Trends in atrazine use and pollution in Wisconsin

Atrazine use

Application rate

The Atrazine Rule in Wisconsin reduced the allowed application rate, which immediately reduced the average application rates used by farmers. The application rate at which atrazine is used is considered to be one of the most important factors as to whether atrazine and its metabolites will become a problem for groundwater, a concept that influences DATCP’s limits on use rates (Hanson et al., 1997). In fact, the USGS used application rate as the strongest predictor for water quality problems in its atrazine pollution model (Stackelberg et al., 2012). In 1990, Wisconsin corn farmers were using atrazine on 58 percent of corn acreage at a rate of 1.29 lbs./acre (NASS, 2015). That translates to a total of 2,790,000 pounds of atrazine applied to the 3.7 million acres in corn production. However, historic rates were likely higher (Wisconsin Statistical Reporting Service, 1971). For example, DATCP recorded one farm’s historical application rates exceeding 5 lbs./acre (DATCP Archive, 1992). In 1961, 5 lbs./acre was actually the rate recommended by at least one county agricultural agent for fields in continuous corn production in 1961 (Buchholz, 1961). In 1991 the first year of atrazine regulation in Wisconsin, there was a sharp decline in the average application rate from 1.29lbs/acre to 1.01 lbs./acre as well as a decline in the extent of its use (to 52 percent of corn acres). This was in spite of the 100,000 additional corn acres planted that year. The initial reduction in application rate continued, with some outlying years, and atrazine was used at its lowest recorded rate in 2010 at 0.71lbs/acre (Figure 1).
Figure 1. Mean application rate of atrazine for corn in Wisconsin from 1970-2010 (NASS, 2015; Wisconsin Statistical Reporting Services, 1971).

*Area treated with atrazine*

The percent of corn acres treated with atrazine has fluctuated over the years. After regulation began in 1991, there was a dip in the percent of acres treated from 58 percent in 1990 to 52 percent in 1991. In 1997, 64 percent of corn acres were treated with atrazine, the highest on record, and in 1999, only 37 percent of acres were treated, the lowest on record. The most recent trend is an increase in the percent of acres treated, with 62 percent treated in 2010, up from 54 percent in 2005 (Figure 2).
Due to the decreased application rate and the only slight increase in the percent of acres on which atrazine is used; there have been overall decreases in the total amount of atrazine used in Wisconsin corn. From 1990 to 2010, the total atrazine applied in Wisconsin has decreased from 2,790,000 lbs. to 1,627,000 lbs. for an overall reduction of more than one million pounds (Figure 3). This reduction highlights that although the amount of corn planted has increased over the past twenty-five years, the overall amount of atrazine use has decreased.
Figure 3. Total atrazine applications in Wisconsin (Source: NASS, 2015).

The reduction in the total atrazine used in Wisconsin seems to be greatly correlated with the reduction in application rate. The reduced application rate was most likely a result of lowered allowable rates and the availability and use of other products. The DATCP evaluation of 1997 stated that the reduction in the application rate observed in the early 1990s was due to using atrazine in combination with other herbicides, applying it in a band over the row, and using more mechanical weed control (Postle et al., 1997). Farmers were aware of the pollution caused by atrazine, and also feared the possibility that the government would completely take away the ability to use atrazine. Farmers voluntarily reduced atrazine in order to avoid stricter regulations. In addition, Postle et al. (1997) described the reduction in use as being attributed towards fear that atrazine could damage the following year's crop, concern for the environment, availability of alternatives, conversion to practices requiring less herbicide, and finding other solutions to weed problems not controlled by atrazine.

Over the period of 1990-2010, there have been two main changes to the way corn is grown: the use of genetically modified herbicide tolerant corn seeds and the increased use of minimal or no-tillage farming systems. Specifically, the introduction of Roundup Ready corn marks a shift to reliance on glyphosate herbicides. In addition to the availability of GMO corn, other herbicides such as acetochlor became
available weed control tools in the mid 1990s. For example, acetochlor, a selective herbicide for broadleaf weeds and annual grasses, was granted registration in 1994 by the EPA in an effort to reduce the use of atrazine and other herbicides in corn (EPA, 2009).

