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Follow Up to the Grade A
Dairy Farm Well Water
Quality Survey

Follow Up to the Grade A Dairy Farm Well Water Quality Survey

Wisconsin Department of Natural Resources
PUBL-WR 301-92
February 1992

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FOLLOW UP

TO THE

GRADE A DAIRY FARM

WELL WATER QUALITY SURVEY

PUBL-WR-301-92

Wisconsin Department of Natural Resources
P.O. Box 7921
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February 1992

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February 29, 1992

To Citizens Concerned about Wisconsin's Groundwater:

Approximately 570 million gallons of groundwater per day are withdrawn from private and public wells and about 70% of Wisconsin residents rely upon groundwater for drinking. Because of the importance of groundwater to the state of Wisconsin, we are concerned about protecting its quality for present and future generations.

The Grade A dairy farm follow up study described in this report was undertaken by the Department of Natural Resources to enhance the knowledge of groundwater pesticide contamination in the state.

Initial studies of Grade A dairy farm wells by the Department of Agriculture, Trade and Consumer Protection and the Department of Natural Resources revealed that pesticides, particularly atrazine and alachlor are found in groundwater in rural areas of the state. The follow up study was designed to resample the Grade A dairy farm wells with pesticide detections plus expand sampling to nearby areas for comparison and delineation of the extent of pesticide contamination.

This report entitled "Follow Up To The Grade A Dairy Farm Well Water Quality Survey" contains a synopsis of the original Grade A Dairy Farm Well Water Quality Survey as well as a summary and discussion of the follow up study results. Results from the study indicated that pesticide detections remained prevalent in the originally sampled wells and, as expected, were less prevalent in nearby wells. Atrazine remained the predominant detectable pesticide.

Groundwater professionals, policy makers as well as the general public may find this report useful in understanding both the occurrence and extent of pesticide contamination in our state.

Sincerely,

Lyman F. Wible, Administrator
Division for Environmental Quality

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Department of Natural Resources Groundwater Management Section
101 South Webster Street
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Special thanks are due to the 69 Grade A dairy farmers who allowed resampling of their wells as well as 212 of their neighbors, without whom this survey would have been impossible.

We would also like to thank the following staff at the Department of Natural Resources:

BUREAU OF WATER RESOURCES MANAGEMENT
Groundwater Management Section

Kevin Kessler, Chief
Michael D. Lemcke, Hydrogeologist

EXECUTIVE SUMMARY

Original Study

In 1988 and 1989, 534 randomly selected Grade A dairy farm wells across Wisconsin were sampled by the Wisconsin Department of Agriculture, Trade and Consumer Protection for pesticides and Nitrate+Nitrite Nitrogen (NO_3+NO_2 N). The 95% confidence interval for the proportion of Grade A dairy farm wells with detectable levels of pesticides and NO_3+NO_2 N was determined. The study also helped assess the effectiveness of pesticide regulations in protecting groundwater from pesticide contamination. Of these 534 wells, 71 contained detectable levels of pesticides. Atrazine was most prevalent (detected alone in 64 wells and in combination with alachlor or metolachlor in two wells). Alachlor alone was found in three wells and in combination with metribuzin in one well. Metribuzin alone was detected in only one well.

The results indicated that 10% to 16% of Grade A dairy farm wells across the state have detectable pesticide concentrations. Detectable NO_3+NO_2 N concentrations statewide were between 61% and 69%. A chi-square analysis indicated an association between NO_3+NO_2 N detections, both above the PAL and enforcement standard (ES) of 10 mg/l, and pesticide detections. Furthermore, areas of geographic atrazine contamination were found which did not correspond directly with extensive atrazine usage. These areas were believed to be more susceptible due to medium and coarse-textured soils and intensive or prolonged use of atrazine.

Follow Up Study

In the Follow Up to the Grade A Dairy Farm Well Water Quality Survey, the Wisconsin Department of Natural Resources targeted the 71 wells which originally contained pesticides for resampling. There was also an interest in determining whether these wells were representative of the groundwater quality in the area. Therefore, the follow up study design was for an average of three wells in the vicinity of the impacted well to also be sampled. This study was conducted to confirm the original detections, delineate the extent of contamination, and collect data to aid in future assessments of pesticide contamination. Sixty-nine (69) of the original 71 wells with pesticide detects were resampled, and 57 of these 69 wells still contained a detectable concentration of at least one pesticide. Atrazine remained the most prevalent pesticide, found alone in 50 wells and in combination with alachlor, metolachlor or cyanazine in 6 wells. Only one well contained alachlor alone. Pesticide and NO_3+NO_2 N detection frequency remained high. Pesticides were still detected in 83% of these wells and NO_3+NO_2 N was detected in 97% of the wells. The concentration of atrazine was significantly different between the original and follow up samplings of the 64 wells that originally contained atrazine.

Based on the number of follow up results which decreased from the original sampling, it was concluded that reported atrazine concentrations had declined. This decline as well as the minimal difference between the two median values of 0.04 µg/l is not necessarily due to actual declines of atrazine in groundwater.

A total of 212 nearby wells were sampled. Pesticides were detected in 30% of these wells and 89% contained NO_3+NO_2 N. Atrazine was the most frequently detected pesticide and was found either alone or with alachlor, metribuzin, metolachlor or cyanazine in all of the impacted wells. As anticipated these wells were more frequently contaminated than the statewide proportion estimates calculated from the original study.

"Atrazine", as used in this report, refers to atrazine parent compound, not to the combination of the parent compound and metabolites.

INTRODUCTION

The majority of Wisconsin residents rely on groundwater for their drinking water. Concerns over the quality of this resource were heightened in the early 1980s when aldicarb, an insecticide used on potatoes, was detected in groundwater in central Wisconsin. In 1984, Wisconsin adopted comprehensive legislation to preserve groundwater quality. A cornerstone of this groundwater law is the process for establishing health-based, numerical standards, consisting of an Enforcement Standard (ES) and a Preventive Action Limit (PAL). The PAL and ES can be thought of as a yellow light and red light for regulatory agencies. If the PAL is violated measures must be considered to ensure that, at a minimum, the ES is not violated, and unless it is not feasible, that the PAL is complied with. If the ES is violated, regulatory agencies must stop the activity or practice that has resulted in the contamination.

In 1988, the Wisconsin Department of Agriculture, Trade and Consumer Protection (WDATCP) conducted a survey of well water quality on Grade A dairy farms (Grade A farms produce milk meeting standards for the fresh market). It identified atrazine as the predominant pesticidal contaminant of groundwater. At the same time, the Wisconsin Department of Natural Resources (WDNR) adopted groundwater standards for atrazine and alachlor (trade name Lasso), both herbicides widely used on corn crops in Wisconsin.

In this report, "Follow Up to the Grade A Dairy Farm Well Water Quality Survey", the results from the original survey are summarized, and the results of the follow up survey are presented. The follow up study consisted of resampling each contaminated well from the original survey, as well as an average of three wells in proximity to the original well.

Recently, the occurrence of atrazine metabolites in groundwater (deethylatrazine, deisopropylatrazine and diaminoatrazine) has been recognized as a significant concern. The state groundwater enforcement standards and preventive action limit for atrazine have been amended to include the above chlorinated metabolites in addition to parent compound (effective 2/1/92). The original Grade A Dairy Farm Study, as well as the Follow Up Study discussed in this report were conducted before the State of Wisconsin has the routine capability to analyze for atrazine metabolites, therefore "atrazine" as used in this report refers to atrazine parent compound, not to the combination of the parent compound and metabolites.

ORIGINAL GRADE A DAIRY FARM SURVEY

Objectives

The primary objective of the original Grade A dairy farm study was to estimate the proportion of Grade A dairy farm wells with detectable levels of commonly used pesticides and NO_3+NO_2 N. Such a statistically unbiased estimate of pesticide contamination of groundwater had not been derived up to that time. Additionally, this study served as a database to help assess the statewide extent of pesticide contamination, which was needed because of the new groundwater standards for atrazine and alachlor adopted in October 1988 (ch. NR 140, Wis. Admin. Code) (1,2).

Methods

Sampling Strategy

A total of 550 private water supply wells on Grade A dairy farms were randomly selected for sampling from the state's nine Agricultural Statistics Districts (ASDs) as shown in Figure 1. Proportional allocation was used to select the number of Grade A dairy farm wells in each ASD. Thus, the number of Grade A dairy farm wells sampled in each district was based upon the number of Grade A farms in the district in proportion to the total number of Grade A farms in the state. Grade A dairy farms were targeted since they were accessible to WDATCP Food Division inspectors and most of these farms use wells which meet specifications set forth in Chapter NR 112, Wis. Admin. Code. In addition, since Grade A dairy farms are present throughout much of the state, the results might be used to estimate the prevalence of pesticides in rural groundwater (1,2).

