Groundwater QUALITY

Transpiration

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Runoff

Livestock waste storage pit

Septic System

Groundwater Table

Private well

Direction of Groundwater Movement

agricultural CHEMICALS in WISCONSIN groundwater

MAY 2002

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agricultural CHEMICALS in WISCONSIN groundwater

FINAL REPORT

MAY 2002

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chemicals in GROUNDWATER

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abstract

Between October 2000 and April 2001 336 private drinking water wells were sampled as part of a statewide survey of agricultural chemicals in Wisconsin groundwater. The purpose of the survey was to obtain a current picture of agricultural chemicals in groundwater and to compare the levels in the 2001 survey with levels founds in earlier surveys conducted in 1994 and 1996. Wells were selected using a stratified random sampling procedure and were used to represent Wisconsin groundwater exploitable by private wells. Samples were analyzed for 18 compounds including herbicides, herbicide metabolites, and nitrate - nitrogen.

Based on statistical analysis of the sample results, it was estimated that the proportion of wells in Wisconsin that contained a detectable level of a herbicide or herbicide metabolite was 37.7%. The two most commonly detected compounds were the metabolites alachlor ESA and metolachlor ESA with proportion estimates of 27.8 and 25.2%, respectively.

The estimate of the proportion of wells that contained atrazine total chlorinated residues (atrazine and three chlorinated metabolites) was 11.6%. Estimates of the mean detect concentrations were generally less than 1.0 ug/l. The estimate of the proportion of wells that exceeded the 3 ug/l enforcement standard for atrazine total chlorinated residues was 1.1%. The estimate of the proportion of wells that exceeded the 10 mg/l enforcement standard for nitrate - nitrogen was 14.1%.

The proportion of wells that contained a detectable level of parent atrazine showed a statistically significant decline between 1994 and 2001. The statewide proportion of wells with detects of atrazine total chlorinated residues did not show a statistically significant decline over this time period, but there were some interesting trends in groups of similar agricultural statistics districts. No other compound showed a significant decline from 1994 to 2001.

introduction

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

The specific objectives of the 2001 survey were 1) to establish the frequencies of detection and concentrations for atrazine, other herbicides and nitrate - nitrogen in rural drinking water wells in Wisconsin and 2) to determine if there have been measurable changes in atrazine and nitrate-nitrogen levels in Wisconsin groundwater over time.

Seven of the analytes that were tested for in this study -- atrazine, alachlor, metolachlor, acetochlor, cyanazine, metribuzin, and simazine -- are herbicide parent compounds. These are the active ingredients in many commonly used herbicide products. Health standards have been established for all of these compounds except acetochlor.

Ten of the analytes -- deethyl atrazine, deisopropyl atrazine, diamino atrazine, cyanazine amide, and the oxanillic acid (OA) and ethane sulfonic acid (ESA) breakdown products of alachlor, metolachlor, and acetochlor) are herbicide metabolites. These are related chemical compounds that are formed when the parent compounds break down in the soil and groundwater. With the exception of atrazine metabolites and alachlor ESA, these metabolite compounds do not yet have health standards.

The purpose of this report is to provide the results of the 2001 survey and to compare these results to earlier surveys. All three surveys were designed to allow for statistical comparisons.

materials and METHODS

Survey Design

The desired target population for the three surveys was Wisconsin groundwater. Obtaining a representative sample of all Wisconsin groundwater is not an easy task, however, 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 three surveys can be best described as groundwater in rural areas exploited by private wells.

All three surveys used a stratified, random sampling procedure to allocate samples throughout the state (Baldock, 1993). Nine agricultural statistics districts (ASD), which are groups of adjoining counties, formed the sampling strata. The number of samples collected in each district was based on the number of acres in agriculture in the district. To allocate the samples in each district, a random sample was drawn from a list of all the civil sections (excluding those covered by water or publicly owned). Civil sections were used

because no comprehensive current list of private wells exists. 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.

The 1994 and 1996 surveys attempted to minimize the statistical variance of the proportion and concentration estimates by increasing the number of samples in districts that had shown large variances in atrazine results in previous surveys. This optimization step was not used in the 2001 survey because it did not reduce the variance sufficiently in the 1994 / 1996 surveys to justify the increase in complexity. All three surveys used a 50% sample rotation scheme in which half the wells in the 1996 and 2001 surveys had been part of the previous survey and half were newly selected. This allowed additional statistical tests to be used that can detect changes in pesticide levels over time.

Sample Collection and Analysis

We collected 336 water samples from private drinking water wells as part of the 2001 survey. Figure 1 shows the sampling locations and the boundaries of the agricultural statistics districts.

For each of the surveys, sample collection began with a list of randomly selected civil sections with a 10-acre parcel identified in each. The parcel was visited to determine if a private well existed within that 10-acres. If so, we made three attempts to contact the owner and determine their willingness to participate in the survey. If we did not identify a well or willing well owner, we spiraled out in a clockwise manner to other 10-acre parcels in the section until we found a well and willing owner. If we did not find a well or willing well owner in the entire section, we selected a replacement section and random 10-acre parcel from a second random list of sections in the district.

