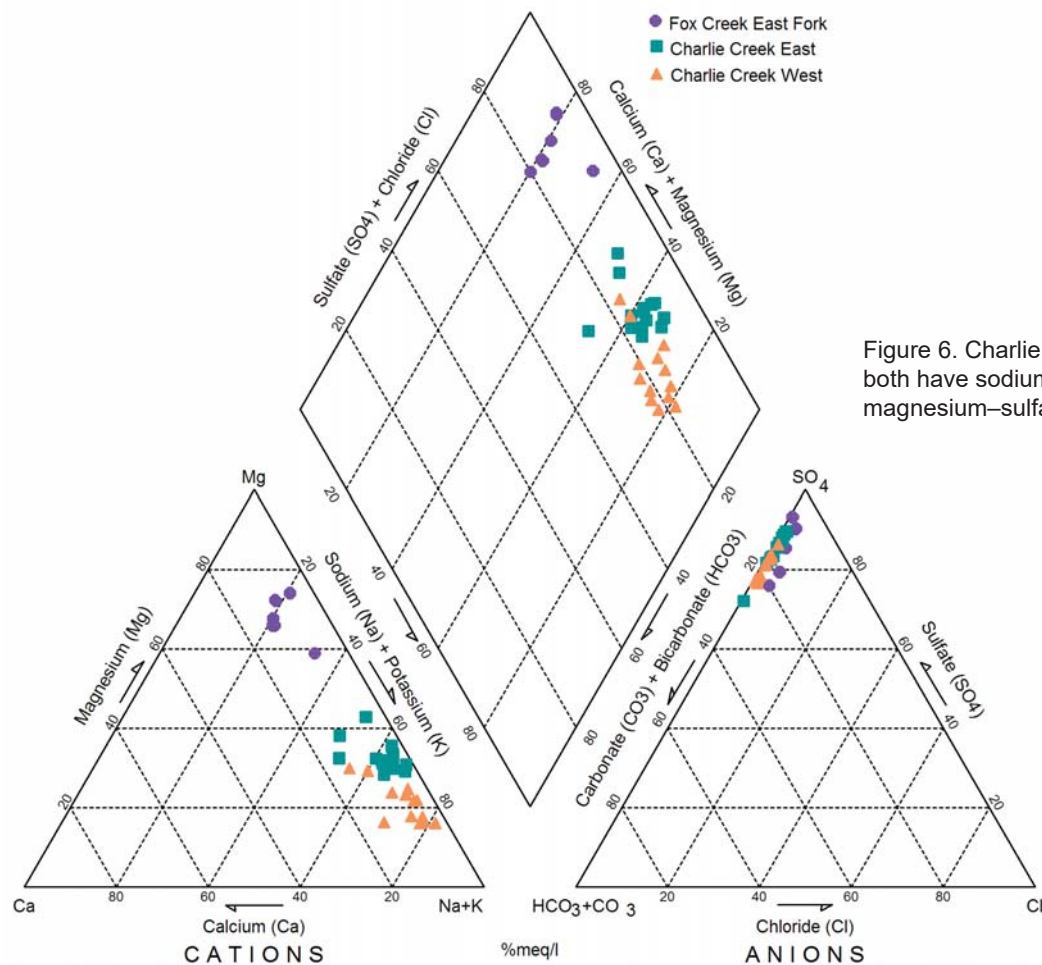
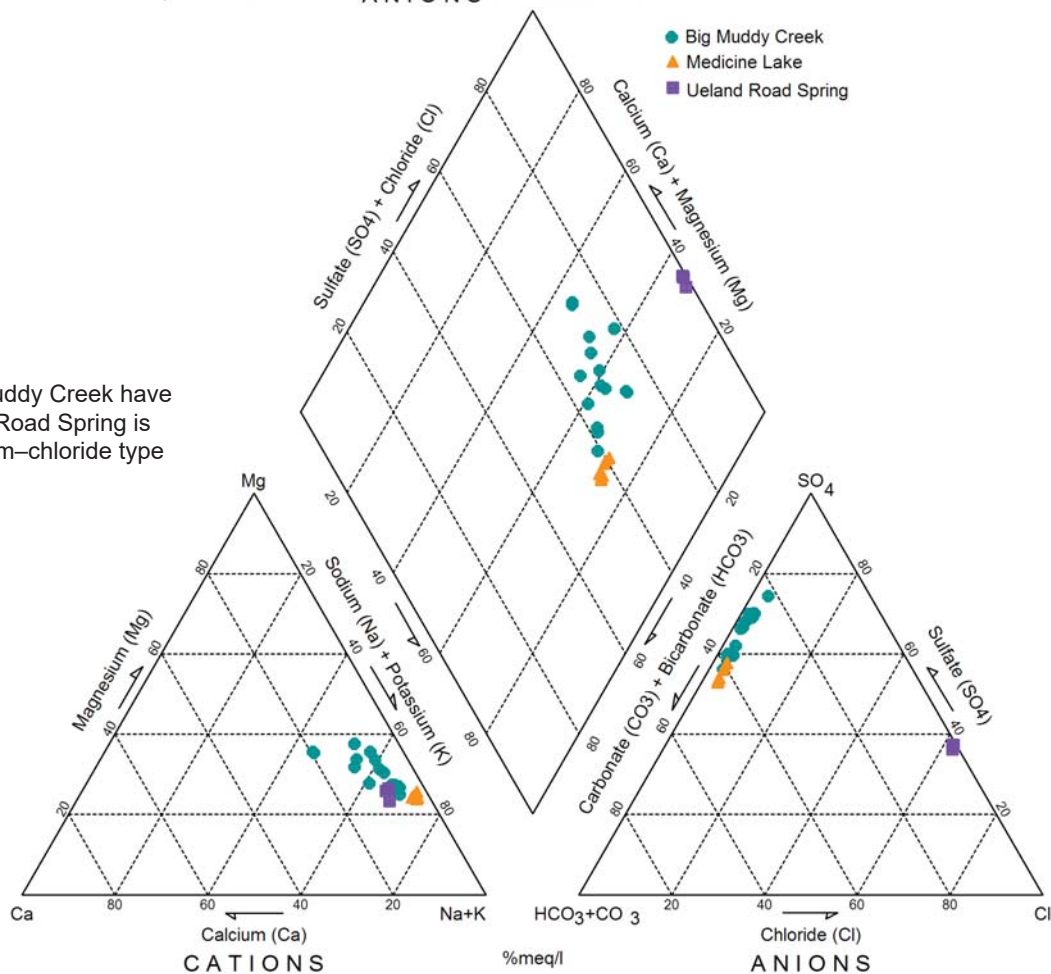


Figure 6. Charlie Creek East and Charlie Creek West both have sodium–sulfate type water. Fox Creek has magnesium–sulfate type water.

Figure 7. Medicine Lake and Big Muddy Creek have sodium–sulfate type water. Ueland Road Spring is unique in this area in that it is sodium–chloride type water.



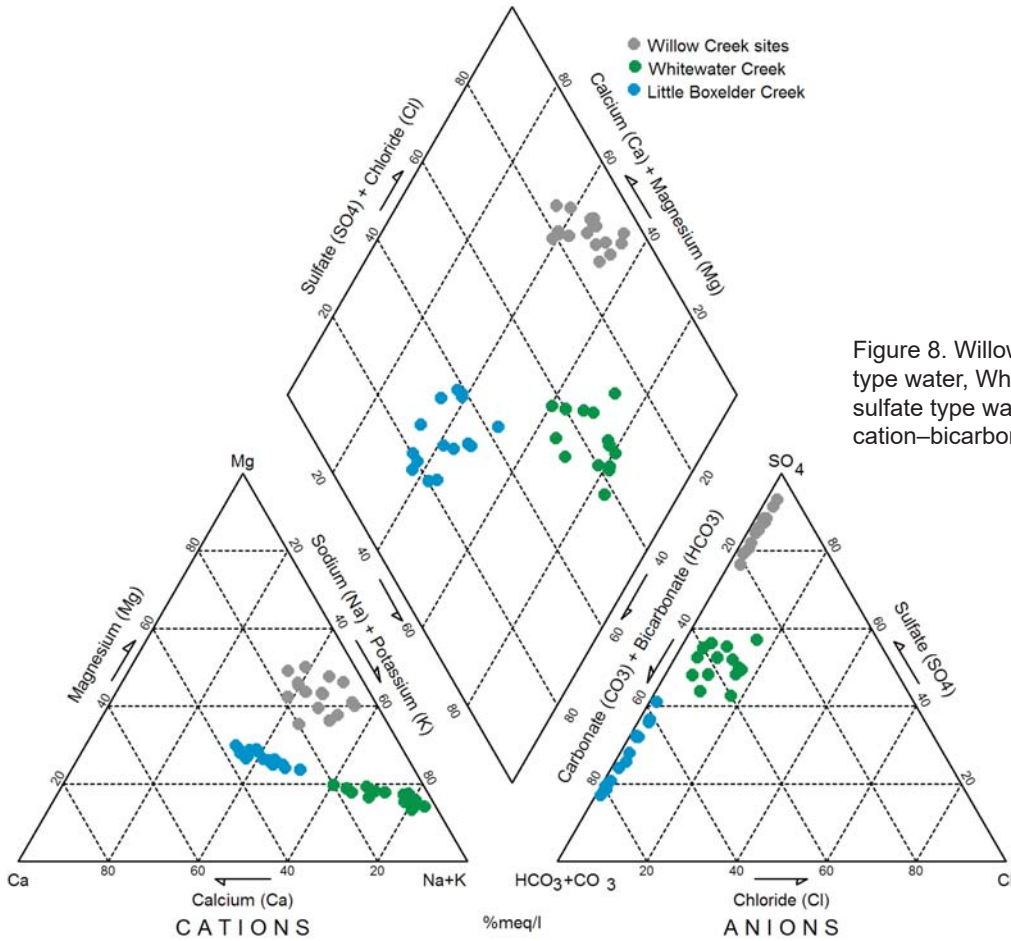


Figure 8. Willow Creek is sodium/magnesium–sulfate type water, Whitewater Creek is sodium–bicarbonate/sulfate type water, and Little Box Elder Creek is mixed cation–bicarbonate type water.

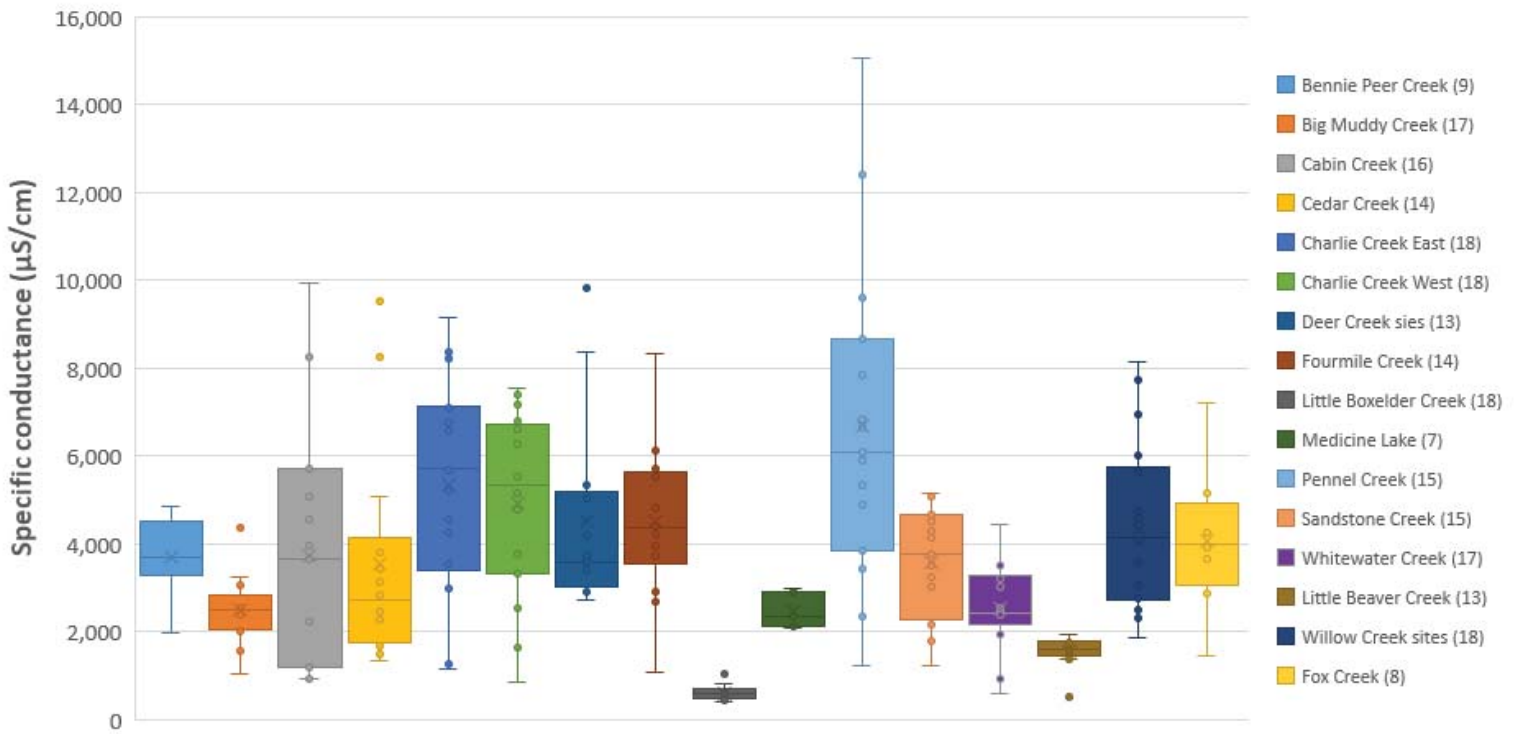


Figure 9. Box and whisker plot of specific conductance of surface-water sites.

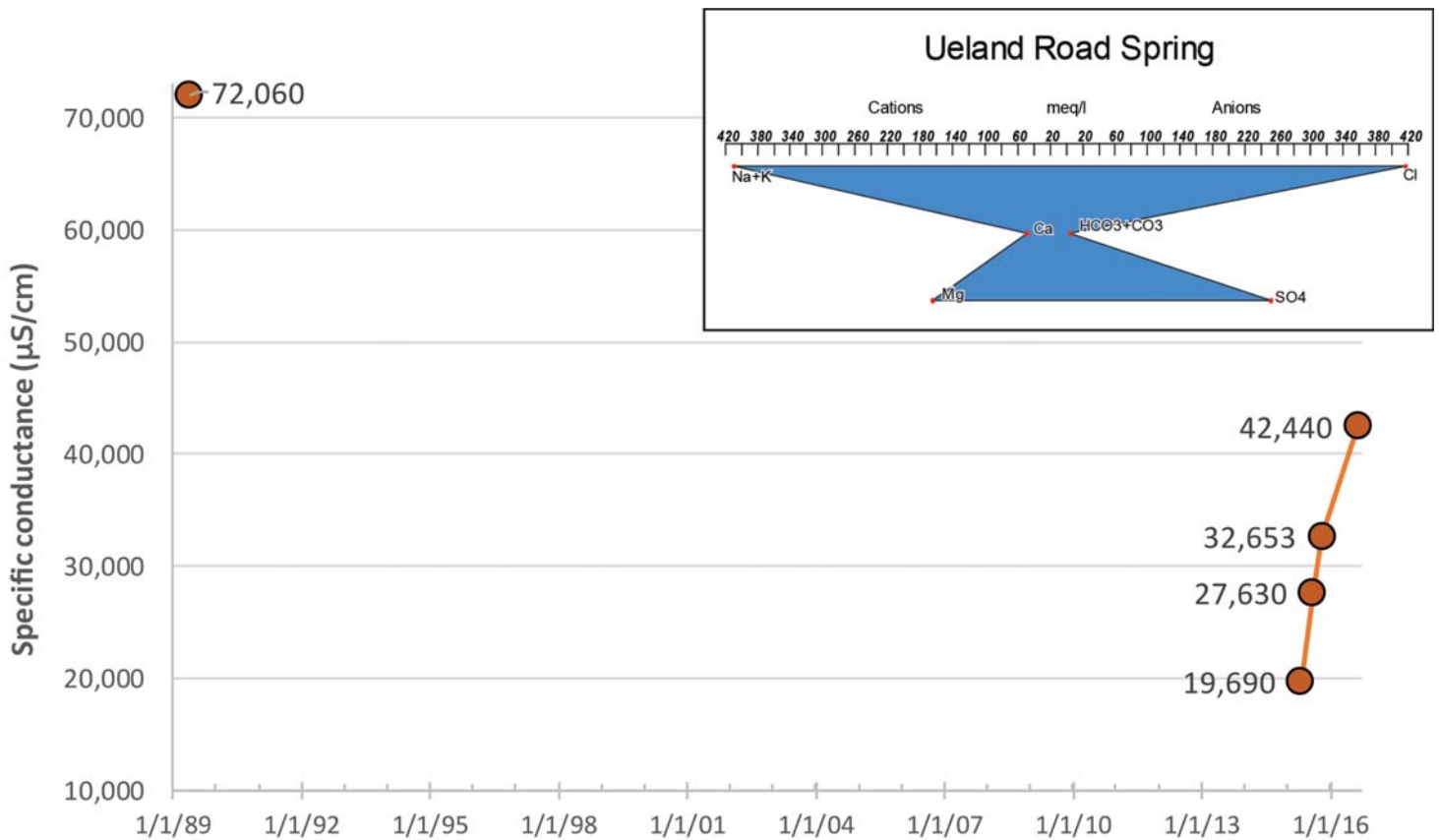


Figure 10. Ueland Road Spring has a historical high SC with a current increasing trend. The spring has high chloride (embedded Stiff diagram) that is not typical of natural waters in this area.

contamination (see Contamination Index). Salinity of this spring cannot be displayed on the same axis as the other sampled streams and lake (fig. 9) because it has SC values ranging from 4 to 9 times higher than the median SC values of the other streams.

Salinity in streams is often related to flow rate. In general, high flow rates imply an influx of low-salinity precipitation (either rain runoff or snowmelt), which will lower the total salinity of the stream. Alternatively, high flow rates may be the result of increased groundwater baseflow to the stream through elevated groundwater levels. In this situation, the salinity of the stream may increase. The behavior of a stream’s salinity to flow rate relationship can help decipher the source of surface water.

Stream flow rates are highly variable from year to year in the Northern Great Plains. The USGS gauging station on Big Muddy Creek shows flows peak in the spring, with the highest peak since 2012 at over 1,200 cfs in 2013, with subsequent years showing lower and lower peaks and no distinguishable peak in 2016 (fig. 11). Many of the other creeks measured during this project have the same seasonal flow variations and

overall decreasing flow trend over the study period. Most of the streams had flow rates below 1 cfs, which can be difficult to measure with accuracy. Additionally, streams with low flow rates such as these may be subject to evapoconcentration of salts, which can complicate comparisons between streams and identification of the source of salts.

Salinity and flow rates were plotted to observe seasonal trends in selected creeks. Willow Creek (fig. 12) and Big Muddy Creek (fig. 13) show a freshening of surface water in the spring followed by higher salinity at baseflow in winter. During snowmelt or large rain events, precipitation can flow directly into the creeks, increasing the flow rate and freshening the water quality. Charlie Creek East (fig. 14) and Cabin Creek (fig. 15) show spring freshening on a dramatic scale. In contrast, Little Boxelder Creek (fig. 16) and Little Beaver Creek (fig. 17) have stable salinity values despite variable flow rates.

