Chippewa County Nitrate Occurrence and Source Investigation

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We would like to thank all of the Chippewa County community members that agreed to submit samples or have samples collected from their wells. Without their interest and willingness to participate, this report would not have been possible.

Executive Summary

Groundwater is the principal water supply for Chippewa County municipalities, industries, and rural residents. While municipal water supplies are regularly monitored and required to meet drinking water standards, private well owners must make decisions regarding when and what to test for and what to do if there is a problem. This work summarizes a one-year effort of Chippewa County and the University of Wisconsin – Stevens Point to investigate sources and occurrence of nitrate in groundwater. The intent is that the information be used to assist rural residential landowners with management of groundwater and private well water systems.

Previous work in Chippewa County identified and selected wells that are tested annually for common water quality parameters such as nitrate-nitrogen, chloride, alkalinity, total hardness, pH, and conductivity. These wells are intended to provide an annual assessment of groundwater quality from wells that are representative of Chippewa County's diverse soils, geology, land-use, and well construction. A total of 151 Chippewa Trend Monitoring (CTM) wells were tested in 2022. In addition to monitoring trends in water quality of common parameters, historical data from these private wells was used to create a nitrate risk assessment model for Chippewa County.

The model was used to select wells for a nitrate occurrence and source investigation. Nitrate is the most widespread groundwater contaminant in Wisconsin. Understanding the occurrence and sources of nitrate allows for more effective outreach efforts and deployment of conservation dollars to improve water quality. Nitrate Source Investigation (NSI) wells accounted for an additional 142 wells sampled in 2022 that were selected from areas predicted to have nitrate above natural levels in groundwater.

Samples collected from the CTM and NSI wells sampled for nitrate-nitrogen had mean concentrations 4.7 and 7.6 mg/L respectively. The model used to predict the occurrence of elevated nitrate-nitrogen resulted in 82% (greater than 2 mg/L) and 60% (greater than 5 mg/L), which is significantly better than the 63% (greater than 2 mg/L) and 40% (greater than 5 mg/L) which would have been expected by random sampling. Additional refining of the predictive model was conducted to further improve nitrate risk assessment tools in Chippewa County.

A subset of wells (n=24) were tested for source tracers (i.e. common pesticides, neonicotinoid compounds, per and poly fluoroalkyl substances (PFAS), pharmaceuticals, and personal care products). Analysis of the source tracers helps to determine potential sources of human-impacted groundwater, which is why only wells with greater than 2 mg/L of nitrate-nitrogen and/or greater than 10 mg/L of chloride were selected for this additional testing. Because some of these compounds also have health standards associated with them, the information provides insight into other important tests for well owners to consider. Analysis of the nitrate source data revealed that 88% (21/24) contained common pesticides, 71% (17/24) contained pharmaceuticals and/or personal care products, 17% (4/24) contained PFAS, and 17% (4/24) contained neonicotinoid compounds. All wells (n=24) contained at least one of the categories of source tracing compounds. Wells that detected evidence of one or more pesticide compounds had greater mean nitrate-nitrogen concentrations; while wells detecting one or more pharmaceuticals/personal care products had greater mean chloride concentrations.

This work provides insight into the utility of statistical models to effectively target well water outreach and testing in areas that are more at risk for nitrate contamination. In addition, we show that wells containing elevated nitrate have a high probability of detecting other compounds common to land-use. The information will be useful for future outreach and land management efforts in Chippewa County.

Well Selection and Sampling

Only wells assigned a Wisconsin Unique Well Number and locatable well construction information (i.e. well depth, casing depth, static water level) were sampled as part of this project. In addition to well construction information, additional information on soil drainage, geology, and land cover within a 500 m buffer was also summarized for each well.

A total of 291 landowners participated in the 2022 well monitoring efforts. This included 151 private wells that are part of the long-term Chippewa Trend Monitoring (CTM) program. A predictive model developed using previous testing data was used to select wells for Nitrate Source Investigation (NSI). This resulted in an additional 142 private well samples submitted from areas of elevated nitrate risk. Grid cells with a predicted nitrate-nitrogen concentration greater than 5 mg/L were used to select potential landowners for participation in the NSI component of the project (Figure 1). CTM well water results are intended to be representative of Chippewa County groundwater in general, and provide a comparison dataset for wells selected from NSI regions.

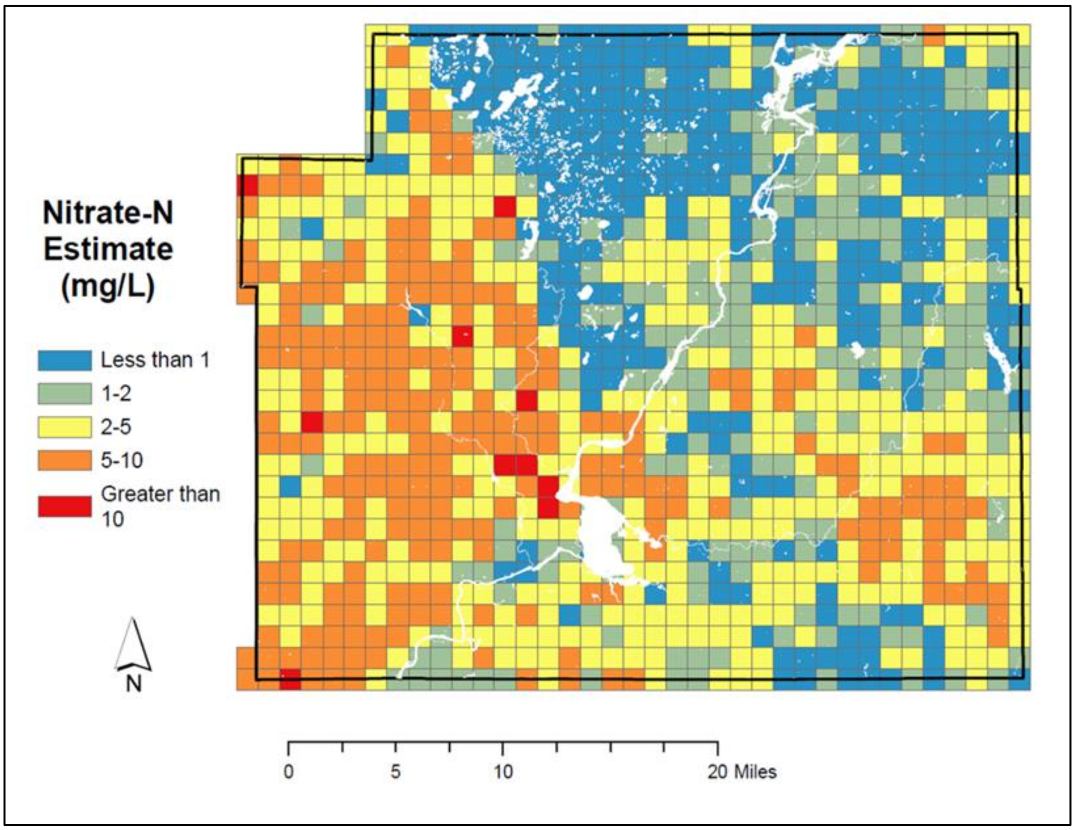


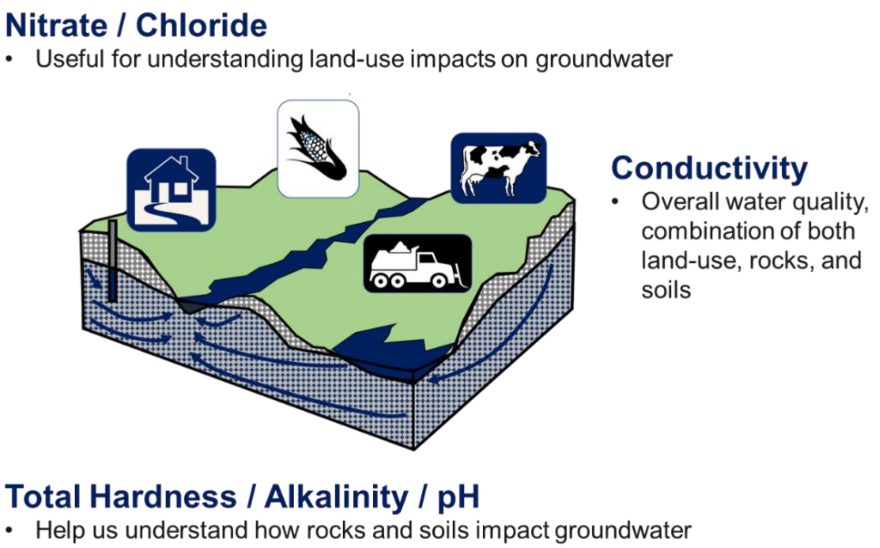
Figure 1. Gridded data from statistical model predicting areas of Chippewa County with elevated nitrate-nitrogen. Wells (n=142) sampled for Nitrate Source Investigation (NSI) were selected from grid cells with a predicted nitrate level of greater than 5 mg/L.

While CTM participants have sampled annually since 2019, NSI participants had to be recruited. Recruitment materials for NSI participants consisted of a recruitment letter describing why the landowner was being contacted along with additional information about the project. Landowners were asked to respond using a pre-paid postcard. Materials were sent to 487 landowners, 181 indicated interest in participating.

Sampling kits (n=337) were mailed in late July 2022. Each kit included a sample bottle, sampling instructions, and a pre-paid mailer for participants to enclose materials in. Participants were instructed to sample an untreated faucet. If not sure which faucet to use, they were asked to collect the sample from their cold-water kitchen faucet which is generally untreated in most households. Following sample collection, participants were asked to take the pre-paid mailer to a Postal Service counter.

A total of 291/337 (86%) samples were received and analyzed for nitrate-nitrogen, chloride, alkalinity, pH, total hardness, and conductivity. All samples were analyzed by the Water and Environmental Analysis Laboratory which is state-certified to perform the analyses of interest.

Figure 2. All samples (n=291) were analyzed for nitrate-nitrogen, chloride, conductivity, total hardness, alkalinity, and pH.



Individual well test results were mailed to participants following completion of water quality analysis. Each participant received a copy of their individual test results along with an interpretive guide and overall summary of the results. Results were also integrated into an online dashboard that's part of the long-term CTM program. The dashboard can be assessed online at:
http://68.183.123.75:3838/County-Apps/Chippewa/

A total of 24 wells were selected for additional analysis. To be considered, samples had to have nitrate-nitrogen concentrations greater than 2 mg/L and/or chloride concentrations greater than 10 mg/L. This additional analysis included agricultural tracers, pharmaceuticals/personal care products (PPCPs), neonicotinoids, and perfluoroalkyl and polyfluoroalkyl substances (PFAS). Neonicotinoids and PFAS are considered contaminants of emerging concern because less information exists on the extent of these compounds in groundwater. Additional information about these compounds in Chippewa County help establish a baseline for future comparison and could help inform land management efforts into the future.

All of these samples were collected by UW-Stevens Point staff who had been trained in sampling procedures for analytes of interest. Compounds such as PFAS are more sensitive to sampling methods and to ensure sample integrity was maintained, we elected to collect these samples rather than rely on individual homeowners. Homeowners were contacted and a time was arranged to collect the sample or staff was granted permission to sample if the homeowner was not available.

When sampling for these compounds, sampling staff utilized the outside faucet. Materials likely to be free of PFAS compounds were used to flush wells and other procedures were taken to reduce the potential of contaminating samples during the sampling process. Wells were determined to be appropriately flushed when equipment used to monitor the water pH, conductivity, and temperature had stabilized. Stabilization of these parameters indicates that water from plumbing system or stagnant water in the well had been appropriately flushed from the system. At this time the hose was removed and samples were collected in the following order: PFAS followed by sampling for pesticides, PPCPs, and neonicotinoids.

