Long-Term Agroecosystem Research in the Central Mississippi River Basin: Hydrogeologic Controls and Crop Management Influence on Nitrates in Loess and Fractured Glacial Till

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Abstract

Nitrogen from agriculture is known to be a primary source of groundwater NO$_3$–N. Research was conducted in a northeastern Missouri watershed to assess the impact of cropping systems on NO$_3$–N for a loess and fractured glacial till aquifer underlying claypan soils. Three cropped fields with 10 yr of similar management were each instrumented with 20 to 25 monitoring wells, 3 to 15 m in depth, in 1991 to 1992. Wells were sampled and analyzed for NO$_3$–N at least annually from 1991 to 2004. Initial NO$_3$–N concentrations were variable, ranging from undetectable to >24 mg L$^{-1}$ but averaged 7.0 mg L$^{-1}$. Groundwater NO$_3$–N was significantly higher in Field 3, probably the result of concurrent applications of manure and N fertilizer before 1980. Overall changes in NO$_3$–N levels in Fields 1 and 2 were generally small; however, NO$_3$–N levels for Field 3 have decreased an average of 0.28 mg L$^{-1}$ yr$^{-1}$. Excessive loading of N into the matrix of the glacial till may have had a long-term impact on NO$_3$–N for this field. Despite the presence of dissolved O$_2$ in the aquifer, evidence of denitrification in some upper-landscape groundwater wells was found. The greatest decreases in NO$_3$–N concentration occurred as groundwater moved through an in-field tree line or through a riparian zone. While overall conclusions were complicated by the long-term impact of past management, the capacity of the till to buffer changes, hydrogeologic variability found among wells, and the activity of biological processes, we conclude that cropping practices during this study did not increase glacial till NO$_3$–N.

The use of fertilizers and pesticides has increased agricultural grain production to record levels in much of the world, but contamination of water resources from fertilizer use has caused widespread ecological impairment and economic costs to society for clean drinking water (State-EPA Nutrient Innovations Task Group, 2009; Ribaudo et al., 2011). Nitrogen fertilizer is, by mass, the single greatest agrichemical input on cereal grain crops. Production is tremendously enhanced with N fertilization, with yield increases commonly two to four times greater than without fertilization, and N additions are thus a critical input to help reach global food security goals (Tilman et al., 2002). A negative consequence of N fertilizer use is hydrologic transport from farmland. One loss pathway of concern is NO$_3$–N leaching below the root zone and into aquifers. Nitrogen from synthetic fertilizers continues to be considered a primary source of elevated NO$_3$–N in groundwater.

Nitrates are relatively nontoxic to humans and animals; however, it can be reduced to NO$_2$–N by denitrifying bacteria in the upper digestive tract. High concentrations of NO$_2$–N can be toxic to humans, causing a serious blood disorder called infantile methemoglobinemia or cyanosis (Manassaram et al., 2006). Although the disorder is easily treated, in extreme cases it can cause death. The reaction of NO$_2$–N with the hemoglobin of the blood reduces the capability of the blood to carry O$_2$ to the body tissues. Prompt medical attention normally results in quick recovery (Zaporozec, 1983). A few cases of the disease have been associated with foods high in NO$_3$–N or NO$_2$–N, but nearly all cases reported in the United States have resulted from the ingestion of NO$_3$–N in private well water used to prepare infant formula (Walton, 1951; Knobeloch et al., 2000). The risk of methemoglobinemia increases measurably as concentrations increase above 10 mg L$^{-1}$ NO$_3$–N. Recent studies on human NO$_3$ ingestion are mixed, but some have also shown increased risk for digestive tract or endocrine cancers (Ward et al., 2005, 2006). The disorder is easily treated, in extreme cases it can cause death. The reaction of NO$_2$–N with the hemoglobin of the blood reduces the capability of the blood to carry O$_2$ to the body tissues. Prompt medical attention normally results in quick recovery (Zaporozec, 1983). A few cases of the disease have been associated with foods high in NO$_3$–N or NO$_2$–N, but nearly all cases reported in the United States have resulted from the ingestion of NO$_3$–N in private well water used to prepare infant formula (Walton, 1951; Knobeloch et al., 2000). The risk of methemoglobinemia increases measurably as concentrations increase above 10 mg L$^{-1}$ NO$_3$–N. Recent studies on human NO$_3$ ingestion are mixed, but some have also shown increased risk for digestive tract or endocrine cancers (Ward et al., 2005, 2006).

Abbriviations: CMRB, Central Mississippi River Basin; DO, dissolved oxygen; GCEW, Goodwater Creek Experimental Watershed; LTAR, Long-Term Agroecosystem Research; MCL, maximum contaminant level; MSEA, Management Systems Evaluation Area.

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While the 10 mg L\(^{-1}\) NO\(_3\)–N standard has been questioned using modern techniques of epidemiology (Avery, 1999), it still stands as the maximum contaminant level (MCL) by the USEPA.