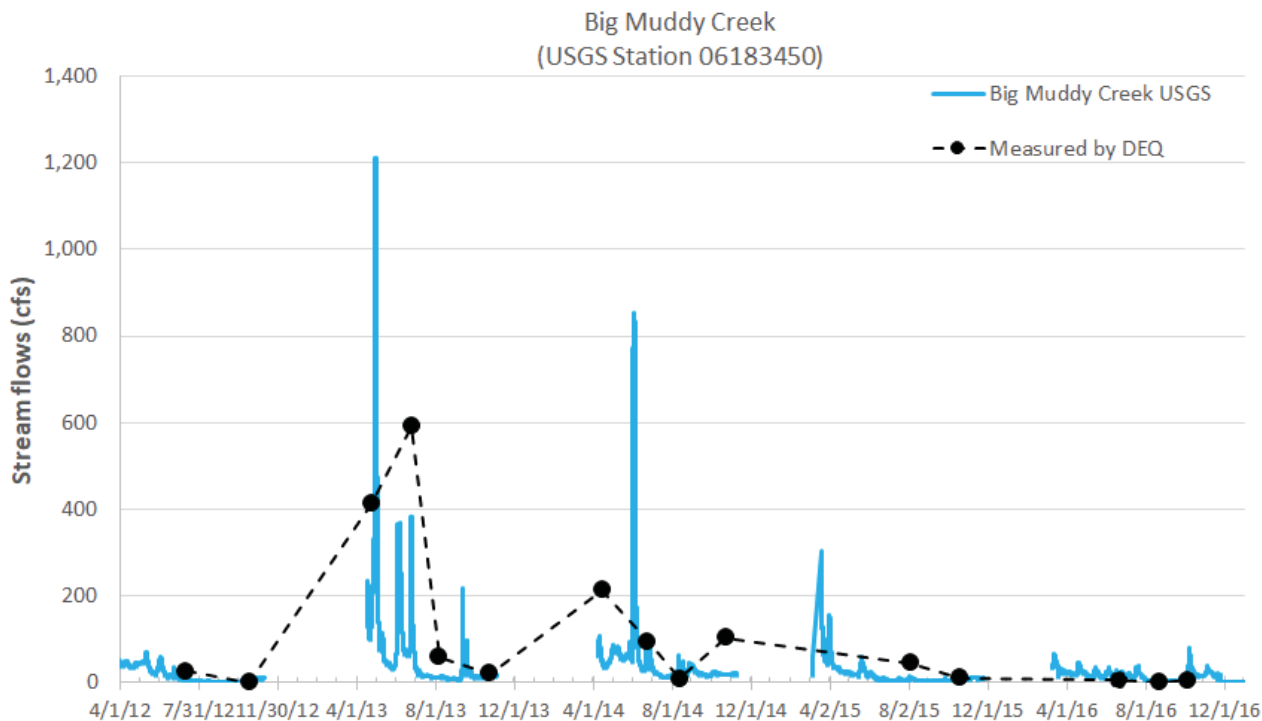


Figure 11. Big Muddy Creek flow rates.

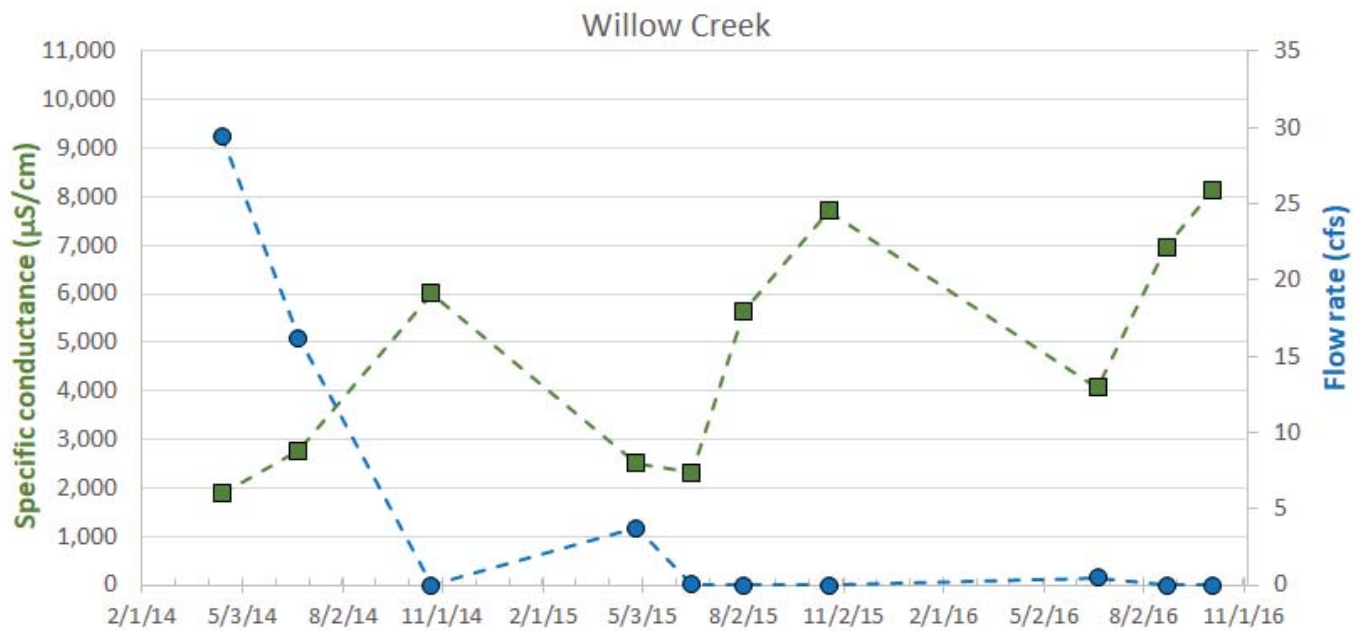


Figure 12. Willow Creek salinity and flow rate with time.

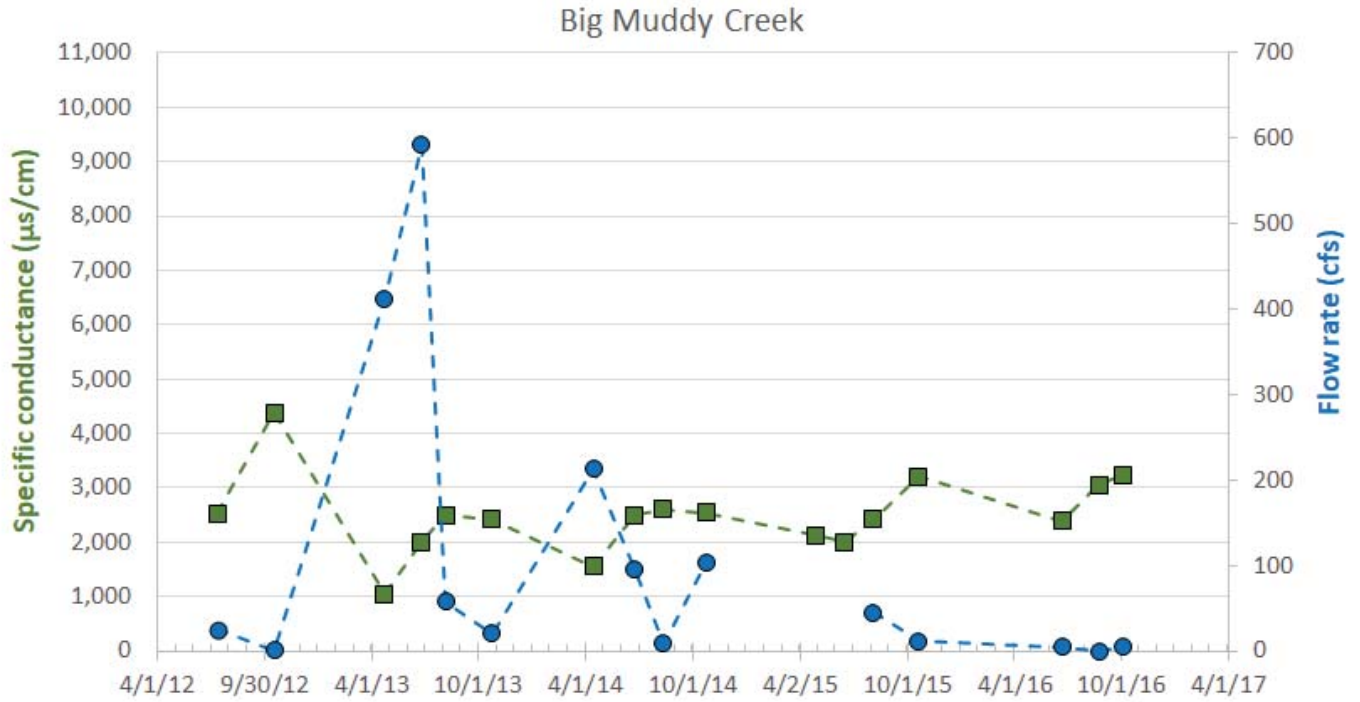


Figure 13. Big Muddy Creek salinity and flow rate with time.

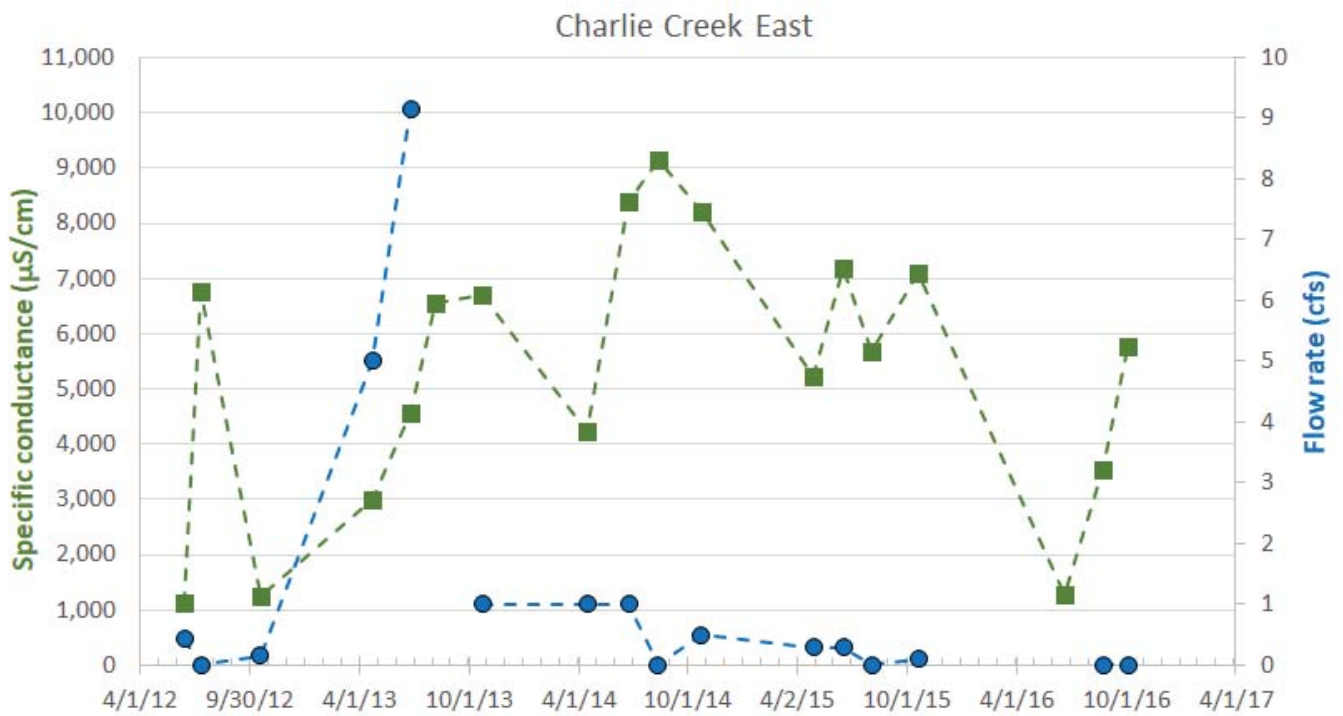


Figure 14. Charlie Creek East salinity and flow rate with time.

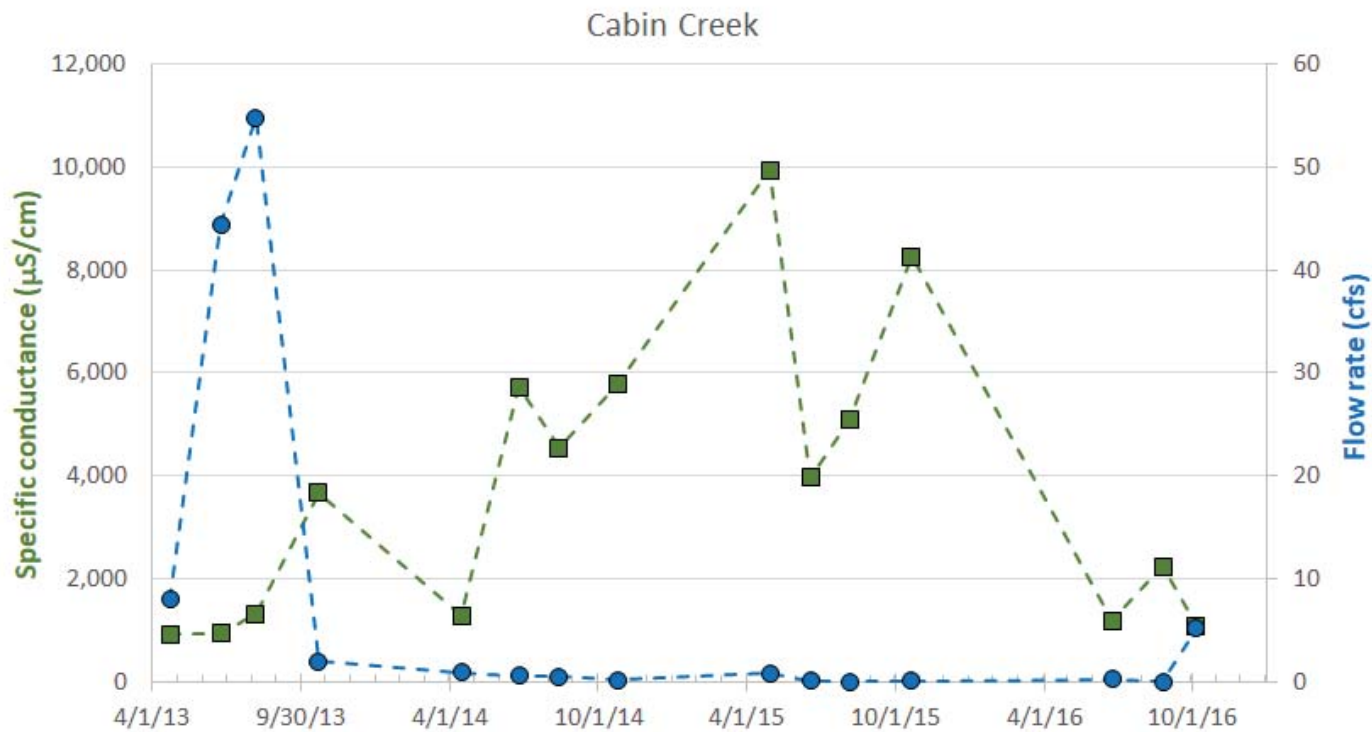


Figure 15. Cabin Creek salinity and flow rate with time.

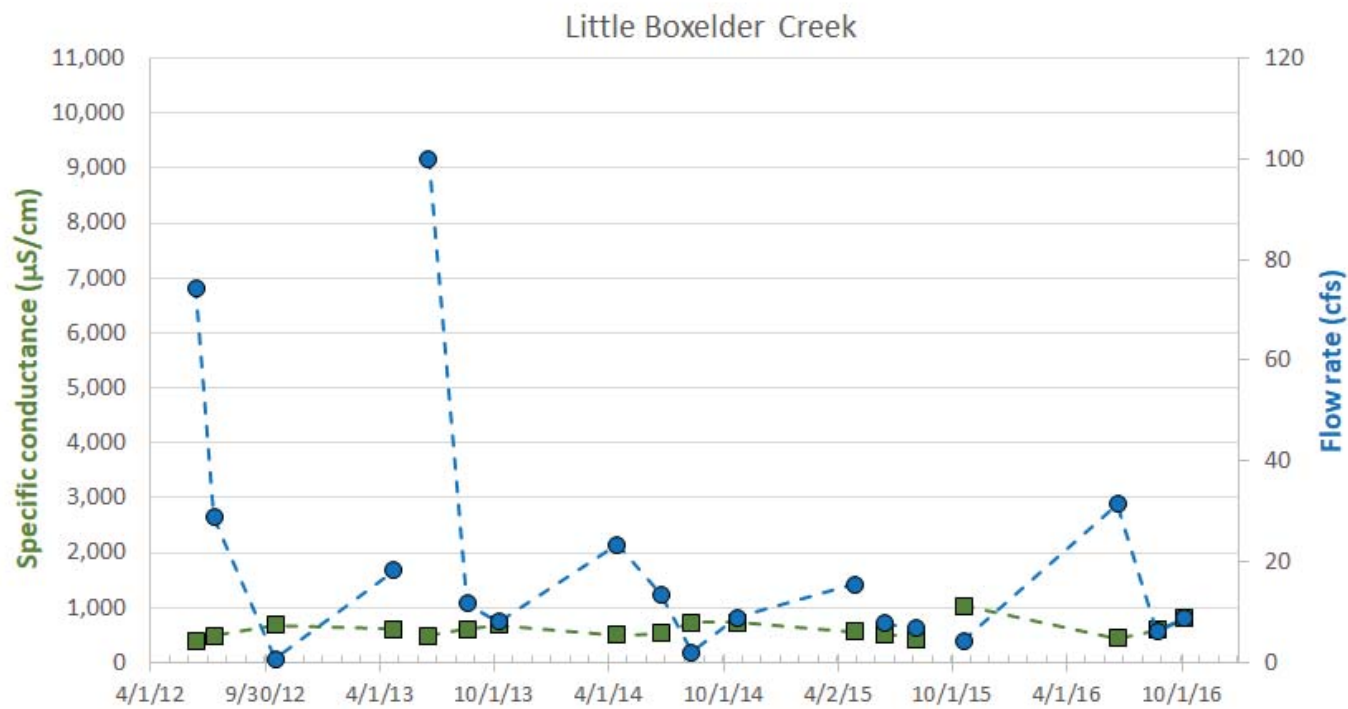


Figure 16. Little Boxelder Creek salinity and flow rate with time.

