

MANGANESE CONCENTRATIONS IN MONTANA'S GROUNDWATER



Ann E.H. Hanson and John I. LaFave

**Montana Bureau of Mines and Geology
Ground Water Assessment Program**

Front photo: Sampling groundwater in the Shields Valley, Montana. Photo by Don Mason, MBMG.

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ABSTRACT

Emerging research indicates that elevated manganese concentrations in drinking water may have adverse neurological effects in children and adults. About 61 percent of Montanans obtain their drinking water from groundwater, which in some locations contains detectable, naturally occurring manganese. This report evaluates manganese concentrations in Montana's principal aquifers based on 3,858 groundwater samples from across the State. For each aquifer, manganese concentrations were compared to the Montana Department of Environmental Quality's recommended health guidelines, and the manganese concentrations were assessed based on geochemical conditions (redox, pH, and iron concentrations) and well depth. Overall, manganese concentrations were low, with 85 percent of samples containing ≤ 0.1 mg/L, which is considered safe to drink for all ages. Fifteen percent of samples exceeded 0.1 mg/L, which is the recommended limit for infants and children 6 yr and younger, and about half of these samples (7 percent of the total) exceeded 0.3 mg/L, which is the recommended health standard limit for adults and children older than 6.

Low manganese concentrations were most common in western fractured-bedrock and basin-fill aquifers. Elevated concentrations (>0.3 mg/L) were most frequently detected in eastern alluvial and layered sedimentary rock aquifers. In several subsets of the principal aquifers, including the Lonepine basin-fill aquifer southwest of Flathead Lake, the buried-valley aquifers in central and northeast Montana, and the Missouri River alluvial aquifers, greater than 24% of samples contained elevated manganese (>0.3 mg/L). Multiple linear regression using censored statistics (which accounts for manganese concentrations below the laboratory detection limit) generally demonstrated positive correlations between manganese and iron; inverse correlations between manganese and redox and manganese and pH; and inconsistent to no correlations with well depth. The aquifer material composition, geothermal waters, and/or legacy mining impacts can affect local groundwater chemistry and obscure hydrogeochemical relationships. However, low redox and, to a lesser extent, low pH were commonly associated with elevated manganese and iron concentrations in groundwater. Water managers, local government officials, and homeowners may use these data to understand the distribution of manganese in groundwater across the State. These data may guide sampling efforts and support education about drinking water quality.

INTRODUCTION

Manganese (Mn) is a naturally occurring element present in sediments and rocks throughout Montana and the world. Its concentration in groundwater can vary considerably depending on the abundance of manganese in the aquifer materials and the aquifer geochemical conditions. The extent to which manganese can dissolve in groundwater is related to the reduction-oxidation (redox) conditions and the pH (acidity) of the water (Hem, 1985). In general, water that is reducing (which will generally have less oxygen and be considered more anoxic) and slightly acidic (pH <7) will more readily dissolve manganese (Hem, 1972). Redox (and dissolved oxygen) typically decreases along groundwater flow paths, further downgradient and with depth in aquifers. Elevated iron (Fe) concentrations typically accompany manganese (Ayotte and others, 2011).

Small concentrations of manganese are commonly ingested through food and are essential for human

health. However, drinking water that contains elevated manganese is an aesthetic and potential human-health concern. The U.S. Environmental Protection Agency (EPA) has set a secondary maximum contaminant level for manganese at 0.05 milligrams per liter (mg/L) because it stains plumbing fixtures and laundry, and can impart a bitter taste to water (EPA, 2004, 2021). Emerging research indicates that elevated manganese in drinking water may be linked with memory, attention, and motor skill problems; children younger than 6 may be adversely affected by low concentrations of manganese (Bouchard and others, 2007; ATSDR, 2012; Avila and others, 2013; Montana DEQ, 2021). Because of these human-health concerns, the Montana Department of Environmental Quality (MDEQ) recommends the following guidelines for manganese concentrations in drinking water:

- Less than 0.10 mg/L for those 6 yr old and under
- Less than 0.30 mg/L for those older than 6

These MDEQ human-health guidelines for manganese are not regulatory standards.

In Montana, groundwater obtained from wells and springs is the source of drinking water for about 61% of the population (Dieter and others, 2018). In most rural areas, groundwater supplies all the domestic, stock, and ranch needs. In some of Montana's cities, such as Missoula, Kalispell, and Sidney, groundwater is the public water supply source.

The purpose of this report is to describe the natural occurrence and distribution of manganese in Montana's principal aquifers using existing water-quality data. The data were compiled largely by the Montana Bureau of Mines and Geology's (MBMG) Ground Water Assessment Program, which has sampled and analyzed groundwater throughout Montana since 1993; these groundwater-quality data are available to the public through the Ground Water Information Center database (<http://mbmggwic.mtech.edu>).

This report discusses manganese concentrations by aquifer, assesses manganese based on the MDEQ human-health guidelines, and evaluates potential relationships between manganese and other aquifer geochemical conditions.

METHODS

Data from wells and springs were compiled from the GWIC database to assess manganese concentrations in Montana groundwater. Criteria used to assemble the dataset included identifying:

- samples collected by the MBMG after 1993 and analyzed by the MBMG analytical laboratory,
- samples with a complete analysis for inorganic compounds,
- samples from sites with a known source aquifer and total depth, and
- analyses with a manganese reporting limit <0.1 mg/L (to remove samples with anomalously high reporting limits).

For sites with more than one sample, the analysis with the highest manganese concentration was used. The complete dataset can be found in appendix A as a Microsoft Excel file.

The resultant dataset includes 3,858 groundwater samples from 3,758 wells and 100 springs. These sample sites are distributed across the State and represent all the principal aquifers (fig. 1). The analyses include major ion and iron (Fe) concentrations, and many include measurements of pH and redox potential. Additional information includes source aquifer and, for wells, depth. Well depth in this report refers to the top of the well-screen perforation where water enters the well. Total well depth is used for wells with an unknown depth to the well-screen. Most of the samples were from domestic (63 percent) or stockwater (13 percent) wells. Wells with reported water uses of monitoring, public water supply, irrigation, or other (e.g., commercial, unused) were also included in this study (fig. 1B).

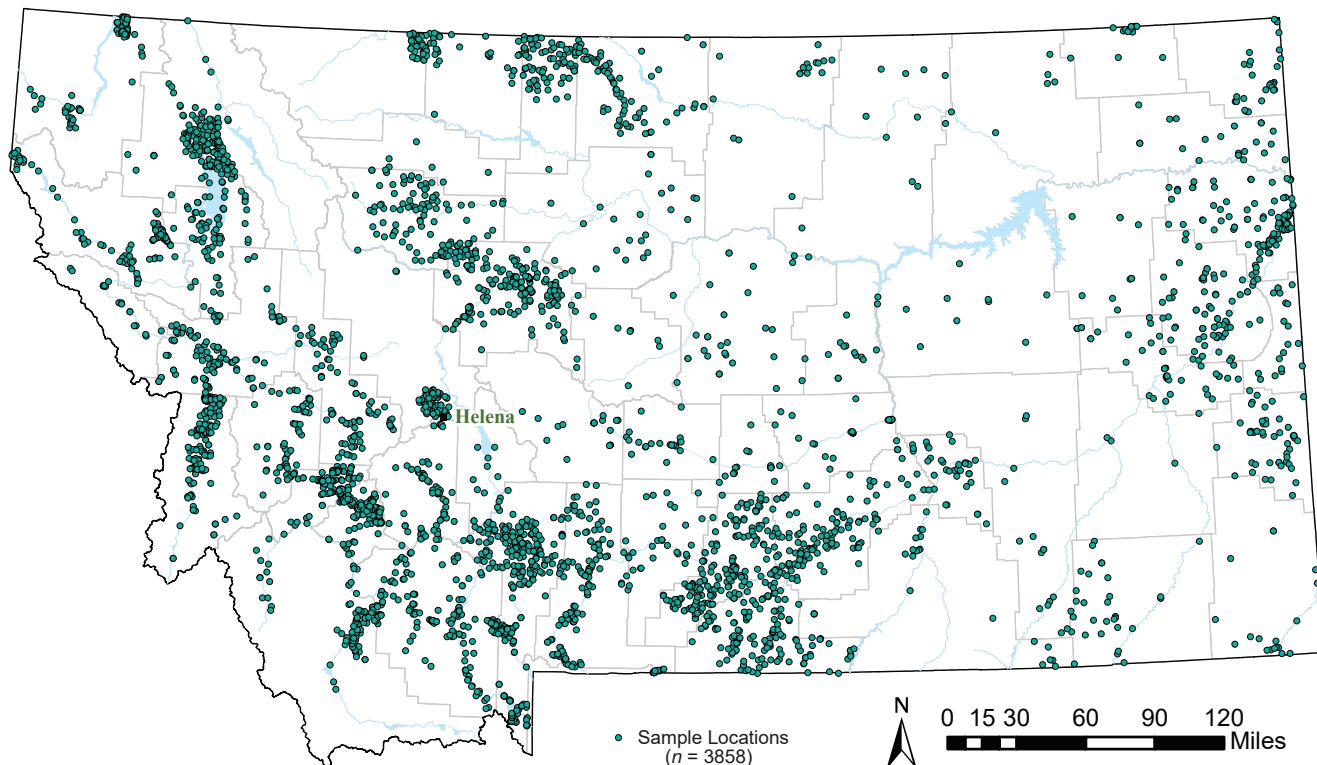
For each aquifer, maps were compiled to show the distribution of manganese concentrations and highlight areal patterns; the concentrations were grouped and symbolized according to the recommended MDEQ health standards into the following ranges:

- ≤ 0.10 mg/L safe to drink,
- >0.10 mg/L and ≤ 0.3 mg/L potentially harmful to those 6 yr old and under
- >0.30 mg/L potentially harmful to all age groups.

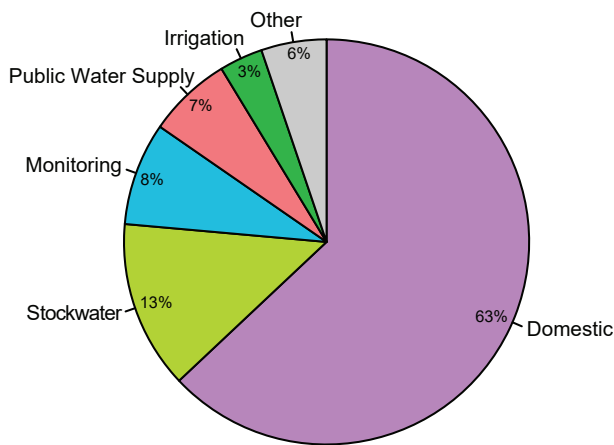
For the purposes of this report, "elevated manganese" refers to concentrations that exceed the MDEQ human-health benchmark of 0.30 mg/L.

The treatment of censored results in this study is important because manganese concentrations were below detection in a large proportion of the samples. Censored values or "non-detects" are concentrations below the analytical detection limit (e.g., <0.001 mg/L if the detection limit was 0.001 mg/L). A censored value does not provide a discrete numerical value; however, it does provide a constraint, or upper limit, on the manganese concentration. Estimates of the overall data distribution are affected by the treatment of censored values, and we applied methods to account for censored values while compiling summary statistics for each aquifer (Helsel, 2011). The Kaplan–Meier method was used to estimate means and medians. Regression-on-order (ROS) techniques were used to estimate non-detected values in censored box plots, including whiskers, first quartile, median, and third

A. Mn Sample Locations



B. Percentage of Samples by Well Use



C. Percentage of Samples by Principal Aquifer

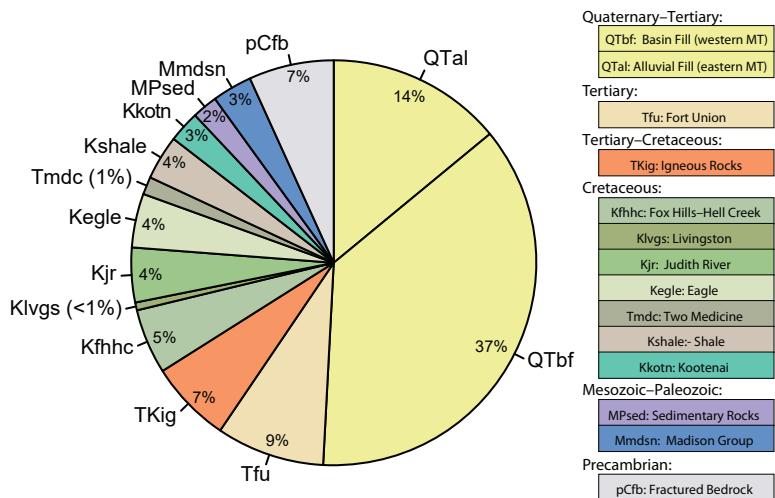


Figure 1. (A) Map showing the location of all Mn samples in this dataset. (B) Pie chart of the well uses in the Mn dataset. The top five well uses are domestic, stockwater, monitoring, public water supply, and irrigation. (C) Pie chart showing the percentage of samples in the Mn dataset from each principal aquifer. Explanation of aquifer abbreviations are found in text. Note that 51% of the wells in this dataset are from QTbf and QTal aquifers.

quartile values that were below the maximum non-detect value. Other calculated statistics such as minimums, maximums, and percentages did not require censored-specific statistical methods.

Multiple linear regression was used to assess the relationship between manganese concentrations and (a) field redox, (b) field pH, (c) iron concentration, and (d) well depth. Because groundwater typically has small manganese and iron concentrations, the distribution of the data is heavily weighted to small values (i.e., a non-normal data distribution); therefore, both manganese and iron concentrations were log-transformed for statistical testing. The correlation between manganese and the explanatory variables (e.g., redox, pH, Fe, well depth) was analyzed using a censored maximum likelihood estimation method (Helsel, 2011; Julian and Helsel, 2021). The measure of strength for the overall maximum likelihood estimation regression relationship is given by the rescaled likelihood R^2 (Helsel, 2011). The explanatory variables were considered statistically significant when they had a p -value ≤ 0.05 . To check for potential statistical complications due to the explanatory variables being too closely related, variance inflation factors (VIF) were assessed. A VIF value greater than 10 suggests potential correlation between the explanatory variables. All VIFs evaluated for this project were less than 1.9. Statistics were calculated in R (R Core Team, 2020) using NADA and NADA2 packages (Helsel, 2011; Lee, 2020; Julian and Helsel, 2021).

MONTANA AQUIFERS

Montana's groundwater is stored within aquifers that are closely tied to the geology of two prominent physiographic regions: (1) the intermontane basins of the northern Rocky Mountains in western Montana and (2) the northern Great Plains in eastern Montana (fig. 2; LaFave, 2020). Each physiographic province represents broad differences in geology and geologic history, creating different hydrogeologic settings and differences in water quality. Generally, the aquifers range from unconsolidated sand and gravel deposits to consolidated sedimentary, metamorphic, igneous, and volcanic rocks.

Within the western intermontane basins, most groundwater occurs in shallow water-table sand and gravel aquifers, and deep confined to semi-confined aquifers in the basin-fill. Both aquifer types contain large amounts of groundwater and are highly productive and utilized. Less productive fractured-rock aquifers occur in Precambrian metasediments and Tertiary–Cretaceous igneous rocks in the mountains that surround the valleys (fig. 3).

In the northern Great Plains region, the principal aquifers consist of layered sedimentary sandstone and limestone, and alluvial sediments (fig. 3). The Tertiary Fort Union Formation (consisting of sandstone, shale, and coal) is the youngest bedrock aquifer and is exposed over the eastern third of Montana. Strati-

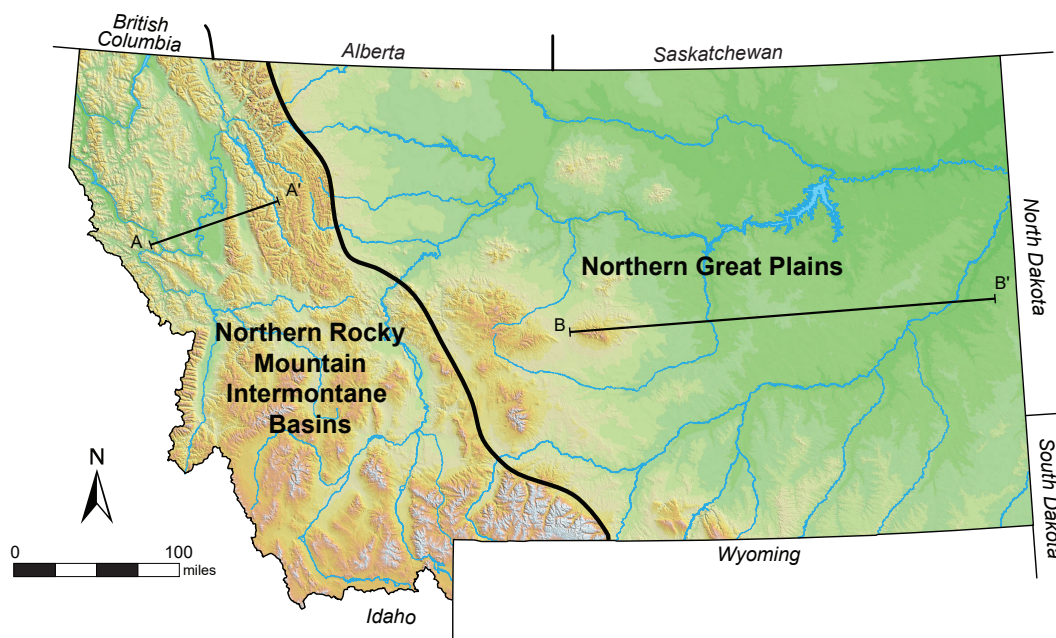


Figure 2. Physical geography of Montana showing the two main regions: northern Rocky Mountain intermontane basins and the northern Great Plains. Lines A–A' and B–B' refer to aquifer cross-sections shown in figure 3.

