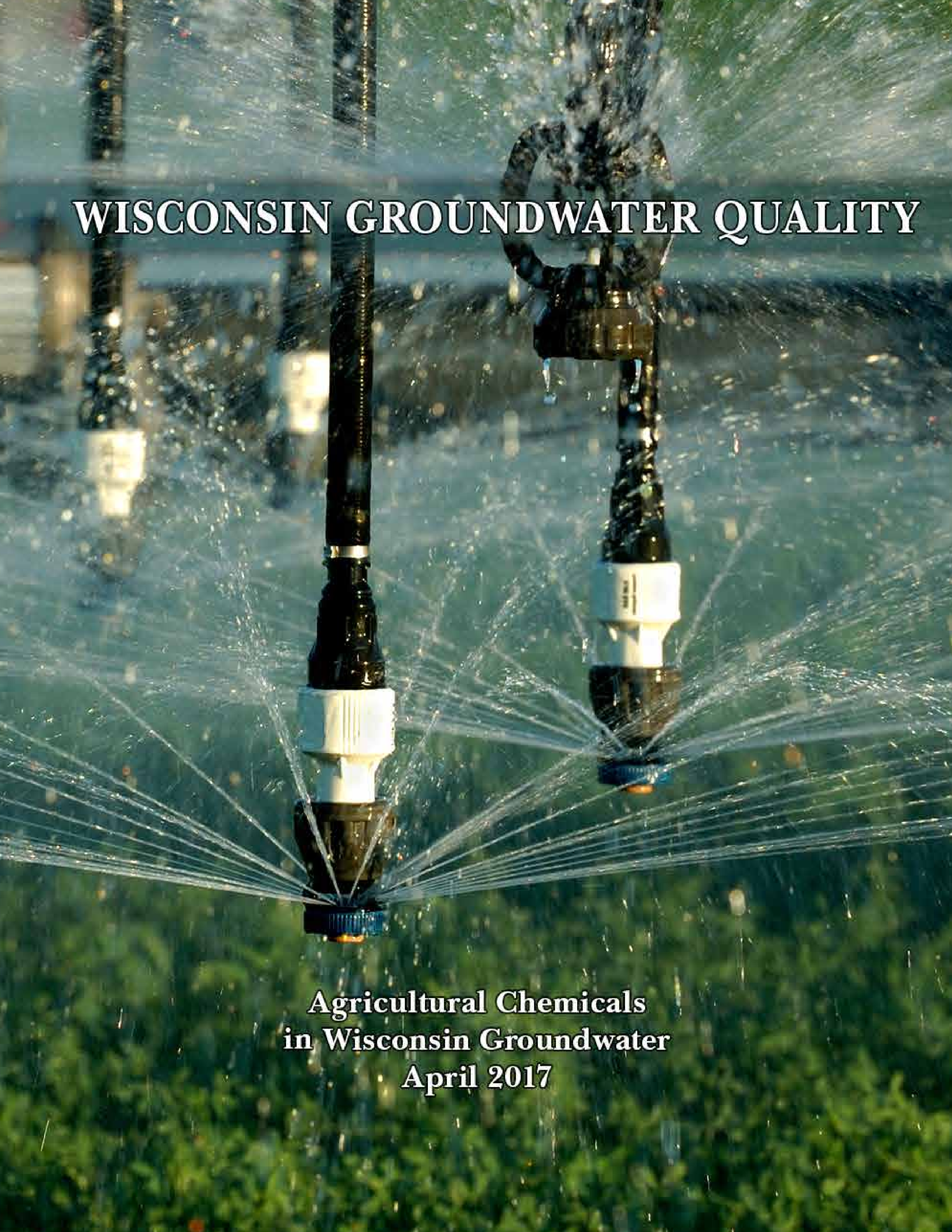

WISCONSIN GROUNDWATER QUALITY

Agricultural Chemicals in Wisconsin Groundwater

April 2017

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AGRICULTURAL CHEMICALS IN WISCONSIN GROUNDWATER

FINAL REPORT
APRIL 2017

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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 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 questionnaire.

Ben Brancel

Greg Bussler

Abstract

As part of a statewide survey of agricultural chemicals in Wisconsin groundwater, 401 private drinking water wells were sampled between March and August 2016. The purpose of the survey was to obtain a current picture of pesticides and pesticide breakdown products in groundwater, and to compare the levels of those found in earlier surveys. Wells were selected using a stratified random sampling procedure and represented Wisconsin groundwater accessible by private wells. Samples in the 2016 survey were analyzed for 101 different compounds, including herbicides, herbicide metabolites (breakdown products), insecticides, fungicides, and nitrate-nitrogen.

Based on a statistical analysis of the sample results, it was estimated that the percentage of wells in Wisconsin that contained a pesticide or pesticide metabolite was 41.7%. This is up from 33.5% in the 2007 survey. The survey generally showed more frequent detections of pesticides and nitrate–nitrogen in the more intensely farmed areas. The most commonly detected individual pesticide compound was the herbicide metabolite metolachlor ESA, found in an estimated 32.2% of wells. The second most commonly detected pesticide compound was the herbicide metabolite alachlor ESA, found in an estimated 21.5% of wells.

The statewide estimate of wells that contained atrazine or one of its total chlorinated residues (TCR) was 22.9%. The estimates of the mean detected concentrations for pesticides were generally less than 1.0 µg/l. The estimate of the percentage of wells with nitrate-nitrogen between the NR 140 Preventive Action Limit of 2 mg/l and the NR 140 Enforcement Standard of 10 mg/l was 29.5%, and the estimate of the percentage of wells with greater than the NR 140 Enforcement Standard for nitrate was 8.2%. A sample collected from one well contained atrazine TCR above the Wisc. Admin. Code NR 140 Enforcement Standard for atrazine TCR of 3.0 µg/l.

Time trend analysis was performed to determine whether the percentage estimates for nitrate-nitrogen, atrazine, TCR, alachlor ESA and metolachlor ESA in private wells had changed between the 2001, 2007 and the 2016 surveys. The percentage estimate for TCR and metolachlor ESA increased dramatically between the 2007 and 2016 surveys.

Introduction

The Wisconsin Department of Agriculture, Trade and Consumer Protection conducted the Atrazine Rule Evaluation Surveys in 1994 (Phase 1) and 1996 (Phase 2) (LeMasters and Baldock, 1997). These surveys were an important part of the department's evaluation of its regulations on the use of the herbicide atrazine. In 2000-2001, a third statewide survey was conducted to provide an update on agricultural chemicals in groundwater and to compare findings with the earlier surveys (Wisconsin Department of Agriculture, Trade and Consumer Protection, 2002).

A fourth statewide survey was completed in 2007 to establish the frequencies of detection and concentrations for pesticides and nitrate-nitrogen in rural drinking water wells in Wisconsin and to determine if there have been measurable changes in pesticide compounds and nitrate-nitrogen levels in Wisconsin groundwater over time, and also to relate groundwater quality to land use (Wisconsin Department of Agriculture, Trade and Consumer Protection, 2007).

The 2016 survey was completed to further estimate the quality of rural drinking water in Wisconsin and to again determine if there have been measurable changes in pesticide compounds and nitrate-nitrogen levels in Wisconsin groundwater over time.

Each water sample was analyzed for 101 compounds including 81 pesticide parent compounds, 18 pesticide metabolites (breakdown products), one pesticide safener, and nitrate-nitrogen. This list was expanded from the 32 analytes included in the 2007 survey. Of the pesticide compounds included in the 2016 survey, 69 were herbicides, 26 were insecticides, four were fungicides, and one was a pesticide safener. A majority of the pesticides included in the 2016 survey are currently registered for use in Wisconsin. However, several are no longer registered for use in Wisconsin, but may have impacted groundwater due to past use. Wisconsin Administrative Code NR 140 Enforcement Standards (NR 140 ES) have been established for 19 of the parent pesticide compounds and eight of the pesticide metabolites.

The purpose of this report is to present the results of the 2016 survey and to compare these results to earlier surveys. All five surveys were designed to allow for statistical comparisons.

Materials and Methods

Survey Design

The desired target sample population for the 1994, 1996, 2001, 2007, and 2016 surveys was Wisconsin groundwater. However, obtaining a representative sample of all Wisconsin groundwater is difficult due to its large three-dimensional extent across the state. In order to sample groundwater in an efficient manner, existing private drinking water wells were used. The actual target population for the five surveys can be best described as "groundwater accessible by private wells."

Each survey used a 50 percent sample rotation scheme, in which about half of the wells in the 1996, 2001, 2007, and 2016 surveys had been part of the previous survey and about half were newly selected. Wells that were tested for the first time in the 2007 survey were tested again in the 2016 survey. Wells that had been in both the 2001 and 2007 surveys were rotated out of the 2016 survey and a sample of new wells was selected. This rotation allowed both for the potential to identify new areas of agricultural chemical detections within the state, and for detecting changes in pesticide levels over time.

The 2016 survey, along with the previous four surveys, used a stratified random sampling procedure to allocate (select) samples throughout the state. The sample allocation procedure used in 2007 and 2016 for the newly-selected wells used NASS land use strata, which are based on how intensively land in Wisconsin is cultivated for agricultural production. 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." The land within each stratum is divided into "area segments" that are typically one square mile in size.

Since no comprehensive list of private wells exists, samples were allocated by randomly selecting a predetermined number of area segments within each agricultural stratum. Strata for entirely 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 groundwater 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 in order 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. The number of samples collected in each of the nine districts was based on the number of acres in farms in each district. Samples were allocated by selecting a random sample list of civil sections in each district (excluding those covered by water or publicly owned). In each civil section, a random 10-acre parcel was selected and the well nearest its center was identified to represent the groundwater of the civil section. A map depicting the NASS agricultural statistics districts can be found at: https://www.nass.usda.gov/Charts_and_Maps/Crops_County/boundary_maps/wi.pdf.

The 2007 and 2016 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.

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

Sample Collection And Analysis

Figure 1 shows the sample locations and the land use categories used in the 2016 survey. For the 2016 survey, 401 samples were collected from private drinking wells throughout Wisconsin.

