INVESTIGATION OF THE INORGANIC GROUNDWATER QUALITY IN THE WEST YELLOWSTONE BASIN, GALLATIN COUNTY, MONTANA

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Cover photo: View of the West Yellowstone Basin looking southeast along the Madison Arm from Horse Butte Peninsula. Photo by Ann Hanson, MBMG.

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LIST OF ACRONYMS

DEQ	Department of Environmental Quality (Mont.)
EPA	Environmental Protection Agency (U.S.)
GWAP	Ground Water Assessment Program
GWIC	Ground Water Information Center
GWIP	Ground Water Investigations Program
LMWL	Local Meteoric Water Line
MBMG	Montana Bureau of Mines and Geology
MCL	Maximum Contaminant Level
SMCL	Secondary Maximum Contaminant Level
TDS	Total Dissolved Solids
USGS	U.S. Geological Survey
VSMOW	Vienna Standard Mean Ocean Water
YCGA	Yellowstone Controlled Groundwater Area
YNP	Yellowstone National Park

UNIT ABBREVIATIONS

gpm	gallons per minute
meq/L	milliequivalents per liter
mg/L	milligrams per liter
mV	millivolts
µg/L	micrograms per liter
pCi/L	picocuries per liter
‰	per mil (or) parts per thousand

ABSTRACT

The West Yellowstone Basin is located predominantly in Gallatin County, Mont.; it extends west from Yellowstone National Park (YNP, Teton and Park Counties, Wyo.) and north from the Madison Plateau to Hebgen Lake (Mont.). Previous groundwater samples have measured arsenic and fluoride concentrations above the Environmental Protection Agency (EPA) drinking water standards in the southwest part of the basin. To begin to address these concerns, the Montana Bureau of Mines and Geology (MBMG) Ground Water Investigation Program (GWIP) completed an investigation of inorganic groundwater quality in the West Yellowstone Basin outside of YNP. For this study, 42 wells completed in bedrock or basin-fill aquifers were sampled for major ions, trace elements, radon, and stable isotopes (oxygen, hydrogen, and strontium) in the fall of 2021, and previous and ongoing MBMG groundwater sampling data were compiled from 24 additional sites. Bedrock aquifers occur along the basin margins and are composed of Precambrian metamorphic rocks, Paleozoic–Mesozoic sedimentary rocks, and Tertiary–Quaternary volcanic rocks. The basin-fill aquifer is predominately composed of Quaternary outwash deposits, with till along the west–southwest margin and alluvial fan deposits along the northwest margin.

Overall, the sampling results from the 66 sites show the water is dilute with low total dissolved solids (median concentration = 133 mg/L) and meets EPA drinking water standards with the exception of arsenic, fluoride, iron, and manganese. Arsenic exceeded the EPA Maximum Contaminant Level (MCL) of 10 µg/L in 11 samples from sites near the Madison River and in some areas where the groundwater had low reduction/oxidation potential. Fluoride exceeded the EPA secondary maximum contaminant level (SMCL) of 2 mg/L in 17 samples, with 5 of the samples exceeding the EPA MCL of 4 mg/L. These samples were from wells completed in outwash deposits and volcanic bedrock; the highest fluoride concentrations were near the Madison River. Calculation of Kendall's τ shows arsenic has a statistically significant, positive correlation with fluoride in the basin. Iron exceeded the EPA SMCL of 0.3 mg/L in two samples. Manganese exceeded the EPA SMCL of 0.05 mg/L in six samples. Groundwater radon concentrations ranged from 221 to 3,850 pCi/L, with one sample at approximately 35,000 pCi/L; concentrations were generally higher in bedrock aquifers than in basin-fill aquifers. Hydrogen and oxygen isotope samples show that water recharging the bedrock and basin-fill aquifers is primarily from winter snowpack. Groundwater in the center of the basin, near the Madison River and Horse Butte Peninsula, has hydrogen and oxygen isotopes that are relatively depleted compared to groundwater near the northern and southwestern margins. Distinct groundwater strontium isotope ratios in the study area were consistent with values published for local bedrock units, suggesting groundwater flows from bedrock units on the margins of the basin to locally derived, basin-fill deposits.

INTRODUCTION

The West Yellowstone Basin is located predominantly in Gallatin County, Mont.; it extends west from Yellowstone National Park (YNP, Teton and Park Counties, Wyo.) and north from the Madison Plateau to the northwestern point of Hebgen Lake (fig. 1). The Town of West Yellowstone (hereafter referred to as West Yellowstone) is the basin's main population center and serves as a gateway community for the West Entrance to YNP. The population of West Yellowstone remained relatively consistent at approximately 1,270 permanent residents between 2010 and 2020 (U.S. Census Bureau, 2022). However, in the summer, the tourist population increases to as high as 10,000 people. With both winter and summer tourism popular in the area, up to four million people visit West Yellowstone each year (NPS, 2022a; Town of West Yellowstone, 2022).

Groundwater serves as the municipal supply for West Yellowstone and provides domestic water for residences around Denny Creek and the South Fork of the Madison River, the Madison and Grayling Arms of Hebgen Lake, and the Horse Butte Peninsula (fig. 1). According to the Montana Bureau of Mines and Geology (MBMG) Ground Water Information Center (GWIC), there are approximately 840 wells in the basin, with about 200 wells drilled since 2000 (MBMG, 2022). Most wells and springs in the West Yellowstone Basin are within the Yellowstone Controlled Groundwater Area (YCGA; Metesh and Kougioulis, 1999; Metesh, 2004). The YCGA includes land in Montana that is adjacent to YNP and serves as a buffer to protect hydrothermal features within YNP from

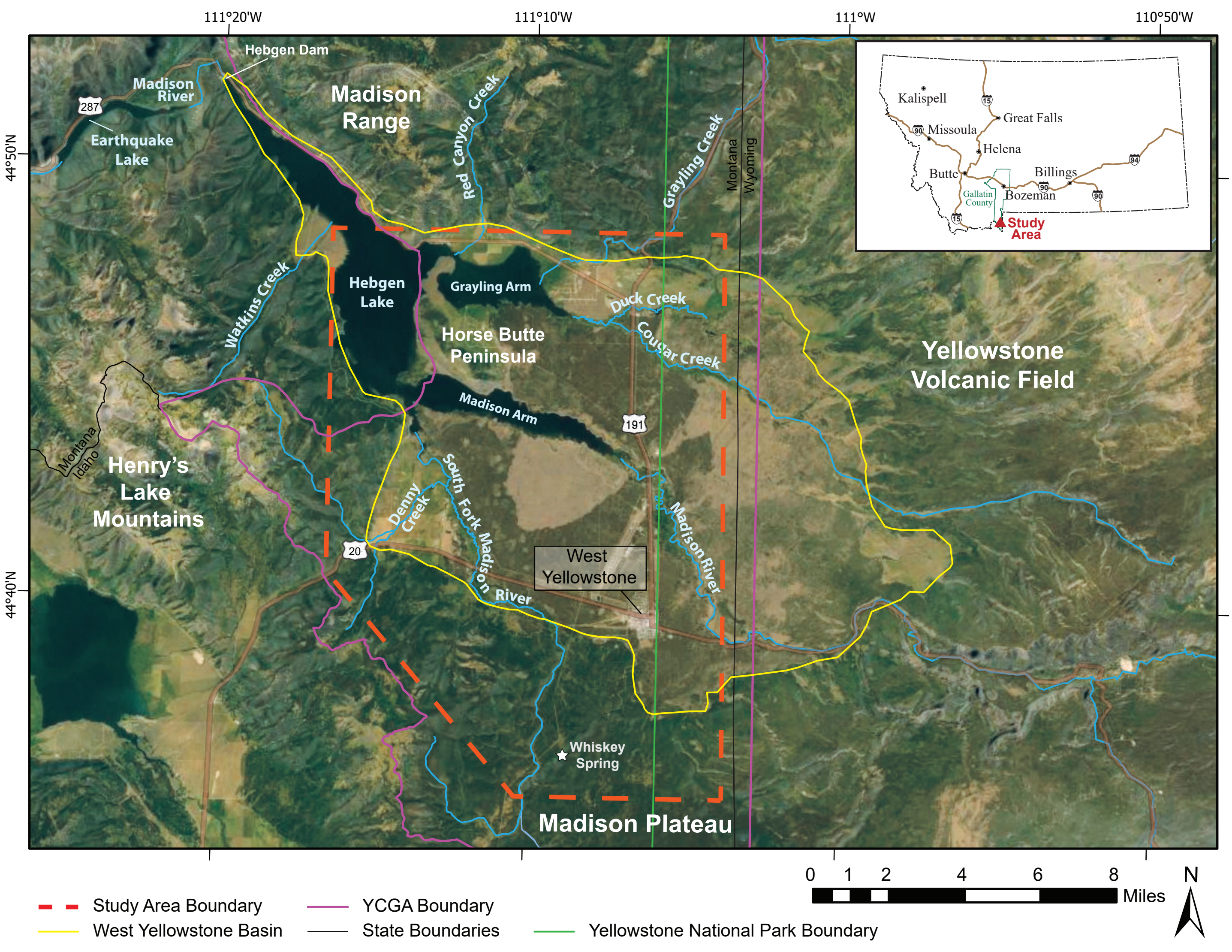


Figure 1. The West Yellowstone Basin is approximately 140 mi^2 and is bordered by the Madison Range to the north, Yellowstone Volcanic Field to the east, Madison Plateau to the south, and Henry's Lake Mountains to the west. The West Yellowstone Basin is almost entirely within the Yellowstone Control Groundwater Area (YCGA).

development outside of the park (fig. 1). The MBMG maintains a monitoring network within the YCGA to track long-term groundwater level and water-quality changes (National Park Service Compact, 85-20-401 MCA).

Concentrations of naturally occurring arsenic that exceed the Environmental Protection Agency (EPA) maximum contaminant level (MCL) have been documented in groundwater near the Madison River (Carstarphen and LaFave, 2018; English and others, 2021). Additionally, concentrations of naturally occurring fluoride that exceed the EPA MCL and/or secondary maximum contaminant level (SMCL) have been documented throughout the basin (LaFave and others, 2017; Johnson, 2020; Brown, 2022). One groundwater sample from an artesian well located along the west side of the basin had radon concentrations above the proposed EPA MCL for groundwater radon (Carstarphen and LaFave, 2018). Prior to this study, only nine wells in the basin had been sampled for radon (Carstarphen and LaFave, 2018), so the extent of elevated levels of radon is unknown.

Purpose and Scope

The purpose of the project was to better understand the inorganic groundwater chemistry in the West Yellowstone Basin and identify locations where groundwater constituents exceeded EPA inorganic drinking water standards. This report presents the results for water-quality sampling of wells and springs in the West Yellowstone Basin (fig. 1). The sampled sites were selected based on location within the basin and landowner access; all sampled sites were outside the YNP boundary. Samples were collected in the fall of 2021 and analyzed for major ions and trace elements; radon; and isotopes of oxygen, hydrogen, and strontium. Additional samples previously collected by the MBMG in the West Yellowstone Basin were also used for interpretation.

Description of the West Yellowstone Basin

The West Yellowstone Basin is a structural and topographic basin that covers an area of about 140 mi^2 (fig. 1). The term “West Yellowstone Basin” was first used by the USGS (1964) in reports following the 1959 Hebgen Lake earthquake. The basin is bounded by the Madison Plateau to the south and southeast, the Henry’s Lake Mountains to the west and southwest, and the Madison Range to the northwest and north; the basin floor is delineated by the topographic change between the bedrock and surficial units (figs. 1, 2). The eastern edge of the basin is not as well defined, but is considered here to be where the hilly terrain of the Yellowstone volcanic field meets the relatively flat basin floor.

Geologic Setting

The West Yellowstone Basin is bounded by normal faults on the south, west, and north sides, and has been forming by northeast–southwest crustal extension since the late Tertiary (Witkind and others, 1964; Myers and Hamilton, 1964). Precambrian through Quaternary bedrock surrounds the basin and includes metamorphic, sedimentary, and volcanic rocks (fig. 2). The structure is complex, with folding and/or faulting of all the bedrock formations. The Precambrian metamorphic rocks form the crystalline basement and include granite, gneiss, schist, amphibolite, and quartzite (O’Neill and Christiansen, 2002, 2004). The Precambrian basement rocks crop out along the west and northwest margins of the basin and on the west end of Horse Butte Peninsula (fig. 2). Isolated outcrops are also mapped on the north and northeastern side of the basin, where they are blanketed by Tertiary–Quaternary volcanic rocks. Paleozoic and Mesozoic sedimentary rocks are mapped near the southwest side of the basin, and along the northwest shore and Grayling Arm area of Hebgen Lake (fig. 2). To the southwest, these sedimentary rocks are folded and partially covered by Tertiary–Quaternary volcanic rocks. Along the northwest shore and Grayling Arm of Hebgen Lake, the Paleozoic and Mesozoic rocks have been folded and thrust towards the northeast (Witkind and others, 1964; O’Neill and Christiansen, 2002, 2004). The Tertiary–Quaternary volcanic rocks are mapped all around the margins of the basin (fig. 2). These rocks include Tertiary volcanic rocks of the Absaroka Supergroup (primarily andesitic), the Quaternary Huckleberry Ridge and Lava Creek Tuffs, and Quaternary Plateau rhyolite and basalt lava flows. The rhyolite and basalt lava flows are younger than the tuffs (Hamilton, 1964; Christiansen, 2001).