Prior to collecting for PFAS, samplers cleaned hands using alcohol-based hand-sanitizer and then put on nitrile gloves before touching sample bottles. Sample bottles (including a field blank) were removed from a plastic bag designed to keep them from contacting any materials that might contain PFAS. The field blank is PFAS free water that accompanied each sample kit. The field blank was poured into a separate 250 mL HDPE sample bottle at the sampling location as a way to assess potential sampling contamination. The field blank was only analyzed if PFAS compounds were measured in the well water sample. Following the field blank, two 250 mL HDPE bottles were filled with well water. The two PFAS samples and field blank were placed in a plastic bag and sealed with a zip tie before being placed in a cooler that maintained a temperature of -20 degrees Celsius. Freezing samples has been suggested to reduce the potential of PFAS degradation prior to sample analysis. Samples were stored at -20 degrees Celsius until they could be delivered to the laboratory. Samples for PFAS were analyzed at the Wisconsin State Laboratory of Hygiene using EPA Method 537.1.

Samples for pesticides, neonicotinoids, and PPCPs were collected in in 1L glass amber bottles that had been cleaned and rinsed with acetone. Following collection, samples were placed in a cooler that maintained samples at 4 degrees Celsius until they could be returned to the laboratory. Samples were analyzed at the UW-Stevens Point Water and Environmental Analysis Lab. One field blank and sample duplicate were also collected as part of a quality control/quality assurance plan for these parameters.

Project Results for Common Well Water Quality Parameters

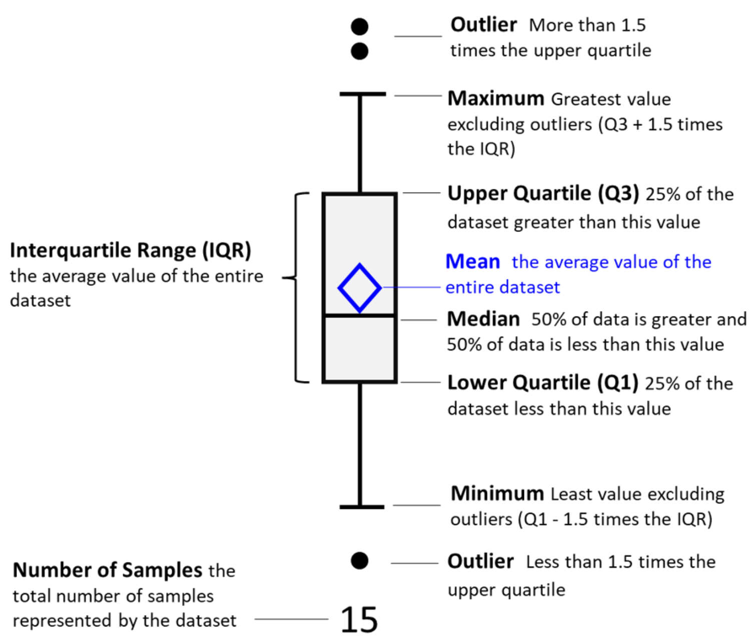
The following information summarizes the 2022 water testing results for all 291 well water samples that were anaylzed for common water quality parameters. In this section we provide information on each of the parameters and overall summaries of the results.

Table 1. Summary statistics for 2022 well water samples.

	Total Hardness*	Alkalinity	Conductivity	pH	Nitrate-Nitrogen	Chloride
	mg/L as $CaCO_3$	mg/L as $CaCO_3$	umhos/cm		mg/L	mg/L
Minimum	5	4	35	4.04	<0.1	0.5
Mean	93.7	52	246.8	7	6.1	24.2
Median	82.5	32	220	7	5	14.3
Maximum	305	241	1365	8.8	28.8	366
# of samples	268	291	291	291	291	291

*Softened samples removed from summary statistics for Total Hardness.

Boxplots are used to summarize results by individual municipalities. The following diagram describes how to interpret boxplots used in subsequent pages.



Total Hardness

The total hardness test measures the amount of calcium and mangnesium in water. Calcium and magnesium are essential nutrients, which generally come from naturally sources of these elements in rock and soils (i.e. carbonate rocks). The amount present in drinking water is generally not a significant source of these nutrients compared with a healthy diet. There are no health standards associated with total hardness in your water, however; too much or too little hardness can be associated with various aesthetic issues that can impact plumbing and other functions.

Results from the project suggest that Chippewa County well water generally contains lower levels of hardness than what is typically found in other parts of Wisconsin. Low values (less than 150 mg/L) associated with soft water were most commonly detected in wells that access the Cambrian sandstone in western Chippewa County or sand/gravel aquifers along the Chippewa River or next to Lake Wissota. These aquifer materials generally contain less carbonate rock and may result in water that is more corrosive. Wells drilled into glacial sediments or crystalline bedrock common for wells of northeastern Chippewa County are more likely to contain levels of hardness associated with hard water (greater than 200 mg/L).

Why Test for Total Hardness
Because total hardness is related to the rocks and soils that water flows through on its way to a well, we would expect total hardness concentrations to be fairly stable from year to year. Any changes observed in total hardness concentrations may help us better understand the influence of climate variability on well water quality on an individual well. Because hardness concentrations have been shown to increase when nitrate and/or chloride increase, the total hardness test is a good complement to other tests.

Interpreting Total Hardness Concentrations

Hard Water:
Water with a total hardness value greater than 200 mgL is considered hard water. Hard water can cause lime buildup (scaling) in pipes and water heaters. Elements responsible for water hardness can also react with soap decreasing its cleaning ability, can cause buildup of soap scum, and/or graying of white laundry over time. Some people that use hard water for showering may notice problems with dry skin.

If you are experiencing problems with hard water: Consider softening water using a water softener. Water softeners remove calcium and magnesium and replace those elements with a different cation (usually sodium). Many people choose not to soften the cold-water tap used for drinking/cooking and the outdoor faucet used for yard watering. *Note: the water softening industry measures hardness in grains per gallon. 1 grain per gallon = 17.1 mg/L as $CaCO_3$*

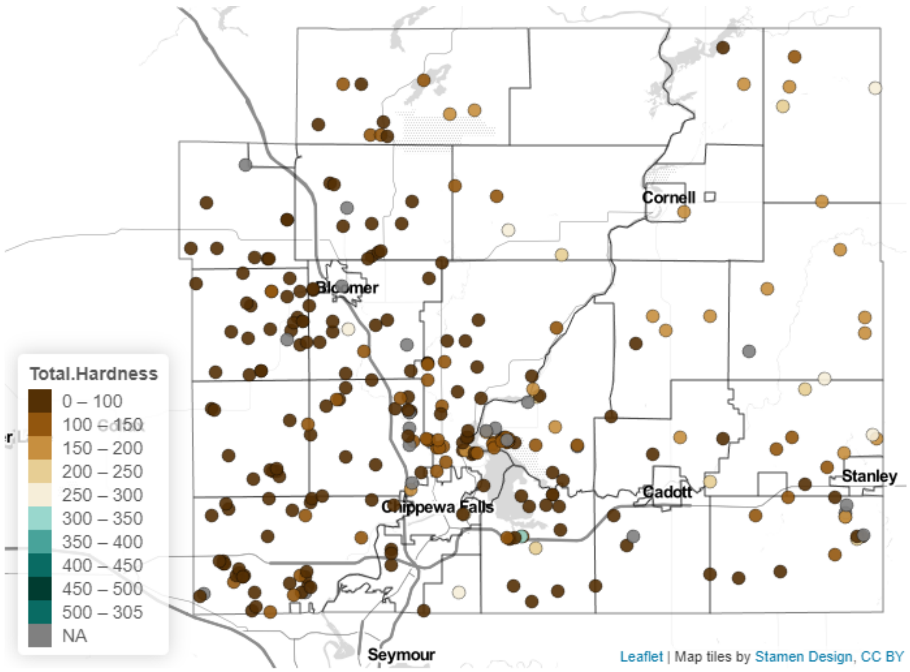
Soft Water:
Water with a total hardness concentration less than 150 mg/L is considered soft. Water with too little hardness is often associated with corrosive water, which can be problematic for households with copper plumbing or other metal components of a plumbing system.

If you are experiencing problems with soft water or corrosion of household plumbing: You may want to consider a water treatment device (called a neutralizer) designed to make water less corrosive. Newer homes with plastic plumbing generally don't need to be as concerned with corrosive water with respect to the plumbing.

Ideal:
Water with total hardness between 150-200 mg/L is generally an ideal range of water hardness because there are enough ions to protect against corrosion, but not too many that they contribute to scale formation. While it is a personal preference, households with hardness in this range generally don't require additional treatment.

Sources of Total Hardness
Primarily dissolved carbonate minerals from soil and rock materials. When carbonate minerals dissolve, they increase the amount of calcium and magnesium ions in water.

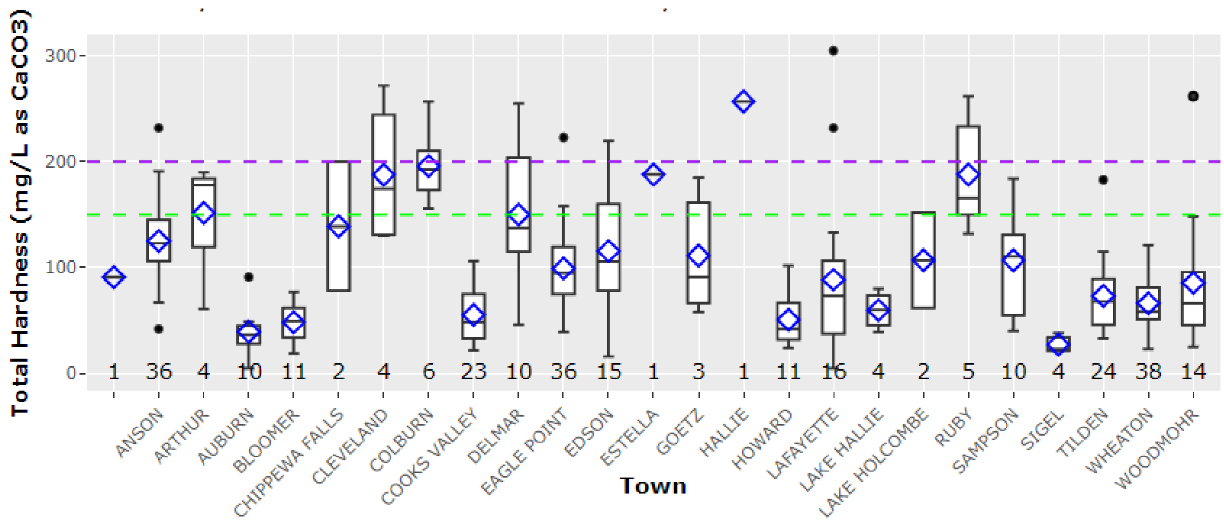
Figure 3. Total hardness well water quality results for 2022.



Total Hardness (mg/L CaCO3)	Number of Samples	Percent
Less than 50*	90	31%
51 – 100	96	33%
101 – 200	89	31%
201 – 300	14	5%
301 – 400	1	<1%
Greater than 400	0	0%

*Samples with less than 50 mg/L are likely softened or partially softened

Figure 4. Boxplots of total hardness by town.