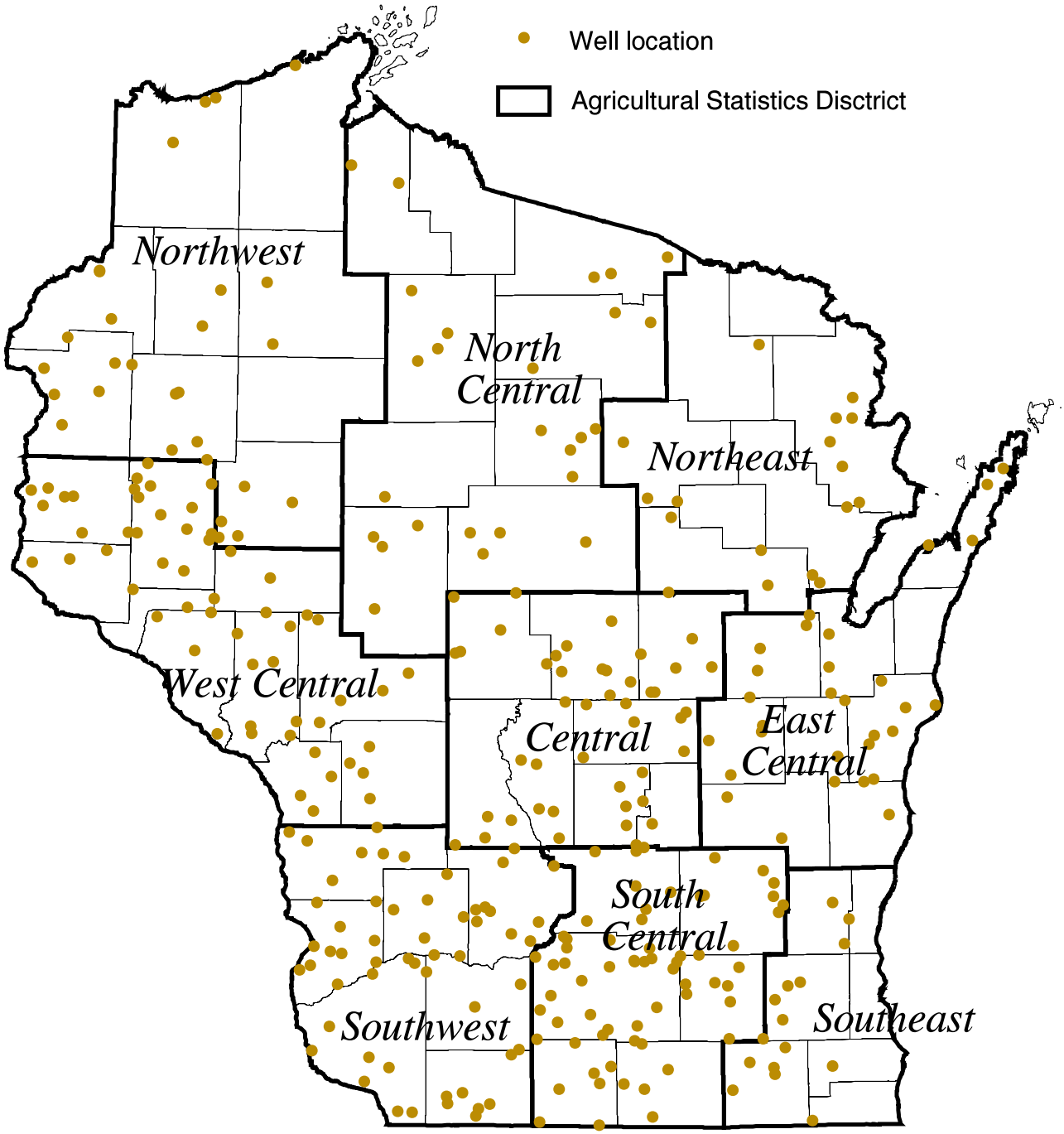
Once we identified a well and willing well owner, we collected a sample using the existing well and pump. The sampling technician interviewed the owner and inspected the plumbing system to see if there was a water treatment device. If we could not obtain a sample that did not pass through a water treatment device, we selected a replacement well using the process described above. We collected samples through the cold water faucet after allowing the water to run for approximately 10 minutes. We filled two one-liter amber glass jars with Teflon lined caps from each site and promptly placed the sample on ice. We filled out sample collection records and maintained sample integrity through delivery to the DATCP laboratory.

Each water sample was analyzed for the following 18 compounds at the DATCP laboratory:

- atrazine and its metabolites deethyl atrazine, deisopropyl atrazine and diamino atrazine (the sum of these four compounds is referred to as total chlorinated residues of atrazine or TCR)
- alachlor, metolachlor and acetochlor and their ESA and OA metabolites
- cyanazine and its metabolite cyanazine amide
- metribuzin
- simazine
- nitrate-nitrogen

figure 1

Sampling Locations and Agricultural Statistics District Boundaries



results of the 2001 SURVEY

Herbicide and Nitrate-N Detections

Table 1 is a tabulation of the results of the 2001 survey. One hundred thirty five (135) of the 336 samples contained a detectable concentration of one or more herbicides or herbicide metabolites. The most commonly detected herbicide compounds were alachlor ESA (103 detects), metolachlor ESA (88 detects), and atrazine total chlorinated residues or TCR (48 detects). Figures 2-4 are maps showing the geographic distribution of the results for these three parameters. It is also interesting to note that acetochlor metabolites were detected in ten wells six years after the use of acetochlor products began in Wisconsin.

Five of the 48 samples that contained detectable residues of TCR exceeded the Wisconsin groundwater enforcement standard of 3 micrograms per liter (µg/l) (parts per billion). No samples exceeded the alachlor ESA interim health advisory of 20 ug/l. A standard has not been established for metolachlor ESA.

