Final Project Report for DNR-235:
Identification of naturally-occurring fluoride and selected metals in northwest Wisconsin groundwater

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- University of Wisconsin-Extension in Ashland County, Iron County, and the Spooner Agricultural Research Station
- Barron County Department of Health and Human Services
- Bayfield County Health Department
- Douglas County Health Department
- Rusk County Health and Human Services
- Polk County Health Department
- Mercer Public Library
- Barbara Wist and the Madeline Island Public Library
- Jim and Ruth Brennan
- Price County Fair
- Burnett County Agricultural Society Fair

There were many local newspapers and regional journalists who helped to spread the word about the *Northwest Wisconsin Groundwater Monitoring Project*, without which we would have never been able to distribute and receive as many samples as we did.

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EXECUTIVE SUMMARY

According to Wisconsin Department of Natural Resources (WDNR) well construction reports (http://prodoasext.dnr.wi.gov/inter1/watr$.startup, accessed 23 October 2017), residents within eleven northwestern Wisconsin counties obtain their drinking water from over 56,000 wells, including more than 48,000 private wells. Although groundwater in northwestern Wisconsin aquifers may not be as impacted by anthropogenic contaminants as groundwater in other areas of the state, baseline data regarding naturally-occurring inorganic contaminants and metals is severely lacking. Within the past ten years, commercial interests in the region have led to actual and proposed large-scale land use changes that have the potential to impact groundwater quality. A comprehensive set of baseline data are needed in order to measure these impacts long term.

Fluoride and the metals aluminum, arsenic, iron, lead, and manganese are groundwater contaminants that may impact public health, and for which little is known regarding baseline concentrations present in northwestern Wisconsin aquifers. Fluoride is a naturally-occurring inorganic ion, which has a narrow range of therapeutic concentrations. Aluminum, arsenic, iron, and manganese are naturally-occurring metals that could be present in groundwater depending upon the underlying geology and water quality of the aquifer. Lead is introduced to drinking water most commonly by corrosion of plumbing materials which contain lead. Corrosive groundwater can dissolve lead and other metals from these plumbing materials and contaminate drinking water. It is also possible that corrosive groundwater may cause lead-containing minerals in aquifers to leach lead.

The objectives of this research were to:

1. Identify naturally-occurring fluoride and selected metals in groundwater within northwestern Wisconsin.
2. Increase the groundwater quality data available to residents of northwestern Wisconsin.

Data to support these objectives were obtained through private drinking water samples collected by volunteers who were supplied with drinking water sample kits, and were instructed on how to collect well water samples. All samples were analyzed for fluoride, and a randomly-selected subset of private drinking water samples were analyzed for aluminum, arsenic, iron, manganese, and lead. At the end of the project, the findings from this study were presented at several regional venues from which volunteers were recruited. The summarized data from this monitoring effort is presented in Table 1.

Table 1. Range and Average Concentrations of Parameters Measured during the Northwest Wisconsin Groundwater Monitoring Project.

Parameter	Minimum (mg/L)	Average (mg/L)	Maximum (mg/L)	Enforcement Std.* (mg/L)
Fluoride	<0.015	0.11	2.0	4.0 mg/L
Iron	<0.025	0.64	24.9	0.30 mg/L
Manganese	<0.0066	0.045	0.57	0.30 mg/L
Aluminum	<0.0016	0.0075	0.31	0.20 mg/L
Lead	<0.00054	0.0011	0.018	0.015 mg/L
Arsenic	<0.00035	0.0012	0.010	0.010 mg/L

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1 INTRODUCTION

The geology of aquifers plays a large role in determining the naturally-occurring inorganic contaminants present in groundwater. Contaminants such as radium, arsenic, nickel, cobalt, fluoride, strontium, aluminum, and manganese are known to be present in Wisconsin groundwater (Luczaj and Masarik, 2015). Northwestern Wisconsin, including the counties of Ashland, Barron, Bayfield, Burnett, Douglas, Iron, Polk, Price, Rusk, Sawyer, and Washburn (Figure 1), is dominated by Precambrian geology consisting of crystalline igneous and metamorphic rock, predominately red granite (Luczaj and Masarik, 2015). Granite rocks are a natural source of fluoride, with a reported average fluoride concentration of 810 mg/kg worldwide (Brindha and Elango, 2011). The weathering of these rocks, particularly in alkaline conditions with a pH between 7.6 and 8.6, can cause dissolution of fluoride into groundwater (Brindha and Elango, 2011). High fluoride concentrations have been reported in several areas of Wisconsin, including parts of Marathon County in central Wisconsin and areas within north- and southeastern Wisconsin (Ozsvath, 2006; Luzaj and Masarik, 2015). Arsenic, a naturally-occurring heavy metal, has been measured in Wisconsin groundwater in various concentrations ranging from <1 µg/L to over 15,000 µg/L with elevated levels known to be present in Paleozoic bedrock, glacial sediment, and Precambrian bedrock (Luzaj and Masarik, 2015). In a survey of data from private wells in rural Wisconsin, researchers found concentrations of aluminum, arsenic, iron, lead, and manganese exceeded groundwater enforcement standards in 1.2%, 2.4%, 20.6%, 1.8%, and 3.6% of samples, respectively (Knobeloch et al., 2013).

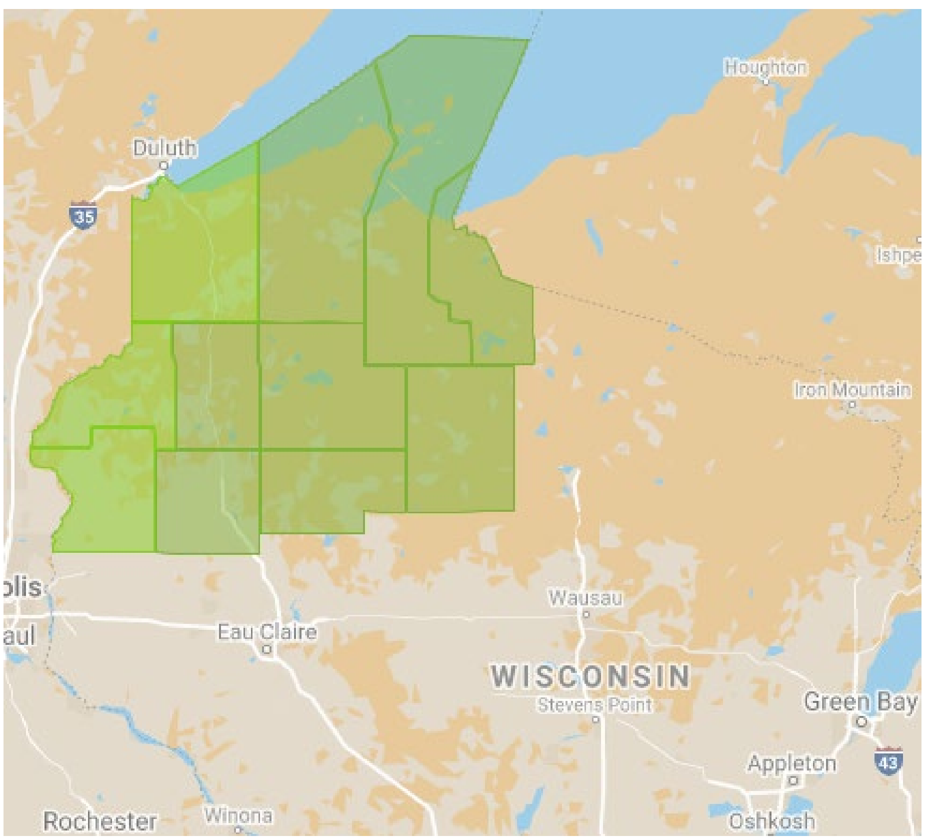

Figure 1. Map Showing the 11-County, Northwest Wisconsin Monitoring Study Area (Counties Shaded in Green). Map created using Google My Maps.

These naturally-occurring groundwater contaminants and lead, which only occurs naturally under specific water quality conditions, can impact public health, depending upon the concentrations present, and baseline data are needed for northwestern Wisconsin in order to better understand the range of concentrations of fluoride, aluminum, arsenic, iron, lead, and manganese to which residents obtaining their drinking water from public and private wells are exposed. Within the last decade, residents of northwest Wisconsin have seen several large-scale land use changes as a result of new and expanding industries in the region. There have also been several proposed industries within northwest Wisconsin that could have impacted groundwater quality. This includes active industrial sand facilities (e.g., frac sand mining) in Barron and Rusk County, proposed development of an iron ore mining operation in Ashland and Iron County (Gogebic Iron Range), a proposed concentrated animal feeding operation (CAFO) in Ashland County, the pending development of a CAFO in Burnett County, and proposed rerouting of an oil pipeline through Ashland and Iron County. Land use changes such as these necessitate a comprehensive set of baseline data from which to measure long-term groundwater quality changes.

Despite research-based evidence of the presence of naturally-occurring fluoride, aluminum, arsenic, iron, and manganese and non-naturally occurring lead in Wisconsin groundwater, there is very little baseline monitoring data for northwestern Wisconsin, an area with underlying geology that may be conducive to dissolution of these inorganic contaminants. According to WDNR well construction reports, residents within eleven northwestern Wisconsin counties obtain their drinking water from over 56,000 wells, of which 48,000 are private wells that are not regulated under the federal Safe Drinking Water Act and have no routine monitoring requirement. In reality, the number of public and private wells within these primarily rural counties is much higher, given that electronic records are only readily available for wells constructed after 1987. Although groundwater in northwestern Wisconsin aquifers may not be as impacted by anthropogenic contaminants as groundwater in other areas of the state, baseline data regarding naturally-occurring inorganic contaminants and metals is severely lacking. In addition, despite the high percentage of residents obtaining drinking water through public and private wells, many homeowners in the region are unaware that their private water supply should be tested regularly.

1.1 Study Objectives

The goal of this monitoring study, known as the *Northwest Wisconsin Groundwater Monitoring Project*, was to obtain much-needed baseline data in northwestern Wisconsin regarding the naturally-occurring concentrations of fluoride, aluminum, arsenic, iron, and manganese that residents are exposed to in the well water they drink. Lead, which does not readily leach from minerals into groundwater unless specific water quality conditions are present, and is present in groundwater due to human sources of contamination, was also measured as part of this study. This project was conducted to inform the public of the need for regular well water testing and which parameters should be measured. It involved volunteers and citizen scientists in the data collection effort, and the results were fed back into the public in the form of public seminars that were offered throughout the eleven-county study area. The objectives of the *Northwest Wisconsin Groundwater Monitoring Project* were to:

1. Monitor naturally-occurring fluoride concentration in groundwater samples collected from eleven counties in northwestern Wisconsin, and determine concentrations of aluminum, arsenic, iron, lead, and manganese in a subset of these samples.

2. Foster public awareness among northwestern Wisconsin residents about the need for regular private well water testing, and increase the publicly-available groundwater data within the region.

1.2 Fluoride

The American Dental Association recommends fluoride supplementation in drinking water containing less than 0.7 mg/L fluoride to prevent dental caries (Rozier et al., 2010). Conversely, drinking water fluoride concentrations greater than 1.5 mg/L can cause dental fluorosis and negatively impact bone health in children (Table 2).

Table 2. Effects of Fluoride Ingestion on Human Health (Adapted from Ozsvath, 2006).

Fluoride Concentration (mg/L)	Effect on Human Health
<0.7	Conducive to dental caries
0.7 – 1.5	Promotes development of strong bones and teeth
1.5 – 4.0	Promotes dental fluorosis in children
>4.0	Promotes dental and skeletal fluorosis
>10.0	Crippling skeletal fluorosis, possibly cancer

Given the very small range of beneficial fluoride concentrations, it is especially important for northwestern Wisconsin families who obtain their drinking water from public and private wells to be aware of the fluoride concentration in their primary source of drinking water in order to make informed decisions on whether fluoride supplementation is necessary for their children. This is even more important for residents with infants drinking formula reconstituted with well water, as infants may be exposed to multiple sources of fluoride and could be at risk of developing fluorosis (Table 3; Rozier et al., 2010).

Table 3. American Dental Association Recommendations for Fluoride Supplementation, According to Fluoride Concentration in Drinking Water (Rozier et al., 2010).

Age	Fluoride Concentration Present in Drinking Water (mg/L)		
	<0.3	**0.3 – 0.6**	**>0.6**
Birth to 6 months	None	None	None
6 months to 3 years	0.25 mg/day	None	None
3 to 6 years	0.50 mg/day	0.25 mg/day	None
6 to 16 years	1.00 mg/day	0.50 mg/day	None

There is no requirement for fluoride monitoring in non-community public water systems, and fluoride is not a parameter that is typically measured during a new well installation or property transfer. The maximum contaminant level (MCL) for fluoride is 4 mg/L; once fluoride concentrations reach 6 mg/L in drinking water it has been reported that 100% of the population experiences some level of dental fluorosis (Ozsvath, 2009). The secondary maximum contaminant level for fluoride is 2 mg/L, a concentration reported to cause mild to moderate dental fluorosis in at least 60% of the United States population (Ozsvath, 2009).

1.3 Iron and Manganese

Iron and manganese are both found in groundwater from natural, geologic sources. In a study conducted on samples collected 2005 – 2013 from within the glacial aquifer system, which includes the State of Wisconsin, both iron and manganese were detected at high concentrations across approximately 50% of the glacial aquifer system (Erickson et al., 2019). These metals are considered "secondary" contaminants whose presence in drinking water may cause an unpleasant smell, taste, appearance, or cause staining. Therefore, secondary drinking water standards have been set for iron and manganese. The standard for iron is 0.3 mg/L and the standard for manganese is 0.05 mg/L, concentrations above which drinking water may not be aesthetically pleasing. However, it is also true that exposure to elevated levels of iron and manganese can have human health effects. Iron exposure has been associated with the development of diabetes and cardiovascular disease. Manganese exposure has been known to cause central nervous system toxicity (Knobeloch et. al, 2013).

1.4 Aluminum

Aluminum is another naturally-occurring metal that is found in groundwater. Chronic exposure to high levels of aluminum have been associated with central nervous system toxicity and reproductive effects (Knobeloch et al., 2013). The MCL for aluminum is 0.20 mg/L.

1.5 Arsenic

Chronic exposure to arsenic has been associated with cancer, nerve damage, and cardiovascular disease. All community (i.e., municipal water systems, mobile home parks, apartment buildings, and long-term care facilities) and non-transient, non-community (i.e., schools, day care centers, industrial facilities, and other businesses) public water systems in Wisconsin are required to monitor for arsenic. Arsenic may be measured in private wells during property transfers, but may not otherwise be measured annually according to WDNR guidelines (2011) because homeowners may be unaware that these guidelines exist. The MCL for arsenic is 0.01 mg/L.