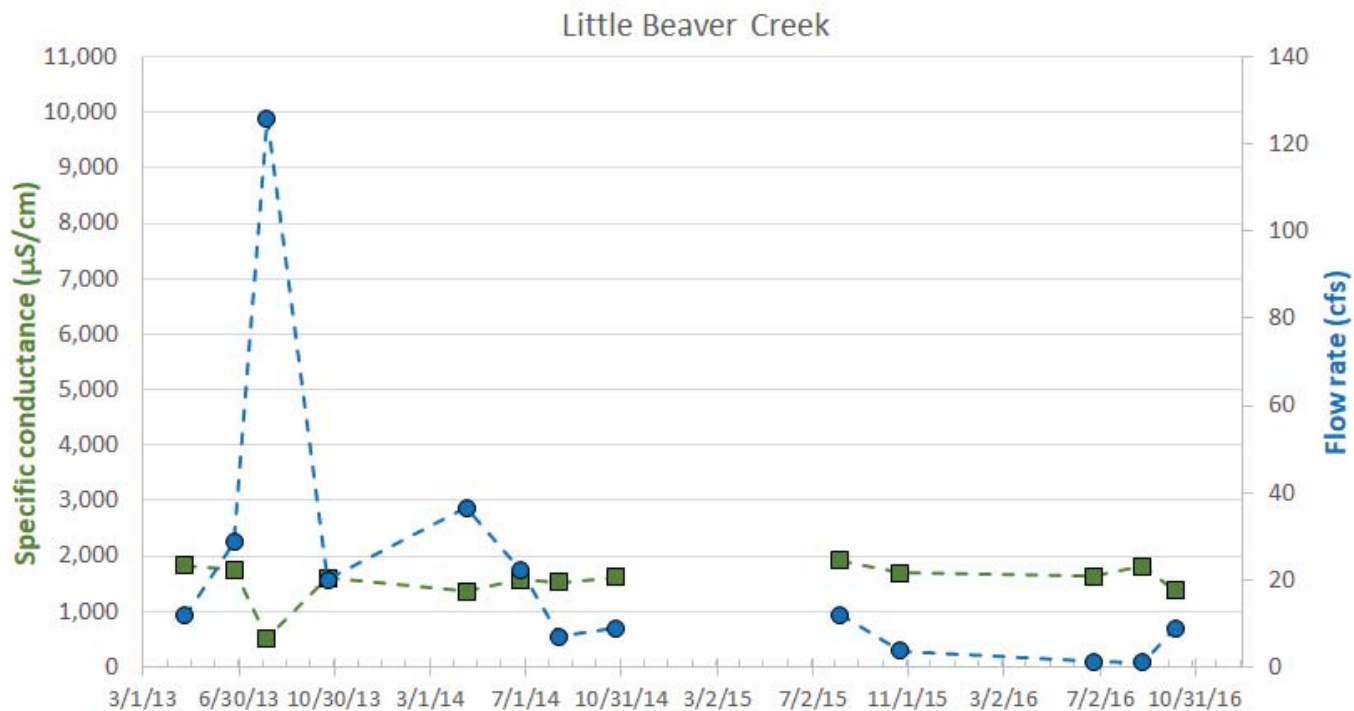


Figure 17. Little Beaver Creek salinity and flow rate with time.

Groundwater quality

In 2015 and 2016, MBMG collected groundwater-quality samples from the alluvium, glacial outwash, Fort Union, and Fox Hills/Hell Creek aquifers (appendix D). For this analysis, the aquifers within the Fort Union, which can include major sandstone units such as the Tongue River Member or coals and shales, are not differentiated. Similarly, the Fox Hills and Hell Creek aquifers are also considered as one hydrogeologic unit. Groundwater samples were also collected from wells in Sheridan County known to be contaminated with brine disposal and cuttings from oil well drilling. The contaminated wells have completions in glacial outwash aquifers that are less than 42 ft deep.

Alluvium and glacial outwash aquifers have similar groundwater quality. The aquifers do not have a dominate cation type; however, a few samples have a slightly higher percent sodium composition. The anions are a mix of both bicarbonate- and sulfate-type (figs. 18, 19).

The Fort Union and Fox Hills/Hell Creek bedrock aquifers show a progression from calcium dominated cation chemistry to sodium dominated (figs. 20, 21). This progression in geochemistry may indicate location along flow paths within the aquifers. Recently recharged groundwater is generally dominated by

calcium and magnesium; older groundwater becomes progressively more sodium dominated (Brinck and others, 2008). The anions in the Fort Union and Fox Hills–Hell Creek aquifer are generally a mix of bicarbonate/sulfate; however, some Fox Hills–Hell Creek aquifer samples are bicarbonate/chloride type water.

Five previously sampled wells completed in locations known to have brine contamination were resampled during this project. The chemistry is sodium-chloride type, which reflects the influence of the oil brine contamination (fig. 22). These wells have a water-quality history from 1989 to 2015. Over time, the specific conductance of the groundwater has become more saline at three wells (890933, 221691, 890422) and freshened at two wells (221574, 221722) (fig. 23). This may represent brine plume migration and dilution.

Box plots were used to compare the specific conductance of the four major aquifers (fig. 24; appendix D). The average specific conductance values were under 2,000 µS/cm for the alluvium, glacial outwash, and Fox Hills–Hell Creek aquifers. The Fort Union aquifer had the highest average value of about 2,500 µS/cm. For comparison, drinking water guidelines recommend a specific conductance less than 800–1,000 µS/cm.

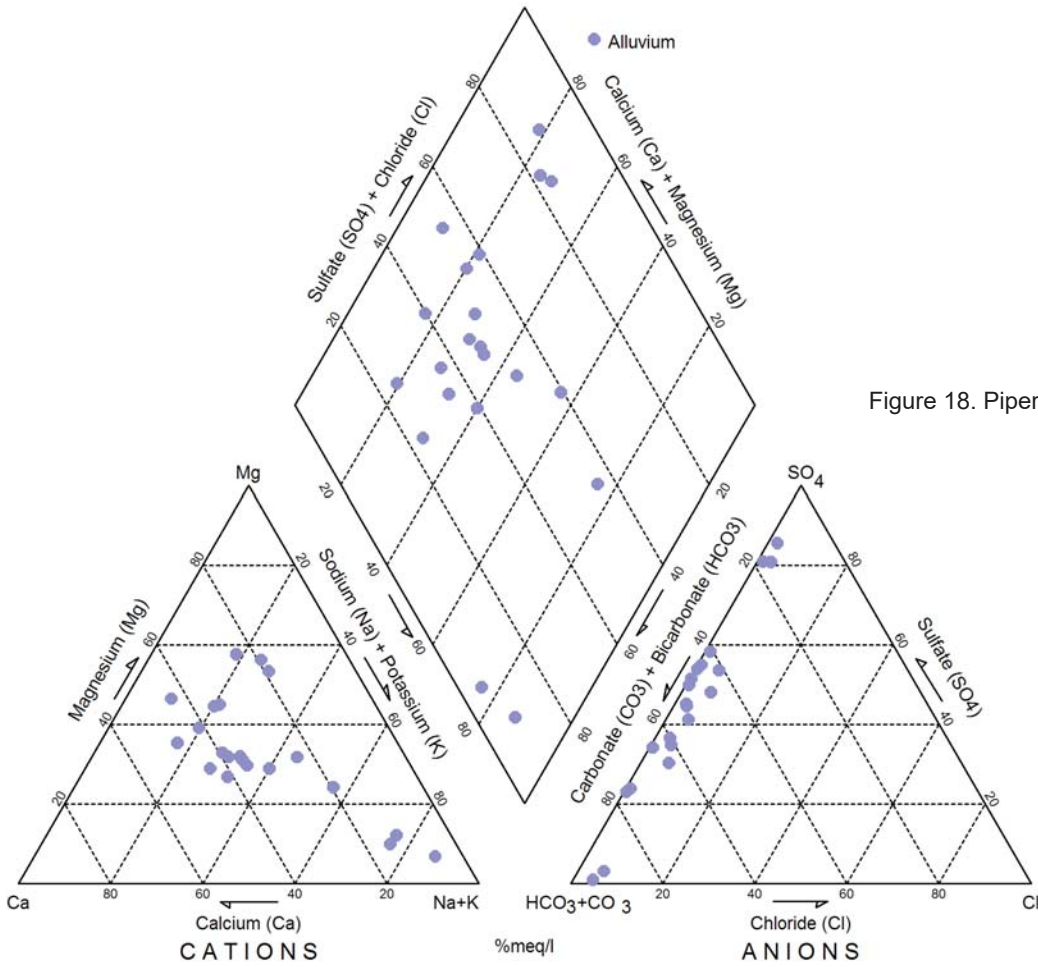


Figure 18. Piper diagram of alluvial groundwater.

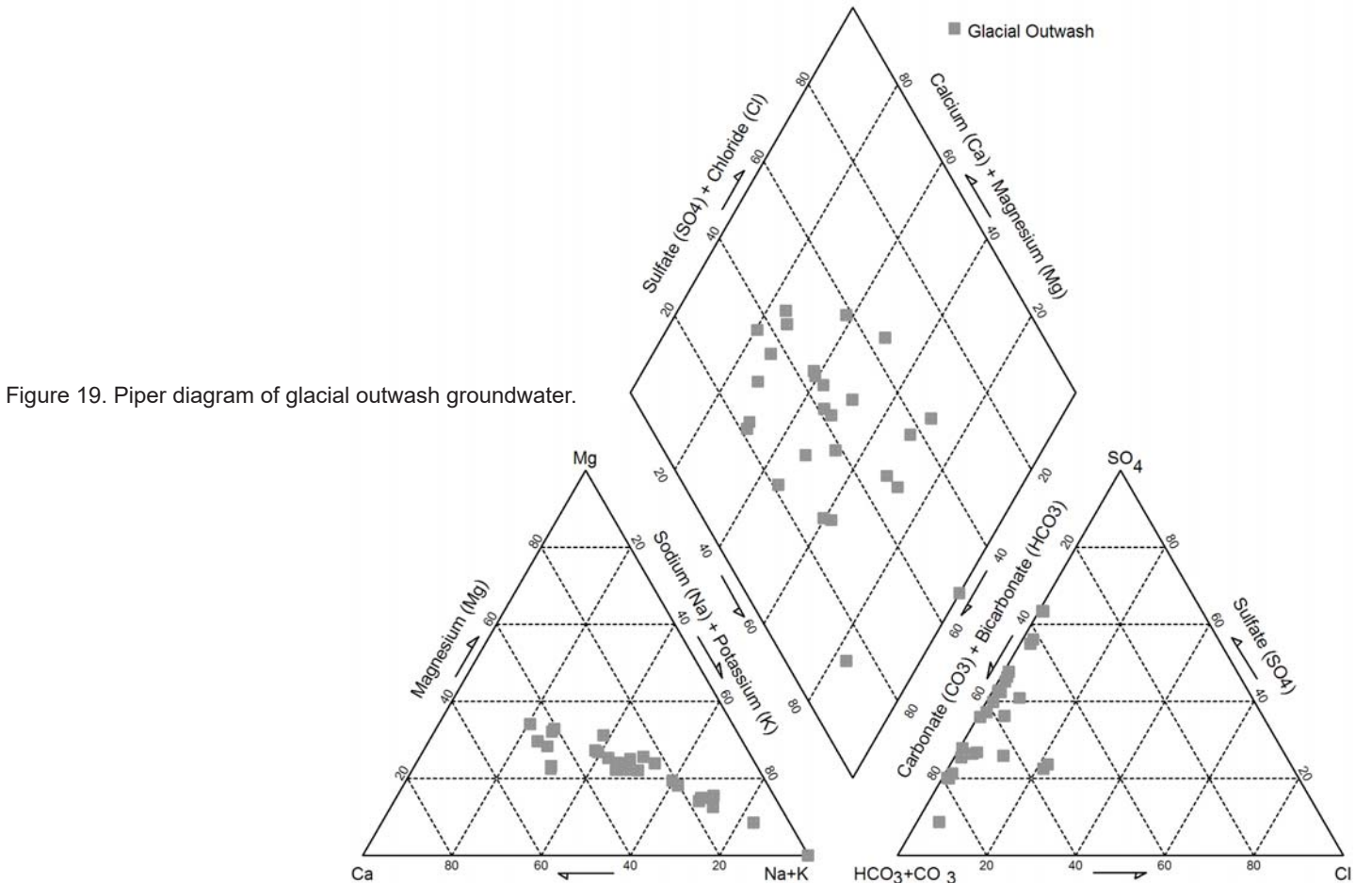


Figure 19. Piper diagram of glacial outwash groundwater.

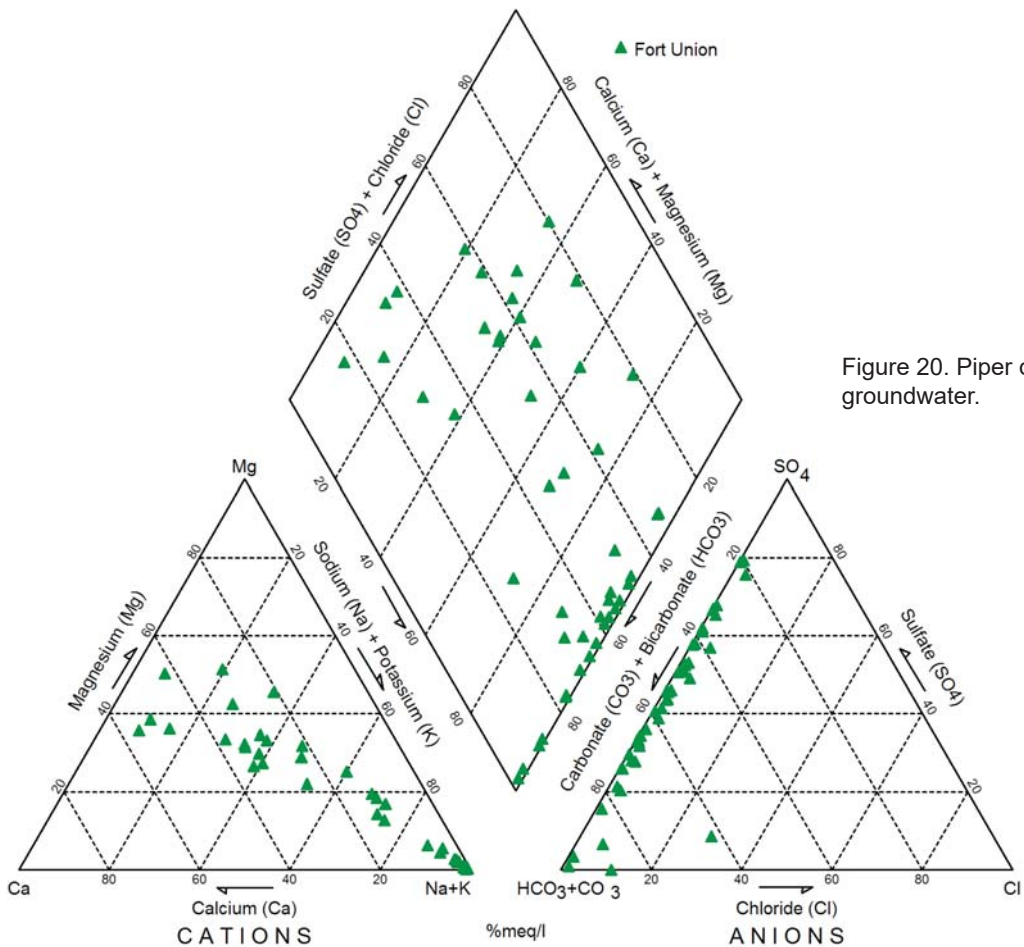


Figure 20. Piper diagram of Fort Union Formation groundwater.

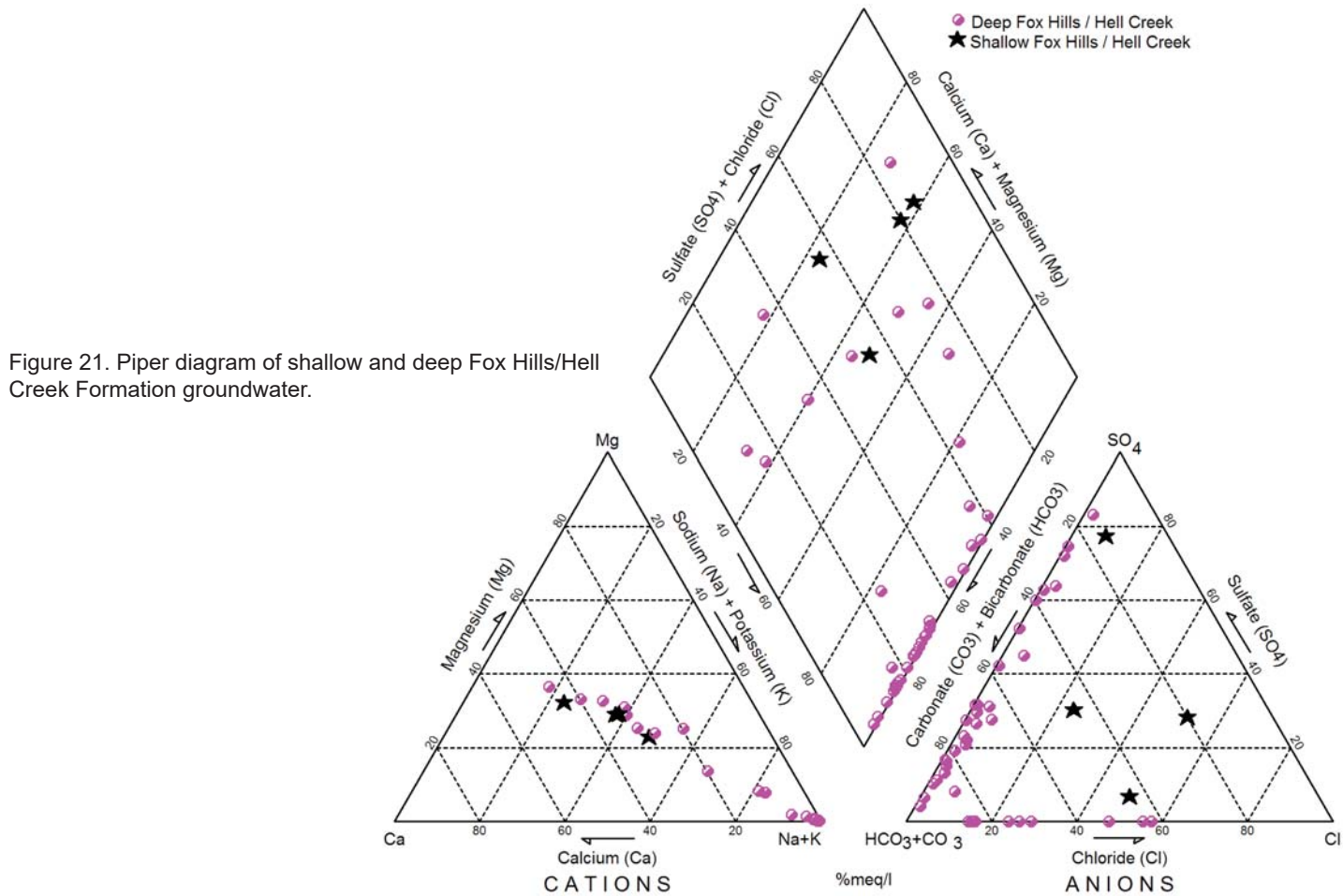


Figure 21. Piper diagram of shallow and deep Fox Hills/Hell Creek Formation groundwater.

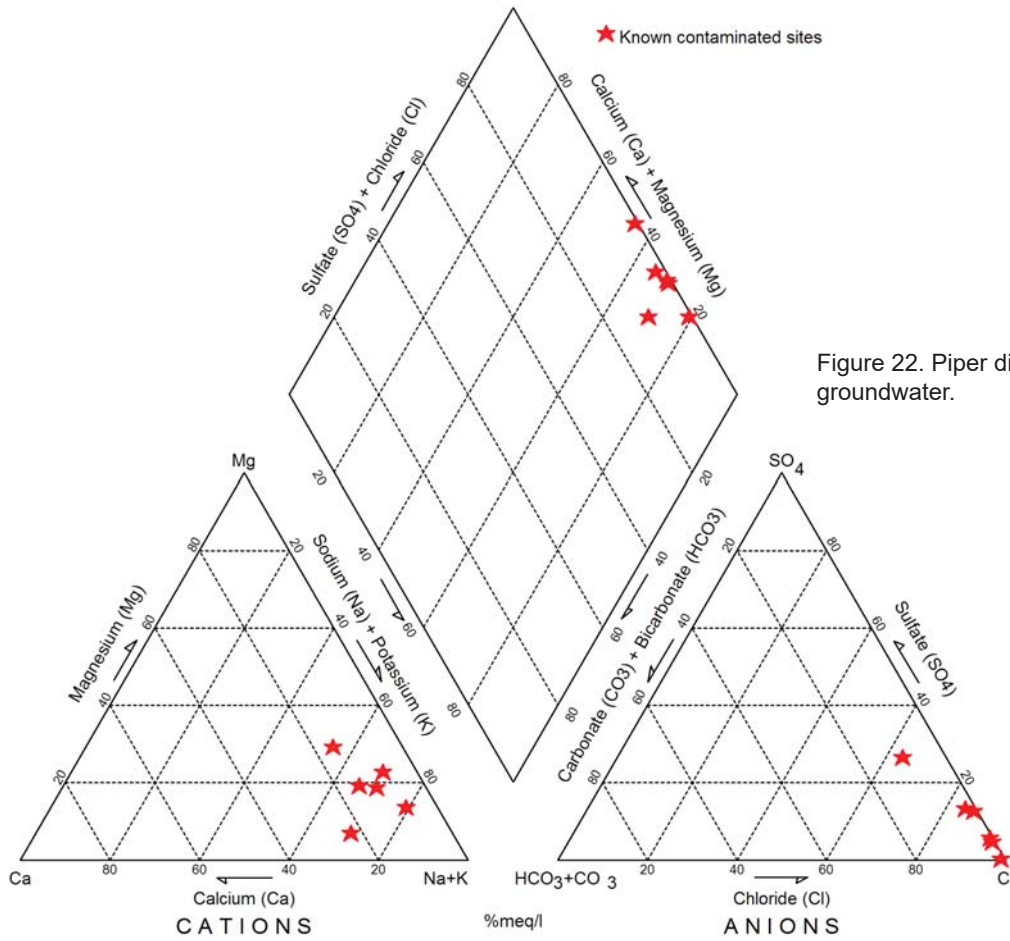


Figure 22. Piper diagram of known brine-contaminated groundwater.

