Atrazine in Minnesota Groundwater: A Summary Report

By

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Groundwater Monitoring Program

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INTRODUCTION

Atrazine is an herbicide used to control broad leaf and some grass weed species. First registered for use in the United States in 1958 atrazine has historically been one of the most heavily used herbicides in Minnesota. Atrazine is primarily used on corn although it may also be used in turf applications and other field crops. According to the Minnesota Agricultural Statistics Service atrazine was used on an estimated 45% of corn acreage in Minnesota during the 2003 cropping season. Based on soil conditions and cropping systems atrazine use patterns may be quite variable in the state.

According to US-EPA's Interim Reregistration Eligibility Decision[1] *"Atrazine is mobile and persistent in the environment and, as such, atrazine is expected to be present in surface and groundwater. This is confirmed by widespread detection in surface water and groundwater"*. In addition, product labels advise that areas containing sandy soil material with shallow underlying groundwater, and geographic locations containing sinkholes are the areas most susceptible to groundwater contamination by atrazine.

This report consists of atrazine data the Minnesota Department of Agriculture, Agronomy and Plant Protection Division, Monitoring and Assessment Unit has collected since the fall of 1985. Data from the original groundwater monitoring network, the central sand plain monitoring network, and a recently completed drinking water survey is included along with a summary comparison of USGS data for Illinois, Iowa, Minnesota and Wisconsin. Within this document you will find sample results tables, graphical summaries, statistical analyses and summary interpretations of atrazine impacts on Minnesota's groundwater. Detailed data reports are available on the MDA web page at

http://www.mda.state.mn.us/appd/ace/maace.htm

and cover all phases of the water quality monitoring program at the MDA.

[1] US-EPA. January 2003 Interim Reregistration Eligibility Decision for Atrazine Case No. 0062.

I. Summary of the MDA Groundwater Monitoring Program.

The Minnesota Department of Agriculture began monitoring groundwater for atrazine, along with other pesticides, in the fall of 1985. A network of existing wells, selected from an earlier project, was sampled from 1985 through 1996. The wells in this original network consisted of monitoring wells, observation wells, and private drinking water wells. In January of 2000, following three years of development, the MDA implemented a new legislatively approved monitoring network of wells specifically installed for monitoring pesticide impacts to groundwater. This new network, termed the Central Sands (CS) groundwater monitoring network, was conceived by the MDA and designed in consultation with the Minnesota Department of Health, Pollution Control Agency and Department of Natural Resources, along with twelve counties, the University of Minnesota, St. Cloud State University, the Natural Resource Conservation Service, and the United States Geological Survey. The Minnesota Pollution Control Agency, the Minnesota Department of Natural Resources, and local water well contractors assisted with well design and installation. The CS network consists entirely of water quality monitoring wells designed to sample the very top portion of the shallowest aquifer in the state's major sand plain region. The central sands area is considered one of the most vulnerable regions in the state with respect to potential pesticide movement to groundwater. Accordingly the network was designed to detect changes in pesticide presence in groundwater in the shortest possible time. Of particular interest to the program are effects on groundwater pesticide detections as a result of changes in management practices promoted by the MDA's Pesticide Management Plan.

Sampling of properly constructed, located and maintained public and private drinking water wells in the late 1980's and early 1990's indicated relatively few detections of atrazine. When detected in drinking water wells atrazine was usually present at low concentrations. In 2003 the MDA designed a new well sampling effort to answer the question of whether current conditions in drinking water wells are similar to the previous results. In early 2004 the MDA conducted a survey sampling of public non-community and private drinking water wells. The drinking water survey followed a random grid based procedure for selecting wells and sampled those wells where well owners agreed to participate. A total of 71 wells were sampled. Each sample was analyzed for atrazine and a suite of other chemicals including pesticide breakdown products.

Most recently, the groundwater monitoring program designed and implemented a regional groundwater monitoring network utilizing pre-existing monitoring wells similar to the original network. The regional delineations were based on crops, soils, climate and existing ecoregion boundaries. Wells were selected from four of the department's ten preliminary monitoring regions for inclusion in the network. The wells were chosen from existing monitoring or observation wells maintained by the state. Figure 1 shows the MDA preliminary monitoring regions and also displays the locations of the wells selected for the regional network. Samples were collected from this network in September 2004. Unfortunately many of the wells were dry or otherwise unable to be sampled. Laboratory analytical results are not yet available for the samples that were collected; therefore no further discussion of this network will appear in this report.

A cooperative effort between the MPCA and MDA was developed in 2004 for the collection of samples from wells located in urban areas. All the urban wells are part of an MPCA urban monitoring program and are sampled by MPCA staff when at the well for their sampling events. No results are yet available for these wells.

To account for potential atmospheric impacts on groundwater the MDA sampled rainfall for pesticides at eight locations across the state from 1993 through 1996. Although specific funding for the venture ceased in the mid 1990's the MDA has kept one station operating at the Crystal Springs fish hatchery in Winona County. Atrazine frequently occurred in historic rainfall samples and continues to be present in the one remaining site. Results of precipitation sampling will not be further discussed here although a report covering all aspects of the program through 1996 was prepared by the United States Geological Survey in 1997 and is available at http://mn.water.usgs.gov/atmospheric/atmospheric.html.

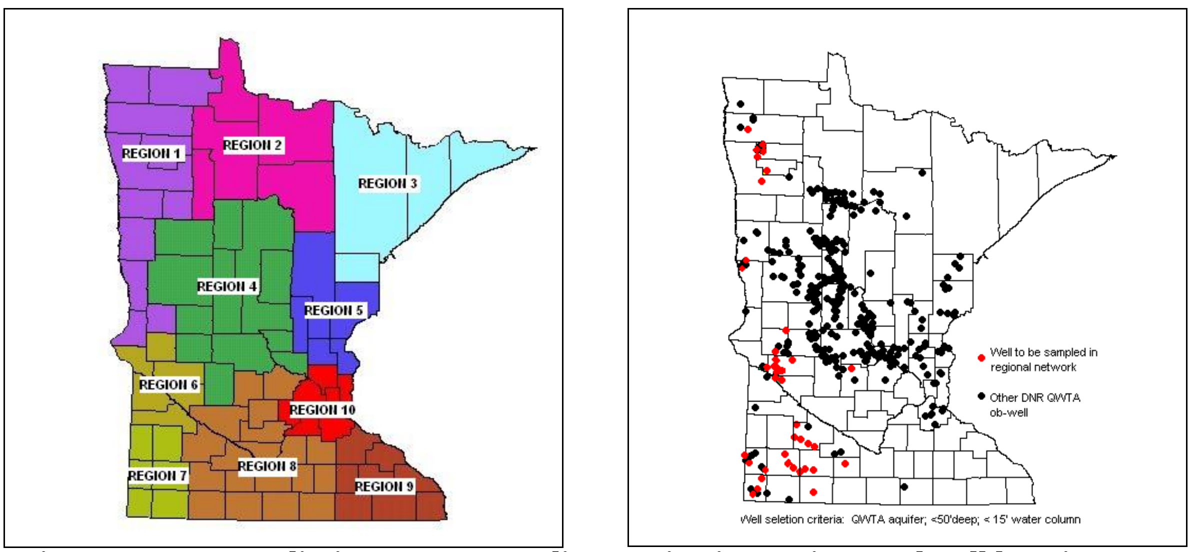


Figure 1. MDA preliminary water quality monitoring regions and well locations selected for sampling as part of the regional groundwater monitoring program.

