Montana Bureau of Mines and Geology
Hydrogeologic Map 10

Fluoride Concentrations in Montana's Groundwater

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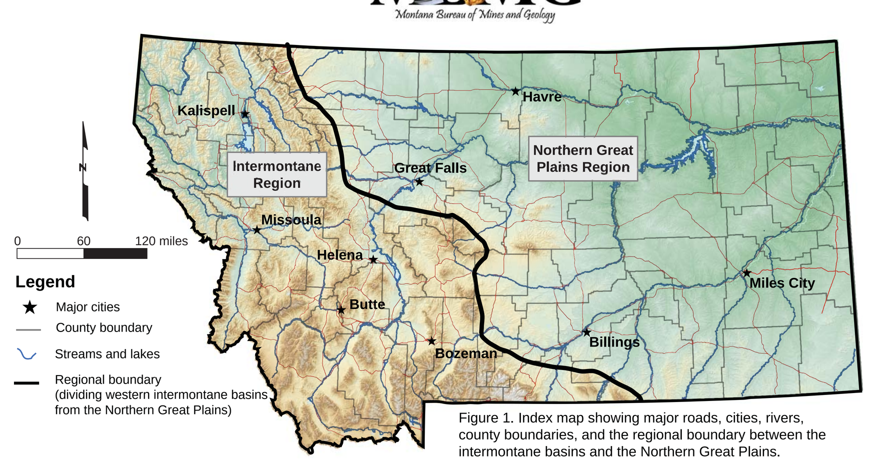

Figure 1. Index map showing major roads, cities, rivers, county boundaries, and the regional boundary between the intermontane basins and the Northern Great Plains.