Sample Collection

Sampling was conducted by WDATCP Food Division inspectors from August 1988 through February 1989. Samples were drawn from wells which supplied the two-compartment wash sink in the milkhouse. All samples were collected from the cold water tap of the two-compartment wash sink after the water was allowed to run for at least five minutes. Pesticide samples were collected in decontaminated, one-liter amber glass bottles with teflon-lined caps. The NO_3+NO_2 N samples were collected in decontaminated 125 milliliter (ml) polypropylene bottles. Samples were shipped, in insulated shipping containers refrigerated with prefrozen ice packs, and received within 24 hours at the WDATCP General Laboratory via courier service (1).

Laboratory Analysis

Pesticides were analyzed by the WDATCP Bureau of Laboratory Services using the Neutral Extractable Method of the State Laboratory of Hygiene Organics Section Method 1200, which has a

limit of detection (LOD) of approximately 0.15 micrograms/liter (μg/l) for pesticides. Table 1 illustrates the detectable analytes for this method and Table 2 contains the LODs for atrazine, alachlor, metolachlor, metribuzin and cyanazine. NO_3+NO_2 N samples were analyzed by the Cadmium Reduction Method 418C with a detection limit of 0.5 milligrams/liter (mg/l). Approximately 150 NO_3+NO_2 N samples were analyzed at the WDATCP laboratory with the remainder completed by the State Laboratory of Hygiene (1).

Results

Sixteen of the 550 selected farms went out of business before a sample could be collected. Of the 534 wells sampled, 71 wells had detectable levels of one or more pesticides. A total of 64 wells contained atrazine alone, while 2 wells had atrazine plus another pesticide. The median (see Appendix A for definition) atrazine concentration of wells with atrazine detections was 0.45 μg/l and the ES of 3.5 μg/l* was exceeded in 3 wells. Alachlor was detected in 5 wells, all above the enforcement standard (ES) of 0.5 μg/l. Of the detectable pesticides analyzed (Table 1), only metribuzin and metolachlor were also detected (1 well each). Overall, 48% of the wells exceeded the NO_3+NO_2 N PAL (2 mg/l) and 10% exceeded the ES (10 mg/l) (1).

*Note: At the time of this survey and analysis, the ES for atrazine was 3.5 μg/l for parent compound. The ES has changed to 3.0 μg/l (as a total of parent compound and metabolites), effective 2/1/92.

Discussion

Based on the results of the survey, the proportion of Grade A dairy farm wells in the state with pesticide detections was estimated to be from 10% to 16% at a 95% confidence level. Between 5% and 9% of Grade A dairy farm wells across the state, at the 95% confidence level, are estimated to contain atrazine above the PAL of 0.35 μg/l and from 7% to 13% of the wells have NO_3+NO_2 N above the ES of 10 mg/l. Additionally, approximately 61% to 69% of the Grade A dairy farm wells statewide were estimated to contain detectable levels of NO_3+NO_2 N (1). A chi-square test of association indicated that wells with NO_3+NO_2 N above the PAL and ES are significantly more likely to contain pesticides (at α's of 0.01 and 0.05 respectively) (1). An explanation of this statistic and some of its limitations is in Appendix A.

Particularly relevant were the geographic patterns of atrazine detections compared to atrazine usage patterns. Table 3 illustrates the number and frequency of detections for each ASD in order of 1985 atrazine usage. Approximately the same percentage of Grade A dairy farms in each ASD were sampled (ranging from 2.4% in the Southeast ASD to 2.2% in the East Central ASD). The frequency of atrazine detection is not directly related to the number of acres on which atrazine is

used. Although the first three leaders in atrazine usage follow a corresponding decreasing detection frequency, the Central and Northeast ASDs deviate from this pattern. Detections were most prevalent in the South Central ASD and Dane County in particular. Detections did occur in other ASDs, but with less frequency. The frequency of detections in the South Central ASD is thought to be due to the presence of medium-textured and coarse-textured soils, as opposed to heavier soils in eastern Wisconsin, and intensive or prolonged use of atrazine (3).

FOLLOW UP GRADE A DAIRY FARM SURVEY

Objectives

There were three objectives in the follow up study. First, original Grade A dairy farm wells with pesticide detections were targeted for resampling for comparison to original data. Secondly, nearby wells were selected for sampling to assess the extent of groundwater contamination in the area. A third objective was data collection to aid in future assessments of pesticide contamination.

Methods

Sampling Strategy

The 71 wells with pesticide detections from the original study were to be resampled. In addition, an average of three wells in the vicinity of each original well were to be sampled. Best professional judgement and availability of cooperative well owners was used to select the vulnerable wells in the vicinity of the impacted well. Thus, unlike the original study, these samples were not random and selection criteria for nearby wells likely varied.

Sample Collection

Wells were sampled by the WDNR District Water Supply staff from October 1989 through September 1990. The distribution of sample dates for the two surveys and the time that elapsed between samplings are shown in Figure 2. Unlike the original study, considerable variability existed in sample collection sites, ranging from milkhouse sinks to kitchen faucets. All samples were collected in a manner consistent with the WDNR Manual of Groundwater Sampling Procedures Guidelines (4). These collection methods are identical to those utilized in the original Grade A dairy farm survey. Samples were packed in pre-refrigerated shipping containers and received within 24 hours at the State Laboratory of Hygiene.

Laboratory Analysis

All samples were analyzed by the State Laboratory of Hygiene. Pesticide samples were analyzed in accordance with the

State Laboratory of Hygiene Organics Sections Neutral Extractable Method 1210 (5). The pesticides analyzed and the LODs for this method are in Table 2. Nitrate samples were analyzed using the State Laboratory of Hygiene Cadmium Reduction Method (LOD 0.1 mg/l) (6). The analytical method for pesticide analysis was virtually identical to the original study, although the limits of detection did vary between the WDATCP Bureau of Laboratory Services and the State Laboratory of Hygiene. The NO_3+NO_2 N limit of detection change, as compared to the original survey, was due to analysis of acidified samples (7).

Results

WDNR staff were able to resample 69 of the original 71 contaminated wells. The two wells not resampled were located in the Northeast and the Central ASDs. For purposes of discussion, their nearby wells will be included since the two unsampled wells did originally have pesticide detections. Statistical formulas, brief definitions and some of their limitations are presented in Appendix A.

Original Wells

Pesticide detections for the original wells and resampled wells are compared in Table 4, and a detailed comparison of the pesticide results, arranged by ASDs, is in Appendix B. Of the 69 resampled wells, 57 had detectable levels of one or more pesticides. A total of 50 wells contained atrazine alone while four wells had atrazine and alachlor; one well contained atrazine and metolachlor; one well contained atrazine, alachlor and cyanazine and one well contained alachlor alone. The median atrazine concentration of wells with atrazine detections was 0.36 µg/l, only two wells equaled or exceeded the atrazine ES of 3.5 µg/l and 31 of the wells contained atrazine at or above the PAL of 0.35 µg/l. The median atrazine concentration of the 64 wells which originally contained atrazine (recall that 66 wells originally contained atrazine, but two of these wells were unable to be resampled) was 0.38 µg/l. All alachlor detections were above the PAL of 0.05 µg/l. Additionally, 67 wells showed NO_3+NO_2 N detections with a median concentration of 9.4 mg/l. NO_3+NO_2 N was found at or above the PAL of 2 mg/l in 66 of the wells and in 32 of the wells at or above the ES of 10 mg/l.

Nearby Wells

A total of 212 nearby wells were sampled. Pesticide detections between resampled and nearby wells tabulated by ASDs are compared in Table 5. The detailed results are in Appendix C. One or more pesticides were detected in 63 (30%) of these wells. Atrazine alone was found in 57 wells; atrazine and alachlor were discovered in three wells; one well contained atrazine and metribuzin; one well contained atrazine, alachlor, metribuzin and cyanazine and one well had atrazine and metolachlor. The median atrazine concentration of wells with atrazine detections was

0.31 µg/l. Only one well equaled or exceeded the atrazine ES and 27 wells equaled or exceeded the PAL. A total of 188 wells showed NO_3+NO_2 N detections with a median concentration of 6.5 mg/l. It should also be noted that three of these wells contained NO_3+NO_2 N below 0.5 mg/l (the LOD for the original study), the median is 6.6 mg/l when these wells are omitted. NO_3+NO_2 N was found at or above the PAL in 168 of the wells and in 62 of the wells at or above the ES.

Discussion

Original Wells

A comparison of the original results for the 71 wells versus the 69 wells which were resampled confirms that a high percentage of wells are contaminated by pesticides and NO_3+NO_2 N. Pesticides were detected in 83% of the follow up wells and NO_3+NO_2 N detected in 97% of these wells. From the original study, 61% to 69% of the Grade A dairy farm wells statewide were estimated to contain NO_3+NO_2 N. Differences between ASDs were also noted which may help affirm the original study's observation of geographic distribution. Originally 90% of the wells in these impacted areas contained atrazine alone, whereas the follow up study indicated that only 72% of the wells contained solely atrazine. Alachlor remained a concern since all follow up detections were above the PAL.