National surveys (USEPA, 1990; Mueller et al., 1995), national syntheses of local and regional surveys and studies (Madison and Brunett, 1985; Fedkiw, 1991; Spalding and Exner, 1993; Burow et al., 2010), regional surveys (Burkart and Kolpin, 1993; Richards et al., 1996; Centers for Disease Control and Prevention, 1998; Gormly and Spalding, 1979), and numerous state and local studies have investigated the extent of and factors related to NO\(_3\)–N contamination of groundwater. The percentage of wells with NO\(_3\)–N exceeding the MCL varies from study to study depending on the biases inherent in the data sets, such as whether a study focused on public water supply or domestic wells, agricultural or urban settings, or was dominated by known or suspected problem areas. Numerous studies have documented two primary factors in NO\(_3\)–N contamination. The highest occurrence of wells in which NO\(_3\)–N exceeds the MCL is when the screened interval of the wells is shallow (defined differently in various studies, but generally less than either 15 or 30 m) and/or when the wells are in agricultural areas. Within agricultural areas, there are numerous sources of N, all of which could contribute to NO\(_3\)–N contamination. These include levels of N fertilizer use, animal waste, septic tanks, atmospheric deposition, and soil N. Contamination due to N fertilizer could be from either point sources (e.g., spills or back-siphoning of chemigation water) or nonpoint source from normal fertilizer use. Contamination due to animal waste could be from either point sources or nonpoint source from manure use on fields. Important well characteristics include such factors as the age, depth, diameter, and construction method (dug, driven, or drilled) of the well and the proximity of the well to cropland, chemical mixing sites, septic systems, or livestock areas. These various factors are not mutually exclusive. For example, Richards et al. (1996) noted that older wells are more likely to be dug rather than drilled and that dug wells are likely to be shallow.

The hydrogeologic setting imposes additional factors affecting the vulnerability of groundwater to NO\(_3\)–N contamination. These factors include soil texture, which controls infiltration and percolation rates, aquifer type and depth, precipitation, geochemical attenuation processes within the soil and aquifer, and surface topography (Nolan and Hitt, 2006; Liao et al., 2012). Land uses and land management practices that affect the nature and extent of N inputs are then imposed on the hydrogeologic setting. The existence of multiple factors and complex interactions between the geophysical setting and anthropogenic activities confounds the ability to isolate the impact of any single factor. Thus, determining the impact of nonpoint-source N fertilizer on groundwater quality requires a detailed understanding of the hydrogeology and land uses impacting an aquifer.

To better understand the combined effects of hydrogeology and crop management effects, a long-term groundwater NO\(_3\)–N data set was generated within the Goodwater Creek Experimental Watershed (GCEW) (Lerch et al., 2015). Beginning in 1991, a network of 97 wells installed within the glacial till aquifer of the GCEW was monitored for NO\(_3\)–N concentrations. Seventy-two of the wells were adjacent to or within three research field sites (Fig. 1), and 25 wells were distributed throughout the watershed. Details of the well locations, depth below the ground surface, and sampling frequency were reported by Lerch et al. (2015). Descriptions of the geophysical setting, historic land uses and anthropogenic activities, and weather data were provided as part of the data documentation for the GCEW (Sadler et al., 2015). The data have served to develop our understanding of the hydrogeology, the spatial and temporal variation in contamination, and the effects of landscape features on the fate of NO\(_3\)–N for a shallow glacial aquifer underlying claypan soils. In addition, it provides an example of the insights that can be gained through the long-term and comprehensive development of the data sets collected within the GCEW. The specific objectives of this research were to provide a detailed understanding of the hydrogeologic controls on NO\(_3\)–N transport and the effects of three different cropping systems on groundwater NO\(_3\)–N concentrations within the GCEW from 1991 to 2004. The knowledge gained from this study has enhanced our understanding of the importance of vegetation and hydrogeologic controls on NO\(_3\)–N contamination of streams within the region.
Materials and Methods

Site Description

The study site is the 7250-ha GCEW in north-central Missouri (Fig. 1). The GCEW is near the southern terminus of glaciation in the Dissected Till Plains physiographic province, which includes significant portions of Kansas, Nebraska, Iowa, and Missouri. This watershed is typical of the 2.8 million ha Central Claypan region of Missouri and Illinois (NRCS, 1981). This region is typified by the presence of a claypan, a naturally occurring argillic soil horizon (clay content 450–650 g kg$^{-1}$) that typically occurs at a depth of 10 to 40 cm, depending on erosion exposure.

Quaternary stratigraphic relationships for north-central Missouri (Guccione, 1983; Sharp, 1984) were adapted for the watershed based on core samples collected during this study (Fig. 2). Two pre-Illinoian till units (200,000–750,000 yr; Rovey and Balco, 2011) separated by a paleosol were found at most locations. Erosion has removed the upper or lower till units at some locations. A paleosol was also present at the top of the glacial till which has been mantled by Illinoian (300,000–120,000 yr) and Wisconsinian (100,000–25,000 yr) loess. The area has since been subject to considerable weathering and stream dissection. The loess and till decrease in thickness from summit positions to lower landscape positions near the creek. The loess can be >3 m thick and overlies as much as 15 m of till. The till overlies Pennsylvanian age deposits of shale, limestone, and clay, and in some locations pre-glacial sediments include peat. Alluvial deposits are present near the creeks. Near the outlet of the GCEW, the loess, till, and Pennsylvanian deposits have been completely eroded and alluvium directly overlies the Mississippian age Burlington Limestone. The loess and glacial till have sufficient permeability and yield for domestic use (Blanchard and Donald, 1997) and are referred to here as the glacial aquifer.

The predominant soils including the Putnam (Mollic Albaurals), Mexico (Udollic Ochraqualfs), Adeo (Albauric Hapludalfs), and Leonard (Vertic Ochraqualfs) series developed on the Wisconsin loess (NRCS, 1995). The claypan formed in the loess by the accumulation of clay in the illuvial B horizon. The low permeability of the claypan restricts percolation and promotes the development of interflow and surface runoff (Sharp, 1984). Additional details on the glacial material and soil morphology of the GCEW landscape were provided by Sadler et al. (2015).

