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# Kansas Geological Survey

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## Results of Agrichemical Survey of Ground Water in Kansas, 1993-1994

by

M.A. Townsend, D.P. Young and J. Healey

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The University of Kansas, Lawrence, KS 66047 Tel. (913) 864-3965

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# **Results of Agrichemical Survey of Ground Water in Kansas, 1993-1994**

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## **ABSTRACT**

During 1993-1994 the Kansas Geological Survey sampled 78 wells in the state of Kansas as part of the Novartis Crop Protection atrazine reregistration study. Wells were selected for sampling based on availability of wells logs and stratigraphic information, and presence of a shallow water table. Of the 78 wells sampled, 58 had well logs and for the remaining 20, well logs were added from wells in the same or an adjacent quarter section. Well depth ranged from 6.6 m to 64 m with a mean of 26 m. Depth to water ranged from 2.6 to 29 m with a mean of 10 m.

Samples were analyzed for atrazine, several metabolites of atrazine, and nitrate. Atrazine concentrations ranged from no detect ( $< 0.1$  ppb) to 5.1 ppb. Of the 78 samples collected, 60 were  $< 0.10$  (detection limit), 16 were between 0.10 and 3.0 ppb (drinking water limit), and 2 were  $> 3.0$  ppb. The two samples with atrazine above the drinking water limit had probable point sources of contamination.

The most common metabolite, deethylatrazine, was detected in 23 samples. Of those 23, five wells had no detectable atrazine. This suggests that the daughter products may be more mobile and/or persistent than the parent product.

Deethylatrazine/atrazine ratios (DAR) have been used by other researchers to evaluate the rate of movement of agrichemicals to ground water with values  $> 1.0$  indicating rapid movement. In this study, DAR ranged from 0.12 to 5.0 indicating that the rate of movement of atrazine and its metabolites varies widely.

The less common daughter products deisopropylatrazine and hydroxy-atrazine occurred together in 7 samples and were each detected separately in 4 additional samples. All 15 of these samples had detectable atrazine.

Nitrate-N concentrations ranged from 0.04 to 40.2 ppm with a mean concentration of 8.4 ppm. Of the samples collected, 25 were  $< 3$  mg/L, 28 were between 3 and 10 mg/L, and 25 were  $\geq 10$  mg/L (drinking water limit). In terms of numbers of samples above the drinking water limit, nitrate contamination appears of greater concern than either atrazine or its metabolites.

Factors related to the occurrence of atrazine, atrazine metabolites, and nitrate in ground water are occurrence of clay in the stratigraphic column, soil permeability, depth to water, distance from chemical application or mixing point, irrigation well density, the occurrence of surface water/ground water interaction, and geographic location.

## Introduction

Many studies in the United States and worldwide have found that agricultural chemicals are a major source of nonpoint source contamination. The two most common classes of agricultural chemicals that can impact the usability of ground water are nitrogen sources such as commercial fertilizers, animal wastes, and soil organic nitrogen; and pesticides. In many midwestern states, herbicides are the most common class of pesticides used in farming; atrazine is the dominant chemical used in areas growing corn and grain sorghum in the midwest (Burkart and Kolpin, 1993; Ciba-Geigy Corp, 1992). The most commonly studied compounds are nitrate and atrazine and its metabolites deethylatrazine and deisopropylatrazine. Atrazine, deethylatrazine, and nitrate are commonly found in both surface and ground waters. Deisopropylatrazine is most often found in surface rather than ground waters. Recent research indicates that although hydroxyatrazine rarely occurs in ground water its presence in surface water may be more common than previously known (Lerch et al., 1998).

Review of the literature indicates that in the more western portion of the midwestern corn belt, higher percentages of herbicide detections, particularly atrazine and its metabolites, are found in the surface and ground water than in the eastern portion (Kolpin and Burkart, 1993). In Kansas much of the work evaluating the occurrence of herbicides has been done on surface water, particularly in northeastern Kansas where primarily corn and sorghum are grown. In this part of the state the mean annual rainfall is approximately 35 inches/year and generally occurs during the growing season of April through September. The topography, geology, and soils in this area make it conducive for overland flow to streams and rivers in the area rather than infiltration to the ground water. As a result, atrazine concentrations are generally highest in the streams after the spring flush and decrease with time (Pope, 1995; Stamer et al., 1994). Because much of the surface drainage feeds into reservoirs used for drinking water supplies, recreational use, and irrigation, storage of the spring runoff with higher concentrations of atrazine can

result in delayed release of water with atrazine concentrations above the 3 ppb EPA drinking water limit (Stamer et al., 1994).

Another result of spring runoff can be the infiltration of surface water with higher atrazine concentration into adjacent alluvial aquifers. The excess surface water is stored as bank storage and then released as base flow as the surface-water level decreases. This can result in two conditions: (1) the continued detection of high atrazine concentration in the surface water and the possible use of this water by downstream municipalities that rely on surface water for drinking water, or (2) the mixing of bank-stored surface water with regional ground water and the movement of these contaminated waters to wells installed in the alluvial aquifer. Both of these scenarios could result in limitations on the use of the ground and surface water and affect the volume of potable water available within a particular aquifer.

Nitrate concentrations in surface water in Kansas are generally below the accepted background level of 3 ppm (Madison and Brunett, 1985). In contrast, many studies of nitrate in ground water have shown concentrations well above the drinking water limit (Townsend and Young, 1994; Townsend and Sleezer, 1995; Townsend et al., 1993).

Statewide studies on the occurrence of atrazine and nitrate in ground water in Kansas have generally been limited to one-time surveys to determine the presence or absence of the compound. The studies discussed below do not consider the potential seasonal/temporal or spatial variations that may have an impact on the occurrence of atrazine or nitrate in ground water.

Steichen et al. (1989) found that 4 out of 100 wells sampled in a random sampling design across Kansas had atrazine concentrations above the drinking water limit. A total of 8 wells in the study had other pesticide(s) detected in the well water. In contrast 28 wells had nitrate-N above the drinking water limit of 10 ppm.

In a study to identify the factors affecting water quality in Kansas, Koelliker et al. (1987) found that nitrate concentrations were related to geographical and precipitation regions of the state. Higher nitrate levels were found in the northeast,

north-central, and south-central regions of Kansas and in regions where precipitation ranged from 26-35 inches per year.

A study by Perry and Anderson (1988) showed that of 41 chemigation and 70 conventional irrigation wells, 4.5 % of the wells had atrazine detects but that all values were below the 3 ppb drinking water limit. The areas with the detections have shallow water tables and coarse-textured soils, favorable conditions for the movement of atrazine to ground water. Of the wells sampled, approximately 10% had nitrate-N above the drinking water limit of 10 ppm.

Factors that may affect the movement of atrazine and nitrate through the unsaturated zone to ground water include: management of agrichemicals and water, surface soil type, and vadose zone stratigraphy. The resulting occurrence of atrazine or nitrate in ground water may also be affected by depth to water, depth of the well, and irrigation well density.

A site study done by Sophocleous et al. (1990) in south-central Kansas showed by means of flood recharge experiments that atrazine did not move through the unsaturated zone to the ground water in spite of evidence of macropore flow at one of the sites. Atrazine metabolites were detected in the soil water but not the ground water indicating that atrazine was degraded enroute through the unsaturated zone, but was not moving fast enough with the soil water to reach the ground water, at least during the time period of the study. The stratigraphy of the unsaturated zone and the aquifer included interfingered non-continuous sand and silty clay layers. The results of the experiment suggested that atrazine was degraded because the retardation of water by silty-clay layers permitted adsorption of the atrazine onto the clays and also permitted biodegradation processes to occur.

In contrast, nitrate was found at all depths of soil water and in concentrations above the drinking water limit throughout the aquifer. The presence of high nitrate concentrations and no atrazine or metabolites in the ground water suggests that the unsaturated zone may be a relatively effective barrier to the movement of atrazine but not to the movement of nitrate. Unlike the results of studies in Nebraska

(Spalding and Exner, 1993) high nitrate concentrations in the ground water in Kansas do not necessarily indicate an increased likelihood of atrazine being present.

The vertical and areal distribution of nitrate below an irrigated field in sandy soil indicated that clay layers in the unsaturated and saturated zones retard but do not prevent the movement of water and nitrate through the system (Townsend et al., 1993). High nitrate-N concentrations (> 10 mg/L) occurred both in the unsaturated zone and in the shallow aquifer (10 - 20 m). Clay layers retarded the movement of nitrate and occasionally caused perched zones where some denitrification occurred, but overall the nitrate moved unchanged from the land surface to the ground water.

### **Current Study**

The Kansas Department of Agriculture (KDA) was contracted by Waterborne Environmental Inc. to conduct a survey of the occurrence of atrazine in ground water as part of a 22 state study for the reregistration of atrazine with the U. S. EPA by Novartis Inc. (previously Ciba-Geigy). This study was to evaluate the occurrence of atrazine in shallow ground water in areas of the state of Kansas, and elsewhere, where corn and/or grain sorghum were most frequently grown. As a secondary objective, the Kansas Geological Survey elected to sample for nitrate-N to assess the variability of nitrate in ground water across the state.

This study is a point-in-time reconnaissance study. No attempt was made to link the concentrations of nitrate or atrazine and its metabolites to seasonal changes or specific farming methods used within the area of study.

## **Methods**

The Kansas Geological Survey (KGS) was subcontracted by the Kansas Department of Agriculture and Waterborne Environmental, Inc. to do site selection and ground-water sampling from the fall of 1993 to fall of 1994. Criteria for site selection, sampling protocols, and record keeping were presented to the KGS by

Waterborne Environmental, Inc. Samples were collected and sent to Novartis, Inc. for atrazine and atrazine daughter product analysis; the detection limit was 0.1 ppb for both atrazine and daughter products. Final results from the laboratory were received in the summer of 1995. In addition to atrazine, deethylatrazine and deisopropylatrazine were analyzed as well as hydroxyatrazine and some additional daughter products, which are not commonly tested for in ground water. Duplicate samples were sent to KDA for atrazine analysis (detection limit of 0.04). A separate set of samples was collected for and analyzed for nitrate by the Ultraviolet column method in the KGS Analytical Services Laboratory (Hathaway, 1990). The detection limit was 0.04 ppm as nitrate-nitrogen for this analysis. All chemical analyses are reported in Appendix B. Duplicate samples are indicated by a "B" in the sample ID number.

### **Well Site Selection Criteria**

An attempt was made to select sites that met the following criteria: shallow depth to ground water of less than 10 m (30 ft); limited amount of clay in the subsurface; located near irrigated fields planted with corn or sorghum in recent years; domestic or municipal wells, although monitoring wells were also acceptable; availability of lithologic well log; and permission of well owner. The amount of clay in the stratigraphic section was difficult to minimize because of the quantity of clay present in the alluvial aquifers of Kansas.

Location of irrigated sites was used as a preliminary tool for selection of wells to be sampled. An inventory of irrigation use for corn, grain sorghum, and multiple crops for the eastern two-thirds of Kansas for 1991 was used to select counties for possible well selection sites (Darrel Eklund, KWO, 1994, personal communication). Use of this data base permitted selection from areas of the state where the crops of interest were grown.

Well-drillers' logs, available at the KGS, include information on type of well, well depth, screen depth, depth to water, grout interval, legal location, and lithologic

log. These records were evaluated for the counties of interest and locations of sites verified using 7.5 minute topographic maps and rural county phone books.