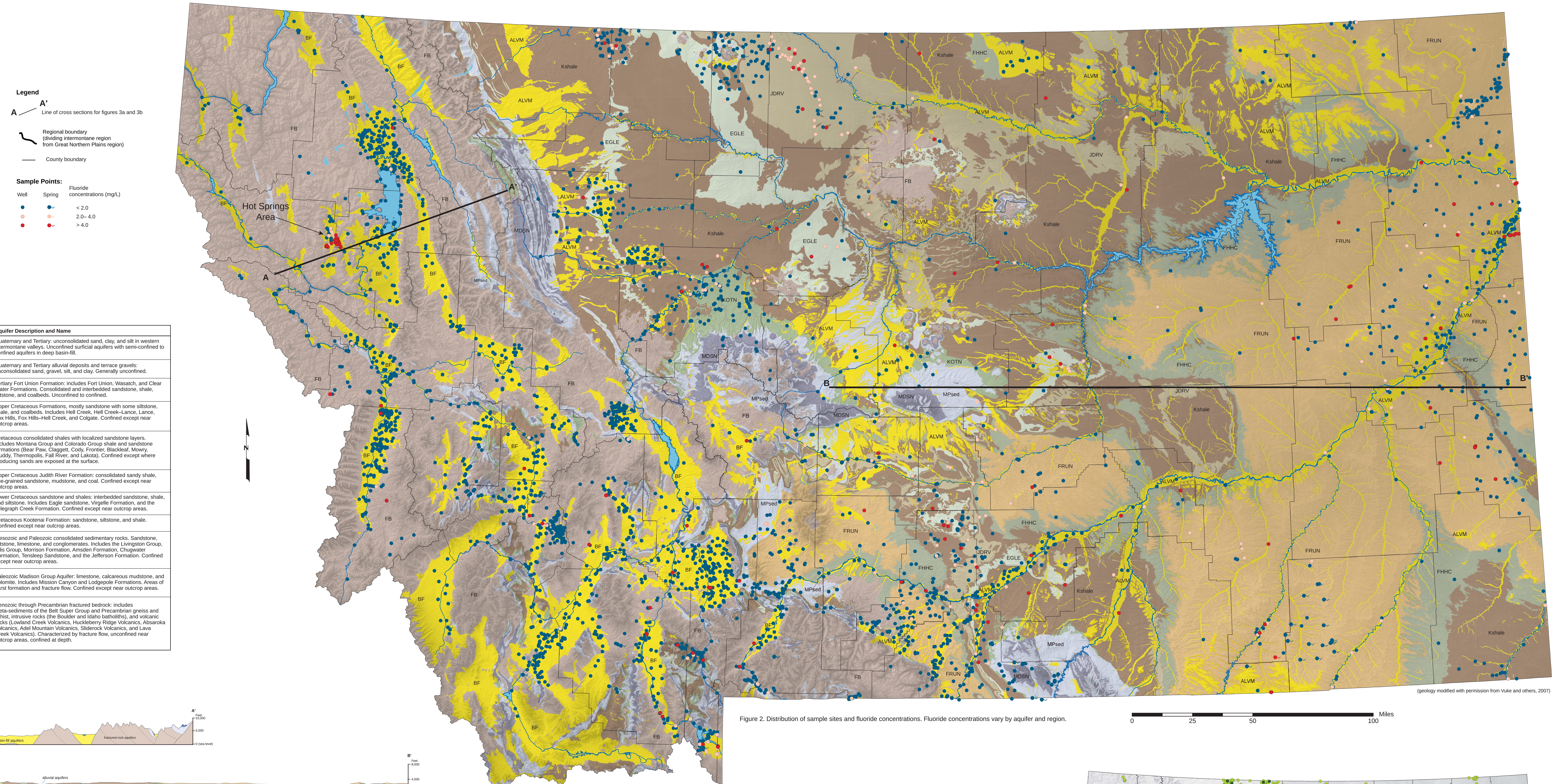

Figure 2. Distribution of sample sites and fluoride concentrations. Fluoride concentrations vary by aquifer and region.

INTRODUCTION

Fluoride is a naturally occurring element in rocks, soils, and groundwater. Elevated fluoride concentrations in drinking water can cause bone damage, staining of teeth, and fluorosis; the U.S. Environmental Protection Agency (EPA) has a maximum contaminant level (MCL) of 4.0 milligrams per liter (mg/L) for fluoride, and a secondary MCL (SMCL) of 2.0 mg/L (the MCL is currently under review). However, the U.S. Public Health Service (PHS) currently recommends a fluoride concentration of 0.7 mg/L in drinking water to prevent tooth decay (HHS, 2011).

Approximately 60 percent of Montana's population obtains their drinking water from groundwater. This map provides information on the range and extent of naturally occurring fluoride in Montana's groundwater.

MONTANA GROUNDWATER

Groundwater is stored within aquifers closely tied to the geology of Montana's two physiographic regions: (1) the intermontane basins in western Montana and (2) the Northern Great Plains in central and eastern Montana (fig. 1). Each physiographic province represents broad differences in geology and geologic history that result in different hydrogeologic settings.

Montana's geologic units range from unconsolidated sand and gravel deposits, to consolidated sedimentary rocks, to fractured metamorphic and igneous rocks. Figure 2 is a generalized geologic map that shows the distribution of major geologic units across the State (modified from Vuke and others, 2007). The major aquifers are described in table 1.

In the intermontane basins, groundwater occurs in shallow unconfined alluvial aquifers as well as deeper confined to semi-confined aquifers buried at depth within several thousand feet of Quaternary and Tertiary basin-fill sediments (basin-fill aquifers, yellow areas in western valleys, fig. 2). These aquifers contain large amounts of groundwater, are highly productive, and are heavily used. The western basins are bounded by mountains (gray areas, fig. 2) composed of meta-sedimentary rocks (e.g., Belt Super Group and Precambrian gneiss and schist), intrusive rocks (e.g., Idaho and Boulder batholiths), and volcanic rocks (e.g., Lowland Creek and Elkhorn Mountain Volcanics) that host less productive fractured-rock aquifers. Figure 3a is a cross section that illustrates the relationship between the basin-fill and fractured-rock aquifers in western Montana.

