

Linking ground-water age and chemistry data along flow paths: Implications for trends and transformations of nitrate and pesticides

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Abstract

Tracer-based ground-water ages, along with the concentrations of pesticides, nitrogen species, and other redox-active constituents, were used to evaluate the trends and transformations of agricultural chemicals along flow paths in diverse hydrogeologic settings. A range of conditions affecting the transformation of nitrate and pesticides (e.g., thickness of unsaturated zone, redox conditions) was examined at study sites in Georgia, North Carolina, Wisconsin, and California. Deethylatrazine (DEA), a transformation product of atrazine, was typically present at concentrations higher than those of atrazine at study sites with thick unsaturated zones but not at sites with thin unsaturated zones. Furthermore, the fraction of atrazine plus DEA that was present as DEA did not increase as a function of ground-water age. These findings suggest that atrazine degradation occurs primarily in the unsaturated zone with little or no degradation in the saturated zone. Similar observations were also made for metolachlor and alachlor. The fraction of the initial nitrate concentration found as excess N_2 (N_2 derived from denitrification) increased with ground-water age only at the North Carolina site, where oxic conditions were generally limited to the top 5 m of saturated thickness. Historical trends in fluxes to ground water were evaluated by relating the times of recharge of ground-water samples, estimated using chlorofluorocarbon concentrations, with concentrations of the parent compound at the time of recharge, estimated by summing the molar concentrations of the parent compound and its transformation products in the age-dated sample. Using this approach, nitrate concentrations were estimated to have increased markedly from 1960 to the present at all study sites. Trends in concentrations of atrazine, metolachlor, alachlor, and their degradates were related to the timing of introduction and use of these compounds. Degradates, and to a lesser extent parent compounds, were detected in ground water dating back to the time these compounds were introduced.

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1. Introduction

There has been growing concern about the consequences of increases in the amounts of anthropogenic N circulating in the atmosphere, hydrosphere, and biosphere in recent years (e.g., Galloway et al., 2003; Schlesinger et al., 2006). In particular, the land application of N fertilizer and pesticides to cropland has resulted in contaminant loads beneath fields that have adversely

affected the quality of drinking water and stream ecosystems. Nitrogen fertilizer applications to the land surface have increased 20-fold since 1945 (Puckett, 1995) and four-fold since 1960 (Howarth et al., 2002). Many commonly used pesticides have also been introduced in the past few decades (e.g., atrazine in 1958; alachlor in 1969; and metolachlor in 1976; U.S. Department of Agriculture, 1994; U.S. Environmental Protection Agency, 1995, 1998). Elevated concentrations of nitrate and

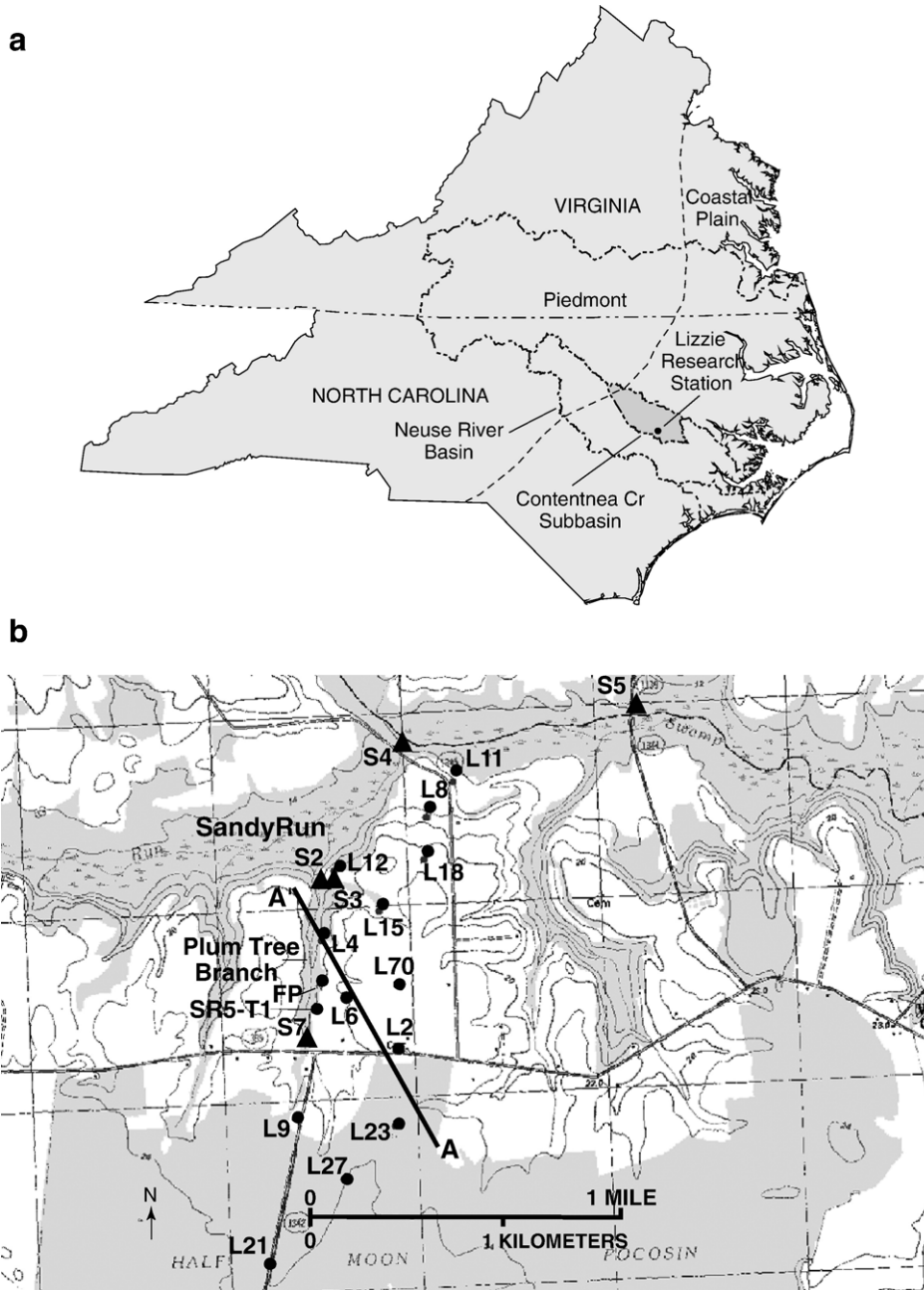


Fig. 1. Locations of (a) the Neuse River and Contentnea Creek Basins and (b) sampling sites at the Lizzie Research station.

pesticides tend to occur in recently recharged ground water (e.g., Barbash et al., 2001; Nolan et al., 2002). While the contamination of recently recharged ground-water can be a concern on its own, most drinking-water supplies and ground-water discharge to streams are composed, in part, of older water from deeper parts of the ground-water system. In many instances this older water has relatively low concentrations of nutrients and pesticides because it recharged the aquifer prior to increases in the use of these compounds. As a result, while ground water that is now used for drinking water supplies or discharging to streams today may contain only a small fraction of water that recharged during periods of intensive nutrient and pesticide application, steadily declining water quality may result as the fraction of water that pre-dates industrial agriculture decreases with time, regardless of the magnitude of future contaminant loading (e.g., Fogg et al., 1999; Tomer and Burkart, 2003). Furthermore, linking land-use practices with the age of ground water is essential when evaluating the effectiveness of best management practices (e.g., Wassenaar et al., 2006).

Tracking the changes in constituent concentrations along flow paths has been successfully used to assess the fate and trends of contaminants in the ground-water system, particularly when coupled with age-dating information. In these studies, wells are sampled along flow paths and analyzed for contaminants and their degradation products, as well as for other constituents that can be used to characterize the geochemical environment. When coupled with information on ground-water velocities, transformation rates can be estimated. It is known that many contaminants degrade at vastly different rates depending on the redox conditions of the aquifer (e.g., Tesoriero et al., 2000; Cozzarelli et al., 2001). However, a lack of understanding of denitrification rates in ground water remains one of the major limitations in evaluating the implications of industrial fertilizer production on the nitrogen cycle (Galloway et al., 2004).

While redox conditions may affect the transformation of pesticides (Barbash, 2003), other factors can also be important. The biodegradation of pesticides is thought to occur primarily in the soil root zone, an observation that is thought to be a consequence of the fact that microbial populations, organic carbon concentrations and temperatures are all typically higher in the shallower portions of the unsaturated zone (Barbash and Resek, 1996, and references therein). Once in ground water, pesticides and their degradates may persist for decades (e.g., Puckett and Hughes, 2005).

In this paper we have linked data on ground-water residence times (also referred to as ground-water age) and

water chemistry to examine the influence of hydrogeologic setting on the fate and transport of nitrate and pesticides along flow paths. Specifically, we examine the effects of redox conditions and the thickness of the unsaturated zone on the fate of nitrate and pesticides. Transformations and trends of nitrate and pesticides are elucidated by relating parent and degradate concentrations to ground-water age and redox conditions. This is one of the first studies to examine the concentrations of nitrate, atrazine, metolachlor, and alachlor—and their respective transformation products—as functions of ground-water age across multiple study areas. Examining the prevalence of degradates as a function of ground-water age at sites having different hydrogeologic settings provides new field-based evidence for both the trends in, and the factors affecting transformations of nitrate and pesticides in ground water.

