2022 Targeted Sampling Program

ANNUAL REPORT

Wisconsin Department of Agriculture, Trade and Consumer Protection
Agricultural Resource Management Division
Environmental Quality Unit

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Introduction

In 2022, the Wisconsin Department of Agriculture, Trade and Consumer Protection (DATCP) continued the Targeted Sampling Program to document the effect of pesticide use on selected private potable wells in Wisconsin. In total, 81 wells located in Door, Oneida, and Rock counties were sampled between July and November. This document provides a narrative of the activities and summarizes the analytical data of the DATCP 2022 Targeted Sampling Program. It is anticipated that the program will be paused in 2023 and resume in 2024 due to the 2023 Statewide survey.

A compilation of acronyms and definitions used throughout this document is provided in Appendix A – Acronyms and Definitions.

Purpose of Targeted Sampling

Agriculture contributes about $104.8 billion annually to Wisconsin's economy (Wisconsin Department of Agriculture, Trade and Consumer Protection, 2023). Growers use millions of pounds of pesticides and millions of tons of fertilizers annually to grow a wide variety of crops. Through the Targeted Sampling Program, DATCP utilizes a targeted approach to select private potable wells that are at risk of being impacted by agricultural chemicals. DATCP Targeted Sampling Program helps the agency meet its statutory obligation to monitor groundwater. Wisconsin's groundwater law, Chapter 160, requires regulatory agencies to sample and monitor groundwater for substances that have a reasonable probability of entering the groundwater resources of the state. The regulation applies to activities such as waste disposal, agricultural practices, and industrial activities that have the potential to contaminate groundwater. Under this regulation, agencies are required to determine whether Preventive Action Limits (PALs) or Enforcement Standards (ESs)[1] of a substance in groundwater, have been exceeded at a specific location, depth, or distance from a facility, activity, or practice. The statute further specifies that agencies develop monitoring plans that include provisions for conducting four types of monitoring (Wis. Stats., Ch. §160.05 and §160.27):

- Problem assessment monitoring, to detect substances in the groundwater and to assess the significance of the concentrations of the detected substances;
- Regulatory monitoring, to determine if PALs or ESs are attained or exceeded and to obtain information necessary for the implementation of responses for specific sites;
- At-risk monitoring, to define and sample at-risk potable wells in areas where substances are detected in the groundwater or where PALs or ESs are attained or exceeded; and
- Management practice monitoring, to assure practices are within compliance regulations.

Program Approach and Selection Criteria

The potential for agricultural chemicals to affect groundwater quality at any particular location depends on site-specific conditions. Criteria used to select study areas for the Targeted Sampling Program testing focus on conditions that make groundwater prone to contamination. These criteria vary from year to year and between study areas.

Criteria used for study area selection include:

- Areas susceptible to groundwater contamination due to geology (i.e., sandy soils with shallow groundwater, shallow depth to bedrock, or karst features);
- Areas where prior testing by others (county government, university, private owner, etc.) indicates concerning concentrations of nitrate, pesticides, or other compounds;
- Areas in or near an existing atrazine prohibition area (PA), or areas where other restrictions on pesticide use have occurred out of concern for groundwater protection;

[1] An essential part of Wisconsin's groundwater protection laws was the creation of water quality standards for different substances, outlined in Wis. Admin. Code Chapter NR 140. The Wisconsin Department of Natural Resources sets standards for substances of public health concern based on recommendations from the Wisconsin Department of Health Services. The groundwater standards have two components, an enforcement standard (ES) and preventative action limit (PAL). The ES is a concentration that, if exceeded requires intervention from the appropriate authority. The PAL is a percentage of the ES; 10% of the ES for carcinogenic, mutagenic, or teratogenic properties, and 20% of the ES for the remaining substances. The intention of the PAL is for it to act as a trigger for intervention before a pollutant becomes a serious risk to public health or the environment.

- Areas with little to no crop rotation (e.g. corn, soybeans, potatoes grown year after year) and a high likelihood of repetitive pesticide use in the area;
- Areas where the grown crops require extensive chemical or fertilizer inputs and/or irrigation; and
- Areas where pesticides with characteristics of high mobility in soil and resistance to degradation are used.

Planning for the Targeted Sampling Program is usually performed early in the year, with DATCP staff and management agreeing on the number of samples to be collected for the coming year. Program goals vary from year to year. In addition to assessing groundwater quality in areas of potential concern for groundwater contamination, DATCP also investigates groundwater quality trends over time by resampling wells about every five years. Relationships between groundwater quality observations and well construction properties, such as well depth, casing depth, well age, and geologic formation at the screen, are also explored through analysis of data collected through the program.

Permission to sample private potable wells is generally obtained in advance through letters and permission slips mailed to the well owners. Once the sample is collected and analyzed through the DATCP Bureau of Laboratory Services (BLS), DATCP hydrogeologists provide homeowners with a copy of their analytical results within 10 days of receiving the data from BLS. DATCP staff assist with the interpretation of results and in resolving any water contamination issues. Whenever a concentration of a certain compound exceeds an ES or a Wisconsin Department of Health Services (DHS) Drinking Water Health Advisory, the owner receives drinking water advisory information.

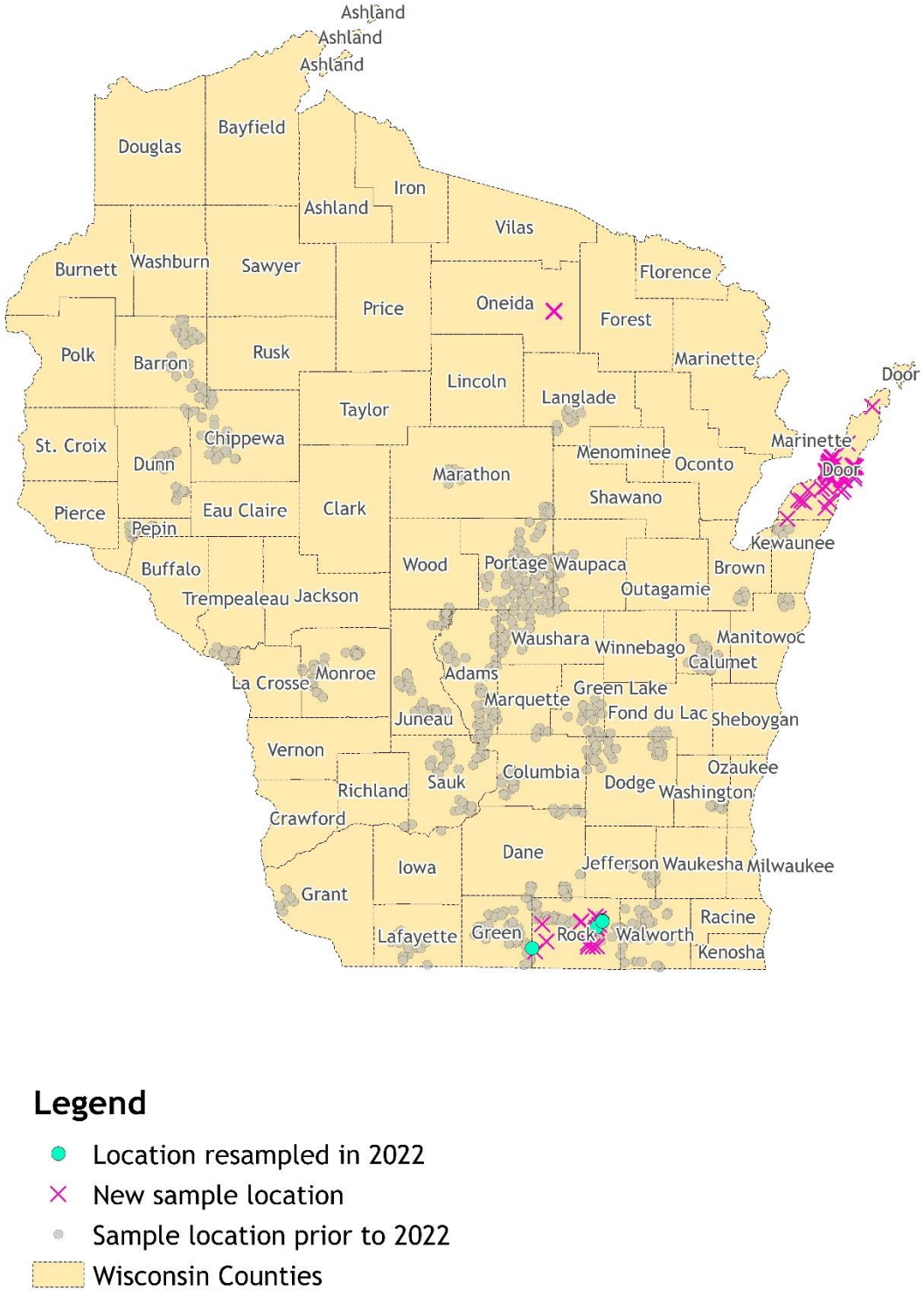
2022 PROGRAM SPECIFICS

In 2022, DATCP reached out to 116 homeowners inviting them to participate in the Targeted Sampling Program. Ultimately, 81 homeowners agreed to have their private potable wells tested. Among these participants, 77 homeowners had wells that had not previously been examined under the program while four homeowners had already undergone sampling in 2017 or 2018 and had granted approvals for further testing. Program staff collected 81 samples from private potable wells in agricultural areas across three counties between July and November 2022. Specifically, 54 samples were collected in Door County, seven samples in Oneida County, and 20 samples in Rock County. The number of samples collected and their locations in each county are shown in Table 1. The sampling locations of 2022, and those sampled in previous years, are shown on Figure 1. It is noteworthy that while four private potable wells in Rock County were part of past sampling efforts, Door and Oneida County wells were included in the program for the first time in 2022.

Table 1. 2022 Targeted Sampling Program Sample Location Summary

County	Municipalities	Number of Samples
Door	Brussels, Egg Harbor, Forestville, Gardner, Liberty Grove, Nasewaupee, Sevastopol, Sturgeon Bay, Union	54
Oneida	Stella	7
Rock	Avon, Harmony, Janesville, La Prairie, Magnolia, Spring Valley	20

Figure 1. 2022 Targeted Sampling Program Well Locations



Notes: *Figure 1 shows locations for all 81 Targeted Program wells tested in 2022. Wells that were sampled through the Targeted Sampling Program in 2022 for the first time are marked with a cross. Wells that were sampled in 2017 or 2018 in addition to 2022 through the Targeted Sampling Program are marked with a light green circle. Historic Targeted sampling locations from all samples collected since 2010 are marked with a grey circle.*

Sample Collection and Analysis

Sample collection followed Wisconsin Department of Natural Resources (DNR) and DATCP standard opertating procedures (Wisconsin Department of Natural Resources, 1996). Groundwater samples were collected from either an outside spigot or a valve/sampling port at the water system pressure tank to ensure the collection of raw and untreated water (i.e. water not passing through a water treatment system). Whenever a sample was collected from an outside spigot, the water ran through a pumping cycle to ensure the water was fresh from the underground water supply. Groundwater samples were collected by directly filling one laboratory-provided one-liter amber-colored glass sampling bottle at the designated sampling location. Bottles were then placed in a cooler on ice along with a properly completed sample collection form. Packages were hand delivered to the DATCP Bureau of Laboratory Services (BLS) for pesticide and nitrogen analyses. A summary of the analytical data for the 2022 Targeted Sampling Program is included in Appendix B. Detailed analytical reports are available upon request.

BLS performed groundwater analytical testing using GC/MS/MS and LC/MS/MS methods in accordance with ISO 17025 accreditation standards. Each sample was tested for 106 pesticides or pesticide metabolites, and nitrate plus nitrite as nitrogen (N). Table B 1 of Appendix B lists the parameters and corresponding laboratory reporting limits. The laboratory reporting limit is the minimum analyte concentration that can be reliably quantified and reported by the laboratory. If the concentration of a certain compound is reported to be less than the respective laboratory reporting limit, we consider the compound ***not detected*** in the water sample. If the concentration of a certain compound is reported to be greater than the respective laboratory reporting limit, we consider the compound ***detected*** in the water sample. We are unable to determine if the water samples contain other compounds than those listed in Table B 1 of Appendix B.

Results

A total of 81 groundwater samples were collected and submitted for chemical analysis as a part of the DATCP's 2022 Targeted Sampling Program. A full listing of compounds analyzed and compounds' concentrations is included in Table B 1 of Appendix B along with Wisconsin's groundwater quality standards referencing both Wisconsin Administrative Code (Wis. Admin. Code) ch. NR 140 PALs and ESs, and DHS Drinking Water Health Advisories.

SUMMARY

Below is a summary of the sampling results, followed by a detailed narrative for the 2022 data. For a more comprehensive understanding of the compounds detected, the range of concentrations, and exceedances of established groundwater standards, please refer to Table 2.

Detections

Detected compounds and respective detection rates[2] for the 2022 Targeted Sampling Program are shown on Figure 2.

- Of the 106 pesticide analytes included in the laboratory testing methods, 19 were detected in the 2022 Targeted Sampling Program data. Detections include seven herbicides, nine herbicide metabolites, and three insecticides.
- No nitrate or pesticide compounds were detected in five of the 81 samples collected.
- Nitrate was detected in 75 samples or 92.6% of the samples.
- One or more pesticide compounds were detected in 71 samples or 87.6% of the samples.
- The highest number of pesticides detected in a single sample was eight.
- Metolachlor Ethane Sulfonic Acid (ESA) was the most detected pesticide compound (59.3% detection rate).
- The second most detected compound overall was diamino atrazine (44.4% detection rate).
- De-ethyl atrazine was the third most detected compound (28.4% detection rate).

[2] The detection rate (%) is calculated as follow: $\frac{number\ of\ detects}{total\ number\ of\ samples}\ x\ 100$

- Atrazine Total Chlorinated Residue (TCR), i.e. the sum of atrazine parent material and its breakdown products (de-ethyl atrazine, de-isopropyl atrazine, and diamino atrazine), was detected in 59.3% of the samples collected.
- At least one neonicotinoid compound was detected in 22 samples or 27.2% of the samples. Clothianidin was the most frequently detected neonicotinoid compound.

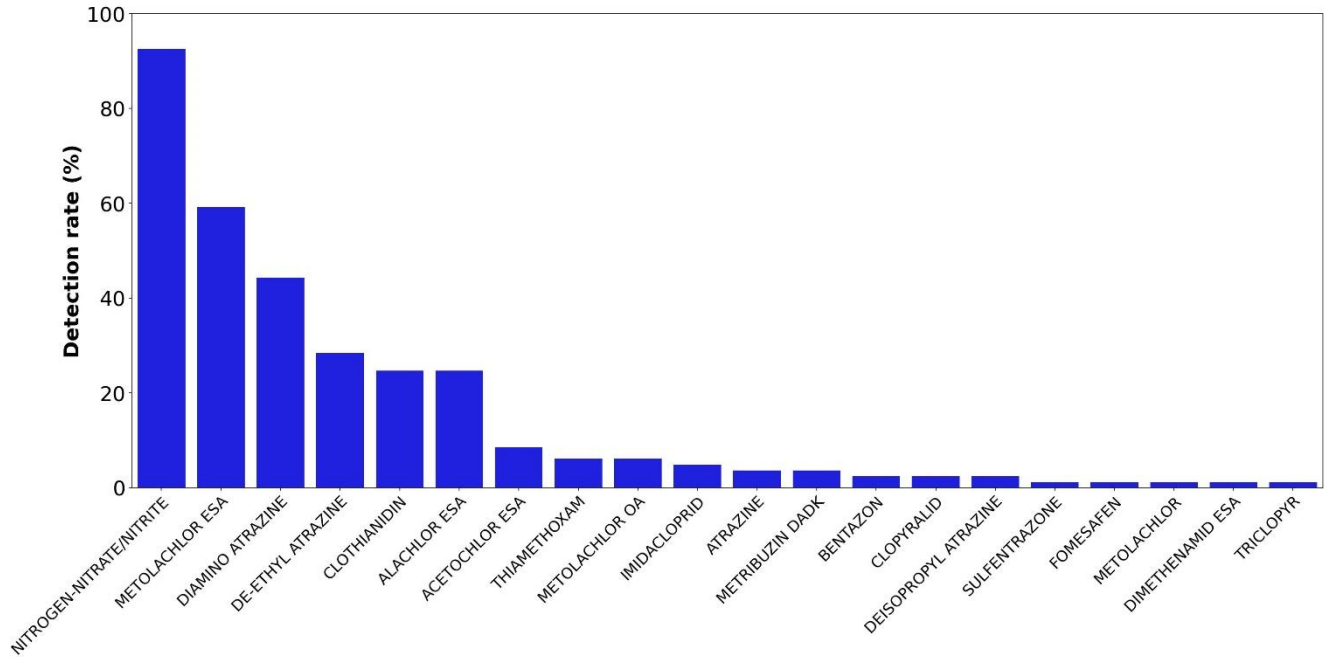
Table 2. Summary of compounds detected in 2022 DATCP Targeted Sampling Program

Compound Detected	*Range Detected (µg/L or mg/L for nitrate plus nitrite)*	*Detections*				*PAL / ES*	*DWHA*
		Total	*>=PAL*	*>=ES*	*>=DWHA*		
Nitrate plus nitrite as N	1.38 - 32.7	*75*	*73*	*21*	---	*2 / 10*	---
Acetochlor ESA	0.0621 - 0.211	*7*	*0*	*0*	---	*46 / 230*	---
Acetochlor Metabolites	0.0621 - 0.211	7	0	0	---	46 / 230	---
Alachlor ESA	0.0802 - 3.29	20	0	0	---	4 / 20	---
Atrazine TCR	0.0507 - 1.1349	43	14	0	---	0.3 / 3.0	---
Atrazine	0.0608 - 0.131	3	0	0	---	0.3 / 3.0	---
De-Ethyl Atrazine	0.0507 - 0.345	23	2	0	---	0.3 / 3.0	---
Deisopropyl Atrazine	0.0571 - 0.0984	2	0	0	---	0.3 / 3.0	---
Diamino Atrazine	0.154 - 0.672	36	10	0	---	0.3 / 3.0	-
Bentazon	0.085 - 1.8	2	0	0	---	60 / 300	---
Clopyralid	0.131 - 0.38	2	---	---	---	---	---
Clothianidin	0.01 - 0.599	20	---	---	0	---	1,000
Dimethenamid ESA	0.0596	1	---	---	---	---	---
Fomesafen	0.276	1	---	---	0	---	25
Imidacloprid	0.0481 - 0.0869	4	---	---	0	---	0.2
Metolachlor	0.0549	1	0	0	---	10 / 100	---
Metolachlor ESA	0.0523 - 13.1	48	0	0	---	260/1,300	---
Metolachlor OA or OXA	0.297 - 5.94	5	0	0	---	260 / 1,300	---
Metolachlor Metabolites	0.0523 - 17.14	48	0	0	---	260 / 1,300	
Metribuzin DADK	0.464 - 0.94	3	---	---	---	---	---
Sulfentrazone	0.194	1	---	---	0	---	1,000
Thiamethoxam	0.0222 - 1.01	5	---	---	0	---	120
Triclopyr	0.0774	1	---	---	---	---	--

Notes: Units: Nitrogen = mg/L (milligrams per liter, equivalent to parts per million) and Pesticides = µg/L (micrograms per liter, equivalent to parts per billion).

--- Standard not established.
Acetlachlor Metabolites = Sum of Acetochlor ESA and Acetochlor OA
DADK Desaminodiketo
DWHA Wisconsin Department of Health Services Drinking Water Health Advisory
ES Enforcement Standard as defined in Wisconsin Administrative Code Chapter NR 140.
ESA Ethanesulonic acid
OA Oxanilic acid
Metolachlor Metabolites = Sum of Metolachlor ESA and Metolachlor OA
PAL Preventive Action Limit as defined in Wisconsin Administrative Code Chapter NR 140.
TCR Total Chlorinated Residues of atrazine. It is the sum of atrazine (parent material) and its three metabolites (de-ethyl, deisopropyl, and diamino atrazine).