Surficial deposits in the West Yellowstone Basin are dominated by Pleistocene till and outwash from the Bull Lake (ca. 150,000 years ago) and Pinedale (ca. 30,000 years ago) glaciations (Pierce, 1979; O’Neill and Christiansen, 2002, 2004). During the Bull Lake glaciation ice flowed into the basin from

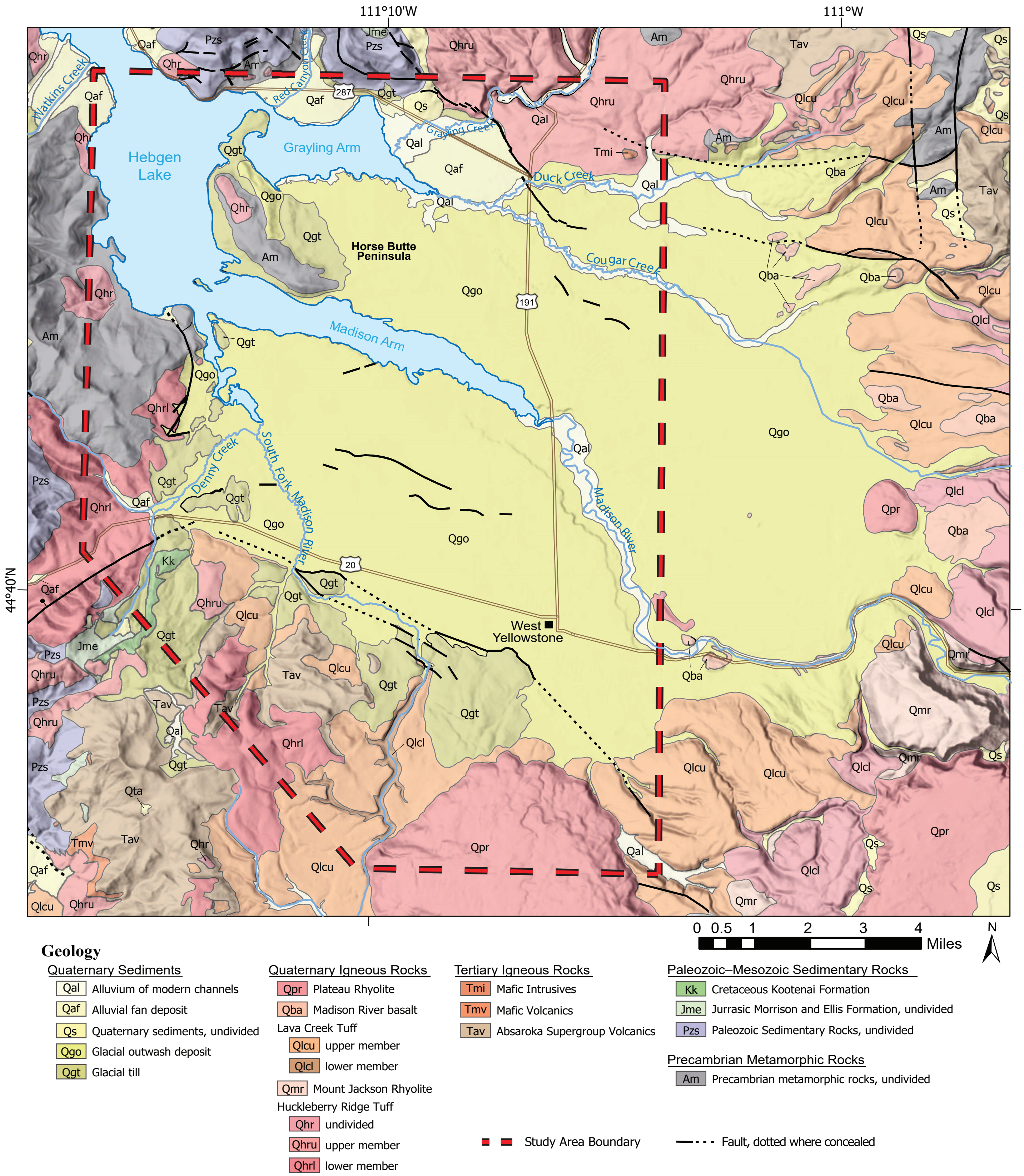


Figure 2. Geologic map of the study area modified from O'Neill and Christiansen (2004) and Christiansen (2001). Major geologic units include the Quaternary glacial outwash deposits and the Quaternary volcanic rocks of the Yellowstone Plateau volcanic field (e.g., Plateau Rhyolite, Lava Creek Tuff, and Huckleberry Ridge Tuff). Note that the ~2.1 Ma Huckleberry Ridge Tuff (O'Neill and Christiansen, 2004) is now considered Quaternary according to the most recent geologic timeline divisions.

the southeast and northeast, depositing terminal and lateral moraines along the south, west, and north sides of the basin and around Horse Butte Peninsula (fig. 2; Pierce, 1979, fig. 9, p. 17). Glacial lake bed sediments interbedded with till are described by Richmond (1964), and were probably deposited behind the moraines shortly after recession of the Bull Lake ice. The Bull Lake glacial deposits are overlain by younger colluvium and alluvium along the north side of the basin, Pinedale outwash deposits through the central part of the basin, and Yellowstone Plateau rhyolite flows in the southern part of the basin (fig. 2; Richmond, 1964). During the Pinedale glaciation a lobe of ice flowed southwestward to the eastern margin of the basin, and another lobe flowed down the Madison River Canyon to the southeast margin of the basin (Pierce, 1979). Although the ice did not flow into the basin, extensive outwash deposits consisting of obsidian and rhyolite sands were deposited by glacial meltwater (Pierce, 1979).

Hydrogeologic Setting

Groundwater occurs in the bedrock units and basin-fill deposits, and flows from the recharge areas in the surrounding mountains toward the discharge area at the regional topographic low, Hebgen Lake. Most of the groundwater and surface water exits the basin through the bedrock canyon at Hebgen Dam (fig. 1). Regionally, groundwater flow is assumed to follow surface topography with localized flow towards the rivers and creeks. The basin is drained by the upper Madison River, South Fork of the Madison River, Duck Creek, Cougar Creek, Grayling Creek, Red Canyon Creek, Denny Creek, and Watkins Creek (fig. 1). These streams likely provide some recharge to the basin-fill deposits along losing reaches; however, this has not been documented. Within the basin-fill there are surficial unconfined aquifers and localized confined aquifers at depth. Approximately 3 ft of snowpack accumulates on the basin floor each winter (Western Regional Climate Center for West Yellowstone, MT, 2022), and spring snowmelt (usually in April) likely provides significant areal recharge to the basin-fill sediments.

METHODS

Data Management

Data collected for this investigation are archived in MBMG's GWIC database (http://mbmggwic.mtech.edu/), and summarized in appendix A, which is available as a downloadable Excel spreadsheet from the website for this publication. Groundwater sampling locations referred to in this report are denoted by their GWIC identification numbers (e.g., well 247335 and spring 183242).

Water-Quality Sampling

Water-quality data were obtained from 66 sites (58 wells, 8 springs). Forty-two sites were sampled during the fall of 2021 as part of this study, while 24 sites were sampled from 2010 to 2021 as part of other MBMG studies (fig. 3). About 88 percent of the study area is public land with few wells (fig. 3); therefore, samples were generally collected from the four residentially developed areas: (1) the northern part of the basin near Duck Creek and Grayling Creek, (2) Horse Butte Peninsula, (3) the southeast part of the basin near West Yellowstone and the upper Madison River, and (4) the southwest part of the basin near the South Fork of the Madison River and Denny Creek (fig. 3). For this report, these areas will be referenced as: the "Grayling–Duck Creek," "Horse Butte Peninsula," "Madison River," and "South Fork–Denny Creek" areas, respectively. Most samples were from sites used for domestic purposes (47) or public water supplies (12). Other uses included stockwater (1), monitoring (1), and unknown (5).

At each site water-quality field parameters [specific conductance, dissolved oxygen, pH, temperature, and reduction/oxidation potential (redox)] were measured and samples were collected in accordance with MBMG standard operating procedures (Gotkowitz, 2022). All samples were analyzed by the MBMG Analytical Laboratory for major ions, trace metals, and nutrients (appendix A, table A.1). Sample results were compared to EPA drinking water standards. Although EPA drinking water standards only apply to public water supplies, they are useful benchmarks to assess private water supplies. Samples from 62 of the 66 sites were analyzed for stable isotopes of hydrogen and oxygen (hereafter referred to as stable water isotopes; appendix A, table A.2). Four sites that were sampled as part of earlier studies did not include stable water

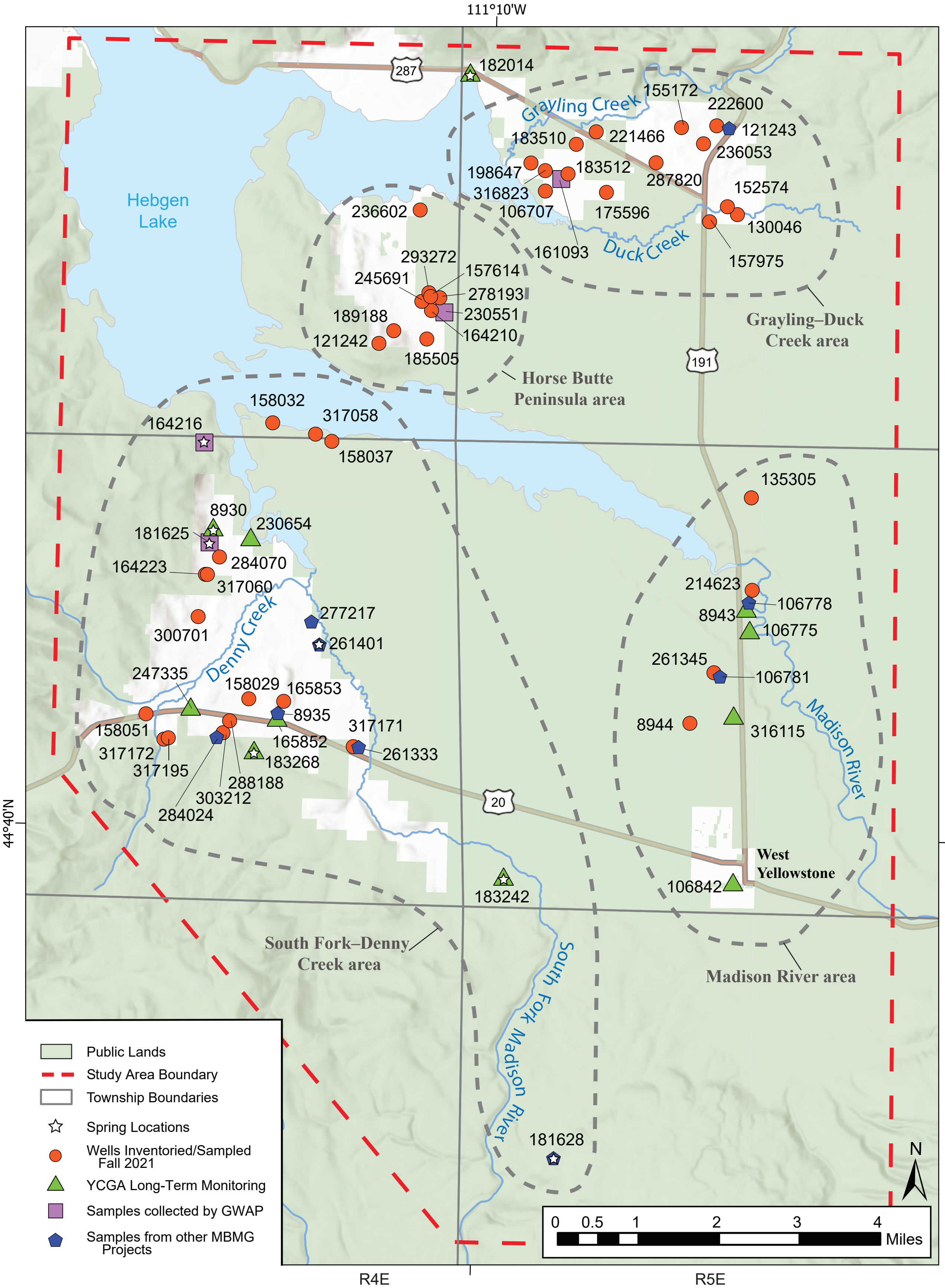


Figure 3. Inorganic water-quality sampling sites from this study (collected fall 2021) and previous MBMG studies (Carstarphen and LaFave, 2018; YCGA monitoring and inventories, etc.). Sampling locations were broadly grouped into four regions: the Grayling−Duck Creek, Horse Butte Peninsula, Madison River, and South Fork–Denny Creek areas.

isotope analyses. The stable water isotope values are reported in delta (δ) notation (in per mil, ‰) relative to Vienna Standard Mean Ocean Water (VSMOW).

Samples were also collected for strontium isotopes (^{87}Sr and ^{86}Sr) from 31 of the 66 sites. Twenty-seven of the samples were collected during the fall of 2021 as part of this study, while 4 were previously analyzed samples from the YCGA (English, unpublished data). Strontium isotope samples were filtered into 500-mL high-density polyethylene bottles and kept at or below 4°C. The samples were analyzed by the University of Georgia Center for Applied Isotope Studies Plasma Chemistry Laboratory. Strontium isotope values are reported as a strontium ratio $^{87}Sr/^{86}Sr$. Error (2σ) on the strontium ratios ranged from 0.000018 to 0.000035 (appendix A, table A.3). Strontium isotopes from the MBMG Analytical Laboratory were interpreted in combination with the strontium concentrations from the University of Georgia Center for Applied Isotope Studies Plasma Chemistry Laboratory.

Radon (^{222}Rn) samples were collected from 40 of the 66 sites in the fall of 2021. Samples were collected following the procedures described in Timmer (2020). Samples were collected in a 125-mL glass bottle with a Teflon™-lined cap. Water from the well was discharged into a 5-gal bucket and allowed to flow continually while sampling. The sample bottle was placed near the bottom of the bucket and then uncapped and filled. The samples were checked to ensure there were no air bubbles, labeled with the time of collection, kept on ice, and transported to the laboratory within 24 h. Samples were analyzed by the MBMG Analytical Laboratory using a liquid scintillation counter (Timmer, 2020). Six additional radon samples previously collected in the study area between 1994 and 1998 were used to assess radon levels in groundwater (appendix A, table A.4).

Quality Assurance

Duplicate samples were collected to assess the analytical reproducibility. Duplicates for inorganic elements, water isotopes, and radon were collected successively during sampling. Three duplicates were collected for inorganic elements and water isotopes, one duplicate was collected for strontium isotopes, and two duplicates were collected for radon. Relative percent differences were greater than 10% for only one major or trace element from each duplicate (sodium for 106707, boron for 165853, and zirconium for 278193; appendix A, table A.1). For most elements, the relative percent differences were less than 5%. Water isotope duplicate values differed by ≤0.2‰ for $\delta^{18}O$ and did not differ for $\delta^{2}H$. The relative percent difference between the duplicate $^{87}Sr/^{86}Sr$ ratios was 0.005%. The relative percent differences for the radon duplicates were less than 7.5%. The results demonstrate overall consistency, providing confidence in the field collection procedures and laboratory analyses.