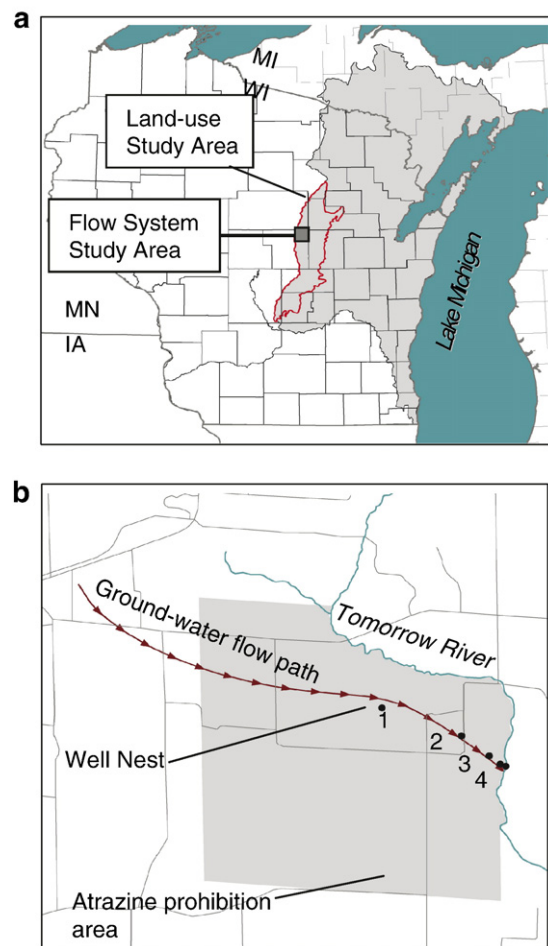


Fig. 2. Locations of (a) land use study and flow system study areas in the Western Lake Michigan Study area (shaded), and (b) well locations in the flow system study area in the Tomorrow River watershed. Ground-water flow paths based on model simulations (Saad, *in press*). Shaded area delineates atrazine prohibition area established in 1995.

2. Site descriptions

Site maps for each of the study areas are provided in Figs. 1–4 and site descriptions are given below.

2.1. Lizzie, North Carolina

This study area is located in the Contentnea Creek subbasin of the Neuse River in Greene County, North Carolina (Fig. 1a). The site includes a first-order drainage, known locally as Plum Tree Branch, that drains to Sandy Run, a third-order stream (Fig. 1b). The water table is typically 1.5 to 3 m below land surface. Head measurements indicate that ground water flow in the surficial aquifer is predominantly towards Plum Tree Branch (Tesoriero et al., 2005). It is hypothesized that

much of the recent recharge in the surficial aquifer is diverted to tile drains. Along the alluvial valley of Sandy Run (e.g., sites L8 and L11 in Fig. 1b), recently recharged water occurs at greater depths than in upland areas, suggesting that the alluvial aquifer receives more recharge than the surficial aquifer. Small upward vertical gradients were observed in this area, but appreciable flow from deeper portions of the ground-water system was not indicated (Tesoriero et al., 2005). This area has greater depths to the water table than the surficial aquifer and is not artificially drained. Land use in the area is primarily agricultural, with row crops typically consisting of corn and soybeans. A confined hog feeding operation with lagoon and spray field waste treatment began operating on the site in early 1995. Spray fields encompass much of the area between well L15 and well L2 (Fig. 1b).

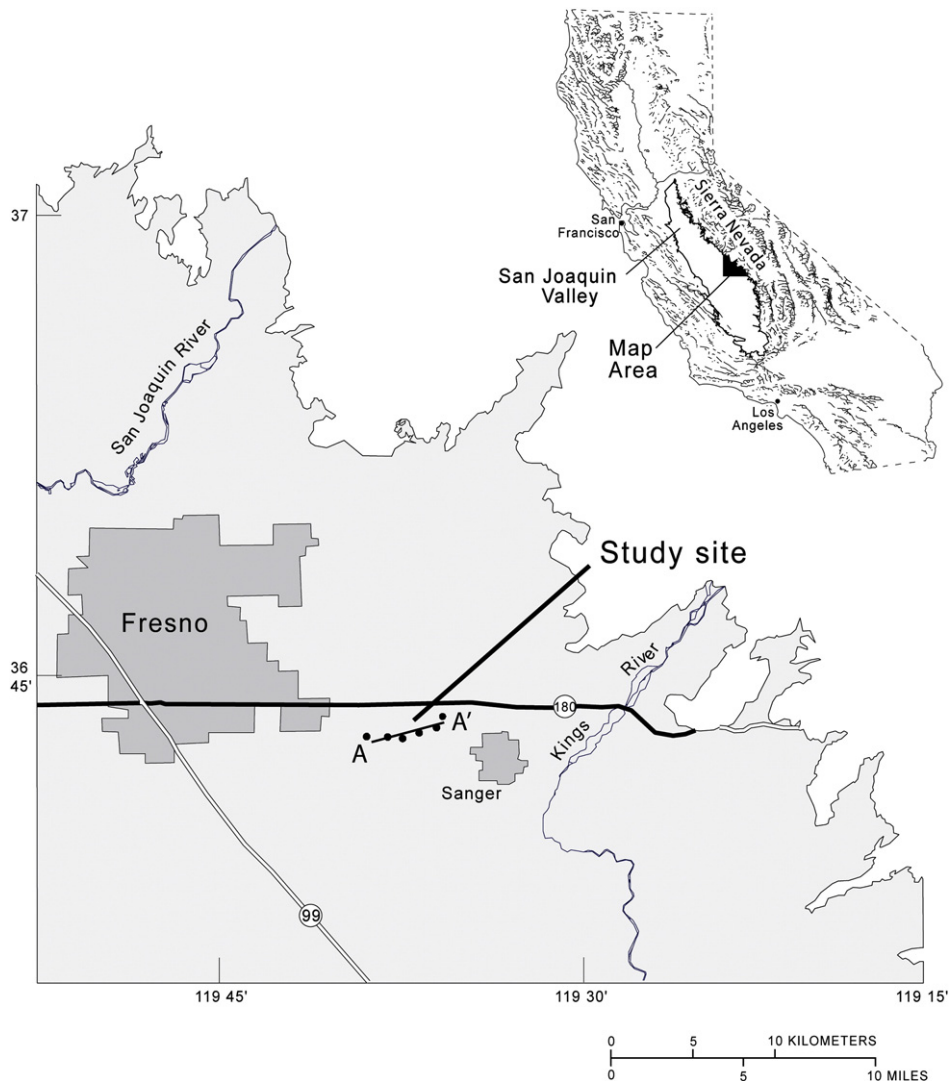


Fig. 3. Study area near Fresno in the eastern San Joaquin Valley, California.

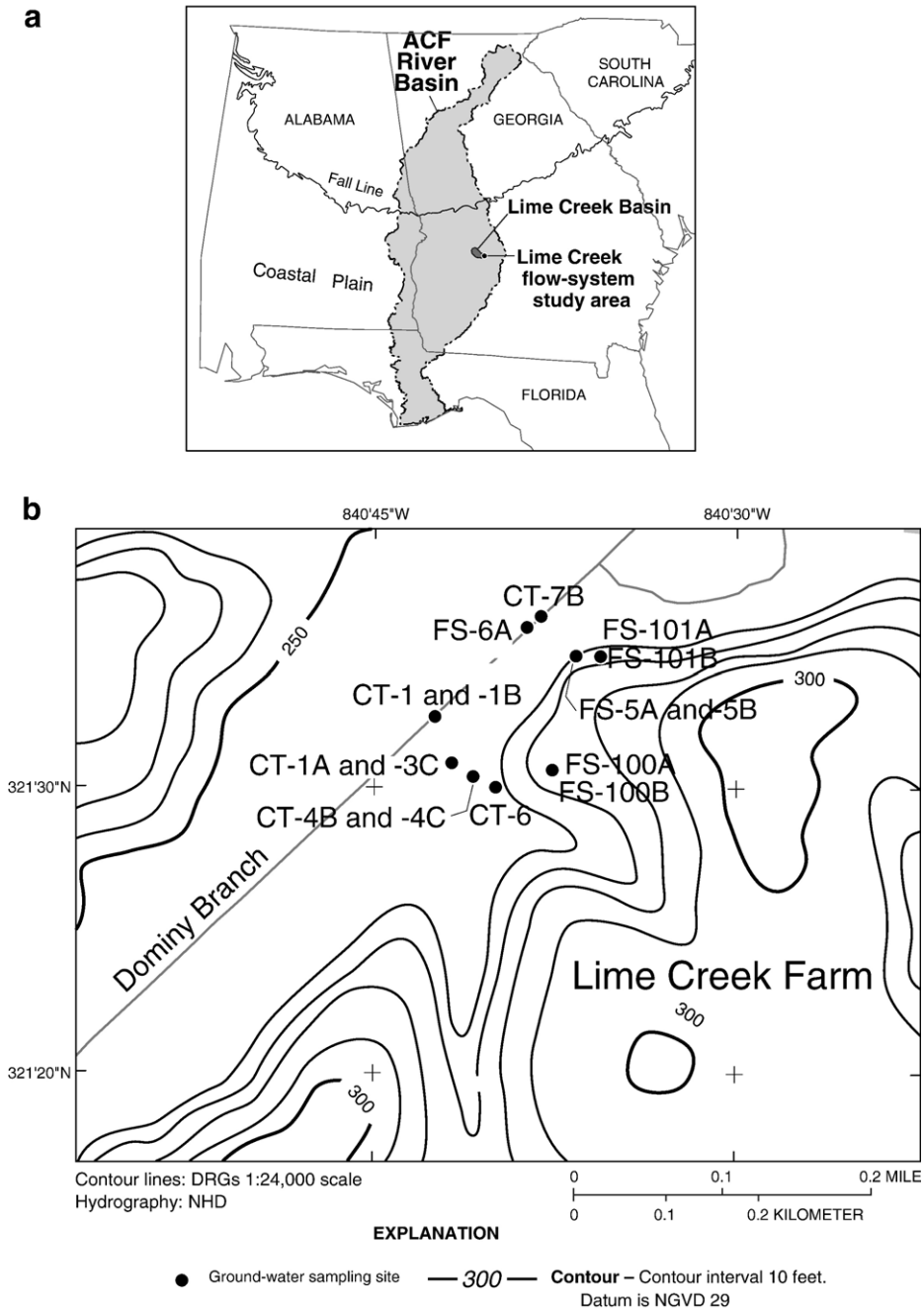


Fig. 4. Locations of (a) the Apalachicola–Chattahoochee–Flint (ACF) River Basin and Lime Creek Basin and (b) sites sampled in 2004 as part of the Lime Creek Flow-System Study in Georgia.