Collectively the efforts described here represent one of the most comprehensive monitoring programs for pesticides in groundwater of any state in the U.S. The most extensive set of data for Minnesota is available for wells completed in the state's highly sensitive shallow sand and gravel aquifers. Atrazine data (parent compound and degradates) from sand plain wells will form the bulk of this section of the report although all atrazine ground water data is reported and discussed.

Degradation of atrazine in the environment can lead to one or more breakdown products (degradates). Prior to 1995, the MDA was not able to analyze water samples for atrazine degradates. Because there is much atrazine parent data from pre-1995 sampling, this report is divided into two major sections: Section II.A. presents data from 1985 to present for atrazine only, while section II.B. presents data from 1995 to present for atrazine and its major degradates. Accordingly, the long-term detection and concentration data in Section IIA for the atrazine parent molecule is presented as an indicator of overall trends in product use. The groundwater concentration data in Section IIB is presented for both atrazine and its degradates, and is compared to applicable drinking water standards.

The MDA laboratory method for atrazine has remained fairly consistent since the inception of the monitoring program. Although analysis is currently confirmed by mass spectrometry, the lowest level of detection of atrazine has remained constant at 0.05 micrograms per liter. The analysis of atrazine degradates has been further developed over time with more reliable means of detecting the low concentrations typically found. Capability to analyze water samples for additional products of atrazine degradation has also been developed. Recently an additional atrazine degradate, diaminoatrazine, has been analyzed for, and detected, in water samples collected in Wisconsin and elsewhere. The MDA laboratory is currently researching the best method for analysis of diaminoatrazine.

IIA. Summary of MDA Groundwater Monitoring Program Atrazine Data

Sand Plain Time-Trend Monitoring Well Results.
In the fall of 1987 a set of 19 sand plain wells that had a history of atrazine detections were selected for continued time trend monitoring. These wells were all previously sampled in the initial short-term project begun in 1985. Atrazine data from these wells was combined with data from the 84 CS network sites to form the complete data set for this report. Specific design details on the original network and the CS network may be obtained by calling the MDA at 651-297-3994 or through e-mail by sending a request to john.w.hines@state.mn.us.

Data has generally shown that between 25 and 75 percent of the samples collected from shallow sand plain wells contain atrazine in any given sampling period (see Figure 2 and Table 1). Frequency of detection of atrazine in wells since the inception of monitoring shows a slight decreasing trend, however it is not statistically significant (slope = -0.0016; $p > 0.05$). When data collected prior to the installation of the central sands network is removed from the data set no unequivocal trend is evident (slope = -0.0034; $p >> 0.05$). There is a measurable difference in the average quarterly frequency of detection of the original network versus the new central sands network; however this difference is not statistically significant. Lack of significance of the test may be due to the relatively small number of quarterly samples available for the new network (15) vs. the old network (42). Figure 3 displays the percent of samples by quarter that contained atrazine at greater than 0.10 μg/L. The graph shows a clear and statistically significant decreasing trend (- 0.0069; $p<<0.05$) in the percentage of detections above 0.10 μg/L. The 50th (median) and 75th percentile quarterly atrazine concentrations have both decreased over time (Figures 4 and 5). Median concentrations show a statistically significant decreasing trend of -0.000026µg/L per day; while 75th percentile concentrations show a trend of -0.00010µg/L per day. Atrazine quarterly median concentrations are frequently below analytical limits of detection meaning that more than 50 percent of the samples have no quantifiable concentrations associated with them. This tendency is particularly evident in recent monitoring (see Figure 4.).

Table 1. Statistical analysis of the frequency of detection of atrazine in MDA sand plain trend-monitoring wells. LCL = Lower Confidence Limit; UCL = Upper Confidence Limit.

	---------All samples--------	
Parameter	**Mean % Detection**	**Median % Detection**
Value	48.35088	50
95% LCL	43.91961	44
95% UCL	52.78215	52

Samples From	# of Quarters	Mean % detection	95% LCL of Mean % detection	95% UCL of Mean % detection
New network	15	43.06667	37.97194	48.1614
Old network	42	50.23809	44.50742	55.96877

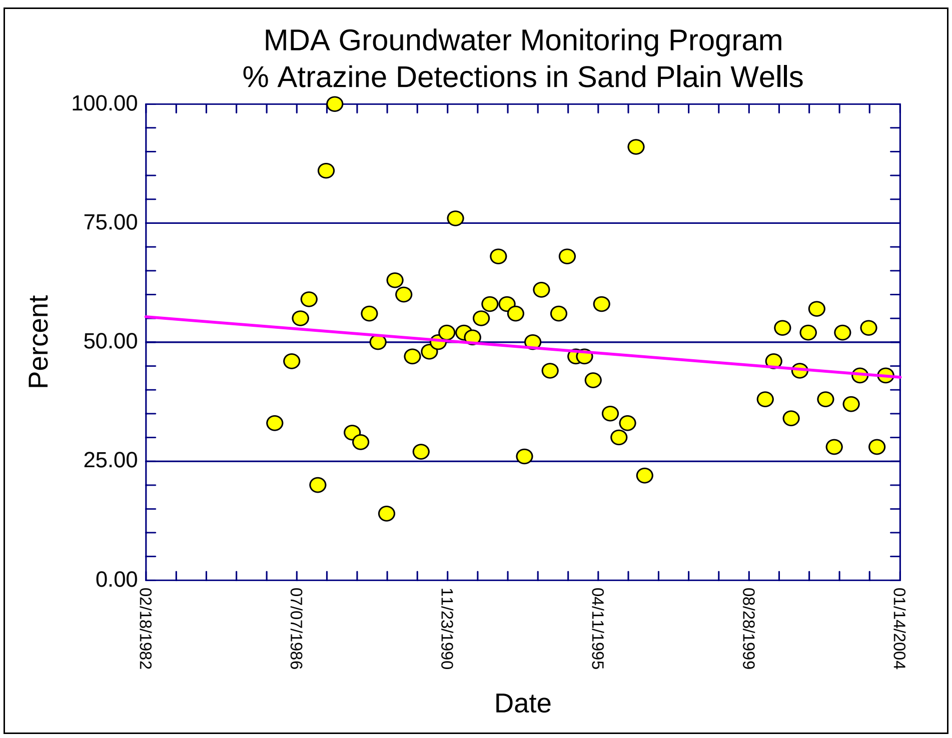


Figure 2. Quarterly percent detections over time of atrazine in sand plain trend-monitoring wells. A linear regression trend line is also shown.

