Mass Balance of Nitrogen and Phosphorus in an Agricultural Watershed: The Shallow Groundwater Component

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Edward Mehnert, William S. Dey, Hue-Hwa Hwang & Donald A. Keefer
Illinois State Geological Survey

Thomas R. Holm
Illinois State Water Survey

Thomas M. Johnson, Will C. Beaumont & Matthew C.F. Wander
University of Illinois at Urbana-Champaign
Department of Geology

Robert A. Sanford, Jennifer M. McDonald & Shawn M. Shiffer
University of Illinois at Urbana-Champaign
Department of Civil and Environmental Engineering

ABSTRACT

Mass balances for nitrogen (N) and phosphorus (P) were conducted in a tile-drained, agricultural watershed by a multidisciplinary team. While cooperating researchers studied N and P fluxes for crops, soils, surface water, and atmospheric deposition, our efforts focused on the flux of N and P through shallow groundwater. The overall mass balance was conducted under the Water Quality Strategic Research Initiative, which was sponsored by the Illinois Council on Food and Agricultural Research (C-FAR).

This mass balance was conducted in the Big Ditch watershed of northern Champaign County. In this watershed, the shallow geologic materials were deposited during the Wisconsin Episode and modern times and consist of thin loess overlying clayey glacial diamictons interbedded with sorted sediments (sand and silt). Monitoring wells were installed to monitor the water table at 11 sites and to monitor the deeper sand-and-gravel layers at 9 of these sites. An analytical, steady state, groundwater flow model was developed and calibrated using water levels and stream flow data.

Groundwater samples were collected from the 20 monitoring wells on 28 occasions from May 2000 through June 2003. Overall, N concentrations in the groundwater tended to be low. Only 6 of the 20 wells (5 shallow & 1 deep) had total N concentrations that consistently exceeded 1 mg/L. Nitrate comprised almost 100% of the N in the two wells with the highest total N concentrations. These two wells had median total N of 8 and 18 mg/L. In the other 18 wells, organic N generally comprised 10 to 40% of the total N. Nitrate was rarely detected in the deep wells, while ammonia was rarely detected in the shallow wells. Phosphorus was rarely detected in groundwater samples. Thus, the watershed soils appear to be a sink for P, binding it and preventing its transport into shallow groundwater.

Denitrification in the subsurface appears to be a significant N sink. Stable isotope ratios of O and N in nitrate from shallow groundwater samples revealed enrichments in the heavy isotopes, relative to the initial values determined from tile drain samples. These enrichments suggested that denitrification in shallow groundwater was generally greater than 50% complete, but varied from 0% to 98% complete across the watershed. Denitrifying bacteria varied in abundance by a factor of 10 in water bearing layers throughout the watershed, but were considered sufficiently abundant to denitrify a significant amount of N. Denitrification rates were dependent on the availability of biodegradable organic carbon and averaged 0.82 mg N/kg-d with an amendment of 0.2 mM carbon as acetate (2.4 mg/L as C).

To estimate the dynamics of nitrogen in the shallow groundwater of the watershed, we adopted a simple approach. We assumed that N concentrations in very shallow groundwater (i.e., soil water within and below the root zone) are generally high, as shown by the N concentrations in tile drainage and soil pore water. These high N concentrations entering shallow groundwater are reduced to zero (by denitrification) by the end of the flow path, where groundwater discharges to the stream. At base flow, when groundwater comprises all water in the stream, N concentrations in the stream are essentially zero. During base flow conditions, nitrate-N concentrations in Big Ditch were <0.06 mg/L and the stream flow varied from year to year (from 0.12 to 7 cfs). To estimate steady-state groundwater recharge, stream flow was assumed to vary from 0.86 to 2.8 cfs. Groundwater recharge was determined by steady-state groundwater flow modeling. Using this approach, the estimates of mass of N denitrified were equivalent to 0.3 to 6.4% of the N applied, with the best estimates being

2.3% of N applied for water year 2000, 1.2% of N applied for water year 2001, and 3.1% of N applied for water year 2002. Our estimates of N denitrified in shallow groundwater also are equivalent to 9% to 27% of the estimated N exported from the watershed via surface water. However, these estimates should be considered minimums because our approach does not account for transient flow. Additional N transported by transient groundwater flow, such as groundwater flow following precipitation events, probably remains in the subsurface long enough to be at least partially, and possibly completely, denitrified.

In this report, we have summarized the groundwater research conducted for the mass balances of the nutrients, N and P. In a future report, we will help develop a comprehensive mass balance for N and P and will assist the other researchers compile a report regarding the flux of nutrients through the watershed.

1. INTRODUCTION

Nitrogen (N) is a common contaminant in the surface water and groundwater of Illinois and the United States (Nolan et al., 1997). With the emergence of hypoxia as a national concern (Burkart and James, 1999; Goolsby and Battaglin, 2000), the fate and transport of nitrogen in the environment has received considerable interest from researchers, regulators, and the public. To address this concern, the fate and transport of nitrogen in an agricultural watershed was investigated by a multidisciplinary team. The mass balance of nitrogen in this agricultural watershed (Figure 1.1) included estimates of N input to and N exported from the watershed. Nitrogen inputs included additions from fertilizer, precipitation, dry deposition, and soybeans. Release of N from soil organic-N (ammonification in Figure 1.1) was not considered, although it may be a significant source of dissolved N. Estimates of N exported from the watershed included N removed with crops or livestock, via surface water, and via groundwater. A similar mass balance was developed for another nutrient, phosphorus (P).

The mass balances for N and P were conducted in the Big Ditch watershed, which covers approximately 38 square miles in northern Champaign County (Figure 1.2). The predominant land use is agriculture, with some commercial and industrial land use in the eastern portion of the watershed (west of Rantoul). The major crops are corn, soybeans, and seed corn. Instruments were installed throughout the watershed to monitor precipitation, tile flow, stream flow, and groundwater flow.
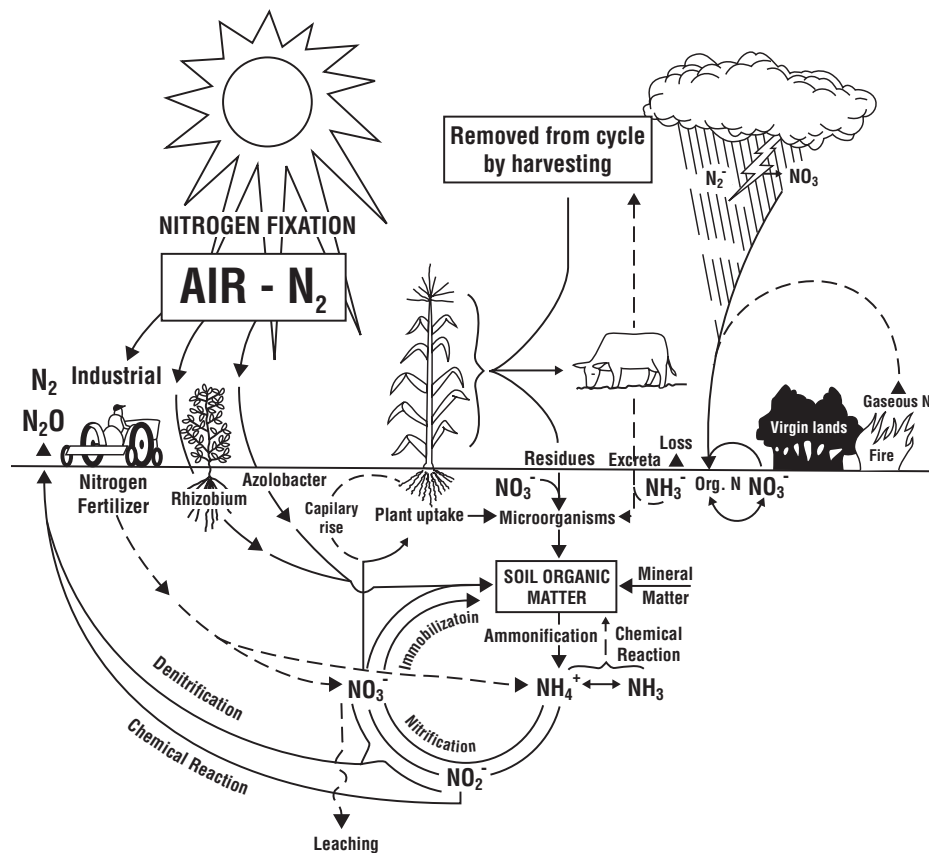

