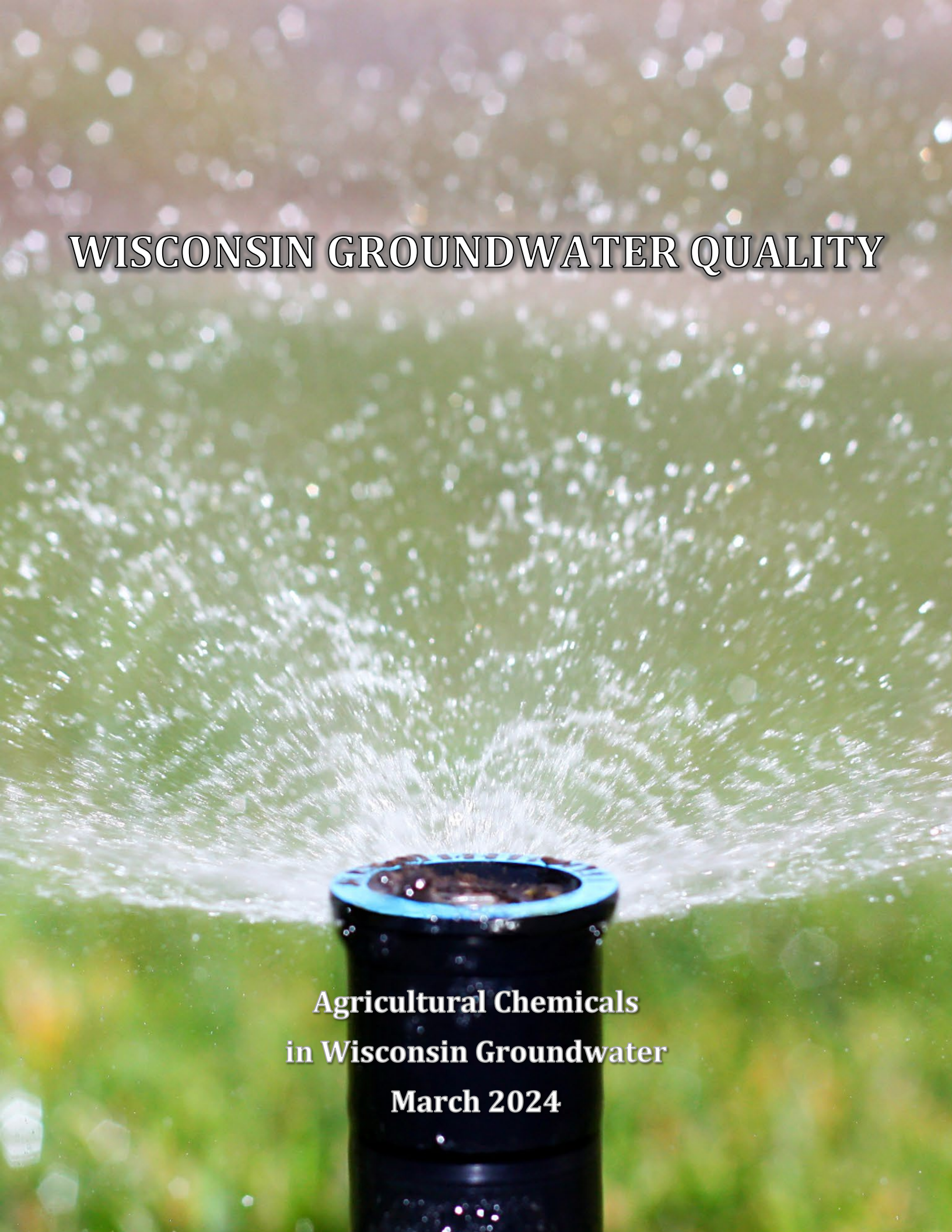

WISCONSIN GROUNDWATER QUALITY

Agricultural Chemicals in Wisconsin Groundwater

March 2024

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AGRICULTURAL CHEMICALS IN WISCONSIN GROUNDWATER

FINAL REPORT
March 2024

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A COOPERATIVE PROJECT OF THE:

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Randy Romanski, Secretary

And,

United States Department of Agriculture - National Agricultural Statistics Service
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The Wisconsin Department of Agriculture, Trade and Consumer Protection (DATCP) and the Wisconsin Field Office of the National Agricultural Statistics Service (NASS) conducted this statewide survey of agricultural chemicals as a cooperative effort. For this project, DATCP was responsible for the overall project management, laboratory analysis, data analysis and report preparation while NASS developed the survey procedures, managed the collection of the water samples, and summarized the laboratory results.

DATCP administers many water quality and agricultural chemical programs that are designed to protect Wisconsin's groundwater. This survey provides factual information on the chemical compounds found in water used by Wisconsin residents with private wells.

Special thanks to the residents who participated in the survey and the many NASS enumerators who collected the water samples and administered the survey questionnaire.

Randy Romanski

Greg Bussler

ABSTRACT

Between March and August 2023, 380 private drinking water wells were sampled as part of a statewide survey of agricultural chemicals in Wisconsin groundwater. The survey aimed to obtain an updated assessment of pesticides and pesticide breakdown products in groundwater, and to compare their concentrations with those found in earlier surveys. The wells were selected using a stratified random sampling procedure and represented Wisconsin groundwater accessible by private wells. Samples collected in the 2023 survey were analyzed for 107 different compounds, including herbicides, herbicide metabolites (breakdown products), insecticides, fungicides, and nitrate plus nitrite as nitrogen N, or nitrate in this manuscript. In addition to the 102 compounds tested in 2016, the following six compounds were also tested in 2023: bifenthrin, cyantraniliprole, dacthal mono-acid, dachtal di-acid, desthio prothioconazole, and permethrin.

A statistical analysis of 2023 samples revealed that an estimated 43.1% of wells in Wisconsin contained a pesticide or pesticide metabolite. This is greater than the estimates reported for the 2016 (41.7%) and the 2007 (33.5%) surveys. The 2023 survey also showed that detections of pesticides and nitrate concentrations over 10 mg/l were more frequently found within areas with a higher percentage of cultivated land.

The most frequently detected pesticide compound was the herbicide metabolite metolachlor Ethane Sulfonic Acid (ESA). It was found in an estimated 36.1% of the wells sampled in 2023. The second most frequently detected pesticide compound was the herbicide metabolite alachlor ESA. It was found in an estimated 19.6% of the wells sampled in 2023.

An estimated 19.9% of wells contained atrazine Total Chlorinated Residue (TCR), which is the sum of atrazine and its metabolites.

Neonicotinoids (clothianidin, imidacloprid, or thiamethoxam) were estimated to be found in 5.3 % of the wells. In one sample, imidacloprid was found to exceed the Wisconsin Department of Health Services (DHS) Drinking Water Health Advisory of 0.2 µg/l. Imidacloprid was detected in only one well in 2016. No clothianidin or thiamethoxam were detected in the previous survey.

The 2023 survey estimated that the statewide detection rate for nitrate between the NR 140 Preventive Action Limit of 2 mg/l and the NR 140 Enforcement Standard of 10 mg/l was 32.7%. The 2023 statewide survey estimated detection rate of nitrate exceeding the NR 140 Enforcement Standard for nitrate was 7.3%.

A time trend analysis was performed to determine whether the estimated detection rates for metolachlor ESA, alachlor ESA, atrazine, atrazine TCR, neonicotinoids, and nitrate in private wells had changed between the previous survey and the 2023 surveys. Results show that no statistically significant changes were observed for alachlor ESA, atrazine, and nitrate. The statewide estimated detection rates for metolachlor ESA and atrazine TCR remained consistent with the 2016 findings but increased compared to the 2007 results. Neonicotinoids detection rate estimated for Wisconsin increased since 2016.

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INTRODUCTION

Every five to 10 years, the Wisconsin Department of Agriculture, Trade and Consumer Protection (DATCP) collaborates with the United States Department of Agriculture - National Agricultural Statistics Service (NASS) for a comprehensive statewide survey of Wisconsin groundwater. This survey focuses on sampling private potable wells in rural areas, aiming to evaluate the presence of agricultural chemicals in groundwater and to raise awareness among residents regarding potential contaminants in their drinking water.

Since 1994, DATCP has completed five statewide surveys. The initial Atrazine Rule Evaluation Surveys in 1994 and 1996, as documented by LeMasters and Baldock [1], played a pivotal role in evaluating regulations concerning the herbicide atrazine. Subsequent surveys in 2000-2001, 2007, and 2016 were conducted to establish detection frequencies and concentrations of pesticides and nitrate plus nitrite as N, or nitrate in this manuscript, in rural drinking water wells across Wisconsin. These surveys aimed to also determine if there have been measurable changes in pesticides and nitrate concentrations in Wisconsin groundwater over time [2, 3, 4].

The 2023 survey was completed to provide an updated overview of agricultural chemicals in groundwater and to compare these findings with the results from earlier surveys.

Each water sample collected in 2023 was analyzed for 107 compounds, including 56 herbicides, 16 herbicides metabolites, four fungicides, one fungicide metabolite, 26 insecticides, two insecticides metabolites, one pesticide safener, and nitrate. Most of the pesticides included in the 2023 survey are currently registered for use in Wisconsin. However, certain compounds, such as alachlor, are no longer registered for use in Wisconsin, but may have affected groundwater due to past use. Wisconsin Administrative Code NR 140 Enforcement Standards (ES) and Preventive Action Limit (PAL) have been established for 32 of the compounds tested. The Department of Health Services (DHS) has also set Drinking Water Health Advisories for 17 other compounds or group of compounds. No PALs, ES, or DHS Drinking Water Health Advisories have been established for the remaining compounds.