In the Northern Great Plains of central and eastern Montana, aquifers occur in layers of sedimentary sandstone and limestone, and Quaternary and Tertiary alluvium. The Quaternary and Tertiary deposits are grouped as "alluvial" aquifers (yellow areas in east on fig. 2). Most of these aquifers are located in the major river valleys, localized gravel terraces or "benches," and in buried stream channels. The alluvial aquifers are thin (median well depth of sampled wells is 50 ft) and unconfined, with a few exceptions such as the buried channel gravels in northeastern Montana (the Clear Lake aquifer). The sedimentary bedrock aquifers underlie large parts of central and eastern Montana; although these aquifers are not as productive as the alluvial aquifers, they are highly utilized. The major sedimentary rock aquifers include:

- the Fort Union aquifer (FRUN),
- the Fox Hills–Hell Creek aquifer (FHHC), which underlies the Fort Union in much of the region,
- the Judith River Formation (JDRV),
- the Eagle/Virgelle Formation (EGLE),
- the Kootenai Formation (KOTN),
- and the Madison Group (MDSN), which outcrops along the Rocky Mountain Front, Little Belt Mountains, and Big Snowy Mountains.

There are other sandstone and limestone units that produce water in areas where they crop out or are close to the surface; for the purposes of this map these units are grouped together as Mesozoic–Paleozoic sedimentary rocks (MPsed, table 1). Also, broad areas of north-central Montana are underlain by Cretaceous shale (Kshale). In places, local sandstones within the shale may produce water to wells; however, water quantity and quality are generally poor. A schematic cross section of the Plains region's major sandstone and limestone aquifers and Cretaceous shales is shown in figure 3b.

DATA

The Montana Bureau of Mines and Geology (MBMG) has collected and analyzed groundwater samples from aquifers across the State. These data are stored in and available from the Montana Ground Water Information Center (GWIC) database (http://mbmggwic.mtech.edu).

The objective of this evaluation was to assess the "natural" or background concentrations and variability of fluoride in groundwater from the State's major aquifers. Although the GWIC database houses more than 62,000 water-quality analyses from 18,000 sites, this data set was limited to samples that:

- were collected by the MBMG between May 1993 and Nov 2015 and analyzed by the MBMG analytical laboratory,
- have a complete major-ion analysis,
- have a known source aquifer, and
- represent background conditions.

For sites with more than one sample, the analysis with the highest fluoride concentration was used. To facilitate regional and inter-aquifer comparisons, and comparisons to health benchmarks, censored values with a laboratory reporting limit greater than "< 1.0" mg/L were not included in the dataset (51 samples). The final data set includes 3,587 samples from 3,475 wells and 112 springs. Most of the samples were obtained from domestic wells (59 percent), but stock water, public water supply, irrigation, and monitoring wells were also sampled (table 2).

Table 2. Reported well use of sampled sites. Fifty-nine percent of samples are from domestic wells and springs.

Water Use	Number of Samples
Domestic	2,111
Monitoring	469
Stockwater	434
Public Water Supply	245
Other	167
Irrigation	120
Industrial/commerical	41
Total	3,587

DATA ANALYSIS AND CONCLUSIONS

The distribution of groundwater samples is shown in figure 2. There are areas where the sample distribution is sparse, but others where many samples are clustered. Therefore, the data set may not be statistically representative of all aquifers. Nevertheless, the data set includes samples from every county and all the major aquifers (fig. 4). Over half the samples are from the basin-fill and alluvial aquifers (54 percent), followed by the fractured-rock aquifers (13 percent). Twenty-three percent of samples are collectively from the sedimentary-bedrock aquifers in the Plains region (see fig. 4 for all percentages).

Most fluoride in groundwater occurs naturally from dissolution of fluoride-bearing minerals (e.g, fluorite, apatite, and mica). These minerals are present in many igneous and sedimentary rocks but have low solubility (Hem, 1992). Therefore, elevated fluoride concentrations occur in aquifers with fluoride-bearing minerals and long groundwater residence times—typically deep aquifer systems with low groundwater-flow rates. High fluoride concentrations are also associated with groundwater undergoing cation exchange and geothermal water (Brunt and others, 2004).

Table 1. Description of major aquifer units.