Nitrate-nitrogen was detected in 216 of the 336 samples in concentrations ranging from 0.5 milligrams per liter (mg/l) (parts per million) to 41.6 mg/l. Fifty-three of the samples exceeded the nitrate-nitrogen enforcement standard of 10 mg/l. Figure 5 is a map showing the geographic distribution of the nitrate-nitrogen results.

table 1

Results of the 2001 Survey.

Compound	Number of detects	Limit of detection (ug/l)	Groundwater enforcement standard (ug/l)	Groundwater samples over standard	Concentration range (ug/l)
atrtrazine	20	0.15			0.168-1.58
deethyl atrazine	31	0.30			0.309-2.76
deisopropyl atrazine	14	0.30			0.30-3.75
diamino atrazine	24	0.50			0.54-3.1
TCR	48	#	3	5	0.271-6.26
alachlor	1	0.15	2		0.69
alachlor ESA	103	0.10	20*		0.101-14.8
alachlor OA	16	0.10			0.145-13.5
metolachlor	0	0.25	15		
metolachlor ESA	88	0.10			0.103-10.2
metolachlor OA	23	0.10			0.103-5.89
acetochlor	0	0.10			
acetochlor ESA	10	0.10			0.104-0.809
acetochlor OA	1	0.10			0.155
cyanazine	0	0.50	1		
cyanazine amide	4	0.50			0.553-0.998
metribuzin	1	0.05	250		0.078
simazine	0	0.15	4		
nitrate-nitrogen	216	0.50+	10+	53	0.551-41.6+

* interim health advisory
\+ nitrate-nitrogen results are in mg/l
\# TCR is the sum of four analytes and does not have a limit of detection

