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WR05R003

NITRATE AND PESTICIDE PENETRATION INTO A NORTHERN MISSISSIPPI VALLEY LOESS HILLS AQUIFER

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Nitrate and Pesticide Penetration into a Northern Mississippi Valley Loess Hills Aquifer

A Report for University of Wisconsin System
Groundwater Research Project WR05R003

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PROJECT SUMMARY

Title: **Nitrate and Pesticide Penetration into a Northern Mississippi Valley Loess Hills Aquifer**

Project I.D.: WR05R003

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Background/Need: The leakage of NO_3 and pesticide residues from agricultural landscapes to groundwater degrades drinking water resources and exports contaminants to surface waters, threatening both freshwater and marine ecosystems. This leakage has increased greatly over the last several decades, driven by increasing fertilizer and pesticide use particularly over the period of about 1960 to 1990. Given that the increase in pollutant leakage is recent compared with the residence time of ground water in many aquifers, aquifer pollutant loads may not generally be at a steady-state with pollutant leakage in many agricultural regions. In the absence of a steady-state, pollutants will continue to penetrate more deeply into aquifers, increasing pollutant load and pollutant export to surface water.

Objectives: Determine (1) the pollutant leakage chronology of a Northern Mississippi Valley Loess Hills aquifer, (2) whether a modern pollutant load penetrates the entire aquifer thickness, (3) if degradation mechanisms limit pollutant penetration, and (4) what pollutant conditions might develop in the future.

Methods: The study location was on the University of Wisconsin-Platteville Pioneer Farm in the upper Fever River watershed. We accessed the subsurface through a borehole that provided a 62 m aquifer profile instrumented at discrete depths for sample collection. We employed "groundwater stratigraphy" methods to establish in the aquifer profile the depth structure of NO_3, denitrified-NO_3, pesticide residues, groundwater recharge age-date, and other dissolved constituents. Age-date information was used to establish a pollutant leakage chronology.

Results and Discussion: Groundwater was the Ca – Mg – HCO_3 type with summed ion concentrations of 437-667 mg L^{-1}. Shallow groundwater (upper 7 m) was well oxygenated (dissolved oxygen > 5.0), but deeper groundwater was suboxic, though strong reducing conditions were generally contraindicated by small concentrations of Fe, Mn, and denitrified-N, and by larger concentrations of SO_4.

Nitrate and denitrified N were the dominant forms of nonatmospheric dissolved N in the aquifer. The NO_3-N averaged 7.2 mg L^{-1} and ranged from 19.8 mg L^{-1} near the water table to 0.2 mg L^{-1} at 29 m. Ground water shallower than 7 m exceeded the MCL (maximum contaminant level; a US drinking water standard) of 10 mg L^{-1} of NO_3-N. Denitrified N averaged 1.7 mg L^{-1}, and relative to NO_3-N had a narrow range, 0.1 to 3.6 mg L^{-1}. The small amount of denitrified-N relative to initial NO_3-N (the sum of denitrified and measured NO_3-N) indicates that denitrification cannot be relied upon to substantially reduce NO_3 concentrations in groundwater nor control export to surface waters.

Groundwater age dates in the profile ranged from 1957 to 1984. Hence, the profile contained a 27 yr chronology of pollutant leakage to ground water from the landscape. A smooth age-date decline (1984 to 1979) was apparent in the upper 7 m of the profile spanning a highly transmissive dissolution zone, but age dates dropped abruptly to 1959 by 8.5 m. Deeper groundwater exhibited age dates of 1957 to 1969. Nitrate, initial NO_3 (NO_3 and denitrified NO_3), and Cl concentrations increased with increasing groundwater age date. The increase was 17-fold for initial NO_3-N and 14-fold for Cl during the 1957-1984 period. Concentrations of NO_3-N, initial NO_3-N, and Cl were still increasing at the end of the chronology, by about 0.8 mg L^{-1} yr^{-1}. We attribute the steep rise to intensification of agricultural practices including increased use of chemical fertilizers during the period.

Detected pesticide residues were atrazine and its deethyl-atrazine degradate, alachlor ESA, metolachlor ESA and OA. Not detected were acetochlor residues, diamino-atrazine, alachlor, alachlor OA, metolachlor, metolachlor OA, nor many others potentially detectable by the analytical methods. Summed pesticide residues ranged to 7.2 µg L^{-1}. Metolachlor metabolites were found in greatest concentrations, up to 5.2 µg L^{-1}. Alachlor ESA was also detected frequently, at concentrations up to 1.4 µg L^{-1}. Atrazine and its degradate deethylatrazine were also found, but only in the upper 5 m of the aquifer, and at concentrations of only about 0.3 µg L^{-1}. Larger pesticide residue concentrations (>1 µg L^{-1}) were found only in the upper 7 m in groundwater with age dates of 1979 to 1984. We attribute the pesticide depth and age date patterns to the rise of pesticide use during the period.

