

# Agriculture-Related Trends in Groundwater Quality of the Glacial Deposits Aquifer, Central Wisconsin

David A. Saad\* USGS

Measuring and understanding trends in groundwater quality is necessary for determining whether changes in land-management practices have an effect on groundwater quality. This paper describes an approach that was used to measure and understand trends using data from two groundwater studies conducted in central Wisconsin as part of the USGS NAWQA program. One of the key components of this approach, determining the age of sampled groundwater, gave a temporal component to the snapshots of water quality that were obtained through synoptic-sampling efforts. This approach can be used at other locations where groundwater quality data are collected, groundwater age can be determined, and associated temporal data are available. Results of these studies indicate measured concentrations of nitrate and atrazine plus deethylatrazine were correlated to historical patterns of fertilizer and atrazine use. Concentrations of nitrate in groundwater have increased over time; concentrations of atrazine plus deethylatrazine increased and then decreased. Concentrations of nitrate also were correlated to well depth below the water table and concentrations of dissolved  $O_2$ ; concentrations of atrazine plus deethylatrazine were correlated to dissolved  $O_2$  and annual precipitation. To measure trends in concentrations of atrazine plus deethylatrazine, the data, collected over a near-decadal period, were adjusted to account for changes in laboratory-reporting levels and analytical recoveries. Only after accounting for these changes was it apparent that the median concentrations of atrazine plus deethylatrazine decreased over the near-decadal interval between sampling efforts.

THE effects of agricultural chemical use on groundwater quality in Wisconsin have been described by many investigators (Bundy et al., 1994a, Chern et al., 1999; LeMasters and Doyle, 1989; Jackson et al., 1987; Postle et al., 1997; Rheineck and Postle, 2000; Saad, 1997; Vanden Brook et al., 2002; Warzecha et al., 1995; Wisconsin Department of Natural Resources, 2004, 2002, 2000, 1994, 1990, 1987, 1986; Wisconsin Groundwater Coordinating Council, 1994, 1992; Wollenhaupt et al., 1990). The most frequently detected contaminant in groundwater in the State, nitrate, commonly exceeds the U.S. Environmental Protection Agency (USEPA) drinking-water standard ( $10 \text{ mg L}^{-1}$  as N) in agricultural areas due to applications of nitrogen for crops (Chern et al., 1999). Agricultural pesticides in groundwater have been a concern in Wisconsin since 1980 when aldicarb (see Table 1 in Rosen and Lapham, 2007 [this issue] for pesticide chemical names) was first detected in central Wisconsin (Rothschild et al., 1982). Since that time it has been shown that some of the most heavily used pesticides, such as atrazine, often correspond to the most commonly detected pesticides in groundwater (Vanden Brook et al., 2002; Wisconsin Department of Natural Resources, 1994, 2004). In an effort to improve groundwater quality where it has been adversely affected, the State has restricted or prohibited the use of some agricultural chemicals (Wisconsin Department of Agriculture, Trade, and Consumer Protection, 2004a, 2004b). For example, the use of atrazine was restricted beginning in 1991 as part of the Atrazine Rule (Wisconsin Department of Agriculture, Trade, and Consumer Protection, 1991). Efforts have also been made to determine whether changes in agricultural chemical use have resulted in an improvement in groundwater quality (Vanden Brook et al., 2002; LeMasters and Baldock, 1997; Postle et al., 1997; Postle, 1996). To determine whether changes in agricultural chemical use are having the desired effect, it is necessary to measure trends in groundwater quality and to be able to correlate changes in water quality with changes in chemical use. It is also important to understand other factors, such as climate and geology, that can have an effect on groundwater quality. There is interest in measuring and understanding trends in groundwater quality in Wisconsin, but there have been relatively few publications describing such studies.

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\*Corresponding author (dasaad@usgs.gov).  
© ASA, CSSA, SSSA  
677 S. Segoe Rd., Madison, WI 53711 USA

U.S. Geological Survey, 8505 Research Way, Middleton, WI 53562. The use of trade names in this paper is for identification purposes only and does not constitute endorsement by the U.S. Geological Survey.

**Abbreviations:** USGS, United States Geological Survey; NAWQA, National Water-Quality Assessment; USEPA, United States Environmental Protection Agency; Nitrate, nitrite plus nitrate as nitrogen ( $\text{NO}_2 + \text{NO}_3 - \text{N}$ ); CFC, chlorofluorocarbon.



Often the source of sampled groundwater is not known. The locations of wells sampled as part of land-use studies are selected so as to be downgradient from a specific type of land use. However, the actual groundwater flowpaths are assumed to originate beneath the upgradient land use; detailed flowpath locations are not verified. Flow-system wells are installed at multiple depths and at multiple locations along an inferred or simulated groundwater flowpath and are designed to provide a better understanding of the source and fate of the sampled groundwater.

Groundwater age (i.e., the time since recharge occurred) can vary from days to many years throughout an aquifer. Typically, shallow groundwater is younger (i.e., it was recharged more recently) than water in deeper parts of the aquifer. Because of this variability in age, changes in chemical inputs at the land surface do not have a uniform effect on changes in groundwater quality throughout an aquifer. Knowledge of the age of sampled groundwater is important for understanding trends in groundwater quality and relating those trends to historical changes in chemical use. Groundwater age data were not widely collected before the 1990s. In recent years, however, the use of chemical tracers, such as chlorofluorocarbons (CFCs) (Busenberg and Plummer, 1992), sulfur hexafluoride (Busenberg and Plummer, 2000), tritium (Bradbury, 1991), and tritium/helium (Plummer et al., 2000), to date groundwater has been more common. Apparent groundwater ages of water samples collected from the land-use study and flow-system study wells were estimated using CFCs and tritium. Knowledge of groundwater age allows groundwater chemistry to be correlated to temporally variable factors, such as chemical use and climate conditions at the time of recharge.

The objective of this paper is to describe an approach to measure and understand trends in groundwater quality in central Wisconsin using data from two groundwater studies. The approach can be used at other locations where groundwater quality data are collected, groundwater age of the sample water can be determined, and associated temporal data (such as historical chemical use) are available. The combination of data analysis and statistical techniques described here is likely unique. However, the key component of this approach, relating groundwater quality to historical chemical use through the use of groundwater age, has been documented previously (Böhlke and Denver, 1995; Saad, 1997; Böhlke, 2002; Puckett and Cowdery, 2002; Browne and Guldan, 2005).

## Description of the Study Areas

The land-use and the flow-system study areas described in this report are in an agricultural area of central Wisconsin in the Western Lake Michigan Drainages NAWQA study unit (Fig. 1). Brief descriptions of the study areas are given herein; additional information about the land-use study area can be found in Saad (1997).

The land-use study includes 30 wells in the glacial deposits aquifer in an area that covers approximately 4400 km<sup>2</sup> (Fig. 1). The flow-system study site, which is nested within the land-use study area, includes 17 monitor wells and two mini-piezometers completed in the glacial deposits aquifer in the Tomorrow River Watershed in Portage County, Wisconsin (Fig. 1 and 2). Located in the north-central United States, this area has a temperate, continental climate characterized by a large annual range in air temperature and

little monthly variation in precipitation. Annual precipitation can vary considerably. From 1950 to 2003, annual precipitation ranged from 54.9 cm (in 1976) to 114 cm (in 1984), with a median and average of 81 cm (Fig. 3) (National Climatic Data Center, 2006).

Land use throughout the land-use study area is primarily agriculture and forest (covering 48 and 41% of the area, respectively). However, land immediately upgradient from the land-use wells is mainly used to grow corn and alfalfa, the main crops commonly used in rotation by dairy farmers in Wisconsin (Robertson and Saad, 1996). Land use at the flow-system study site is mainly forest, grassland, and agriculture (also mainly corn and alfalfa) (Fig. 2). Upgradient from the flow-system study site, land use includes irrigated and non-irrigated agriculture (mainly corn), forest, and grassland. In 1995, the immediate vicinity around the flow-system study area was designated as an atrazine prohibition area through use of the Atrazine Rule. Although atrazine use was not allowed in the prohibition area (LeMasters and Baldock, 1997), its use was not prohibited farther upgradient from the flow-system study site (Fig. 2).

Soils in the study areas (compiled from the SSURGO database; Natural Resources Conservation Service, 2007) are generally permeable with minimal organic matter content. Saturated hydraulic conductivity (based on the thickness-weighted average of soil characteristics for the soil map unit at each well location) in the land-use study area ranges from 4 to 108  $\mu\text{m s}^{-1}$ . Organic-matter content ranges from 0.3 to 5%. Soils characteristics at the flow-system study site varied minimally between well locations, ranging from 53 to 60  $\mu\text{m s}^{-1}$  for saturated hydraulic conductivity and from 0.4 to 0.5% for organic matter content.

Surficial deposits in the study areas are remnants of glacial outwash and ice-contact deposits (Olcott, 1968) and are generally described as sand or sand and gravel (Richmond and Fullerton, 1983). These deposits are generally 20 to 60 m thick (Olcott, 1968), and, where saturated, they constitute the glacial deposits aquifer (Lapham et al., 2005), which is the primary source of groundwater used in the study area. Hydraulic conductivities determined from slug tests conducted in the land-use study monitor wells ranged from about 0.09 to 50  $\text{m d}^{-1}$ , with a median of 8.2  $\text{m d}^{-1}$  (Saad, 1997). Hydraulic conductivity data were not collected in the flow-system study.

## Groundwater Quality and Historical Agricultural Chemical Use in Wisconsin

Of the chemicals that contaminate groundwater in Wisconsin, nitrate is the most commonly detected (Wisconsin Department of Natural Resources, 2004). It has been estimated that 10% of wells in Wisconsin (and up to 60% of wells in agricultural areas of the State) exceed the USEPA drinking water standard for nitrate (10  $\text{mg L}^{-1}$  as N) (Chern et al., 1999).