2.2. Portage County, Wisconsin

This site is in the Tomorrow River Watershed in Portage County, Wisconsin (Fig. 2b). The geology at the study site consists of glacial and fluvial deposits overlying

Precambrian crystalline bedrock. Ground-water movement is primarily through permeable glacial deposits to nearby streams such as the Tomorrow River (Fig. 2b). An upward gradient was observed in piezometers installed in the streambed. The underlying Precambrian rocks are

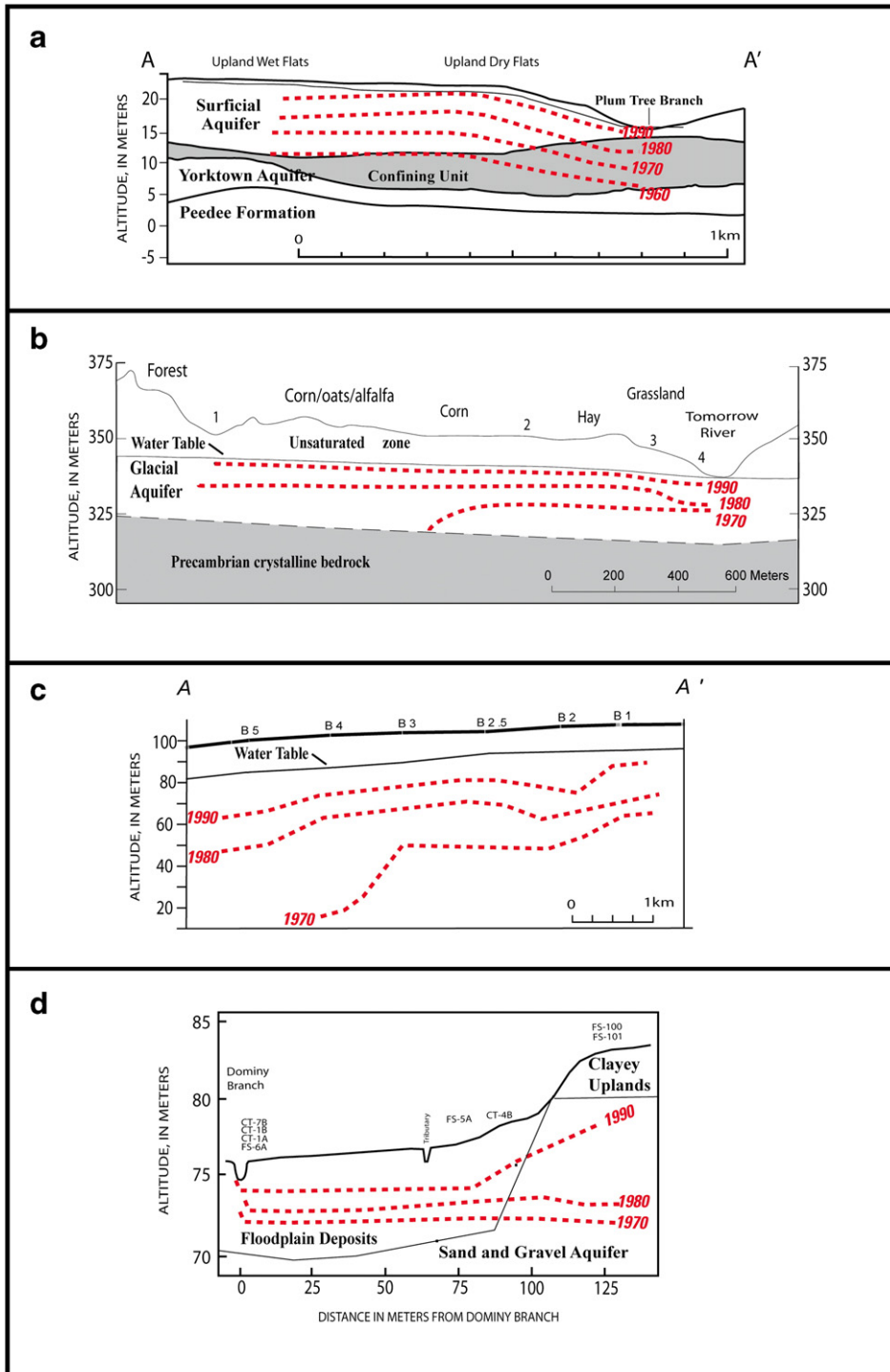


Fig. 5. Apparent recharge date isopleths along transects in (a) North Carolina, (b) Wisconsin, (c) California and (d) Georgia. Water quality sampling for this study was conducted in the portion of each aquifer where isopleths are shown. Vertical scales are greatly exaggerated. See Figs. 1–4 for site maps. Vertical datum is mean sea level.

generally considered impermeable and represent the base of the ground-water flow system. The water table is 8 to 10 m below land surface across most of the study area. Corn, oats, and soybeans have been the primary crops grown in this region for more than 40 years (U.S. Department of Agriculture, 2006).

2.3. Eastern San Joaquin Valley, California

This study area is west of the foothills of the Sierra Nevada and east of the San Joaquin Valley trough on the high alluvial fan of the Kings River in Fresno County, California (Fig. 3). The alluvial sediments consist primarily of interlayered lenses of gravel, sand, silt, and clay deposited by the Kings River. The water table is typically 11 to 15 m below land surface in this study area. Ground-water recharge dates were estimated along the monitoring well transect from chlorofluorocarbon (CFC) concentrations in samples collected in 1994–95 (Burow et al., 1999) and 2003 (Fig. 5c). A detailed analysis of ground-water ages at this site is provided elsewhere (Burow et al., *in press*). Near the monitoring well transect, vineyards are the dominant land use. The distribution of land use near the transect has remained relatively constant over time; however, some individual fields were converted from vineyards to other crops (primarily orchards) between 1987 and 2000 (California Department of Water Resources, 1971, 2001).

2.4. Sumter County, Georgia

This study site is located in the Lime Creek subbasin of the Flint River in Sumter County, Georgia (Fig. 4a and b). The uplands at the site are unconsolidated sediments or weathered residuum composed of clay, silt, and sand underlain by sand and sandy limestone aquifers (Claiborne Aquifer and upgradient remnants of the Upper Floridan aquifer). Tile drains and ditches drain shallow ground water where it is perched above discontinuous clay layers. The depth to the water table is typically less than 2 m, but the water table is deeper (4.5 to 8 m) on the fringe of the uplands (e.g., site FS-100A, Fig. 4b). Deposits in the forested floodplain along Dorniny Branch (Fig. 4b) contain higher concentrations of organic matter. Similar to the Wisconsin site, upward gradients were observed in piezometers installed in the streambed. Corn, soybeans, and peanuts were the major crops grown in the Lime Creek basin until the early 1990s, when cotton became the top crop grown by acreage. At the study site (Lime Creek Farm), cotton was exclusively planted on the three upgradient center-pivot irrigated fields from 1994 to 2004.

3. Methods

At each study site, monitoring wells were installed at 4 or 5 locations along hypothesized ground-water flow paths. Typically 3 or 4 wells are installed at each of these locations, with well screens placed at various depths. Well screens were generally 1 m or less in length. The uppermost well was screened near the water table. The remaining wells at each location were screened at various depths to intercept likely flow paths. Monitoring wells were installed and sampled according to protocols established by the USGS National Water Quality Assessment program (Lapham et al., 1995; Koterba et al., 1995). Dissolved oxygen and pH were measured while water was being pumped, using electrodes placed in a flow cell chamber to minimize atmospheric interactions. Water samples for nutrients and pesticides were filtered with a 0.45- μm capsule filter. Descriptions of the analytical methods for nutrients and pesticides are provided elsewhere (Fishman, 1993; Zaugg et al., 1995). Dissolved organic carbon was analyzed by ultraviolet-promoted persulfate oxidation and infrared spectrometry. Samples were also collected and analyzed for chlorofluorocarbons (trichlorofluoromethane, CFC-11; dichlorodifluoromethane, CFC-12; trichlorotrifluoroethane, CFC-113) as described in Busenberg et al. (2006). Chlorofluorocarbon (CFC) concentrations, coupled with known trends in the atmospheric concentrations of these compounds over time, were used to provide estimates of ground-water age, which is defined as the time of travel from the water table to the point of sampling.

Samples were also collected and analyzed for N_2 and Ar gas to estimate the amount of nitrogen derived from denitrification (Busenberg et al., 1993). N_2 and Ar are incorporated in ground water during recharge by air–water equilibration processes and by entrainment of air bubbles (“excess air”) (Heaton and Vogel, 1981). Because denitrification, which produces N_2 , is not expected to occur under aerobic conditions, aerobic samples were used to determine the relation between N_2 and Ar as well as to infer the mean recharge temperature at each site. Using this method, mean recharge temperatures of 19, 17, 14, and 8.5 °C were estimated for the Georgia, California, North Carolina, and Wisconsin sites, respectively. These estimated recharge temperatures for these sites are similar to the mean annual temperatures of the study sites, which were: 18.3, 17.2, 15.0, and 6.7 °C for the Georgia, California, North Carolina, and Wisconsin locations, respectively (National Climatic Data Center, 2006). Estimates of excess N_2 from denitrification were then calculated by subtracting the estimated concentration of atmospheric nitrogen, derived from both air–water equilibration and excess air,

from that of the total amount of nitrogen gas measured in the ground-water sample (Dunkle et al., 1993).

4. Results and discussion

4.1. Chemical transformations: implications for the fate of nitrate and pesticides

4.1.1. Dissolved oxygen loss

The reduction of oxygen (aerobic respiration) is the most energetically favorable reaction that microorganisms use to oxidize organic material or other electron donors (e.g., pyrite). As a result, other reduction reactions (e.g., denitrification) typically do not occur until most dissolved oxygen has been consumed.