	Code	Aquifers	Aquifer Description and Name
	BF	Basin–Fill Aquifers	Quaternary and Tertiary: unconsolidated sand, clay, and silt in western intermontane valleys. Unconfined surficial aquifers with semi-confined to confined aquifers in deep basin-fill.
	ALVM	Alluvial Aquifers	Quaternary and Tertiary alluvial deposits and terrace gravels: unconsolidated sand, gravel, silt, and clay. Generally unconfined.
	FRUN	Fort Union Aquifer	Tertiary Fort Union Formation: includes Fort Union, Wasatch, and Clear Water Formations. Consolidated and interbedded sandstone, shale, siltstone, and coalbeds. Unconfined to confined.
	FHHC	Fox Hills–Hell Creek Aquifer	Upper Cretaceous Formations, mostly sandstone with some siltstone, shale, and coalbeds. Includes Hell Creek, Hell Creek–Lance, Lance, Fox Hills, Fox Hills–Hell Creek, and Colgate. Confined except near outcrop areas.
	Kshale	Cretaceous Shales	Cretaceous consolidated shales with localized sandstone layers. Includes Montana Group and Colorado Group shale and sandstone formations (Bear Paw, Claggett, Cody, Frontier, Blackleaf, Mowry, Muddy, Thermopolis, Fall River, and Lakota). Confined except where producing sands are exposed at the surface.
	JDRV	Judith River Aquifer	Upper Cretaceous Judith River Formation: consolidated sandy shale, fine-grained sandstone, mudstone, and coal. Confined except near outcrop areas.
	EGLE	Eagle Aquifer	Lower Cretaceous sandstone and shales: interbedded sandstone, shale, and siltstone. Includes Eagle sandstone, Virgelle Formation, and the Telegraph Creek Formation. Confined except near outcrop areas.
	KOTN	Kootenai Aquifer	Cretaceous Kootenai Formation: sandstone, siltstone, and shale. Confined except near outcrop areas.
	MPsed	Mesozoic–Paleozoic Sedimentary Rocks	Mesozoic and Paleozoic consolidated sedimentary rocks. Sandstone, siltstone, limestone, and conglomerates. Includes the Livingston Group, Ellis Group, Morrison Formation, Amsden Formation, Chugwater Formation, Tensleep Sandstone, and the Jefferson Formation. Confined except near outcrop areas.
	MDSN	Madison Group Aquifer	Paleozoic Madison Group Aquifer: limestone, calcareous mudstone, and dolomite. Includes Mission Canyon and Lodgepole Formations. Areas of karst formation and fracture flow. Confined except near outcrop areas.
	FB	Fractured Rock Igneous, Meta-Sedimentary and Metamorphic Rocks	Cenozoic through Precambrian fractured bedrock: includes meta-sediments of the Belt Super Group and Precambrian gneiss and schist, intrusive rocks (the Boulder and Idaho batholiths), and volcanic rocks (Lowland Creek Volcanics, Huckleberry Ridge Volcanics, Absaroka Volcanics, Adel Mountain Volcanics, Sliderock Volcanics, and Lava Creek Volcanics). Characterized by fracture flow, unconfined near outcrop areas, confined at depth.