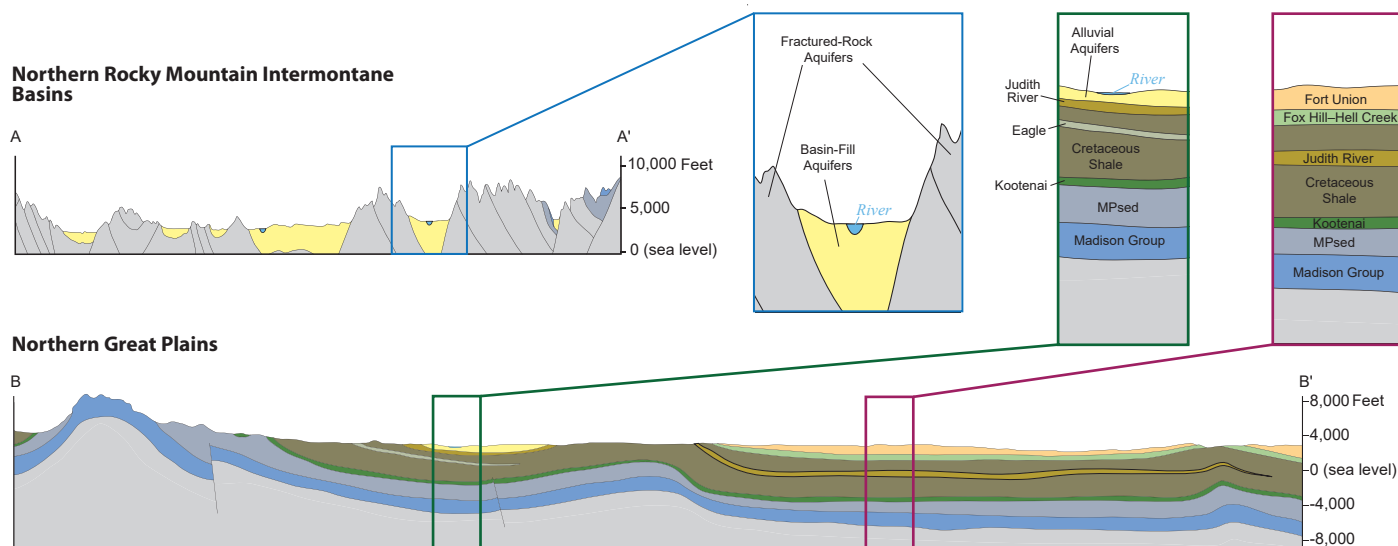


Figure 3. Representative cross-sections of the northern Rocky Mountain intermontane basins and the northern Great Plains with principal aquifers labeled (after Crowley and others, 2017). Note the very different geologic structure between the two regions (e.g., faulted/folded vs. flat-lying). Cross-section lines are shown in figure 2.

graphically below the Fort Union is a sequence of Cretaceous sandstone aquifers that are separated by thick shale units; from youngest to oldest they are: the Fox Hills–Hell Creek, the Judith River, the Eagle, and the Kootenai. The basal (deepest, stratigraphically) principal aquifer of the Montana plains is the Madison Group limestone. Although it underlies most of eastern Montana, the Madison is only a fresh-water aquifer near outcrop areas where it is relatively close to the surface. Local-scale aquifers that are also important groundwater sources include alluvial aquifers within the Missouri and Yellowstone River watersheds, terrace “benches” off the Rocky Mountain Front, and buried-valley aquifers in northeast and central Montana.

DATA AND RESULTS

Of the 3,858 analyses, manganese concentrations ranged from below detection limits to 51.3 mg/L, with a median of 0.003 mg/L. Detection limits ranged from 0.001 to 0.031 mg/L, and many of the samples (43 percent) had manganese concentrations below the method detection limits (censored values).

Overall, concentrations were low; 85 percent of samples had concentrations less than the “safe” limit of 0.10 mg/L, 8 percent of the samples had concentrations between 0.10 and 0.30 mg/L (exceeds recommendation for children 6 yr old and younger), and 7 percent (291) of the samples exceeded the recommended health standard of 0.30 mg/L. Each principal

aquifer contained some sites with elevated manganese (>0.3 mg/L), but concentrations exceeding 0.3 mg/L were most frequently detected in the eastern Montana alluvial aquifers (QTal) and the Cretaceous shale aquifers (Kshale; fig. 4).

Aquifer Comparison

Manganese concentrations for the principal aquifers are summarized on the boxplots in figure 4; the box plots are ordered by increasing estimated median manganese concentration. Overall, lower manganese concentrations occur in the western Montana basin-fill and fractured-rock aquifers, whereas the higher manganese concentrations occur in the eastern Montana sandstone and alluvial aquifers. However, there are some geographic patterns within and among the principal aquifers. The following discussion summarizes the manganese concentration by aquifer and evaluates the degree to which redox, pH, iron, and well depth are related to manganese solubility.

Basin-Fill (QTbf) and Alluvial (QTal) Aquifers

The western Montana intermontane basin-fill aquifers (QTbf) and the eastern alluvial and terrace “bench” aquifers (QTal, hereafter referred to as alluvial aquifers) are some of the most productive and utilized aquifers in the State. Manganese oxides that coat alluvial sediments may serve as a source of manganese in these aquifers (Hem, 1985; Warner and Ayotte, 2015). Fifty-one percent of the sampled wells are from these two aquifer systems (fig. 1C). Overall,

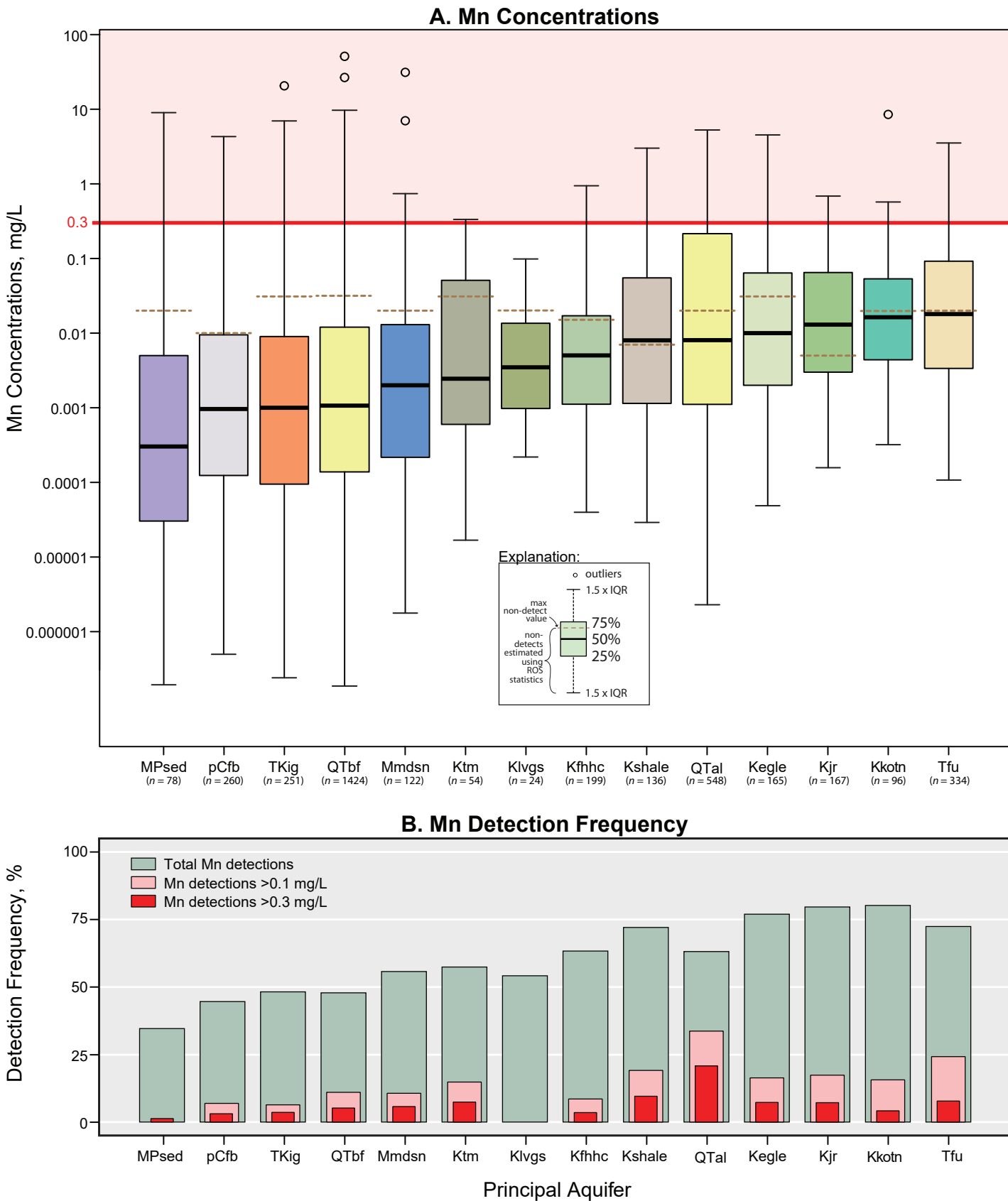


Figure 4. (A) Boxplots of Mn concentrations among the principal aquifers in order of increasing median. The portion of the boxplots below the maximum non-detect line (brown dash) contains estimated values using regression-on-order (ROS) statistics (Helsel, 2011). Note that the y-axis scale is lognormal. (B) Frequency plot of total Mn detections, Mn detections >0.1 mg/L, and Mn detections >0.3 mg/L in each principal aquifer. IQR, interquartile range.

manganese concentrations ranged from below detection limits to 51.3 mg/L; however, concentrations are generally lower in the western basin-fill aquifers (table 1; fig. 5).

Of the 1,424 western basin-fill samples, 89 percent had manganese concentrations less than 0.1 mg/L, 6 percent were between 0.1 and 0.3 mg/L, and 5 percent (74) exceeded 0.3 mg/L (fig. 5). One area of notable manganese occurrence in the western basin-fill is the Lonepine aquifer that underlies the Little Bitterroot Valley near Hot Springs (figs. 5, 6). The Lonepine sand and gravel aquifer is confined by a thick sequence of glacial lake clay and silt, generally occurs more than 200 ft below the land surface, is the main source of water locally, and is geothermal in places (LaFave and others, 2004; Abdo, 1997). All of the Lonepine samples (34) had detectable manganese, and 32 percent of these exceeded 0.3 mg/L; the median concentration was 0.146 mg/L (fig. 6; table 2).

The Kalispell valley, north of Flathead Lake, also had a relatively high manganese detection frequency. Manganese was detected in 53 percent of the Kalispell Valley basin-fill samples, with 24 percent exceeding 0.1 mg/L, and 9 percent exceeding 0.3 mg/L (fig. 6). The other western Montana basin-fill aquifers had a lower frequency of manganese detection (less than 50 percent) and lower concentrations (fig. 6).

Overall, the elevated manganese concentrations in the western basin-fill aquifers are associated with more reducing conditions and lower pH values; manganese is also associated with elevated iron concentrations (fig. 7), but the manganese concentrations do not have a statistically significant relationship with well depth (fig. 7).

Of the 548 eastern Montana alluvial aquifer (QTal) samples, 66 percent had concentrations less than 0.1 mg/L, 13 percent were between 0.1 and 0.3 mg/L, and 21 percent (114) exceeded 0.3 mg/L (fig. 5). There are distinct geographic patterns to the elevated manganese occurrence in the eastern alluvial aquifers that are related to the hydrogeologic setting. The highest frequency of detection and the highest concentrations occur in the buried-valley aquifers in northeast Montana and near Great Falls (figs. 5, 6). The Clear Lake and West Crain buried-valley aquifers near Plentywood and Sidney, respectively, occupy preglacial valleys and are productive sources of

Table 1. Manganese summary statistics for Montana's principal aquifers.

Aquifer Name	Aquifer Abbreviation	No. of Samples	% Detected	% of Detections >0.1 mg/L and ≤0.3 mg/L	% of Detections >0.3 mg/L	Mean ¹ (mg/L)	Median ¹ (mg/L)	Minimum (mg/L)	Maximum (mg/L)	Median Redox ² (mV)	Median pH ²	Median Well Depth ³ (ft)
Basin-fill (western MT)	QTbf	1,424	47.9	5.8	5.2	0.129	0.001	<0.001	51.3	175	7.6	84
Alluvial fill (eastern MT)	QTal	548	62.6	12.8	20.6	0.247	0.008	<0.001	5.25	91	7.5	38
Fractured bedrock	pCfb	260	44.6	3.8	3.1	0.044	0.001	<0.001	4.30	151	7.7	200
Tertiary-Cretaceous igneous rocks	TK'ig	251	48.2	2.8	3.6	0.170	0.001	<0.001	20.6	210	7.5	134
Fort Union	Tfu	334	72.4	16.4	7.8	0.090	0.018	<0.001	3.53	30	7.6	105
Fox Hills-Hell Creek	Kfhhc	199	63.3	5.0	3.5	0.039	0.005	<0.001	0.938	-64	8.5	140
Livingston	Klvgs	24	54.2	0.0	0.0	0.013	0.004	<0.001	0.098	168	7.9	99
Judith River	Kjr	167	79.6	10.2	7.2	0.068	0.014	<0.001	0.686	12	8.0	110
Two Medicine	Ktm	54	57.4	7.4	7.4	0.046	0.003	<0.001	0.334	128	7.6	90
Eagle	Kegle	165	77.0	9.1	7.3	0.109	0.010	<0.001	4.53	51	7.6	136
Cretaceous Shale	Kshale	136	72.1	9.5	9.6	0.116	0.008	<0.001	3.01	24	7.7	94
Kootenai	Kkotn	96	80.2	11.4	4.2	0.142	0.017	<0.001	8.60	114	7.6	315
Mesozoic-Paleozoic sedimentary rocks	MPsed	78	34.6	0.0	1.3	0.123	<0.001	<0.001	9.00	194	7.6	144
Madison Group	Mmdsn	122	55.7	5.0	5.7	0.351	0.003	<0.001	31.2	130	7.5	312

¹Estimated using Kaplan-Meier method (Helsel, 2011; Julian and Helsel, 2021).

²Redox and pH values were not available for all well sites; median redox and median pH were calculated with available data.

³Determined from depth of screened interval, if available; otherwise total depth of well.