Although nitrate can occur naturally in groundwater, elevated concentrations of 2  $\text{mg L}^{-1}$  (USGS, 1999) are commonly associated with leakage from septic systems or with agricultural sources of nitrogen (fertilizer and manure) used to grow crops (Bundy et al., 1994a; Chern et al., 1999). Shaw (1994) estimated that 90% of the nitrate in groundwater in Wisconsin comes from

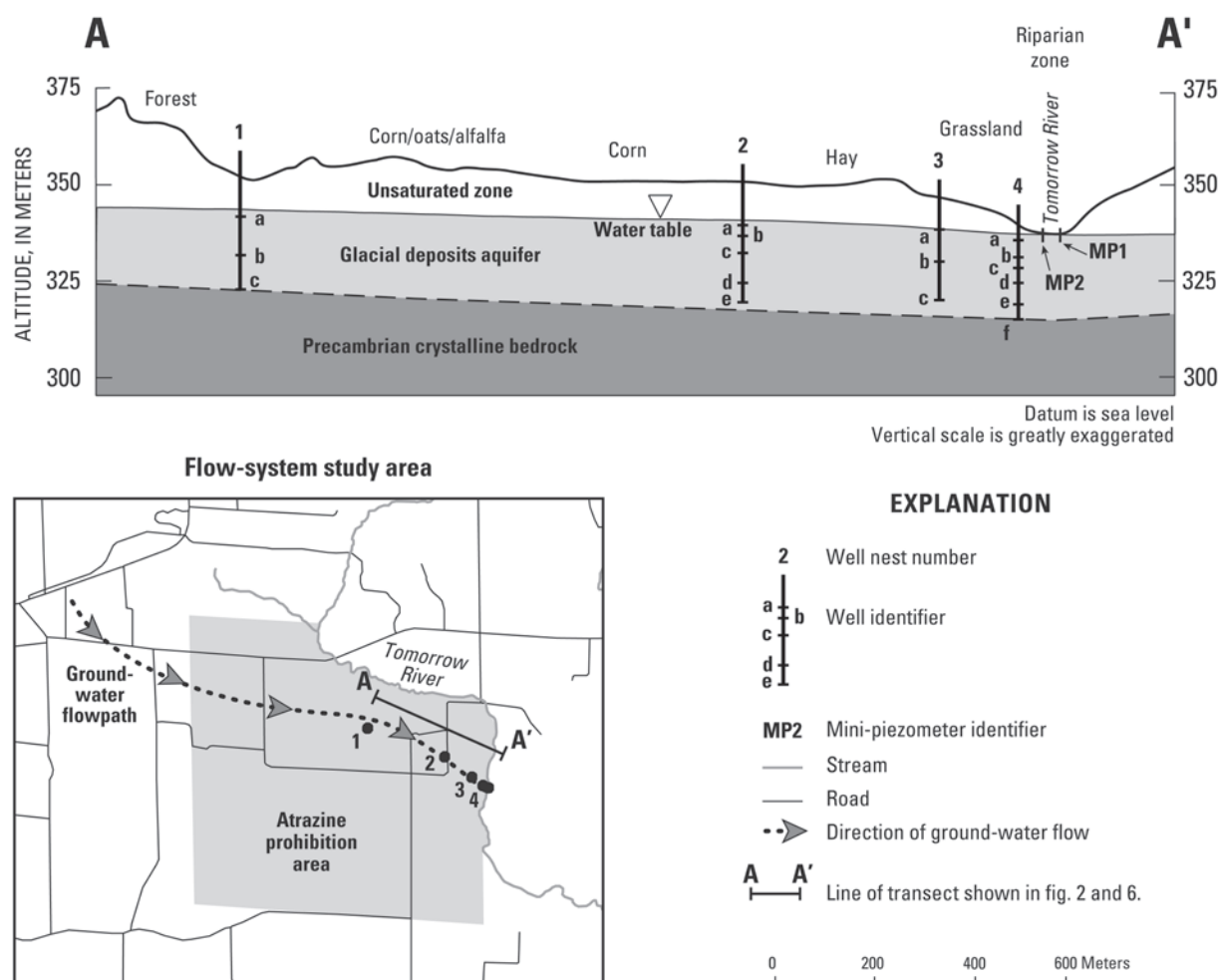


Fig. 2. Water table, geology, land cover, and location of sampled wells and mini-piezometers at the flow-system study area near the Tomorrow River in the Western Lake Michigan Drainages study unit of the USGS National Water Quality Assessment Program.

agricultural sources. In addition to fertilizer and manure, other important sources of nitrogen in agricultural areas can include soil mineralization, atmospheric deposition, and nitrogen fixation from legumes (Böhlke, 2002). Soil mineralization can be a

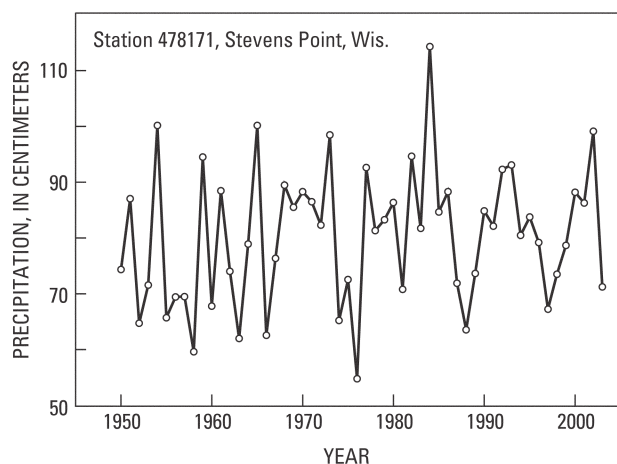


Fig. 3. Historical annual precipitation near the land-use and flow-system study areas (National Climatic Data Center, 2006).

large source of nitrogen, but it is difficult to quantify, and some estimates of mineralization rates seem to be highly correlated to historical fertilizer use (Böhlke, 2002). Atmospheric deposition is a relatively minor source of nitrogen in agricultural areas, and there are limited historical data available. Fixation of nitrogen by legumes, such as alfalfa and soybeans, can be a major source of nitrogen. Statewide, the number of acres planted in alfalfa was relatively unchanged from 1971 to 2000, whereas soybean acres steadily increased. Soybeans have not historically been included in the crop rotation patterns used in the study areas.

Statewide histories of fertilizer and manure use were compiled from various sources (Alexander and Smith, 1990; Battaglin and Goolsby, 1995; National Agricultural Statistics Service, 2006a; Peters and Kelling, 2002; Ruddy et al., 2006). Based on the compiled data, the amount of fertilizer used in Wisconsin increased dramatically from 1950 to about 1985 but has generally stabilized and fluctuated only slightly since then. Manure use has decreased slightly over that same period and is associated with a decrease in the number of milk cows in Wisconsin. Most of the fertilizer use in Wisconsin is for corn. For the period 1994 to 2002, an average of 66% of fertilizer used in Wisconsin was used

on corn (National Agricultural Statistics Service, 2006b, c, d). Considering all of the sources, fertilizer use likely represents the greatest change in nitrogen inputs in the study areas since 1950.

Agricultural pesticide contamination of groundwater generally originates from direct field application or activities related to the handling of pesticides (Wollenhaupt et al., 1990). Many of the pesticides used in Wisconsin have been detected in groundwater (Matzen and Saad, 1996). Atrazine, which has been one of the most heavily used pesticides in Wisconsin since the mid-1960s (Warzecha et al., 1995), has also been one of the most commonly detected in groundwater (LeMasters and Baldock, 1997; LeMasters and Doyle, 1989; Matzen and Saad, 1996; Saad, 1997; Wisconsin Department of Natural Resources, 1994).

Atrazine was first registered as a pesticide in 1958 (USEPA, 2006), and the first widespread use in Wisconsin was the early 1960s (Wollenhaupt et al., 1990). Data compiled from the Wisconsin Agricultural Statistics Service (1979, 1986, and 1991), the National Agricultural Statistics Service (2006e), and Ribaudo and Bouzahr (1994) indicate that statewide atrazine use increased steadily from the 1960s until the mid-1980s and then began to decrease. Starting in 1991, the Atrazine Rule limited the amount of atrazine that farmers could use per acre and established areas in the State in which atrazine use was prohibited. Since the adoption of the Atrazine Rule, atrazine use in Wisconsin has been relatively stable with slight yearly fluctuations.

Although the use of agricultural chemicals has varied considerably over the last 50 years, it also varies on a shorter time scale in the study areas after the corn and alfalfa crop rotation commonly used in the study areas. A typical crop rotation in the land-use study area is 2 to 3 yr of corn followed by 3 to 4 yr of alfalfa (Saad, 1997). In years when corn is planted, fertilizer and herbicides (such as atrazine) are applied to the fields. When alfalfa is planted, herbicides (not including atrazine) and fertilizers are used minimally or not at all (Jackson et al., 1987). Although it would be difficult to compile chemical use information that follows the crop rotation pattern, the fact that it does occur should be considered when trying to understand chemical inputs and the related impacts on groundwater quality.

## Study Design and Methods

Data described in this report were analyzed to determine trends and understand the factors that affect trends in groundwater quality. The water quality data were originally collected as part of NAWQA land-use and flow-system studies conducted in the Western Lake Michigan Drainages. Details of network design, well construction, sample collection, laboratory analysis, groundwater age dating, data adjustments, and statistical method are described below. All land-use study and flow-system study data described in this report are included in Appendixes 1 and 2 (available online at JEQ).

## Network Design, Well Construction, and Sample Collection

The network of wells installed for the land-use study was designed to determine the status and trends in groundwater quality affected by agricultural practices associated with growing corn

and alfalfa. The well sites were chosen using a stratified-random-selection method (Saad, 1997) and were located immediately downgradient from fields planted in corn and alfalfa. The entire network of wells is to be sampled at near-decadal intervals.

The network of wells installed for the flow-system study site was designed to provide an understanding of the source and fate of nutrients and pesticides throughout the entire thickness of the glacial deposits aquifer in an area used to grow corn and alfalfa. The flow-system site was to be nested within the land-use study area, and potential sites were chosen with the aid of a two-dimensional, steady state, analytic-element groundwater flow model (GFLOW) (Haitjema, 1995) constructed for use as a screening tool. Detailed examples of constructing a screening model using GFLOW are given by Hunt et al. (2003) and Feinstein et al. (2006). The near-field portion of the GFLOW model extent includes the Tomorrow River watershed in Portage and Waupaca Counties (Fig. 1). The far-field portion of the GFLOW model includes all or part of the rivers and streams that surround the Tomorrow River. A single layer representing the bulk average properties of the glacial deposits aquifer was simulated and divided into four zones of hydraulic conductivity based on soil properties and slug test results. Near-field surface-water features were simulated using linesinks with resistance (0.3 d); far-field linesinks had no resistance. Hydraulic conductivity and a global uniform recharge rate were varied until a reasonable fit between 42 hydraulic head targets (residual mean error = 0.03 m and absolute residual mean error = 2.9 m) and two stream flow targets (baseflow estimates of 0.6 and 5.4 m<sup>3</sup> s<sup>-1</sup> were simulated as 0.7 and 5.5 m<sup>3</sup> s<sup>-1</sup>, respectively) was obtained. In addition to simulating the 42 head targets, the model also reasonably simulated that portion of a published water-table map of Portage County (Holt, 1965) covered by the screening model. The final hydraulic conductivity values used in the model ranged from 4.5 to 11 m d<sup>-1</sup>; recharge was 26.4 cm yr<sup>-1</sup>.