Figure 1.1 N cycle for an agricultural setting (from Brown and Johnson, 1996, Ohio State University Extension)
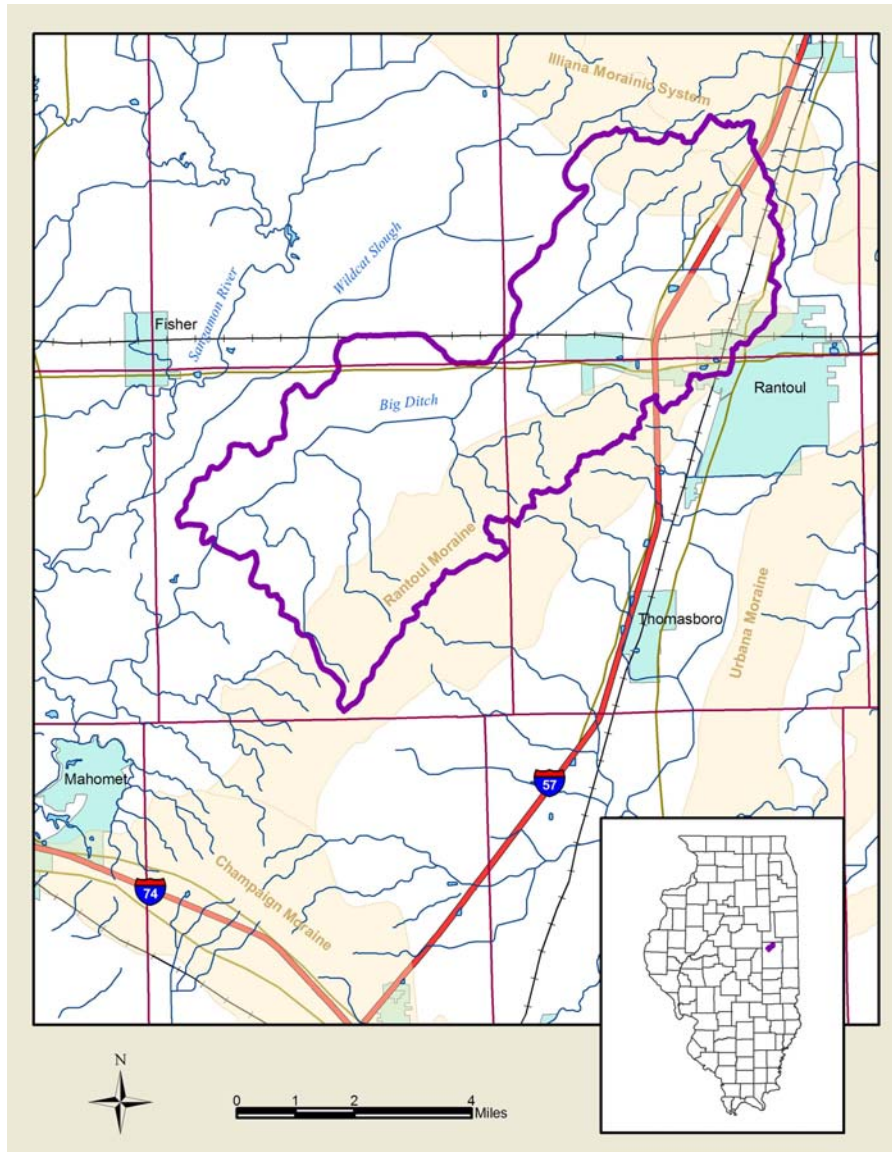
Figure 1.2 Map showing the study area and its cultural, hydrologic, and selected geologic features

Our investigations included field sampling and laboratory studies to estimate the flux of nitrogen and phosphorus in the shallow (<50 feet below ground surface) groundwater of the watershed. In the subsurface, N and P are transported by groundwater. Some groundwater discharges to local streams such as Big Ditch, and some groundwater recharges deeper aquifers. While in the subsurface, nitrogen can transform amongst various forms (nitrate, nitrite, organic N, & ammonia) depending upon local geochemical conditions (Korom, 1992). In addition, naturally occurring microbes transform nitrate into nitrogen gas, thus removing N from the liquid phase. This process, denitrification, may be an important sink for N in the Big Ditch watershed. Because many researchers consider nitrogen loss via denitrification to be among the most uncertain of all estimates in the N mass balance, denitrification rates were quantified by microbial and isotopic methods. In the subsurface, phosphorus generally adsorbs to soil particles and is removed from groundwater (NRC, 1993). Thus, soils and geologic materials are possible sinks for P.

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1.1 Objectives
Within the context of developing comprehensive mass balances for N and P in an agricultural watershed, we provided data regarding the subsurface portions for these mass balances. The objectives of this project were three-fold:
> 1) To assess the mass flux of nutrients (N and P) in the shallow groundwater of an agricultural watershed.
> 2) To assess denitrification in shallow groundwater by isotopic methods.
> 3) To assess denitrification in shallow groundwater by microbial methods.

This report describes the methods used to collect and analyze the data for the subsurface portion of these mass balances. This report was prepared prior to the completion of the report for the comprehensive mass balances; thus, some of the interpretations may be revised based on information gained from other components of the mass balance.

1.2 Background
In this section, the literature concerning the fate and transport of nitrogen and phosphorus in shallow groundwater is briefly summarized.

1.2.1 Background-- Nitrate in Shallow Groundwater
Nitrate is considered the most common and widespread contaminant in groundwater in the U.S. (Freeze and Cherry, 1979; Hallberg and Keeney, 1993) and around the world (Spalding and Exner, 1993). In the U.S., the highest nitrate concentrations are found in domestic wells of agricultural areas, specifically in areas of intensive row crop production (Mueller and Helsel, 1996). The nitrate concentrations in the groundwater and surface water of U.S. agricultural areas are 3 to 60 times higher than those in forested or grassland areas (NRC, 1993). In the U.S., based on samples collected by USGS scientists from 1992 to 1995, nitrate was detected (concentrations ≥ 0.2 mg/L) in 71%, organic nitrogen in 5.3%, and ammonia in 5.1% of all groundwater samples, while nitrite was not detected at concentrations above 0.2 mg/L (Nolan and Stoner, 2000). Factors that generally increase nitrate concentration in groundwater include well-drained soils, fractured bedrock, and irrigation, while factors that mitigate nitrate concentrations in groundwater include poorly drained soils, greater depth to groundwater, artificial drainage systems, intervening layers of unfractured bedrock, low rate of groundwater recharge, and anaerobic conditions in aquifers (Nolan and Stoner, 2000). These factors essentially confirm those described previously by Spalding and Exner (1993).

Nationally, 12% of domestic wells exceed the drinking water standard of 10 mg/L for nitrate-nitrogen (Mueller and Helsel, 1996). This percentage is similar to domestic wells in Illinois, where nitrate-nitrogen was ≥ 10 mg/L in 10.5% of rural domestic wells (Goetsch et al., 1992). In rural Illinois, wells completed in shallow aquifers (<50 feet) are more likely to be contaminated with nitrate than wells in deeper aquifers (>50 feet) (Goetsch et al., 1992; Mehnert et al., 1995).

The fate and transport of N in the subsurface are highly variable due to the natural variability of the hydraulic and geochemical properties of the geologic materials. Key hydraulic properties include the length of flow path and hydraulic conductivity, which can easily vary over 7 orders of magnitude within tens of feet in the subsurface. These changes in properties can result in widely varying travel times—from hours to transport water from the soil surface to water table (Landon et al., 2000) to

decades for transport through the longer flow lines of a watershed (Böhlke and Denver, 1995; USGS, 1999).