Alkalinity

Alkalinity is a measure of water's ability to neutralize acids. Alkalinity is associated with carbonate minerals and is commonly found in areas where groundwater is stored or transported in carbonate aquifers. Carbonate minerals may be found in the glacial sediments of northeastern Chippewa County, but are generally lacking in much of western and southern Chippewa County. As a result, well water in Chippewa County was found to contain low levels of alkalinity. Lower values correlated with those areas found to have lower total hardness values. Well water in much of the county is likely to be aggressive or corrosive to metal plumbing components.

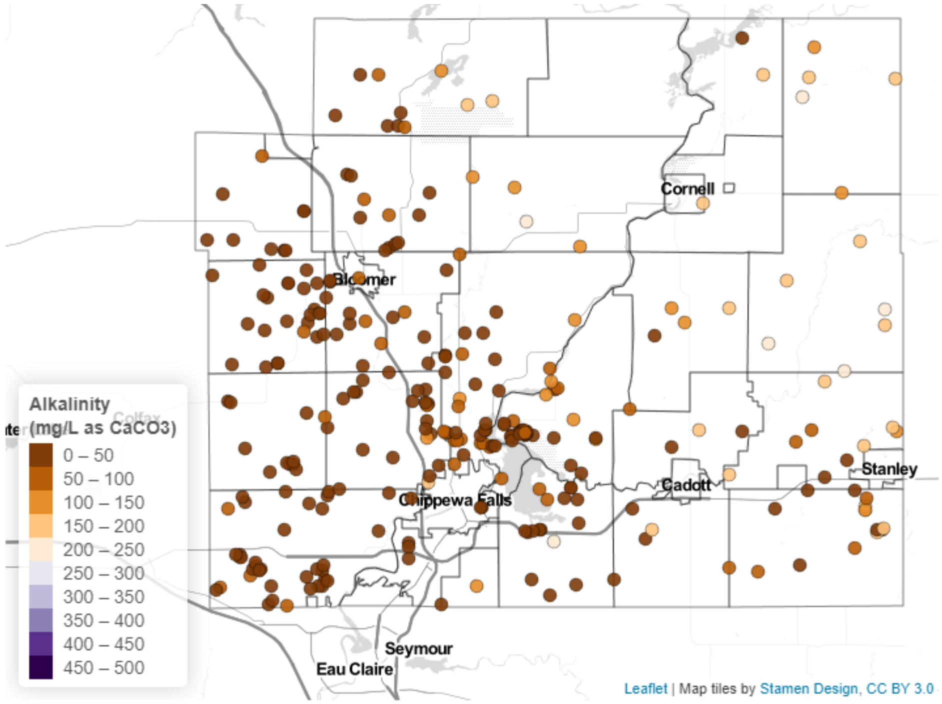
Why Test for Alkalinity

Because alkalinity is related to the rocks and soils that water flows through on its way to a well, we would expect alkalinity concentrations to be relatively stable from year to year. Any changes observed in alkalinity concentrations may help us better understand the influence of climate variability on well water quality from year to year, or make sense of broader water quality results from Chippewa County. Particularly in wells that are uninfluenced by human activity, alkalinity concentrations may help us better understand which aquifers wells are accessing groundwater from.

Interpreting Alkalinity Concentrations

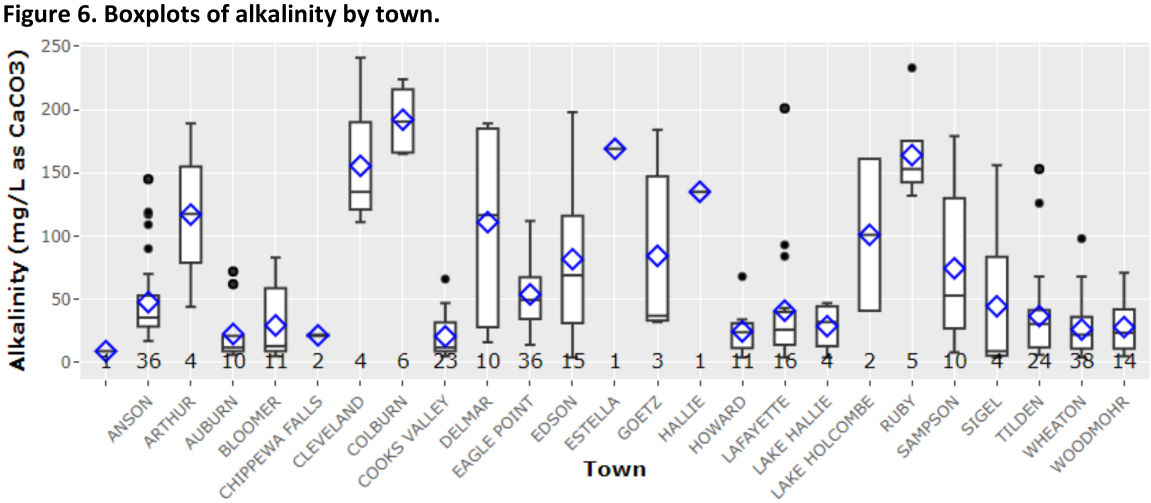
There are no health concerns associated with having alkalinity in water. Alkalinity should be roughly 75-100% of the total hardness value in an unsoftened sample. Water with low levels of alkalinity (less than 150 mg/L) is more likely to be corrosive. High alkalinity water (greater than 200 mg/L), may contribute to scale formation. If total hardness is half or less than the alkalinity result, it likely indicates that your water has passed through a water softener. If alkalinity is significantly less than total hardness, it might be related to elevated levels of chloride or nitrate in a water sample.

Figure 5. Alkalinity well water quality results for 2022.



Alkalinity (mg/L $CaCO_3$)	Number of Samples	Percent
Less than 50	197	68%
51 – 100	47	16%
101 – 200	40	14%
201 – 300	6	2%
301 – 400	0	0%
Greater than 400	0	0%

Figure 6. Boxplots of alkalinity by town.



Conductivity

Conductivity measures the amount of dissolved substances (or ions) in water; but does not give an indication of which minerals are present. Conductivity is a measure of both naturally occurring ions such as calcium, magnesium, and alkalinity; as well as ions that are often associated with human influences such as nitrate and chloride. Changes in conductivity over time may indicate changes in your overall water quality.

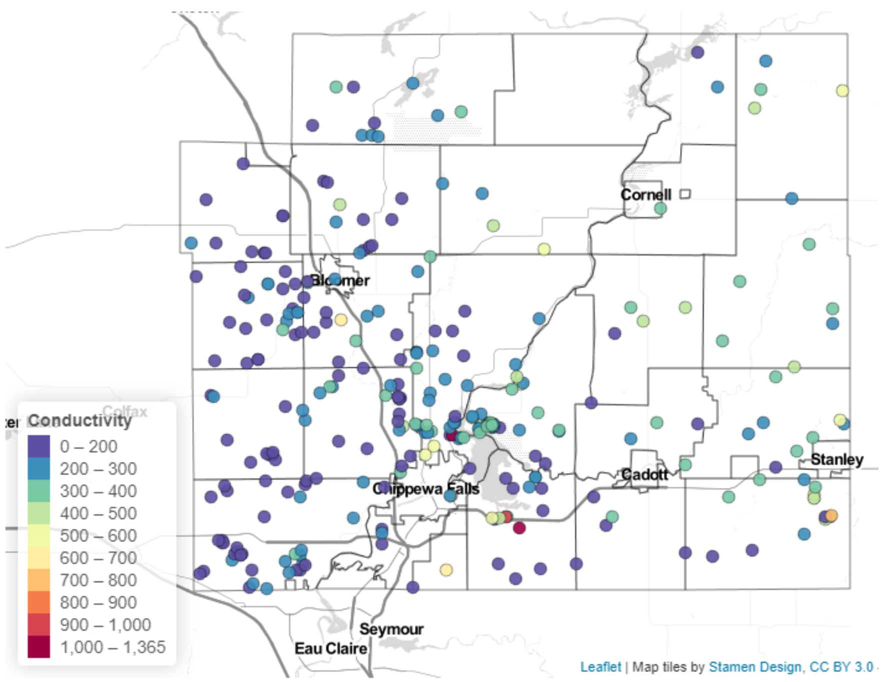
Why Test for Conductivity

Conductivity is relatively easy to measure for and sensors for conductivity are reliable. Information learned from changes in conductivity during this project may be useful for designing future monitoring strategies for Chippewa County or even individual households to inexpensively track changes in well water quality continuously on their own.

Acceptable results:

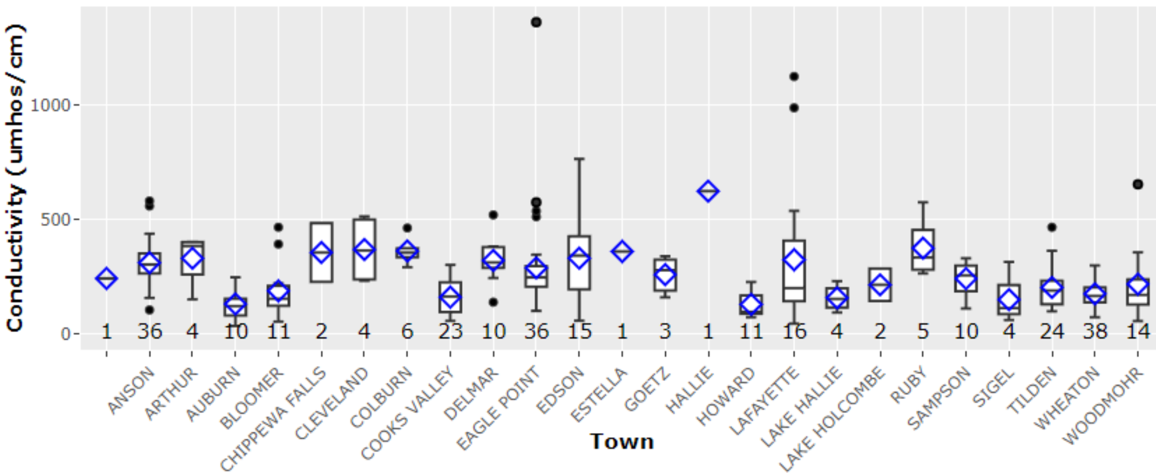
There is no health standard associated with conductivity. A normal conductivity value measured in umhos/cm is roughly twice the total hardness as mg/L $CaCO_3$ in unsoftened water samples. If conductivity is significantly greater than twice the hardness, it may indicate the presence of other human-influenced or naturally occurring ions such as chloride, nitrate, or sulfate.

Figure 7. Conductivity results for 2022 Chippewa County well sampling.



Conductivity (umhos/cm)	Number of Samples	Percent
Less than 100	29	10%
101 – 250	145	50%
251 – 500	100	34%
501 – 750	12	4%
751 – 1000	2	<1%
Greater than 1000	2	<1%

Figure 8. Boxplots of conductivity by town.