Elemental Trend Statistics

Previous studies have shown elevated concentrations of arsenic, fluoride, lithium, boron, and molybdenum co-occur in surface waters that drains hydrothermal features in YNP (e.g., Thompson, 1979; Stauffer and Thompson, 1984; NPS, 1994; Nimick and others, 1998; Chaffee and others, 2007; McCleskey and others, 2022). Correlation relationships among arsenic, fluoride, lithium, boron, molybdenum, pH, and redox were investigated to evaluate if these elements co-occur throughout the West Yellowstone Basin, and how they may relate to pH and redox. The strength of the correlations, in combination with the spatial distribution of the elements in the study area, were used to interpret possible reasons and source(s) for the elevated arsenic and fluoride concentrations. The strength of the correlation relationships was calculated using the nonparametric Kendall's τ correlation coefficient for censored (non-detect) data. Calculation of Kendall's τ does not assume a distribution of the data and it evaluates the strength of any monotonic trend (not just linear relationships; Julian and Helsel, 2021). In this study, a correlation was considered strong when the absolute value of Kendall's τ was ≥0.50, moderate at $0.50 > |\tau| > 0.30$, and weak at $|\tau| \leq 0.30$. The statistical significance of τ was tested and a p-value of less than 0.05 indicated that the correlation was not random at a 95% confidence. All trace element data were log-transformed before testing. Statistical testing was performed in R (R Core Team, 2020) using the NADA2 package (Julian and Helsel, 2021).

RESULTS AND DISCUSSION

Aquifer Lithology of Sampled Wells

The hydrogeologic units in the basin were grouped into (1) basin fill and (2) bedrock (fig. 4). The basin-fill deposits consist predominantly of outwash, with lesser amounts of till and alluvial fan deposits (figs. 2, 4). Richmond (1964) described the outwash deposits as being up to 100 ft thick, but a recently drilled monitoring well (well 316112, adjacent to well 316115; fig. 3) shows they are at least 246 ft thick near the West Yellowstone Airport. Well logs show till underlies outwash deposits in the Horse Butte Peninsula and the South Fork–Denny Creek area (fig. 3). Alluvial fan deposits along the north side of the basin are also included in the basin-fill aquifer. Most of the sampled wells in this study are completed in basin-fill deposits at depths less than 200 ft.

The bedrock produces water from Precambrian metamorphic rock, Paleozoic–Mesozoic sedimentary rocks, and Tertiary–Quaternary volcanic rocks along the margins of the basin or under the surficial deposits. Most of the sampled bedrock wells are in the Grayling–Duck Creek and South Fork–Denny Creek areas. The Tertiary–Quaternary volcanic rocks are the most developed bedrock formations in the basin (appendix A, table A.1). There are linearly oriented springs located along the west side of the basin in the South Fork–Denny Creek area that discharge from the basin-fill, and appear to be fault controlled and sourced from the

Aquifer	Geology		Lithologic description
Basin-fill	Quaternary alluvial fan deposits		Sand and gravel that form deposits at the mouths of Red Canyon and Grayling Creek
	Quaternary glacial outwash		Generally poorly sorted sand, obsidian sand, and gravels forming the Obsidian-Sand Outwash Plain interpreted to be deposited during Pinedale glaciation
Bedrock	Quaternary Plateau Rhyolite		Rhyolitic flow containing moderate to abundant phenocrysts
Basin-fill	Quaternary glacial till		Poorly sorted, unconsolidated clay, silt, and sand that commonly overlies sand and gravel; deposits dominantly form terminal moraines interfingered with lake bed sediments from the Bull Lake glaciation
Bedrock	Quaternary Lava Creek Tuff	Upper member	Light gray, fine-grained to aphanitic, densely welded ash-flow tuff overlying welded tuff that divides the two members; proportion of phenocrysts (8–35%) decrease with depth
		Lower member	Light gray, fine-grained to aphanitic, densely welded ash-flow tuff, 25–35% phenocrysts
	Quaternary Huckleberry Ridge Tuff	Upper member	Pinkish gray to brown welded tuff with 10–25% phenocrysts
		Lower member	Gray, densely to partly welded tuff with <5% phenocrysts
	Tertiary Absaroka Supergroup Volcanics		Fine-grained to aphanitic pyroxene trachyte porphryry
	Cretaceous Kootenai Formation		Interbedded mudstone, siltstone, and sandstone with minor limestone
	Jurassic Morrison and Ellis Formations, undivided		Siltstone, mudstone, and shale overlying calcareous sandstone, limestone, and shale
	Paleozoic sedimentary rocks, undivided		Limestone, dolomite, shale, and sandstone
	Precambrian metamorphic rocks, undivided		Granite and granitic gneiss, quartzite, and mica schist

Figure 4. Simplified geologic section of the West Yellowstone Basin and the associated aquifers. Lithologic descriptions are summarized from O'Neill and Christiansen (2002, 2004), Christiansen (2001), and Pierce (1979).

underlying metamorphic rocks. Corey Spring, located on the north side of the basin in the Grayling–Duck Creek area, discharges 3,000 to 6,000 gpm from the Madison Group limestone (182014; fig. 3). Whiskey Spring (181628; fig. 3), the West Yellowstone municipal supply, is the largest developed spring in the basin and discharges between 1,500 and 3,000 gpm from the base of the rhyolite flow south of West Yellowstone (fig. 2, unit Qpr).

Field Parameters

Most sites (62) had temperatures less than 15°C (cold-water sites) and four (wells 8943, 106775, and 230654; spring 183268; fig. 3) had temperatures between 15 and 22°C (warm-water sites; fig. 5). Within the YCGA, groundwater that exceeds 15°C is used as an indicator of possible thermal activity (Metesh, 2004). The warm-water sites are part of the YCGA long-term monitoring program (English and others, 2021).

The pH of groundwater is a measure of acidity. Redox potential is a measure of oxidizing/reducing conditions, and positive redox (oxidizing conditions) is generally associated with high levels of dissolved oxygen. For this study, dissolved oxygen values greater than or equal to 0.5 mg/L were considered "oxic" conditions following Zogorski and others (2006). For the sampled sites, the pH ranged from 5.5 to 9.0, with most sites (42) having a neutral to slightly basic pH between 7 and 8 (fig. 5; appendix A, table A.1). The lower-pH water (pH less than 7.0) is found along the Madison River and Duck Creek (fig. 5). Redox ranged from -375 mV to 728 mV (fig. 5), with most sites having positive redox (51 of the 60 sites with measured redox) and dissolved oxygen greater than 0.5 mg/L (52 of the 58 sites with measured dissolved oxygen; appendix A, table A.1). All samples with strongly negative redox values (<-100 mV) also had low dissolved oxygen (<0.5 mg/L dissolved oxygen); one site (well 8944) had low dissolved oxygen with a positive redox value. Low redox and anoxic conditions (≤0.5 mg/L dissolved oxygen) were generally present in the confined basin-fill, in addition to the one sample from the Kootenai Formation (well 284024; appendix A, table A.1).

Total Dissolved Solids

Total dissolved solids (TDS) is a measure of the amount of dissolved minerals in water and an indicator of water's suitability for use. The EPA has a SMCL for TDS of 500 mg/L (EPA, 2022b); none of the samples exceeded 500 mg/L (appendix A, table A.1). Groundwater in the basin is dilute; TDS ranged from 56 to 440 mg/L with a median of 133 mg/L (fig. 5). The median values from Grayling–Duck Creek and Horse Butte Peninsula areas (115 mg/L and 113 mg/L, respectively) were slightly lower than the median values from the South Fork–Denny Creek (146 mg/L) and Madison River areas (169 mg/L; fig. 6). The highest TDS concentrations were detected in well 303212 and spring 183268 in the South Fork–Denny Creek area, discharging from volcanic rocks (figs. 5, 6).

Major Ions and Trace Element Chemistry

<u>*Major Ions*</u>

The chemistry of groundwater can be classified by the proportional concentration of major cations (sodium + potassium, calcium, and magnesium) and anions (chloride, bicarbonate + carbonate, and sulfate) expressed in meq/L. In the Grayling–Duck Creek and Horse Butte Peninsula areas, the dominant water type is calcium–bicarbonate (figs. 7, 8). Most of these wells are completed in the Huckleberry Ridge Tuff, Precambrian metamorphic rocks, alluvial fan deposits, or till. Three samples in the Grayling–Duck Creek area have higher sodium (fig. 8); these three samples are from sites along Duck Creek completed in outwash deposits (figs. 7, 8; appendix A, table A.1). These samples are more similar to those in the Madison River area (see below). One outlier in the Grayling–Duck Creek area, Corey Spring (182014), has higher sulfate and TDS compared to the other bedrock samples in the area (fig. 8); this is the only site in the two areas that is discharging from Paleozoic–Mesozoic sedimentary rocks, specifically the Madison Limestone (English and others, 2021).

In the Madison River area, sodium–bicarbonate is the dominant water type (figs. 7, 8). All but one of the wells are completed in the outwash sediments. The outwash deposits are sourced from Plateau rhyolite flows to the east and south of the basin (Pierce, 1979). Weathering of the rhyolite (which is proportionally higher in sodium compared to other bedrock units in the basin) is the likely source of sodium to the

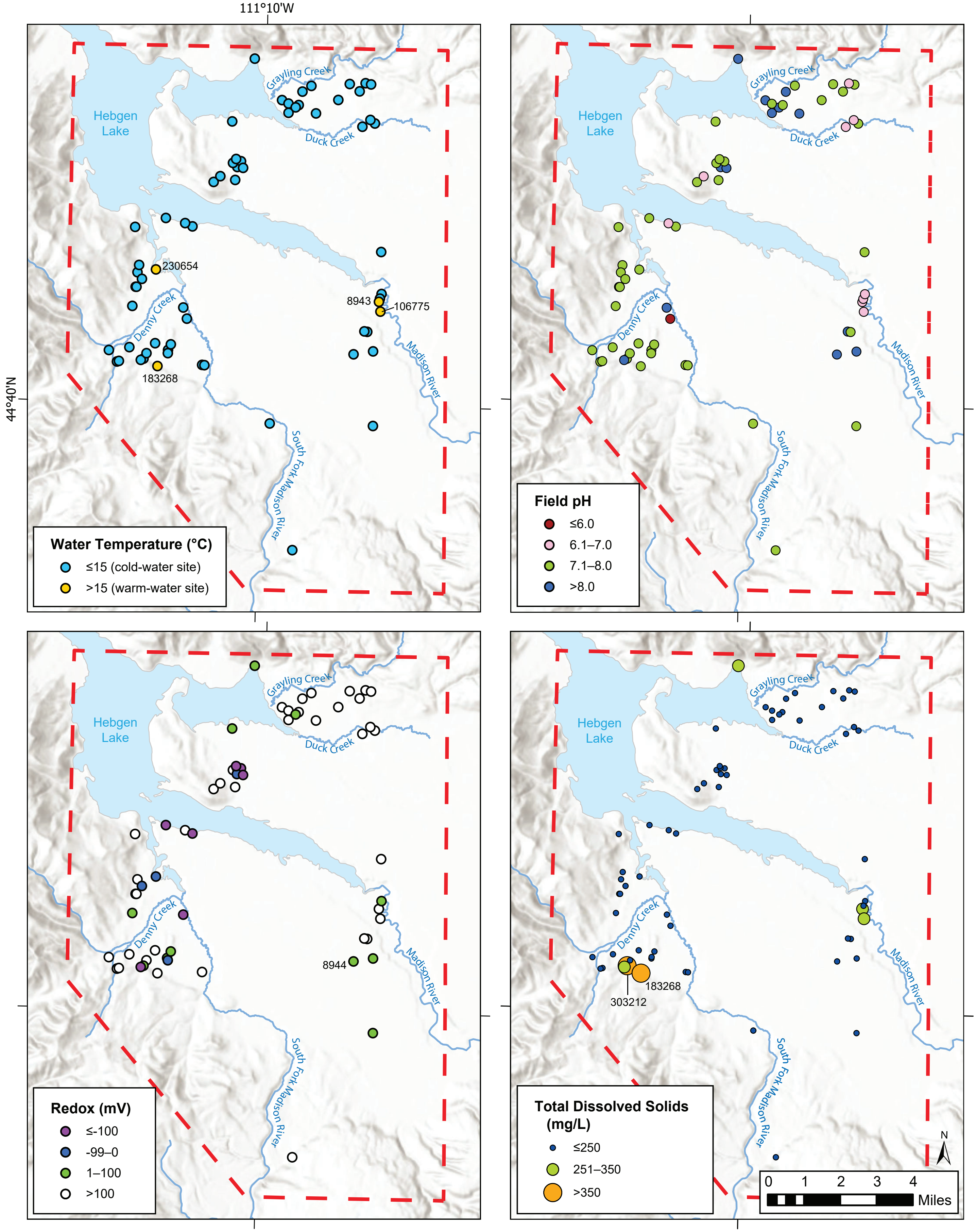


Figure 5. Spatial distribution of groundwater temperature, pH, redox, and total dissolved solids (TDS) in the study area. TDS provides a basic measure of groundwater quality while pH and redox influence the groundwater chemistry. GWIC numbers labeled for sites mentioned in text.