Domestic wells were selected in areas where irrigation well records existed, where there was an indication that corn or grain sorghum had been planted in recent years, and where a well log existed for the domestic well. An attempt was made to select several farmsteads within an area as alternatives in case permission to sample was denied, the farmstead was abandoned, or a well log did not exist for a particular site. The Kansas Department of Agriculture sent notification to well owners requesting permission to sample and indication of times the well owner would be available to answer a questionnaire concerning their well. Several municipal wells were selected because of past records of detections of atrazine in the well water. These wells were sampled if a well log was available, personnel were available to assist in sampling the wells, and the well fields were located near irrigated corn or sorghum growing areas.

### **Overview of Sampling Procedures**

All water samples obtained throughout the state of Kansas were collected in strict compliance with the protocols established by the US Environmental Protection Agency (EPA). These established protocols, including Good Laboratory Practices (GLP) and Standard Operating Procedures (SOP), were followed to minimize data collection errors in accordance to the guidelines and instructions of Waterborne Environmental Inc. (WEI) and Quality Environmental (QE). All data forms and other paperwork were composed by WEI. The forms include: well information and inspection, sketch of well location with respect to buildings and other physical features, purging parameters, and chain of custody (Appendix A).

Eighty-four samples (78 water samples plus 6 duplicates) across the state were collected. Sampled wells may be divided into two groups according to required sampling protocols. The two groups are: 1) domestic and public water supply wells and 2) monitoring wells. Ninety five percent of the wells sampled were in service for

domestic or municipal use. The municipal wells comprised 14% of the total samples. The remaining 5% of the sampled wells are monitoring wells owned, maintained, and periodically sampled by regional Groundwater Management Districts.

### **Available Databases**

The STATSGO (NRCS, 1994) and 24K Soil Survey Data (NRCS, 1995) soil databases were used to obtain soil texture classifications for each sampling point. The ARC-INFO package, v. 7.0.4, (ESRI, 1994) and ARC-VIEW, v. 3.0 (ESRI, 1996) were used to plot the sampling points, chemical values, and soil polygons. Irrigation well density was determined from the WIMAS data base (KS Dept. Agriculture, 1993).

### **Irrigation Well Density Calculation**

Irrigation well density was determined by constructing circles with radii of 1.6 km (1 mile) and 3.2 km (2 miles) around the sampling point. The number of wells falling within the circumference of the circle was used as the irrigation well density associated with that point.

### **Statistical Data Analysis**

Statistical analyses were performed using the SAS statistical package, v.6.12, (SAS Institute, 1996). Data analysis included use of the nonparametric statistical method Mann-Whitney U test (similar to Student's t-test). Because much of the herbicide data was censored (less than the detection limit of 0.10 ppb) the nonparametric methods permit limited data analysis. This method relies on ranking of the data and using an averaged rank value for samples with the same value. Use of substitution of a smaller value for the censored value (in this case 0.01) permits evaluation of the data without utilizing the actual values of the data.

Because much of the atrazine and the daughter product data is censored (below detection limit) it is possible to calculate a median value for the dataset but not a mean. The Mann-Whitney test was set up as a two-tailed test. This means that the test determines if a statistical difference exists between the proposed categories but it does not determine if one category is larger than another. We used this form of the test for the evaluation of the atrazine data.

The Mann-Whitney test can also be set up as a directional test. In this case the test determines if a statistical difference exists and also which category is larger. We used this method for the nitrate tests because we had measurable values for all of the sampling points.

The value for determining acceptance or rejection of a test result is  $p \leq \alpha$  where  $\alpha = 0.10$ . This level of significance means that there is a one in ten chance of rejecting the null hypothesis when in fact it is true. Considering the sample size (78) and the fact that the sampling points were not randomly selected by use of a random number generator or other impartial device, we feel that 0.10 is an acceptable limit. Only those results which were found to be significant are reported in this study.

## **Results and Discussion**

The locations for sites used in this study are shown in figure 1. Legal locations and data associated with these points are listed in Appendix B of this report. This section is divided into two subsections: evaluation of the total data set and evaluation of regional data sets.

Statistical analyses were run on the complete data set (78 samples) to determine trends and relationships between parameters. Because of observed differences in a number of the variables due to geographical regions, the data was also separated by region (northeast and south-central Kansas) and various relationships were evaluated.



## **Potential Factors Affecting Concentrations of Atrazine and Nitrate**

Many studies have evaluated land use, soil properties, hydrologic and geologic factors, as well as agricultural factors such as crops grown, agrichemicals used, and density of irrigation wells near the sampled well to determine a suite of factors that describe the best predictors for determining the vulnerability of a given site (Kolpin et al., 1997; Kolpin and Burkhart, 1995; Druliner et al., 1996; Chen and Druliner, 1987; Exner and Spalding, 1990). Based on the results of work from other states cited previously, the relationships of various factors with the observed concentrations of nitrate and/or atrazine and its daughter products in ground water were evaluated. The factors evaluated included: distance of application area of agrichemicals from sampled well, volume of clay in the upper 3 m of the stratigraphic profile, depth of well, depth to water, irrigation well density near a sampling point, soil texture estimates, age of well, depth to top of well screen, total clay above well screen, and geographic location of sample site. Only the tests with statistically significant results are discussed.

## **Summary of Basic Statistics for Total Dataset**

A summary of basic statistics (minimum, maximum, mean and median) for all samples collected in the study is given in table 1. The factors listed in this table reflect the parameters that were evaluated. Many of the factors were found to have a significant effect on the concentration of atrazine and/or nitrate-N in ground water in other parts of the United States. No mean values are presented for the atrazine, deethylatrazine, and deisopropylatrazine values in table 1 because of the large number of non-detects in the study.

**Table 1. Summary of Basic Statistics for Factors Examined in Study**

Factor	Number Samples	Minimum Value	Maximum Value	Mean	Median
Well Depth (m) *	78	6.6	64	26	25
Top of Screen (m) *	78	2.3	50.6	18.5	17
Well age (yrs)	78	0.33	63	14.4	12.5
Depth to Water (m) *	78	1.8	38.8	10.2	7.5
Application Distance (m) *	78	0	883	102.6	33.3
Total Clay above screen (m) *	78	0	41.6	7.4	5.3
Volume of Clay in Upper 3.3 m *	78	0	100	45.9	46
Volum of Clay in Upper 8.3 m *	78	0	100	50.2	49.3
Nitrate-N (ppm)	78	<0.04	40.2	8.4	6.5
Atrazine (ppb)	78	<0.1	5.1		<0.10
Deethylatrazine (ppb)	78	<0.1	1.1		<0.10
Deisopropylatrazine (ppb)	78	<0.1	0.32		<0.10
SUM (Atr + Daughter Products)	26	0.11	6.03	1.02	0.62
DAR (Atrazine/Deethylatrazine)	17	0.12	5	1.4	0.62
Soil Texture Estimate	78	1	8	5.1	6
Irrigation Well Density 1.6 km **	78	0	19	4	4
Irrigation Well Density 3.2 km **	78	0	48	15	14

\*Multiply meter values by 3.281 to obtain feet. \*\* 1.6 km = 1 mile; 3.2 km = 2 miles.

### **Distribution of Atrazine and Nitrate-N Values**

Preliminary evaluation of the atrazine data shows that 77% of the wells sampled had atrazine levels below the detection limit of 0.1 ppb; 21% of the samples were between 0.1 and 3 ppb (U. S. EPA drinking water limit for atrazine; and 2% were above 3 ppb and are considered indicative of probable point sources (fig. 2). Figure 3 shows the distribution of atrazine concentration at the sampling sites.

Preliminary evaluation of the nitrate-N data shows that 32% of the sampled wells had nitrate-nitrogen levels below the background level of 3 ppm; 36% of the samples had nitrate-N concentration between 3 ppm and 10 ppm; and 32% of the wells had concentrations greater than the drinking water limit (fig. 2). These preliminary results indicate that nitrate in ground water in Kansas is of potentially

greater concern than the occurrence of atrazine. Figure 4 shows the distribution of nitrate-N concentrations at the sampling sites.

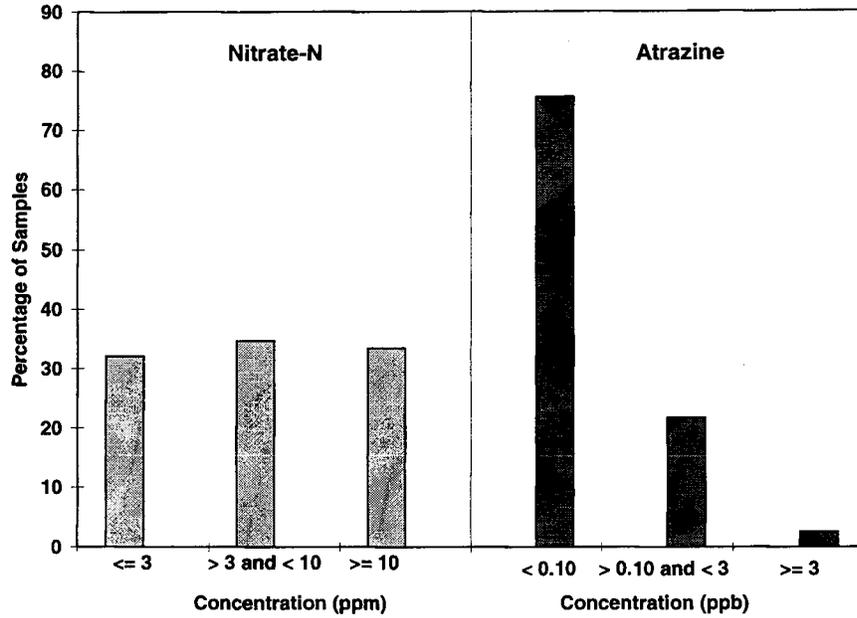


Figure 2. Range of atrazine and nitrate-N values for total data set (78 samples). Graph illustrates that nitrate-nitrogen contamination of ground water may be of greater concern than atrazine. Numbers above bars indicate number of samples in each class.