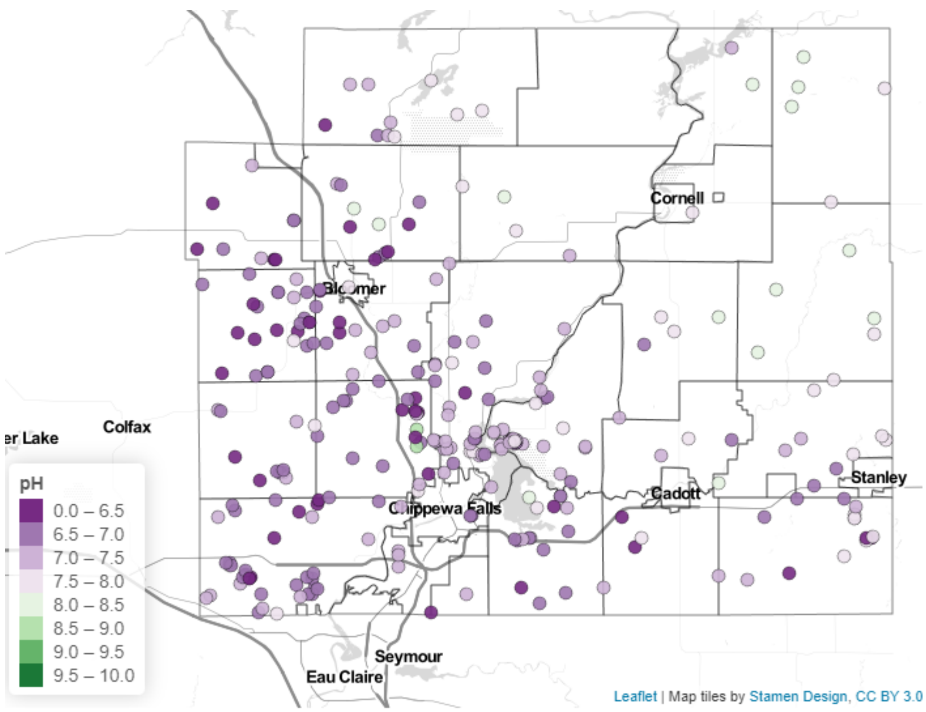
pH

The pH test measures the concentration of hydrogen ions in a solution. The concentration of hydrogen determines if a solution is acidic or basic. The lower the pH, the more corrosive water will be. The pH of well water in Chippewa County is slightly acidic, with 51% of wells tested indicating a pH less than 7.0. Lower pH water is commonly found in western and southern Chippewa County, particularly those that rely on the sandstone aquifers for water. Higher pH levels are common in the northeaster portions of Chippewa County and correlate to wells drilled into unconsolidated glacial deposits.

Acceptable results:
There is no health standard for pH but corrosive water (pH less than 7) is more likely to contain elevated levels of copper or lead if these materials are in your household plumbing. Typical groundwater pH values in Wisconsin range from 6.0 to 9.0.

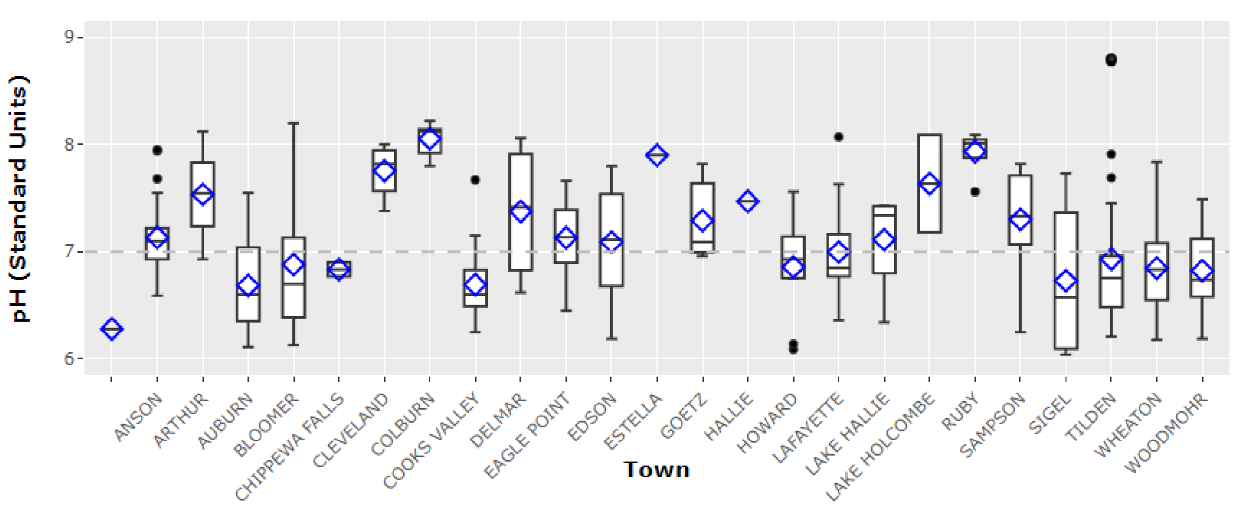
Sources: Elevated levels are usually the result of carbonate minerals which help raise the pH and also buffer against changes in pH. Conversely, low values of pH are most often caused by lack of carbonate minerals in the aquifer. Low pH combined with low mineral content makes water aggressive or corrosive, particularly to metal plumbing components.

Figure 9. The pH well water quality results for 2022.



pH	Number of Samples	Percent
Less than 5.00	1	<1%
5.01 – 6.00	2	<1%
6.01 – 7.00	143	49%
7.01 – 8.00	129	44%
8.01 – 9.00	15	5%
Greater than 9.00	0	0%

Figure 10. Boxplots of pH by town.



Chloride

In most areas of Wisconsin, chloride concentrations are naturally low (usually less than 10 mg/L). Higher concentrations may serve as an indication that the groundwater supplied to your well has been impacted by various human activities. Sixty-two percent of wells tested as part of the 2022 Chippewa County well water sampling suggest evidence that land-use has impacted the well water quality.

Why Test for Chloride

Chloride is a test that allows us to understand the influence of human activities on well water quality. Measuring chloride concentrations in well water will also allow us to better understand whether well water quality is getting better, worse, or staying the same with respect to certain land-uses (see Sources).

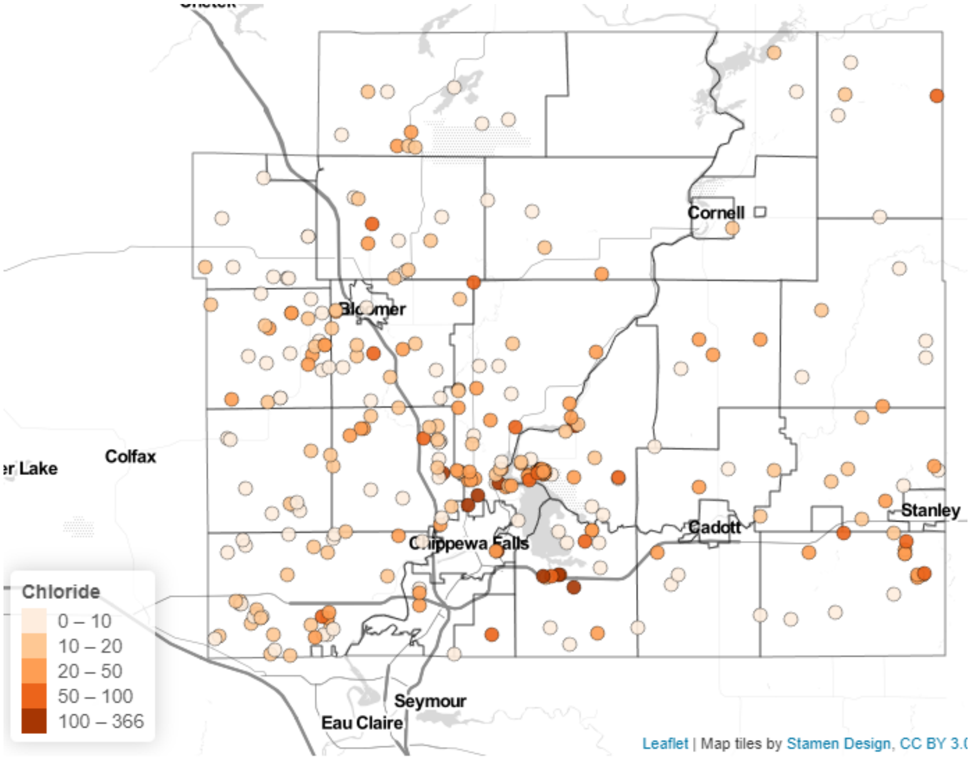
Interpreting Chloride Concentrations

Chloride is not toxic at typical concentrations found in groundwater. Unusually high concentrations of chloride (greater than 100 mg/L) are often associated with road salt and may be related to nearby parking lots or road culverts where meltwater from winter deicing activities often accumulates. Water with concentrations greater than 250 mg/L are likely to contain elevated sodium and are sometimes associated with a salty taste; high chloride levels are also more likely to be corrosive to certain metals.

Sources of Chloride

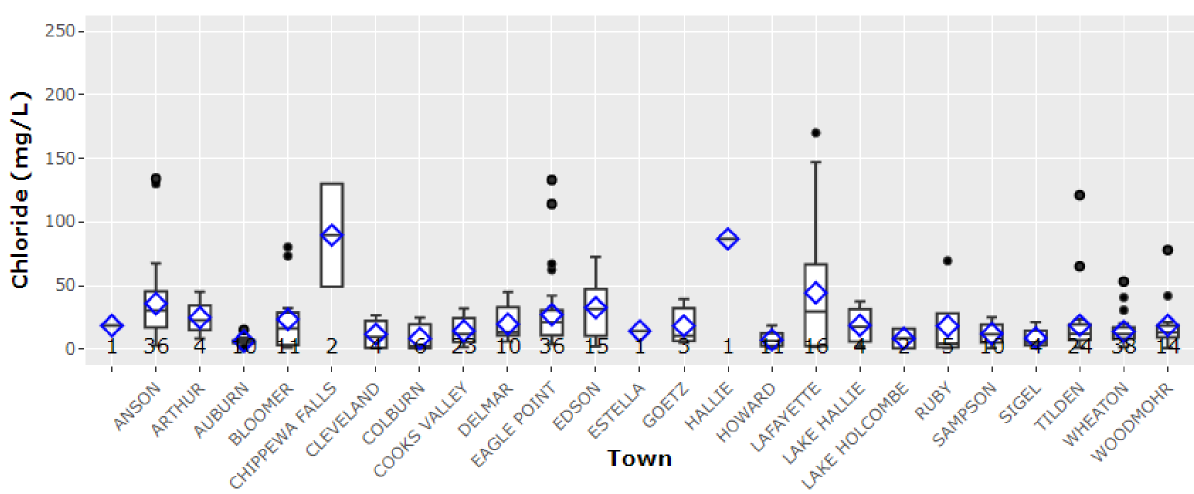
- Agricultural Fertilizers (chloride is a companion ion of potash fertilizers
- Manure and other biosolids
- Septic Systems
- Road Salt

Figure 11. Chloride results for 2022 Chippewa County well testing.



Chloride (mg/L)	Number of Samples	Percent
Less than 0.1	1	<1%
Less than 10	107	37%
11 – 50	152	52%
51 – 100	20	7%
101 – 200	8	3%
Greater than 200	2	<1%

Figure 12. Boxplots of chloride by town for Year 4.



Nitrate

This test measures the amount of nitrate-nitrogen in a well. Nitrate is a form of nitrogen commonly found in agricultural and lawn fertilizer that easily dissolves in water. Nitrate is also formed when waste materials such as manure or septic effluent decompose. The natural level of nitrate in Wisconsin's groundwater is less than 1 mg/L. Levels greater than this suggest groundwater has been impacted by various land-use practices. There is a health-based drinking water standard of 10 mg/L of nitrate-nitrogen.