This report aims to showcase the outcomes of the 2023 survey while drawing comparisons with data from previous surveys. By doing so, it offers valuable information about agricultural chemicals in Wisconsin's groundwater.

MATERIALS AND METHODS

SURVEY DESIGN

The goal of the 1994, 1996, 2001, 2007, 2016, and 2023 surveys was to assess the presence of agrichemicals in Wisconsin's groundwater, a task made challenging due to its vast, three-dimensional spread across the state. To efficiently tackle this challenge, existing private drinking water wells were chosen as sampling points, defining the actual target as "groundwater accessible by private wells." Each survey used a 50% sample rotation scheme, in which about half of the wells in the 1996, 2001, 2007, 2016, and 2023 surveys had been part of the previous survey and about half were newly selected. Approximately half of the wells sampled for the first time in the 2016 survey were retested in 2023. Wells that were part of both the 2007 and 2016 surveys were excluded from the 2023 study, and new wells were chosen instead. This rotation strategy enabled the identification of new areas with agricultural chemical presence within the state and allowed for tracking changes in pesticide concentrations over time.

The 2023 survey, along with the previous five surveys, used a stratified random sampling procedure to allocate (select) samples throughout the state. The sample allocation procedure used in 2007, 2016 and 2023 for the newly-selected wells used the NASS Land Use Strata, which are based on how intensively land in Wisconsin is cultivated for agricultural production [5]. Each NASS stratum includes land areas falling into a specific range of intensity of cultivation. The exception to this is the stratum presented as "Agri-Urban", which is defined as being "mixed agriculture and residential with 100 or more dwellings per square mile" [6]. The land within each stratum is divided into "area segments" that are typically one square mile in size.

Samples were allocated by randomly selecting a predetermined number of area segments within each agricultural stratum. Strata consisting entirely of urban, non-agricultural, and water-covered areas were excluded from sampling. Since area segment boundaries are typically roads, staff chose a starting corner in each segment and the water samplers were instructed to travel clockwise within the segment until they found a well owner willing to participate in the survey. In a few sparsely-populated segments, the samplers had to contact a well owner in an adjoining segment to collect a sample.

The 1994, 1996, and 2001 surveys also used a stratified random sampling procedure to allocate samples, but the strata in those surveys were the nine NASS Agricultural Statistics Districts, which are groups of adjoining counties [7]. The number of samples collected in each of the nine districts was based on the number of farmed acres in each district. Samples were allocated by selecting a random sample list of Public Land Survey System (PLSS) sections in each district (excluding those covered by water or publicly owned). In each PLSS section, a random 10-acre parcel was selected and the well nearest its center was identified to represent the groundwater of the PLSS section.

The 2007, 2016, and 2023 stratification method offered several benefits over the previously used method. First, samples were allocated proportional to agricultural intensity throughout the state. Second, the current method allows for comparisons of water quality to agricultural intensity in addition to location within the state.

To compare the frequencies of detections of agricultural chemicals over time, a Geographic Information Systems (GIS) software was used to re-stratify the results of the 1994, 1996, and 2001 surveys into the same strata used in the 2007, 2016, and 2023 surveys. This re-stratification allowed the data from the previous surveys to be weighted so that the older data could be compared to the 2007, 2016, and 2023 data.

SAMPLE COLLECTION AND ANALYSIS

In Figure 1, the sample locations for the 2023 survey are shown alongside the most recent (2016) NASS Land Use Strata [8]. A total of 380 samples were collected from private drinking wells across Wisconsin.

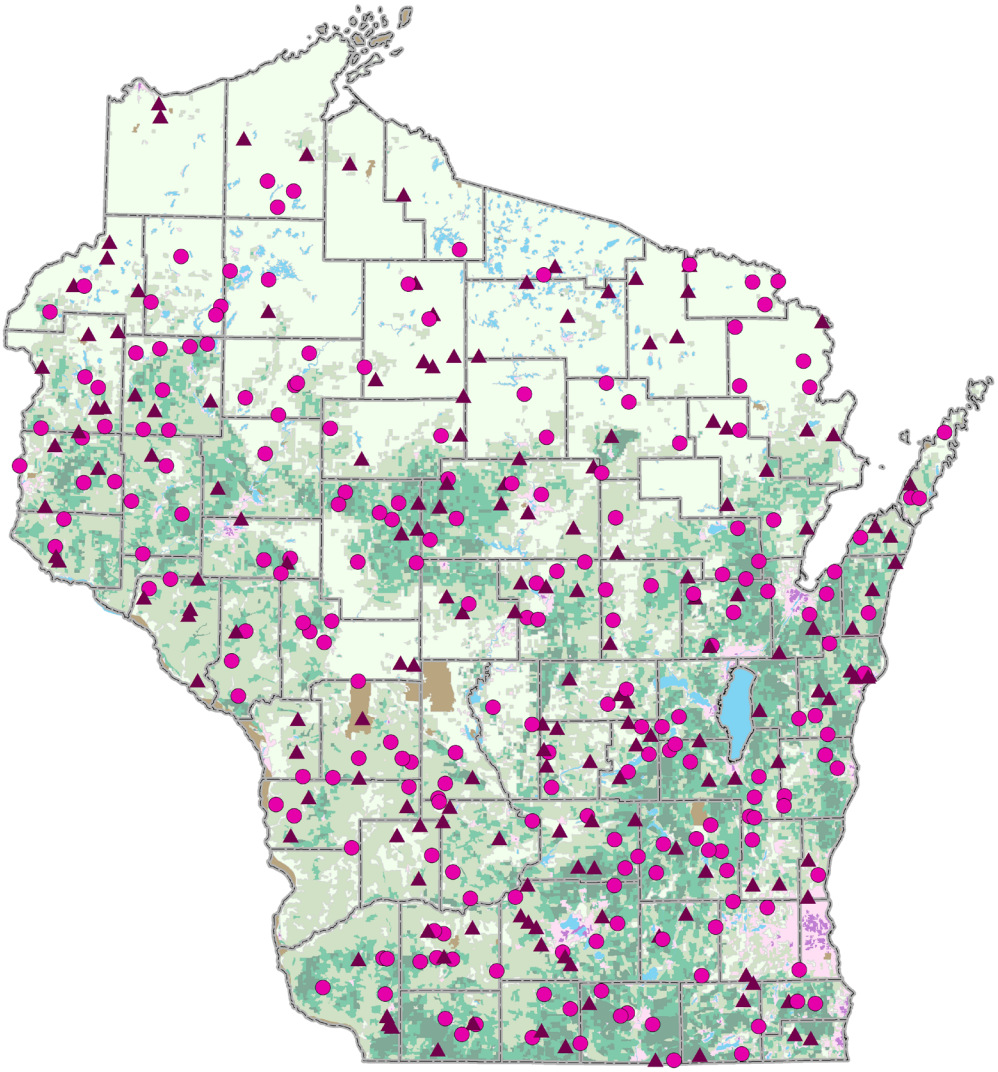
Among these, 173 groundwater samples were collected from wells that were previously tested in the 2016 survey. Groundwater samples were obtained only from wells that had not had any structural changes since the last survey. This was to guarantee that water samples were collected from the same location within the aquifer for valid comparisons.

Water samples were taken from 207 newly-selected wells that replaced those rotated out of the 2016 survey. Once a new well was selected, the samplers interviewed the owner to gather information on the well and ascertain the presence of any water treatment devices. Sampling was conducted exclusively if untreated, raw water was accessible. If a sampler was unable to obtain an untreated sample, an alternative well was selected the same selection process.

Water samples were collected from a cold water supply after running the water for approximately five minutes. A one-liter amber glass bottle with a Teflon-lined cap was filled at each site and promptly placed in an insulated box with ice. Sample collection records were completed, and the samples were either hand-delivered to the DATCP Bureau of Laboratory Services or shipped using an overnight delivery service.

FIGURE 1

2023 SURVEY SAMPLING LOCATIONS AND LAND USE CATEGORIES



Legend

2023 Sampling Locations

- Wells sampled in 2023
- Wells sampled in 2016 and 2023
- **Wisconsin Counties**

NASS 2016 Land Use Strata

- < 15% Cultivated
- 15 - 50 % Cultivated
- 51 - 75 % Cultivated
- > 75 % Cultivated
- Agri-Urban
- Commercial
- Non Agricultural
- Water

RESULTS OF THE 2023 SURVEY

PESTICIDE AND NITRATE DETECTS

Table 1 summarizes the results of the 2023 survey. A compound is considered *not detected* if its concentration is reported to be less than the respective reporting limit. If the concentration of a compound is reported to be greater than the respective laboratory reporting limit, that compound is considered *detected* in the water sample. The laboratory reporting limits (RL) for each tested compound in 2023 are provided in Table 1. For confidentiality reasons, the exact values pertaining to the number of detections and concentration ranges of Table 1 have been withheld for compounds detected in one or two (less than three) samples.

Of the 380 samples collected, 201 contained detectable concentrations of one or more pesticides or a pesticide metabolite. The most frequently detected pesticide compounds were the herbicide metabolite metolachlor Ethane Sulfonic Acid (metolachlor ESA) and alachlor Ethane Sulfonic Acid (alachlor ESA). Metolachlor ESA is a metabolite of metolachlor and s-metolachlor, which are active ingredients used in many corn herbicides. Metolachlor ESA was detected in 170 samples collected in the 2023 statewide survey.