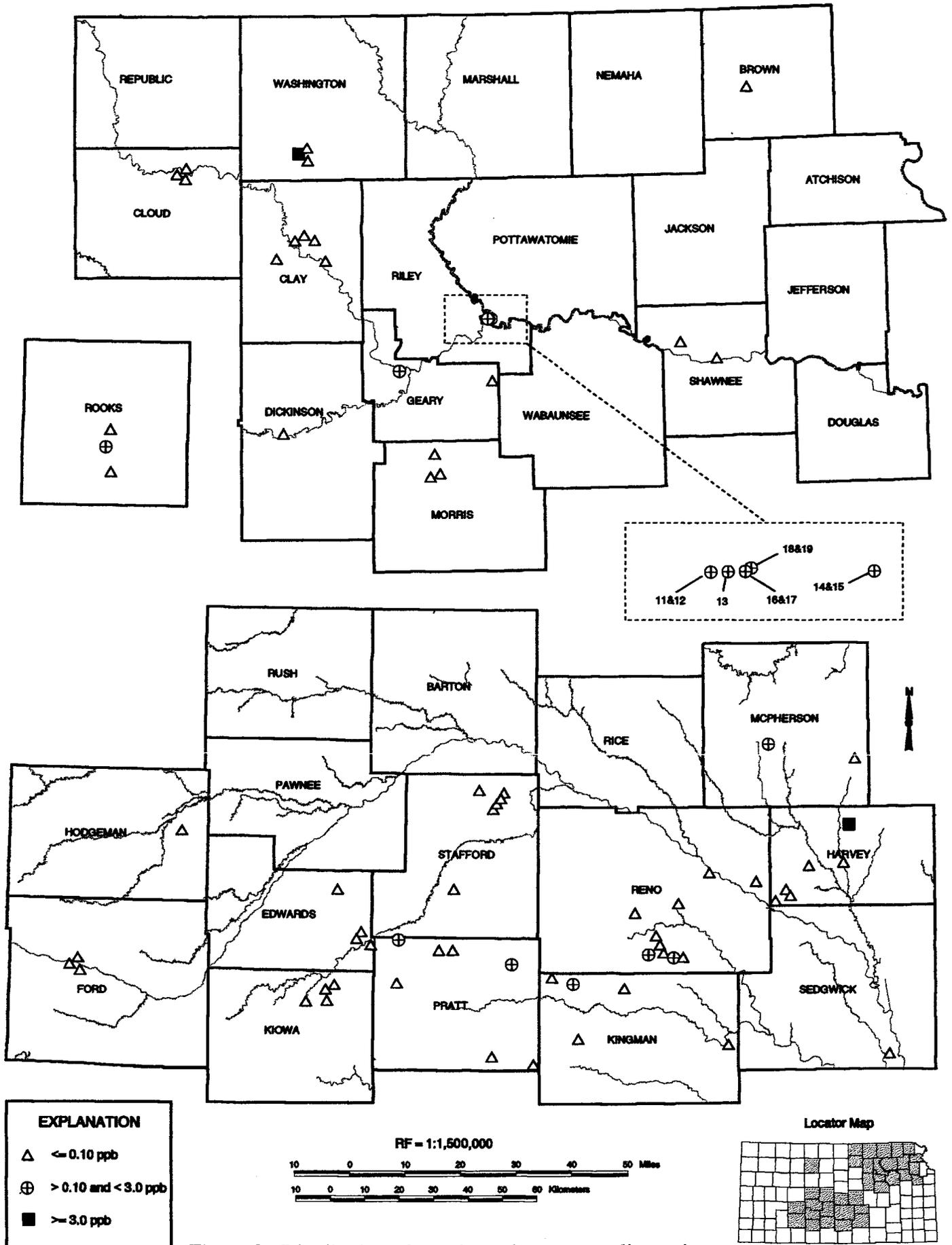


Figure 3. Distribution of atrazine values at sampling points.

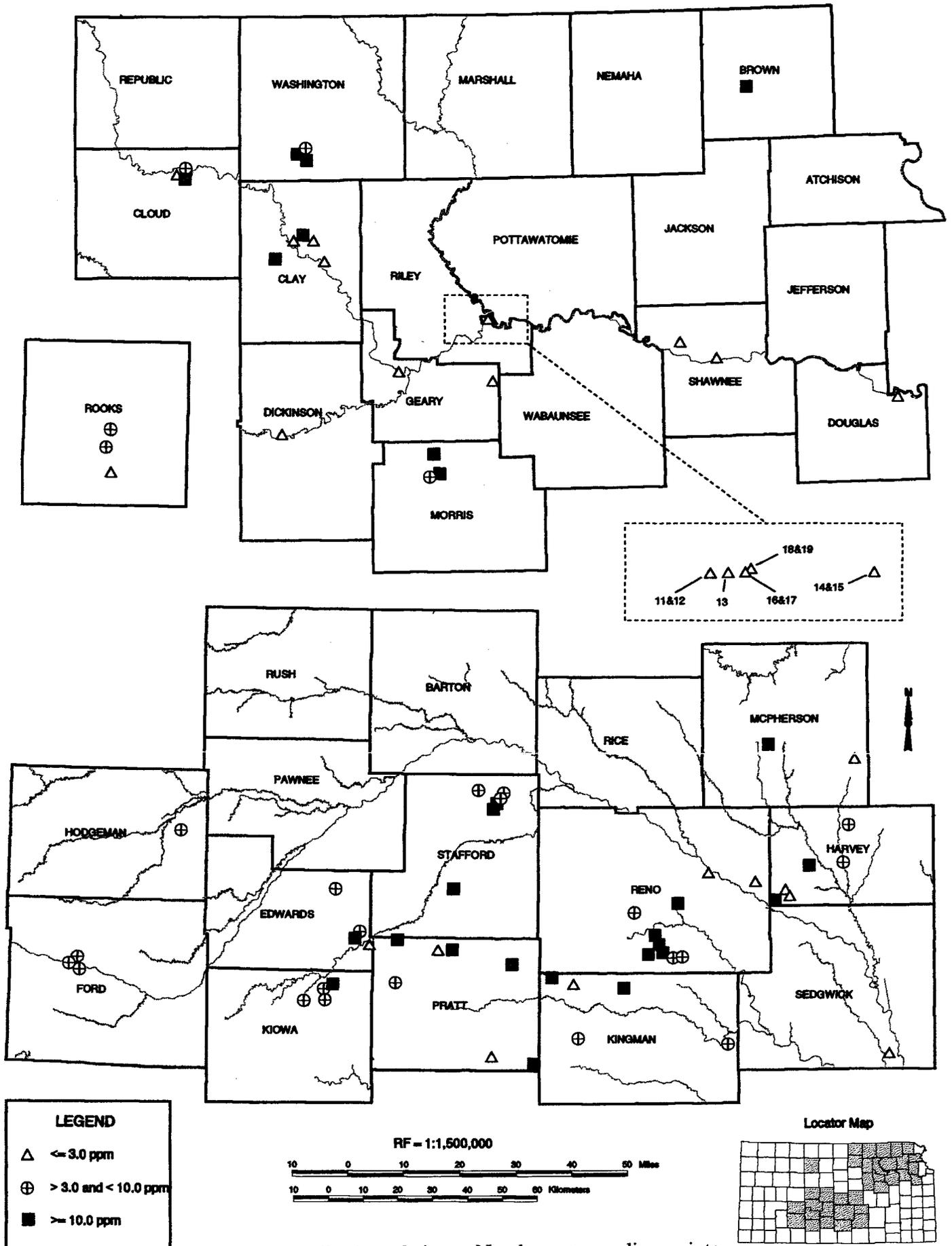


Figure 4. Distribution of nitrate-N values at sampling points.

## **Atrazine**

The factors found to be statistically related to the occurrence of atrazine in ground water in Kansas are: irrigation well density within a 3.2 km radius of the sampled well; depth of well; depth to the water table; and distance of application area from sampled well. These factors are similar to findings from other studies (Kolpin et al., 1995; Burkart and Kolpin, 1993; Exner and Spalding, 1990).

### **Irrigation Well Density**

Irrigation well density is one of the factors most likely to impact the movement of atrazine through the unsaturated zone to ground water. The density of wells within a given area gives an estimate of the intensity of farming and the potential volume of water being applied within that portion of the state. Figure 5 shows the distribution of irrigation wells within the study area (WIMAS database, KDA, 1993). The figure clearly shows that in northeastern and central Kansas, the irrigation well distribution follows the major river channels. In south-central Kansas there is a tendency for irrigation well density to follow the major river channels but not the smaller channel systems (figs. 3, 4, 5). The density is higher because of the increased need for irrigation due to lower rainfall in this part of the state.

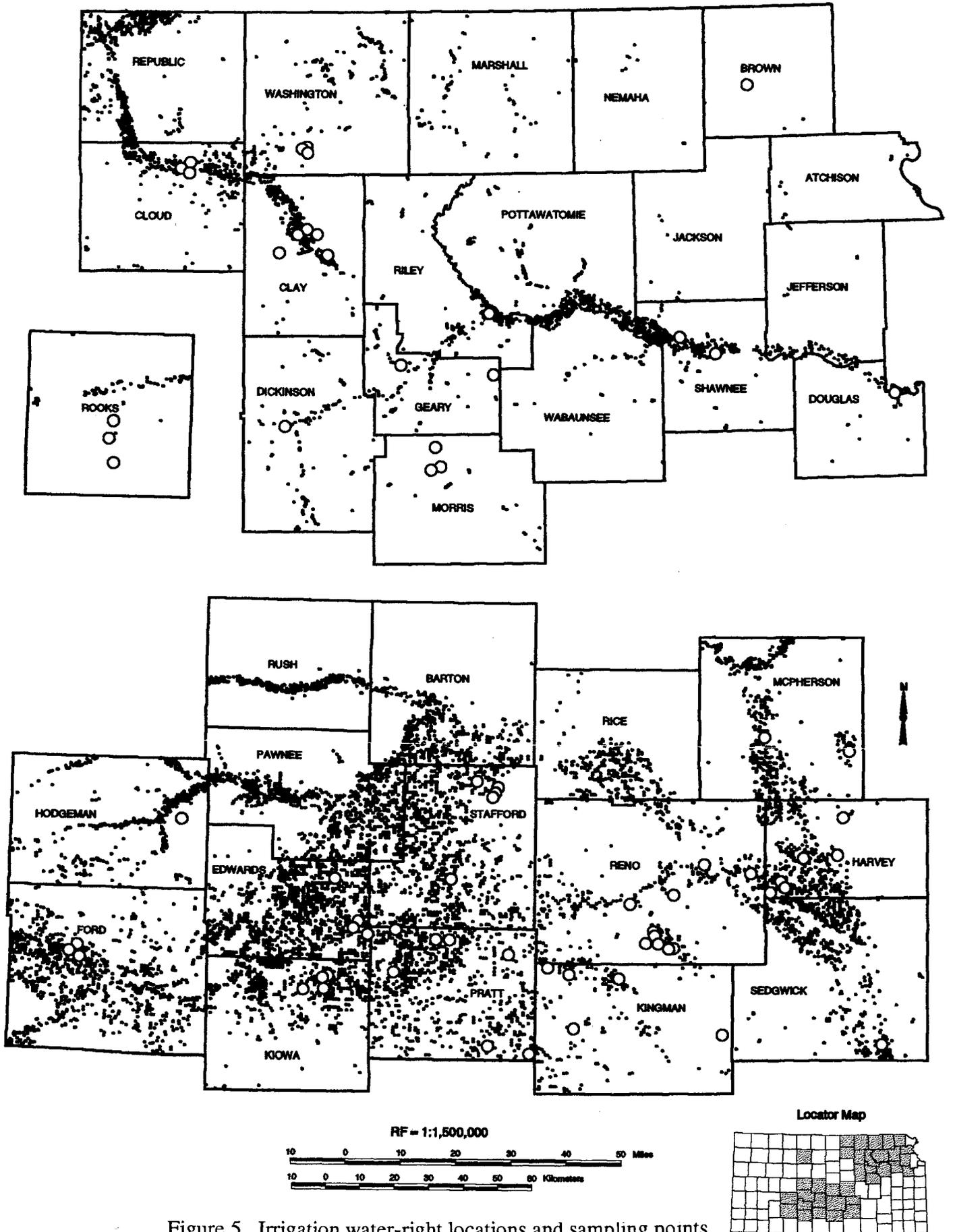


Figure 5. Irrigation water-right locations and sampling points.

Figure 6 shows the distribution of atrazine concentration with irrigation well density for 3.2 km radius. Sampled wells with no irrigation wells within 3.2 km were not included. The Mann-Whitney U test showed that a statistical difference existed between density levels of  $\leq 15$  wells or  $> 15$  wells ( $p = 0.0122$ ). The results indicate that more atrazine detections occurred at the  $\leq 15$  well density level and that more non-detections were present in the  $> 15$  well density level. These results are the opposite of what we expected. A possible explanation is that more detections of atrazine occurred in the alluvial deposits of the Kansas River where less irrigation takes place than in south-central Kansas (fig. 5). This is an area that needs more evaluation.

