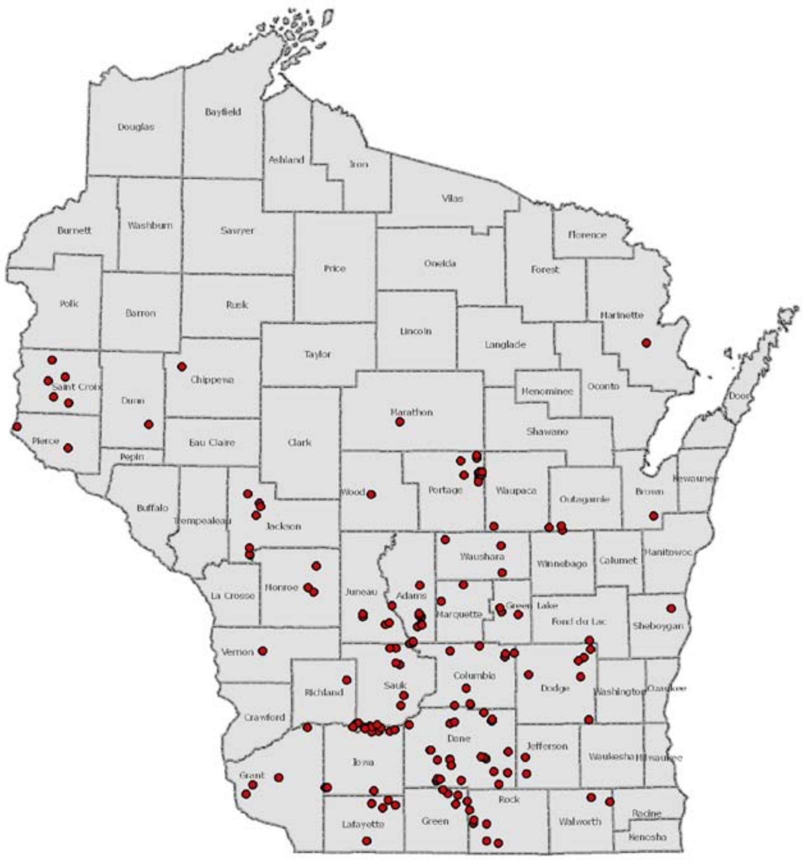
Fifteen Years of the DATCP Exceedence Well Survey



Wisconsin Department of Agriculture, Trade and Consumer Protection

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Fifteen Years of the DATCP Exceedence Well Survey

Introduction/Background

The Department of Agriculture, Trade and Consumer Protection (DATCP) Groundwater Program initiated the Exceedence Survey (EX Survey) in 1995 in order to follow private drinking water wells that had exceeded a groundwater enforcement standard for a pesticide. Most of the wells in this program were included due to high levels of atrazine and its metabolites. The results of the survey are used to provide information to well owners, gauge the success of atrazine prohibition areas (PAs), and determine how long it takes for atrazine to dissipate in groundwater in various geologic settings after a PA is put in place. The list of wells sampled in the EX Survey changes over time as some wells are abandoned and new wells are added when testing in other programs shows they exceed an enforcement standard. As the pesticide concentrations in survey wells decreases or becomes non-detectable, the sampling frequency also decreases.

Objectives

The specific objectives of this program are to:

- Track changes in the concentration of pesticides and nitrate in highly-impacted wells.
- Determine what changes well owners have made to their water supplies.
- Identify wells that meet the first condition for repeal of a PA under the atrazine rule.
- Provide a service to private well owners.