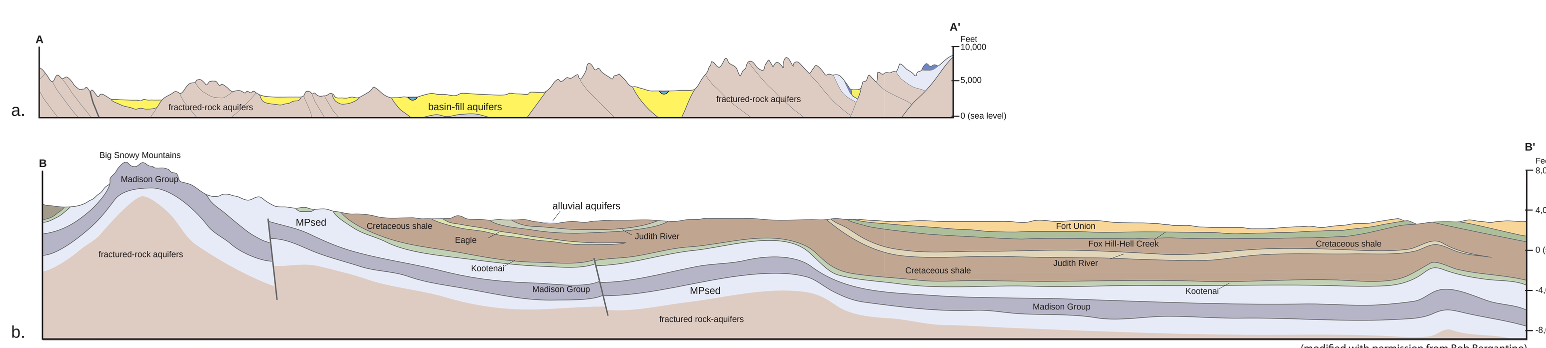

Figure 3. Generalized cross sections illustrating Montana aquifers. (a) Cross section A–A' illustrates the complexly folded and faulted geology of Montana's western intermontane basins. Most of the groundwater development is located in the productive basin-fill aquifers. Less productive fractured-rock aquifers along the valley margins supply many residential wells. (b) Cross section B–B' shows eastern Montana's regional flat-lying aquifers and non-aquifers. Groundwater occurs in the Tertiary Fort Union Formation, Cretaceous sandstone (Fox Hills–Hell Creek, Judith River, Eagle, and Kootenai Formations) and the Mississippian Madison Group.

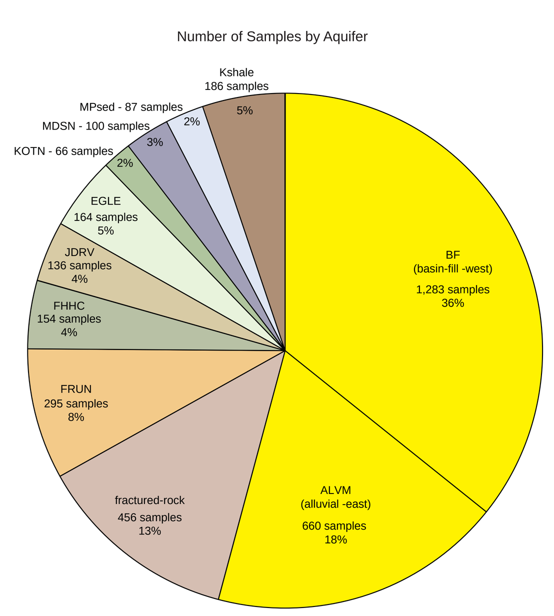

Figure 4. Sample breakdown by aquifer. Fifty-four percent of samples were collected from the basin-fill and alluvial aquifers.

Deep aquifer systems require deep wells. The depth water enters (DWE) is the distance below land surface to the top of perforations or open interval in a well; it represents the depth to an aquifer's production zone. Figure 5 summarizes the DWE of the sampled wells by aquifer. In general, the sedimentary-rock aquifers in eastern Montana have the deepest production zones, but their depths below land surface are the most variable. The geologic cross section (fig. 3b) illustrates the relative position of the aquifers with respect to the land surface and each other. Some aquifers occur at the land surface near "outcrop areas," but are deeply buried distant from outcrops—and even buried below other aquifers (for example see the Fox Hills–Hell Creek aquifer in eastern Montana, fig. 3b). All of the sampled wells from bedrock aquifers in eastern Montana have a median DWE greater than 100 ft; the median DWE for the Fox Hills–Hell Creek, Kootenai, and Madison wells, is greater than 190 ft. The median DWE of the sampled basin-fill wells in western Montana (79 ft) is nearly double that of the alluvial wells in eastern Montana (41 ft), reflecting the greater thickness of the intermontane basin-fill.