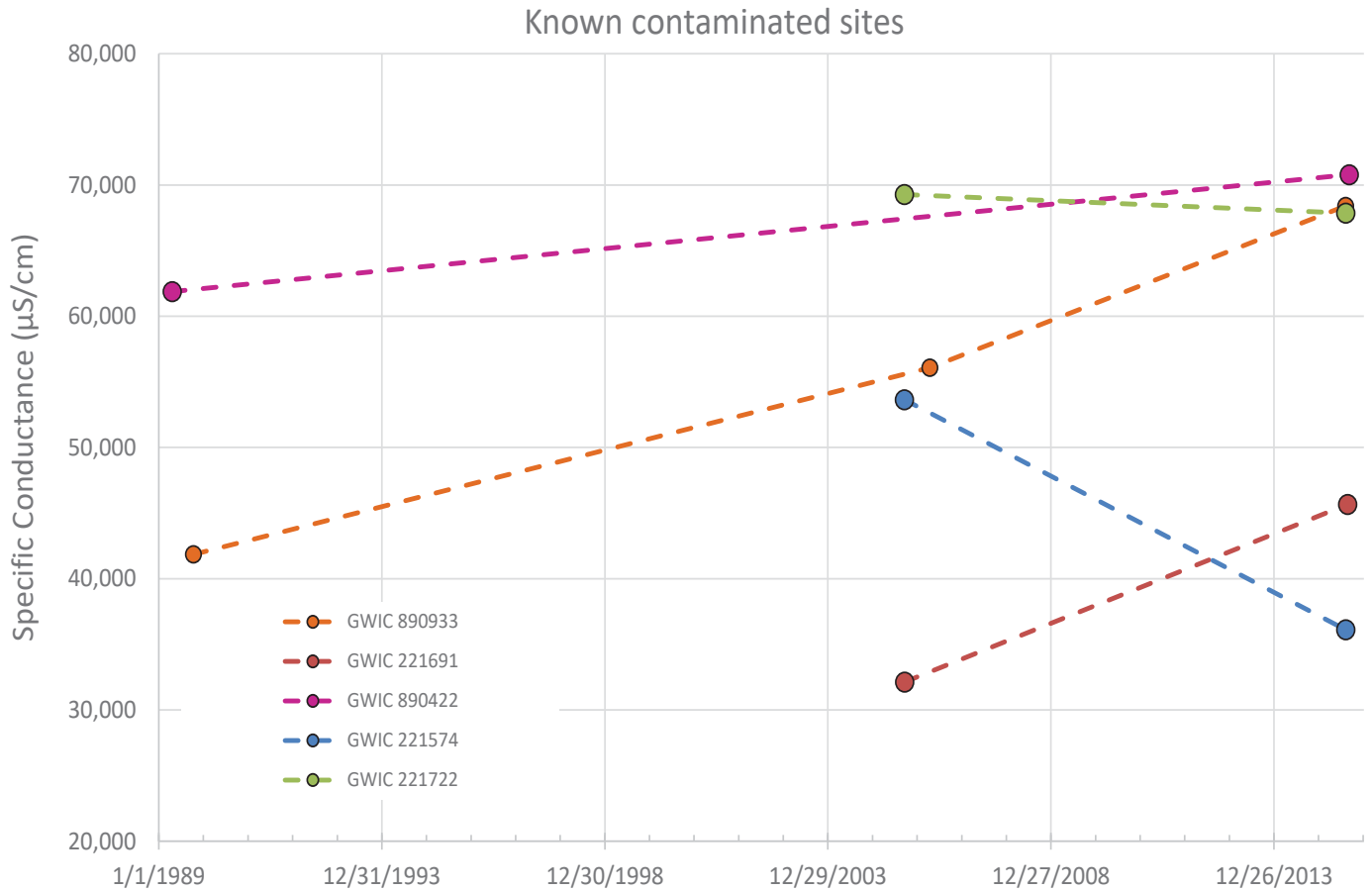


Figure 23. Specific conductance trends with time for selected sites of known brine-contaminated groundwater.

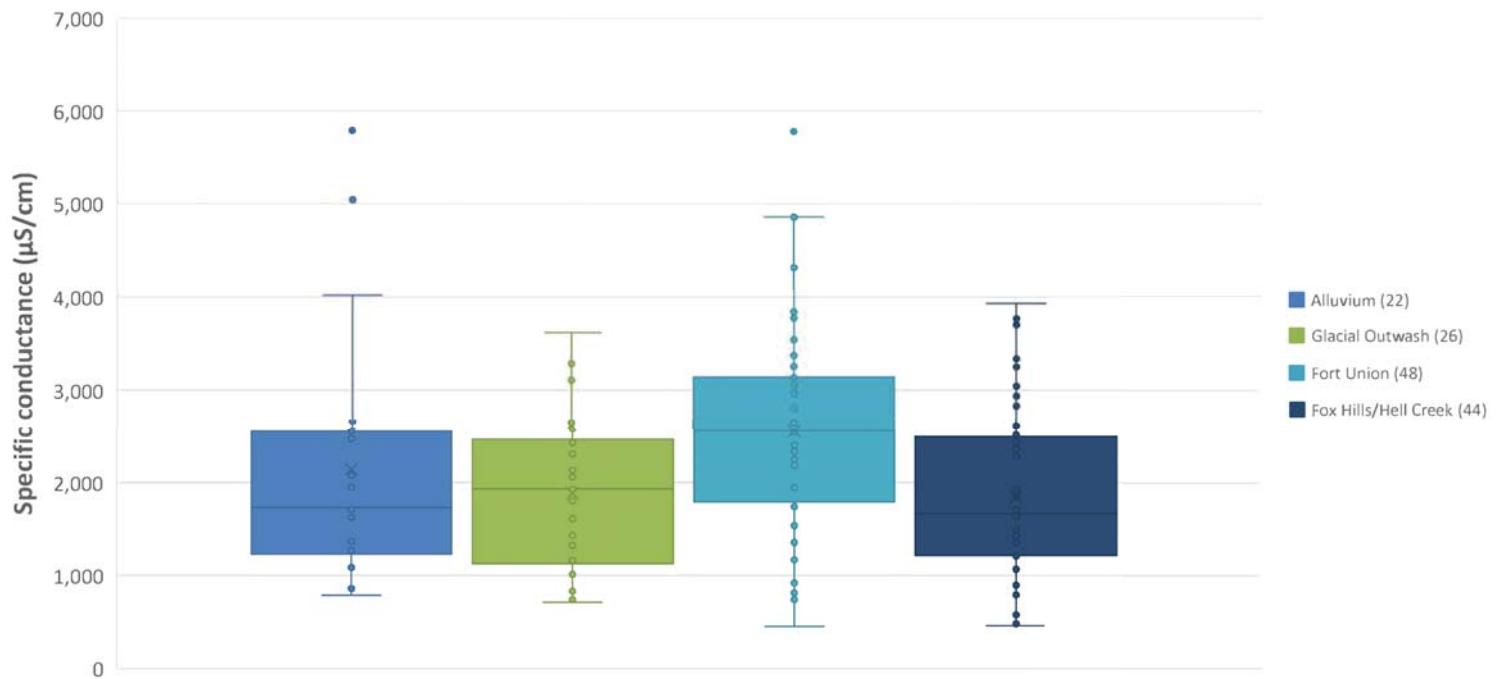


Figure 24. Box plot showing distribution of salinity in groundwater by aquifer.

Sodium adsorption ratio

Agriculture is one of the dominant economic drivers in eastern Montana; therefore an important consideration for the quality of the water resources is its suitability for irrigation. The sodium adsorption ratio (SAR) is the ratio of sodium to magnesium and calcium (defined here in milliequivalents per liter):

$$SAR = \frac{[Na]}{\sqrt{\frac{[Ca] + [Mg]}{2}}}$$

As a water-quality parameter, SAR is used to determine the suitability of water for irrigation. Several factors in addition to SAR are considered in determining the suitability, including soil type and water salinity. In general, however, for typical salinities found in eastern Montana groundwater and surface water, the SAR should be less than 7 to be considered a low sodium hazard and between 7 and 14 to be a medium sodium hazard (USDA, 1954). Continued use of high SAR irrigation water on fields can result in a loss in soil structure.

The SAR values for the four aquifers and the surface-water samples were compared in figure 25; the red line indicates a 7 SAR value. Most samples from the alluvium and glacial outwash have SAR values

below the irrigation guideline. The bedrock aquifers of the Fort Union and Fox Hills–Hell Creek have a wide range in SAR values that are mostly above the irrigation standard, indicating that prolonged use as irrigation water is not recommended. The surface-water samples (all sites) have an average SAR value of 10.37, and 66% of the samples were over 7 (fig. 25). With careful management, which can include use of soil amendments and sufficient leaching fractions (addition of water in excess of the evapotranspiration demand), suboptimal water may at times be used for irrigation. Certain crops would not be able to tolerate associated salinity levels. Irrigation from small eastern Montana streams usually occurs during early spring runoff when water has fewer salts.

Comparison of surface water to groundwater types by region. Streams interact with groundwater by gaining or losing water through the streambed. The water chemistry of the groundwater and surface water can provide clues to the degree and nature of connectivity between the two. Stiff diagrams visually represent the major ion composition of a water sample by presenting measured concentrations of major cations on the left and anions on the right (fig. 26). Figure 26 presents the water chemistry by geographic location for selected samples. The most recent sample is presented for surface-water sites. Bedrock groundwater samples near the surface-water sample sites were selected for display.

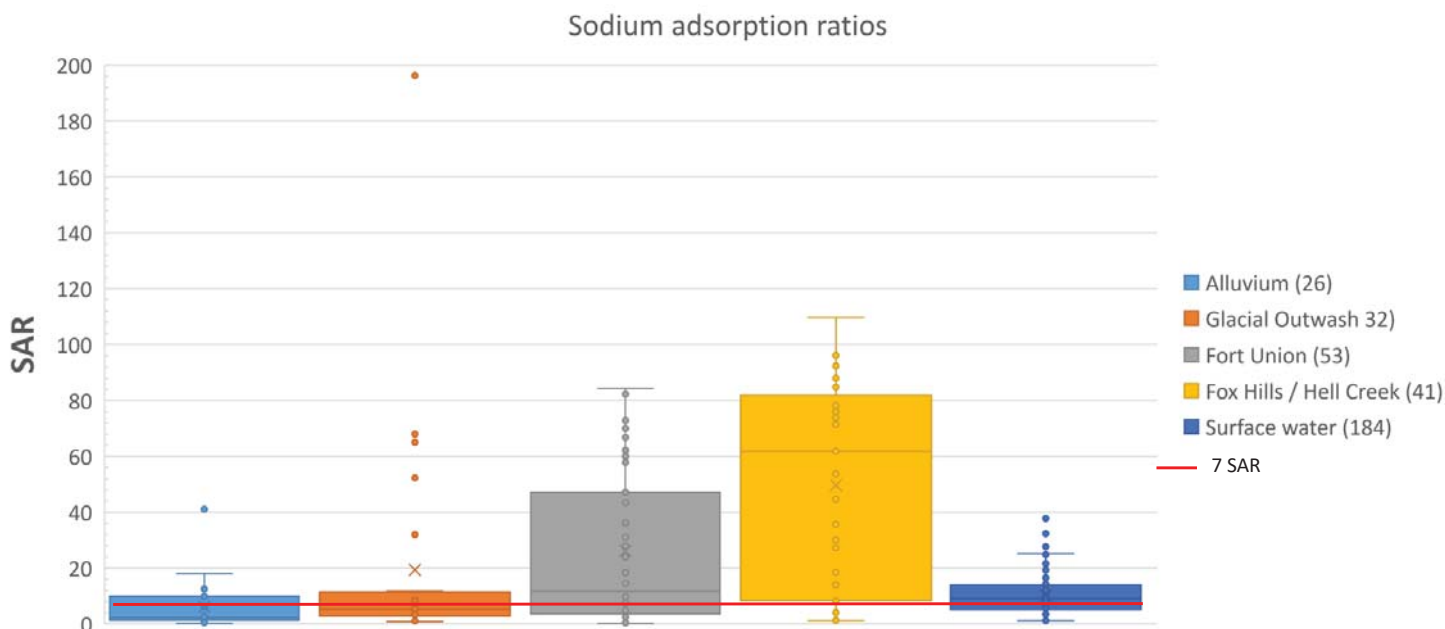


Figure 25. Box plot showing distribution of SAR of groundwater and surface water.

Two distinct regions of water types are evident in both surface water and groundwater (fig. 26). Sodium and sulfate become progressively more dominant in surface-water samples from south to north. Groundwater tends to be more saline, and increases are primarily in sodium and bicarbonate, from south to north. The surface and subsurface geologic units (fig. 2) directly influence the regional water types. Stream sample sites south of Glendive fall along the Cedar Creek Anticline, one of Montana's first major oil and gas development areas. These streams, including Cedar Creek, Cabin Creek, Pennel Creek, Sandstone Creek, and Little Beaver Creek, receive bedrock contributions from the Fox Hills–Hell Creek aquifer and, to a lesser extent, the Fort Union Formation aquifer. North of Glendive, the prevalence of unconsolidated alluvial and glacial outwash aquifers increases. These shallow aquifers are likely significant sources of magnesium and sulfate salts increasing the salinity of streams north of Glendive, including Deer Creek and streams north.

Groundwater samples were collected from existing domestic and stock wells; most residents in the area preferentially complete wells in deeper aquifers. Therefore, outside of monitoring wells completed in contaminated areas, few alluvial or outwash aquifer wells were available for sampling. Consequently, our knowledge of the quality of the groundwater contri-

bution to streams north of Glendive is limited. The bedrock aquifers in this area are often confined (have impermeable geologic layers between the aquifer and the surface), which would prevent bedrock groundwater from interacting with surface water. Where stream chemistry is dramatically different from the bedrock groundwater chemistry (fig. 26), this is likely the cause.

Bicarbonate is present at similar levels in both groundwater and surface water, but surface water has an additional, important sulfate component (fig. 26). The elevated sulfate is matched by elevated magnesium in surface waters as compared to groundwater. Increases in magnesium and sulfate concentrations due to dissolution of soluble salts, including epsomite ($MgSO_4$) naturally present in surficial geology and soils, have been shown in similar settings in northeastern Wyoming (Wheaton and Brown, 2005).

The higher overall salinity of surface water as compared to groundwater may reflect: (1) interaction with more saline surficial aquifers in glaciated areas; (2) evaporative concentration in these small streams; or (3) land-use effects.

While some deep (>900 ft) Fox Hills–Hell Creek aquifer groundwater can be naturally sodium–chloride or sodium–chloride/bicarbonate type, the salinity of the bedrock groundwater is much lower. The spring's