The USDA–ARS has maintained climate and surface hydrology instrumentation on the watershed since 1970. During a 43-yr period (1970–2012), the average annual precipitation has been 98.1 cm. Average annual stream flow exiting the watershed (1992–2010) is 28.7 cm, with surface runoff accounting for ~85% of the total stream flow. Groundwater recharge has previously been documented to occur primarily between the months of November and May (Blanchard and Donald, 1997). Other details of the GCEW ground and surface hydrology were provided by Sadler et al. (2015).

Three farm fields (Fig. 1 and 3) approximately 2.5 km apart from each other were selected in fall 1990 for assessing the impact of cropping systems on ground and surface water quality. The fields were chosen because they have soils typical of the Central Claypan region, were located at topographic divides, were suitable for ground and surface water monitoring, and had been managed similarly the decade before initiating this research. Farming practices and evaluation associated with the Management Systems Evaluation Area (MSEA) project began on the fields in 1991. Annual N fertilizer rates along with the crop rotation sequence for the three field cropping systems were typical for the region and are provided in Table 1. Tracking of N inputs and other crop management details ceased at the end of the 2001 growing season for Fields 2 and 3.

Well Drilling and Construction

Groundwater wells were drilled in the spring of 1991, before the implementation of the prescribed farming systems. Each field was instrumented with five well nests, with three to four wells in each nest (Fig. 3). At least three nests per field were located within the field boundary, with the additional nests positioned along the field edge. The wells within each nest were within close proximity of each other, with the total nest area encompassing about 25 m². No agrichemicals were applied to the well nest area. The 5.08-cm-diameter polyvinyl chloride (PVC) wells were installed through 16.5-cm-diameter hollow-stem augers. The borehole annulus was backfilled with sand to 30 cm above the well screen, followed by 2 m of bentonite and, from the top of the bentonite to the land surface, with a cement–bentonite grout. These initial wells had 1.2-m-long slotted PVC screens. The wells in each nest were screened at different depths to determine water quality differences with depth. The deepest well in each nest was

<table>
<thead>
<tr>
<th>Thickness Range (m)</th>
<th>Strata Mean Hydraulic Conductivity (m/sec)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wisconsin Loess</td>
<td>2-4</td>
</tr>
<tr>
<td>Claypan</td>
<td>8.7 x 10⁻²</td>
</tr>
<tr>
<td>Illinoian Loess</td>
<td>2.5</td>
</tr>
<tr>
<td>Upper Till Paleosol</td>
<td>5.2 x 10⁻⁵</td>
</tr>
<tr>
<td>Upper Glacial Till</td>
<td>2-7</td>
</tr>
<tr>
<td>Lower Till Paleosol</td>
<td>5.2 x 10⁻⁵</td>
</tr>
<tr>
<td>Lower Glacial Till</td>
<td>2-5</td>
</tr>
<tr>
<td>Pre-glacial sediments</td>
<td>5.3 x 10⁻⁴</td>
</tr>
<tr>
<td>Pennsylvania Shale</td>
<td>0.5-1</td>
</tr>
</tbody>
</table>

Fig. 2. A general representation of the stratigraphic relationships of loess and glacial till layers originally described for north-central Missouri (Guccione, 1983) but modified for the Goodwater Creek Watershed based on drill core samples collected during this study. Hydraulic conductivity was obtained from wells of this study as previously reported (Blanchard and Donald, 1997). Hydraulic tests of the upper and lower tills and the two paleosols were averaged for representing those respective layers.
Fig. 3. Field boundaries and elevation for the three fields intensively monitored for groundwater nitrates. Letters show well nest locations.

Table 1. Nitrogen input and cropping history of fields.

<table>
<thead>
<tr>
<th>Year</th>
<th>Applied N</th>
<th>Cropping history†</th>
<th>Cropping history§</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Field 1</td>
<td>Field 2</td>
<td>Field 3</td>
</tr>
<tr>
<td></td>
<td>kg ha⁻¹</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1991</td>
<td>190</td>
<td>101</td>
<td>118</td>
</tr>
<tr>
<td>1992</td>
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<td>2001</td>
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<td>144</td>
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<td>2002</td>
<td>0</td>
<td>NA‡</td>
<td>NA</td>
</tr>
<tr>
<td>2003</td>
<td>190</td>
<td>NA</td>
<td>NA</td>
</tr>
</tbody>
</table>

Assessment annual mean§: 96, 68, 81
Assessment total§: 1250, 749, 890

† Nitrogen fertilization occurred in late February or March for wheat and April or May for corn and sorghum.
‡ NA, not available.
§ Mean and total are 13 yr for Field 1 and 11 yr for Fields 2 and 3.
screened at the bottom of the till, except for the deepest wells in nests 3B, 3C, and 3E, which were screened in preglacial peat just below the till (Fig. 2). The screened intervals of the succeeding shallower wells in each nest were chosen to correspond with fractures, sand lenses, and color changes observed in continuous cores collected during well drilling. In 1992, 10 additional wells were installed, one at each nest where the water table was higher than the shallowest well installed in 1991. These 10 wells were in the loess and have 0.6-m slotted PVC screens. Thus, for the three fields, a total of 72 monitoring wells were installed. Elsewhere, 18 additional glacial aquifer wells at depths from 3 to 10 m and five alluvial wells at depths from 2 to 8 m were drilled in 1990 within the surrounding GCEW (Fig. 1). Two extra shallow wells were installed in 1992 along a riparian corridor bordering the west side of Field 3.

Core Collection and Analysis

A continuous core sample was collected during the drilling of the deepest well at each well nest. The samples were collected with a 1.6-m-long, 7.62-cm-diameter core barrel that had a removable acetate liner. The core barrel advanced ahead of the augers and was mounted on a bearing to prevent rotation of the core barrel. The core barrel was retrieved every 1.6 m, and the liner was removed, capped, numbered, and placed in a cooler. The core samples were brought to the laboratory at the end of the day and refrigerated.