Conclusions/Implications/Recommendations: Pollutant leakage in the upper Fever watershed increased greatly from 1957 through 1984 during the period of increasing use of chemical fertilizers and pesticides. Net NO_3-N concentrations in groundwater recharge increased from 0.2 mg L^{-1} to about 19 mg L^{-1} during the period. Denitrification processes were able to attenuate only about 1.7 mg L^{-1} of initial NO_3-N, and thus little of the NO_3 leakage in the latter part of the chronology. Net NO_3-N leakage rates increased from <1.0 to 28.5 kg ha^{-1} yr^{-1} during the 1957 through 1984 period. Chloride leakage followed that of NO_3 closely.

Detected residues were atrazine and its deethyl-atrazine degradate, alachlor ESA, metolachlor ESA and OA. Larger pesticide residue concentrations (>1 µg L^{-1}) were found only in the upper 7 m in groundwater with age dates of 1979 to 1984.

Pollutants have only partially penetrated the aquifer in the upper Fever watershed. Degradation mechanisms appear unable to control further NO_3 penetration into the aquifer, but the picture is less clear for pesticide residues. Progression toward a steady state at local scales may be manifested as increasing pollutant concentrations in drinking water. At large scales, the progression could be manifested by increased surface water pollutant loads with corresponding ecological harms, such as an intensification of marine hypoxia.

Future work in this study area could focus on elucidating groundwater flow patterns from the landscape to local, intermediate, and regional groundwater flow systems, with the goal of predicting the increase in aquifer pollutant concentrations and pollutant export to surface water over time

Key Words: nitrate, pesticides, groundwater, pollutant penetration

INTRODUCTION

This study addresses groundwater pollution by NO_3 and pesticide residues in part of the Northern Mississippi Valley Loess Hills region (Figure 1). Specifically we examine whether pollutant loads in aquifers (the mass of pollutant in aquifer storage) there are increasing, or conversely, that aquifer pollutant loads are in an equilibrium with pollutant leakage from the landscape surface. The Northern Mississippi Valley Loess Hills (NMVLH; NRCS, 2006) covers 57,520 km^2; about one-fifth of Wisconsin (including most of the “driftless area”) plus adjacent parts of Minnesota, Iowa, and Illinois. The study site was on the University of Wisconsin – Platteville Pioneer Farm in the upper Fever River watershed.

The leakage of NO_3 and pesticide residues (“pollutants”) from agricultural landscapes to groundwater degrades drinking water resources (Postle et al., 2004, Nolan et al., 2002, Fan and Steinberg, 1996) and exports contaminants to surface waters, which threatens both freshwater (Rouse et al., 1999; Johnston et al., 1999; Howe et al., 1998; Hayes et al., 2003) and marine ecosystems (e.g., Rabalais et al., 2007). This leakage has increased greatly over the last several decades, driven by increasing fertilizer and pesticide use particularly over the period of about 1960 to 1990 (Hallberg et al., 1989; Böhlke and Denver, 1995; Kellog et al., 2000). Given that the increase in pollutant leakage (pollutant mass per landscape area - time) is recent compared with the residence time of groundwater in many aquifers, aquifer pollutant loads may not generally be at a steady-state with pollutant leakage in many agricultural regions. "Steady-state" is defined here as the condition in which the mass of a pollutant and its spatial distribution in an aquifer remain more-or-less constant over time. In the absence of a steady-state, pollutants will continue to penetrate more deeply into an aquifer, increasing the aquifer's pollutant load and its pollutant export to surface water. A steady-state develops when modern groundwater and its accompanying pollutants penetrate an aquifer's entire thickness, or when pollutants in an aquifer degrade at a rate equal to their leakage.