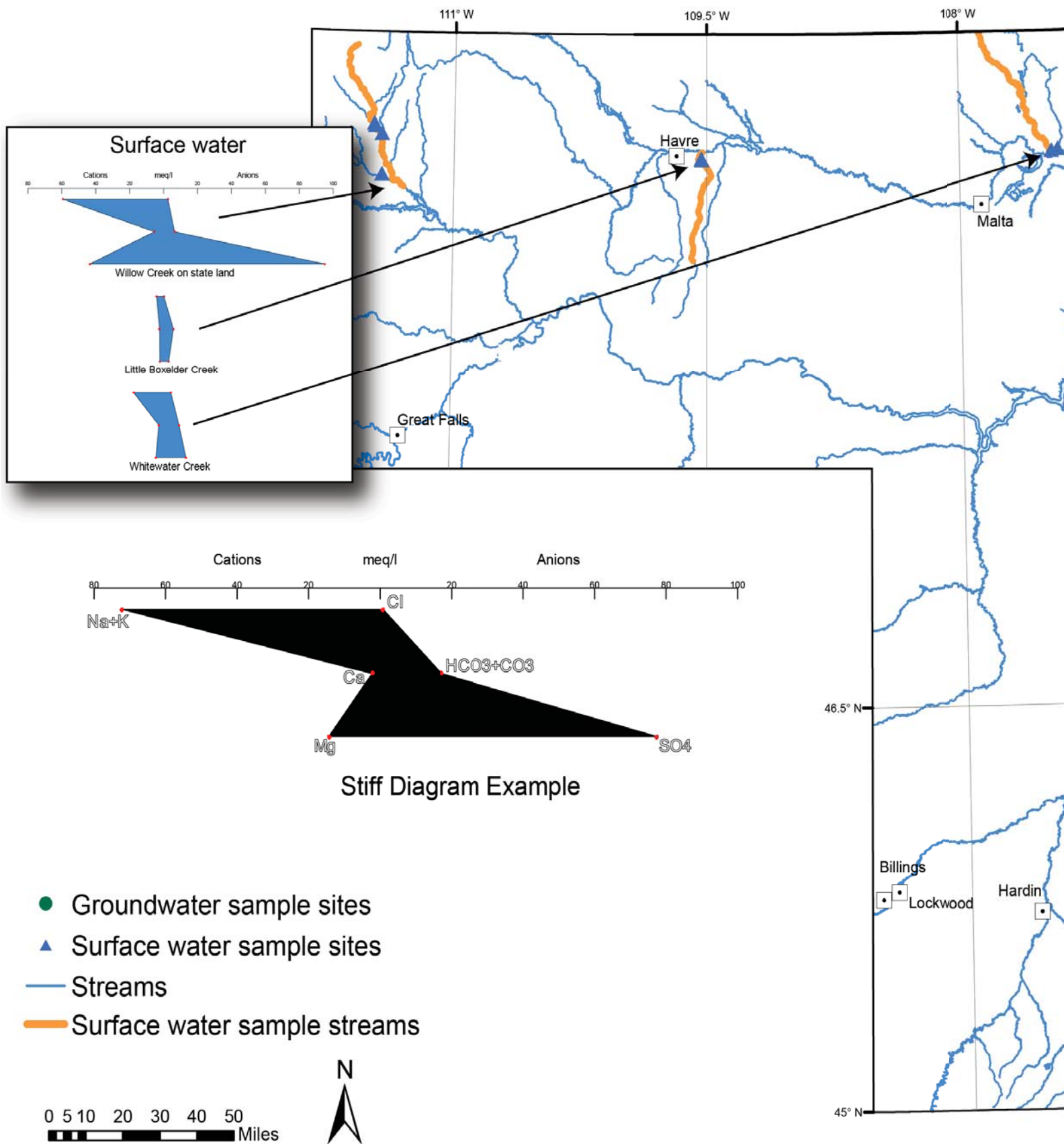
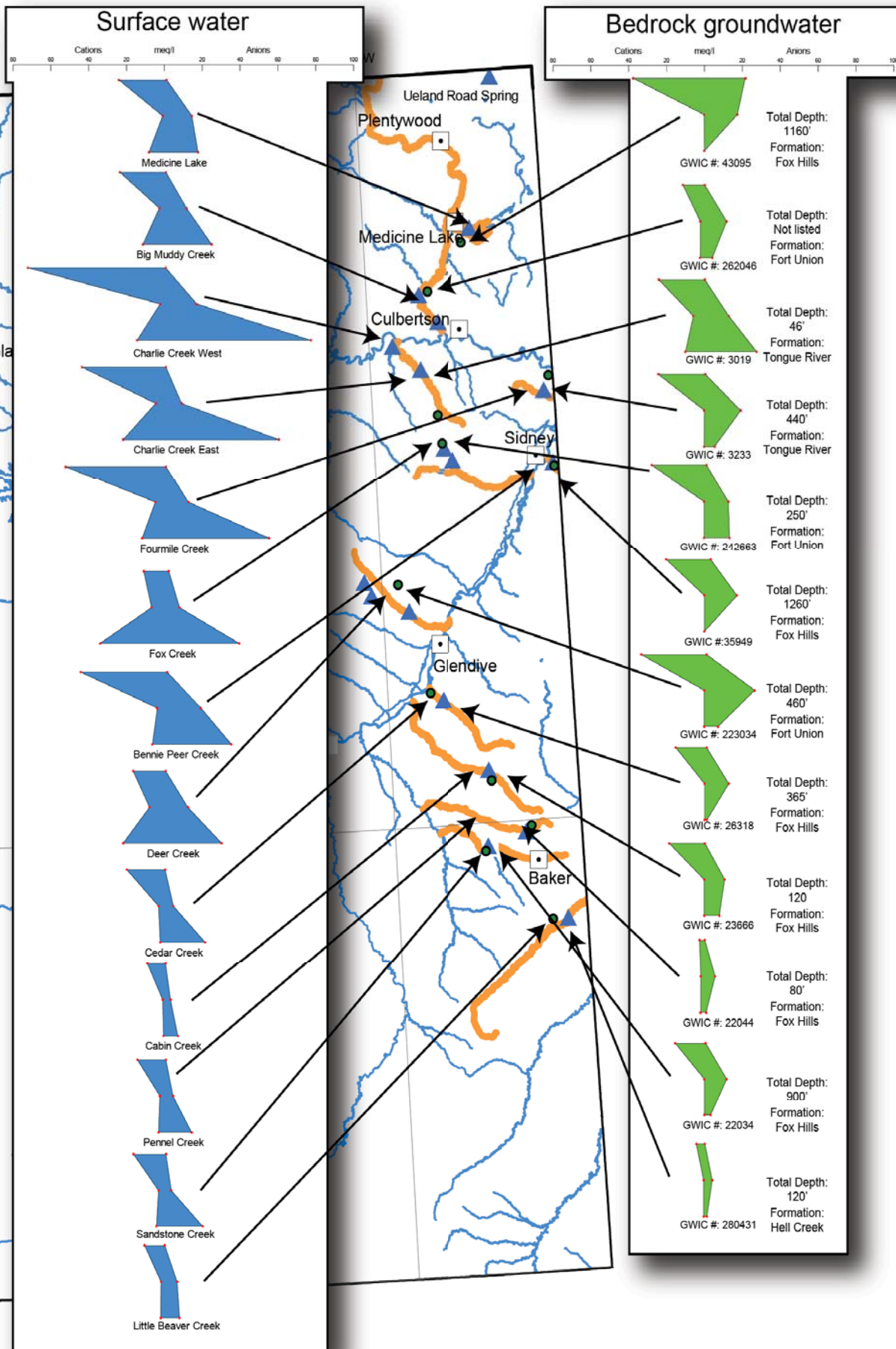


Figure 26. Surface water and groundwater type by location.



sodium–chloride water type is unique among surface-water samples. High salinity associated with sodium and chloride is a signature of oil-field brines.

pH and Mobilization of Trace Metals

The pH of water generally increases along its flow path because water/rock interaction typically consumes acidity (Stumm and Morgan, 1996). Measured pH of surface-water samples had a range from 6.93 to 10.1. The median pH is 8.59. One exception, a measurement of 5.05 on Willow Creek, was not duplicated in the other Willow Creek samples, which ranged from 8.50 to 8.97. The median pH of groundwater is 7.4154, with a pH range from 6.28 to 9.10.

In pH neutral to acidic waters, arsenic (as arsenate [As(V)] and arsenite [As(III)]) adsorbs onto iron-oxides, aluminum-oxides, and clays, making it immobile. However, in the high pH surface and groundwater of eastern Montana (those over 7.7 or 8 depending upon the arsenic species), arsenic will desorb and become mobile. Iron-oxides can adsorb sufficiently high concentrations of arsenic that the subsequent desorption can cause water to exceed the human health standard (Hinkle and Polette, 1999). This was found to be true in 1999 when the arsenic standard was 50 µg/L; in 2001 the standard was lowered to 10 µg/L.

Aluminum as an ion, Al³⁺, is only mobile in acidic waters with pH less than 3.5. In neutral pH waters aluminum will complex with oxide and precipitate as aluminum-oxide [Al(OH)₃]. As pH continues to increase from 7.5 to 9.5, this precipitate is re-dissolved as Al(OH)₂⁺ (Hem and Robertson, 1967).

Organic Constituents

Surface-water detections

All detections of the presence of organic constituents (not including methane and organic carbon) in the sampled streams occurred in 2013 (April, June, August, and October), with one exception, a detection of total extractable petroleum hydrocarbons in a Medicine Lake sample collected in 2016 (appendix E). Additionally, there were detections in all blank water analyses from 2013. There were no other detections in blanks in other years. Blank detections included acenaphthylene (April), naphthalene (April, June, August, and October), fluorene (August), and phenanthrene (August).

The June 2016 Medicine Lake sample had a total extractable petroleum hydrocarbon concentration of 321 µg/L; however, this sample was collected in duplicate, and the duplicate sample did not have a detectable concentration. This analyte was only measured on Medicine Lake samples and there were no other detections.

Streams with detections in 2013 include: Bennie Peer Creek, Big Muddy Creek, Cabin Creek, Cedar Creek, Charlie Creek East, Charlie Creek West, Fourmile Creek, Little Beaver Creek, Little Boxelder Creek, Pennel Creek, Sandstone Creek, and Willow Creek. Detectable constituents include: acenaphthene, acenaphthylene, anthracene, chrysene, fluoranthene, fluorene (all but one detection impacted by positive blank detection), methanol, naphthalene (all detections impacted by positive blank detection), total extractable petroleum hydrocarbons, phenanthrene (all but two detections impacted by positive blank detection), and pyrene (appendix E).

Outside of those constituents that are impacted by positive blank detections, no stream had any constituent detected in more than one sample (outside of duplicates). The lack of reproducibility and the fact that all detections occurred in the 2013 sampling, which had problems with blank contamination, makes it difficult to conclude that the organic constituents detected in the 2013 samples are indications of oil and gas contamination.

Groundwater detections

Low levels of organic constituents can be found in many aquifers in eastern Montana (appendix F); however, they are most prevalent in the shallow unconsolidated aquifers near Medicine Lake in areas with historic contamination from oil and gas production. In 158 samples collected by the MBMG, detectable concentrations of total purgeable hydrocarbons was measured in 20 samples, and 43 samples had total extractable hydrocarbons.

- Total purgeable hydrocarbon (TPH)
 - 20 total detections (15 Sheridan, 4 Roosevelt, 1 Dawson Counties)
 - 18 were from shallow unconsolidated aquifers (15 were from monitoring wells in known contamination areas)
 - 2 were from Fort Union aquifer

- Total extractable hydrocarbon (TEH)
 - 43 total detections
 - 37 were from shallow unconsolidated aquifers (34 were from monitoring wells in known contamination areas)
 - 3 were from Fort Union, 3 were from Fox Hills–Hell Creek aquifers

Several detections were found in benzene, toluene, ethylbenzene, and xylene (BTEX) range. One detection each of benzene and ethylbenzene were from the same sample (well 221574) in a known contaminated site, but this sample may be affected by contaminated blank water. Eleven samples had detectable toluene, with concentrations ranging from 0.49 to 32 $\mu\text{g/L}$ collected in Sheridan, Roosevelt, and Richland Counties. Five samples had detectable xylene, with one exception all in the form of m+p xylene. The sample with the highest concentration of total xylene (1.9 $\mu\text{g/L}$ from well 40257) also had o-xylene.

Seventeen wells had detectable C5-C8 Aliphatics (11 to 387 $\mu\text{g/L}$) from Sheridan (12), Roosevelt (4), and Dawson (1) Counties. Two wells had detectable C9-C12 Aliphatics, both from Sheridan County.

Montana Salinity Control Association samples had detectable levels of total petroleum hydrocarbons–diesel range organics (C10-C28) in six samples located in Dawson, Richland and Daniels Counties (collected from wells 30256, 38701, 137915, 249758, 261518, and 703740). The samples ranged in concentration from 0.071 to 0.42 mg/L . While several wells have no information about drilling depths or lithology, based on their locations and what is known about completion depths, we classify them as likely completed in the Fort Union Formation.

Methane, Ethene, and Ethane Concentrations

Methane (CH_4) is naturally prevalent in eastern Montana aquifers. Over half of the samples analyzed for methane (58 percent, 95 of 163 analyses) had detectable concentrations. Concentrations are generally low; 82 percent (79 of 95 detections) of samples with detectable methane had concentrations below 1 mg/L . Only two samples had concentrations over 10 mg/L : 18 and 21 mg/L from wells 154904 (840 ft deep) and 43095 (1,160 ft deep), completed in the Fox Hills–Hell Creek aquifer. In general, well owners do not

need to take remedial action for methane concentrations below 10 mg/L because the likelihood for fire or explosion is low. Some remediation is recommended for methane concentrations between 10 and 28 mg/L . The methane explosive limit is reached at concentrations of 28 mg/L and above, and extreme caution is required (Eltschlager and others, 2001).

A similar prevalence of methane was found in surface-water samples. Low levels of methane were detected in 75 percent of samples analyzed for methane (198 detections of 265 methane analyses). All concentrations were well below 1 mg/L , with the highest concentrations, 0.036 and 0.039 mg/L , from Fox Creek and Deer Creek, respectively. The source of naturally occurring methane in surface water is from groundwater baseflow to the stream. Therefore, we find the concentrations and prevalence of methane in surface water are consistent with those in groundwater.

One groundwater sample collected from a known contaminated site had detectable ethene (C_2H_4) (0.0013 mg/L ; well 3767). Ethane (C_2H_6) was also detected in 12 other samples, with concentrations ranging from 0.0011 to 0.0088 mg/L . Of the 12 detections, 8 samples were collected from Richland County, 1 from Roosevelt County, and 3 from Sheridan County. Four of these samples, those collected in August 2015, may be impacted by contaminated blank water; this includes the two shallowest samples. The two shallowest samples were from the Fort Union (35945: 148 ft deep) and unconsolidated aquifer in the known contaminated area (221574: 28 ft deep). The other 10 samples were collected from the Fox Hills–Hell Creek aquifer from wells with depths ranging between 1,160 to 1,500 ft deep. Ethane was therefore present in 60 percent (10 of 17) of sampled wells greater than 900 ft deep. Ethene and ethane were not analyzed in surface-water samples.

Ethane can be found naturally in groundwater not associated with oil production (Humez and others, 2016; Schloemer and others, 2016). Schloemer and others (2016) found that 27 percent of approximately 1,000 sampled wells in a major natural-gas-producing area in Germany had detectable concentrations of ethane. Their work showed that biogenic methane concentrations in uncontaminated systems are usually 200 times—or more—the concentrations of ethane and propane. Eastern Montana groundwater has methane concentrations 225 to 5,000 times greater than ethane

concentrations, with the exception of well 221574 (a known contaminated site), which had a ratio of 19. Based on these ratios and the fact that most of the samples from wells 900 ft or deeper had detectable ethane, we conclude it is unlikely the presence of ethane in the Fox Hills–Hell Creek aquifer is contamination from oil production.

Isotopic Composition of Methane

The original source of methane in groundwater, either through biological respiration or through thermocatalytic processes, can be deciphered through the carbon isotope ratio (^{13}C to ^{12}C) of methane (Clark and Fritz, 1997). Biogenic (biological) methane has a more-negative signature—generally less than -50 per mil—than thermocatalytic methane does. Biogenic methane is common in eastern Montana aquifers, whereas thermocatalytic methane is generally only found in deep aquifers not commonly used for water wells. Therefore, the presence of thermocatalytic methane in shallow aquifer systems and surface water would indicate the migration of methane from deeper systems or contamination from surface disposal of oil brines.

Comparing surface water to groundwater isotopic results is complicated by the sampling bias required by the different laboratories used. The carbon isotope ratios of methane in groundwater samples were analyzed by Isotech Laboratory, which suggests a minimum methane concentration of 1 mg/L for best results. This resulted in analyzing only a handful of groundwater samples with the highest concentrations. The carbon isotope ratio of methane in surface-water samples was analyzed by the University of Arkansas Stable Isotope Laboratory, which reports isotope ratios on methane concentrations of 2 $\mu\text{g/L}$ and higher (detection limit is 2 $\mu\text{g/L}$). Of 49 samples sent for isotope measurement, 24 of the surface-water samples could not be accurately measured because the methane concentration was below the detection limit.

No conclusion should be drawn from the apparent discrepancy in methane concentrations between surface water and groundwater in figure 27 and table 3 because of the previously described sampling bias. The carbon isotope ratio of methane in sampled groundwater is well within the general cutoff for biogenic methane (below -50 per mil; fig. 27). The majority of surface-water samples, while overall less

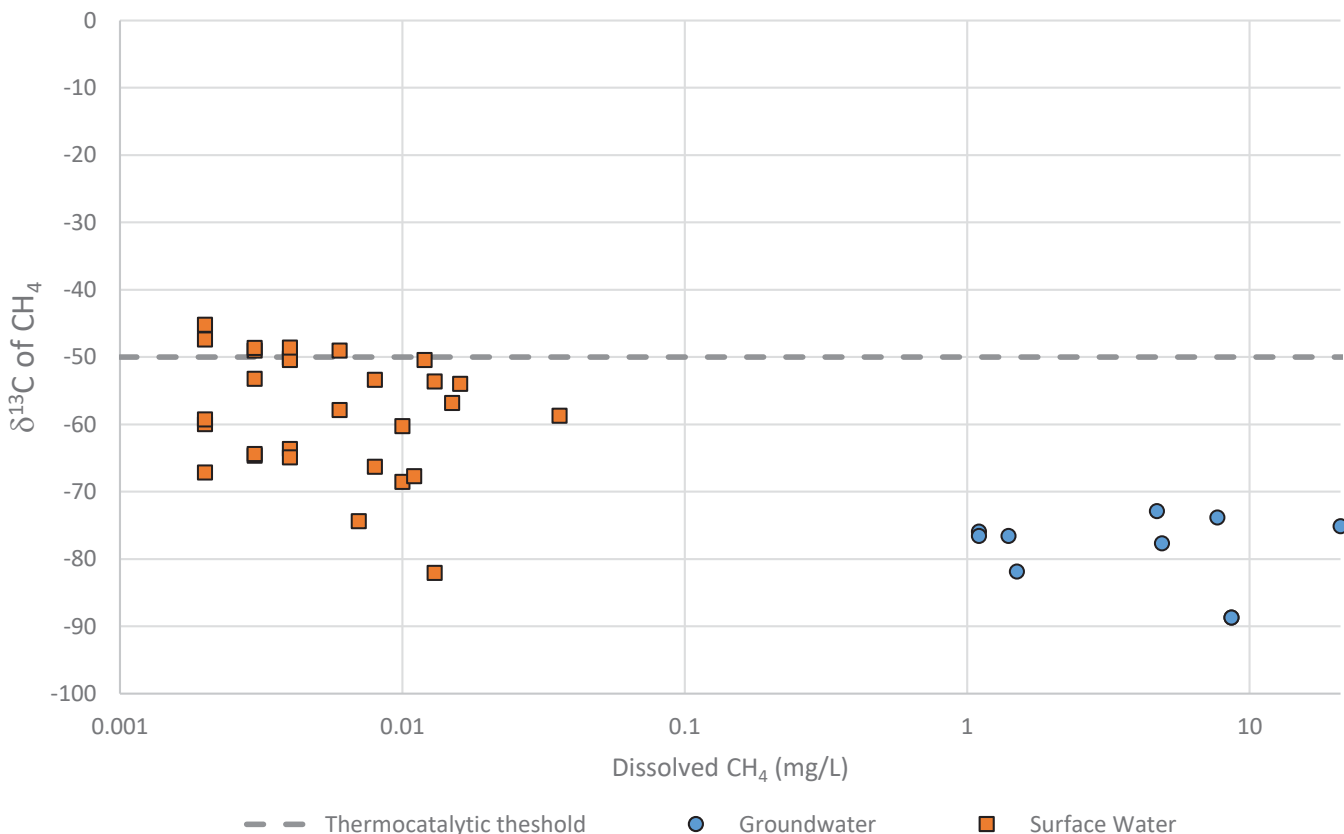


Figure 27. Methane concentration versus carbon isotope ratio for surface and groundwater.

Table 3. Carbon isotope ratios of methane.

	Site	June 2016		August 2016		October 2016	
		d ¹³ C ‰	CH ₄ (mg/L)	d ¹³ C ‰	CH ₄ (mg/L)	d ¹³ C ‰	CH ₄ (mg/L)
Surface Water (creek name)	Big Muddy Creek	-47.39	0.002			-45.18	0.002
	Charlie Creek East	-57.86	0.006	-63.65	0.004	-64.66	0.003
	Charlie Creek West	-59.96	0.002	-67.69	0.011		
	Deer Creek	-82.07	0.013				
	Fourmile Creek	-68.53	0.010	-50.43	0.004	-64.40	0.003
	Fox Creek	-66.31	0.008	-58.73	0.036	-53.62	0.013
	Fox Creek (duplicate)	-74.37	0.007			-53.99	0.016
	Little Beaver Creek	-50.13	0.004	-53.24	0.003		
	Little Boxelder Creek	-49.04	0.003	-48.60	0.004		
	Pennel Creek	-59.29	0.002	-60.26	0.010	-67.13	0.002
	Sandstone Creek			-56.81	0.015	-48.64	0.003
	Whitewater Creek	-50.43	0.012	-53.39	0.008	-49.02	0.006
	Willow Creek					-64.88	0.004
	Groundwater (GWIC ID number)	3483					-72.88
3772						-88.70	8.6
3772 (Dup)						-88.69	8.6
35876						-76.59	1.4
35945						-81.88	1.5
38755						-73.82	7.7
43095						-75.13	21
79510						-77.68	4.9
142679						-75.91	1.1
274382						-76.56	1.1

negative than the groundwater samples, are still within the definition of biogenic methane. If anaerobic fermentation is contributing methane to the streams (such as in a marsh), that would contribute an isotope ratio of approximately -55 per mil, which could account for some of the upward shift from groundwater isotope ratios. However, samples from Big Muddy Creek and Box Elder Creek suggest there may be some component of thermogenic methane. The total concentrations of methane in these samples is low, at or near the 2 µg/L detection limit (table 3), which increases the error associated with the analyses.