Figure 2 shows the sampled well locations and fluoride concentrations. Fluoride concentrations were grouped based on water-quality benchmarks:

●	Below SMCL	< 2.0 mg/L (includes non-detects)
○	Above SMCL	2.0–4.0 mg/L
●	Above MCL	> 4.0 mg/L (exceeds EPA-recommended health level)

Fluoride concentrations for each aquifer are statistically summarized in table 3 and figure 6. Summary statistics (median and percentile concentrations) were calculated using the Kaplan–Meier method (Helsel, 2012). Overall, fluoride concentrations ranged from <0.05 to 19.93 mg/L, with a median concentration of 0.33 mg/L. Most of the samples (89 percent) had fluoride concentrations less than 2.0 mg/L; 4 percent had concentrations greater than 4.0 mg/L MCL. Although exceedances of the MCL occurred in samples from all aquifers, there were differences in fluoride concentrations among the aquifers. Concentrations exceeding the SMCL (2.0 mg/L) and MCL (4.0 mg/L) occurred most frequently in samples from sandstone aquifers in eastern Montana (fig. 7). More than 30 percent of the Fox Hills–Hell Creek and more than 40 percent of the Judith River samples exceeded the SMCL. The MCL was exceeded most frequently in samples from Fox Hills–Hell Creek (12 percent), Judith River (10 percent), and Kootenai (8 percent). These aquifers contain deep regional flow systems that have long groundwater residence times in which water undergoes cation exchange (Henderson, 1985; Smith and others, 1999).

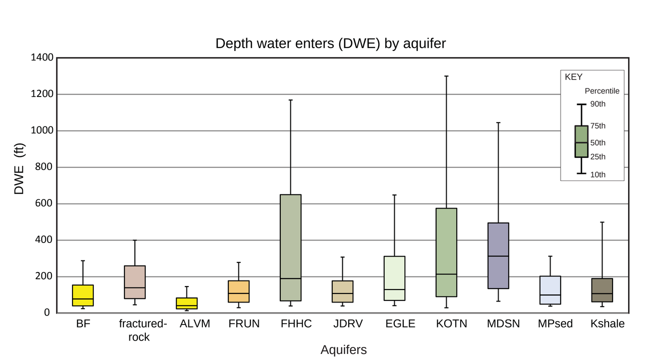

Figure 5. Depth water enters (DWE) is the depth to the first open interval in a well. The deepest sampled wells were in the Madison Limestone, Kootenai, and Fox Hills–Hell Creek aquifers.

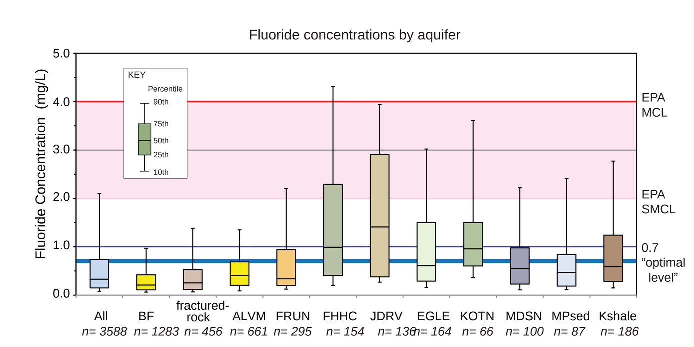

Figure 6. Box plots of fluoride concentrations by aquifer. The highest concentrations are observed in the sandstone aquifers in the Northern Great Plains. Many of these aquifers have samples that fall between EPA's SMCL and MCL (shaded pink area). Samples from intermontane basins have concentrations that fall mostly below "optimal" level (< 0.7 mg/L).

Table 3. Fluoride concentration summary statistics for Montana's major aquifers. Concentrations are variable among and within the aquifers.

Aquifers	Number of Samples	Minimum Fluoride Concentration (mg/L)	Median Fluoride Concentration (mg/L *)	Maximum Fluoride Concentration (mg/L)	Number of Samples with Optimal F Concentration (0.7 mg/L)	Samples below Optimal F Concentration (< 0.7 mg/L)	Number of Secondary MCL Exceedances (2.0–4.0 mg/L)	Number Primary MCL Exceedances (> 4.0 mg/L)
Intermontane basin-fill aquifers	1283	0.01	0.21	13.02	33	77	41	32
Fractured rock: igneous, metasedimentary, and metamorphic	456	< 0.05	0.26	15.00	15	71	13	21
Central and Eastern alluvial aquifers	660	< 0.05	0.41	8.76	37	70	32	8
Fort Union aquifer	295	< 0.05	0.34	8.82	10	65	25	12
Cretaceous shale	186	< 0.05	0.59	19.93	10	50	18	12
Fox Hills–Hell Creek aquifer	154	< 0.05	0.99	6.86	4	40	32	18
Judith River aquifer	136	< 0.05	1.41	10.00	5	28	45	13
Eagle aquifer	164	0.03	0.61	13.61	13	49	20	9
Kootenai aquifer	66	0.17	0.96	11.07	5	33	6	5
Mesozoic–Paleozoic Sedimentary rocks	87	0.07	0.47	7.89	3	68	8	1
Madison Group aquifer	100	0.05	0.55	5.08	4	59	10	1