Basin-Fill (QTbf) and Alluvial Fill (QTal) Aquifers

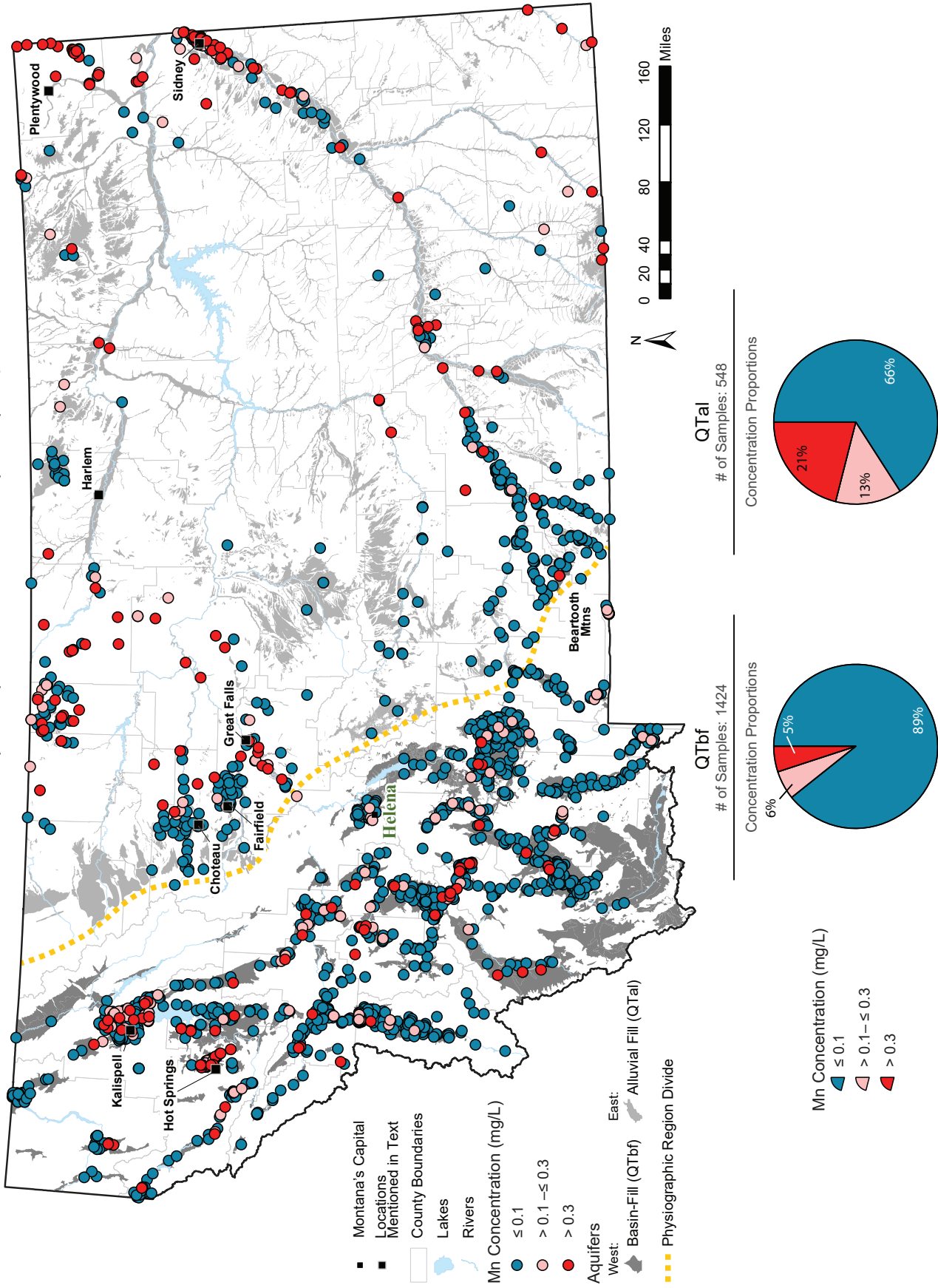
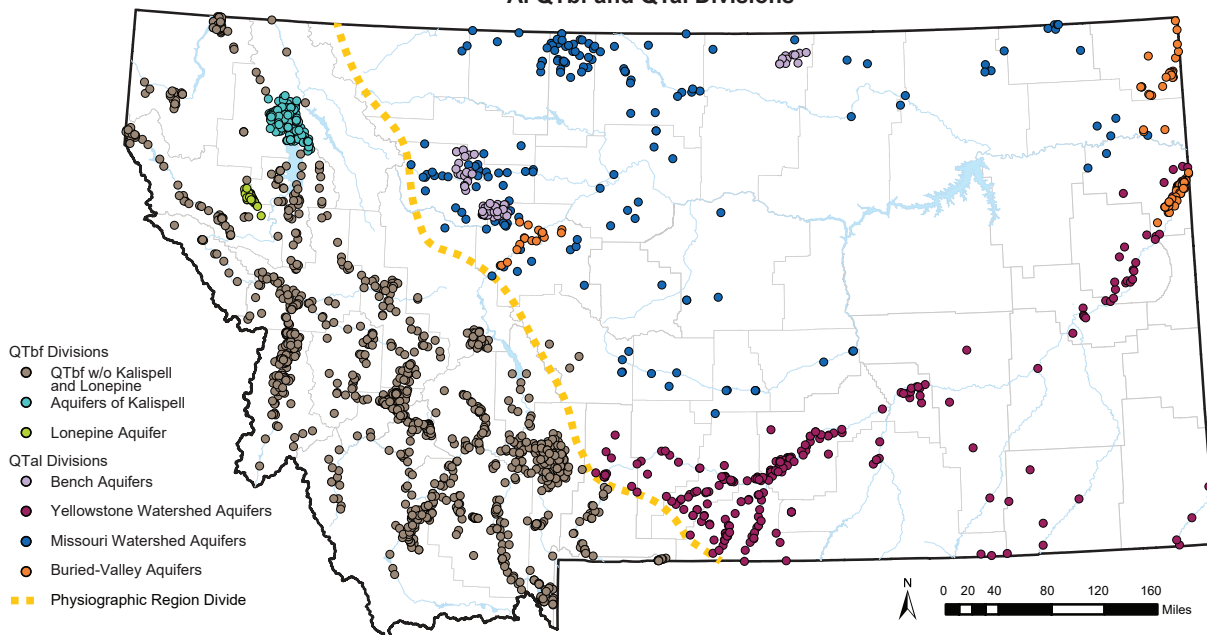
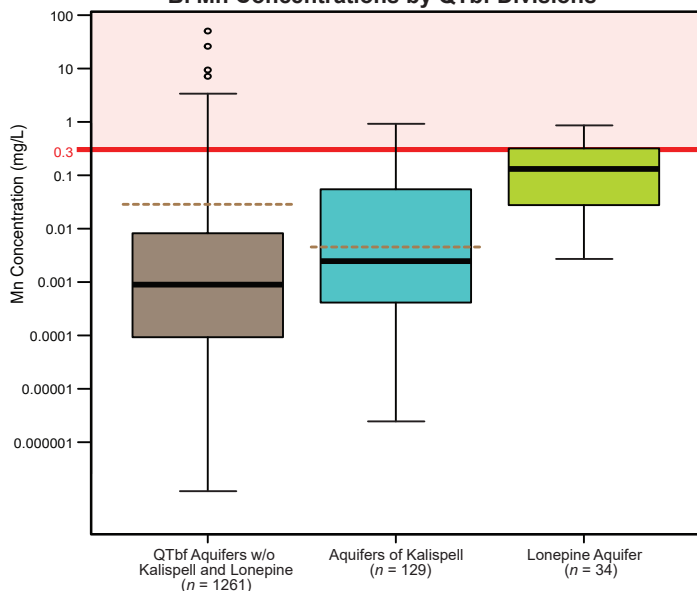


Figure 5. Distribution of Mn concentrations in the Basin Fill (QTbf) and Alluvial Fill (QTal) principal aquifers. Pie charts of Mn concentrations in each aquifer display the three Mn groups: blue, safe to drink; pink, potentially harmful to those ≤6 years old; and red, exceeds recommended guideline for all age groups. QTbf and QTal aquifers are grouped by physiographic region (e.g., all samples west of the physiographic region divide are QTbf and all samples east of the physiographic region divide are QTal).

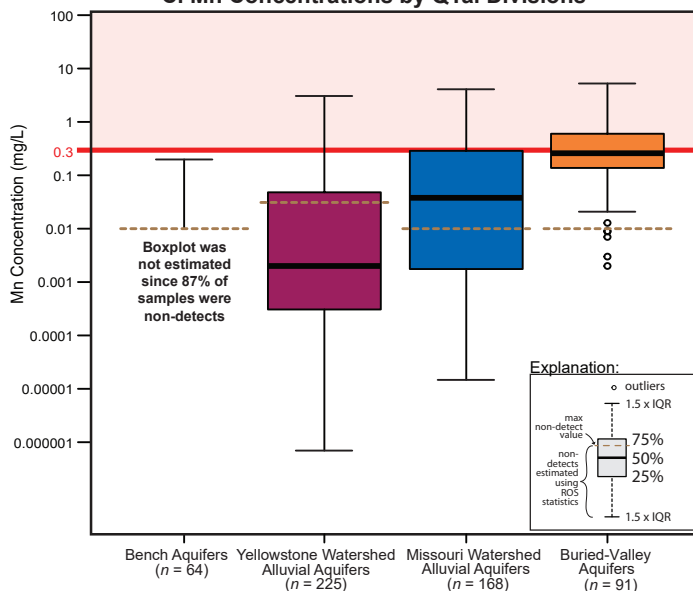
A. QTbf and QTal Divisions



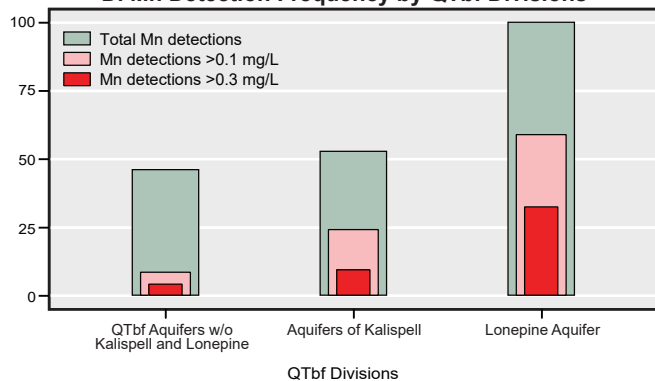
B. Mn Concentrations by QTbf Divisions



C. Mn Concentrations by QTal Divisions



D. Mn Detection Frequency by QTbf Divisions



E. Mn Detection Frequency by QTal Divisions

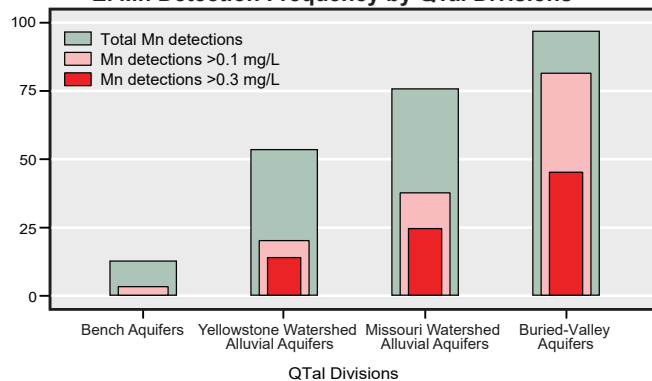


Figure 6. (A) Map showing location of QTbf and QTal Mn samples that were grouped based on notable Mn concentration in specific aquifers/locations. (B, C) Boxplots of Mn concentrations for QTbf (B) and QTal (C) divisions in order of increasing median. The portion of the boxplots below the maximum non-detect line (brown dash) contains estimated values using regression-on-order (ROS) statistics (Helsel, 2011). Note that the y-axis scale is lognormal. (D, E) Frequency plot of total Mn detections, Mn detections >0.1 mg/L, and Mn detections >0.3 mg/L for the for QTbf (D) and QTal (E) divisions.

Table 2. Manganese summary statistics for QTbf aquifer divisions.

Aquifer	No. of Samples	% of Detections		Mean ¹ (mg/L)	Median ¹ (mg/L)	Minimum (mg/L)	Maximum (mg/L)	Median Redox ² (mV)	Median pH ²	Median Well Depth ³ (ft)
		% Detected	>0.1 mg/L and ≤0.3 mg/L							
QTbf w/o Kalispell and LonePine	1,261	46.0	4.4	0.130	0.001	<0.001	51.3	181	7.5	77
Kalispell	129	52.7	14.7	0.089	0.002	<0.001	0.970	185	7.6	169
LonePine	34	100.0	26.4	0.248	0.146	0.003	0.907	-87	8.2	275

¹Calculated using Kaplan–Meier method (Helsel, 2011; Julian and Helsel, 2021)

²Redox and pH values were not available for all well sites; median redox and median pH were calculated with available data.

³Determined from depth of screened interval, if available, otherwise total depth of well.

irrigation and domestic water (Reiten, 2002; Chandler and Reiten, 2020). Near Great Falls, the course of the preglacial Sun River forms a buried-valley aquifer that is a source of domestic water (Lemke and Maughan, 1977). These aquifers are generally deeper than other eastern Montana alluvial aquifers and are more likely to be confined or semi-confined. Most of the samples from these aquifers had detectable manganese, with 81 percent of the samples exceeding 0.1 mg/L, and 45 percent exceeding 0.3 mg/L; the median manganese concentration was 0.259 mg/L (fig. 6; table 3).

The lowest alluvial manganese concentrations occur in the terrace-bench aquifers off the Rocky Mountain Front and in north-central Montana. The Greenfields bench near Fairfield, the Burton bench north of Choteau, and the Turner–Hogland bench northeast of Harlem are all characterized by surficial sand and gravel aquifers generally less than 50 ft thick on top of Cretaceous shales that are recharged by irrigation water (Miller and others, 2002; Patton, 1988, 1991). The low manganese concentrations on the terrace-bench aquifers likely reflect the irrigation water that is conveyed and applied across the benches; irrigation water is the main source of aquifer recharge. These aquifers are used for municipal, domestic, and irrigation supply. Manganese concentrations in samples from these aquifers were low: 13 percent had detectable manganese, only two samples exceeded 0.1 mg/L, and no samples exceeded 0.3 mg/L (figs. 5, 6).

The other main eastern Montana alluvial aquifers are associated with the Missouri River to the north and the Yellowstone River to the south (fig. 6). Manganese concentrations were generally higher in the alluvial aquifers within the Missouri River watershed. Seventy-six percent of the samples had detectable manganese: 38 percent of the samples exceeded 0.1 mg/L, 24 percent exceeded 0.3 mg/L, and the median concentration was 0.041 mg/L (fig. 6, table 3). The alluvial aquifers within the Yellowstone River watershed had a lower manganese detection frequency; about half of the samples had detectable manganese, 20 percent exceeded 0.1 mg/L, and the estimated median was 0.002 mg/L. The Yellowstone alluvial aquifer dataset includes a large number of samples from Stillwater and Carbon Counties; the alluvial aquifers in these counties receive snowmelt recharge with low total dissolved solids from the Beartooth Mountains. Where elevated manganese occurs in the central and lower parts of the Yellowstone watershed (figs. 5, 6), the

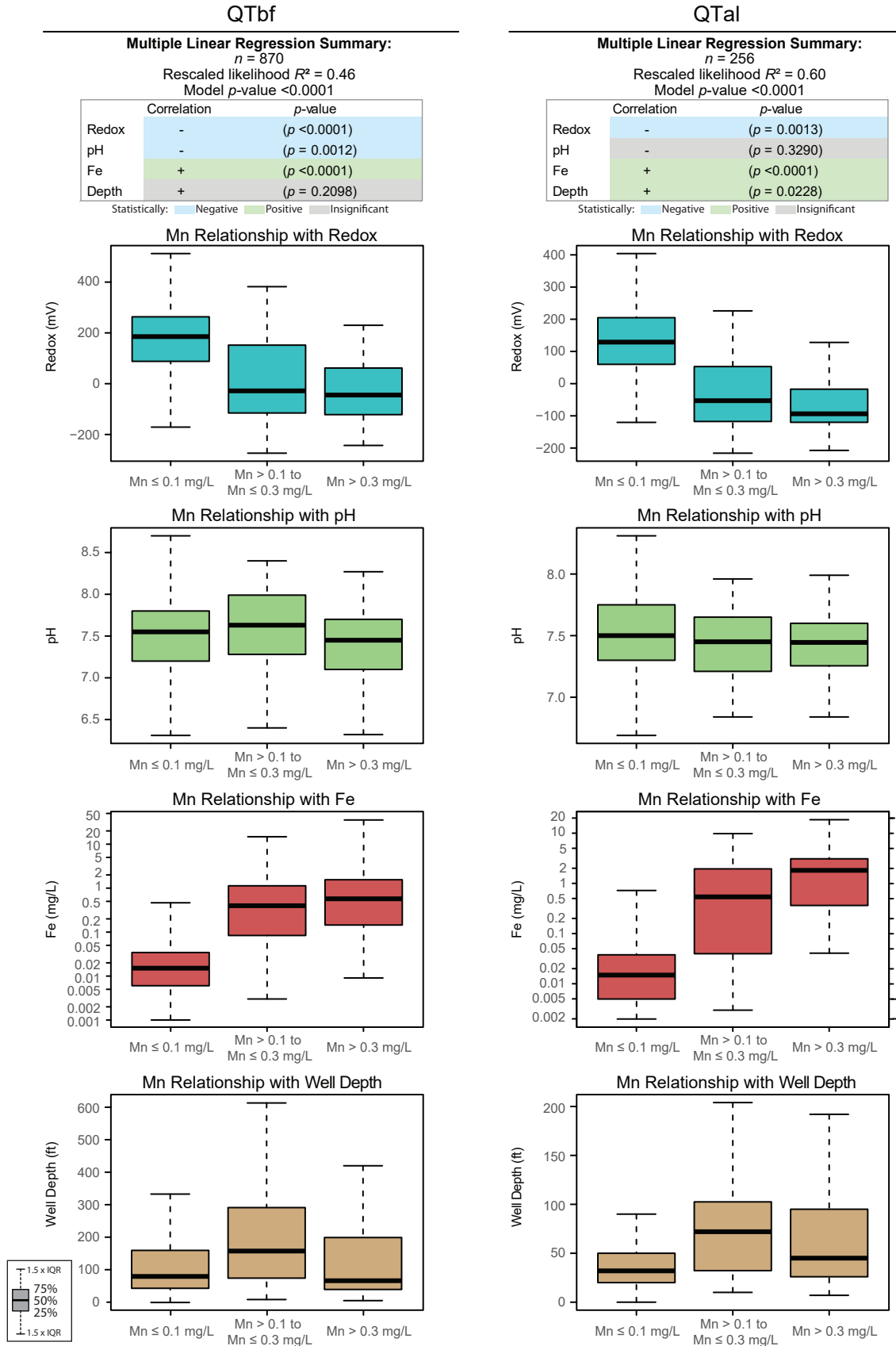


Figure 7. Summary of the multiple linear regression for QTbf and QTal aquifers including number of samples with data for all four explanatory variables, rescaled likelihood R^2 , and overall *p*-value. Direction (positive, negative) and *p*-values for the correlation between Mn and redox, pH, Fe, and well depth are given in the summary table; *p*-values ≤ 0.05 suggest a statistically significant correlation. Boxplots of Mn concentrations with available redox, pH, Fe, and well depth provide a visual examination of correlation relationships. Whiskers extend to data no more than 1.5 x IQR (interquartile range), which includes 95% of the data for a normal distribution. Note that the y-axes vary among figures.