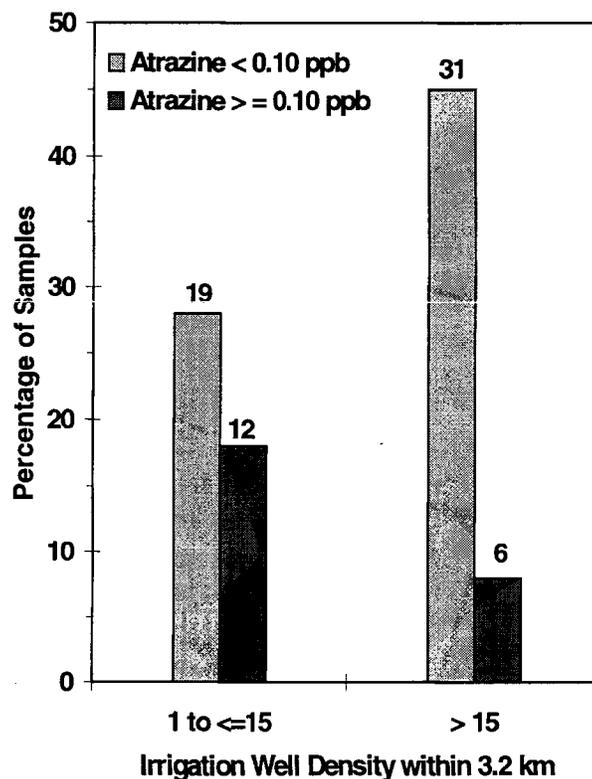


Figure 6. Distribution of atrazine detections in ground water based on irrigation well density within 3.2 km of sampled well. Graph shows percentage of total samples (68). Numbers above bars indicate number of samples in each class.

## Depth of Well

The median depth of well sampled in this study was 25 m (table 1). This value was used to test the hypothesis that concentrations of atrazine in ground water decrease with depth. Figure 7 shows the distribution of atrazine concentration with depth of well. The Mann-Whitney U test of this hypothesis showed that atrazine concentration was related to depth of well ( $p= 0.094$ ). The figure shows the trend that there are fewer detects at depth than in the shallower wells. This result is similar to findings from other studies (Kolpin et al., 1993; Exner and Spalding, 1990).

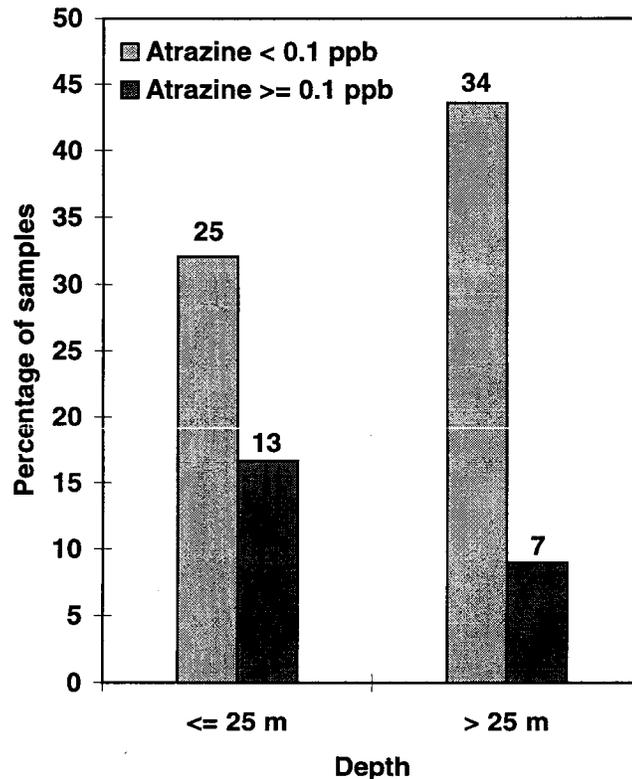


Figure 7. Distribution of atrazine detections in ground water based on median depth of well (25 m). Note that more non-detects occur in deeper wells. Percentage of total wells (78) shown. Numbers above bars indicate number of samples in each class.

## Depth to Water Table

One of the most frequently cited factors related to the occurrence of atrazine in ground water is the depth to the water table. Generally atrazine is found most frequently in areas with a shallow water table. A shallow water table reflects a thin unsaturated zone which implies a potentially faster movement of agrichemicals from the land surface to ground water.

The Mann-Whitney U test of the relationship of atrazine with depth to water was statistically significant ( $p=0.0516$ ). As illustrated figure 8, the trend of the data appears to be more detections in shallow water and more non-detections in areas with a deeper water table. These findings are similar to those found in other studies and suggest that areas with a shallow water table are more vulnerable to potential contamination than other areas. These results are also similar to those shown for the depth of well factor discussed above.

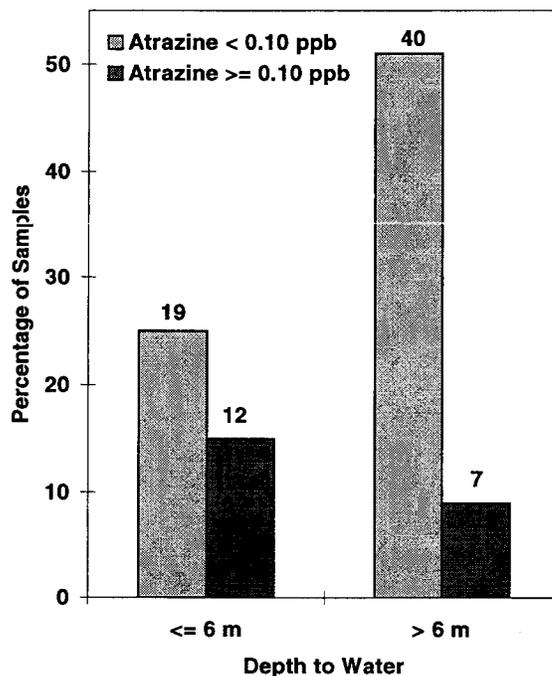


Figure 8. Distribution of atrazine detections based on depth to water. Note that more non-detects occur at deeper depth to water. Figure shows percent of samples within each category. Number above bars indicate number of samples in each class.

## Application Distance

The distance of the sampled well from potential sources of nonpoint source contamination, such as cropland, may be an important consideration to determine if atrazine is getting into the ground water. The Mann-Whitney U test of relationship of atrazine with application distance to the sampled well showed a statistically significant difference ( $p=0.0273$ ). Figure 9 indicates the possible trend that the presence of atrazine occurs more frequently when the application distance is less than the median value of 33 m.

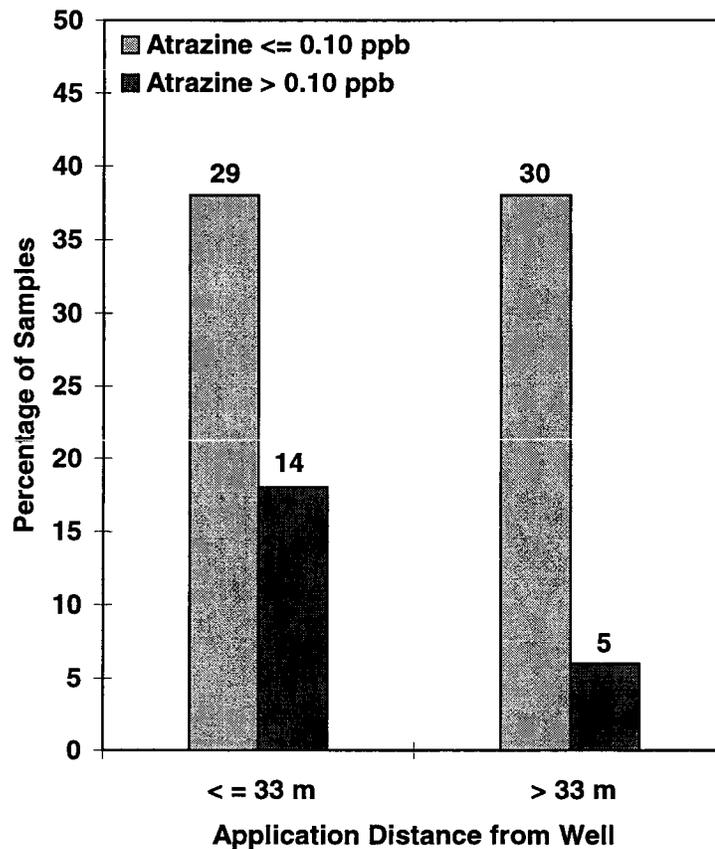


Figure 9. Distribution of atrazine detections based on application distance from well. More samples with detects occur in ground water when application distance is less than 33 m. Percentage of total samples (78) shown. Numbers above bars show number of samples in each class.

### Volume of Clay in Upper Stratigraphic Section

The volume of clay in the upper stratigraphic section is based on thickness of clay reported from available well logs. These values are gross estimates at best with no core to examine to determine if the lithologic description is accurate. The Mann-Whitney U test of a relationship of atrazine with the volume of clay in the upper 3 m showed that there is a significant difference ( $p=0.0424$ ) between the two groups. However, the bar plot of the results showed that more detections occurred in areas with more clay rather than less clay in the upper 3 m of soil. Figure 10 shows the distribution of atrazine detects based on the quantity of clay reported in the section.

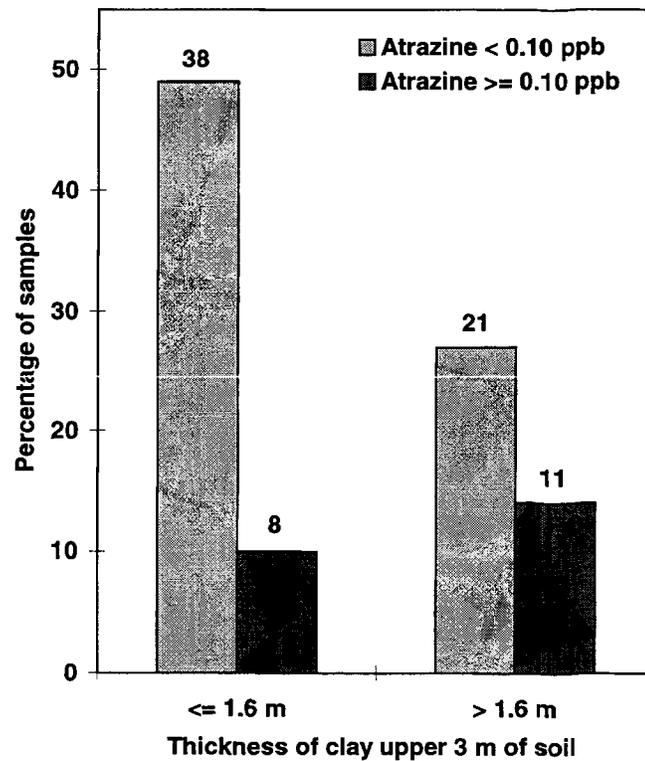


Figure 10. Distribution of atrazine detection based on thickness of clay in upper 3 m of stratigraphic profile. Note that number of detections increase with increased clay content in upper 3m. Percentage of total samples (78) shown. Numbers above bars show number of samples in each class.