Nitrogen occurs in natural aquatic systems mainly as the inorganic species ammonia (NH_4-N), nitrite (NO_2-N), and nitrate (NO_3-N) and "organic nitrogen" (Org-N), which includes amino acids, peptides, proteins, and amino sugars (Mulvaney et al., 2001). The various N species are interconverted by an array of microbial processes in the subsurface (Stumm and Morgan, 1996). Therefore, although almost all nitrogen fertilizer applied in the Big Ditch watershed is in the form of anhydrous ammonia, one or more N species may be found in groundwater in the watershed. Nitrate is very soluble and mobile in soil and aquifers. Ammonium ion (NH_4^+) may be sorbed to clay minerals by cation exchange (Drever, 1982). The N species in groundwater depend on many factors, including the pH, temperature, age of the water, microbial populations, minerals in the soil and aquifer, and the concentrations of dissolved oxygen and organic matter. Therefore, an estimate of N flux must consider all N species.

Denitrification is a microbially mediated process, where most denitrifying bacteria are facultative anaerobes (Firestone, 1982). When oxygen becomes limited, these bacteria begin to use nitrate as an electron acceptor. The most common electron donor is organic carbon, although sulfur and ferrous iron can also serve as electron donors (Tesoriero et al., 2000). Variations in geochemical properties, such as the variation in the availability of organic matter and dissolved oxygen, can control the denitrification rate (Korom, 1992). Relative position within a watershed, underlain by an unconfined sand and gravel aquifer, was shown to control denitrification (Tesoriero et al., 2000). Higher denitrification rates were observed adjacent to a stream, while lower rates were observed in shallow flow paths in upland areas. Martin et al. (2004) noted similar patterns for denitrification in an agricultural watershed in France. For a tile-drained agricultural watershed in Iowa, denitrification varied by soil type and was greatest in unoxidized loess (Cambardella et al., 1999).

Determination of *in situ* denitrification rates was identified as a research need about 10 years ago (Korom, 1992). Since that time, a great deal of research has focused on the fate and transport of N in the environment (e.g., Delgado, 2002). Mass balances of N have been completed at the national, regional, and farm scales (NRC, 1993). Some of these mass balances have included groundwater (e.g., Cambardella et al., 1999; Lampert and Brunner, 1999; Puckett et al., 1999) and others have ignored groundwater or assumed it to be insignificant (e.g., David and Gentry, 2000; Tavener and Iqbal, 2003). Ignoring groundwater could be a major mistake, because nitrate leaching is a major avenue for N loss in humid regions (Meisinger and Delgado, 2002) and in some hydrogeologic settings most nitrate in the surface water comes from groundwater (NRC, 1993). Rosenberry (2003) noted that groundwater has historically been ignored in watershed studies, but argued that it should be included in similar studies today.

Finally, altering the nutrient inputs to a watershed may not have an immediate effect on the water quality within the watershed. For example, nitrate discharge to aquatic systems may be delayed for decades due to the transitory retention of excess nitrogen in soil water, soil organic matter, groundwater, and riparian vegetation (Haag and Kaupenjohann, 2001). Tomer and Burkart (2003) demonstrated this delay for two small watersheds in Iowa, where the effects of high nitrate fertilization were observable in the shallow groundwater 30 years after implementation.

1.2.2 Background-- Phosphorus in Shallow Groundwater

In contrast to N, phosphorus (P) is relatively immobile in the subsurface. The orthophosphate ion (PO_4^{3-}) readily sorbs to clay and oxide minerals. Therefore, dissolved P is expected to be found only where the sorption capacity is nearly saturated. In most regions of the U.S, phosphorus leaching to groundwater is not a problem (NRC, 1993). In a recent study of U.S. groundwater quality, the median orthophosphate concentration in areas of agricultural land use was 0.01 mg/L (Nolan and Stoner, 2000). Limited phosphorus solubility and mobility in water were cited by Nolan and Stoner (2000) to explain this low orthophosphate concentration. Recent research has shown that phosphorus leaching may be observed in soils with sandy texture, with high organic matter, or with macropores (Lemunyon and Daniel, 2002).

2. GEOLOGIC DESCRIPTION OF THE WATERSHED

In this chapter, the geology of the watershed will be described. Because shallow groundwater is most important for this research, this description will emphasize the geologic materials above the bedrock, i.e., the Quaternary materials. The methods used to collect and describe geologic materials also will be discussed.

2.1 Background

This field research was conducted in the Big Ditch watershed, which drains into the Sangamon River. The watershed is located in northern Champaign County, Illinois, and covers approximately 38 square miles. Land use in this watershed is predominantly agricultural. The major crops include corn, soybeans, and seed corn. The watershed also includes some commercial and urban land uses on the west side of Rantoul.

2.2 Methods

The methods used to define the geology, hydrogeology, and hydrology of the watershed are described.

2.2.1 Compilation of Available Geologic Information

The geologic description of this watershed was developed based mostly on previous interpretations by Wickham (1979) and Soller et al. (1999). In addition, geologic data were obtained from ISGS and ISWS well logs. Well logs from 4 townships and 12 surrounding townships (T20N, R7E thru R10E; T21N, R7E thru R10E; T22N, R7E thru R10E; T23N, R7E thru R10E) were reviewed to develop this geologic description. The watershed is primarily located in 4 townships (T21N, R8E; T21N, R9E; T22N, R8E; T22N, R9E).

From the available well logs, one or two logs per section were included in the project database. Well logs with data from ground surface to bedrock and with the greatest detail, such as those with sample sets described by an experienced geologist, were given highest priority for inclusion in the project database. In some sections, well logs with driller's descriptions were the only logs available. These logs are useful, but are more variable in quality. The well logs were compiled in a project database using RockWorks 2002 version 2.1 (RockWare, Inc., Golden, CO). RockWorks allows one to develop two-dimensional maps and cross-sections of the geologic materials.

2.2.2 Collection of Additional Geologic Materials

To supplement the available geologic information, additional geologic materials were obtained in a phased approach. First, geologic materials were collected with a percussion drive rig (ISGS AMS Powerprobe 9600) in January 2000. Data from this field work were used to design the second phase– collection of geologic samples and installation of monitoring wells. Most monitoring wells were installed in April 2000, using a hollow-stem auger rig (ISGS CME 75 rig) and 6⅝-inch auger (OD). Four monitoring wells (1S, 4S, 6S, & 10S) were installed using a solid stem auger rig (ISGS Giddings rig) in July 2000.