Table 3. Manganese summary statistics for QTal aquifer divisions.

Aquifer	No. of Samples	% Detected	% of Detections >0.1 mg/L and ≤0.3 mg/L	% of Detections >0.3 mg/L	Mean ¹ (mg/L)	Median ¹ (mg/L)	Minimum (mg/L)	Maximum (mg/L)	Median Redox ² (mV)	Median pH ²	Median Well Depth ³ (ft)
Benches	64	12.5	3.1	0.0	0.007	<0.001	<0.001	0.198	138	7.7	20
Missouri Watershed	168	75.6	13.1	24.4	0.302	0.041	<0.001	4.09	72	7.5	34
Yellowstone Watershed	225	53.3	6.2	13.8	0.162	0.002	<0.001	3.06	111	7.4	33
Buried Valleys	91	96.7	36.2	45.1	0.526	0.259	<0.001	5.25	-92	7.5	89

¹Calculated using Kaplan–Meier method (Helsel, 2011; Julian and Helsel, 2021).

²Redox and pH values were not available for all well sites; median redox and median pH were calculated with available data.

³Determined from depth of screened interval, if available, otherwise total depth of well.

climate is drier (and therefore, receives less recharge), and the alluvium is underlain by shale.

Overall, manganese concentrations in the eastern alluvial aquifers are associated with low redox and elevated Fe (fig. 7); concentrations are higher under reducing conditions, and manganese co-occurs with Fe. Elevated manganese is also associated with deeper aquifers, reflecting the samples from the buried-valley aquifers. There was no statistical association between manganese concentrations and pH (fig. 7).

Fractured-Bedrock (pCfb and TKig) Aquifers

Fractures in Precambrian metasedimentary rocks (Belt Supergroup), gneiss, and schist (pCfb) and Tertiary and Cretaceous igneous rocks (TKig) provide sources of groundwater in mountainous areas in western Montana (fig. 8). These “fractured-rock” aquifers contain sufficient secondary permeability (fractures) to yield small supplies of water to wells. The occurrence, size, and orientation of fracture openings are spatially variable, resulting in large variations in well yields (Crowley and others, 2017; LaFave, 2020). The host rocks (metasedimentary and igneous rocks) are mostly composed of low-solubility minerals. The majority (93 percent) of fractured-rock aquifer samples had manganese concentrations less than 0.1 mg/L: 3–4 percent of the samples were between 0.1 mg/L and 0.3 mg/L, and 3–4 percent were greater than 0.3 mg/L (fig. 8). Samples with elevated manganese also had elevated Fe; however, there was no statistically significant relationship between manganese and redox, pH, or well depth (fig. 9).

Fractured-bedrock wells that yield groundwater with elevated manganese are scattered across western Montana—many are located close to wells with low manganese, reflecting the local heterogeneities in permeability and geology (fig. 8). Elevated manganese concentrations in Precambrian fractured-rock aquifers (pCfb) are associated with lower redox conditions (redox <100 mV; fig. 9) and elevated manganese in the Tertiary and Cretaceous igneous rocks (TKig) is associated with lower pH water (generally pH <6.9; fig. 9). However, the lack of a statistical correlation between manganese and redox (for pCfb groundwater) and manganese and pH (for TKig groundwater) suggests that water with low redox conditions and high acidity does not always have high manganese concentrations.

Fractured-Bedrock Aquifers (pCfb and TKig)

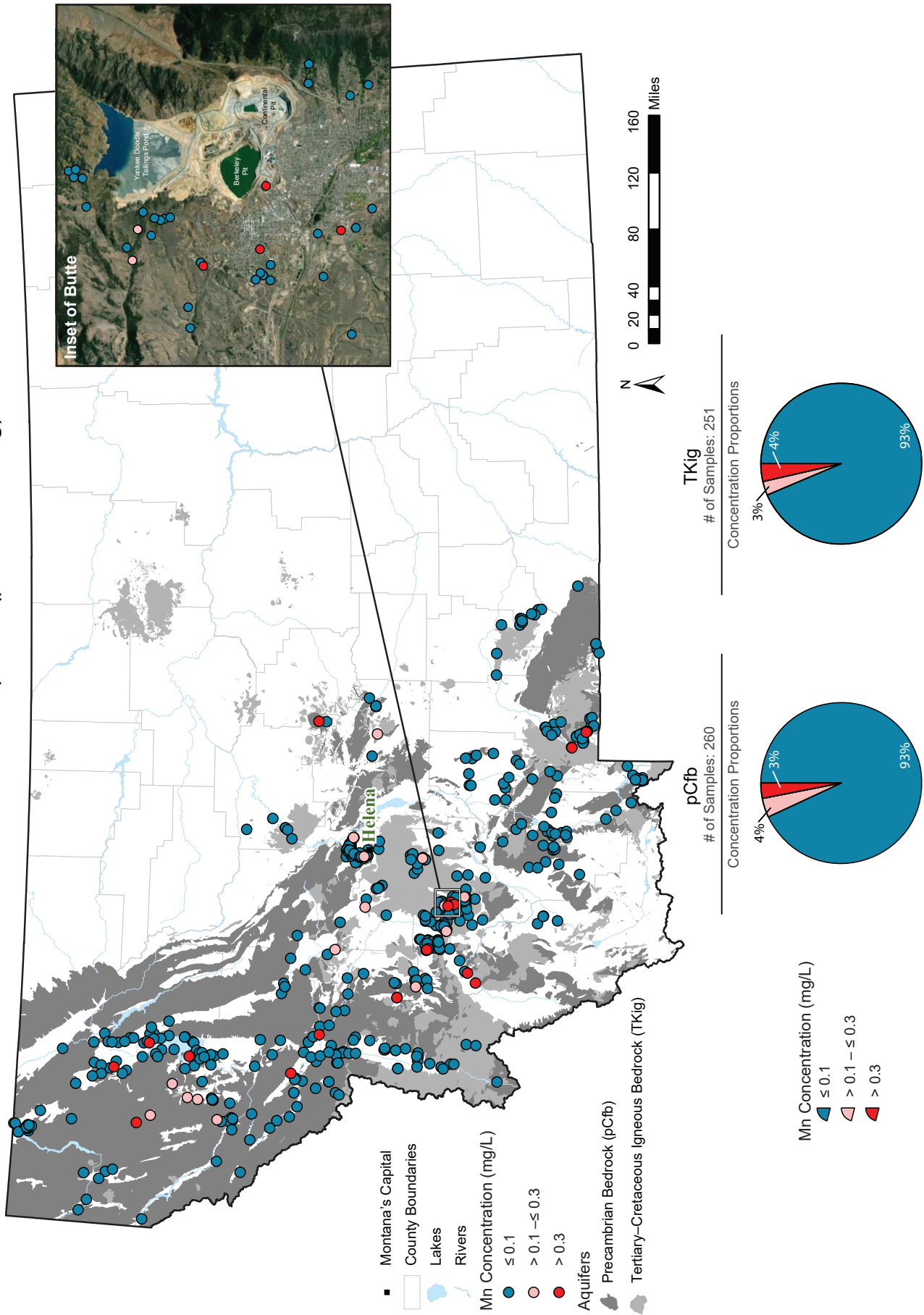


Figure 8. Distribution of Mn concentrations in the fractured bedrock principal aquifers (pCfb and TKig). Inset of high Mn concentrations in Butte attributed to legacy mine operations. Pie charts of Mn concentrations in each aquifer display the three Mn groups: blue, safe to drink; pink, potentially harmful to those <6 years old; and red, exceeds recommended guideline for all age groups.

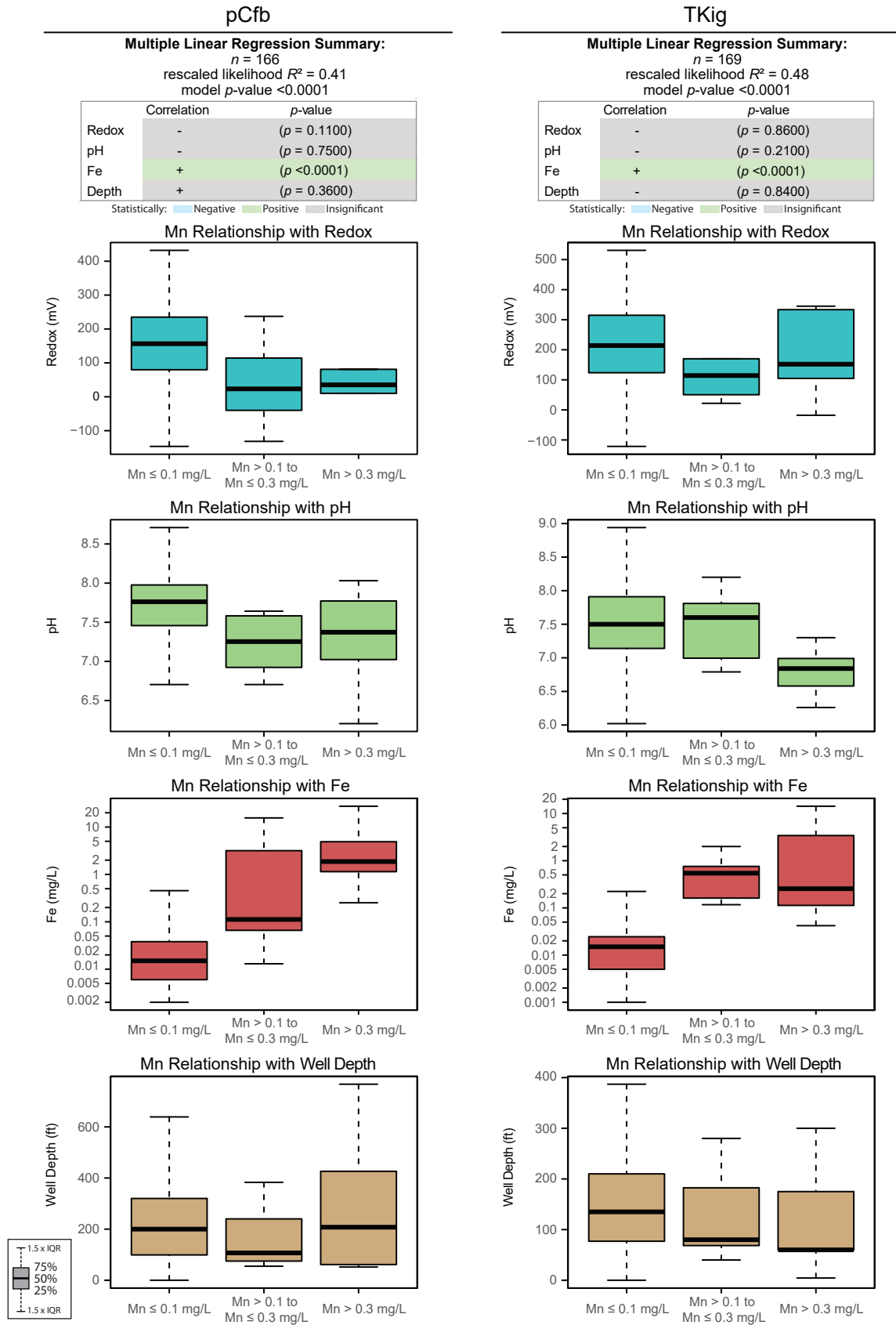


Figure 9. Summary of the multiple linear regression for pCfb and TKig aquifers including number of samples with data for all four explanatory variables, rescaled likelihood R^2 , and overall p -value. Direction (positive, negative) and p -values for the correlation between Mn and redox, pH, Fe, and well depth are given in the summary table; p -values ≤ 0.05 suggest a statistically significant correlation. Only Mn correlation with Fe is statistically significant for these two aquifers. Boxplots of Mn concentrations with available redox, pH, Fe, and well depth provide a visual examination of correlation relationships. Whiskers extend to data no more than 1.5 x IQR (interquartile range), which includes 95% of the data for a normal distribution. Note that the y-axes vary among figures.

Some of the highest manganese concentrations (between 5 and 20 mg/L) were detected in the Summit Valley near Butte (fig. 8), specifically from wells near legacy mine operations that produce acid rock drainage. The localized occurrence of very high manganese concentrations is most likely attributable to the mineralized bedrock and the land-use disturbance from historic mining (Duaine and others, 2021).

Fort Union (Tfu) Aquifer

The Tertiary Fort Union Formation (Tfu) is characterized by interbedded sandstone, coal, shale, and mudstone originally deposited in a nonmarine, alluvial environment (Vuke and others, 2007). It is exposed across south-central and eastern Montana and is an important source of domestic and stockwater. Groundwater in the Fort Union Formation occurs in sandstone and coal layers that are interbedded with shale and mudstone; the interbedded layers result in a great deal of vertical and horizontal anisotropy (Smith and others, 2000; Crowley and others, 2017; LaFave, 2020).

A total of 334 Fort Union samples from across south-central and eastern Montana were evaluated (fig. 10). Manganese was detected in 72 percent of the samples, with concentrations ranging up to 3.5 mg/L (table 1). Concentrations greater than 0.1 mg/L were detected in 24 percent of the samples, and the median concentration of 0.018 mg/L was the highest of the principal aquifers (table 1).

Iron was typically detected with manganese, and elevated manganese concentrations were associated with low redox values and pH values less than 7.5 (fig. 11, redox and pH boxplots); there was not a statistically significant relationship between manganese and well depth. However, wells with elevated manganese were generally shallower (fig. 11). Most of the elevated concentrations were detected in the lower Yellowstone Valley of eastern Montana; concentrations were generally lower in south-central Montana (fig. 10). Samples from the Fort Union in south-central Montana had a median pH of 7.8 and median redox of 120 mV, whereas in eastern Montana the Fort Union samples had a lower median pH of 7.5 and lower median redox of -27 mV, conditions that favor manganese dissolution (fig. 11).

Fox Hills–Hell Creek (Kfhhc) and Livingston (Klvgs) Aquifers

For this report the Fox Hills–Hell Creek (Kfhhc) and Livingston (Klvgs) aquifers are considered together because of their geographic proximity; there were 199 samples from the Fox Hills–Hell Creek aquifer and 24 from the Livingston aquifer (fig. 12).

Sandstone beds of the upper Cretaceous Fox Hills Sandstone and the lower part of the Hell Creek Formation are hydraulically connected and form an extensive aquifer that is widely used in eastern Montana. The Fox Hills–Hell Creek aquifer occurs at depths of 600 to 1,600 ft below land surface throughout most of eastern Montana except near outcrop areas. Mudstones in the Hell Creek Formation confine the top of the aquifer and the Bearpaw/Pierre Shale confines the base of the aquifer. Wells in the Fox Hills–Hell Creek aquifer are concentrated near outcrop areas and in the lower Yellowstone River Valley (LaFave, 2020).

The Cretaceous Livingston Group aquifer (Klvgs) is characterized by layers of volcanoclastic sandstone, conglomerate sandstone, tuffaceous siltstone, shale, and mudstone (Vuke and others, 2007). The aquifer occurs predominately in the Shields Valley, north of Livingston between the Bridger Mountains on the west and the Crazy Mountains on the east.