figure 2

Alachlor ESA and OA Results from the 2001 Survey

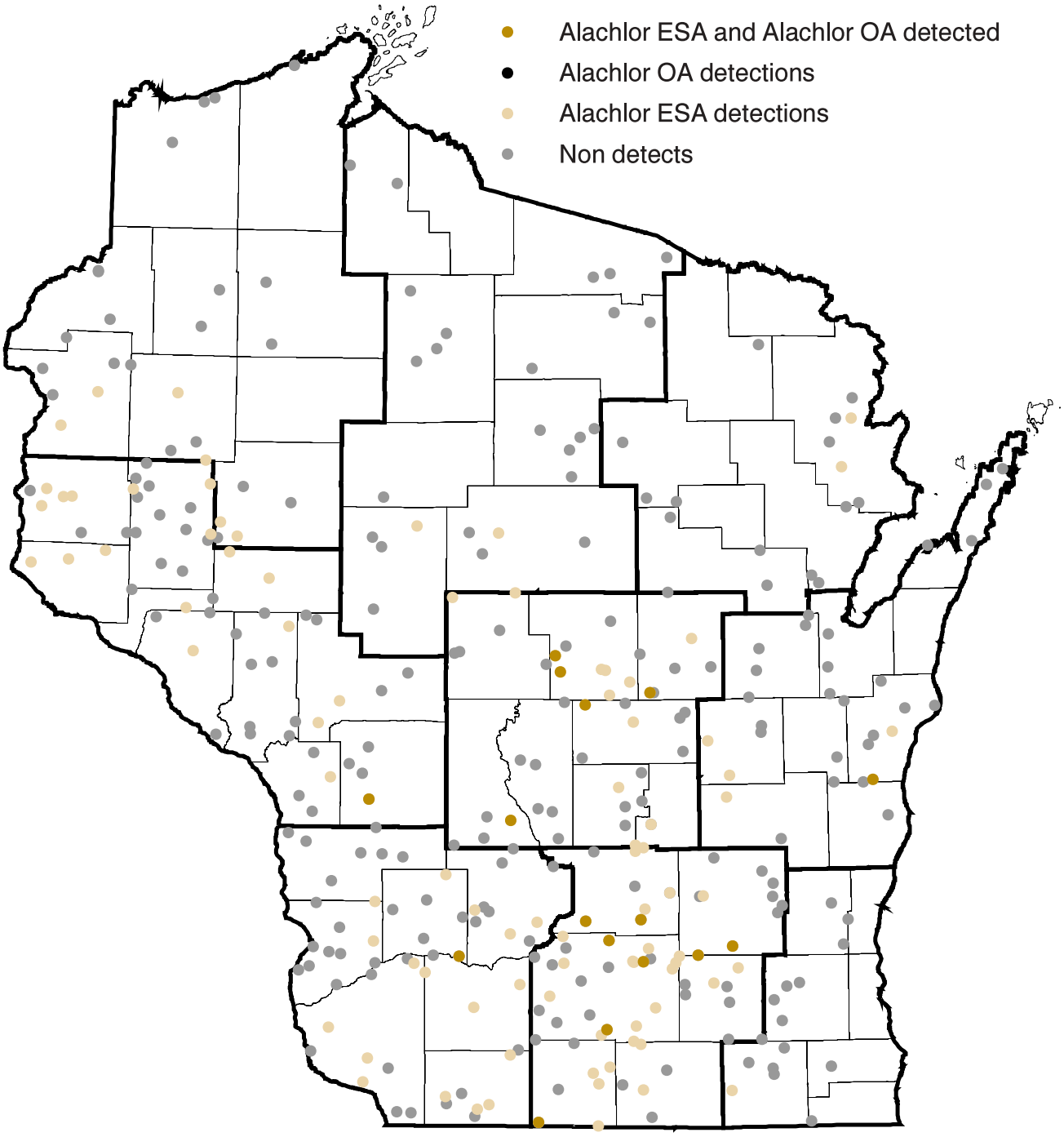


figure 3

Metolachlor ESA and OA Results from the 2001 Survey