Did the Atrazine Levels Decline?

Two issues must be addressed before considering if the levels of atrazine have declined.

First, are two samples representative of any trend in atrazine concentrations? No, the following statistic and decision that atrazine concentrations have declined only apply to the two samplings. The overall trend may be that atrazine concentrations are declining, rising or stable. Without long term monitoring, extrapolation of these results to a trend is impossible.

Secondly, have the levels of atrazine changed between the original sampling of the 64 wells and the follow up samples from the same wells? Procedures to be used by regulatory agencies to determine if a change in concentrations has occurred are provided by ch. NR 140.14 (2), Wis. Admin. Code. "The regulatory agency shall use one or more valid statistical procedures to determine if a change in the concentration of a substance has occurred. A significance level of 0.05 shall be used for all tests." The Wilcoxon paired-sample test was used since the data was not normally distributed (as determined using the procedure of D'Agostino (8)) and was symmetric around the median (9). From the Wilcoxon test, the atrazine concentrations in the follow up samples were found to be significantly different (α = 0.05) than

those in the original samples (Appendix D). Upon examination of the data, 40 of the original 64 wells with atrazine detections had a decrease in atrazine concentrations. Based upon these results, it has been concluded that there was a decrease in reported atrazine concentrations. These results do not apply to the entire population of all Grade A dairy farm wells statewide. Another random sample of wells from the entire Grade A dairy farm well population would be required rather than these follow up wells which were originally contaminated.

The median atrazine concentration of the 64 wells with original atrazine detections was 0.42 µg/l in the original study versus 0.38 µg/l for these same wells with atrazine detections in the follow up study. While the 64 originally sampled wells all had atrazine detections, only 54 of these same wells had atrazine detections in the follow up survey.

The difference between the two medians of 0.04 µg/l or decrease in reported concentrations is not necessarily due to a decrease in groundwater atrazine concentrations. Since two laboratories were used, the Department of Agriculture Trade and Consumer Protection laboratory in the original study and the State Lab of Hygiene in the follow up study, bias between laboratories and even variability in the analytical method are factors to be considered. Every laboratory has an associated bias, or deviations from a true value. Bias is tested by having each laboratory analyze split samples. Unfortunately this was not done in either the original or follow up studies and no other information on bias between the Department of Agriculture Trade and Consumer Protection laboratory and the State Lab of Hygiene atrazine analyses was available. In addition to interlaboratory error, intralaboratory error is also present. Variability in analytical method is inherent within laboratories due to both experimental and random error. Sampling error may also be present, since different samplers were used for the follow up study (the original study used WDATCP Food Division inspectors whereas the follow up study employed WDNR Water Supply samplers). One of these explanations or a combination of them could readily account for the 0.04 µg/l difference in median concentrations and could also explain the decrease in reported atrazine concentrations.

It is also possible that the difference in reported concentrations was a result of actual declines in amounts of atrazine in groundwater. There are several environmental factors which might explain such a decline.

Surveys of pesticide use by Wisconsin farmers have shown that use of atrazine has declined between 1985 and 1990, as shown in Table 6. Due in part to a reduction in the corn acres planted, about 1.3 million fewer acres were treated in 1990 than in 1985. Time may also be a factor. The original Grade A samples were collected during the winter of one of the most severe droughts on record, while the follow up samples were collected during the spring and summer of a period of more normal

rainfall. Also, an average of 482 days elapsed between the two samplings, as shown in Figure 2. During this time the well owners may have modified their atrazine handling practices due to their participation in the survey as well as due to the general heightened awareness among farmers about this issue. Given the slow rate of groundwater flow, it is difficult to conclude that enough time had elapsed for such changes to be manifested in the lower reported atrazine concentrations.

Nearby Wells

As anticipated, the nearby wells had less frequent contamination than the resampled wells, but were more frequently contaminated than the state proportion estimates calculated from the original Grade A study. Only 30% of nearby wells had detections of pesticides versus 83% for the resampled wells. Atrazine alone was found in 72% of the resampled wells whereas in only 27% of the nearby wells. NO_3+NO_2 N detections also followed this pattern—from 97% in the resampled wells to 89% in the nearby wells.

Table 7 compares the statewide and ASD proportion estimates for atrazine detections with the atrazine detection proportions observed in the nearby wells. The nearby wells are located in geographic areas identified from the original survey as having significant atrazine contamination. Therefore it was anticipated that atrazine would be detected more frequently in these wells than indicated by the statewide proportion estimates calculated from the original Grade A survey. This is confirmed by noting the statewide proportion of 0.30 for the nearby wells, which is considerably higher than the statewide upper bound of 0.15 estimated from the original study. This is largely due to the contribution of 33 detections from the South Central ASD. From Table 8, these wells are located mostly in Dane (17 of 36, p = 0.47) and Columbia (8 of 9, p = 0.89). Dane County had the highest frequency of atrazine detections in the original Grade A survey (12 of 22, p = 0.55), while Columbia County had the highest frequency of atrazine detections among the nearby wells.

Table 9 compares the statewide and ASD estimates for atrazine detections at or above the PAL with the nearby wells at or above the PAL. For nearby wells, the statewide proportion is only slightly above the upper bound from the original study. Again, the nearby wells in the South Central ASD contributed half of the wells at or above the PAL.

Sources of Contamination

The Grade A survey demonstrated that atrazine is the predominant pesticide contaminant in Wisconsin groundwater. A review of atrazine's use history may offer some explanations.

Prior to the late 1950s, farmers relied on mechanical cultivation to control weeds in corn. In 1958 the Geigy

Corporation made available research samples of a number of triazine derivative compounds, including atrazine, for evaluation for agricultural uses. At that time, atrazine was registered only for use as an industrial or non-selective herbicide. It performed very well in field trials, offering several advantages over simazine, which had been registered for agricultural use on field corn in 1958. Atrazine was more water soluble than simazine, could be utilized either in a pre- or post-emergence application, and was less persistent in soils than simazine. The successful performance of atrazine in field trials in 1958 resulted in it's registration for use on corn beginning in 1959.

Atrazine quickly became the most popular herbicide for broadleaf weed control in corn in Wisconsin. It was formulated as either a wettable powder or as a water dispersible granule. Most farmers did their own applications, mixing the product with about 25 gallons of water per acre to be treated. Recommended application rates were in the range of 2 to 4 pounds active ingredient per acre, with the higher rates used to control quackgrass in alfalfa fields being planted to corn. By 1969, 75% of Wisconsin's corn crop was treated with herbicides, primarily atrazine. That same year, atrazine first became available as a liquid, containing 4 pounds active ingredient per gallon of solution. By 1985, of the 4.2 million acres of corn treated with herbicides, 3.3 million, or 78%, were treated with atrazine.

Until recently, atrazine was thought to be very safe to handle and use, based on studies showing it had a low acute toxicity. As a result, until the 1991 growing season farmers did not have to receive any training and/or certification whatsoever to purchase and use atrazine. From visits to numerous farms and discussions with farmers, it appears that atrazine was handled in a very casual manner until the last several years. It was often mixed near the well, using a garden hose connected to a frost-proof hydrant, with no backflow prevention. Excess spray solution was often used to treat roadside brush or to control weeds around the farmstead. Rinse water from cleaning operations also may often have been released near the well.

Given the use history of atrazine, it is not surprising that many people believe that it's detection in Wisconsin groundwater is due solely to improper use. To attempt to resolve this issue, WDNR and WDATCP have jointly funded a number of research projects. Two of these are being conducted in Dane County, Wisconsin. One research group studied atrazine in groundwater at a Grade A dairy farm north of Madison. The soils on the farm are formed in loess (windblown silts of glacial origin) and the underlying glacial drift and are among the most productive soils in the state. Atrazine was detected in monitoring wells downgradient from corn fields where atrazine had not been mixed/loaded. However, the highest concentrations were detected in the well downgradient from the mixing/loading site, which may also have been influenced by corn fields in that same direction. The preliminary results from this study suggest that both use and

misuse appear to contribute to the contamination on this farm (12).

A second team of researchers studied atrazine in groundwater in the unglaciated landscape of western Dane County. The soils at this site are formed in loess and the underlying residuum from limestone bedrock. Atrazine was detected in monitoring wells finished in bedrock downgradient from corn fields where atrazine had been used and where no mixing/loading had been done (13).

The results of these two studies are supported by similar studies in other midwestern states, both in the field and under controlled laboratory conditions.

In summary, it is clear that atrazine has been mishandled during its long use history, and that some groundwater has been contaminated by such practices. Research conducted since the Grade A survey has demonstrated that atrazine can reach groundwater when applied to corn fields at label rates. Both processes have in all likelihood contributed to the pattern of atrazine detections in Wisconsin groundwater.