1.6 Lead

Lead is the only parameter measured in this monitoring study that does not occur naturally in groundwater unless certain water quality conditions exist. Chronic exposure to lead has been determined to cause developmental effects and decreased renal function (Yang et al., 2019). The MCL for lead is 0.015 mg/L. The presence of lead in drinking water that is sourced from groundwater is generally attributable to copper plumbing with lead-based solder, brass or bronze fixtures, lead pipes, and galvanized pipes (Yang et al., 2019). Lead measured in private well water may also be coming from well components containing lead (e.g., screens, packing collars, and old submersible pumps; Yang et al., 2019). Leaching of lead from plumbing and well components can be exacerbated if groundwater is corrosive. The corrosivity of groundwater is characterized by pH, calcium ion concentration, hardness, alkalinity, dissolved solids, and temperature (https://www.usgs.gov/mission-areas/water-resources/science/all-about-corrosivity?qt-science_center_objects=0#qt-science_center_objects; accessed July 2020). Two indicators are commonly used to determine groundwater corrosivity: Langelier Saturation Index (LSI) and the chloride-to-sulfate mass ratio (CSMR). The LSI indicates the potential for calcium carbonate to form a scale, and considers the pH of the water and a derived pH at which calcium carbonate saturation occurs (Belitz et al., 2016). Negative LSI values indicate that calcium carbonate scaling is unlikely to occur inside pipes and other components of the well/plumbing system; lead and other metals would more readily leach from plumbing into groundwater under these conditions. In a study conducted by the U.S. Geological Survey of untreated groundwater samples collected from 20,962 sites within the U.S., Wisconsin was characterized as "intermediate" based upon the average LSI -0.14 (Belitz et al., 2016). The CSMR, in combination with alkalinity, is used to characterize the potential for galvanic corrosion in water distribution systems. Elevated CSMR values in groundwater can increase the potential for galvanic corrosion, and the probability that lead or other metals present in plumbing systems may leach into groundwater (Johnson, no date). In the 2016 U.S. Geological Survey study, Wisconsin was characterized as "moderate" based on less than 50% of wells sampled classified as having a low potential to promote galvanic corrosion (PPGC), and 25% of wells sampled classified as having a high PPGC (Belitz et al., 2016).

Under elevated CSMR conditions, lead-containing minerals naturally present in aquifers (e.g., galena, plattnerite, cerussite, and/or hydrocerussite) may also leach lead into groundwater. This generally occurs when groundwater has a pH<6 or pH>11 with little to no calcium carbonate present (Johnson, no date). When groundwater pH is between 6 and 11, these minerals are not readily soluble and the lead contained within them would not be mobile in groundwater (Johnson, no date).

2 METHODS

2.1 SAMPLE KIT DISTRIBUTION AND VOLUNTEER RECRUITMENT

A total of 704 volunteer-collected fluoride samples and 115 volunteer-collected metals samples were targeted for this study. This study used a random sample design, with the objective of having at least one distribution site where volunteers could obtain a sample collection kit in each of the 11 northwest Wisconsin counties in the study area. Volunteers were recruited to participate in this study through a combination of social media postings, press releases, and outreach events. The citizen-scientist organization SciStarter was also utilized, although this platform did not result in any volunteers. In order to participate in the monitoring study, volunteers had to use well water as their primary drinking water source and had to reside in one of the 11 counties in the study (Ashland, Barron, Bayfield, Burnett, Douglas, Iron, Polk, Price, Rusk, Sawyer, or Washburn).

Assembled sample kits were delivered to each of the 26 distribution sites (Table 4) from 15 July 2018 through 30 April 2019. Interested volunteers were encouraged to pick up a sample collection kit at one of the distribution sites (Table 4) located throughout the 11-county study area (Figure 2). For each distribution site, an average of 16% of sample collection kits assembled were randomly selected to contain both fluoride and metals sample collection bottles (Table 4).

Each sample kit that was assembled was uniquely identified and labeled for tracking purposes. Each distribution site received a tracking log at the time of sample kit delivery. When a study volunteer picked up a sample kit, the volunteer completed an entry in the tracking log for the kit that was assigned to them, including their name, phone number and/or e-mail address, and date of sample kit pickup. This allowed the pickup and receipt of each sample kit to be tracked, and provided a mechanism for communication with each volunteer if a kit was received without a sample collection form, with missing information on the sample collection form, or if a kit was not received at all.

Table 4. List of Sample Collection Kit Distribution Sites, by County, and Total Number of Kits Housed at Each Location.

Distribution Site/Outreach Event Name	Location (Town/City, County)	Number of Kits Delivered	Number of Kits with Metals Sample Bottle
Madeline Island Public Library	La Point, Ashland	35	7
NorthLakes Community Clinic - Ashland Downtown	Ashland, Ashland	20	3
NorthLakes Community Clinic – Ashland Children's	Ashland, Ashland	20	3
Morse Groundwater Education Event – Morse Town Hall	Morse, Ashland	17	4
University of Wisconsin-Extension Ashland County	Ashland, Ashland	100	12
Barron County Department of Health and Human Services	Barron, Barron	60	8
NorthLakes Community Clinic - Turtle Lake	Turtle Lake, Barron	20	3
Bayfield County Health Department	Washburn, Bayfield	10	1
NorthLakes Community Clinic - Iron River	Iron River, Bayfield	20	4
NorthLakes Community Clinic - Washburn	Washburn, Bayfield	20	3
Burnett County Agricultural Society Fair	Grantsburg, Burnett	15	2
Douglas County Department of Health and Human Services	Superior, Douglas	10	1
Lake Superior Day	Superior, Douglas	1	0
University of Wisconsin-Superior – Lake Superior Research Institute	Superior, Douglas	43	8
The River Talks – Wisconsin Sea Grant	Superior, Douglas	5	1
Mercer Public Library	Mercer, Iron	39	12
University of Wisconsin-Extension Iron County	Hurley, Iron	36	3
Polk County Health Department	Balsam Lake, Polk	20	3
NorthLakes Community Clinic - Balsam Lake	Balsam Lake, Polk	20	3
Price County Fair	Phillips, Price	18	3
Rusk County Department of Health and Human Services	Ladysmith, Rusk	50	5
NorthLakes Community Clinic – Hayward Rivers Edge	Hayward, Sawyer	20	3
NorthLakes Community Clinic – Hayward Hospital	Hayward, Sawyer	20	3
NorthLakes Community Clinic - Birchwood	Birchwood, Washburn	18	3
NorthLakes Community Clinic - Minong	Minong, Washburn	36	8
Spooner Agricultural Research Station - University of Wisconsin-Extension	Spooner, Washburn	31	9
Total Number of Sample Kits Delivered to Distribution Sites		**704**	**115**

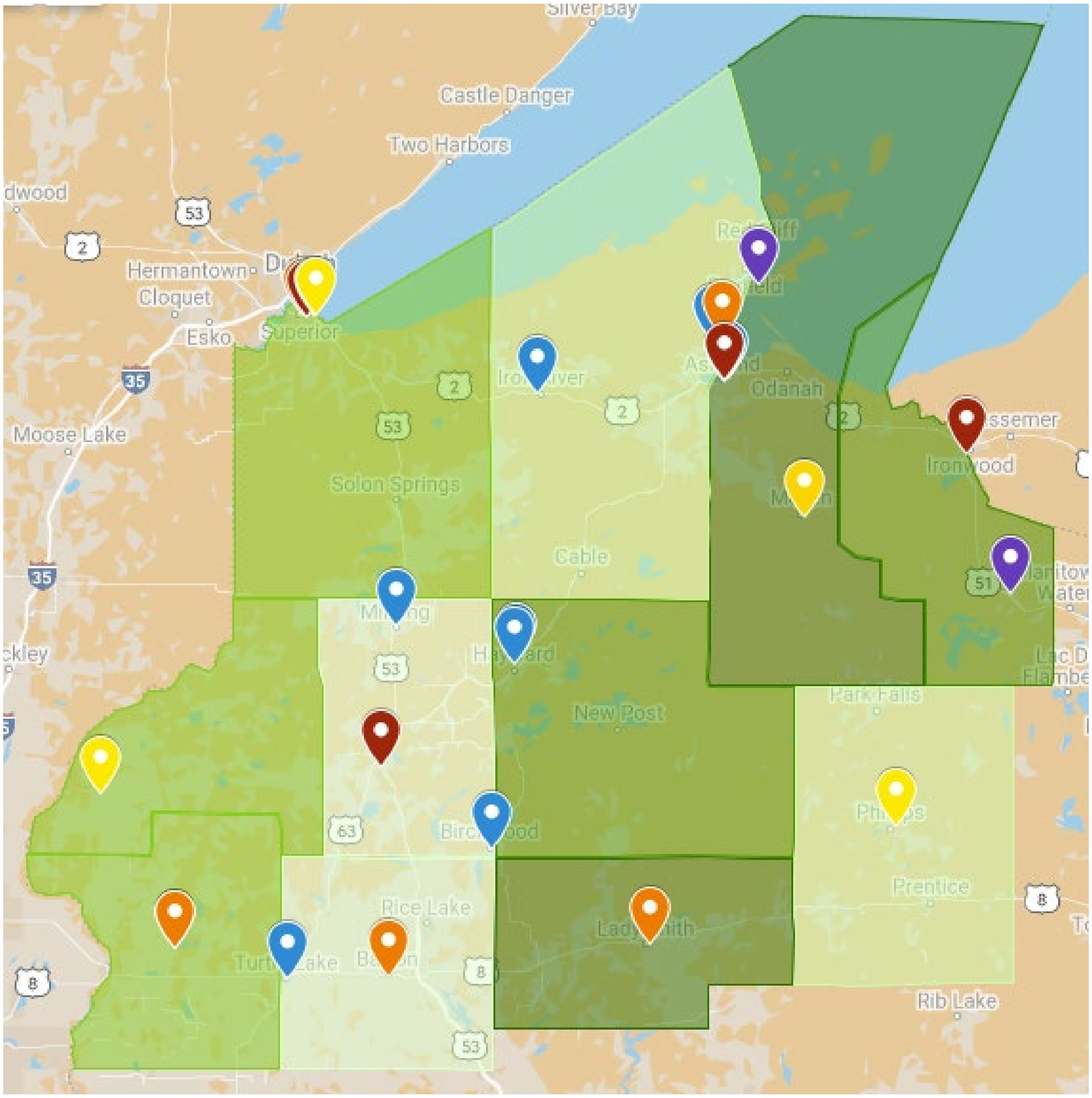

Figure 2. Google Map of 11-County Study Area Showing the Sample Kit Distribution Sites. Blue pins represent NorthLakes Community Clinics, orange pins represent county public health departments, red pins indicate University of Wisconsin-Extension, purple pins represent public libraries, and yellow pins indicate outreach events.

2.2 Sample Collection

Each sample collection kit contained either one (fluoride-only) or two (fluoride + metals) sample bottles, instructions for sample collection, a sample collection form, and a pre-paid shipping label (Figure 3). Sample kits located at distribution sites within Douglas County and at NorthLakes Community Clinic locations in Iron River or Minong did not contain shipping labels, as they were either delivered directly to the University of Wisconsin-Superior Lake Superior Research Institute or were picked up from the distribution site after collection. The sample bottles were labeled with the unique identifier used for each kit.

Figure 3. Photo of Sample Bottles and Pre-Paid Shipping Label Contained in Sample Kit (Left), and Photo of Assembled Sample Kits Prepared for Delivery to Distribution Sites (Right). Pictured right: Mikaela Shepard, Project Undergraduate Research Assistant.

In order to ensure these volunteer-collected samples were collected following the same method, much care was taken when writing the sample collection instructions. Photos were used to provide volunteers with a visual aid, and volunteers were encouraged to contact the project principal investigator with any questions. Volunteers were asked to collect samples from three possible sample location options within their residence:

1. Sampling faucet located between private well and the pressure tank (preferred collection location).
2. Sample faucet located after the pressure tank but before a filter or other water treatment system.
3. Sample faucet (indoor sink) located after the pressure tank and filter/water treatment system.

Samples were collected into 125-mL, wide-mouth containers that were pre-cleaned to meet or exceed EPA requirements for drinking water (QEC Level 2; Quality Environmental Containers; Beaver, WV). Volunteers were asked to collect a sample into the provided bottle(s) after running cold water at a high flow rate for at least five minutes to clear the lines. Following sample collection, volunteers were instructed to complete Sections 1 and 2 of the provided sample collection form (Appendix 1). Information requested from the study volunteers included: collection date and time, collection location, presence/absence and type of water treatment system and whether the sample was collected before or after the treatment system, well owner's contact information, well information (address, completion date, well number, construction type), and address to send results to after completion of analysis.

Volunteers were asked to return the collected samples to the University of Wisconsin-Superior Lake Superior Research Institute within 14 days of collection. This requirement allowed the metals samples to be preserved by the project team, rather than asking volunteers to handle bottles containing the acid preservative. The samples were placed into zip-top plastic bags and placed into the cardboard box along with the sample collection form. For those kits with pre-paid shipping labels, the label was affixed to the outside of the box and shipped via two-day priority mail. Kits were also returned by volunteers to the Lake Superior Research Institute, Douglas County Department of Health and Human Services, NorthLakes Clinic – Iron River, and NorthLakes Clinic – Minong. The kits that were dropped off by volunteers in Iron River and Minong were picked up by the project principal investigator and transported to the Lake Superior Research Institute for analysis.

2.3 Sample Analysis

2.3.1 Sample Receipt and Handling

Upon receipt of sample kits at the Lake Superior Research Institute, a sample receipt checklist (Appendix 2) was completed by the project staff checking in the sample. The samples were inspected to determine whether the LSRI-supplied container was used and was intact and whether sufficient sample volume was present in the bottle. The sample collection form, if present, was examined to determine whether Sections 1 and 2 had been completed. If the sample collection form was not present in the returned kit, or had missing information, the volunteer was contacted by a member of the project staff in order to obtain the necessary information. Any samples for which the sample collection date could not be determined were deemed invalid. For those samples for which the sample collection date was known, the project staff member checking in the samples verified the sample was received within the holding time. The fluoride samples required no temperature or chemical preservation, and were held at room temperature for a maximum of 28 days prior to analysis. The metals samples were preserved upon receipt using trace metal grade nitric acid to pH<2. The pH of the preserved sample was measured using low-range pH paper to confirm preservation. The preserved metals samples were held at room temperature for up to six months prior to analysis.

After receipt of each sample kit, an attempt was made to locate the well record from which the sample(s) was collected. The well address supplied by the project volunteer was used to determine the section, range, and township from which the groundwater sample was collected. The Wisconsin Department of Natural Resources Well Construction Information System was used to conduct the well record research, and any well records that were successfully obtained were included in the volunteer's report and the data were entered into a MS Excel spreadsheet containing all well and sample analysis data from the study.

2.3.2 Fluoride

Fluoride analysis was conducted on a Thermo Scientific Dionex Integrion HPIC (High Performance Ion Chromatography) system following US EPA Method 300.0 (1993). The system consisted of the Integrion HPIC, an AS-DV autosampler, an IonPac™ AG22-Fast-4µm RFIC™ 4 x 30 mm guard column, an IonPac™ AG22-Fast-4µm RFIC™ 4 x 150 mm analytical column, an AERS 500 suppressor and a 10 µL sample loop. The Integrion HPIC was equipped with a conductivity detector. The eluent used for the analysis was a mixture containing 0.45M sodium carbonate and 0.14M sodium bicarbonate in deionized water. The flow rate of the eluent was 1.2 mL/minute.