Manganese concentrations in the Fox Hills–Hell Creek aquifer were low; of the 199 samples, 91 percent were less than 0.1 mg/L, 5 percent were between 0.1 and 0.3 mg/L, and 4 percent exceeded 0.3 mg/L (fig. 12). There were only 24 samples from the Livingston aquifer, all of which had manganese concentrations less than 0.1 mg/L.

The Fox Hills–Hell Creek samples had the lowest median redox and the highest median pH of all the aquifers (table 1). Despite the prevalence of low redox values, which tend to favor manganese solubility, manganese concentrations were low, possibly due to the relatively high pH values (median of 8.5; table 1). The Fox Hills–Hell Creek samples with elevated manganese concentrations generally had lower pH values and also had detectable (elevated) Fe concentrations (fig. 13). There is a cluster of wells with elevated manganese in Fallon County near the North Dakota border (fig. 12). The manganese concentration in these wells may be affected by their proximity to exposed portions of Pierre Shale, which can degrade water quality

Fort Union Aquifer (Tfu)

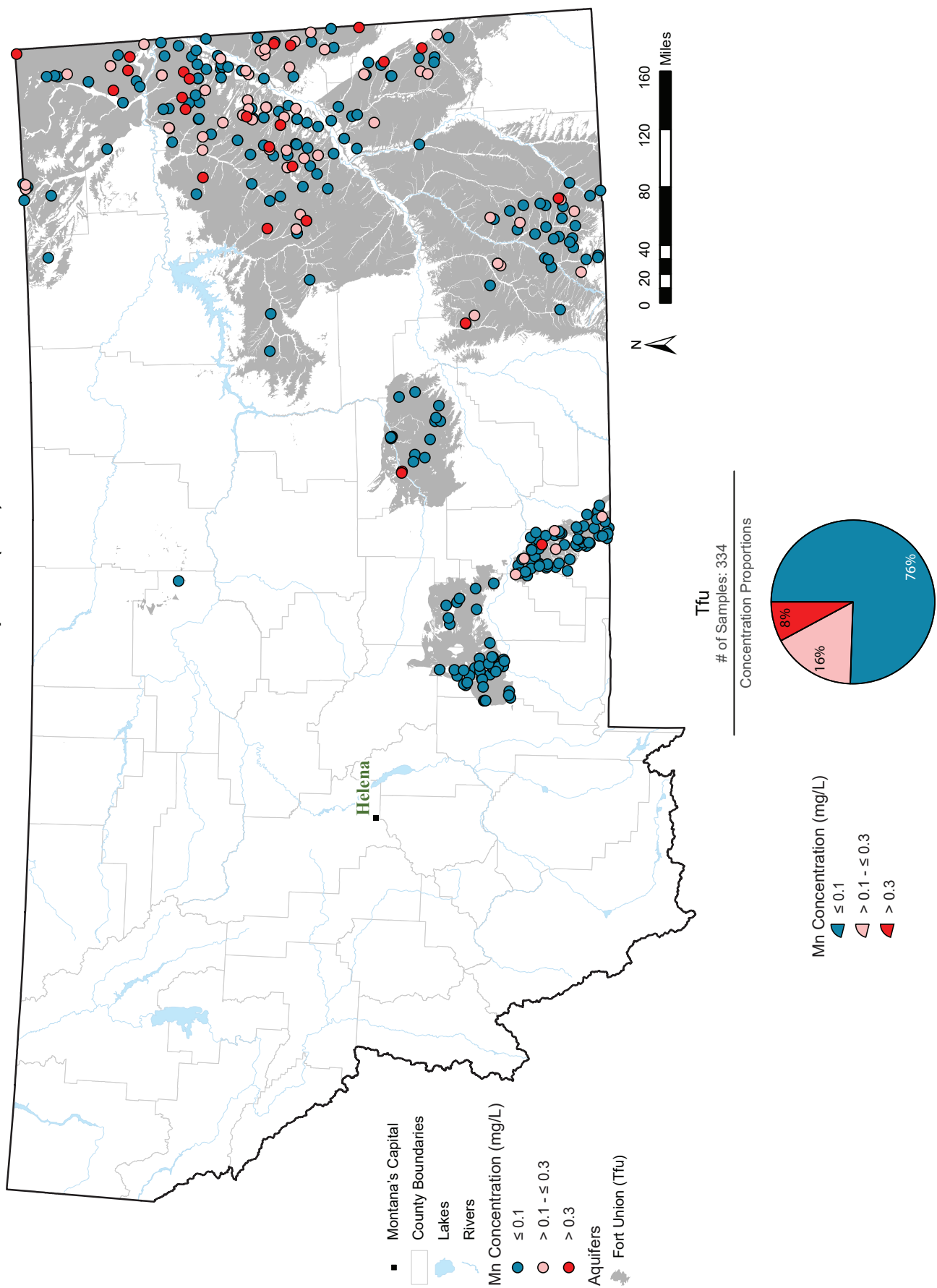


Figure 10. Distribution of Mn concentrations in the Fort Union (Tfu) principal aquifer. A pie chart of Mn concentrations display the three Mn groups: blue, safe to drink; pink, potentially harmful to those ≤6 years old; and red, exceeds recommended guideline for all age groups.

Tfu

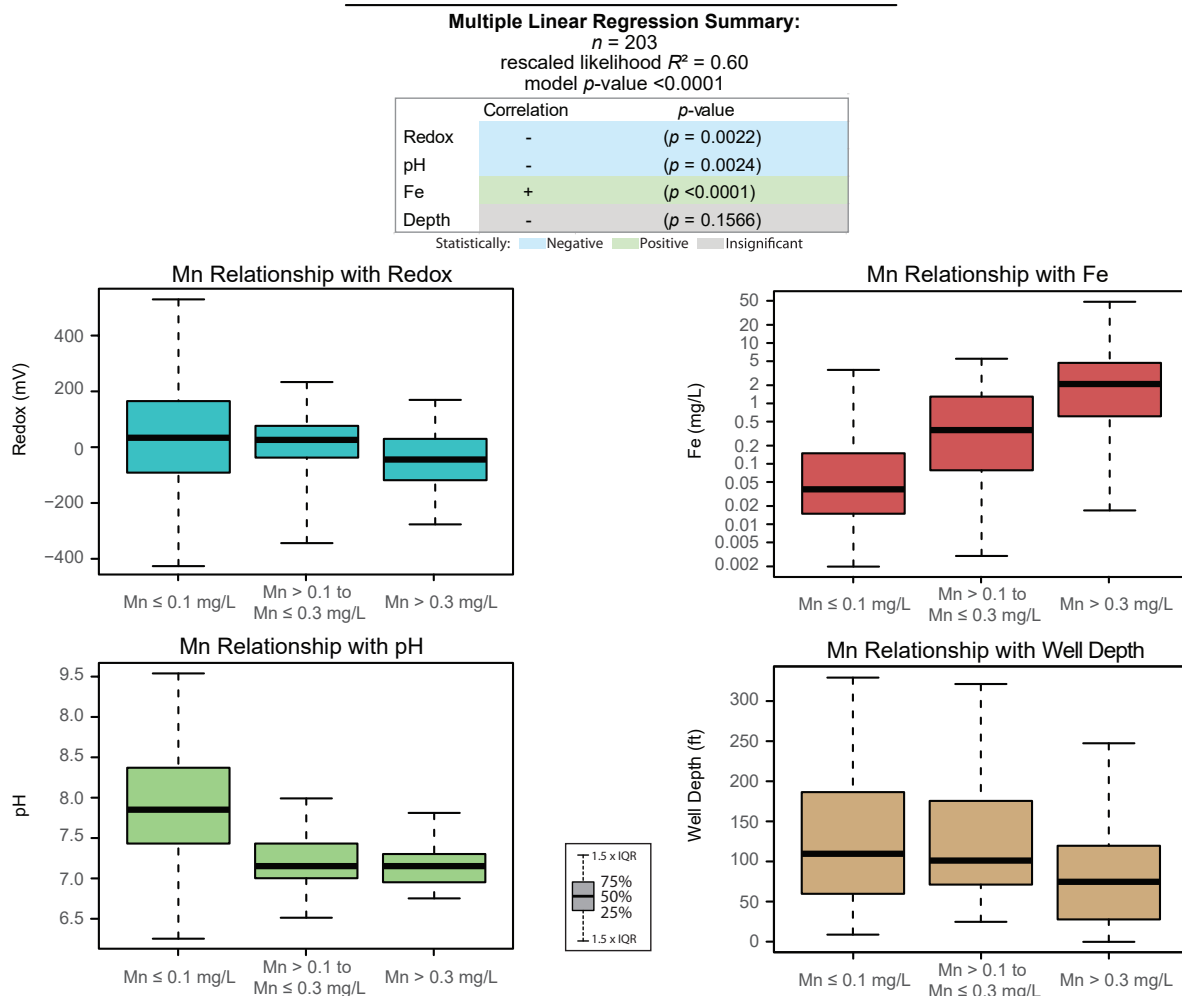


Figure 11. Summary of the multiple linear regression for the Tfu aquifer including number of samples with data for all four explanatory variables, rescaled likelihood R^2 , and overall p -value. Direction (positive, negative) and p -values for the correlation between Mn and redox, pH, Fe, and well depth are given in the summary table; p -values ≤ 0.05 suggest a statistically significant correlation. Boxplots of Mn concentrations with available redox, pH, Fe, and well depth provide a visual examination of correlation relationships. Whiskers extend to data no more than $1.5 \times$ IQR (interquartile range), which includes 95% of the data for a normal distribution. Note that the y-axes vary among figures.

(LaFave, 1998) and lower pH values compared to other wells in the area.

The small number of samples from the Livingston aquifer and the overall low manganese concentrations precluded the creation of concentration boxplots. However, the few wells with detectable manganese concentrations generally had lower redox and pH values. There appeared to be no relationship between manganese concentrations and Fe concentrations or well depth.

Judith River (Kjr), Two Medicine (Ktm), and Eagle (Kegle) Aquifers

The Judith River Formation (Kjr), Two Medicine Formation (Ktm), and Eagle Formation (Kegle) are a series of upper Cretaceous sandstone aquifers present

throughout central Montana. The aquifers are typically confined, except near outcrop areas, and are important sources of domestic and stockwater (Crowley and others, 2017; LaFave, 2020). They are generally characterized by interbedded sandstone, shale, siltstone, and/or mudstone that were deposited in environments ranging from alluvial to marine (Lopez, 2002; Vuke and others, 2007; Crowley and others, 2017). The samples from these aquifers had very similar manganese concentrations: most (83–86 percent) were less than 0.1 mg/L, 7–10 percent were between 0.1 mg/L and 0.3 mg/L, and 7 percent exceeded 0.3 mg/L (fig. 14).

Although the concentrations were similar, the relationships with other geochemical parameters varied. The variations may be a result of insufficient data (e.g., not all well samples having redox or pH mea-

Fox Hills-Hell Creek (Kfhhc) and Livingston (Klvgs) Aquifers

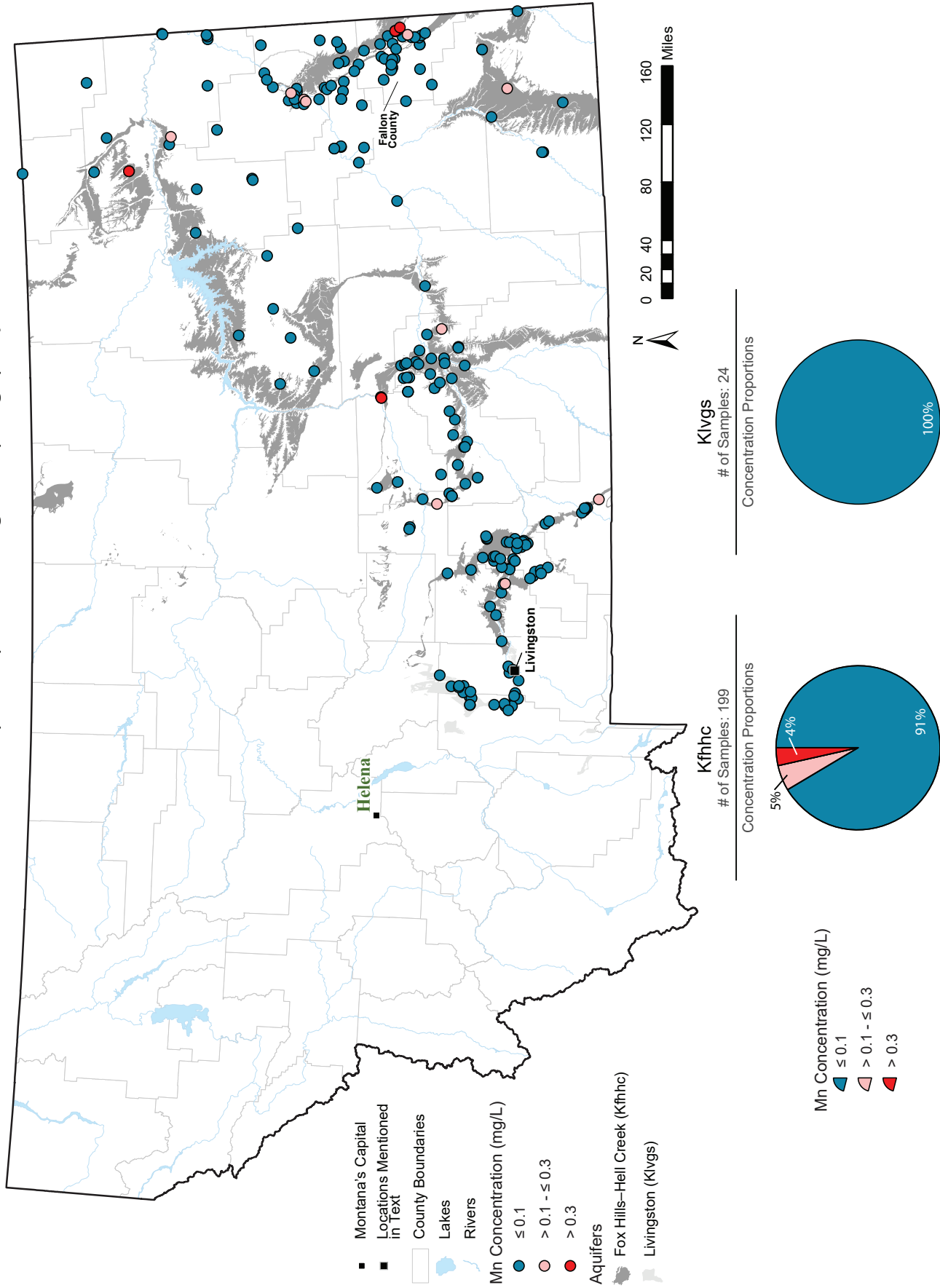


Figure 12. Distribution of Mn concentrations in the Fox Hills-Hell Creek and Livingston principal aquifers. Pie charts of Mn concentrations in each aquifer display the three Mn groups: blue, safe to drink; pink, potentially harmful to those ≤6 years old; and red, exceeds recommended guideline for all age groups.