Conclusions

Original Wells

Resampling the 69 wells confirmed the presence of pesticides and nitrates and also differences in detections between ASDs. The data collected also increased the database of information which might aid in future decisions. There was a statistical difference between atrazine concentrations as detected in the 64 wells which originally contained atrazine versus atrazine concentrations in these same wells in the follow up study. Based upon the number of detections which decreased, it has been concluded that there was a decrease in reported atrazine concentrations. This decline does not necessarily imply a trend in atrazine reduction and several explanations for the median difference of 0.04 μg/l and decrease in atrazine concentrations were listed. Laboratory error (both bias and variability in laboratory method) and possibly sampling error could account for the 0.04 μg/l median difference and decrease in reported atrazine concentrations between the original and follow up samples. If the difference in reported concentrations was a result of actual declines in amounts of atrazine in groundwater, several environmental factors were proposed to explain such a decline. Changes in atrazine usage and handling practices along with seasonal changes and the time elapsed between samplings were cited as possible reasons for the differences in reported concentrations. A study akin to the original Grade A survey will be conducted by WDATCP in 1992-93, which will add to the picture of atrazine in Wisconsin groundwater.

Nearby Wells

Differences exist between the resampled and nearby wells. As anticipated, the nearby wells had less frequent contamination than the resampled wells, but were more frequently contaminated than the state proportion estimates calculated from the original Grade A study. Unfortunately, since well construction information was not readily available, no attempt was made to choose the nearby wells in the same aquifer as the original well. Distance and orientation (upgradient and downgradient) to the original wells was also not uniform. Thus, the extent of contamination cannot be determined, although the differing results between nearby and resampled wells do appear to suggest limited areas of contamination. Differences in detection frequency between the ASDs also exist for the nearby wells, although these differences are less pronounced than for the resampled wells.

Table 1. Detectable Analytes for State Laboratory of Hygiene Organics Section, Method 1200 (1).

ANALYTE	NITROGEN/PHOSPHORUS DETECTOR	ELECTRON CAPTURE DETECTOR
ALACHLOR	X	X
ALDRIN		X
ATRAZINE	X	
BENEFIN	X	X
BHC		X
BLADEX	X	
CASORON	X	X
CHLORDANE		X
CHLORDENE		X
CHLOROTHANLONIL	X	
CHLORPYRIFOS	X	X
DACTHAL	X	X
DDT & ANALOGUES		X
DIAZINON	X	X
DIELDRIN		X
DIMETHOATE	X	X
DISULFOTON	X	X
ENDOSULFAN		X
ENDRIN		X
EPTAM	X	X
FONOFOS	X	X
HCB		X
HEPTACHLOR		X
HEPTACHLOR EPOXIDE	X	
LINDANE		X
LINURON	X	X
MALATHION	X	X
METHAMIDAPHOS	X	X
METOLACHLOR	X	X
METHOXYCHLOR		X
METHYL PARATHION	X	X
PARATHION	X	X
PCB'S		X
PCNB		X
PENDAMETHALIN	X	X
PHORATE	X	
PHORATE-OXYGEN ANALOGUE	X	
PTHALATES		X
PROMETONE	X	X
SENCOR	X	X
SIMAZINE	X	
SUTAN	X	X
TERBUFOS	X	X
TRIFLURALIN	X	X

Note: Even though many compounds show up on both detectors, the nitrogen/phosphorus detector is specific for the organonitrogen and the organophosphorus analytes.

Table 2. Limits of Detection for Selected Pesticides for the State Laboratory of Hygiene Organics Section, Method 1210 (6).

ORIGINAL STUDY (samples analyzed at WDATCP Bureau of Laboratory Services)

PARAMETER	LOD --µg/l--
ALACHLOR (trade name Lasso)	0.15
ATRAZINE	0.15
CYANAZINE (trade name Bladex)	0.50
METOLACHLOR (trade name Dual)	0.30
METRIBUZIN (trade name Sencor)	0.05

FOLLOW UP STUDY (samples analyzed at the State Laboratory of Hygiene)

PARAMETER	LOD --µg/l--
ALACHLOR (trade name Lasso)	0.10
ATRAZINE	0.10
CYANAZINE (trade name Bladex)	0.90
METOLACHLOR (trade name Dual)	0.20
METRIBUZIN (trade name Sencor)	0.05

Table 3. Atrazine Detections and Usage for Grade A Dairy Farms (1).

Agricultural District	Total Grade A dairy farms	Number Sampled	Detects	(%)	Acres Treated With Atrazine in 1985
South Central	3,464	80	23	(28.8)	730,000
Southwest	3,422	78	13	(16.7)	506,000
West Central	3,899	87	10	(11.5)	501,000
East Central	3,725	82	6	(7.3)	443,000
Central	1,640	38	5	(13.2)	347,000
Northwest	2,755	64	4	(6.2)	244,000
North Central	2,178	48	2	(4.2)	233,000
Southeast	1,130	27	1	(3.7)	204,000
Northeast	1,330	30	2	(6.7)	144,000
Totals	**23,543**	**534**	**66**	**(12.6)**	**3,362,000**

Table 4. Results of Resampling 69* of the 71 Wells in the Grade A Dairy Farm Survey That Contained One or More Pesticides, by Agricultural Statistics District

Agricultural Statistics District	Original Wells With A Pesticide Detection	Wells Resampled	Pesticide Detections: Atrazine Original	Atrazine Resampled	Alachlor Original	Alachlor Resampled
Northwest	5	5	4	3	1	0
North Central	2	2	2	1	0	0
Northeast	2	1	2	0	0	0
West Central	11	11	10	9	1	1
Central	6	5	5	2	0	1
East Central	6	6	6	5	0	0
Southwest	15	15	13	15	0	2
South Central	23	23	23	20	1	2
Southeast	1	1	1	1	0	0
Total	71	69	66	56	3	6

Agricultural Statistics District	Pesticide Detections: Metolachlor Original	Metolachlor Resampled	Metribuzin Original	Metribuzin Resampled	No Pesticide Detected in Resampled Wells
Northwest	0	0	0	0	2
North Central	0	0	0	0	1
Northeast	0	0	0	0	1
West Central	0	0	0	0	1
Central	0	0	0	0	3
East Central	0	0	0	0	1
Southwest	1	1	1	0	0
South Central	0	0	0	0	3
Southeast	0	0	0	0	0
Total	1	1	1	0	12

* Unable to resample 2 wells

Table 5. Results of Resampling 69* of the 71 Wells in the Grade A Dairy Farm Survey That Contained One or More Pesticides and 212 Nearby Wells, by Agricultural Statistics District

Agricultural Statistics District	Sample Count		Pesticide Detections			
			Atrazine		Alachlor	
	Resampled Wells	Nearby Wells	Resampled	Nearby	Resampled	Nearby
Northwest	5	15	3	1	0	0
North Central	2	6	1	0	0	0
Northeast	1	7	0	0	0	0
West Central	11	31	9	11	1	0
Central	5	19	2	5	1	1
East Central	6	18	5	3	0	0
Southwest	15	44	15	10	2	0
South Central	23	69	20	33	2	3
Southeast	1	3	1	0	0	0
Total	69	212	56	63	6	4

Agricultural Statistics District	Pesticide Detections				No Pesticide Detected	
	Metolachlor		Metribuzin			
	Resampled	Nearby	Resampled	Nearby	Resampled	Nearby
Northwest	0	0	0	0	2	14
North Central	0	0	0	0	1	6
Northeast	0	0	0	0	1	7
West Central	0	0	0	0	1	20
Central	0	0	0	2	3	14
East Central	0	0	0	0	1	15
Southwest	1	1	0	0	0	34
South Central	0	0	0	0	3	36
Southeast	0	0	0	0	0	3
Total	1	1	0	2	12	149

* Unable to resample two wells

NOTE: Cyanazine was not detected in any of the resampled wells. It was detected in a single nearby well in the Central Agricultural Statistics District.

Table 6. Atrazine Use on All Crops, by Agricultural Statistics District, for 1985 and 1990 (10,11)

Agricultural Statistics District	Planted		Treated			
	x 1000 acres		x 1000 acres		Percent of Planted	
	1985	1990	1985	1990	1985	1990
Northeast	277.0	245.0	244.5	172.9	88	71
North Central	243.0	194.0	233.1	169.3	96	87
Northwest	189.0	152.0	143.8	61.0	76	40
West Central	622.0	566.0	500.8	405.4	81	72
Central	413.2	330.0	346.8	214.2	84	65
East Central	661.8	527.0	443.3	207.6	67	39
Southwest	700.0	573.0	505.7	289.2	72	50
South Central	970.2	811.0	729.9	440.0	75	54
Southeast	346.0	302.0	203.8	97.7	59	32
Other	14.0	--	10.2	--	73	--
Statewide	4436.2	3700.0	3361.9	2057.3	76	56

Table 7. Atrazine Detection Frequencies for the 212 Nearby Wells Sampled in the Grade A Follow Up, and Proportion Estimates for Atrazine Detects from the Original Grade A Survey.