Alachlor ESA, a metabolite of alachlor — an active ingredient historically employed in herbicides targeting grass and broadleaf control — was identified in 97 samples from the same survey, despite the absence of currently registered alachlor products in Wisconsin. No samples exceeded the NR 140 ES for alachlor ESA (20 micrograms per liter, µg/l) or the NR 140 ES for metolachlor ESA (1,300 µg/l).

Atrazine Total Chlorinated Residues (TCR) was detected in 95 samples. Atrazine TCR is defined as the sum of atrazine, which is the active ingredient in many corn herbicides used for grass and broadleaf control, and its three primary breakdown products (de-ethyl atrazine, de-isopropyl atrazine, and di-amino atrazine). None of the 95 samples containing atrazine TCR exceeded the NR 140 ES of 3.0 µg/l.

Neonicotinoids are a class of insecticides widely used in Wisconsin. Clothianidin, imidacloprid, and thiamethoxam — all belonging to the neonicotinoid class — were detected in multiple water samples collected during the 2023 statewide survey. Clothianidin was the most detected neonicotinoid compound, with 26 detects. Imidacloprid was detected in three samples, and thiamethoxam was detected in two samples. In total, 27 samples contained one or more of these neonicotinoids. One sample contained imidacloprid at a concentration exceeding the DHS Drinking Water Health Advisory of 0.2 µg/l.

The geographic distribution of the compounds described above is shown on Figures 2-5.

Nitrate was detected in 215 of the 380 samples at concentrations ranging from 0.51 milligrams per liter (mg/l) to 37.9 mg/l. Nitrate concentrations exceeded the NR 140 ES 10 mg/l in 40 samples. The geographic distribution of nitrate results are shown on Figure 6.

TABLE 1

RESULTS OF THE 2023 SURVEY

Compound	Number of Detects	Reporting Limit (RL) (µg/l)	Health Standard[1] (µg/l)	Number of Samples Exceeding Health Standard	Concentration Range (µg/l)
Nitrate plus nitrite as N	215	0.50 mg/l	10 mg/l	40	0.51 - 37.90
2,4,5-T	0	0.05	--	0	--
2,4,5-TP	0	0.05	50	0	--
2,4-D	3	0.05	70	0	0.05 - 0.16
2,4-DB	0	1	--	0	--
2,4-DP	0	0.05	--	0	--
Acetamiprid	0	0.01	--	0	--
Acetochlor	0	0.05	7	0	--
Acetochlor ESA	40	0.05	230	0	0.05 - 5.30
Acetochlor Metabolites[2]	40	--	230	0	0.05 - 5.30
Acetochlor OA	0	0.3	230	0	--
Acifluorfen	< 3	0.05	--	0	> RL
Alachlor	0	0.05	2	0	--
Alachlor ESA	97	0.05	20	0	0.05 - 6.86
Alachlor OA	3	0.25	--	0	0.68 - 0.75
Aldicarb Sulfone	0	0.05	--	0	--
Aldicarb Sulfoxide	0	0.071	--	0	--
Aminopyralid	0	0.15	--	0	--
Atrazine	18	0.05	3	0	0.05 - 0.20
Atrazine TCR[3]	95	--	3	0	0.05 - 2.71
Azoxystrobin	0	0.05	--	0	--
Benfluralin	0	0.05	--	0	--

Compound	Number of Detects	Reporting Limit (RL) (µg/l)	Health Standard[1] (µg/l)	Number of Samples Exceeding Health Standard	Concentration Range (µg/l)
Bentazon	8	0.05	300	0	0.05 - 0.38
Bicyclopyrone	0	0.05	--	0	--
Bifenthrin	< 3	0.005	--	0	> RL
Bromacil	< 3	0.05	--	0	> RL
Carbaryl	0	0.05	40	0	--
Carbofuran	0	0.05	40	0	--
Chloramben	0	0.32	150	0	--
Chlorantraniliprole	< 3	0.05	16,000	0	> RL
Chlorothalonil	0	0.1	--	0	--
Chlorpyrifos	0	0.05	2	0	--
Chlorpyrifos Oxon	0	0.05	--	0	--
Clomazone	0	0.05	--	0	--
Clopyralid	0	0.05	--	0	--
Clothianidin	26	0.01	1,000	0	0.01 - 2.22
Cyantraniliprole	0	0.05	10	0	--
Cyclaniliprole	0	0.2	--	0	--
Cyfluthrin	0	0.05	--	0	--
Cypermethrin	0	0.1	--	0	--
Cyprosulfamide	0	0.05	--	0	--
Dacthal	0	0.05	70	0	--
Dacthal di-acid	< 3	0.5	70	0	> RL
Dacthal mono-acid	0	0.5	70	0	--
Dacthal Total[4]	< 3	--	70	0	> RL
De-ethyl atrazine	92	0.05	3	0	0.05 - 0.61
De-isopropyl atrazine	9	0.05	3	0	0.06 - 0.22
Desthio prothioconazole	0	0.05	--	0	--

Compound	Number of Detects	Reporting Limit (RL) (µg/l)	Health Standard[1] (µg/l)	Number of Samples Exceeding Health Standard	Concentration Range (µg/l)
Di-amino atrazine	29	0.15	3	0	0.15 - 2.25
Diazinon	0	0.05	--	0	--
Diazinon oxon	0	0.05	--	0	--
Dicamba	0	0.2	300	0	--
Dichlobenil	0	0.05	--	0	--
Dimethenamid	0	0.05	50	0	--
Dimethenamid ESA	4	0.05	--	0	0.06 - 0.12
Dimethenamid OA	0	0.05	--	0	--
Dimethoate	0	0.05	2	0	--
Dinotefuran	0	0.01	--	0	--
Diuron	0	0.05	--	0	--
EPTC	0	0.05	250	0	--
Esfenvalerate	0	0.025	--	0	--
Ethalfluralin	0	0.05	--	0	--
Ethofumesate	0	0.05	--	0	--
Flumetsulam	0	0.05	10,000	0	--
Flupyradifurone	0	0.05	--	0	--
Fluroxypyr	0	0.05	--	0	--
Fomesafen	< 3	0.05	25	0	> RL
Halosulfuron methyl	0	0.05	--	0	--
Hexazinone	0	0.05	400	0	--
Imazapyr	4	0.05	--	0	0.05 - 0.18
Imazethapyr	0	0.05	--	0	--
Imidacloprid	3	0.01	0.2	1	0.03 - 1.59
Isoxaflutole	0	0.05	3	0	--
Isoxaflutole DKN	0	0.05	3	0	--

Compound	Number of Detects	Reporting Limit (RL) (µg/l)	Health Standard[1] (µg/l)	Number of Samples Exceeding Health Standard	Concentration Range (µg/l)
Isoxaflutole Total[5]	0	--	3	0	--
lambda-Cyhalothrin	0	0.02	--	0	--
Linuron	0	0.05	--	0	--
Malathion	0	0.05	--	0	--
MCPA	0	0.05	--	0	--
MCPB	0	0.1	--	0	--
MCPP	0	0.05	--	0	--
Mesotrione	0	0.1	--	0	--
Metalaxyl	< 3	0.05	800	0	> RL
Methyl Parathion	0	0.05	--	0	--
Metolachlor	4	0.05	100	0	0.09 - 0.31
Metolachlor ESA	170	0.05	1,300	0	0.05 - 18.30
Metolachlor Metabolites[6]	170	--	1,300	0	0.05 - 29.40
Metolachlor OA	16	0.27	1,300	0	0.28 - 13.20
Metribuzin	4	0.065	70	0	0.06 - 1.75
Metribuzin DA	< 3	0.1	--	0	> RL
Metribuzin DADK	5	0.12	--	0	0.13 - 5.07
Metsulfuron methyl	0	0.05	--	0	--
Nicosulfuron	0	0.05	--	0	--
Norflurazon	0	0.05	15	0	--
Oxadiazon	0	0.05	--	0	--
Pendimethalin	0	0.05	--	0	--
Permethrin	0	0.03	--	0	--
Picloram	< 3	0.05	500	0	> RL
Prometon	0	0.05	--	0	--
Prometryn	0	0.05	--	0	--

Compound	Number of Detects	Reporting Limit (RL) (µg/l)	Health Standard[1] (µg/l)	Number of Samples Exceeding Health Standard	Concentration Range (µg/l)
Propiconazole	0	0.05	--	0	--
Saflufenacil	0	0.05	460	0	--
Simazine	0	0.05	4	0	--
Sulfentrazone	0	0.05	1,000	0	--
Sulfometuron methyl	0	0.05	--	0	--
Tebupirimphos	0	0.05	--	0	--
Tembotrione	0	0.1	--	0	--
Thiacloprid	0	0.01	--	0	--
Thiamethoxam	< 3	0.01	120	0	> RL
Thiencarbazone methyl	0	0.05	10,000	0	--
Triclopyr	< 3	0.05	--	0	> RL
Trifluralin	0	0.05	7.5	0	--

[1] Wis. Admin. Code, ch. NR 140 Enforcement Standard or Wisconsin Department of Health Services Drinking Water Health Advisory

[2] Acetochlor Metabolites is the sum of acetochlor metabolites (acetochlor ESA and acetochlor OA)

[3] Atrazine TCR is the Total Chlorinated Residue (TCR) for atrazine. It is the sum of atrazine (parent material) and its three metabolites (de-ethyl, deisopropyl, and diamino atrazine)

[4] Dacthal Total is the sum of dacthal (parent material) and its two metabolites (dacthal di-acid and dacthal mono-acid)

[5] Isoxaflutole Total is the sum of isoxaflutole (parent material) and its metabolite (isoxaflutole DKN)

[6] Metolachlor Metabolites is the sum of metolachlor metabolites (metolachlor ESA and metolachlor OA)

-- In column *Reporting Limit* indicates that no reporting limits are available for calculated values. In column *Health Standard* indicates that no groundwater standards or DHS health advisory is established for that compound. In column *Concentration Range* indicates that the concentration was not found in excess of the reporting limit.