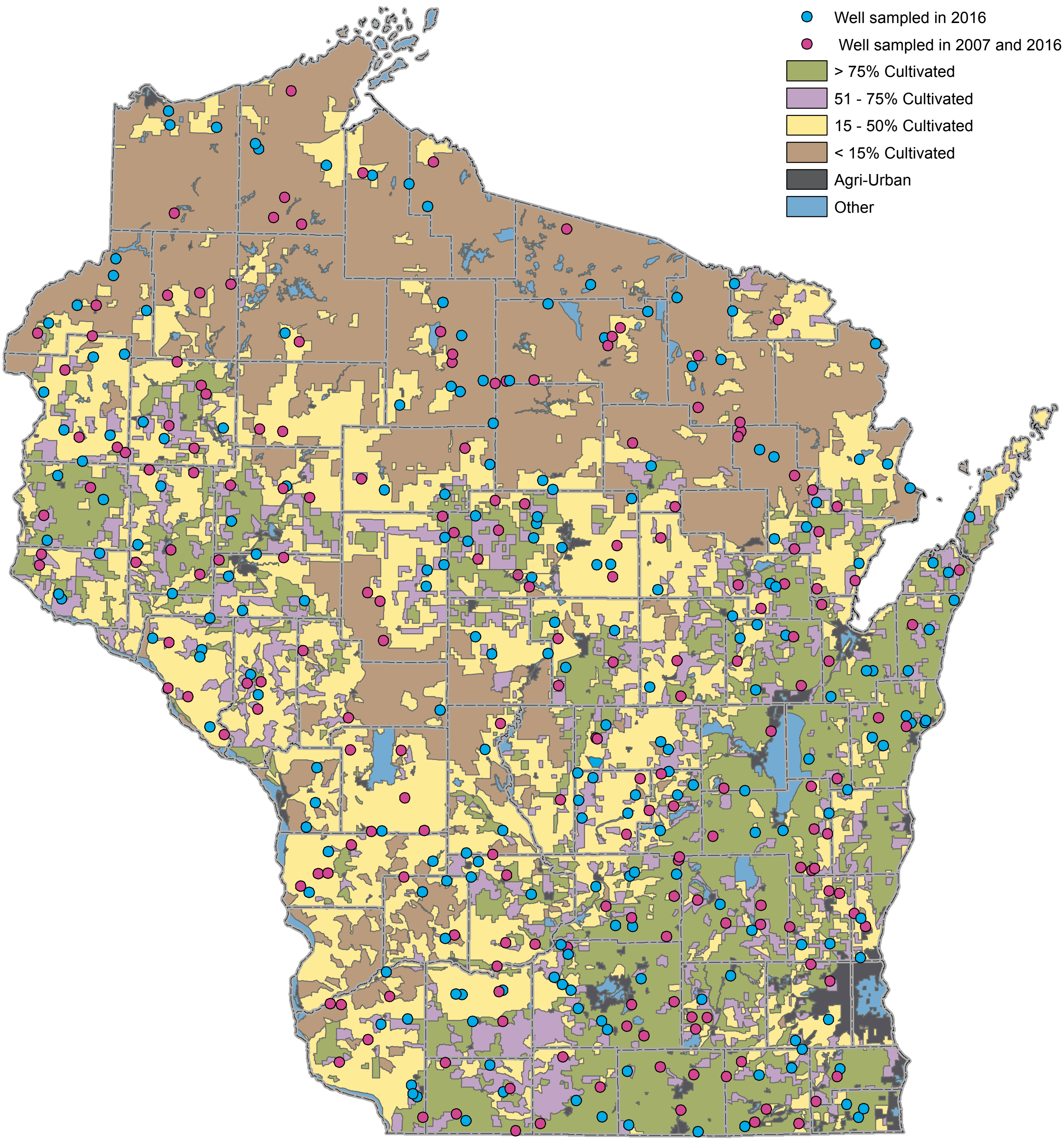
Water samples were collected from 191 wells that were first tested in the 2007 survey. Water samples were obtained only from wells that had not had any structural changes since the last survey. This was to ensure that water samples were collected from the same location in the aquifer as the previous survey in order to make comparisons valid.

Water samples were taken from 210 newly-selected wells that replaced those rotated out of the 2007 survey. Once a new well was selected, the samplers interviewed the owner to obtain well information and inspected the plumbing system to determine if there was a water treatment device. Samples were collected only if untreated, raw water could be obtained. If a groundwater sampler was not able to obtain an untreated sample from a well, another well was selected using the process described above.

Samples were collected through 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 bottles were delivered to the DATCP laboratory using an overnight delivery service or by hand.

Figure 1

Sampling Locations and Land Use Categories for the 2016 Survey



Results of the 2016 Survey

Pesticide and Nitrate-Nitrogen Detections

Table 1 shows the results of the 2016 survey. Of the 401 samples collected, 200 contained a detectable concentration (above the reporting limit) of one or more pesticide or pesticide metabolite (pesticide breakdown product). The most commonly detected pesticide compounds were the herbicide metabolites (breakdown products) metolachlor ethane sulfonic acid (metolachlor ESA) with 159 detections, and alachlor ethane sulfonic acid (alachlor ESA) with 113 detections. Atrazine total chlorinated residues (TCR) was detected a total of 106 times. TCR is defined as the total of atrazine or any of its three primary breakdown products (de-ethyl atrazine, de-isopropyl atrazine, di-amino atrazine). Figures 2-4 show the geographic distribution of the results for these three parameters.

One of the 106 samples that contained TCR exceeded the NR 140 ES of 3.0 micrograms per liter (µg/l). No samples exceeded the NR 140 ES for alachlor ESA of 20 µg/l or the NR 140 ES for metolachlor ESA of 1,300 µg/l.

Nitrate-nitrogen was detected in 225 of the 401 samples at concentrations ranging from 0.52 milligrams per liter (mg/l) to 31.2 mg/l, with 43 of the samples exceeding the nitrate-nitrogen NR 140 ES of 10 mg/l. Figure 5 is a map showing the geographic distribution of the nitrate-nitrogen results.

Table 1

Results of the 2016 Survey

Compound	Number of Detections Above Repoting Limit (RL)	Reporting Limit (µg/L)	NR 140 ES (µg/l)	Groundwater Samples Over NR 140 ES	Range of Concentrations (Above Reporting Limit) (µg/l)
N-Nitrate/Nitrite*	225	0.50 mg/L	10	43	0.52 - 31.2
2,4,5-T	0	0.05			
2,4,5-TP	0	0.05	50		
2,4-D	0	0.05	70		
2,4-DB	0	0.57			
2,4-DP	0	0.058			
Acetamiprid	0	0.05			
Acetochlor	1	0.05	7	0	0.05
Acetochlor ESA	30	0.05	230	0	0.05 - 3.60
Acetochlor OA	1	0.3	230	0	1.39

Compound	Number of Detections Above Repoting Limit (RL)	Reporting Limit (µg/L)	NR 140 ES (µg/l)	Groundwater Samples Over NR 140 ES	Range of Concentrations (Above Reporting Limit) (µg/l)
Acifluorfen	1	0.056			0.10
Alachlor	0	0.05	2		
Alachlor ESA	113	0.05	20	0	0.05 - 6.03
Alachlor OA	2	0.25			0.30 - 0.38
Aldicarb Sulfone	0	0.059			
Aldicarb Sulfoxide	0	0.13			
Aminopyralid	0	0.05			
Atrazine	31	0.05	3	0	0.05 - 1.77
De-ethyl atrazine	100	0.05	3	0	0.05 - 1.08
De-isopropyl atrazine	17	0.05	3	0	0.05 - 0.47
Di-amino atrazine	26	0.28	3	1	0.30 - 3.05
TCR	106	**	3	1	0.05 - 4.32
Azoxystrobin	0	0.05			
Benfluralin	0	0.05			
Bentazon	2	0.05	300	0	0.47 - 1.48
Bicyclopyrone	0	0.05			
Bromacil	0	0.084			
Carbaryl	1	0.067	40	0	0.14
Carbofuran	0	0.051	40		
Chloramben	0	0.57	150		
Chlorantraniliprole	0	0.2			
Chlorothalonil	0	0.16			
Chlorpyrifos	0	0.05	2		
Chlorpyrifos Oxon	0	0.05			
Clomazone	0	0.05			
Clopyralid	1	0.078			0.34
Clothianidin	0	0.067			
Cyclaniliprole	0	2			
Cyfluthrin	0	0.1			
Cypermethrin	0	0.15			
Cyprosulfamide***	0	0.074			
Dacthal	0	0.05	70		
Diazinon	0	0.05			
Diazinon oxon	0	0.05			

** Nitrate-Nitrite Concentration is in mg/l*

*** TCR is the sum of atrazine, de-ethyl atrazine, de-isopropyl atrazine, di-amino atrazine and does not have a reporting limit*

**** Cyprosulfamide is a pesticide safener, not a pesticide active ingredient*

Compound	Number of Detections Above Repoting Limit (RL)	Reporting Limit (µg/L)	NR 140 ES (µg/l)	Groundwater Samples Over NR 140 ES	Range of Concentrations (Above Reporting Limit) (µg/l)
Dicamba	0	0.89	300		
Dichlobenil	0	0.05			
Dimethenamid	0	0.05	50		
Dimethenamid ESA	1	0.05			0.08
Dimethenamid OA	0	0.054			
Dimethoate	0	0.05			
Dinotefuran	0	0.05			
Diuron	0	0.18			
EPTC	0	0.05	250		
Esfenvalerate	0	0.05			
Ethalfluralin	0	0.074			
Ethofumesate	0	0.05			
Flumetsulam	0	0.17			
Flupyradifurone	0	0.05			
Fluroxypyr	0	0.32			
Fomesafen	0	0.05			
Halosulfuron methyl	0	0.08			
Hexazinone	3	0.05			0.06 - 1.51
Imazapyr	0	0.05			
Imazethapyr	0	0.05			
Imidacloprid	1	0.05			0.08
Isoxaflutole	0	0.32			
Isoxaflutole DKN	0	0.47			
Lambda-Cyhalothrin	0	0.05			
Linuron	0	0.087			
Malathion	0	0.05			
MCPA	0	0.05			
MCPB	0	0.21			
MCPP	0	0.055			
Mesotrione	0	0.18			
Metalaxyl	1	0.05			0.09
Methyl Parathion	0	0.078			
Metolachlor	0	0.05	100		
Metolachlor ESA	159	0.05	1300	0	0.05 - 14.7

** Nitrate-Nitrite Concentration is in mg/l*

*** TCR is the sum of atrazine, de-ethyl atrazine, de-isopropyl atrazine, di-amino atrazine and does not have a reporting limit*

**** Cyprosulfamide is a pesticide safener, not a pesticide active ingredient*

Compound	Number of Detections Above Repoting Limit (RL)	Reporting Limit (µg/L)	NR 140 ES (µg/l)	Groundwater Samples Over NR 140 ES	Range of Concentrations (Above Reporting Limit) (µg/l)
Metolachlor OA	11	0.27	1300	0	0.30 - 2.82
Metribuzin	1	0.05	70	0	0.07
Metribuzin DA	1	0.1			0.10
Metribuzin DADK	5	0.12			0.15 - 0.85
Metsulfuron methyl	0	0.094			
Nicosulfuron	0	0.05			
Norflurazon	0	0.058			
Oxadiazon	0	0.05			
Pendimethalin	0	0.05			
Picloram	0	0.05	500		
Prometon	0	0.05	100		
Prometryn	0	0.05			
Propiconazole	0	0.055			
Saflufenacil	0	0.2			
Simazine	1	0.05	4	0	0.08
Sulfentrazone	0	0.75			
Sulfometuron methyl	0	0.05			
Tebupirimphos	0	0.05			
Tembotrione	0	0.21			
Thiacloprid	0	0.067			
Thiamethoxam	0	0.067			
Thiencarbazone methyl	0	0.38			
Triclopyr	1	0.1			0.15
Trifluralin	0	0.05			

** Nitrate-Nitrite Concentration is in mg/l*

*** TCR is the sum of atrazine, de-ethyl atrazine, de-isopropyl atrazine, di-amino atrazine and does not have a reporting limit*