In January 2000, a total of 130 feet of core (i.e., geologic samples) were collected from 6 boreholes in the watershed (Figure 2.1). The texture, weathering, soil structure, and color of these geologic samples were described in the field.
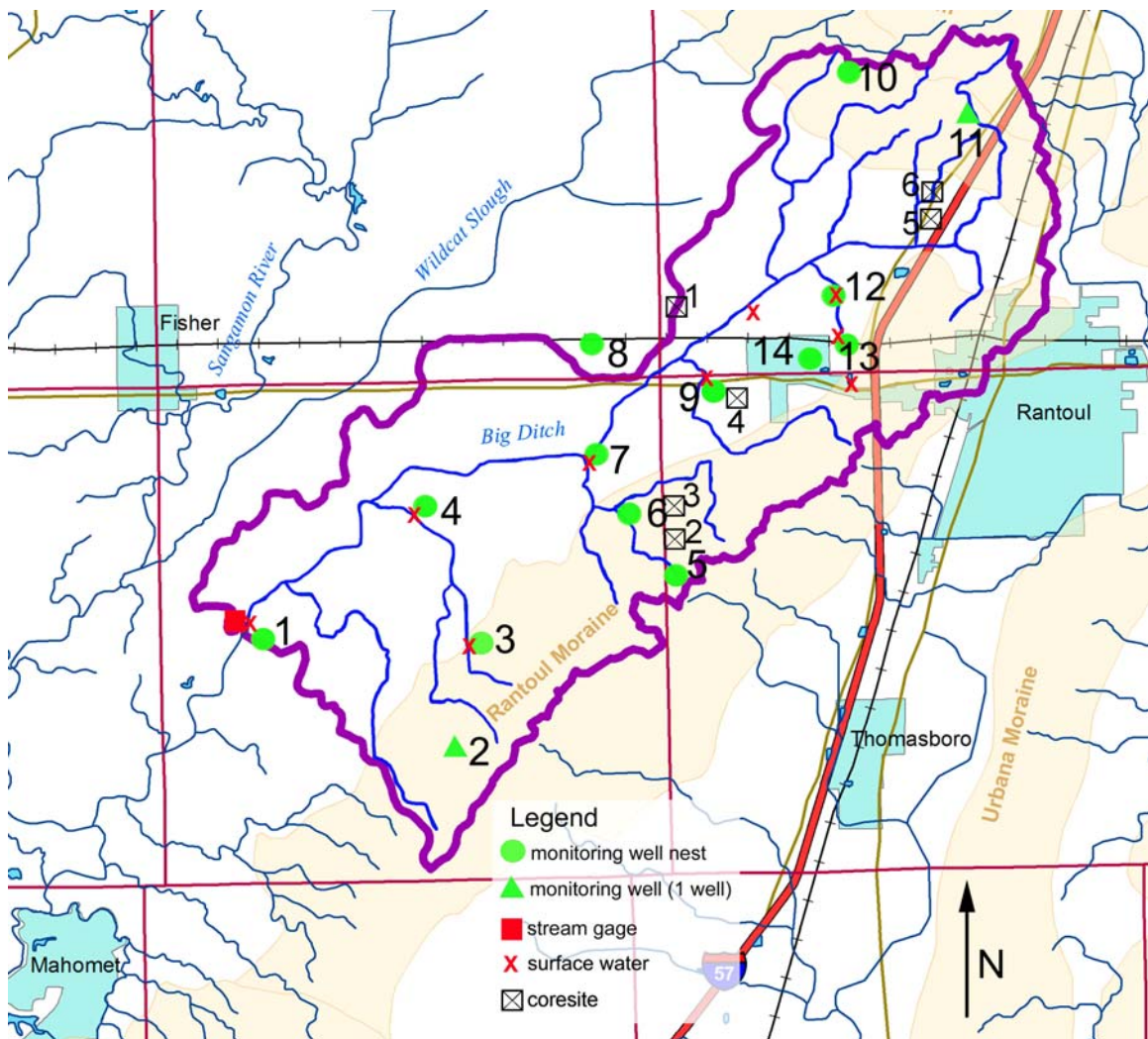
Figure 2.1 Map of study area showing monitoring wells, stream gage, core sites and surface water stations

The design of the monitoring well network was based on the information available in Wickham (1979) and on coring done at selected locations throughout the watershed. The 1.75-inch cores were collected using an AMS PowerProbe 9600. The monitoring well network was designed by balancing the data needs of all members of the groundwater research team, other C-FAR researchers, and available funds. These needs included:

1. Need to cover the entire watershed
2. Need to establish transects along the main stem of the stream and 2 or more transects perpendicular to the stream
3. Need to locate at sites where tile drainage was monitored
4. Need to avoid sites where nitrogen isotopes (^{15}N) were used for agronomic experiments due to possible interference with our isotopic experiments
5. Need to determine groundwater flow in 3 dimensions.

Once the network was designed, permission to drill and install monitoring wells was sought from land owners. Most landowners were very cooperative once they understood the project's purpose. Monitoring wells were installed at 11 locations (Figure 2.1). A well nest consists of one well to monitor the water table and a second well to monitor deeper groundwater within a sand deposit. The water table wells were typically completed at a depth of 12 feet, while the maximum depth of the deep wells was approximately 50 feet. Deeper wells were not installed at 2 locations because no sand was found between the base of the shallow wells and 50 feet. The monitoring wells were constructed with 2-inch, schedule 40 PVC screens and casing, as shown in Figure 2.2. The casing for most wells extended approximately 2 feet above ground surface. Steel well protectors, with locking covers, were installed to prevent damage to the wells. The boreholes were backfilled with quartz sand, bentonite, and cement as shown in Figure 2.2.
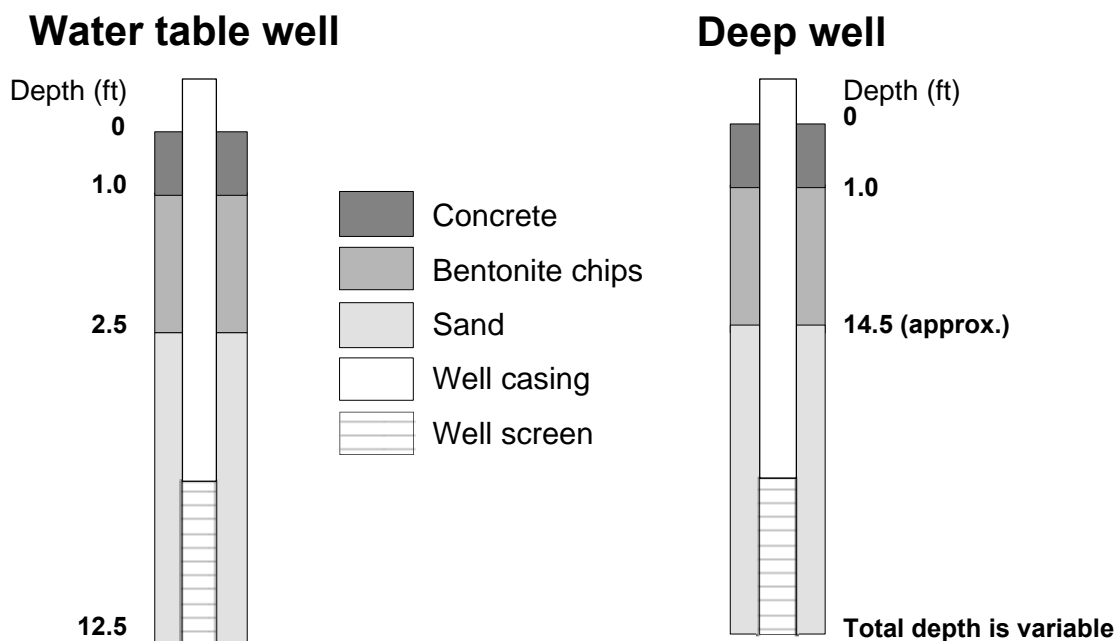

Figure 2.2 Schematic diagram of water table and deep monitoring wells installed in the Big Ditch watershed

The water table wells were screened at depths of approximately 7.5 to 12.5 feet, and sand-packed from depths of approximately 2.5 to 12.5 feet (Table 2.1). This well design allowed us to sample shallow groundwater throughout the year. The deep wells were screened and sand-packed at various depths. We sought to separate the sand packs of the water table and deep wells by at least 2 feet.

Table 2.1 Well construction details for monitoring wells in the Big Ditch watershed

Well #	Depth (ft)					
	bottom of screen	top of screen	bottom of sand pack	top of sand pack	bottom of bentonite	top of bentonite
1S	12.6	7.6	15.0	2.5	2.5	1.0
1D	30.7	25.7	30.7	21.3	18.6	1.0
2S	12.5	7.5	16.3	2.5	2.5	1.0
3S	10.0	5.0	10.0	2.0	2.0	1.0
3D	30.0	25.0	30.0	10.5	10.5	6.6
4S	12.6	7.6	13.1	2.5	2.5	1.0
4D	26.3	21.3	28.5	20.2	20.2	1.1
5S	11.9	6.9	12.3	2.5	2.5	1.0
5D	24.5	19.5	25.0	14.2	14.2	2.5
6S	16.1	11.1	16.6	2.5	2.5	1.0
6D	32.0	27.0	32.5	26.4	26.4	1.0
7S	12.5	7.5	13.0	2.5	2.5	1.0
7D	25.0	20.0	30.0	16.8	16.8	1.0
8S	13.2	8.2	13.8	2.5	2.5	1.0
8D	43.4	38.4	44.0	21.4	21.4	1.0
9S	13.0	8.0	13.5	2.5	2.5	1.0
9D	25.5	20.5	28.0	20.1	20.1	1.0
10S	19.0	14.0	19.5	2.5	2.5	1.0
10D	40.0	35.0	41.0	34.0	34.0	2.5
11S	12.6	7.6	13.1	2.5	2.5	1.0
12S	9.8	4.8	10.0	7.0	7.0	1.5
12D	33.3	28.3	nr	nr	nr	Nr
13S	12.5	7.5	12.5	4.8	4.8	3.2
13D	25.4	20.4	nr	nr	nr	Nr
14S	13.5	8.5	13.5	3.5	3.5	1.5
14D	28.8	23.8	nr	nr	nr	Nr

nr= not recorded

Additional well nests (12, 13 & 14) were installed in July 2002 with funding from the Illinois Groundwater Consortium (IGC). The focus of this IGC-funded research effort was to evaluate any potential differences in the groundwater beneath a commercial area and the larger agricultural watershed. These wells were installed with the same methods and materials described above.