Kfhhc

Multiple Linear Regression Summary:

$n = 115$
 rescaled likelihood $R^2 = 0.53$
 model p -value < 0.0001

	Correlation	p -value
Redox	-	($p = 0.0071$)
pH	-	($p = 0.0001$)
Fe	+	($p < 0.0001$)
Depth	-	($p = 0.2478$)

Statistically: Negative Positive Insignificant

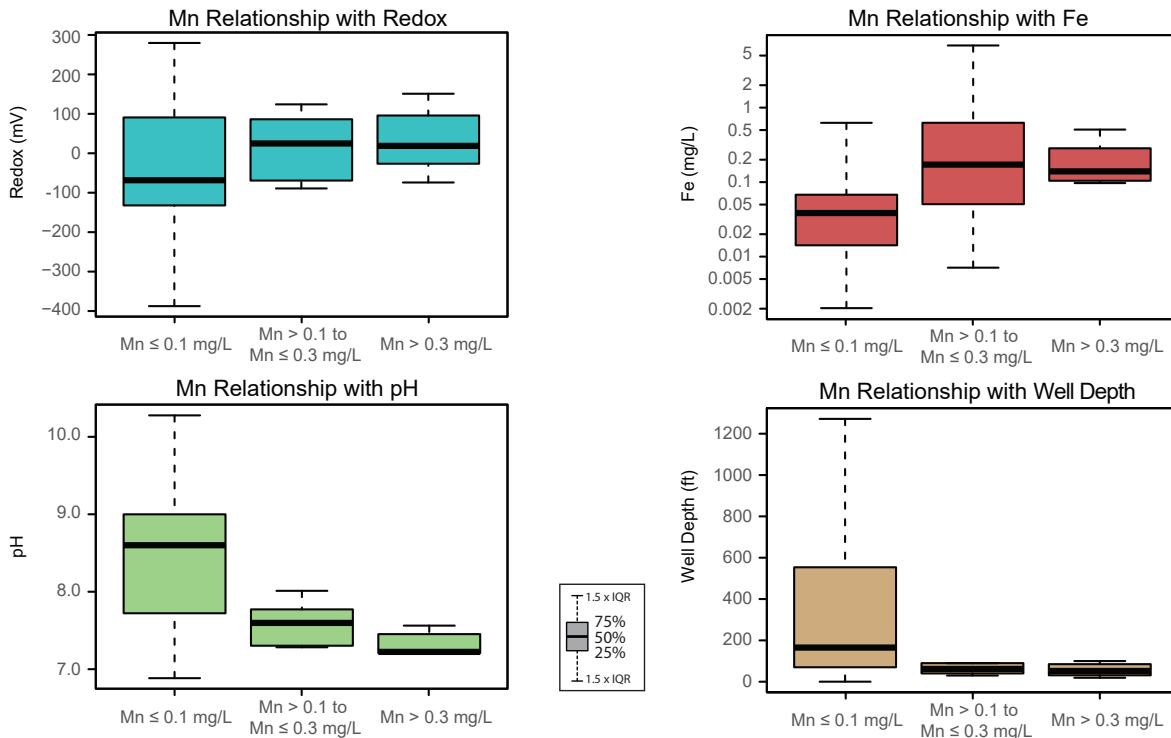


Figure 13. Summary of the multiple linear regression for the Kfhhc aquifer including number of samples with data for all four explanatory variables, rescaled likelihood R^2 , and overall p -value. Direction (positive, negative) and p -values for the correlation between Mn and redox, pH, Fe, and well depth are given in the summary table; p -values ≤ 0.05 suggest a statistically significant correlation. Boxplots of Mn concentrations with available redox, pH, Fe, and well depth provide a visual examination of correlation relationships. Whiskers extend to data no more than $1.5 \times$ IQR (interquartile range), which includes 95% of the data for a normal distribution. Note that the y-axes vary among figures.

surements) and/or the data may have had non-linear relationships that were not predicted by the correlation technique. The Judith River samples showed manganese concentrations associated with lower redox, shallower wells (well depth less than 100 ft), and elevated iron concentrations (fig. 15). Elevated manganese concentrations also appear to be related to lower pH values; however, the p -value is high ($p = 0.47$), indicating a lack of statistical support for a correlation between manganese concentrations and pH. This is likely driven by some samples with low manganese concentrations and low pH, and some samples with high manganese concentrations and high pH.

Samples from the Eagle and Two Medicine aquifers did not show a statistical relationship between manganese concentrations and other geochemical

parameters (redox and pH) or well depth. The small number of samples with a complete set of reported parameters (only 19 of the 54 samples had redox values) likely contributed to the lack of statistical relationships apparent in samples from the Two Medicine aquifer. However, visual examination of the boxplots suggests that elevated manganese concentrations generally occur with elevated iron and lower pH and redox values (fig. 15). There was no apparent relationship between well depth and manganese concentrations for samples from the Eagle aquifers, but elevated manganese in the Two Medicine aquifer generally occurred in deeper wells (well depth > 135 ft; fig. 15).

The spatial distribution of elevated manganese in these aquifers appears random, with wells containing high manganese very close to wells with low con-

Two Medicine (Ktm), Eagle (Kegle), and Judith River (Kjr) Aquifers

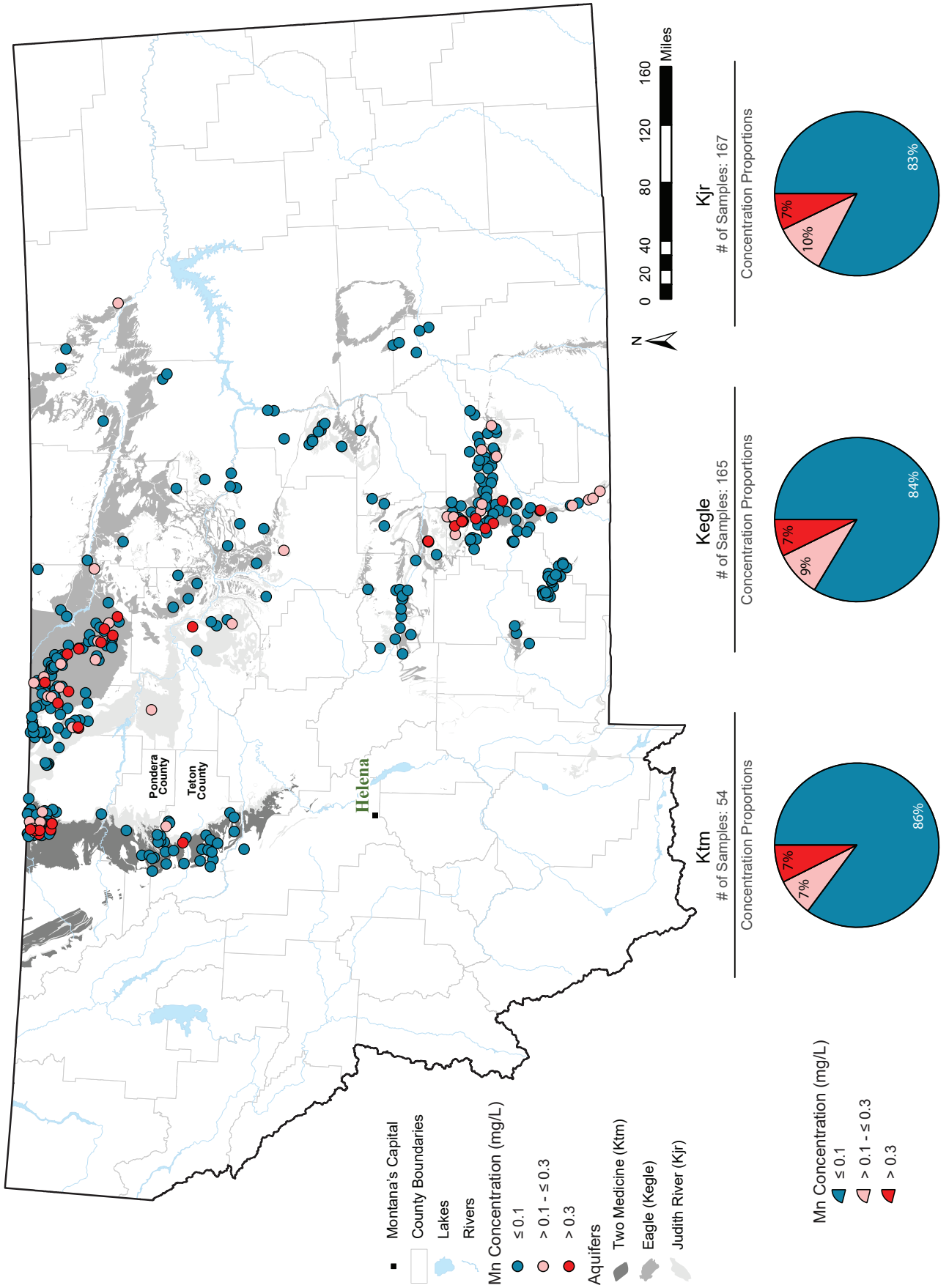


Figure 14. Distribution of Mn concentrations in the Two Medicine (Ktm), Eagle (Kegle), and Judith River (Kjr) principal aquifers. Pie charts of Mn concentrations in each aquifer display the three Mn groups: blue, safe to drink; pink, potentially harmful to those ≤6 years old; and red, exceeds recommended guideline for all age groups. Counties discussed in text are labeled.

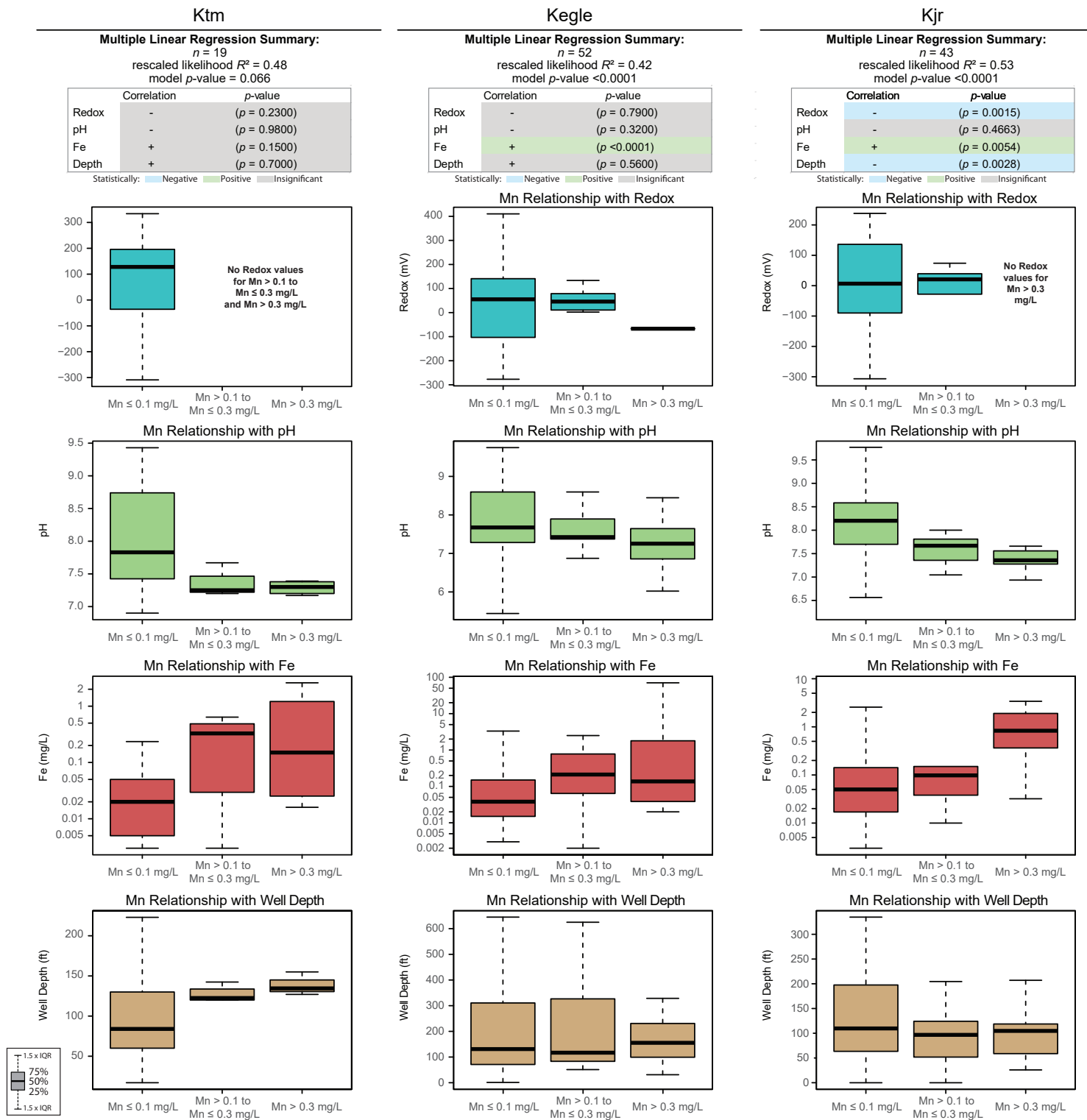


Figure 15. Summary of the multiple linear regression for Ktm, Kegl, and Kjr aquifers including number of samples with data for all four explanatory variables, rescaled likelihood R^2 , and overall p -value. Direction (positive, negative) and p -values for the correlation between Mn and redox, pH, Fe, and well depth are given in the summary table; p -values ≤ 0.05 suggest a statistically significant correlation. Boxplots of Mn concentrations with available redox, pH, Fe, and well depth provide a visual examination of correlation relationships. Whiskers extend to data no more than 1.5 x IQR (interquartile range), which includes 95% of the data for a normal distribution. Note that the y-axes vary among figures.

centrations (fig. 14). However, in general, samples from the southern part of the Two Medicine aquifer in Pondera and Teton Counties had concentrations less than 0.1 mg/L.

Cretaceous Shale (Kshale) Confining Units

Thick sequences of shales separate the Cretaceous sandstone aquifers (e.g., Kfhhc, Klvg, Kjr, Kegl; Crowley and others, 2017; fig. 3). These shales were deposited as marine sediments during regressive/transgressive cycles of the Western Interior Seaway (Rogers, 1998) and include the Bearpaw/Pierre, Claggett, and Colorado Group shales (Crowley and others, 2017). Sandy layers within the Cretaceous shales may produce water to wells, and in some places may be the only source of domestic and stockwater. Although the shale formations are stratigraphically and hydrologically distinct, for the following water-quality discussion they are combined as the Cretaceous shale aquifers (Kshale).

The samples from Kshale wells are scattered throughout central Montana, and in the Big Sky area and southwest Powell County in western Montana (fig. 16). Overall, 80 percent of the samples had manganese concentrations less than 0.1 mg/L, 10 percent were between 0.1 and 0.3 mg/L, and 10 percent exceeded 0.3 mg/L (fig. 16).

Manganese concentrations were related to lower pH, deeper wells, and iron concentrations (fig. 17). The samples from shale wells generally had low redox conditions; the median redox value was 24 mV (table 1). The low redox values combined with relatively lower pH creates favorable conditions for manganese dissolution. In western Montana, the Kshale samples had low manganese concentrations (most less than 0.1 mg/L); elevated manganese was more frequently detected in Colorado group shales in and around Cascade County (fig. 16).

Kootenai (Kkotn) Aquifer

The lower Cretaceous Kootenai Formation consists of sandstone, siltstone, and shale and is overlain by the Colorado Group shales. These sedimentary rocks were originally deposited as alluvial plain sediments on an eroded Jurassic surface in a fluvio-deltaic environment that marks the onset of Cretaceous sea-level rise (Vuke and others, 2007; Schwartz and Vuke, 2019). The basal sandstones, which form the primary aquifer,

are informally referred to as the Third Cat Creek Sandstone (central Montana); the Sunburst Sandstone or the Cutbank Sandstone (northwestern plains); and the Pryor Conglomerate or the Lakota Sandstone (eastern Montana). The Kootenai aquifer is an important source of domestic and stockwater near Great Falls, off the north flank of the Little Belt Mountains, and in the Judith Basin, off the northeast flank of the Big and Little Snowy Mountains. To a lesser extent it is also used near Big Sky, along the northern Pryor Mountains (between Billings and Red Lodge), and in the southeast corner of the State (fig. 18; Crowley and others, 2017; LaFave, 2020).

The sampled Kootenai wells are some of the deepest in the dataset (table 1); the well depth ranged up to 2,832 ft with a median of 315 ft. Although manganese was detected in about 80 percent of the Kootenai samples, the concentrations were generally low. Of the 96 samples, 84 percent had manganese less than 0.1 mg/L, 12 percent had concentrations between 0.1 and 0.3 mg/L, and 4 percent exceeded 0.3 mg/L (fig. 18).

Elevated manganese in the Kootenai aquifer was detected most frequently in samples from Cascade County near Great Falls and from a few wells near Big Sky (fig. 18). Elevated manganese was associated with Fe, but not with redox, pH, or well depth (fig. 19).

Mesozoic--Paleozoic Sedimentary Rock (MPsed) Aquifers

The Mesozoic and Paleozoic sedimentary rock (MPsed) aquifers are a collection of water-yielding sandstone, siltstone, conglomerate, limestone, and dolomite formations deposited during the Mesozoic and Paleozoic eras (Crowley and others, 2017). These formations are collectively grouped together because of the small number of wells each aquifer contains. These wells are located throughout south-central and southwestern Montana (fig. 20). Some of the formations within this assemblage include sandstones and limestones in the Jurassic Morrison Formation and Ellis Group, the Triassic Chugwater Formation, and the Pennsylvanian Amsden Formation and Tensleep sandstone.