Six calibration standards (0.0, 0.020, 0.080, 0.200, 0.800 and 2.0 mg/L) were prepared from a fluoride containing mixed anion stock (150 mg/L in each anion). The Thermo Scientific Chromeleon software used the data from the analysis of the standards to generate a calibration curve that determined the concentration of fluoride in samples. The mixed anion standards, quality control standards and samples were prepared for analysis by adding a concentrated solution of sodium carbonate and sodium bicarbonate (100X eluent) so that the concentration of these components were the same in the standards and samples. By making the concentration of carbonate and bicarbonate in the standards and samples the same as in the eluent, the water dip that frequently interferes with the integration of the fluoride peak was eliminated.

The Limit of Detection (LOD) and Limit of Quantitation (LOQ) for fluoride was determined annually during this project following LSRI SOP SA/35, Determination of Limit of Detection and Limit of Quantitation (LSRI, 2019). For both determinations, a minimum of eight-25 µg/L unpreserved fluoride standards were prepared in reagent water and analyzed over the course of a minimum of three days annually. The 25 µg/L standard was prepared by diluting 16.6 µL of the Mixed Anion Stock solution (containing chloride, fluoride, nitrate-N, nitrite-N, *o*-phosphate-P and sulfate) to 100 mL and adding 0.100 mL 100X eluent (0.45 M sodium carbonate and 0.14 M sodium bicarbonate), which is used to get rid of the water dip that interferes with the fluoride peak. The standard deviation from the analyses was multiplied by the t-value for the relevant degrees of freedom to determine the LOD. The LOQ was 10/3 the LOD value. Prior to 21 February 2019, the LOD for fluoride was 0.008 mg/L and the LOQ was 0.025 mg/L. After 21 February 2019, the LOD for fluoride was 0.017 mg/L and the LOQ was 0.057 mg/L.

2.3.3 Metals

Analysis of the five metals studied for this project was conducted on the PerkinElmer PinAAcle 900T Atomic Absorption Spectrometer. The instrument was equipped with both flame and graphite furnace capabilities. Hollow cathode lamps (HCLs) were utilized for the analysis of aluminum, iron, manganese and lead. An electrodeless discharge lamp (EDL) was used to analyze arsenic. The PerkinElmer AS 900 autosampler was employed when analyzing samples by graphite furnace technique. The operation of the system was controlled by PerkinElmer Syngistix software.

Calibration standards were prepared from a purchased multi-element metals standard (Centripur® Certified Reference, EMD Millipore, Billerica, MA) and used for the generation of calibration curves. For flame analysis, the reagent blank and five calibration standards were used. The reagent blank was acidified deionized water. Graphite furnace analysis employed the reagent blank and four calibration standards. All standards and samples were acidified with trace metal grade nitric acid to a pH of <2 before being analyzed. The Syngistix software generated calibration curves based on the reagent blanks and analytical standards and used this data to calculate the concentration of metal in the samples being analyzed. LOD and LOQ values for all metals analyzed by either flame or furnace were determined by spiking reagent water with a low concentration of the metal of interest and analyzing nine spiked reagent water samples over three analysis days (LSRI, 2019). The standard deviation of the nine analyses was multiplied by the t-value for eight degrees of freedom (2.896) to determine the LOD. The LOQ is 10/3 the value of the LOD.

2.3.3.1 Flame Atomic Absorption Spectrometry

Samples analyzed for iron and manganese were analyzed by flame atomic absorption spectrometry following standard methods (Greenberg et al., 1992). Iron was analyzed using the 248.3 nm wavelength and manganese at 279.5 nm. The flame used for the analysis of both metals was a clean air/acetylene flame. The Syngistix software was programmed to make three 3-second absorbance readings for each standard and sample and to report the individual absorbance readings and concentrations, as well as, the mean, standard deviation and percent relative standard deviation of the values. The LOD (LOQ) value for iron was determined to be 0.025 mg/L (0.083 mg/L). The LOD (LOQ) value for manganese was 0.0066 mg/L (0.022 mg/L).

2.3.3.2 Graphite Furnace Atomic Absorption Spectrometry

Aluminum, arsenic and lead were analyzed by graphite furnace technique following US EPA Method 200.9 (1994). This method was used for these metals instead of the flame technique because the concentration of the metals in the samples was below the detection limit of the flame method. Zeeman background correction was used in the analysis of each of these metals. Table 5 provides the wavelength, pyrolysis and atomization temperatures and the matrix modifier employed in the analysis of these metals. The LOD (LOQ) value for aluminum was determined to be 1.6 µg/L (5.3 µg/L), arsenic 0.35 µg/L (1.2 µg/L), and lead 0.54 µg/L (1.8 µg/L).

Table 5. Analysis Method Summary for Graphite Furnace Atomic Absorption Spectrometry Analysis of Aluminum, Arsenic, and Lead.

Metal	Wavelength	Pyrolysis Temp. (°C)	Atomization Temp. (°C)	Matrix Modifier
Aluminum	309.3 nm	1300	2400	Magnesium nitrate
Arsenic	193.7 nm	1000	2100	Palladium and Magnesium nitrate
Lead	283.3 nm	850	1700	Ammonium phosphate monobasic and Magnesium nitrate

Triplicate injections of each of the standards and samples were made by the autosampler. Each injection consisted of 5 µL of matrix modifier and 20 µL of standard or sample. The mean, standard deviation and percent relative standard deviation of the concentration based on the triplicate injections was provided by the Syngistix software.

2.3.4 Quality Control

Quality control samples were employed during the analysis of both fluoride and metals to ensure that the data generated was of good quality. After the calibration standards were analyzed and the calibration curve was established, a metals reference standard from a second source (ERA, Golden, CO) or a fluoride reference standard from a second source (Ricca Chemical Company, Arlington, TX) was analyzed during respective analyses. For the calibration curve to be acceptable for use, the correlation coefficient had to be ≥0.995 and the obtained value for the reference standard had to be within ±10% of the certified value. Additionally, a calibration verification standard and a calibration (reagent) blank were analyzed after every ten samples and at the end of the analysis. The obtained value for the calibration verification standard had to be within ±10% of the known value for the standard and the value for the calibration blank had to be less than the limit of detection for fluoride and metals.

Additionally, at least 10% of the samples were spiked in duplicate to determine both duplicate agreement and spike recoveries. The relative percent difference of the duplicate spikes had to be ≤20%. The spike recoveries for metals analysis had to be 70-130%, and the spike recoveries for fluoride analysis had to be 80-120% to be acceptable.

2.4 DATA ANALYSIS

Microsoft Excel was used to enter and track all data associated with each of the 704 sample kits that were delivered to the distribution sites. The date of kit delivery, receipt at LSRI, date of analysis, concentrations of fluoride, aluminum, arsenic, iron, lead, and manganese were entered by hand from the raw data and checked for errors by a separate member of the project team. In addition, well information, such as water treatment system, sample collection location, collection before/after treatment, geospatial data, Wisconsin Unique Well Number (WUWN), well completion date, well construction type, and well depth were entered into MS Excel by hand and then checked for errors by a separate member of the project team.

MS Excel was used to summarize the well information data. The sample analysis data were summarized using box-and-whisker plots, also created using MS Excel, to show the distribution of fluoride and metals concentrations by county. For those samples having a result of less than the limit of detection, one-half the limit of detection for each parameter analyzed was used for statistical analysis of the data. The Enforcement Standard and Preventative Action Limit for each parameter analyzed in this study was referenced from Wisconsin Administrative Code Chapter NR 140 (Groundwater Quality). One of the stated purposes of this chapter is to evaluate groundwater monitoring data, and stated limits were used to put the data into context and evaluate the potential for human health impacts with this baseline set of data.

Maps of the sample collection locations and the sample analysis results were created using ArcGIS Online (Esri; Redlands, CA). The well address provided on each completed sample collection form was distilled into township, range, and section centroids for the State of Wisconsin and the geospatial data was linked to the sample analysis results. There was a total of 15 samples for which Public Land Survey System references were not available for the well address provided, therefore, these samples are not represented on any of the mapped data. A general bedrock type underlay and county outlines with labels were added to provide context to the mapped data.

2.5 REPORTING TO PROJECT VOLUNTEERS

Following sample analysis, if any of the substances of public health concern (i.e., aluminum, arsenic, fluoride, and lead as defined by Wisconsin Ch. NR 140 – Wisconsin Groundwater Quality Standard) exceeded the enforcement standard the project principal investigator immediately contacted the project volunteer to notify the volunteer of this exceedance. Volunteers were provided contact information for the public health department located in their county of residence for further resources and information.

Once data entry and quality control checks were completed, a report was written by a member of the project team to be received by each volunteer that participated in the project. The fluoride concentration, and if applicable, concentrations of arsenic, aluminum, iron, lead, and manganese were reported along with the Public Health Enforcement Standard listed in Wisconsin Ch. NR 140. The report also contained human health information on each of the analytes measured in the study, and resources for interpreting the results, as well as a copy of the sample collection form, sample receipt form, and the well record (if one was located).

Results from this study were also presented publicly at locations throughout the 11-county study area. The public presentations were an opportunity not only to convey the results from this monitoring study to residents of northwest Wisconsin, but to provide residents with information on the hydrologic cycle, groundwater storage, well construction, water supply systems, groundwater contaminants, and testing frequency recommendations. Each presentation also provided the contact information for the public health department and UW-Extension office for the county in which the presentation took place. Presentation dates and locations are as follows:

- 23 October 2019: Spooner Agricultural Research Station (Spooner, Washburn County)
- 30 October 2019: Mercer Community Center (Mercer, Iron County)
- 18 November 2019: Vaughan Public Library (Ashland, Ashland County)

3 Results and Discussion

3.1.1 Sample Kit Return

In total, 704 sample kits (115 kits containing a metals sample bottle) were delivered to distribution sites within the 11-county study area beginning 15 July 2018 and ending 30 April 2019. The objective of having at least one distribution site in each of the 11 counties was met, which greatly increased the probability that samples would be collected from every county. All 704 sample kits had been picked up by project volunteers as of 08 May 2019. Samples were received at UWS-LSRI beginning 23 July 2018, with the last sample received on 08 August 2019. Given that samples were collected over the timespan of a little more than one year, this monitoring dataset is reflective of natural, seasonal variation in groundwater quality.

Of the 704 sample kits that were picked up by project volunteers, 461 kits (65.5%) were returned to UWS-LSRI (Figure 4). In nearly all cases, an attempt was made to contact each project volunteer who did not return their sample kit. This resulted in 42 sample kits that were confirmed to have been lost or discarded, meaning 503 out of 704 kits (71.5%) were accounted for at the end of the sample collection period (i.e., either returned or confirmed lost/discarded) and 201 out of 704 kits (28.5%) were not returned and could not be accounted for (Figure 4). In total, the data from 450 samples returned to LSRI-UWS were utilized for project data analysis. Four samples were collected from outside of the study area (i.e., one each from Lincoln, Oneida, St. Croix, and Vilas counties; Figure 5), one sample was municipal water, and the collection date for six returned samples could not be confirmed.

Return rate for kits containing a second sample bottle for metals analysis was slightly better. Of the 115 sample kits that contained a metals sample bottle, 81 (70.4%) were returned to UWS-LSRI (Figure 4). There were 11 kits that were confirmed by volunteers to be either lost or discarded, resulting in 92 kits accounted for (80%) and 23 that were not returned and were not unaccounted for in this study (Figure 4). In total, the data from 80 metals samples returned to LSRI-UWS were utilized for project data analysis; the data from one metals sample was not reported because the collection date could not be confirmed and the sample may have exceeded the maximum hold time (Figure 4).

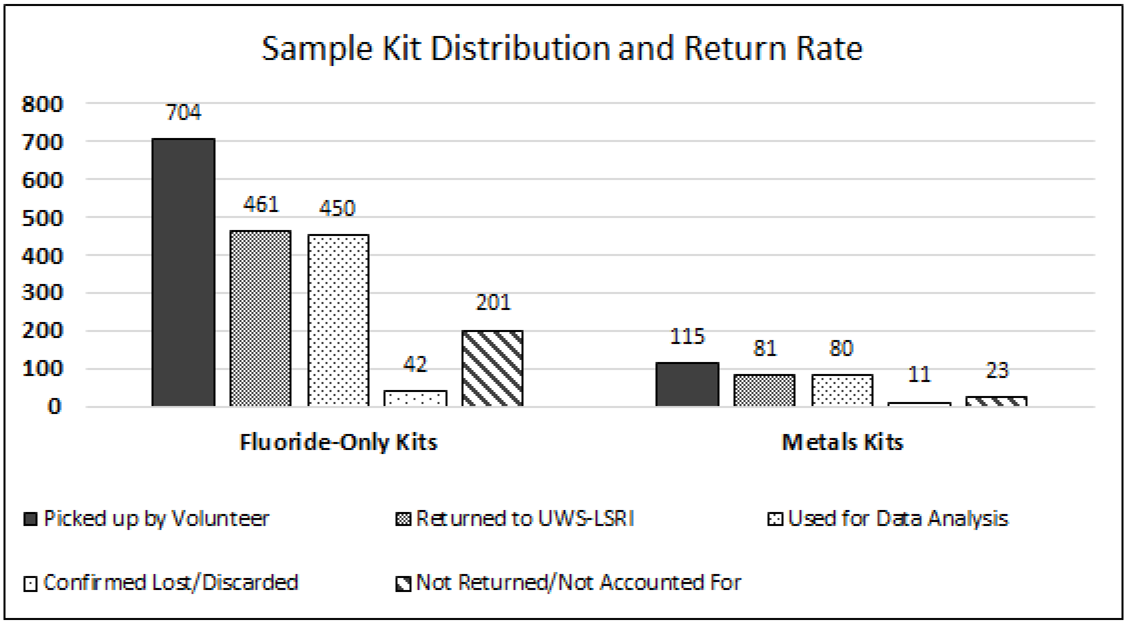

Figure 4. Breakdown of Number of Sample Kits Returned, Confirmed Lost/Discarded, and Unaccounted for out of 704 Total Sample Kits (115 Containing Metals Sample Bottle) Picked up by Project Volunteers.

Groundwater samples were collected from all 11 counties in the study area (Figure 5). The county with the most returned samples was Bayfield, with a total of 88 samples representing 20% of the 450 samples that were used for data analysis (Figure 5; Table 6). Nearly 50% of samples in the study originated from three counties: Bayfield, Ashland, and Douglas (Figure 5; Table 6). Burnett and Price were the counties with the lowest representation, with 13 and 11 samples collected, respectively (Table 6). This is likely due to each county having only one distribution site, which was an outreach event held at each county fair.