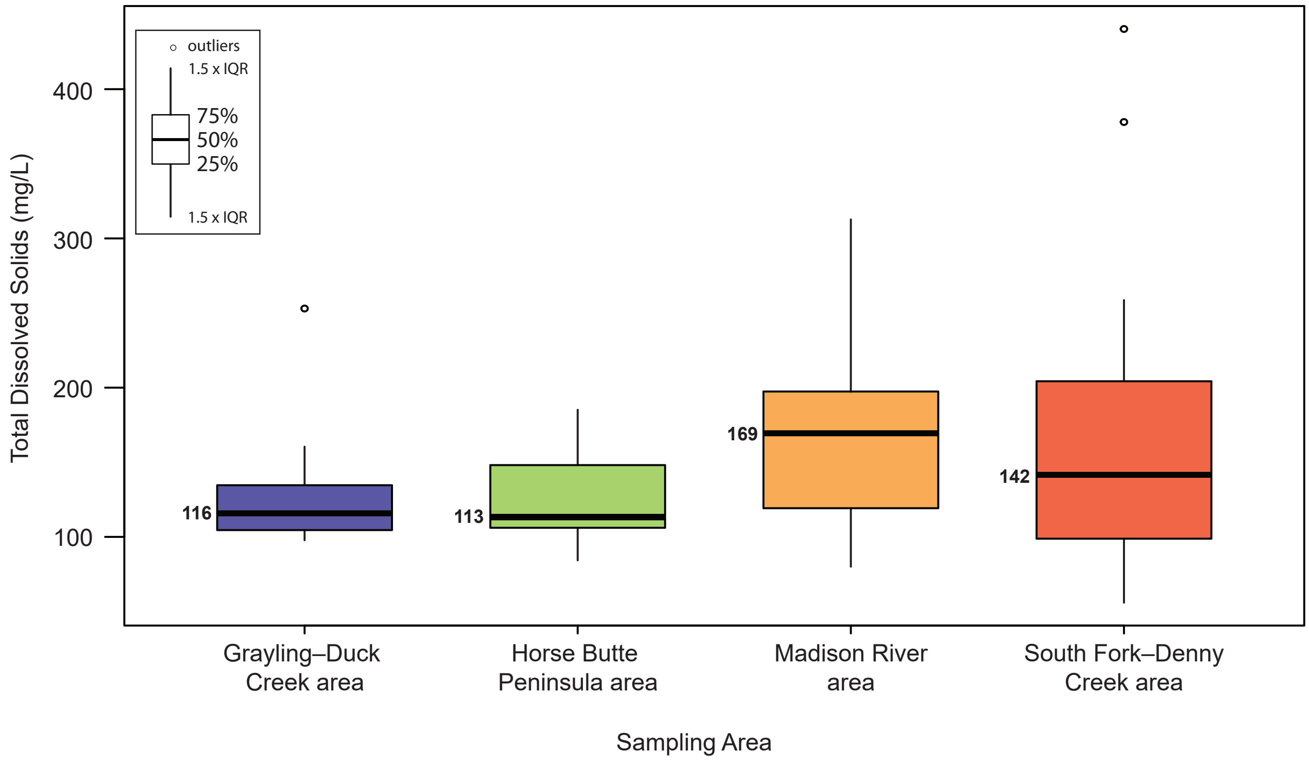


Figure 6. Boxplots summarizing total dissolved solids concentrations for the four sampling areas. Medians are given next to the boxplot. IQR is the interquartile range.

groundwater. The sodium–bicarbonate groundwater near the Madison River area is similar to, but not the same as, the sodium–bicarbonate–chloride type water in the Madison River (Nimick and others, 1998). Two wells in the Madison River area produce a calcium–bicarbonate type water, similar to the outwash wells in the Grayling–Duck Creek area (figs. 7, 8). These two samples are from well 135305, the most northern sample in the Madison River area, and well 316115, a new 119-ft-deep monitoring well drilled by the MBMG (for reference, wells in the Madison River area are between 45 and 300 ft; fig. 3).

Water types vary in the South Fork–Denny Creek area—ranging from calcium–bicarbonate to sodium–bicarbonate, with three different water types within a mile of each other (figs. 7, 8). The variability in water type is attributed to the complex geology in the area. Samples along the South Fork of the Madison River drainage, and where the South Fork of the Madison River enters Hebgen Lake, generally are proportionally higher in sodium compared to samples along the Denny Creek drainage (fig. 7). Both the sodium–bicarbonate and calcium–bicarbonate wells were completed in various lithologies (outwash, till, Huckleberry Ridge Tuff, volcanics, Precambrian rocks, and not determined; fig. 8). Samples from wells completed in till are generally calcium–bicarbonate type water whereas samples from wells completed in outwash are calcium–sodium–bicarbonate to sodium–bicarbonate type water (fig. 8). The water with proportionally higher sodium generally coincides with outwash deposits (fig. 2).

Three sites in the South Fork–Denny Creek area had very different water quality, possibly reflecting different sources (figs. 7, 8). The sample from well 284024 was a sodium–bicarbonate type water with the fourth highest TDS concentration in the study area. This well is interpreted to be completed in the Kootenai Formation (Paleozoic–Mesozoic sedimentary rocks). The sample from "Stinky Spring," a warm spring (183268), had a calcium–bicarbonate–sulfate water type. Stinky Spring and nearby Targhee Sulphur Spring (which is less than 0.5 mi southeast of Stinky Spring) have sulfur-rich water and are thought to represent deep-circulating discharge along the northwest-trending normal fault that bounds that part of the basin (English and others, 2021). Well 303212 is also along that fault trend, and its sample was also relatively enriched in sulfate (calcium–sulfate type); it is completed in volcanics.

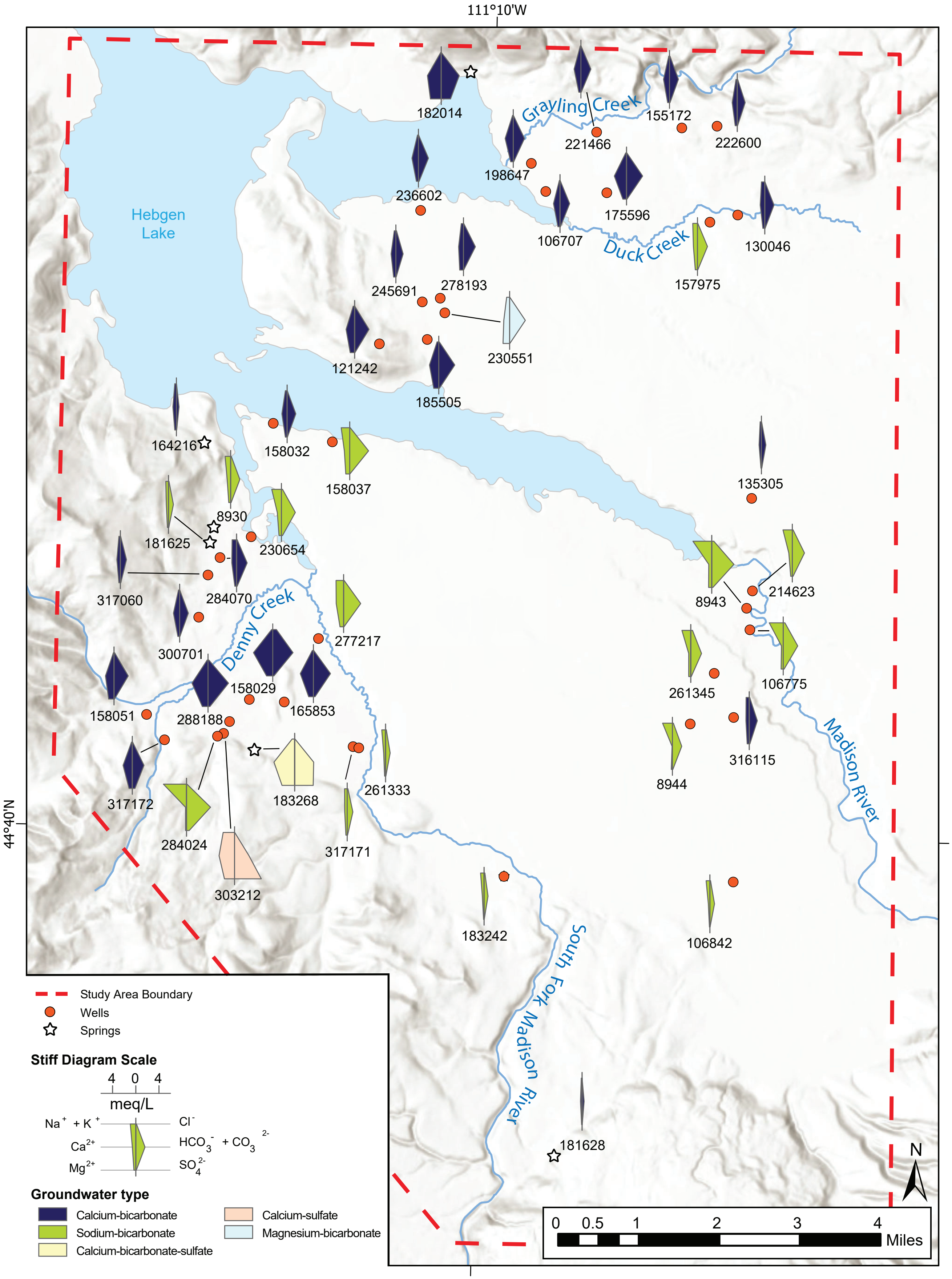


Figure 7. Stiff diagrams from a representative subset of samples across the study area. Groundwater type generally ranges from calcium–bicarbonate water in the northern and western portions of the study area to sodium–bicarbonate water in the eastern portion of the study area and southern Hebgen Lake.

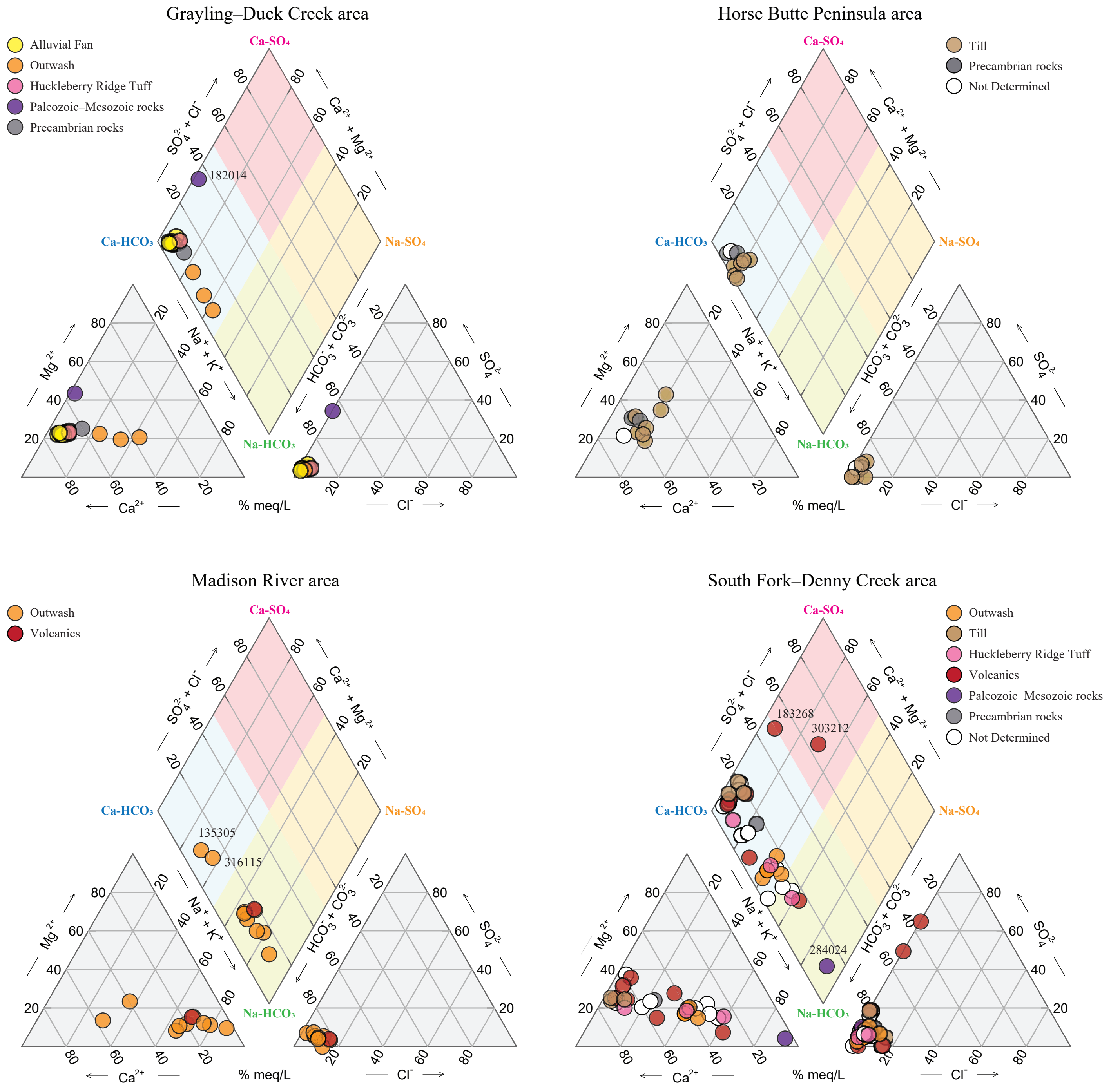


Figure 8. Piper plots for the four sampling areas. Samples are colored by the geologic material that the well is completed in. GWIC numbers labeled for sites mentioned in text.

Select Major and Trace Elements

Figure 9 shows the estimated concentration range for select major ions and trace elements for the sampled sites. The concentrations of aluminum, antimony, barium, beryllium, cadmium, chromium, copper, lead, nitrate-N, selenium, silver, thallium, and zinc did not exceed any MCLs or SMCLs. Several sites exceeded MCLs or SMCLs for arsenic, fluoride, iron, and manganese, which are discussed below (fig. 9).