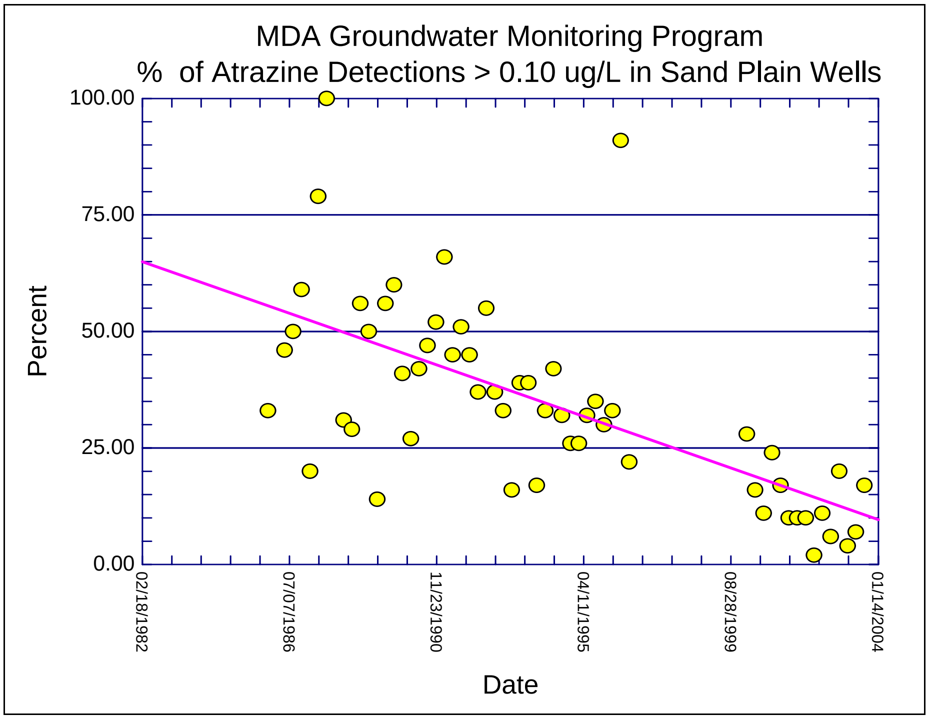


Figure 3. Quarterly percent of sand plain time trend well samples containing atrazine at or above 0.10 μg/L.

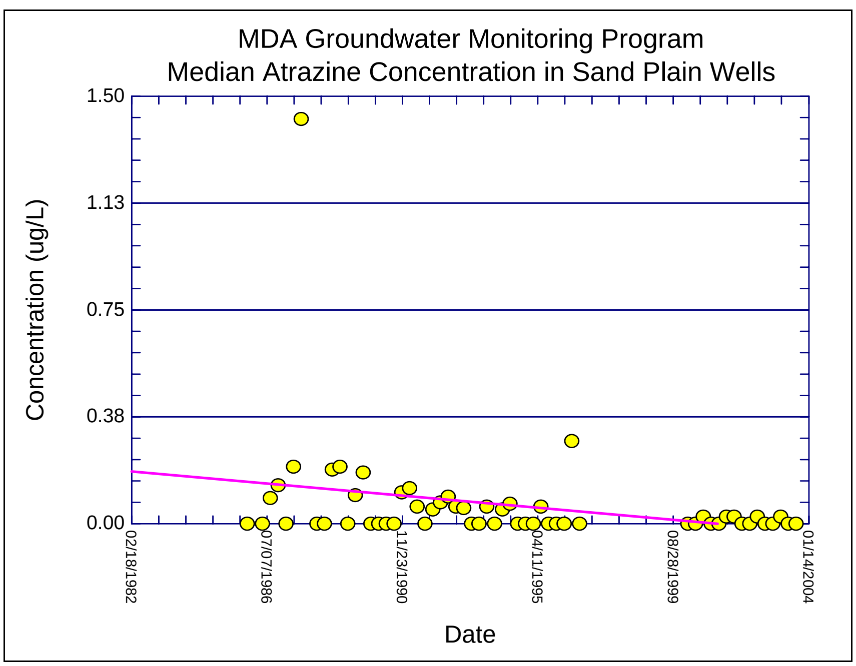


Figure 4. Median atrazine concentration in sand plain trend monitoring wells.

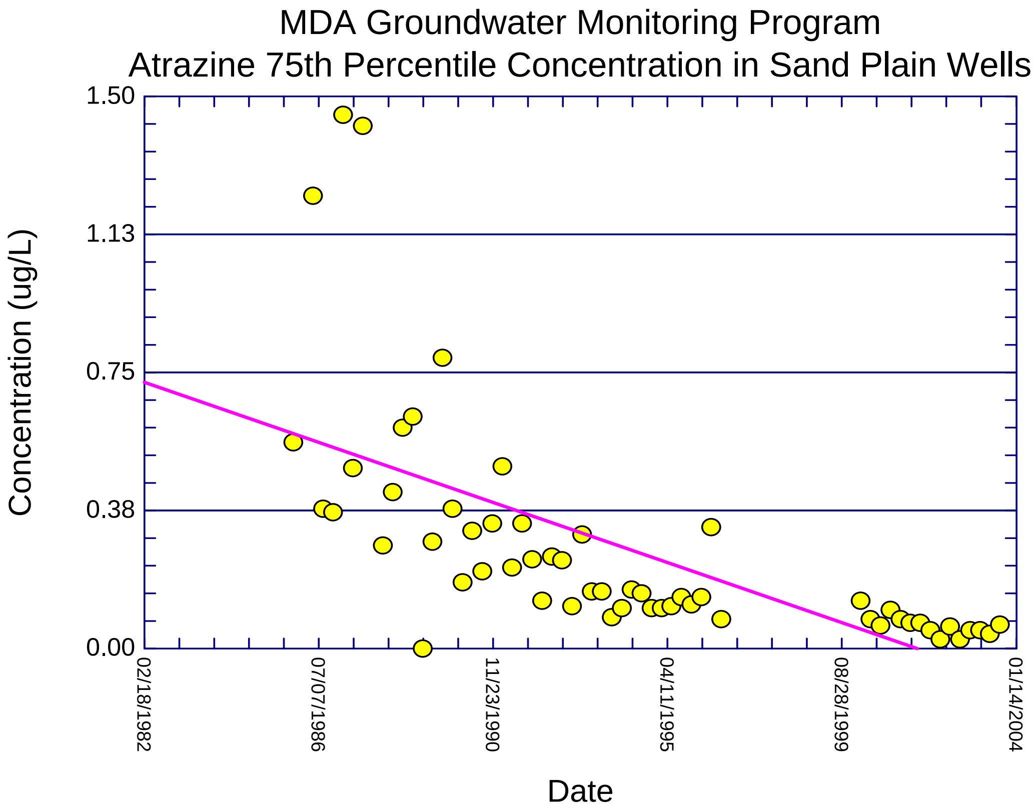


Figure 5. Atrazine 75th percentile concentrations in sand plain trend monitoring wells.

As would be expected from the previous discussion atrazine quarterly median concentrations over time for each season of the year have decreased (see Figure 6). All seasonal medians have trended toward non-detectable concentrations. Table 2 displays long-term medians, 75th percentiles and detection frequencies for the various seasons of the year.

Table 2. Seasonal atrazine sample results from all samples collected from original time-trend network and central sands network.

Season	Median Concentration (µg /L)	75th percentile concentration (µg /L)	Frequency of detection (%)
Winter	ND	0.15	44
Spring	0.09	0.26	58
Summer	0.06	0.28	52
Fall	0.04	0.27	50

Tabulated results indicate there is little change in concentrations detected in all seasons except the winter. There is also a rather large difference in detection frequencies when comparing winter and other seasons of the year. This type of difference is intuitive in the sense that spring snow-melt and summer rainfall is an excellent source of water to carry pesticide residues downward to groundwater during and shortly after pesticide application. Winter samples represent a time of year when neither pesticide application nor significant groundwater recharge is occurring.