The rate of oxygen reduction in each of the four aquifers was evaluated by relating dissolved oxygen concentrations to ground-water age using the approach described by Böhlke et al. (2002). At both the California and Georgia sites dissolved oxygen concentrations show no trend with ground-water age, suggesting that oxygen reduction is negligible in these systems over the time period examined. In contrast, data from the Wisconsin and North Carolina sites indicate that oxygen loss was substantial in both systems. Estimates of the rate of oxygen reduction were made using a zero-order rate expression:

$$C = C_0 - k_0 t \quad (1)$$

where C is the concentration of the reactant (i.e., dissolved oxygen) at the time of interest, C_0 is the initial concentration of the reactant, k_0 is the zero-order reaction coefficient and t is time.

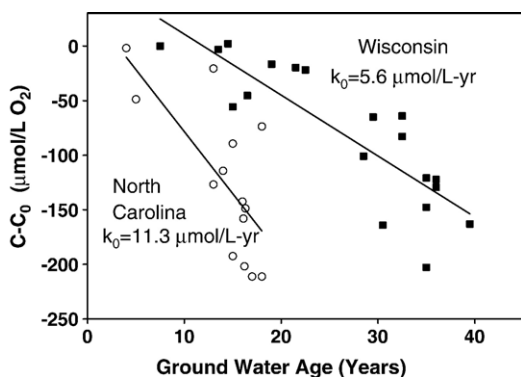


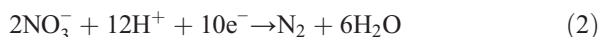
Fig. 6. Dissolved O_2 consumption rates in aquifers at the North Carolina and Wisconsin sites. C_0 is the initial concentration of dissolved O_2 in the aquifer and was assumed to be 230 mmol/L and 301 mmol/L for North Carolina and Wisconsin, respectively. C is the sample concentration of dissolved oxygen. k_0 refers to the zero-order rate constant in Eq. (1).

Initial concentrations of dissolved oxygen (C_0) were estimated to be 230 $\mu\text{mol/L}$ and 301 $\mu\text{mol/L}$ at the North Carolina and Wisconsin sites, respectively. These values are similar to the concentrations of dissolved oxygen in the youngest ground water sampled at these sites. The zero-order rate constant was determined by fitting a linear regression curve to plots of $C-C_0$ versus ground water age (Fig. 6) using only data from samples taken from the oxic zone. The zero-order rate constants were estimated to be 11.3 $\mu\text{mol/L-yr}$ and 5.6 $\mu\text{mol/L-yr}$ for the North Carolina and Wisconsin sites, respectively (Fig. 6). First-order rate expressions were also examined but did not result in a better fit to the observed data.

The fact that ground water temperatures at the North Carolina site (recharge temp. $\approx 14^\circ\text{C}$) were higher than at the Wisconsin site ($\approx 8.5^\circ\text{C}$) is likely to have been responsible for some of the increased oxygen reduction rates observed at the North Carolina site. However, the presence of electron donors, such as organic carbon may also be an important factor influencing reduction rates in aquifers and riparian zones (e.g., Starr and Gillham, 1989, 1993; Vidon and Hill, 2004). It has been hypothesized that in areas with shallow water tables, the residence time of water in the unsaturated zone is too short to allow for much of the labile organic carbon generated in the soil zone to be oxidized by soil microbes (Starr and Gillham, 1993; Malard and Hervant, 1999). The observation of a higher oxygen reduction rate at the North Carolina site, relative to the Wisconsin site, is consistent with this hypothesis because the unsaturated zone is substantially thinner at the North Carolina site.

4.1.2. Nitrate reduction and excess N_2 fraction

The extent to which elevated nitrate concentrations affect ground water or streams is dependent upon the redox conditions in the portions of the aquifer downgradient from the locations where high nitrate concentrations are observed. Denitrification is a microbial respiratory process where nitrate is used as an electron acceptor and is reduced to N_2 by the following generalized half-reaction:



Facultative anaerobes begin to use nitrate as an electron acceptor when oxygen becomes limited. As such, little denitrification is expected in the Wisconsin, California, and Georgia sites as these aquifers are largely oxic. In contrast, only the upper few meters of saturated thickness at the North Carolina site are oxic. It was therefore not surprising that the concentrations of excess N_2 were highest at the North Carolina site and were generally low or nondetectable elsewhere.

Expressing solute concentrations as a mole fraction of the sum of reactant and product concentrations provides an indication of which compound(s) predominate(s) in a particular location. In this approach, the fraction for a given product, $X(\text{Product}_i)$, is calculated as follows:

$$X(\text{Product}_i) = \frac{[\text{Product}_i]}{\sum_{i=1}^n [\text{Product}_i] + [\text{Reactant}]} \quad (3)$$

where $[\text{Product}_i]$ and $[\text{Reactant}]$ are the molar concentrations of Product i and the reactant compound respectively, in moles per liter, and n is the number of products examined. Values of $X(\text{Product}_i)$ range from zero, when no Product i is present to unity, when neither the reactant nor any of its other products (other than product i) are detected. The utility of Eq. (3) for tracking reaction progress will be limited when Product i has subsequently degraded and/or in those instances where one or more of the products travel through ground water at rates that are substantially different from that of their parent compound. Neither nitrate nor N_2 are significantly retarded in ground-

water systems, so Eq. (3) should adequately represent the progress of nitrate reaction in ground water.

Comparing the fractions of excess N_2 (as N) at the four sites as a function of ground-water age permits a cross-study comparison of transformation progress that is normalized for ground-water age. Fractions of excess N_2 at the North Carolina site are initially low and increase as ground-water age increases, indicating denitrification in ground water (Fig. 7a). In fact, excess N_2 fractions approaching unity at the North Carolina site indicate that virtually all of the nitrate in ground water older than 25 years has undergone denitrification in this location. By contrast, with a few exceptions, excess N_2 fractions remain low as ground water age increases at the remaining sites, indicating that little or no denitrification occurs in ground water at these sites (Fig. 7a).

4.1.3. Pesticide transformations and degradate fractions

Atrazine, metolachlor and alachlor were the most commonly detected pesticides in the four systems examined in this paper. These compounds are also among the pesticides detected most frequently in ground water in the United States (Gilliom et al., 2006). Degradates of these compounds were typically found more frequently and at higher concentrations than their parent compounds in most of the samples analyzed for this study. These and other observations (e.g., Kolpin et al., 1996; Scribner et al., 2005) indicate that the degradates of several high-use pesticides are more persistent in the hydrologic system than their parent compounds. By examining parent and degradate concentrations as a function of age we are able to evaluate the persistence of these compounds in the four different hydrogeologic settings.

4.1.3.1. Atrazine. Previous research has suggested that the concentrations of pesticide biotransformation products, relative to those of their parent compounds, are likely to be lower in runoff than in ground water, tile drainage or other waters that spend more time in contact with the soil (e.g., Adams and Thurman, 1991; Burkart and Kolpin, 1993; Phillips et al., 1999). In addition, pesticide degradation rates generally decrease with increasing depth in the soil (e.g., Blume et al., 2004) and in aquifer sediments (e.g., McMahon et al., 2006), primarily as a result of the decrease in the populations of microorganisms responsible for the biotransformation of compounds – and the organic matter that supports them – with depth (Barbash and Resek, 1996). For atrazine, redox conditions may also be a factor affecting transformation rates because its oxidation to deethylatrazine and other dealkylated products occurs more readily under oxic conditions (Nair and Schnoor, 1992; DeLaune et al., 1997). Short residence times in the

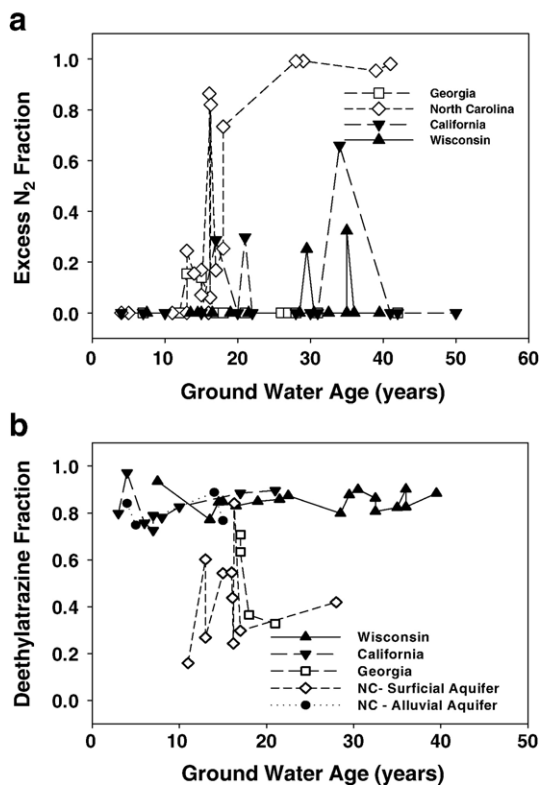


Fig. 7. (a) Relation between excess N_2 (as N) fraction and ground water age. Excess N_2 fraction is mol/L of excess N_2 (as N) divided by mol/L nitrate (as N) plus mol/L excess N_2 (as N). (b) Relation between deethylatrazine (DEA) fraction and ground water age. DEA fraction is mol/L of DEA divided by mol/L DEA plus mol/L atrazine.

shallow soil horizon, particularly when coupled with reducing conditions, would thus be likely to promote the persistence of atrazine.

Ground-water samples were not analyzed for atrazine degradates other than deethylatrazine (DEA) because of considerations related to analytical detection limits and cost. Hydrolysis of atrazine to hydroxyatrazine is the principal degradation pathway for atrazine (Skipper et al., 1967), but since this degradate sorbs much more strongly to soils than either atrazine or DEA (Armstrong et al., 1967), its occurrence in deeper ground water may be limited.