FIGURE 2

2023 SURVEY RESULTS FOR METOLACHLOR ESA

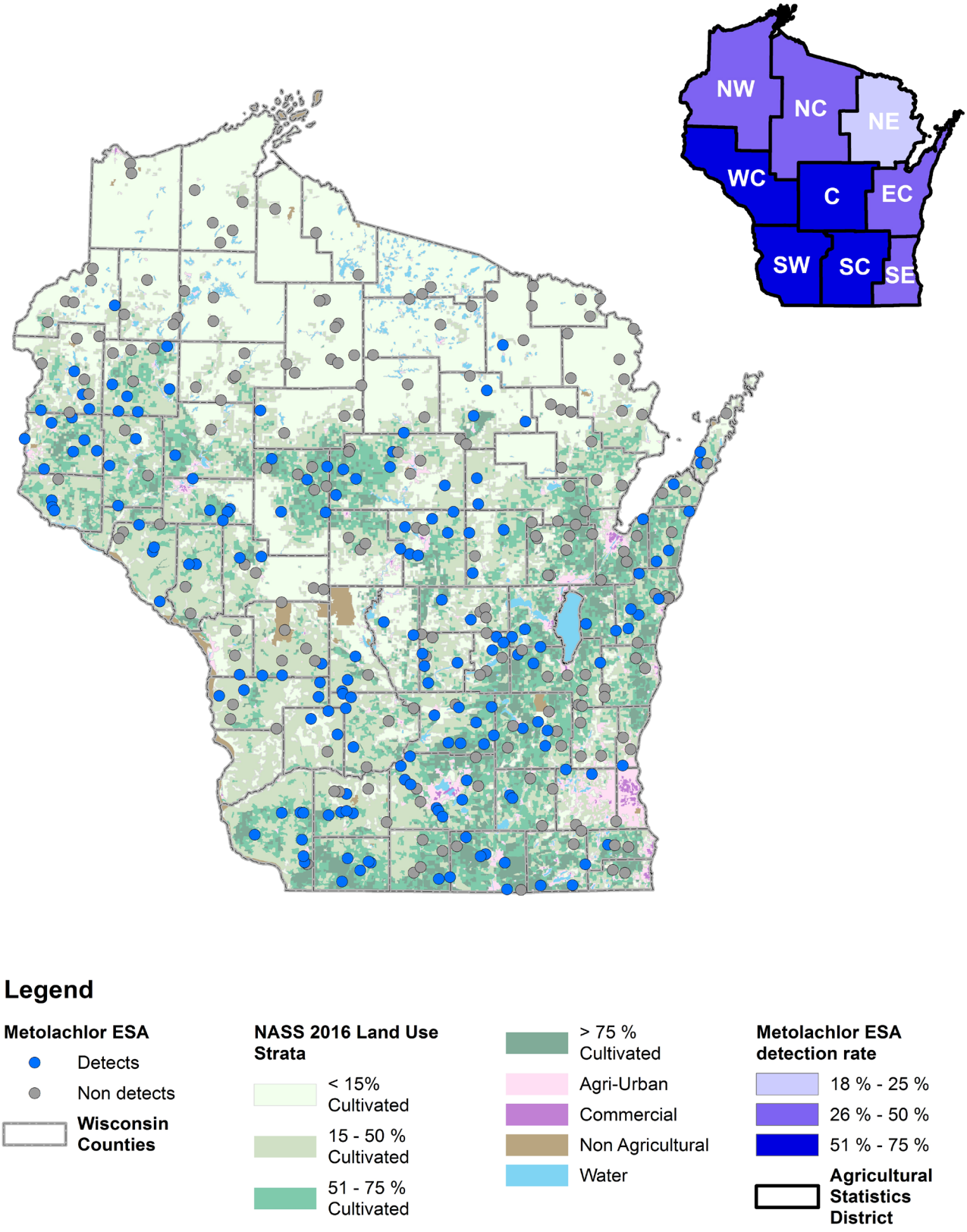


FIGURE 3

2023 SURVEY RESULTS FOR ALACHLOR ESA

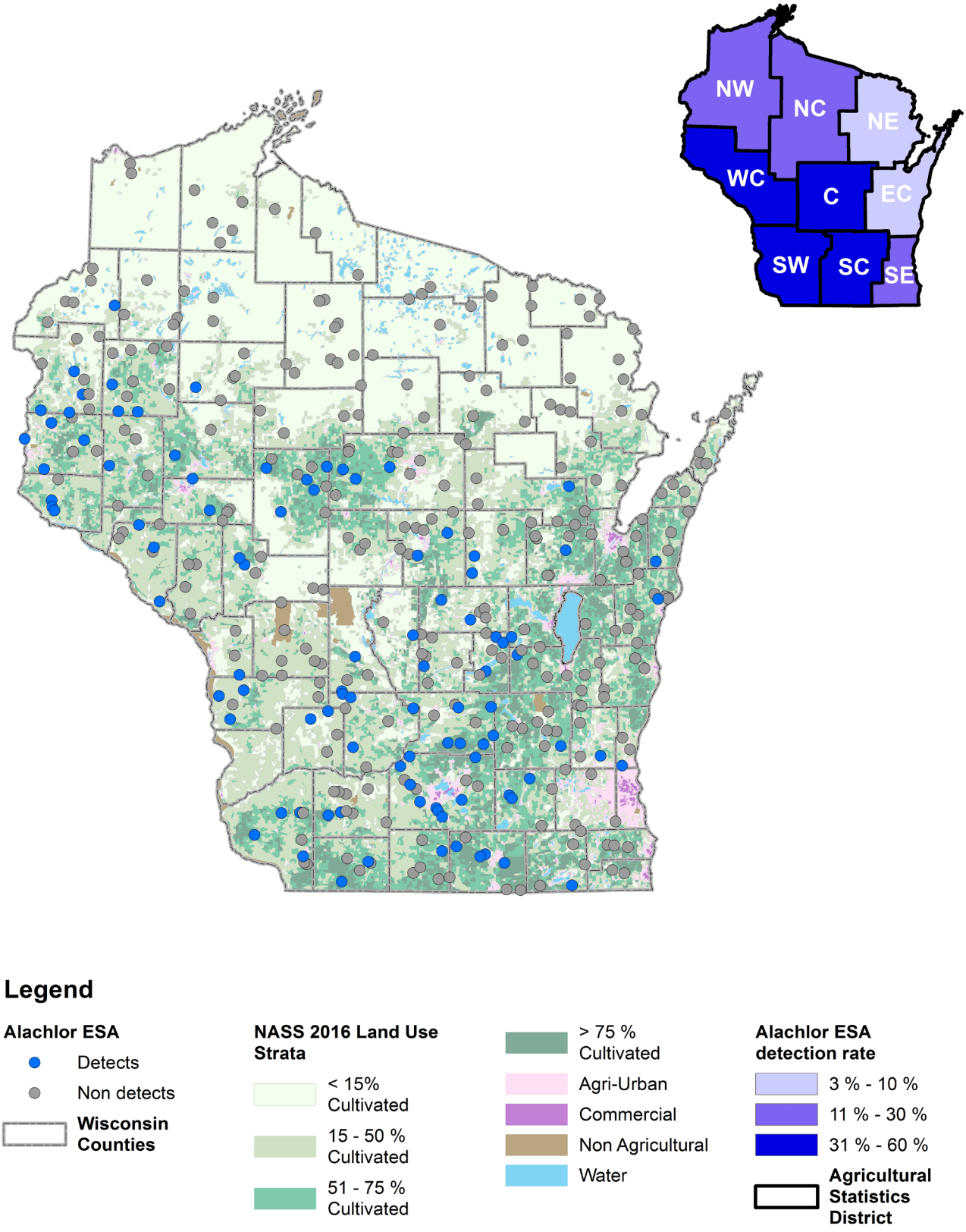
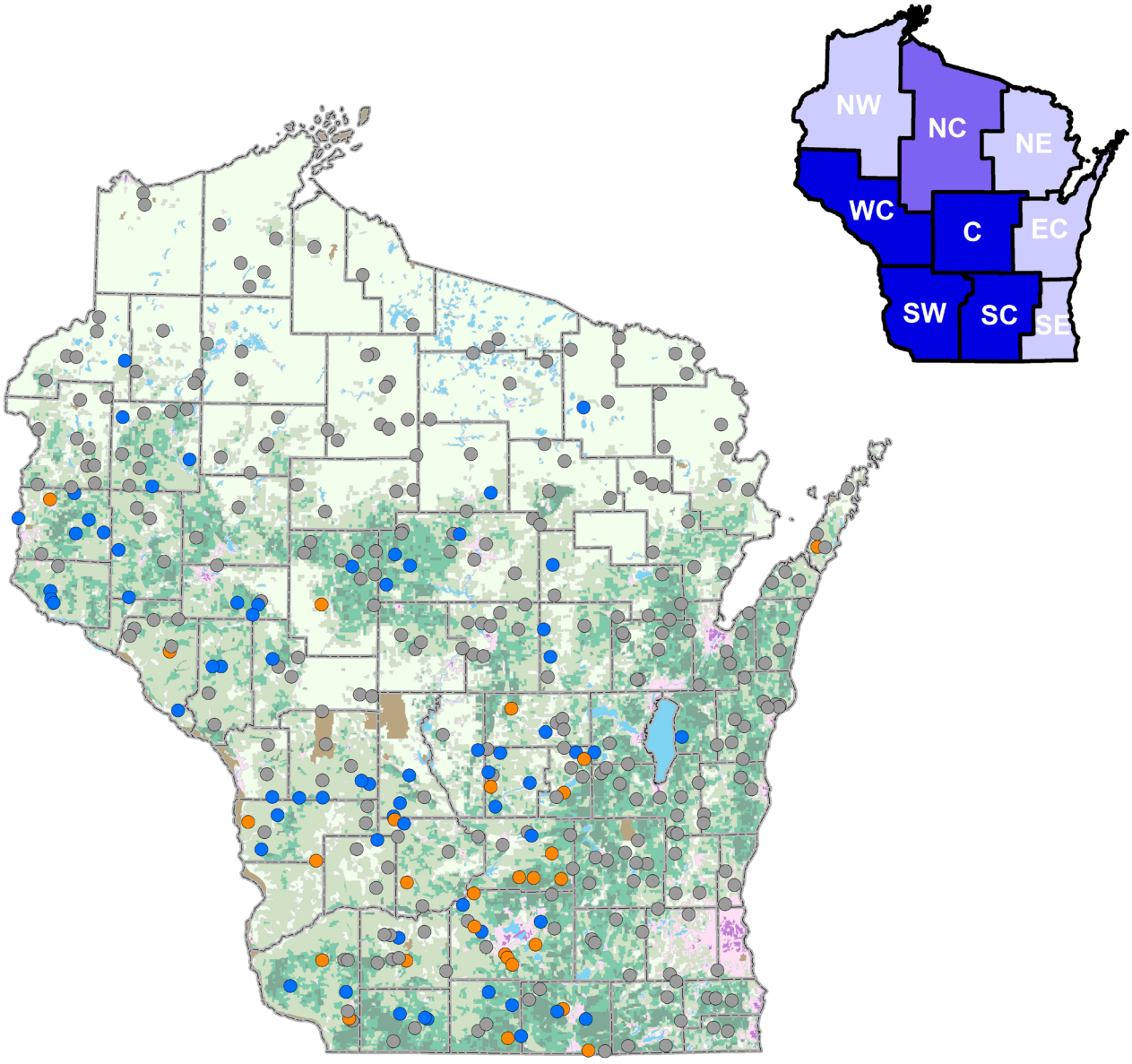