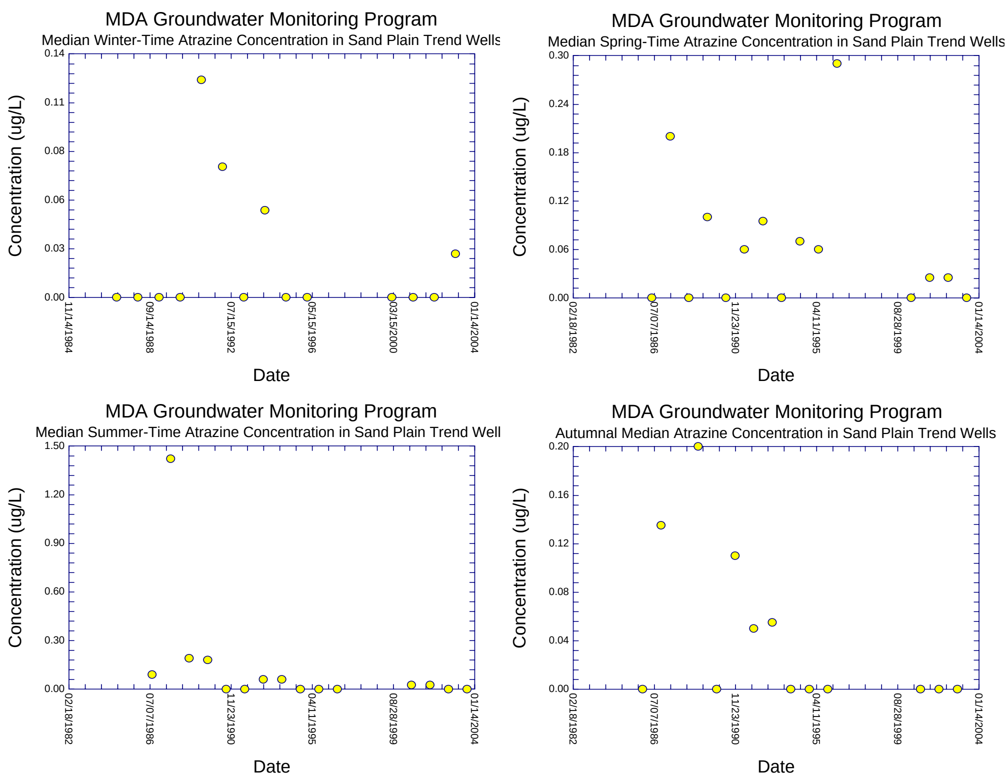


Figure 6. Trends in atrazine quarterly median concentrations over time for samples collected in winter, spring, summer, and autumn (1996 to 2004). Winter season represents January through March; spring , summer and autumn follow accordingly.

Sand Plain Monitoring Reconnaissance Well Sample Results

From 1986 through 1996, 984 samples were collected from 215 sand plain wells in the original network. These 215 wells do not include the 19 wells in the sand plain which were sampled quarterly during the same span of years for time trend analysis. Table 3 summarizes results from the original 215 well network on an annual basis for the life of the old monitoring network (from 1985 through 1996). As can be seen most of the samples showed no detectable levels of atrazine. The data however does suggest that, on a broad scale, detection frequencies as high as 20 percent may be expected in these types of shallow water table wells in sand plain areas. Annual detection frequencies in this set of wells have been lower than in the time trend wells because the old network trend wells were chosen based on a history of previous atrazine detections. The general reconnaissance wells (summarized in Table 3) also varied in depth and sensitivity to a much greater extent than the trend wells, and not every reconnaissance well was sampled every year.

Table 3. Results of sampling sand plain reconnaissance wells from old MDA groundwater monitoring network (1986 to 1996).

Year	Wells Sampled	Wells Positive	Samples Collected	Samples Positive	Median (μg /L)	75th %-ile (μg /L)	Maximum (μg /L)
1985	7	0	7	0	ND	ND	ND
1986	41	18	93	29	ND	0.16	7.22
1987	36	7	44	7	ND	ND	4.87
1988	37	2	74	2	ND	ND	0.18
1989	28	4	48	4	ND	ND	0.25
1990	58	12	81	12	ND	ND	3.60
1991	91	17	119	19	ND	ND	7.00
1992	77	19	92	21	ND	ND	3.43
1993	118	31	138	33	ND	ND	1.75
1994	78	19	106	25	ND	ND	1.36
1995	77	16	98	20	ND	ND	5.77
1996	52	9	84	9	ND	ND	1.13

Monitoring Results In Minnesota's Southeastern Karst Topography

During the mid 1980's the MDA also began sampling a set of domestic drinking water wells in southeast Minnesota's karst, or soluble fractured bedrock region, for trends in pesticides over time. Four wells were selected based on previous detections of atrazine. The wells were sampled every quarter from early 1986 through mid 1995. As there are only four karst wells in this time series program, evaluation of changes in atrazine detection over time holds little information. Analysis of quarterly atrazine detection frequency over time for the karst area trend wells shows no trend. More data richness is available for atrazine concentration over time as seen in Figures 7 and 8. As the figures illustrate, there is little change over time in concentration values. Least squares regression results indicate an increasing trend over time although it is not statistically significant (slope + 0.00002 μg/L per quarter @ $p >> 0.05$). Higher concentrations of atrazine as evidenced by the chart of 75th percentile values over time (Figure 8) indicate a slight decreasing trend although this relationship is also not statistically significant.

During the period represented by the earlier karst monitoring program atrazine was clearly present in the sampled wells and showed a strong likelihood for continued detectable levels. The data also suggests that the higher concentration values may have been declining. Unfortunately the data-set is not sufficient for such determination overall.

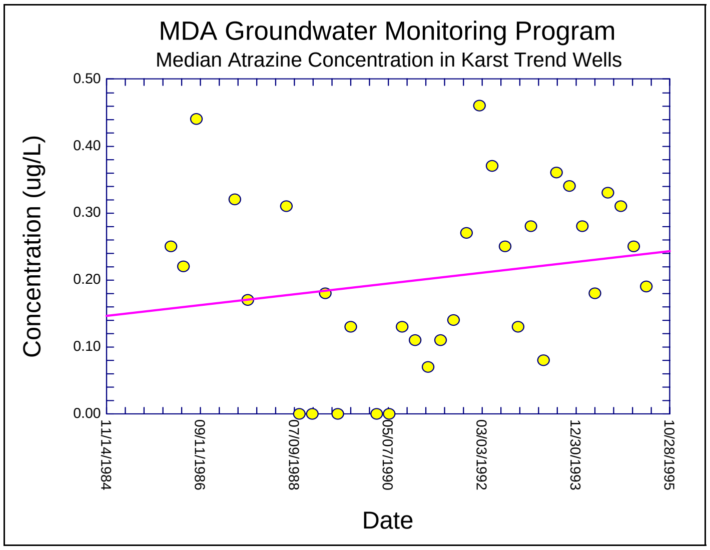


Figure 7. Atrazine median quarterly concentrations over time in MDA karst geology trend monitoring wells. Data is from the original monitoring network operated from 1986 through 1995.