The manganese detection frequency and concentrations were low (fig. 4). All of the 78 samples had manganese concentrations below 0.1 mg/L except one. The one sample with an elevated concentration (9.0 mg/L) was from a well completed in the Swift Forma-

Cretaceous Shale (Kshale) Confining Unit

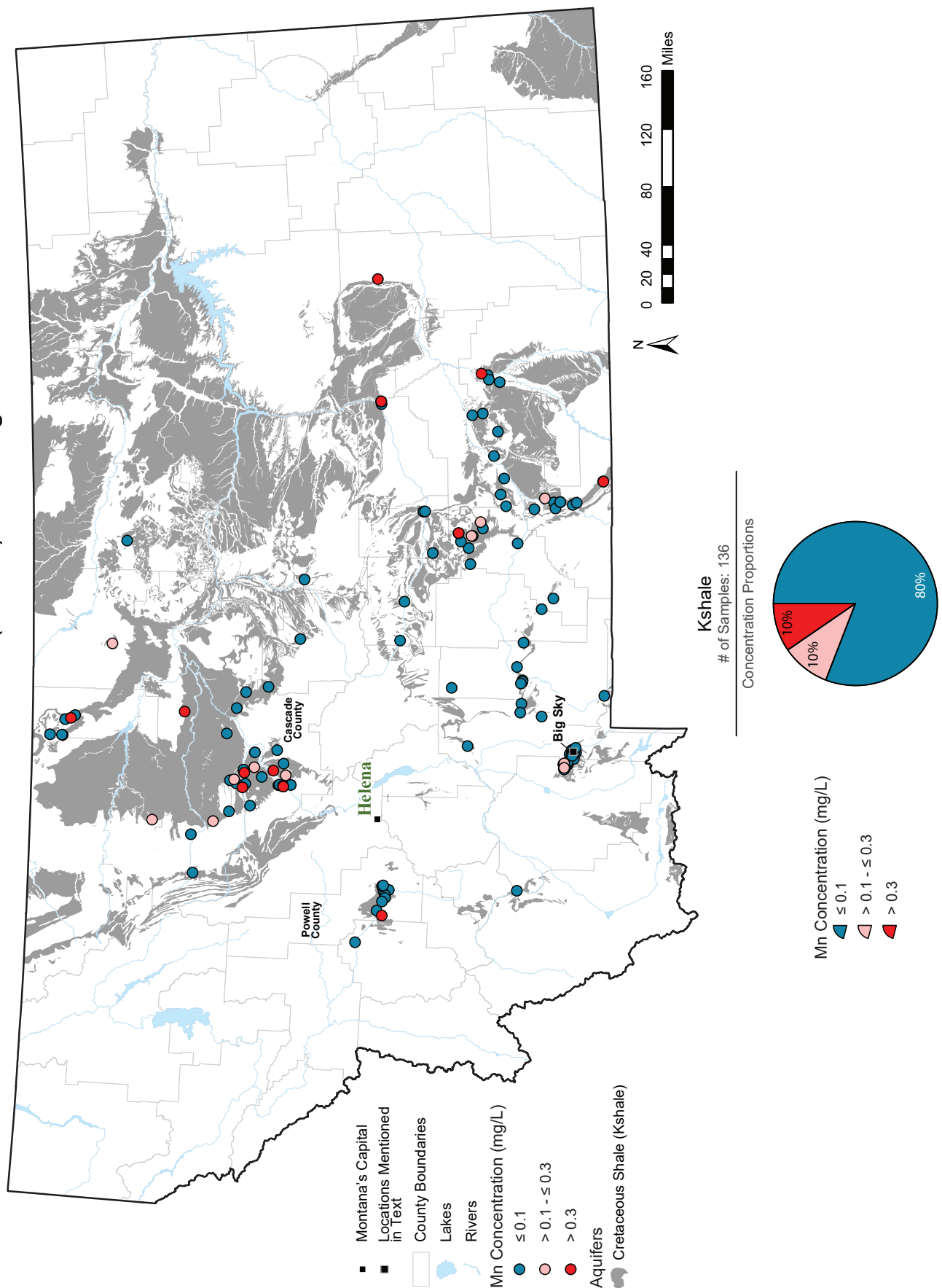


Figure 16. Distribution of Mn concentrations in the Cretaceous shale (Kshale) confining units. A pie chart of Mn concentrations display the three Mn groups: blue, safe to drink; pink, potentially harmful to those ≤6 years old; and red, exceeds recommended guideline for all age groups.

Kshale

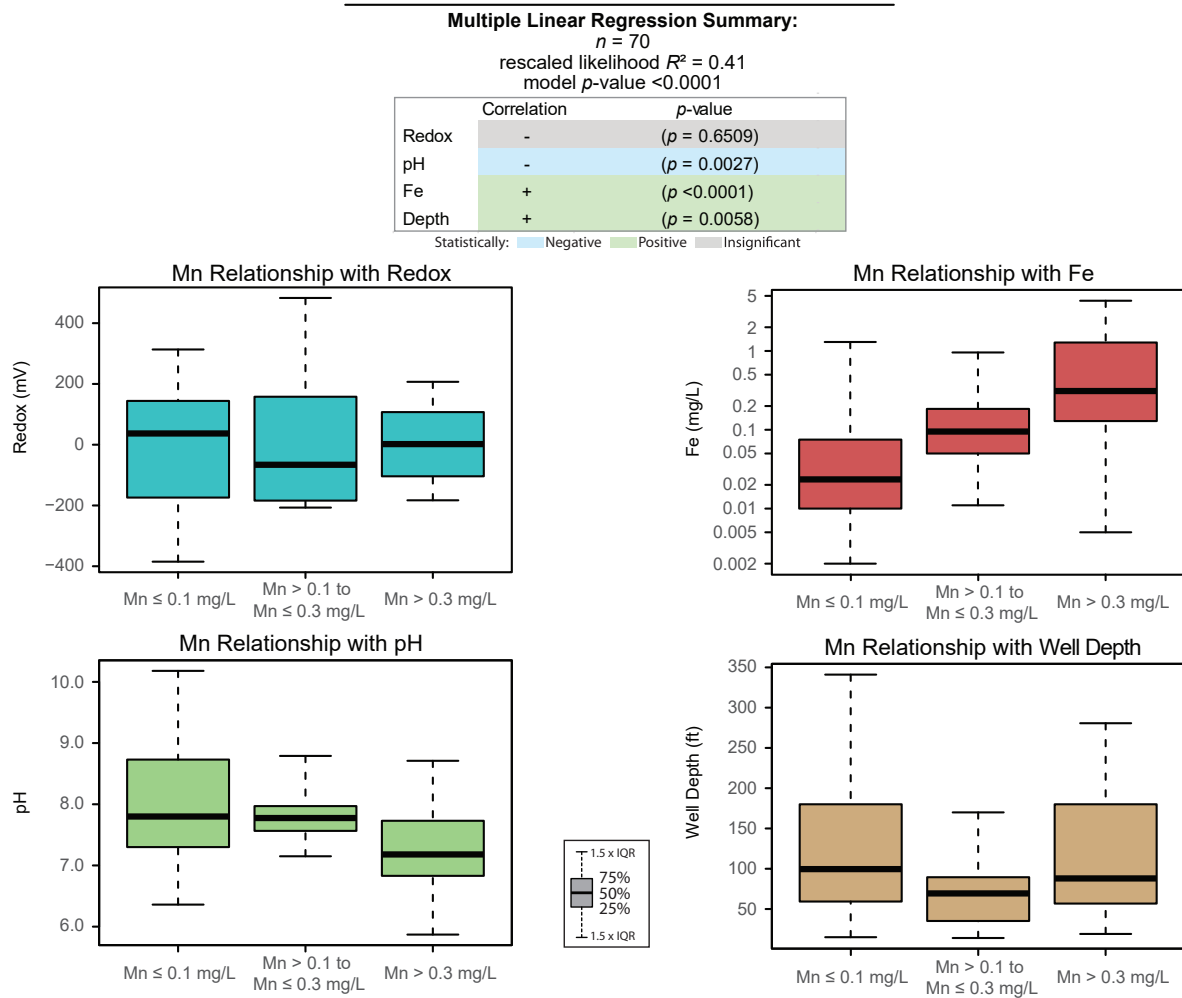


Figure 17. Summary of the multiple linear regression for the Kshale confining units including number of samples with data for all four explanatory variables, rescaled likelihood R^2 , and overall p -value. Direction (positive, negative) and p -values for the correlation between Mn and redox, pH, Fe, and well depth are given in the summary table; p -values ≤ 0.05 suggest a statistically significant correlation. Boxplots of Mn concentrations with available redox, pH, Fe, and well depth provide a visual examination of correlation relationships. Whiskers extend to data no more than 1.5 x IQR (interquartile range), which includes 95% of the data for a normal distribution. Note that the y-axes vary among figures.

tion south of Great Falls, near the Kootenai wells that also had elevated manganese concentrations (fig. 20). The samples with detectable manganese generally had detectable Fe. There were no statistically supported correlations between manganese and redox, pH, and well depth.

Madison (Mmdsn) Aquifer

Within the Paleozoic sedimentary rocks are a sequence of marine limestone, dolomite, and evaporite deposits that form the Mississippian Madison (Mmdsn) Group (Vuke and others, 2007; Crowley and others, 2017). Although this formation underlies most of eastern Montana, it is only a freshwater aquifer near outcrop areas where it is relatively close to the surface. In central Montana, the Madison Group crops out

mainly along the northern flanks of the Little Belt and Big Snowy Mountains; it is also prominently exposed along the northeast flank of the Pryor Mountains and in narrow exposures in mountain ranges in southwest Montana. Groundwater flows outward from the mountain recharge areas through fractures and karst features. In general, water in the Madison aquifer is confined except near outcrop areas (Crowley and others, 2017; LaFave, 2020). Most of the Madison wells are in Cascade County between the Little Belt Mountains and the Missouri River near Great Falls, where they are used for domestic water. Other wells completed in the Madison are near outcrop areas (fig. 21).

Manganese concentrations in the Madison aquifer are generally low: 89 percent of Madison samples

Kootenai Aquifer (Kkotn)

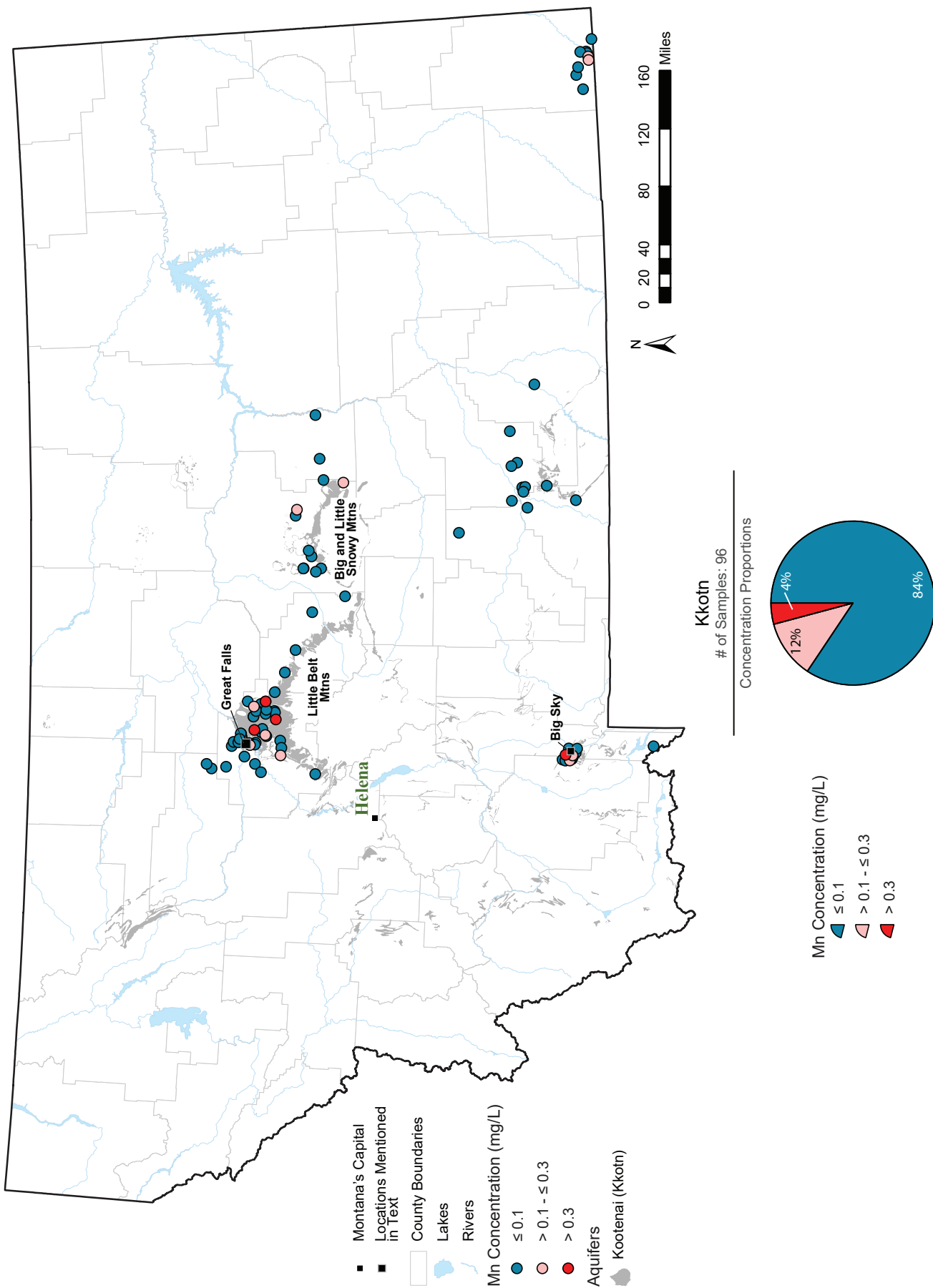


Figure 18. Distribution of Mn concentrations in the Kootenai (Kkotn) principal aquifer. A pie chart of Mn concentrations display the three Mn groups: blue, safe to drink; pink, potentially harmful to those ≤6 years old; and red, exceeds recommended guideline for all age groups.

Kkotn

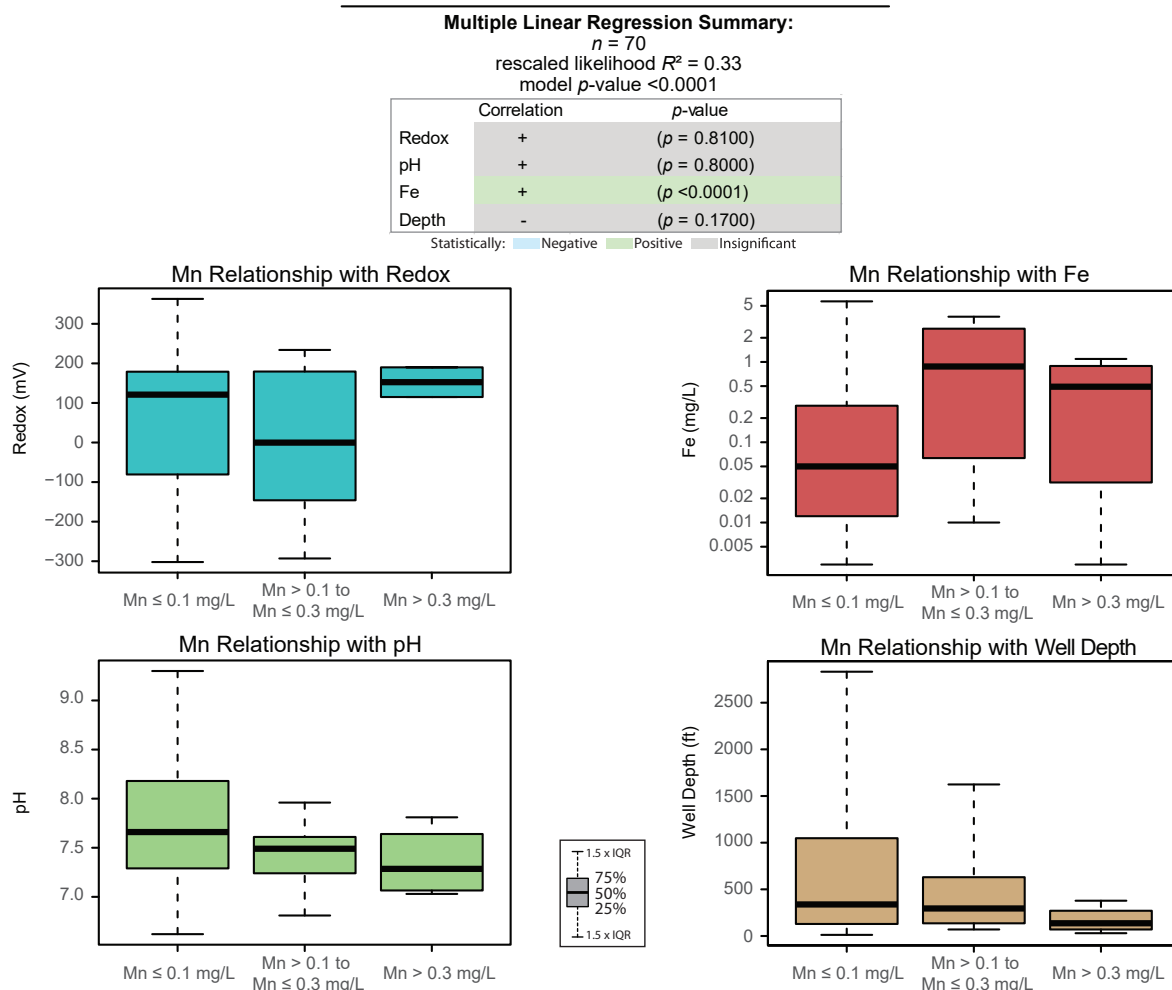


Figure 19. Summary of the multiple linear regression for the Kkotn aquifer including number of samples with data for all four explanatory variables, rescaled likelihood R^2 , and overall p -value. Direction (positive, negative) and p -values for the correlation between Mn and redox, pH, Fe, and well depth are given in the summary table; p -values ≤ 0.05 suggest a statistically significant correlation. Boxplots of Mn concentrations with available redox, pH, Fe, and well depth provide a visual examination of correlation relationships. Whiskers extend to data no more than $1.5 \times$ IQR (interquartile range), which includes 95% of the data for a normal distribution. Note that the y-axes vary among figures.

had manganese concentrations less than 0.1 mg/L, 5 percent were between 0.1 and 0.3 mg/L, and 6 percent exceeded 0.3 mg/L (fig. 21). All the wells with elevated manganese (14), except one, were located in Cascade County south of Great Falls.