Simulated flow paths, using the particle tracking options in GFLOW, were used to identify several suitable flow-system study sites. Field reconnaissance and land-owner cooperation narrowed the possible sites to the final location. The flow-system study site is on the west side of the Tomorrow River in northeast Portage County and includes four nests of wells installed near a simulated groundwater flowpath that discharges to the river (Fig. 2).

Most wells sampled for the land-use and flow-system studies were installed by the USGS using hollow-stem augers following protocols and procedures described by Lapham et al. (1995). Land-use study wells were constructed of 5.1-cm PVC with 1.5-m screens and ranged in depth from 3 to 39 m (Appendix 1). Water levels were generally 3 to 11 m but were as much as 31 m below land surface. The screen depth below the measured water level ranged from 0 to 14.9 m (median 4.3 m). More details about the wells used in this study can be found in Saad (1997). Flow-system study wells were constructed of 5.1-cm PVC with 0.9- to 3-m screens (Appendix 2). The well nests are located west and upgradient from the Tomorrow River at distances of 65 m (Well Nest 4), 220 m (Well Nest 3), 600 m (Well Nest 2), and 1500 m (Well Nest 1) (Fig. 2). Well depths range from 3.5 to 30 m and penetrate the entire thickness of the glacial deposits aquifer (Appendix 2). Depth to water ranged from about 1.8 to 9.4 m below land sur-

face, and the screen depth below the measured water level ranged from 0 to 20.4 m. These well nests represent the downgradient part of the entire flowpath length that discharges to the stream at this location. The full length of the flowpath, estimated with the screening model, is about 3.5 to 4.5 km (Fig. 2).

In addition to the 17 monitor wells at the four well nest locations, two mini-piezometers (located at the downgradient end of the simulated flowpath) were sampled as part of flow-system study (Fig. 2). The mini-piezometers were driven into the stream bed (one near the center of flow and the other at the stream edge closest to the other monitor wells) to a depth of about 1.5 m. They were constructed of 1.3-cm, high-density polyethylene plastic tubing and a 15-cm-length stainless steel mesh screen.

Sampling protocols of the USGS (Koterba et al., 1995) were followed in the collection of all water samples from the land-use study and flow-system study wells. The samples were collected using a positive displacement pump (monitor wells) or a peristaltic pump (mini-piezometers). Sample lines were constructed of Teflon or copper (used for collecting CFC samples).

Water quality data described in this paper are limited generally to nutrients, pesticides, and field measurements. Data for these and other water quality constituents measured in samples from land-use and flow-system study wells can be found in Saad (1997) and in Appendixes 1 and 2.

The land-use study wells were sampled during late summer in 1994 and 2002 in an effort to minimize interannual variability (seasonal effects), although such short-term variability may not be an issue because of the wide range in age of the sampled water. Groundwater age information (described below) collected for this study indicates that recharge to the wells in the land-use study network occurred over a period of 40 yr or more. Although all samples were collected in late summer, it is likely that recharge to the wells in the network represents each of the major recharge periods that occur each year, thus minimizing any bias due to intra-annual variability.

### Laboratory Analysis, Recovery, and Re-Coding

Water samples collected in 1994 and 2002 for the land-use study and in 2004 for the flow-system study were analyzed for nutrients and pesticides by the USGS National-Water Quality Laboratory. Nutrients were analyzed using methods described in Fishman and Friedman (1989). The samples collected in 1994 and 2002 were analyzed for pesticides using methods described by Zaugg et al. (1995) and Werner et al. (1996). Pesticides in flow-system study samples from 2004 were analyzed using methods described by Sandstrom et al. (2001) and the USGS Organic Geochemistry Research Lab (USGS, 2006a).

Because pesticide data produced by the USGS National-Water Quality Laboratory are not automatically adjusted for analytical recovery (a measure of how well laboratory-reported concentrations represent environmental concentrations), it was necessary to adjust reported concentrations on the basis of laboratory recovery performance for several pesticides. Thus, the atrazine and deethylatrazine concentrations shown in graphs and used in statistical analyses in this paper were adjusted for laboratory recoveries based on an analysis of historical laboratory recovery data (Bexfield, 2007 [this

issue]; Laura Bexfield, USGS, written commun., 4 Nov. 2005). Recoveries for atrazine in the samples collected in 1994 for the land-use study ranged from 87.8 to 88.1% (average 87.9%); deethylatrazine recoveries averaged 33.5% (range 33.1–33.8%). Atrazine recoveries averaged 110% during the 2002 sampling effort; deethylatrazine averaged 62.9% recovery and ranged from 62.7 to 63%. For the samples collected during the 2004 flow-system study, atrazine recovery was 108%, and deethylatrazine recovery was 36%. Because the variability in atrazine and deethylatrazine recoveries during each sampling period was minimal, the average recoveries reported here were used to adjust laboratory-reported concentrations. Recoveries of nitrate did not change and were consistently near 100% from 1993 to 2004 (Rupert, 2007 [this issue]; Michael Rupert, USGS, written commun., 21 Oct. 2005).

To make low-level concentration data (values at or below the laboratory reporting limit) from 1994 and 2002 comparable, results were uniformly re-coded using an approach suitable for comparisons using nonparametric statistics (described in more detail by Bexfield, 2007 [this issue]). Specifically, all “less than” data were re-coded to one half of the lowest reporting limit or lowest estimated value, and estimated values were used as quantified values. For nitrate and deethylatrazine, “less than” values were set to one half of the lowest estimated value ( $0.015 \text{ mg L}^{-1}$  for nitrate and  $0.0015 \text{ } \mu\text{g L}^{-1}$  for deethylatrazine), and estimated values were used as quantified values. For atrazine, all “less than” values were set to  $0.0005 \text{ } \mu\text{g L}^{-1}$  (one half of the lowest reporting limit); there were no estimated values for atrazine.

Throughout this article, values are reported for concentrations of atrazine plus deethylatrazine. These values represent the sum of the concentrations of atrazine and deethylatrazine in micrograms per liter as atrazine. For instances in which atrazine or deethylatrazine were re-coded, the re-coded values were included in the sum. Before summing, concentration values of deethylatrazine were converted to equivalent atrazine units based on the molar ratio of atrazine (molecular weight = 215.69) to deethylatrazine (molecular weight = 186.60) (Lee et al., 2002). Units of deethylatrazine were multiplied by 1.156 ( $215.69/186.60$ ) to determine equivalent atrazine units. Unless otherwise noted, all concentrations described in text and figures and included in statistical analyses in this paper were re-coded to a uniform reporting level and, in the case of atrazine and deethylatrazine, adjusted for analytical recovery. Data included in Appendixes 1 and 2 represent original data and are not re-coded to a uniform reporting level and are not adjusted for recovery.

### Groundwater Age Dating

The recharge date of most of the sampled water from the land-use and flow-system study wells (Appendixes 1 and 2) was estimated using chlorofluorocarbons  $\text{CFCl}_3$  (CFC-11),  $\text{CF}_2\text{Cl}_2$  (CFC-12), and  $\text{C}_2\text{F}_3\text{Cl}_3$  (CFC-113). The CFC concentrations in the samples were related to historical atmospheric CFC mixing ratios corresponding to the time of recharge using Henry's Law following methods developed by Busenberg and Plummer (1992). This method requires an estimate of temperature and atmospheric pressure in the unsaturated zone above the water table at the time of recharge. For the land-use study samples, temperature and pres-

sure were estimated using mean annual air temperature ( $7.5^{\circ}\text{C}$ ) and elevation of the sampling location (Appendix 1). For the flow-system study samples, elevation was used to estimate pressure, and recharge temperature was estimated using dissolved argon and nitrogen gas data (Busenberg et al., 1993). Estimates of recharge temperature ranged from 6 to  $10^{\circ}\text{C}$ , with a median of  $8.6^{\circ}\text{C}$  (Appendix 2). Uncertainty in CFC-based groundwater recharge dates can vary from a year or two to more than 5 yr. For CFC samples collected from land-use study wells, uncertainty in recharge temperatures is probably the largest source of error in estimates of groundwater recharge date (changes in elevation are relatively small). On the basis of an uncertainty in recharge temperature of  $1^{\circ}\text{C}$  ( $7.5 \pm 1^{\circ}\text{C}$ ), recharge dates varied from within 1 yr (for older waters) to more than 5 yr from the original estimate (for youngest waters). This uncertainty analysis indicates that the recharge date for most samples may be expected to vary within  $\pm 2$  yr of the original estimate. Most of the recharge dates described in this paper were based on the median apparent age from CFC-12 data. The CFC-12 apparent ages were generally consistent between replicate samples collected at every well and were similar to corresponding CFC-11 and CFC-113 apparent ages in oxic samples. Additional details of the methods used to estimate groundwater recharge dates for the land-use study wells can be found in Saad (1997). Additional details of the CFC sample collection and analytical methods, as well as additional references describing groundwater age dating, are described by the USGS (2006b).

The recharge date for one land-use study well (Well 23, Fig. 1) was estimated on the basis of tritium levels following methods described by Bradbury (1991). Tritium levels measured in a sample from this well in 1994 were  $0.5 \text{ pCi L}^{-1}$ , which indicates the water recharged before 1955. For purposes of graphical display and statistical correlations, the recharge date for the water sample from this well was arbitrarily assigned to be 1950, but the water sample could be older.