FIGURE 4

2023 SURVEY RESULTS FOR ATRAZINE TCR



Legend

Atrazine TCR
- Concentration > 0.3 µg/l (PAL)
- Concentration < 0.3 µg/l (PAL)
- Non detects
- **Wisconsin Counties**

NASS 2016 Land Use Strata
- < 15% Cultivated
- 15 - 50 % Cultivated
- 51 - 75 % Cultivated
- > 75 % Cultivated
- Agri-Urban
- Commercial
- Non Agricultural
- Water

Atrazine TCR detection rate
- 0 % - 10 %
- 11 % - 25 %
- 26 % - 50 %
- **Agricultural Statistics District**

FIGURE 5

2023 SURVEY RESULTS FOR CLOTHIANIDIN, IMIDACLOPRID, AND THIAMETHOXAM (NEONICOTINOIDS)

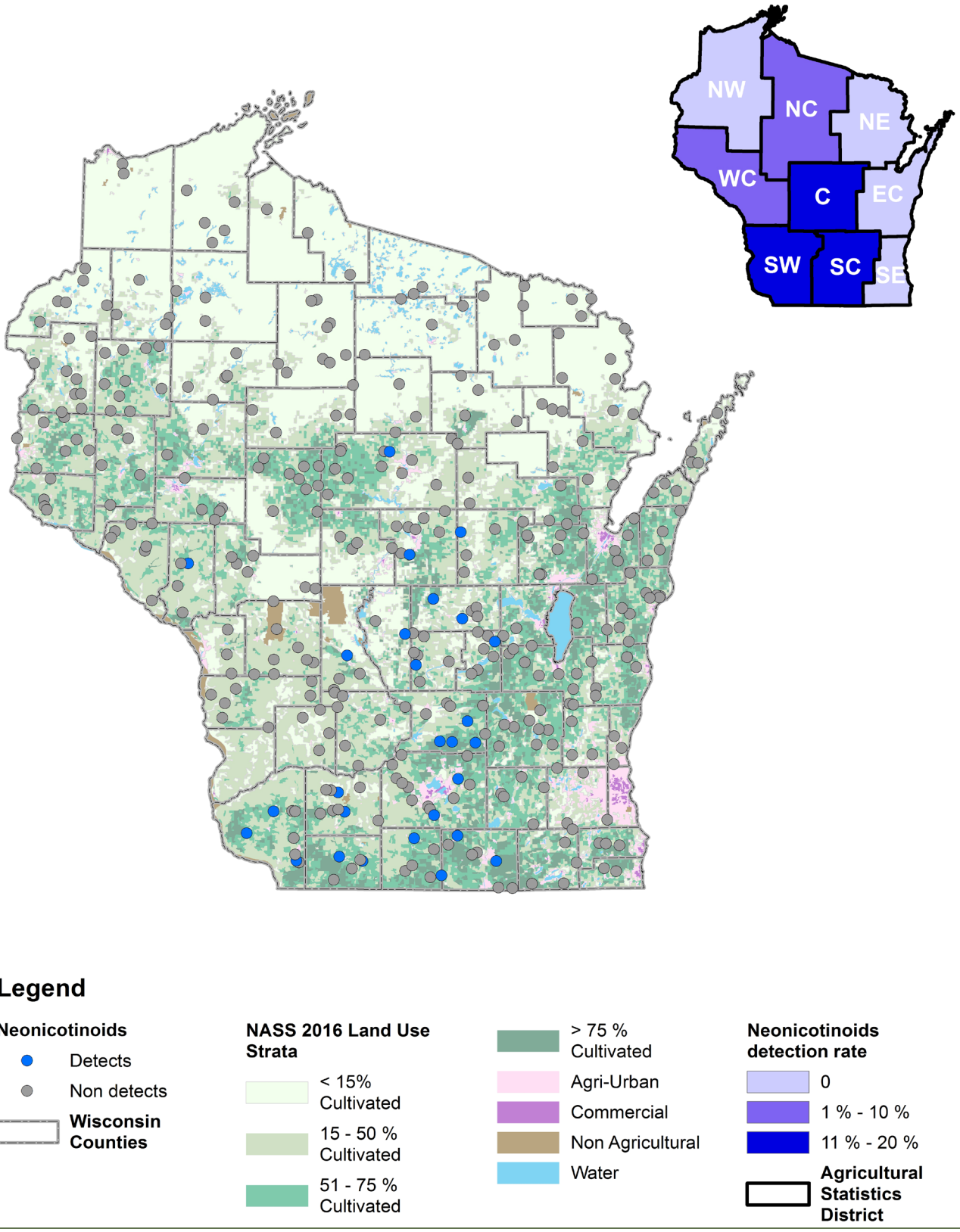
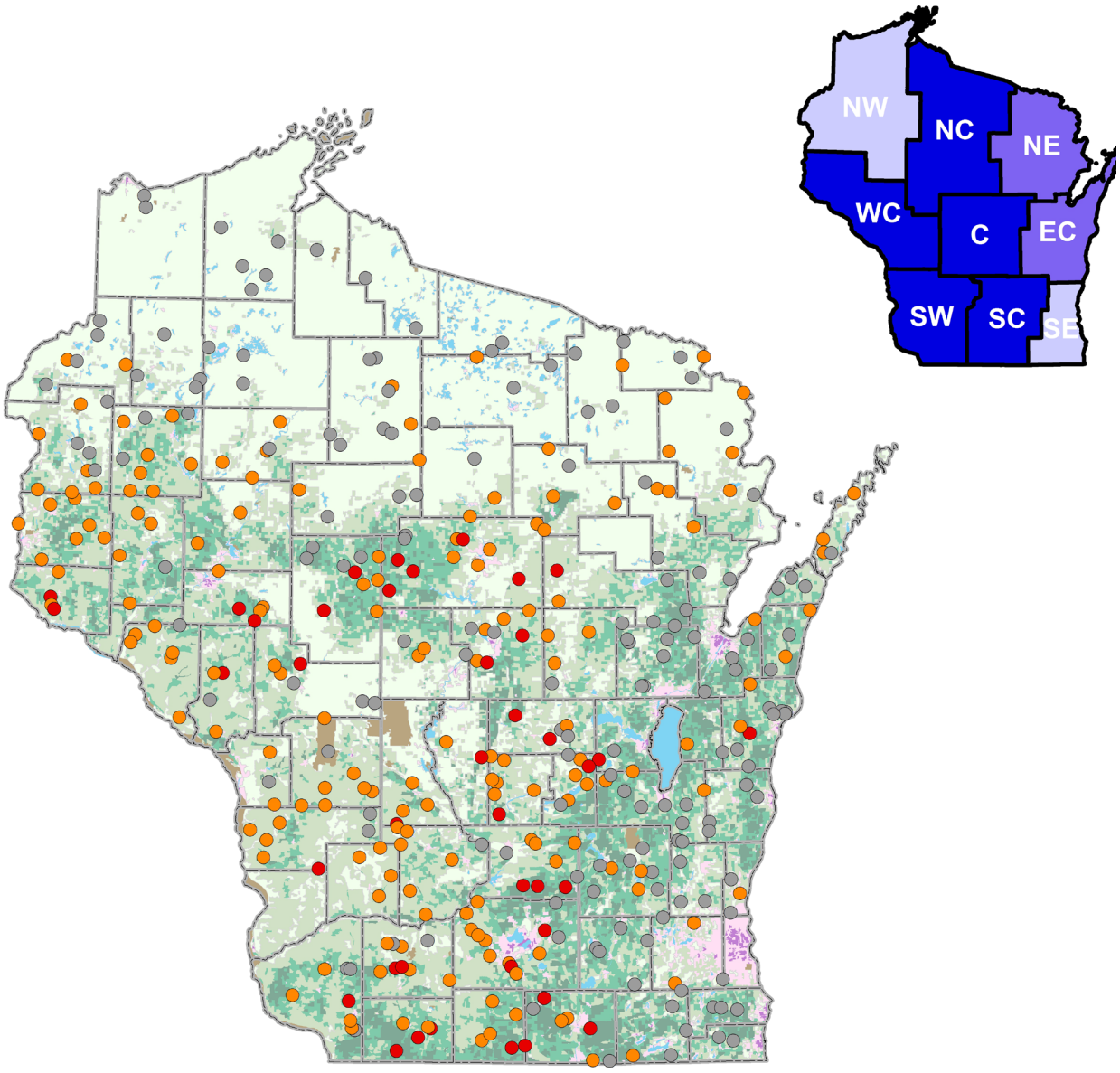