In the laboratory, the core samples were divided horizontally according to soil horizons or visible textural or color changes. Where the core appeared uniform, it was divided into 30-cm increments. The core segments were divided longitudinally twice. One quarter of each sample was sent to the USDA Soil Tilth Laboratory (now the USDA National Laboratory for Agriculture and the Environment) for NH$_4$–N and NO$_3$–N analysis. Soil NH$_4$–N and NO$_3$–N were extracted with 2 mol L$^{-1}$ KCl (Keeney and Nelson, 1982). Nitrate was measured colorimetrically by reduction to NO$_3$–N using a Cd column and a continuous-flow autoanalyzer (Lachat Instruments). The detection limit for this method was 0.5 mg N kg$^{-1}$ dry soil. A second quarter of each sample was sent to the University of Missouri-Columbia Soil Characterization Laboratory for analysis following accepted methods (Soil Survey Laboratory Staff, 1996) including particle size (pipette method), cation exchange capacity and exchangeable cations (1 mol L$^{-1}$ NH$_4$OAc extractable at pH 7.0), saturated paste pH, and organic C content (dry combustion).

Well Tests, Sampling, and Analysis

Hydraulic conductivity (K) was measured on wells in 1992. For most wells, a falling-head slug test using a water-tight 2.54- by 1.52-cm PVC displacement cylinder provided reproducible results. For some wells, this procedure produced no appreciable response and a rising-head after-pumping test was used. Models suitable for unconfined aquifers were considered when calculating K, with additional details documented by Heidenreich and Blanchard (1993).

Wells were sampled quarterly from March 1991 to March 1996 and semiannually from March 1996 through 2004. Not all wells were sampled each quarter because some wells were dry at the scheduled time of sampling, but in at least one quarter each year every well was sampled. Sampling was discontinued at the end of 2001 for Field 2. Each well was equipped with a dedicated Waterra (Waterra Pumps, Ltd.) hand pump. The hand pump was composed of 1.59-cm (0.625-in) o.d. high-density polyethylene tubing with a Delrin (DuPont, Inc.) plastic foot valve. Three well volumes of water were purged from each well before sample collection. Samples were collected in 900-mL amber glass bottles, placed in a cooler, and transported to the laboratory at the end of the day.

Chemical Analyses

Water samples for NO$_3$–N analyses were filtered within 48 h of sampling through 0.45-μm nylon syringe filters to remove suspended sediment. From 1991 to 1993, samples were preserved before analysis by H$_2$SO$_4$ treatment to a pH of approximately 2 and refrigerated (Lerch et al., 2015). Analysis for NO$_3$–N was done within 28 d. Beginning in 1993, samples were filtered, refrigerated, and normally analyzed within 5 d of collection. If samples could not be analyzed within 5 d, they were frozen and analysis was done within 30 d of collection. The Cd reduction method was used to determine NO$_3$–N concentrations using different instrumentation over time as described by Lerch et al. (2015). The detection limit for the analyses was 0.05 to 0.10 mg L$^{-1}$ NO$_3$–N. Initially, separate analyses of NO$_3$–N and NO$_2$–N + NO$_3$–N were conducted. Nitrite proved to be insignificant relative to NO$_3$–N and the separate NO$_3$–N analyses were discontinued after 1992. We refer to (NO$_3$ + NO$_2$)–N results as NO$_3$–N.

Dissolved O$_2$ (DO) measurements were conducted using a Hydrolab H20G multiprobe (Hydrolab Corp.), which allows simultaneous in situ logging of pH, specific conductance, DO, and oxidation–reduction potential. After calibration, the probe was deployed in the well so that the sensors were at the level of the well screen. One well volume of water was purged from the well before datalogging. To maintain flow past the sensors, the well was pumped while continuously measuring the parameters. The test was considered complete when all parameters remained steady for 3 min.

Statistical Analyses

Descriptive statistics of NO$_3$–N concentrations were obtained by field and well nest, and were related to other well properties to explore potential meaningful relationships of management to hydrologic properties of the GCEW. Trends in NO$_3$–N concentration changes within each well during the 13-yr period (11 yr for Field 2) were statistically tested by comparing the first half of the assessment time with the second half using a Wilcoxon–Mann–Whitney ranked sums test (Helsel and Hirsch, 2002). Wells found to be different using this test ($α = 0.05$) were then further tested using simple linear regression with decimal year as the independent variable, adjusted for autocorrelation when the Durbin–Watson statistic was significant ($α = 0.05$). Slopes of the regressions were used to represent when significant changes had occurred ($F$ test $α = 0.05$; $Ho$: linear slope during assessment period = 0).

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Results and Discussion
Hydrogeology of the Study Site

Nitrate transport by groundwater cannot be evaluated without an understanding of the hydrogeology of the site. The hydrogeology of the study site and its influence on the transport of herbicides and herbicide metabolites was discussed in detail by Blanchard and Donald (1997). A brief summary is provided here to aid in the interpretation of NO\textsubscript{3}– transport processes. The glacial aquifer hydrology is complex; it behaves in most locations as a water table aquifer, but in other locations the paleosols or preglacial clays act as leaky confining units. Sharp (1984) noted that field-measured hydraulic conductivities of pre-Illinoian till in Missouri are two to four orders of magnitude higher than those determined on small laboratory samples. The hydraulic conductivity tests conducted on the study wells (Heidenreich and Blanchard, 1993) were consistent with that finding and are summarized in Fig. 2. The low topographic slope of the GCEW is reflected in the hydraulic gradients in the study area, which are in the range of 0.005 to 0.02. Transport of mobile herbicide metabolites through the aquifer was rapid, especially at Fields 2 and 3 (Blanchard and Donald, 1997). Rapid transport in this system is consistent with preferential flow through fractured till. Blanchard and Donald (1997) concluded that the upper till paleosol is hydrologically the limiting unit for transport of dissolved chemicals that have reached the water table.