Groundwater recharge dates for 2002 land-use study samples (Appendix 1) were assigned using the recharge date from the 1994 water samples plus 8 yr (the time between sampling). Justification for using a single recharge date estimate for multiple samples is based on the assumption that the groundwater gradient and thus the water residence time in the vicinity of the sampled wells was not significantly different for the samples collected in 1994 and 2002. Residence time is calculated as the sampling date minus the recharge date and is controlled by the average linear groundwater velocity. For example, a faster velocity produces a shorter residence time. The average linear velocity is directly proportional to hydraulic conductivity ( $K$ ) and hydraulic gradient ( $i$ ) and inversely proportional to porosity (Freeze and Cherry, 1979). Hydraulic conductivity and porosity in the vicinity of sampled wells is static; however, the groundwater gradient is not static. The hydraulic gradient is affected by recharge associated with precipitation during the entire time of groundwater residence and should be less variable with distance away from discharge locations (like a stream or pumping well). The locations of the land-use study wells were selected to be distant from streams and pumping wells. A statistical comparison (using the Wilcoxon signed-rank test, described in the Statistical Methods section) of

mean precipitation during the residence times for 1994 samples and the residence times implied for 2002 samples showed no significant difference ( $p = 0.3$ ). Based on this analysis, it seems reasonable to apply recharge dates from the 1994 samples plus 8 yr to the 2002 samples for the WMIC land-use study wells.

## Statistical Methods

The Wilcoxon signed-rank test was used to determine if there was a difference in median concentrations of nitrate and atrazine plus deethylatrazine between paired samples collected in 1994 and 2002 from land-use study wells. The null hypothesis of the signed-rank test is that the median difference of paired samples is zero (Helsel and Hirsch, 2002). Spearman's rho was used to measure monotonic relationships between measured concentrations and variables expected to have a causal relationship to concentration. Additionally, Spearman's rho was used to measure monotonic relationships between causal variables to determine which are highly correlated to each other. The null hypothesis of the Spearman's rho test is that there is no correlation between the two variables ( $\rho = 0$ ). Annual agricultural chemical use and annual precipitation corresponding to the year of recharge for each sample were used in calculating Spearman's rho for those variables. Moving averages for chemical use and annual precipitation were also tested for monotonic relationships to concentration. These tests were done to improve correlations by minimizing variability due to the uncertainty associated with the assigned year of recharge (based on CFCs) and agricultural-chemical use (after the 5- to 7-yr corn and alfalfa rotation). Three-year and 5-year moving averages were calculated for chemical use and annual precipitation using the years before, during, and after the year of recharge. For example, the 5-yr moving average is based on the 2 yr before, 2 yr after, and the assigned year of recharge. Additionally, 2-, 3-, and 4-yr "pre" moving averages were calculated using only the years before and the assigned year of recharge to determine whether correlations improved using only antecedent information. Wilcoxon signed rank test and Spearman's rho analyses were performed using the computer program SAS (SAS Institute, Inc., 1999).

To determine if concentrations of nitrate and pesticides in samples from individual wells were significantly different between the 1994 and 2002 samples, measured concentrations were compared with known measures of sample variability (variability attributed to factors such as sample collection, processing, shipping, and analysis). Using measures of variability calculated for nutrients (Muelier and Titus, 2005) and pesticides (Martin, 2002), in replicate samples collected for the NAWQA program, 95% confidence intervals were calculated for measured values of nitrate, atrazine, and deethylatrazine. If the 95% confidence intervals for paired samples overlapped, there was no difference in the concentrations measured in the samples collected in different years.

Concentration data plotted by recharge date were aggregated and smoothed to graphically show historical trends. Data were aggregated into 5-yr intervals based on recharge date and displayed in boxplots. Data were smoothed with a locally weighted least squares smooth (LOESS) algorithm using computational methods described by Cleveland and Grosse (1991). Boxplots and smooth lines were generated us-

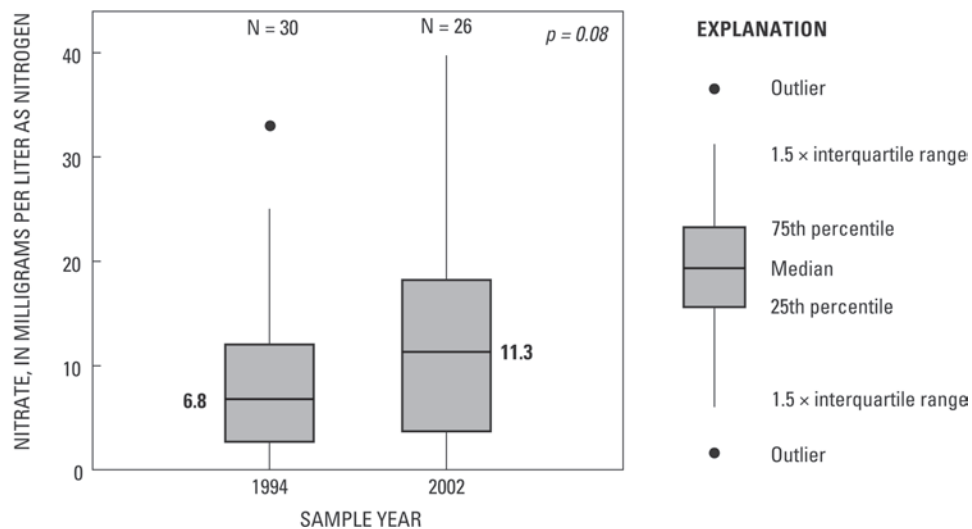


Fig. 4. Distribution of concentrations and signed-rank test results ( $p$  value) of nitrate by sample year for land-use study wells.

ing the computer program S-PLUS (Insightful Corporation, 2001). Smooth lines were created using a span of 0.5, which represents the percentage of all adjacent data used to calculate the local smooth value.

For statistical analyses used in this study, the probability (or  $p$  value) that the measured difference or monotonic relationship occurs by chance is described in the text or shown on graphs. In this paper,  $p \leq 0.05$  was generally considered significant;  $p \leq 0.1$  was considered significant for the Wilcoxon signed-rank test.

## Results and Discussion

### Trends in Groundwater Quality

#### Trend Analysis Using Near-Decadal Data

**Nitrate.** Of the 30 land-use wells sampled in 1994, 26 were resampled in 2002. During this near-decadal interval, the median concentration of nitrate in samples from the land-use study wells increased by  $4.5 \text{ mg L}^{-1}$  as N (Fig. 4). After re-coding the data to a uniform laboratory reporting limit and accounting for sample variability, the concentrations of nitrate increased in 13 of 26 resampled wells, decreased in six wells, and did not change in seven wells. Results of the signed-rank test for paired data indicate that the median difference in the concentration of nitrate was significantly different from zero ( $p = 0.08$ ). This indicates that for shallow groundwater in the glacial deposits aquifer, downgradient from agricultural fields used primarily to grow corn and alfalfa, concentrations of nitrate were significantly higher in samples collected in 2002 than those collected in 1994.

**Atrazine and Deethylatrazine.** After re-coding the atrazine and deethylatrazine data to uniform laboratory reporting limits and accounting for laboratory analytical recovery, it was determined that median atrazine and deethylatrazine concentrations decreased from  $0.08$  to  $0.04 \text{ } \mu\text{g L}^{-1}$  and  $0.25$

to  $0.2 \text{ } \mu\text{g L}^{-1}$ , respectively, from 1994 to 2002 (Fig. 5). Results of the signed-rank test for paired data indicate that the median difference in the concentrations of atrazine and deethylatrazine was significantly different from zero ( $p = 0.09$  and  $p = 0.03$ , respectively). To determine changes in total measured atrazine, atrazine and deethylatrazine concentrations were combined into a single value (expressed as atrazine plus deethylatrazine, in micrograms per liter as atrazine). The median difference in the concentration of atrazine plus deethylatrazine was significantly different from zero ( $p = 0.02$ ) (Fig. 5). Of the

26 wells sampled in 1994 and 2002, the concentration of atrazine plus deethylatrazine decreased in 13, increased in three, and was unchanged in 10.

It is important to note the sensitivity of the signed-rank test results to the pre-test data adjustments for the concentrations of atrazine plus deethylatrazine. If a comparison of atrazine plus deethylatrazine data were based only on data re-coded to uniform laboratory reporting limits, it would seem that 13 of 26 resampled wells had greater concentrations in 2002 and 13 had lower concentrations and that the median concentration increased slightly ( $0.17$ – $0.2 \text{ } \mu\text{g L}^{-1}$ ). The signed-rank test would have indicated that the median difference was not significantly different from zero ( $p = 0.78$ ). Only after accounting for laboratory analytical recovery is it apparent that median concentrations of atrazine plus deethylatrazine decreased from 1994 to 2002 and that the difference was significant (Fig. 5). Had considerations not been given to all of the necessary data adjustments, conclusions about trends in concentrations of atrazine plus deethylatrazine from 1994 to 2002 would have been incorrect.

#### Trend Analysis Using Groundwater Age

Knowledge of groundwater age allows snapshots of groundwater quality in time to be compared with temporally variable factors, such as climate and agricultural chemical use. Groundwater age information associated with water samples collected from wells at the land-use study and flow-system study sites was used to put concentration data into a temporal context beyond that associated with changes determined only from the sampling interval. The results described in this section demonstrate the value of groundwater age information in displaying and understanding trends in groundwater quality.