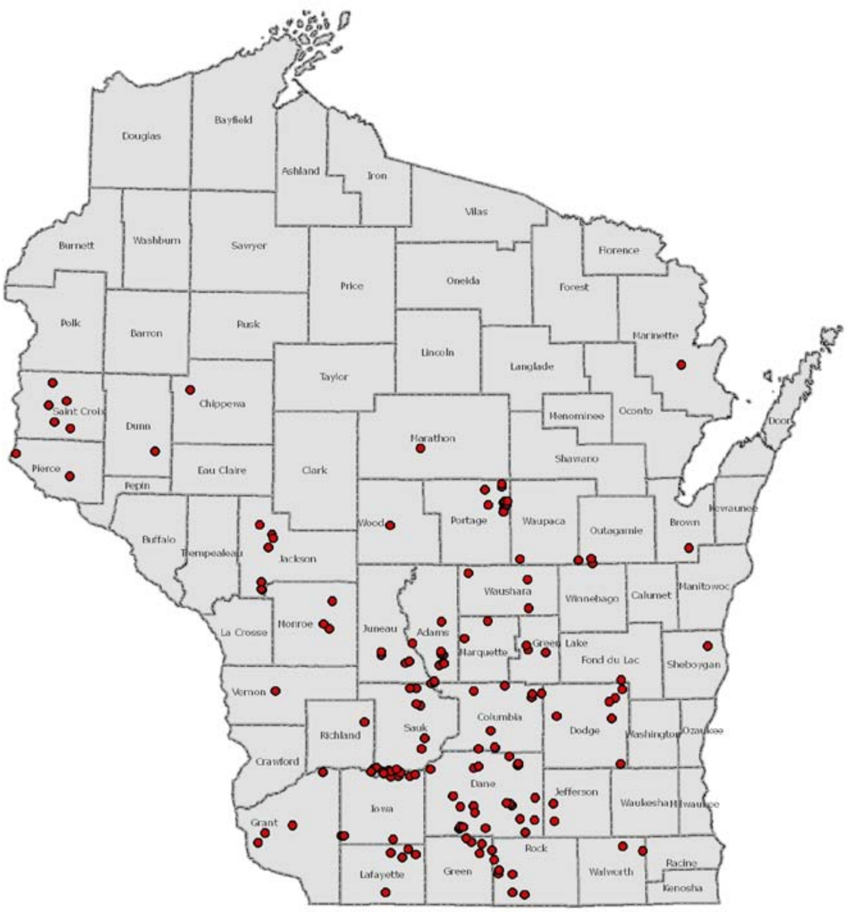
Sample Collection and Analysis

Figure 1 shows the location of the 161 wells that have been sampled in the EX Survey. All wells are sampled according to standard procedures. Samples are collected through an untreated cold water supply line after purging the well for at least five minutes. Samples are then transported to the DATCP laboratory in chilled containers. Sample collection records are completed and bottles are sealed to maintain sample integrity. Each year samples are collected from September through November to minimize any effects of seasonality.

The list of analytes that samples are analyzed for has changed over the fifteen years of the survey as new methods have become available. In year two of the survey (1996) samples were analyzed at the Syngenta laboratory. Currently samples are analyzed at the DATCP laboratory for the following 17 agricultural chemicals including pesticides, pesticide metabolites, and nitrate:

- Atrazine and its three chlorinated metabolites (deethyl atrazine, deisopropyl atrazine and diamino atrazine)
- Alachlor, metolachlor and acetochlor and their ESA and OA metabolites
- Metribuzin
- Cyanazine
- Simazine
- Nitrate-N

Figure 1. Map of Exceedence Survey Well Locations



Well Construction

Only nine of the wells in the EX Survey have complete well construction reports available, but many have partial information such as date of installation, depth to static water level and well casing depth. Table 1 summarizes the well construction information that is available for the 161 wells in the survey. Many of the wells are older with a mean installation date of 1972 for the 54 wells with known age.