Figure 2. Compounds detected through the 2022 Targeted Sampling Program and respective detection rates



Notes: *On the x-axis, the list of compounds detected, i.e. found with concentrations greater than laboratory reporting limits. On the y-axis, the detection rate in percentage for each detected compound. The most frequently detected compound was nitrate plus nitrate as N, followed by metolachlor ESA and diamino atrazine.*

Exceedances of Drinking Water Standards

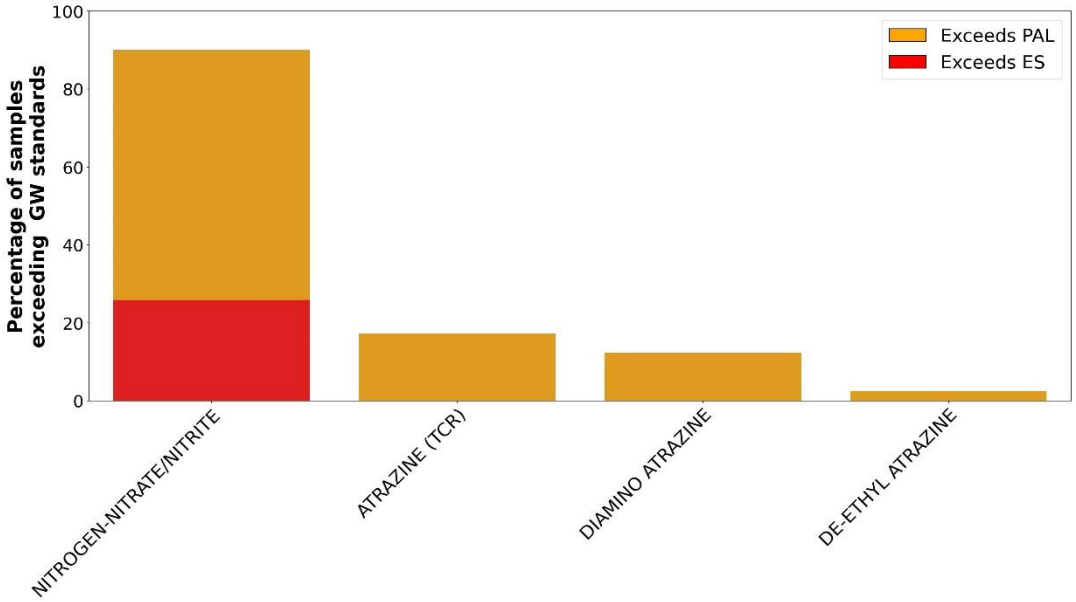
Compounds exceeding groundwater standards and respective percentage of exceedances for the 2022 Targeted Sampling Program are shown on Figure 3.

- Nitrate was detected in exceedance of the Wis. Admin. Code ch. NR 140 PAL of 2 milligram per liter (mg/L) in 75 samples (90.1%)
- Nitrate was detected in exceedance of the Wis. Admin. Code ch. NR 140 ES of 10 mg/L in 21 samples (25.9%)

No pesticide analytes were detected at a concentration exceeding respective Wis. Admin. Code ch. NR 140 ESs or DHS Drinking Water Health Advisories (DWHAs). PAL exceedances are as follows:

- Atrazine TCR was detected in exceedance of the Wis. Admin. Code ch. NR 140 PAL of 0.3 microgram per liter (µg/L) in 14 samples (17.3%)
- Diamino atrazine was detected in exceedance of the Wis. Admin. Code ch. NR 140 PAL of 0.3 microgram per liter (µg/L) in 10 samples (12.3%)
- De-ethyl atrazine was detected in exceedance of the Wis. Admin. Code ch. NR 140 PAL of 0.3 microgram per liter (µg/L) in two samples (2.5%)

Figure 3. Compounds exceeding the Wis. Admin. Code ch. NR 140 Preventive Action Limit (PAL), or Wis. Admin. Code ch. NR 140 Enforcement Standard (ES) and respective exceedances rates

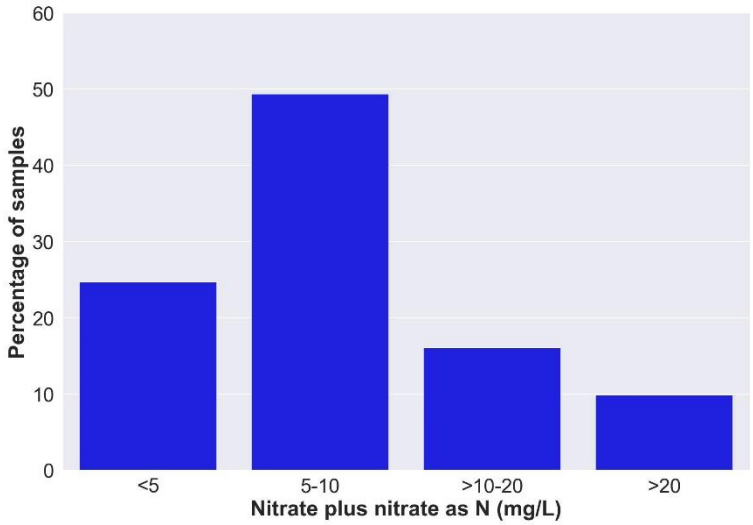


NITROGEN

Nitrate plus nitrite as N was detected in 92.6% of samples collected through the 2022 DATCP Targeted Sampling Program. Nitrogen occurrence data is summarized below and shown on Figure 4.

- < 5 mg/L: 20 samples (24.7%)
- 5 to 10 mg/L: 40 wells (49.4%)
- > 10 to 20 mg/L: 13 wells (16%)
- > 20 mg/L: eight wells (9.9%)

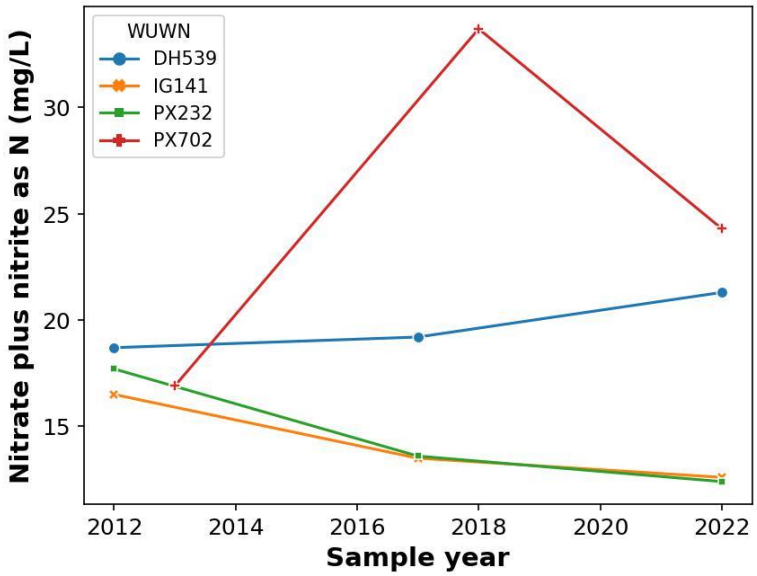
Figure 4. Nitrate plus nitrite as N occurrence data



The PAL of 2 mg/L and the ES of 10 mg/L for nitrate plus nitrite as N was exceeded in 90.5% and 25.9% of the samples, respectively. The percentage of samples (and wells) exceeding the ES is higher than results from the 2017 statewide sampling survey. In that random survey, only 8% of wells sampled exceeded the ES for nitrogen (Wisconsin Department of Agriculture & United States Department of Agriculture, 2017). A greater exceedance rate was expected for the DATCP Targeted Sampling Program data because it is a biased method of sampling for pesticides and nitrogen.

As mentioned in the 2022 Program Specifics section, four wells in Rock County were sampled for the 2022 Targeted Sampling Program were previously sampled. The observed nitrogen concentrations for the samples collected from these wells in 2012 or 2013, 2017 or 2018, and 2022 are shown on Figure 5. Analysis of the available data indicates that nitrogen concentrations decreased in two wells (IG144 and PX232). Conversely, at well DH539, nitrogen concentrations increased. Nitrogen concentrations at well PX702 displayed significant variability. Due to the limited number of data points (three) obtained from each well, drawing definitive conclusions about trends in contaminant concentrations at specific locations is challenging. To gain a more comprehensive understanding of long-term trends, additional samples from these wells would be needed in future years. This may then provide a more robust basis for evaluating contaminant concentrations over time.

Figure 5. Nitrogen Concentration over time



Notes: WUWN Wisconsin Unique Well Number

PESTICIDES

One or more pesticide or pesticide metabolite compounds were detected in 87.6% of samples collected in 2022 (71 of the 81 samples). A total of 19 different pesticides or pesticide metabolites were detected in samples (Table 2 and Figure 2). The five most frequently detected compounds (with more than a 10% detection rate) are listed below along with the number of times (n) and detection rate (%) each compound was detected.

- Metolachlor ethanesulonic acid (ESA) (n=48, detection rate=59.3%)
- Diamino atrazine (n=36, detection rate=44.4%)
- De-ethyl atrazine (n=23, detection rate=28.4%)
- Alachlor ESA (n=20, detection rate=24.7%)
- Clothianidin (n=20, detection rate=24.7%)

Four of the most frequently detected compounds are metabolites of the herbicides metolachlor, alachlor, and atrazine. Each of these compounds is in products commonly used to control weeds in corn or other crops grown in the state. Metolachlor ESA and alachlor ESA were reported as the two most frequently detected

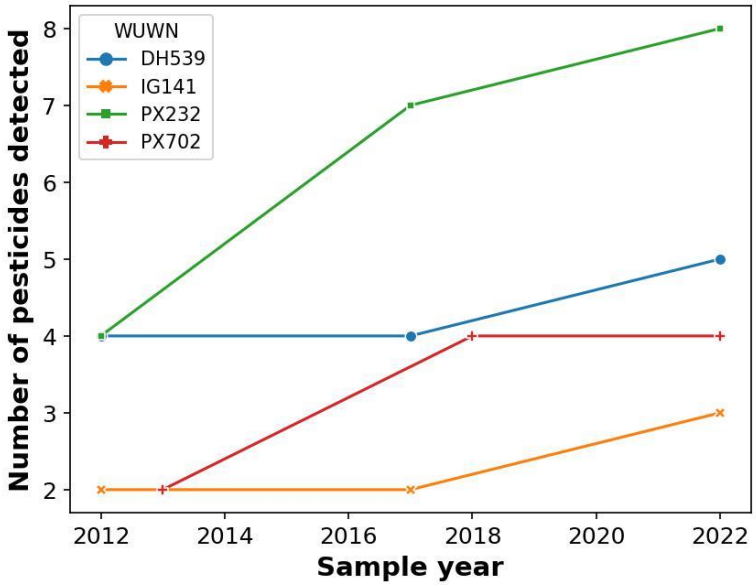
pesticide residues in the 2016 statewide sampling of private wells conducted by DATCP (Wisconsin Department of Agriculture & United States Department of Agriculture, 2017). Alachlor ESA concentrations are expected to decline over time because alachlor is a cancelled product and growers significantly reduced use prior to cancellation in June 2016 (Environmental Protection Agency, 2016). The compound clothianidin is a systemic neonicotinoid insecticide that is used to control insects in corn, small grains, soybeans, and vegetable crops. Two additional neonicotinoid insecticides that were also detected less frequently include imidacloprid (n=4, detection rate= 4.9%) and thiamethoxam (n=5, detection rate= 6.2%).

Pesticides or pesticide metabolites detected in 2022 Targeted Sampling Program were compared to existing groundwater quality standards listed in Wis. Admin. Code ch. NR 140 (NR 140) and DHS Drinking Water Health Advisories. Of the 106 compounds tested for, there are 30 compounds with established regulatory groundwater standards and 17 compounds with Drinking Water Health Advisories. Table 2 shows established Wis. Admin. Code ch. NR 140 PALs, ESs, and DHS Drinking Water Health Advisories (DWHAs) for the compounds detected. Five pesticide compounds (clothianidin, fomesafen, imidacloprid, sulfentrazone and thiamethoxam) were detected in one or more samples. While DHS Drinking Water Health Advisories are currently available, no groundwater quality standards have not been established for these compounds at this time. Four pesticide compounds (clopyralid, dimethenamid ESA, metribuzin DADK, and triclopyr) were detected in one or more samples, but currently have no groundwater quality standards or Drinking Water Health Advisories.

Two pesticide metabolites, diamino atrazine and de-ethyl atrazine, were detected above groundwater standards. Diamino atrazine was detected in exceedance of the Wis. Admin. Code ch. NR 140 PAL of 0.3 µg/L in 12.3% of the samples (10 samples). De-ethyl atrazine was detected in exceedance of the Wis. Admin. Code ch. NR 140 PAL of 0.3 µg/L in 2.5% of the samples (2 samples). Atrazine TCR (the sum of atrazine plus its three metabolites) exceeded the 0.3 µg/L PAL in 17.3% of the sample (14 samples).

Four wells in Rock County underwent sampling as part of both previous sampling efforts and the 2022 Targeted Sampling Program. The observed number of pesticides detected for the samples collected from these wells in 2012 or 2013, 2017 or 2018, and 2022 are shown on Figure 6. The data recorded that an overall increase of the number of pesticides detected over time for all the four wells resampled.

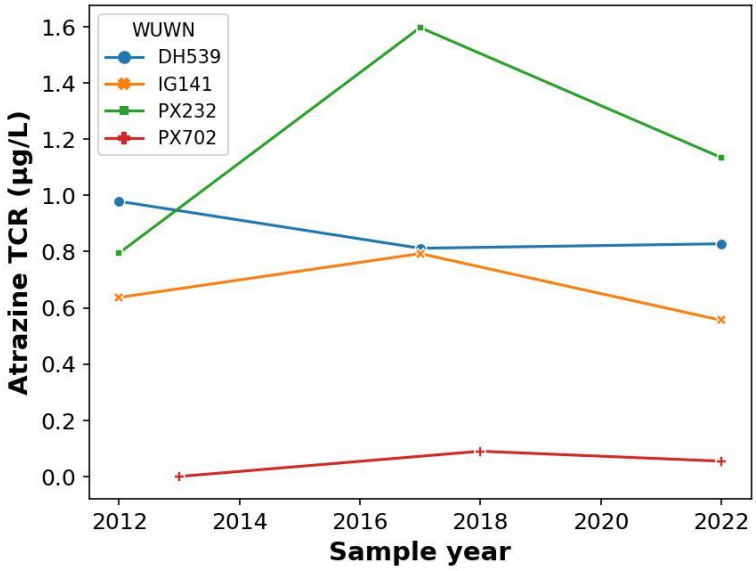
Figure 6. Number of pesticides detected over time



Notes: WUWN Wisconsin Unique Well Number

The concentrations of Atrazine TCR remained relatively stable over time at wells DH539, IG141, and PX702, showing no significant changes. Although the concentration of atrazine TCR at well PX232 decreased compared to 2017, it remains higher than the recorded concentration in 2012 (Figure 7). Additional data is needed to confirm these trends.

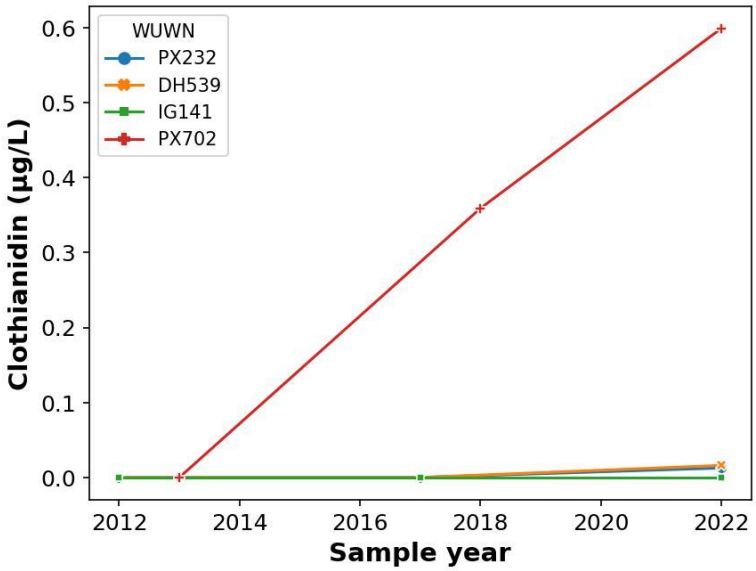
Figure 7. Atrazine TCR concentration over time



Notes: WUWN Wisconsin Unique Well Number

Clothianidin was the only neonicotinoid compound detected at these resampled wells. As shown on Figure 8, clothianidin concentration increased significantly over time at PX702, increased slightly at PX232 and DH539, and was not detected at IG141.

Figure 8. Clothianidin concentration over time



Door County – Detailed Summary

DATCP collected water samples from 54 private potable wells in Door County in the summer of 2022 as part of the Targeted Sampling Program (Figure 9).

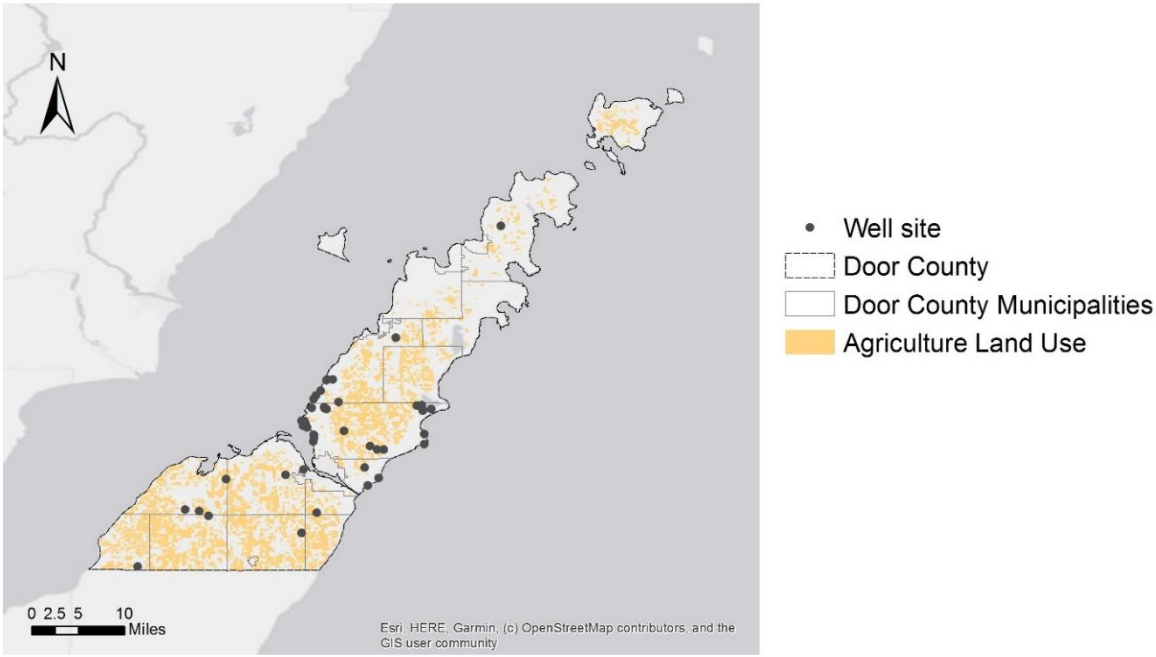
Door County is highly susceptible to groundwater contamination (Schmidt, Robin R; Kessler, Kevin, 1989). The Silurian Dolomite is the upper bedrock unit and the primary aquifer system of the area. The Silurian Dolomite lies below a thin and low-permeable layer of fine-grained soils, which may locally prevent groundwater contamination. However, the dense fracture network and karst features of the dolomite promote rapid groundwater recharge and increase the aquifer susceptibility to contamination from the land surface (Wisconsin Geological and Natural History Survey, 2023). In Door County, about 30% of the land is devoted to agricultural procedures (Wisconsin Department of Natural Resources, 2019). While it is acknowledged that agriculture operations favor regional economic development, concern is continuously raised about their impact on water quality.

Results of the 2022 DATCP sampling effort show that nitrogen and several pesticides, such as atrazine metabolites and neonicotinoids, were detected in groundwater samples. Only three wells exceeded the nitrogen drinking water standard of 10 mg/L. No other compound was found at a concentration exceeding the respective drinking water standard.

SELECTION OF SAMPLING LOCATIONS AND SAMPLING METHOD

Between 2019 and 2022, Door County collected about 900 water samples from private potable wells through the Door County Private Well Monitoring Program (University of Wisconsin - Oshkosh, 2023). The samples were tested for nitrate- N (as nitrogen), and a nitrogen concentration above 5 mg/L was found at 79 wells. Since nitrogen-based fertilizers are often used in combination with pesticides, DATCP selected these wells to further evaluate groundwater quality for pesticide active ingredients and nitrogen. Letters and permission slips were mailed to 75 of these well owners and 51 of them granted DATCP permission to test their wells. Three additional samples were collected from wells that, to our knowledge, were never tested for nitrogen before. A total of 54 private potable wells were sampled by DATCP in July and August 2022. Groundwater sample collection followed procedure explained in the Sample Collection and Analysis section.

Figure 9. Sampling locations in Door County for the Targeted Sampling Program in 2022



Notes: Agricultural land use from Wiscland 2.0 (Wisconsin Department of Natural Resources, 2019).