Estimates of recharge date for water samples collected from land-use study wells in 1994 and 2002 ranged from 1950 to 2002 (Appendix 1). Recharge dates for samples collected in 2004 from flow-system study wells ranged from 1964 to 1996

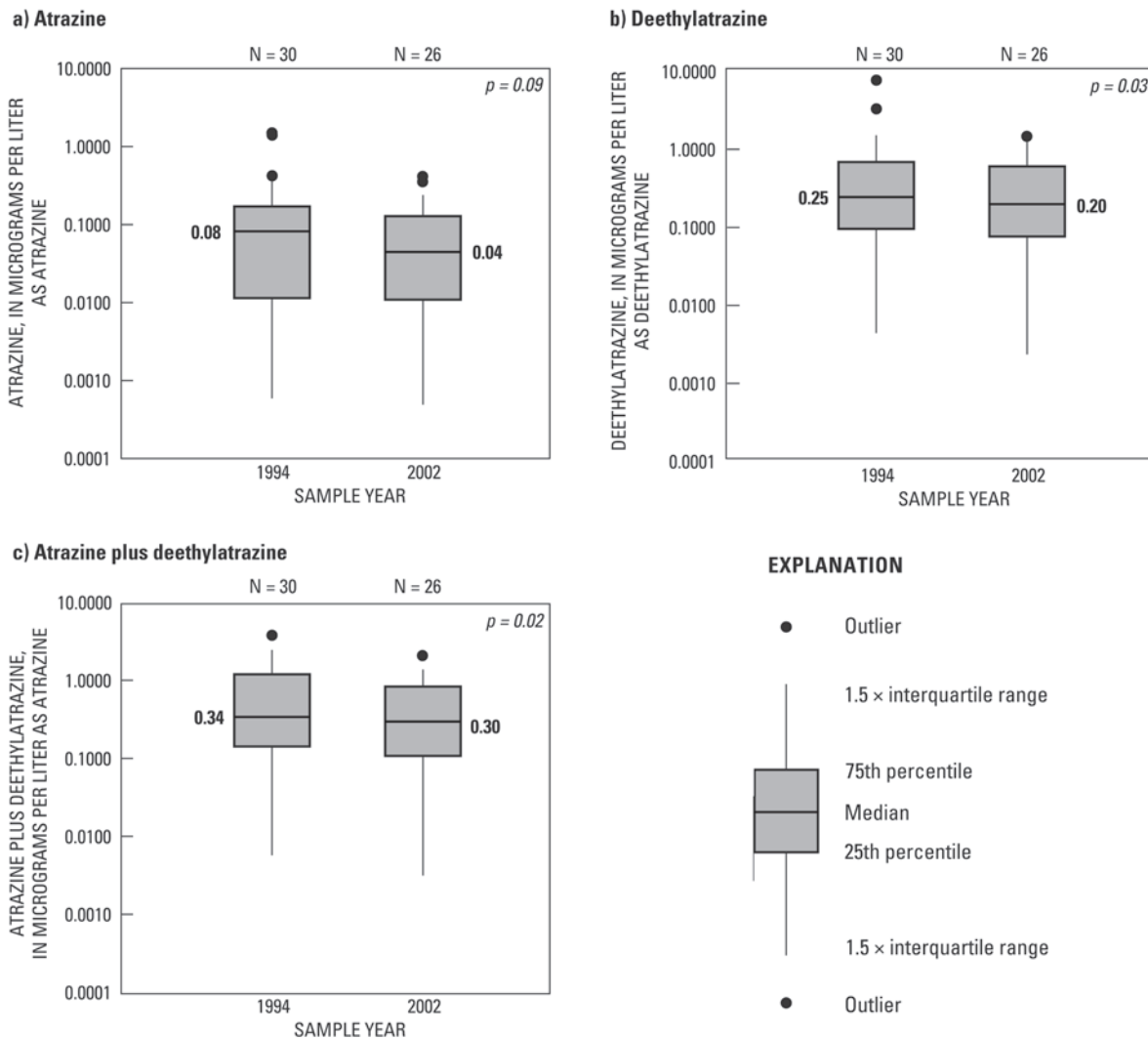


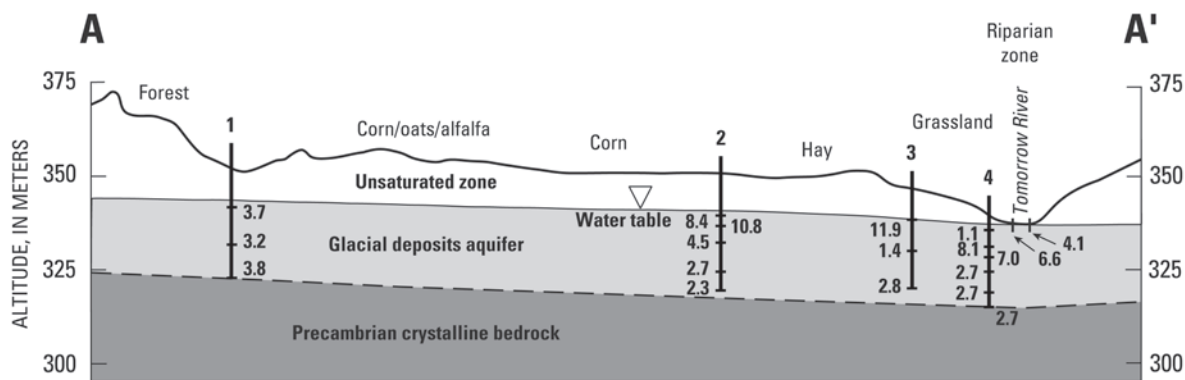
Fig. 5. Distributions of concentrations and signed-rank test results (p value) of (a) atrazine, (b) deethylatrazine, and (c) atrazine plus deethylatrazine by sample year for land-use study wells.

(Appendix 2). Groundwater ages generally increase with depth and with distance along the flowpath as expected based on flow directions determined from measured heads (Fig. 6c). Several of the flow-system study wells (Wells 1a, 3a, and 4a) have screened intervals that intersect the water table. Samples from these wells likely represent a mixture of recently recharged (<1 yr old) and older water. Wells typically produce a mixture of water of different ages. The range of sampled ages can be minimized by sampling wells with short screens and avoiding zones of converging groundwater flowpaths. Most of the flow-system study wells have short screens ( $\leq 0.9$  m) and are away from zones of convergence. However, the water-table wells have longer screens (1.5–3 m) and to some degree are nearer zones of convergence (recently recharged water converging with older, upgradient water near the water table). Concentrations of nitrate and atrazine in wells that produce waters of mixed ages do not necessarily mirror the trends in agricultural-chemical use (Fig. 6a and 6b). For this reason, the analysis of flow-system study data focuses primarily on the non-water-table wells.

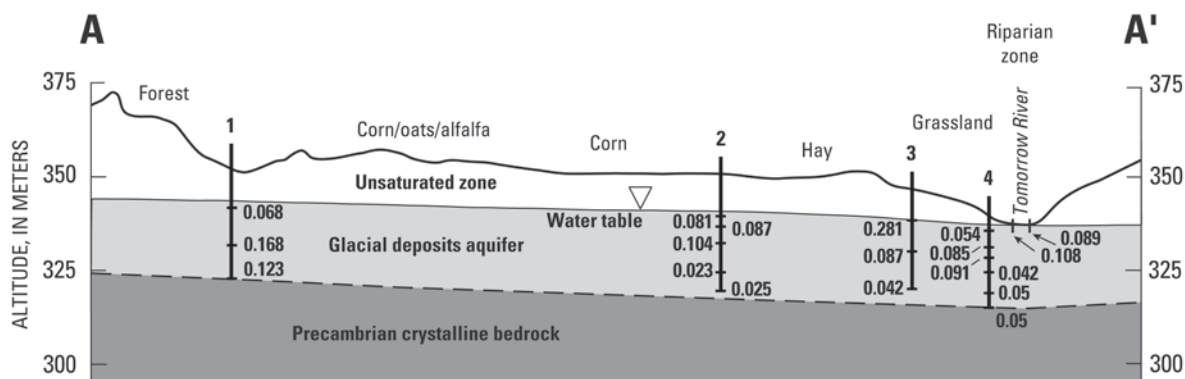
**Nitrate.** Concentrations of nitrate in samples from the land-use study wells are plotted by groundwater recharge date in Fig. 7. The general pattern indicates that the highest concentrations of nitrate are typically found in younger water. The concentrations of nitrate in samples collected from flow-system study wells follows a similar pattern (Fig. 8). In addition to being screened at the water table, Wells 1a and 4a (Fig. 6a) are located in areas that may not be strongly affected by upgradient agricultural, providing an additional reason why concentrations of nitrate in these wells do not necessarily mirror the trend in fertilizer use (Fig. 8).

Data aggregation and smoothing techniques were used to identify general patterns or trends in the concentrations of nitrate and pesticides over time. These techniques were not applied to the flow-system study data because of the limited number of samples and the fact that the wells were installed to represent effects from various types of land use. The concentrations of nitrate from the land-use study wells were aggregated into 5-yr intervals and are displayed as boxplots at

a) Nitrate, in milligrams per liter as nitrogen



b) Atrazine plus deethylatrazine, in micrograms per liter as atrazine



c) Chlorofluorocarbon-based ground-water recharge dates

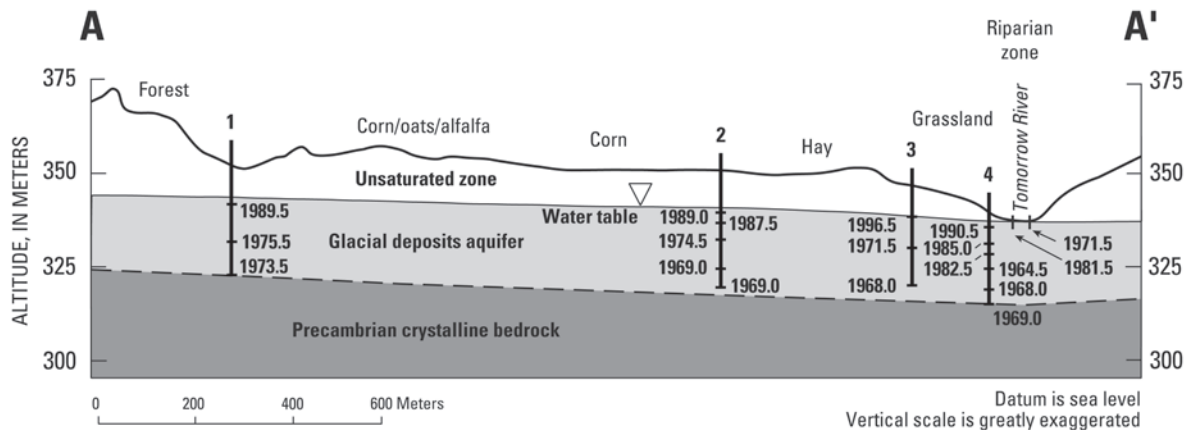


Fig. 6. Distribution of (a) nitrate and (b) atrazine plus deethylatrazine concentrations in groundwater and (c) chlorofluorocarbon-based groundwater recharge dates at the flow-system study site. For more information describing transect A–A', see Fig. 2.

the midpoint of the 5-yr interval (Fig. 7). The boxplots show that the median and highest concentrations of nitrate increase steadily to the mid 1990s and then decrease. A LOESS smooth line through the data shows a similar pattern (Fig. 7). The pattern of increasing concentrations mirrors the increasing trend in fertilizer nitrogen use in Wisconsin. Without additional data, it is impossible to say whether the downward trend in nitrate concentration after the mid 1990s is real or is an artifact of the few samples available to represent water that

recharged after the mid 1990s. Most of the samples collected in 1994 and 2002 represent water that recharged the aquifer during the period of increasing fertilizer use. Therefore, it is reasonable to assume that, as a result of increased fertilizer use, concentrations of nitrate did increase from 1994 to 2002, as indicated by the signed-rank test described previously.