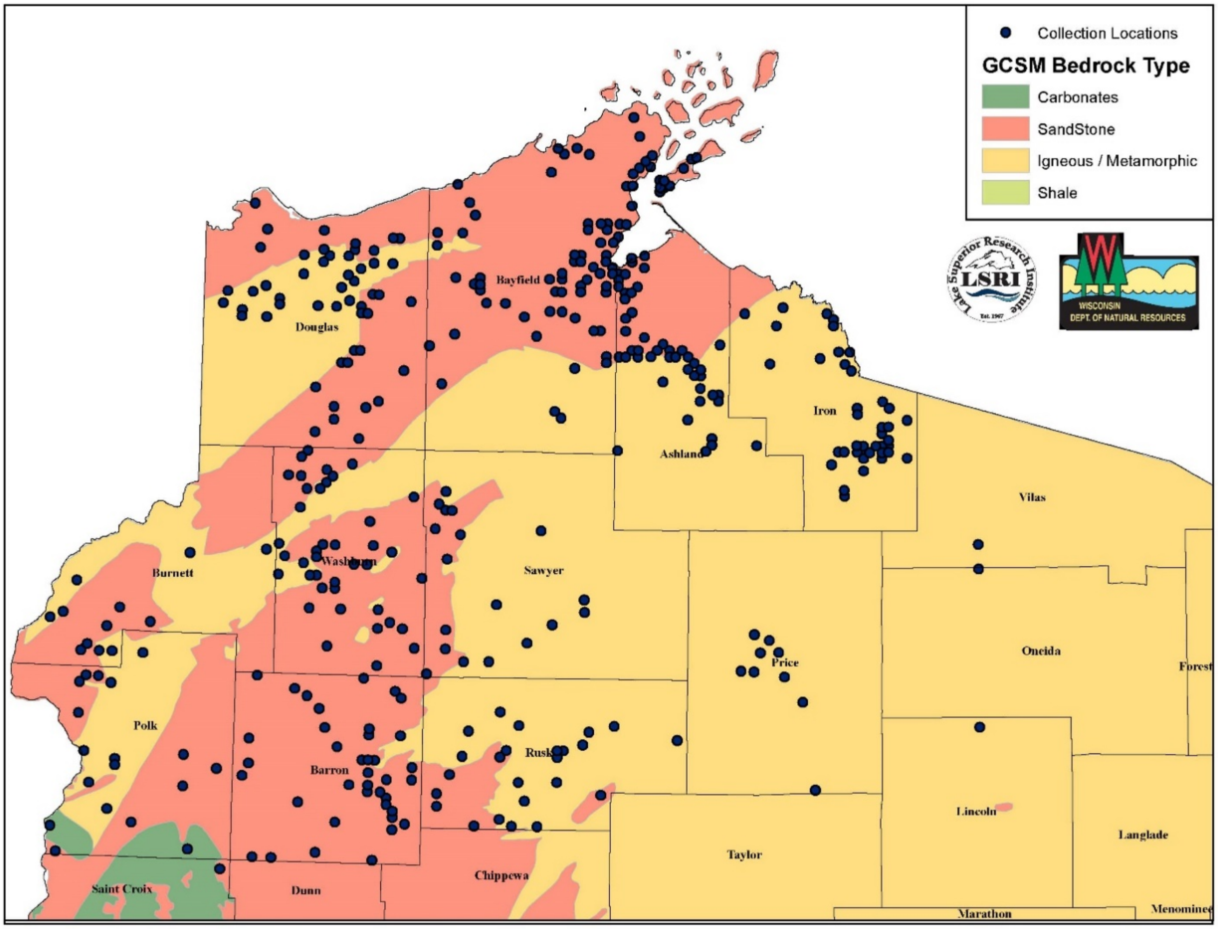

Figure 5. Map Indicating the Location of each Sample Collected by Volunteers Participating in the Northwest Wisconsin Groundwater Monitoring Project.

Table 6. Number of Sample Kits Returned by County.

County	Number of Sample Kits Returned	Return Rate (% of Total Returned Kits used for Data Analysis)
Ashland	74	16
Barron	43	10
Bayfield	88	20
Burnett	13	3
Douglas	59	13
Iron	53	12
Polk	20	4
Price	11	2
Rusk	26	6
Sawyer	19	4
Washburn	44	10

3.1.2 Private Well Characteristics

The samples collected by volunteers participating in this study represent a variety of well construction types, with the vast majority (75%) of volunteers having drilled wells (Figure 6). Of the 450 volunteers whose data were included in this study, 73 (16%) did not know their well's construction type (Figure 6). Driven point/sand point wells represented 7% of the wells from which samples were collected (Figure 6). Less common well construction, each representing less than 1% of the wells sampled, were dug, artesian, sand point, fracked, and jetted wells (Figure 6).

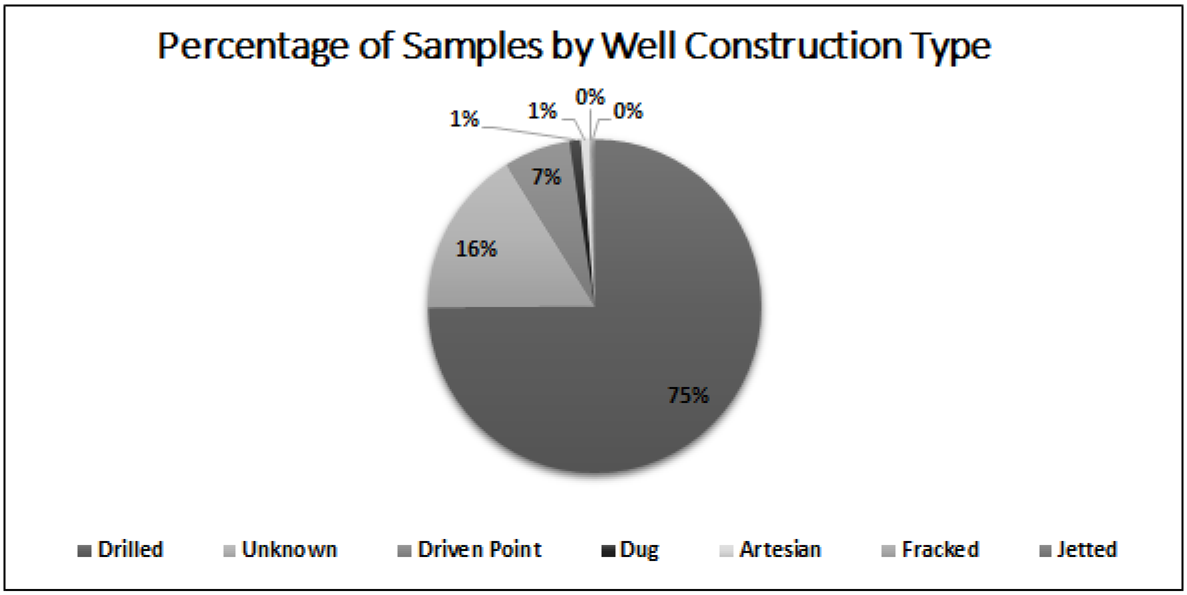

Figure 6. Breakdown of Well Construction Types from which Samples were Collected within the Northwest Wisconsin Study Area.

Well records were located for only a portion of the samples collected in this study, therefore, well age and depth for the private wells from which these samples were collected are largely unknown (Figures 7 and 8). The age could not be determined for over 180 wells in this study. Of those wells for which age was determined, the majority of samples were collected from wells that were constructed between 26 and 50 years ago (Figure 7).

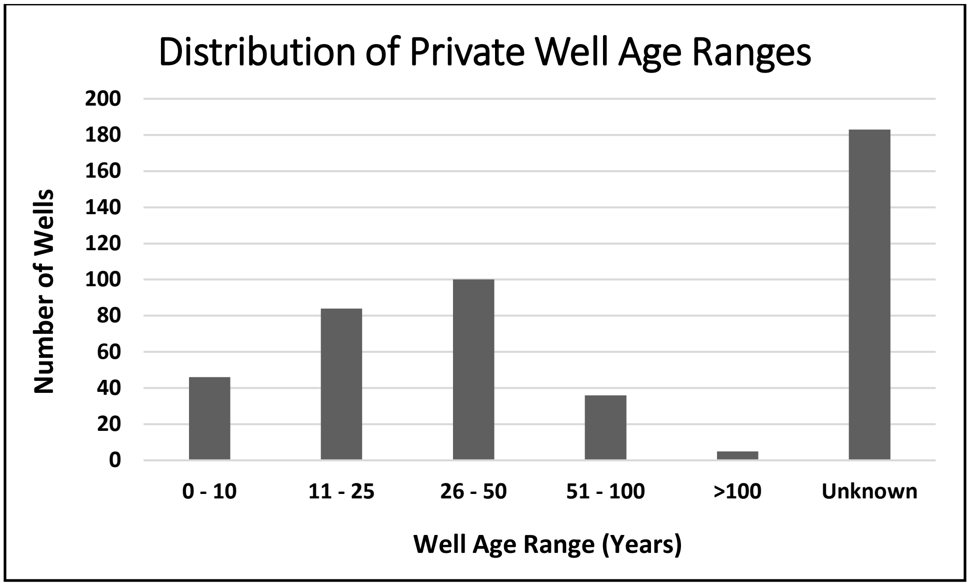

Figure 7. Distribution of Well Age Ranges from which Samples were Collected within the Northwest Wisconsin Study Area.

Well depth could not be determined for over 250 of the private wells sampled in this study (Figure 8). For those wells for which depth could be determined, 68 of the samples were collected from wells ranging in depth from 51 to 100 feet (Figure 8). The shallowest well sampled in this study was 28 feet, while the deepest well was 576 feet. No correlation could be made between well age and/or well depth and the parameters measured in this study due to the lack of available well records.

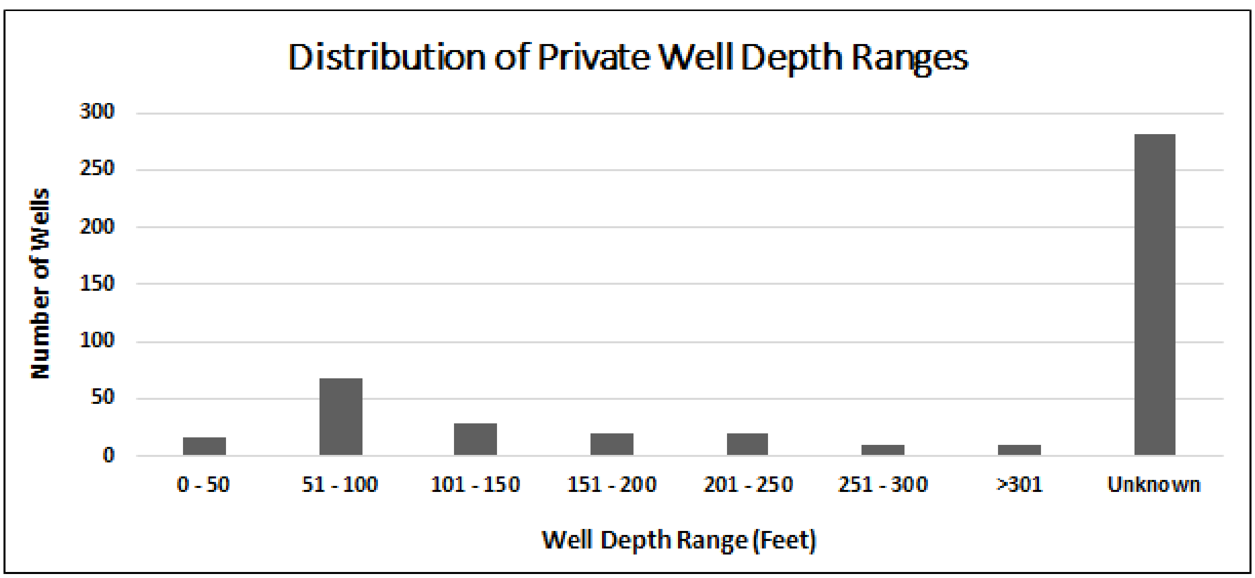

Figure 8. Distribution of Well Depth Ranges from which Samples were Collected within the Northwest Wisconsin Study Area.

The vast majority of wells sampled in this study (64%) had no water treatment system in place (Figure 9). Of the 36% that did have a water treatment system, a variety of methods were employed (Figure 9): water softener (14%), carbon filter (6%), multiple treatment methods (5%), sediment filter (5%), and iron filter (2%). Those wells having multiple treatment methods (Figure 9) generally employed a combination of carbon filtration and water softener, in a small number of wells, carbon filtration, iron filtration, and a water softener were employed simultaneously. The impact of water treatment on parameters measured in samples collected after a water treatment system (*n*=69 sample kits) was taken into consideration during data analysis. None of the water treatments employed would have impacted the concentrations of fluoride, aluminum, arsenic, or lead concentrations. However, samples collected after an iron filter would have an underestimated iron concentration. None of the samples collected after an iron filter were metals samples. It is also possible that samples collected after a water softener would have resulted in a slight underestimate of both iron and manganese concentrations, although the impact is likely very minimal. There were only four metals samples that were collected after a water softener.

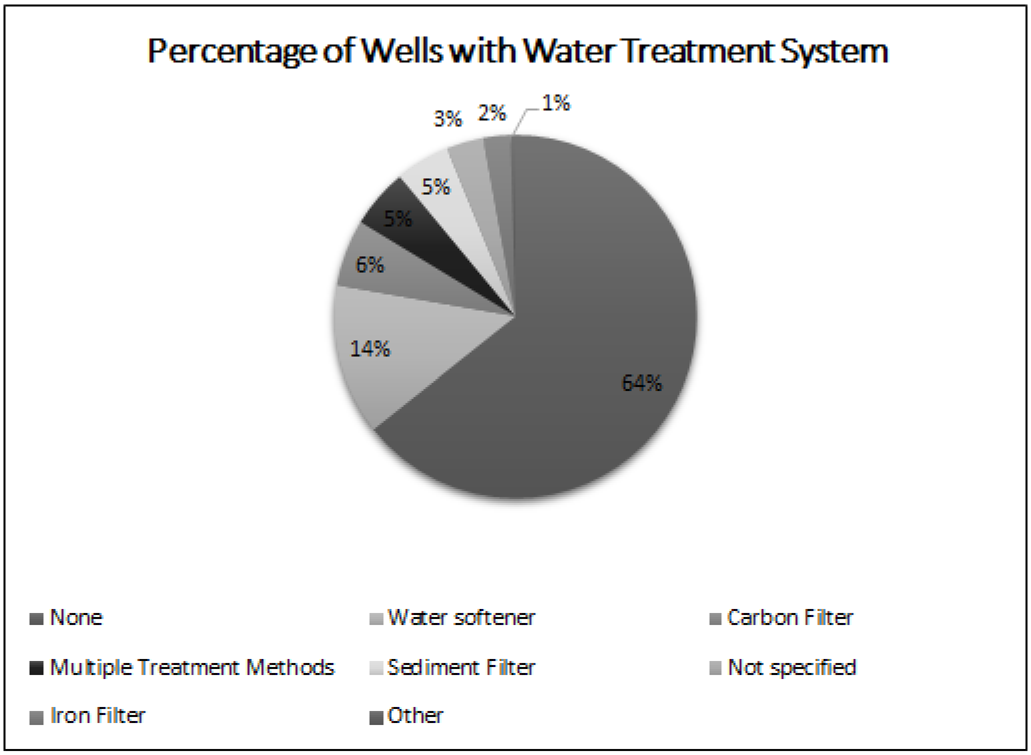

Figure 9. Percentage of Samples Collected from Wells with and without Water Treatment Systems.