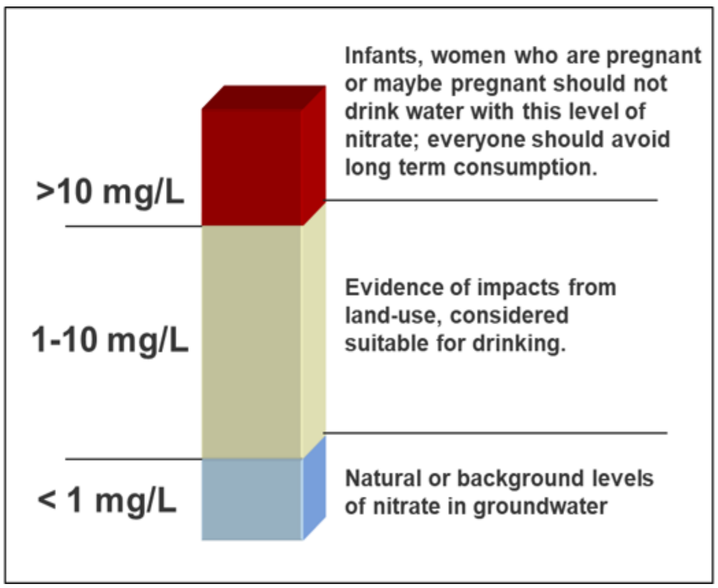
Why Test for Nitrate

Nitrate is an important test for determining the safety of well water for drinking. In addition, nitrate is a test that allows us to understand the influence of human activities on well water quality. Because it moves can come from a variety of sources and moves easily through soil, it serves as a useful indicator of certain land-use activities. An annual nitrate test is useful for better understanding whether water quality is getting better, worse, or staying the same with respect to certain land-uses/sources mentioned above.

Health Effects of Nitrate in Drinking Water

Nitrate-nitrogen levels greater than 10 mg/L may result in the following potential health concerns:

- **Infants less than 6 months old –** blue baby syndrome or methemoglobinemia is a condition that can be fatal if left untreated
- **Women who are or may become pregnant –** may cause birth defects
- **Everyone –** may cause thyroid disease and increase the risk for certain types of cancer



Infants less than 6 months old and women who are or may become pregnant should not drink water or consume formula made with water containing more than 10 mg/L of nitrate-nitrogen. Everyone should avoid long-term consumption of water with greater than 10 mg/L of nitrate-nitrogen.

Ways to reduce nitrate in your drinking water

Sometimes drilling a new well or reconstructing an existing well may provide water with less nitrate. If this is not possible, or you need an alternative solution because of time or cost, another way to reduce nitrate is to install a water treatment device approved for removal of nitrate. Please note that if using treatment for nitrate, routine testing is necessary to make sure its functioning properly.

Treatment for Nitrate
Ideally, we would work to reduce nitrate in groundwater rather than rely on treatment, however water treatment may be necessary short-term or long-term solution for obtaining safe drinking water. Treatment for nitrate is very specific and requires certain treatment technologies. The following types of systems may be appropriate depending on the amount of water you are looking to treat:

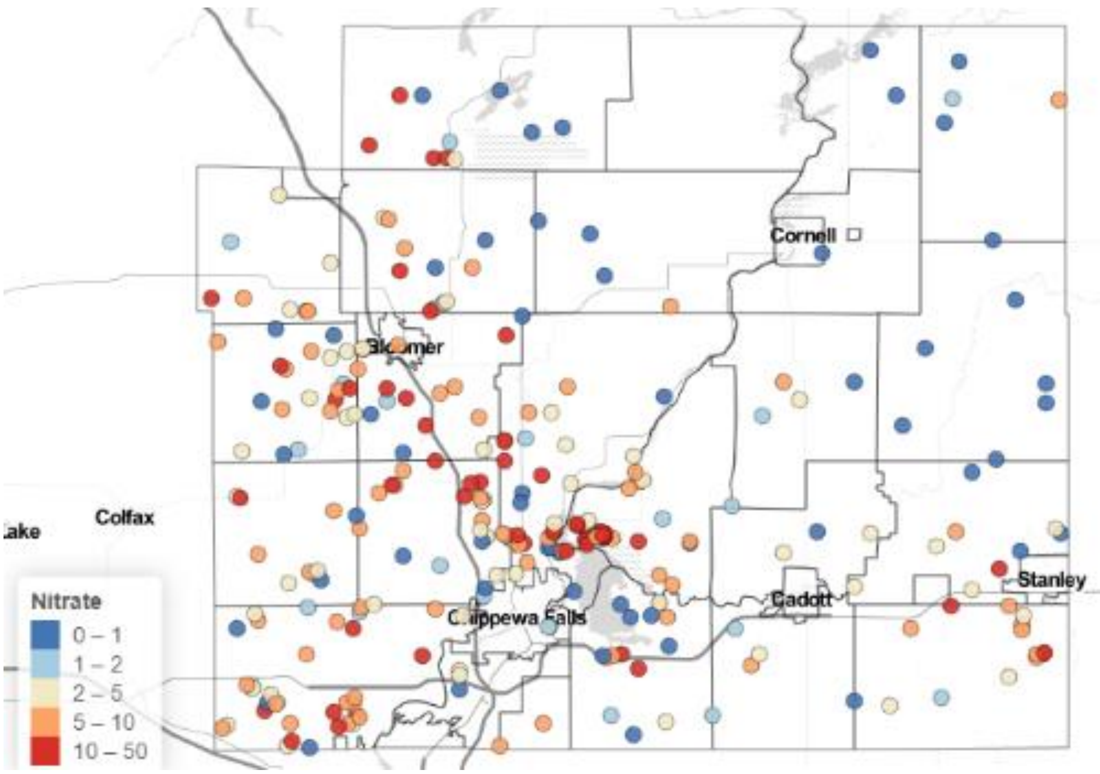
Point-of-use devices treat enough water for drinking and cooking needs

- Reverse Osmosis
- Distillation

Point-of-entry systems treat all water distributed throughout the house

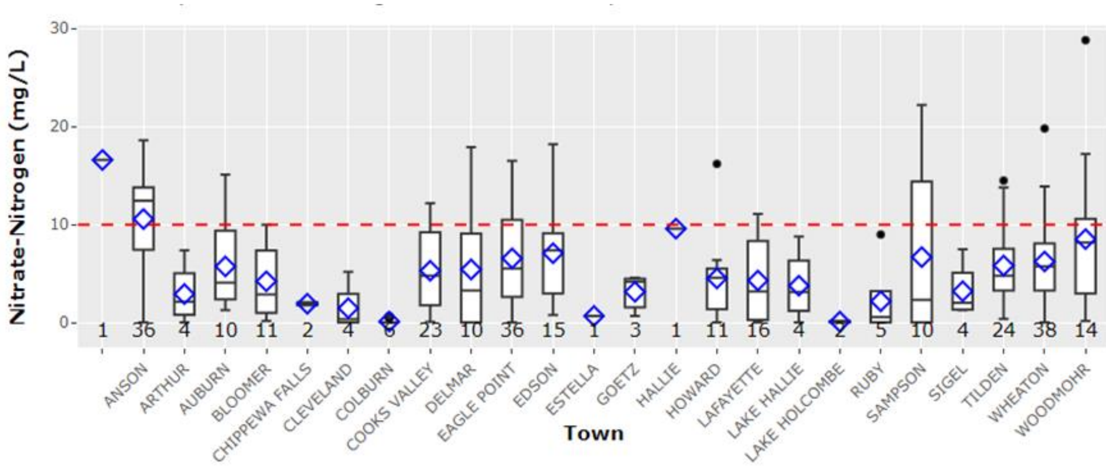
- Anion Exchange

Figure 13. Nitrate-nitrogen results for the 2022 well testing.



Nitrate-Nitrogen (mg/L)	Number of Samples	Percent
Less than 0.1	29	10%
0.1 – 2.0	52	18%
2.1 – 5.0	65	22%
5.1 – 10.0	78	27%
10.1 – 20.0	64	22%
Greater than 20.0	2	<1%

Figure 14. Boxplots of nitrate-nitrogen by town for 2022.



Nitrate Source Tracers

When looking at most of the source tracing compounds, it is important to point out that many either do not have health standards associated with them or the levels that we typically detect them in groundwater do not often exceed levels that have been determined to impact health. Source tracing compounds are often stable compounds that help us understand potential sources of nitrate or other chemicals of concern. The following section outlines different categories of source tracing compounds that were analyzed in 24 samples with elevated nitrate and/or chloride.

Pharmaceuticals and personal care products (PPCPs)

The purpose of testing for artificial sweeteners, pharmaceuticals, and other personal care products is that they are ubiquitous in food and other personal care products. After ingesting or using these products, they are excreted and become part of our household wastewater stream; which in rural households often goes to a septic system. While septic systems are designed to reduce bacteria, highly mobile compounds such as nitrate and artificial sweeteners may pass through the soil below a drainfield. If artificial sweeteners and other wastewater tracers are detected in a well, it suggests that some of the nitrate contamination likely originates from a nearby septic system or other wastewater source.

Agricultural Tracers

The agricultural tracers look for the breakdown products (metabolites) of two pesticides commonly used on corn and soybeans in Wisconsin. According to a 2017 WI Department of Agriculture, Trade, and Consumer Protection report, breakdown components of metolachlor and alachlor are the most commonly detected pesticide compounds in Wisconsin's groundwater. If these compounds are detected, it is likely that some of the nitrate in the well is coming from agricultural sources.

Neonicotinoids Compounds

Neonicotinoids are increasingly used as seed coatings on corn to prevent against insect pressure; these compounds are taken up by the plant and distributed throughout the tissue as the plant develops. Some of the seed coating ultimately can be washed off the seed and be transported via infiltration to groundwater. In addition to the negative impacts this class of chemicals plays in bee populations, groundwater standards have been proposed for imidachloprid, chlothianidin, and thiamethoxam.

Neonicotinoids are a more recent class of chemical; with the use of these compounds increasing dramatically in the past decade. Because of the lag time between what happens on the land surface and the groundwater quality that reaches wells and streams, we have yet to learn the full extent of neonicotinoids on our water resources. Collecting data on these compounds now provides some baseline regarding occurrence in groundwater accessed by private wells.

Table 2. Summary of common pesticides, PPCPs, and neonicotinoid compounds.

Parameter	Samples	Limit of Detection	Samples with detections		Health value*	Min	Median	Mean	Max
	n	ug/L	n	%	ug/L or parts per billion				
Alachlor OA[1]	24	0.08	0	0		NA	NA	NA	NA
Alachlor ESA[1]	24	0.08	10	42		0.13	0.49	0.53	1.28
Metolachlor OA[1]	24	0.08	2	8		0.12	0.17	0.17	0.22
Metolachlor ESA[1]	24	0.08	21	88		0.12	0.61	0.95	6.01
	n	ng/L	n	%	ng/L or parts per trillion				
Acesulfame[2]	24	5	10	42		5.6	10.8	1,500	13,100
Sucralose[2]	24	25	11	46		27	43	1934	16,100
Caffeine[2]	24	12	3	13		12	12.3	14	18.7
Paraxanthine[2]	24	5	0	0		NA	NA	NA	NA
Carbamazepine[2]	24	2	1	4		7.6	7.6	7.6	7.6
Sulfamethoxazole[2]	24	5	2	8		64	117.5	117.5	171
Acetamiprid[3]	24	1.7	0	0		NA	NA	NA	NA
Clothianidin[3]	24	1.5	4	17	1,000,000	2.5	18.1	18.2	34.1
Dinotefuran[3]	24	0.7	0	0		NA	NA	NA	NA
Imidacloprid[3]	24	2.4	1	4	200	18.7	18.7	18.7	18.7
Thiamethoxam[3]	24	1.5	1	4	1,200,000	47.9	47.9	47.9	47.9

[1]Common pesticides

[2]Pharmaceuticals and personal care products (PPCPs)

[3]Neonicotinoid compounds

*If this column is absent it means that there is no recommended health value available due to low risk or lack of health/toxicity research on those compounds.