Time Zero Nitrate

Initial groundwater samples were collected in spring and early summer of 1991 as the project farming systems were being implemented on the farm fields. Nitrate concentrations in these three field baseline samples were quite variable, ranging from undetectable to >24 mg L\textsuperscript{−1} (Fig. 4). The median and mean NO\textsubscript{3}–N concentrations were 5.0 and 7.0 mg L\textsuperscript{−1}, respectively, with 24% of the samples exceeding the MCL. From these baseline samples, the highest concentrations for each field occurred at the 6- to 11-m well depth (Fig. 5), with concentrations generally lower above and below. However, due to the wide variance in NO\textsubscript{3}–N concentration with depth, statistical significance of concentration as a function of well depth was weak for each field (best-fit quadratic or cubic model R\textsuperscript{2} values of 0.28, 0.19, and 0.36 for Fields 1–3, respectively).

All the wells in this study were <15 m deep and would have been classed as shallow wells in the national and regional surveys. The initial median and mean for surrounding GCEW well NO\textsubscript{3}–N concentrations were 1.6 and 5.2 mg L\textsuperscript{−1}, respectively, with 28% of the samples above the MCL. Taken as a whole, the NO\textsubscript{3}–N in wells from the three fields was statistically similar to that of the wells in the surrounding watershed (Fig. 4), although some wells from Field 3 were identified as outliers when field results were combined. On a field-by-field basis, NO\textsubscript{3}–N results from Field 3 were significantly different from Fields 1 and 2. A plot of NO\textsubscript{3}–N in the initial well samples vs. NO\textsubscript{3}–N in the corresponding core samples (Fig. 6) shows that Fields 1 and 2 were similar overall, but many of the Field 3 well and core samples were higher in NO\textsubscript{3}–N than those of Fields 1 and 2. The well samples represent water from fractures, while the core samples represent an estimate of the matrix NO\textsubscript{3}–N.

Because these three fields had been managed in a similar manner in the 10 yr before this research began, no major differences in groundwater quality had been anticipated. Field history records and interviews with landowners and farm managers were used to create a timeline of management history (i.e., crops, rotations, N fertilizer management, and manure management) of the three fields from 1930 to 1990 (Kitchen et al., 1997). From 1930 to 1980, Field 3 had apparently received a greater total N application than the other two fields. Corn was grown more often in the 1970s on this field, and between 1930 and 1981, manure was spread from nearby (but hydrologically separate) livestock feeding areas. Livestock animals were also occasionally overwintered on Field 3.

Impact of Cropping Systems on Nitrate

As noted, a primary goal of the Missouri MSEA was to assess the water quality impacts of typical cropping systems within the GCEW. For the 6 yr before this study (1985–1990), N fertilizer input was accounted for from farmer records and the average annual N input was 34, 67, and 45 kg ha\textsuperscript{−1} for Fields 1, 2, and 3, respectively. Crop rotations and associated N fertilizer management for the farming systems of this study are presented.

Fig. 4. Groundwater NO\textsubscript{3}–N concentrations shown for initial (1991 all fields) and final (2004 for Fields 1 and 3, 2001 for Field 2) samplings. Results exclude shallow wells drilled in 1992. Values from the field wells are contrasted with values obtained from 18 watershed wells.
Thus with the initiation of the research, N inputs on Field 2 were similar to pre-investigation years and Fields 1 and 3 represented increased N fertilization.

Nitrate-N concentrations of the initial field and watershed samples are summarized and compared with the final samples taken 11 or 13 yr later (Fig. 4). The annual average NO$_3$–N concentration is also summarized by field during the 13 yr (Table 2). Combined across fields, the final median and mean NO$_3$–N concentrations were 5.2 and 6.1 mg L$^{-1}$, respectively. For the watershed, final median and mean NO$_3$–N concentrations were 4.0 and 6.7 mg L$^{-1}$, respectively. While the final mean values are slightly lower than the initial samples for the fields and slightly higher for the watershed, at this aggregate level no significant difference using the Wilcoxon rank sum test was found between the beginning and the end samplings. The 90th percentile of NO$_3$–N concentrations in the watershed wells has increased dramatically due to three wells that have increased by 8 to 10 mg L$^{-1}$. The N input in the vicinity of these wells was unknown, although we suspect that irrigation management of a nearby pivot system (not common in the watershed) was a factor.

Nitrate-N concentration by field, nest, and each individual well are shown for the period of this assessment (Fig. 7). On each field, some wells appear to have decreased with time, some increased, and some have remained nearly invariant in NO$_3$–N. For many wells, NO$_3$–N changes have been small and gradual, but a few wells have shown significant temporal fluctuations (discussed below). Seasonal or crop-rotational trends in NO$_3$–N concentration were not present or were not obvious.