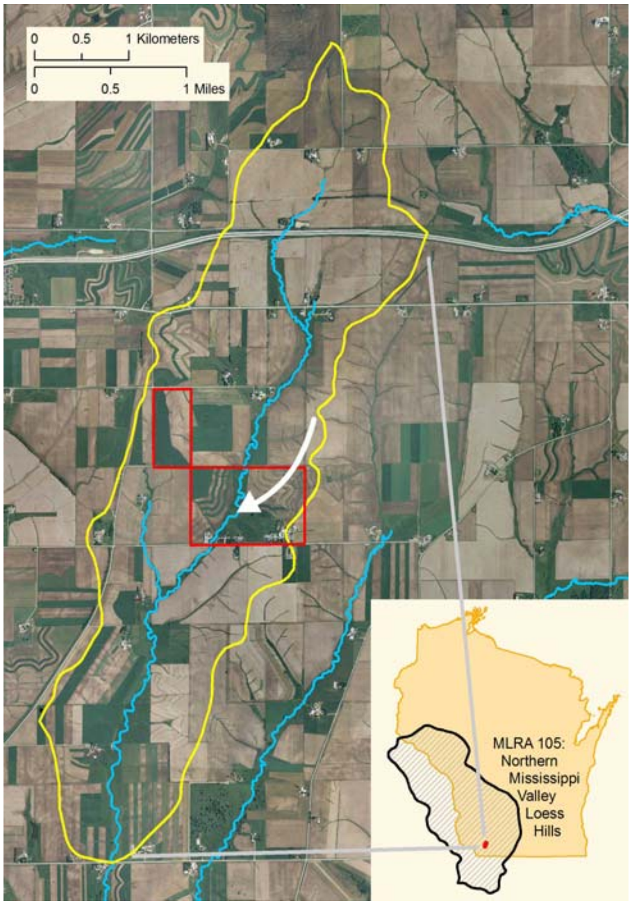

Figure 1. Location and boundaries of the upper Fever watershed in the Northern Mississippi Loess Hills. Pioneer Farm is shown in red; inferred flow line to study borehole shown in white.

In this study, we examine pollutant penetration in a dominantly agricultural part of the NMVLH of southwestern Wisconsin to determine whether a modern pollutant load penetrates the entire aquifer thickness there, if degradation mechanisms limit pollutant penetration, and what pollutant conditions might develop in the future. Our approach employed "groundwater stratigraphy" methods (Böhlke, 2002), establishing and interpreting in an aquifer profile the depth structure of NO_3, denitrified-NO_3, pesticide residues, groundwater recharge age-date, and other dissolved constituents; and then using age-date information to establish a pollution leakage chronology.

Study Area

The NMVLH is characterized by rolling to hilly uplands dissected by tributaries of the Mississippi

River (NRCS, 2006). Silt loam soils several meters thick cover thick sequences of Paleozoic sandstones and dolostones. Soils are generally well-drained, and artificial drainage is rare. Much of the landscape is agricultural, and groundwater quality impairments are common. In the Wisconsin part of the NMVLH, 25% of wells exceed the nitrate MCL (LeMasters and Baldock, 1995), 11% contain atrazine residues, 32% contain alachlor residues, and 34% contain metolachlor residues (Postle et al., 2004). Nitrate exports from watersheds are large; in the upper Fever River watershed NO_3-N exports amounted to over 25 kg ha^{-1} yr^{-1} (Masarik et al., 2007). This is in the uppermost category of the classification scheme of Goolsby et al. (2001) for the Mississippi drainage (15-31 kg ha^{-1} yr^{-1}).

We used a 62 m deep groundwater profile at the Pioneer Farm in the upper Fever River watershed (Figure 2) to infer the chronology of pollutant leakage from the landscape to groundwater and the pollutant status of the aquifer. The upper Fever watershed and surroundings have >90% agricultural land cover, much of which is in row crops utilizing large inputs of fertilizer and pesticides. The land surface is gently rolling with slopes averaging about 6%, directed toward drainages spaced at 1 to 3 km intervals. Through most of the area, 1-4 m of loess-derived soils are typically present, covering 0-4 m of unconsolidated/“loose rock” material derived from the underlying Galena formation (Figure 2). The Galena dolostone thickness in the study profile is 37 m thick. Important underlying units are Decorah dolostone (11 m thickness), Spechts Ferry shale (1-2 m), Platteville Formation dolostone (19 m), and Glenwood shale (1.5 m). Underlying the Glenwood is the St. Peter sandstone of possibly 10-100 m thickness, and about 300 m of other Paleozoic rocks that behave as aquifers and aquitards. In the profile, a large vertical hydraulic gradient across the Glenwood exists, where an apparent 28 m head loss occurs over just a few meters. The rock units overlying the St. Peter formation are grouped hydrostratigraphically as the “Maquoketa confining unit” (Young, 1992). Despite the “confining unit” moniker, these units commonly yield water sufficient for supplying domestic and farm needs, and convey much of the landscape’s runoff to surface water in shallow, local flow systems. The permeability and water yielding abilities of the rocks are largely controlled by the degree of weathering and fracturing. Additional details are being compiled in a separate report (Kraft et al., in progress).

As a working conceptual model of groundwater hydraulics, we propose a four layer flow system (Figure 2). Flow in the uppermost layer occurs in the shallow Galena, i.e., that within 10 m or so of the water table, through a well connected and highly transmissive conduit network. The underlying second layer, about 50 m thick, is marked by a lower permeability and possibly dominated by matrix flow (as opposed to conduit flow), and contains low conductivity units that may impede vertical flow. The third layer is the Glenwood shale, a barrier that impedes flow from overlying layers to the St. Peter sandstone aquifer, the highly permeable fourth layer. In this conceptual model, groundwater flow in layers 1 and 2 conforms to the local topography, and is largely captured by local discharge to the Fever River. Some water in layer 2 likely becomes regional flow, either by escaping capture by the Fever River and exiting the watershed, or by crossing the Glenwood and joining regional flow in the St. Peter aquifer and underlying units. The St. Peter aquifer also receives underflow from the east (Young, 1992) and transmits underflow to the west. The recharge areas in the upper Fever watershed most likely to contribute to deep, regional flow systems are those located near groundwater divides, which here coincide with the topographic boundaries of the watershed (Toth, 1963).