DEA was found at higher concentrations than atrazine in ground water from the sites with thicker unsaturated zones (Wisconsin and California, alluvial aquifer in North Carolina, Fig. 8), while the reverse was generally true for the sites with thinner unsaturated zones (surficial aquifer, North Carolina and Georgia, Fig. 8). In the relatively thick unsaturated zone settings, DEA fractions computed using Eq. (3), are high (>0.8) for very young ground water and remain at essentially the same level as ground-water ages increase (Fig. 7b). Much lower DEA fractions (typically <0.6) are observed in the thin unsaturated zone settings found in the surficial aquifer at the North Carolina site and at the Georgia site.

The North Carolina and Georgia sites have relatively high water tables that often lead to saturated soil conditions. The high water table at these sites is also likely to lead to shorter residence times in the unsaturated zone where, as noted earlier, transformation of the herbicide to DEA is most likely to occur. Reduced residence times in these locations may result either from percolation through the thin unsaturated zone or from more rapid preferential flow through cracks in the clayey soil (e.g., Helmke et al., 2005).

No trends in DEA fractions with age were observed at any of the four sites (Fig. 7b). While this may have been a consequence of the fact that atrazine and DEA show similar rates of transformation in surface soils (e.g., Kruger et al., 1997), it is also possible that relatively little degradation of either compound was occurring in the saturated zone. This is consistent with the finding by Wehtje et al. (1983) that, in the saturated zone, atrazine appears to undergo negligible rates of dealkylation (which requires microbial assistance), and only slow rates of hydrolysis (which does not).

4.1.3.2. Metolachlor and alachlor. Alachlor and metolachlor undergo transformation relatively rapidly in aerobic soil, but much more slowly in water alone

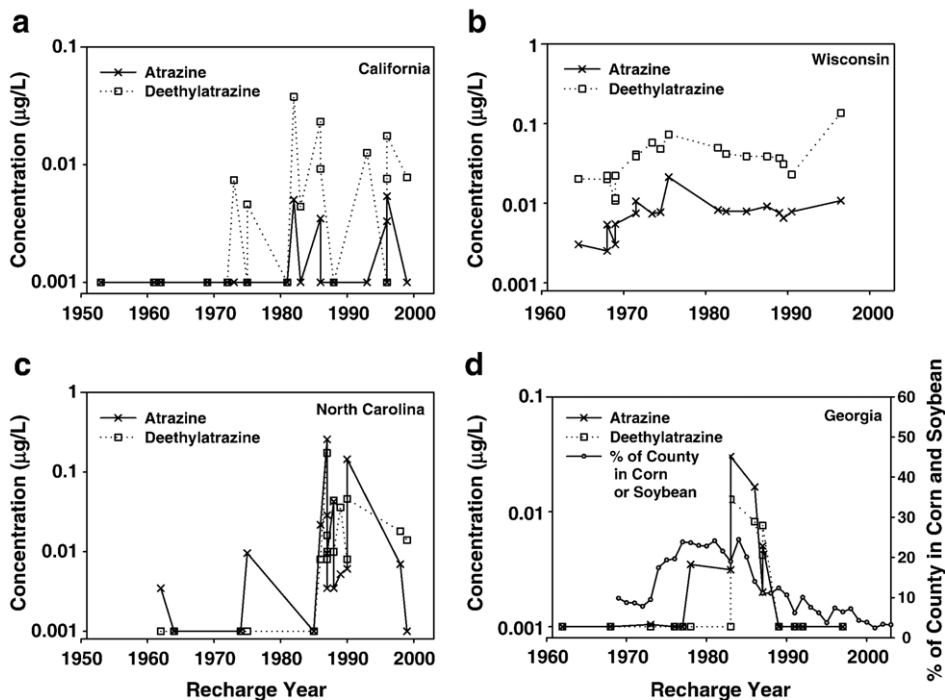


Fig. 8. Concentrations of atrazine and deethylatrazine versus recharge year at each study site: a) California, b) Wisconsin, c) North Carolina, and d) Georgia. Values with non-detectable concentrations were plotted at a value of 0.001 µg/L. Atrazine was registered for use in 1958 (U.S. Department of Agriculture, 1994). Georgia graph also includes the percentage of the study site county (Sumter) that was planted in corn or soybeans (National Agricultural Statistics Service, 2006).

(Gilliom et al., 2006). Product analyses indicate that both compounds may be transformed by a large number of different pathways in the hydrologic system, many of which require microbial assistance. This results in the production of at least 22 different degradates for alachlor and at least 21 for metolachlor (Stamper and Tuovinen, 1998; Lee and Strahan, 2003; Hladik et al., 2005).

Among the degradates for which analyses have been carried out on environmental media for alachlor and metolachlor, the two that have been detected most frequently in surface and ground waters are their ethane sulfonic acid (ESA) and oxanilic acid (OA) metabolites. However since alachlor OA and metolachlor OA were

generally found in much lower concentrations than alachlor ESA and metolachlor ESA, the OA metabolites are not discussed in this paper. Microbial degradation under aerobic conditions is the predominant pathway for the transformation of metolachlor in soil (e.g., Miller et al., 1997). Specifically, laboratory experiments have found that under aerobic conditions, metolachlor degrades only in nonsterile surface soils (Accinelli et al., 2001). However, slow hydrolysis of the herbicide in aqueous solution has also been observed (Carlson and Roberts, 2002). Alachlor also degrades microbially under aerobic conditions, abiotic degradation in aquifer sediments has also been reported (e.g., Schwab et al., 2006).

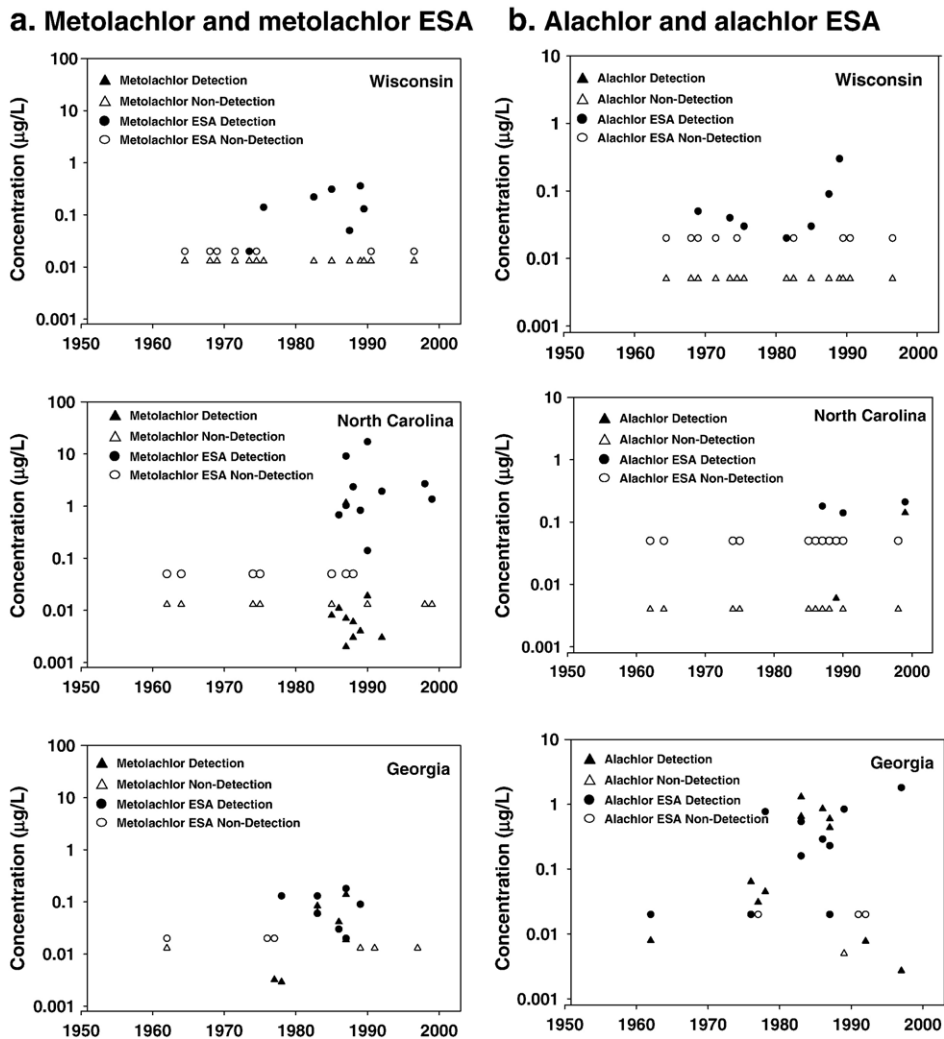


Fig. 9. Relation between herbicide (and degradate) concentrations and recharge date for each study area. a) Metolachlor and metolachlor ESA, and b) alachlor and alachlor ESA. Non-detections are plotted with open symbols at the reporting level. Metolachlor and alachlor were registered for use in 1976 and 1969, respectively (U.S. Environmental Protection Agency, 1995, 1998).