**Atrazine Plus Deethylatrazine.** Concentrations of atrazine plus deethylatrazine in water samples from the land-use study wells are plotted by groundwater recharge date in Fig. 9. The general

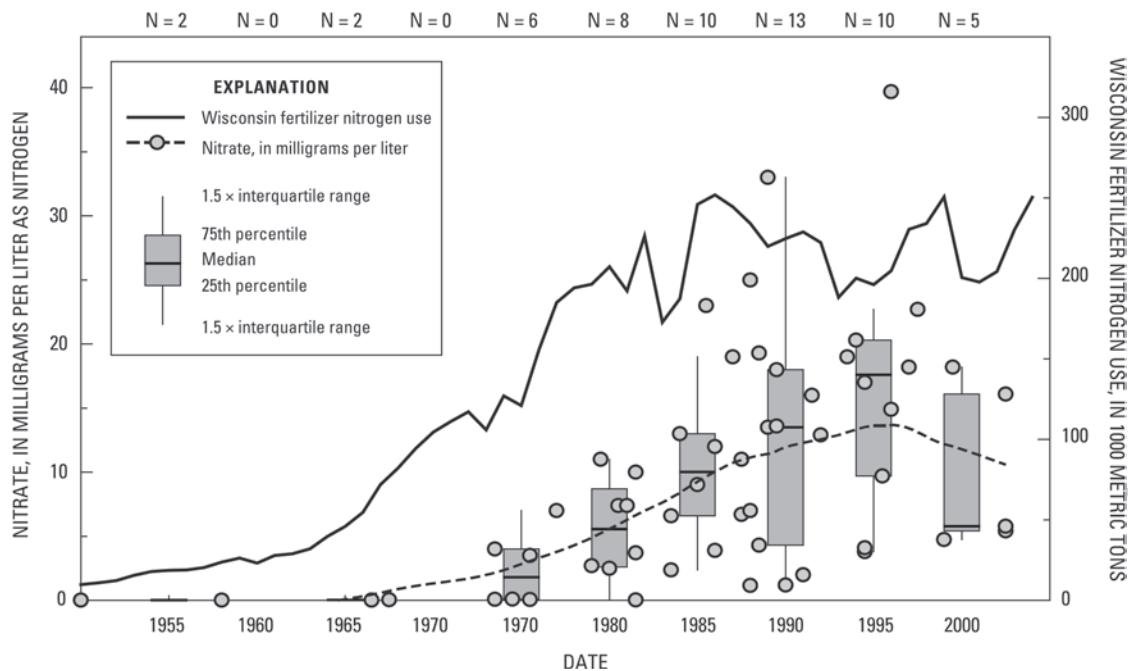


Fig. 7. Concentrations of nitrate in samples from land-use study wells plotted by groundwater recharge date, boxplots of nitrate grouped by 5-yr groundwater recharge date intervals and historical fertilizer use in Wisconsin. The number of samples for each boxplot is shown at the top of the figure. The dashed line is a locally weighted least squares smooth of nitrate concentrations using a span of 0.5.

pattern indicates that concentrations were typically highest in water that recharged during the mid 1980s; concentrations were slightly lower in younger water and much lower in older water. Boxplots and a LOESS smooth line through the data show a similar pattern: generally increasing concentrations to the mid 1980s, followed by a decrease to the early 1990s, followed by steady concentrations (Fig. 9). The concentration pattern over time is similar to the historical pattern of atrazine use on corn in Wisconsin (Fig. 9). The samples collected in 1994 and 2002

represent water that recharged during the periods of increasing and decreasing atrazine use. Slightly more than half of the land-use study samples represent water that recharged after 1985 and the subsequent years of decreasing atrazine use. This agrees with the results of the signed-rank test described previously: a slight but statistically significant decrease in concentrations of atrazine plus deethylatrazine from 1994 to 2002.

Concentrations of atrazine plus deethylatrazine in water samples from flow-system study wells (Fig. 6b) are plotted by recharge

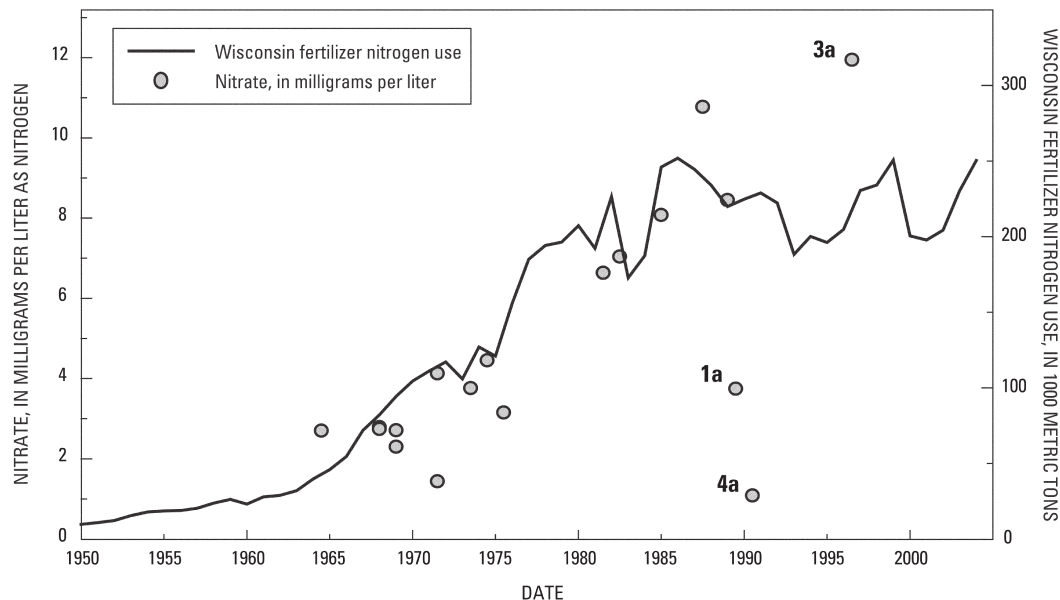


Fig. 8. Concentrations of nitrate in samples from flow-system study wells plotted by groundwater recharge date and historical fertilizer use in Wisconsin. Labeled wells are those with screened intervals that intersect the water table.

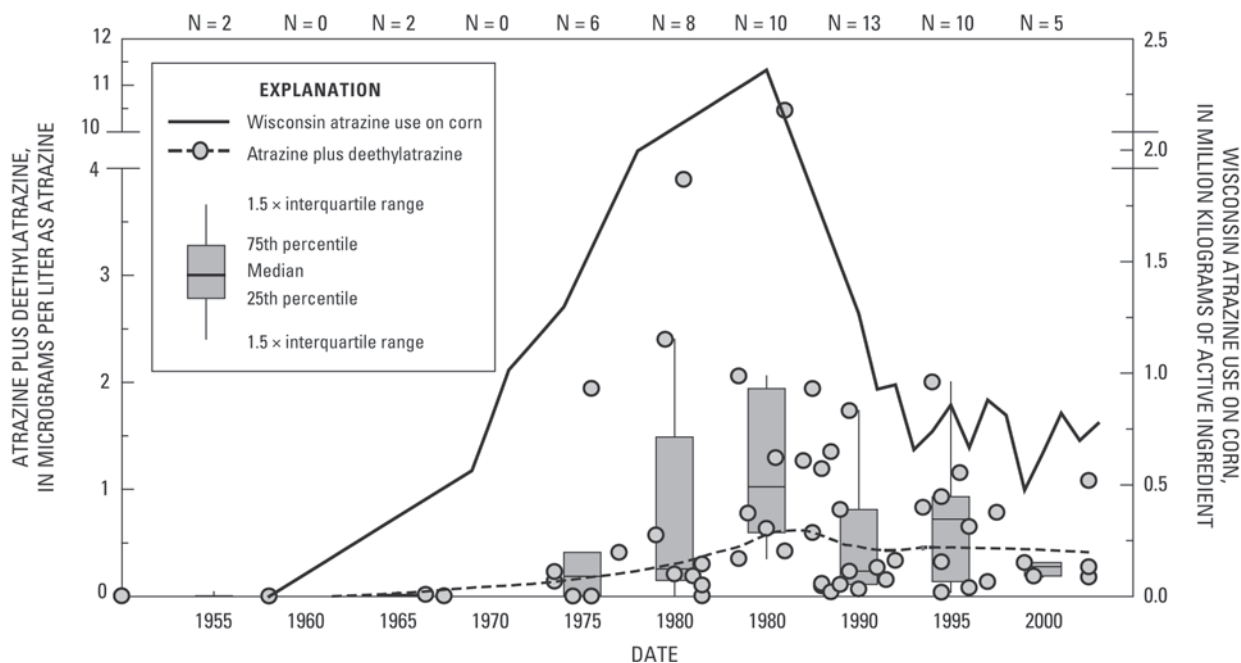


Fig. 9. Concentrations of atrazine plus deethylatrazine in samples from land-use study wells plotted by groundwater recharge date, boxplots of atrazine plus deethylatrazine grouped by 5-yr groundwater recharge date intervals and historical atrazine use on corn in Wisconsin. The number of samples for each boxplot is shown at the top of the figure. The dashed line is a locally weighted least squares smooth of atrazine plus deethylatrazine concentrations using a span of 0.5.

date in Fig. 10. The general pattern showed increasing concentrations to the mid to late 1970s, followed by decreasing concentrations. Atrazine use was prohibited in the vicinity of the flow-system study starting in 1995, so the highest concentration in Well 3a (CFC-based recharge date = 1996) is likely anomalous and due to mixing of waters of difference ages as described previously. Except for Well 3a, the peak in concentration seems to be earlier than the

peak in statewide atrazine use. This could indicate that atrazine use in the flow-system study area peaked before the statewide average.