Instrumentation

The Pioneer Farm is instrumented with 12 boreholes, each fitted with multiple piezometers that terminate at different aquifer elevations. These have been used to infer the local hydrogeology (Kraft et al., in progress). Two boreholes constructed to 43 m and 77 m (Figure 2) were used to establish the groundwater profile used in this study. The shallower hole was instrumented with a Flute^{TM} (http://www.flut.com/about.html) multilevel piezometer device equipped with 8 ports screened 10 to 41 m below ground surface (3 to 34 m below the water table, all depths to screen midpoint). The second

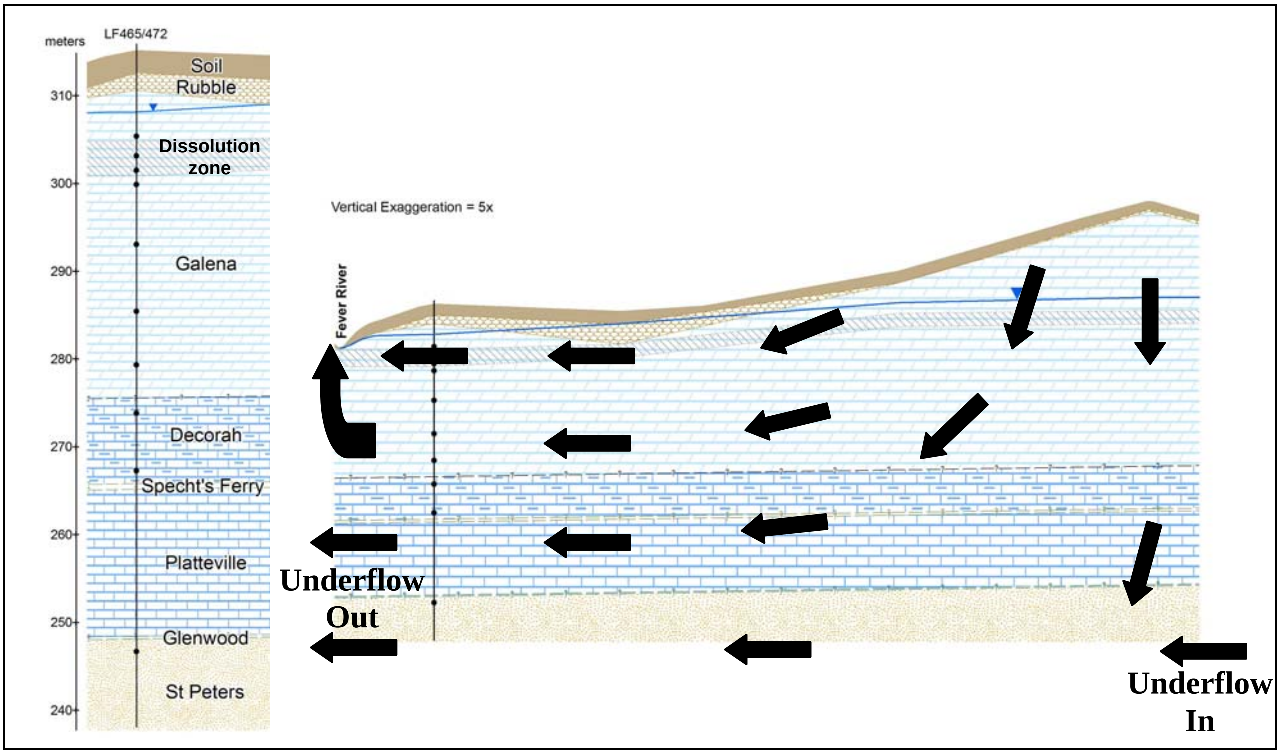

Figure 2. Left: Stratigraphy and sampling depths at the study site. Right: Conceptual model of groundwater flow from the landscape to study site along flowpath shown in Figure 1.

borehole was instrumented with two standard PVC piezometers screened at 48 and 69 m depths (41 and 62 m below the water table). The upper three screens were constructed into an apparently laterally continuous dissolution zone. The fourth screen crossed a possibly poorly connected vuggy horizon, screens 5 through 9 were placed at depths seemingly lacking substantial dissolution features, and screen 10 was placed beneath the Glenwood shale in the St. Peter sandstone.