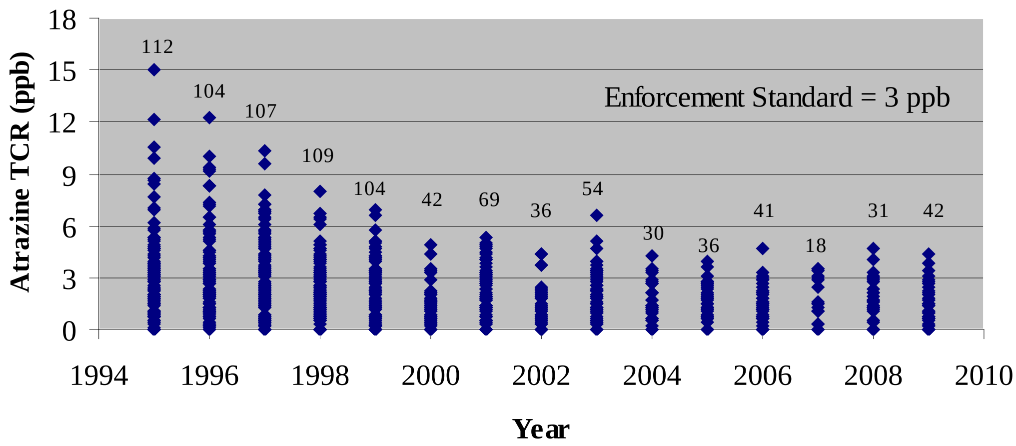
Table 1. Well Construction Information for the EX Survey.

	Number of wells with data	***Minimum (ft. or year)***	***Maximum (ft. or year)***	***Mean (ft. or year)***
Installation Date	54	1907	2000	1972
Depth to Static Water Level	21	12	94	45
Casing depth	21	19	211	72
Total well depth	9	50	248	124

Results – Atrazine and its Metabolites

Figure 2 shows the distributions of atrazine total chlorinated residue (TCR) results for the fifteen years of the EX Survey. This figure shows that in general the atrazine TCR concentrations have gone down over time and that there are fewer results over the 3 parts per billion (ppb) ES in recent years. This downward trend is expected since atrazine prohibition areas were created around these wells when they were found to exceed the ES. This figure should only be interpreted for general trends, however, since the group of wells sampled each year varies. As mentioned previously, during the survey some wells have been abandoned and some new wells have been added. Also, as the levels in a given well decrease towards the level of detection, less emphasis is placed on sampling it annually.

Figure 2. Distribution of Atrazine TCR Results and Number of Samples in the EX Survey, by Year



Dissipation of Atrazine in Exceedence Survey Wells

Another topic of interest in the EX Survey is how long it takes for atrazine and its metabolites to dissipate after an atrazine prohibition area is established around a well. Dissipation time is known to vary depending on geologic setting, well depth and construction, size of the atrazine plume in groundwater, precipitation patterns and possibly other variables. In general, deeper wells intercept groundwater with longer flow paths and more time is needed for the aquifer and the well to clean up.

To determine dissipation time for atrazine in survey wells, a subset of eight wells was chosen that had longer sampling histories and a relatively linear decline in atrazine TCR levels over time. The atrazine TCR levels for these wells were plotted over time and a visual determination was made of the approximate dissipation time from the establishment date of the PA until the concentration reached or approached the level of detection (0.15 ppb for parent atrazine, 0.30 ppb for deethyl and deisopropyl atrazine and 0.50 ppb for diamino atrazine). The eight wells were selected from different geologic settings around Wisconsin to determine a range of dissipation times. Figure 3 shows an example of the atrazine TCR results over time for well FF907 in southeastern Dane County. Many of the wells in the survey have not shown such a clear linear downward trend.