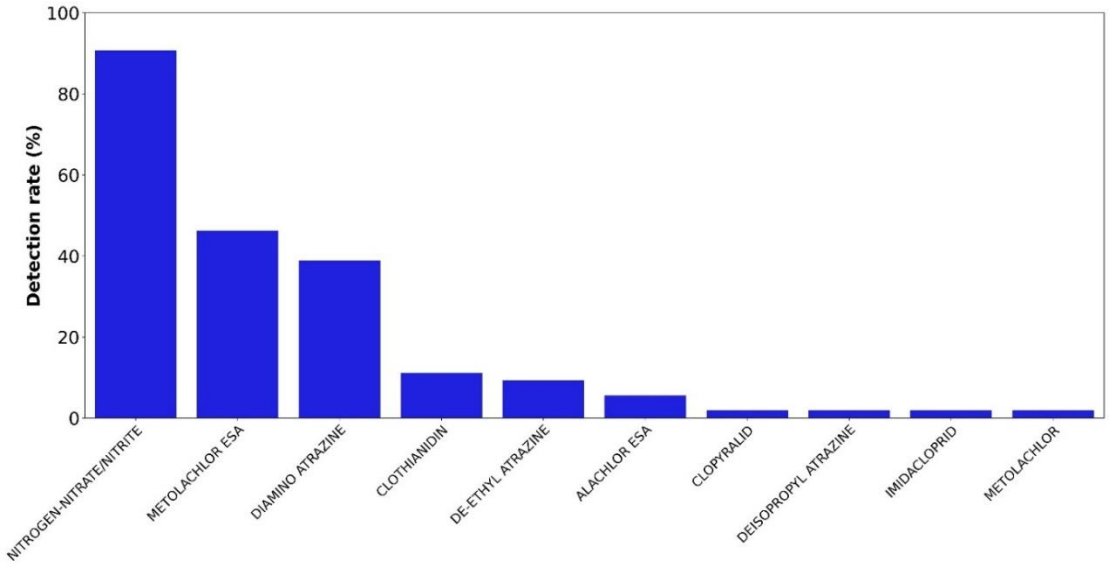
RESULTS

Detections and comparisons to standards

Nitrogen and nine pesticides were detected in 2022 Door County Targeted Program samples (Figure 10 and Table B 2 in Appendix B). Below is a summary of the detection rate, the range of values detected for each compound, and the exceedance rate of the respective Wis. Admin. Code ch. NR 140 PAL and ES or DHS Drinking Water Health Advisory.

- Nitrate plus nitrite as N was detected at 49 wells (detection rate of 90.7%) at concentrations between 1.68 mg/L and 13.4 mg/L. The 2 mg/L PAL was exceeded at 48 wells (88.9%), and the 10 mg/L ES was exceeded at three wells (5.6%).
- Metolachlor ESA was detected at 25 wells (46.3%) at concentrations between 0.0539 µg/L and 0.954 µg/L. None of the samples exceeded the 260 µg/L PAL and the 1,300 µg/L ES for this compound.
- Diamino atrazine, a metabolite of atrazine, was detected at 21 wells (38.9%) at concentrations ranging from 0.145 µg/L and 0.362 µg/L. The 0.3 µg/L PAL was exceeded at one well (1.9%). No samples exceeded the 3 µg/L ES for total atrazine (the sum of atrazine parent material plus its metabolites).
- Clothianidin, a neonicotinoid insecticide, was detected at six wells (11.1%) at concentrations ranging from 0.01 µg/L and 0.0335 µg/L. No PAL and ES standards have been established for this compound at this time. All clothianidin detections were less than the DHS Drinking Water Health Advisory of 1,000 µg/L.
- De-ethyl atrazine, a metabolite of atrazine, was detected at five wells (9.3%) at concentrations ranging from 0.0507 µg/L and 0.0611 µg/L. No samples exceeded the 0.3 µg/L PAL or the 3 µg/L ES for total atrazine (the sum of atrazine parent material and its metabolites).
- Alachlor ESA was detected at three wells (5.6%) at concentrations ranging from 0.158 µg/L and 0.403 µg/L. No samples exceeded the 4 µg/L PAL or the 20 µg/L ES for this compound.
- Clopyralid was detected at one well (1.9%) at a concentration of 0.38 µg/L. No PAL, ES, DHS Drinking Water Health Advisory have been established for this compound at this time.
- Deisopropyl atrazine was detected at one well (1.9%) at a concentration of 0.0984 µg/L. No samples exceeded the 0.3 µg/L PAL or the 3 µg/L ES for this compound.
- Imidacloprid, a neonicotinoid insecticide, was detected at one well (1.9%) at a concentration of 0.0707 µg/L. No PAL and ES standards have been established for this compound at this time. The Wisconsin Department of Health Services (DHS) has set the Drinking Water Health Advisory for imidacloprid at 0.2 µg/L. No samples exceeded the imidacloprid DHS Drinking Water Health Advisory.
- Metolachlor was detected at one well (1.9%) at a concentration of 0.0549 µg/L. The sample did not exceed the 10 µg/L PAL or the 100 µg/L ES for this compound.

Figure 10. Compounds detected through the 2022 Targeted Sampling Program in Door County and respective detection rates



Notes: *On the x-axis, the list of compounds detected, i.e. found with concentrations greater than laboratory reporting limits. On the y-axis, the detection rate in percentage for each detected compound.*

While atrazine parent material was not detected in any 2022 samples collected in Door County, three atrazine metabolites (diamino atrazine, de-ethyl atrazine, and deisopropyl atrazine) were detected. Atrazine TCR (sum of atrazine and its metabolites) yielded concentrations between 0.0507 µg/L and 0.3764 µg/L. Atrazine TCR exceeded the PAL of 0.3 µg/L at two wells, but it never exceeded the 3 µg/L ES.

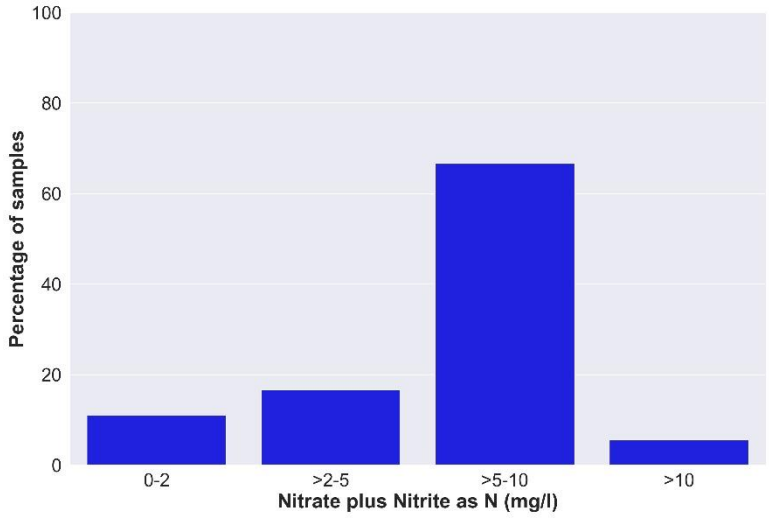
Metolachlor Metabolites is the sum of metolachlor ESA and metolachlor OA (or OXA). Metolachlor OA was not detected in any of the samples collected. Metolachlor Metabolites yielded concentrations between 0.0539 µg/L and 0.954 µg/L. No PAL (260 µg/L) or ES (1,300 µg/L) standards were exceeded.

Nitrogen

Although nitrate plus nitrite as N was detected in 49 of 54 samples collected, it only exceeded the 10 mg/L ES at three wells. It was most frequently detected between 5 and 10 mg/L. The distribution of nitrate plus nitrite as nitrogen concentrations is summarized below and shown on Figure 11.

- 0-2 mg/L: six wells (11%)
- >2 to 5 mg/L: nine wells (17%)
- >5 to 10 mg/L: 36 wells (67%)
- >10 mg/L: three wells (5%)

Figure 11. Nitrate plus nitrite as N occurrence data in Door County



As shown on Figure 12, two wells with high nitrogen levels (greater than 10 mg/L) are near other sampling locations where nitrogen concentrations ranged between 0 and 6.65 mg/L (area in the black squares of Figure 12). However, no regional pattern could be interpreted based on the limited size of the data set and the lack of additional information, such as well properties and fracture network properties around the wells.

To track the nitrogen contamination in-depth and to better identify what factors control the contamination, we retrieved information on well depth, casing bottom depth, static water level, bedrock depth, and installation date from publicly available construction reports. Only 32 of the 54 well samples had complete construction reports.

Figure 13 shows the nitrogen concentration versus the difference between the depth of the water table at the time of construction (static water level) and the bottom depth of the well casing. This plot shows how deep below the water table nitrogen exceeds drinking water standards. As shown, nitrogen exceeded 10 mg/L at 65 feet below the water table at one well. Nitrogen concentrations between 5 and 10 mg/L were found between 20 and 140 feet below the water table.

Figure 12. Nitrate plus nitrite as N concentration for each sampling location in Door County

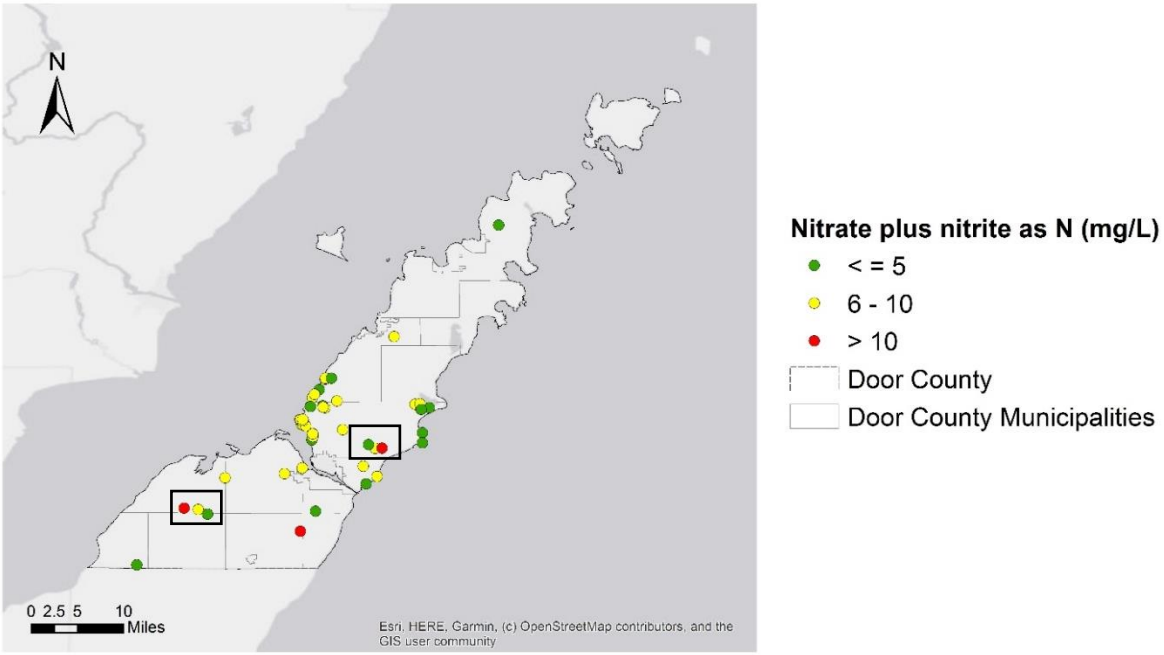
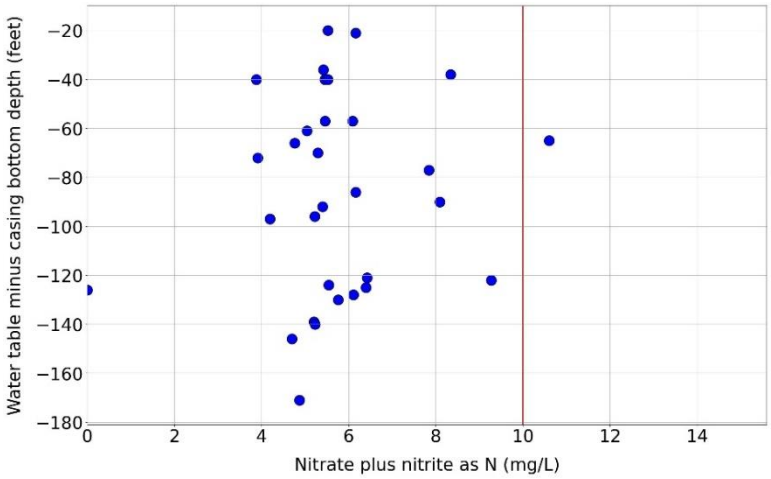


Figure 13. Nitrate and nitrite as nitrogen versus the difference between the water level and the casing depth in Door County



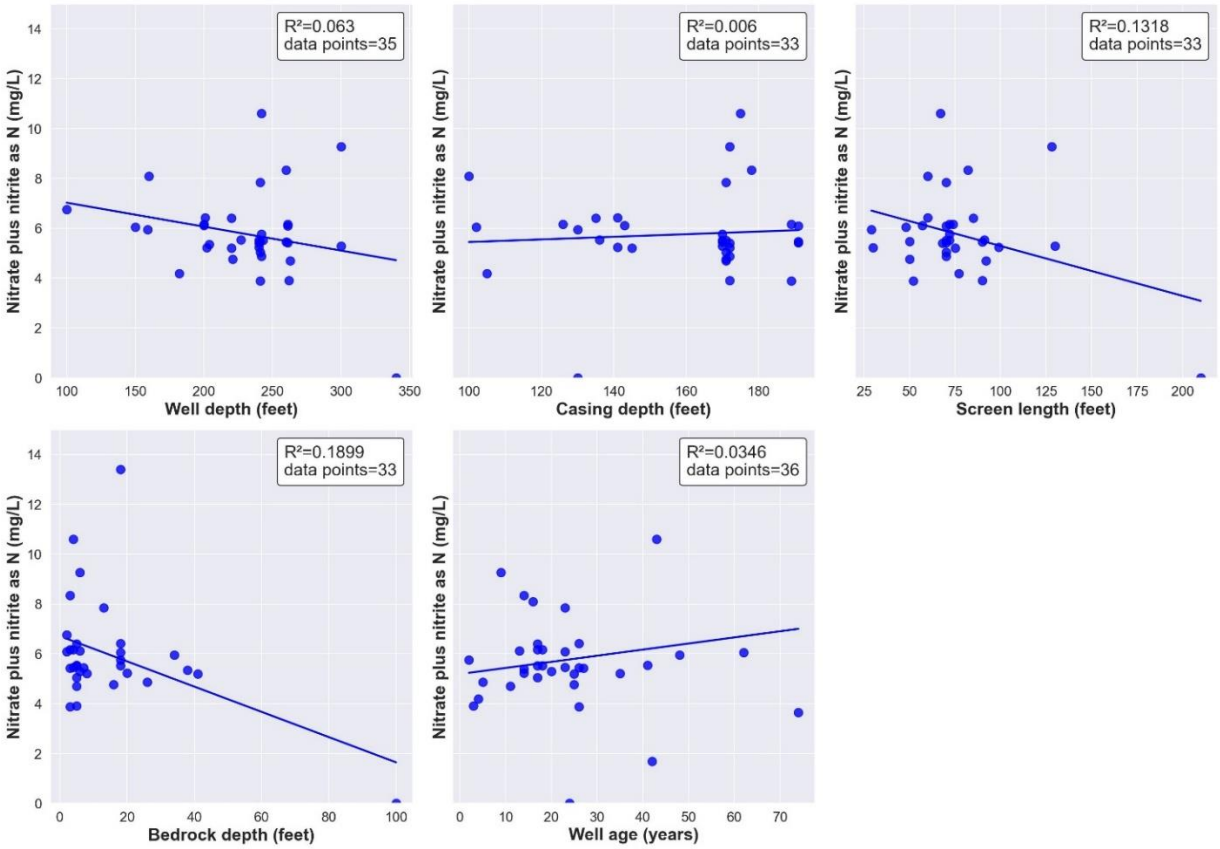
Notes: The red line represents the ES for nitrogen (10 mg/L).

No relationships were found between nitrogen concentration and well depth, casing depth, or well age. Nitrogen concentration is negatively correlated with the screen length: the longer the screen or the open (uncased) interval to the sourrounding geology, the lower the nitrogen concentration. However, the goodness of fit of this linear relationship is very low (R^2=0.1318), and it is strongly affected by a single data point with a screen length of 210 feet (Figure 14). Nitrogen concentration is negatively correlated with the bedrock depth: the shallower the bedrock, the higher the nitrogen concentration. However, the goodness of fit of this linear relationship is also very low (R^2=0.1899), and it is strongly affected by a single data point with a bedrock depth of 100 feet (Figure 14).

Through Geographic Information Systems (ArcMap), we calculated the distance between each sampling point and the nearest agricultural field (Figure 15). Wiscland 2.0 was used as land cover data (Wisconsin

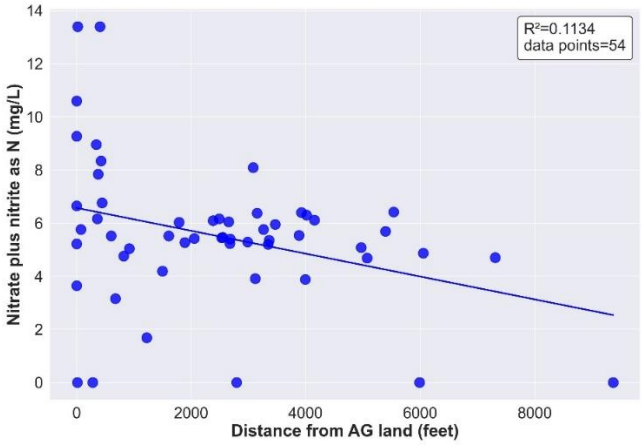
Department of Natural Resources, 2019). Although the goodness of fit is low (R^2=0.1134), the data show a weak negative correlation between nitrate levels and the distance of each sampling location to the nearest agricultural field. The higher the distance from an agricultural field, the lower the nitrogen concentration. For example, the wells with nitrogen concentrations exceeding 10 mg/L are all located within 150 feet from an agricultural field.

Figure 14. Nitrate plus nitrite as N as a function of well depth, casing depth, static water level, bedrock depth, and well age in Door County



Notes: The well age is defined as the difference between the year of sampling (2022) and the year of the well construction. The well screen length defined as the difference between the well depth and the casing depth. The box on the top right includes the goodness of fit (R^2) and the number of data used for each relationship.

Figure 15. Nitrate plus nitrate as nitrogen versus the distance from an agricultural field in Door County



As mentioned in the Selection of sampling locations and sampling method section, 51 of the 54 wells were tested at least once for nitrate-N in the last four years through the Door County Private Well Monitoring Program. For five of the 51 wells, additional nitrogen data collected between 2016 and 2022 were available on the Groundwater Retrieval Network website (Wisconsin Department of Natural Resources, 2023). This data includes samples collected by either the Wisconsin Department of Natural Resources (DNR) or the constructor (driller) during the well construction process. In general, the nitrogen levels recorded through the 2022 DATCP Targeted Sampling program were not substantially different from the past nitrogen levels (Table 3).

Table 3. Nitrogen concentration changes for the wells that at least once were tested for nitrogen prior the 2022 DATCP sampling effort in Door County

Nitrogen comparison for 51 wells sampled between 2016 and 2022		
Increased Nitrogen Two locations	**No or minimal change 40 locations**	**Decreased Nitrogen Nine locations**
One increased by 2 to 5 mg/L	34 decreased less than 2 mg/L Six increased less than 2 mg/L	Five decreased by 2 to 5 mg/L
One increased by 5 to 10 mg/L		Three decreased by 5 to 10 mg/L
None increased more than 10 mg/L		One decreased more than 10 mg/L

Neonicotinoids

Neonicotinoids are a class of insecticides widely used in Wisconsin. These insecticides are usually applied as seed treatments on major Wisconsin crops, such as corn, soybeans, beans, potatoes, small grains, vegetables, fruit crops, and more. Clothianidin, imidacloprid, and thiamethoxam are neonicotinoid compounds and active ingredients of 557 registered products in Wisconsin (Kelly Solutions, 2023). In 2016, DATCP sampled 10 wells in Door County and neonicotinoids were not detected (Wisconsin Department of Agriculture, Trade and Consumer Protection, 2019). However, the analytical results of the sampling effort for 2022 showed, that clothianidin was detected at six wells and imidacloprid w at one well (Figure 16). While imidacloprid is a parent compound, clothianidin can be either a parent compound or a metabolite of thiamethoxam. Hence, clothianidin may be associated with the use of pesticides containing either clothianidin or thiamethoxam. The concentrations of imidacloprid and clothianidin detected in 2022 samples remain below DHS Drinking Water Health Advisories. Neonicotinoids were only found in the Egg Harbor and Sevastopol municipalities, in topographically low lying areas located at the edges of a local recharge area (Preliminary Regional Groundwater Recharge/Discharge Map in Cutright, 1982).

The neonicotinoid concentrations (either imidacloprid or clothianidin) were evaluated in relation to the difference between the water depth and the casing depth (Figure 17). Information on the well properties is available for four of the six locations where neonicotinoids were detected. Clothianidin and imidacloprid were detected to a maximum depth of 121 and 36 feet below the water table, respectively.