2.2.3 Collection of Geophysical Data

High-resolution seismic data were collected and interpreted by Dr. Andre Pugin and Dr. Tim Larson, as part of a research project funded by the Illinois Board of Higher Education. These data were collected west of well 1 and southwest of the Big Ditch watershed. These data were used to define the general sequence of the Quaternary materials and depth to bedrock. The methods to collect and interpret these geophysical data were described by Pugin and Larson (2001) and Pugin et al. (2003).

2.2.4 Collection of Hydrogeologic Data

Water levels in the monitoring wells and surface water at selected locations were monitored on a regular basis. Water levels were monitored weekly or biweekly. Data loggers were installed in 10 wells (1S, 1D, 4S, 4D, 9S, 9D, 10S, 10D, 12S & 12D). These dataloggers were programmed to record water levels on an hourly basis.

Water levels were determined manually using a water-level meter, which allows one to measure the distance from the top of the well casing to the water level in the well. These measurements were recorded to the nearest 0.01 ft. The pressure transducers installed for this project were vibrating wire type transducers which record the depth of water above the pressure transducer. These transducers also recorded water levels to the nearest 0.01 ft. Data loggers, which store the data output from the pressure transducers, from Solinst (wells 10S, 10D, 12S & 12D), Slope Indicator (wells 4S & 4D), and Campbell Scientific (wells 1S, 1D, 9S & 9D) were used for this project. The data loggers were serviced every 2 or 3 weeks. Servicing involved downloading data, checking or replacing batteries and desiccant, and ensuring that the pressure transducers were working properly.

The elevations of all water-level measuring points were determined by level surveying, based on the known elevations of five benchmarks throughout the watershed. Three benchmarks were set by Illinois Department of Transportation and are located along U.S. Highway 136. Another benchmark was set by the Champaign County Highway Department and is located on the bridge over Big Ditch on County Road 900 E. The fifth benchmark was set by the U.S. Geological Survey and is located east of the intersection of C.R. 3300N and C.R. 1600E. Level surveying was conducted with an automatic level (Wild NA2) and a micrometer. The micrometer allowed elevations to be measured to the fourth decimal place. All measuring points were determined to the nearest 0.01 foot.

To determine hydraulic conductivity, slug tests were conducted in 20 monitoring wells following the procedures described by Butler (1998). This procedure involved inserting or removing a solid plastic pipe or "slug" of known volume and recording the water level in a well over time. The slug test data were analyzed to estimate hydraulic conductivity using AquiferWin32, version 2 (Environmental Simulations, Inc.).

2.2.5 Collection of Hydrologic Data

The ISWS collected stream flow data at the outlet of the watershed. We occasionally collected additional stream flow data throughout the Big Ditch watershed and in Wildcat Slough (watershed just north of Big Ditch) to help define the spatial variability of groundwater discharge to the streams and collect data needed to calibrate the groundwater flow model. Stream gauging was generally conducted at low flow conditions, using a current meter following USGS methods (Rantz, 1982).

A Global Water current meter (model FP-101) was used to measure the mean flow velocity. Velocity measurements were taken at one or more locations, depending on the stream width and discharge. Measurement locations were selected along stream reaches that were straight and had relatively uniform flow. The meter was held at a depth (from the water surface) of 0.6 times the stream depth (D). We applied the 0.6D approximation to estimate the mean discharge at a number of locations across the stream. When the flow was too low to turn the current meter, the velocity was estimated by timing the movement of suspended material over a specified distance.

2.2.6 Estimation of Groundwater Flow

To estimate groundwater flow, a two-dimensional, steady-state groundwater flow model was developed for the Big Ditch watershed and surrounding areas. This model was developed using GFLOW 2000 (version 1.3), an analytical element modeling software package (Haitjema, 1995). This software allows one to develop conceptual models of groundwater flow based on steady-state water elevations, such as mean water levels in streams, lakes, and wells.

2.3 Geologic Description of the Watershed

The unconsolidated geologic deposits throughout the watershed consist of a sequence of glacial and post-glacial deposits that range in thickness from 260 to 400 feet (Soller et al., 1999) and overlie Mississippian and Devonian bedrock (Willman and others, 1967). The topography of the bedrock surface (Figure 2.3) shows a NE-SW trending valley beneath Big Ditch. This valley is the Mahomet bedrock valley, which holds the Mahomet aquifer.

2.3.1 Quaternary and Recent Geological Materials

This watershed is predominantly an intermorainal landscape, but includes portions of the Rantoul Moraine in the S-SE part of the watershed and the Illiana Morainic System in the NE part of the watershed. These moraine positions suggest a significant amount of glacial meltwater flowed through the watershed. Sand and gravel deposits associated with these streams are found within the shallow subsurface of this watershed. The exact layout of buried glacial stream deposits, however, is unknown and can only be inferred from surficial landforms, and the limited borehole and geophysical data.

In the northernmost end of the watershed, the land surface elevation peaks at 827 feet above mean sea level (MSL). The lowest elevation in the watershed is 694 feet, at the outlet of the watershed. The intermorainal area of the watershed ranges in elevation between 696 and 732 feet above MSL with a general NE-SW trending slope. The crest of the Illiana Morainic System within the watershed is typically about 771 feet above MSL. The crest of the Rantoul Moraine is typically between 771 and 787 feet above MSL.
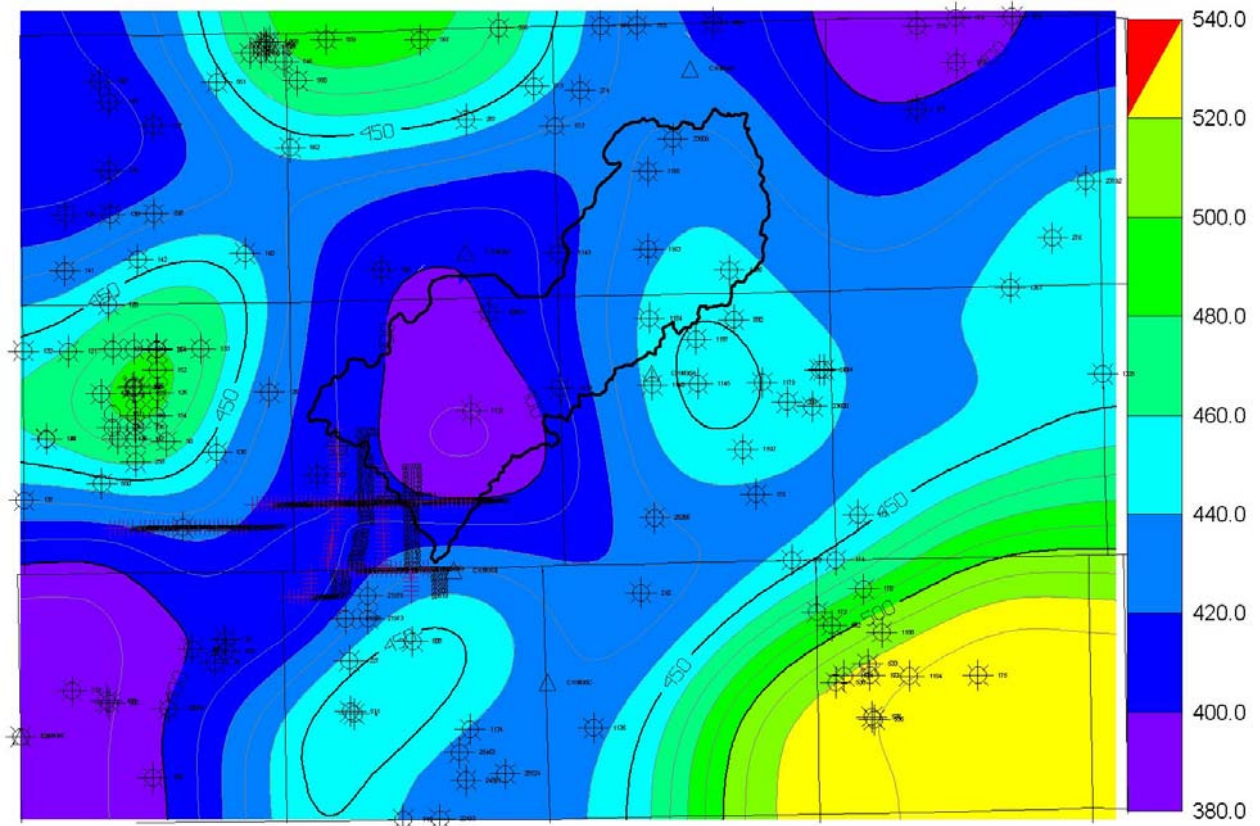
Figure 2.3 Contour map of bedrock elevation in northern Champaign County (10 ft contour interval, seismic data are marked as +, other symbols represent wells). The watershed boundary is also shown.