Figure 3. Atrazine TCR Results over Time in Well FF907

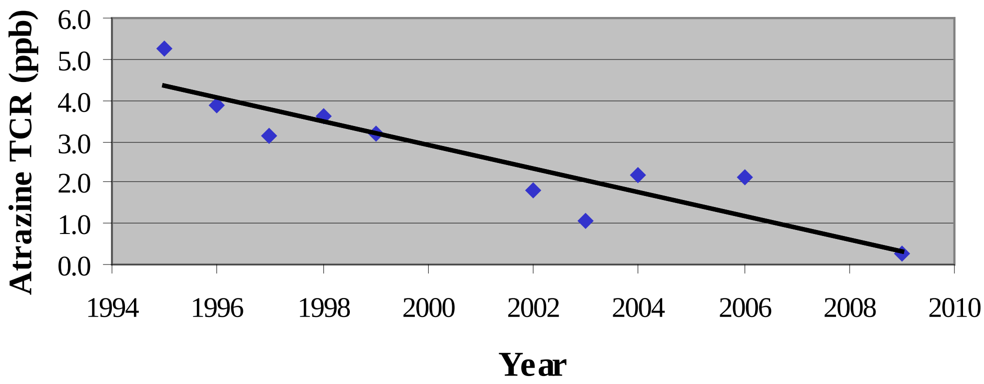


Table 2 shows the results of the dissipation analysis for the eight wells. The dissipation times ranged from approximately 11 years in a sand and gravel aquifer in the Lower Wisconsin River Valley to 17 years in a bedrock well in Dane County. The approximate dissipation time is the number of years from when the PA was established around the well until the concentration of atrazine TCR reached or approached the level of detection. Unfortunately, none of the eight wells have well constructions reports available so it was not possible to relate variables such as well depth and casing depth to dissipation time. For these same eight wells the time required for the atrazine TCR level to go below the 3 ppb ES ranged from 2-7 years.

Table 2. Atrazine TCR Dissipation Time for Eight Wells in the EX Survey.

Well	***County***	***Year PA Established***	***Initial Concentration* (ppb)***	***Approximate Dissipation Time after PA Established (years)***
FF907	Dane	1993	5.27	17
FB451	Dane	1993	4.83	15
DH609	Dane	1993	3.25	16
DJ531	Iowa	1993	3.82	11
BL878	Portage	1995	3.56	13
EX537	Jackson	1994	4.61	16
FC345	Sauk	1993	12.1	13
GQ383	Waushara	1996	6.89	15

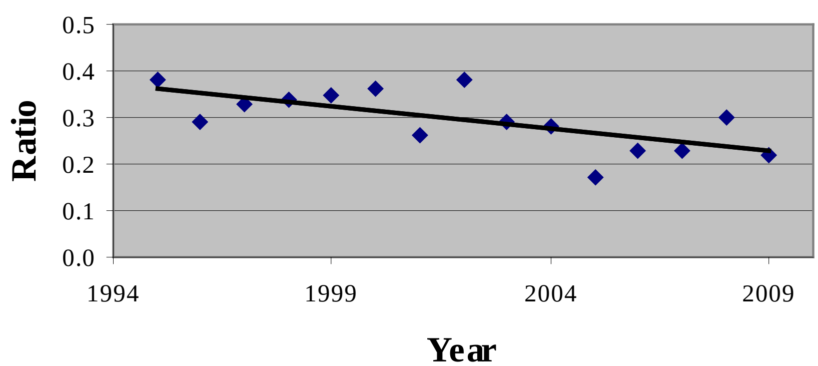
* This is the initial concentration in the Exceedence Survey. There may be additional sample results from other sampling programs.

For the small number of wells in the survey that have not shown a relatively steady decrease in atrazine levels following the establishment of a PA, there are several possible explanations: not enough time for the atrazine plume to dissipate or move past the well, illegal atrazine use or handling in the PA, residues of other triazine herbicides (cyanazine or simazine) contributing to shared triazine metabolite levels, the well is too close to the edge of the PA (PA not large enough), or an unidentified point source near the well. Field investigations around three EX survey wells where atrazine TCR levels did not go down as expected did not discover a clear explanation. In one case lingering higher levels of TCR were attributed to cyanazine use after the atrazine PA was established.

Ratio of Parent Atrazine to Atrazine TCR

As atrazine TCR dissipates in a well, and if no new atrazine is introduced into the soil and aquifer, it is expected that the ratio of parent atrazine to atrazine TCR will decrease as more of the atrazine is converted to its metabolites over time (Adams and Thurman, 1991). Atrazine is first converted to deethyl atrazine and deisopropyl atrazine and then to diamino atrazine as its degradation progresses. Figure 4 shows the average ratio of atrazine to atrazine TCR for each year of the EX Survey. This graph shows an overall decrease over time, as expected, but with considerable variability around the general trend line. This analysis is limited by the fact that the same wells were not always sampled in each year of the survey. It is also not known how much of the degradation of atrazine occurred in the soil versus the groundwater.