	Grade A Follow Up Nearby Wells			
Agricultural Statistics District	Wells Sampled	Wells With Atrazine	P	Proportion Estimates from Original Grade A For Atrazine Detects*
Northwest	15	1	.07	.01 - .15
North Central	6	0	0	0 - .10
Northeast	7	0	0	0- .16
West Central	31	11	.35	.06 - .20
Central	19	5	.26	.04 - .28
East Central	18	3	.17	.01 - .13
Southwest	44	10	.23	.10 - .28
South Central	69	33	.48	.19 - .39
Southeast	3	0	0	0 - .12
Statewide	212	63	.30	.09 - .15

* 95 percent confidence interval

Table 8. Original and Follow Up Sampling Results in the Counties of the South Central Agricultural Statistics District

	Follow Up Sampling					
	Number of Wells		No Pesticide Detect			
County	Resampled	Nearby	Resampled	P	Nearby	P
Columbia	3	9	0/3	0	1/9	0.11
Dane	12	36	3/12	0.25	19/36	0.53
Green	4	12	0/4	0	9/12	0.75
Rock	4	12	1/4	0.25	7/12	0.58
Totals	23	69	4/23	0.17	36/69	0.52

	Pesticide Detects					
	Initial Sampling		Follow Up Sampling			
County	Detects	P	Resampled	P	Nearby	P
Columbia	3/8	0.38	3/3	1.0	8/9	0.89
Dane	12/22	0.55	9/12	0.75	17/36	0.47
Green	4/9	0.44	4/4	1.0	3/12	0.25
Rock	4/10	0.40	3/4	0.75	5/12	0.42
Totals	23/80	0.29	19/23	0.83	33/69	0.48

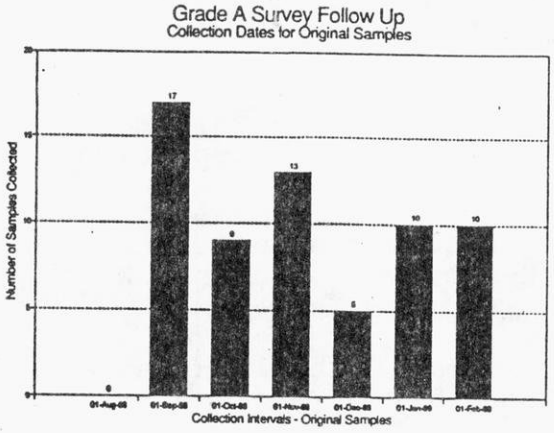
Table 9. Frequency of Detection of Atrazine Above the Preventive Action Limit (PAL) in the Grade A Follow Up and the Proportion Estimates from the Original Grade A Survey.

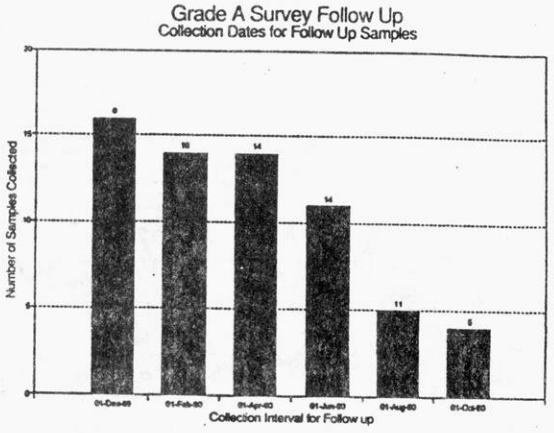
	Grade A Follow Up Nearby Wells With Atrazine Above PAL		
Agricultural Statistics District	Count	P	Proportion Estimates From Original Grade A Survey for Atrazine Above PAL*
Northwest	0	0	0 - .10
North Central	0	0	0 - .10
Northeast	0	0	0 - .09
West Central	5	0.16	.02 - .12
Central	3	0.16	0 - .17
East Central	0	0	N/A
Southwest	4	0.09	.03 - .15
South Central	12	0.17	.11 - .24
Southeast	0	0	0 - .12
Statewide	24	0.11	.05 - .09

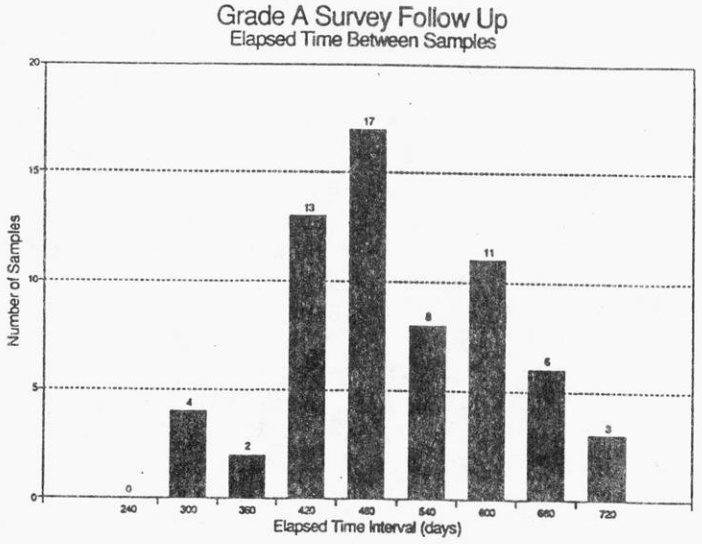
* 95 percent confidence interval

Figure 1. Wisconsin Agricultural Statistics Districts

Figure 2. Collection Dates and Elapsed Times for Original and Follow Up Samples







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APPENDIX

APPENDIX A. Statistical Formulas and Terms

Median

The middle concentration value of wells with detections.

95% Confidence Interval

In repeated sampling, with an infinite amount of samples, the computed confidence interval should contain the true population proportion 95% of the time.

$$\frac{N_i}{N} \pm 1.96 \sqrt{\frac{\frac{N_i}{N}\left(1 - \frac{N_i}{N}\right)}{N}}$$

N_i = number of elements in the i^{th} stratum

N = number of elements in the population

q = $1 - N_i$

Chi-square

Utilized a 2 X 2 contingency table with the null hypothesis that there is not an association between NO_3+NO_2 N detections at or above the PAL or ES and pesticide detections. α is the value at which the null hypothesis is rejected. It also shows the probability, with an infinite number of samples, that the null hypothesis would be rejected when it was true.

Wilcoxon Signed Rank Test

A nonparametric test that permits both the signs and the magnitudes of the differences to influence the inference. The only additional population assumption required is that of symmetry about the true median or median difference (8).

APPENDIX B. Results from Original Grade A Wells

District	County	Wuwn	Pesticide Detected in Original Sample	Concentration (µg/l)	Pesticide Detected in Follow-up Sample	Concentration (µg/l)
Northwest	Barron	CK580	Atrazine	.39*	Atrazine	.23
		CK585	Atrazine	1.05*	Atrazine	2.0*
		CK589	Atrazine	.19	ND	
	Chippewa	CK602	Atrazine	.46*	Atrazine	.51*
		CK611	Alachlor	.71**	ND	
		CK611	Metribuzin	.17	ND	
North Central	Clark	CK614	Atrazine	.53*	ND	
	Marathon	CK467	Atrazine	.55*	Atrazine	.39*
Northeast	Shawano	CK518	Atrazine	1.22*	No sample collected	
		CK524	Atrazine	.23	ND	
West Central	Eau Claire	CK658	Atrazine	.25	ND	
	Jackson	CK660	Atrazine	.38*	Atrazine	.30
		CK661	Atrazine	.53*	Atrazine	.57*
	Monroe	CK681	Atrazine	.31	Atrazine	.32
	Pierce	CK689	Atrazine	.37*	Atrazine	.40*
		CK690	Atrazine	.45*	Atrazine	.58*
	St. Croix	CK711	Atrazine	2.53*	Atrazine	2.8*
		CK718	Atrazine	.25	Atrazine	.27
		CK719	Atrazine	.15	Atrazine	.21
		CK722	Atrazine	.48*	Atrazine	.61*
	Trempealeau	CK747	Alachlor	5.87**	Alachlor	3.2**
Central	Green Lake	CK433	Atrazine	.16	Atrazine	.66*
					Alachlor	.49*
					Cyanazine	2.3*
		CK434	Atrazine	4.16**	Atrazine	5.8**
	Juneau	CK667	Atrazine	.64*	ND	
	Portage	CK512	Metribuzin	.44	ND	
	Waupaca	CK537	Atrazine	.86*	ND	
		CK542	Atrazine	.16	No sample collected	
East Central	Brown	CK393	Atrazine	.29	ND	
	Door	CK409	Atrazine	.16	Atrazine	.19
	Fond Du Lac	CK420	Atrazine	.33	Atrazine	.20
		CK422	Atrazine	.27	Atrazine	.24
		CK424	Atrazine	.27	Atrazine	.16
	Outagamie	CK495	Atrazine	.18	Atrazine	.28
Southwest	Grant	CK266	Atrazine	.35*	Atrazine	.22
		CK267	Alachlor	.50**	Atrazine	.14
		CK277	Atrazine	.25	Atrazine	.16
	Iowa	CK293	Atrazine	.35*	Atrazine	.50*
		CK299	Atrazine	.30	Atrazine	.26
		CK304	Atrazine	.62*	Atrazine	.37*
	Lafayette	CK317	Alachlor	1.95**	Alachlor	.82**
					Atrazine	.12
		CK321	Atrazine	.20	Atrazine	.24
		CK322	Atrazine	.62*	Atrazine	.46*
	Richland	CK334	Atrazine	1.05*	Atrazine	1.0*
	Sauk	CK346	Atrazine	.27	Atrazine	.10
		CK348	Atrazine	.25	Atrazine	.27
		CK353	Atrazine	.33	Atrazine	.18
					Alachlor	.21*
		CK355	Atrazine	19.40**	Atrazine	2.5*
		CK355	Metolachlor	.56	Metolachlor	.34
		CK356	Atrazine	1.91*	Atrazine	1.8*
South Central	Columbia	CK202	Atrazine	.58*	Atrazine	.54*
		CK205	Atrazine	4.43	Atrazine	7.3**
		CK206	Alachlor	.53**	Alachlor	.47*
		CK206	Atrazine	2.93*	Atrazine	3.3*