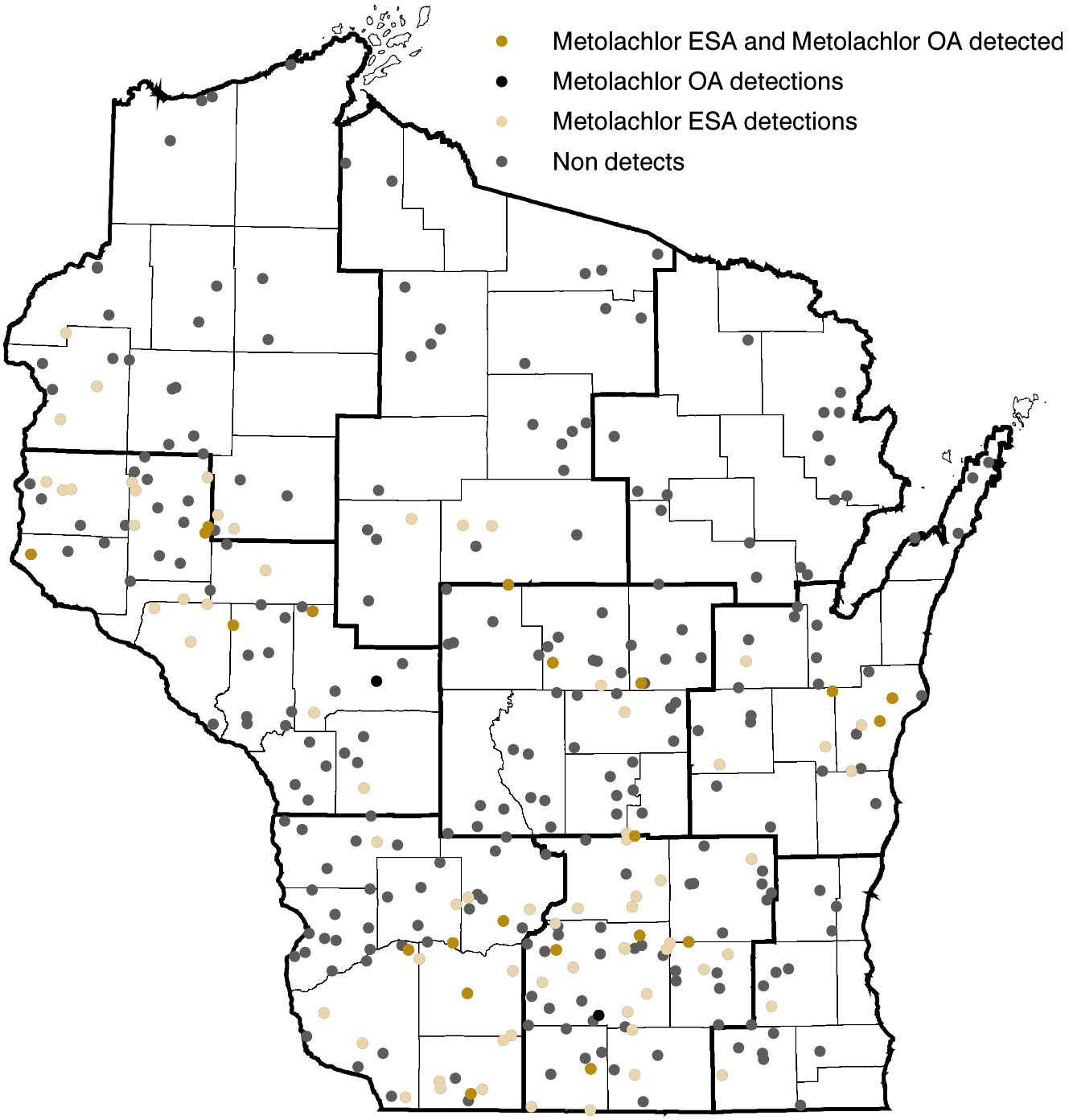


figure 4

TCR Results from the 2001 Survey

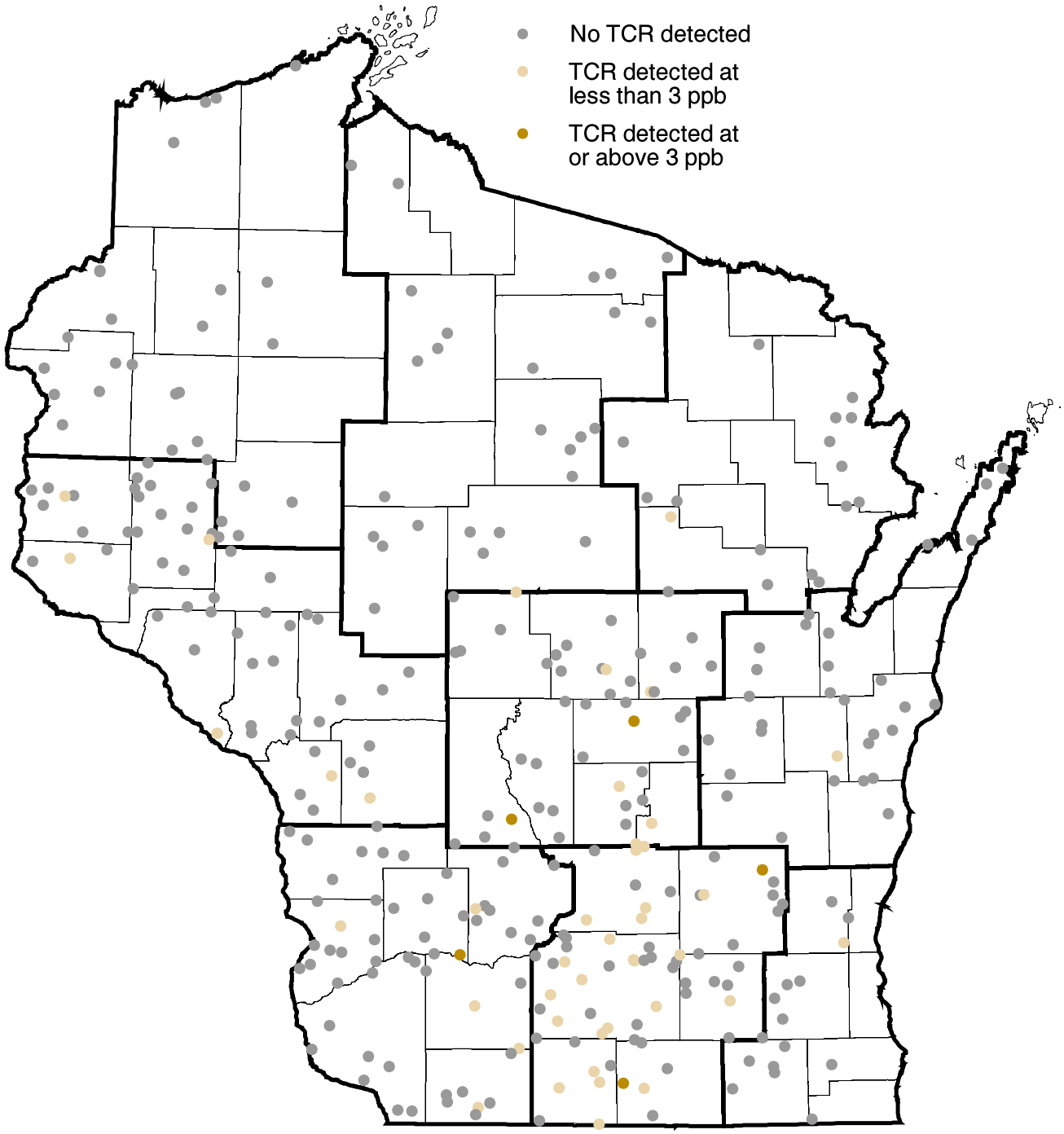
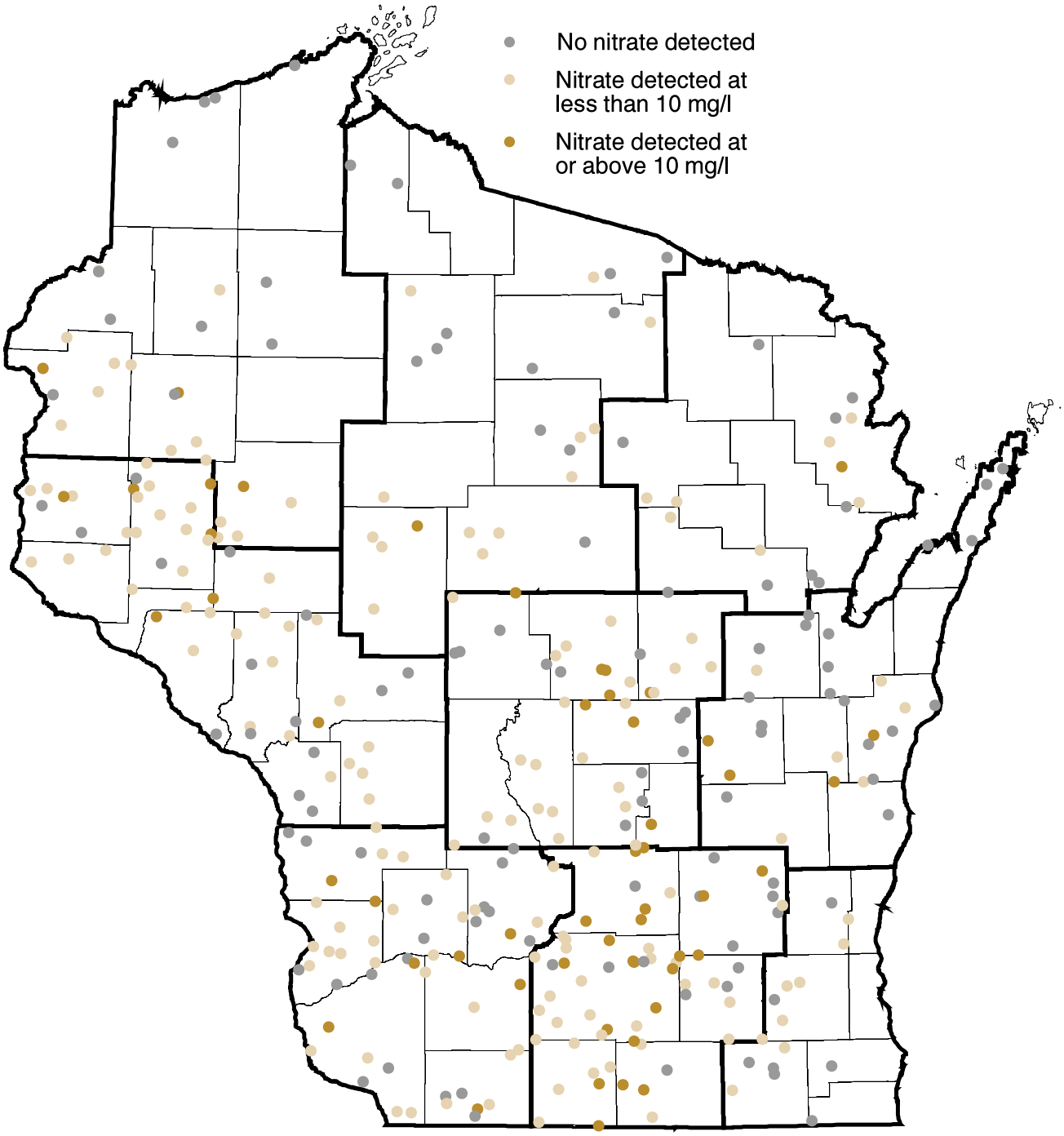