3.1.3 Fluoride

None of the samples collected and analyzed for fluoride in this study exceeded the Wisconsin Public Health Groundwater Quality Enforcement Standard of 4.0 mg/L (Wisconsin Adm. Ch. NR 140 – Groundwater Quality). The Wisconsin Public Health Groundwater Quality Preventative Action Limit of 0.8 mg/L was exceeded in only four of 450 samples analyzed (0.9%); these samples were collected in Ashland (2), Douglas (1), and Iron (1) County.

In terms of the beneficial impact of fluoride ingestion on bone and tooth development in children, only two samples had fluoride concentrations between 0.7 mg/L and 1.5 mg/L (Figure 10), the range of beneficial fluoride concentration that promotes the development of strong bones and teeth in children (Ozsvath, 2006). Three samples, collected in Ashland (2) and Iron (1) counties, had fluoride concentrations greater than 1.5 mg/L (Figure 10). Fluoride concentrations above 1.5 mg/L in a primary drinking water source could promote dental fluorosis in children (Ozsvath, 2006). The vast majority of samples analyzed as part of this study had fluoride concentrations below 0.7 mg/L (Figure 10), indicating that fluoride supplementation is likely needed for children residing within the study area who use well water as their primary drinking water source.

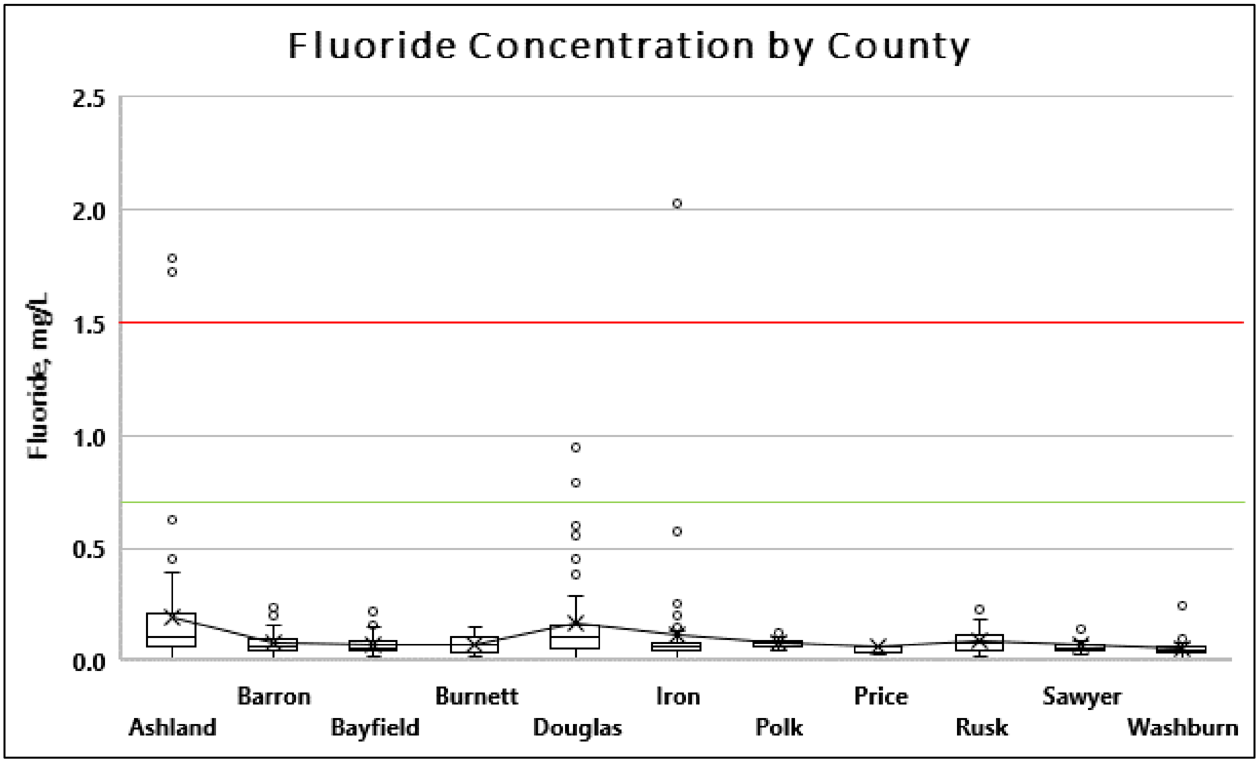

Figure 10. Distribution of Fluoride Concentration in Groundwater Samples Collected from 11 Counties in Northwest Wisconsin. The green line indicates the fluoride concentration of 0.7 mg/L, children whose primary drinking water source contains fluoride concentrations <0.7 mg/L would need fluoride supplementation. The red line indicates the fluoride concentration of 1.5 mg/L, children whose primary drinking water source contains fluoride concentrations >1.5 mg/L may have issues with dental fluorosis due to ingestion of excess fluoride.

A map of the fluoride concentrations in volunteer-collected samples indicates that for nearly all of the counties within the study area, all samples collected had fluoride concentrations <0.3 mg/L (Figure 11), which is well below the beneficial range of 0.7 – 1.5 mg/L. Only three counties, located in the north-northeastern portion of the study area, had samples with fluoride concentrations above 0.7 mg/L: Ashland, Douglas, and Iron (Figure 11). Within each of these counties, the samples having the highest fluoride concentrations were collected from locations near Lake Superior, although there was one sample collected from northern Iron County that had a relatively high fluoride concentration (Figure 11).

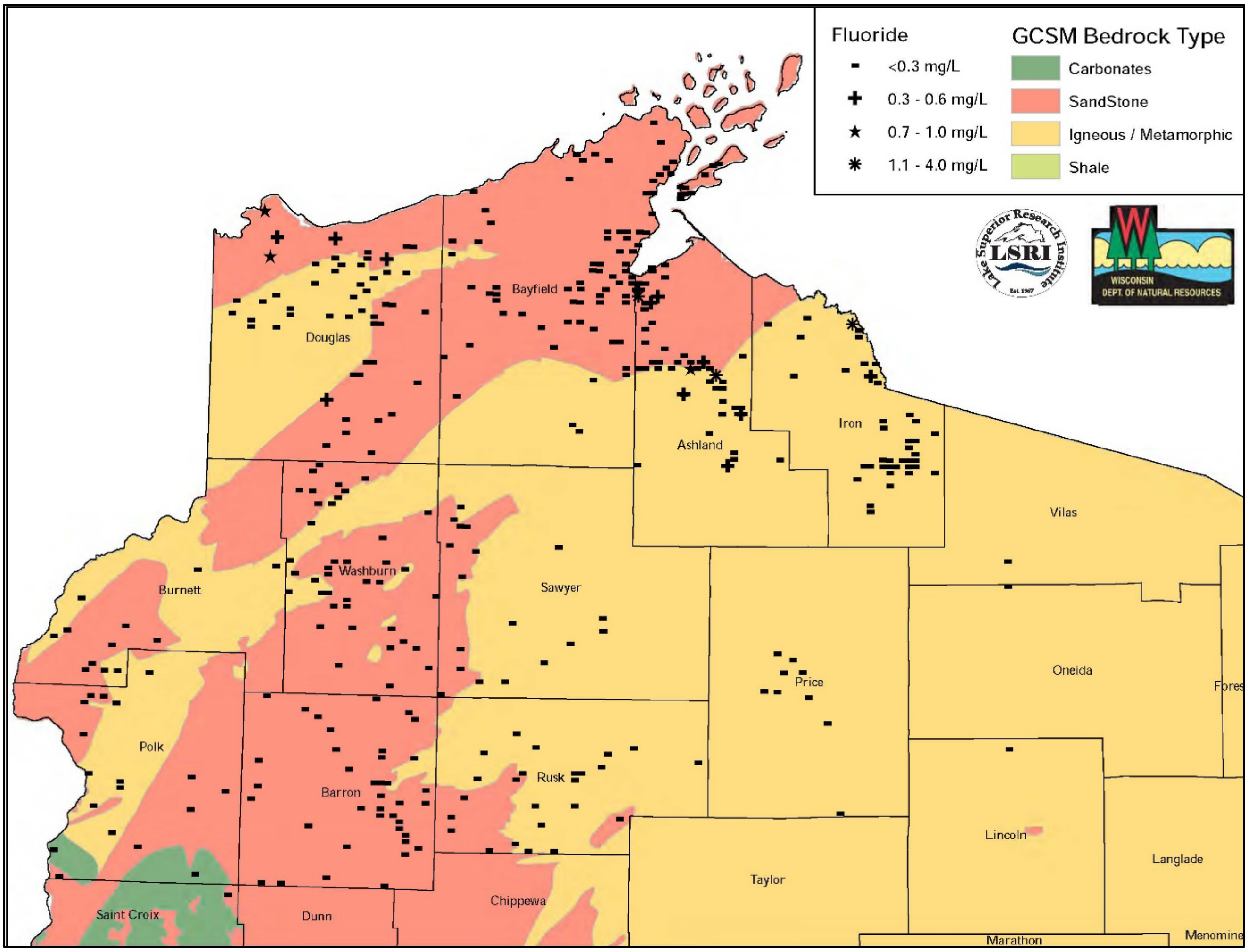

Figure 11. Map of Fluoride Sample Collection Locations and Ranges of Concentrations, Including General Bedrock Types within the Study Area.

3.1.4 Metals by Flame Atomic Absorption Spectrometry

3.1.4.1 Iron

Of the 80 metals samples included in data analysis, 20 (25%) had iron concentrations greater than 0.15 mg/L, the State of Wisconsin Public Welfare Groundwater Quality Standard Preventative Action Limit (Wis. Adm. Ch. NR 140) and 16 (20%) had iron concentrations greater than the 0.3 mg/L Enforcement Standard. One sample, collected in Iron County, had an iron concentration of 24.9 mg/L, far surpassing any other sample collected in this study (Figure 12). That sample, shown in Figure 13, had to be filtered for analysis, which could have resulted in a slight underestimate of the metals concentrations.

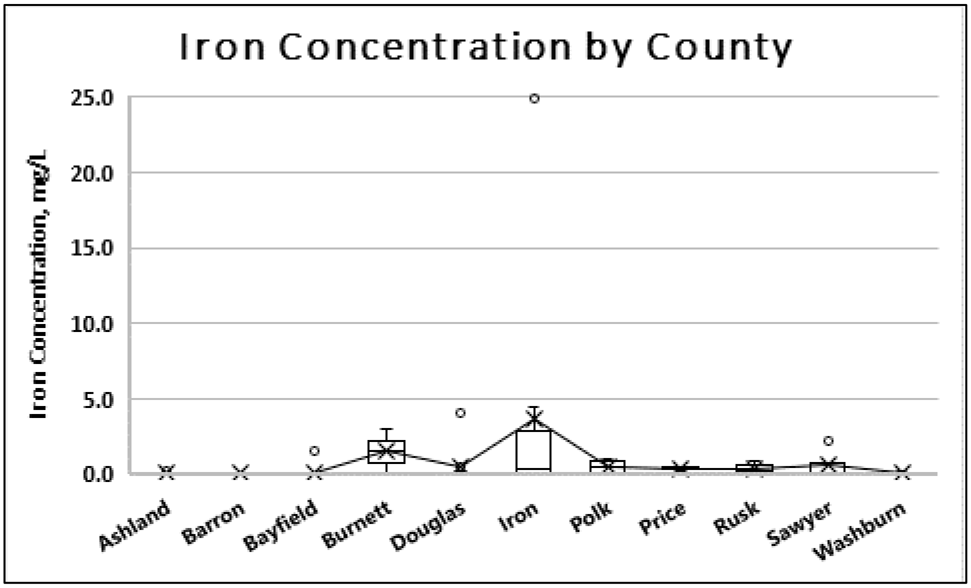

Figure 12. Distribution of Iron Concentration in Groundwater Samples Collected from 11 Counties in Northwest Wisconsin.

Figure 13. Private Well Sample Collected from Iron County with Iron Concentration of 24.9 mg/L.

Figure 14 shows the distribution of the iron data, by county, of those samples with an iron concentration of 5.0 mg/L or less (i.e., 24.9 mg/L sample is not shown). Of the 11 counties in the study area, 7 counties

(Burnett, Douglas, Iron, Polk, Price, Rusk, and Sawyer) had an average iron concentration at or above 0.3 mg/L (Figure 14).

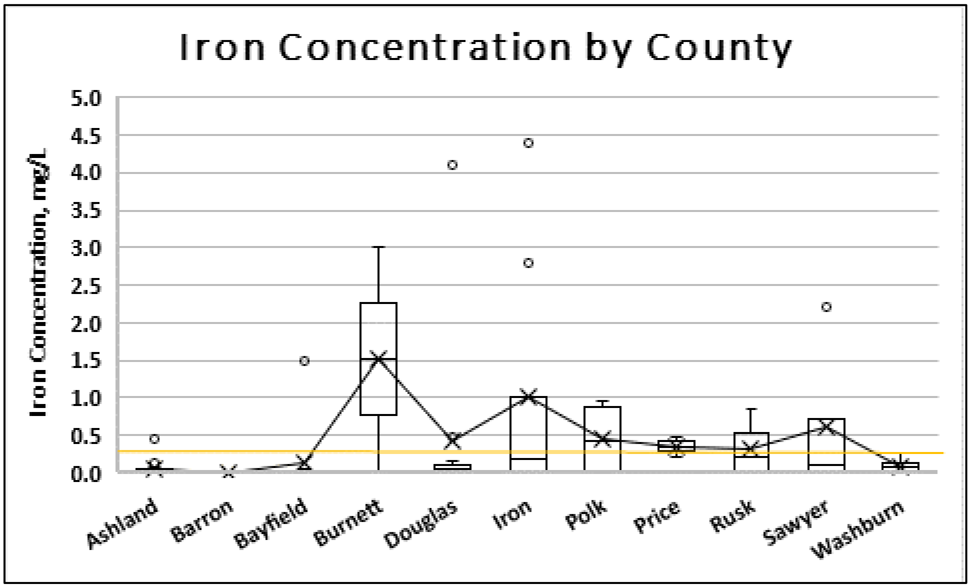

Figure 14. Distribution of Iron Concentration in Groundwater Samples Collected from 11 Counties in Northwest Wisconsin. Not included in this chart is one sample from Iron County with 24.9 mg/L iron. The yellow line indicates the Wisconsin Public Welfare Groundwater Quality Standard Enforcement Standard of 0.3 mg/L.