*Values calculated with the Kaplan–Meier method (Helsel, 2012).

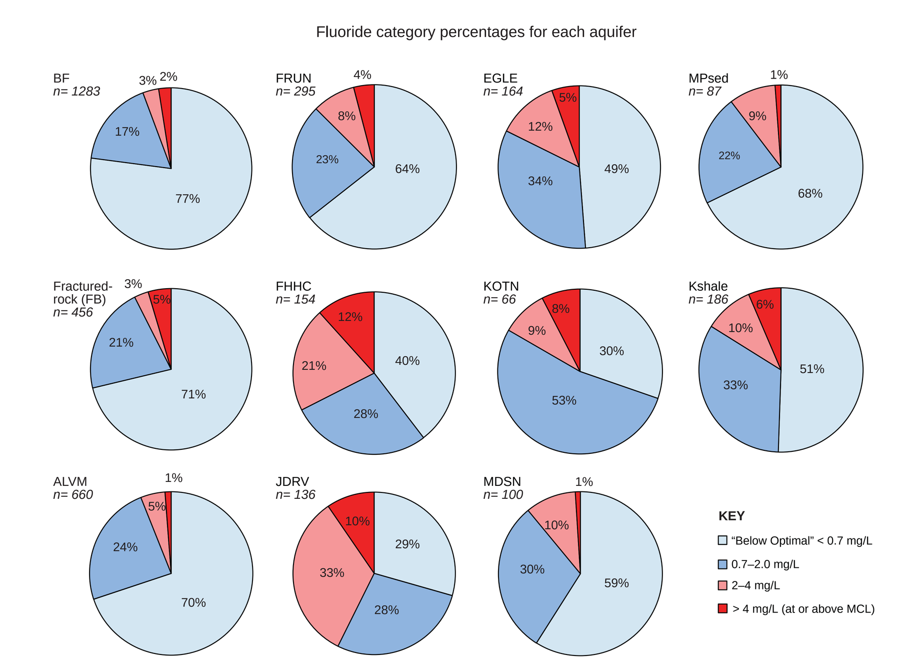

Figure 7. Fluoride concentrations by aquifer with respect to health benchmarks. Samples from sandstone aquifers in the Plains region had the most SMCL/MCL exceedances. The alluvial, basin-fill, and fractured-rock aquifers have the highest percentage of samples with concentrations below "optimal" (< 0.7 mg/L).

In general, samples from the western basin-fill and fractured-rock aquifers had low fluoride concentrations, with median concentrations of 0.21 and 0.26 mg/L, respectively (table 3; fig. 6; fig. 7). However, there is a cluster of elevated concentrations in samples from wells completed in basin fill near Hot Springs in Sanders and Lake Counties. Near Hot Springs, deep-sourced, fluoride-enriched, geothermal water discharges into the fractured-rock and basin-fill aquifers (Abdo, 1997).

Fluoride concentrations below the PHS "optimal" concentration of 0.7 mg/L were observed in 66 percent of the samples. Only 139 samples (4 percent) were optimal. Below optimal concentrations were observed less frequently in the eastern bedrock aquifers, but more frequently (>70 percent of the samples) in the alluvial, basin-fill, and fractured-rock aquifers (fig. 7). Figure 8 shows that most of the sample locations with optimal and below optimal fluoride concentrations occur in the western part of the State, with the exception of alluvial and Fort Union samples near the Montana–North Dakota border.