**** Cyprosulfamide is a pesticide safener, not a pesticide active ingredient*

Figure 2

Alachlor ESA and Alachlor OA Results from the 2016 Survey

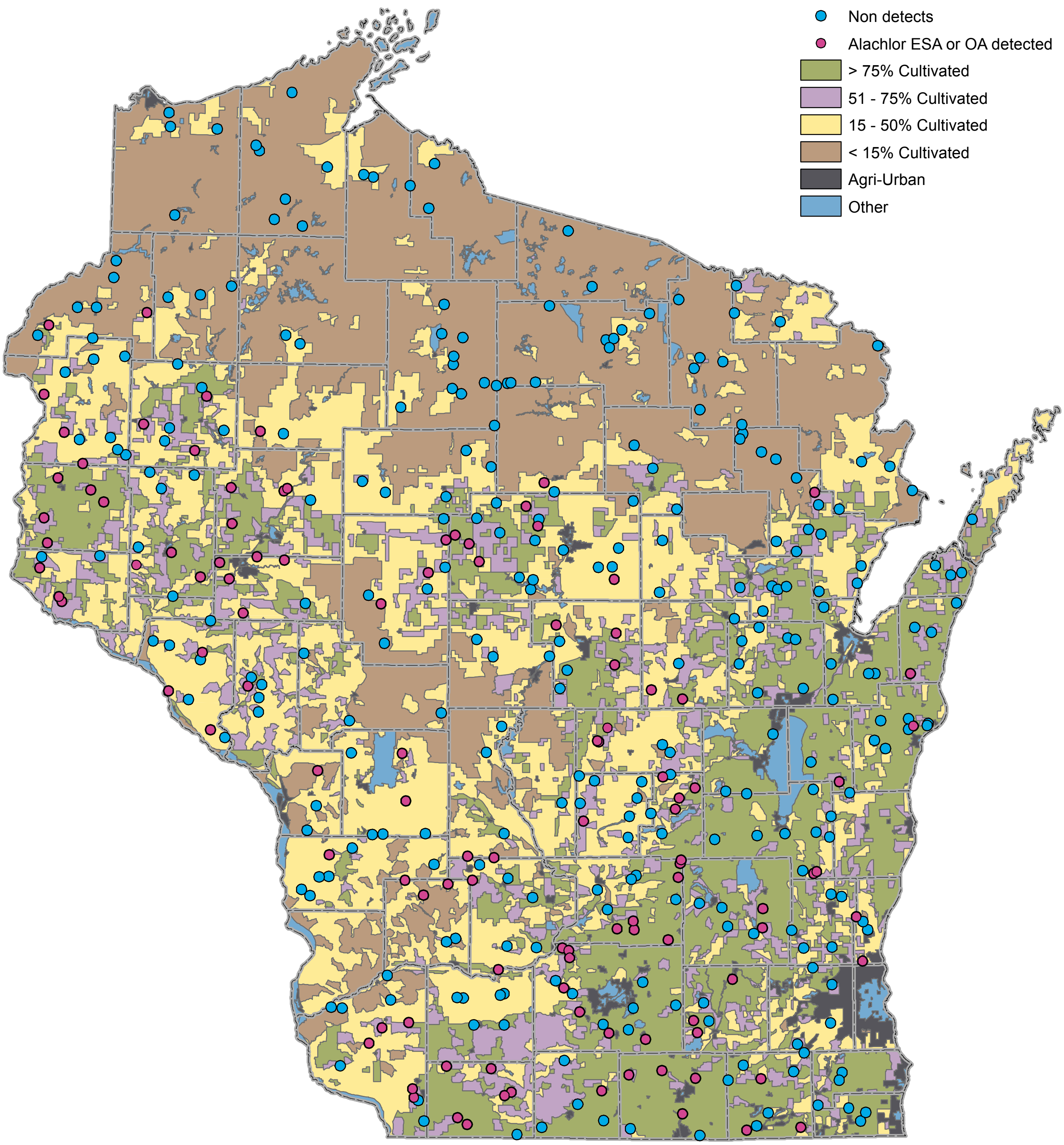


Figure 3

Metolachlor ESA and Metolachlor OA Results from the 2016 Survey

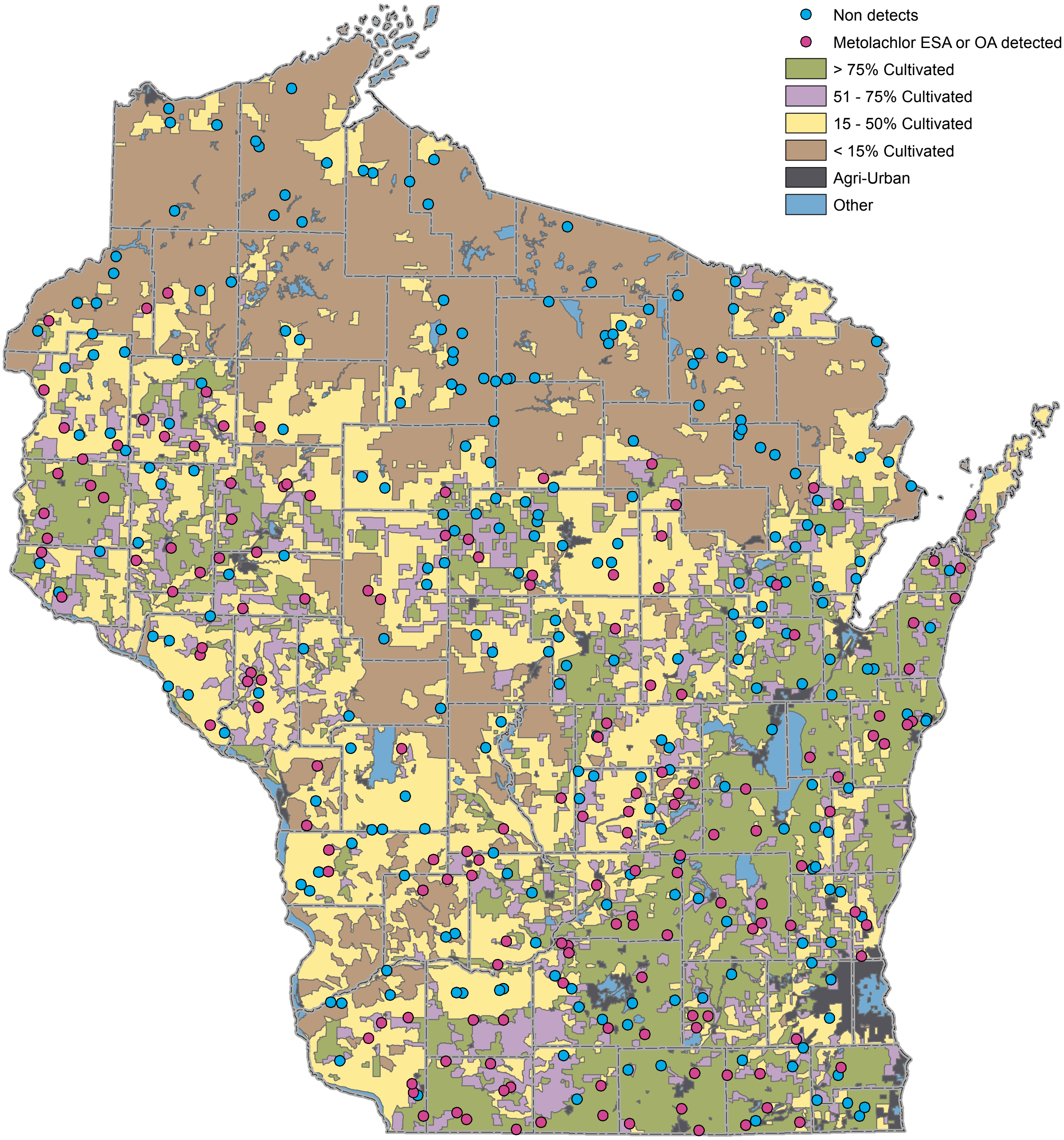


Figure 4

Atrazine TCR Results from the 2016 Survey

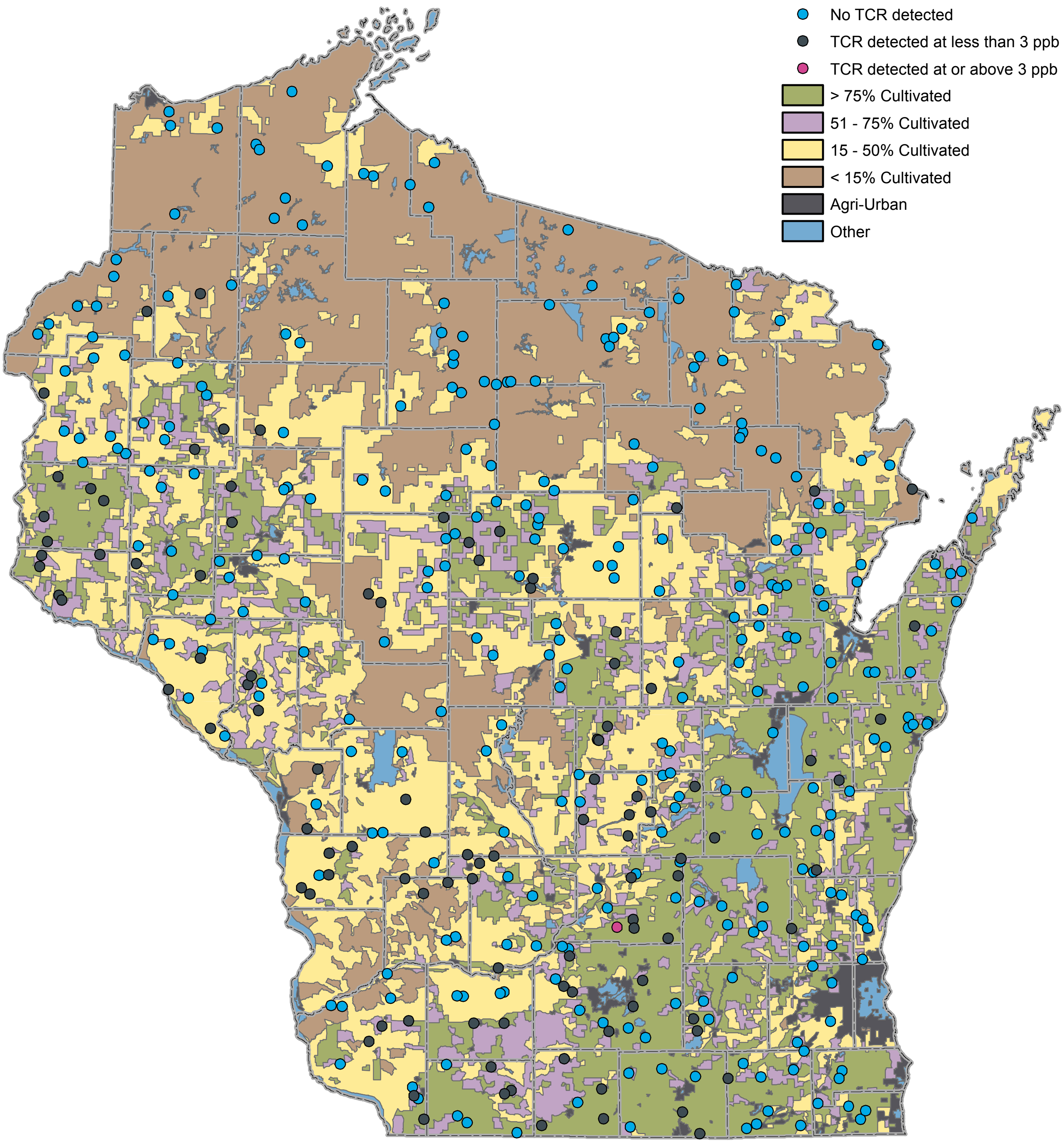
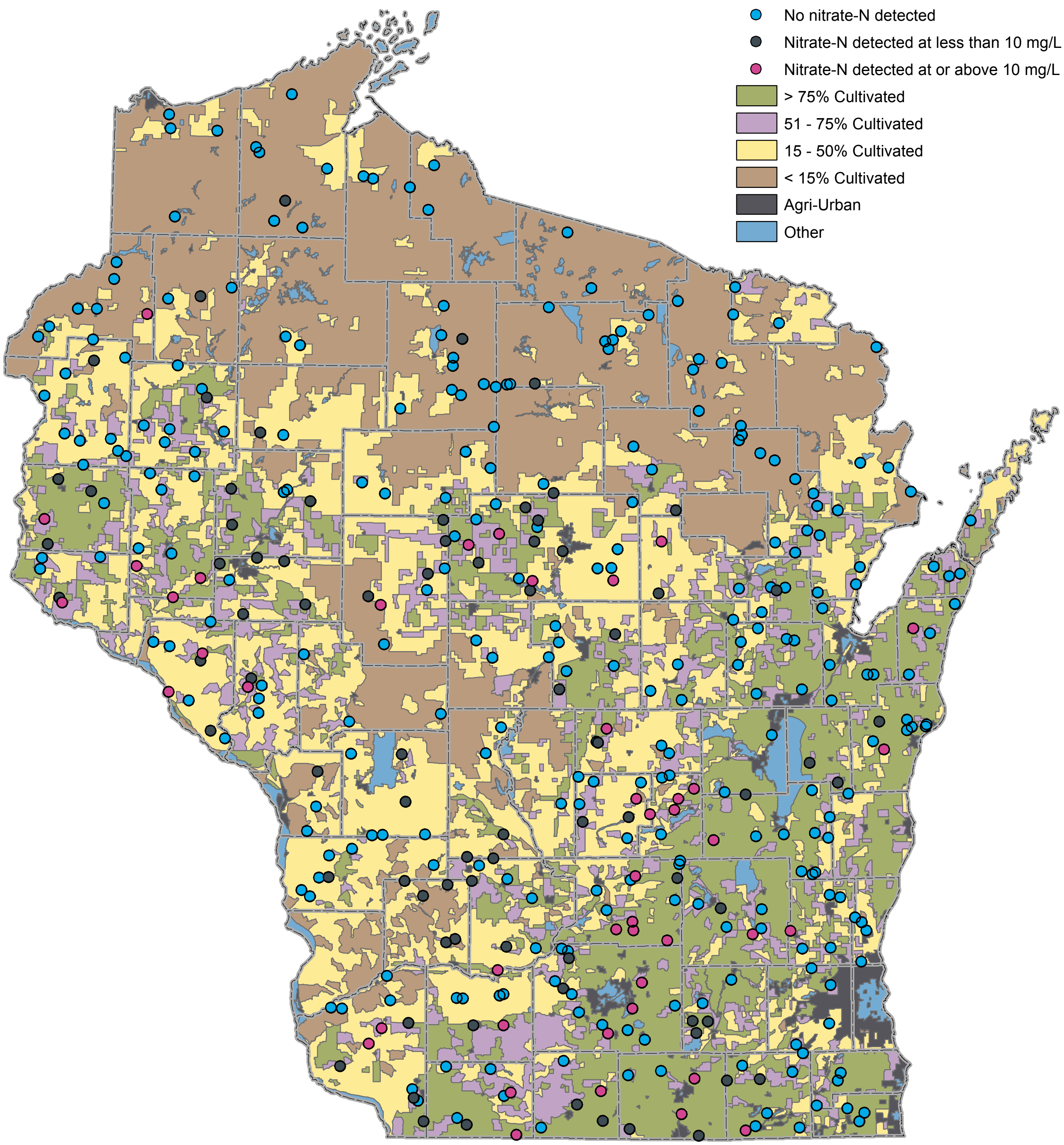


Figure 5

Nitrate-Nitrogen Results from the 2016 Survey



Detection Frequencies in the Strata

Table 2A shows the number of detections and Table 2B shows the percentage of detections in the NASS strata for the most commonly detected compounds in the 2016 survey.

TABLE 2A

Number of Detections Above Reporting Limit by NASS Strata and Parameter in the 2016 Survey

Strata	Description	Number of Samples	Number of Detections					
			Atrazine	TCR	Alachlor ESA	Metolachlor ESA	Nitrate-N	Nitrate>10
11	>75% Cultivated	133	12	42	55	78	82	27
12	51-75% Cultivated	57	4	18	17	23	37	3
20	15-50% Cultivated	150	13	39	40	51	87	12
40	<15% Cultivated	58	2	6	1	7	19	1
31	Agri-Urban	3	0	1	0	0	0	0
Total		401	31	106	113	159	225	43

TABLE 2B

Percentage of Detections Above Reporting Limit by NASS Strata and Parameter in the 2016 Survey

Strata	Description	Number of Samples	Percentage of Detections					
			Atrazine	TCR	Alachlor ESA	Metolachlor ESA	Nitrate-N	Nitrate>10
11	>75% Cultivated	133	9.0	32	41	59	62	20
12	51-75% Cultivated	57	7.0	32	30	40	65	5.3
20	15-50% Cultivated	150	8.7	26	27	34	58	8.0
40	<15% Cultivated	58	3.4	10	1.7	12	33	1.7
31	Agri-Urban	3	0	33	0	0	0	0

Statewide Statistical Estimates of the Percentage of Detections

Using the results from each stratum and the methods described by Cochran (1977) and Thomson (1992), statewide estimates of the percentage of detections were calculated for 11 parameters. These estimates apply to rural Wisconsin groundwater accessible by private wells. Table 3 shows these estimates and their 95% confidence intervals. Similar to the 2007 survey, metolachlor ESA and alachlor ESA had the highest percentage estimates for individual pesticide compounds with 32.2% and 21.5%, respectively. The estimate of the percentage of wells with TCR was calculated to be 22.9%. The estimate of the percentage of wells that exceeded the 10 mg/l NR 140 ES for nitrate-nitrogen was 8.2%

TABLE 3

Statewide Estimates of the Percentage of Detections and 95% Confidence Intervals for 11 Parameters in the 2016 Survey

Compound	Statewide number of detections	Statewide estimate of the percentage of detections	95% Confidence Interval (%)*
Any pesticide or metabolite	200	41.7	34.8- 48.6
TCR	106	22.9	16.8 - 28.9
TCR>3.0	1	0.2	**
Atrazine	31	6.7	4.2 - 9.2
Alachlor ESA	113	21.5	18.1 - 25.0
Alachlor OA	2	0.4	**
Acetochlor ESA	30	6.8	4.1 - 9.5
Metolachlor ESA	159	32.2	27.8 - 36.6
Metolachlor OA	11	2.4	0.8 - 4.0
Nitrate-nitrogen	225	50.1	44.8 - 55.4
Nitrate-Nitrogen>10***	43	8.2	5.7 - 10.6

* 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
***Nitrate-Nitrogen values are in mg/l

CONCENTRATIONS

Table 4 shows the average concentration for nine parameters and their 95% confidence intervals. The estimates of mean detected concentrations for pesticides ranged from 0.15 µg/l for atrazine to 1.04 µg/l for metolachlor OA.

TABLE 4

Estimates of the Mean Concentration of Detections and 95% Confidence Intervals for Nine Parameters in the 2016 Survey