#### Factors Affecting Concentrations of Agricultural Chemicals in Groundwater

Spearman's rho correlations were used to provide statistical support to the visual relation between concentrations of agricultural chemicals in groundwater and their use on crops and to identify significant relations to other causal factors

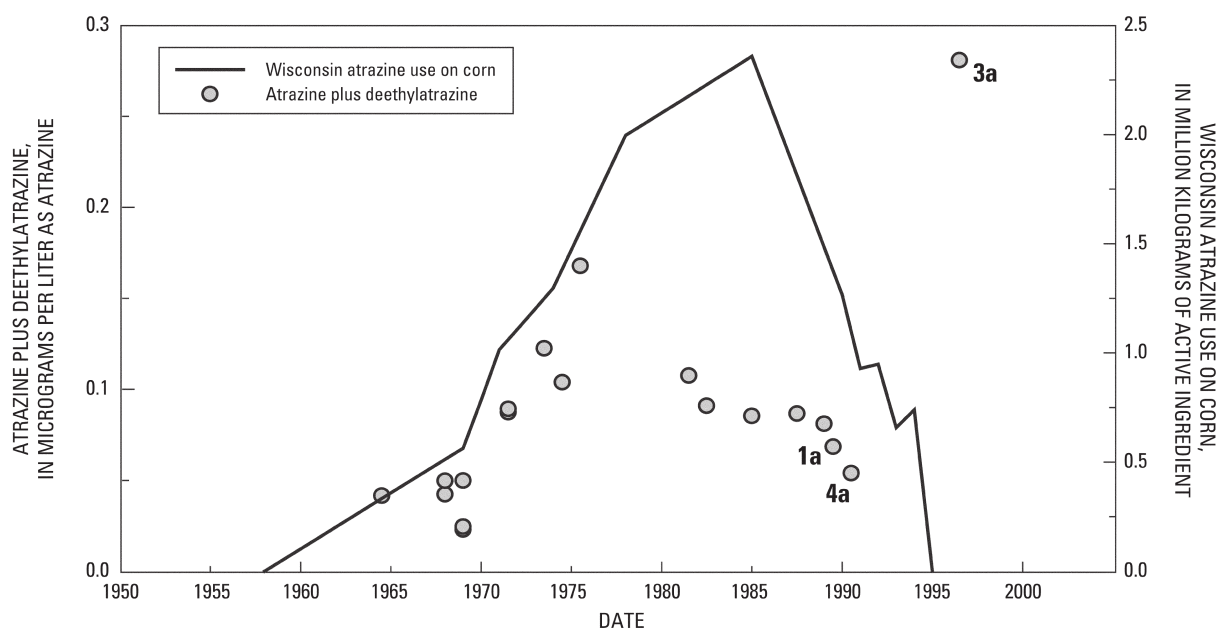


Fig. 10. Concentrations of atrazine plus deethylatrazine in samples from flow-system study wells plotted by groundwater recharge date and historical atrazine use on corn in Wisconsin. Labeled wells are those with screened intervals that intersect the water table. Statewide atrazine use data modified to show local atrazine prohibition beginning in 1995.

that were expected to have an effect on those concentrations. Factors included in the analysis and expected to have a causal relation are shown in Table 1.

**Nitrate.** The only factors that were significantly correlated to concentrations of nitrate in samples collected from the land-use study wells include historical fertilizer use, groundwater residence time, and concentrations of dissolved oxygen in groundwater (Table 1). Fertilizer use and dissolved oxygen are positively correlated to concentrations of nitrate, whereas residence time is negatively correlated. Fertilizer use is highly correlated to residence time and dissolved oxygen. The median concentration of dissolved oxygen in land-use study wells was 6.8 mg L<sup>-1</sup>. However, dissolved oxygen concentrations were generally lower in older water, and concentrations in the oldest water samples (recharged before 1970) were all less than 0.5 mg L<sup>-1</sup> (Appendix 1). The reducing conditions in the older water samples make denitrification a possible factor in producing water samples with low concentrations of nitrate. In the absence of oxygenated samples of old water, it is difficult to distinguish between the effects of denitrification and of less fertilizer use on concentrations of nitrate in older water. For water samples with concentrations of dissolved oxygen greater than 0.5 mg L<sup>-1</sup>, Spearman's rho correlation between concentrations of nitrate and fertilizer use was not significant at the 0.05 level. For these same samples, concentrations of nitrate were significantly correlated to screen depth below water level (Table 1).

Moving averages of fertilizer use for all land-use study samples slightly improved correlations of concentrations of nitrate to fertilizer use for the 5-yr and pre-3-yr averages (Table 2). For oxygenated samples (dissolved oxygen >0.5 mg L<sup>-1</sup>), the 5-yr and pre-3-yr moving averages improved correlations of concentrations of nitrate to fertilizer use and were significant at the 0.05 level.

Spearman's rho correlations using only those flow-system study samples collected from nonwater table wells show significant correlations of nitrate to fertilizer use, dissolved oxygen, residence time, well depth, and screen depth below water level (Table 3). Fertilizer use, residence time, dissolved oxygen, and the depth factors are all highly correlated to each other (Table 3). In the flow-system study wells, dissolved oxygen and the depth factors likely represent surrogates for groundwater age, which is highly correlated to fertilizer use (Table 3). Dissolved oxygen concentrations in all flow-system study wells were greater than 0.5 mg L<sup>-1</sup>, indicating that denitrification is not a major factor in the lower concentrations of nitrate in older water. It has been reported elsewhere that denitrification can be minimal in oxygenated, sand, and gravel aquifers (Korom, 1992). Although a number of factors seem to be significantly correlated to concentrations of nitrate at the flow-system study site, the primary factor affecting concentrations is likely fertilizer use.

**Atrazine Plus Deethylatrazine.** The factors that were significantly correlated to concentrations of atrazine plus deethylatrazine in samples collected from the land-use study wells include historical atrazine use, annual precipitation, and dissolved oxygen (Table 1). The pre-2-, 3-, and 4-yr moving averages of atrazine use samples slightly improved correlations to concentrations of atrazine plus deethylatrazine (Table 2). Three- and 5-yr moving averages had little effect on correlations of use to concentrations.

Table 1. Spearman's rho correlation coefficients between concentrations of nitrate and atrazine plus deethylatrazine in samples from land-use study wells and environmental characteristics (N = 56 except where noted).

|                                                           | Fertilizer use | Atrazine use | Well depth | Water level | Screen depth below water level | Residence time | Aquifer hydraulic conductivity | Soil organic matter content | Soil saturated hydraulic conductivity | Annual precipitation | Dissolved oxygen |
|-----------------------------------------------------------|----------------|--------------|------------|-------------|--------------------------------|----------------|--------------------------------|-----------------------------|---------------------------------------|----------------------|------------------|
| Nitrate, mg L <sup>-1</sup> (all samples)                 | 0.49*          | -†           | 0.16       | 0.16        | 0.25                           | -0.51*         | 0.04                           | 0.04                        | -0.09                                 | 0.05                 | 0.40*            |
| Nitrate, mg L <sup>-1</sup> (DO > 0.5 mg/L, N = 47)       | 0.27           | -            | 0.16       | 0.06        | 0.35*                          | -0.28          | -0.02                          | -0.03                       | 0.02                                  | -0.14                | 0.17             |
| Atrazine plus deethylatrazine, µg L <sup>-1</sup>         | -              | 0.34*        | 0.22       | 0.22        | 0.24                           | -0.21          | 0.25                           | 0.05                        | 0.06                                  | 0.30*                | 0.51*            |
| Fertilizer use, 1000 metric tons of N per year            | 1              |              |            |             |                                |                |                                |                             |                                       |                      |                  |
| Atrazine use, million kg active ingredient per year       | 0.21           | 1            |            |             |                                |                |                                |                             |                                       |                      |                  |
| Well depth, m                                             | 0.09           | -0.18        | 1          |             |                                |                |                                |                             |                                       |                      |                  |
| Water level, m                                            | 0.13           | -0.15        | 0.91*      | 1           |                                |                |                                |                             |                                       |                      |                  |
| Screen depth below water level, m                         | 0.14           | -0.02        | 0.57*      | 0.27*       | 1                              |                |                                |                             |                                       |                      |                  |
| Residence time, yr                                        | -0.52*         | 0.27*        | -0.19      | -0.32*      | 0.07                           | 1              |                                |                             |                                       |                      |                  |
| Aquifer hydraulic conductivity, m d <sup>-1</sup>         | -0.10          | 0.01         | 0.19       | 0.34*       | -0.17                          | -0.14          | 1                              |                             |                                       |                      |                  |
| Soil organic matter content, %                            | 0.08           | -0.02        | -0.32*     | -0.30*      | -0.12                          | -0.11          | -0.33*                         | 1                           |                                       |                      |                  |
| Soil saturated hydraulic conductivity, µm s <sup>-1</sup> | 0.00           | -0.01        | 0.07       | -0.02       | 0.18                           | 0.10           | 0.09                           | -0.48*                      | 1                                     |                      |                  |
| Annual precipitation, cm                                  | -0.06          | 0.02         | -0.09      | -0.03       | -0.12                          | -0.23          | 0.09                           | 0.11                        | -0.05                                 | 1                    |                  |
| Dissolved oxygen, mg L <sup>-1</sup>                      | 0.32*          | -0.06        | 0.61*      | 0.69*       | 0.31*                          | -0.56*         | 0.40*                          | -0.23                       | 0.09                                  | 0.14                 | 1                |

\* Significant at the 0.05 level.

† Coefficient not calculated.