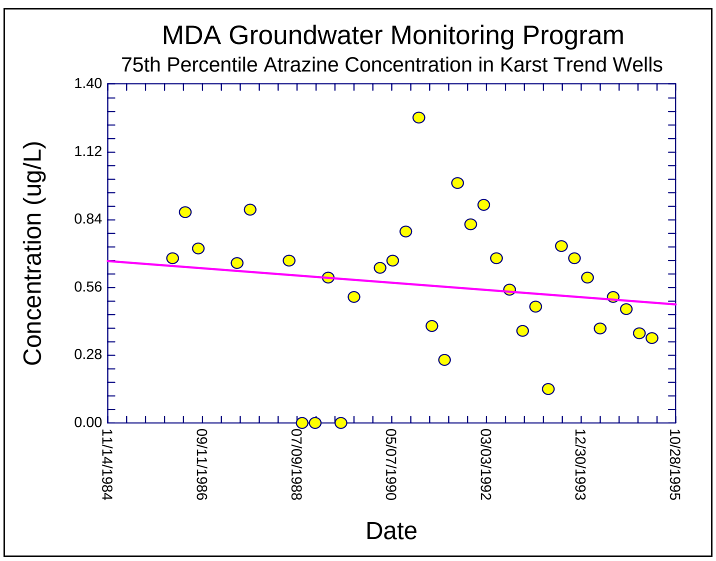


Figure 8. Atrazine median quarterly concentrations over time in MDA karst geology trend monitoring wells. Data is from the original monitoring network operated from 1986 through 1993.

In response to the shortness of data available to make generalized statements, an analysis of the data for each individual well was conducted. The results of this time series assessment is presented in Table 4 and indicates there is no indisputable trend present in three of the wells. The three wells with questionable trends all have fitted lines with increasing slopes. There is a statistically significant decreasing trend present in well number 852005. Data collected for this effort was insufficient to determine the possible cause of the decrease in atrazine concentration in this particular well.

Table 4. Results of linear trend regression analysis of atrazine quarterly sample concentrations over time for domestic drinking water wells used for monitoring trends in southeast Minnesota's karst region, 1986 to mid-1995.

Well number	Trend slope estimate (μg/L per Qtr)	Trend slope estimate p value	significant at $\alpha = 0.05$?
852001	+ 0.0011	0.23	No
852002	+ 0.0037	0.37	No
852004	+ 0.0016	0.16	No
852005	- 0.011	0.04	Yes

As drinking water wells are not the best indicator of large area impacts due to pesticide use in karst terrains, the program began monitoring two springs at the Crystal Springs fish hatchery in Winona County during 1993. Analysis from these springs is presented in Figure 9 and indicates a significant decreasing trend for spring #2. Spring #1 has a decreasing trend also, although it is not statistically significant. Four additional springs, two at the Lanesboro and two at Peterson, were added to the monitoring network in southeast Minnesota in 2003. Table 5 summarizes data currently available from these springs. At this time insufficient data is available from these springs for evaluation of concentration trends.

Table 5. Atrazine detection frequencies and concentrations for springs sampled at Lanesboro and Peterson.

Spring	Year	Number of Samples	Number of Detections	Median Concentration (μg /L)	75th Percentile Concentration (μg /L)
Lanesboro 1	2003	9	7	0.07	0.075
	2004	7	7	0.08	0.09
Lanesboro 2	2003	9	6	0.08	0.082
	2004	7	7	0.08	0.10
Peterson 1	2003	9	3	ND	0.037
	2004	8	7	0.037	0.057
Peterson 2	2003	9	5	ND	0.065
	2004	8	7	0.06	0.07

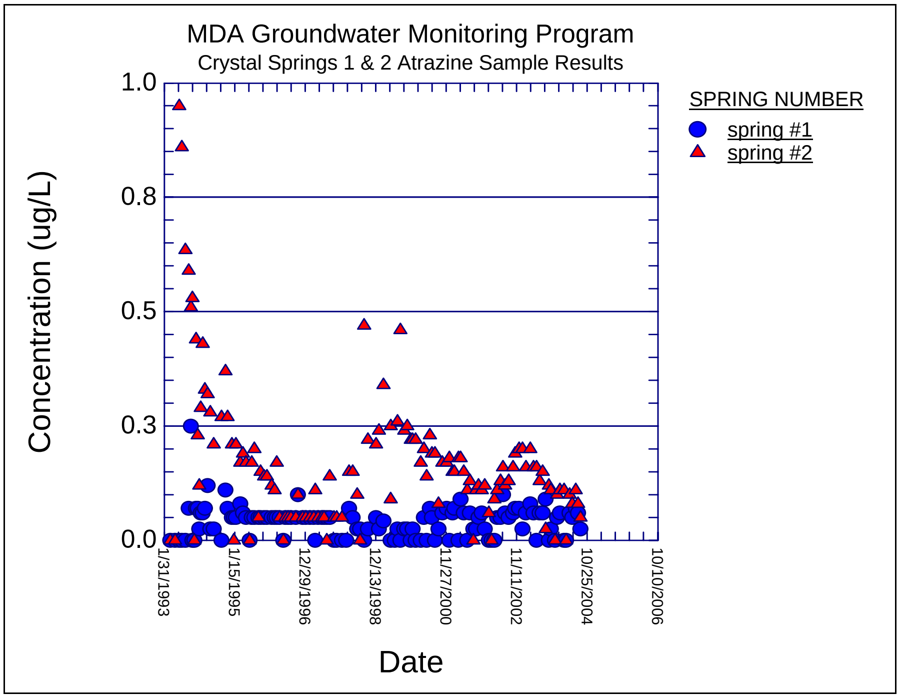


Figure 9. Atrazine sample results over time for Crystal Springs sample site.

As can be seen in the table below, a number of reconnaissance wells within the karst region were sampled in the original network. There were a highly variable number of samples collected each year making evaluations over time impossible. The data however may be used as an index of what conditions may be within an individual year. Table 6 lists the results of atrazine sample analysis for karst wells and shows that detections of atrazine are likely to occur in samples collected from domestic wells in the area. Concentrations tend to be quite low with significantly less than half the wells or samples containing measurable levels of atrazine. Locating appropriate representative wells for

Table 6. Results of sampling karst region reconnaissance wells from old MDA groundwater monitoring network.

Year	Wells Sampled	Wells Positive	Samples Collected	Samples Positive	Median (µg /L)	75th %-ile (µg /L)	Maximum (µg /L)
1986	11	6	31	9	ND	0.09	1.75
1987	10	3	17	3	ND	ND	0.11
1988	4	0	11	0	ND	ND	ND
1989	3	0	5	0	ND	ND	ND
1990	9	0	9	0	ND	ND	ND
1991	78	22	108	31	ND	0.07	1.60
1992	15	3	15	3	ND	ND	1.70
1993	0	NA	NA	NA	NA	NA	NA
1994	0	NA	NA	NA	NA	NA	NA
1995	1	0	1	0	ND	ND	ND
1996	0	NA	NA	NA	NA	NA	NA

monitoring groundwater conditions in karst terrain is extremely difficult and time consuming. For several reasons, including well construction and pesticide source issues, the MDA has determined that springs are the best groundwater monitoring point in karst conditions. The Department plans on continuing the effort to locate and sample springs as time and financial resources permit.