Compound	Statewide number of detections	Statewide estimate of the mean detection concentration (µg/l)	95% confidence Interval* (µg/l)	NR 140 ES (µg/l)
TCR	106	0.37	0.19 - 0.56	3
Atrazine	31	0.15	0.05 - 0.24	3
Alachlor ESA	113	0.32	0.22 - 0.41	20
Alachlor OA	2	0.18	* *	Not established
Acetochlor ESA	30	0.32	0.07 - 0.56	230
Acetochlor OA	1	0.46	* *	230
Metolachlor ESA	159	0.77	0.35 - 1.20	1300
Metolachlor OA	11	1.04	0.00 - 2.07	1300
Nitrate-Nitrogen* * *	225	5.58	4.88 - 6.27	10

* 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
* * *Nitrate-Nitrogen values are in mg/l

Results for the Expanded List of analytes in the 2016

The 2016 survey included 73 additional analytes compared to the 2007 survey. These analytes (see materials and methods section) were added in 2016 because of historic or increased use of the compound in Wisconsin, information suggesting leaching potential, or improved laboratory capabilities. Additionally, five compounds that were included in the 2007 survey were not included in the 2016 survey due to analytical method difficulties. These compounds include glyphosate, glyphosate AMPA cyanazine, mesotrione MNBA and mesotrione AMBA.

Of the 73 new analytes, seven were detected in the 2016 survey. Table 5 shows the results for these compounds.

TABLE 5

Results for the Expanded List of analytes in the 2016 Survey.

Compound	Statewide number of detections	Concentration (µg/l)	NR 140 ES (µg/l)
Acifluorfen	1	0.10	Not established
Carbaryl	1	0.14	40
Imidacloprid	1	0.08	Not established
Metalaxyl	1	0.09	Not established
Metribuzin DA	1	0.10	Not established
Metribuzin DADK	5	0.15 - 0.85	Not established
Triclopyr	1	0.15	Not established

Comparing Results Between Surveys

The estimate of the percentage of detections and the respective 95% confidence intervals for atrazine, TCR, metolachlor ESA, and alachlor ESA were compared to determine if there were any statistically significant changes between 2001 and 2016. The TCR data had to be adjusted to allow for changes in the detection / reporting limits between the 2007 and 2016 surveys. Additionally, this 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.

Similarly, the estimate of the percentage of detections and the respective 95% confidence intervals for concentrations of nitrate-nitrogen between 2 mg/l and 10 mg/l and the concentration of nitrate-nitrogen greater than 10 mg/l were compared to determine if there were any statistically significant changes between1994 and 2016.

All five surveys could be used for this evaluation because the analytical methods for nitrate-nitrogen were comparable for all surveys.

Figure 6a shows that there is a dramatic increase in the percentage of wells that contain TCR and metolachlor ESA between the 2007 and 2016 surveys. Since there is no overlap in confidence intervals, the increase in the percentage of wells with metolachlor ESA is considered to be statistically significant. Figure 6A also shows that there was no statistically significant difference in the percentage of wells containing atrazine or alachlor ESA for this same time period. Figure 6b shows that there were no statistically significant changes (all confidence intervals overlap) for the percentage of wells containing nitrate nitrogen greater than 10 ppm, and Figure 6C shows that there were no statistically significant changes for the percentage of wells containing nitrate-nitrogen between 2 mg/l and 10 mg/l.