figure 5

Nitrate-Nitrogen Results from the 2001 Survey



Detection Frequencies in Agricultural Statistics Districts

Table 2 shows the number of detects in each agricultural statistics district for the most commonly detected compounds in the 2001 survey. The number of samples by district varies because of the stratified sampling design.

table 2

Number of Detects, by Agricultural Statistics District and Parameter.

District	Number of Samples	Number of Detects				
		Atrazine	TCR	Alachlor ESA	Metolachlor ESA	Nitrate-N
SE	14	0	1	1	2	7
SC	65	9	25	34	26	52
SW	56	3	6	18	19	36
EC	30	0	1	5	8	10
CE	44	2	8	16	6	31
WC	56	6	6	19	19	41
NE	17	0	1	2	0	8
NC	26	0	0	2	3	14
NW	28	0	0	6	5	17
Total	336	20	48	103	88	216

In the 2001 survey over half of the detections of TCR were in the South Central agricultural statistics district which includes Columbia, Dane, Dodge, Green, Jefferson and Rock counties. In this district 38% of the wells had a detection of TCR. Alachlor ESA and metolachlor ESA were detected in 52% and 40% of the wells, respectively, in the South Central district. Detection rates were next highest in the Central district, followed by the Southwest and West Central districts. Detection patterns in 2001 were similar to those documented in 1994 and 1996.

Statewide Statistical Estimates of the Proportion of Detections

Using the results from each stratum (agricultural statistics district) and the methods described by Cochran (1977) and Thomson (1992), we calculated estimates of the proportions of detections for eleven parameters. These estimates apply to rural Wisconsin groundwater exploited for private use. Table 3 shows these estimates and their 95% confidence intervals.

table 3

Statewide Estimates of the proportion of detections and 95% confidence intervals for eleven parameters in the DATCP 2001 statewide well sampling program.

Compound	Statewide number of detects	Statewide estimate of the proportion of detects (%)	95% confidence interval (%)
any herbicide or metabolite	135	37.7	32.7-42.8
TCR	48	11.6	8.6-14.7
TCR>3.0	5	1.1	0.076-2.2
atrazine	20	5.1	2.8-7.3
alachlor ESA	103	27.8	23.2-32.3
alachlor OA	16	3.7	1.9-5.6
acetochlor ESA	10	2.6	0.9-4.3
metolachlor ESA	88	25.2	20.6-29.8
metolachlor OA	23	6.4	3.8-9.1
nitrate-nitrogen	216	61.7	56.5-67.0
nitrate-nitrogen>10	53	14.1	10.5-17.7

Concentrations

We also estimated average concentrations for nine parameters. These concentration estimates are based on data from wells that contained detectable levels of herbicides or nitrate-nitrogen. If wells without detections had been included, the statewide average concentration estimates would be different. Table 4 shows these estimates and their 95% confidence intervals.

table 4

Estimates of the mean concentration of detects and 95% confidence intervals for nine parameters in the DATCP 2001 statewide well sampling program.

Compound	Statewide number of detects	Statewide estimate of the mean detect concentration (ug/l)	95% confidence interval (ug/l)	Enforcement Standard (ug/l)
atrazine TCR	48	0.967	0.589-1.36	3
atrazine	20	0.362	0.051-0.673	
alachlor ESA	103	1.00	0.755-1.25	20+
alachlor OA	16	1.84	1.24-2.44	
acetochlor ESA	10	0.154	0.072-0.236	
acetochlor OA	1	0.021		
metolachlor ESA	88	0.785	0.533-1.038	
metolachlor OA	23	0.569	0.071-1.066	
nitrate-nitrogen*	216	6.86	5.86-7.86	10

+ interim health advisory

* nitrate-nitrogen results are in mg/l or parts per million

Comparing Results Between Surveys

Two statistical tests were used to determine whether the levels of atrazine, TCR and nitrate-nitrogen in private wells had changed from 1994 to 2001.

We compared the estimates of the proportion of detects and the respective 95% confidence intervals for atrazine, TCR, and nitrate - nitrogen over 10 mg/l to see if there were any changes between 1994 and 2001. The results from 1994 and 2001 where used because they provided the greatest amount of elapsed time between sampling dates. This analysis showed that the proportion of wells with a detection of parent atrazine had a statistically significant decline between 1994 and 2001. In 1994 the estimated proportion of wells with parent atrazine was 11.1% (95% confidence interval 7.4% to 14.8%) and in 2001 the estimated proportion was 5.1% (95% confidence interval 2.8% to 7.3%). No statistically significant declines were found for the proportion of wells with TCR detections or nitrate-nitrogen over 10 mg/l. This analysis is shown graphically in Figure 6.