Soller et al. (1999) provided a framework for the regional Quaternary stratigraphy (Figure 2.4). A north-south cross-section (Figure 2.5) through west-central Champaign County and the Big Ditch watershed (at section J-J' on Figure 2.5) depicts the two-dimensional arrangement of the Quaternary materials and the uneven bedrock surface.

Wickham (1979) and Hansel and Johnson (1996) provided a detailed framework for the regional stratigraphy of the Wisconsin Episode. Wickham (1979) proposed a conceptual model of glacial movement and ice margin position that describes the identified sequence of deposits.   Cost constraints and project objectives prevented our study from confirming the stratigraphic framework within the study area. Lithologies identified in core samples, however, appear to generally agree with Wickham's interpretations of ice movement and ice margin locations.

Four different glacial diamictons were identified in the cores from the shallow subsurface. Except for the bottom diamicton unit, the textures within the diamicton sequence fined upward from a sandy loam to a silty clay loam. The lowermost diamicton encountered was a weak red, silty clay
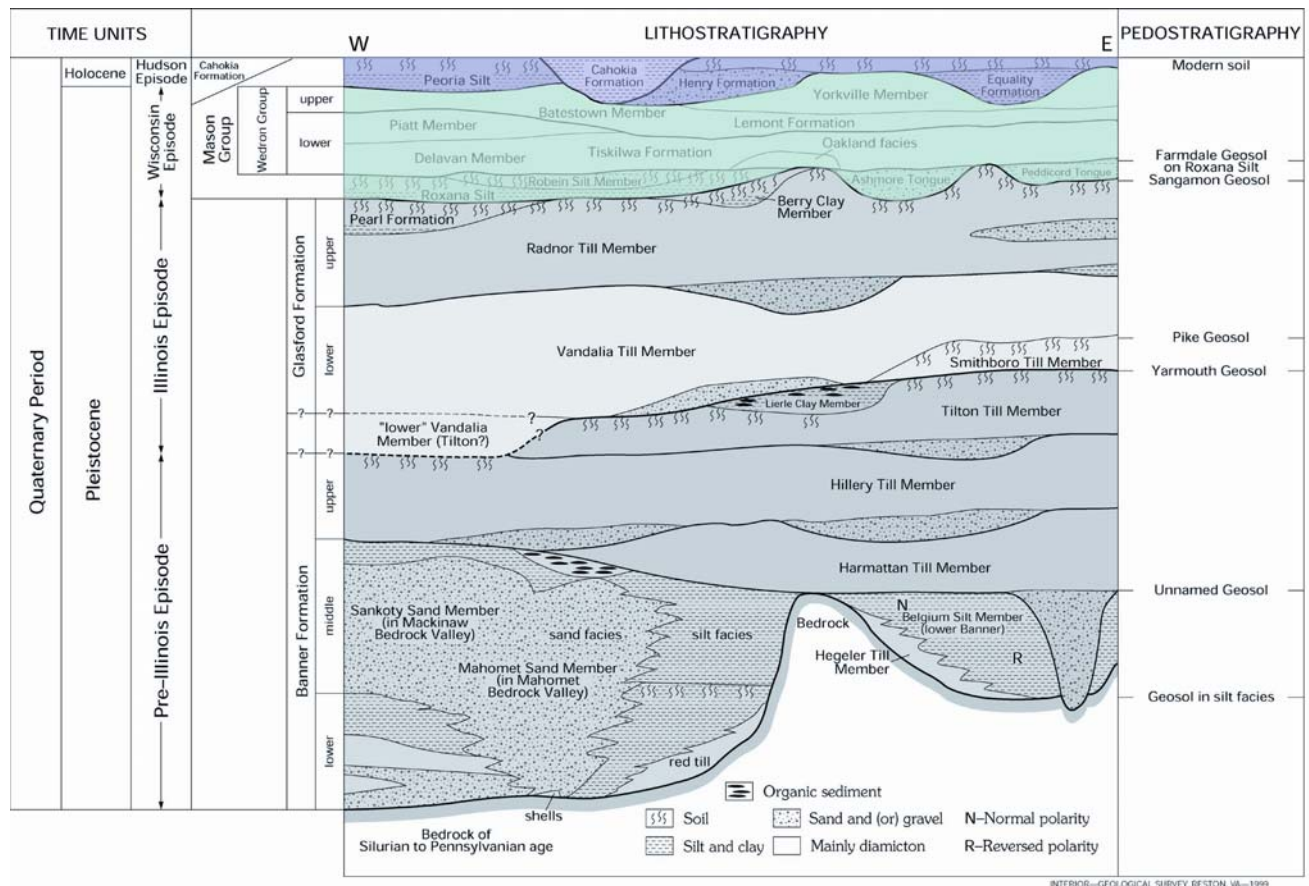
Figure 2.4 Stratigraphic column for Quaternary sediments in east-central Illinois (from Soller et al., 1999)

loam that appeared to correlate with the undifferentiated Tiskilwa Formation. This unit was only encountered in a few cores in the intermorainal area of the watershed. Above that diamicton in some cores, and typically the lowermost unit observed, was a gray sandy loam diamicton that appeared to correlate to the Piatt Member of the Tiskilwa Formation. This unit appeared at elevations of approximately 700 feet above MSL in the intermorainal area and rose to elevations around 745 feet above MSL beneath the Rantoul Moraine. This gray diamicton appeared to correlate with Wickham's descriptions of the Piatt Member, which he described as forming the core of the Rantoul Moraine. This diamicton was separated from overlying diamictons by a sequence of sorted materials. Above this sandy loam diamicton were two loam to silty loam diamictons that were bounded by packages of sorted sediments. These deposits appear to correlate with the Batestown Member of the Lemont Formation (Figure 2.4) (Wickham 1979; Hansel and Johnson 1996).
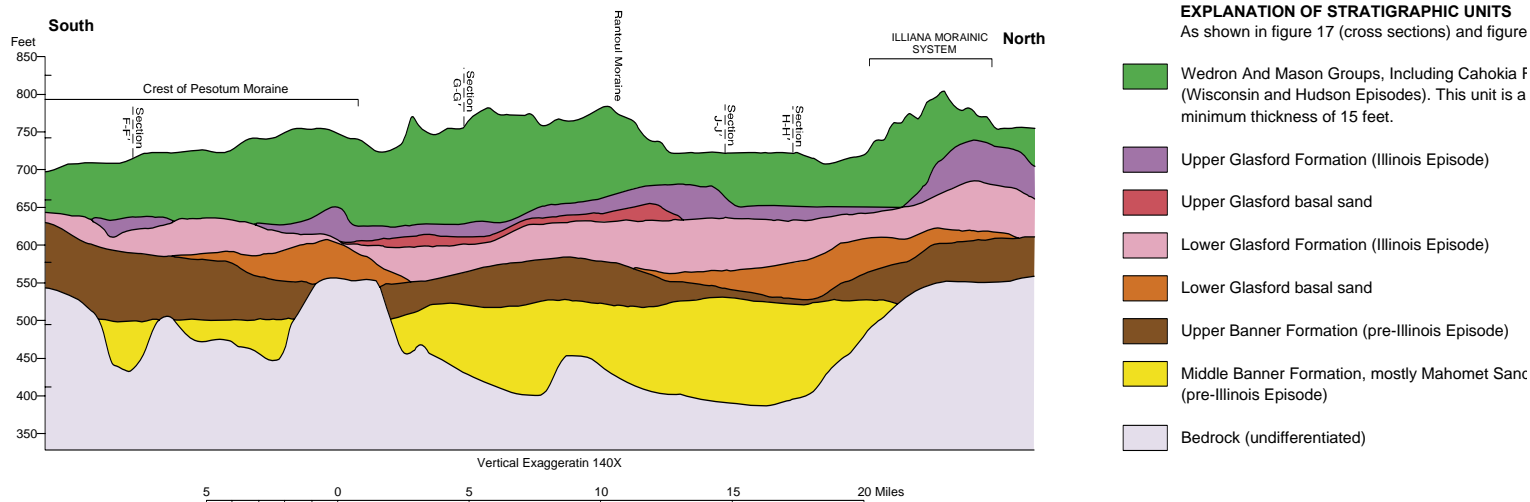
EXPLANATION OF STRATIGRAPHIC UNITS
As shown in figure 17 (cross sections) and figure