A map of the iron concentrations in volunteer-collected samples indicates that Ashland, Barron, Bayfield, and Washburn counties had samples that were all below 1.0 mg/L, with all samples in Barron County having <0.15 mg/L iron (Figure 15). All other counties had at least one sample with iron >0.3 mg/L, with Iron County having the highest average iron concentration (3.7 mg/L) in private well samples (Figure 14) followed by Burnett County with an average of 1.5 mg/L iron (Figures 12 and 14).

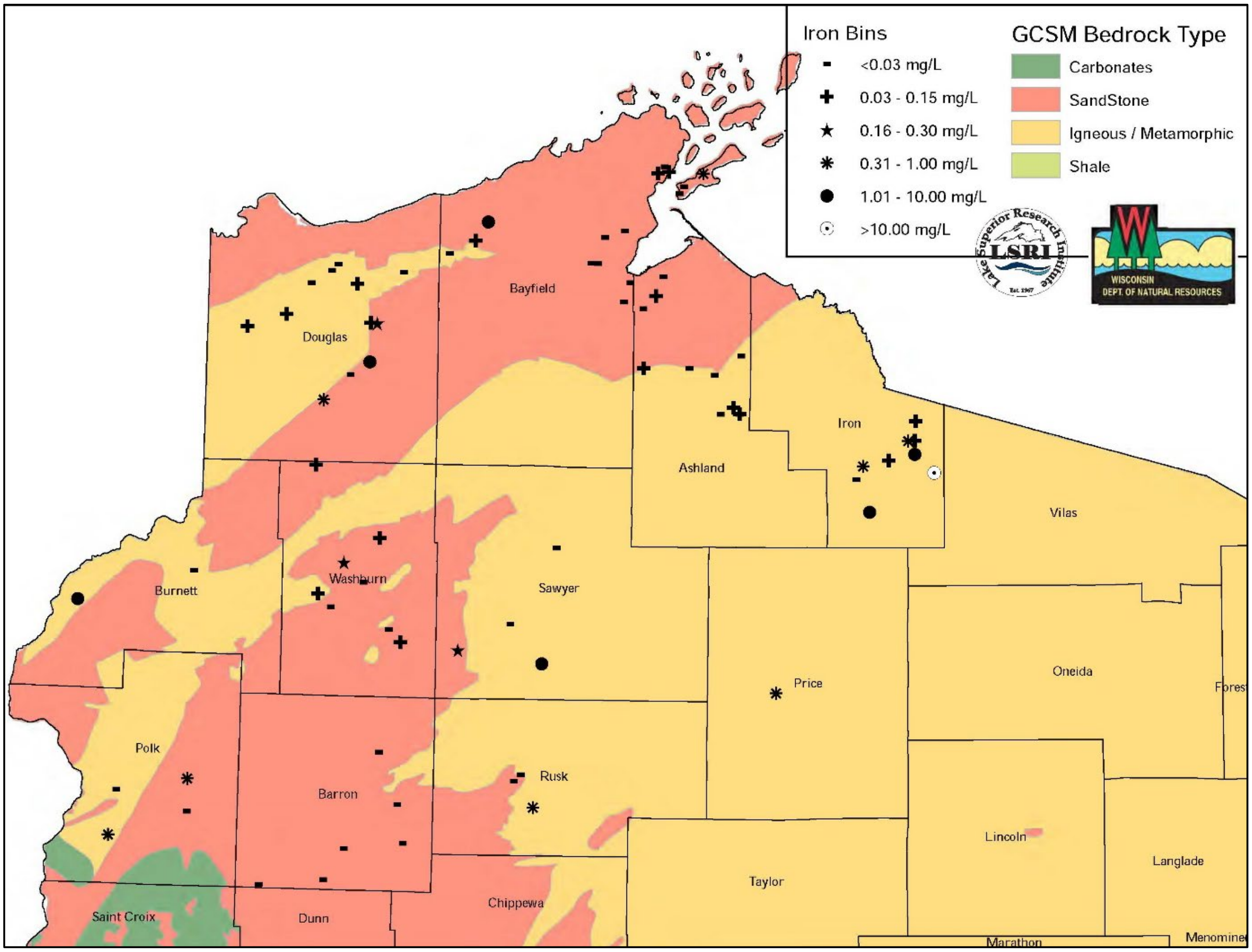

Figure 15. Map of Iron Sample Collection Locations and Ranges of Concentrations, Including General Bedrock Types within the Study Area. Note: Two samples were collected from Price County, one sample (0.210 mg/L iron) is not pictured because it did not have an associated Public Land Survey System reference.

3.1.4.2 Manganese

There were 80 manganese samples analyzed and included in Figures 16 and 17 below, and of these, 14 samples (17.5%) had manganese concentrations greater than the Wisconsin Public Health Groundwater Quality Standard Preventative Action Limit (i.e., >60 µg/L; Wis. Admin. Code Ch. NR 140) and 4 samples (5%) were above the Enforcement Standard of 300 µg/L. There were five counties with manganese concentrations that were on average higher than the Preventative Action Limit: Barron, Burnett, Iron, Polk, and Rusk (Figure 16).

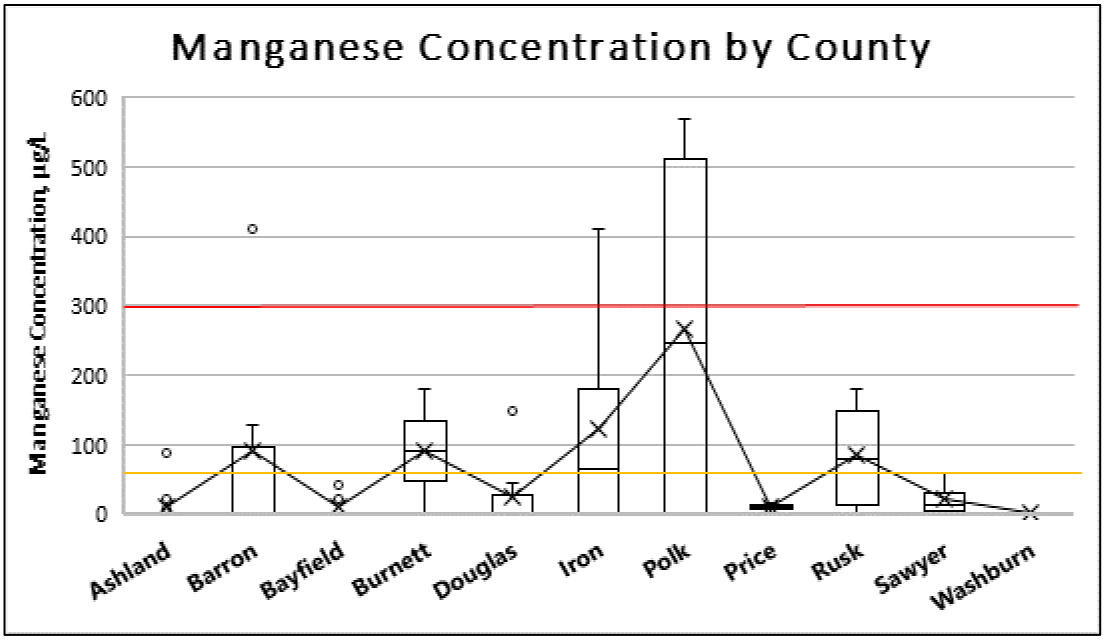

Figure 16. Distribution of Manganese Concentration in Groundwater Samples Collected from 11 Counties in Northwest Wisconsin. The yellow line indicates the Wisconsin Public Health Groundwater Quality Standard Preventative Action Limit of 60 µg/L and the red line indicates the Enforcement Standard of 300 µg/L.

A map of the manganese concentrations measured in volunteer-collected samples indicates that the samples having the highest concentrations were collected from the far southern and eastern portions of the study area, while the north and central portions of the study area have concentrations of <60 µg/L (Figure 17).

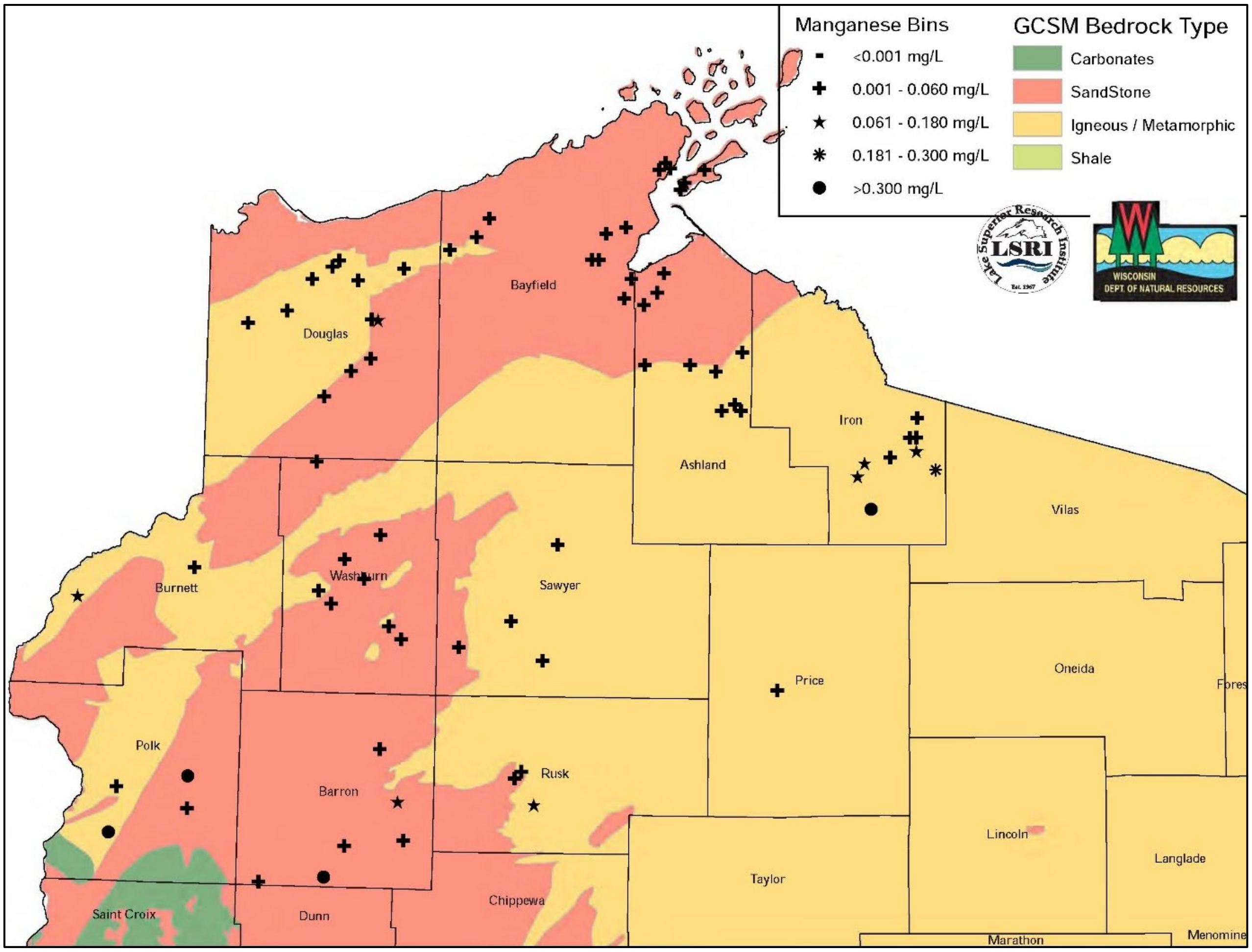

Figure 17. Map of Manganese Sample Collection Locations and Ranges of Concentrations, Including General Bedrock Types within the Study Area. Note: Two samples were collected from Price County, one sample (0.017 mg/L or 17 µg/L manganese) is not pictured because it did not have an associated Public Land Survey System reference.

3.1.5 Metals by Graphite Furnace Atomic Absorption Spectrometry

3.1.5.1 Aluminum

Overall, aluminum concentrations in samples collected as part of this study were quite low (Figure 18). Of the 80 samples included in data analysis, there were two (2.5%) that were >40 µg/L, which is the Wisconsin Public Health Groundwater Quality Standard Preventative Action Limit (Wis. Adm. Code Ch. NR 140; Figure 18). There was only one sample (1.25%) that exceeded the Enforcement Standard of 200 µg/L (Wis. Adm. Code Ch. NR 140; Figure 18). That sample had an aluminum concentration of 307 µg/L, which far exceeded the concentration of any other sample collected in this study (Figure 18).

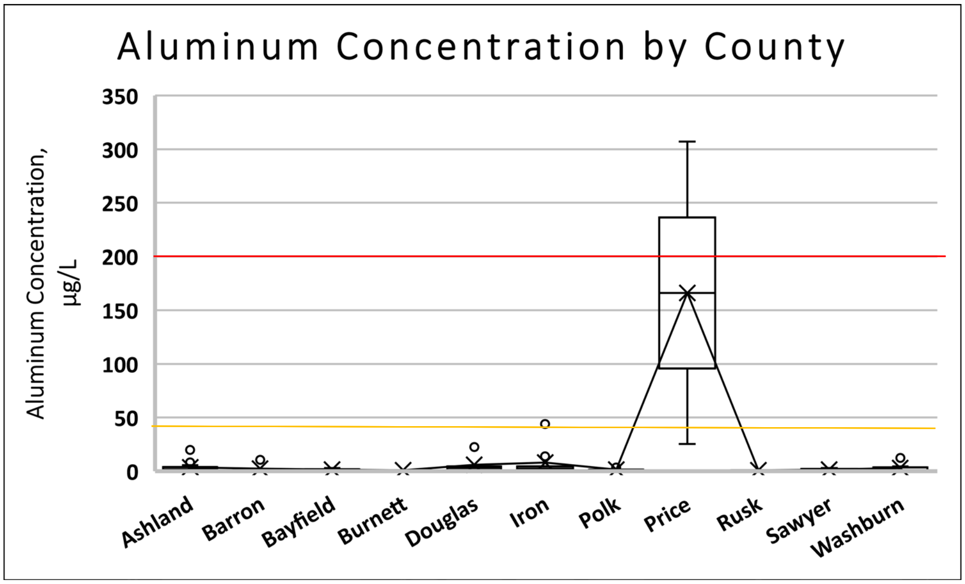

Figure 18. Distribution of Aluminum Concentration in Groundwater Samples Collected from 11 Counties in Northwest Wisconsin. The yellow line indicates the Wisconsin Public Health Groundwater Quality Standard Preventative Action Limit of 40 µg/L and the red line indicates the Enforcement Standard of 200 µg/L.

A map of the volunteer-collected samples in this study shows that for 9 of 11 counties in the study area, aluminum concentrations were <4.0 µg/L for every sample collected (Figure 19). In Iron County, one sample had an aluminum concentration of 43.9 µg/L (Figure 19). The maximum aluminum concentration measured in this study was collected in Price County (not pictured in Figure 19 because the sample did not have a Public Land Survey System reference associated with it).