* Equals or exceeds preventive action limit
** Equals or exceeds enforcement standard
ND not detected

APPENDIX B. Results from Original Grade A Wells (cont'd)

District	County	Wuwn	Pesticide Detected in Original Sample	Concentration (µg/l)	Pesticide Detected in Follow-up Sample	Concentration (µg/l)
	Dane	CK215	Atrazine	.49*	Atrazine	.30
		CK217	Atrazine	1.24*	Atrazine	.45*
		CK219	Atrazine	.52*	Atrazine	.36*
		CK221	Atrazine	.57*	Atrazine	.74*
					Alachlor	.17
		CK224	Atrazine	.47*	Atrazine	.36*
		CK225	Atrazine	.20	ND	
		CK227	Atrazine	2.80*	Atrazine	1.1*
		CK228	Atrazine	.83*	Atrazine	.35*
		CK229	Atrazine	.45*	Atrazine	.26
		CK230	Atrazine	.18	Atrazine	.13
		CK233	Atrazine	.16	Atrazine	.98*
		CK234	Atrazine	.27	ND	
	Green	CK282	Atrazine	.23	Atrazine	.24
		CK284	Atrazine	1.41*	Atrazine	1.4*
		CK285	Atrazine	.26	Atrazine	.27
		CK288	Atrazine	.64*	Atrazine	1.1*
	Rock	CK337	Atrazine	.45*	Atrazine	.38*
		CK338	Atrazine	.80*	Atrazine	.72*
		CK339	Atrazine	.68*	ND	
		CK343	Atrazine	.19	Atrazine	.13
Southeast	Washington	CK377	Atrazine	.57*	Atrazine	.48*

* Equals or exceeds preventive action limit
** Equals or exceeds enforcement standard
ND not detected

APPENDIX C. Results of Follow Up Sampling

Agricultural Statistics District	County	Original	Follow Up	Follow Up NO_3-N (mg/l)	Follow Up Pesticide	Follow Up Concentration (µg/l)
Northwest	Barron	CK580		1.4	Atrazine	.23
			DL542	1.0	ND	
			DL543	4.8*	Atrazine	.23
			DL544	ND	ND	
			DL545	.1	ND	
		CK585		9.5*	Atrazine	2.0*
			DL539	3.6*	ND	
			DJ075	2.6*	ND	
		CK589		7.4*	ND	
			DL536	5.2*	ND	
			DL537	9.2*	ND	
			DL538	10.3**	ND	
	Chippewa	CK611		8.5*	ND	
			DL583	2.0*	ND	
			DL584	4.9*	ND	
			DL585	.2	ND	
		CK602		12.5**	Atrazine	.51 *
			DL623	3.7*	ND	
			DL624	.6	ND	
			DL625	2.5*	ND	
North Central	Clark	CK614		5.6*	ND	
			DL626	2.5*	ND	
			DL627	3.4*	ND	
			DL628	6.6*	ND	
	Marathon	CK467		7.1*	Atrazine	.39 *
			AV461	2.7*	ND	
			CH443	6.7*	ND	
			DJ856	5.9*	ND	
Northeast	Shawano	CK518	No sample collected			
			DM001	.5	ND	
			DM002	ND	ND	
			DM003	6.9*	ND	
			AO980	4.9*	ND	
		CK524		3.3*	ND	
			DJ750	11.8**	ND	
			DM004	15.2**	ND	
			DM005	22.8**	ND	
West Central	Eau Claire	CK658		5.0*	ND	
			DL608	3.5*	ND	
			DL609	3.1*	ND	
			DL610	4.4*	ND	
	Jackson	CK660		15.2**	Atrazine	.30
			DL606	9.8*	ND	
			DL607	5.6*	ND	
		CK661		5.5*	Atrazine	.57 *
			DL598	3.9*	Atrazine	.42 *
			DL604	22.7**	ND	
			DL605	14.6**	Atrazine	.21
	Monroe	CK681		5.7*	Atrazine	.32
			BG478	7.2*	ND	
			DL581	25.1**	ND	
			DL582	7.3*	ND	

* Equals or exceeds preventive action limit
** Equals or exceeds enforcement standard
ND not detected

APPENDIX C. Results of Follow Up Sampling (cont'd)

Agricultural Statistics District	County	Original	Follow Up	Follow Up NO_3-N (mg/l)	Follow Up Pesticide	Follow Up Concentration (µg/l)
West Central	Pierce	CK689		17.3**	Atrazine	.40 *
			DL601	ND	ND	
			DL602	3.5*	ND	
			DL603	5.1*	ND	
		CK690		7.7*	Atrazine	.58 *
			DL597	1.4	ND	
			DL599	11.4**	ND	
			DL600	6.0*	ND	
	St. Croix	CK711		4.6*	Atrazine	2.8 *
			DL592	4.3*	ND	
			DL593	4.0*	Atrazine	.13
			DL594	7.3*	ND	
		CK718		9.0*	Atrazine	.27
			DL586	10.1**	Atrazine	.56 *
			DL587	11.3**	Atrazine	.31
			DL590	11.9**	ND	
		CK719		6.8*	Atrazine	.21
			DL588	11.3**	Atrazine	.42 *
			DL589	13.0**	Atrazine	.17
			DL591	5.1*	Atrazine	.13
		CK722		3.8*	Atrazine	.61 *
			DK204	3.9*	Atrazine	.33
			DL595	2.6*	Atrazine	.51 *
			DL596	3.4*	Atrazine	.57 *
	Trempealeau	CK747		4.2*	Alachlor	3.2 **
			DL621	2.9*	ND	
			DL622	1.0	ND	
Central	Green Lake	CK434		13.0**	Atrazine	5.8 **
			AN895	13.9**	Atrazine	1.5 *
			AN899	30.4**	Atrazine	.30
			AP509	5.4*	ND	
		CK433		27.9*	Atrazine	.66*
					Alachlor	0.49*
					Cyanazine	2.3*
			AN987	16.8**	Atrazine	1.0 *
					Alachlor	.29*
					Cyanazine	1.5*
					Metribuzin	.33
			AN988	20.4**	Atrazine	.52 *
					Metribuzin	.18
			AN989	12.5**	Atrazine	.22
	Juneau	CK667		19.4**	ND	
			AA493	ND	ND	
			AW813	6.5*	ND	
			DJ852	5.4*	ND	
Central	Portage	CK512		ND	ND	
			AB970	1.7	ND	
			AO430	ND	ND	
			DJ845	ND	ND	

* Equals or exceeds preventive action limit
** Equals or exceeds enforcement standard
ND not detected

APPENDIX C. Results of Follow Up Sampling (cont'd)