Detections of one or more agricultural compounds (common pesticides and neonicotinoids) occurred in 88% (21/24) samples. Metolachlor ESA was the most commonly detected agricultural compound detected. Neonicotinoids were detected much less frequently and only occurred in samples that also contained Alachlor ESA and/or Metolachlor ESA. Because neonicotinoids are relatively new compounds these detections could point to wells that access young or recently recharged groundwater. Compounds maybe more common as newer water replaces older groundwater within Chippewa County aquifers.

One or more PPCPs were detected in 71% (17/24) of the samples. Sucralose was detected most frequently followed by acesulfame and caffeine; these are widely used or consumed products and we would anticipate detections more frequently then pharmaceuticals which may be used infrequently or only by a few individuals. Because these are compounds that humans routinely consume at higher levels than were detected here, we assume that there is little to no health risk associated. The occurrence of PPCPs compounds does provide evidence that at least a portion of the water is likely being influenced by human wastewater sources. Higher concentrations could indicate a more concentrated flowpath.

Perfluoroalkyl and Polyfluoroalkyl Substances

Perfluoroalkyl and polyfluoroalkyl substances are a class of chemicals that have been used in industrial applications and consumer products since the 1950s. Recent investigations in Wisconsin have shown them to occur in groundwater below or near areas where firefighting foams have been used/discharged, other industrial sites/settings, and near areas where bio-solids have been land spread. Limited information exists on their occurrence in private wells beyond a few key investigations near La Crosse, Marinette, and Dane Counties. For the Chippewa County testing, samples were sent to the Wisconsin State Laboratory of Hygiene where samples were analyzed for 44 different PFAS compounds using EPA Method 537.1.

Detections of one or more PFAS compounds occurred in 17% (4/24) of the samples. One of those samples exceeded the 20 ng/L health value for PFOA. One sample only detected one compound (PFBA) at levels just above the limit of detection. The other three samples that contained PFAS compounds detected between 8 and 11 different compounds. It is important to note that this is a very small number of samples to characterize PFAS occurrence at a county scale. This information does however provide initial baseline data to inform future sampling for PFAS in Chippewa County. For instance, additional sampling near the well that contained PFOA greater than the health value could be beneficial for determining whether more wells might contain levels of concern.

Table 3. Summary of per- and polyfluoroalkyl substances in 2022 Chippewa County sampling efforts.

Parameter	Samples	Limit of Detection	Samples with detections		Health value*	Min	Median	Mean	Max
	n	ng/L	n	%	ng/L	ng/L or parts per trillion			
PFOA	24	0.107	3	13	20	2.94	3.19	8.78	20.20
PFOS	24	0.141	2	8	20	0.17	0.61	0.61	1.04
FOSA	24	0.153	0	0		NA	NA	NA	NA
N-EtFOSA	24	0.686	0	0		NA	NA	NA	NA
N-EtFOSE	24	0.21	0	0		NA	NA	NA	NA
N-EtFOSAA	24	0.21	0	0		NA	NA	NA	NA
Total of 6 above					20				
PFNA	24	0.146	1	4	30	0.19	0.19	0.19	0.19
PFHxS	24	0.14	3	13	40	0.19	1.22	3.21	8.23
HFPO-DA	24	0.19	0	0	300	NA	NA	NA	NA
PFDA	24	0.161	1	4	300	0.149	0.149	0.149	0.149
PFDoA	24	0.268	0	0	500	NA	NA	NA	NA

Table 3. Continued

Parameter	Samples	Limit of Detection	Samples with detections		Health Value*	Min	Median	Mean	Max
	n	ng/L	n	%	ng/L	ng/L or parts per trillion			
DONA	24	0.127	0	0	3,000	NA	NA	NA	NA
PFUnA	24	0.219	0	0	3,000	NA	NA	NA	NA
PFBA	24	0.342	4	17	10,000	1.23	6.35	15.31	47.30
PFTeDA	24	0.173	0	0	10,000	NA	NA	NA	NA
PFHxA	24	0.202	3	13	150,000	0.67	0.91	1.05	1.57
PFBS	24	0.228	3	13	450,000	0.26	2.05	4.77	12.00
PFPeA	24	0.148	3	13		0.26	0.80	0.76	1.22
PFHpA	24	0.148	2	8		0.36	3.42	3.42	6.49
PFTrDA	24	0.191	0	0		NA	NA	NA	NA
PFPrS	24	0.255	1	4		0.46	0.46	0.46	0.46
PFPeS	24	0.134	2	8		0.39	1.41	1.41	2.43
PFHpS	24	0.188	0	0		NA	NA	NA	NA
PFNS	24	0.18	0	0		NA	NA	NA	NA
PFDS	24	0.254	0	0		NA	NA	NA	NA
PFDoS	24	0.393	0	0		NA	NA	NA	NA
PFECHS	24	0.189	0	0		NA	NA	NA	NA
4:2 FTSA	24	0.188	0	0		NA	NA	NA	NA
6:2 FTSA	24	0.269	0	0		NA	NA	NA	NA
8:2 FTSA	24	0.259	0	0		NA	NA	NA	NA
10:2 FTSA	24	0.203	0	0		NA	NA	NA	NA
FPrPA	24	0.247	0	0		NA	NA	NA	NA
FPePA	24	0.383	0	0		NA	NA	NA	NA
FHpPA	24	0.435	1	4		1.11	1.11	1.11	1.11
FHUEA	24	0.285	0	0		NA	NA	NA	NA
FOUEA	24	0.215	0	0		NA	NA	NA	NA
FDUEA	24	0.362	0	0		NA	NA	NA	NA
PFBSA	24	0.427	1	4		1.23	1.23	1.23	1.23
PFHxSA	24	0.478	0	0		NA	NA	NA	NA
N-MeFOSA	24	0.988	0	0		NA	NA	NA	NA
N-MeFOSE	24	0.278	0	0		NA	NA	NA	NA
N-MeFOSAA	24	0.216	0	0		NA	NA	NA	NA
9Cl-PF3ONS	24	0.18	0	0		NA	NA	NA	NA
11Cl-PF3OUdS	24	0.147	0	0		NA	NA	NA	NA

*Health values only listed for those compounds for which WI Department of Health Services has reported a recommended health value. If this column is absent it means that there is no recommended health value available due to a lack of health/toxicity research on those compounds.

“NA” stands for Not Applicable. Compounds that were not detected have no summary statistics to report.

Investigating sources of nitrate and chloride using source tracer data

The majority of samples contained evidence of both agricultural tracers and PPCPs, however some additional data analysis was performed to try and understand the relative contribution of each source to nitrate and chloride concentrations. We investigated nitrate and chloride as they relate to the occurrence of agricultural or PPCPs tracers in well water samples.

What we observed was that nitrate-nitrogen concentrations were generally greater in samples associated with partial or only agricultural influence (Table 4). Meanwhile, chloride concentrations were greater in samples associated partially or only to PPCPs compounds.

Table 4. Summary of nitrate-nitrogen and chloride data by nitrate source tracers. Standard deviation in parentheses.

		Nitrate-Nitrogen	Chloride
	n	**mg/L**	
Agricultural Tracers[1]	21	9.8(5.1)	20.4(13.8)
PPCPs[2]	17	8.8(5.4)	35.8(60.1)
Only Agricultural Tracers[3]	6	10.0(5.2)	19.2(14.9)
Only PPCP[4]	3	4.7(5.2)	105(137)

[1]Samples that detected one or more common pesticides or neonicotinoids
[2]Samples that detected one or more PPCP compounds
[3]Samples that detected one or more common pesticides or neonicotinoids but no detects of PPCP compounds
[4]Samples that detected one or more PPCP compounds but no detects of pesticides or neonicotinoids

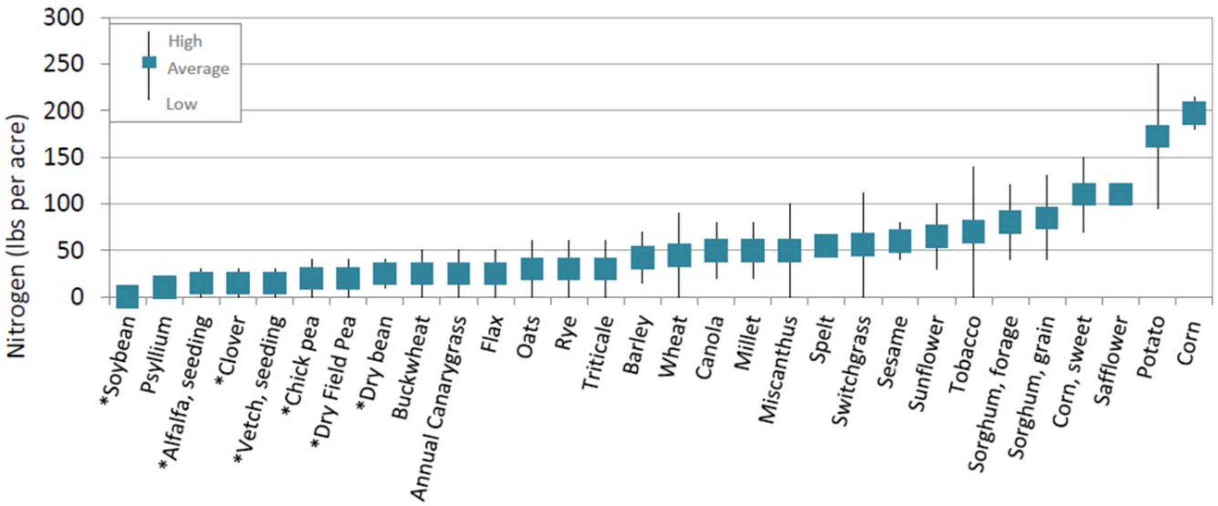
Both agricultural activities and septic systems drainfields contribute to elevated nitrate concentrations in groundwater, however, as the data above shows, higher nitrate concentrations are often associated with agricultural activity. Higher levels of chloride appear to be associated with residential development where septic systems and road salt impacts are likely to be more evident. More data would be beneficial to support these findings, however the chemical source tracing data summarized here does support current and previous statistical models that have investigated relationships to various land cover and geologic factors.

As mentioned previously, nitrate and chloride are both useful for understanding the degree to which land-use is impacting groundwater quality. Background or natural levels of nitrate-nitrogen are generally less than 1 mg/L, while background levels of chloride would be expected to be less than 10 mg/L.

Agriculture and nitrate

Starting with nitrate first, we know that various factors influence the amount of nitrate that gets into groundwater. This is because the amount of nitrogen utilized on agricultural fields is in much greater quantities than what we would anticipate from human wastewater. And while significant amounts of nitrogen are taken up by crops, not all of the nitrogen applied as fertilizer/manure is removed via the harvested portion of the plant. Heavy rains during the growing season can push nitrate past the reach of plant roots. Meanwhile, any nitrate left over in the soil at harvest time is likely to leach into groundwater with autumn rains and/or spring snow melt.

Figure 15. Nitrogen fertilizer recommendations (in pounds per acre) for various crops growing in Wisconsin. Asterisk (*) indicates legumes. (Source: Nutrient application guidelines for field, vegetable, and fruit crops in Wisconsin. A2809. Laboski and Peters, 2012. University of Wisconsin-Madison).