Figure 4. Year vs. Average Ratio of Parent Atrazine to Atrazine TCR



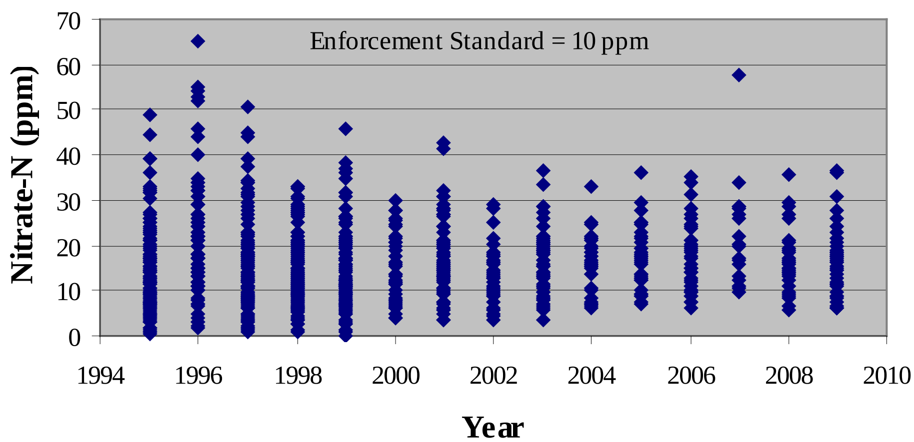
Repealing Atrazine PAs under ATCP 30.375

The atrazine rule includes a provision for the potential repeal of PAs if three conditions are met. Repeal condition one states that the level of atrazine TCR in each well that lead to the creation of a PA must fall to below one half the 3 ppb ES for three consecutive samples in order to consider repealing the PA. The EX Survey is the mechanism that the department uses to evaluate this condition. To date 72 wells in PAs have met repeal condition one. Twenty-two PAs qualify for repeal based on condition one alone. However, repeal conditions two and three, which consider atrazine levels in other wells in a PA and scientific evidence on the likelihood that renewed use of atrazine will cause additional contamination, have not been met. These results were presented to the ATCP Board on June 28, 2006. DATCP decided, with support from the Atrazine Technical Advisory Committee, not to consider repealing PAs at that time (WDATCP, 2008a).

Results - Nitrate

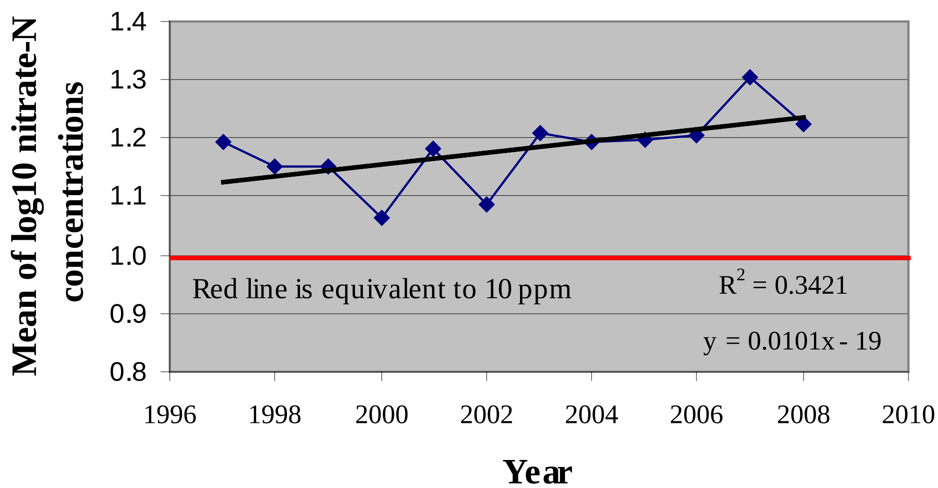
Although atrazine and its metabolites are the compounds of most interest in the EX Survey, the program has also generated a large amount of valuable data for nitrate-nitrogen. The EX Survey represents a good source of data for repeat sampling of private wells in Wisconsin. Not surprisingly, the wells in the survey have high levels of nitrate-N because they are known to be impacted by agricultural activities. Figure 5 shows the nitrate results by year for the 161 wells in the EX Survey. Eighty-eight percent (141 of 161) of these wells have exceeded the 10 parts per million (ppm) enforcement standard for nitrate-N.