The samples with elevated manganese were generally associated with lower pH and contained iron (fig. 22). There was no statistical relationship between manganese concentrations and redox and well depth (fig. 22).

SUMMARY AND CONCLUSIONS

Montana is characterized by a wide variety of aquifers containing different amounts of manganese-bearing minerals and with varying geochemical

conditions; manganese concentrations in groundwater reflect these variable conditions. A total of 3,858 groundwater samples from the principal aquifers across Montana were used to compare manganese concentrations to human health benchmarks and assess the degree to which observed concentrations are related to redox conditions, pH, and well depth.

Overall, manganese concentrations were low; most of the samples (85 percent) had concentrations below 0.1 mg/L or below detection levels. MDEQ's human-health guideline of 0.3 mg/L for adults and children older than 6 yr was exceeded in 7 percent (291) of the samples, and the guideline of 0.1 mg/L for children age 6 and younger was exceeded in 15 percent (591) of samples. Elevated concentrations were detected in at least one sample in all the principal aquifers, except

Mesozoic and Paleozoic Sedimentary Rock Aquifer (MPsed)

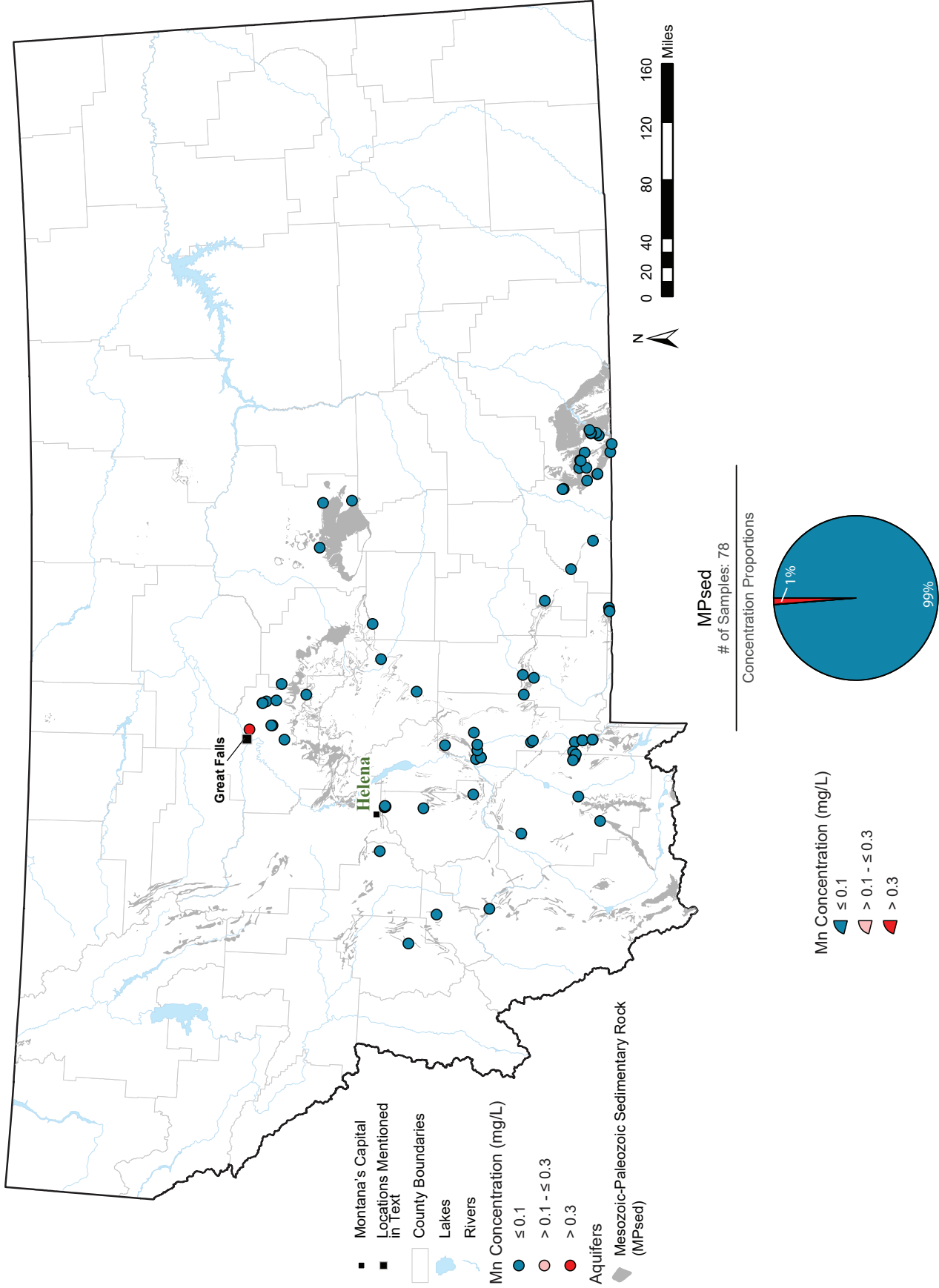


Figure 20. Distribution of Mn concentrations in the Mesozoic and Paleozoic sedimentary rock (MPsed) principal aquifer. A pie chart of Mn concentrations display the three Mn groups: blue, safe to drink; pink, potentially harmful to those ≤6 years old; and red, exceeds recommended guideline for all age groups. Boxplots were not created for the MPsed principal aquifer since only one sample was >0.1 mg/L.

Madison Aquifer (Mmdsn)

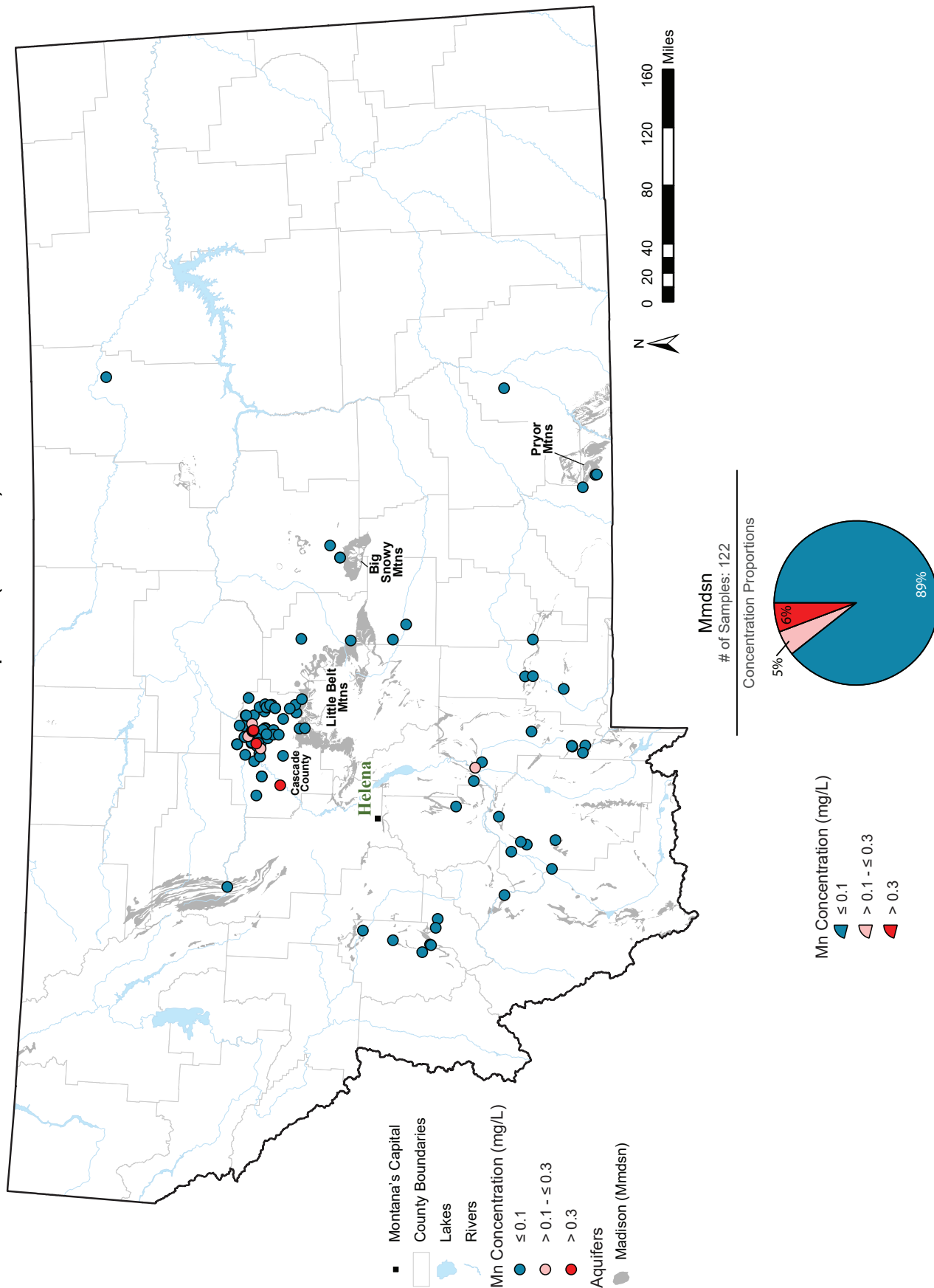


Figure 21. Distribution of Mn concentrations in the Mesozoic Madison (MMDsn) principal aquifer. A pie chart of Mn concentrations display the three Mn groups: blue, safe to drink; pink, potentially harmful to those ≤ 6 years old; and red, exceeds recommended guideline for all age groups. Locations mentioned in text are labeled.

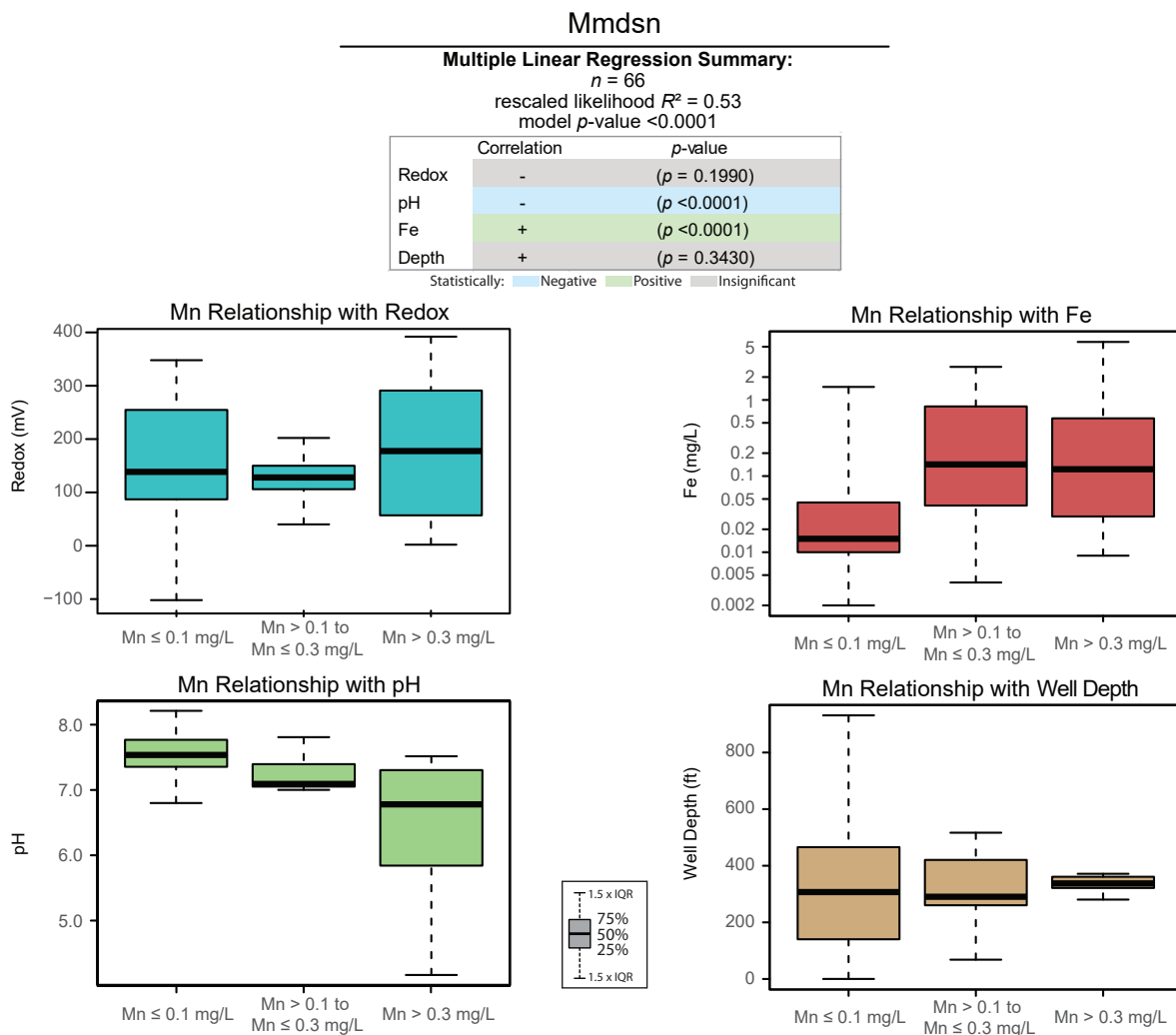


Figure 22. Summary of the multiple linear regression for the Mmdsn aquifer including number of samples with data for all four explanatory variables, rescaled likelihood R^2 , and overall p -value. Direction (positive, negative) and p -values for the correlation between Mn and redox, pH, Fe, and well depth are given in the summary table; p -values ≤ 0.05 suggest a statistically significant correlation. Boxplots of Mn concentrations with available redox, pH, Fe, and well depth provide a visual examination of correlation relationships. Whiskers extend to data no more than 1.5 x IQR (interquartile range), which includes 95% of the data for a normal distribution. Note that the y-axes vary among figures.

the Livingston Group. The occurrence of elevated manganese varied regionally and by aquifer. Elevated concentrations were detected most frequently in samples from the Lonepine basin-fill aquifer southwest of Flathead Lake, in the buried-valley aquifers in central and northeast Montana, and in the Missouri River alluvial aquifers. Of the bedrock aquifers, elevated concentrations were detected most frequently in the Fort Union, Cretaceous shale, and Judith River aquifer samples.

Redox conditions and pH are strong controls on manganese solubility. In the basin-fill and alluvial aquifers, manganese was inversely correlated with redox and to a lesser extent pH. Manganese concentrations in Fort Union and Judith River aquifers/samples also showed an inverse correlation to redox. The redox

and pH conditions that favor manganese solubility also favor the dissolution of iron; therefore, most of the aquifers showed a positive correlation between manganese and iron concentrations. In general, there was little correlation between manganese and well depth; only samples from the alluvial and Cretaceous shale aquifers showed a statistical increase in manganese concentrations and deeper wells.

Statistical relationships among manganese, redox, and pH were not supported in all aquifers. The results may be limited by the lack of data. For instance, not all of the samples had measurements of redox (42 percent). Another limitation to this dataset may be that the spatial distribution of the samples does not capture the range of conditions for each aquifer. Continued groundwater sampling across Montana will improve

our understanding of the distribution of manganese in groundwater and the geochemical conditions that are associated with higher manganese concentrations. The results presented herein provide a synthesis of almost three decades of data on manganese occurrence and the associated solubility controls in Montana's groundwater.

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