Figure 16. Sampling locations in Door County where clothianidin and imidacloprid were detected

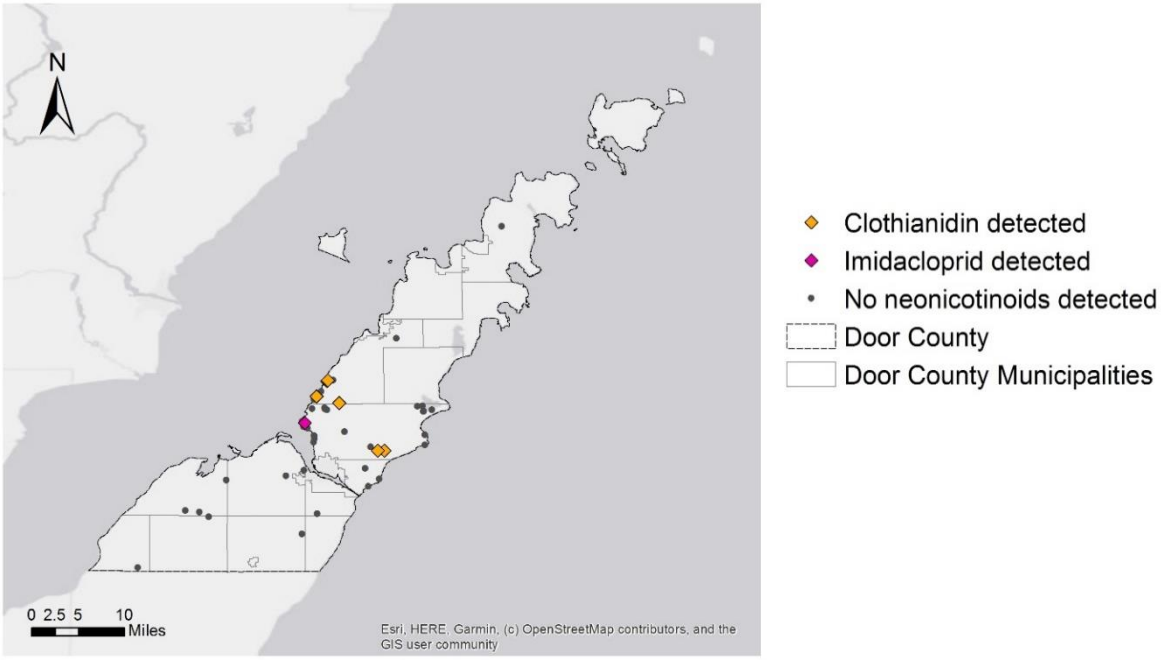
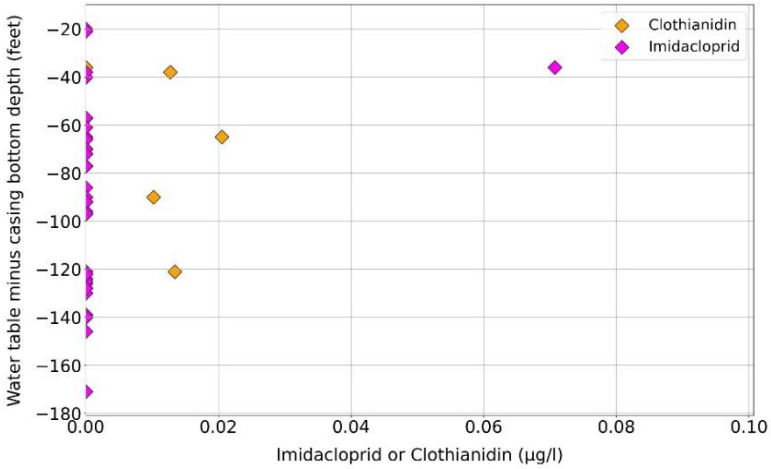


Figure 17. Imidacloprid or clothianidin concentration versus the difference between the water level and the casing depth in Door County

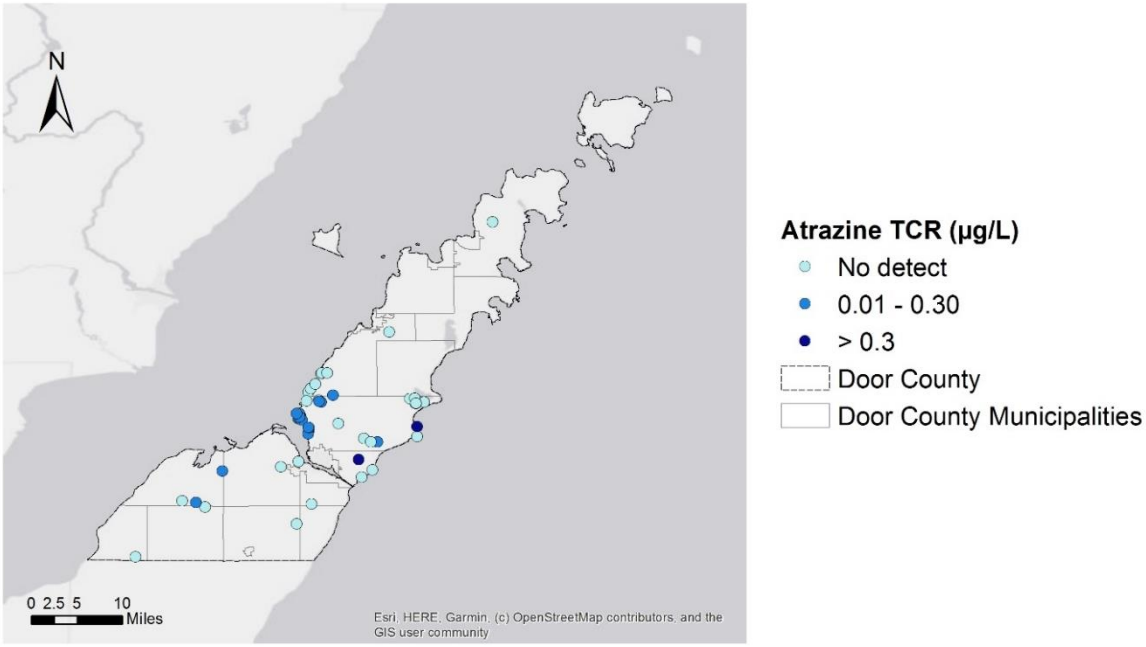


Atrazine

Atrazine is an herbicide used to selectively control weeds on several crops, such as field corn, sweet corn, sorghum, and sugarcane. In Wisconsin, it is registered as a restricted-use pesticide and prohibited in 101 areas (prohibition areas). There are currently no atrazine prohibition areas in Door County.

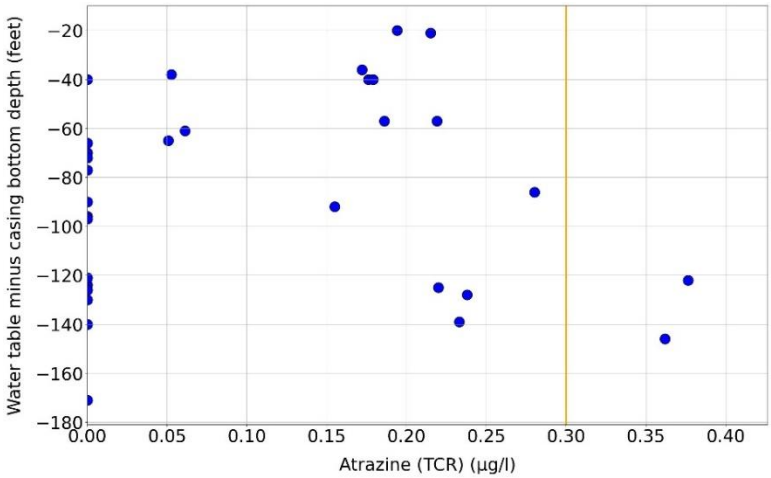
Atrazine metabolites were detected at 24 wells. The sum of the atrazine metabolites (atrazine TCR) exceeded the PAL in two locations (Figure 18). At least one atrazine metabolite was detected in the wells along the west shoreline of the Sevastopol municipality. These wells are located in areas where agriculture is limited or absent (see Figure 9). The detection of atrazine metabolites at these wells is likely associated with the use of atrazine at upgradient agricultural fields.

Figure 18. Sampling locations in Door County where Atrazine Total Chlorinated Residue (TCR) was detected



Atrazine TCR was found between 20 and 146 feet below the water table (Figure 18). Higher concentrations of Atrazine TCR were found at greater depths below the water table.

Figure 19. Atrazine Total Chlorinated Residue (TCR) concentration versus the difference between the water level and the casing depth in Door County



Notes: *The orange line represents the PAL for Atrazine TCR (0.3 µg/L).*

CONCLUSION AND RECOMMENDATIONS

Groundwater samples collected between July and August 2022 from 54 Door County wells were tested for nitrate and 106 pesticides. Only three samples exceeded the 10 mg/L Enforcement Standard (ES) for nitrogen. Nitrogen was detected between 5 and 10 mg/L at most of the wells sampled. This is similar to findings from previous sampling efforts conducted by Door County and the DNR. Nitrogen concentration increased by more than 5 mg/L at one well and decreased by more than 5 mg/L at four wells. We advise resampling these wells in the near future (annually) to better assess the nitrogen concentration trends. It is likely that the considerable difference from past measurements is due to the rapid recharge rate of the Silurian dolomite aquifer. Regional well yields are estimated to be between 100 and over 500 gallons per

minute (Devaul, 1975), and strongly depend on the degree of secondary porosity of the Silurian dolomite. Heterogeneities in fracture apertures, the orientation of karst features, and fracture connectivity may also justify the differences in nitrogen concentrations found in adjacent wells (black squares on Figure 12). No strong linear relationships were found between nitrogen concentrations and well properties or nitrogen concentration and distance to an agricultural field. Additional data are needed to confirm these trends.

Several pesticides were detected, but no pesticide concentrations exceeded their respective ESs. Atrazine metabolites are the only compounds detected above PAL. In 2021, over 55,000 acres of Door County were devoted to corn and alfalfa production (United States Department of Agriculture, 2021). Since atrazine may be used on these cover crops and is not prohibited in Door County, it was foreseeable that atrazine metabolites would be detected. Imidacloprid and clothianidin were both detected in 2022 samples. To our knowledge, this is the first time that neonicotinoids were detected in private potable wells of Door County. Additional sampling is needed to better understand neonicotinoids trends and occurrence. (Note: DATCP is unable to track the type or amount of pesticide used on any specific field, county, or statewide.)

DATCP will consider resampling wells where pesticides of interest (atrazine, clothianidin, and imidacloprid) were detected. Since no PAL, ES, or DHS Drinking Water Health Advisory have been established for Clopyralid, we are currently unable to assess the health risk associated with the detection of this compound. The detection of other pesticides does not raise noteworthy concerns regarding risks to human health and the environment.

Oneida County – Detailed Summary

The Wisconsin Department of Agriculture, Trade and Consumer Protection (DATCP) collected water samples from seven private potable wells in the town of Stella, Oneida County, in the summer of 2022 as part of the Targeted Sampling Program (Figure 20).

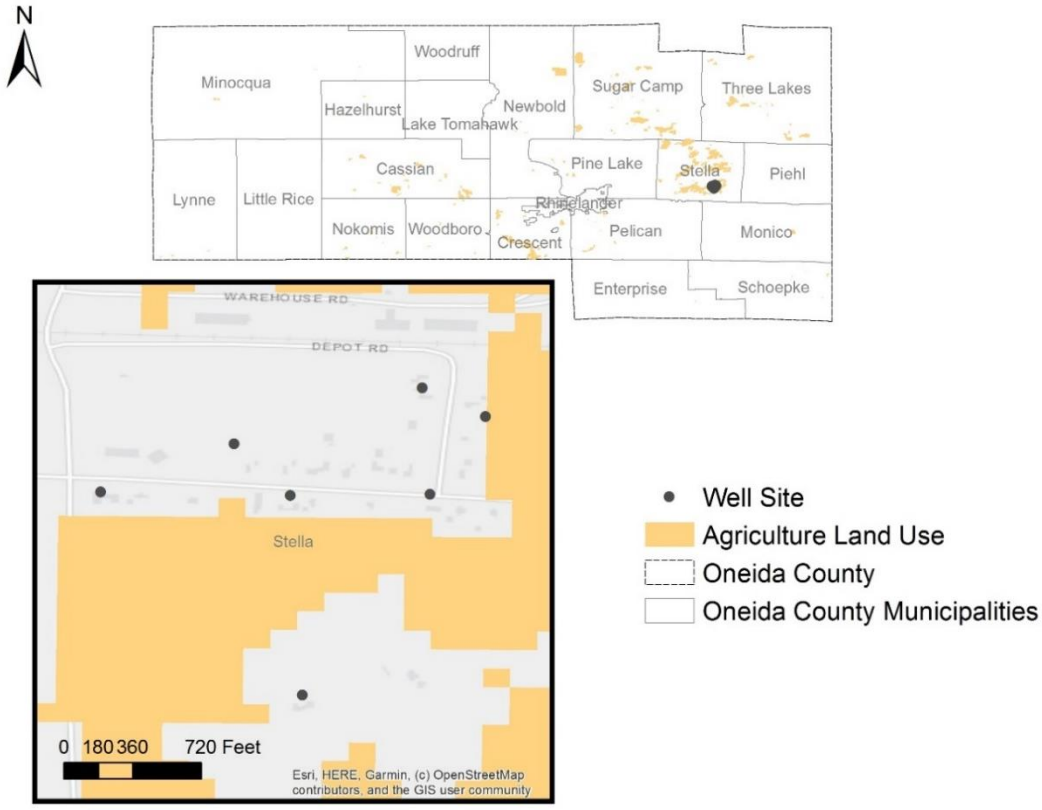
Oneida County is highly susceptible to groundwater contamination due to its geologic characteristics (Schmidt, Robin R; Kessler, Kevin, 1989). The county comprises Proterozoic Bedrock, which is exposed in certain areas and extends up to a depth of 300 feet (Trotta & Cotter, 1973). Above the bedrock, there are Quaternary surficial deposits consisting of sand and gravel. These deposits were formed approximately 20,000 years ago during the recession of the margin of the ice lobes (Attig & Rawling, 2020). As a result, the county exhibits two distinct aquifer systems: a sand and gravel aquifer and a bedrock aquifer. In the case of the sand and gravel aquifer, water flows through the porous nature of the deposits. Conversely, the bedrock aquifer relies on water transmission through fractures (Wisconsin Geological and Natural History Survey, 2023). These aquifer systems facilitate rapid groundwater recharge but also increase the susceptibility of the aquifers to contamination from the land surface. In Oneida County, less than 2% of the land is devoted to agricultural procedures (Wisconsin Department of Natural Resources, 2019). However, the majority of the agricultural use area is localized in the town of Stella (Figure 20).

Results of the 2022 DATCP sampling effort show that, despite the limited agriculture land use, nitrogen and several pesticides, such as atrazine metabolites and neonicotinoids were detected in groundwater samples. The nitrogen drinking water standard of 10 mg/L was exceeded in one sample. No other compound was found at a concentration exceeding the respective drinking water standard.

SELECTION OF SAMPLING LOCATIONS AND SAMPLING METHOD

During the summer of 2022, DNR conducted a comprehensive statewide survey of groundwater to assess the presence of per- and polyfluoroalkyl substances (PFAS) in private potable wells. The survey revealed the existence of PFAS contamination at multiple wells situated within the town of Stella. This discovery prompted concerns regarding the overall vulnerability of the aquifer to potential contaminations. For this reason, the same wells where PFAS contamination was found were selected to be included in the 2022 DATCP Targeted Sampling Program. Seven private potable wells were sampled by DATCP in October 2022. Groundwater sample collection followed procedure explained in the Sample Collection and Analysis section.

Figure 20. Sampling locations in Oneida County for the Targeted Sampling Program in 2022



RESULTS

Detections and comparisons to standards

Nitrogen and seven pesticides were detected in 2022 Oneida County samples (Figure 21 and Table B 3 in Appendix B). Below is a summary of the detection rate, the range of values detected for each compound, and the exceedance rate of the respective Wis. Admin. Code ch. NR 140 PAL and ES or DHS Drinking Water Health Advisory.

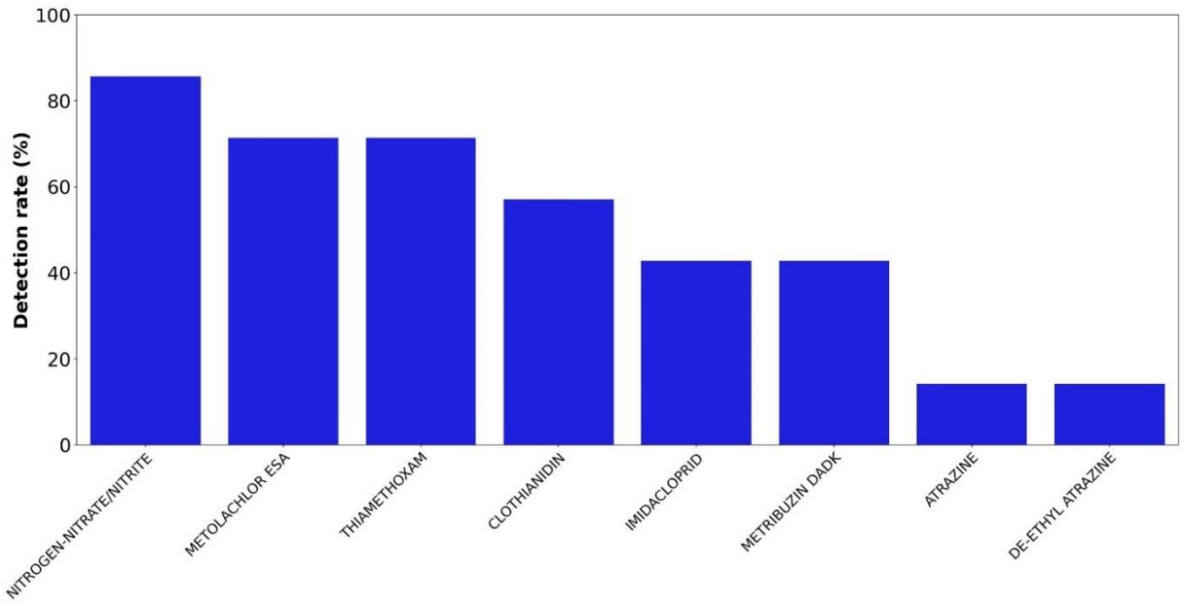
- Nitrate plus nitrite as N was detected at six wells (detection rate of 85.7%) at concentrations between 1.38 mg/L and 10.1 mg/L. The 2 mg/L PAL was exceeded at five wells (71.4%), and the 10 mg/L ES was exceeded at one well (14.3%).
- Metolachlor ESA was detected at five wells (71.4%) at concentrations between 0.0523 µg/L and 0.173 µg/L. All detections did not exceed the 260 µg/L PAL and the 1,300 µg/L ES for this compound.
- Thiamethoxam, a neonicotinoid insecticide, was detected in five wells (71.4%) at concentrations between 0.0222 µg/L and 1.01 µg/L. No PAL and ES standards have been established for this compound at this time. All clothianidin detections did not exceed the DHS Drinking Water Health Advisory of 120 µg/L.
- Clothianidin, a neonicotinoid insecticide, was detected at four wells (57.1%) at concentrations ranging from 0.0145 µg/L and 0.0599 µg/L. No PAL and ES standards have been established for this compound at this time. All clothianidin detections did not exceed the DHS Drinking Water Health Advisory of 1,000 µg/L.
- Imidacloprid, a neonicotinoid insecticide, was detected at three wells (42.9%) at concentrations ranging from 0.0481 µg/L and 0.0869 µg/L. No PAL and ES standards have been established for this compound at this time. All clothianidin detections did not exceed the DHS Drinking Water Health Advisory of 0.2 µg/L.

- Metribuzin DADK was detected at three wells (42.9%) at concentrations ranging from 0.464 µg/L and 0.94 µg/L. No PAL, ES, or DHS Drinking Water Health Advisory have been established for this compound at this time.
- Atrazine was detected at one wells (14.3%) at a concentration of 0.131 µg/L. No samples exceeded the 0.3 µg/L PAL and the 3 µg/L ES for this compound.
- De-ethyl atrazine, a metabolite of atrazine, was detected at one wells (14.3%) at a concentration of 0.128 µg/L. No samples exceeded the 0.3 µg/L PAL and the 3 µg/L ES for this compound.

Atrazine TCR (sum of atrazine and its metabolites) yielded a concentration of 0.259 µg/L. Atrazine TCR exceeded the PAL of 0.3 µg/L at two wells, but did not exceed the 3 µg/L ES.

Metolachlor Metabolites is the sum of metolachlor ESA and metolachlor OA (or OXA). Metolachlor OA was not detected in any of the samples collected. Metolachlor Metabolites yielded concentrations between 0.0523 µg/L and 0.173 µg/L. No PAL (260 µg/L) or ES (1,300 µg/L) standards were exceeded.

Figure 21. Compounds detected through the 2022 Targeted Sampling Program in Oneida County and respective detection rates



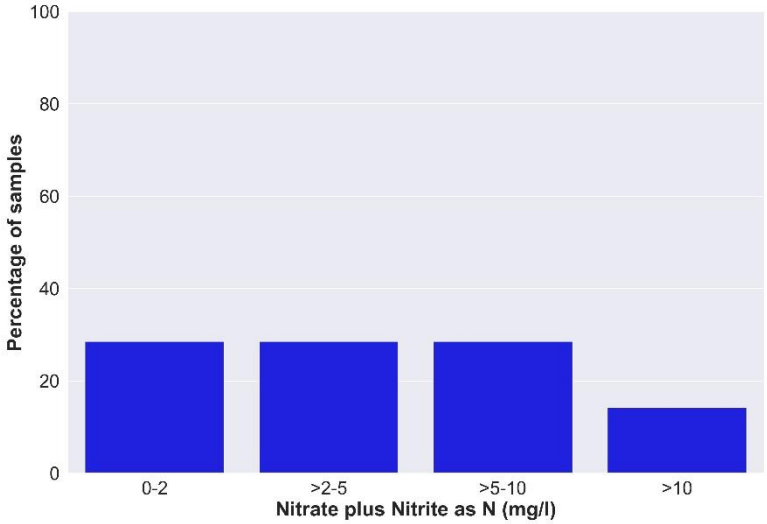
Notes: On the x-axis, the list of compounds detected, i.e. found with concentrations greater than laboratory reporting limits. On the y-axis, the detection rate in percentage for each detected compound.