Figure 5. Nitrate-N Results by Year in the EX Survey



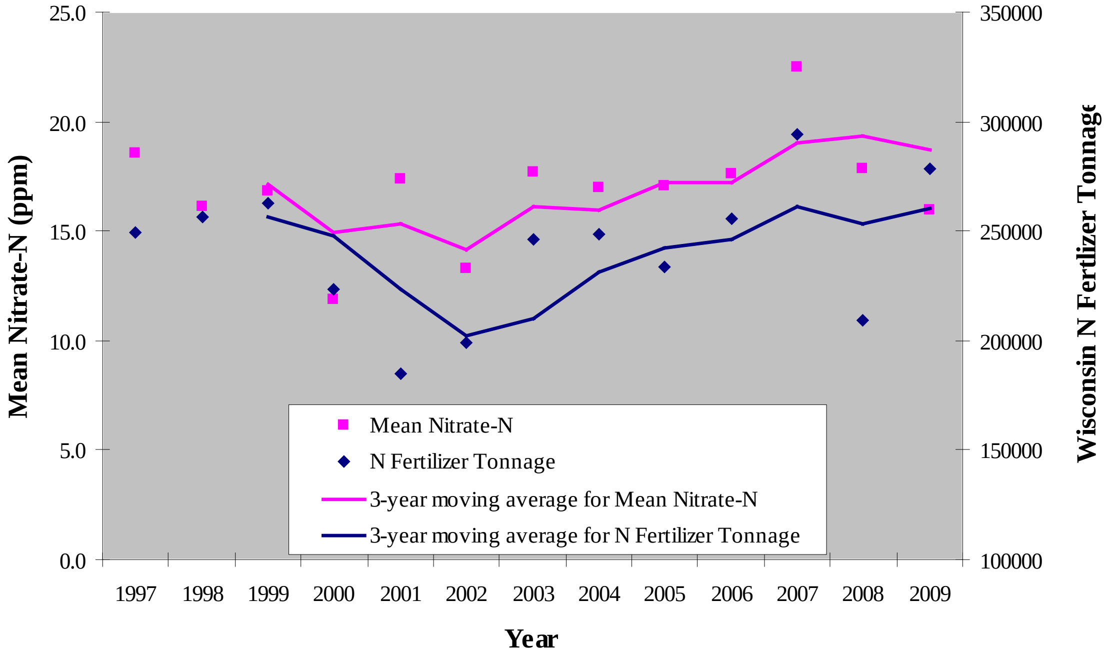
Additional analysis was conducted to determine whether nitrate levels have changed significantly over time in EX Survey wells. For this trend analysis, a subset of 46 wells with the longest history of sampling was chosen and regression analysis was performed for time (year) vs. (log10 transformed) mean annual nitrate-N concentrations. Figure 6 shows the results of this analysis. (A log 10 value of “1” in this figure corresponds to the 10 ppm ES level, i.e. the log of 10 =1.) The R^2 value of 0.34 is significant at p=0.05 indicating a statistically significant increase in nitrate-N levels over time. The regression equation shown on the chart indicates a predicted increase in mean nitrate-N concentration of about 0.37 ppm per year after converting from the log 10 scale.

Figure 6. Year vs. Mean of log10 Transformed Nitrate-N Concentrations in the EX Survey



To learn more about factors related to nitrate in these private wells, we compared trends in the nitrate-N results from the same subset of 46 survey wells to the annual nitrogen fertilizer tonnage in Wisconsin in each year of the survey. Nitrogen fertilizer tonnage was chosen as a possible explanatory variable because annual data is readily available (WDATCP, 2010) and it was hypothesized that there might be a relationship between nitrate-N levels in groundwater and the amount of N fertilizer used. Figure 7 shows the trends in the mean nitrate-N levels compared to the corresponding trends in the annual N fertilizer tonnage in Wisconsin from 1997-2009. This figure shows surprisingly similar trends between N tonnage and the mean nitrate-N levels in this group of wells.