Other Reconnaissance Wells Not Classified As Sand Plains Or Karst

In response to Department needs to evaluate groundwater across the state a number of reconnaissance monitoring wells were sampled between 1986 and 1993. Table 7 lists the results of the sample analysis from these wells. Relative to previous data atrazine was detected infrequently in the general reconnaissance wells and in low concentrations. All but one annual maximum concentration was below 1.0 micrograms per liter and annual medians were below detection limits in each year of monitoring. Many of these wells were completed in areas where heavier or higher organic matter soil material was present. Some of these wells may also have been deeper than the typical sand plain well. All of the wells were representative of shallow groundwater conditions in the area where they were sampled.

Table 7. Results of sampling reconnaissance wells other than those located in karst or sand plain areas.

Year	Wells Sampled	Wells Positive	Samples Collected	Samples Positive	Median (μg /L)	75th %-ile (μg /L)	Maximum (μg /L)
1985	1	0	1	0	ND	ND	ND
1986	32	5	73	6	ND	ND	0.71
1987	30	3	45	3	ND	ND	0.15
1988	21	2	29	2	ND	ND	0.20
1989	22	0	22	0	ND	ND	ND
1990	31	8	33	9	ND	0.7	1.10
1991	60	1	64	1	ND	ND	0.05
1992	9	0	10	0	ND	ND	ND
1993	2	0	2	0	ND	ND	ND

Atrazine occurrence in MDA drinking water survey wells.

With the assistance of the MDH and the MPCA the MDA developed and implemented a random survey of drinking water wells throughout the agricultural regions of the state in early 2004. A grid structured to locate 100 points across the state's primary agricultural regions was randomly placed across the state. Wells nearest to the grid line intersections (Figure 10.) were located and sampled during January, February and March of 2004. Figure 10 also indicates sample point locations, sample status and occurrence of atrazine. Of the 71 wells sampled four contained atrazine with an average concentration of 0.08 μg /L and a maximum detection of 1.52 μg /L.

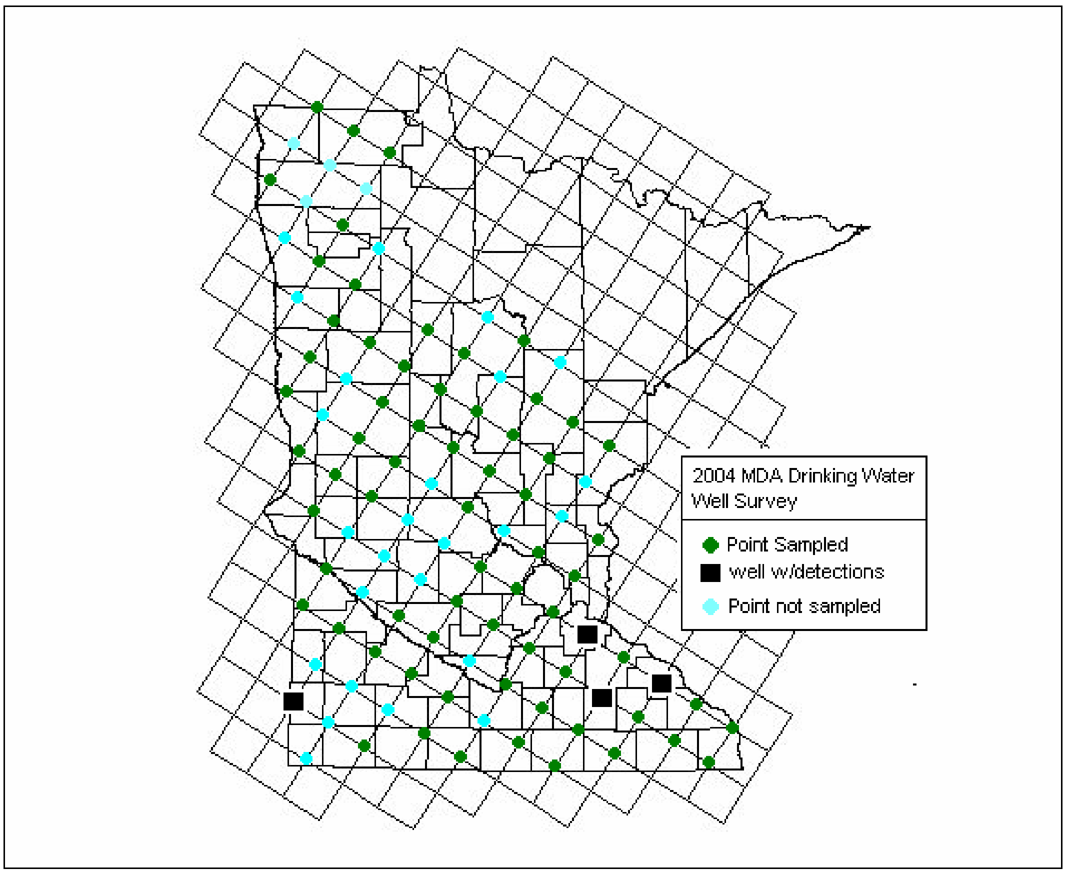


Figure 10. MDA 2004 drinking water well survey grid points, sample status and detections of atrazine.

II.B. Summary of Atrazine Monitoring In Other Midwestern States

The United States Geological Survey as part of its National Water Quality Assessment program has collected several hundred samples from other Midwestern states. Figure 11 displays results of NAWQA atrazine sample analysis. Because of dissimilar methods, comparisons between NAWQA data and the MDA groundwater monitoring program cannot be made directly, therefore Figure 11 includes Minnesota data from the Upper Mississippi River Basin NAWQA project. Figure 11 clearly shows that Minnesota groundwater conditions with respect to atrazine are very similar to surrounding corn-belt states, which is to be expected. NAWQA data is currently inadequate for tracking long-term concentration trends leaving no direct time series comparison between MDA and USGS NAWQA data. Very generally it appears NAWQA data may be displaying a decrease over time in Wisconsin and Minnesota without much change in Illinois or Iowa. Additional work by the USGS in the coming years may lead to more conclusive analysis.