Nitrogen

Although nitrate plus nitrite as N was detected in six of seven samples collected, it only exceeded the 10 mg/L ES at one well. The distribution of nitrate plus nitrite as nitrogen concentrations is summarized below and shown on Figure 22.

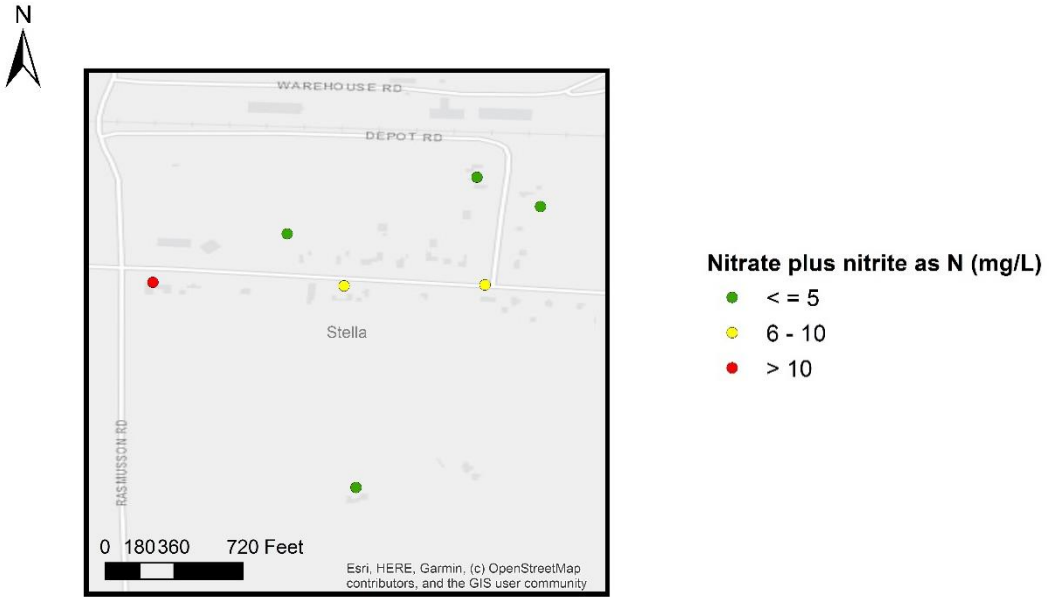
- 0-2 mg/L: two wells (28.56%)
- >2 to 5 mg/L: two wells (28.56%)
- >5 to 10 mg/L: two wells (28.56%)
- >10 mg/L: one well (14.3%)

Figure 22. Nitrate plus nitrite as N occurrence data in Oneida County



No regional pattern could be interpreted based on the limited size of the data set and the extent of the sampling area (Figure 23).

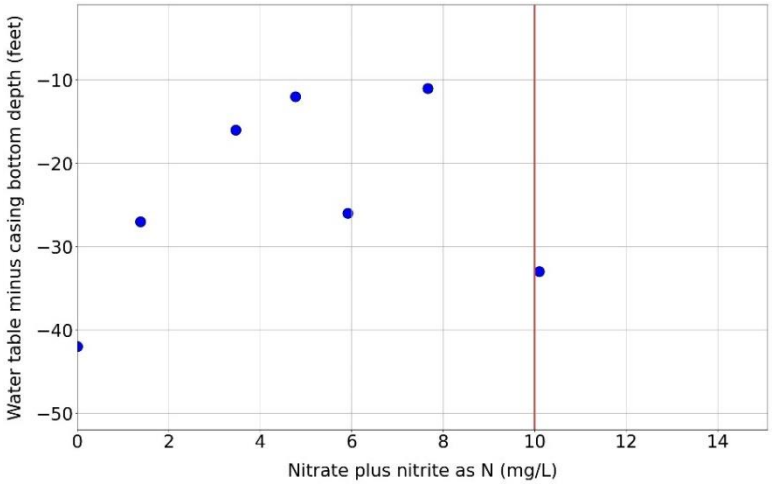
Figure 23. Nitrate plus nitrite as N concentration for each sampling location in Oneida County



To track the nitrogen contamination in-depth and to better identify what factors control the contamination, we retrieved information on well depth, casing bottom depth, static water level, bedrock depth, and installation date from publicly available construction reports.

Figure 24 shows the nitrogen concentration versus the difference between the depth of the water table at the time of construction (static water level) and the bottom depth of the well casing. This plot shows how deep below the water table nitrogen exceeds drinking water standards. As shown, nitrogen exceeded 10 mg/L at 33 feet below the water table at one well. Nitrogen concentrations between 5 and 10 mg/L were found between 11 and 26 feet below the water table.

Figure 24. Nitrate and nitrite as nitrogen versus the difference between the water level and the casing depth in Oneida County



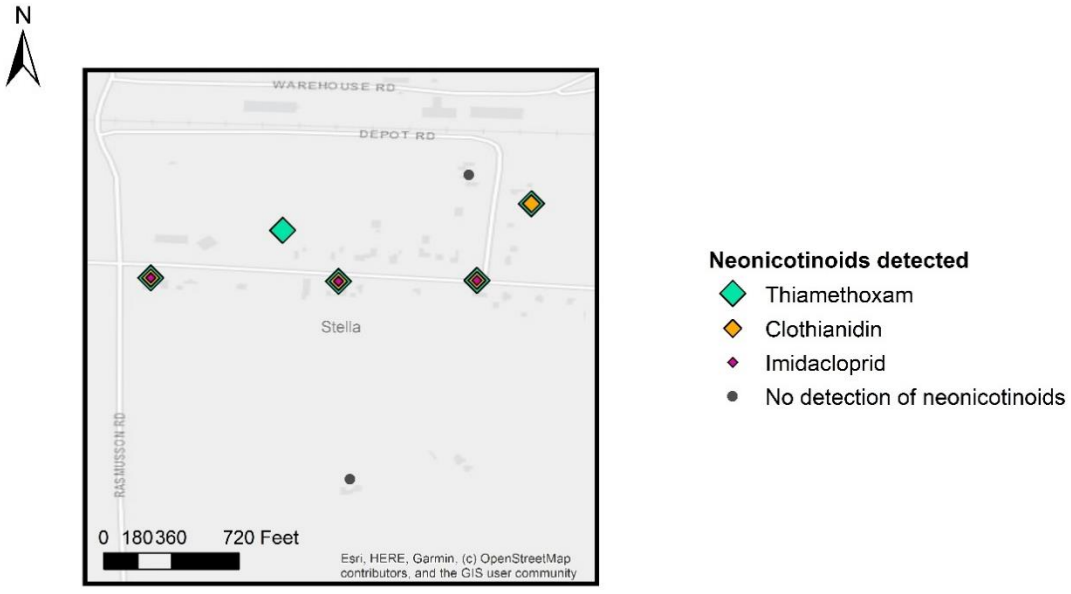
Notes: The red line represents the ES for nitrogen (10 mg/L).

Due to the insufficient quantity of data and the restricted geographic coverage within Oneida County, it is not feasible to conduct comprehensive statistical analyses that would enable us to examine the correlation between nitrate levels and well properties, as well as the distance between wells and agricultural land fields.

Neonicotinoids

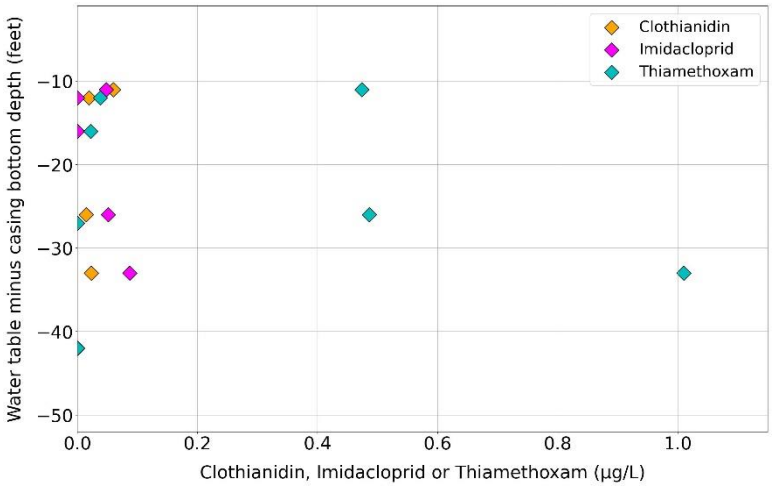
In 2016, DATCP sampled several wells in Door County and neonicotinoids were not detected (Wisconsin Department of Agriculture, Trade and Consumer Protection, 2019). However, the analytical results of the sampling effort for 2022 showed that clothianidin, imidacloprid, and thiamethoxam were instead detected at four, three, and five wells, respectively (Figure 25). While imidacloprid is a parent compound, clothianidin can be either a parent compound or a metabolite of thiamethoxam. Clothianidin may be associated with the use of pesticides containing either clothianidin or thiamethoxam. The concentrations of clothianidin, imidacloprid, and thiamethoxam detected in 2022 samples remain below DHS Drinking Water Health Advisories.

Figure 25. Sampling locations in Oneida County where neonicotinoids were detected



The neonicotinoid concentrations (either imidacloprid or clothianidin) were evaluated in relation to the difference between the water depth and the casing depth (Figure 26). Information on the well properties is available for four of the six locations where neonicotinoids were detected. Clothianidin and imidacloprid were detected at maximum depths of 121 and 36 feet below the water table, respectively.

Figure 26. Neonicotinoids concentrations versus the difference between the water level and the casing depth in Oneida County



Atrazine

There are currently no atrazine prohibition areas in Oneida County. Atrazine and de-ethyl atrazine were detected at one well. The sum of the atrazine metabolites (atrazine TCR) did not exceeded any groundwater standards at this location (Figure 27). Atrazine and de-ethyl atrazine (or atrazine TCR for the sum) were found at 27 feet below the water table (Figure 28).

Figure 27. Sampling location in Oneida County where Atrazine Total Chlorinated Residue (TCR) was detected

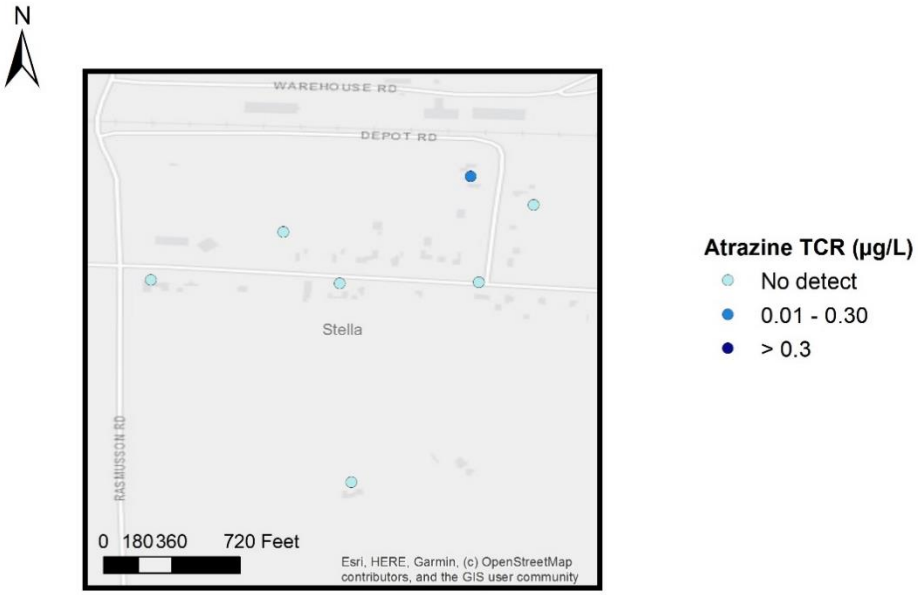
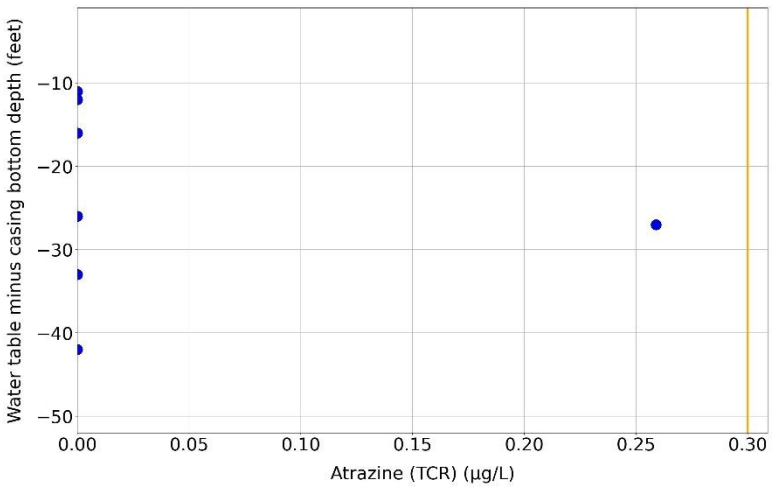


Figure 28. Atrazine Total Chlorinated Residue (TCR) concentration versus the difference between the water level and the casing depth in Oneida County



Notes: The orange line represents the PAL for Atrazine TCR (0.3 µg/L).

CONCLUSION AND RECOMMENDATIONS

Groundwater samples collected between July and August 2022 from seven Oneida County wells were tested for nitrate and 106 pesticides. Only one sample exceeded the 10 mg/L Enforcement Standard (ES) for nitrogen.

Several pesticides were detected but no pesticide concentrations exceeded their respective PAL or ES standards. Clothianidin, imidacloprid, and thiamethoxam were also detected in 2022 samples. To our knowledge, this is the first time that neonicotinoids were detected in private potable wells of Oneida County. Additional sampling is needed to better understand neonicotinoids trends and occurrence. (Note: DATCP is unable to track the type or amount of pesticide used on any specific field, county, or statewide.)

DATCP will consider resampling wells where pesticides of interest (clothianidin, imidacloprid, and thiamethoxam) were found in future sampling efforts. Since no PAL, ES, or DHS Drinking Water Health Advisories have been established for Metribuzin DADK, we are currently unable to assess the health risk associated with the detection of this compound. The detection of other pesticides does not raise noteworthy concerns regarding risks to human health and the environment.

Rock County – Detailed Summary

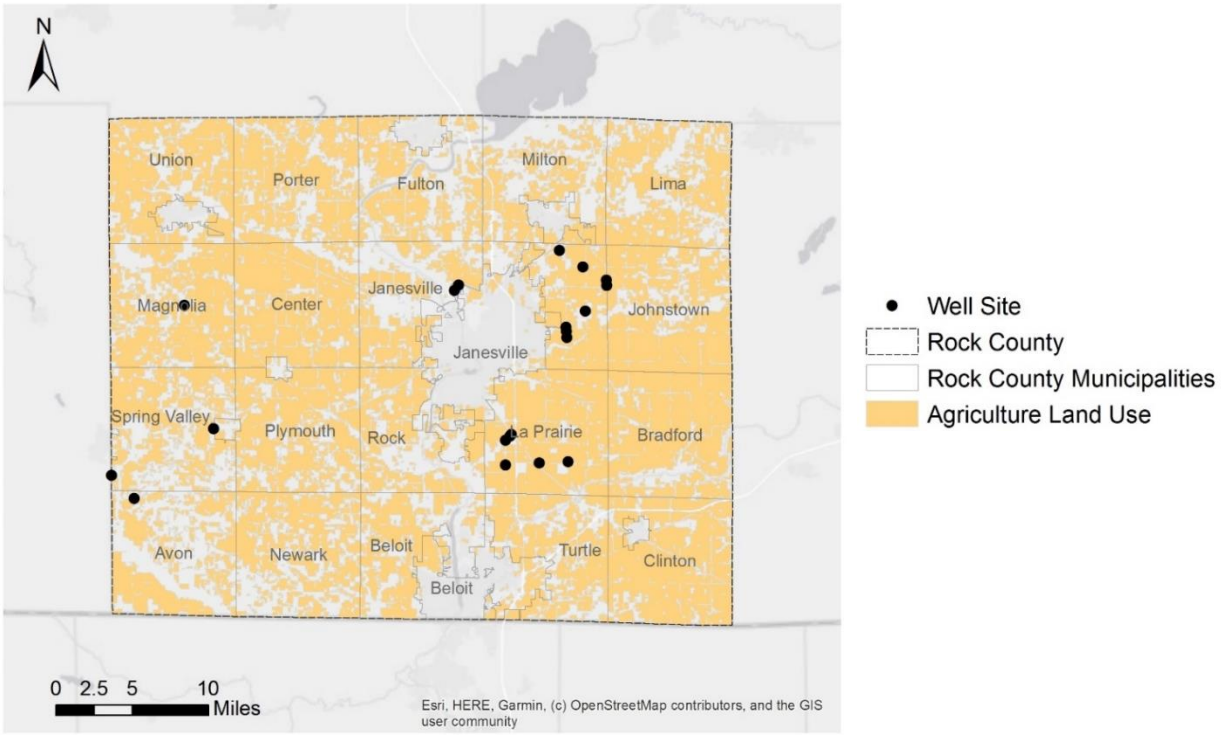
The Wisconsin Department of Agriculture, Trade and Consumer Protection (DATCP) collected water samples from 20 private potable wells in Rock County in the fall of 2022 as part of the Targeted Sampling Program (Figure 29).

Rock County is highly susceptible to groundwater contamination (Schmidt & Kessler, 1989). Groundwater in Rock County is hosted in three aquifer systems (LeRoux, 1963). Domestic water supplies are primarily sourced from the sand and gravel aquifer. The water quality in this shallow, unconfined aquifer is highly affected by activities on the land surface. Outwash deposits range up to 400 feet thick (Wisconsin Department of Natural Resources, 2022). However, in some areas, such as southern Rock County, outwash deposits have been completely eroded. Dolomites of the Sinnipee Group are found on the eastern side of the county beneath glacial deposits of variable thickness (Wisconsin Geological and Natural History Survey, 1982). Secondary porosity due to dense fracture networks and karst features promotes fast groundwater recharge and rapid infiltration of contaminants in groundwater. Drinking water is also sourced from aquifers made up of the Ordovician and Cambrian sandstones. The Cambrian sandstone represents the deepest aquifer unit throughout the entire county and is commonly found beneath the Ordovician sandstone. The Ordovician sandstone is usually underlying the Sinnipee group. However, in some areas of the county, such as between Orfordville and Hanover, the dolomite layer is absent, and the sandstone aquifer is buried underneath a thin layer of outwash deposits (Wisconsin Geological and Natural History Survey, 1982). Groundwater contamination for the sandstone aquifers is highly dependent on local hydro stratigraphy and

land activities. In Rock County, over 66% of the land is devoted to agricultural procedures (Wisconsin Department of Natural Resources, 2019). While it is acknowledged that agriculture operations favor regional economic development, concern is continuously raised about how these affect water quality.

Results of the 2022 DATCP sampling effort show that nitrogen and 15 pesticides, including atrazine metabolites and neonicotinoids were detected in groundwater samples. Seventeen of the 20 well samples exceeded the nitrogen drinking water standard of 10 mg/L. No other compound was found at a concentration exceeding the respective drinking water standard.

Figure 29. Sampling locations in Rock County for the Targeted Sampling Program in 2022



***Notes**: Agricultural land use from Wiscland 2.0 (Wisconsin Department of Natural Resources, 2019).*

SELECTION OF SAMPLING LOCATIONS AND SAMPLING METHOD

Between 2012 and 2022, Rock County collected hundreds of water samples from private potable wells. The samples were tested for nitrate-N and a nitrogen concentration greater than 20 mg/L was found at 232 wells. Since nitrogen-based fertilizers are often used in combination with pesticides, DATCP selected 20 of these wells to further evaluate groundwater quality for pesticide active ingredients and nitrogen. Two wells located down gradient of agricultural fields where best management practices are being implemented (Rock County, 2023) were also selected. DATCP selected six wells to resample that were included in the Targeted Sampling program for 2012, 2013, and 2018. At these wells, nitrogen concentrations exceeded the Wisconsin Administrative Code Chapter NR 140 Enforcement Standards (ES) of 10 mg/L and at least two pesticide compounds were detected. Two additional wells that were found with a nitrogen concentration over 30 mg/L were also selected from the DNR Groundwater Retrieval Network website. Letters and permission slips were mailed to 30 well owners and 19 of them granted permission to DATCP to test their wells. One additional sample was also collected from a second well for one of the owners. A total of 20 private potable wells were sampled by DATCP in October and November 2022. Of these 20 wells, four were previously sampled by DATCP and 12 were previously sampled by Rock County. Groundwater sample collection followed procedure explained in the Sample Collection and Analysis section.