Agricultural Statistics District	County	Original	Follow Up	Follow Up NO_3-N (mg/l)	Follow Up Pesticide	Follow Up Concentration (µg/l)
Central	Waupaca	CK537		17.9**	ND	
			A0979	4.8*	ND	
			DJ746	7.0*	ND	
			DJ747	7.4*	ND	
		CK542	No sample collected			
			DJ745	12.0**	ND	
			DJ748	8.7*	ND	
			DJ749	6.3*	ND	
			CM051	ND	ND	
East Central	Brown	CK393		ND	ND	
			A0975	ND	ND	
			A0976	ND	ND	
			A0977	ND	ND	
	Door	CK409		6.9*	Atrazine	.19
			A0973	6.4*	Atrazine	.13
			A0974	7.8*	Atrazine	.23
			EF014	6.2*	Atrazine	.12
	Fond du Lac	CK420		3.0*	Atrazine	.20
			AM388	ND	ND	
			AM389	ND	ND	
			AM430	ND	ND	
		CK424		12.4**	Atrazine	.16
			AM384	ND	ND	
			AM385	11.2**	ND	
			AM421	ND	ND	
		CK422		9.2*	Atrazine	.24
			AM386	3.0*	ND	
			AM387	2.9*	ND	
			AM429	2.4*	ND	
	Outagamie	CK495		11.6**	Atrazine	.28
			DM007	ND	ND	
			DM008	14.4**	ND	
			DM009	ND	ND	
Southwest	Grant	CK266		10.0**	Atrazine	.22
			AM433	16.7**	Atrazine	.31
			AM436	3.7*	ND	
			AM439	3.9*	ND	
		CK267		11.6**	Atrazine	.14
			AN661	6.2*	ND	
			AN662	5.5*	ND	
			AN670	6.4*	ND	
		CK277		4.7*	Atrazine	.16
			AN663	7.3*	ND	
			AN669	2.6*	ND	
Southwest	Iowa	CK293		9.4*	Atrazine	.50 *
			AM361	3.5*	ND	
			AM362	2.4*	ND	
			AM363	6.8*	Atrazine	.10

* Equals or exceeds preventive action limit
** Equals or exceeds enforcement standard
ND not detected

APPENDIX C. Results of Follow Up Sampling (cont'd)

Agricultural Statistics District	County	Original	Follow Up	Follow Up NO_3-N (mg/l)	Follow Up Pesticide	Follow Up Concentration (µg/l)
Southwest	Iowa	CK304		4.3*	Atrazine	.37 *
			AM364	4.5*	ND	
			AM365	3.2*	ND	
			AM366	4.6*	ND	
		CK299		12.5**	Atrazine	.26
			AM367	27.8**	Atrazine	1.4 *
			AM368	6.6*	ND	
			AM369	2.3*	ND	
	Lafayette	CK317		5.6*	Atrazine	.12
					Alachlor	.82 **
			AM395	3.2*	ND	
			AM396	2.6*	ND	
			AM397	2.3*	ND	
		CK321		11.4**	Atrazine	.24
			AM434	8.3*	Atrazine	.10
			AM435	9.5*	Atrazine	.26
			AN990	10.0**	ND	
		CK322		9.4*	Atrazine	.46 *
			AM394	3.0*	ND	
			AM431	8.5*	Atrazine	.86 *
			AN668	5.8*	Atrazine	2.5 *
	Richland	CK334		9.2*	Atrazine	1.0 *
			AM399	.9	ND	
			AM437	2.3*	Atrazine	.64 *
			AM438	.1	ND	
	Sauk	CK346		6.4*	Atrazine	.10
			AM465	1.5	ND	
			AM466	6.1*	ND	
			AM467	1.3	ND	
		CK348		20.6**	Atrazine	.27
			AM463	.5	ND	
			AM464	.9	ND	
			AM469	6.8*	ND	
		CK353		7.2*	Atrazine	.18*
					Alachlor	.21
			AM503	9.7*	ND	
			AM504	17.5**	ND	
			AM505	12.6**	ND	
		CK355		8.5*	Atrazine	2.5 *
					Metolachlor	.34
			AP498	15.0**	Atrazine	3.5 **
					Metolachlor	2.7 *
			AP499	3.7*	Atrazine	.12
			AP500	3.3*	ND	
		CK356		14.7**	Atrazine	1.8 *
			AN891	ND	ND	
			AN892	28.9**	ND	
			AN893	7.3**	ND	

* Equals or exceeds preventive action limit
** Equals or exceeds enforcement standard
ND not detected

APPENDIX C. Results of Follow Up Sampling (cont'd)

Agricultural Statistics District	County	Original	Follow Up	Follow Up NO_3-N (mg/l)	Follow Up Pesticide	Follow Up Concentration (µg/l)
South Central	Columbia	CK202		17.3**	Atrazine	.54*
			AM370	3.4*	ND	
			AM398	20.0**	Atrazine	.38*
					Alachlor	.56**
			AM400	13.1**	Atrazine	.20
		CK205		22.3**	Atrazine	7.3**
			AP492	17.1**	Atrazine	.26
			AP493	14.9**	Atrazine	0.89*
			AP494	1.6	Atrazine	0.18
			AP495	1.3	Atrazine	.89*
		CK206		14.2**	Atrazine	3.3*
					Alachlor	.47*
			AP496	17.2**	Atrazine	.31
			AP497	48.1**	Atrazine	1.9*
	Dane	CK215		15.5**	Atrazine	.30
			AM372	4.0*	ND	
			AM373	8.2*	ND	
			AM374	4.8*	ND	
		CK217		4.8*	Atrazine	.45 *
			AM501	ND	ND	
			AM502	1.6	ND	
			AM530	1.1	ND	
		CK219		16.2**	Atrazine	.36 *
			AM381	15.5**	ND	
			AM382	14.6**	ND	
			AM390	17.4**	Atrazine	.26
		CK221		8.0*	Atrazine	.74 *
					Alachlor	.17 *
			DL482	7.6*	Atrazine	.32
			DL489	4.2*	ND	
			DL490	17.0**	Atrazine	.11
		CK224		11.5**	Atrazine	.36 *
			AM471	6.5*	ND	
			AM472	7.2*	ND	
			AM473	21.7**	ND	
		CK225		15.2**	ND	
			AM474	18.4**	Atrazine	.27
			AM475	5.0*	Atrazine	.11
			AM476	1.9	ND	
		CK227		25.6**	Atrazine	1.1 *
			DL497	19.6**	ND	
			DL511	9.4*	Atrazine	.25
			AM529	24.4**	Atrazine	1.0 *
		CK228		4.2*	Atrazine	.35 *
			AM416	18.7**	Atrazine	2.3 *
					Alachlor	.15 *
			DL498	11.6**	ND	
			DL499	3.4*	ND	
		CK229		10.4**	Atrazine	.26
			AM377	8.6*	ND	
			AM426	15.0**	Atrazine	.30
			AM428	11.2**	Atrazine	.29

* Equals or exceeds preventive action limit
** Equals or exceeds enforcement standard
ND not detected

APPENDIX C. Results of Follow Up Sampling (cont'd)

Agricultural Statistics District	County	Original	Follow Up	Follow Up NO_3-N (mg/l)	Follow Up Pesticide	Follow Up Concentration (µg/l)
South Central	Dane	CK230		3.8*	Atrazine	.13
			AM375	16.3**	Atrazine	1.2 *
			AM376	19.7**	Atrazine	1.1 *
					Alachlor	0.12 *
			AM378	10.6**	Atrazine	.26
		CK233		17.0**	Atrazine	.98 *
			DL486	12.5**	Atrazine	.28
			DL487	32.3**	ND	
			DL488	17.3**	Atrazine	.51 *
		CK234		6.7*	ND	
			DL483	24.9**	Atrazine	.82 *
			DL484	2.6*	ND	
			DL485	15.7**	Atrazine	.12
	Green	CK282		11.4**	Atrazine	.24
			AM412	10.9**	Atrazine	.18
			AM417	1.2	ND	
			AM418	7.3*	ND	
		CK284		13.8**	Atrazine	1.4 *
			AM413	ND	ND	
			AM414	13.1**	Atrazine	1.7 *
			AM415	8.4*	ND	
		CK285		11.5**	Atrazine	.27
			AM468	17.0**	Atrazine	.39 *
			AM525	4.5*	ND	
			AM526	2.5*	ND	
		CK288		22.8**	Atrazine	1.1 *
			AM419	10.5**	ND	
			AM420	4.6*	ND	
			AO409	4.8*	ND	
	Rock	CK337		16.8**	Atrazine	.38 *
			AM422	32.6**	Atrazine	.15
			AM477	7.9*	ND	
			AM480	12.8**	ND	
		CK338		17.3**	Atrazine	.72 *
			AM461	6.6*	Atrazine	0.44 *
			AM462	ND	ND	
			AM470	13.2**	Atrazine	.49 *
		CK339		5.3*	ND	
			AM423	11.0**	Atrazine	.25
			AM424	4.4*	Atrazine	.12
			AM479	3.3*	ND	
		CK343		9.2*	Atrazine	.13
			AM371	5.4*	ND	
			AM379	2.0*	ND	
			AM380	8.6*	ND	
Southeast	Washington	CK377		10.6**	Atrazine	.48 *
			DK803	ND	ND	
			DK804	ND	ND	
			DK808	ND	ND	

* Equals or exceeds preventive action limit
** Equals or exceeds enforcement standard
ND not detected