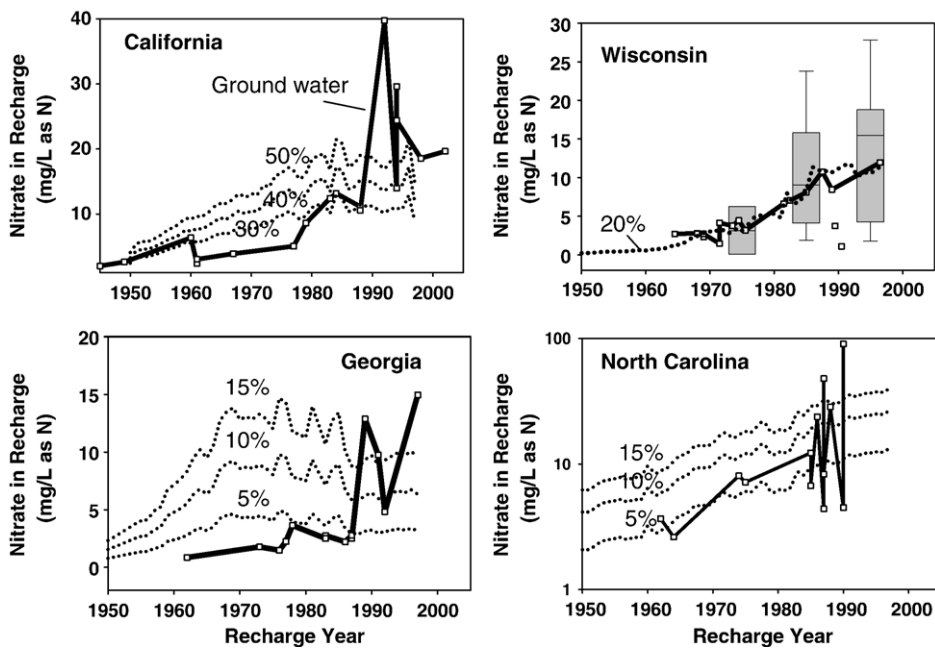


Fig. 10. Relation between nitrate concentrations in recharge and recharge year (open squares and solid line). Dotted lines indicate concentrations that result from dissolution of fertilizer (includes inorganic fertilizer and manure) in recharging ground water. These estimates are based on recharge estimates and the percentage of fertilizer applied reaching the water table (indicated on each graph). Annual recharge estimates used in these calculations were as follows: Wisconsin, 25 cm; California, 50 cm; North Carolina, 10 cm; and Georgia, 20 cm. Box plots in the Wisconsin graph show nitrate concentrations in ground water from a larger land use study area (Fig. 2a).

The detection of metolachlor ESA and alachlor ESA—but not the parent compounds—at the Wisconsin site, even in very recent recharge, suggests that the parent compounds are readily transformed in the shallow saturated zone or, more likely, in the unsaturated zone at this location (Fig. 9). This is consistent with the rapid degradation of metolachlor and alachlor found in surface soils (e.g., Accinelli et al., 2001; Aga and Thurman, 2001) as well as with the prevalence of their degradates in ground water (e.g., Kolpin et al., 1996; Kolpin et al., 2004). In contrast, at the sites with relatively thin unsaturated zones (North Carolina and Georgia), metolachlor and alachlor were both detected in ground water. As with atrazine, we hypothesize that these detections of metolachlor and alachlor were a consequence of the shorter residence times for water and solutes in the unsaturated zone at these locations, relative to the Wisconsin site, where neither of these parent compounds were detected. Furthermore, the presence of detectable concentrations of metolachlor and alachlor in ground water recharged at least 15 years ago at the Georgia and North Carolina sites suggests that while these compounds degrade over time scales of weeks to months in soils, degradation rates are markedly slower in the saturated zone. Metolachlor, alachlor or their degradates were not detected at the California site reflecting the low usage of the parent compounds at this site.

4.2. Trends in Nitrate and Pesticide Concentrations

4.2.1. Nitrate

Nitrate trends were determined at each of the four sites by reconstructing concentrations of nitrate at the time of recharge using the results from age dating (from CFCs) and water-quality sampling. Specifically, the concentration of nitrate at the time of recharge was estimated with the following equation:

$$[\text{NO}_3^-]^t = [\text{NO}_3^-]^{t+\Delta t} + [\text{excess N}_2]^{t+\Delta t} \quad (4)$$

where $[\text{NO}_3^-]^{t+\Delta t}$ and $[\text{excess N}_2]^{t+\Delta t}$ are the concentrations (as N) of these compounds at the time of sampling and $[\text{NO}_3^-]^t$ is the concentration of nitrate (as N) at the time of recharge.

This analysis suggests that two-to five-fold increases in nitrate concentrations have occurred in recharging ground water in these aquifers since the 1960s (Fig. 10). This has important implications for nitrate trends in ground-water derived drinking water supplies and streams. These resources may be composed of old ground water or of mixtures containing some fraction of older water (e.g., Manning et al., 2005; Browne and Guldán, 2005). If the proportions of water from the low nitrate period decreases, nitrate concentrations in these waters will increase.

Comparing changes in fertilizer applications over time with trends in reconstructed nitrate concentrations facilitates the examination of how changes in land-use practices may be affecting ground-water quality. In the United States, industrial fertilizer production has increased nearly four-fold between 1960 and 2000, rising from 3.1×10^9 to 11.2×10^9 kg N/yr (Howarth et al., 2002). To determine the amount of fertilizer applied in each county we summed the amount of inorganic fertilizer (1950–1997) used and manure (1982–1997) generated in each county (estimated by Alexander and Smith, 1990; Ruddy et al., 2006). Only manure from confined feeding operations was used for this analysis since manure from unconfined feeding operations is generally not applied to cropland (Kellogg et al., 2000). Manure produced in each county prior to 1982 was not included in this analysis because data are not available, however trends in the numbers of livestock and poultry in confined feeding operations would suggest that manure was not a major source of nitrogen applied to fields in these study areas during this time. In recent years, manure has become a major source of applied nitrogen in the North Carolina study area (Greene County); at all other sites inorganic fertilizer is the major source of applied nitrogen.

The fraction of applied fertilizer that would be required to reach the water table in order to explain reconstructed nitrate concentrations in recharge was estimated using the method described in Böhlke (2002). In this method, the concentration of N in recharge is determined by dividing the amount of fertilizer from both inorganic and manure sources in each county by the volume of water into which this fertilizer is “dissolved.” This volume of water is determined by multiplying the fertilized land in the county (estimated from the Census of Agriculture data compiled by the National Agricultural Statistics Service) by the annual recharge. These concentrations are multiplied by a fraction (e.g., 0.2) to fit the observed reconstructed nitrate concentrations in ground water. This approach assumes that county-level fertilizer use data accurately represent fertilizer use at the study site, recharge occurred in cropland, and that the fraction of applied fertilizer reaching the water table is constant over time. It should also be noted that these are “equivalent” fractions since we did not track actual fertilizer application and other sources of nitrate are present.

In Wisconsin, agreement between fertilizer-derived nitrate concentrations and reconstructed concentrations is obtained when it is assumed that the equivalent of 20% of the fertilizer applied to the land in this county reaches the water table (Fig. 10). The two data points that have much lower concentrations than those predicted by the equivalent of 20% of the fertilizer applied are directly below

forested and riparian areas, land uses that are not representative of most the study site (Fig. 5b). The Wisconsin site was unique among the four study areas because it has both nitrate data and ground-water age dates from a larger study area (land use study area in Fig. 2a). Median nitrate concentrations from the larger land use study area closely match nitrate concentrations found in the smaller flow system study area (Fig. 10). This suggests that the trends observed at the small scale are not unique, but rather are representative of the larger land-use study area.

The trends in nitrate concentrations in ground water predicted from fertilizer use did not match the reconstructed nitrate concentrations as closely at the Georgia, North Carolina, and California sites as they did at the Wisconsin site. This may indicate that fertilizer use at the first three study areas was not adequately represented by county-level data, or that the fractions of applied fertilizer reaching the water table in these areas have changed over time. While it is not possible to identify the equivalent fraction of applied nitrogen that reached the water table at the North Carolina, California and Georgia sites with any certainty, plotting several fractions on Fig. 10 permits an assessment of the likely range in these values. At the North Carolina site, these calculations suggest that the equivalent of 5 to 15% of the applied fertilizer reached ground water. At the California site, reconstructed nitrate concentrations were generally within the range of values estimated when the equivalent of 30% to 50% of the fertilizer in the county reached the water table. It should be noted that the recirculation of ground-water nitrate by pumping for irrigation complicates comparisons between applied nitrogen and reconstructed nitrate concentrations at this site. In Georgia, reconstructed nitrate concentrations do not appear to be related to county level fertilizer data (Fig. 10), suggesting that county level fertilizer data do not represent local applications or that other sources of nitrogen are present.

4.2.2. Atrazine, metolachlor and alachlor

Reconstructing historic concentrations of pesticide concentrations in recharging ground water is more difficult than it is for nitrate because in most cases (1) not all pesticide degradates are measured, and (2) pesticides and their degradates may be retarded – and to varying extents – in ground water. Sorption of pesticides and their degradates onto sediment may thereby result in the detection of these compounds in ground water that recharged after the time when application occurred. With these limitations in mind, the pesticide results from this study may be used to examine the extent to which trends in the concentrations in ground water of atrazine and DEA (Fig. 8), as well as metolachlor, alachlor and their ESA

degradates (Fig. 9) may reflect the history of use of the parent compounds.

The Wisconsin site provides a particularly valuable opportunity to examine changes in the concentrations of atrazine and DEA in recharging water, given the fact that both compounds were detected in every sample taken at this location (Fig. 8b). Atrazine and DEA concentrations at the site were observed to increase from the early 1960s to the mid to late 1970s. From the late-1970s to the early 1990s, concentrations of DEA declined slightly, while atrazine concentrations were stable. Use of atrazine was prohibited in this area beginning in 1995. The only sample that has a recharge date after 1995 had relatively high concentrations of both atrazine and DEA. It is likely that this well represents a mixture of water from both before and after the ban on atrazine use in this area (Saad, *in press*).

Atrazine and DEA concentrations at the Georgia site (Fig. 8d) increased in the late 1970s and then declined to nondetectable levels in the late 1980s. Atrazine was commonly used on corn and soybeans, the production of which increased sharply in the early 1970s and decreased in the mid-1980s in this area (Fig. 8d). Atrazine and DEA concentrations began to rise about 5 years after the increase in corn and soybean production and declined to nondetectable levels about 5 years after production of these crops had peaked (Fig. 8d). While trends in the concentrations of atrazine and DEA were less apparent at the California and North Carolina sites (Fig. 8a and c, respectively), higher frequencies of detection and higher concentrations were found in water recharged after 1980 in both systems.