PROCEDURES AND METHODS

Approach and Conceptual Model

The "groundwater stratigraphy" approach (Böhlke 2002) used in this study relies on the premise that the pollutant leakage and fate chronology of a landscape is retained in the profile of an aquifer, and that this chronology can be extracted using the general principles that "are applied commonly in stratigraphic analysis of sedimentary rocks," using pollutant analysis and groundwater age-date techniques. Previous studies using this approach have been done mainly in simpler hydrogeologic systems that behave in accordance with the hydraulics described by King (1899) and Hubbert (1940). That is, groundwater systems that are unconfined, receive areally-distributed recharge (and diffuse-source pollutants), discharge to surface water features, and have a spatial structure in which younger groundwater overlies older groundwater. In this sort of system, younger, shallower groundwater originates as recharge nearer to an observation point, while older, deeper groundwater originates farther upgradient, closer to a groundwater divide. In the upper Fever watershed, the hydrogeology is more complicated, involving alternating high and low permeability strata, and local to regional flow systems. However, the basic premise still hold that the pollutant leakage and fate chronologies is retained and can be extracted. Böhlke (2002) points out that in a single borehole, the spatial influences of land use heterogeneities (i.e., land uses near the borehole are different than those farther from it) on water quality could be difficult to separate from temporal influences (changes in agricultural management through time). At scales important to this study, the land uses in the upper Fever River watershed are homogeneous, without apparent bias with distance upgradient from the borehole. We expect therefore that temporal influences dominated spatial ones in the variability observed in groundwater quality with aquifer depth.

Sampling and Analyses

Groundwater was sampled in July 2007. Standard PVC piezometers were purged from near the hydrostatic surface of at least 5 volumes of water prior to sampling. During sampling, the sample tubing was dropped into the screened zone of the piezometer. Purging and sampling utilized a Wattera^{TM} inertial pump. General sampling procedures for the Flute^{TM} piezometer tubes is provided at http://www.flut.com/meth_2.html. Tubes were purged slowly (27 L d^{-1}) for 30 days prior to sampling. Samples for inorganic and pesticide analyses were collected using routine protocols (e.g., WDNR, 1996) for filtering and preservation as appropriate for individual analytes. Samples for dissolved gas analyses (chlorofluorocarbons (CFCs), Ar, N_2, N_2O) were collected according to USGS laboratory specified procedures described at http://water.usgs.gov/lab/. Field measurements (temperature, pH, specific conductance, and dissolved oxygen) were obtained using a multiparameter sonde equipped with a flow cell to avoid exposure of sample to the atmosphere during measurement. Metals (Al, Ca, Mg, K, Na, Mn, Fe), Si, and S (reported as SO_4) were analyzed by inductively coupled plasma AES (APHA 1995 methods 311B, 3111D, and 3129B). Chloride, NO_2+NO_3-N, NO_2, NH_4, and total Kjeldahl N (TKN) were analyzed using automated colorimetry (APHA 1995 methods 4500 E, F, H, and G). ANC (acid neutralizing capacity) was analyzed by titration (APHA 1995, method 2320B). Dissolved organic carbon was measured by a combustion infrared method (APHA 1995, method 5310 B). We calculated a "summed ion concentration" as the sum of concentrations of all ions present at greater than 0.5 mg L^{-1}, as a surrogate for total dissolved solids. For this calculation, ANC was converted to HCO_3.

The pesticide emphases of this study were the residues of atrazine (parent atrazine and the chlorinated degradates deethyl-, deisopropyl-, and diamino-atrazine), and the chloroacetanlides alachlor, acetochlor, and metolachlor (parents plus their ethane sulfonic acid (ESA) and oxanilic acid (OA) degradates). These are common groundwater pollutants in much of the midwestern US (Postle et al., 2004, Kalkhoff et al., 1998). Though the parent compounds are relatively rare, ESA and OA degradates are widespread (Kalkhoff et al., 1998, VandenBrook et al., 2002). Atrazine, atrazine degradates, alachlor, metolachlor, acetochlor, metribuzin, and 24 other pesticides were analyzed by GC/MS (modified EPA method 8270, USEPA, 1996) with an extraction method developed to isolate the more water soluble atrazine degradates (WSLH, 2003). Total atrazine residues were calculated by summing parent and degradates. Chloroacetanilide degradates were determined using solid-phase extraction and high performance liquid chromatography/diode array detection as described by Zimmerman et al. (2000).