Nitrate concentration during the 13-yr assessment period was statistically evaluated to determine where changes have occurred (Fig. 8). Average annual NO$_3$–N change rates are shown relative to the initial well NO$_3$–N concentrations. Some wells from all three fields statistically increased in NO$_3$–N concentration (five, nine, and two wells for Fields 1, 2, and 3, respectively), although no wells showed an average annual increase of >0.35 mg L$^{-1}$ yr$^{-1}$. An initial concentration <12 mg L$^{-1}$ seemed to have no bearing on whether NO$_3$–N levels increased. Wells showing significant increases averaged only 0.16, 0.17, and 0.15 mg L$^{-1}$ yr$^{-1}$ for Fields 1 to 3, respectively. Likewise, all three fields had some wells that significantly decreased in NO$_3$–N (three, nine, and nine wells for Fields 1, 2, and 3, respectively). By far, decreases were most prominent from Field 3, with the average of wells showing decreases being 0.70 mg L$^{-1}$ yr$^{-1}$ compared with 0.44 mg L$^{-1}$ yr$^{-1}$ for Field 1 and 0.23 mg L$^{-1}$ yr$^{-1}$ for Field 2. In some cases, all wells within a nest changed similarly. For example, all wells in Nest 2B significantly increased and all wells in Nests 2C and 2D decreased. However, one third of field well nests had at least one well that increased and one that decreased, suggesting multiple processes at work controlling NO$_3$–N transport and storage within these fields.

The decrease in NO$_3$–N concentrations from Field 3 was especially notable in the up-gradient well nests (3A and 3B), which had the highest concentrations in 1991. This decrease reflects the influence of both the pre-1990 management and the management during this assessment period. Judging by the long-term impact of management shown by the pre-study samples at Field 3, it was difficult to make definitive statements regarding the impact of the prescribed cropping systems even after the

<table>
<thead>
<tr>
<th>Year</th>
<th>Mean NO$_3$–N (mg L$^{-1}$)</th>
</tr>
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<tbody>
<tr>
<td>1991</td>
<td>4.2</td>
</tr>
<tr>
<td>1992</td>
<td>4.5</td>
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<tr>
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<td>5.1</td>
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<tr>
<td>2004†</td>
<td>4.8</td>
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</tbody>
</table>

† First quarter only.
Fig. 7. Quarterly groundwater NO$_3$–N concentrations shown by field, nest, and individual well during this investigation period. Note that well depth in meters is provided on the nest legend.
decade plus of monitoring represented by this investigation. Nevertheless, some statements can be made based on the data.

Field 1, which had the highest N input, showed a slight upward trend in mean NO$_3$–N concentrations (Table 2). However, averaging among individual wells as shown in Fig. 8 (increasing, decreasing, and no change), the rate of change has been minor (~0.003 mg L$^{-1}$ yr$^{-1}$). This slight decrease suggests that minimal NO$_3$–N is transported through the loess and upper till paleosol, making it extremely difficult to assess the impact of subtle differences in cropping system N fertilizer inputs. This is supported by measurements that show that of the three fields, the groundwater system at Field 1 is the slowest hydrologically as a result of a lower hydraulic gradient and the influence of a thicker and/or less permeable upper till paleosol (discussed below). An additional indication that the Field 1 farming system had not yet affected the majority of Field 1 wells is the fact that fewer herbicides and herbicide metabolites have been detected at Field 1 than at Fields 2 and 3, even though Field 1 had the highest herbicide application rates (Blanchard and Donald, 1997). More recent results showed that atrazine [6-chloro-N-ethyl-N”-(1-methylethyl)-1,3,5-triazine-2,4-diamine] and metabolite concentrations at Field 1 have increased with time, but the concentrations were still very low because of the low hydraulic conductivity of the claypan (Pagan, 2009).

Field 2, which is most similar to pre-study N management, showed a small decrease in the mean NO$_3$–N values. Averaging across all wells, the rate of decrease was only 0.03 mg NO$_3$–N L$^{-1}$ yr$^{-1}$.

Field 3 showed a major decrease in NO$_3$–N concentrations, especially in the up-gradient well nests (3A and 3B in Fig. 7). The decrease for all wells averaged 0.31 mg L$^{-1}$ yr$^{-1}$. This decrease reflects both the influence of excessive N loading with concurrent N fertilizer and manure applications before 1980 (Kitchen et al., 1997) and the modest N application since then (average 68 kg N yr$^{-1}$ for 1985–2001). A quantitative record of N applications before 1985 is unavailable, and thus the impact of concurrent N fertilizer and animal manures before 1980 on aquifer loading is uncertain. If available, such records would allow quantification of the lag effect of inputs on groundwater NO$_3$–N for this hydrologic setting. If the lag times were no more than a few years, we could conservatively estimate, using the regression results for wells decreasing in NO$_3$–N concentrations, that these same wells were 5 to 15 mg L$^{-1}$ higher in 1980 than they were for the initial sampling in 1991.

Hydrogeologic Controls and Impact on Nitrates

Differences among the fields were mainly attributed to the variable hydrogeologic controls that impact NO$_3$–N transport in the glacial aquifer. These controls vary in depth from the surface to the preglaclial deposits and include both physical and biochemical controls (Liao et al., 2012). While the low hydraulic conductivity of the claypan significantly limits recharge, site-specific preferential flow through the subsoil and till material can dominate over matrix flow, as has been well described previously for this research site (Blevins et al., 1996; Blanchard and Donald, 1997; Kitchen et al., 1998; Wilkison and Blevins, 1999; Pagan, 2009). For this investigation, other relationships were examined to try to better understand hydraulic control within the till. Hydraulic conductivity ($K$) as a function of well depth showed no meaningful relationship because both shallow and deeper wells exhibited low and high $K$ (Fig. 9). Hydraulic conductivity trended lower with higher clay content in the till of the fields, but this relationship was weak ($R^2 = 0.21$, 0.19, and 0.07 for Fields 1–3, respectively; Fig. 10). When we examined the initial sampled NO$_3$–N concentration (Fig. 11) or variation in