Figure 6A

Comparison of percentage estimates and 95% Confidence Intervals for 2001, 2007, and 2016

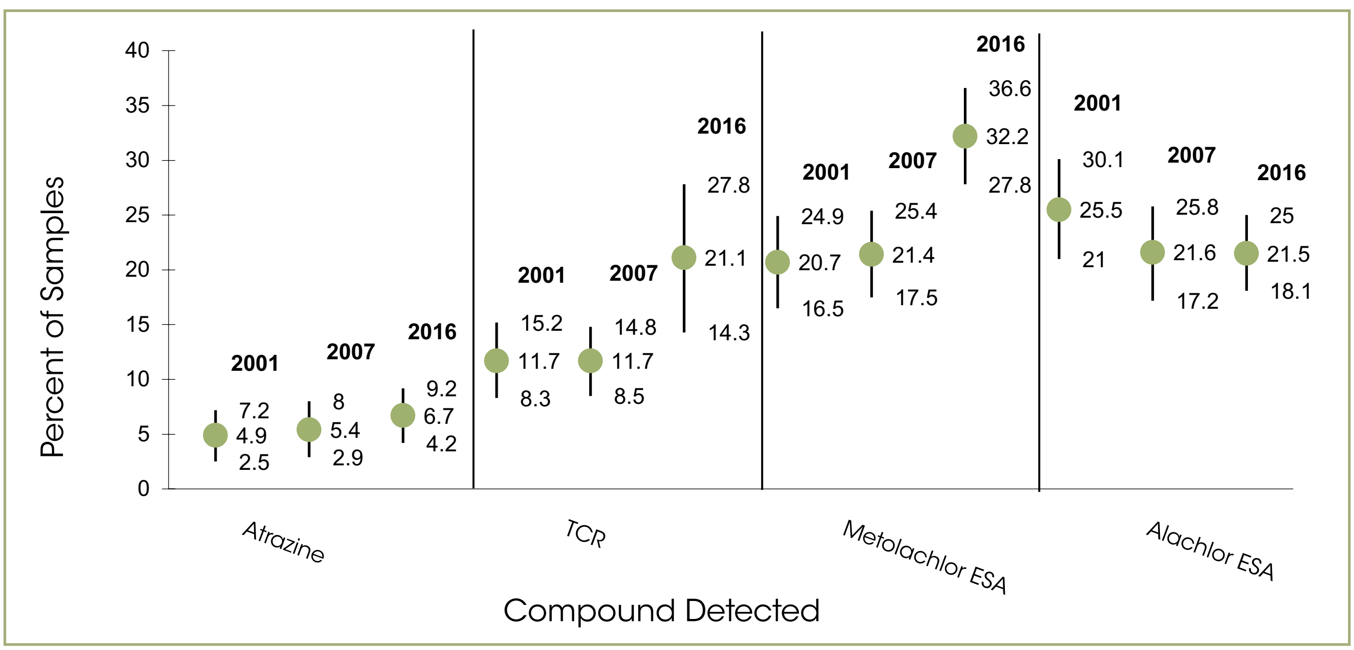


Figure 6B

Comparison of percentage estimates and 95% Confidence Intervals between 1994 and 2016.

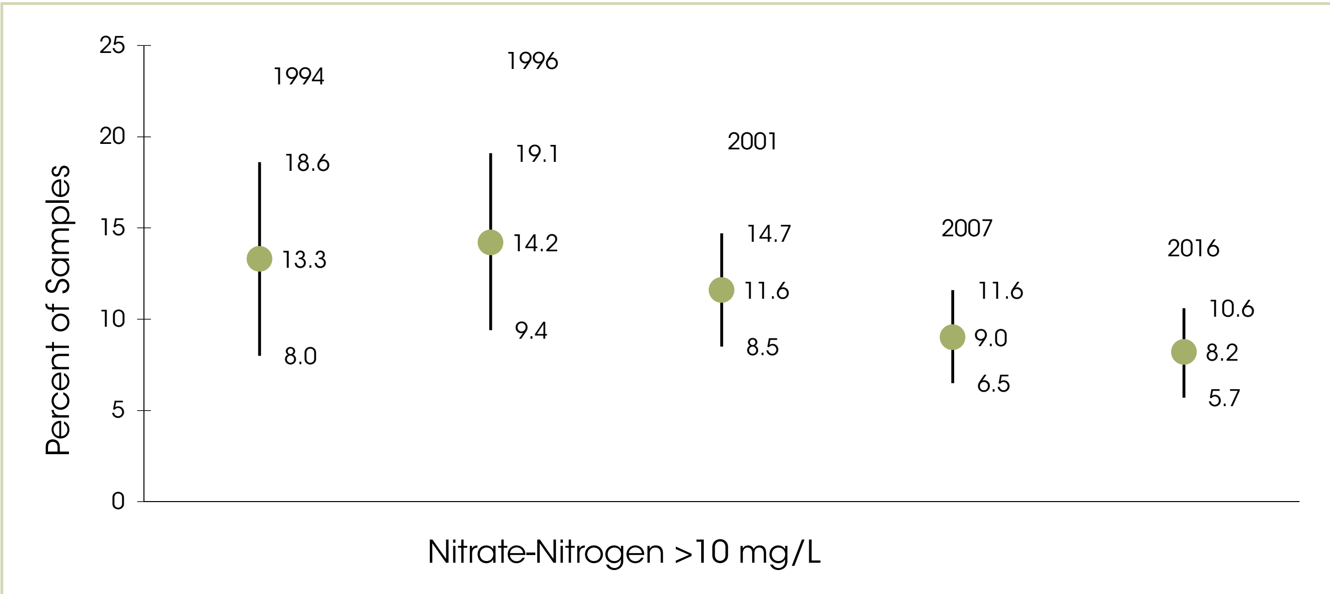
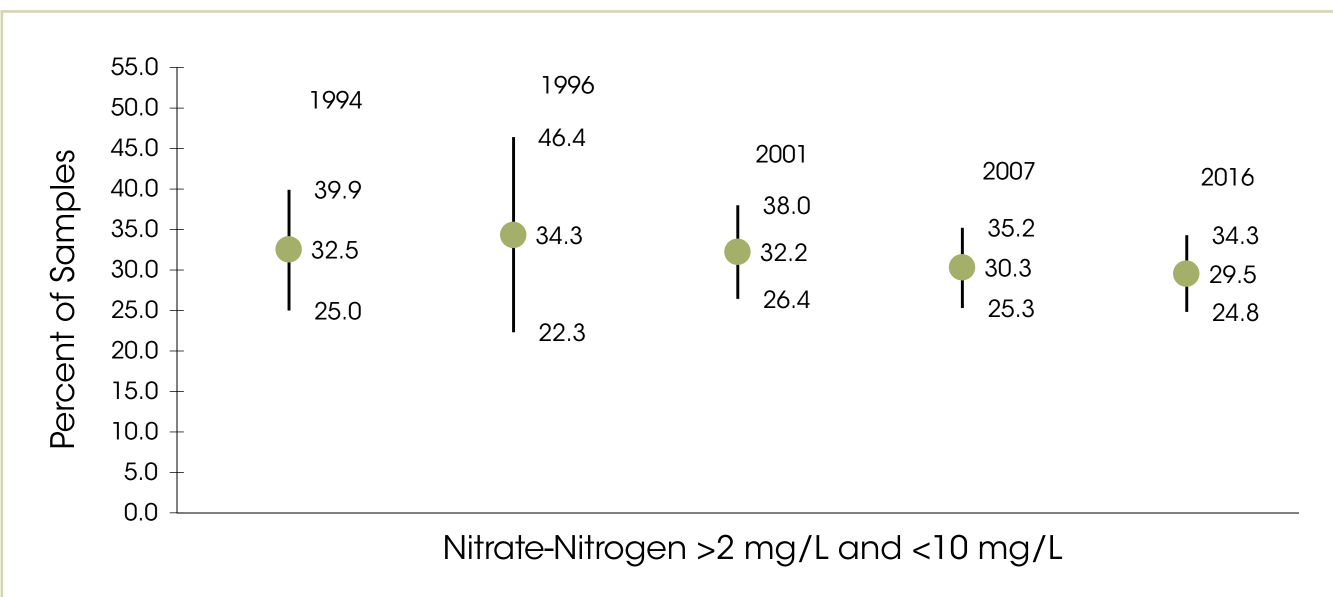


Figure 6C

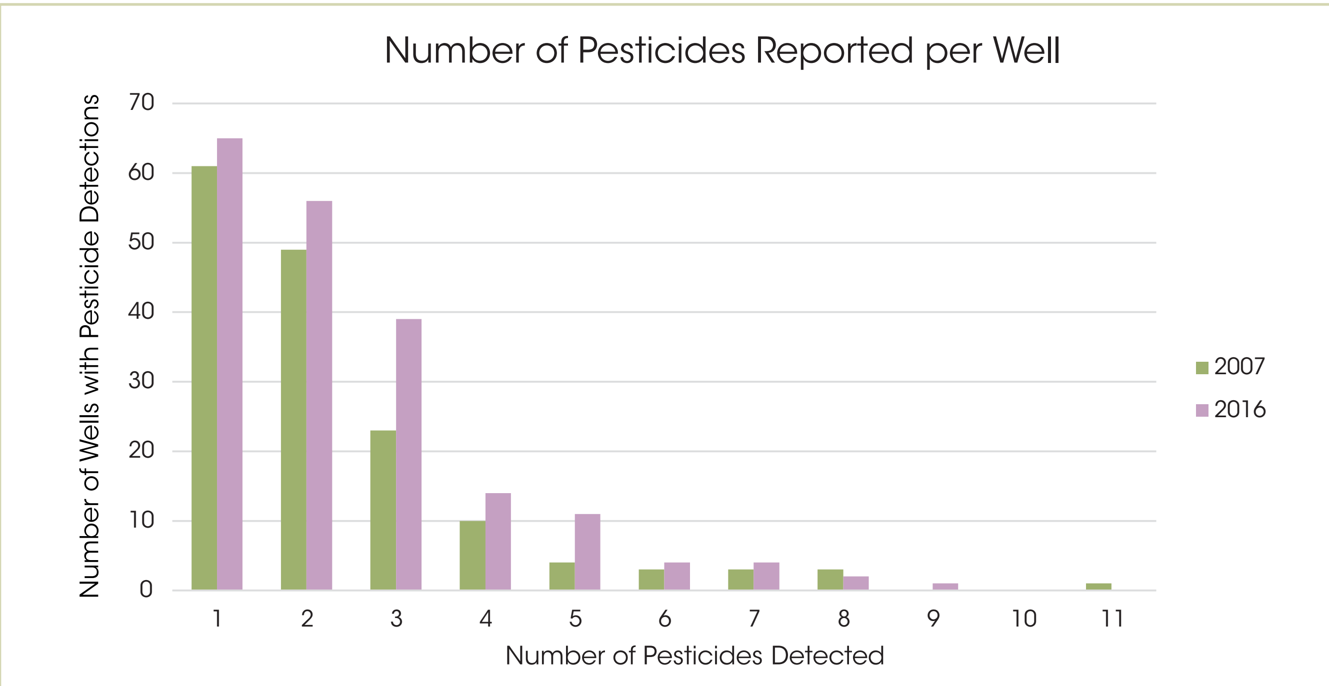
Comparison of percentage estimates and 95% Confidence Intervals between 1994 and 2016.



Finally, we compared the number of wells in the 2007 survey that had only one pesticide to the number of wells with only one pesticide in 2016. This comparison is followed by how many wells had only two pesticides, then three, then four, etc., until all wells with detectable levels of pesticides were included. To eliminate bias in comparison, only pesticides that were included on the analytical list for both the 2007 and 2016 surveys were included in this evaluation. Additionally, the data were adjusted for differences in detection / reporting limits between the two surveys. Figure 7 shows that the number of pesticides detected in wells generally increased between the 2007 and 2016 surveys.