The results of this test were the opposite of findings from other studies in Nebraska and Iowa. One explanation may be that the distribution and type of clay throughout the study area varies greatly. In south-central Kansas, clays occur in layers of variable thickness in the upper 3 m thus making an estimate of the volume of clay in the profile difficult. In northeastern Kansas, more clay is present in a given volume in the upper 3 m profile. The type and volume of clay in the profile may result in macropore development because of shrink swell processes thus permitting rapid movement of atrazine to the ground water. Another possibility is that the layering of clays in the subsurface in south-central Kansas may result in mini perched water layers which could enhance biological degradation of the atrazine.

### **Surface Soil Texture**

The soil texture rankings are for the upper 0.3 m of soil (NRCS, 1994). The values selected from the data base are a proxy for infiltration capacity. The values used ranged from 1 (clay to silty clay) to 8 (fine sand). The median textural estimate for the data set is 5. The values only reflect the surface soils and do not imply that similar soil textures occur at depth.

The Mann-Whitney test indicates a statistically significant difference between the two groups ( $p=0.0057$ ). However, a plot of the data distribution shows that more of the measured atrazine detects occurred in the lower soil texture group (fig. 11). A possible reason for this may be that most of the samples with atrazine detections occurred in the Kansas River alluvium which is has more silt and clay present than the sandier soils in south-central Kansas (fig. 15, Geographic Location section).

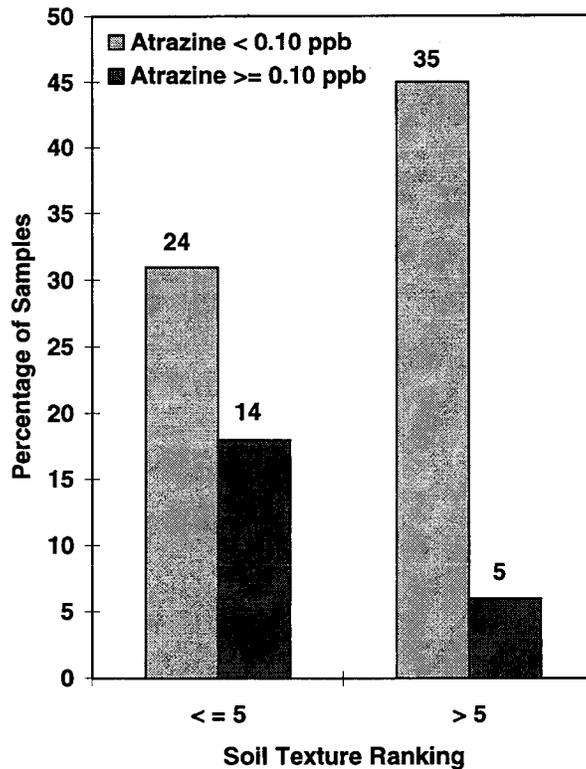


Figure 11. Distribution of atrazine detections with soil texture rankings. More detects occurred in soils with more clay and silt. Percentage of total samples (78) shown. Numbers above bars indicate number of samples in each group.

### Nitrate-Nitrogen

The factors that were statistically related to nitrate-N values in ground water were depth to water and estimate of soil surface permeability (K). These findings are similar to those noted in other studies (Kolpin et al., 1995, Spalding and Exner, 1993, Chen and Druliner, 1987, Druliner et al., 1996).

## Depth to Water

The Mann-Whitney U results for depth to water indicate that higher nitrate-N concentrations occur in wells with depth to water greater than 6.6 m (20 ft;  $p=0.0233$ ; fig. 12). Although an unexpected result, a similar finding of higher nitrate-N concentrations at deeper water levels was also noted in the U. S. Geological Survey NAWQA studies (Mueller et al., 1995). These studies showed a trend of increasing nitrate-N concentrations in well-drained soils with increasing depth to water up to 22 - 33 m (80-100 ft). At greater depths to water the nitrate-N concentrations decreased. Our data appear to fit the model of increased nitrate-N values with increased depth to water. These results also indicate the long-term migration of nitrate throughout the aquifer systems in Kansas possibly enhanced by the mixing of shallow and deeper waters as a result of irrigation.

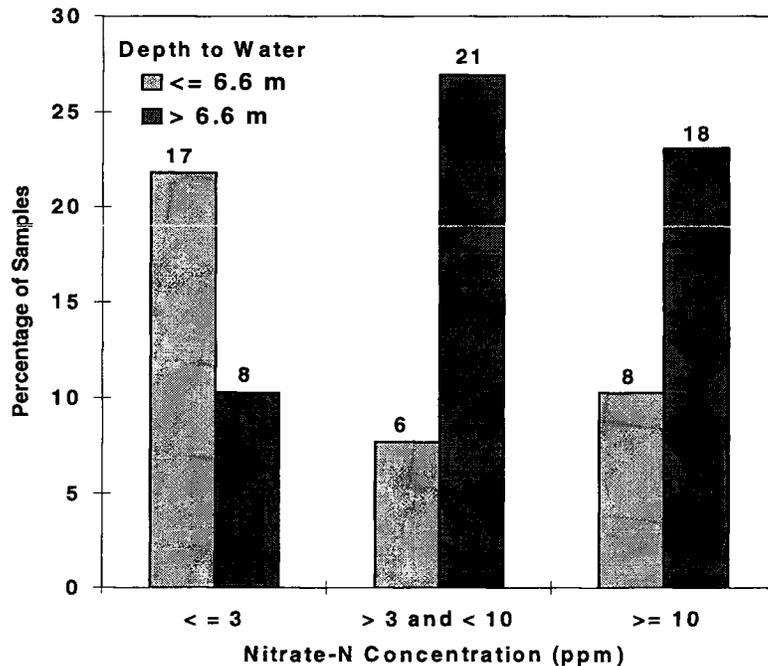


Figure 12. Distribution of nitrate-N concentrations with depth to water. Percentage of total samples (78) shown. Number of samples in each group shown above bar.

## Surface Soil Texture

The Mann-Whitney U tests results for the soil texture estimate showed that higher concentrations of nitrate-N occurred under soils with more sand than under soils with more silt and clay ( $p=0.053$ ) (fig. 13). This finding also suggests that areas in Kansas with more permeable soils are more vulnerable to potential contamination from nitrate sources.

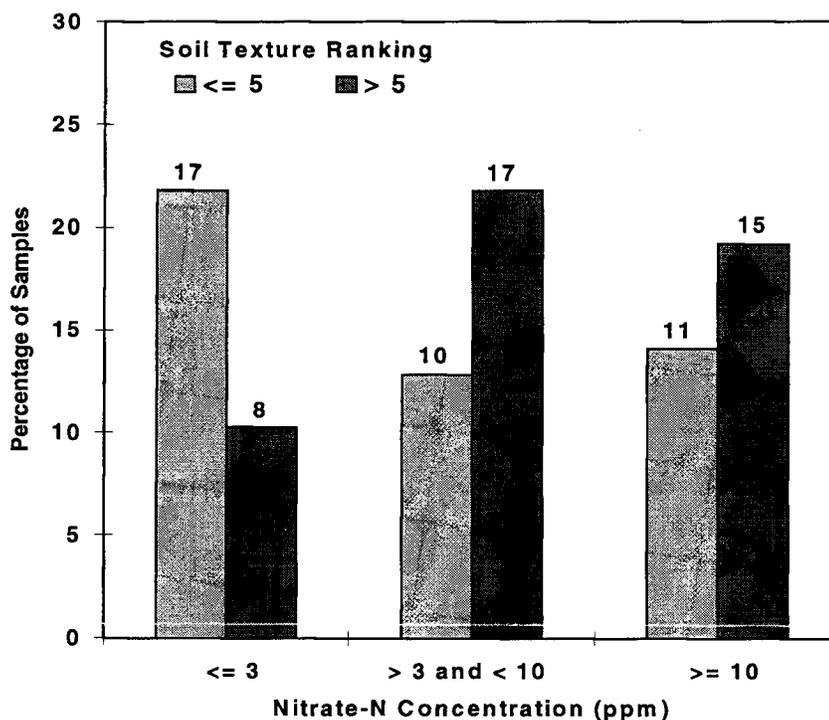


Figure 13. Distribution of nitrate-N concentrations by soil texture ranking. Note that more samples with nitrate-N greater than 3 mg/L occur under soils with more sand. Percentage of total samples (78) shown. Numbers above bars indicate number of samples in each class.

The lack of observed relationship between nitrate-N and most of the factors tested, and the observation that 67% of the samples had nitrate-N concentrations above 3 ppm, strongly suggests that elevated nitrate-N concentrations are widespread. Once nitrate-N concentrations begin increasing, they can be expected to continue to increase under the same water and nitrogen management practices (Hallberg, 1986).

## Geographic Location

Because of differences in soils, rainfall, irrigation well density, depth to water, and depth of well, the data were also evaluated by the two geographic locations that were sampled: northeast and south-central Kansas. Tables 2 and 3 summarize the basic statistics by subregion for all of the factors considered in this study. The volume of clay in the upper 3.3 and 8.3 m of the soil column and the total volume of clay above the well screen are similar for both areas thus suggesting that the use of a gross estimate of clay available from drillers' logs is not sufficient to examine the relationship between quantity of clay in the subsurface and the quantity of atrazine detected in the ground water. Figure 14 shows the distribution of atrazine and nitrate-N by subregion.

**Table 2. Summary of Statistics for Northeast KS and Rooks County, Kansas**

Factor	Number Samples	Minimum Value	Maximum Value	Mean	Median
Well Depth (m) *	28	14	46.6	25	22.6
Top of Screen (m) *	28	6.6	9.3	17	14.6
Well age (yrs)	28	3	61	14.1	11.5
Depth to Water (m) *	28	3.3	29	10	7.6
Application Distance (m) *	28	0	440	45	16.6
Total Clay above screen (m) *	28	0	41.6	6	5
Volume of Clay in Upper 3.3 m	28	0	3.3	4.6	5.5
Volume of Clay in Upper 8.3 m	28	0	8.3	4.4	4.8
Nitrate-N (ppm)	28	0.1	32.1	7.9	43
Atrazine (ppb)	28	<0.1	3.3		<0.10
Deethylatrazine (ppb)	28	<0.1	1.1		<0.10
Deisopropylatrazine (ppb)	28	<0.1	0.18		<0.10
SUM (Atrazine + Metabolites) (ppb)	12	0.2	3.9	0.98	0.62
DAR	9	0.15	3.9	1.3	0.44
Soil Texture Estimate	28	1	8	3.4	4
Irrigation Well Density 1.6 km **	28	0	19	3	1
Irrigation Well Density 3.2 km **	28	0	48	11	11

\* Multiply meter values by 3.28 to obtain measurements in feet. \*\*1.6 km = 1 mile.