Radiochemistry

Surface water to groundwater comparison

The highest alpha and beta values from surface-water samples were from Ueland Road Spring, which is likely contaminated (243, 114, and 91.5 pCi/L alpha and 182, 82, and 78 pCi/L beta). The next highest levels were approximately half those of Ueland Road Spring, from Deer Creek South Fork (46 and 45 pCi/L alpha) and from Fox Creek (43, 39, and 28 pCi/L beta; appendix E). Many of the radiochemistry analyses for

surface water had “U” flags, which indicates that the measured level was not over the Contract Required Quantitation Limit (CRQL); however, for the purposes of this analysis all reported values were considered. The surface-water radiochemistry blank analyses resulted in low levels of alpha and beta radiation. The highest measured blank for alpha and beta was from October 2013 (1.7 pCi/L alpha). This level was considered low compared to natural levels and was therefore interpreted to not interfere with the accuracy of the sample.

Deer Creek was analyzed for an additional set of measurements of radioactive constituents or products of radioactive decay, including of bismuth, cesium, lead, potassium, protactinium, radium, thorium, and uranium, to provide baseline information (appendix G). There does not appear to be a measureable difference between the Deer Creek Middle Fork and the Deer Creek off highway 254+Deer Creek South Fork datasets (appendix G), based upon overlap between 1-standard deviation from the average value between the two sites, the large variability in the blank analyses, and the prevalence of the “U” flag. Groundwater

was not analyzed for these constituents.

The uranium series of radioactivity measurements (U-234, -235, and -238) was only measured on one surface site, Deer Creek South Fork (plus duplicate and blank), and was not measured on groundwater samples. The dissolved uranium concentration of the Deer Creek sample, 40 µg/L, is above the drinking water standard of 30 µg/L. Dissolved uranium concentrations are available in the MBMG GWIC database (MBMG, 2017) for 44 groundwater samples from Dawson County (Deer Creek is in central Dawson County). Of the 44 groundwater samples, 17 had uranium concentrations below detection. The remaining 26 samples had values ranging from 0.4 to 63.3 µg/L, with an average value of 14 µg/L. Two wells had uranium concentrations over the drinking water standard of 30 µg/L. The highest uranium concentrations in Dawson County groundwater were from a mix of aquifers, Fox Hills–Hell Creek, Fort Union, and unconsolidated terrace deposits. While present in the groundwater, uranium concentrations in groundwater

similar to those found in Deer Creek South Fork are unusual in the area but not unheard of.

The highest radiochemistry values from groundwater samples were from well 221691 (282 pCi/L alpha and 471 pCi/L beta). This Medicine Lake monitoring well goes through oil and gas pit material (at 10 ft). The next highest alpha values were from wells 221722 and 221574 (156 and 129 pCi/L alpha, respectively). The next highest beta values were from wells 890933 and 890422 (217 and 67 pCi/L beta, respectively). These four sites are monitoring wells in northeast Sheridan County between Plentywood and Westby. After the three highest values of both alpha and beta, the next highest were half or less (44 pCi/L alpha and 28 pCi/L beta; appendix F).

The variability of alpha and beta radiochemistry is similar in surface and groundwater samples, including the mean and standard deviation (fig. 28). The number and range of outliers is also similar.

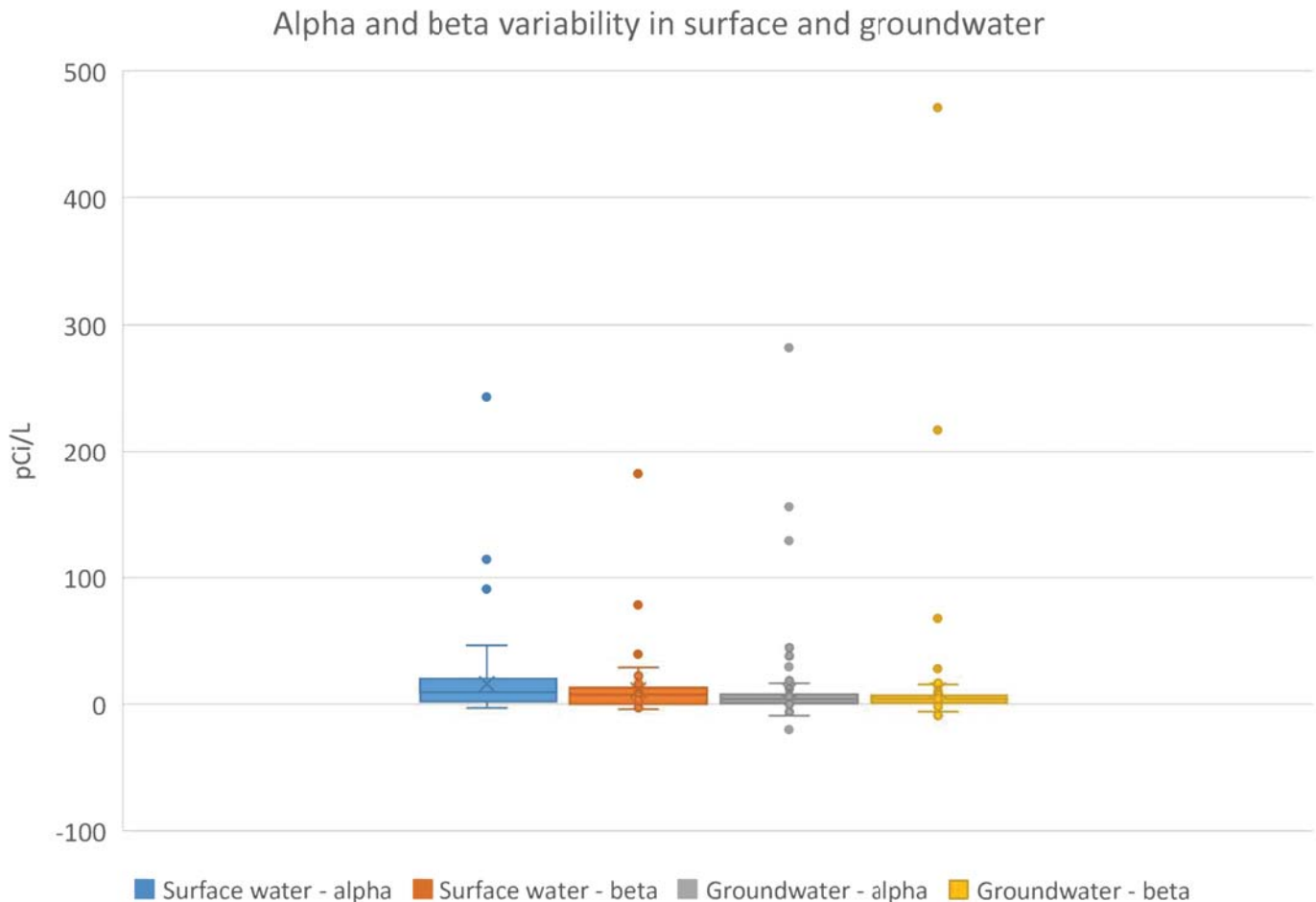


Figure 28. Radiochemistry variability in surface and groundwater.

Inorganic tracers of contamination

Historical oil- and gas-produced brine contamination in northeastern Montana spurred the development of a contamination index (CI) to determine quickly and inexpensively if groundwater salinity was derived, in part, from oil brines (Reiten and Tischmak, 1993; Rouse and others, 2013). This method stipulates that ratios of chloride (mg/L) to specific conductance ($\mu\text{S}/\text{cm}$) greater than 0.035 indicate brine contamination. This method has been shown to be successful in shallow aquifers in northeastern Montana because of the naturally low levels of chloride; therefore, excess chloride in shallow aquifers can often be attributed to brine contamination (Reiten and Tischmak, 1993). Additionally, a bromide to chloride molar ratio $\text{Br}/\text{Cl} > 0.001$ has been shown to be a reliable fingerprint of brine waters in the Marcellus shale in Pennsylvania (Warner and others, 2012). These two methods were evaluated for effectiveness in identifying the presence of brine water contamination in the groundwater and surface-water datasets.

Contamination index

The previously described site of known contamination is easily distinguished on a chart of salinity versus CI (fig. 29). The points fall well above the 0.035 CI threshold that indicates the presence of brine water.

Fifteen Fox Hills–Hell Creek aquifer samples have CI values greater than 0.035; in general, points on the anion triangle of figure 21 that do not fall along the bicarbonate–sulfate anion line exceed this value. Of these, four are less than 100 ft deep (starred points on fig. 21); the remaining 11 range in depth from 840 to 1,720 ft deep. The shallow wells are distinct from deeper wells in that they have a mixture of bicarbonate, sulfate, and chloride anion composition, while anions in samples from the deep wells do not have a sulfate component. Interpreting the origin of the chloride in the four shallow wells as either natural or from brine contamination is complicated by the fact that some Fox Hills–Hell Creek groundwater has natural levels of chloride similar to that found in shallow wells (deep wells in fig. 21). Additionally, despite the close proximity of the shallow Fox Hills–Hell Creek wells (starred points in fig. 21) to operating oil wells, these samples did not have any detectable organic constituents. We conclude that the CI cannot accurately be

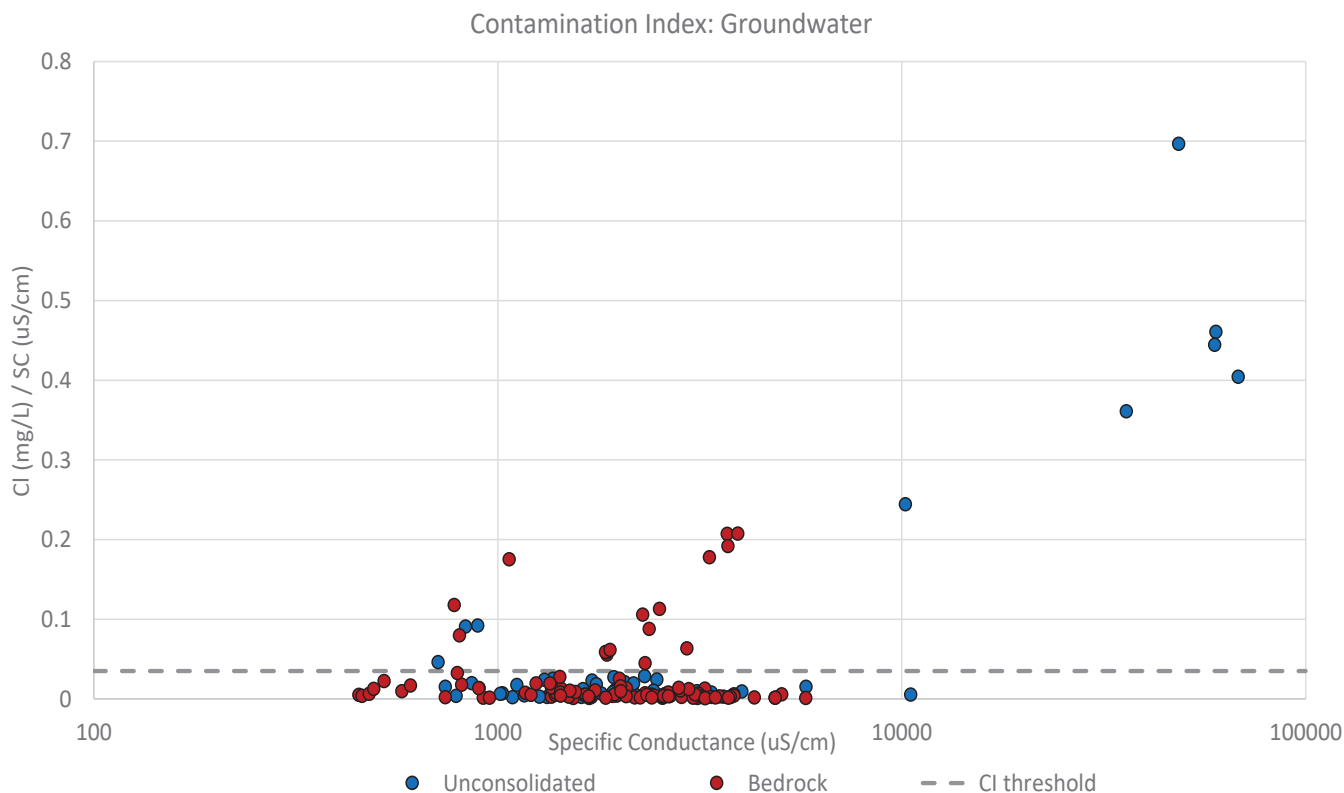


Figure 29. Known contaminated groundwater falls over the contamination index value of 0.035. Natural levels of chloride in the Fox Hills–Hell Creek make this index ineffective for identifying contamination in bedrock aquifers.

applied to Fox Hills–Hell Creek groundwater because of the possibility of naturally occurring chloride in excess of the 0.035 threshold.

Samples collected from Cabin Creek, Ueland Road Spring, and Whitewater Creek consistently exceeded the contamination index of 0.035 (fig. 30). In each case, the majority of samples collected had CI over 0.035: Cabin Creek (11 of 13 samples), Ueland Road Spring (3 of 3), and Whitewater Creek (12 of 15 samples).

The combination of high salinity (19,690–72,060 $\mu\text{S}/\text{cm}$) and high CI (0.35) of Ueland Road Spring matches the signature of the contaminated unconsolidated aquifer by Medicine Lake and may therefore have a component of brine-contaminated groundwater. While the CI of Cabin Creek and Whitewater Creek exceed the 0.035 threshold, the combined signature of salinity and CI are similar to bedrock groundwater, so may just reflect the influence of natural groundwater contribution.

Four creeks, Charlie Creek East, Pennel Creek, Willow Creek, and Fox Creek, each had one or more samples that exceeded the CI threshold but were the minority of samples collected (three or fewer). The CI of these creeks may also just reflect the contribution of

bedrock groundwater baseflow.

Without a specific groundwater/surface-water interaction study to identify sources of baseflow to the sampled creeks, it will not be possible to positively identify the source of chloride and salinity in the creeks as attributable to natural bedrock contributions or to brine water discharges. High CI in bedrock aquifers is generally found in aquifers over 1,000 ft deep, and is therefore unlikely to contribute baseflow to streams. However, the four samples from shallow Fox Hills–Hell Creek wells that had CI over 0.035 suggest that there may be shallow sources of chloride.

Bromide to chloride ratio

Using the site of known contamination as a guide, we find no correlation between the bromide to chloride ratio and the presence of oil brines (fig. 31). This lack of correlation holds for both groundwater and surface-water samples. Bromide concentrations in groundwater are generally low: of 159 samples analyzed for bromide, 59 (37 percent) were below detection. Of the 100 samples with detectable bromide, concentrations ranged from 61 to 6,930 $\mu\text{g}/\text{L}$ in 95 samples. Five samples were significantly higher, with bromide concentrations ranging from 18,850 to 117,200 $\mu\text{g}/\text{L}$, collected from wells in known contaminated groundwater

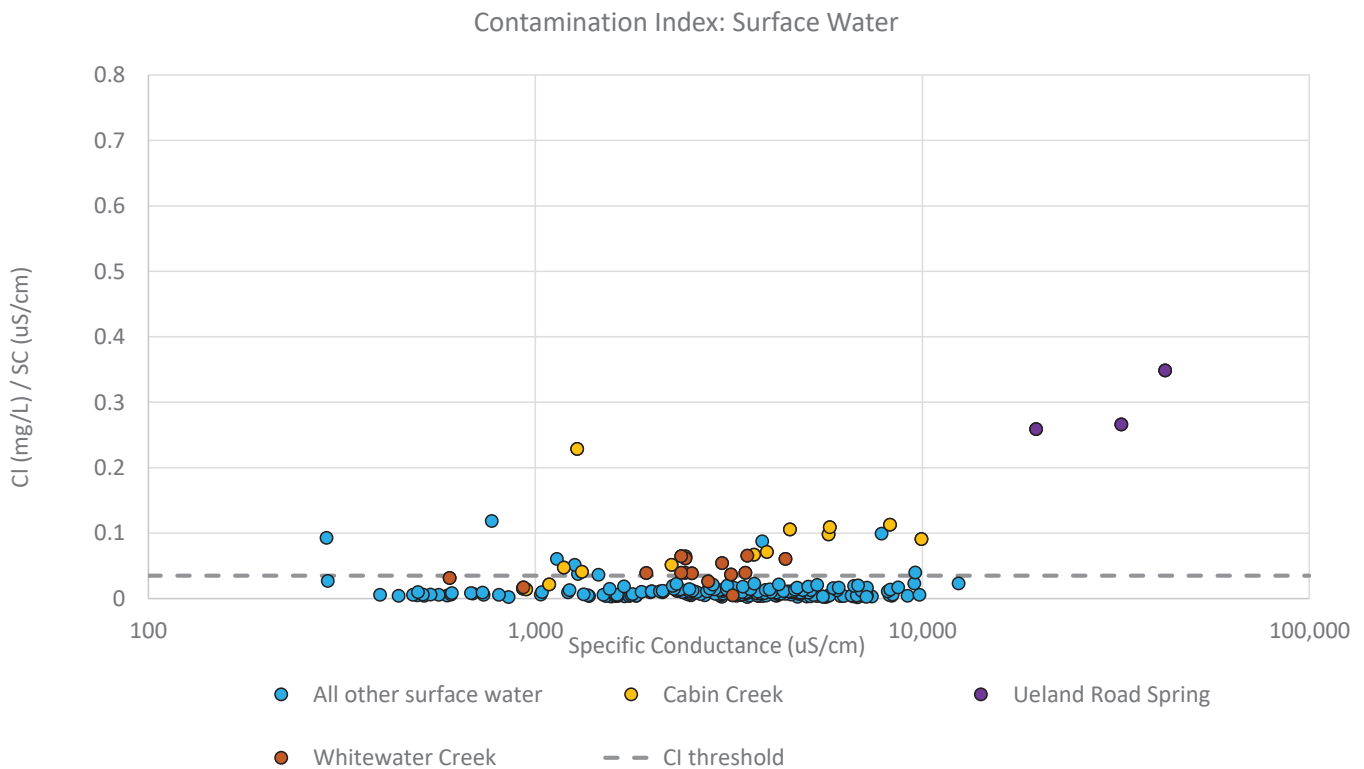


Figure 30. Ueland Road Spring has the hallmarks of contaminated groundwater: high salinity and contamination index over 0.035.