Figure 7

Comparison of Number of Pesticides Detected in Any Well Between the 2007 and 2016 Surveys



Relationship Between Well Characteristics and Frequencies of Detection for Selected Compounds

As part of the 2016 survey, DATCP included two questions on age and depth of wells sampled.

For well age, respondents were asked if their wells were less than six years old, six to 20 years old, or over 20 years old. For well depth, respondents were asked if their wells were less than 50 feet deep, 50-150 feet deep, or over 150 feet deep. This information was used to evaluate the relationships between wells characteristics and detection frequencies for selected agricultural chemicals. Not all respondents were able to provide the age and depth of their wells and those who did generally answered based on memory. Therefore, the correlation between well age / depth and detection frequency should be considered approximate.

Table 6A shows the percentage of detections by well age. The majority of wells in the survey were more than 20 years old. Noticeable trends are higher percentages of detections of atrazine, TCR, alachlor ESA, metolachlor ESA and nitrate-nitrogen with increasing well age.

Table 6B shows the percentage of detections by well depth. The majority of wells in the survey were in the 50-150 feet range. The shallower wells had a higher percentage of detections of nitrate-nitrogen and a higher percentage of wells with nitrate-nitrogen over the 10 mg/l NR 140 ES.

Table 6A

Percentage of Detection for Selected Compounds by Well Age

Well Age* (years)	Number of Samples	Percentage of Detections					
		Atrazine	TCR	Alachlor ESA	MetolachlorESA	Nitrate-N	Nitrate >10
Under 6	9	0	0	11	22	33	0
6-20	103	6	18	19	26	45	4
Over 20	232	7	27	31	42	59	13

* 344 respondents knew the approximate age of their well

Table 6B

Percentage of Detection for Selected Compounds by Well Depth

Well Depth* (feet)	Number of Samples	Percentage of Detections					
		Atrazine	TCR	Alachlor ESA	Metolachlor ESA	Nitrate- N	Nitrate >10
Under 50	38	8	29	26	42	68	18
50-150	153	6	17	24	35	53	9
Over 150	96	13	28	26	32	50	10

* 287 respondents knew the approximate depth of their wells

Summary

- The statewide estimate of the percentage of wells containing atrazine and alachlor ESA did not show statistically significant changes between 2001 and 2007.
- The percentage of wells containing nitrate-nitrogen between the preventive action limit of 2 mg/l and the NR 140 ES of 10 mg/l was estimated to be 29.5%, and the percentage of wells that exceeded the 10 mg/l NR 140 ES for nitrate-nitrogen was estimated to be 8.2%. These percentages are statistically consistent with previous surveys.
- The statewide estimate of the percentage of wells that contained a detectable level of a pesticide or pesticide metabolite was 41.7%, up from 33.5% in 2007.
- Metolachlor ESA and alachlor ESA were the most commonly detected herbicide compounds with percentage estimates of 32.2% and 21.5%, respectively.
- The statewide estimate of the percentage of wells that contained TCR was 22.9%, up from 11.7% in 2007, and the estimate of wells that contained metolachlor ESA was 32.2%, up from 21.6% in 2007. The change in the percentage of wells containing metolachlor ESA is considered to be a statistically significant change.

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Notes

Notes

AGRICULTURAL CHEMICALS IN WISCONSIN GROUNDWATER

FINAL REPORT
APRIL 2017

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A Cooperative Project of the:

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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 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 questionnaire.

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Abstract

As part of a statewide survey of agricultural chemicals in Wisconsin groundwater, 401 private drinking water wells were sampled between March and August 2016. The purpose of the survey was to obtain a current picture of pesticides and pesticide breakdown products in groundwater, and to compare the levels of those found in earlier surveys. Wells were selected using a stratified random sampling procedure and represented Wisconsin groundwater accessible by private wells. Samples in the 2016 survey were analyzed for 101 different compounds, including herbicides, herbicide metabolites (breakdown products), insecticides, fungicides, and nitrate-nitrogen.

Based on a statistical analysis of the sample results, it was estimated that the percentage of wells in Wisconsin that contained a pesticide or pesticide metabolite was 41.7%. This is up from 33.5% in the 2007 survey. The survey generally showed more frequent detections of pesticides and nitrate–nitrogen in the more intensely farmed areas. The most commonly detected individual pesticide compound was the herbicide metabolite metolachlor ESA, found in an estimated 32.2% of wells. The second most commonly detected pesticide compound was the herbicide metabolite alachlor ESA, found in an estimated 21.5% of wells.

The statewide estimate of wells that contained atrazine or one of its total chlorinated residues (TCR) was 22.9%. The estimates of the mean detected concentrations for pesticides were generally less than 1.0 µg/l. The estimate of the percentage of wells with nitrate-nitrogen between the NR 140 Preventive Action Limit of 2 mg/l and the NR 140 Enforcement Standard of 10 mg/l was 29.5%, and the estimate of the percentage of wells with greater than the NR 140 Enforcement Standard for nitrate was 8.2%. A sample collected from one well contained atrazine TCR above the Wisc. Admin. Code NR 140 Enforcement Standard for atrazine TCR of 3.0 µg/l.

Time trend analysis was performed to determine whether the percentage estimates for nitrate-nitrogen, atrazine, TCR, alachlor ESA and metolachlor ESA in private wells had changed between the 2001, 2007 and the 2016 surveys. The percentage estimate for TCR and metolachlor ESA increased dramatically between the 2007 and 2016 surveys.

Introduction

The Wisconsin Department of Agriculture, Trade and Consumer Protection conducted the Atrazine Rule Evaluation Surveys in 1994 (Phase 1) and 1996 (Phase 2) (LeMasters and Baldock, 1997). These surveys were an important part of the department's evaluation of its regulations on the use of the herbicide atrazine. In 2000-2001, a third statewide survey was conducted to provide an update on agricultural chemicals in groundwater and to compare findings with the earlier surveys (Wisconsin Department of Agriculture, Trade and Consumer Protection, 2002).

A fourth statewide survey was completed in 2007 to establish the frequencies of detection and concentrations for pesticides and nitrate-nitrogen in rural drinking water wells in Wisconsin and to determine if there have been measurable changes in pesticide compounds and nitrate-nitrogen levels in Wisconsin groundwater over time, and also to relate groundwater quality to land use (Wisconsin Department of Agriculture, Trade and Consumer Protection, 2007).

The 2016 survey was completed to further estimate the quality of rural drinking water in Wisconsin and to again determine if there have been measurable changes in pesticide compounds and nitrate-nitrogen levels in Wisconsin groundwater over time.

Each water sample was analyzed for 101 compounds including 81 pesticide parent compounds, 18 pesticide metabolites (breakdown products), one pesticide safener, and nitrate-nitrogen. This list was expanded from the 32 analytes included in the 2007 survey. Of the pesticide compounds included in the 2016 survey, 69 were herbicides, 26 were insecticides, four were fungicides, and one was a pesticide safener. A majority of the pesticides included in the 2016 survey are currently registered for use in Wisconsin. However, several are no longer registered for use in Wisconsin, but may have impacted groundwater due to past use. Wisconsin Administrative Code NR 140 Enforcement Standards (NR 140 ES) have been established for 19 of the parent pesticide compounds and eight of the pesticide metabolites.

The purpose of this report is to present the results of the 2016 survey and to compare these results to earlier surveys. All five surveys were designed to allow for statistical comparisons.

Materials and Methods

Survey Design

The desired target sample population for the 1994, 1996, 2001, 2007, and 2016 surveys was Wisconsin groundwater. However, obtaining a representative sample of all Wisconsin groundwater is difficult due to its large three-dimensional extent across the state. In order to sample groundwater in an efficient manner, existing private drinking water wells were used. The actual target population for the five surveys can be best described as "groundwater accessible by private wells."

Each survey used a 50 percent sample rotation scheme, in which about half of the wells in the 1996, 2001, 2007, and 2016 surveys had been part of the previous survey and about half were newly selected. Wells that were tested for the first time in the 2007 survey were tested again in the 2016 survey. Wells that had been in both the 2001 and 2007 surveys were rotated out of the 2016 survey and a sample of new wells was selected. This rotation allowed both for the potential to identify new areas of agricultural chemical detections within the state, and for detecting changes in pesticide levels over time.

The 2016 survey, along with the previous four surveys, used a stratified random sampling procedure to allocate (select) samples throughout the state. The sample allocation procedure used in 2007 and 2016 for the newly-selected wells used NASS land use strata, which are based on how intensively land in Wisconsin is cultivated for agricultural production. 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." The land within each stratum is divided into "area segments" that are typically one square mile in size.

Since no comprehensive list of private wells exists, samples were allocated by randomly selecting a predetermined number of area segments within each agricultural stratum. Strata for entirely 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 groundwater 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 in order 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. The number of samples collected in each of the nine districts was based on the number of acres in farms in each district. Samples were allocated by selecting a random sample list of civil sections in each district (excluding those covered by water or publicly owned). In each civil section, a random 10-acre parcel was selected and the well nearest its center was identified to represent the groundwater of the civil section. A map depicting the NASS agricultural statistics districts can be found at: https://www.nass.usda.gov/Charts_and_Maps/Crops_County/boundary_maps/wi.pdf.

The 2007 and 2016 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.

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

Sample Collection And Analysis

Figure 1 shows the sample locations and the land use categories used in the 2016 survey. For the 2016 survey, 401 samples were collected from private drinking wells throughout Wisconsin.

Water samples were collected from 191 wells that were first tested in the 2007 survey. Water samples were obtained only from wells that had not had any structural changes since the last survey. This was to ensure that water samples were collected from the same location in the aquifer as the previous survey in order to make comparisons valid.

Water samples were taken from 210 newly-selected wells that replaced those rotated out of the 2007 survey. Once a new well was selected, the samplers interviewed the owner to obtain well information and inspected the plumbing system to determine if there was a water treatment device. Samples were collected only if untreated, raw water could be obtained. If a groundwater sampler was not able to obtain an untreated sample from a well, another well was selected using the process described above.

Samples were collected through 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 bottles were delivered to the DATCP laboratory using an overnight delivery service or by hand.

Results of the 2016 Survey

Pesticide and Nitrate-Nitrogen Detections

Table 1 shows the results of the 2016 survey. Of the 401 samples collected, 200 contained a detectable concentration (above the reporting limit) of one or more pesticide or pesticide metabolite (pesticide breakdown product). The most commonly detected pesticide compounds were the herbicide metabolites (breakdown products) metolachlor ethane sulfonic acid (metolachlor ESA) with 159 detections, and alachlor ethane sulfonic acid (alachlor ESA) with 113 detections. Atrazine total chlorinated residues (TCR) was detected a total of 106 times. TCR is defined as the total of atrazine or any of its three primary breakdown products (de-ethyl atrazine, de-isopropyl atrazine, di-amino atrazine). Figures 2-4 show the geographic distribution of the results for these three parameters.

One of the 106 samples that contained TCR exceeded the NR 140 ES of 3.0 micrograms per liter (µg/l). No samples exceeded the NR 140 ES for alachlor ESA of 20 µg/l or the NR 140 ES for metolachlor ESA of 1,300 µg/l.

Nitrate-nitrogen was detected in 225 of the 401 samples at concentrations ranging from 0.52 milligrams per liter (mg/l) to 31.2 mg/l, with 43 of the samples exceeding the nitrate-nitrogen NR 140 ES of 10 mg/l. Figure 5 is a map showing the geographic distribution of the nitrate-nitrogen results.