**Table 3. Summary of Statistics for South-central Kansas**

Factor	Number Samples	Minimum Value	Maximum Value	Mean	Median
Well Depth (m) *	50	6.6	64	26.5	26
Top of Screen (m) *	50	2.3	50.6	19.6	19.3
Well age (yrs)	50	0.3	63	15	13
Depth to Water (m) *	50	2.3	23.3	9.7	8.8
Application Distance (m) *	50	0	883	135	50
Total Clay above screen (m) *	50	0	30	8.3	5.6
Volume of Clay in Upper 3.3 m	50	0	3.3	4.2	4.0
Volume of Clay in Upper 8.3 m	50	0	8.3	4.5	4.2
Nitrate-N (ppm)	50	0.1	40.2	8.8	8.1
Atrazine (ppb)	50	<0.1	5.1		<0.10
Deethylatrazine (ppb)	50	<0.1	1.1		<0.10
Deisopropylatrazine (ppb)	50	<0.1	0.32		<0.10
SUM (Atrazine + Metabolites) (ppb)	14	0.11	6.03	1.04	0.56
DAR	8	0.12	5	1.46	0.73
Soil Texture Estimate	50	2	8	6	6
Irrigation Well Density 1.6 km **	50	0	14	5	5
Irrigation Well Density 3.2 km **	50	0	46	18	18

\* Multiply meter values by 3.28 to obtain measurements in feet. \*\*1.6 km = 1 mile.

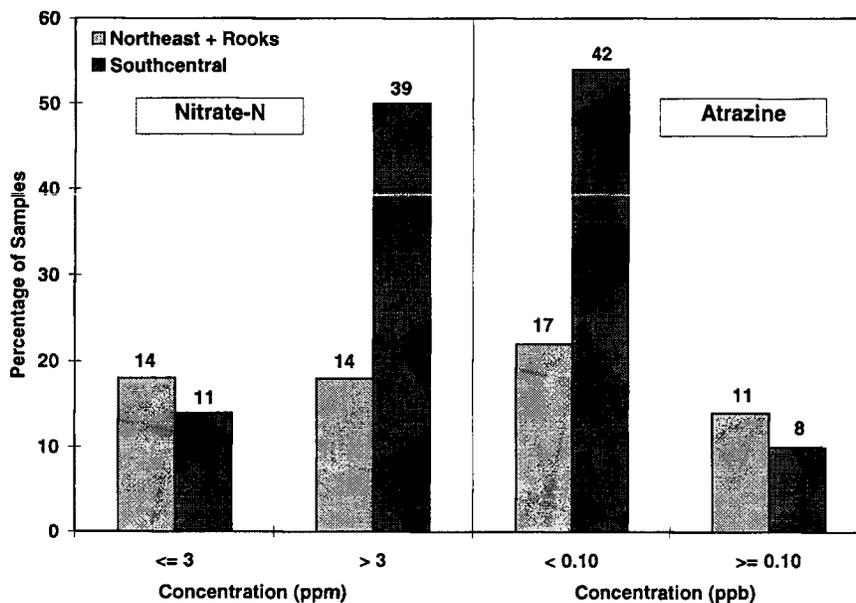


Figure 14. Distribution of atrazine and nitrate-N in northeast and south-central Kansas. Note that higher concentrations of nitrate-N occur in south-central than in northeast Kansas. Also more non-detects of atrazine occur in south-central Kansas and more detections of atrazine occur in northeastern Kansas. Percentage of total samples (78) shown. Numbers above bars indicate number of samples in each class.

Figure 15 shows the distribution of surface soil texture estimates by subregion. Although south-central Kansas has more sandy surface soils, more non-detections of atrazine occur in this area than in northeast Kansas (fig. 14). In addition, more detections (both in terms of absolute numbers and of percentage of sites samples) of nitrate-N concentration above the background level of 3 ppm occur in south-central Kansas. The high percentage of non-detects of atrazine suggests that subsurface clay content in the unsaturated zone in south-central Kansas may have a role in preventing the movement of atrazine to the ground water. The presence of subsurface clay does not appear to impact the movement of nitrate to ground water.

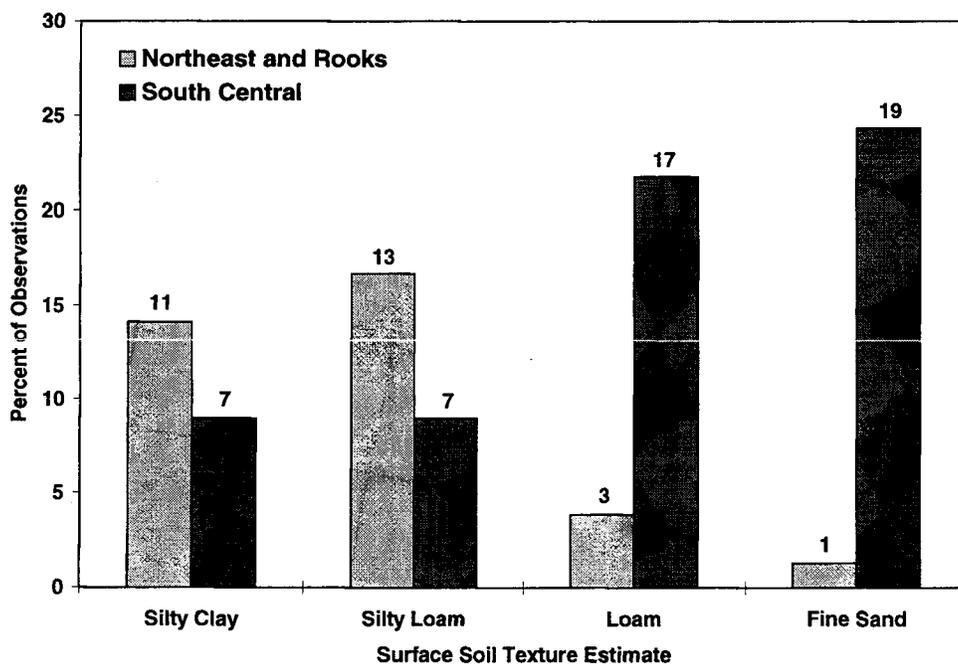


Figure 15. Distribution of surface soil texture rankings for northeast and south-central Kansas. More loam and fine sand are present in south-central and more silty clay and silty loam are present in northeast Kansas. Percentage of total samples shown (78). Numbers above bars indicate number of samples in each class.

## **Statistical Evaluation of Subregional Data**

Of the factors originally proposed three showed significant relationships with the subregional data: atrazine concentration was significantly different between the two areas, nitrate concentration was significantly different between the areas, and soil texture was different between the two areas. The surface soil texture estimates are generally higher in south-central Kansas (fig. 15) suggesting that this area is potentially more vulnerable to agrichemical movement to the ground water.

### **Atrazine**

Detections of atrazine were significantly different between northeastern and south-central Kansas (Mann Whitney U test,  $p=0.013$ ). However, the frequency distribution of the data indicates that more detections of atrazine occur in northeastern Kansas and more non-detects occur in south-central Kansas (fig. 14). Most of the samples with atrazine detects generally occur in the alluvium of the Kansas River in northeastern Kansas. These results may reflect stream-aquifer interaction rather than regional ground-water atrazine concentrations. The higher number of non-detections that are present in south-central Kansas may be the result of adsorption of atrazine to clay lamellae in the subsurface as was discussed previously and as supported by another study done in south-central Kansas (Sophocleous et al., 1990).

### **Nitrate-N**

The Mann-Whitney U test results for determining if geographic location was a factor that helped to explain the occurrence of nitrate in ground water showed a significant difference between northeastern and south-central Kansas ( $p=0.0829$ ) with south-central Kansas having higher concentrations of nitrate in the ground water (fig. 14).

The Mann-Whitney U test for evaluating soil texture estimates as a potential factor on the occurrence of nitrate in ground water showed a significant difference

between the two categories ( $p=0.0001$ ). Comparison of figures 14 and 15 show that south-central Kansas has coarser textured soils and more nitrate nitrogen in the ground water. The coarser textured soils in south-central Kansas, compared to northeastern Kansas, apparently allow more nitrate to leach to the ground water.

### **Atrazine Metabolites**

Previous studies have shown that although atrazine may not be present in ground water, detections of daughter products indicate that atrazine was present in the vadose zone or ground water at some point in time (Thurman et al., 1992; Kolpin et al., 1995). Metabolite concentrations included deethylatrazine of which 69% of the wells were less than the detection limit of 0.10 ppb, and the remaining 31% were  $\geq 0.10$  ppb and  $\leq 1.5$  ppb; and deisopropylatrazine of which 90% were less than the detection limit of 0.10 ppb, and 10% were  $\geq 0.10$  ppb and  $\leq 0.7$  ppb. Hydroxy-atrazine occurred in 11 samples with the range of values between 0.23 and 1.4 ppb. Figure 16 shows the chemical structure of atrazine and the three most often detected metabolites: deethylatrazine, deisopropylatrazine, and hydroxyatrazine. Figure 17 shows the distribution of metabolite concentrations of deethylatrazine, deisopropyl-atrazine, and hydroxyatrazine.

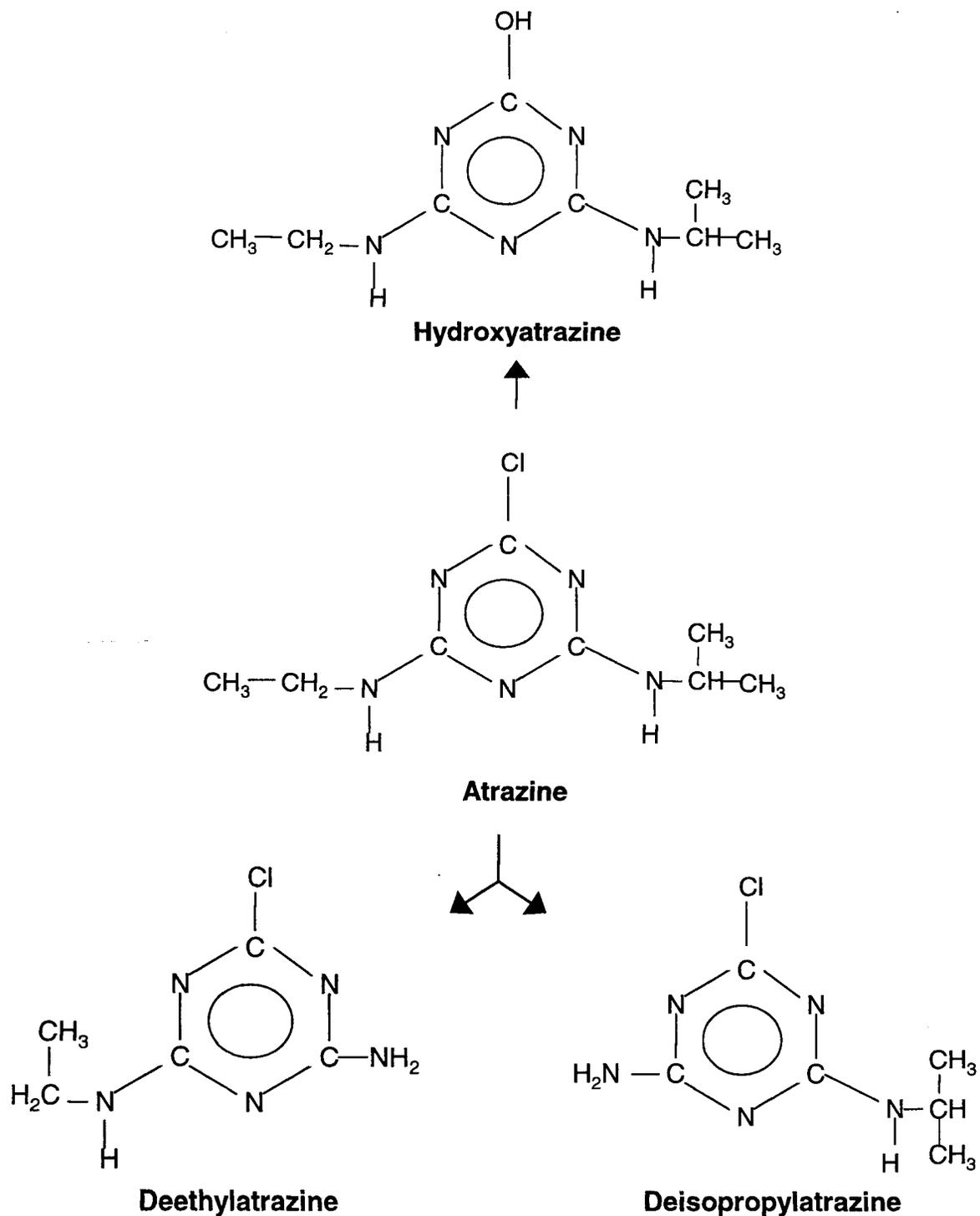


Figure 16. Degradation products of atrazine: chemical processes result in hydroxyatrazine; bacterial degradation processes result in deethylatrazine and/or deisopropylatrazine.