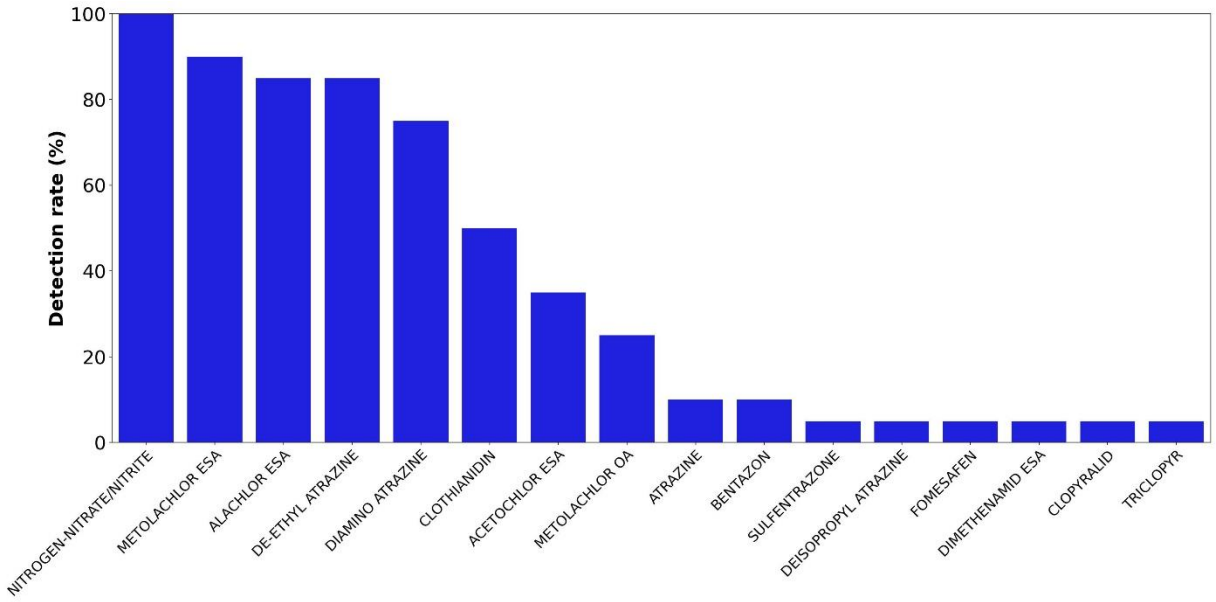
RESULTS

Detections and comparisons to standards

Nitrogen and 15 pesticides were detected in 2022 Rock County samples (Figure 30 and Table B 4 in Appendix B). Below is a summary of the detection rate, the range of values detected for each compound, and the exceedance rate of Preventive Action Limits (PAL) and Enforcement Standards (ES) as defined in the Wisconsin Administrative Code Chapter NR 140.

- Nitrate plus nitrite as nitrogen (N) was detected at 20 wells (detection rate of 100%) at concentrations between 3.89 mg/L and 32.7 mg/L. The 2 mg/L PAL was exceeded at 20 wells (100%), and the 10 mg/L ES was exceeded at 17 wells (85%).
- Metolachlor ESA was detected at 18 wells (90%) at concentrations between 0.1 µg/L and 13.1 µg/L. None of the samples exceeded the 260 µg/L PAL or the 1,300 µg/L ES for this compound.
- De-ethyl atrazine, a metabolite of atrazine, was detected at 17 wells (85%) at concentrations ranging from 0.0545 µg/L and 0.345 µg/L. The PAL of 0.3 µg/L for total atrazine (the sum of atrazine parent material and its metabolites) was exceeded in two samples (10%). No samples exceeded the 3 µg/L ES for total atrazine.
- Alachlor ESA was detected at 17 wells (85%) at concentrations ranging from 0.0802 µg/L and 3.29 µg/L. No samples exceeded the 4 µg/L PAL or the 20 µg/L ES for this compound.
- Diamino atrazine, a metabolite of atrazine, was detected at 15 wells (75%) at concentrations ranging from 0.158 µg/L and 0.672 µg/L. The 0.3 µg/L PAL for total atrazine was exceeded at nine wells (45%). No samples exceeded the 3 µg/L ES for total atrazine.
- Clothianidin, a neonicotinoid insecticide, was detected at 10 wells (50%) at concentrations ranging from 0.0126 µg/L and 0.599 µg/L. No PAL and ES standards have been established for this compound at this time. The Wisconsin Department of Health Services (DHS) has set the Drinking Water Health Advisory for clothianidin at 1,000 µg/L. All clothianidin detections did not exceedare below the DHS Drinking Water Health Advisory.
- Acetochlor ESA was detected at seven wells (35%) at concentrations ranging from 0.0621 µg/L and 0.211 µg/L. No samples exceeded the 46 µg/L PAL or the 230 µg/L ES for this compound.
- Metolachlor OA (or OXA) was detected at five wells (25%) at concentrations ranging from 0.297 µg/L and 5.94 µg/L. No samples exceeded the 260 µg/L PAL or the 1,300 µg/L ES for this compound.
- Atrazine (parent material) was detected at two wells (10%) at concentrations ranging from 0.0608 µg/L and 0.105 µg/L. No samples exceeded the 0.3 µg/L PAL or the 3 µg/L ES for total atrazine.
- Bentazon was detected at two wells (10%) at concentrations ranging from 0.085 µg/L and 1.8 µg/L. No samples exceeded the 60 µg/L PAL or the 300 µg/L ES for this compound.
- Sulfentrazone was detected at one well (5%) at a concentration of 0.194 µg/L. No PAL and ES standards have been established for this compound at this time. DHS has set the Drinking Water Health Advisory for sulfentrazone at 1,000 µg/L. The concentration detected did not exceed the DHS Drinking Water Health Advisory.
- Deisopropyl atrazine was detected at one well (5%) at a concentration of 0.0571 µg/L. This concentration did not exceed the 0.3 µg/L PAL and the 3 µg/L ES for total atrazine.
- Fomesafen was detected at one well (5%) at a concentration of 0.276 µg/L. No PAL and ES standards have been established for this compound at this time. DHS has set the Drinking Water Health Advisory for fomesafen at 25 µg/L. The concentration detected did not exceed the DHS Drinking Water Health Advisory.
- Dimethenamid ESA, a metabolite of dimethenamid, was detected at one well (5%) at a concentration of 0.0596 µg/L. No PAL, ES, or DHS Drinking Water Health Advisories have been established for this compound at this time.
- Clopyralid was detected at one well (5%) at a concentration of 0.131 µg/L. No PAL, ES, or DHS Drinking Water Health Advisories have been established for this compound at this time.
- Triclopyr was detected at one well (5%) at a concentration of 0.0774 µg/L. No PAL, ES, or DHS Drinking Water Health Advisories have been established for this compound at this time.

Figure 30. Compounds detected through the 2022 Targeted Sampling Program in Rock County and respective detection rates



Notes: *On the x-axis, the list of compounds detected, i.e. found with concentrations greater than laboratory reporting limits. On the y-axis, the detection rate in percentage for each detected compound.*

Atrazine Total Chlorinated Residues (TCR) is the sum of atrazine parent material and its metabolites. Atrazine parent material and three atrazine metabolites (diamino atrazine, de-ethyl atrazine, and deisopropyl atrazine) were detected. Atrazine TCR yielded concentrations between 0.0545 µg/L and 1.1349 µg/L. The 0.3 µg/L PAL for Atrazine TCR was exceeded at 12 wells (60%). No samples exceeded the 3 µg/L ES for Atrazine TCR .

Acetochlor Metabolites is the sum of acetochlor ESA and acetochlor OA (or OXA). Acetochlor OA was not detected in any of the samples collected. Acetochlor Metabolites yielded concentrations between 0.0621 µg/L and 0.211 µg/L. No PAL (46 µg/L) or ES (230 µg/L) standards were exceeded.

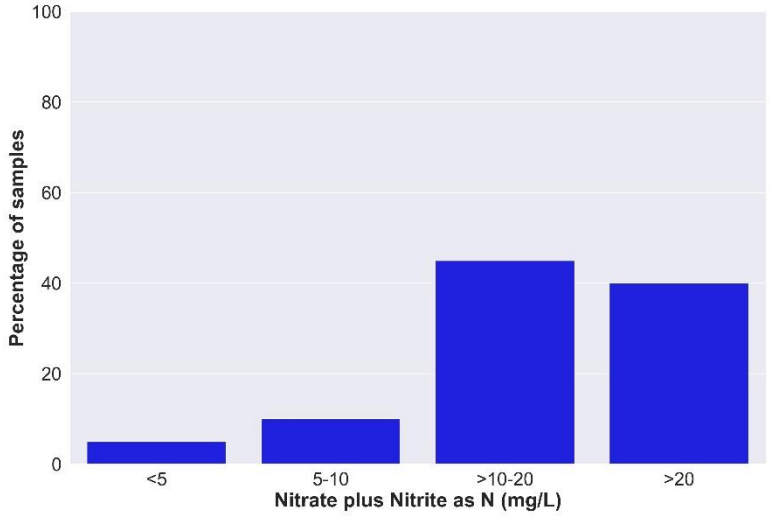
Metolachlor Metabolites is the sum of metolachlor ESA and metolachlor OA (or OXA). Metolachlor Metabolites yielded concentrations between 0.1 µg/L and 17.14 µg/L. No PAL (260 µg/L) or ES (1,300 µg/L) standards were exceeded.

Nitrogen

Nitrate plus nitrite as N was detected in 49 of 54 samples collected. Nitrogen concentrations exceeded the 10 mg/L ES at 17 wells. Nitrogen was most frequently detected between 10 and 20 mg/L. The distribution of nitrate plus nitrite as nitrogen concentrations is summarized below and shown on Figure 31.

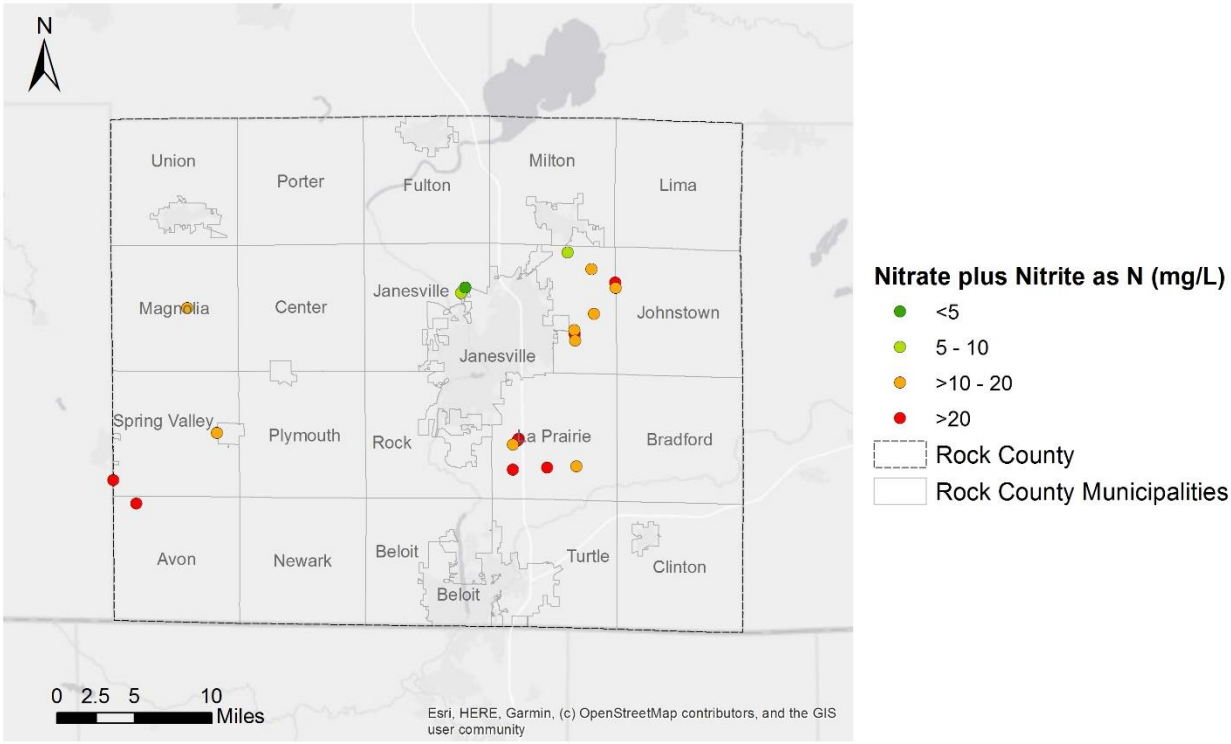
- <5 mg/L: one well (5%)
- 5 to 10 mg/L: two wells (10%)
- >10 to 20 mg/L: nine wells (45%)
- >20 mg/L: eight wells (40%)

Figure 31. Nitrate plus nitrite as N occurrence data in Rock County



As shown on Figure 32, the wells with nitrogen concentrations greater than 10 mg/L (in orange and red) are located in different areas of the county. However, four of the eight wells with a nitrogen concentration greater than 20 mg/L are located in the municipality of La Prairie. This finding may be influenced by the fact that more data was collected in La Prairie compared to other municipalities, such as Avon and Spring Valley.

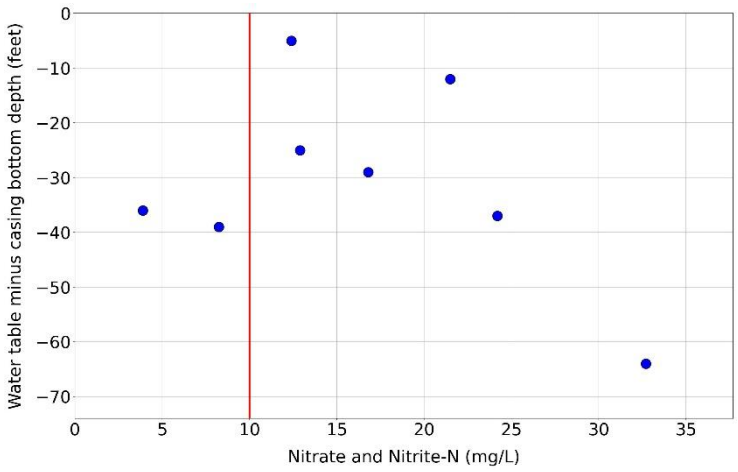
Figure 32. Nitrate plus nitrite as N concentration for each sampling location in Rock County



To track the nitrogen contamination in-depth and to better identify what factors control the contamination, we retrieved information on well depth, casing bottom depth, static water level, bedrock depth, and installation date from publicly available construction reports. Only 11 of the 20 well sampled had complete construction reports.

Figure 33 shows the nitrogen concentration versus the difference between the depth of the water table at the time of construction (static water level) and the bottom depth of the well casing. This plot shows how deep below the water table nitrogen exceeds drinking water standards. As shown, nitrogen exceeded 10 mg/L at depths ranging from four to 64 feet below the water table.

Figure 33. Nitrate and nitrite as nitrogen versus the difference between the water level and the casing depth in Rock County



No relationships were found between nitrogen concentration and casing depth, screen length, or well age (Figure 34). Nitrogen concentration is negatively correlated with the well depth; the shallower the well bottom, the higher the nitrogen concentration. However, the goodness of fit of the linear relationship is very low (R^2=0.1917 for the well depth) and not statistically significant. For example, wells with a depth of about 140 feet show nitrogen concentrations ranging from less than five to almost 15 mg/L. Nitrogen concentration is also negatively correlated with the bedrock depth: the shallower the bedrock, the higher the nitrogen concentration. While the goodness of fit is higher than for the well depth (but still below 0.5, R^2=0.4677), the small sample size (only six data points) limits the reliability of this relationship. Boxplot on Figure 34 shows the nitrogen concentration based on the geology at the well screen (Cb=Carbonate, Snd= Sandstone, S&G= Sand and gravel), with the average nitrogen concentration marked with the white circle. There is no substantial difference in nitrogen average concentration among the different geological deposits at the well screen. The greatest variation in nitrogen concentration is found in wells with a screen in carbonate (or dolomite) deposits.

Since most of the wells selected are within close proximity of agricultural fields, no relationship can be established between nitrogen concentration and the distance from agricultural fields.

Of the 20 samples collected in Rock County through the DATCP 2022 Targeted Program, 17 were previously sampled at least once for nitrate-N by either DATCP, Rock County, or DNR (DNR data available on the Groundwater Retrieval Network website - Wisconsin Department of Natural Resources, 2022). In general, the nitrogen concentrations recorded through the 2022 DATCP Targeted Sampling program are lower than the past nitrogen levels (Table 4).

Figure 34. Nitrate plus nitrite as N as a function of well depth, casing depth, static water level, bedrock depth, and well age in Rock County

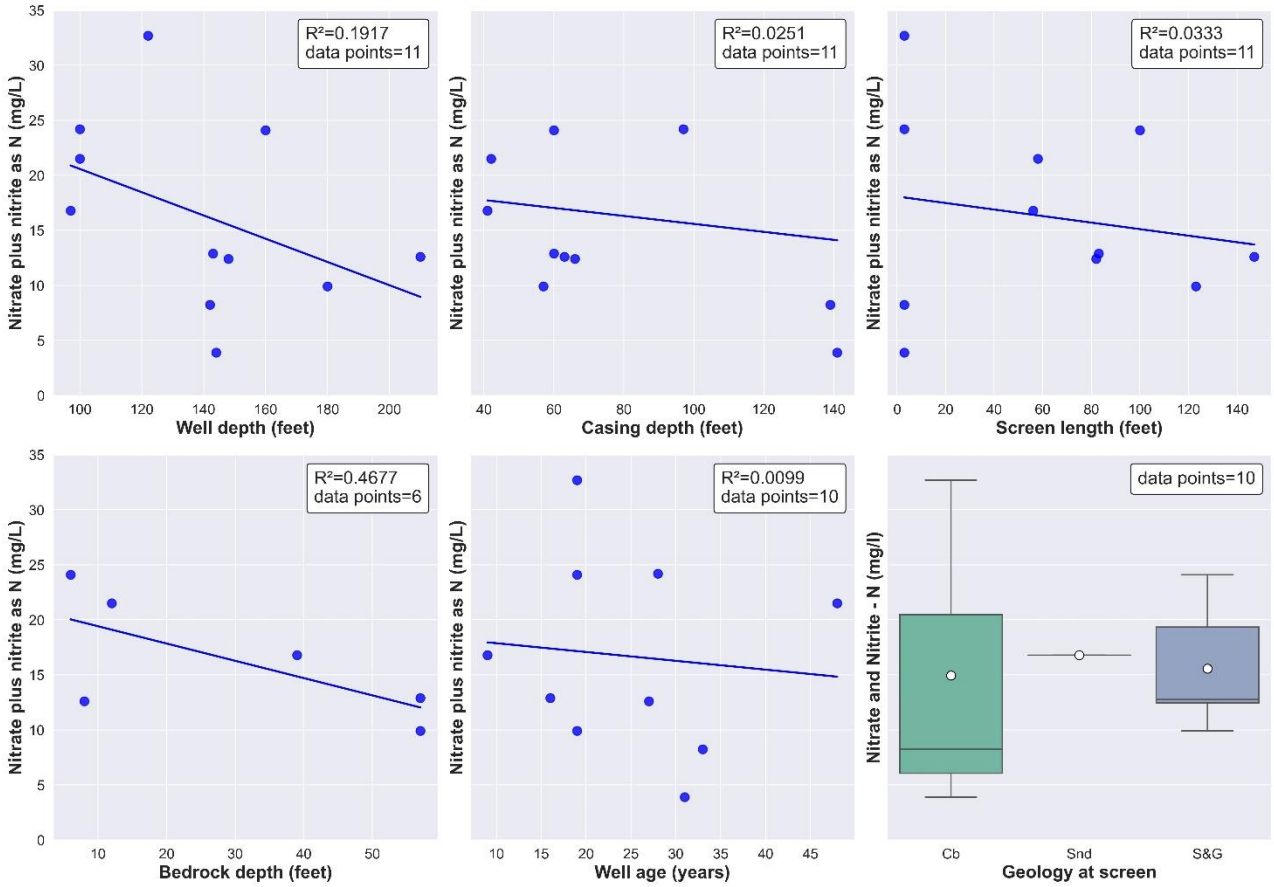


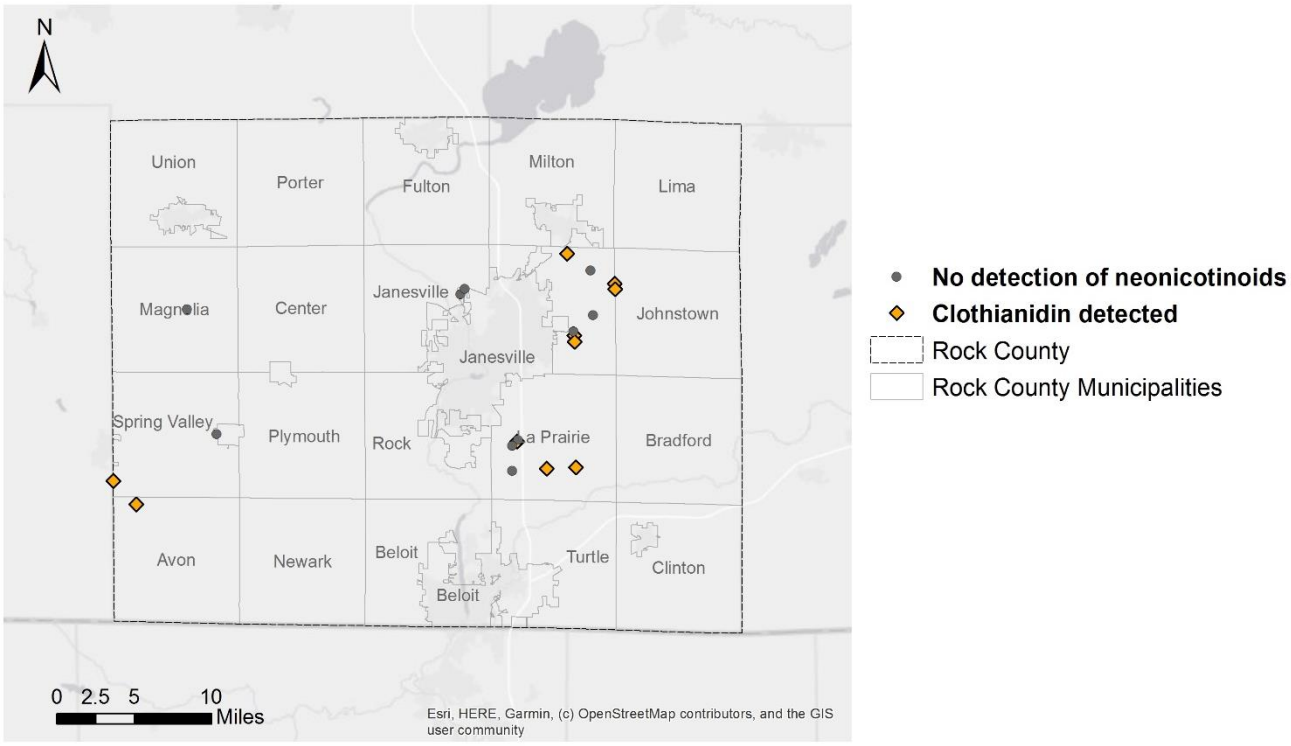
Table 4. Nitrogen concentration changes for the wells that at least once were tested for nitrogen prior the 2022 DATCP sampling effort in Rock County