Exceedances of Water-Quality Standards

Arsenic and Fluoride

The EPA MCL for arsenic is 0.010 mg/L (10 µg/L) and the MCL and SMCL for fluoride is 4.0 mg/L and 2.0 mg/L, respectively (EPA, 2022a). Arsenic concentrations for the sampled sites are summarized in figure 10 and provided in table A.1 in appendix A. Eleven of the 66 samples exceeded the arsenic MCL (>10 µg/L); most of the exceedances (7) were in the Madison River area, but two samples exceeded the MCL in both the Horse Butte Peninsula and South Fork–Denny Creek area (fig. 10). The highest arsenic concentration was 49.6 µg/L at well 8944 in the Madison River area (appendix A, table A.1). Fluoride above the MCL and SMCL co-occurred with elevated arsenic in several locations, but was also elevated in locations where arsenic concentrations were low (fig. 10). Seventeen of the 66 samples had fluoride concentrations above 2.0 mg/L (SMCL), and five samples exceeded the 4.0 mg/L MCL (fig. 10; appendix A, table A.1). Samples with fluoride greater than 2.0 mg/L were generally from sites adjacent to rivers and creeks, including the Madison River, the South Fork of the Madison River, and Duck Creek (fig. 10). Fluoride above 2.0 mg/L was also detected in the southern part of the study area, including Whiskey Springs, the main water source for West Yellowstone (181628; fig. 10). A recent "Quality on Tap Report" for West Yellowstone

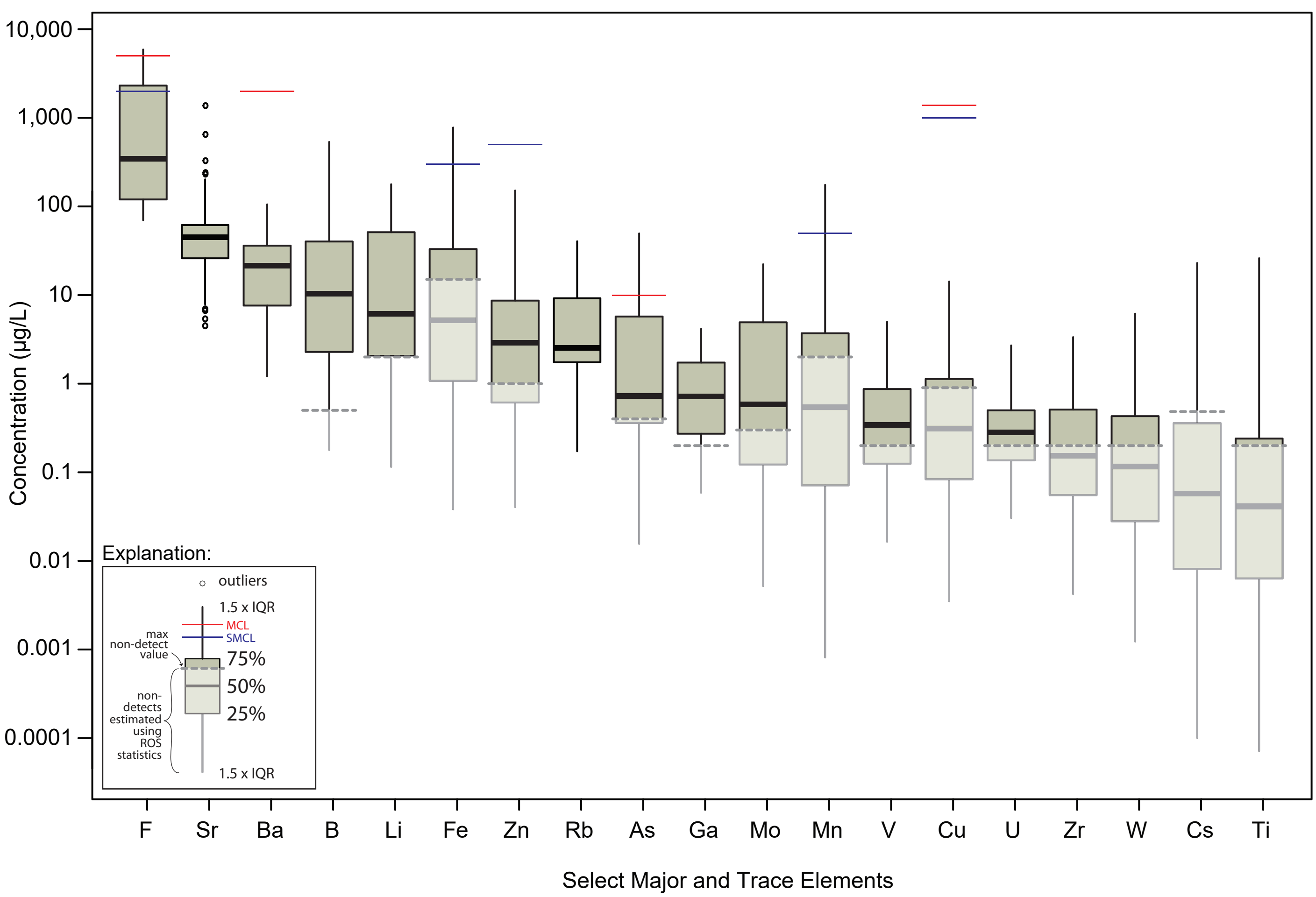


Figure 9. Boxplots of select major and trace elements that had 25% of samples above detection limit, in order of decreasing median. Applicable EPA MCL and SMCL are provided. Note that the y-axis is lognormal. Values within the transparently shaded portion of the boxplot are below the maximum non-detect value (gray dashed line) and contain estimated values using regression-on-order (ROS) statistics (Helsel, 2011). IQR is the interquartile range.

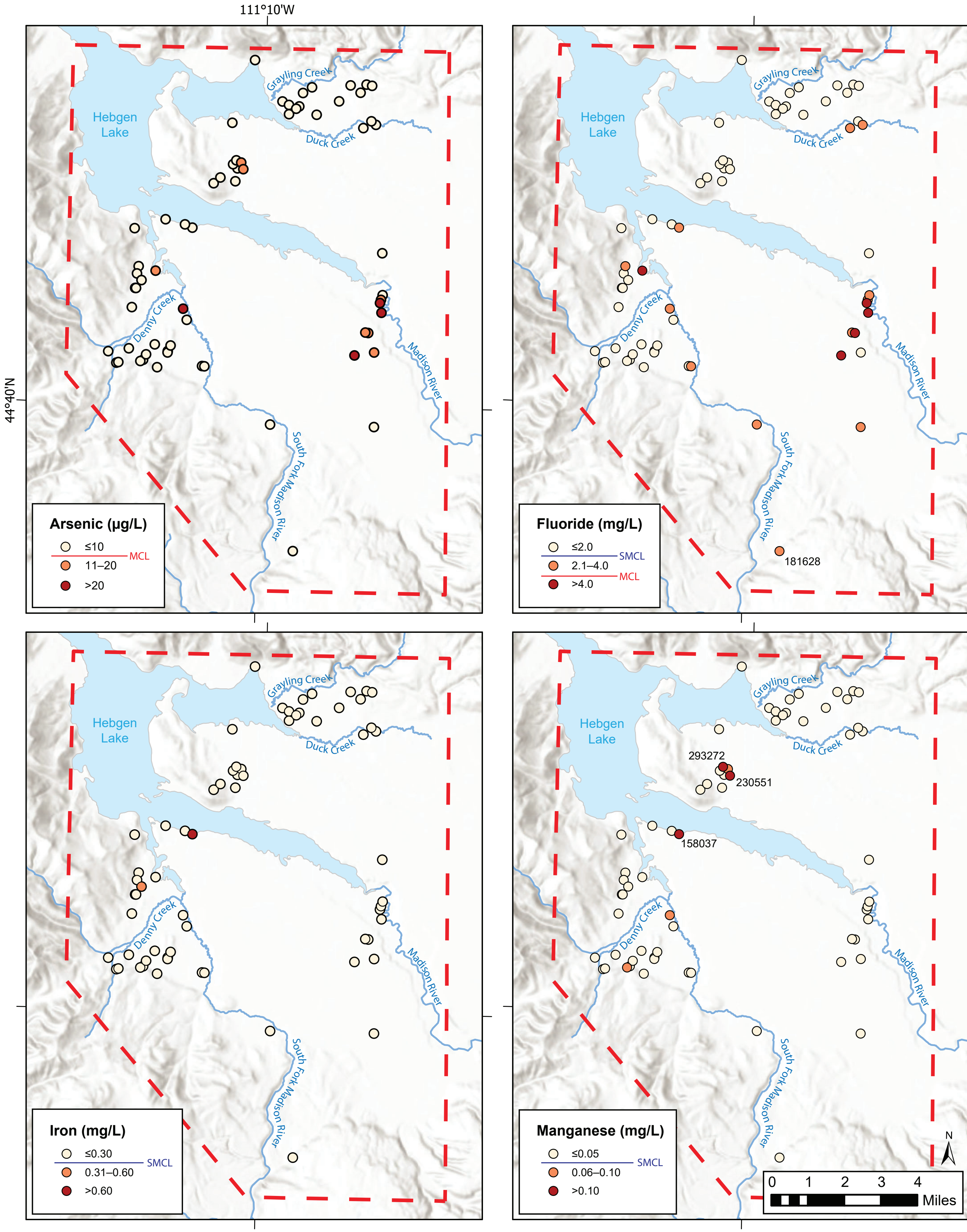


Figure 10. Overview of groundwater arsenic, fluoride, iron, and manganese concentrations in the study area. EPA's maximum contaminant level (MCL) and secondary maximum contaminant level (SMCL) for drinking water standards are indicated on the legend for each element. GWIC numbers labeled for sites mentioned in text.

reported up to 3.8 mg/L fluoride in the public water supplies (Brown, 2021). Elevated fluoride concentrations were generally not found in samples from the alluvial fan deposits, till deposits, and Precambrian bedrock (figs. 2, 10; appendix A, table A.1).

The co-occurrence of fluoride and arsenic in the West Yellowstone Basin is statistically supported with a p-value of <0.0001 and a moderate positive correlation of $\tau = 0.4242$ (fig. 11). Arsenic also had a moderate correlation with lithium, boron, and molybdenum, similar to correlation relationships shown for surface waters in YNP and for the Madison River (Thompson, 1979; Nimick and others, 1998; McCleskey and others, 2022). All non-arsenic pairs between fluoride, lithium, boron, and molybdenum had strong correlations ($\tau \geq 0.50$; fig. 11). The locations of higher concentrations of lithium, boron, and molybdenum are very similar to locations of higher fluoride (fig. 10). The lower strength in arsenic-paired correlations — and the slight differences in locations of high arsenic compared to high fluoride, lithium, boron, and molybdenum—suggest there is potentially different water chemistry and/or different sources influencing the occurrence of arsenic compared to fluoride, lithium, boron, and molybdenum.

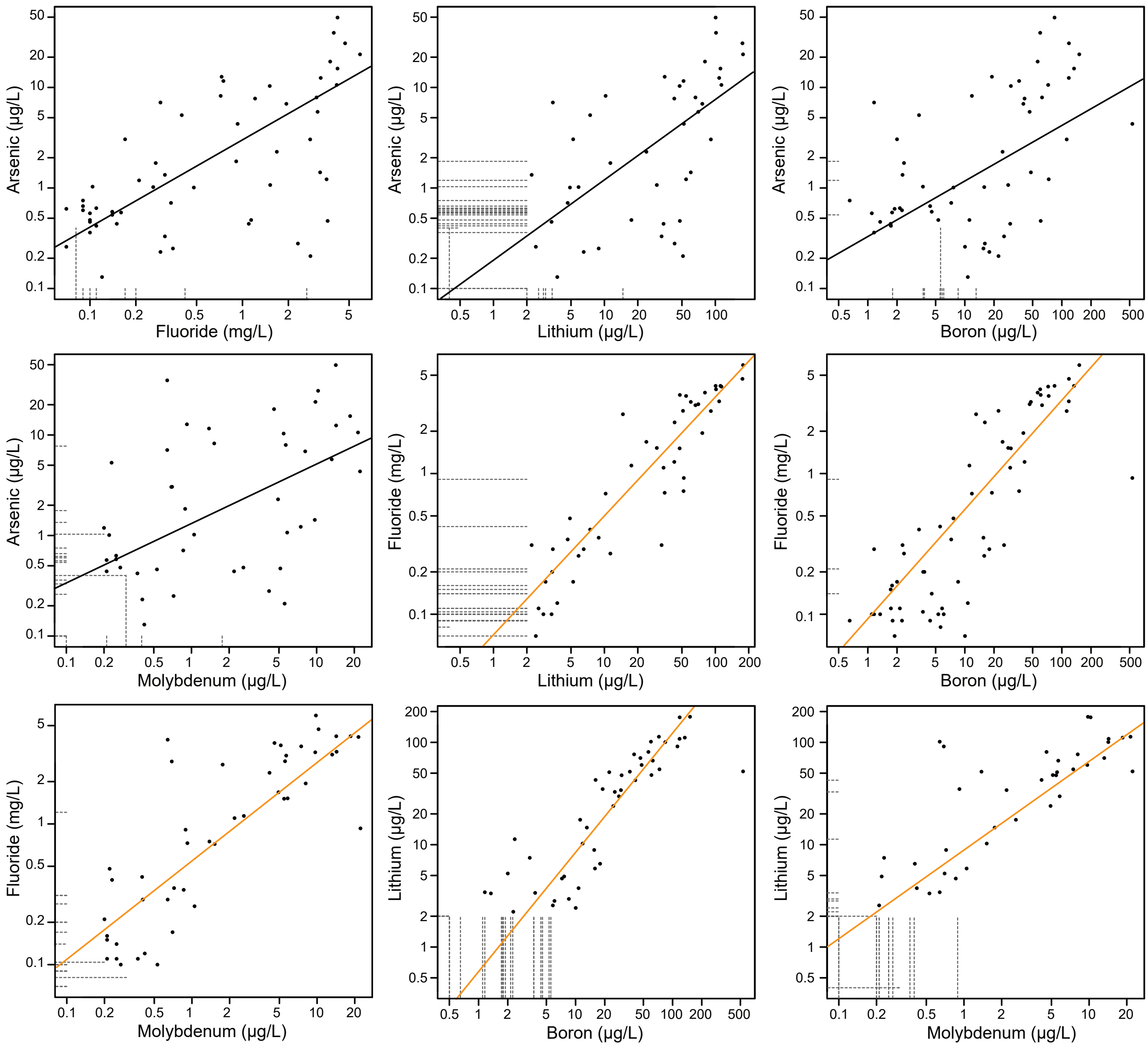
One potential source for arsenic, fluoride, lithium, boron, and molybdenum is recharge from the Madison River. The Madison River drains the geyser basins in the west-central part of YNP and has shown dissolved arsenic concentrations of up to 266 µg/L, fluoride concentrations of 6.2 mg/L, lithium concentrations of 500 µg/L, and boron concentrations of 650 µg/L, with stream sediments containing 6–19 mg/kg of molybdenum (Thompson, 1979; Knapton and Brosten, 1988; NPS, 1994; Chaffee and others, 2007; NPS, 2022b). The elevated concentrations in the Madison River are attributed to hydrothermal leaching of rhyolites in the headwaters area within YNP (e.g., Thompson, 1979; Stauffer and Thompson, 1984; Knapton and Horpestad, 1987; McCleskey and others, 2022). Since the highest groundwater concentrations of these elements are near the Madison River, the Madison River may be losing to groundwater. There is a flowing well (106775) located within 100 ft of the river (fig. 3); no information is available on the depth or lithology of this well. However, this well suggests there is an upward gradient near where the Madison River meets Hebgen Lake; therefore, the Madison River is more likely to be losing upstream where it enters the basin.