For the purposes of this analysis, I evaluated trends for six major herbicides, alachlor, atrazine, acetochlor, dicamba, glyphosate, and s-Metalochlor over the period of 1990-2010 in Wisconsin corn. All of these herbicides are primarily used for pre-emergent weed control. In terms of the percent of acres planted with corn that are treated with atrazine, the percentage has remaining fairly constant between 50 and 60%, except for 1999. The use of acetochlor, introduced in 1994, has steadily increased from 2% in 1994 to 37 percent in 2010. Dicamba, increased from 17% in 1990 to a peak of more the 50% in the late 1990s, but has since experienced a decline in use and was only used on five percent of the acres in 2010. Alachlor experiences a steady decrease from a peak use on 30% of acres in 1993 to not being used in the late 2000’s. s-Metalochlor has increased in use from being used on 16 percent of acres in 1990 to 32% in 2010 (for this analysis metalochlor and s-metalochlor were grouped together if both were used in the same year). Glyphosate and later glyphosate isopropylamine salt have increased from being used on 4% of corn acres in 1990 to 47% in 2010. Because Roundup Ready corn comprises 85% of corn planted, the amount of glyphosate has most likely increased from 47% since 2010. Overall, since 1990, the acres treated with atrazine, acetochlor, glyphosate and s-metalochlor have all increased (Figure 4). Alachlor and dicamba are the only herbicides that experienced a decline in use.
The groundwater law in Wisconsin does not address the issue of chemical mixtures. The exposure to a combination of pesticides can result in both adverse synergistic and additive effects, especially in the potential for estrogenic effects from endocrine disruptors (Hernández et al., 2013). Unlike the EU standard for total pesticides in water of 0.5\( \mu \text{g/L} \), there is no set safety level in the US for combined chemicals. The threat of individual chemicals and chemical mixes to drinking water can be expected to increase as seen in the most recent upward trend in overall herbicide use in Wisconsin (Figure 5).

Figure 4. Percent of corn acres in Wisconsin treated with different herbicides (Source data: NASS, 2015).
There are also specific risks associated with different herbicides that are potential atrazine alternatives. The major herbicide used in corn production is glyphosate, the most commonly used herbicide in the US (Figure 13). Glyphosate, long considered by many to be of low environmental and health risk, is under scrutiny for possible environmental and human health impacts. A 2015 report from the WHO classified glyphosate as a probable carcinogen. Samsel and Seneff (2013) has gained attention because of the hypothesis that links glyphosate exposure to autism and other neurological diseases. These studies linking glyphosate to major health risks have sparked controversy and alarm concerning the high levels of glyphosate use. That a pesticide can be used in a widespread manner in agriculture and other settings without its risks fully understood brings into question how we should best manage chemicals and their risks.

**Groundwater monitoring data**

DATCP took 44,899 groundwater samples to monitor for atrazine or atrazine breakdown products from the time period 1985-2014. 7,732 samples were taken from 1985-1991 and 37,167 samples were taken from 1992-2014. Atrazine concentrations varied dramatically depending on the well site. Atrazine concentrations ranged from zero to 191 µg/L. The samples with the highest concentrations, like the 191 µg/L sample, were most likely
affected by point source well contamination. Improper atrazine handling leading to point source contamination was recorded by DATCP. Samples with concentrations exceeding 30 µg/L were excluded from the analysis because they represent point source contamination instead of leaching from normal atrazine use. Of the 44,899 total samples, 26,314 samples (59%) were positive for total atrazine. The enforcement standard of 3µg/L was exceeded in 963 samples with 602 exceedances occurring from 1985-1991 and 361 exceedances recorded from 1992-2014. Figure 6 visually depicts the atrazine
monitoring, detections, and exceedances using GIS.

Figure 6. Total atrazine concentration results for wells sampled from 1985-2014.
Mixed-effects model

A mixed-effects model, also known as a linear mixed model (LMM) was used to evaluate the longitudinal data set of monitoring data. The mixed-effects model is a procedure that allows for analysis of change over time by fitting an advanced regression model to the longitudinal data set (West, 2009). Mixed-effects models allow the inclusion of both fixed effects as well as random effects. SPSS software was used to create a model that evaluated the change in atrazine concentration over time as well as the impact and interaction effects of the 1991 Atrazine Rule and the creation of the PAs. In the atrazine model, the fixed effects were (a) time, (b) being in a PA or not being in a PA and (c) the year being before or after 1991 (the year of the Atrazine Rule). The random effect in the model was the difference between individual wells.

In order to determine if total atrazine concentrations changed after the Atrazine Rule, I narrowed the analysis to data wells which had at least one detection of atrazine or a breakdown product and overall had more than three samples taken over the time period of 1987-2013. The data from 1985 and 1986 were excluded because there were few readings with many outliers for those years. By excluding wells that always had zero values, I was able to focus on wells where change over time could be documented. Concentrations over 30 µg/L were also excluded from the analysis because they most likely represent point source well contamination and are more than 2.5 standard deviations away from the mean and are not connected to the other data points. This subset of the data set contains 3,719 data points from 610 monitoring wells.