Wedron And Mason Groups, Including Cahokia F (Wisconsin and Hudson Episodes). This unit is a minimum thickness of 15 feet.

Upper Glasford Formation (Illinois Episode)

Upper Glasford basal sand

Lower Glasford Formation (Illinois Episode)

Lower Glasford basal sand

Upper Banner Formation (pre-Illinois Episode)

Middle Banner Formation, mostly Mahomet Sand (pre-Illinois Episode)

Bedrock (undifferentiated)

Figure 2.5 South-north geologic cross-section showing bedrock surface and Quaternary sediments (from Soller et al., 1999) Big Ditch is located at Section J-J'.

Except for areas covered by the Illiana Moraine, these deposits were the uppermost diamictons encountered in the watershed. In the Illiana Moraine, however, these silty loam diamictons were not observed and were likely covered by thick sequences of silty clay loam diamicton of the Yorkville Member of the Lemont Formation. In cores from the flanks of the Illiana Moraine, the diamicton was generally interbedded with thin deposits of sorted sediments. Approximately 5 feet of silt loam material (loess) was found as the surficial deposit in all cores collected in the watershed.

Where encountered, sands and silty sediments were typically in 3 to 5 foot zones with thin interbeds of glacial diamicton. The grain size and degree of sorting within the sand deposits were highly variable. The shallow groundwater flow system will be significantly affected by the lateral continuity and uniformity of texture in these shallow sand deposits. In addition, groundwater flow through fine-grained sediments is commonly controlled by the presence of joints, fractures, and other macropores.

A buried soil (paleosol) was encountered in the upper 10 feet of several boreholes (well 3, well 9 & core 1). The higher content of organic matter in this buried soil, relative to the bounding glacial deposits, may lead to increased denitrification within this horizon. Local variability in the presence and thickness of this paleosol and the presence and magnitude of preferential flow features will affect the variability of denitrification within this horizon.

2.3.2 Surficial Soils
The surficial soils in the Big Ditch watershed are predominantly silt loams and silty clay loams. The five most common soils, Drummer silty clay loam, Raub silt loam, Elliott silt loam, Parr silt loam, and Ashkum silty clay loam, cover approximately 82% of the watershed. Most soils in this watershed are considered somewhat poorly to poorly drained and have moderate to high organic matter content (USDA, 1982). Eight of the 33 soils found in the watershed occur within 250 feet of the wells installed in the watershed (Table 2.2). The proportion of the land within a 250-foot radius covered by these soils are shown in Figure 2.6. The soils around most wells are poorly drained or

somewhat poorly drained. However, 40% of the land around wells 10, 6, and 2 is covered with moderately well drained or well drained soils.

Table 2.2 Description of soils within a 250-foot radius of the shallow wells (USDA, 1982)

| Soil name	Soil map symbol	Soil texture	Soil drainage	Soil organic matter (% by weight)
Swygert	91	silty clay loam	somewhat poorly drained	4 to 5
Elliott	146	silt loam	somewhat poorly drained	4 to 5
Drummer	152	silty clay loam	poorly drained	5 to 7
Parr	221	silt loam	well drained	3 to 5
Varna	223	silt loam	moderately well drained	2 to 3
Ashkum	232	silty clay loam	poorly drained	5 to 7
Ambraw	302	silty clay loam	poorly drained	2 to 3
Raub	481	silt loam	somewhat poorly drained	2 to 4
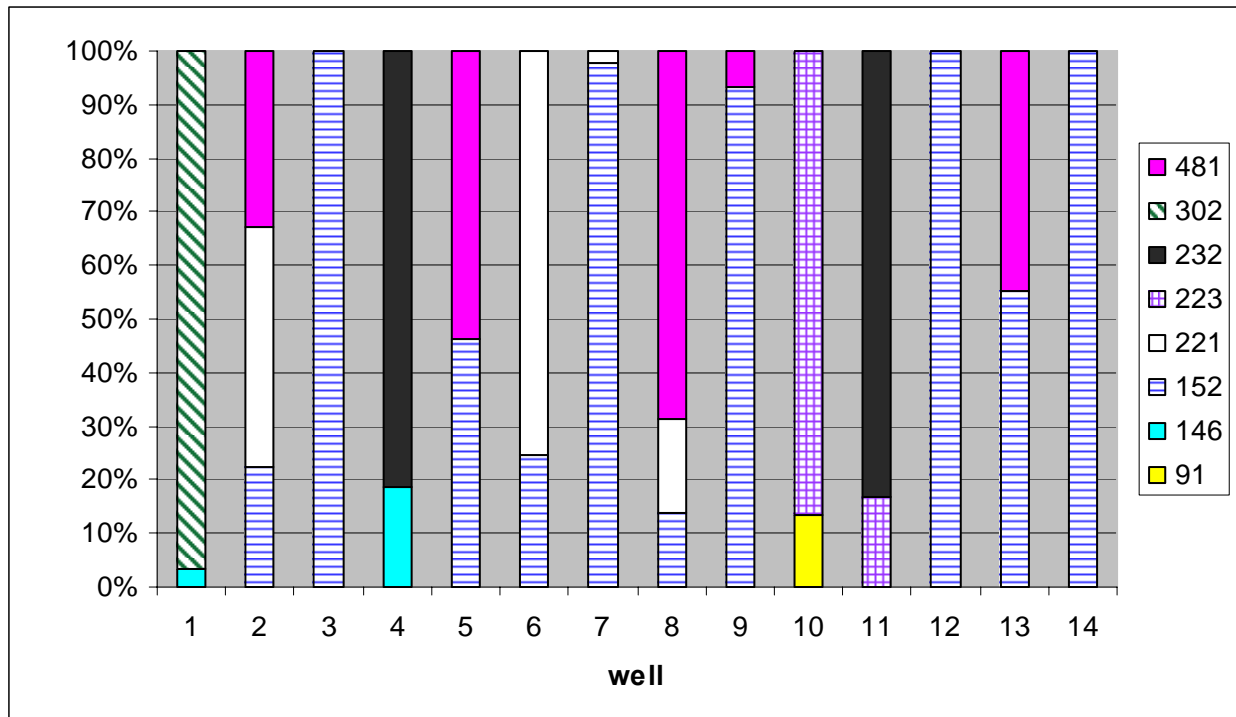
Figure 2.6 Areal coverage of soils within a 250-foot radius of each well (soil series numbers are listed in Table 2.2)