FIGURE 6

2023 SURVEY RESULTS FOR NITRATE PLUS NITRITE AS NITROGEN



Legend

Nitrate + Nitrite (N)
- Concentration > 10 mg/l
- Concentration <= 10 mg/l
- Non detects
- **Wisconsin Counties**

NASS 2016 Land Use Strata
- < 15% Cultivated
- 15 - 50 % Cultivated
- 51 - 75 % Cultivated
- > 75 % Cultivated
- Agri-Urban
- Commercial
- Non Agricultural
- Water

Rate of Nitrate + Nitrite (N) > 10 mg/l
- 0 %
- 1 % - 10 %
- 11 % - 20 %
- **Agricultural Statistics District**

Detection Rate within Each Land Use Stratum

Utilizing Geographic Information Systems (GIS) technology, each well was categorized according to the 2016 NASS Land Use Strata [8] based on their geographical coordinates. Table 2 shows the detection rates within each NASS strata for the most commonly detected compounds in the 2023 survey. For each stratum, the percentage of samples containing one or more pesticide compound was also estimated. In Table 2, the numbers highlighted in bold represent the top three detection rates for a certain variable or compound.

The analysis revealed that areas with a cultivated land percentage exceeding 50% exhibited a greater pesticide detection rate. All selected pesticide compounds were more frequently detected in regions where the proportion of cultivated land exceeded 50%.

Nitrate was detected across all land use categories at a rate exceeding 30%. However, concentrations of nitrate exceeding the NR 140 ES of 10 mg/l were predominantly found at wells located within areas characterized by a high percentage of cultivated land.

Table 2

Detection Rates across NASS Land Use Strata for Selected Compounds Detected in the 2023 Survey

Stratum Description	Samples Collected	Percentage of Samples with at Least One Pesticide Detected	Detection Rate (%)									
			Metolachlor ESA	Alachlor ESA	Atrazine TCR	Atrazine	Clothianidin	Imidacloprid	Thiamethoxam	Neonicotinoids	Nitrate	Nitrate > 10 mg/l
>75% Cultivated	50	**66**	**56**	**42**	**30**	**10**	**14**	4	2	**16**	48	**24**
51-75% Cultivated	90	**69**	**62**	**36**	**33**	**6**	**9**	0	1	**9**	**60**	**16**
15-50% Cultivated	144	**63**	**51**	**27**	**31**	**6**	**7**	1	0	**7**	**69**	**10**
<15% Cultivated	89	17	13	4	6	0	1	0	0	1	37	0
Agri-Urban	7	14	14	14	14	0	0	0	0	0	**57**	0

Detection Rate within Each Agricultural Statistics District

Table 3 and Figures 2-6 provide comprehensive data on both the percentage of samples, with at least one detected pesticide for each NASS Agricultural Statistics District and the detection rates for selected compounds within those districts [7]. In Table 3, the numbers highlighted in bold represent the top three detection rates of detects for a certain variable or compound.

The analysis revealed that greater percentages of samples containing at least one pesticide were found in the West Central, Southwest, and South Central districts.

Metolachlor ESA, alachlor ESA, atrazine TCR, and atrazine exhibited greater detection rates within these districts.

Clothianidin was predominantly detected within the Central, Southwest, and South Central districts, while imidacloprid and thiamethoxam were exclusively found within the Central district.

The West Central, Central, and Southwest districts showed the greatest nitrate detection rates. Concentrations exceeding the NR 140 ES threshold of 10 mg/l were most prevalent within the Central, Southwest, and South Central districts.

Table 3

Detection Rates across Agricultural Statistics District for Selected Compounds Detected in the 2023 Survey

District	Samples Collected	Percentage of Samples with at Least One Pesticide Detected	Detection Rate (%)									
			Metolachlor ESA	Alachlor ESA	Atrazine TCR	Atrazine	Clothianidin	Imidacloprid	Thiamethoxam	Neonicotinoids	Nitrate	Nitrate > 10 mg/l
Northwest	47	32	26	21	9	0	0	0	0	0	45	0
North Central	48	35	27	17	15	2	2	0	0	2	48	15
Northeast	34	26	18	3	6	0	0	0	0	0	47	3
West Central	48	**69**	**63**	**33**	**50**	**13**	2	0	0	2	**85**	12
Central	42	64	57	31	38	7	**17**	**7**	**5**	**19**	**76**	**19**
East Central	52	42	38	10	6	0	0	0	0	0	27	4
Southwest	40	**78**	**70**	**43**	**43**	**10**	**18**	0	0	**18**	**80**	**18**
South Central	49	**80**	**61**	**49**	**45**	**8**	**20**	0	0	**20**	65	**18**
Southeast	20	40	35	15	0	0	0	0	0	0	20	0

Weights were assigned to each land stratum based on their respective total acres coverage within the state. By multiplying the detection rates in each stratum by their corresponding weights and summing these weighted detection values, statewide detection rates were estimated for 12 parameters.

Table 4 shows estimated statewide detection rates and their 95% confidence intervals. Metolachlor ESA and alachlor ESA had the highest estimated statewide detection rates for individual pesticide compounds with 36.1% and 19.6%, respectively. Atrazine TCR statewide detection rate was estimated to be 19.9%. The estimated statewide percentage of wells that exceeded the NR 140 ES of 10 mg/l for nitrate was 7.3%.

TABLE 4

ESTIMATED STATEWIDE DETECTION RATES AND 95% CONFIDENCE INTERVALS FOR 12 PARAMETERS IN THE 2023 SURVEY

Compound	Total Number of Detects	Estimated Statewide Detection Rate (%)	95% Confidence Interval (%)[7]
One or more pesticide detected	201	43.1	38.4 - 47.8
Metolachlor ESA	170	36.1	31.6 - 40.7
Alachlor ESA	97	19.6	15.9 - 23.3
Atrazine TCR	95	19.9	16.1 - 23.8
Atrazine	18	3.4	1.6 - 5.2
Clothianidin	26	5.1	3.1 - 7.1
Imidacloprid	3	0.5	**
Thiamethoxam	2	0.3	**
Neonicotinoids	27	5.3	3.2 - 7.3
Nitrate	215	52.3	46.7 - 57.8
2 < Nitrate <10	135	32.7	27.6 - 37.8
Nitrate > 10 mg/l	40	7.3	4.8 - 9.9

[7] Calculated range of values where there is a 95% probability that the percent of reported detections will fall within that range.

** Not enough data points to calculate a confidence interval

Table 5 shows the estimate statewide average concentration for eight parameters and their 95% confidence intervals. The estimates of mean detected concentrations for pesticides ranged from 0.04 µg/l for thiamethoxam to 0.76 µg/l for metolachlor ESA. The 95% confidence interval for imidacloprid ranged from 0 to 3.77 µg/l. The upper limit of this interval appears unusually high due to a significant outlier; one of the three samples in which imidacloprid was detected had an exceptionally high concentration in comparison to the other two samples.

TABLE 5

ESTIMATED STATEWIDE MEAN CONCENTRATIONS AND 95% CONFIDENCE INTERVALS FOR EIGHT COMPOUNDS DETECTED IN THE 2023 SURVEY

Compound	Estimated Statewide Mean Concentration (µg/l)	95% Confidence Interval (µg/l)[8]	Health Standard (µg/l)[9]
Metolachlor ESA	0.76	0.55 - 0.97	1,300
Alachlor ESA	0.36	0.15 - 0.57	20
Atrazine TCR	0.2	0.16 - 0.24	3
Atrazine	0.05	0.03 - 0.07	3
Clothianidin	0.09	0 - 0.23	1,000
Imidacloprid	0.07	0 - 3.77	0.2
Thiamethoxam	0.04	**	120
Nitrate	5.22 mg/l	4.7 - 5.74 mg/l	10 mg/l

[8] Calculated range of values where there is a 95% probability that the percent of reported detections will fall within that range.