APPENDIX D. Wilcoxon Signed Rank Test

Raw Data For Wilcoxon Signed Rank Test

Wuwn	Count	Original Grade A [Atrazine] (µg/l)	Follow Up Grade A [Atrazine] (µg/l)	Diff	Abs Value of Diff	Rank of Minuses	Count of Minuses
CK681	1	0.315	0.320	-0.005	0.005	1	1
CK282	2	0.235	0.240	-0.005	0.005	2	2
CK284	3	1.41	1.40	0.01	0.01	0	0
CK285	4	0.258	0.270	-0.012	0.012	4	3
CK348	5	0.254	0.270	-0.016	0.016	5	4
CK718	6	0.25	0.270	-0.02	0.02	0	5
CK409	7	0.164	0.190	-0.026	0.026	7	6
CK422	8	0.267	0.240	0.027	0.027	0	0
CK689	9	0.365	0.400	-0.035	0.035	9	7
CK321	10	0.202	0.240	-0.038	0.038	10	8
CK299	11	0.299	0.260	0.039	0.039	0	0
CK202	12	0.581	0.540	0.041	0.041	0	0
CK661	13	0.529	0.570	-0.041	0.041	13	9
CK334	14	1.05	1.00	0.05	0.05	0	0
CK602	15	0.455	0.510	-0.055	0.055	15	10
CK230	16	0.185	0.130	0.055	0.055	0	0
CK343	17	0.187	0.130	0.057	0.057	0	0
CK719	18	0.15	0.210	-0.06	0.06	18	11
CK337	19	0.455	0.380	0.075	0.075	0	0
CK660	20	0.377	0.300	0.077	0.077	0	0
CK338	21	0.802	0.720	0.082	0.082	0	0
CK377	22	0.571	0.480	0.091	0.091	0	0
CK277	23	0.253	0.160	0.093	0.093	0	0
CK495	24	0.182	0.280	-0.098	0.098	24	12
CK424	25	0.267	0.160	0.107	0.107	0	0
CK356	26	1.91	1.80	0.11	0.11	0	0
CK224	27	0.470	0.360	0.110	0.110	0	0
CK690	28	0.454	0.580	-0.126	0.126	28	13
CK420	29	0.326	0.200	0.126	0.126	0	0
CK722	30	0.481	0.610	-0.129	0.129	30	14
CK266	31	0.354	0.220	0.134	0.134	0	0
CK293	32	0.350	0.500	-0.150	0.150	32	15
CK353	33	0.333	0.180	0.153	0.153	0	0
CK580	34	0.387	0.230	0.157	0.157	0	0
CK219	35	0.519	0.360	0.159	0.159	0	0
CK467	36	0.550	0.390	0.160	0.160	0	0
CK322	37	0.621	0.460	0.161	0.161	0	0
CK221	38	0.569	0.740	-0.171	0.171	38	16
CK346	39	0.274	0.100	0.174	0.174	0	0
CK229	40	0.445	0.260	0.185	0.185	0	0
CK589	41	0.193	0.000	0.193	0.193	0	0
CK215	42	0.495	0.300	0.195	0.195	0	0
CK225	43	0.197	0.000	0.197	0.197	0	0
CK524	44	0.234	0.000	0.234	0.234	0	0
CK658	45	0.251	0.000	0.251	0.251	0	0
CK304	46	0.625	0.370	0.255	0.255	0	0
CK711	47	2.53	2.80	-0.27	0.27	47	17
CK234	48	0.272	0.000	0.272	0.272	0	0
CK393	49	0.292	0.000	0.292	0.292	0	0
CK206	50	2.93	3.30	-0.37	0.37	50	18
CK288	51	0.638	1.10	-0.46	0.46	51	19
CK228	52	0.829	0.350	0.479	0.479	0	0
CK433	53	0.164	0.660	-0.496	0.496	53	20
CK614	54	0.528	0.000	0.528	0.528	0	0
CK667	55	0.638	0.000	0.638	0.638	0	0
CK339	56	0.681	0.000	0.681	0.681	0	0
CK217	57	1.24	0.450	0.79	0.79	0	0
CK233	58	0.160	0.980	-0.82	0.82	58	21
CK537	59	0.862	0.000	0.862	0.862	0	0
CK585	60	1.05	2.00	-0.95	0.95	60	22
CK434	61	4.16	5.80	-1.64	1.64	61	23
CK227	62	2.80	1.10	1.70	1.70	0	0
CK205	63	4.43	7.30	-2.87	2.87	63	24
CK355	64	19.4	2.50	16.9	16.9	0	0
					sum	679	24

Wilcoxon Signed Rank Test

Ho: The follow up atrazine concentrations are the same as the original atrazine concentrations

Ha: The follow up atrazine concentrations are not the same as the original atrazine concentrations

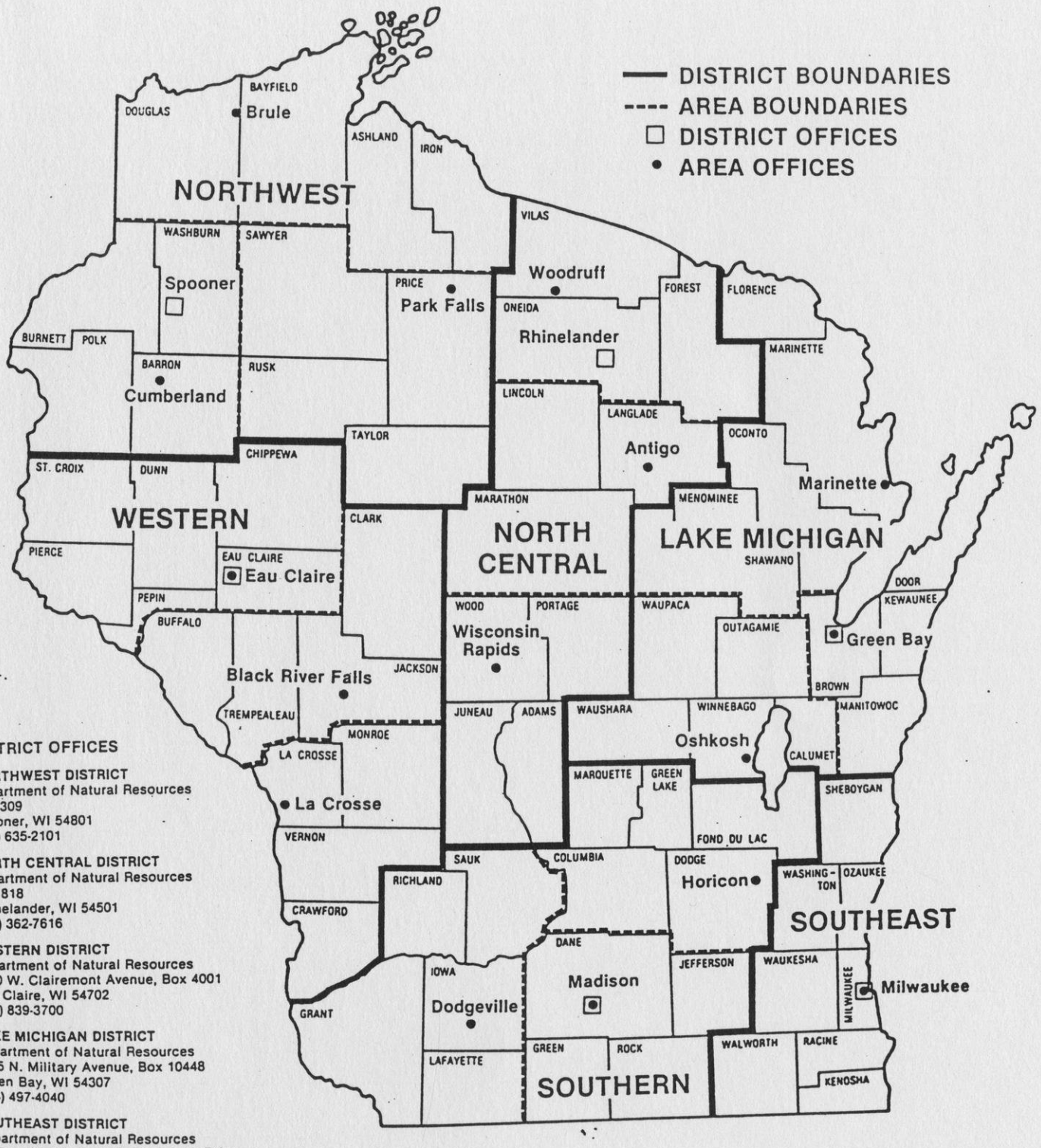
The critical value of T for n=64, two-tailed test, and alpha of 0.05 = 747
T = sum of less frequent ranks = 679, m = count of less frequent ranks = 24, n = 64

$T' = m(n+1)-T = 24(65)-679 = 881$

If either T or T' is less than or equal to the critical value of T (in this case 747), reject the null hypothesis

T = 679 and is less than 747 so the null hypothesis of no difference between original and follow-up atrazine concentrations is rejected

DNR FIELD DISTRICTS AND AREAS



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