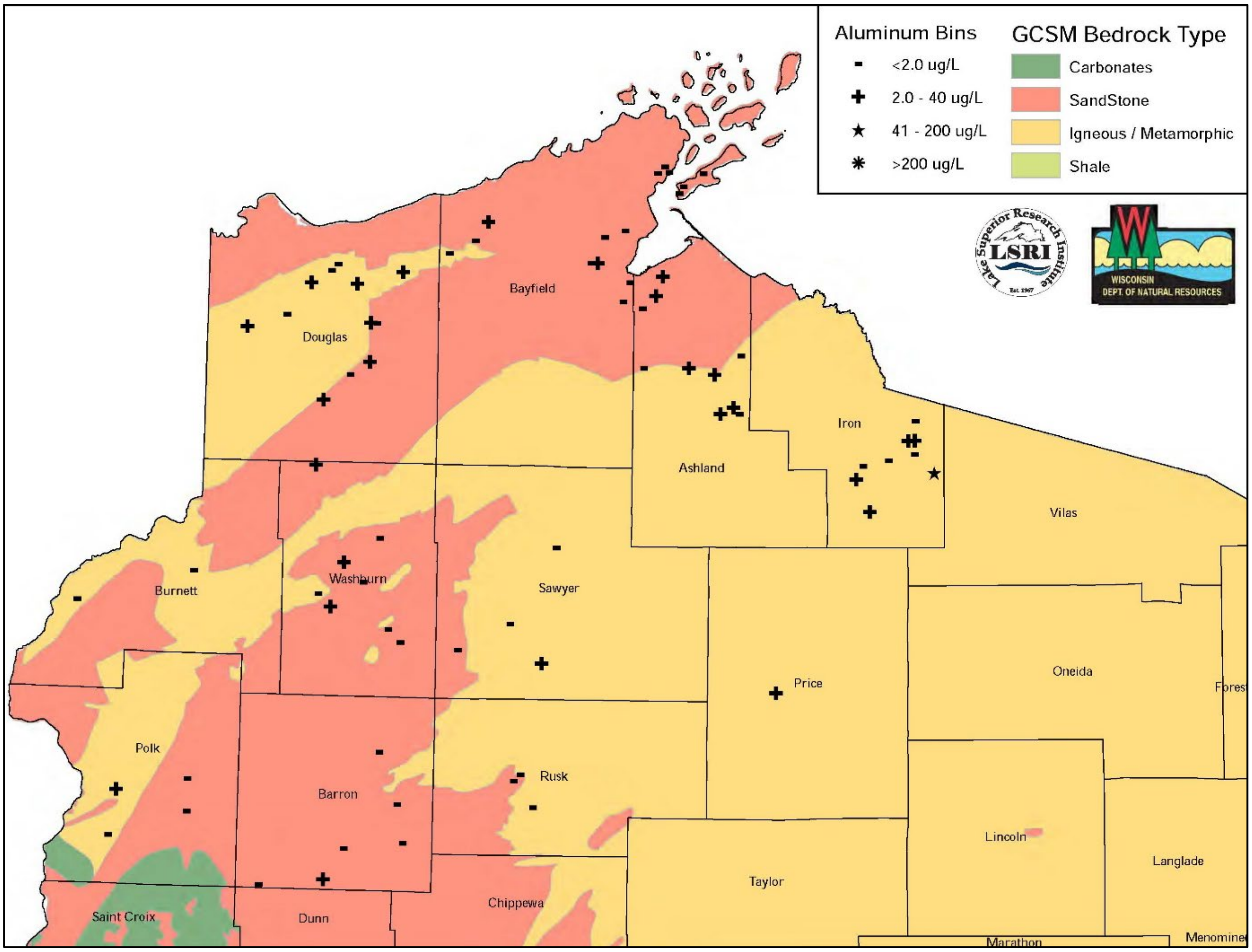

Figure 19. Map of Aluminum Sample Collection Locations and Ranges of Concentrations, Including General Bedrock Types within the Study Area. Note: Two samples were collected from Price County, one sample (307 µg/L aluminum) is not pictured because it did not have an associated Public Land Survey System reference.

3.1.5.2 Arsenic

Out of 80 total samples included in data analysis, 31 (38.8%) had an arsenic concentration at or above the Wisconsin Public Health Groundwater Quality Standard Preventative Action Limit (i.e., >1 µg/L; Wis. Adm. Code Ch. NR 140; Figure 20). Of these, only one sample had an arsenic concentration of 10 µg/L, which is the Enforcement Standard (Wis. Adm. Code Ch. NR 140; Figure 20). On average, arsenic concentrations measured in samples collected from Ashland, Bayfield, Polk, and Rusk were greater than 1 µg/L, with Bayfield County having the highest average of 2.05 µg/L (Figure 20).

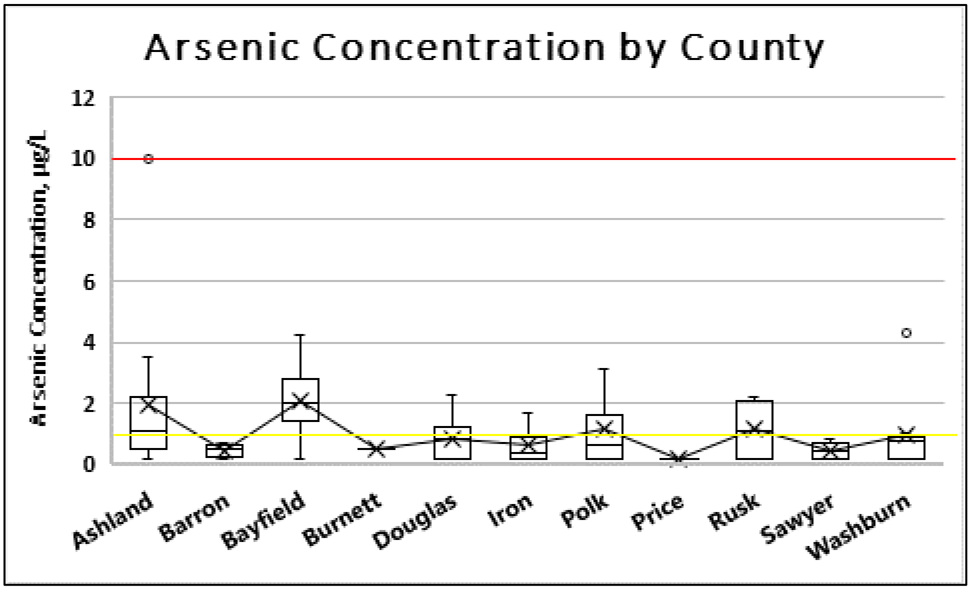

Figure 20. Distribution of Arsenic Concentration in Groundwater Samples Collected from 11 Counties in Northwest Wisconsin. The yellow line indicates the Wisconsin Public Health Groundwater Quality Standard Preventative Action Limit of 1 µg/L and the red line indicates the Enforcement Standard of 10 µg/L.

A map of the arsenic samples collected as part of this study shows relatively low arsenic concentrations in the central and south-central portions of the study area (Barron, Burnett, Price, Sawyer, and Washburn; Figure 21). The highest arsenic values were measured in the northern portion of the study area, particularly around the Chequamegon Bay of Lake Superior (Ashland and Bayfield counties; Figure 21) and the south-east and south-west portions of the study area (Polk and Rusk counties; Figure 21).

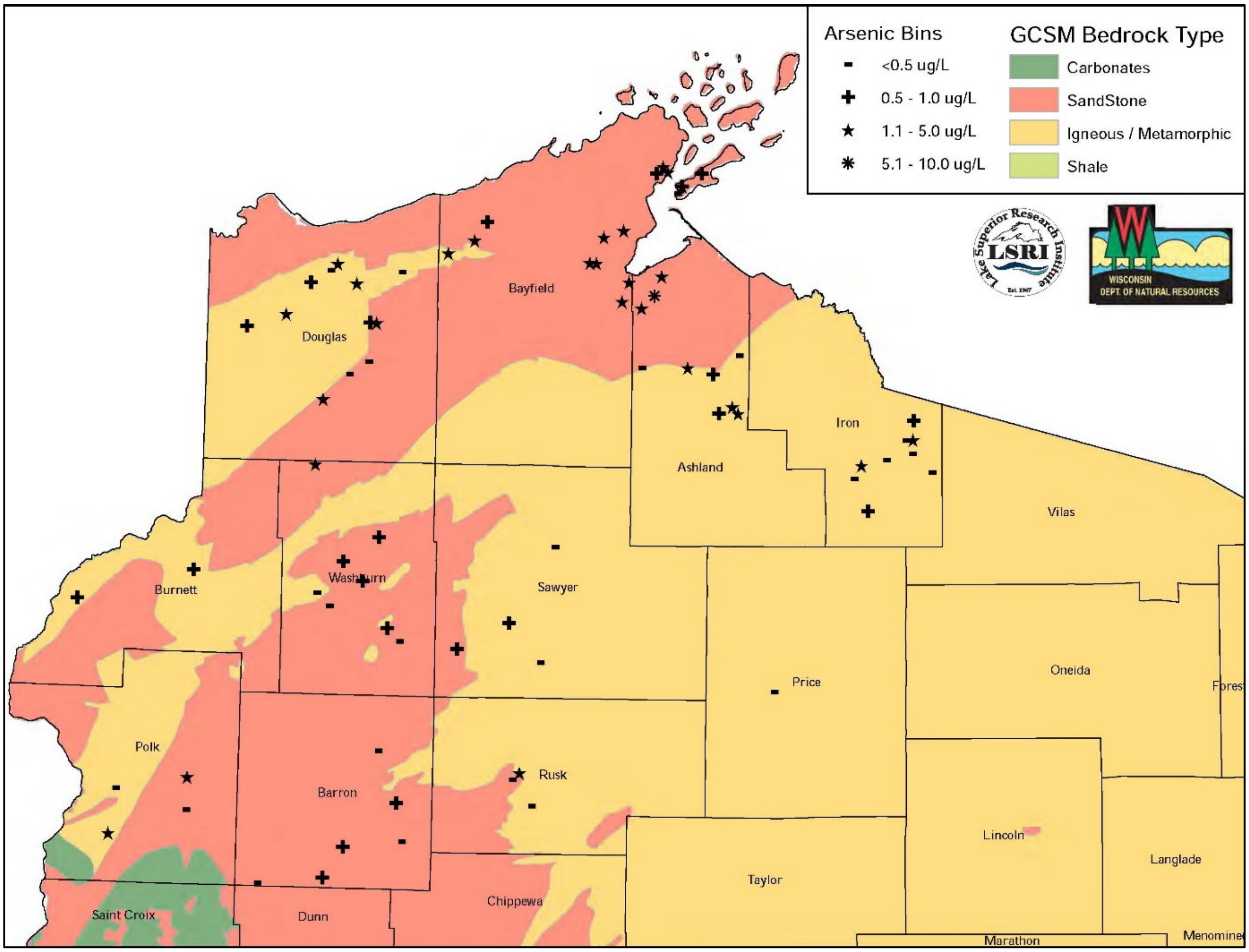

Figure 21. Map of Arsenic Sample Collection Locations and Ranges of Concentrations, Including General Bedrock Types within the Study Area. Note: Two samples were collected from Price County, one sample (<0.35 µg/L arsenic) is not pictured because it did not have an associated Public Land Survey System reference.

3.1.5.3 Lead

Lead was the only parameter included in this monitoring study that generally does not have a natural origin, with the exception of groundwater that has pH <6 or pH>11 with little to no carbonate present. It is important to note that all sample collection volunteers were instructed to run the cold water at the sampling location at a high rate of flow for at least five minutes to ensure that the plumbing had been cleared and the samples contained freshly-drawn groundwater. Since volunteers were not asked to collect a first-draw sample for analysis of lead, the results are presumed to be unconfounded by leaching of lead from indoor plumbing and represent the lead concentrations that would be ingested directly from groundwater. The results show that the majority of samples collected had low lead concentrations, <0.54 µg/L (limit of detection) in many cases. Of the 80 metals samples included in data analysis, there were nine samples (11.3%) with lead concentration at or above 1.5 µg/L (i.e., Wis. Adm. Code Ch. NR 140 Preventative Action Limit; Figure 22). Only one sample, collected from Douglas County, had a lead concentration greater than the Enforcement Standard of 15 µg/L (Wis. Adm. Code Ch. NR 140; Figure 22). The volunteer was contacted to notify them of this result, and it was determined that the sample was collected according to the instructions provided in the kit (i.e., sample collected after five minutes of running cold water). The volunteer was encouraged to contact the Douglas County Department of Health and Human Services, and collect a follow-up sample to confirm this result.

Three counties had average lead concentrations >1.5 µg/L, Douglas, Iron, and Price (Figure 22). Polk County had an average lead concentration of 1.4 µg/L (Figure 22). All other counties in the study area had average lead concentrations below or near the method's limit of detection (0.54 µg/L lead; Figure 22).

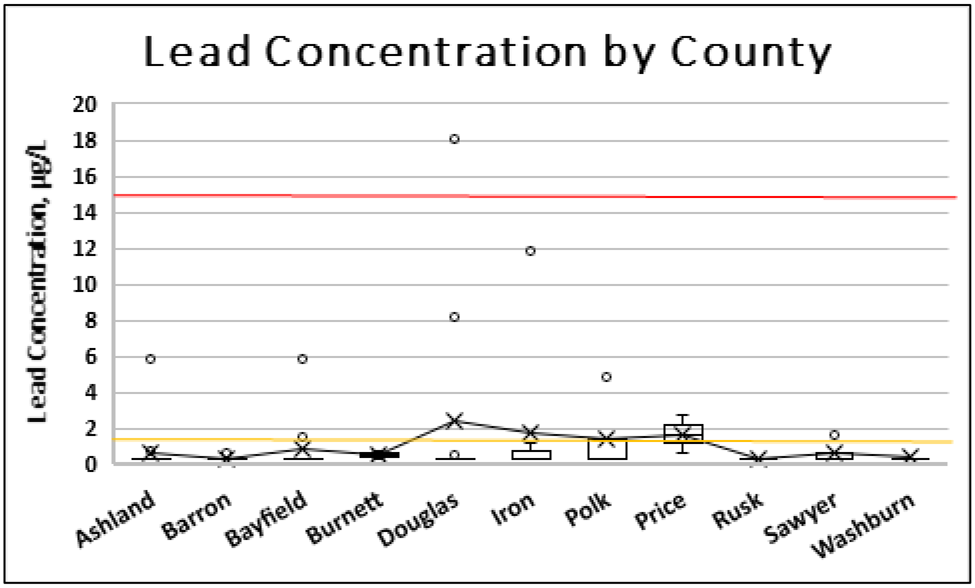

Figure 22. Distribution of Lead Concentration in Groundwater Samples Collected from 11 Counties in Northwest Wisconsin. The yellow line indicates the Wisconsin Public Health Groundwater Quality Standard Preventative Action Limit of 1.5 µg/L and the red line indicates the Enforcement Standard of 15 µg/L.