[9] Wis. Admin. Code, ch. NR 140 Enforcement Standard or Wisconsin Department of Health Services Drinking Water Health Advisory

**Not enough data points to calculate a confidence interval

Relationship Between Well Characteristics and Percentage of Detects for Selected Compounds

For each well tested, detailed well construction information was sourced from well construction reports whenever accessible. This data was utilized to assess the correlations between well characteristics and detection frequencies of specific agricultural chemicals. Unlike previous surveys, where this relationship was established through well owner questionnaire responses, in 2023, we relied on precise well information recorded at the time of construction. This approach ensures greater accuracy, as it eliminates the reliance on individuals' recollection.

Table 6 presents a breakdown of detection rates based on the age of wells. Information pertaining to well age was available for 226 out of the 380 sampled wells, accounting for 60% of the total sample. The majority of wells in the survey were identified as being over 20 years old.

Examining the data, a greater percentage of wells exhibiting at least one pesticide or nitrate detection were observed in older wells. Metolachlor ESA, alachlor ESA, and atrazine were more frequently detected in wells aged between six and 20 years. Atrazine TCR, clothianidin, thiamethoxam, and nitrate concentrations exceeding 10 mg/l were more prevalent in wells constructed within the last six years.

It is worth noting that these trends diverge from the findings of the 2016 survey [4]. For instance, in the previous survey, both the percentage of atrazine TCR detections and nitrate concentrations exceeding 10 mg/l increased with the age of the well. This discrepancy highlights that well age may not be a decisive parameter strongly influencing the likelihood of detecting a specific compound.

Table 6

Percentage of Detects for Selected Compounds By Well Age

Well Age Category (Years)	Samples Collected	Percentage of Samples with at Least One Pesticide Detected	Detection Rate (%)									
			Metolachlor ESA	Alachlor ESA	Atrazine TCR	Atrazine	Clothianidin	Imidacloprid	Thiamethoxam	Neonicotinoids	Nitrate	Nitrate > 10 mg/l
Under 6	12	58	33	17	33	0	17	0	8	17	42	33
6-20	78	65	51	29	26	6	6	1	1	6	47	9
Over 20	136	68	40	24	24	4	7	1	0	7	60	7

Table 7 shows the distribution of detection percentages based on the bottom depth of the wells. Wells within the 50-150 feet range constituted the majority in the survey.

Greater detection rates for metolachlor ESA, clothianidin, nitrate, and nitrate concentrations exceeding 10 mg/l were observed in wells with depths below 50 feet. Conversely, greater detection rates for alachlor ESA, atrazine TCR, and atrazine were found in wells with depths exceeding 150 feet.

This pattern aligns with the 2016 data, which similarly emphasized that shallower wells exhibited a greater percentage of nitrate detections and a greater percentage of wells with nitrate concentrations exceeding 10 mg/l.

TABLE 7

PERCENTAGE OF DETECTS FOR SELECTED COMPOUNDS BY WELL DEPTH

Well Depth Category (feet)	Samples Collected	Percentage of Samples with at Least One Pesticide Detected	Detection Rate (%)									
			Metolachlor ESA	Alachlor ESA	Atrazine TCR	Atrazine	Clothianidin	Imidacloprid	Thiamethoxam	Neonicotinoids	Nitrate	Nitrate > 10 mg/l
Under 50	22	68	55	14	23	0	9	0	0	9	59	14
50-150	122	63	38	25	23	3	7	2	2	7	54	8
Over 150	81	72	48	30	27	7	7	0	0	7	54	10

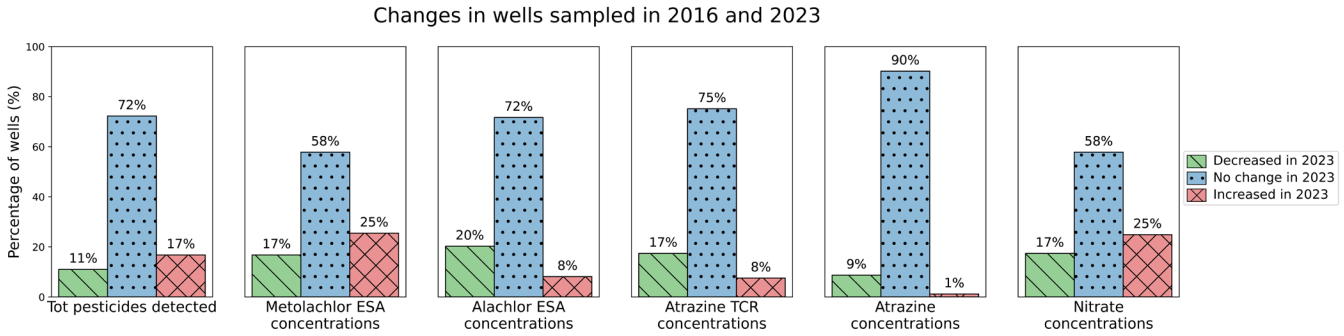
Comparison with Prior Surveys

Trends in Wells Sampled in 2016 and 2023

In 2023, a total of 380 wells were tested, out of which 173 had previously undergone testing in 2016. Figure 7 shows the percentage of wells exhibiting variations in concentrations and total pesticide compounds detected. The graph categorizes wells based on changes in concentration, representing wells with unchanged concentration in blue, increased concentration in red, and decreased concentration in green for specific selected compounds. Overall, the study revealed that the total amount of detected pesticides and concentrations did not change within individual wells since 2016. However, when examining specific changes, it was observed that in a greater percentage of wells, the total number of detected pesticides, as well as metolachlor ESA and nitrate concentrations, increased rather than decreased. Conversely, alachlor ESA and atrazine TCR concentrations experienced a decrease in a greater percentage of wells compared to those where an increase was observed.

Figure 7

Changes in Total Pesticide Detections and Concentrations in Well Sampled in 2016 and 2023



Trends in Statewide Detection Rates

The estimate of the statewide detection rates and the respective 95% confidence intervals for metolachlor ESA, alachlor ESA, atrazine TCR, atrazine, and neonicotinoids were compared to determine if there were any statistically significant changes between 2001 and 2023 (Figure 8). The atrazine and atrazine TCR evaluation did not include the results from prior surveys (1994 and 1996) because comparable lab methods for these compounds did not exist for the 1994 and 1996 surveys. Up to 2016, the statewide estimates relied on the 2001 NASS Land Use Strata [5], while the 2023 data utilized the latest 2016 NASS Land Use Strata [8]. The two NASS Land Use Strata primarily differ in their resolution levels. The 2001 layer was derived from 30-meter resolution aerial imagery, whereas the 2016 layer was derived from a higher resolution of 1-meter aerial imagery. The change in resolution predominantly impacted the acreage assigned to categories with the highest percentage of cultivated area.

Despite this variation, we calculated the 2023 statewide percentage of detects using both layers and found no substantial difference in the results.

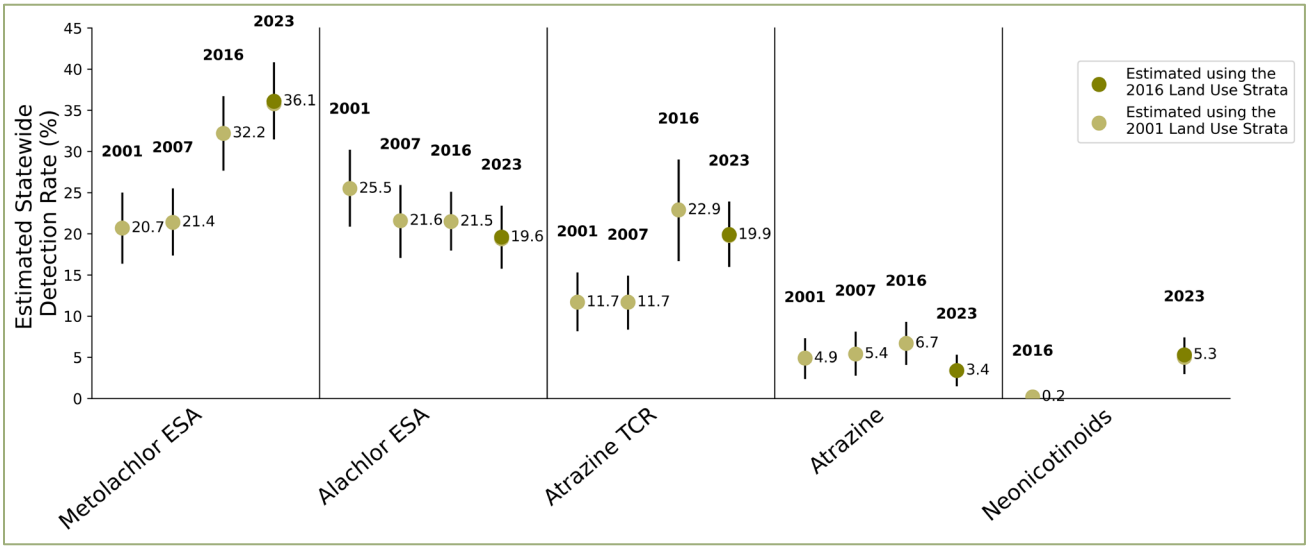
In Figure 8, the metolachlor ESA statewide detection rate is shown to be greater than in 2016. Despite this observed increase, the overlapping confidence intervals in both 2016 and 2023 suggest that the difference is not statistically significant at the 95% confidence level. Hence, it is not possible to confidently assert an increase in the metolachlor ESA statewide percentage of detects since 2016. However, it is confirmed that the metolachlor ESA statewide detection rate has increased when compared to the rates recorded in 2001 and 2007. Similarly for atrazine TCR, no statistically significant changes in the statewide detection rate have been observed since 2016. However, there appears to be an increase in the detection rate when compared to data from 2001 and 2007. The increase in the estimated detection rates for metolachlor ESA and atrazine TCR since 2007 may be partially attributed to the reduction of laboratory reporting limits, initiated in 2016, for a range of tested compounds, including metolachlor ESA, atrazine, and atrazine metabolites. This decrease in reporting limits has subsequently enhanced the laboratory's ability to detect compounds at lower concentrations.