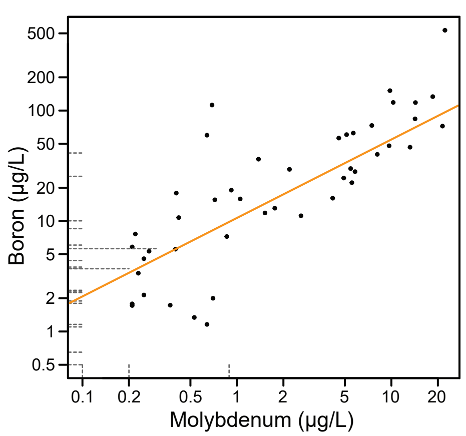
Another likely source for fluoride, lithium, boron, and molybdenum is groundwater interaction with the rhyolitic volcanic rocks that rim the northeast, east, south, and southwest parts of the basin and the basin-fill deposits, which are composed mainly of rhyolitic detritus. Samples from Whiskey Spring (181628), which flows only through Plateau rhyolite, and wells 157975 and 130046 near Duck Creek, have elevated fluoride (2.64 mg/L) but very low arsenic (non-detect to ≤0.280 µg/L). Whole-rock geochemical analyses of the different rhyolite units in YNP show they are relatively enriched in fluorine and alkali metals, including sodium, potassium, and lithium. The alkali-rich YNP volcanic rocks have been invoked by previous research as a source for the fluoride in the upper Madison River system (Hildreth and others, 1984; Thompson, 1979).

Samples with elevated arsenic along the southern part of Hebgen Lake in the South Fork–Denny Creek area and in the Horse Butte Peninsula area are not associated with elevated fluoride but are associated with low redox conditions (≤-100 mV; figs. 5, 10). There was a statistically significant weak positive correlation between arsenic and pH ($\tau = 0.0998$, p-value = 0.0278) and weak negative correlation between arsenic and redox ($\tau = -0.2192$, p-value = 0.0142). All other correlations between elements (fluoride, lithium, boron, molybdenum) and pH or redox were statistically insignificant (p-value > 0.10), with the exception of lithium and redox ($\tau = -0.2034$, p-value = 0.0204). Low redox conditions can increase the solubility and mobility of arsenic (e.g., Gulens and others, 1979; Morin and Calas, 2006, and references therein). Thus, redox and pH conditions in the groundwater likely control the occurrence of arsenic in some locations.

Iron and Manganese

There are no MCLs for iron and manganese. The SMCL for iron is 0.3 mg/L and manganese is 0.05 mg/L. Concentrations above the SMCL can stain laundry and plumbing fixtures, and impart a metallic taste (EPA, 2022b). Recent research suggests that elevated manganese in drinking water may be associated with memory, attention, and motor skill problems (Bouchard and others, 2007; ATSDR, 2012, Avila and others, 2013; DEQ, 2021). Montana Department of Environmental Quality (DEQ) has advised a manganese health guideline of 0.1 mg/L for children 6 yr and younger and 0.3 mg/L for those older than 6 (DEQ, 2021).





Elements Correlated	*τ*	*p*-value
Arsenic–Fluoride	0.4242	<0.0001
Arsenic–Lithium	0.4233	<0.0001
Arsenic–Boron	0.3110	0.0002
Arsenic–Molybdenum	0.3599	<0.0001
Fluoride–Lithium	0.7086	<0.0001
Fluoride–Boron	0.6103	<0.0001
Fluoride–Molybdenum	0.6228	<0.0001
Lithium–Boron	0.7273	<0.0001
Lithium–Molybdenum	0.5907	<0.0001
Boron–Molybdenum	0.5501	<0.0001

Figure 11. Scatter plots showing the correlations among arsenic, fluoride, lithium, boron, and molybdenum. Akritas-Theil-Sen (ATS) lines estimate the slope of the correlation relationship. Gray dotted lines in the scatter plots represent non-detect values and the range that each non-detect value in the dataset may have (e.g., zero to the detection level). Kendall's τ and p-values are given for each correlation. Orange highlighted values and orange slopes are interpreted as strong correlation relationships.

Iron exceeded the SMCL in two samples from the South Fork–Denny Creek area (fig. 10; appendix A, table A.1). Manganese exceeded the SMCL in six samples from the Horse Butte Peninsula area and the South Fork–Denny Creek area; three of these samples also exceeded the DEQ health guideline of 0.1 mg/L for children 6 yr and younger (wells 158037, 230551, 293272; fig. 10; appendix A, table A.1). Elevated manganese detected in samples from the Horse Butte Peninsula area were from wells completed in till deposits, whereas elevated manganese and iron detected in the South Fork–Denny Creek area were from wells completed in various lithologies (outwash, till, Paleozoic–Mesozoic bedrock, and not determined).

The elevated manganese concentrations (greater than 0.05 mg/L) were found in groundwater with redox values less than -100 mV and dissolved oxygen concentrations below 0.28 mg/L (figs. 5, 10; appendix A, table A.1). Similarly, most samples with iron concentrations above 0.05 mg/L had negative redox values and dissolved oxygen below 0.80 mg/L (with a few exceptions; appendix A, table A.1). The two samples with the highest manganese concentrations (wells 230551 and 293272; >0.16 mg/L) were in the Horse Butte Peninsula area; they had relatively low (<0.13 mg/L) iron concentrations and a distinctive smell of hydrogen sulfide when sampling. Dissolved iron in the presence of dissolved sulfur species can produce insoluble iron-sulfides, removing iron from the groundwater (Hem, 1972; Brookins, 1988); this may explain why these high manganese samples have lower iron concentrations. However, in general, negative redox and anoxic groundwater conditions were key indicators for elevated concentrations of dissolved iron and manganese in the West Yellowstone Basin.

Radon

High levels of radon in water can be a health concern because dissolved radon will transfer to indoor air at a ratio of about 1:10,000 (EPA, 2014). The U.S. EPA has a proposed radon MCL of 4,000 pCi/L for states with a mitigation program (EPA, 2014); the Montana DEQ has a Human Health Advisory level of 300 pCi/L (DEQ, 2019). All but two of the samples exceed 300 pCi/L, and one sample from well 230654 exceeded the proposed MCL level of 4,000 pCi/L (fig. 12; appendix A, table A.4). Radon concentrations are generally higher in bedrock wells (Huckleberry Ridge Tuff and Precambrian rocks) and lower in wells completed in the till, outwash, and alluvial fan deposits (figs. 2, 12; appendix A, table A.4). Elevated radon is commonly associated with metamorphosed sediments, felsic volcanics, and granite intrusions (Gundersen and others, 1992). The lower radon concentrations in the basin-fill is likely due to low radon in the sedimentary deposits and the natural decay of radon with increased flow time from bedrock sources (half-life of radon is 3.8 d).

<u>Stable Isotopes</u>

Oxygen and Hydrogen Isotopes

The δ^2H and δ^{18}O values for groundwater in the study area ranged from -130 to -154 and -17.0 to -20.4‰, respectively (fig. 13; appendix A, table A.2). The samples plot along, or below, the YNP local meteoric water line (Kharaka and others, 2002), indicating a meteoric origin of the sampled groundwater; the samples that plot below the line are attributed to secondary evaporative effects during precipitation and/or infiltration (Kharaka and others, 2002; Cecil and others, 2005). The groundwater values all plot close to the average value for winter precipitation observed in southern Idaho and the YNP area (fig. 13; Cecil and others, 2005), suggesting that snowmelt is the primary source of groundwater recharge.

The samples from the center of the basin, near the Horse Butte Peninsula and Madison River areas, are similar and relatively depleted compared to the samples from the basin margins, near the Grayling–Duck Creek and South Fork–Denny Creek areas (fig. 13). Kharaka and others (2002) found similarly depleted water isotope values in YNP Madison River and Cougar Creek drainages and relatively enriched values in the surrounding Madison and Gallatin Ranges.

Strontium Isotopes

The ratio of ^{87}Sr and ^{86}Sr can be used as a natural tracer in identifying groundwater sources and/or surface-water catchments (e.g., Bain and Bacon, 1994; Zou and others, 2018; Miller and others, 2021). Different rock units can have distinctive strontium ratios (^{87}Sr/^{86}Sr). In the simplest case, when groundwater flows through the rock units, strontium will dissolve into the water from the host rocks, and the groundwater will acquire a strontium isotope ratio that matches the rock unit. However, complications in interpreting the strontium ratios can occur if: (1) the groundwater

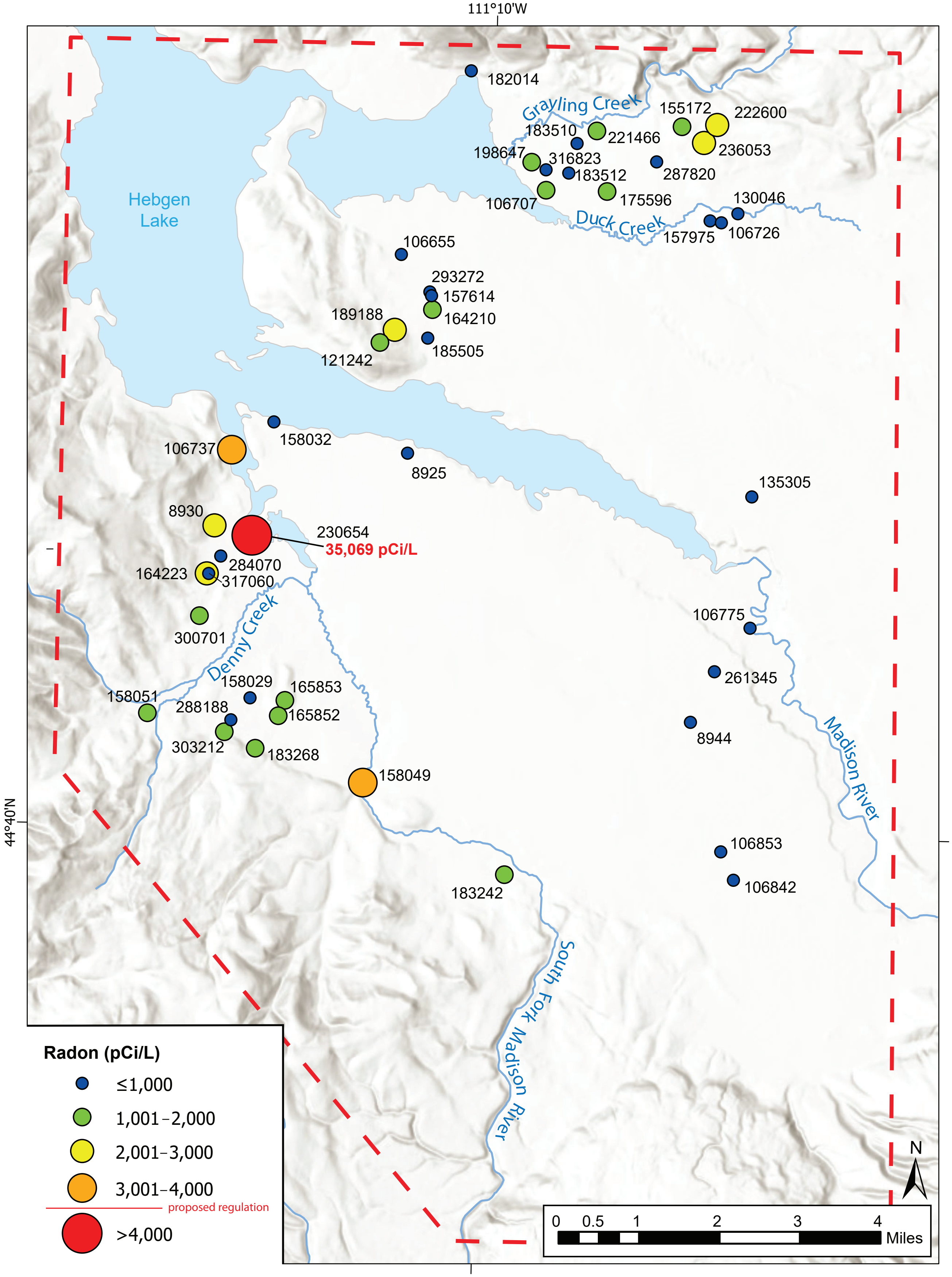


Figure 12. Groundwater radon concentrations throughout study area are higher along the edges of the basin (which flows through bedrock) and lower in the center of the basin (which flows through outwash, till, and alluvial fan deposits; see geology in fig. 2). Well 230654 greatly exceeds the EPA proposed groundwater radon regulation of 4,000 pCi/L.

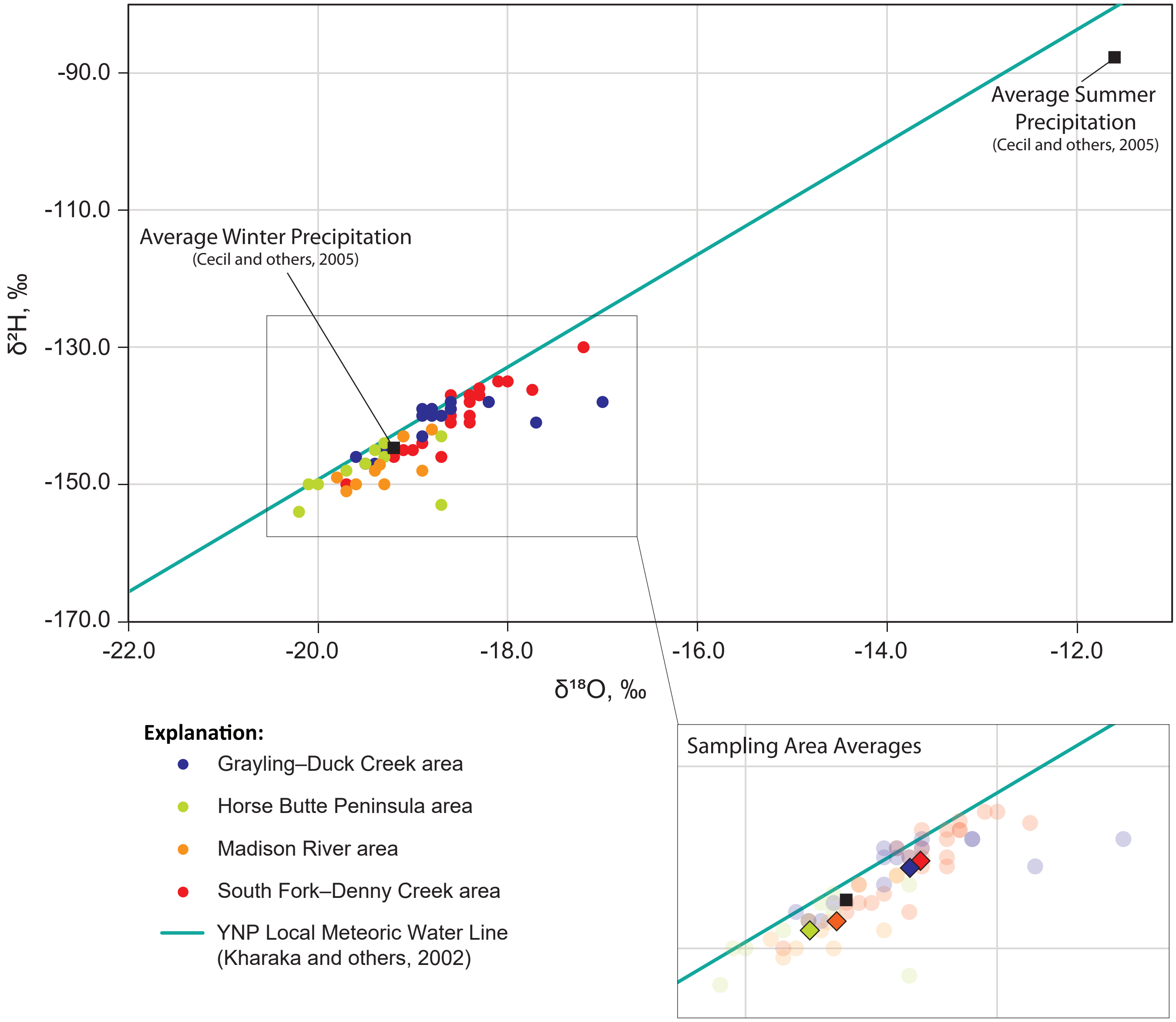


Figure 13. Groundwater isotopes of the study area plot along, or below, the local meteoric water line (LMWL) developed from Yellowstone National Park (YNP) snow samples. The Horse Butte Peninsula and Madison River area have water isotope averages that are relatively depleted compared to the Grayling–Duck Creek and South Fork–Denny Creek areas.