The mapped data do not show any discernable trends (Figure 23). Five counties had statistical outlier samples with relatively high lead concentrations when compared to the data as a whole, Ashland, Bayfield, Douglas, Iron, and Polk (Figure 23). The pH and alkalinity of the samples was not measured upon receipt, as the holding time for these parameters would have been exceeded, but it is possible that the samples containing relatively high lead concentrations could have been the result of a combination of low/high pH groundwater with very low alkalinity causing leaching of lead from lead-containing minerals present in the aquifer.

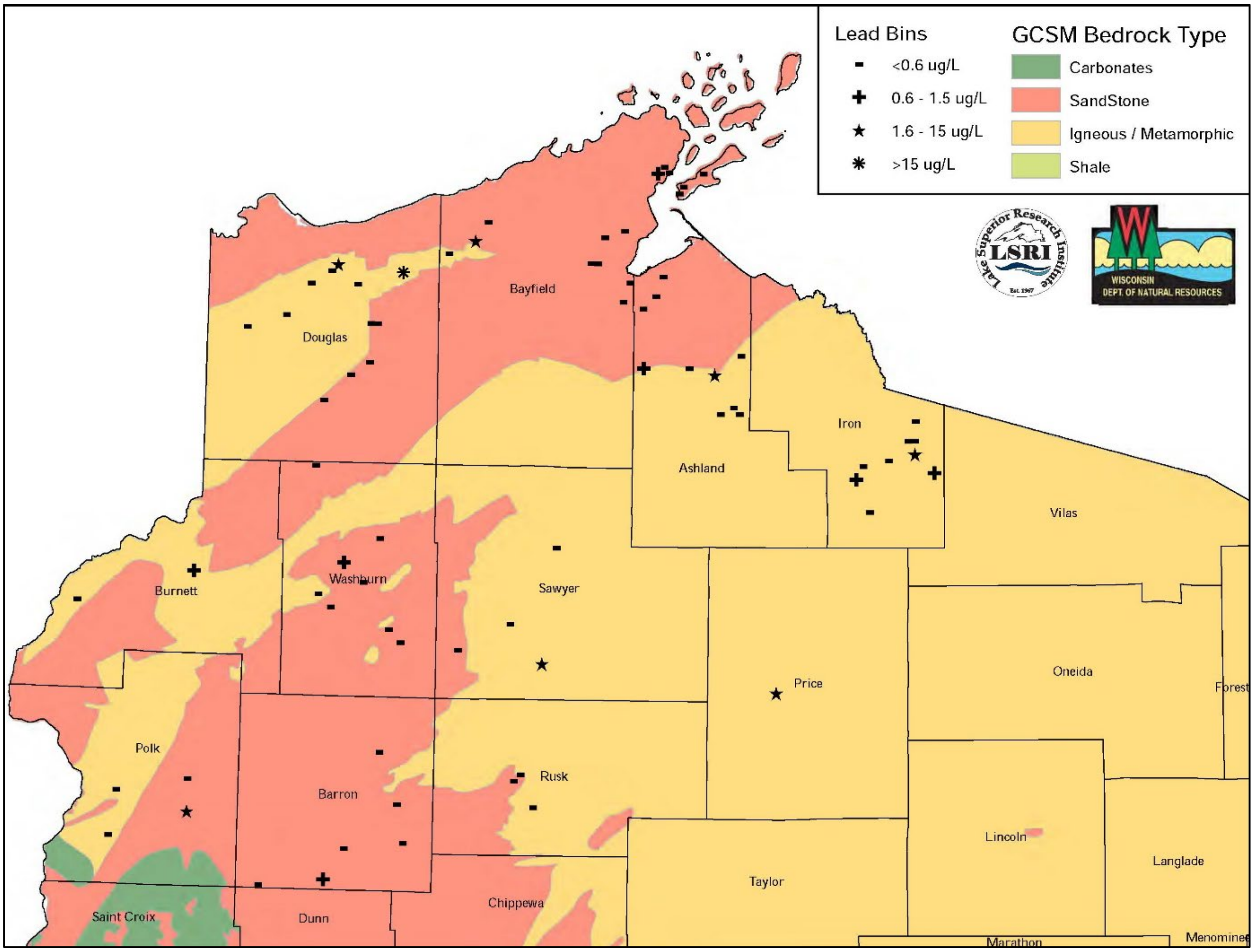

Figure 23. Map of Lead Sample Collection Locations and Ranges of Concentrations, Including General Bedrock Types within the Study Area. Note: Two samples were collected from Price County, one sample (0.63 µg/L lead) is not pictured because it did not have an associated Public Land Survey System reference.

4 CONCLUSIONS AND RECOMMENDATIONS

To the authors' knowledge, this study represents the first baseline groundwater monitoring effort within the northwest Wisconsin region. Volunteer-collected samples allowed for a large number of samples to be targeted over a large region of the state. Although 65% of the sample kits were returned to UWS-LSRI for analysis, this method of sample collection did present a challenge in terms of the time required to follow-up with volunteers who had not returned a kit they had picked up, had not included a sample collection form with their kit, or had not completely filled out the provided sample collection form. The sample kits that contained a metals sample bottle had a higher rate of return than the fluoride-only kits (65% vs. 70%), which could be due to volunteers not realizing that fluoride is naturally-occurring in groundwater and/or an increased interest among residents in the region in metals concentrations in groundwater. For this reason, future studies utilizing volunteers may have greater success if targeted parameters include metals.

With the exception of fluoride and arsenic, the Enforcement Standard (Wis. Adm. Code Ch. NR 140) was exceeded for all parameters measured in this study in at least one sample collected within the northwest Wisconsin study area. The average iron concentration for all 80 samples reported was 0.64 mg/L, which is over twice the Enforcement Standard for this “substance of public welfare concern” (Wis. Adm. Code Ch. NR 140). Despite 20% of samples having an iron concentration greater than 0.3 mg/L, water treatment was not utilized by the vast majority of volunteers in this study. Only 36% of wells sampled utilized a drinking water treatment system with just over 2% of volunteers employing an iron filter for treatment of their drinking water.

Based on the results from this study, fluoride supplementation would be needed for most children in northwest Wisconsin whose primary drinking water is sourced from groundwater. However, higher levels of fluoride were measured in Ashland, Douglas, and Iron counties, and it is recommended that families residing in those counties have the fluoride concentration in their private wells tested to determine whether supplementation is necessary.

Five of 11 counties in the study area had manganese concentrations that were on average at or above the Preventative Action Limit of 60 µg/L. Iron and Polk counties had the highest manganese concentrations on average, with one out of eight samples in Iron County and two out of four samples in Polk County measuring above the Enforcement Standard of 300 µg/L. High manganese concentrations in groundwater, particularly public well water, has also been found to be an issue in Ironwood, MI, which is directly adjacent to Iron County, WI (Meyer, 2019).

Aluminum concentrations were relatively low throughout northwest Wisconsin, with the exception of two samples all were below the Preventative Action Limit of 40 µg/L. One sample collected from Iron County had an aluminum concentration of 43.9 µg/L. The maximum aluminum concentration measured in this study was substantially higher than all other samples collected at 307 µg/L, and was collected from Price County. It is highly recommended that future studies in Price County include additional aluminum samples, as this county’s history includes a large tannery (U.S. Hide and Leather Company; Prentice, WI).

All of the samples collected and analyzed for arsenic were at or below the Enforcement Standard of 10 µg/L; one sample collected in Ashland County had 10.0 µg/L arsenic. Ashland, Bayfield, Douglas, Polk, Rusk, and Washburn all had average arsenic concentrations at or above the Preventative Action Limit of 1 µg/L.

Lead was the only parameter measured in this study with no natural origin under groundwater conditions having pH between 6 and 11. Samples collected during this study were collected after running cold water for at least five minutes to reduce the influence of lead leachate from plumbing. Surprisingly, one sample collected from Douglas County had a lead concentration greater than the Enforcement Standard of 15 µg/L. Douglas, Iron, and Price counties had average lead concentrations that were at or above the Preventative Action Limit of 1.5 µg/L lead. Although pH and alkalinity were not measured at the time of sample receipt due to sample holding time exceedance, some information on these parameters is available from the Wisconsin Well Water Quality Viewer (https://gissrv3.uwsp.edu/webapps/gwc/pri_wells/, accessed July 2020). The pH range in Douglas County for a total of 219 samples is 6.55 – 9.95, and alkalinity ranges from no detection to 788 mg/L $CaCO_3$ (*n*=216). Given that 15% of samples collected in Douglas County had an alkalinity <50 mg/L $CaCO_3$, it is possible that groundwater quality conditions in some areas of Douglas County may be conducive to leaching lead from minerals present in the aquifer, although the pH range of measured samples suggests that the pH condition is not optimal for this to occur. Alkalinity ranges are even lower in Iron County, ranging from no detection to 288 mg/L $CaCO_3$ (*n*=102), and pH ranges from 5.75 – 9.91 (*n*=102), which confirms that conditions exist that could lead to naturally-occurring lead in groundwater. Similarly, in Price County, in a total of 820 samples collected, the pH ranges from 5.92 – 9.78, and alkalinity ranges from 12 – 404 mg/L $CaCO_3$ (*n*=817). Therefore, relatively high lead measurements in Price County could be from naturally-occurring sources.

This study utilized a random sample design, and the next logical step is to conduct targeted sampling in areas with contaminant-level values in groundwater samples. There is not a need to conduct targeted sampling of fluoride based on the results from this study, but additional, targeted sampling of iron, manganese, aluminum, arsenic, and lead is highly recommended. Further, it is recommended that any targeted sampling be conducted on wells for which a well record exists, so that correlations may be made between well characteristics and sample analysis results. In terms of naturally-occurring compounds in groundwater, it would be beneficial to add radium and radon groundwater monitoring in future studies conducted in northwestern Wisconsin.

The methods utilized in this study can easily be replicated by citizen-science groups and others who are interested in monitoring groundwater quality on a local level. This may increase groundwater data available to the public within the northwest Wisconsin region. In order to better measure short-term trends and long-term changes in regional groundwater quality, the development of a public groundwater quality database for northwest Wisconsin is recommended.

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APPENDIX 1: SAMPLE COLLECTION FORM – NORTHWEST WISCONSIN GROUNDWATER MONITORING PROJECT

Sample Collection Form: NW WI Groundwater Monitoring Project

SECTION 1: TO BE COMPLETED BY THE SAMPLE COLLECTOR

Collection Date (MM-DD-YYYY):		**Collection Time:**	**Circle: AM PM**
Sample Collection Location:	☐Faucet Between Well and Pressure Tank ☐Faucet After Pressure Tank but Before Filter(s)/Water Treatment System (if applicable) ☐Faucet After Pressure Tank and After Filter(s)/Water Treatment System (if applicable) ☐Other (Please Specify):		
Water Treatment System(s):	☐None – Not Applicable ☐Water Softener ☐Carbon Filter ☐Reverse Osmosis ☐Iron Filter ☐Other (Please Specify):		
Was sample collected before or after water treatment system(s)?	☐Before ☐After ☐Not Applicable		

Well Owner's Contact Information		Private Well Information (Leave Blank if not Known)	
Name:		**Well Address (Street or Legal Description):**	
Telephone Number:		**Town or City/County:**	
Address:		**Well Completion Date:**	
		Wis. Unique Well Number:	
		Well Construction Type:	☐Drilled ☐Jetted ☐Driven Point ☐Dug ☐Other (Please Specify):

SECTION 2: SEND RESULTS TO (COMPLETED BY THE SAMPLE COLLECTOR)

Preferred Method to Communicate Results:	☐Mail Hard Copy ☐E-mail Electronic Copy ☐Both ☐Other (Please Specify):
Send Results To (Name and Street/E-mail Address):	

SECTION 3: TO BE COMPLETED BY THE LABORATORY

Requested Analysis:	☐Fluoride (Bottle #1; US EPA Method 300.0, v.2.1) ☐Metals (Bottle #2 – Arsenic, Iron, Manganese, Lead, and Aluminum; US EPA Method 200.9, v.2.2)

Sample Receipt and Preservation Data

Date Received (MM-DD-YYYY):		**Time Received (HH:MM):**		**Received by:**	
Was Sample Accepted for Analysis?	☐Yes ☐No				
If No, Why?	☐Received Past Hold Time ☐Shipping Problem ☐Frozen during Transit ☐Other (Specify):				
Description of Water Appearance (Color, Strong Odor, Particulates):					

Laboratory Result(s)

Analyte	Result	Public Health Enforcement Standard (Wis. Ch. NR 140)	Public Health Preventative Action Limit (Wis. Ch. NR 140)
Arsenic (μg/L):		10 μg/L	1 μg/L
Aluminum (μg/L):		200 μg/L	40 μg/L
Fluoride (mg/L):		4 mg/L	0.8 mg/L
Iron (mg/L):		0.3 mg/L	0.15 mg/L
Lead (μg/L):		15 μg/L	1.5 μg/L
Manganese (mg/L):		300 μg/L	60 μg/L
Date Reported to Volunteer/Reported By:			

Data Reviewed by (Laboratory Manager or Quality Assurance Manager) Signature:

APPENDIX 2: SAMPLE RECEIPT CHECKLIST – NORTHWEST WISCONSIN GROUNDWATER MONITORING PROJECT

Lake Superior Research Institute; University of Wisconsin-Superior
Wisconsin DNR Certification #816003540
801 North 28th Street; Superior, WI 54880
(715)394-8422
kprihoda@uwsuper.edu

SAMPLE RECEIPT CHECKLIST: NW WI Groundwater Monitoring Project

Sample ID Code:		Date of Sample Receipt:	
Collection Date/Time:			
Courier:	☐Volunteer ☐FedEx ☐USPS ☐Sample Picked Up (NL-IR, NL-MG)		
Courier Tracking Number:			

Sample Login

QUESTION	ANSWER	COMMENTS
Sample Collection Form Present?	☐Yes ☐No ☐Not Applicable	
Sample Collection Form Filled Out Completely?	☐Yes ☐No ☐Not Applicable	
Samples Arrived within Hold Time?	☐Yes ☐No ☐Not Applicable	
Sufficient Sample Volume?	☐Yes ☐No ☐Not Applicable	
LSRI-Supplied Container(s) Used?	☐Yes ☐No ☐Not Applicable	
Containers Intact?	☐Yes ☐No ☐Not Applicable	
Sample Label(s) Match Sample Collection Form?	☐Yes ☐No ☐Not Applicable	

Sample Preservation Data

Metals Only: Adjusted pH of Sample to <2 using nitric acid?	☐Yes	☐No
Metals Only: Measured pH		
Metals Only: Low-Range pH Paper Lot #/Exp. Date		

Client Notification/Resolution

Person Contacted:	
Contacted By and Date/Time:	
Comments/Resolution:	

Sample Storage/Analyst Notification

Fluoride		Metals	
Sample Storage Location:		Sample Storage Location:	
"Analyze By" Date:		"Analyze By" Date:	
Notified Analyst(s) of Sample Receipt and "Analyze By" Date?		☐Yes	☐No

QAM OR Project PI Review:	
Date:	

Version: 22 Aug 2018