Both statewide detection rates for alachlor ESA and the active ingredient atrazine showed no statistically significant changes, as indicated by overlapping confidence intervals.

Samples were not tested for clothianidin, imidacloprid, and thiamethoxam in 2001 and 2007. In 2016, only one detection of imidacloprid was recorded, resulting in an estimated statewide detection rate of 0.2% for neonicotinoids. Between 2016 and 2023, the statewide detection rate for neonicotinoids increased by approximately 5%. In 2016, the reporting limits for clothianidin, imidacloprid, and thiamethoxam were 0.067 µg/l, 0.05 µg/l, and 0.067 µg/l, respectively. By 2023, these reporting limits had been lowered to 0.01 µg/l. The adjustment in reporting limits may have contributed to the higher number of detections recorded in 2023 compared to 2016. For example, if the reporting limit had remained the same as in 2016, clothianidin would have been detected only three times instead of the recorded 26 instances of 2023.

FIGURE 8

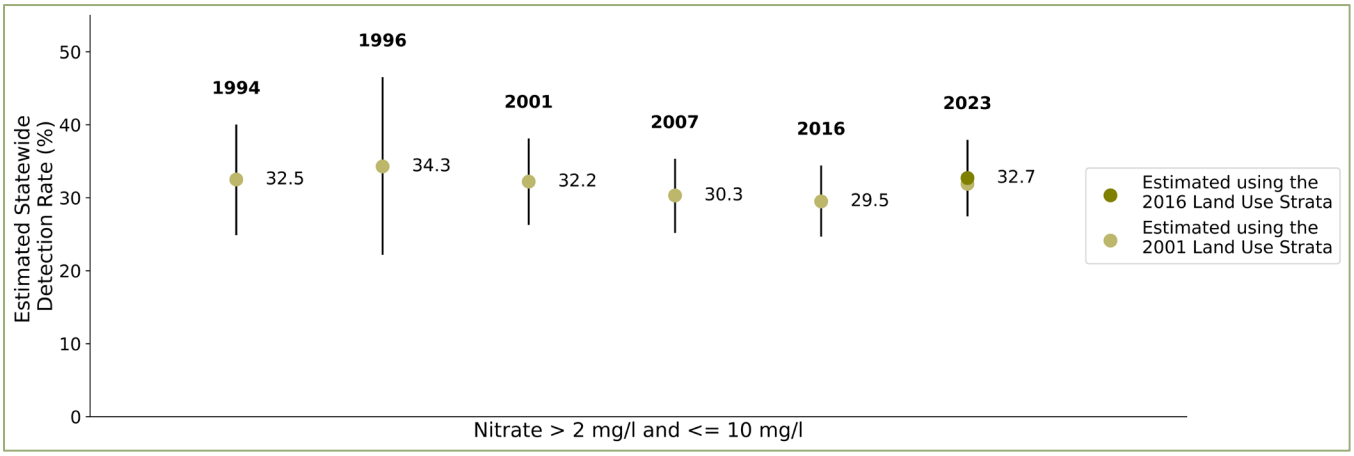
STATEWIDE PERCENTAGE OF DETECTS AND 95% CONFIDENCE INTERVALS FOR SELECTED PESTICIDES IN 2001, 2007, 2016, AND 2023 SURVEYS

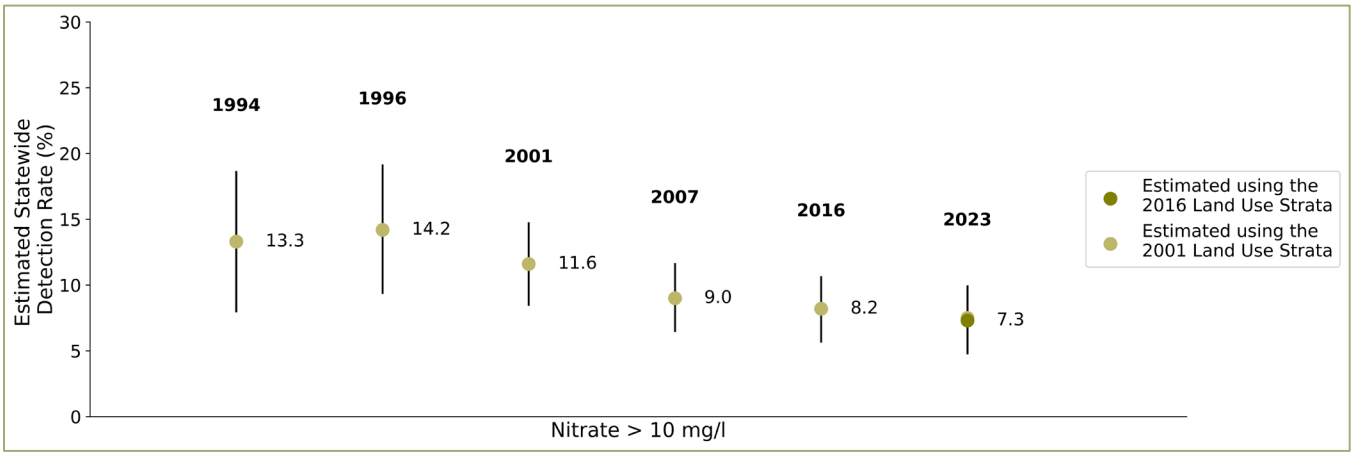


Similarly, the study compared statewide estimates and their respective 95% confidence intervals for nitrate concentrations as N, ranging from 2 mg/l to 10 mg/l, as well as concentrations exceeding 10 mg/l between the years 1994 and 2023 (Figure 9). All five surveys were suitable for this analysis due to the consistent analytical methods employed for nitrate across the surveys. Figure 9 shows that there has been no statistically significant change in the estimated statewide detection rate of nitrate between 2 mg/l and 10 mg/l since 1994. Similarly, since the first survey was completed in 1994, the percentage of wells containing nitrate greater than 10 mg/l has also remained unchanged.

FIGURE 9

STATEWIDE PERCENTAGE OF DETECTS AND 95% CONFIDENCE INTERVALS FOR NITRATE IN 2001, 2007, 2016, AND 2023 SURVEYS





SUMMARY

- The 2023 statewide survey estimate of the percentage of wells that contained a detectable concentration of a pesticide or pesticide metabolite was 43.1%, up from 41.7% of 2016 and 33.5% in 2007.
- In 2023 metolachlor ESA and alachlor ESA were the most commonly detected herbicide compounds with estimated statewide detection rates of 36.1% and 19.6%, respectively.
- The 2023 statewide survey estimate of wells that contained metolachlor ESA was 36.1%. The observed percentages in 2023 were not statistically significantly different from those recorded in 2016 (32.2%). Nevertheless, both the 2023 and 2016 statewide estimates of wells with metolachlor ESA were greater than the 21.4% recorded in 2007. The increase in the estimated detection rate for metolachlor ESA since 2007 may be partially attributed to the reduction in laboratory reporting limits initiated in 2016.
- The 2023 statewide survey estimate of the percentage of wells containing atrazine (active ingredient) and alachlor ESA did not show statistically significant changes between 2001 and 2023.
- The 2023 statewide survey estimate of the percentage of wells that contained atrazine TCR was 19.9%, similar to the 22.9% estimated in 2016, and up from 11.7% estimated in 2007. The increase in the estimated detection rate for atrazine TCR since 2007 may be partially attributed to the decrease in laboratory reporting limits initiated in 2016.
- The 2023 statewide survey estimate of the percentage of wells that contained neonicotinoids (clothianidin, imidacloprid, and/or thiamethoxam) was 5.3%, up from 0.2% estimated in 2016. The increase in the detection rate in 2023 can be attributed, in part, to the reduction of laboratory reporting limits for neonicotinoid compounds following 2016.
- The 2023 statewide survey percentage of wells containing nitrate between the NR 140 Preventive Action Limit of 2 mg/l and the NR 140 Enforcement Standard of 10 mg/l was estimated to be 32.7%. The statewide percentage of wells that exceeded the 10 mg/l NR 140 Enforcement Standard of 10 mg/l for nitrate in 2023 was estimated to be 7.3%. These percentages are statistically consistent with previous surveys.

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ACRONYMS AND DEFINITIONS

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

ACRONYMS

µg/l	Micrograms per liter (a liquid equivalent of ppb)
DADK	Desaminodiketo
DATCP	Wisconsin Department of Agriculture, Trade and Consumer Protection
DHS	Wisconsin Department of Health Services
ES	Enforcement Standard
ESA	Ethane Sulfonic Acid
GC	Gas Chromatography
mg/l	Milligrams per liter (a liquid equivalent of ppm)
N	Nitrogen
NASS	National Agricultural Statistics Service
OA	Oxanilic Acid
PAL	Preventive Action Limit
TCR	Total Chlorinated Residues
USDA	U.S. Department of Agriculture
Wis. Admin. Code	Wisconsin Administrative Code

DEFINITIONS

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

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)