flows through two or more host-rock sources, (2) the groundwater does not interact long enough with the host rock, or (3) two different host-rock sources in the study area have overlapping strontium ratios. For this study, groundwater strontium isotope ratios were compared to previously published strontium values of local bedrock sources (Peterman and others, 1970; Leeman and others, 1977; Doe and others, 1982; Horton and others, 1999; Miller and others, 2021). The similarities between groundwater and bedrock isotopes were used to interpret the geologic units the groundwater flowed through in the different sampling areas. Overall, the $^{87}Sr/^{86}Sr$ ratios ranged from 0.707332 to 0.728794, with strontium concentrations between 4.51 and 1,390 µg/L (fig. 14; appendix A, table A.3).

In the Grayling–Duck Creek area, samples from wells completed in the Huckleberry Ridge Tuff or alluvial fan deposits have strontium ratios that suggest the groundwater has interacted with both Precambrian bedrock and Huckleberry Ridge Tuff (figs. 2, 14). Although the bedrock that underlies the Huckleberry Ridge Tuff in the northeastern part of the study area is poorly exposed, Precambrian bedrock crops out in numerous locations on both sides of Grayling Creek, suggesting that Precambrian rock likely underlies the Huckleberry Ridge Tuff throughout this area (fig. 2). Additionally, the alluvial fan deposits are composed of Precambrian crystalline, Paleozoic–Mesozoic sedimentary, and rhyolitic detritus (Richmond, 1964); the rhyolitic detritus is likely derived from the nearby Huckle-

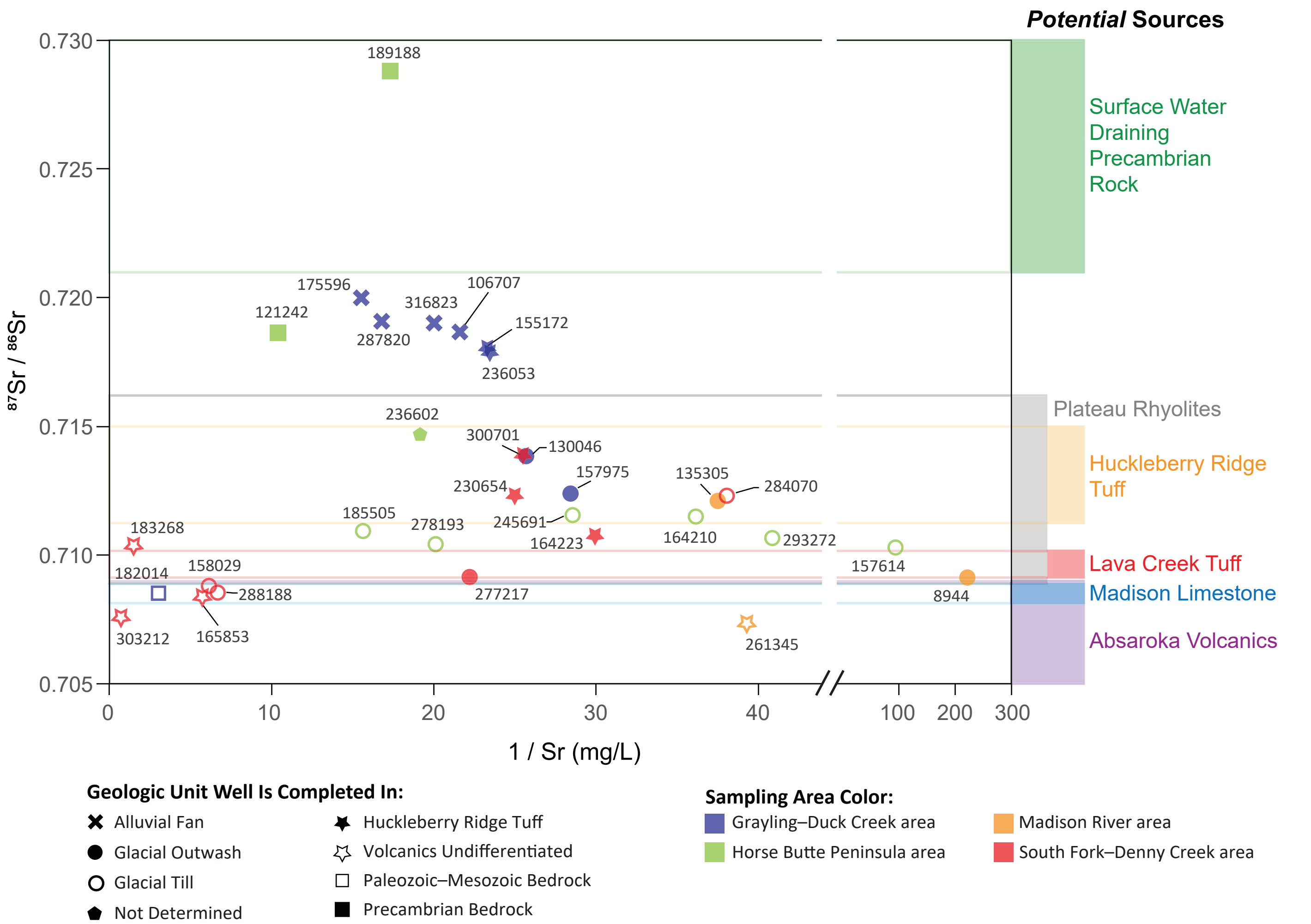


Figure 14. Groundwater strontium ratios in the study area (with associated GWIC numbers) in comparison with potential geologic sources (data from Doe and others, 1982; Miller and others, 2021 and references therein). Values for the Plateau Rhyolites overlap Huckleberry Ridge Tuff and Lava Creek Tuff.

berry Ridge Tuff. Thus, as water in the Grayling–Duck Creek area flows from higher elevation towards Hebgen Lake, it would flow through the bedrock fractures of Huckleberry Ridge Tuff and Precambrian rocks and alluvial fan deposits composed of Precambrian and Huckleberry Ridge Tuff—acquiring both mixed strontium ratios and similar water chemistry.

The samples in the Grayling–Duck Creek area that were chemical outliers also have distinct strontium ratios. Spring 182014, which discharges from the Madison Limestone, had an elevated sulfate concentration and a strontium ratio that is consistent with Madison Limestone. Also, the Grayling–Duck Creek samples that had proportionally higher sodium have strontium ratios that are similar to ratios in the Plateau rhyolites that weathered to form the outwash deposits.

Samples from wells completed in basin-fill deposits (till and outwash) in the Horse Butte Peninsula and Madison River area have strontium ratios between 0.709132 and 0.714679, consistent with glacial sediments derived from the Plateau rhyolites, Huckleberry Ridge Tuff, and Lava Creek Tuff. However, the strontium concentrations of these samples vary from 4.51 to 64 µg/L. Overall, the Madison River area and the Horse Butte Peninsula area basin-fill deposits have similar isotopic (strontium, hydrogen, and oxygen) signatures, but different water chemistry.

The two Precambrian bedrock wells of the Horse Butte Peninsula area (189188 and 121242) have significantly higher strontium ratios than nearby wells completed in basin-fill and fall in or are close to the range given by Horton and others (1999) for water sourced from Precambrian rocks. The one bedrock well in the Madison River area is completed in volcanics of an unknown geologic unit. The strontium ratio of groundwater from well 261345 plots in the range of strontium ratios for Absaroka volcanics, suggesting

Absaroka volcanics are underneath the outwash sediments in the Madison River area.

Finally, strontium ratios vary across the South Fork–Denny Creek area. A cluster of three wells on the southeast side of Denny Creek (wells 158029, 288188, and 165853) have tightly grouped strontium ratios of approximately 0.70857 (figs. 7, 14). Well 277217, about a mile northeast of these sites, has a similar strontium ratio, but a very different strontium concentration; this sample also has proportionally higher sodium, arsenic, and fluoride than most other sites in the South Fork–Denny Creek area. Three wells on the northwest side of Denny Creek (300701, 230654, and 164223) are completed in Huckleberry Ridge Tuff and have a range of strontium ratios that is consistent with values from the Huckleberry Ridge Tuff bedrock. Spring 183268 and well 303212 have chemically distinct water types (calcium–bicarbonate–sulfate and calcium–sulfate type waters, respectively) and the highest strontium concentrations of all sampled sites (fig. 14; appendix A, table A.1). Well 303212 is interpreted to be completed in volcanics; however, the strontium concentration (~1,390 μg/L) is consistent with limestone, possibly suggesting the water is sourced from the Paleozoic–Mesozoic sedimentary rocks. The other chemically distinct site, spring 183268, has a strontium ratio that is consistent with discharge from volcanics (e.g., Lava Creek and/or Huckleberry Ridge Tuff). Thus, the southern portion of the South Fork–Denny Creek area has chemically and isotopically distinct groundwater; the extent to which these groundwaters mix is currently unknown.

CONCLUSIONS

This study evaluated the inorganic groundwater chemistry in four areas across the West Yellowstone Basin. Forty-two samples collected in the fall of 2021 and 24 samples from previous and ongoing MBMG studies were used to characterize major ion and trace element chemistry; radon concentrations; and isotope ratios of hydrogen, oxygen, and strontium. Overall, the water is dilute; the median total dissolved solids concentration was 133 mg/L. Most of the sampled sites produce calcium–bicarbonate to sodium–bicarbonate type water. In places, arsenic and fluoride were detected at concentrations above their respective MCLs, and iron or manganese were detected above their respective SMCLs.

Elevated arsenic and fluoride concentrations occur in the basin-fill aquifer near the Madison River, close to where it drains into the Madison Arm of Hebgen Lake. The Madison River is known to have high arsenic and fluoride concentrations (from draining hydrothermal features in YNP) and it potentially recharges the aquifer where it enters the West Yellowstone Basin. Elevated arsenic concentrations are weakly negatively correlated with redox conditions. Elevated fluoride concentrations also occur in basin-fill and bedrock aquifers away from the Madison River, specifically in wells completed in outwash sediments and wells completed in Quaternary volcanic bedrock. Much of the Quaternary volcanic bedrock is rhyolitic, while the outwash sediments are derived from weathering of rhyolitic rocks. It is likely that nonhydrothermal groundwater interaction with the alkali-rich rhyolites and rhyolitic sediments increases the fluoride concentrations in the southern and eastern part of the West Yellowstone Basin. The Huckleberry Ridge Tuff, although also rhyolitic, is generally not associated with groundwater containing elevated fluoride. Elevated manganese and iron concentrations were associated with reducing and anoxic groundwater conditions, most commonly from wells completed in basin-fill deposits with interbedded sand and clay layers.

Groundwater is dominantly recharged by winter precipitation. Samples in the center of the basin, near the Madison River and Horse Butte Peninsula, have water isotopes that are relatively depleted compared to samples near the basin margins in the Grayling–Duck Creek and South Fork–Denny Creek areas. Between Grayling and Duck Creek, strontium isotopes are consistent with groundwater flowing from the Precambrian and Huckleberry Ridge Tuff bedrock to the alluvial fan deposits. Strontium isotope samples from wells completed in basin-fill deposits right next to Duck Creek, near the Madison River, and from Horse Butte Peninsula are consistent with groundwater flow through till and outwash sediments. In the southwest part of the basin, there are multiple groundwater types and distinct strontium isotope ratios.

RECOMMENDATIONS

A detailed hydrogeologic investigation and additional groundwater sampling are recommended to better interpret water quality throughout the West Yellowstone Basin. Installation of monitoring wells on public lands (U.S. Forest Service land and YNP) in the central and eastern part of the basin, where there are few wells, will better define the geology, hydrogeology, and water quality in the basin. Additional well sampling in the Town of West Yellowstone, the alluvial fans near Red Canyon Creek and Watkins Creek, the north and south shores of Hebgen Lake, and the southwest corner of the basin is also recommended, as sampling in these areas was limited or not completed. Additional groundwater strontium isotope analyses would be helpful for interpreting groundwater mixing. Whole-rock chemistry analyses and leaching tests on the volcanic rocks and the obsidian sands of the outwash would be helpful in evaluating which geologic units contribute the most fluoride to the groundwater.

Discharge measurements and investigations of groundwater/surface-water interactions along the Madison River, the South Fork of the Madison River, and major tributary streams within the West Yellowstone Basin are needed to determine where the rivers and streams are losing to or gaining from the basin-fill aquifer. Currently the only surface-water discharge measurements are collected by the USGS on the Madison River near West Yellowstone (monitoring location 06037500). Discharge measurements locations should include at least one site where the Madison River enters the basin and one where the Madison River flows into Hebgen Lake. Surface-water sampling of the Madison River as it enters the basin and between West Yellowstone and Hebgen Lake would be helpful for comparisons with groundwater near the river. Additional discharge measurements and surface-water sampling (including hydrogen and oxygen isotopes) along Cougar Creek are needed to evaluate the extent to which this drainage influences groundwater recharge and quality in the west and central part of basin.