Table 2. Spearman's rho correlation coefficients between concentrations of nitrate and atrazine plus deethylatrazine in samples from land-use study wells and moving averages for selected environmental characteristics.

|                                                     | Nitrate<br>(all samples)<br><i>N</i> = 56 | Nitrate<br>(DO > 0.5 mg L <sup>-1</sup> )<br><i>N</i> = 47 | Atrazine plus<br>deethylatrazine<br><i>N</i> = 56 |
|-----------------------------------------------------|-------------------------------------------|------------------------------------------------------------|---------------------------------------------------|
|                                                     | mg L <sup>-1</sup>                        |                                                            | μg L <sup>-1</sup>                                |
| Fertilizer use, 1000 metric tons of N per year      | 0.49*                                     | 0.27                                                       | -†                                                |
| Fertilizer use, 3-yr moving average                 | 0.49*                                     | 0.26                                                       | -                                                 |
| Fertilizer use, 5-yr moving average                 | 0.53*                                     | 0.31*                                                      | -                                                 |
| Fertilizer use, pre-2-yr moving average             | 0.47*                                     | 0.23                                                       | -                                                 |
| Fertilizer use, pre-3-yr moving average             | 0.52*                                     | 0.29*                                                      | -                                                 |
| Fertilizer use, pre-4-yr moving average             | 0.47*                                     | 0.22                                                       | -                                                 |
| Atrazine use, million kg active ingredient per year | -                                         | -                                                          | 0.34*                                             |
| Atrazine use, 3-yr moving average                   | -                                         | -                                                          | 0.32*                                             |
| Atrazine use, 5-yr moving average                   | -                                         | -                                                          | 0.33*                                             |
| Atrazine use, pre-2-yr moving average               | -                                         | -                                                          | 0.35*                                             |
| Atrazine use, pre-3-yr moving average               | -                                         | -                                                          | 0.38*                                             |
| Atrazine use, pre-4-yr moving average               | -                                         | -                                                          | 0.36*                                             |
| Annual precipitation, cm                            | 0.05                                      | -0.14                                                      | 0.30*                                             |
| Annual precipitation, 3-yr moving average           | -0.03                                     | -0.12                                                      | 0.16                                              |
| Annual precipitation, 5-yr moving average           | 0.00                                      | -0.16                                                      | 0.23                                              |
| Annual precipitation, pre-2-yr moving average       | 0.04                                      | -0.08                                                      | 0.29*                                             |
| Annual precipitation, pre-3-yr moving average       | 0.04                                      | -0.07                                                      | 0.34*                                             |
| Annual Precipitation, pre-4-yr moving average       | 0.13                                      | -0.01                                                      | 0.38*                                             |

\* Significant at the 0.05 level.

† Coefficient not calculated.

For the nonwater table flow-system study wells, only atrazine use and residence time were significantly correlated to concentrations of atrazine plus deethylatrazine (Table 3).

#### Expected Future Trends in Groundwater Quality

This article has shown that historical trends in groundwater quality of the glacial deposits aquifer in an agricultural area of central Wisconsin are significantly correlated to agri-

cultural chemical use. It is likely that future trends in groundwater quality will also reflect recent and future trends in agricultural chemical use. Changes measured at individual locations vary depending on a number of factors, including the source and age of the sampled groundwater.

The land-use study wells represent groundwater that is affected by the application of agricultural chemicals on the nearby, upgradient land used to grow corn and alfalfa. The typical age of sampled water from these wells is approximately 10 to 20 yr old. Data from the land-use study wells indicate that changes in fertilizer use is likely the primary factor in determining changes in nitrate in shallow groundwater. Therefore, because fertilizer use leveled off around 1985 and continues to remain relatively steady, most concentrations of nitrate in the shallow part of the glacial deposits aquifer should have reached relative stability during the period from about 1995 to 2005 and beyond. As the groundwater gets older and oxygen becomes depleted (i.e., as it moves downgradient in the aquifer), denitrification could also become an important factor in decreasing concentrations of nitrate.

Data from the land-use study wells indicate that atrazine use and annual precipitation are important factors in determining concentrations of atrazine plus deethylatrazine in groundwater. Because atrazine use and annual precipitation are temporally variable, making predictions of future trends in concentrations of

Table 3. Spearman's rho correlation coefficients between concentrations of nitrate and atrazine plus deethylatrazine in samples from flow-system study wells and environmental characteristics (*N* = 19 except where noted).

|                                                                                                | Fertilizer use | Atrazine use | Well depth | Water level | Screen depth below water level | Residence time | Annual precipitation | Dissolved O <sub>2</sub> |
|------------------------------------------------------------------------------------------------|----------------|--------------|------------|-------------|--------------------------------|----------------|----------------------|--------------------------|
| Nitrate, mg L <sup>-1</sup> (all samples)                                                      | 0.65*          | -†           | -0.38      | 0.09        | -0.41                          | -0.57*         | -0.33                | 0.49*                    |
| Atrazine plus deethylatrazine, μg L <sup>-1</sup> (all samples)                                | -              | 0.39         | -0.33      | -0.13       | -0.39                          | -0.54*         | -0.22                | 0.40                     |
| Nitrate, mg L <sup>-1</sup> (excluding water table wells, <i>N</i> = 16)                       | 0.82*          | -            | -0.53*     | 0.01        | -0.59*                         | -0.84*         | -0.33                | 0.72*                    |
| Atrazine plus deethylatrazine, μg L <sup>-1</sup> (excluding water-table wells, <i>N</i> = 16) | -              | 0.64*        | -0.29      | -0.19       | -0.31                          | -0.58*         | -0.15                | 0.40                     |
| Fertilizer use, 1000 metric tons of N per year                                                 | 1              |              |            |             |                                |                |                      |                          |
| Atrazine use, million kg of active ingredient per year                                         | 0.80*          | 1            |            |             |                                |                |                      |                          |
| Well depth, m                                                                                  | -0.58*         | -0.40        | 1          |             |                                |                |                      |                          |
| Water level, m                                                                                 | 0.04           | 0.04         | 0.68*      | 1           |                                |                |                      |                          |
| Screen depth below water level, m                                                              | -0.72*         | -0.37        | 0.92*      | 0.24        | 1                              |                |                      |                          |
| Residence time, yr                                                                             | -0.91*         | -0.58*       | 0.57*      | -0.03       | 0.82*                          | 1              |                      |                          |
| Annual precipitation, cm                                                                       | -0.42          | -0.35        | 0.26       | -0.16       | 0.44                           | 0.43           | 1                    |                          |
| Dissolved O <sub>2</sub> , mg L <sup>-1</sup>                                                  | 0.83*          | 0.54*        | -0.74*     | -0.18       | -0.91*                         | -0.86*         | -0.38                | 1                        |

Note: Aquifer hydraulic conductivity and soil properties were not available or not spatially variable for the flow-system study wells.

\* Significant at the 0.05 level.

† Coefficient not calculated.

atrazine plus deethylatrazine is difficult. For discussion purposes, if it were assumed that future precipitation would equal the historical average and that atrazine use would remain relatively stable, after peaking around 1985 then decreasing until about 1990, then the concentrations of atrazine plus deethylatrazine in shallow groundwater should continue to decrease until reaching relative stability during the period from about 2000 to 2010 and beyond.

The flow-system study wells represent a range of land-uses and depths throughout the glacial deposits aquifer. The age of water sampled from most of the flow-system study wells is 30 to 40 yr old or less than 20 yr old. If the fertilizer-use scenario described above (stable use after 1985) is assumed, many of the wells producing 30- to 40-yr-old water should see increasing concentrations of nitrate for another 10 to 20 yr before the concentrations became stable. The wells that now produce younger water (<20 yr old) should already have relatively stable concentrations of nitrate.

At the flow-system study site, atrazine use likely peaked around 1980 to 1985 and then decreased until about 1990 before being prohibited in 1995 (Fig. 10). Farther upgradient from the study site, where atrazine may still be used, the level of use has likely been stable since 1990, after peaking in the 1980s (based on the statewide use pattern). Again, assuming future precipitation will equal the historical average, concentrations of atrazine plus deethylatrazine in wells producing older water (30–40 yr old) that originated in the prohibition area should continue to increase for another 10 to 20 yr, then begin decreasing and continue to decrease. Wells producing older water that originated upgradient from the prohibition area could have concentrations of atrazine plus deethylatrazine that continue to increase for another 10 to 20 yr, before decreasing and then stabilizing. All young water (less than about 20 yr old) from flow-system study wells likely originates from within the atrazine prohibition area. Concentrations of atrazine plus deethylatrazine in these wells should already be decreasing and continue to decrease in the future. In the prohibition area, it is not known how long it will take for concentrations of atrazine plus deethylatrazine to reach levels less than the laboratory detection limit.

## Conclusions

Data collected from spatially distributed wells of a NAWQA land-use study and from locally nested wells of a NAWQA flow-systems study were analyzed to measure and understand trends in the concentrations of nitrate and atrazine plus deethylatrazine in groundwater in the glacial deposits aquifer in an agricultural area of central Wisconsin. Those analyses showed that concentrations were significantly correlated to historical fertilizer and atrazine use patterns over time. Following the trends in chemical use, concentrations of nitrate in groundwater have increased over time, and concentrations of atrazine plus deethylatrazine increased and then decreased. In addition to being correlated to agricultural chemical use, concentrations of nitrate were correlated to dissolved oxygen concentrations and screen depth below water level. Concentrations of atrazine plus deethylatrazine were correlated to annual precipitation. Understanding the factors affecting trends of concentrations of nitrate and atrazine plus deethylatrazine required knowledge of

the source and age of the sampled groundwater and the history of nitrogen and atrazine use, as well as other ancillary information such as well construction, geology, climate, and water chemistry. Additionally, it was important to apply appropriate adjustments to the water-quality data so that concentrations measured in 1994 could be compared with concentrations measured in 2002.

Data from two types of NAWQA groundwater studies provided for a better understanding of agriculture-related trends in groundwater quality of the glacial deposits aquifer than could the data from either study alone. The land-use study wells provided information for a relatively large area (but only for the shallow part of the aquifer) with assumed knowledge about the groundwater source areas. Based on land-use study samples collected in 1994 and 2002, concentrations of nitrate were higher in samples collected in 2002, whereas concentrations of atrazine plus deethylatrazine were significantly lower. The flow-system study wells provided a better understanding of source areas and the quality of water throughout the entire aquifer thickness but were limited to a small area. The findings in this type of study clearly indicate that changes in chemical inputs at the land surface do not uniformly affect concentrations of those chemicals throughout the aquifer.

Expected future trends in groundwater quality in the study areas should reflect recent and future trends in agricultural chemical use. For shallow groundwater of the land-use study, future concentrations of nitrate and atrazine plus deethylatrazine should remain relatively stable if fertilizer and atrazine use remains stable. For the flow-system study, concentrations of nitrate and atrazine plus deethylatrazine in the deeper, agriculture-impacted wells (producing old water) should continue to increase. Shallow flow-system study wells, which produce relatively young water, should have stable concentrations of nitrate. Concentrations of atrazine plus deethylatrazine from shallow wells producing water that originated within the prohibition area should be decreasing in the future.

One of the most valuable components of each of these studies is the groundwater age dating information. Knowledge of groundwater age, determined by analysis of chemical tracer data, allowed snapshots of water quality in time to be compared with temporally variable factors. Without such information, displaying and measuring trends in concentration over time and establishing correlations to historical chemical use and climate data would not have been possible.

## Appendixes

Appendixes 1 and 2 are available online at <http://jeq.scijournals.org>.

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