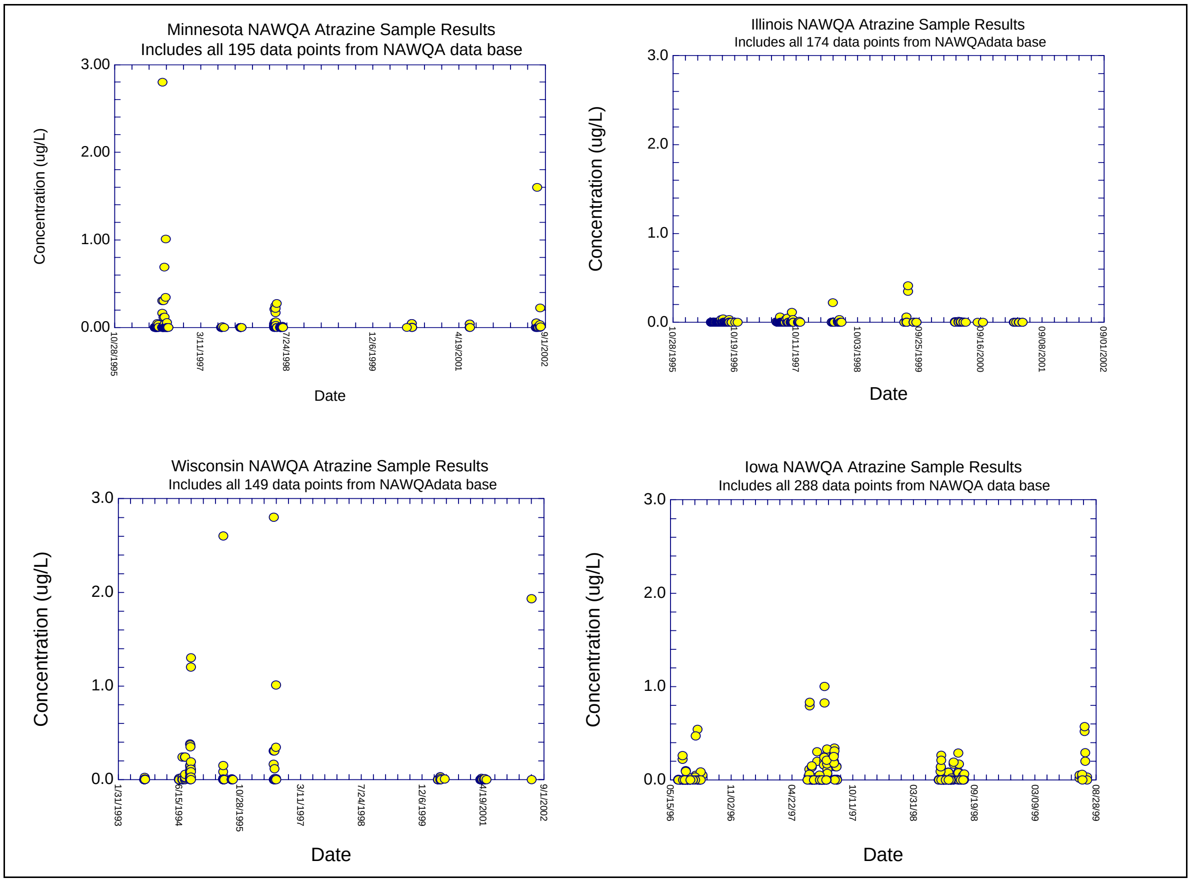


Figure 11. Atrazine sample results from the USGS-NAWQA program in four Midwestern states. Data downloaded from NAWQA web data base.

III. Summary of MDA Groundwater Monitoring Program Atrazine and Atrazine Degradate Data

The MDA began analyzing water samples for atrazine breakdown products (degradates) in late 1995. Desethylatrazine and deisopropylatrazine are the two degradates the MDA includes in its analysis of water samples. A small number of samples from the old network were analyzed for degradates before the network was abandoned in 1996. All samples from the Central Sands monitoring network have been analyzed for atrazine and its primary degradates. From late 1995 through the closing of the original network 174 samples were analyzed for desethylatrazine and deisopropylatrazine. Twenty-nine (17%) of the samples contained desethylatrazine while 13 (7%) contained deisopropylatrazine. Table 8 displays the results of atrazine degradate analysis for samples collected from wells in the CS network. Degradate detections clearly outnumber and have higher concentrations than detections of parent atrazine.

Table 8. Results of atrazine parent and degradate analysis from water samples in the MDA Central Sand Plain network. A total of 87 wells were sampled. All results included.

Degradate Analyte	Wells with Detections	Samples Collected	Samples with Detections	Median Concentration (µg /L)	75th %-ile Concentration (µg /L)	Maximum Concentration (µg /L)
Desethylatrazine	76 of 87	664	425	0.09	0.18	1.28
Deisopropylatrazine	43 of 87	664	221	ND	0.10	3.40
Atrazine parent	62 of 87	664	292	ND	0.06	0.74
Atrazine+degradates	76 of 87	664	479	0.14	0.38	4.50

Currently, toxicologists recommend summing the parent and degradates together when determining potential health or ecological risk associated with atrazine exposure. Figure 12 are charts of atrazine and its degradate medians for each quarter of sampling from the Central Sands network. The data shows that there is no discernable trend in degradate median quarterly concentrations since the inception of the CS network. Figure 12 further shows the value of analyzing water samples for pesticide degradates.

In karst areas desethylatrazine concentrations appear to be decreasing over time (see Figure 13.). Analysis of the results for desethylatrazine over time indicates that the apparent trend for either spring is not statistically significant for the entire data set. In 1997 analytical methods were further refined to provide a quantification of the actual amount of atrazine degradates present in the springs. Prior to that point in time results for the springs were reported as detected or not detected. Data collected since 1997 for spring 1 continues to show no significant trend, while spring 2 shows a statistically significant decreasing trend. Detections of deisopropylatrazine are so few that no trend can be seen.