No trends in metolachlor ESA concentrations were found in samples that had detectable concentrations of this compound (Fig. 9). Not surprisingly, the frequencies of detection of metolachlor ESA are higher in ground water that recharged after 1977, when metolachlor was introduced, than before. Metolachlor ESA was detected in 75% (24 of 32) of the samples with recharge dates after 1977 at the sites where this compound or its parent was found (i.e., North Carolina, Georgia and Wisconsin). Conversely, only 2 of the 13 samples that recharged prior to 1977 had detections of metolachlor ESA. The two samples with detections had recharge dates in the mid-1970s, so only a small amount of mixing would have been needed to capture water that recharged after metolachlor was introduced. Alachlor ESA was also detected frequently (48%, 19 of 40) in samples that recharged after the year that use of this compound began (1969). While there were few samples that recharged prior to 1969, the frequency of detection of alachlor ESA was lower during this time (20%, 1 of 5).

5. Conclusions

Estimated ground-water ages were used in conjunction with data on the concentrations of pesticides, pesticide degradates, nitrogen species, and other redox-active constituents in ground water at four locations across the United States to examine the importance of application history, unsaturated-zone thickness, redox conditions and other factors in controlling the concentrations of agrichemicals in ground water. Conclusions drawn from these analyses include:

1. O₂ reduction rates that are faster at the North Carolina site than at the other sites results in an oxic zone below the water table that is less than 5 m thick. In the anaerobic zone of this aquifer, nitrate has been denitrified to N₂. In contrast, slower O₂ reduction rates at the other sites allow oxic zones to persist to greater depths, inhibiting denitrification for greater distances below the water table. O₂ reduction rates at the North Carolina site may be due, in part, to the high ground-water temperatures and shallow water table observed at this site.
2. Deethylatrazine (DEA), a transformation product of atrazine, was typically present at higher concentrations than atrazine at study sites with thick unsaturated zones but not at sites with thin unsaturated zones. Furthermore, the fraction of atrazine plus DEA that was present as DEA did not increase as a function of ground-water age. These findings suggest that atrazine degradation occurs primarily in the unsaturated zone with little or no degradation taking place in the saturated zone at these study sites. Similar patterns were also observed for alachlor and metolachlor.
3. Nitrate concentrations in recharging ground water have increased markedly from 1960 to the present at all study sites. Trends in nitrate concentrations are related to increases in fertilizer (inorganic and/or manure) applications at the Wisconsin, California and North Carolina sites.
4. Trends in the concentrations of atrazine, alachlor, metolachlor and selected degradates are largely consistent with the years in which use of these herbicides was first initiated. Detections of these compounds—or their degradates—in ground waters recharged prior to the first use of the parent compounds could have been accounted for through mixing with younger waters.

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References

- Accinelli, C., Dinelli, G., Vicari, A., Catizone, P., 2001. Atrazine and metolachlor degradation in subsoils. *Biology and Fertility of Soils* 33, 495–500.
- Adams, C.D., Thurman, E.M., 1991. Formation and transport of deethylatrazine in the soil and vadose zone. *Journal of Environmental Quality* 20, 540–547.
- Aga, D.S., Thurman, E.M., 2001. Formation and transport of the sulfonic acid metabolites of alachlor and metolachlor in soil. *Environmental Science and Technology* 35, 2455–2460.
- Alexander, R.A., Smith, R.A., 1990. County-level estimates of nitrogen and phosphorus fertilizer use in the United States, 1945–1985. USGS Open-File Rep. 90–130, Reston, VA.
- Armstrong, D.E., Chesters, G., Harris, R.F., 1967. Atrazine hydrolysis in soils. *Proceedings – Soil Science Society of America* 31, 61–66.
- Barbash, J.E., 2003. The Geochemistry of Pesticides. In: Sherwood-Lollar, B., Holland, H.D., Turekian, K.K. (Eds.), *Treatise on Geochemistry. Environmental Geochemistry*, vol. 9. Elsevier Pergamon, London, UK, pp. 541–577.
- Barbash, J.E., Resek, E.A., 1996. Pesticides in ground water. *Ann Arbor Press*, Chelsea, MI.
- Barbash, J.E., Thelin, G.P., Kolpin, D.W., Gilliom, R.J., 2001. Major herbicides in ground water: results from the National Water Quality Assessment. *Journal of Environmental Quality* 30, 831–845.
- Blume, E., Bischoff, M., Moonman, T.B., Turco, R.F., 2004. Degradation and binding of atrazine in surface and subsurface soils. *Journal of Agricultural and Food Chemistry* 52, 7382–7388.
- Böhlke, J.K., 2002. Groundwater recharge and agricultural contamination. *Hydrogeology Journal* 10, 153–179.
- Böhlke, J.K., Wanty, R., Tittle, M., Delin, G., Landon, M., 2002. Denitrification in the recharge area of a transient agricultural nitrate plume in a glacial outwash sand aquifer, Minnesota. *Water Resources Research* 38 (7). doi:10.1029/2001WR000663.
- Browne, B.A., Guldan, N.M., 2005. Understanding long-term base-flow water quality trends using a synoptic survey of the ground water — surface water interface, central Wisconsin. *Journal of Environmental Quality* 34, 825–835.
- Burkart, M.R., Kolpin, D.W., 1993. Hydrologic and land-use factors associated with herbicides and nitrate in near-surface aquifers. *Journal of Environmental Quality* 22, 646–656.
- Burow, K.R., Panshin, S.Y., Dubrovsky, N.M., Vanbrocklin, D., Fogg, G.E., 1999. Evaluation of processes affecting 1,2-dibromo-3-chloropropane (DBCP) concentrations in ground water in the Eastern San Joaquin Valley, California: analysis of chemical data and ground water flow and transport simulations. U.S. Geological Survey Water Resources Investigation Report, vol. 99-4059.
- Burow, K.R., Dubrovsky, N.M., Shelton, J.L., Jurgens, B., in press. Temporal trends in concentrations of DBCP and nitrate in ground water in the eastern San Joaquin Valley, California, USA. *Hydrogeology Journal*. doi:10.1007/s10040-006-0148-7.
- Busenberg, E., Weeks, E.P., Plummer, L.N., Bartholomay, R.C., 1993. Age dating groundwater by use of chlorofluorocarbons (CCl_3F and CCl_2F_2), and distribution of chlorofluorocarbons in the saturated zone, Snake River Plain Aquifer, Idaho National Engineering Laboratory, Idaho. U.S. Geological Survey Water Resources Investigation Report, pp. 93–4054.
- Busenberg, E., Plummer, L.N., Cook, P.G., Solomon, D.K., Han, L.F., Gröning, M., Oster, H., 2006. Sampling and analytical methods. Use of Chlorofluorocarbons: A Guidebook. International Atomic Energy Agency (IAEA) STI/PUB/1238. ISBN: 92-0-100805-8, pp. 199–220. chapt. 12.
- California Department of Water Resources, 1971. Land use in California: an index to surveys conducted by the California Department of Water Resources. *Bulletin* 176 (16 pp.).
- California Department of Water Resources, 2001. Land use for Fresno County, California, for 2000 [digital data]. California Department of Water Resources, Division of Planning and Local Assistance, Statewide Planning Branch, Land and Water Use.
- Carlson, D.L., Roberts, A.L., 2002. Acid- and base-catalyzed hydrolysis of chloroacetamide herbicides. Preprint Extended Abstracts. *American Chemical Society Division of Environmental Chemistry* 42 (2).
- Cozzarelli, I.M., Bekins, B.A., Baedeker, M.J., Aiken, G.R., Eganhouse, R.P., Tuccillo, M.E., 2001. Progression of natural attenuation at a crude-oil spill site: I. Geochemical evolution of the plume. *Journal of Contaminant Hydrology* 53, 369–385.
- DeLaune, R.D., Devai, I., Mulbah, C., Crozier, C., Lindau, C.W., 1997. The influence of soil redox conditions on atrazine degradation in wetlands. *Agriculture, Ecosystems & Environment* 66, 31–40.
- Dunkle, S.A., Plummer, L.N., Busenberg, E., Phillips, P.J., Denver, J.M., Hamilton, P.A., Michel, R.L., Coplen, T.B., 1993. Chlorofluorocarbons (CCl_3F and CCl_2F_2) as dating tools and hydrologic tracers in shallow groundwater of the Delmarva Peninsula, Atlantic Coastal Plain, United States. *Water Resources Research* 29, 3837–3860.
- Fishman, M.J. (Ed.), 1993. *Methods of analysis by the U.S. Geological Survey National Water Quality Laboratory-Determination of inorganic and organic constituents in water and fluvial sediments*. U.S. Geological Survey Open-File Report 93–125. 217 pp.
- Fogg, G.E., Labolle, E.M., Weissmann, G.S., 1999. Groundwater vulnerability assessment: hydrogeologic perspective and example from Salinas Valley, California in Assessment of Non-Point Source Pollution in the Vadose Zone. In: Corwin, D.L., Loague, K., Ellsworth, T.R. (Eds.), *Geophys., Monogr. Ser.*, vol. 108. AGU, Washington, DC, pp. 45–61.
- Galloway, J.N., Aber, J.D., Erisman, J.W., Seitzinger, S.P., Howarth, R.W., Cowling, E.B., Cosby, B.J., 2003. The nitrogen cascade. *BioScience* 53, 341–356.
- Galloway, J.N., Dentener, F.J., Capone, D.G., Boyer, E.W., Howarth, R.W., Seitzinger, S.P., Asner, G.P., Cleveland, C.C., Green, P.A., Holland, E.A., Karl, D.M., Michaels, A.F., Porter, J.H., Townsend, A.R., Vöosmarty, C.J., 2004. Nitrogen cycles: past, present, and future. *Biogeochemistry* 70, 153–226.
- Gilliom, R.J., Barbash, J.E., Crawford, C.G., Hamilton, P.A., Martin, J.D., Nakagaki, N., Nowell, L.H., Scott, J.C., Stackelberg, P.E., Thelin, G., Wolock, D.M., 2006. The quality of our nation's waters: pesticides in the nation's streams and ground water, 1992–2001. U.S. Geological Survey Circular 1291 (172 pp.).
- Heaton, T.H.E., Vogel, J.C., 1981. “Excess air” in groundwater. *Journal of Hydrology* 50, 201–216.
- Helmke, M.F., Simpkins, W.W., Horton, R., 2005. Fracture controlled nitrate and atrazine transport in four Iowa till units. *Journal of Environmental Quality* 34, 227–236.
- Hladik, M.L., Hsiao, J.J., Roberts, A.L., 2005. Are neutral chloroacetamide herbicide degradates of potential environmental concern? Analysis and occurrence in the upper Chesapeake Bay. *Environmental Science and Technology* 39 (17), 6561–6574.