The extent of confining conditions within the basin-fill deposits is relatively unknown. Conducting aquifer tests in the basin-fill deposits, installing test wells, and developing a potentiometric-surface map for the basin would greatly improve the hydrogeologic understanding of the West Yellowstone Basin.

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REFERENCES

Agency for Toxic Substances and Disease Registry (ATSDR), 2012, Toxicological profile for manganese, available at https://www.atsdr.cdc.gov/toxprofiles/tp151.pdf [Accessed July 2022].

Avila, D.S., Puntel, R.L., and Aschener, M., 2013, Manganese in health and disease: Metal Ions in Life Sciences, v. 13, p. 199–227, doi: 10.1007/978-94-007-7500-8_7.

Bain, D.C., and Bacon, J.R., 1994, Strontium isotopes as indicators of mineral weathering in catchments: Catena, v. 22, no. 3, p. 201–214.

Bouchard, M., Laforest, F., Vandelac, L., Bellinger, D., and Mergler, D., 2007, Hair manganese and hyperactive behaviors: Pilot study of school-age children exposed through tap water: Environmental Health Perspectives, v. 115, no. 1, p. 122–127.

Brookins, D.G., 1988, Eh-pH diagrams for geochemistry: New York, Springer-Verlag, 176 p.

Brown, J., 2021, Quality on tap report 2021: Town of West Yellowstone PWSID MT#0003136, available at https://www.townofwestyellowstone.com/wp-content/uploads/2022/06/West-Yellowstone-2022-CCR-for-2021-Monitoring-Period.pdf [Accessed July 2022].

Brown, J., 2022, Important information about your drinking water elevated fluoride levels detected in the drinking water for Town of West Yellowstone: https://www.townofwestyellowstone.com/wp-content/uploads/2022/05/Fluoride-Information-1.pdf [Accessed August 2022].

Carstarphen, C.A., and LaFave, J.I., 2018, Groundwater quality of Gallatin and Madison Counties, southwest Montana: Montana Bureau of Mines and Geology Montana Ground-Water Assessment Atlas 8-03, 2 sheets.

Cecil, L.D., Hall, L.F., Benjamin, L., Knobel, L.L., and Green, J.R., 2005, Comparison of local meteoric water lines in southeastern Idaho, western Wyoming, and south-central Montana and the associated hydrologic implications: Journal of the Idaho Academy of Science, v. 41, no. 2, p. 13–29.

Chaffee, M.A., Carlson, R.R., King, H.D., and Chapter, K., 2007, Environmental geochemistry in Yellowstone National Park—Natural and anthropogenic anomalies and their potential impact on the environment: U.S. Geological Survey Professional Paper 1717, 29 p.

Christiansen, R.L., 2001, The Quaternary and Pliocene Yellowstone Plateau volcanic field of Wyoming, Idaho, and Montana: U.S. Geological Survey Professional Paper 729-G, 120 p.

Doe, B.R., Leeman, W.P., Christiansen, R.L., and Hedge, C.E., 1982, Lead and strontium isotopes and related trace elements as genetic tracers in the Upper Cenozoic rhyolite–basalt association of the Yellowstone Plateau Volcanic Field: Journal of Geophysical Research: Solid Earth, v. 87, no. B6, p. 4785–4806.

English, A., LaFave, J.I., and Richter, M., 2021, Yellowstone Controlled Groundwater Area, Montana long-term monitoring program: Data summary report: Montana Bureau of Mines and Geology Open-File Report 743, 126 p.

Environmental Protection Agency (EPA), 2014, Basic information about radon in drinking water, available at https://archive.epa.gov/water/archive/web/html/basicinformation-2.html [Accessed August 2022].

Environmental Protection Agency (EPA), 2022a, National primary drinking water regulations, available at https://www.epa.gov/ground-water-and-drinking-water/national-primary-drinking-water-regulations [Accessed July 2022].

Environmental Protection Agency (EPA), 2022b, Secondary drinking water standards: Guidance for nuisance chemicals, available at https://www.epa.gov/ground-water-and-drinking-water/national-primary-drinking-water-regulations [Accessed July 2022].

Gotkowitz, M.B., 2022, Standard procedures and guidelines for field activities, Montana Bureau of Mines and Geology: Montana Bureau of Mines and Geology Open-File Report 746, 96 p

Gulens, J., Champ, D.R., and Jackson, R.E., 1979, Influence of redox environments on the mobility of arsenic in groundwater, *in* Jenne, E.A., ed., Chemical Modeling in Aqueous Systems: American Chemical Society, Washington D.C., p. 221–226.

Gundersen, L.C., Schumann, R.R., Otton, J.K., Dubiel, R.F., Owen, D.E., and Dickinson, K.A., 1992, Geology of radon in the United States: Geological Society of America Special Paper, v. 271, p. 1–16.

Hamilton, W., 1964, Volcanic rocks of the West Yellowstone and Madison Junction quadrangles, Montana, Wyoming, and Idaho: U.S. Geological Survey Professional Paper 435-G, p. 209–222.

Helsel, D.R., 2011, Statistics for censored environmental data using Minitab and R, second ed.: New York, John Wiley & Sons.

Helsel, D.R., Hirsch, R.M., Ryberg, K.R., Archfield, S.A., and Gilroy, E.J., 2020, Statistical methods in water resources: U.S. Geological Survey Techniques and Methods, book 4, chap. A3, 458 p., doi: https://doi.org/10.3133/tm4a3 [Supercedes USGS Techniques of Water-Resources Investigations, book 4, chap. A3, version 1.1.].

Hem, J.D., 1972, Chemical factors that influence the availability of iron and manganese in aqueous systems: Geological Society of America Bulletin, v. 83, no. 2, p. 443–450.

Hildreth, W., Christiansen, R.L., and O'Neil, J.R, 1984, Catastrophic isotopic modification of rhyolitic magma at times of caldera subsidence, Yellowstone Plateau volcanic field. Journal of Geophysical Research: Solid Earth, v. 89, p. 8339–8369.

Horton, T.W., Chamberlain, C.P., Fantle, M., and Blum, J.D., 1999, Chemical weathering and lithologic controls of water chemistry in a high-elevation river system: Clark's Fork of the Yellowstone River, Wyoming and Montana: Water Resources Research, v. 35, no. 5, p. 1643–1655.

Johnson, Greg, 2020, Important information about your drinking water elevated fluoride levels detected at Town of West Yellowstone, available at https://www.townofwestyellowstone.com/wp-content/uploads/2021/06/June-2021-Fluoride-Report.pdf [Accessed July 2020].

Julian, P., and Helsel, D., 2021, Data Analysis for Censored Environmental Data, R package version 1.0.0, available at https://cran.r-project.org/package=NADA2 [Accessed January 2023].

Kharaka, Y.K., Thordsen, J.J., and White, L.D., 2002, Isotope and chemical compositions of meteoric and thermal waters and snow from the greater Yellowstone National Park region: U.S. Geological Survey Open-File Report 02-194, 18 p.

Knapton, J.R., and Brosten, T.M., 1988, Arsenic and chloride data for five streams in the Madison River drainage, Montana, 1988, U.S. Geological Survey Open-File Report 88-722, 12 p.

Knapton, J.R., and Horpestad, A.A., 1987, Arsenic and chloride data for streams in the upper Missouri River Basin, Montana and Wyoming, U.S. Geological Survey Open-File Report 87-124, 28 p.

LaFave, J.I., Carstarphen, C.A., and Crowley, J., 2017, Fluoride concentrations in Montana's groundwater: Montana Bureau of Mines and Geology Hydrogeologic Map 10, 1 sheet.

Leeman, W.P., Doe, B.R., and Whelan, J., 1977, Radiogenic and stable isotope studies of hot-spring deposits in Yellowstone National Park and their genetic implications: Geochemical Journal, v. 11, no. 2, p. 65–74.

McCleskey, R.B., Nordstrom, D.K., Hurwitz, S., Colman, D.R., Rother, D.A., Johnson, M., and Boyd, E.S., 2022, The source, fate, and transport of arsenic in the Yellowstone hydrothermal system—An overview: Journal of Volcanology and Geothermal Research, doi: https://doi.org/10.1016/j.jvolgeores.2022.107709.

Metesh, J.J., 2004, Spring inventory, Yellowstone controlled ground-water area: Montana Bureau of Mines and Geology Open-File Report 510, 54 p.

Metesh, J.J., and Kougioulis, J., 1999, Yellowstone National Park controlled ground water area, Montana: Well inventory and baseline sampling: Montana Bureau of Mines and Geology Report of Investigation 8, 25 p.

Miller, F.R., Ewing, S.A., Payn, R.A., Paces, J.B., Leuthold, S.J., and Custer, S.G, 2021, Sr and U isotopes reveal the influence of lithologic structure on groundwater contributions along a mountain headwater catchment (Hyalite Canyon, MT): Journal of Hydrology, 594, doi: https://doi.org/10.1016/j.jhydrol.2020.125653.

Montana Bureau of Mines and Geology (MBMG), 2022, Ground Water Information Center (GWIC) online database, available at https://mbmggwic.mtech.edu/ [Accessed December 1, 2022].

Montana Department of Environmental Quality (DEQ), 2019, Water Quality Division, Water Quality Planning Bureau, Water Quality Standards and Modeling Section, DEQ-7 Montana Numeric water quality standards, available at https://deq.mt.gov/files/Water/WQPB/Standards/PDF/DEQ7/DEQ-7.pdf [Accessed August 2022].

Montana Department of Environmental Quality (DEQ), 2021, Manganese in Montana's drinking water: Frequently asked questions, available at https://deq.mt.gov/files/Water/PWSUB/Documents/Manganese/MT_Mn_FAQs_Final_2-26-21.pdf [Accessed July 2022].

Morin, G., and Calas, G., 2006, Arsenic in soils, mine tailings, and former industrial sites: Elements, v. 2, p. 97–101.

Myers, W.B., and Hamilton, W., 1964, Deformation accompanying the Hebgen Lake Earthquake of August 17, 1959: U.S. Geological Survey Professional Paper 435-G, p. 55–98.

National Park Service (NPS), 1994, Baseline water quality data inventory and analysis, Yellowstone National Park, NPS Technical Report NPS/NRWRD/NRTR-94/22, 1083 p.

National Park Service (NPS), 2022a, Annual Park recreation visits (1904–last calendar year), available at https://irma.nps.gov/STATS/Reports/Park/YELL [Accessed November 2022].

National Park Service (NPS), 2022b, Water quality in the Madison River near West Yellowstone, MT, available at https://www.nps.gov/articles/000/madison-river-water-quality.htm [Accessed December 2022]

Nimick, D.A., Moore, J.N., Dalby, C.E., and Savka, M.W., 1998, The fate of geothermal arsenic in the Madison and Missouri Rivers, Montana and Wyoming: Water Resources Research, v. 34, p. 3051–3067.

O'Neill, J.M., and Christiansen, R.L., 2002, Geologic map of the Hebgen Lake 30′ x 60′ quadrangle, Beaverhead, Madison, and Gallatin Counties, Montana, Park and Teton Counties, Wyoming, and Clark and Fremont Counties, Idaho: Montana Bureau of Mines and Geology Open-File Report 464, 21 p., 1 sheet, scale 1:100,000.

O'Neill, J.M., and Christiansen, R.L., 2004, Geologic map of the Hebgen Lake quadrangle, Beaverhead, Madison, and Gallatin Counties, Montana, Park and Teton Counties, Wyoming, and Clark and Fremont Counties, Idaho: United States Geological Survey Scientific Investigations 2816, 1 sheet, scale 1:100,000.

Peterman, Z.E., Doe, B.R., and Prostka, H.J., 1970, Lead and strontium isotopes in rocks of the Absaroka Volcanic Field, Wyoming: Contributions to Mineralogy and Petrology, v. 27, no. 2, p. 121–130.

Pierce, K.L., 1979, History and dynamics of glaciation in the northern Yellowstone National Park area: U.S. Geological Survey Professional Paper 729-F, 90 p.

R Core Team, 2020, R: A language and environment for statistical computing: R Foundation for Statistical Computing, available at http://www.R-project.org [Accessed January 2023].

Richmond, G.W., 1964, Glacial geology of the West Yellowstone basin and adjacent parts of Yellowstone National Park: U.S. Geological Survey Professional Paper 435-G, p. 223–236.

Stauffer, R.E., and Thompson, J.M., 1984, Arsenic and antimony in geothermal waters of Yellowstone National Park, Wyoming, USA: Geochimica et Cosmochimica Acta, v. 48, p. 2547–2561.

Thompson, J.M., 1979, Arsenic and fluoride in the upper Madison River system: Firehole and Gibbon Rivers and their tributaries, Yellowstone National Park, Wyoming, and southeast Montana: Environmental Geology, v. 3, p. 13–21.

Timmer, Jacqueline, 2020, MBMG Analytical Laboratory: Quality assurance manual: Montana Bureau of Mines and Geology Open-File Report 729, 8 p.

Town of West Yellowstone, 2022, Home page, available at https://www.townofwestyellowstone.com/ [Accessed August 2022].

U.S. Census Bureau, 2022, Explore census data, available at https://data.census.gov/cedsci/table?q=West+Yellowstone%2C+MT+2020 [Accessed August 2022].

U.S. Geological Survey (USGS), 1964, The Hebgen Lake, Montana, earthquake of August 17, 1959: U.S. Geological Survey Professional Paper 435, 242 p.

Western Regional Climate Center, 2022, West Yellowstone, Montana (248847), available at https://wrcc.dri.edu/cgi-bin/cliMAIN.pl?mtwesy [Accessed September 15, 2022].

Witkind, I.J., Hadley, J.B., and Nelson, W.H., 1964, Pre-Tertiary stratigraphy and structure of the Hebgen Lake area: U.S. Geological Survey Professional Paper 435-G, p. 199–208.

Zogorski, J.S., Carter, J.M., Ivahnenko, T., Lapham, W.W., Moran, M.J., Rowe, B.L., Squillace, P.J., and Toccalino, P.L., 2006, Volatile organic compounds in the nation's ground water and drinking-water supply wells: U.S. Geological Survey Circular 1292, 101 p., doi: https://doi.org/10.3133/cir1292.

Zou, J., Yang, Y., and Zhang, H., 2018, Sr isotope fingerprinting of multiple water-source characterizations and its environmental implications in a complex lake-groundwater system, Wudalianchi, Northeast China: Chemosphere, v. 212, p. 1095–1103.