Figure 7. Mean Nitrate-N Concentrations in 46 Exceedence Survey Wells and N Fertilizer Tonnage, by Year



Results - Other Pesticides and Pesticide Metabolites

In addition to atrazine, several other pesticides have been detected in Exceedence Survey wells. The list of compounds detected is similar to other DATCP surveys (WDATCP, 2008b), but the detection frequencies are higher in the Exceedence Survey because the wells are known to be susceptible to impacts by agricultural activities. The EX Survey wells are not representative of all private wells in Wisconsin; rather they are known to be highly impacted by agricultural activities which is why they were included in the survey.

As in DATCP statewide surveys (WDATCP, 2008b), metolachlor and alachlor metabolites are commonly detected herbicides in the EX Survey. Metolachlor ESA has been detected in 88% (84 of 96) of EX Survey wells that have been tested. (Note that fewer wells have been tested for metolachlor and acetochlor metabolites and alachlor OA because there was not an analytical method for these compounds until 2001.) Table 3 shows a summary of the commonly detected compounds in the EX Survey.

Table 3. Detection Frequencies and Maximum Concentrations for the Compounds included in the EX Survey.

Compound	*Number of wells tested*	*Number of wells with detects*	*Maximum concentration (ppb)*	*Enforcement Standard (ppb)*
Nitrate-N	161	161	65	10 ppm
Atrazine TCR	161	159	37.1	3
Atrazine	161	145	31.7	
Deethyl atrazine	161	149	11.4	
Deisopropyl atrazine	161	103	4.31	
Diamino atrazine	161	130	8.1	
Metolachlor	161	25	68.6	100
Metolachlor ESA	96	84	27.8	1,300
Metolachlor OA	96	56	16.4	1,300
Alachlor	161	22	6.39	2
Alachlor ESA	161	135	45.2	20
Alachlor OA	96	36	9.06	
Acetochlor	148	2	2.8	7
Acetochlor ESA	96	35	9.52	230
Acetochlor OA	96	9	2.71	230
Metribuzin	158	16	10.1	70
Cyanazine	161	5	1.4	1
Simazine	155	7	0.699	4

Figures 8 and 9 show the annual distribution of results for metolachlor ESA and alachlor ESA, the most commonly detected pesticide compounds after atrazine TCR. The flat trend line (in red) for metolachlor ESA does not suggest any significant increase or decrease over this time period. Alachlor ESA, in contrast, shows some downward trend. The difference in the trends for these two compounds is probably related to their use history in Wisconsin. Metolachlor is very popular (applied on over 1.2 million acres in 2005) whereas alachlor use has declined considerably over the last ten years (USDA/NASS, 2006).