The model was created using a log transformation of the total atrazine concentrations found in the wells. The values for concentration were widely variable between the early monitoring data and the later monitoring data. For example, in 1987 the variance for well concentration was 19.03, whereas the variance in well concentration in 2013 was 0.81. Large differences between variances such as the one between 1987 and 2013 break the linear model’s assumption of heteroscedasticity. After the log transformation, the variances in concentration are substantially more stable over time. After transformation, the variance in 1987 was 9.95 and the variance in 2013 was 8.47.

To test for the best fit of the model to the data, the model was executed with a variety of parameters including random slopes, random intercepts, both random slopes
and intercepts, and also with no random effects. The random effects did not improve the model’s fit to the data. The mixed-effects model was used even though there were no random effects in order to specify the covariance structure, which was first order autoregressive heterogeneous (AR1 heterogeneous). AR1 heterogeneous means that variances in concentration will be more similar the closer the time periods are to one another. AR1 is often the most appropriate covariance structure for a longitudinal model. The heterogeneous AR1 model was selected because the data set includes differences in variance for the different sampling years. The final model included the following three independent variables as fixed effects: year, status of being in a PA as an interaction with year, and an interaction of year being after 1991 and year. These two interaction effects test whether the slope of the mean concentration changed when a site became a PA and if the slope changed after the 1991 Atrazine Rule.

Change over time

The data set used in the model and analysis was reduced from the original set of 44,899 samples to 3,719 samples that met our criteria. For these samples, the mean atrazine concentration peaked in 1992 at 3.0 µg/L and experienced a variable yet consistent decline to 0.67 µg/L in 2013 (Figure 9).

![Figure 9. Mean concentration of total atrazine over time.](image)

The mixed-effects model was used to evaluate if the creation of the 1991 Atrazine Rule reduced atrazine concentration. For the data set, the model shows
that concentrations in wells experienced a steady and statistically significant decline from year to year. The log-transformed concentration allows us to report the decline in concentration as a percent decline per year rather than the change in concentration in µg/L. The model showed that for each additional year, the total atrazine concentration in wells experienced a 16% decrease ($F(1, 179) =, p = <0.005$, 95% CI [14%, 19%]). The difference of slopes is statistically different for wells sampled before and after 1991 ($p = <0.005$) (Figure 10). From 1987-1991, the data from 821 samples from 370 wells showed an increase in year-to-year atrazine concentration of 26.7% ($F(1, 369) = 7.826, p = <0.005$, 95% CI [7%, 40%]). From 1992-2013, the data from 2,898 sampled from 519 wells showed that the slope of the well concentrations declined year-to-year by 17% ($F(1, 704) = 172.401, p = <0.001$, 95% CI [-27%, -20%]). The shift from a positive slope before 1992 to a negative slope from 1992-2013 indicated a shift from the atrazine problem getting worse to the situation improving.

![Figure 10. The year-to-year change in atrazine concentration as characterized by the mixed-effects model.](image-url)
This model did not detect a difference between the rate of concentration decline for wells inside and outside of PAs. The model found that 1267 samples from 423 wells that were not in a PA experienced a year-to-year decline in concentration of 21% after 1991 ($F(1, 226) = 151.409, p = <0.001, 95\% \text{CI} [-27\%, -20\%]$). For the 1631 samples from 290 wells that entered PAs after 1991, the decline in concentration was also 21% ($F(1, 393) = 149.733, p = <0.001, 95\% \text{CI} [-27\%, -20\%]$). These findings suggest that the most important intervention by DATCP was the 1991 Rule that decreased application rates for atrazine statewide. There is a decline in atrazine concentration over time, and this decline is present only after 1991. The model does not show that the institution of the PAs had an effect on atrazine concentration decline. Because a reduced data set is used in the model, there is the possibility that wells that were not frequently sampled were not part of the analysis and their absence may have influenced the findings.

**Conclusion**

The Atrazine Rule in Wisconsin is a policy that has contributed towards strong improvements in water quality protection. This policy can be seen as a first step in the types of policies that are needed nationwide to control herbicide pollution. In addition to limiting the use of herbicides like atrazine that easily enters water sources, there is a need to regulate total pesticide concentrations in water in order to avoid the hazard of chemical mixtures.