We also analyzed the data using logistic regression analyses (Agresti, 1996) to look for trends in the detection frequencies of atrazine, TCR and nitrate over the three survey years (1994, 1996 and 2001). Logistic regression makes maximum likelihood estimations based on categorical variables (e.g. detect, no detect) and is analogous to linear regression for continuous variables (e.g. 1,2,3). Agricultural statistics districts with no detections were eliminated from these analyses because they only had data in one category.

Atrazine - For the parent atrazine analysis, the West Central and Southwestern ASDs and the Central and South Central ASDs were grouped because they had similar patterns of detection frequencies. Both these groups showed a statistically significant decrease in the proportion of atrazine detections from 1994 to 2001. Figure 7 shows the trends in the proportions of parent atrazine detections for these two groups of ASDs.

figure 6

Comparison of proportion estimates and 95% Confidence Intervals for 1994 and 2001

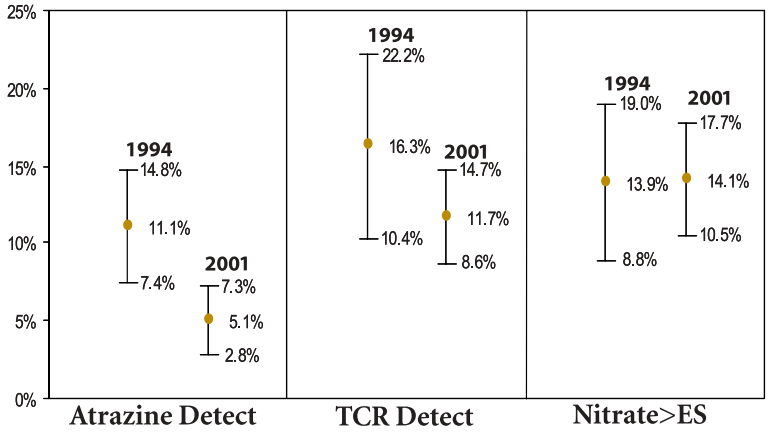
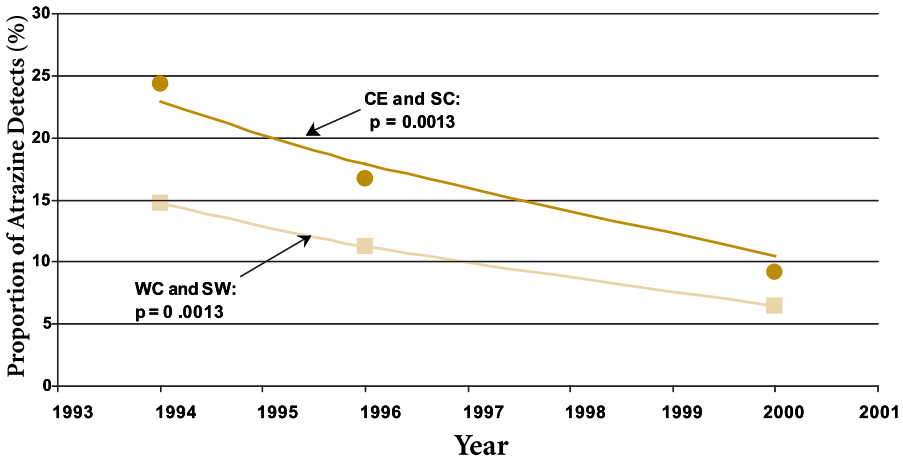


figure 7

Parent Atrazine

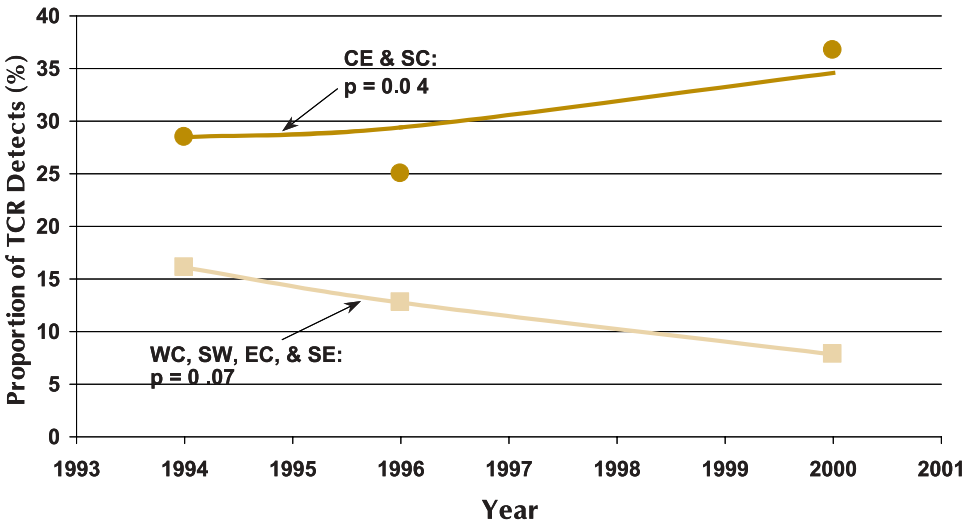


Total Chlorinated residues (TCR)