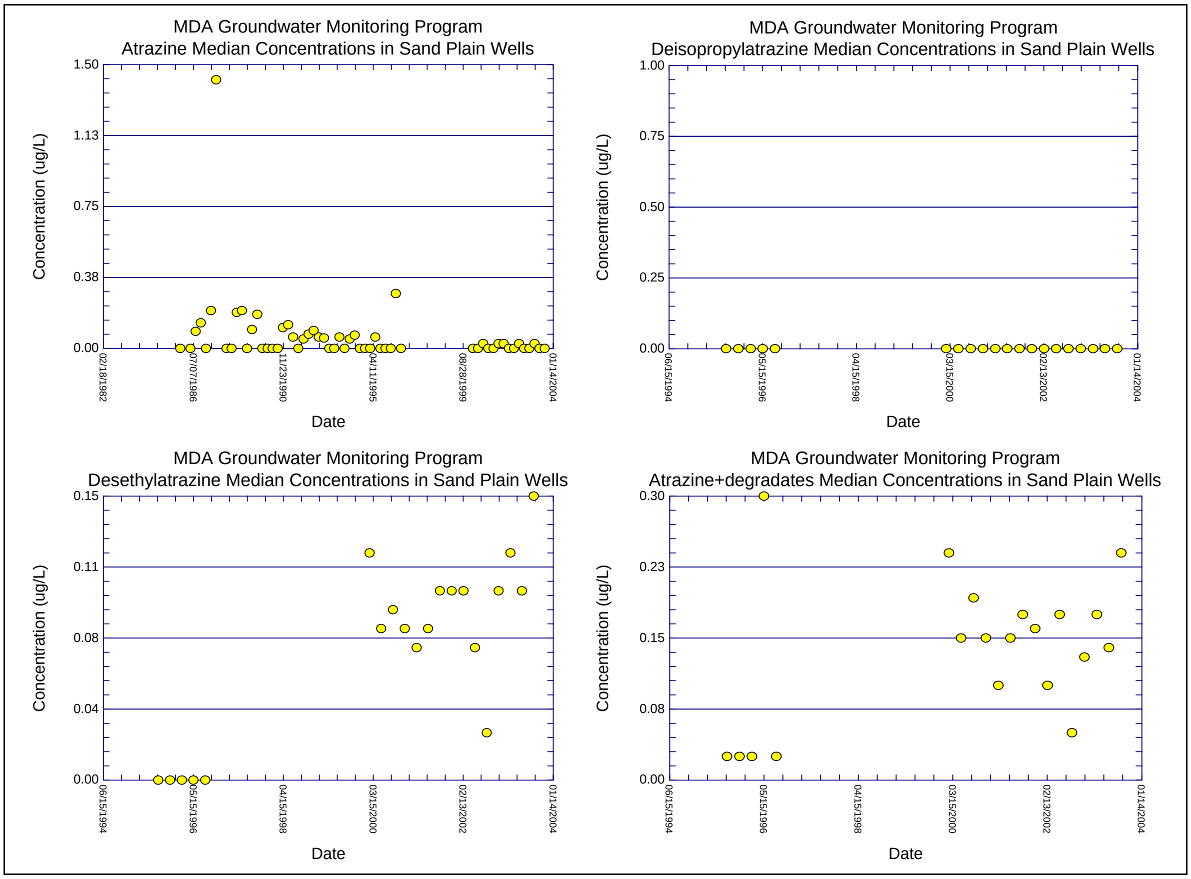


Figure 12. Quarterly median concentrations in µg/L of atrazine and its degradates over time for the MDA Central Sand Plain groundwater monitoring network. Non-detectable levels are represented as 0.00 on the graphs. Notice the date axis difference between atrazine parent and the other three graphs.

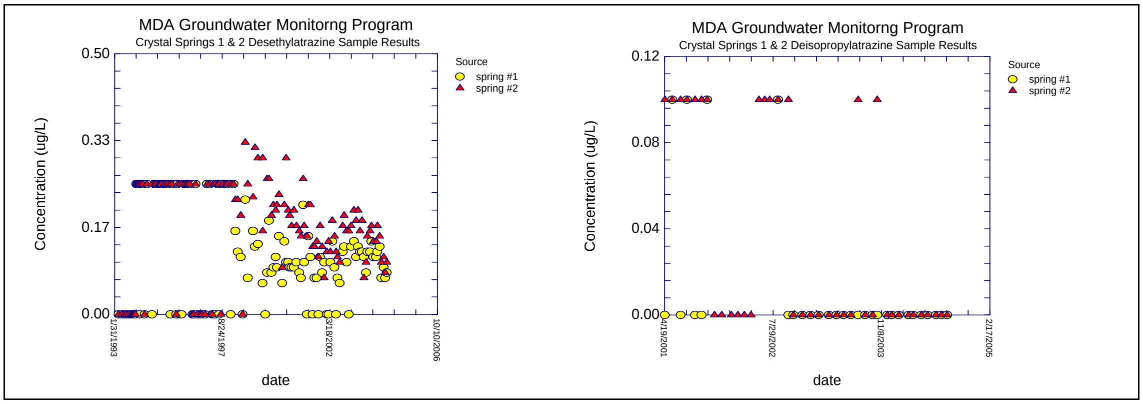
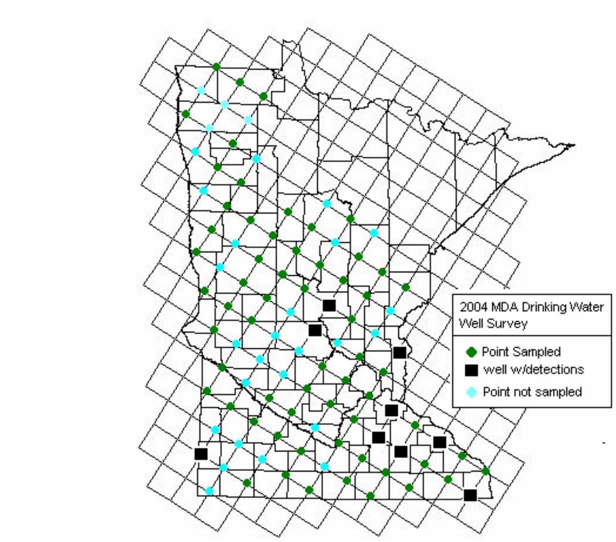
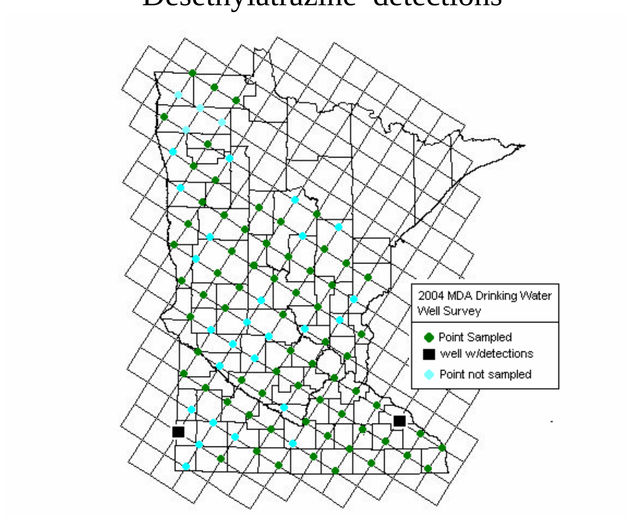


Figure 13. Concentrations in µg/L of atrazine and its degradates over time for the MDA Crystal Springs monitoring. Values for desethylatrazine (top graph) prior to 1998 were reported as present or absent only. For deisopropylatrazine no quantifiable levels have yet been detected. The values at 0.1 µg/L deisopropylatrazine are unquantifiable detections.

The statewide survey of drinking water wells showed results highlighting the importance of analyzing samples for atrazine degradates. Four wells contained atrazine parent material (Figure 10.) while desethylatrazine was detected in nine wells and deisopropylatrazine was detected in two wells (Figure 14). Overall the result was that 10 of the 71 wells in the statewide drinking water well survey contained some form of atrazine, six more than for the atrazine parent compound alone. Detectable concentrations of desethylatrazine ranged from the very limit of detection to 0.65 µg/L with a median value of 0.09 µg/L, and deisopropylatrazine had values of barely detectable to 0.35 µg/L.



Desethylatrazine detections



Deisopropylatrazine detections

Figure 14. Detections of atrazine breakdown products in 2004 MDA statewide drinking water well survey.

IV. Synopsis

Atrazine frequently occurs in groundwater in Minnesota and is present in many different locations. Concentrations are typically below 1.0 μg/L although detection frequencies in the 90% range may be expected in some situations. Atrazine overall detection frequency in shallow sand plain areas is declining as are median concentration values. There is a smaller seasonal influence on atrazine detections and concentrations in sand plain wells than anticipated. In karst areas there appears to be a decreasing trend in atrazine concentrations over time when springs and wells are considered collectively.

Atrazine breakdown products frequently occur in groundwater and typically form the majority of the total atrazine present in the Central Sand Plain, karst springs and drinking water survey programs. Trends in degradate results are similar to those for the parent atrazine. Analysis of water samples for atrazine degradates is a key in determining the significance of atrazine presence in the state's groundwater.

Results of trend analysis reveal that in all cases where a statistically significant trend is measurable the corresponding trend is always downward. This indicates clear evidence that, in a general sense, the concentration of atrazine and its degradates is declining in Minnesota's groundwater. Specific reasons for this decline cannot be directly determined by available data, although inference may be possible through correlations with label application rates and available pesticide use survey information. This inference is beyond the scope of this document and would be a useful future analysis on this set of data.