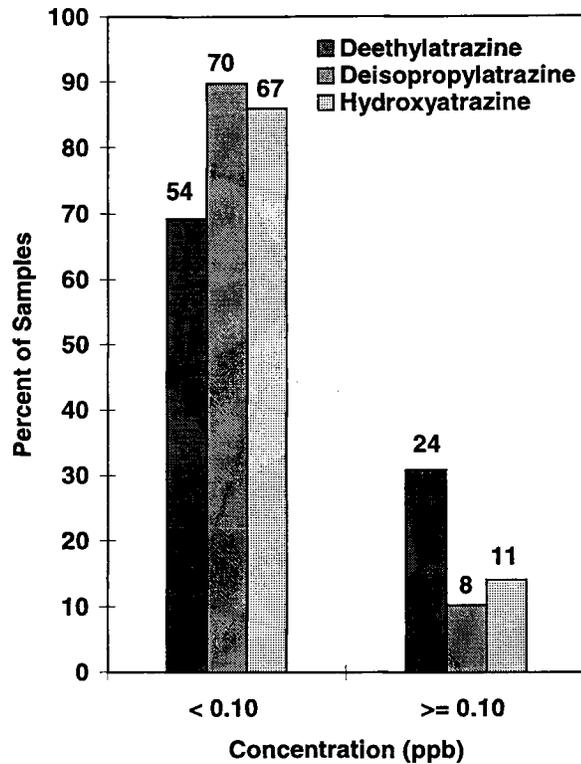


Figure 17. Distribution of daughter products. The majority of samples are less than 0.10 ppb (detection limit). Percentage of total samples (78) shown. Numbers above bars indicate number of samples in each class.

Of the metabolites, deethylatrazine occurs most often as a microbial degradation product caused by slow movement of atrazine through the unsaturated zone. Because this type of degradation takes time, a significant microbe population, and nutrients for the microbes, calculation of **DAR** [**D**eethylatrazine (mol/L)/**A**trazine (mol/L **R**atio)] has been suggested as a possible tracer for the pathway of atrazine movement to ground and surface water and as an indicator of possible point or non-point source contamination (Thurman et al., 1992; Squillace et al., 1993). Work using the DAR (deethylatrazine/atrazine ratio) indicates that the greater the ratio value the longer the residence time in the soil and ground water and thus greater opportunity for the atrazine to be broken down into its metabolites.

Work by Adams and Thurman (1991) first showed the possible use of this ratio. A DAR value  $< 1.0$  suggests a rapid movement of atrazine via overland flow into a stream or by macropore flow to ground water and usually results in a large atrazine concentration and a low deethylatrazine concentration. A DAR value  $> 1.0$  suggests that relatively slow travel time has occurred through the unsaturated zone to the ground water. Figure 18 illustrates these concepts.

DAR values  $> 1.0$  are considered indicative of non-point source contamination (Thurman and Adams, 1991). Nitrate-nitrogen values above 3 ppm are considered indicative of anthropogenic sources of contamination. Figure 19 shows the lack of relationship between nitrate-N and DAR values. This is not unexpected considering the lack of statistical relationship between the occurrence of atrazine and nitrate-N in the ground water. In some studies it is likely that use of DAR values and occurrence of nitrate in ground water could be used to define areas of non-point source contamination.

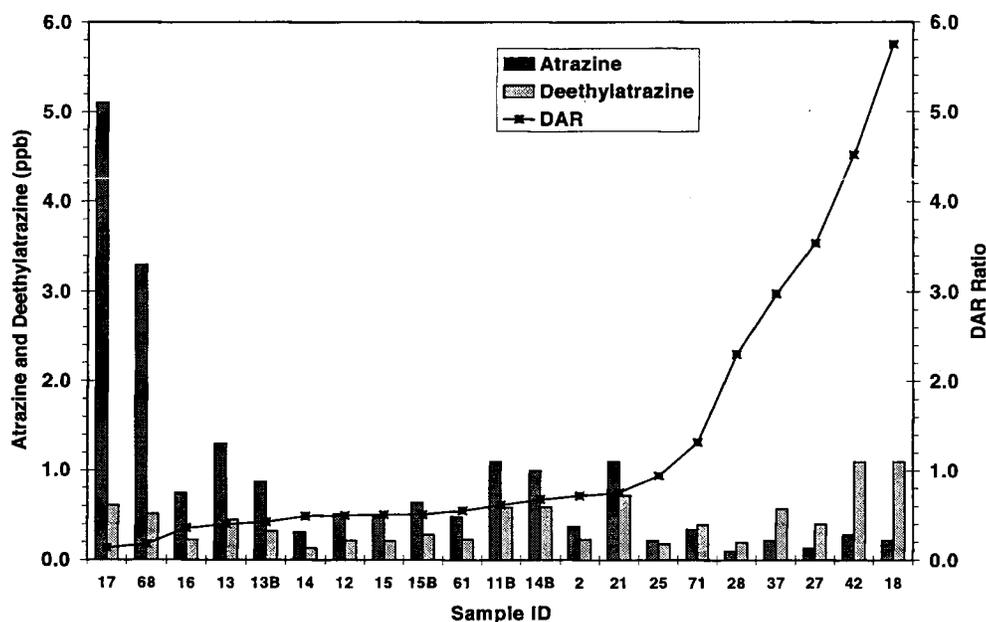


Figure 18. Relationship between atrazine and deethylatrazine concentrations and DAR values. Increased DAR indicates breakdown of atrazine in unsaturated zone and probable nonpoint source for atrazine. Low DAR ( $< 1.0$ ) and measurable atrazine suggest overland flow to streams or macropore flow to ground water resulting in little residence time for breakdown of atrazine to metabolites.

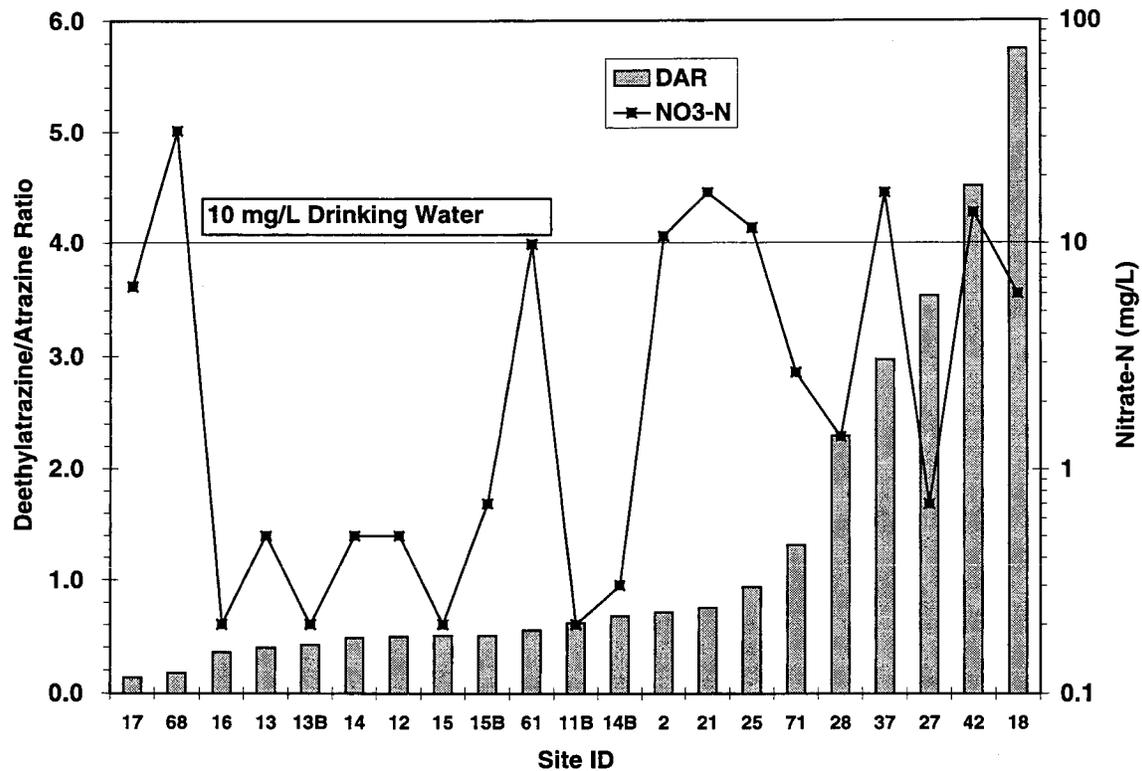


Figure 19. Relationship between nitrate concentrations and DAR values. Low DAR values indicate possible point source contamination. High DAR values indicate possible nonpoint source contamination.

Table 4 lists the values of atrazine, deethylatrazine, deisopropylatrazine, DAR, and nitrate-N values for selected sites from the study. A number of the wells have DAR values of < 1.0 and low nitrate-N concentrations suggesting the possibility of nonpoint source contamination by bank storage effects from stream-aquifer interaction (table 4, wells 11,16; Squillace et al., 1992). Work by the Kansas Department of Health and Environment indicates that atrazine is the most often detected herbicide in surface water in Kansas thus providing a potential source for the observed concentrations in alluvial wells (Carney et al., 1991).

**Table 4. Atrazine, metabolites, DAR, and nitrate-N values for selected sites.**

ID	Atrazine ppb	DEA* ppb	DAR**	DIA* ppb	HA* ppb	NO <sub>3</sub> -N ppm	Well Location
17	5.1	0.61	<b>0.138</b>	0.32		6.4	Hesston
68A	3.3	0.51	<b>0.178</b>	0.11		32.1	Palmer
16	0.74	0.23	<b>0.357</b>	0.12	0.44	0.2	Junction City
13A	1.3	0.45	<b>0.398</b>	0.18	1.4	0.5	Manhattan
13B	0.87	0.32	<b>0.423</b>	0.15	0.77	0.2	Manhattan
14A	0.31	0.13	<b>0.482</b>		0.32	0.5	Manhattan
12	0.51	0.22	<b>0.496</b>		0.31	0.5	Manhattan
15A	0.48	0.21	<b>0.503</b>		0.51	0.7	Manhattan
15B	0.64	0.28	<b>0.503</b>	0.13	0.54	0.2	Manhattan
61	0.48	0.23	<b>0.551</b>			9.9	Macpherson
11	1.1	0.59	<b>0.617</b>	0.30		0.2	Manhattan
14B	1.0	0.59	<b>0.678</b>	0.28		0.3	Manhattan
2	0.37	0.23	<b>0.715</b>			10.7	White City
21	1.1	0.72	<b>0.753</b>			16.8	Reno County
25	0.22	0.18	<b>0.941</b>			11.7	Preston
71	0.34	0.39	<b>1.319</b>			2.7	Penalosa
28	0.1	0.2	<b>2.299</b>			1.4	Rossville
37	0.22	0.57	<b>2.979</b>			16.8	Byers
27	0.13	0.4	<b>3.583</b>			0.7	Topeka
42	0.28	1.1	<b>4.517</b>			13.7	Clay Center
18	0.22	1.1	<b>5.749</b>	0.19		6	Reno County
78	0.63				0.23	11.4	Rooks County

\* DEA - Deethylatrazine; DIA - Deisopropylatrazine; HA - Hydroxyatrazine

\*\* DAR - Deethylatrazine/Atrazine molar ratio.