The statewide proportion of TCR detections showed a downward trend from 1994 to 2001, but the decline was not statistically significant at the 95% confidence level. Also, a grouping of the West Central, Southwest, East Central, and Southeast ASDs, which had similar patterns of detection frequencies, showed a decline in proportions of detects from 1994 to 2001 that was significant at the 93% confidence level (p=0.07). In contrast, the grouping of the Central and South Central ASDs showed an increase in the proportion of TCR detects that is significant at the 96% confidence level (p=0.04). Figure 8 shows the trends in the proportion of TCR detects over the survey period for these two groups of ASDs.

figure 8

Total Chlorinated Residues (TCR)

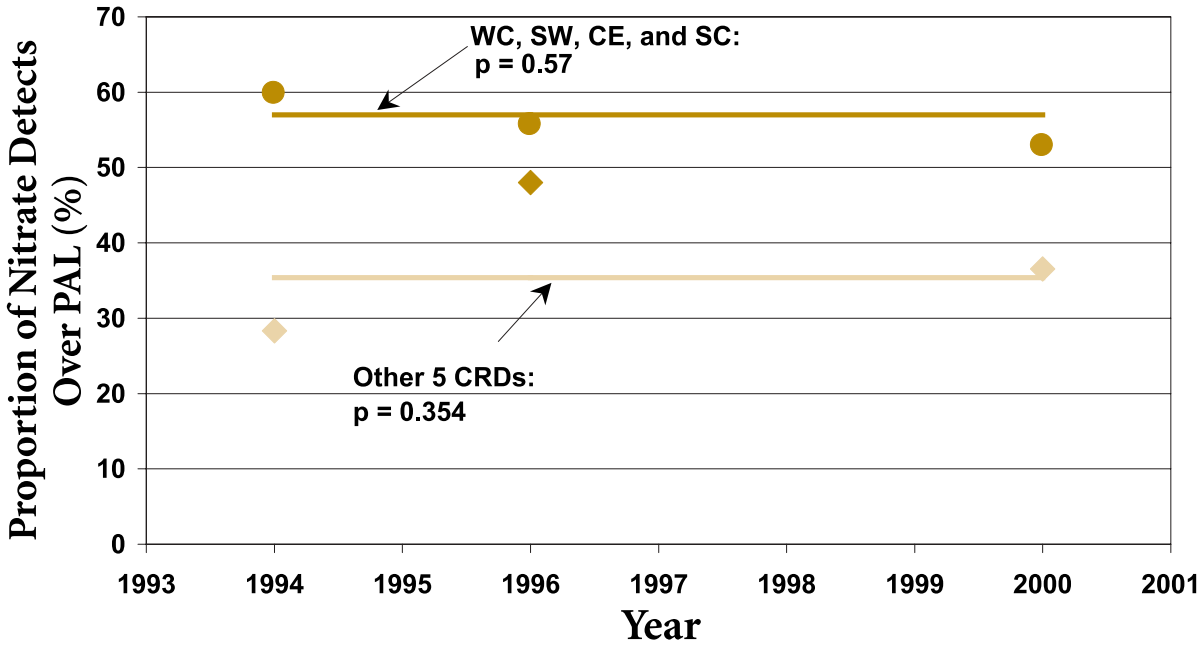


NITRATE - NITROGEN

The logistic regression analysis for nitrate-nitrogen evaluated changes over time in the proportion of detects over the preventive action level (PAL), which is 2 mg/l. Because of the low number of wells without detects of nitrate, it was not possible to conduct the analysis using the categorical detect/non-detect data. Results of this analysis (Figure 9) did not indicate a significant change over time in nitrate detects over 2 mg/l in two grouping of ASDs with similar frequencies of detections.

figure 9

Nitrate-Nitrogen



summary

- the statewide estimate of the proportion of wells that contained a detectable level of a herbicide or herbicide metabolite was 37.7%

- alachlor ESA and metolachlor ESA were the most commonly detected herbicide compounds with proportion estimates of 27.8 and 25.2%, respectively

- the South Central agricultural statistics district (Columbia, Dane, Dodge, Green, Jefferson and Rock counties) had the highest estimates of the proportion of wells containing TCR and other herbicide compounds

- the statewide estimate of the proportion of wells that contained TCR was 11.6%

- the statewide estimate of the proportion of wells containing parent atrazine showed a statistically significant decline between 1994 and 2001

- the statewide estimate of the proportion of wells containing TCR did not show a statistically significant change between 1994 and 2001, but a subset of the state consisting of the Central and South Central districts showed a statistically significant increase over this time period

- the estimate for the proportion of wells that exceeded the 3 ug/l enforcement standard for TCR was 1.1%

- the estimate for the proportion of wells that exceeded the 10 mg/l enforcement standard for nitrate-nitrogen was 14.1%

literature cited

Agresti, A. 1996. An Introduction to Categorical Data Analysis. John Wiley and Sons, Inc. New York.

Cochran, William G. 1977. Sampling Techniques. 3rd ed. John Wiley and Sons, Inc. New York 428 p.

LeMasters, Gary and Jon Baldock. 1997. A Survey of Atrazine in Wisconsin Groundwater. Wisconsin Department of Agriculture, Trade and Consumer Protection-Agricultural Resource Management Division publication 26a. Madison, Wisconsin.

Thomson, Steven K., 1992. Sampling. John Wiley and Sons, Inc. New York 343 p.