Table 1

Results of the 2016 Survey

Compound	Number of Detections Above Repoting Limit (RL)	Reporting Limit (µg/L)	NR 140 ES (µg/l)	Groundwater Samples Over NR 140 ES	Range of Concentrations (Above Reporting Limit) (µg/l)
N-Nitrate/Nitrite*	225	0.50 mg/L	10	43	0.52 - 31.2
2,4,5-T	0	0.05			
2,4,5-TP	0	0.05	50		
2,4-D	0	0.05	70		
2,4-DB	0	0.57			
2,4-DP	0	0.058			
Acetamiprid	0	0.05			
Acetochlor	1	0.05	7	0	0.05
Acetochlor ESA	30	0.05	230	0	0.05 - 3.60
Acetochlor OA	1	0.3	230	0	1.39

Compound	Number of Detections Above Repoting Limit (RL)	Reporting Limit (µg/L)	NR 140 ES (µg/l)	Groundwater Samples Over NR 140 ES	Range of Concentrations (Above Reporting Limit) (µg/l)
Acifluorfen	1	0.056			0.10
Alachlor	0	0.05	2		
Alachlor ESA	113	0.05	20	0	0.05 - 6.03
Alachlor OA	2	0.25			0.30 - 0.38
Aldicarb Sulfone	0	0.059			
Aldicarb Sulfoxide	0	0.13			
Aminopyralid	0	0.05			
Atrazine	31	0.05	3	0	0.05 - 1.77
De-ethyl atrazine	100	0.05	3	0	0.05 - 1.08
De-isopropyl atrazine	17	0.05	3	0	0.05 - 0.47
Di-amino atrazine	26	0.28	3	1	0.30 - 3.05
TCR	106	**	3	1	0.05 - 4.32
Azoxystrobin	0	0.05			
Benfluralin	0	0.05			
Bentazon	2	0.05	300	0	0.47 - 1.48
Bicyclopyrone	0	0.05			
Bromacil	0	0.084			
Carbaryl	1	0.067	40	0	0.14
Carbofuran	0	0.051	40		
Chloramben	0	0.57	150		
Chlorantraniliprole	0	0.2			
Chlorothalonil	0	0.16			
Chlorpyrifos	0	0.05	2		
Chlorpyrifos Oxon	0	0.05			
Clomazone	0	0.05			
Clopyralid	1	0.078			0.34
Clothianidin	0	0.067			
Cyclaniliprole	0	2			
Cyfluthrin	0	0.1			
Cypermethrin	0	0.15			
Cyprosulfamide***	0	0.074			
Dacthal	0	0.05	70		
Diazinon	0	0.05			
Diazinon oxon	0	0.05			

** Nitrate-Nitrite Concentration is in mg/l*

*** TCR is the sum of atrazine, de-ethyl atrazine, de-isopropyl atrazine, di-amino atrazine and does not have a reporting limit*

**** Cyprosulfamide is a pesticide safener, not a pesticide active ingredient*

Compound	Number of Detections Above Repoting Limit (RL)	Reporting Limit (µg/L)	NR 140 ES (µg/l)	Groundwater Samples Over NR 140 ES	Range of Concentrations (Above Reporting Limit) (µg/l)
Dicamba	0	0.89	300		
Dichlobenil	0	0.05			
Dimethenamid	0	0.05	50		
Dimethenamid ESA	1	0.05			0.08
Dimethenamid OA	0	0.054			
Dimethoate	0	0.05			
Dinotefuran	0	0.05			
Diuron	0	0.18			
EPTC	0	0.05	250		
Esfenvalerate	0	0.05			
Ethalfluralin	0	0.074			
Ethofumesate	0	0.05			
Flumetsulam	0	0.17			
Flupyradifurone	0	0.05			
Fluroxypyr	0	0.32			
Fomesafen	0	0.05			
Halosulfuron methyl	0	0.08			
Hexazinone	3	0.05			0.06 - 1.51
Imazapyr	0	0.05			
Imazethapyr	0	0.05			
Imidacloprid	1	0.05			0.08
Isoxaflutole	0	0.32			
Isoxaflutole DKN	0	0.47			
Lambda-Cyhalothrin	0	0.05			
Linuron	0	0.087			
Malathion	0	0.05			
MCPA	0	0.05			
MCPB	0	0.21			
MCPP	0	0.055			
Mesotrione	0	0.18			
Metalaxyl	1	0.05			0.09
Methyl Parathion	0	0.078			
Metolachlor	0	0.05	100		
Metolachlor ESA	159	0.05	1300	0	0.05 - 14.7

** Nitrate-Nitrite Concentration is in mg/l*

*** TCR is the sum of atrazine, de-ethyl atrazine, de-isopropyl atrazine, di-amino atrazine and does not have a reporting limit*

**** Cyprosulfamide is a pesticide safener, not a pesticide active ingredient*

Compound	Number of Detections Above Repoting Limit (RL)	Reporting Limit (µg/L)	NR 140 ES (µg/l)	Groundwater Samples Over NR 140 ES	Range of Concentrations (Above Reporting Limit) (µg/l)
Metolachlor OA	11	0.27	1300	0	0.30 - 2.82
Metribuzin	1	0.05	70	0	0.07
Metribuzin DA	1	0.1			0.10
Metribuzin DADK	5	0.12			0.15 - 0.85
Metsulfuron methyl	0	0.094			
Nicosulfuron	0	0.05			
Norflurazon	0	0.058			
Oxadiazon	0	0.05			
Pendimethalin	0	0.05			
Picloram	0	0.05	500		
Prometon	0	0.05	100		
Prometryn	0	0.05			
Propiconazole	0	0.055			
Saflufenacil	0	0.2			
Simazine	1	0.05	4	0	0.08
Sulfentrazone	0	0.75			
Sulfometuron methyl	0	0.05			
Tebupirimphos	0	0.05			
Tembotrione	0	0.21			
Thiacloprid	0	0.067			
Thiamethoxam	0	0.067			
Thiencarbazone methyl	0	0.38			
Triclopyr	1	0.1			0.15
Trifluralin	0	0.05			

** Nitrate-Nitrite Concentration is in mg/l*

*** TCR is the sum of atrazine, de-ethyl atrazine, de-isopropyl atrazine, di-amino atrazine and does not have a reporting limit*

**** Cyprosulfamide is a pesticide safener, not a pesticide active ingredient*

Detection Frequencies in the Strata

Table 2A shows the number of detections and Table 2B shows the percentage of detections in the NASS strata for the most commonly detected compounds in the 2016 survey.

TABLE 2A

Number of Detections Above Reporting Limit by NASS Strata and Parameter in the 2016 Survey

Strata	Description	Number of Samples	Number of Detections					
			Atrazine	TCR	Alachlor ESA	Metolachlor ESA	Nitrate-N	Nitrate>10
11	>75% Cultivated	133	12	42	55	78	82	27
12	51-75% Cultivated	57	4	18	17	23	37	3
20	15-50% Cultivated	150	13	39	40	51	87	12
40	<15% Cultivated	58	2	6	1	7	19	1
31	Agri-Urban	3	0	1	0	0	0	0
Total		401	31	106	113	159	225	43

TABLE 2B

Percentage of Detections Above Reporting Limit by NASS Strata and Parameter in the 2016 Survey

Strata	Description	Number of Samples	Percentage of Detections					
			Atrazine	TCR	Alachlor ESA	Metolachlor ESA	Nitrate-N	Nitrate>10
11	>75% Cultivated	133	9.0	32	41	59	62	20
12	51-75% Cultivated	57	7.0	32	30	40	65	5.3
20	15-50% Cultivated	150	8.7	26	27	34	58	8.0
40	<15% Cultivated	58	3.4	10	1.7	12	33	1.7
31	Agri-Urban	3	0	33	0	0	0	0

Statewide Statistical Estimates of the Percentage of Detections

Using the results from each stratum and the methods described by Cochran (1977) and Thomson (1992), statewide estimates of the percentage of detections were calculated for 11 parameters. These estimates apply to rural Wisconsin groundwater accessible by private wells. Table 3 shows these estimates and their 95% confidence intervals. Similar to the 2007 survey, metolachlor ESA and alachlor ESA had the highest percentage estimates for individual pesticide compounds with 32.2% and 21.5%, respectively. The estimate of the percentage of wells with TCR was calculated to be 22.9%. The estimate of the percentage of wells that exceeded the 10 mg/l NR 140 ES for nitrate-nitrogen was 8.2%

TABLE 3

Statewide Estimates of the Percentage of Detections and 95% Confidence Intervals for 11 Parameters in the 2016 Survey

Compound	Statewide number of detections	Statewide estimate of the percentage of detections	95% Confidence Interval (%)*
Any pesticide or metabolite	200	41.7	34.8- 48.6
TCR	106	22.9	16.8 - 28.9
TCR>3.0	1	0.2	**
Atrazine	31	6.7	4.2 - 9.2
Alachlor ESA	113	21.5	18.1 - 25.0
Alachlor OA	2	0.4	**
Acetochlor ESA	30	6.8	4.1 - 9.5
Metolachlor ESA	159	32.2	27.8 - 36.6
Metolachlor OA	11	2.4	0.8 - 4.0
Nitrate-nitrogen	225	50.1	44.8 - 55.4
Nitrate-Nitrogen>10***	43	8.2	5.7 - 10.6

* 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
***Nitrate-Nitrogen values are in mg/l

CONCENTRATIONS

Table 4 shows the average concentration for nine parameters and their 95% confidence intervals. The estimates of mean detected concentrations for pesticides ranged from 0.15 µg/l for atrazine to 1.04 µg/l for metolachlor OA.

TABLE 4

Estimates of the Mean Concentration of Detections and 95% Confidence Intervals for Nine Parameters in the 2016 Survey

Compound	Statewide number of detections	Statewide estimate of the mean detection concentration (µg/l)	95% confidence Interval* (µg/l)	NR 140 ES (µg/l)
TCR	106	0.37	0.19 - 0.56	3
Atrazine	31	0.15	0.05 - 0.24	3
Alachlor ESA	113	0.32	0.22 - 0.41	20
Alachlor OA	2	0.18	**	Not established
Acetochlor ESA	30	0.32	0.07 - 0.56	230
Acetochlor OA	1	0.46	**	230
Metolachlor ESA	159	0.77	0.35 - 1.20	1300
Metolachlor OA	11	1.04	0.00 - 2.07	1300
Nitrate-Nitrogen***	225	5.58	4.88 - 6.27	10

* 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
***Nitrate-Nitrogen values are in mg/l

Results for the Expanded List of analytes in the 2016

The 2016 survey included 73 additional analytes compared to the 2007 survey. These analytes (see materials and methods section) were added in 2016 because of historic or increased use of the compound in Wisconsin, information suggesting leaching potential, or improved laboratory capabilities. Additionally, five compounds that were included in the 2007 survey were not included in the 2016 survey due to analytical method difficulties. These compounds include glyphosate, glyphosate AMPA cyanazine, mesotrione MNBA and mesotrione AMBA.

Of the 73 new analytes, seven were detected in the 2016 survey. Table 5 shows the results for these compounds.

TABLE 5

Results for the Expanded List of analytes in the 2016 Survey.