Figure 8. Metolachlor ESA Results in the EX Survey by Year

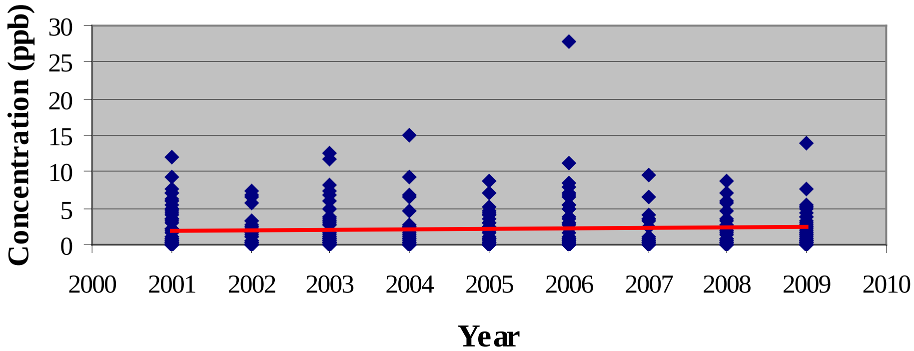
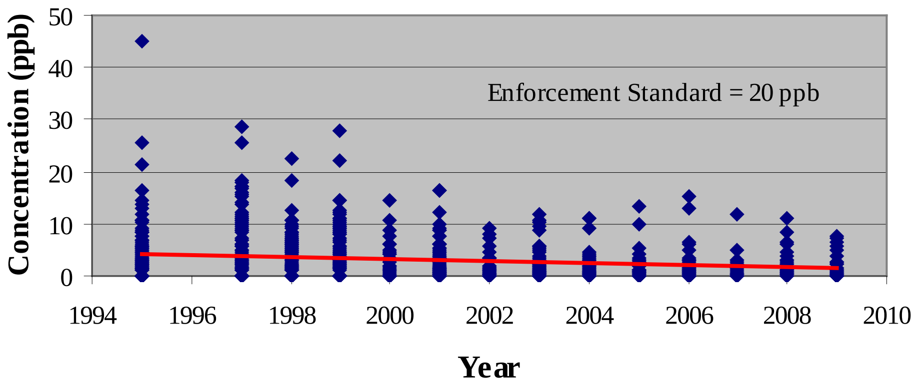


Figure 9. Alachlor ESA Results in the EX Survey by Year



Well Owner Responses to Well Contamination

One of the objectives of the EX Survey is to follow the actions well owners have taken in response to high levels of pesticides and nitrate in the well water. At the beginning of the EX Survey, a phone interview was conducted with 195 well owners whose well had exceeded an ES for a pesticide (WDATCP, 1996). This was the pool of potential participants for the EX Survey. From this well owner survey it was documented that:

- 97 (50%) were using the original well
- 44 (23%) had drilled a new well at an average cost of $6,300
- 13 (6.5%) were drinking bottled water
- 12 (6%) have installed a water treatment system
- 11 (5.6% were hauling water from another source

- 2 had deepened their well
- 2 had connected to a municipal source

Since the original phone survey, 27 additional EX Survey wells have been abandoned and replaced due to contamination by pesticides and nitrate. Some well owners have installed filters but since EX Survey samples are collected from unfiltered water it is not known how successful the filters are in removing pesticides from the water. In general carbon filters are being used to remove pesticide residues and reverse osmosis filters are being used to remove nitrate.

Case Studies

Participation in the EX Survey is voluntary, and in the vast majority of cases, well owners have been very cooperative and eager to have their wells tested. In fact one of the objectives of the survey is to provide a service to participating well owners as they make decisions about their water supply.

As could be expected, however, a few wells owners were less than cooperative about having their well sampled. In one case a well owner had one sample result with atrazine TCR over the ES but did not want a second confirmatory sample because he did not want an atrazine PA to be established in the area. To prevent any chance of a second sample from being collected, the well owner ran over his well head with his truck. The well owner subsequently worked with his State Legislator to pass a law prohibiting the department from creating a PA in the area around the destroyed well.

Another interesting case involved two EX Survey wells in the Lower Wisconsin River Valley. These two neighboring wells had been in the survey since 1995 and their once high atrazine TCR levels had declined to below the ES in response to the PA which covers the entire valley. In 2006, however, the levels of the shared triazine metabolites went up in these wells causing the atrazine TCR concentration to again exceed the 3 ppb ES. An investigation in the area determined that use of the triazine herbicide simazine in the area was causing the contamination and in response voluntary agreements were reached with nearby farmers to discontinue simazine use. The two wells will continue to be sampled to see the effects of the discontinuation of simazine use.

Another case involved very high nitrate-N levels in an EX Survey well in Waupaca County. When the nitrate-N level reached 57 ppm, the well owner contacted the DATCP Groundwater Program for assistance. Inquires to other agencies discovered that a nearby agricultural field had been receiving hog manure and several other nitrogen-containing waste substances beyond what should have been permitted. Unfortunately these well owners had to replace their well.

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