![Fig. 9. Hydraulic conductivity ($K$) of wells in this investigation was not a function of well depth.](image9)

![Fig. 10. Hydraulic conductivity ($K$) of wells in this investigation was weakly related to total clay in the matrix.](image10)

![Fig. 8. Trends in NO$_3$–N concentration during the 13-yr assessment period (11 yr for Field 2) for the first- and third-quarter samples. Wells with significant change are shown as points off the zero-slope line.](image8)
The high pre-study NO$_3$–N water in the fracture and the immobile water of the matrix were in the 2.5 to 8 mg L$^{-1}$ range, which indicated that NO$_3$–N also declined. Declining NO$_3$–N concentrations from 1991 to 1993. During this time period, Well 3B4 showed a dramatic decline in NO$_3$–N concentration of approximately 10 mg L$^{-1}$ (Fig. 7). The drill core samples from the depth range of 3B2 and 3B4 were some of the highest of all the wells, with NO$_3$–N in the 2.5 to 3 mg kg$^{-1}$ range. Therefore, long-term storage of NO$_3$–N had occurred in these parts of the aquifer.

To better understand the hydrogeologic processes occurring in the aquifer, sampling for NO$_3$–N and measurements of hydraulic head were conducted weekly for these three wells from March 1994 to March 1995 (Fig. 12). Vertical hydraulic gradients were due to the lower permeability of the lower till paleosol between 3B4 and 3B2 and by about 60 cm of preglacial clay between 3B2 and 3B1. Despite these zones of lower permeability, all wells in this nest had detections of herbicide metabolites (Blanchard and Donald, 1997), thus demonstrating that hydraulic connectivity exists from the land surface to the base of the aquifer. The NO$_3$–N concentration in 3B1 (the peat well) was highly dependent on the flux of NO$_3$–N from above (3B2). When the head in 3B2 was higher than in 3B1, the rate of NO$_3$–N transport into the till apparently exceeded the rate of denitrification within the peat. When the head difference between 3B2 and 3B1 declined, the 3B1 NO$_3$–N concentration declined. Between August and November 1994, the head in 3B1 was higher than in 3B2. Therefore the only NO$_3$–N transport between the till and the peat was by diffusion and the 3B1 NO$_3$–N became undetectable. During this time period, NO$_3$–N in 3B2 declined from around 13 to 8 mg L$^{-1}$. This decline can be explained as a combination of advection of zero-NO$_3$–N water from the peat into the till and continued diffusion of NO$_3$–N from the till into the peat. From March to July 1994 and December 1994 to March 1995, the NO$_3$–N concentration in 3B2 had only relatively minor fluctuations, similar to 3B4 for the entire year. These relatively minor fluctuations were probably a combination of complicated variations in advection and diffusion between the fractures and the matrix. Quarterly samples from wells located in the peat down-gradient from 3B1 had undetectable concentrations of NO$_3$–N in the water but little or undetectable NO$_3$–N in the corresponding core samples. These wells were located at two summit positions within Field 3 (Nests 3A and 3B in Fig. 3) and were representative of the recharge zone of the aquifer. There were some wells (Fig. 6) that had significant concentrations of NO$_3$–N in the peat. It is unknown if insufficient time has passed to allow large amounts of NO$_3$–N to diffuse into the peat or if these were locations where denitrifying conditions existed within the peat. This fate and transport description is consistent with all known data from the site.

A dramatic example of the hydrogeochemical complexity of NO$_3$–N transport in the till and preglacial deposits was found at Nest 3B, which is located at a summit position within Field 3. Well 3B1 (14.0-m depth) is screened in preglacial peat below the till, 3B2 (11.7-m depth) is screened near the base of the lower till, and 3B4 (8.1-m depth) is screened in the upper till. We hypothesized that this high organic C zone would be conducive to denitrification (Puckett, 2004). Major fluctuations (>8 mg L$^{-1}$) were noted in 3B1 and 3B2 during quarterly sampling in 1991 and 1993. During this time period, Well 3B4 showed a dramatic decline in NO$_3$–N concentration of approximately 10 mg L$^{-1}$ (Fig. 7). The drill core samples from the depth range of 3B2 and 3B4 were some of the highest of all the wells, with NO$_3$–N in the 2.5 to 3 mg kg$^{-1}$ range. Therefore, long-term storage of NO$_3$–N had occurred in these parts of the aquifer.

Fig. 11. Initial NO$_3$–N concentrations as a function of hydraulic conductivity (K) of wells.
Thus, the interaction of these variations in advective transport with the chemical processes of diffusion and denitrification was so complex that a single sample in time could never represent the NO3–N contamination of the portion of the aquifer sampled by Wells 3B1 and 3B2.

Riparian Zone Influence on Nitrates

Glacial aquifer water flow has been well characterized for this study area, showing that the aquifer acts as a water table aquifer, that flow within the aquifer is toward the creeks, and that as the water table drops, the creek completely dries and there is no flow (Hesemann, 1979; Blanchard and Donald, 1997). The glacial aquifer within the watershed is not currently used as a significant source of drinking water. However, the base flow of Goodwater Creek, like many other streams within the Mississippi River basin, is due to groundwater discharge. Base flow represents only 15% of the total stream flow of Goodwater Creek. However, that base flow would represent a significant mass of N if it had the average NO3–N concentration of the glacial aquifer wells (~7 mg L−1). In actuality, base-flow NO3–N concentrations in the creek averaged only 0.59 mg L−1 from 1991 to 2004 (Baffaut et al., 2009). There are several plausible reasons for the difference in concentration. Some alluvial wells show seasonal changes in NO3–N, with concentrations in March and June being less than in September and December (Fig. 13). Nitrate values from some wells changed by >5 mg L−1 in two successive quarters. This was consistent with the process of N uptake by riparian vegetation, which would probably be highly effective at NO3–N uptake based on riparian width, vegetation type, and flow pathway (Mayer et al., 2007). However, wells slightly deeper and more associated with groundwater flow to stream base flow had greater evidence of denitrification. One well (3G1) had no detectable NO3–N for most of the monitoring period (Fig. 13). This same well was known to give off a distinct odor of H2S, indicating that the system was more reducing than necessary for denitrification.