The wells with low DAR values (<1.0) and nitrate-N values greater than 3 ppm indicate a possible anthropogenic source of contamination in the aquifer (Madison and Brunett, 1985) by rapid recharge to the aquifer either because of faulty well design (table 4, well 17), macropore flow, or rapid recharge through a very permeable unsaturated zone (table 4, wells 18, 21). The wells with nitrate-N concentrations greater than 10 ppm strongly indicate a possible point source (table 4, wells 2, 21, 25, 61, and 68). The well sample 68 is a shallow dug well which may explain the high nitrate value and low DAR value.

The remaining wells with DAR values > 1.0 indicate a slow travel time for the atrazine so that considerable degradation occurred before the soil water reached the ground water. However, the presence of high nitrate-N in some of these wells

suggests that although conditions exist for the breakdown of atrazine because of the presence of lower permeable zones in the unsaturated and saturated zones, agrichemicals are still reaching the aquifer and can cause impairment of the water quality both by atrazine metabolites and nitrate.

### **Hydroxyatrazine**

Hydroxyatrazine is the result of a chemical hydrolysis reaction on atrazine. The reaction occurs in the environment via chemical, biological, or photochemical hydrolysis of the of atrazine or dealkylated atrazine metabolites with a replacement of the Cl with a hydroxyl group at the 2-position of the atrazine ring (Lerch et al., 1998; fig. 16).

In this study hydroxyatrazine was detected in 11 samples (table 4). Of those samples, 10 were located in the alluvium of the Kansas river and one was a large dug well. The samples taken from the alluvial wells near the Kansas River had atrazine, deethylatrazine, deisopropylatrazine, and hydroxyatrazine concentrations. The presence of all of these chemicals in the alluvial wells plus low DAR values (table 4) helps to support the hypothesis that these wells are representative of stream-aquifer mixing reactions rather than only ground water. The presence of the hydroxyatrazine, which is not normally found in ground water (Lerch, 1995; Kruger, 1996), but has been found in surface waters in Kansas and Missouri (Adams and Randtke, 1992; Lerch et al., 1998) suggests that the theory of Squillance et al. (1993) of mixing of surface- and ground-water via a bank storage mechanism may be in effect.

Hydroxyatrazine is known to bind strongly to clay particles (Armstrong et al., 1967; Weber, 1970). The presence of hydroxyatrazine in the samples suggests that overland flow has moved these chemicals into the surface water either as a dissolved phase or attached to sediments (Lerch et al., 1998; Adams and Randtke, 1992). The release of hydroxyatrazine from sediments to the surface water might be accomplished by the mechanism proposed by Lerch et al. (1998). Their theory is

that hydroxyatrazine is contributed to surface water via a dissolved phase during overland flow but may also be desorbed from bottom sediment by ground water flowing through hydroxyatrazine contaminated sediments in the streambed.

The samples listed in table 4 were collected at different times, some in the late fall and some in early spring (Appendix B). The presence of atrazine as well as the various daughter products suggests that the source of the atrazine may be from either local sources or from reservoirs upstream that are known to be storage points for atrazine (Adams and Randtke, 1992). In addition, the theory that Lerch et al. (1998) proposed of desorption of the hydroxyatrazine by inflow of ground water through the river base sediments could be occurring.

This brief discussion of the occurrence of atrazine and its metabolites in surface and ground water suggests that herbicides plus their metabolites may have a future greater impact on water quality than previously envisioned. If this is indeed the case, then future water-quality studies will have to address the metabolite issue as well as the major herbicides and nitrate sources as possible threats to the usability of the water.

## **CONCLUSIONS**

The results of the one-time statewide ground-water quality survey showed that atrazine is not present in the majority of wells tested. Of the 78 samples collected, 77% were below the detection limit, 21% had detections above 0.10 ppb (detection limit) but below 3 ppb, and 2% were above the drinking water limit of 3 ppb. The primary factors related to the occurrence of atrazine or its daughter products in ground water are application distance of the chemical from the sampled well, irrigation well density within a 3.2 km radius of the sampled well, quantity of clay in the upper 3 m of the soil profile, depth to water, depth of well, and soil textures.

The majority of samples that had atrazine or daughter product occurred in wells that are in the alluvium of the Kansas River. These samples had DAR values

of <1.0 that may indicate that these wells are influenced by stream-aquifer mixing and the atrazine and daughter product detects are coming from the surface water rather than from the regional ground water.

Results of the nitrate testing indicate that 32% of the sampled wells are below background level (3 ppm as nitrate-N), 36% are between 3 and 10 ppm (drinking water limit for nitrate-N), and 32% of the samples are above the 10 ppm limit. These numbers show that elevated nitrate concentrations are occurring, and suggest that the occurrence of nitrate in ground water is of potentially greater concern than the occurrence of atrazine. Factors found to relate to the concentration of nitrate in ground water were soil texture estimates and depth to water.

Analysis of the data by geographic location (northeastern versus south-central Kansas) showed some relationships. The number of atrazine detections was higher in northeastern than in south-central Kansas. This result is probably related to the location of many of the wells in the Kansas River alluvium which suggests that stream-aquifer interaction may be influencing the water quality at these sites.

Nitrate concentrations were higher in south-central than in northeastern Kansas. The higher concentrations may be related to the combination of sandier soils, higher irrigation well density, and the likelihood that fertilizer use in south-central Kansas has occurred over a longer period of time than that of atrazine.

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## **Appendix A. Sampling Protocols**

### **Standard Operating Procedures**

The Standard Operating Procedures (SOPs) for the study were established by the Waterborne Environmental, Inc. (WEI) and Quality Environmental (QE) companies and followed without deviation. The various SOPs established include those for temperature, pH, conductivity meters (Meter SOP) , Well Purging and Sampling SOP, packaging and maintenance of collected samples, and transport SOP. Along with water samples, the SOP paper work was delivered to the end user (Novartis, Inc.). Each activity listed above had its own SOPs as discussed below.

### **Meter SOP**

The sampling procedure involves standardization of temperature (T), pH, and conductivity (CND) meters following established SOPs. The meters required routine maintenance, inspection, and calibration every day that sampling was to be completed. Temperature meters required little maintenance while the pH and CND meters required calibration in known solutions and adjustment as needed. All adjustments made to any meter were recorded on the appropriate instrument log sheet. If the meter adjustment had no effect on the accuracy of the meter or failure occurred at anytime, a backup meter could be used. Backup instruments required the same testing and calibrations. If a meter was repaired or backup used, documentation was required on the well purge and instrument log forms.

All maintenance, pre- or post-sampling was logged and remained on record for the duration of the study. Damaged instruments were returned to WEI and another was issued.

## **Well Purging and Sampling SOPs, Domestic and Monitoring Wells**

The sampling protocols varied greatly for the domestic, municipal, and monitoring wells. The domestic and municipal wells have pumping equipment installed for immediate water needs whereas the monitoring wells are small diameter piezometers screened within specific water bearing strata. Sampling these wells required the installation of water sampling equipment or other such devices.

The meters used during the study gave the user chemical properties of the water; readings had to stabilize prior to sampling. Temperature, pH, and conductivity were measured at specified intervals until the values were stabilized to ensure the sample was representative of formation water.

In domestic wells the control parameters (T, pH, COND) were measured every 5 minutes until consistent readings were obtained and again after the sample was collected. The selected collection point was chosen by: first, proximity to the well, second, whether any equipment was necessary for cleanliness and ease of water sampling (GLP) and third, owner's request. Ideally, the sampling point was located between the well and any water treatment equipment (such as water softeners), had easy access where discharge water could be collected without the addition of hoses, and waste water was not a inconvenience for the owner. Under these conditions, stabilization of the T, pH, and COND parameter was met in the 10-minute window as suggested in the SOP. Stabilization criteria of the control parameters were: temperature is stable if two readings taken five minutes apart were within one degree centigrade, pH was stable if two readings taken five minutes apart were within 0.2 pH units, and conductivity was stable if the two readings taken five minutes apart were within 10  $\mu$ S.

For monitoring wells where no pumping equipment existed, the SOP required that the well be "purged". The wells used in the study were purged using a 1.5" diameter bailer. Sampling monitoring wells was time consuming because of equipment set up and the manual extraction of predetermined well volumes.

The procedure for purging was: 1) A tarp was laid upon the ground to keep the bailer and bailing line soil free. 2) Using sterile gloves, the water-level indicator and the bailer and its line were cleaned with distilled water. 3) The water level was measured and recorded and the total depth of the well was recorded from the well log. 4) A calculation of the volume of water to be purged was determined and recorded (water column length in feet (static water level to the total well depth) multiplied by the casing diameter constant, converted to gallons, and multiplied by three. 5) While removing this predetermined volume of water the temperature, pH, and conductivity parameters were measured and recorded. The parameters were measured again upon completion of bailing the predetermined volume of water. 6) Bailing continued if the measurement parameters had not stabilized. 7) Once stabilization of measurements occurred, the samples were collected directly from the bailer. 8) A final set of parameter readings were taken and recorded. All storage of samples whether from domestic or monitoring wells, followed the same SOP for shipping and handling.

### **SOP for Packing and Handling**

The SOP for shipping and handling was completed following the guidelines established for this study. Upon completion of sampling and the filling of all sample bottles, the caps were screwed in place and secured with black electrical tape. Each bottled was labeled with a self-adhesive form provided by Novartis, Inc. which included all pertinent information regarding the well site sample number, date, and name of person collecting the sample. The self adhesive label was then secured to the bottle using clear adhesive packing tape. For temporary storage until shipment, the bottles were placed in Zip lock <sup>(TM)</sup> bags and stored in coolers filled with enough ice to keep the samples cool overnight.

The sample-shipment containers were prepared for shipment by Federal Express on the following day. This included freezing the ice packs overnight, arranging samples in appropriate boxes, and preparing a bill of lading specifying the

handling and shipment of samples. All packing crates were filled with bottles to complete one "six pack". The shipment could contain empty sample bottles so as to complete the six pack. An airbill was completed and secured to the shipment box. A copy of the airbill was removed and retained for the chain of custody records. All boxes were shipped the following day by air express mail to the Novartis, Inc. (Ciba-Geigy) lab for analysis.

### **Documentation**

Copies of all paperwork associated with each well was mailed to Waterbourne, Inc. within a few weeks of sample collection and delivery of samples to Ciba-Geigy. Paperwork included sampling records, copies of well-logs (if available), and records of equipment calibration or recorded problems. If discrepancies were found by Waterbourne, Inc. additional materials were sent on request.