Dissolved gas (N_2, CH_4, CO_2, and Ar) analyses were performed at the USGS lab in Reston VA, using procedures described at http://water.usgs.gov/lab/. Analyses were done in duplicate. The procedure for estimating denitrified NO_3-N ("denitrified-N") from total dissolved N_2 and Ar follows. Total dissolved N_2 in groundwater consists of three components: (1) N_2 gas acquired during recharge by equilibrium with air, (2) N_2 gas acquired during recharge by incorporation of excess air, and (3) nonatmospheric excess N_2 gas produced after recharge by denitrification (Böhlke, 2003). Ar is a recharge temperature dependent tracer of the amount of total air (components 1 + 2) contained in a water sample. In a water sample that has behaved as a closed system since recharging, only two of the three components can be resolved directly from measurements of Ar and N_2. Consequently, the concentration of excess non-atmospheric N_2 (denitrified-N) in a sample can only be estimated by assuming a value for the recharge temperature or by assuming a value for the amount of excess air in a sample. "Normal" excess air values are 0 to 3 ml L^{-1}, but values up to 10 ml L^{-1} or more have been observed in some fractured rock and arid areas (http://water.usgs.gov/lab/). We assumed a recharge temperature of 9.5 C (local groundwater temperature) for the results presented here, which produces excess air estimates in individual samples of 0.8 to 5.4 ml L^{-1}. Estimates of denitrified N_2-N would increase by an average 2 mg L^{-1} by assuming no excess air, and recharge temperatures of about 6 C. Estimates of denitrified-N of zero could be produced by assuming recharge temperatures of up to 17 C and excess air up to 9 ml L^{-1} at STP.

Chlorofluorocarbons (CFCs, CFC 11, 12, and 113) for groundwater age dating were analyzed at the USGS lab in Reston VA, using procedures described at http://water.usgs.gov/lab/. Analyses were done in duplicate or triplicate. Sample age dates were assigned on the basis of comparison of CFC equilibrium partial pressures, corrected for recharge temperature, with the chronology of atmospheric partial pressures (Busenberg and Plummer, 1992). A recharge temperature of 9.5 C was used; age date estimates were not greatly sensitive to the use of warmer or cooler temperatures in a realistic range. Potentially three estimates, one from each CFC, could be generated for each sample. As is not uncommon in many groundwater age date studies, CFC 12 contamination (i.e., CFC 12 originating from a source other than the atmosphere) resulted in concentrations above that possible with atmospheric equilibrium. These were excised from the data set. Also excised from the data set were young CFC 12 age date estimates that were incongruent with CFC 11 and CFC 113 estimates and with age date estimates from adjacent piezometer screens.

RESULTS AND DISCUSSION

Groundwater age dates and general geochemistry

Groundwater was the Ca – Mg – HCO_3 type with summed ion concentrations of 437-667 mg L^{-1} (Figure 3). The pH, ANC, and DOC averaged 7.4, 322 mg L^{-1} as $CaCO_3$, and 6.3 mg L^{-1}, respectively. Shallow groundwater (upper 7 m) was well oxygenated (dissolved oxygen > 5.0), though deeper groundwater was somewhat oxygen depleted (dissolved oxygen 0.8 to 1.5 mg L^{-1}). Fe was elevated at the 8.5 m depth (1.0 mg L^{-1}), but strong reducing conditions were generally contraindicated by small concentrations of Fe, Mn, and denitrified-N, and large concentrations of SO_4. (Note that all depths are referenced from the water table.) Summed ions were roughly 50% greater in the upper 7 m of groundwater compared with deeper groundwater, but NO_3 and Cl were much greater still.

Nitrate and denitrified N were the dominant forms of nonatmospheric dissolved N in the aquifer. The NO_3-N averaged 7.2 mg L^{-1} and ranged from 19.8 mg L^{-1} near the water table (Figure 3) to 0.2 mg L^{-1} at 29 m. Groundwater shallower than 7 m exceeded the MCL (maximum contaminant level; a US drinking water standard) of 10 mg L^{-1} of NO_3-N. (The MCL is a useful threshold, as it sets a standard below which groundwater is perceived by many as safe for drinking water.) Denitrified N averaged 1.7 mg L^{-1}, and relative to NO_3-N had a narrow range, 0.1 to 3.6 mg L^{-1}. Because the denitrified-N range was small, initial NO_3-N (measured NO_3-N + denitrified-N) followed NO_3-N closely, averaging 8.3 and ranging 1.3 to 22.3 mg L^{-1} (Figure 3).

Groundwater age dates (Figure 3) ranged from 1957 to 1984. Hence, the profile contained a 27 yr chronology of pollutant leakage to groundwater from the landscape. We presume that younger (post-1984) water resided in the 3 m of aquifer overlying the shallowest monitoring point. Groundwater age dates did not decline smoothly with depth as is common in more homogeneous groundwater environments (Böhlke, 2002; Kraft et al., 2008). A smooth age-date decline (1984 to 1979) was apparent in the upper 7 m of the profile spanning the highly transmissive dissolution zone, but age dates dropped abruptly to 1959 by 8.5 m, and reached a profile minimum of 1957 at 15.4 m. Age dates rebounded linearly to 1969 at 41 m, declining again to 1962 at 62 m, in the upper St. Peter sandstone.