Nitrogen comparison for 17 wells sampled between 2012 and 2022		
Increased Nitrogen One location	**No or minimal change Three locations**	**Decreased Nitrogen 13 locations**
One increased by 2 to 5 mg/L	Two decreased less than 2 mg/L One increased less than 2 mg/L	None decreased by 2 to 5 mg/L
None increased by 5 to 10 mg/L		Four decreased by 5 to 10 mg/L
None increased more than 10 mg/L		Nine decreased more than 10 mg/L

Neonicotinoids

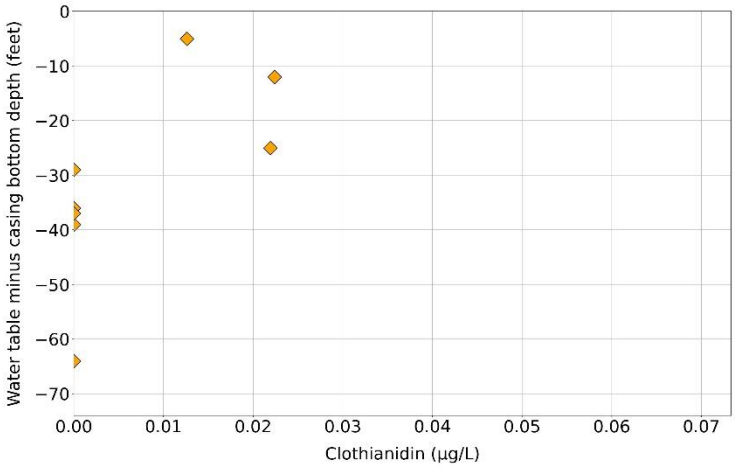
From 2008 to 2016, DATCP sampled several wells in Rock County and no neonicotinoids were detected. However, since 2018, clothianidin has been detected at several private potable wells of Rock County (unpublished data). The analytical results of the sampling effort for 2022 confirmed that clothianidin was the only neonicotinoid detected. In 2022, clothianidin was detected at concentrations greater than the laboratory detection limit at 10 wells (Figure 35). Clothianidin can be either a parent compound or a metabolite of thiamethoxam and hence may be associated with the use of pesticides products containing either clothianidin or thiamethoxam as active ingredients. The clothianidin concentrations recorded through the 2022 DATCP Targeted Sampling program did not exceed the DHS Drinking Water Health Advisory level of 1,000 µg/L.

Figure 35. Sampling locations in Rock County where neonicotinoids were detected



Clothianidin concentrations were evaluated in relation to the difference between the water depth and the casing depth (Figure 36). Information on the well properties is available for eight of the 10 locations where clothianidin was detected. Clothianidin was detected to a maximum depth of 25 feet below the water table.

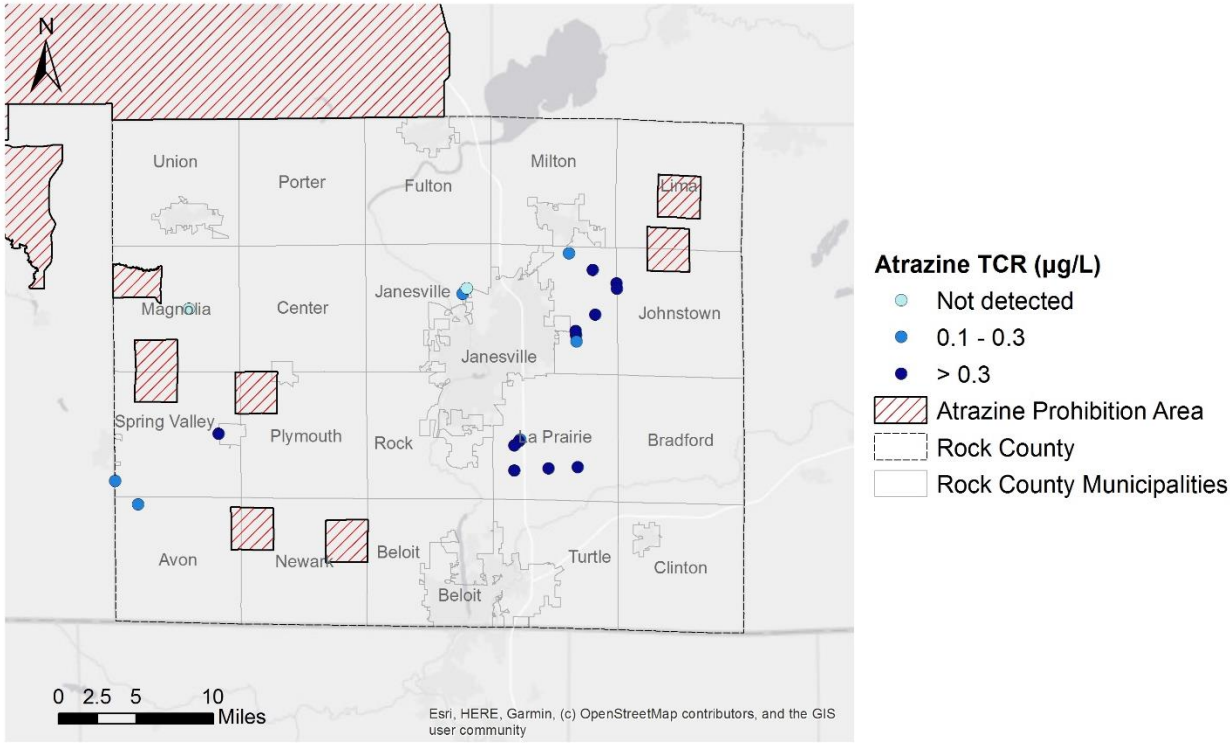
Figure 36. Clothianidin concentration versus the difference between the water level and the casing depth



Atrazine

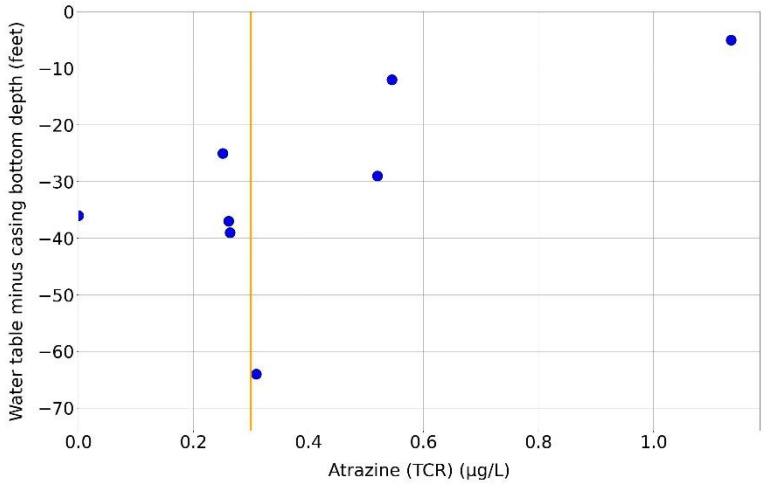
There are currently seven prohibition areas in Rock County (Figure 37). Atrazine metabolites were detected at 18 of the 20 wells. The sum of the atrazine metabolites (atrazine TCR) exceeded the PAL of 0.3 µg/L at 12 locations (Figure 37). The majority of these locations are within the eastern portion of the County.

Figure 37. Sampling location in Rock County where Atrazine Total Chlorinated Residue (TCR) was detected



Atrazine TCR was found between 5 and 64 feet below the water table (Figure 38). Higher concentrations of Atrazine TCR were found at shallower depths below the water table.

Figure 38. Atrazine Total Chlorinated Residue (TCR) concentration versus the difference between the water level and the casing depth in Rock County



CONCLUSION AND RECOMMENDATIONS

Groundwater samples collected between October and November 2022 from 20 Rock County wells were tested for nitrate and 106 pesticides. Seventeen of these samples exceeded the 10 mg/L. Enforcement Standard (ES) for nitrogen, which is similar to findings from prior sampling efforts conducted by Rock County and the DNR. Nitrogen concentrations declined at 13 locations. Although nitrogen concentrations remained above 10 mg/L in the 2022 samples collected from 12 wells, the nitrogen concentration declined to a concentration less than 10 mg/L at one well. This may be related to a decrease in nitrogen inputs, the potential adoption of best management practices, the timing of sampling, and/or hydrogeological factors. Below average precipitation occurred in 2022 in Rock County than in previous years (since 2013) (NOAA National Centers for Environmental information, 2022). Lower precipitations may have reduced the infiltration of contaminants in groundwater. No strong linear relationships were found between nitrogen concentrations and well properties or nitrogen concentration. Additional data is needed to confirm these conclusions.

Several pesticides were detected but no pesticide concentrations exceeded their respective ESs. Atrazine metabolites are the only compounds detected at concentrations greater than the PAL of 0.3 µg/L. In 2022, over 177,000 acres of Rock County were devoted to corn and alfalfa production (United States Department of Agriculture, 2022). Since atrazine may be used on these crops and is not prohibited in most of Rock County, it was foreseeable that atrazine metabolites would be detected. Clothianidin was detected in the 2022 samples, but no imidacloprid or thiamethoxam were detected. Additional sampling is needed to better understand neonicotinoids trends and occurrence. (Note: DATCP does not track the type or amount of pesticides used on specific fields, by county, or statewide.)

DATCP will consider resampling wells where pesticides of interest (atrazine and clothianidin) were found in future sampling efforts. Since no PAL, ES, or DHS Drinking Water Health Advisories have been established for Dimethenamid ESA, Clopyralid, and Triclopyr, we are currently unable to assess the health risk associated with the detection of these compounds. The detections of the remaining pesticides are of minimal regulatory concern regarding risks to human health. For example, metolachlor and metolachlor ESA were both found at concentrations below established water quality standards.

Recommendations

The occurrence of nitrogen and pesticides in groundwater is influenced by environmental factors including soil, geology, depth to groundwater, and weather events, as well as land management practices such as crops grown, cultivation, agrichemicals used, tile drainage, and irrigation, near the wells in this study. Other factors including well construction, casing depth, total depth, and proximity to agricultural fields may also influence potential impacts to groundwater quality. Identifying the extent to which these variables interact and contribute to the contaminants observed at each sample location presents challenges beyond the scope of this report. Regardless, information in this report may help others to make changes with local land management or influence chemical use decisions that benefit water quality.

DATCP will:

- Share this summary report with health departments and land conservation departments in the counties where sampling occurred.
- Share monitoring data and report findings with United States Environmental Protection Agency, Wisconsin Department of Natural Resources, and Wisconsin Department of Health Services to help identify pesticides of interest for national tracking purposes or state standards development.
- Share this report with Groundwater Coordinating Council (GCC) members and member agencies.
- Collect verification samples from wells where pesticide or pesticide metabolite concentrations exceed existing Wis. Admin. Code ch. NR 140 ES or DHS drinking water quality advisories.
- Attempt to resample all wells in five years (2026) to further evaluate trends in groundwater quality.

Acknowledgments

ACM's financial information includes the state fiscal year (FY) 2022 from July 1, 2021 through June 30, 2022. Federal grants operate October 1, 2021 through September 30, 2022. This report covers those portions of the federal grants that occurred during the state fiscal year. The primary sources of revenue for ACM are industry fees for licenses, permits, registrations, and tonnage under the feed, fertilizer, soil and plant additive, lime, and pesticide programs. ACM recognizes these important partnerships with industry and the federal government and works hard to maximize the use of this funding for the benefit of the industry, consumers, and the environment.

The raw data required to reproduce the above findings are available upon request. For any questions and clarifications, please do not hesitate to reach out to us at DATCPGW@wisconsin.gov or at (608) 224-4502.

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Appendix A

The acronyms and terminology included on this list are generic definitions intended to help understand the Targeted Sampling Program. Some of these terms are more specifically defined in various regulations.

ACRONYMS

µg/L	Micrograms per liter (a liquid equivalent of ppb)
ACM	Bureau of Agrichemical Management
BLS	Bureau of Laboratory Services
DADK	Desaminodiketo
DATCP	Department of Agriculture, Trade and Consumer Protection
DHS	Wisconsin Department of Health Services
DNR	Wisconsin Department of Natural Resources
EPA	United States - Environmental Protection Agency
ES	Enforcement Standard
ESA	Ethane Sulfonic Acid
GC	Gas Chromatography
GCC	Wisconsin Groundwater Coordinating Council
ISO	International Organization for Standardization
LC	Liquid Chromatography
mg/L	Milligrams per liter (a liquid equivalent of ppm)
MS	Mass Spectroscopy
N	Nitrogen
ND	No Detect concentrations are less than laboratory reporting limits
NOAA	National Oceanic and Atmospheric Administration
OA	Oxanilic Acid
PAL	Preventive Action Limit
TCR	Total chlorinated residues
USDA	U.S. Department of Agriculture
WGNHS	Wisconsin Geological and Natural History Survey
Wis. Admin. Code	Wisconsin Administrative Code
WUWN	Wisconsin Unique Well Number

DEFINITIONS

Analyte - A chemical substance that has a defined Chemical Abstract Service (CAS) number

Atrazine Prohibition Area - An area where atrazine use is currently prohibited under Administrative Code ATCP 30

Compound - A substance formed by the chemical union of two or more ingredients

Detection - When an analyte has a concentration that can be quantified (i.e., a concentration greater than the Laboratory Reporting Limit)

Enforcement Standard (ES) - The Enforcement Standard (ES) is set to ensure that the concentration of a compound in groundwater does not exceed a specific level that could harm human health or the environment. If the ES for a certain compound in groundwater is exceeded, intervention from the appropriate authority is required

Herbicide - A pesticide used to kill or inhibit the growth of plants, weeds, or grasses

Insecticide - A pesticide used to kill or inhibit the growth of insects

Metabolite or Residual compound or Breakdown product - A chemical substance left behind by a parent compound that has degraded through natural chemical breakdown and/or been metabolized by bacteria

Neonicotinoids - Insecticides that target the neurological systems of insects. The neonicotinoid family includes acetamiprid, clothianidin, dinotefuran, imidacloprid, nitenpyram, nithiazine, thiacloprid, and thiamethoxam

NR140 - Wisconsin administrative code which establishes groundwater quality standards and required responses when the standards are exceeded

Pesticide - Substance used to kill, repel, or control certain forms of plant or animal life that are considered to be pests. The pesticide category includes herbicides, insecticides, rodenticides, fungicides, and bactericides

Preventive Action Limit (PAL) - The Preventive Action Limit (PAL) is a percentage of the Enforcement Standard (ES); 10% of the ES for carcinogenic, mutagenic, or teratogenic properties, and 20% of the ES for the remaining substances. The intention of the PAL is for it to act as a trigger for intervention before a pollutant becomes a serious risk to public health or the environment

Reporting limit - The minimum analyte concentration that can be reliably quantified and reported by the laboratory

Total chlorinated residues (TCR) of atrazine - Sum of atrazine and atrazine metabolites (de-ethyl atrazine, de-isopropyl atrazine, and diamino atrazine)

Appendix B

Table B 1. Summary of analytical results for the 2022 Targeted Sampling Program

2022 Targeted Sampling Program Results					Wisconsin Admin. Code Chapter NR 140		Wisconsin Department of Health Services
Pesticide Name	Pesticide Class	Number of detects	Reporting Limit (µg/L)	Concentration Range (µg/L)	Preventive Action Limit (µg/L)	Enforcement Standards (µg/L)	Drinking Water Health Advisory (µg/L)
2,4,5-T	Herbicide	ND	0.05	---	---	---	---
2,4,5-TP	Herbicide	ND	0.05	---	5	50	---
2,4-D	Herbicide	ND	0.05	---	7	70	---
2,4-DB	Herbicide	ND	1	---	---	---	---
2,4-DP	Herbicide	ND	0.05	---	---	---	---
ACETAMIPRID	Insecticide	ND	0.01		---	---	---
ACETOCHLOR	Herbicide	ND	0.05	---	0.7	7	---
ACETOCHLOR ESA	Metabolite	7	0.05	0.0621 - 0.211	46	230	---
ACETOCHLOR OA	Metabolite	ND	0.3	---	46	230	---
ALACHLOR METABOLITES	Sum of acetochlor metabolites	7	---	0.0621 - 0.211	46	230	
ACIFLUORFEN	Herbicide	ND	0.05	---	---	---	---
ALACHLOR	Herbicide	ND	0.05	---	0.2	2	---
ALACHLOR ESA	Metabolite	20	0.05	0.0802 - 3.29	4	20	---
ALACHLOR OA or OXA	Metabolite	ND	0.25	---	---	---	---
ALDICARB SULFONE	Insecticide	ND	0.05	---	---	---	---
ALDICARB SULFOXIDE	Insecticide	ND	0.071	---	---	---	---
AMINOPYRALID	Herbicide	ND	0.15	---	---	---	---
ATRAZINE	Herbicide	3	0.05	0.0608 - 0.131	0.3	3	---
DE-ETHYL ATRAZINE	Metabolite	23	0.05	0.0507 - 0.345	0.3	3	---
DEISOPROPYL ATRAZINE	Metabolite	2	0.05	0.0571 - 0.0984	0.3	3	---
DIAMINO ATRAZINE	Metabolite	36	0.15	0.154 - 0.672	0.3	3	---
ATRAZINE (TCR)	Sum of atrazine and atrazine metabolites	43	---	0.0507 - 1.1349	0.3	3	---
AZOXYSTROBIN	Fungicide	ND	0.05	---	---	---	---
BENFLURALIN	Herbicide	ND	0.05	---	---	---	---
BENTAZON	Herbicide	2	0.05	0.085 - 1.8	60	300	---
BICYCLOPYRONE	Herbicide	ND	0.05	---	---	---	---
BIFENTHRIN	Insecticide	ND	0.005	---	---	---	---
BROMACIL	Herbicide	ND	0.05	---	---	---	---
CARBARYL	Insecticide	ND	0.05	---	4	40	---
CARBOFURAN	Insecticide	ND	0.05	---	8	40	---
CHLORAMBEN	Herbicide	ND	0.32	---	30	150	---
CHLORANTRANILIPROLE	Insecticide	ND	0.05	---	---	---	16,000
CHLOROTHALONIL	Fungicide	ND	0.1	---	---	---	---
CHLORPYRIFOS	Insecticide	ND	0.05	---	0.4	2	---
CHLORPYRIFOS OXYGEN ANALOG	Metabolite	ND	0.05	---	---	---	---
CLOMAZONE	Herbicide	ND	0.05	---	---	---	---
CLOPYRALID	Herbicide	2	0.05	0.131 - 0.38	---	---	---
CLOTHIANIDIN	Insecticide	20	0.01	0.01 - 0.599	---	---	1,000
CYANTRANILIPROLE	Insecticide	ND	0.05	---	---	---	16,000
CYCLANILIPROLE	Insecticide	ND	0.2	---	---	---	---