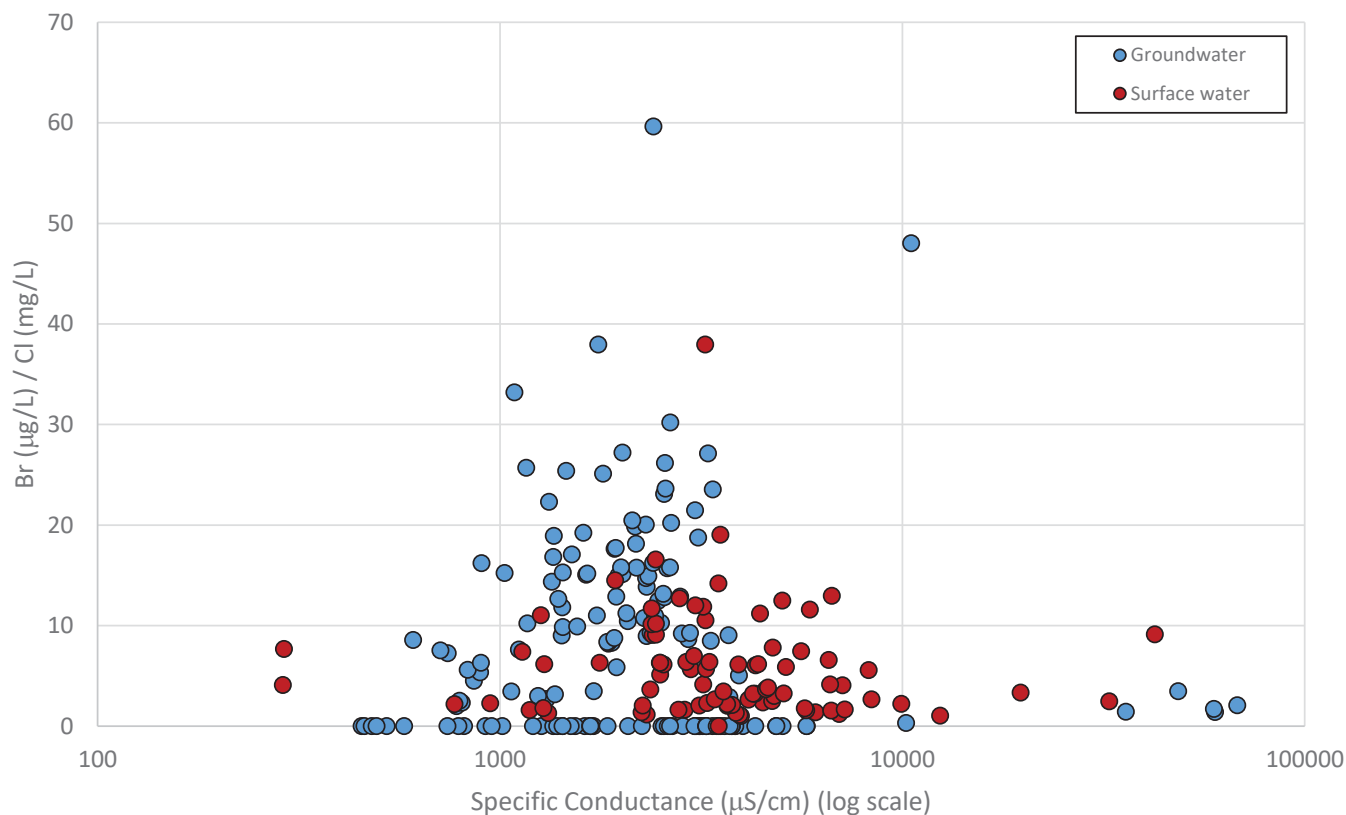


Figure 31. There is no correlation between the ratio of bromide to chloride and elevated salinity.

(wells 209938, 209935, 209933, 210036, 209978). However, in all five of these samples, the chloride concentrations were also correspondingly high, resulting in Br/Cl ratios that fall in the middle of the Br/Cl range for all collected groundwater samples (fig. 31). While the highest ratios were generally from wells in the contaminated area, there was no distinct inflection point in the Br/Cl ratios indicating two populations of water. The highest ratio was measured in a well (153570) with no additional indications of contamination such as high salinity or the presence of organic constituents.

Bromide concentrations in surface water are generally similar to those in groundwater. Of the 264 surface-water samples (including duplicates) analyzed for dissolved bromide, 157 (60 percent) had non-detectable bromide concentrations. Of the 107 samples with measurable bromide, the concentrations ranged from 30 to 5,200 $\mu\text{g/L}$ in 102 samples. Five samples (1 duplicate) had significantly higher concentrations of 17,000 to 136,000 $\mu\text{g/L}$, all collected from Ueland Road Spring. Similar to the findings for groundwater in this area, the Br/Cl ratio for Ueland Road Spring fell in the middle of the range because it also has correspondingly high chloride values. The Br/Cl ratios for

the surface-water sample set (for those samples with measurable bromide) ranged from 1 to 38; the 7 highest values are from samples collected from Whitewater Creek, which had no detectable organic analytes that might also suggest the presence of brine water (fig. 31).

While the Br/Cl ratio was successfully used in Pennsylvania oil and gas fields (Warner and others, 2012) to fingerprint oil brines, the known brine contaminated groundwater in Montana does not hold to this pattern. Overall, the typically low chloride concentrations were matched by bromide concentrations that were below detection in Montana waters. Where high bromide concentrations were measured, they were matched by high chloride.

SUMMARY

Montana citizens are concerned about the risks to their water resources from enhanced oil recovery techniques and the resulting increased oil and gas activity. The increased level of development is seen by some as increasing the risk of water supplies being contaminated by oil-field brines. The results of surface- and groundwater sampling presented in this report found contamination from oil and gas activities is primarily confined to areas previously known to be contaminated from historical oil and gas drilling techniques, which put oil brines and tailings in contact with shallow groundwater. This extends to the surface-water sampling site that this study identified as contaminated, Ueland Road Spring. While not previously known to be contaminated, the spring is an expression of groundwater at ground surface in an area known to have brine-contaminated groundwater. Current oil and gas drilling regulations require careful containment of tailings, drilling fluids, and produced water (brines). All brines are required to be injected into deep aquifers that have a similarly high salinity. Injecting the brines greatly reduces the risk of contamination to potable water.

Groundwater sampling in areas of known brine contamination in Sheridan County illustrates what contaminated water can look like: high salinity, high chloride, high radiochemistry, and the presence of organic constituents. Groundwater-quality sampling outside known contaminated areas has shown that, individually, these qualities can also occur naturally. High chloride to salinity ratios and the presence of ethane is found naturally in deep (>1,000 ft) wells completed in the Fox Hills–Hell Creek aquifer. Groundwater analyses found light hydrocarbons in the Fort Union Formation wells. Therefore, the combination of more than one indicator is key to identifying the presence of contamination from oil/gas development activities.

A combination of factors (salinity, chloride, and radiochemistry) was used to conclude the Ueland Road Spring surface-water sampling site in northeastern Montana exhibits the presence of contaminated groundwater—despite the lack of detectable organic constituents, including methane. Elevated levels of alpha radiation in some streams demand further investigation to determine if it represents mobilization of contamination from historic drill cuttings and/or brine storage or reflects the natural variability in radiochem-

istry. Based on the range of measured values in surface and groundwater, alpha radiation, more so than beta, appears to be a better indicator of contamination. The high alpha radiation values associated with brines are more easily distinguished from baseline.

A few groundwater samples had detections of unusual constituents, such as toluene. However, organic constituent analyses have only been performed once on each of these wells, and this work has shown that these analyses are sensitive to contamination; it is premature to draw conclusions at this time.

The contamination index (Reiten and Tischmak, 1993; Rouse and others, 2013) proved to be a successful indicator of contamination in shallow, unconsolidated groundwater and a spring in this study. However, the natural levels of chloride in some samples from the Fox Hills–Hell Creek aquifer make this metric unsuitable for use in bedrock aquifers. The connection between bedrock aquifers and surface water indicates that this metric is also unsuitable to use as a single line of evidence for surface water.

Arsenic is shallow, biogenic generation that is unlikely to have migrated from deep oil and gas reservoirs. Some surface-water samples had isotopic signatures on the margin that may reflect high analytical error associated with low methane concentrations, the influence of surficial processes, or a contribution of thermogenic methane.

Water resource sampling such as this is imperative to protect both the individual water users from degradation of their resources and the oil and gas industry from inappropriate attribution of naturally occurring conditions to development activities. Expanding efforts to understand the natural variability of eastern Montana's water resources, especially of characteristics generally associated with brines, will protect and aid in the orderly development of Montana's resources.

RECOMMENDATIONS

The findings of this work are consistent with those found by McMahon and others (2014), which looked at samples collected by the USGS from Fort Union Formation wells in the Williston Basin in Montana and North Dakota. They found no evidence of contamination from oil activities. Their analyses also included carbon-14 age dating, which concluded most sampled groundwater was 1,000 to 30,000 years old. Calculated groundwater velocities imply that contaminants from improperly cemented oil wells would be less than 0.5 km of the well location. These conclusions led to the cautionary statement that, for contamination screening, domestic wells might not be as suitable as shallow wells completed near the water table. They also found that a long-term commitment to monitoring bedrock groundwater would be required to assess the effects of energy development on domestic groundwater supplies and recommended monitoring close to development to increase the early detection of potential contamination.

Outside of direct spills into streams, contamination from oil and gas activities will flow through the groundwater systems to the streams. The most likely pathway is through shallow, highly conductive aquifers, but the potential exists for movement through bedrock systems as well. Paired groundwater/surface-water investigations that take into account the connectivity between the two systems will identify more conclusively sources of constituents of concern (e.g., salinity, arsenic, radioactivity, and/or uranium).

The presence of what is currently interpreted to be naturally occurring organic constituents and radioactivity in the Fort Union and Fox Hills–Hell Creek Formations requires further investigation. Positive detections of organic constituents in groundwater or surface water could lead to a mistaken conclusion of contamination from oil and gas development if these constituents occur naturally. A combination of the following will help protect the oil and gas industry from misplaced blame: (1) a more detailed organic analyte suite and a larger sampling area will help create a “fingerprint” of naturally occurring organic and radioactive constituents in bedrock aquifers; and (2) conducting baseline sampling prior to new oil and gas development.

Timing, Frequency, and Analyses of Future Sampling

The high-frequency sampling of surface water from 2012 to 2016, performed quarterly, was important to define the current state and natural variability of the sampled streams. However, outside of characterization efforts, analyses specific to contamination identification could be done on a less frequent basis. Contamination-specific analyses, performed annually for both surface water and groundwater, could include fewer constituents, focusing on organic analyses that measure a broad range of organics such as TEH/TPH/GRO/DRO assays. Detection in these ranges would call for more detailed analysis. These organic analyses should be performed in addition to standard total dissolved solids (which includes chloride concentrations) and flow rate measurements.

The analysis of uranium concentration performed on Deer Creek illustrates the potential for surface water to have uranium in excess of the human health standard. Uranium is regularly measured in groundwater and being able to pair groundwater uranium characteristics with surface water would help identify the source of uranium in both systems.

Incorporating a broad array of isotopic analyses of dissolved constituents, including boron ($^{11}\text{B}/^{10}\text{B}$), lithium ($^6\text{Li}/^7\text{Li}$), strontium ($^{87}\text{Sr}/^{86}\text{Sr}$), hydrogen ($^2\text{H}/^1\text{H}$) of H_2O , oxygen ($^{18}\text{O}/^{16}\text{O}$) of H_2O , and radium ($^{228}\text{Ra}/^{226}\text{Ra}$), has been shown to characterize oil brines and hydraulic fracturing fluids and identify their presence in the environment (Peterman and others, 2010; Vengosh and others, 2013; Warner and others, 2012, 2014). This work been done in Pennsylvania and Texas oil and gas fields; a similar characterization is recommended for Bakken Formation brines and hydraulic fracturing fluids to fingerprint potential oil- and gas-related contamination sources.

Data Storage and Availability

Housing both surface-water and groundwater data in one database would facilitate and improve overall hydrologic interpretations. Publicly available data in a format that makes comparisons between sites straightforward—including table format, consistent unit reporting, and consistent laboratory analyses and methods—will improve the usability of the data for future sampling and characterization efforts and make additional interpretation more efficient.

Prevention of Sample Contamination

In both surface-water and groundwater sampling for organic constituents, contamination of samples was an issue. The source of contamination in the blank samples collected for surface water is unknown, but will be further investigated by DEQ. In the case of groundwater sampling, the source of contamination was the water used to clean equipment. Deionized water from one vendor was found to contain organics and alpha and beta particles despite being specifically designated for decontamination of sampling equipment. Investing in high-grade, certified, organic-free deionized water from a reputable vendor was found to be the best solution to prevent blank contamination. By testing the blank water prior to sample collection and immediately after, and promptly evaluating the results, the impact of the poor quality blank water can be reduced or eliminated.

ACKNOWLEDGMENTS

This work would not have been possible without the cooperation of landowners throughout central and eastern Montana who allowed access to wells, streams, and springs. The area Conservation Districts provided support and valuable feedback to ensure the information collected will meet the needs of local water users.

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APPENDIX A
LIST OF ANALYTES

Appendix A: List of analytes

Surface water		Groundwater	
Inorganic	Organic and radiochemistry	Inorganic (dissolved)	Organic and radiochemistry
Alkalinity, total as CaCO ₃	Acenaphthene	Acidity to 4.5	Aromatic (C11-C22) (ug/L)
Aluminum Dissolved	Acenaphthylene	Acidity to 8.3	Benzene
Aluminum Total Recoverable	Anthracene	Alkalinity	C5 to C8 Aliphatics
Arsenic Dissolved	Benz[a] anthracene	Aluminum	C9 to C10 Aromatics
Arsenic Total Recoverable	Benzene	Ammonia	C9 to C12 Aliphatics
Arsenic Total Recoverable Dry	Benzene	Antimony	Diesel Range Organics (DRO)
Barium Dissolved	Benzo(b) fluoranthene	Arsenic	Ethane
Barium Total Recoverable	Benzo[a] pyrene	Arsenic (III)	Ethene
Bicarbonate as HCO ₃ Total	Benzo[ghi] perylene	Arsenic (other)	Ethylbenzene
Boron Dissolved	Benzo[k] fluoranthene	Arsenic (V)	Gasoline Range Organics (GRO)
Boron Total Recoverable	C5-C8 Aliphatics	Barium	Gross Alpha
Bromide Total	C9-C12 Aliphatics	Berrilium	Gross Beta
Cadmium Dissolved	Chrysene	Boron	m+p-Xylenes
Cadmium Total Recoverable	Dibenz[a,h] anthracene	Bromide	Methane
Cadmium Total Recoverable	Ethylbenzene	Cadmium	Methyl tert-butyl ether (MTBE)
Calcium Free Available	Fluoranthene	Caesium	Naphthalene
Calcium Dissolved	Fluorene	Calcium	o-Xylene
Calcium Dissolved	Formaldehyde	Cerium	Surr: o-Terphenyl
Calcium Dissolved	Hydrocarbons, total purgeable	Chloride	Surr: Trifluorotoluene
Calcium Total Recoverable	Indeno[1,2,3-cd] pyrene	Chromium	Surr: VPH Aliphatics
Carbonate as CO ₃ Total	m,p-Xylene	CO ₃ (mg/l)	Surrogate
Chloride Total	Methane	Cobalt	Surr: VPH Aromatics
Chromium Dissolved	Methanol	Copper	Surrogate
Copper Dissolved	Methyl tert-butyl ether	Dissolved Inorganic Carbon	Toluene
Copper Total Recoverable	Naphthalene	Dissolved Organic Carbon	Total Extractable
Copper Total Recoverable Dry	Organic carbon	Floride	Hydrocarbons
Inorganic nitrogen (nitrate and nitrite) as N Total	o-Xylene	Gallium	Total Purgeable
Iron Dissolved	Petroleum hydrocarbons, total extractable	Hardness (mg/l)	Hydrocarbons
Iron Total Recoverable	Phenanthrene	HCO ₃ (mg/l)	Total Purgeable
Iron Total Recoverable Dry	Pyrene	Iron	Hydrocarbons
Lead Dissolved	Toluene	Kjeldahl-N (mg/l)	Total Purgeable
Lead Total Recoverable	Xylene	La (ug/l)	Hydrocarbons
Magnesium Dissolved	Gross alpha radioactivity	Lead	Xylenes, Total
Magnesium Total Recoverable	Gross beta radioactivity	Lithium	
Manganese Dissolved	Bismuth-212 Total	Magnesium	
Manganese Total Recoverable	Lead-210	Mangenes	
Mercury Total	Lead-212	Mercury	
Mercury Total Dry	Lead-214	Molybdenum	
Nickel Dissolved	Potassium-40	Neodymium	
Nickel Total Recoverable	Radium-226	Nickel	
Nutrient-nitrogen Total	Radium-228	Niobium	

Appendix A: List of analytes

Surface water		Groundwater	
Inorganic	Organic and radiochemistry	Inorganic (dissolved)	Organic and radiochemistry
Phosphate-phosphorus as P Total	Thorium-228	NO ₂ -N (mg/l)	
Potassium Free Available	Thorium-234	NO ₃ +NO ₂ -N (mg/l)	
Potassium Dissolved	Cesium-134	NO ₃ -N (mg/l)	
Potassium Total Recoverable	Cesium-137	OH ⁻ (mg/l)	
Selenium Dissolved	Protactinium-234	OPO ₄ -P (mg/l)	
Selenium Total Recoverable	Radium as Ra226	Palladium	
Sodium adsorption ratio	Radium-226	Potassium	
Sodium Free Available	Radium-228	Praseodymium	
Sodium Dissolved	Uranium-234/235/238	Rubidium	
Sodium Dissolved	Uranium-234	SAR	
Sodium Dissolved	Uranium-235	Selenium	
Sodium Total Recoverable	<u>Uranium-238</u>	Silver	
Strontium Dissolved		SiO ₂ (mg/l)	
Strontium Total Recoverable		SO ₃ (mg/l)	
Sulfate Total		SO ₄ (mg/l)	
Total dissolved solids		Sodium	
Total suspended solids		Strontium	
Zinc Dissolved		Thallium	
Zinc Total Recoverable		Thorium	
<u>Zinc Total Recoverable Dry</u>		Tin	
		Titianium	
		Total Dissolved Solids (mg/l)	
		Total N as N (mg/l)	
		Total Organic Carbon (mg/l)	
		Tungston	
		Uranium	
		Vanadium	
		Zinc	
		<u>Zirconium</u>	

APPENDIX B
SAMPLE LOCATIONS

Appendix B. Sample locations

MBMG GWIC ID / DEQ SITE ID	Latitude	Longitude	County	Type	Aquifer	Td
SURFACE WATER SAMPLES						
Y23BENPC03	47.6722	-104.0721		River/ Stream		
M50BMDYC11	48.1653	-104.6303		River/ Stream		
M50BMDYC12	48.2571	-104.7236		River/ Stream		
Y23CABNC08	46.6643	-104.5041		River/ Stream		
Y23CEDRC04	46.9081	-104.7157		River/ Stream		
M51CHLYC04	48.0109	-104.7360		River/ Stream		
M51CHLYC05	48.0922	-104.8770		River/ Stream		
Y23DRMFC01	47.3126	-105.0912		River/ Stream		
Y23DEERC01	47.2090	-104.8661		River/ Stream		
Y23DRSFC01	47.2660	-105.0568		River/ Stream		
M51FORMC04	47.9142	-104.0960		River/ Stream		
Y23FXEFC01	47.7031	-104.5945		River/ Stream		
Y23FXEFC02	47.7451	-104.6366		River/ Stream		
Y27LBVRC13	46.1571	-104.1469		River/ Stream		
M42LBOXC05	48.5279	-109.5330		River/ Stream		
M42LBOXC06	48.5260	-109.5314		River/ Stream		
M50MEDL01	48.4692	-104.4357		Lake		
Y22PENELC02	46.4537	-104.3320		River/ Stream		
Y22SNSTC04	46.4140	-104.5298		River/ Stream		
M52ULDSP01	48.9651	-104.2771		Spring		
M39WHTWC09	48.5504	-107.4269		River/ Stream		
M39WHTWC10	48.5450	-107.4620		River/ Stream		
M17WILOC03	48.6385	-111.4696		River/ Stream		
M17WILOC02	48.6482	-111.4740		River/ Stream		
M17WILOC04	48.6100	-111.4296		River/ Stream		
M17WLWFC01	48.4601	-111.4250		River/ Stream		
GROUNDWATER SAMPLES						
MBMG 2015 sampling						
26318	46.9441	-104.7788	DAWSON	WELL	211FXHL	365
27743	47.0163	-104.8219	DAWSON	WELL	111ALVM	33
27857*	47.0311	-104.8050	DAWSON	WELL	111TRRC	50
29237	47.0951	-104.7710	DAWSON	WELL	211HLCK	100
186354	47.0334	-104.8558	DAWSON	WELL	211HLCK	230
222411	46.8835	-104.7005	DAWSON	WELL		236
231796	47.0187	-104.8290	DAWSON	WELL	211HLCK	58
276839	47.1687	-104.9224	DAWSON	WELL	125FRUN	80
16570*	46.0747	-104.1894	FALLON	WELL	125FRUN	154
19127*	46.2877	-104.2252	FALLON	WELL	211FHHC	300
20506	46.3956	-104.3053	FALLON	WELL	211HLCK	280
20590*	46.3713	-104.1777	FALLON	WELL	211FXHL	100
20600*	46.3375	-104.1477	FALLON	WELL	211HLCK	40
21998*	46.4161	-104.5672	FALLON	WELL	211HLCK	441
22003	46.4072	-104.5409	FALLON	WELL	211FXHL	900
22005	46.4788	-104.4258	FALLON	WELL	211FXHL	1087
22015	46.4575	-104.4502	FALLON	WELL	211FXHL	985
22016*	46.4552	-104.4255	FALLON	WELL	125FRUN	120
22044*	46.4817	-104.3004	FALLON	WELL	211FXHL	80
23666	46.6396	-104.4894	FALLON	WELL	211FHHC	120
123789	46.3241	-104.2414	FALLON	WELL	211FXHL	150
130084	46.5627	-104.4241	FALLON	WELL	125FRUN	260
134414	46.4099	-104.5501	FALLON	WELL	211FHHC	660
139756	46.3649	-104.1720	FALLON	WELL	211FXHL	100