While in-stream or riparian vegetation seemed to be responsible for the removal of some NO3–N in the riparian corridor, denitrification was probably more important in changing concentration values as water moved into the base flow of the stream. Average base-flow NO3–N in Goodwater Creek was ~2 mg L−1 in January when vegetative utilization presumably was at a minimum, while it was <1 mg L−1 in August when vegetative usage would be high. This, along with the difference in NO3–N concentration between upland glacial till and base flow, suggested that the primary mode of NO3–N loss was by denitrification within either the riparian zone or the streamed, and that uptake by riparian or in-stream vegetation was of secondary importance in this setting. Others have reported the magnitude of denitrification in riparian areas to be about 4 to 20 times higher than vadose-zone denitrification rates found upslope (Liao et al., 2012). Our findings of multiple processes causing changes in NO3–N along a flow path through riparian areas and into streams are consistent with summarized studies (Puckett, 2004).

Tree Line Influence on Nitrates

In a non-riparian setting, deep-rooted trees within or on the edges of fields may also alter shallow aquifer NO3–N concentrations. An example was Nest 1B, located 20 m north of an old fence row that today has overgrown with native shrubs and trees 15 to 20 m in height. Because the groundwater flow direction in this field is north to northwest (Pagan, 2009), these wells are on the “downstream” side of this tree line. Nitrate-N concentrations from wells in this nest have consistently been some of the lowest for this field, averaging 1.5 mg L−1 compared with 6.9 mg L−1 for the nest “upstream” from the tree line (Fig. 7, 1A). With a low hydraulic gradient in this field, shallow groundwater
flow through the tree line is slow, and this apparently facilitated significant plant uptake of N. The tree line is relatively young. There was little visible evidence of trees in this fence row in a 1939 aerial photo of the field. Images taken in the late 1950s indicate small trees growing along the fence row, although a 1982 aerial image shows many of the trees removed. Yet within a decade of that photo, and at the time the groundwater wells were installed on this field (1991), trees and large shrubs had been allowed to return and remained during the time of groundwater monitoring. During the study, the tree-line width was approximately 10 to 12 m, and growth into the field was controlled with tillage and occasional root pruning.

Conclusions

The study provided a long-term investigation of the impact of farming systems on groundwater quality. The use of within-field, properly constructed monitoring wells eliminates many of the complicating factors that have limited the interpretability of water quality surveys. A number of important key points can be made from this study.

There was no clear evidence that the farming practices used during this investigation contributed to increased nonpoint-source NO₃⁻N groundwater contamination; however, interpretation was complicated by the long-term impact of past management, the capacity of the till to buffer changes in NO₃⁻N, the hydrogeologic variability found among well sites, and the activity of biological processes. It was apparent that for one field, significant contamination occurred due to prior farming practices in which excess N loading from concurrent applications of manure and fertilizer contributed to high NO₃⁻N in the groundwater. In this case, the long-term impact has lasted more than 20 yr and current practices are resulting in decreased contamination.

The majority of groundwater recharge for this setting is from November to May. Therefore, minimizing the NO₃⁻N in the recharge water requires minimizing soil NO₃⁻N during this recharge period. Applying fertilizer N in accordance with best management practices is considered essential for the protection of groundwater quality.

Hydrogeologic processes controlling the transport of NO₃⁻N concentrations in groundwater resulted from a combination of diffusion from the aquifer matrix and site-specific preferential flow. Variation in the properties of the glacial aquifer (such as the slope and thickness of the loess, tills, and paleosols) had a profound impact on NO₃⁻N transport. The dual-porosity system of the till provides the opportunity for rapid solute transport in the fractures, but matrix diffusion can buffer the solute concentrations and thus retard transport. Changes in till NO₃⁻N concentrations with time were generally minor. However, concentrations were temporal dynamic where solute concentrations and thus retard transport. Changes in NO₃⁻N, the hydrogeologic variability found among well sites, and the activity of biological processes. It was apparent that for one field, significant contamination occurred due to prior farming practices in which excess N loading from concurrent applications of manure and fertilizer contributed to high NO₃⁻N in the groundwater. In this case, the long-term impact has lasted more than 20 yr and current practices are resulting in decreased contamination.

The results from this investigation within the GCEW represent the broader Salt River Basin (6417 km² or 2478 mi²) and establish an improved understanding of groundwater hydrology for the Central Mississippi River Basin (CMRB) site of the USDA-ARS Long-Term Agroecosystem Research (LTAR) network. As such, this investigation provides a better understanding of the interactions and complexities that exist when combining the effects of spatially heterogeneous hydrogeology, groundwater geochemistry, and crop management. The treatment imposed at the initiation of this work (e.g., cropping system) in the presence of this complexity yielded few definitive answers. In the end, the data provoked inquiry and additional sampling and measurements that resulted in improved understanding of the hydrogeology and the factors influencing spatial and temporal variation in NO₃⁻N contamination for this setting.

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