- Howarth, R.W., Boyer, E.W., Pabich, W.J., Galloway, J.N., 2002. Nitrogen use in the United States from 1961–2000 and potential future trends. *Ambio* 31, 88–96.
- Kellogg, R.L., Lander, C.H., Moffitt, D.C., Gollehon, N., 2000. Manure nutrients relative to the capacity of cropland and pastureland to assimilate nutrients — Spatial and temporal trends for the United States. National Resources Conservation Service, U.S. Department of Agriculture, Washington, DC. available online at: <http://www.nrcs.usda.gov/technical/land/pubs/mannt.html>.
- Kolpin, D.W., Thurman, E.M., Goolsby, D.A., 1996. Occurrence of selected pesticides and their metabolites in near surface aquifers of the Midwestern United States. *Environmental Science and Technology* 30, 335–340.
- Kolpin, D.W., Schnoebelen, D.J., Thurman, E.M., 2004. Degradates provide insight to spatial and temporal trends of herbicides in ground water. *Ground Water* 42, 601–608.
- Koterba, M.T., Wilde, F.D., Lapham, W.W., 1995. Ground-water data-collection protocols and procedures for the National Water Quality Assessment program: collection and documentation of water-quality samples and related data. U.S. Geol. Surv., Open-file Report 95-399.
- Kruger, E.L., Rice, P.J., Anhalt, J.C., Anderson, T.A., Coats, J.R., 1997. Comparative fates of atrazine and deethylatrazine in sterile and nonsterile soils. *Journal of Environmental Quality* 26, 95–101.
- Lapham, W.W., Wilde, F.D., Koterba, M.T., 1995. Ground-water data-collection protocols and procedures for the National Water-Quality Assessment Program: selection, installation, and documentation of wells and collection of related data. U.S. Geological Survey Open-File Report 95-398.
- Lee, E.A., Strahan, A.P., 2003. Methods of Analysis by the U.S. Geological Survey Organic Geochemistry Research Group-Determination of Acetamide Herbicides and Their Degradation Products in Water Using Online Solid-Phase Extraction and Liquid Chromatography/Mass Spectrometry. U.S. Geological Survey Open-File Report 03-173.
- Malard, F., Hervant, F., 1999. Oxygen supply and the adaptations of animals in groundwater. *Freshwater Biology* 41, 1–30.
- Manning, A.H., Solomon, D.K., Thiros, S.A., 2005. $^3\text{H}/^3\text{He}$ Age data in assessing the susceptibility of wells to contamination. *Ground Water* 43, 353–367.
- McMahon, P.B., Dennehy, K.F., Bruce, B.W., Böhlke, J.K., Michel, R.L., Gurdak, J.J., Hurlbut, D.B., 2006. Storage and transit time of chemicals in thick unsaturated zones under rangeland and irrigated cropland, High Plains, United States. *Water Resources Research* 42, W03413. doi:10.1029/2005WR004417.
- Miller, J.L., Wollum, A.G., Weber, J.B., 1997. Degradation of carbon-14 atrazine and carbon-14 metolachlor in soil from four depths. *Journal of Environmental Quality* 26, 633–638.
- Nair, D.R., Schnoor, J.L., 1992. Effect of two electron acceptors on atrazine mineralization rates in soil. *Environmental Science and Technology* 26, 2298–2300.
- National Climatic Data Center, 2006. Climatography of the U.S. No. 81-Supplement # 3: Maps of Annual 1961–1990 Normal Temperature, Precipitation and Degree Days. <http://www.ncdc.noaa.gov/oa/documentlibrary/clim81supp3/clim81.html>2006.
- Nolan, B.T., Hitt, K.J., Ruddy, B.C., 2002. Probability of nitrate contamination of recently recharged groundwaters in the conterminous United States. *Environmental Science and Technology* 36, 2138–2145.
- Phillips, P.J., Wall, G.R., Thurman, E.M., Eckhardt, D.Q., van Hoesen, J., 1999. Metolachlor and its metabolites in tile drain and stream runoff in the Canajoharie Creek watershed. *Environmental Science and Technology* 33, 3531–3537.
- Puckett, L.J., 1995. Identifying the major sources of nutrient water pollution. *Environmental Science and Technology* 29, 408A–414A.
- Puckett, L.J., Hughes, W.B., 2005. Transport and fate of nitrate and pesticides: hydrogeology and riparian zone processes. *Journal of Environmental Quality* 34, 2278–2292.
- Ruddy, B.C., Lorenz, D.L., Mueller, D.K., 2006. County-level estimates of nutrient inputs to the land surfaces of the coterminous United States, 1982–2001. Sci. Investigations Rep. 2006-5012. USGS, Denver CO.
- Saad, D.A., in press. Agriculture-related trends in ground-water quality of the glacial deposits aquifer, central Wisconsin. *Journal of Environmental Quality*.
- Schlesinger, W.H., Reckhow, K.H., Bernhardt, E.S., 2006. Global Change: The nitrogen cycle and rivers. *Water Resources Research* 42, W03S06. doi:10.1029/2005WR004300.
- Schwab, A.P., Splichal, P.A., Banks, M.K., 2006. Persistence of atrazine and alachlor in ground water aquifers and soil. *Water, Air and Soil Pollution* 171, 203–235.
- Scribner, E.A., Thurman, E.M., Goolsby, D.A., Meyer, M.T., Battaglin, W.A., Kolpin, D.W., 2005. Summary of significant results from studies of triazine herbicides and their degradation products in surface water, ground water, and precipitation in the Midwestern United States during the 1990s. U.S. Geological Survey Scientific Investigations Report 2005-5094. 27 pp.
- Skipper, H.D., Gilmour, C.M., Furtick, W.R., 1967. Microbial versus chemical degradation of atrazine in soils. *Soil Science Society of America Proceedings* 31 (5), 653–656.
- Stamper, D.M., Tuovinen, O.H., 1998. Biodegradation of the acetanilide herbicides alachlor, metolachlor, and propachlor. *Critical Reviews in Microbiology* 24 (1), 1–22.
- Starr, R.C., Gillham, R.W., 1989. Controls on denitrification in shallow aquifers. *Contaminant Transport in Ground Water*, pp. 934–947.
- Starr, R.C., Gillham, R.W., 1993. Denitrification and organic carbon availability in two aquifers. *Ground Water* 31, 934–947.
- Tesoriero, A.J., Liebscher, H., Cox, S.E., 2000. The mechanism and rate of denitrification in an agricultural watershed: Electron and mass balance along ground water flow paths. *Water Resources Research* 36, 1545–1559.
- Tesoriero, A.J., Spruill, T.B., Mew, H., Farrell, K., Harden, S.L., 2005. Nitrogen transport and transformations in a coastal plain watershed: influence of geomorphology on flow paths and residence times. *Water Resources Research* 41, W02008. doi:10.1029/2003WR002953 (15 pp.).
- Tomer, M.D., Burkart, M.R., 2003. Long-term effects of nitrogen fertilizer use on ground water nitrate in two small watersheds. *Journal of Environmental Quality* 32, 2158–2171.
- U.S. Department of Agriculture, 1994. Atrazine: Environmental Characteristics and Economics of Management, Agricultural Economic Report 699. <http://www.ers.usda.gov/publications/aer699/AER699.PDF>1994.
- U.S. Department of Agriculture, 2006. National Agricultural Statistics Service. <http://www.nass.usda.gov/index.asp>2006.
- U.S. Environmental Protection Agency, 1995. Reregistration eligibility decision fact sheet for metolachlor. Office of Prevention, Pesticides and Toxic Substances, EPA-738-F-95-007. <http://www.epa.gov/REDs/factsheets/0001fact.pdf>1995.
- U.S. Environmental Protection Agency, 1998. Reregistration eligibility decision fact sheet for alachlor. Office of Prevention, Pesticides and Toxic Substances, EPA-738-F-98-018. <http://www.epa.gov/REDs/factsheets/0063fact.pdf>1998.

- Vidon, P., Hill, A.R., 2004. Denitrification and patterns of electron donors and acceptors in eight riparian zones with contrasting hydrogeology. *Biogeochemistry* 71, 259–283.
- Wassenaar, L.I., Hendry, M.J., Harrington, N., 2006. Decadal geochemical and isotopic trends for nitrate in a transboundary aquifer and implications for agricultural beneficial management practices. *Environmental Science and Technology* 40, 4626–4632.
- Wehtje, G.R., Spalding, R.F., Burnside, O.C., Lowry, S.R., Leavitt, J.R.C., 1983. Biological significance and fate of atrazine under aquifer conditions. *Weed Science* 31, 610–618.
- Zaugg, S.D., Sandstrom, M.W., Smith, S.G., Fehlberg, K.M., 1995. Methods of analysis by the U.S. Geological Survey National Water Quality Laboratory-Determination of pesticides in water by C-18 solid-phase extraction and capillary-column gas chromatography/mass spectrometry with selected-ion monitoring: U.S. Geological Survey Open-File Report 95-181. 60 pp.