Compound	Statewide number of detections	Concentration (µg/l)	NR 140 ES (µg/l)
Acifluorfen	1	0.10	Not established
Carbaryl	1	0.14	40
Imidacloprid	1	0.08	Not established
Metalaxyl	1	0.09	Not established
Metribuzin DA	1	0.10	Not established
Metribuzin DADK	5	0.15 - 0.85	Not established
Triclopyr	1	0.15	Not established

Comparing Results Between Surveys

The estimate of the percentage of detections and the respective 95% confidence intervals for atrazine, TCR, metolachlor ESA, and alachlor ESA were compared to determine if there were any statistically significant changes between 2001 and 2016. The TCR data had to be adjusted to allow for changes in the detection / reporting limits between the 2007 and 2016 surveys. Additionally, this 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.

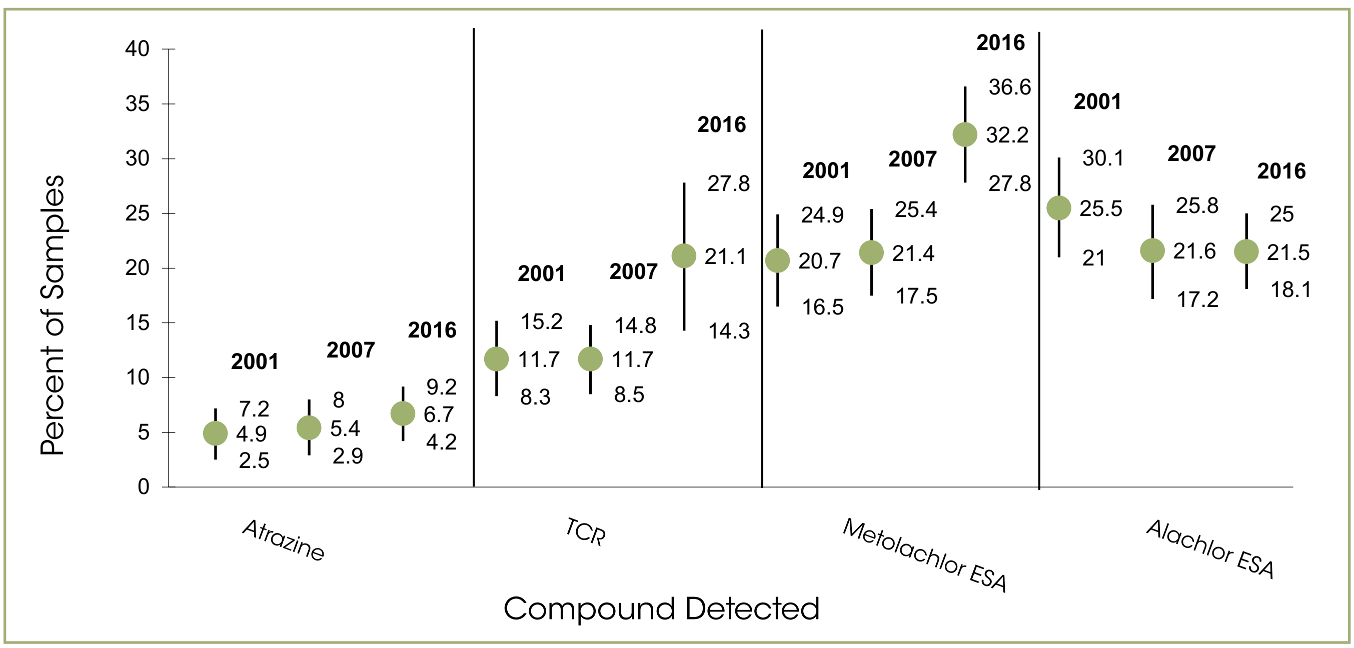
Similarly, the estimate of the percentage of detections and the respective 95% confidence intervals for concentrations of nitrate-nitrogen between 2 mg/l and 10 mg/l and the concentration of nitrate-nitrogen greater than 10 mg/l were compared to determine if there were any statistically significant changes between1994 and 2016.

All five surveys could be used for this evaluation because the analytical methods for nitrate-nitrogen were comparable for all surveys.

Figure 6a shows that there is a dramatic increase in the percentage of wells that contain TCR and metolachlor ESA between the 2007 and 2016 surveys. Since there is no overlap in confidence intervals, the increase in the percentage of wells with metolachlor ESA is considered to be statistically significant. Figure 6A also shows that there was no statistically significant difference in the percentage of wells containing atrazine or alachlor ESA for this same time period. Figure 6b shows that there were no statistically significant changes (all confidence intervals overlap) for the percentage of wells containing nitrate nitrogen greater than 10 ppm, and Figure 6C shows that there were no statistically significant changes for the percentage of wells containing nitrate-nitrogen between 2 mg/l and 10 mg/l.

Figure 6A

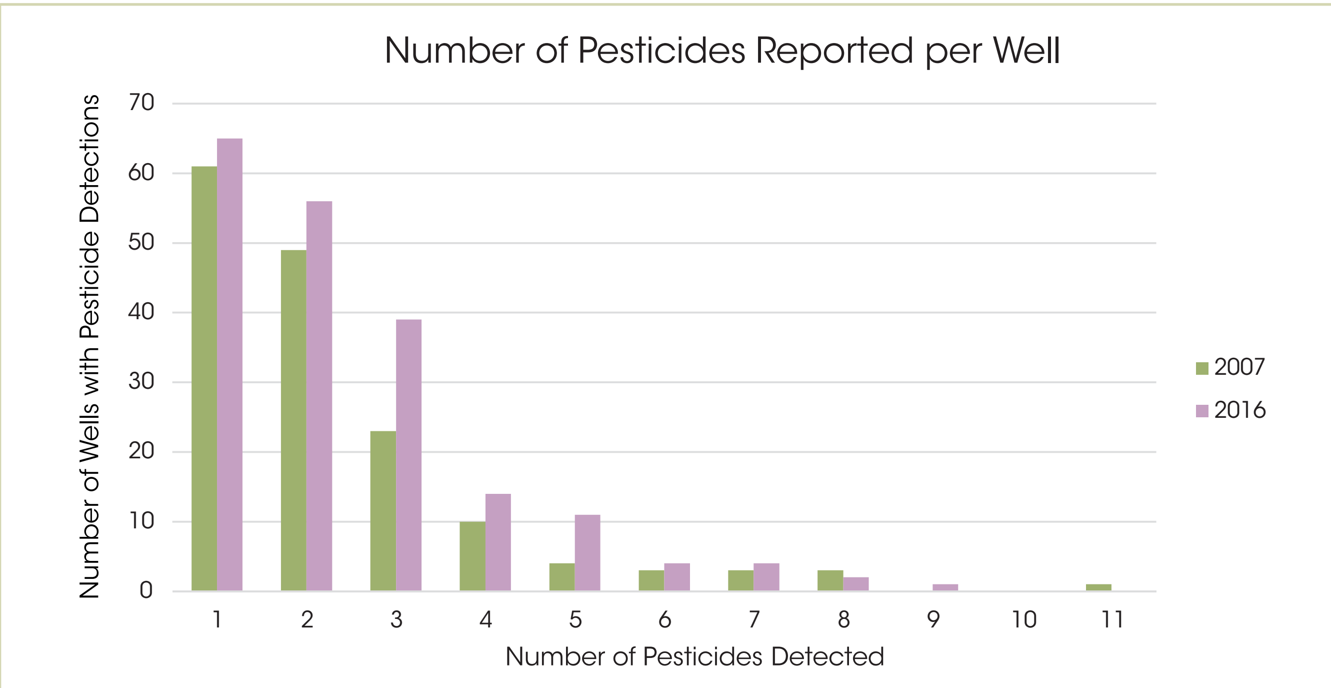
Comparison of percentage estimates and 95% Confidence Intervals for 2001, 2007, and 2016



Finally, we compared the number of wells in the 2007 survey that had only one pesticide to the number of wells with only one pesticide in 2016. This comparison is followed by how many wells had only two pesticides, then three, then four, etc., until all wells with detectable levels of pesticides were included. To eliminate bias in comparison, only pesticides that were included on the analytical list for both the 2007 and 2016 surveys were included in this evaluation. Additionally, the data were adjusted for differences in detection / reporting limits between the two surveys. Figure 7 shows that the number of pesticides detected in wells generally increased between the 2007 and 2016 surveys.

Figure 7

Comparison of Number of Pesticides Detected in Any Well Between the 2007 and 2016 Surveys



Relationship Between Well Characteristics and Frequencies of Detection for Selected Compounds

As part of the 2016 survey, DATCP included two questions on age and depth of wells sampled.

For well age, respondents were asked if their wells were less than six years old, six to 20 years old, or over 20 years old. For well depth, respondents were asked if their wells were less than 50 feet deep, 50-150 feet deep, or over 150 feet deep. This information was used to evaluate the relationships between wells characteristics and detection frequencies for selected agricultural chemicals. Not all respondents were able to provide the age and depth of their wells and those who did generally answered based on memory. Therefore, the correlation between well age / depth and detection frequency should be considered approximate.

Table 6A shows the percentage of detections by well age. The majority of wells in the survey were more than 20 years old. Noticeable trends are higher percentages of detections of atrazine, TCR, alachlor ESA, metolachlor ESA and nitrate-nitrogen with increasing well age.

Table 6B shows the percentage of detections by well depth. The majority of wells in the survey were in the 50-150 feet range. The shallower wells had a higher percentage of detections of nitrate-nitrogen and a higher percentage of wells with nitrate-nitrogen over the 10 mg/l NR 140 ES.

Table 6A

Percentage of Detection for Selected Compounds by Well Age

Well Age* (years)	Number of Samples	Percentage of Detections					
		Atrazine	TCR	Alachlor ESA	MetolachlorESA	Nitrate-N	Nitrate >10
Under 6	9	0	0	11	22	33	0
6-20	103	6	18	19	26	45	4
Over 20	232	7	27	31	42	59	13

* 344 respondents knew the approximate age of their well

Table 6B

Percentage of Detection for Selected Compounds by Well Depth

Well Depth* (feet)	Number of Samples	Percentage of Detections					
		Atrazine	TCR	Alachlor ESA	Metolachlor ESA	Nitrate- N	Nitrate >10
Under 50	38	8	29	26	42	68	18
50-150	153	6	17	24	35	53	9
Over 150	96	13	28	26	32	50	10

* 287 respondents knew the approximate depth of their wells

Summary

- The statewide estimate of the percentage of wells containing atrazine and alachlor ESA did not show statistically significant changes between 2001 and 2007.
- The percentage of wells containing nitrate-nitrogen between the preventive action limit of 2 mg/l and the NR 140 ES of 10 mg/l was estimated to be 29.5%, and the percentage of wells that exceeded the 10 mg/l NR 140 ES for nitrate-nitrogen was estimated to be 8.2%. These percentages are statistically consistent with previous surveys.
- The statewide estimate of the percentage of wells that contained a detectable level of a pesticide or pesticide metabolite was 41.7%, up from 33.5% in 2007.
- Metolachlor ESA and alachlor ESA were the most commonly detected herbicide compounds with percentage estimates of 32.2% and 21.5%, respectively.
- The statewide estimate of the percentage of wells that contained TCR was 22.9%, up from 11.7% in 2007, and the estimate of wells that contained metolachlor ESA was 32.2%, up from 21.6% in 2007. The change in the percentage of wells containing metolachlor ESA is considered to be a statistically significant change.

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