2022 Targeted Sampling Program Results					Wisconsin Admin. Code Chapter NR 140		Wisconsin Department of Health Services
Pesticide Name	Pesticide Class	Number of detects	Reporting Limit (µg/L)	Concentration Range (µg/L)	Preventive Action Limit (µg/L)	Enforcement Standards (µg/L)	Drinking Water Health Advisory (µg/L)
CYFLUTHRIN	Insecticide	ND	0.05	---	---	---	---
CYPERMETHRIN	Insecticide	ND	0.1	---	---	---	---
CYPROSULFAMIDE	Safener	ND	0.05	---	---	---	---
DACTHAL	Herbicide	ND	0.05	---	14	70	---
DACTHAL DI-ACID	Metabolite	ND	0.5	---	---	---	70
DACTHAL MONO-ACID	Metabolite	ND	0.5	---	---	---	70
DACTHAL TOTAL	Sum of dacthal and dacthal metabolites	ND	0.5	---	---	---	70
DESTHIO PROTHIOCONAZOLE	Fungicide metabolite	ND	0.05	---	---	---	---
DIAZINON	Insecticide	ND	0.05	---	---	---	---
DIAZINON OXYGEN ANALOG	Metabolite	ND	0.05	---	---	---	---
DICAMBA	Herbicide	ND	0.2	---	60	300	---
DICHLOBENIL	Herbicide	ND	0.05	---	---	---	---
DIMETHENAMID	Herbicide	ND	0.05	---	5	50	---
DIMETHENAMID ESA	Metabolite	1	0.05	0.0596	---	---	---
DIMETHENAMID OA	Metabolite	ND	0.05	---	---	---	---
DIMETHOATE	Insecticide	ND	0.05	---	0.4	2	---
DINOTEFURAN	Insecticide	ND	0.01	---	---	---	---
DIURON	Herbicide	ND	0.05	---	---	---	---
EPTC	Herbicide	ND	0.05	---	50	250	---
ESFENVALERATE	Insecticide	ND	0.025	---	---	---	---
ETHALFLURALIN	Herbicide	ND	0.05	---	---	---	---
ETHOFUMESATE	Herbicide	ND	0.05	---	---	---	---
FLUMETSULAM	Herbicide	ND	0.05	---	---	---	10,000
FLUPYRADIFURONE	Insecticide	ND	0.05	---	---	---	---
FLUROXYPYR	Herbicide	ND	0.05	---	---	---	---
FOMESAFEN	Herbicide	1	0.05	0.276	---	---	25
HALOSULFURON METHYL	Herbicide	ND	0.05	---	---	---	---
HEXAZINONE	Herbicide	ND	0.05	---	---	---	400
IMAZAPYR	Herbicide	ND	0.05	---	---	---	---
IMAZETHAPYR	Herbicide	ND	0.05	---	---	---	---
IMIDACLOPRID	Insecticide	4	0.01	0.0481 - 0.0869	---	---	0.2
ISOXAFLUTOLE	Herbicide	ND	0.05	---	---	---	3
ISOXAFLUTOLE DKN	Metabolite	ND	0.05	---	---	---	3
ISOXAFLUTOLE TOTAL	Sum of isoxaflutole (IFT) and IFT DKN	ND	0.05	---	---	---	3
LAMBDA-CYHALOTHRIN	Insecticide	ND	0.02	---	---	---	---
LINURON	Herbicide	ND	0.05	---	---	---	---
MALATHION	Insecticide	ND	0.05	---	---	---	---
MCPA	Herbicide	ND	0.05	---	---	---	---
MCPB	Herbicide	ND	0.1	---	---	---	---
MCPP	Herbicide	ND	0.05	---	---	---	---
MESOTRIONE	Herbicide	ND	0.1	---	---	---	---

2022 Targeted Sampling Program Results					Wisconsin Admin. Code Chapter NR 140		Wisconsin Department of Health Services
Pesticide Name	Pesticide Class	Number of detects	Reporting Limit (µg/L)	Concentration Range (µg/L)	Preventive Action Limit (µg/L)	Enforcement Standards (µg/L)	Drinking Water Health Advisory (µg/L)
METALAXYL	Fungicide	ND	0.05	---	---	---	800
METHYL PARATHION	Insecticide	ND	0.05	---	---	---	---
METOLACHLOR	Herbicide	1	0.05	0.0549	10	100	---
METOLACHLOR ESA	Metabolite	48	0.05	0.0523 - 13.1	260	1300	---
METOLACHLOR OA or OXA	Metabolite	5	0.27	0.297 - 5.94	260	1300	---
METOLACHLOR METABOLITES	Sum of metolachlor ESA and metolachlor OA	48	---	0.0523 - 17.14	260	1300	---
METRIBUZIN	Herbicide	ND	0.05	---	14	70	---
METRIBUZIN DA	Metabolite	ND	0.1	---	---	---	---
METRIBUZIN DADK	Metabolite	3	0.12	0.464 - 0.94	---	---	---
METSULFURON-METHYL	Herbicide	ND	0.05	---	---	---	---
NICOSULFURON	Herbicide	ND	0.05	---	---	---	---
NORFLURAZON	Herbicide	ND	0.05	---	---	---	---
OXADIAZON	Herbicide	ND	0.05	---	---	---	---
PENDIMETHALIN	Herbicide	ND	0.05	---	---	---	---
PERMETHRIN	Insecticide	ND	0.03	---	---	---	---
PICLORAM	Herbicide	ND	0.05	---	100	500	---
PROMETONE	Herbicide	ND	0.05	---	20	100	---
PROMETRYN	Herbicide	ND	0.05	---	---	---	---
PROPICONAZOLE	Fungicide	ND	0.05	---	---	---	---
SAFLUFENACIL	Herbicide	ND	0.05	---	---	---	460
SIMAZINE	Herbicide	ND	0.05	---	0.4	4	---
SULFENTRAZONE	Herbicide	1	0.05	0.194	---	---	1,000
SULFOMETURON-METHYL	Herbicide	ND	0.05	---	---	---	---
TEBUPIRIMPHOS	Insecticide	ND	0.05	---	---	---	---
TEMBOTRIONE	Herbicide	ND	0.1	---	---	---	---
THIACLOPRID	Insecticide	ND	0.01	---	---	---	---
THIAMETHOXAM	Insecticide	5	0.01	0.0222 - 1.01	---	---	120
THIENCARBAZONE-METHYL	Herbicide	ND	0.05	---	---	---	10,000
TRICLOPYR	Herbicide	ND	0.05	0.0774	---	---	---
TRIFLURALIN	Herbicide	ND	0.05	---	0.75	7.5	---

Legend:

--- In columns Wisconsin Admin. Code Chapter NR 140 or Wisconsin Department of Health Services indicates that no standards or health advisory is established for that compound. In column Concentration Range indicates that the concentration was found below Reporting Limits.

ND = Not detected at a concentration greater than the reporting laboratory limit.

µg/L = Micrograms per liter or parts per billion.

TCR = Total Chlorinated Residue for Atrazine. Reflects an additive quantity of atrazine and its three metabolites (de-ethyl, de-isopropyl and di-amino atrazine).

Indicates no detects in excess of laboratory reporting limits.

Indicates no detects in excess of laboratory reporting limits, but not in excess of any Preventive Action Limits.

Indicates detects in excess of laboratory reporting limits and Wisc. Admin. Code ch. NR 140 Preventive Action Limit, but not Enforcement standards.

Indicates detects in excess of laboratory reporting limits and Wisc. Admin. Code ch. NR 140 Enforcement standards.

Table B 2. 2022 Targeted Sampling Program analytical results for Door County

WUWN	Sample Date	ALACHLOR ESA	CLOTHIANIDIN	CLOPYRALID	DE-ETHYL ATRAZINE	DEISOPROPYL ATRAZINE	DIAMINO ATRAZINE	ATRAZINE (TCR)	IMIDACLOPRID	METOLACHLOR	METOLACHLOR ESA	METOLACHLOR METABOLITES	NITROGEN-NITRATE/NITRITE	Total compounds detected
8DB275	7/11/2022	ND	ND	ND	ND	ND	ND	ND	ND	ND	0.0539	0.0539	5.54	2
8DB542	7/25/2022	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	5.22	1
8DC404	7/11/2022	ND	ND	ND	ND	ND	ND	ND	ND	ND	0.954	0.954	13.4	2
8DD084	7/21/2022	ND	ND	ND	ND	ND	0.186	0.186	ND	ND	ND	ND	5.95	2
8DD409	7/12/2022	ND	ND	0.38	ND	ND	ND	ND	ND	ND	ND	ND	3.64	2
8DD576	7/26/2022	ND	ND	ND	ND	ND	ND	ND	ND	ND	0.0923	0.0923	6.05	2
8DD729	7/12/2022	ND	0.0205	ND	0.0507	ND	ND	0.0507	ND	ND	0.168	0.168	10.6	4
AAG510	7/25/2022	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	5.76	1
BJ154	7/21/2022	ND	ND	ND	ND	ND	0.267	0.267	ND	ND	ND	ND	6.3	2
BJ162	7/26/2022	ND	ND	ND	ND	ND	0.154	0.154	ND	ND	ND	ND	5.35	2
BJ170	7/20/2022	ND	ND	ND	ND	ND	0.19	0.19	ND	ND	ND	ND	5.27	2
BJ213	7/20/2022	ND	ND	ND	ND	ND	0.202	0.202	ND	ND	ND	ND	5.76	2
BJ301	7/11/2022	ND	ND	ND	0.0553	ND	0.207	0.2623	ND	ND	ND	ND	6.76	3
EX865	8/3/2022	ND	ND	ND	ND	ND	ND	ND	ND	ND	0.406	0.406	1.68	2
IJ897	7/25/2022	ND	ND	ND	ND	ND	ND	ND	ND	ND	0.191	0.191	3.88	2
IJ911	8/2/2022	ND	ND	ND	ND	ND	0.172	0.172	0.0707	ND	ND	ND	5.42	3
KV117	7/11/2022	ND	0.0134	ND	ND	ND	ND	ND	ND	0.0549	ND	ND	6.42	3
KZ425	8/2/2022	ND	ND	ND	ND	ND	0.233	0.233	ND	ND	ND	ND	5.2	2
LG560	7/25/2022	ND	ND	ND	ND	ND	0.176	0.176	ND	ND	0.0609	0.0609	5.45	3
LV374	7/20/2022	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	4.76	1
MQ252	7/26/2022	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
MZ244	7/20/2022	ND	ND	ND	ND	ND	0.219	0.219	ND	ND	ND	ND	5.46	2
MZ283	7/20/2022	ND	ND	ND	ND	ND	0.186	0.186	ND	ND	0.0885	0.0885	6.09	3
NP515	7/25/2022	ND	ND	ND	ND	ND	ND	ND	ND	ND	0.195	0.195	7.84	2
PW501	7/12/2022	0.158	ND	ND	ND	ND	ND	ND	ND	ND	0.256	0.256	5.08	3
PW502	7/12/2022	ND	0.0335	ND	ND	ND	ND	ND	ND	ND	0.124	0.124	6.65	3
PW503	7/11/2022	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
PW504	7/12/2022	ND	ND	ND	ND	ND	ND	ND	ND	ND	0.253	0.253	8.96	2
PW505	7/20/2022	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	13.4	1
PW506	7/21/2022	ND	ND	ND	ND	ND	0.193	0.193	ND	ND	ND	ND	4.68	2
PW507	7/21/2022	ND	0.01	ND	ND	ND	ND	ND	ND	ND	0.397	0.397	5.69	3
PW508	7/21/2022	ND	ND	ND	ND	ND	ND	ND	ND	ND	0.253	0.253	6.37	2
PW509	7/25/2022	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	3.16	1
PW510	7/26/2022	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
PW511	7/26/2022	ND	ND	ND	ND	ND	ND	ND	ND	ND	0.158	0.158	6.03	2
PW512	7/26/2022	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
PW513	8/2/2022	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
QU084	7/11/2022	ND	ND	ND	ND	ND	ND	ND	ND	ND	0.175	0.175	5.29	2
SF341	7/11/2022	ND	ND	ND	0.0611	ND	0.219	0.2801	ND	ND	0.0668	0.0668	6.16	4
SR017	7/20/2022	ND	ND	ND	ND	ND	0.179	0.179	ND	ND	ND	ND	5.52	2
SS795	8/3/2022	ND	ND	ND	ND	ND	0.22	0.22	ND	ND	ND	ND	6.4	2
TG198	8/2/2022	ND	ND	ND	ND	ND	0.194	0.194	ND	ND	ND	ND	5.52	2
TM298	7/21/2022	ND	0.0102	ND	ND	ND	ND	ND	ND	ND	0.356	0.356	8.09	3
TT440	8/2/2022	ND	ND	ND	0.0611	ND	ND	0.0611	ND	ND	ND	ND	5.04	2
TV420	7/21/2022	ND	ND	ND	ND	ND	0.215	0.215	ND	ND	ND	ND	6.16	2
UB179	7/21/2022	ND	ND	ND	ND	ND	0.238	0.238	ND	ND	ND	ND	6.11	2
UM045	7/20/2022	ND	0.0127	ND	0.0526	ND	ND	0.0526	ND	ND	0.345	0.345	8.34	4
UM050	7/20/2022	ND	ND	ND	ND	ND	0.155	0.155	ND	ND	0.0673	0.0673	5.4	3
WL970	7/26/2022	ND	ND	ND	ND	ND	ND	ND	ND	ND	0.0838	0.0838	5.23	2
WR742	7/26/2022	ND	ND	ND	ND	ND	0.362	0.362	ND	ND	ND	ND	4.7	2
XD798	7/12/2022	0.403	ND	ND	ND	0.0984	0.278	0.3764	ND	ND	0.273	0.273	9.27	5
YD197	7/12/2022	0.182	ND	ND	ND	ND	ND	ND	ND	ND	0.14	0.14	4.87	3
ZU124	7/21/2022	ND	ND	ND	ND	ND	ND	ND	ND	ND	0.115	0.115	4.19	2
ZZ495	7/25/2022	ND	ND	ND	ND	ND	ND	ND	ND	ND	0.271	0.271	3.91	2

Legend:

Indicates concentration greater than respective Wis. Admin. Code ch NR 140 PAL.

Indicates concentration greater than respective Wis. Admin. Code ch NR 140 ES.

ND = Not detected at a concentration greater than the reporting laboratory limit.

Concentrations are reported in µg/L with the exception of Nitrate concentrations reported in mg/L.

The "Total compound detected column" excludes the Atrazine TCR, which is the sum of atrazine and its metabolites.

Table B 3. 2022 Targeted Sampling Program analytical results for Oneida County

WUWN	Sample Date	ATRAZINE	DE-ETHYL ATRAZINE	ATRAZINE (TCR)	CLOTHIANIDIN	IMIDACLOPRID	METOLACHLOR ESA	METOLACHLOR METABOLITES	METRIBUZIN DADK	THIAMETHOXAM	NITROGEN-NITRATE/NITRITE	Total compounds detected
8CC087	10/12/2022	0.131	0.128	0.259	ND	ND	ND	ND	ND	ND	1.38	3
DK650	10/10/2022	ND	ND	ND	0.0599	0.0481	0.0523	0.0523	0.535	0.474	7.66	6
EJ981	10/12/2022	ND	ND	ND	0.0191	ND	ND	ND	ND	0.0379	4.77	3
GP608	10/11/2022	ND	ND	ND	0.023	0.0869	0.0834	0.0834	0.94	1.01	10.1	6
UL044	10/12/2022	ND	ND	ND	ND	ND	0.134	0.134	ND	0.0222	3.46	3
UX653	10/10/2022	ND	ND	ND	ND	ND	0.154	0.154	ND	ND	ND	1
VC492	10/11/2022	ND	ND	ND	0.0145	0.0513	0.173	0.173	0.464	0.486	5.91	6

Legend:

Indicates concentration greater than respective Wis. Admin. Code ch NR 140 PAL.

Indicates concentration greater than respective Wis. Admin. Code ch NR 140 ES.

ND = Not detected at a concentration greater than the reporting laboratory limit.

Concentrations are reported in µg/L with the exception of Nitrate concentrations reported in mg/L.

The "Total compound detected column" excludes the Atrazine TCR, which is the sum of atrazine and its metabolites.

Table B 4. 2022 Targeted Sampling Program analytical results for Rock County

WUWN	Sample Date	ACETOCHLOR ESA	ALACHLOR ESA	ATRAZINE	DE-ETHYL ATRAZINE	DIAMINO ATRAZINE	DEISOPROPYL ATRAZINE	ATRAZINE (TCR)	BENTAZON	CLOPYRALID	CLOTHIANIDIN	FOMESAFEN	DIMETHENAMID ESA	METOLACHLOR ESA	METOLACHLOR OA	METOLACHLOR METABOLITES	SULFENTRAZONE	TRICLOPYR	NITROGEN-NITRATE/NITRITE	Total compounds detected
8GC096	10/7/2022	0.0707	0.26	ND	0.118	0.427	ND	0.545	ND	ND	0.0224	0.276	ND	0.1	ND	0.1	0.194	ND	21.5	9
CU836	10/7/2022	ND	0.132	ND	0.0763	0.187	ND	0.2633	ND	ND	ND	ND	ND	0.669	ND	0.669	ND	ND	8.24	5
DH539	10/7/2022	ND	0.25	ND	0.185	0.643	ND	0.828	ND	ND	0.0161	ND	ND	1.09	ND	1.09	ND	ND	21.3	6
DV291	10/7/2022	ND	0.0802	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	0.351	ND	0.351	ND	ND	3.89	3
HR649	10/18/2022	ND	0.149	ND	0.103	0.158	ND	0.261	ND	ND	ND	ND	ND	4.39	0.297	4.687	ND	ND	24.2	6
IG141	10/7/2022	ND	3.29	ND	ND	0.556	ND	0.556	ND	ND	ND	ND	ND	ND	ND	ND	ND	0.0774	12.6	4
PW514	10/7/2022	ND	1.04	0.105	0.302	0.349	ND	0.756	ND	ND	ND	ND	ND	1.09	ND	1.09	ND	ND	11.5	6
PW515	10/7/2022	0.0621	2.55	ND	0.119	0.351	ND	0.47	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	13.4	5
PW516	10/18/2022	ND	0.216	ND	0.115	0.209	ND	0.324	ND	ND	0.0148	ND	ND	4.38	0.343	4.723	ND	ND	21.2	7
PW517	10/18/2022	ND	0.159	ND	0.0978	0.237	ND	0.3348	ND	ND	ND	ND	ND	4.64	0.324	4.964	ND	ND	18.9	6
PW518	10/18/2022	0.211	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	0.469	ND	0.469	ND	ND	19.2	3
PW519	10/18/2022	0.184	ND	ND	0.209	ND	ND	0.209	ND	ND	0.0133	ND	ND	1.5	ND	1.5	ND	ND	24.9	5
PW520	10/20/2022	0.0893	1.77	ND	0.152	0.414	ND	0.566	0.085	ND	0.0246	ND	0.0596	3.83	ND	3.83	ND	ND	17.4	9
PX232	10/7/2022	0.15	0.253	0.0608	0.345	0.672	0.0571	1.1349	ND	ND	0.0126	ND	ND	1.39	ND	1.39	ND	ND	12.4	9
PX702	10/18/2022	ND	ND	ND	0.0545	ND	ND	0.0545	ND	ND	0.599	ND	ND	11.2	5.94	17.14	ND	ND	24.3	5
RK656	11/14/2022	ND	0.122	ND	0.0572	0.252	ND	0.3092	ND	ND	ND	ND	ND	6.37	ND	6.37	ND	ND	32.7	5
RV748	10/7/2022	ND	0.426	ND	0.0696	ND	ND	0.0696	ND	ND	0.0156	ND	ND	0.579	ND	0.579	ND	ND	9.92	5
SD289	11/14/2022	0.156	0.188	ND	0.18	0.34	ND	0.52	ND	0.131	0.0433	ND	ND	13.1	0.895	13.995	ND	ND	24.1	9
ST764	10/7/2022	ND	0.14	ND	0.0659	0.185	ND	0.2509	1.8	ND	0.0219	ND	ND	0.547	ND	0.547	ND	ND	12.9	7
YK117	10/18/2022	ND	0.39	ND	0.0667	0.453	ND	0.5197	ND	ND	ND	ND	ND	3.13	ND	3.13	ND	ND	16.8	5

Legend:

Indicates concentration greater than respective Wis. Admin. Code ch NR 140 PAL.

Indicates concentration greater than respective Wis. Admin. Code ch NR 140 ES.

ND = Not detected at a concentration greater than the reporting laboratory limit.

Concentrations are reported in µg/L with the exception of Nitrate concentrations reported in mg/L.

The "Total compound detected column" excludes the Atrazine TCR, which is the sum of atrazine and its metabolites.