Appendix B. Sample locations

MBMG GWIC ID / DEQ SITE ID	Latitude	Longitude	County	Type	Aquifer	Td
150013	46.3557	-104.1747	FALLON	WELL	211FHHC	245
162134	46.3879	-104.4567	FALLON	WELL		810
183854	46.3701	-104.1852	FALLON	WELL	211FXHL	40
196628	46.4164	-104.5417	FALLON	WELL		440
204658	46.3423	-104.2719	FALLON	WELL		550
237042	46.3713	-104.1787	FALLON	WELL	211FXHL	105
264382	46.4080	-104.5736	FALLON	WELL	125FRUN	94
2926*	47.7575	-104.3241	RICHLAND	WELL	110ALVM	40
3232*	47.9872	-104.0791	RICHLAND	WELL	125TGRV	212
3233*	47.9727	-104.0652	RICHLAND	WELL	125TGRV	440
35876	47.6677	-104.1345	RICHLAND	WELL	211FHHC	1195
35881	47.6658	-104.1461	RICHLAND	WELL	110ALVM	50
35945	47.6752	-104.0736	RICHLAND	WELL	125FRUN	148
35949	47.6719	-104.0648	RICHLAND	WELL	211FXHL	1260
36466	47.7461	-104.3286	RICHLAND	WELL	125TGRV	124
36572	47.7475	-104.1841	RICHLAND	WELL	125FRUN	578
36693*	47.7150	-104.1636	RICHLAND	WELL	110ALVM	40
37319	47.8625	-104.2858	RICHLAND	WELL	211FXHL	1720
38750	47.9803	-104.0450	RICHLAND	WELL	211FHHC	1440
38755	47.9763	-104.0522	RICHLAND	WELL	211FHHC	1442
79510*	47.6658	-104.1464	RICHLAND	WELL	211FHHC	1380
121101*	47.8475	-104.7811	RICHLAND	WELL	125TGRV	90
121774	47.7477	-104.4719	RICHLAND	WELL	125TGRV	540
136651*	47.7569	-104.1260	RICHLAND	WELL	110ALVM	18.7
142083	47.8515	-104.2119	RICHLAND	WELL	112ALVM	40
142679	47.6665	-104.1062	RICHLAND	WELL	211FHHC	1500
151342*	47.7113	-104.1716	RICHLAND	WELL	110ALVM	116
152601	47.8198	-104.7206	RICHLAND	WELL	125FRUN	300
153570	47.7471	-104.4750	RICHLAND	WELL		478
185569	47.9624	-104.7634	RICHLAND	WELL		80
236187	47.8749	-104.6229	RICHLAND	WELL	125FRUN	300
238253	47.7483	-104.7196	RICHLAND	WELL	125FRUN	390
239702*	47.6307	-104.2498	RICHLAND	WELL	112SNGR	107
274382	47.6739	-104.0904	RICHLAND	WELL	211FHHC	1243
279960	47.6008	-104.2556	RICHLAND	WELL	111TRRC	60
3483*	48.1463	-104.1969	ROOSEVELT	WELL	211FHHC	1380
39482*	48.1056	-104.0849	ROOSEVELT	WELL	125FRUN	77
40257	48.1540	-104.5198	ROOSEVELT	WELL		220
40259	48.1522	-104.5170	ROOSEVELT	WELL	112OTSH	84
40296	48.1993	-104.2119	ROOSEVELT	WELL	125FRUN	162
40297*	48.2097	-104.2058	ROOSEVELT	WELL	125FRUN	150
41327*	48.2779	-104.6746	ROOSEVELT	WELL	125FRUN	133
42364*	48.3474	-104.2866	ROOSEVELT	WELL	125FRUN	336
191235	48.1972	-105.1044	ROOSEVELT	WELL		65
195335	48.1993	-104.2173	ROOSEVELT	WELL		392
206201	48.3469	-104.2857	ROOSEVELT	WELL		102
206406*	48.3382	-104.5407	ROOSEVELT	WELL	125FRUN	105
230563	48.2806	-105.1779	ROOSEVELT	WELL		47
239610*	48.1720	-104.2415	ROOSEVELT	WELL	112ALVM	177
249699*	48.2900	-104.1786	ROOSEVELT	WELL	125FRUN	360
262046*	48.1991	-104.6506	ROOSEVELT	WELL	125FRUN	
262050*	48.2489	-104.3448	ROOSEVELT	WELL	125FRUN	
268638	48.1666	-104.5179	ROOSEVELT	WELL		156

Appendix B. Sample locations

MBMG GWIC ID / DEQ SITE ID	Latitude	Longitude	County	Type	Aquifer	Td
284198	48.3397	-104.0574	ROOSEVELT	WELL		
704754*	48.2287	-104.3446	ROOSEVELT	WELL	125FRUN	70
3766*	48.4908	-104.4542	SHERIDAN	WELL	112ALVM	233
3767*	48.4908	-104.4543	SHERIDAN	WELL	112OTSH	118
3858*	48.6138	-104.1444	SHERIDAN	WELL	112OTSH	130
3869*	48.5841	-104.1429	SHERIDAN	WELL	112OTSH	130
3871*	48.5855	-104.1454	SHERIDAN	WELL	112OTSH	98
3872*	48.5855	-104.1455	SHERIDAN	WELL	125FRUN	330
3947*	48.6855	-104.1440	SHERIDAN	WELL	112OTSH	110
43095*	48.4325	-104.4816	SHERIDAN	PETWELL	211FHHC	1160
154904*	48.5215	-104.5006	SHERIDAN	WELL	211FHHC	840
157676	48.5070	-104.4353	SHERIDAN	WELL	125FRUN	260
221574*	48.9876	-104.1044	SHERIDAN	WELL	112TILL	28
221691*	48.5262	-104.2575	SHERIDAN	WELL	112OTSH	38
221722*	48.9547	-104.1878	SHERIDAN	WELL	112TILL	28
262870	48.9741	-104.0720	SHERIDAN	WELL		50
262871	48.9054	-104.0601	SHERIDAN	WELL	112OTSH	115
262872	48.7969	-104.0677	SHERIDAN	WELL	112OTSH	50
271681	48.9906	-104.0951	SHERIDAN	WELL		95
273937*	48.6061	-104.1850	SHERIDAN	WELL	112OTSH	136
283920	48.4917	-104.5181	SHERIDAN	WELL	112OTSH	64
890422*	48.7961	-104.1436	SHERIDAN	WELL	112TILL	42
890933*	48.8485	-104.1000	SHERIDAN	WELL	112OTSH	17
MBMG 2016 sampling						
278374	46.8679	-104.7195	DAWSON	WELL		780
29247	47.0951	-104.7602	DAWSON	WELL	211HLCK	80
287136	47.0938	-104.7590	DAWSON	WELL		120
287744	47.2208	-105.1522	DAWSON	WELL		21
217829	47.1976	-104.9999	DAWSON	WELL		40
282661	47.1976	-104.9999	DAWSON	WELL		200
223034	47.3097	-104.9149	DAWSON	WELL		460
159228	47.4281	-104.8948	DAWSON	WELL		75
287743	47.4121	-104.8173	DAWSON	WELL		33
32661	47.3894	-104.8130	DAWSON	WELL	125TGRV	320
130345	47.6802	-105.0527	DAWSON	WELL	125TGRV	37
284575	46.2096	-104.3310	FALLON	WELL		1080
280431	46.1665	-104.2205	FALLON	WELL		120
227360	46.2616	-104.2540	FALLON	WELL		520
221112	46.2393	-104.2545	FALLON	WELL		260
22009	46.4757	-104.4572	FALLON	WELL	125FRUN	30
22034	46.4133	-104.5121	FALLON	WELL	211FXHL	906
22033	46.4133	-104.5121	FALLON	WELL	211HLCK	360
145248	46.4255	-104.2253	FALLON	WELL		100
246773	46.8374	-104.6858	PRAIRIE	WELL		103
36258	47.7397	-105.0748	RICHLAND	WELL	125TGRV	75
242663	47.7719	-104.6431	RICHLAND	WELL		250
3019*	47.8663	-104.6583	RICHLAND	WELL	125TGRV	46
247437	47.9531	-105.1109	RICHLAND	WELL		201
128173	47.9630	-105.1086	RICHLAND	WELL	211HLCK	100
272365	47.9963	-104.4161	RICHLAND	WELL		295
223679	47.9976	-104.4181	RICHLAND	WELL		245
38693*	47.9958	-104.4161	RICHLAND	WELL	125TGRV	140
194313	48.2652	-105.4401	ROOSEVELT	WELL		80

Appendix B. Sample locations

MBMG GWIC ID / DEQ SITE ID	Latitude	Longitude	County	Type	Aquifer	Td
704694	48.2641	-105.4391	ROOSEVELT	WELL	211HLCK	65
251722	48.4062	-105.0843	ROOSEVELT	WELL		72
203971	48.4056	-105.1460	ROOSEVELT	WELL		120
44354	48.5054	-105.4312	ROOSEVELT	WELL	211HLCK	180
280621	48.4256	-104.4215	SHERIDAN	WELL	112ALVM	59
280618*	48.4251	-104.3890	SHERIDAN	WELL	112ALVM	140
280652*	48.4911	-104.4320	SHERIDAN	WELL	112OTSH	140
221651*	48.4906	-104.4104	SHERIDAN	WELL	112ALVM	248
221649*	48.4907	-104.4103	SHERIDAN	WELL	112OTSH	168
280641*	48.4835	-104.4104	SHERIDAN	WELL	112OTSH	140
280650	48.5240	-104.2636	SHERIDAN	WELL	112OTSH	90
280645*	48.5061	-104.3113	SHERIDAN	WELL	112OTSH	120
280643*	48.4840	-104.3542	SHERIDAN	WELL	112ALVM	248
44466	48.5496	-104.1396	SHERIDAN	WELL	112OTSH	91
3772*	48.5550	-104.1818	SHERIDAN	WELL	125FRUN	318
3773*	48.5550	-104.1819	SHERIDAN	WELL	112OTSH	143
44473	48.5470	-104.1492	SHERIDAN	WELL	112OTSH	100
3777*	48.5338	-104.2056	SHERIDAN	WELL	112OTSH	80
221602*	48.6214	-104.1512	SHERIDAN	WELL	112OTSH	108
221597*	48.6212	-104.1217	SHERIDAN	WELL	112OTSH	128
284270	48.7217	-104.4096	SHERIDAN	WELL		105
45929	48.7163	-104.3606	SHERIDAN	WELL	125FRUN	130
3941*	48.6505	-104.3411	SHERIDAN	WELL	125TGRV	327
215220	48.6936	-104.1213	SHERIDAN	WELL	112OTSH	140
215223	48.6791	-104.0994	SHERIDAN	WELL	112OTSH	140
46940	48.7386	-104.3490	SHERIDAN	WELL		199
206533*	48.7805	-104.0634	SHERIDAN	WELL	112OTSH	80
206546*	48.7515	-104.0779	SHERIDAN	WELL	112OTSH	120
275864	48.9207	-104.7053	SHERIDAN	WELL		264
MSCA sampling 2014 through 2016						
282364	48.6860	-105.6077	DANIELS	WELL		
703510	48.8085	-105.8491	DANIELS	WELL		124
46607	48.8072	-105.6443	DANIELS	WELL	110ALVM	35
46617	48.8128	-105.6274	DANIELS	WELL	125FRUN	60
266680	48.8303	-105.7753	DANIELS	WELL		460
47553	48.8817	-105.4241	DANIELS	WELL	112TILL	54
703740	48.8401	-105.0807	DANIELS	WELL		112
29033	47.1725	-104.7976	DAWSON	WELL	125FRUN	50
30256	47.2667	-105.0618	DAWSON	WELL	125TGRV	102
702410	47.2375	-104.9125	DAWSON	WELL	125FRUN	33
137915	47.2376	-104.9126	DAWSON	WELL	125FRUN	200
250390	47.2262	-104.8947	DAWSON	WELL	211FHHC	700
282972	47.1975	-104.8562	DAWSON	WELL		
198435	47.1839	-104.8236	DAWSON	WELL		360
249758	47.3114	-105.0217	DAWSON	WELL		205
31497	47.2847	-105.0145	DAWSON	WELL	125TGRV	244
279743	46.8615	-109.0907	FERGUS	SPRING		
279677	47.0049	-109.7033	FERGUS	WELL		20
124132	46.9343	-109.5438	FERGUS	WELL		108
279674	46.9320	-109.5101	FERGUS	SPRING		
188806	46.9713	-109.4763	FERGUS	WELL	217KOTN	360
283680	46.9617	-109.4722	FERGUS	WELL		
283672	46.9876	-109.2744	FERGUS	WELL		

Appendix B. Sample locations

MBMG GWIC ID / DEQ SITE ID	Latitude	Longitude	County	Type	Aquifer	Td
25940	46.9944	-108.6653	FERGUS	WELL		1128
223592	47.0736	-109.5065	FERGUS	WELL		380
257754	47.0692	-109.5802	FERGUS	WELL		60
177778	47.0339	-109.5023	FERGUS	WELL		380
28347	47.1234	-109.6872	FERGUS	WELL		20
28396	47.1020	-109.4578	FERGUS	WELL		140
29816	47.2343	-109.4061	FERGUS	WELL		138
277314	47.2209	-109.4786	FERGUS	WELL		60
279679	47.1931	-109.3535	FERGUS	WELL		160
279678	47.1443	-109.3565	FERGUS	SPRING		
30829	47.3112	-109.1835	FERGUS	WELL		392
89179	48.6394	-112.2387	GLACIER	WELL	211VRGL	205
89203	48.6382	-112.2393	GLACIER	WELL	211TMDC	197
89440	48.7275	-112.3653	GLACIER	WELL		175
247510	48.8729	-113.3654	GLACIER	WELL		200
150154*	48.9482	-112.3051	GLACIER	WELL	211TMDC	125
180117	47.0775	-110.2229	JUDITH BASIN	WELL	217KOTN	65
187641	47.0699	-110.1566	JUDITH BASIN	WELL	217KOTN	703
26598	47.0806	-110.1580	JUDITH BASIN	WELL	217KOTN	686
279176	47.0157	-110.1594	JUDITH BASIN	WELL	217KOTN	
248655	47.1722	-110.2000	JUDITH BASIN	WELL	211CLRD	100
28143	47.5754	-110.2201	JUDITH BASIN	WELL	211CLRD	210
28318	47.1505	-110.0016	JUDITH BASIN	WELL	217KOTN	1120
279175	47.1151	-110.0072	JUDITH BASIN	SPRING	112SNGR	
196644	47.2294	-110.2219	JUDITH BASIN	WELL	110TRRC	60
29723	47.2403	-110.2372	JUDITH BASIN	WELL	110TRRC	15
291486	47.5844	-105.6152	MCCONE	WELL		100
252031	47.6107	-105.5669	MCCONE	WELL		102
35534	47.6172	-105.6002	MCCONE	WELL		150
130354	47.9078	-105.2091	MCCONE	WELL		38
257488	48.0704	-105.2444	MCCONE	WELL		85
42005	48.3654	-107.6180	PHILLIPS	WELL	110ALVM	53
122380	48.2605	-112.3381	PONDERA	WELL		120
35683	47.6898	-104.3604	RICHLAND	WELL	125FRUN	300
217571	47.6339	-104.2261	RICHLAND	WELL		
291940	47.6805	-104.1652	RICHLAND	WELL		
284015	47.7908	-104.0907	RICHLAND	WELL		
163340	47.8660	-104.6075	RICHLAND	WELL		200
37249	47.8647	-104.4674	RICHLAND	WELL	125FRUN	495
279185	47.8490	-104.2694	RICHLAND	WELL		120
287543	47.8475	-104.0496	RICHLAND	WELL		
291939	47.7985	-104.0584	RICHLAND	WELL		
291938	47.7986	-104.0586	RICHLAND	WELL		
37875*	47.9021	-105.1703	RICHLAND	WELL	110ALVM	28
38021	47.8898	-104.5492	RICHLAND	WELL	125TGRV	242
268991	47.9240	-104.5370	RICHLAND	WELL		100
203025	47.8970	-104.2017	RICHLAND	WELL		150
121105	47.8682	-104.2698	RICHLAND	WELL	125TGRV	195
291941	47.9207	-104.1292	RICHLAND	WELL		
128171	47.8789	-104.1178	RICHLAND	WELL	125TGRV	156
121169	48.0042	-104.9583	RICHLAND	WELL	211FHHC	353
38568	47.9701	-104.9943	RICHLAND	WELL	125TLCK	353
291942	47.9634	-104.9147	RICHLAND	WELL		

Appendix B. Sample locations

MBMG GWIC ID / DEQ SITE ID	Latitude	Longitude	County	Type	Aquifer	Td
38701	47.9731	-104.3968	RICHLAND	WELL	125TGRV	150
125716*	47.9694	-104.2200	RICHLAND	WELL	125FRUN	290
261518	48.1036	-104.6479	RICHLAND	WELL		195
152494	48.1093	-104.5360	RICHLAND	WELL		315
251847	48.1596	-104.8554	ROOSEVELT	WELL		230
704434	48.1625	-104.8490	ROOSEVELT	WELL		36
704436	48.1622	-104.8480	ROOSEVELT	WELL		36
704437	48.1592	-104.8565	ROOSEVELT	WELL		
40285	48.1509	-104.3833	ROOSEVELT	WELL	125FRUN	130
40286	48.1476	-104.3827	ROOSEVELT	WELL	125FRUN	140
704718	48.2628	-105.0996	ROOSEVELT	WELL	110ALVM	23
3546*	48.2627	-104.6728	ROOSEVELT	WELL	125FRUN	258
41388	48.2536	-104.4809	ROOSEVELT	WELL	125FRUN	95
249699*	48.2900	-104.1786	ROOSEVELT	WELL	125FRUN	360
42274	48.3600	-104.8963	ROOSEVELT	WELL	125FRUN	287
166666	48.3553	-104.2985	ROOSEVELT	WELL		260
255044	48.5295	-104.4095	SHERIDAN	WELL	112OTSH	444
252906	48.6395	-104.1838	SHERIDAN	WELL	112ALVM	130
291935	48.8076	-104.3050	SHERIDAN	WELL		
48280	48.9694	-104.1936	SHERIDAN	WELL	112DRFT	40
168148*	48.0713	-112.0861	TETON	SPRING	110ALVM	
291348	48.5447	-106.0236	VALLEY	WELL		120
274541	48.6075	-106.3143	VALLEY	WELL		30
125231	48.7280	-106.0464	VALLEY	WELL		44
291349	48.7732	-106.3566	VALLEY	WELL		

* Indicates the site has multiple samples

Appendices C–G are available for separate download from our website, in pdf format.