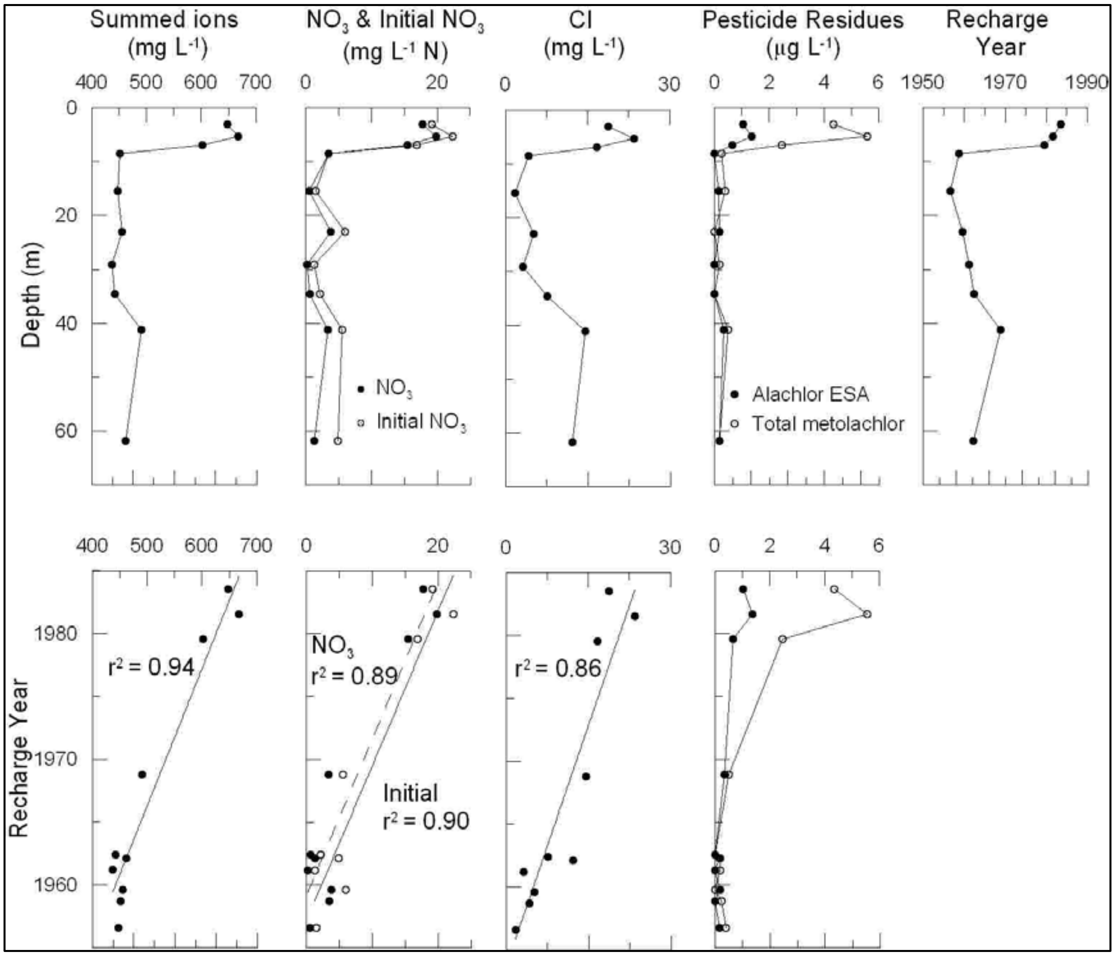

Figure 3. Water quality and age date results by depth and groundwater age date.

Groundwater pollutant chronology

Summed ions, NO_3, initial NO_3, and Cl increased with increasing groundwater recharge age date (Figure 3). Initial NO_3-N increased 17-fold and Cl increased 14-fold in the 1957-1984 chronology. Initial NO_3-N and Cl were still increasing at the end of the chronology, by about 0.8 mg L^{-1} yr^{-1}. We attribute the steep rise to intensification of agricultural practices including increased use of N and KCl fertilizers during the period. Denitrified-N was independent of both initial NO_3 and groundwater age date. This supports that denitrification likely occurred rapidly in the vadose zone or shallow groundwater in “hot spots” or “hot moments” (McClain et al. 2003, Browne et al. 2008) of highly available electron donors, rather than gradually along lengthy flowpaths as has been reported for some study sites (Vogel et al., 1981, Böhlke and Denver, 1995, Tesoriero et al., 2000, Puckett and Cowdery, 2002). Because denitrified-N was small and had a narrow range compared with ever-increasing initial NO_3-N leakage, the denitrified-N fraction of initial NO_3-N decreased over time from up to 80% in about 1960 to 7% in 1984. This indicates that denitrification cannot be relied upon to substantially reduce NO_3 concentrations in groundwater nor export to surface waters.