This report is intended to provide information regarding the distribution of fluoride among Montana's major aquifers. The results indicate that elevated fluoride concentrations occur most frequently in the sandstone aquifers in eastern Montana. However, concentrations greater than the 4.0 mg/L MCL were observed across the State in all aquifers. Fluoride concentrations below the PHS-recommended level of 0.7 mg/L were also observed across the State, but most frequently in the western basin-fill, fractured-rock, and eastern alluvial aquifers. Because of the potential health risk from drinking water with elevated fluoride concentrations, and the variability within each aquifer, well owners are encouraged to test their well water.

All data can be retrieved from the GWIC website: http://mbmggwic.mtech.edu.

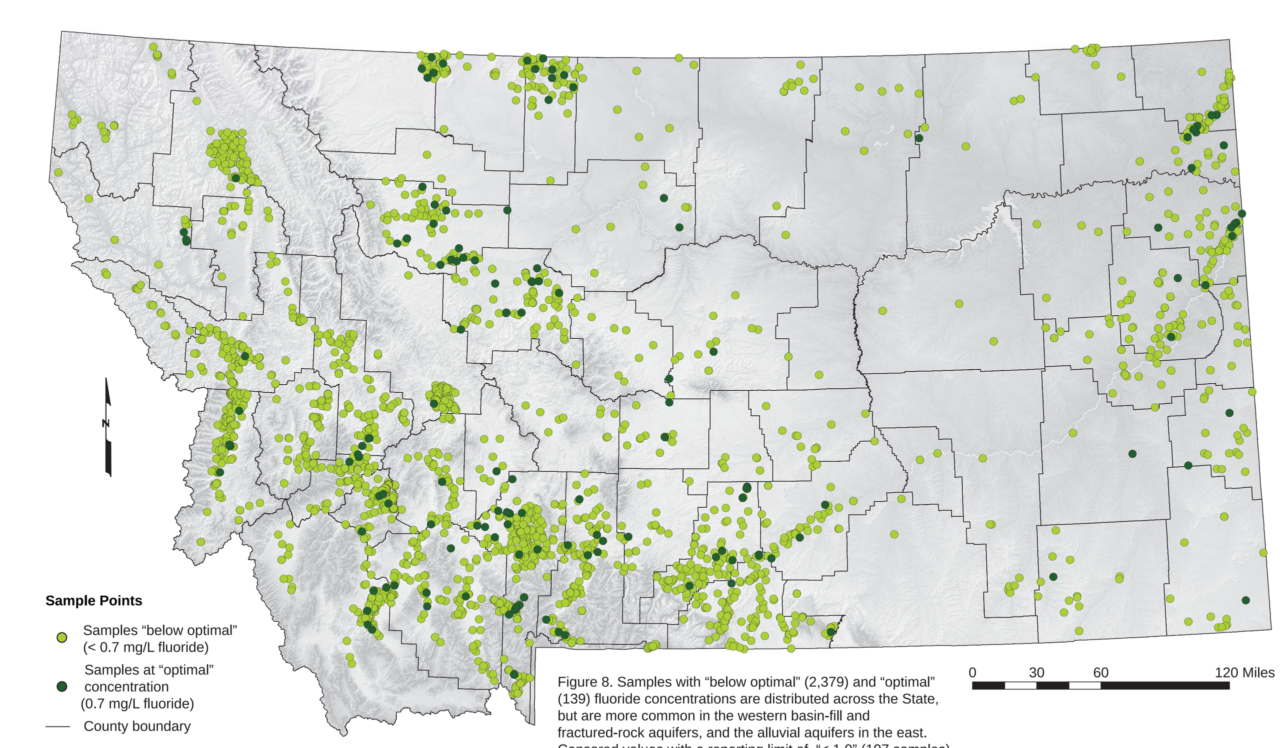

Figure 8. Samples with "below optimal" (2,379) and "optimal" (139) fluoride concentrations are distributed across the State, but are more common in the western basin-fill and fractured-rock aquifers, and the alluvial aquifers in the east. Censored values with a reporting limit of "< 1.0" (197 samples) are not displayed.

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