Nitrate leaching is largely a function of nitrogen fertilizer/manure inputs and the amount of nitrogen removed via harvested material. As a result, nitrate leaching estimates can be made when you know how much fertilizer was applied and the yield that was obtained on that field (Meisinger and Randall, 1991).

This budget approach often reveals that even fields with nutrient management plans are capable of leaching nitrate-nitrogen that is in excess of what is considered suitable for drinking water (i.e. 10 mg/L). Depending on the soil type and other factors, it’s estimated that 20-50% of the nitrogen applied as fertilizer may leach past the root zone into groundwater (Shrethsa et al., 2023). Applying fertilizer at the right rate, time, source, place will maximize profitability and minimize excessive losses of nitrogen to groundwater; however additional practices are often necessary if looking to improve water quality in areas with susceptible soils and geology.

Figure 16. Illustration of the relationship between crop type, the susceptibility of groundwater to contaminants such as nitrate, and the amount of nitrate that leaches under various scenarios. The plane represents the baseline level of nitrate leaching expected as the result of what are generally considered to be acceptable management practices.

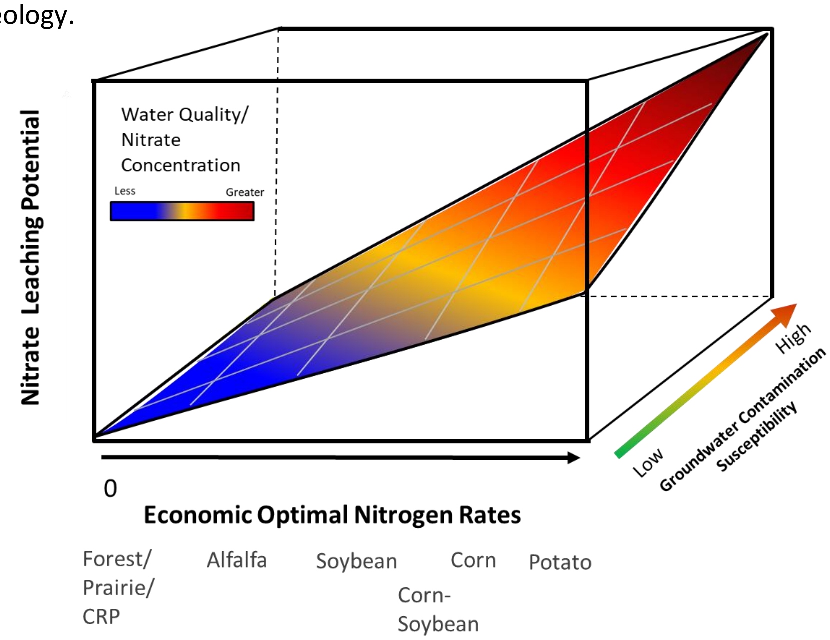
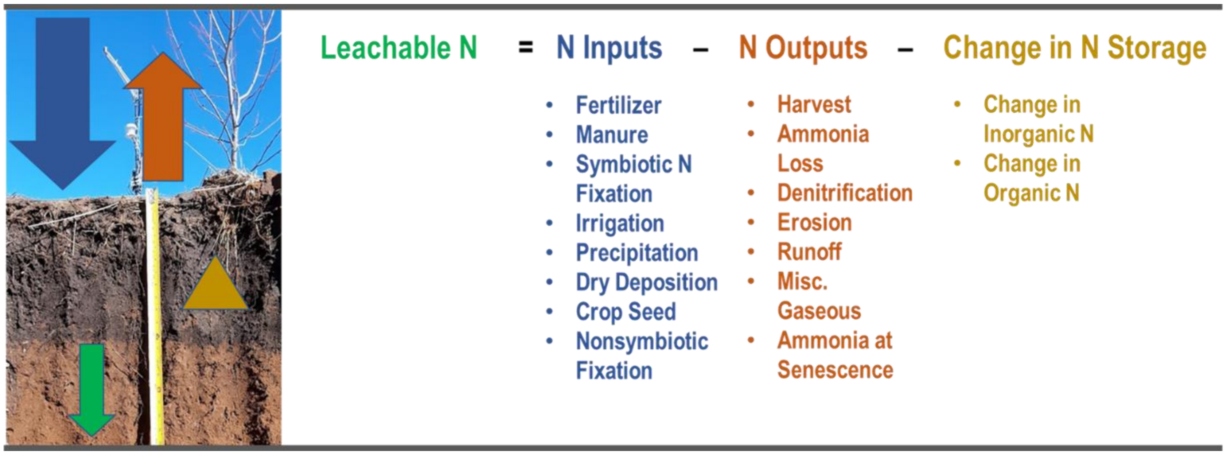


Figure 17. Potential leachable N (nitrate) can be calculated using a nitrogen budget approach. If various inputs are known and a reasonable estimate of yield can be made, estimating leachable nitrogen can be performed.



Minimizing nitrate leaching to groundwater fundamentally requires that we think about how best to maintain nitrogen in the top one to two feet of soil where plants are most likely to capture it. If nitrate in groundwater is an issue, improvements to groundwater quality below agricultural systems will only be observed when the following are achieved: 1) increasing yield with the same amount of nitrogen, 2) achieve the same yield with less nitrogen, 3) increase long-term soil organic matter levels which helps to store organic nitrogen in the soil and also increase water holding capacity, 4) temporary storage of nitrogen by cover crops that can be used to reduce nitrogen inputs to the next year's crop.

While significant nitrate can be lost during the growing season, particularly during wet years, leaching post-harvest through the following planting season may represent the majority of leaching losses during moderate to dry years (Masarik et al., 2014). Therefore, multiple strategies that reduce nitrogen fertilizer inputs, make nitrogen available when the plant needs it most, combined with additional activities that encourage active root systems or minimize decomposition during the fall and spring should all be explored.

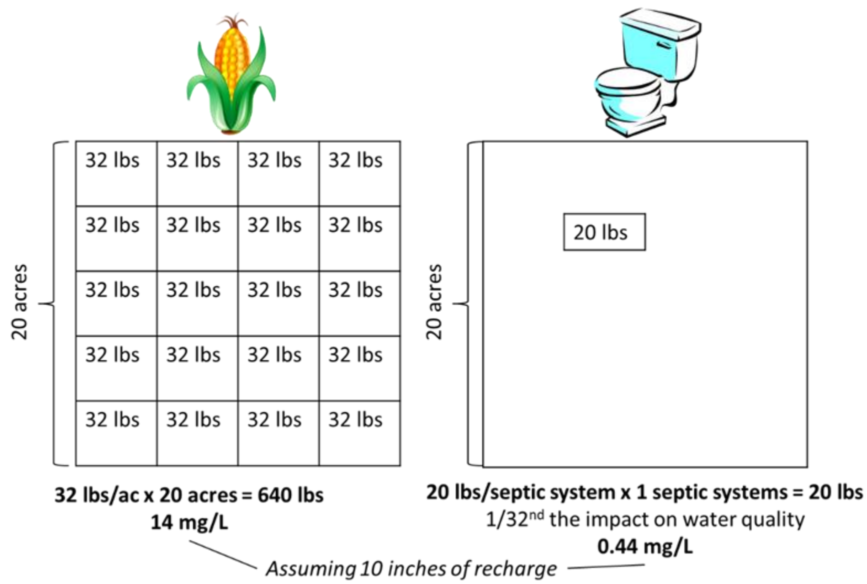
The following ideas are actionable activities that will help to reduce nitrate concentrations in groundwater and nearby wells:

- You may not need as much nitrogen fertilizer as you think, conduct your own on-farm rate trials to develop customized fertilizer response curves for your farm.
- Utilize conservation incentive programs to take marginal land or unprofitable parts of fields out of production.
- Diversify cropping systems to include less nitrogen intensive crops in the rotation (see Figure 15 for list of crops and nitrogen recommendations).
- Explore and experiment with the use of cover crops, intercropping, perennial cropping systems, or managed grazing to reduce nitrate losses to groundwater. Perennial cover, particularly diverse cover with multilayered root systems will have the greatest potential to reduce nitrate losses.

Septic systems and nitrate

Septic systems are designed to deactivate pathogens from wastewater and filter out other potential pollutants such as phosphorus, however other dissolved constituents like nitrate/chloride pass easily through drainfields into groundwater below. It is important to point out here that even properly functioning septic systems are contributors of nitrate to groundwater, although in traditional rural development the degree of influence is much less than agricultural systems.

Figure 18. Illustration of nitrogen leaching estimates for a twenty-acre agricultural field of corn (left) versus a twenty-acre parcel with one septic system drainfield for a 3 person household (right).



We can use a nitrogen budget approach to again understand why this might be the case. On average a septic system would be expected to leach between 16-20 pounds of nitrogen per year (EPA 625/R-00/008). If we compare this to an agricultural field that leaches 32 pounds per acre (Masarik, 2014) they may not seem that different. However, traditional rural development often has one septic system on a large parcel where the impact of nitrate leaching is offset by the rest of the property acreage (Figure 18). In some instances the impacts may be more evident; for instance if a well is directly downgradient of a septic drainfield or there are large numbers of drainfields in close proximity to one another.

When the density of septic systems in a small area increases, there is a greater potential for higher nitrate concentrations as the result of increased nitrate loss. The smaller the lot size the greater potential impact that will result from septic systems in close proximity to one another, not only with respect to nitrate but also other compounds associated with household wastewater (ex. pharmaceuticals, personal care products, PFAS, etc.). For the example in Figure 18, we'd estimate that lot sizes of 0.6 acres in a 20 acre development with septic systems would essentially have the same impact as a 20 acre agricultural field leaching 32 lbs of nitrogen per acre.

Figure 19. (Right) Picture of subdivision with homes served by private wells and septic system drainfields. Groundwater flow direction is from upper-left to lower-right. Orange shapes illustrate hypothetical plumes paths downgradient of drainfields.

Modeling Nitrate and Chloride Risk

Wells selected using the gridded nitrate prediction model (Figure 1) for NSI sampling were compared to the annual CTM sampling results. The CTM results are intended to be a random representative sample of Chippewa County well water quality, while the NSI dataset is from areas specifically thought to have elevated nitrate levels or risk. Results from comparing the datasets (Table 5) are encouraging and show that simple models of readily available datasets (ex. land cover, geology, soils, well construction, etc.) are able to do a relatively good job identifying areas where nitrate is more likely to occur. Nitrate concentrations as well as the percent of samples where nitrate-nitrogen exceeded various thresholds were greater in NSI samples than what would have been expected from random sampling or the percentages observed by CTM samples.

Table 5. Well testing data from 2022 which compares Chippewa Trend Monitoring (CTM) wells to those sampled as part of the Nitrate Source Investigation (NSI) selection process. Standard deviation of mean concentration found in parentheses.

	Nitrate-Nitrogen				
	Samples	Mean Concentration	Greater than 2 mg/L	Greater than 5 mg/L	Greater than 10 mg/L
	n	mg/L	------------------%-------------------		
CTM	151	4.7(4.4)	62	40	12
NSI	142	7.6(5.5)	82	59	34

The modeled data does mean that low nitrate water cannot be obtained in areas of high risk. No model is perfect; factors such as groundwater flow direction, the way in which agricultural fields are managed, errors or interpolations of datasets that do not match real-world conditions all can contribute to errors in the model. These are some of the reasons why simple models such as these cannot predict perfectly which wells will be elevated. We can however, continue to build on existing datasets to further refine these models for future use and improve the reliability.