Leakage and denitrification flux rates (mass per landscape area-time) of initial NO_3-N, NO_3-N, and denitrified-N can be estimated by multiplying concentrations by the estimated groundwater recharge rate of 150 mm yr^{-1}. This indicates initial NO_3-N leakage from the landscape increased from < 1 kg ha^{-1} yr^{-1} in the 1950s to 30 kg ha^{-1} yr^{-1} by 1984. At the end of the groundwater chronology, initial NO_3-N was apparently still increasing at about 0.8 kg ha^{-1} yr^{-1}. Assuming that denitrification removed an average 2.5 kg ha^{-1} yr^{-1} of initial NO_3-N, net NO_3-N leakage amounted to 27.5 kg ha^{-1} yr^{-1} in 1984, and was still increasing by 0.8 kg ha^{-1} yr^{-1}. The 1984 net NO_3-N leakage, if exported to surface water, would place the landscape into the highest NO_3-N yielding category for the Mississippi drainage (15-31.2 kg ha yr^{-1}) in the classification scheme of Goolsby et al. (2001).

Nitrate and Cl patterns with depth and recharge date indicate that modern groundwater recharge and its associated modern pollutant burden have not penetrated the entire aquifer thickness. Neither does evidence support that NO_3 penetration will be greatly limited by denitrification processes. Thus the aquifer load of NO_3 and the aquifer's export of NO_3 to surface water will continue to grow until a steady state is reached or until N leakage from the landscape is substantially reduced. Predicting the growth in load and export, however, is not as straight forward as in simpler hydrogeologic settings (Kraft et al., 2008) and will have to wait until a better understanding of groundwater flow in the upper Fever watershed is gained.

Pesticide residues

Detected residues were atrazine and its deethyl-atrazine degradate, alachlor ESA, metolachlor ESA and OA. Not detected were acetochlor residues, diamino-atrazine, alachlor, alachlor OA, metolachlor, metolachlor OA, nor many others potentially detectable by the analytical methods. Summed pesticide residues ranged to 7.2 µg L^{-1} (Figure 3). Metolachlor metabolites, chiefly ESA but also OA, were found most consistently and in greatest concentrations, up to 5.2 µg L^{-1}. Alachlor ESA was also detected frequently, at concentrations up to 1.4 µg L^{-1}. Atrazine and its degradate deethylatrazine were present only in the upper 5 m of the aquifer and at concentrations of only about 0.3 µg L^{-1}. Summed pesticide residue concentrations exceeding 1 µg L^{-1} were found only shallower than 7 m in groundwater with age dates of 1979 to 1984. Hence, pesticide residues followed NO_3 and Cl depth and age date patterns closely. In the absence of effective degradation processes, pesticide residues will continue to penetrate more deeply into the aquifer, increasing its pesticide residue load and export to surface water.

CONCLUSIONS AND RECOMMENDATIONS

The chronology at the Pioneer Farm Springfield Corners displayed increasing pollutant leakage coinciding with an era of increasing agricultural inputs. Net NO_3-N concentrations in groundwater recharge increased from 0.2 mg L^{-1} in 1957 to about 19 mg L^{-1} in 1984, and were still increasing at 0.8 mg L^{-1} yr^{-1} at the end of the chronology. These concentrations correspond to an increase in net NO_3-N leakage rates from <1.0 to 28.5 kg ha^{-1} yr^{-1} during the same period. As denitrification was not effective in controlling NO_3-N concentrations, aquifer NO_3 will increase over time, as will aquifer export of NO_3-N to surface waters. Predicting the growth in load and export, however, is not easily tractable in the upper Fever by simple models such as those used by Kraft at al. (2008) due to a more complicated hydrogeology. A better understanding of the hydrogeology needs first to be gained.

Chloride concentrations and leakage from the landscape to aquifer grew similarly to NO_3, bolstering confidence that both evolved from the intensification of farming practices that included increases in fertilizer inputs.

The pesticide residues atrazine, deethyl-atrazine, alachlor ESA, and metolachlor ESA and OA were detected in summed concentrations up to 7.2 µg L^{-1}, mainly in groundwater shallower than 7 m and 1979 and younger.

Pollutant penetration appears far from a steady state in the aquifer of the upper Fever watershed and by extension, in the NMVLH. Progression toward a steady state at local scales may be manifested as increasing pollutant concentrations in drinking water. At large scales, the progression could be manifested by increased surface water pollutant loads with corresponding ecological harms, such as an intensification of marine hypoxia. Developing projections regarding how aquifer pollutant loads and exports will increase in the NMVLH could benefit from a better understanding of how groundwater recharge and pollutants are transmitted from the landscape to local, intermediate, and regional groundwater flow systems.

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