Ordinary least squares (OLS) regression was used to further refine the nitrate risk predictive model for Chippewa County. For this current model, additional data from recent nitrate-nitrogen data from Chippewa County well testing efforts was modeled as a function of various land cover, soils, and geologic concerns at a parcel level rather than a 1 square mile grid cell. The percent of agricultural land cover within a 500 meter buffer around the well ($p<0.001$) and soil drainage classification ($p<0.001$) were determined to be significant predictors and used to develop a multiple linear regression model of nitrate. The same attributes were determined for the centroid of every parcel in Chippewa County. The model was then applied to the data for each parcel and is displayed as nitrate risk or likelihood of detecting nitrate in a well from low-medium-high (Figure 20).

Figure 20. Nitrate risk assessment of each land parcel in Chippewa County.

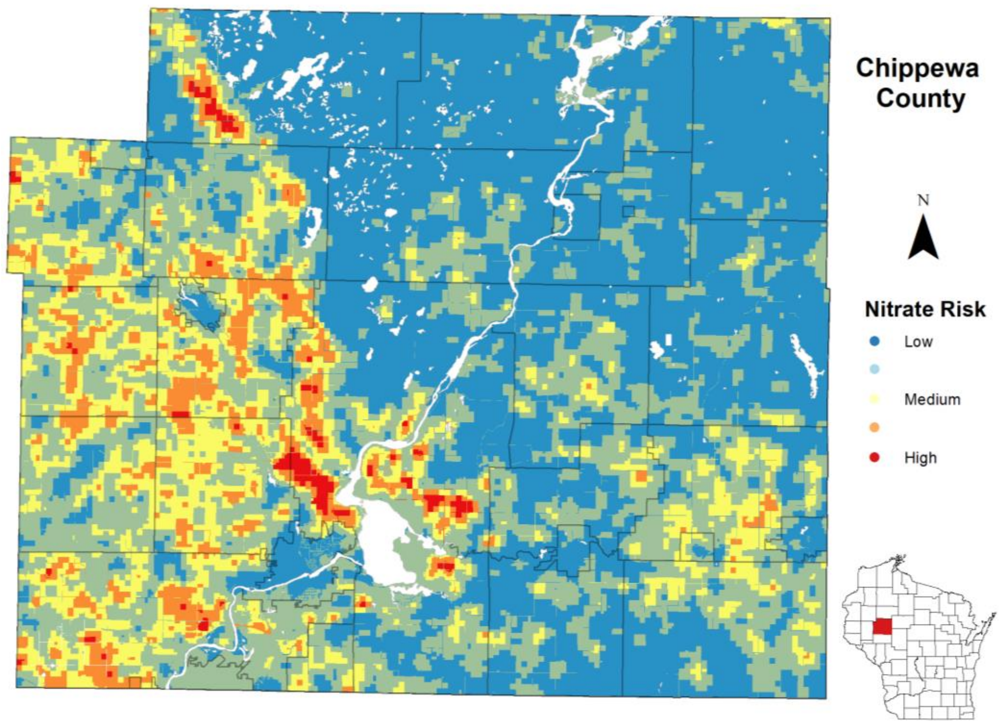
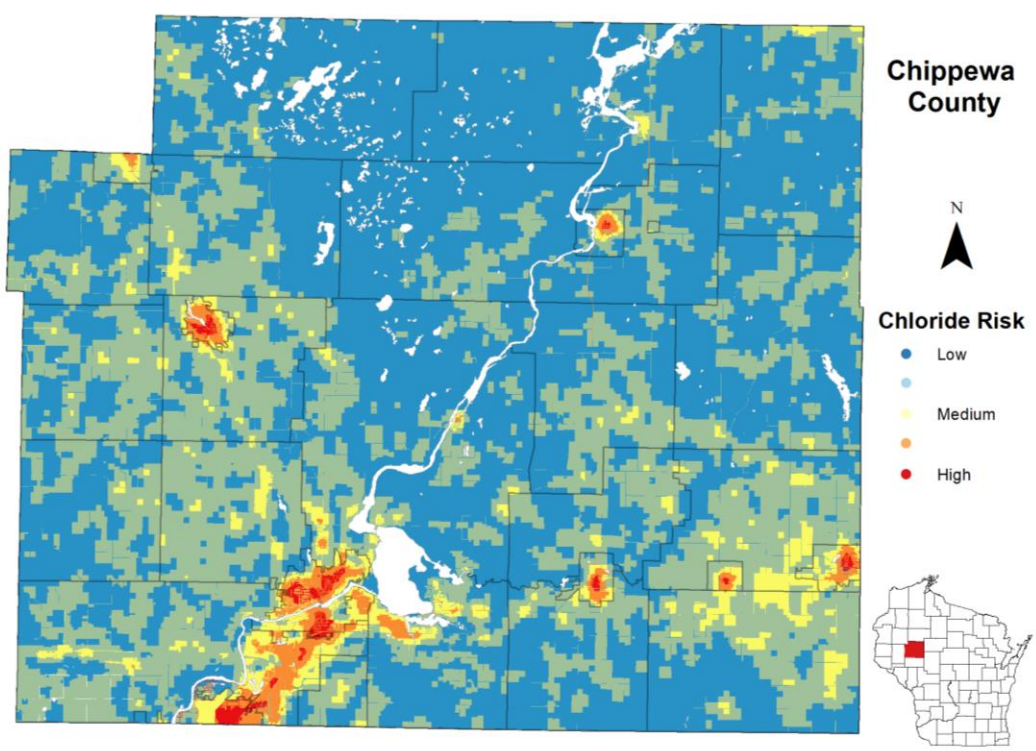


Figure 21. Chloride risk assessment of each land parcel in Chippewa County.



The same approach was used to model chloride risk. When constructing the chloride model percent of agricultural land cover within a 500 m buffer around a well ($p<0.001$), soil drainage classification ($p<0.001$), and the percent of urban land cover within a 500 m buffer were all significant ($p<0.001$). These attributes were obtained for each parcel centroid in Chippewa County. The model was then applied to the data for each parcel to determine the chloride risk or likelihood of finding elevated chloride in a well from low-medium-high (Figure 21).

Conclusions

This report summarizes well testing performed in Chippewa County in 2022. Wells representative of the diverse land cover, soils, and geology that are tested annually as part of a Chippewa Trend Monitoring project were sampled and compared to wells selected from areas predicted to have elevated nitrate concentrations as part of a nitrate source investigation (NSI). A subset of wells with elevated nitrate from NSI wells were also samples for perfluoroalkyl and polyfluoroalkyl substances, neonicotinoids, pharmaceuticals/personal care products, and other common pesticides. Results from this project show that using a predictive model of nitrate concentration to select wells resulted in a significantly greater percentage of wells with elevated nitrate than were measured in the CTM dataset. Analysis of limited source tracer data suggested that higher levels of nitrate are expected from wells influenced by agricultural activity while elevated chloride is associated with developmemt (i.e. septics systems / impervious areas receiving road salt). The results of this study provide baseline data on existing as well as emerging contaminants such as PFAS and neonicotinoids. The information can be used to better assist rural landowners with well water testing and more effectively incentivize or prioritize areas for conservation improvements (i.e. cover crops, nitrate optimization programs, managed grazing, conservation reserve programs, etc.).

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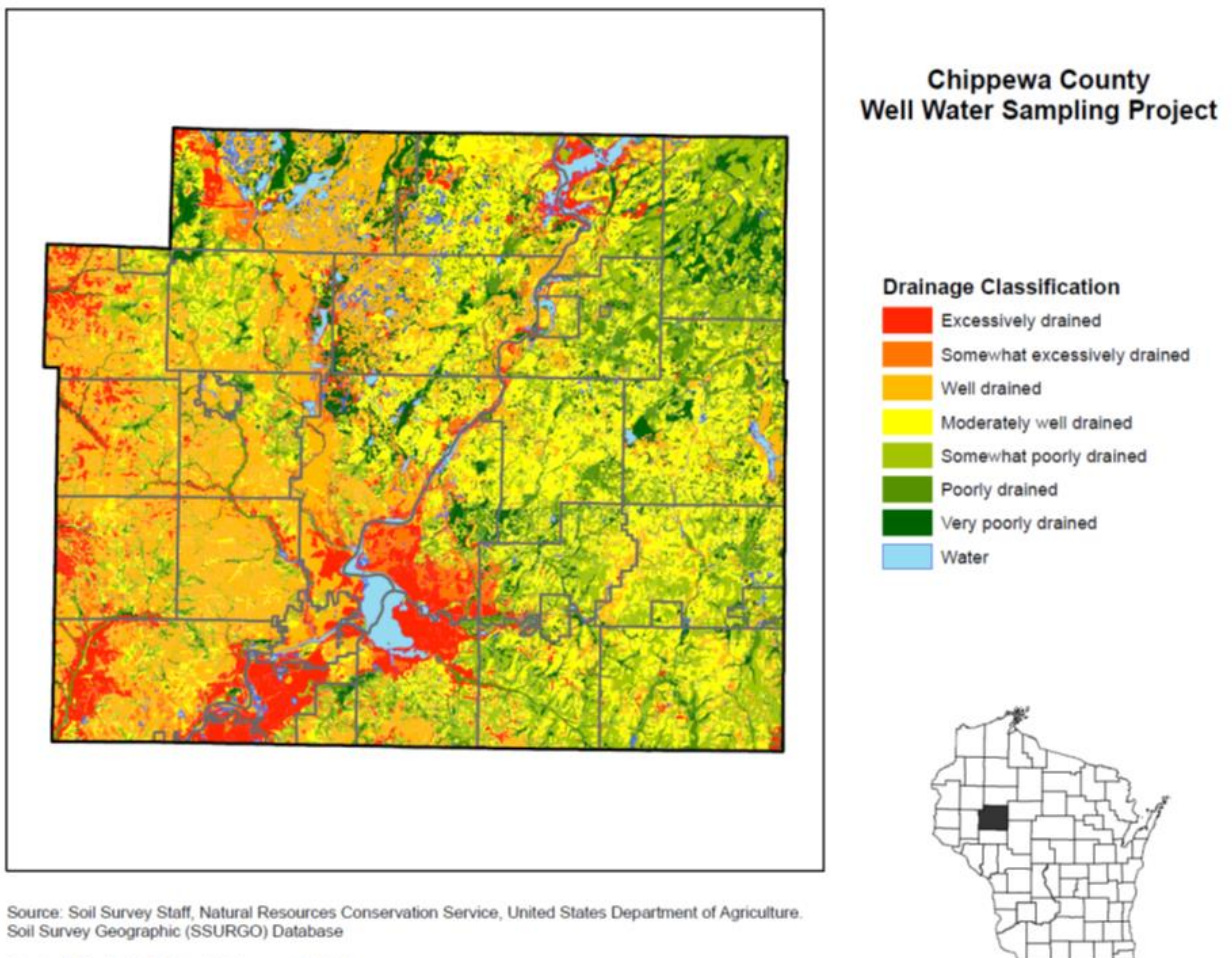
Appendix A

Map of soil drainage used to calculate weighted drainage rank. Weighted drainage rank is a weighted average of soil drainage classification using the area of each drainage classification within a 500 m buffer of the well multiplied by a number (1 very poorly drained to 7 for Excessively drained) and divided by the total area of the 500 meter buffer.



Source: Soil Survey Staff, Natural Resources Conservation Service, United States Department of Agriculture. Soil Survey Geographic (SSURGO) Database

Created: Elizabeth Belmont. February 28, 2022

Appendix B

Agricultural land cover of Chippewa County was summarized within a 500 meter buffer of each well. The percentage of agricultural land was used in the ordinary least squares regression model for determination and prediction of nitrate risk.