2.4 Hydrogeologic Description of the Watershed
2.4.1 Basic Hydrologic Data

Although other members of the WQ-SRI were responsible for monitoring basic hydrologic data such as stream flow and precipitation, these data are necessary to interpret our data so they are presented in this report. Precipitation data were available from stations for Urbana, IL (Mirek, 2001) and Fisher, IL (NOAA station= 113061, http://cdo.ncdc.noaa.gov). Mirek (2001) did not report the source of her precipitation data. Precipitation for these two stations varied slightly, but most dramatically in water year 1999 (Figure 2.7 and Table 2.3). Based on the precipitation, water year 1998 would be considered a wet year (higher than average precipitation), 2002 would be a normal year and 1999, 2000, 2001 and 2003 would be considered dry years.
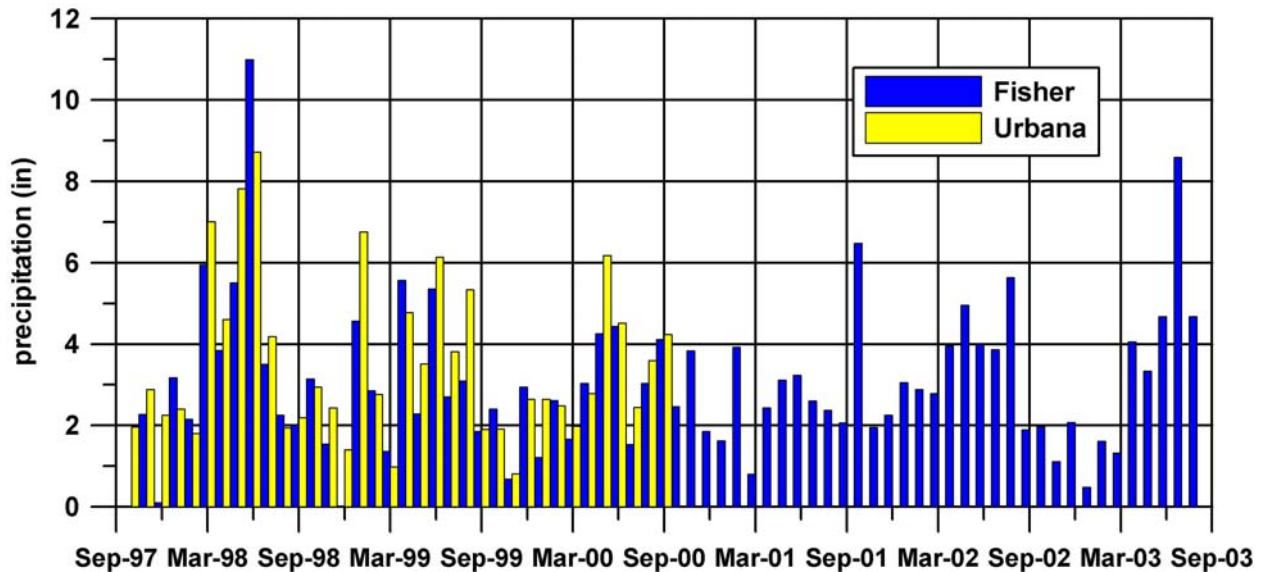

Figure 2.7 Monthly precipitation at Urbana, IL (from Mirek, 2001) and Fisher, IL (from NOAA)

Table 2.3 Annual precipitation at the Urbana and Fisher stations

Water Year	Precipitation (in)		Difference from mean[1] (in)	
	Urbana	Fisher	Urbana	Fisher
1998	47.8	41.8[2]	5.3	-0.7
1999	42.8	34.3	0.3	-8.2
2000	36.3	31.9	-6.2	-10.6
2001		30.3		-12.2
2002		43.7		1.2
2003		35.8[3]		-6.7

1: mean precipitation is 42.5 inches (based on 30 years of data from Urbana station).
2: Data from October 1997 were not available, thus were not included in the annual precipitation
3: Data from September 2003 were not available, thus were not included in the annual precipitation

Stream flow data for Big Ditch and the Sangamon River at Fisher are similar (Figure 2.8). The ISWS provided the flow data for Big Ditch. The gage was located at the outlet of the watershed, near wells 1S & 1D. The data for the Sangamon River (USGS station 05570910) were obtained

from a USGS website (http://nwis.waterdata.usgs.gov/il/nwis/discharge). The USGS gage is located in Fisher, IL, where U.S. 136 crosses the Sangamon River, and is approximately 3 miles north of the ISWS gage. The seasonal nature of flow in the Big Ditch and Sangamon River is easily observed in Figure 2.8— higher flows typically occur in late winter to early spring and low flows in late summer to early fall. The flow in the Sangamon River was almost always greater than the flow in the Big Ditch, as would be expected because of its larger drainage basin (240 sq. miles vs 38 sq. miles).
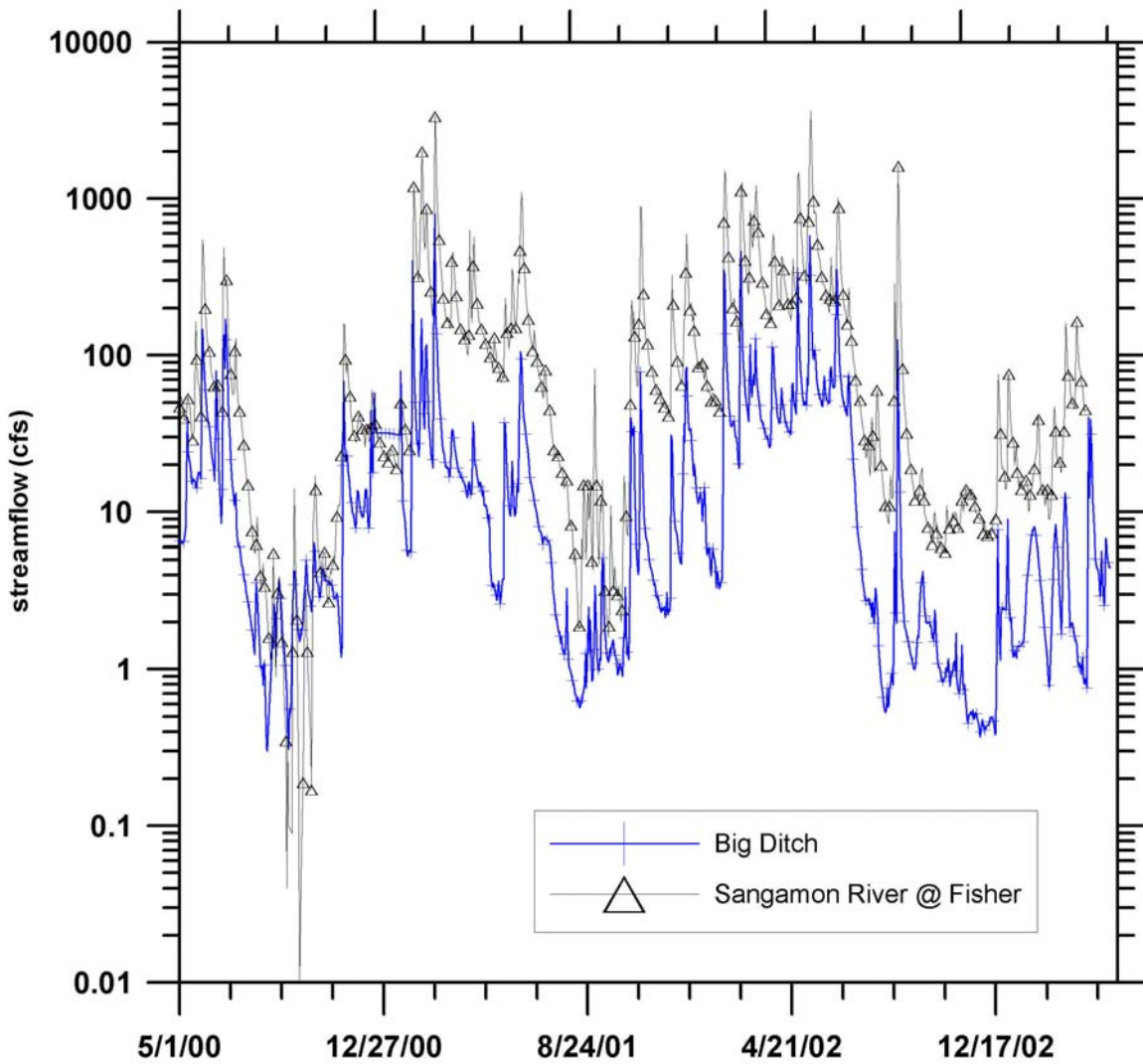
Figure 2.8 Stream flow in the Big Ditch and Sangamon River from May 2000 through April 2003

2.4.2 Groundwater Levels

The groundwater levels in the shallow and deep wells varied seasonally with higher levels in April and May and lower levels in September and October (Figures 2.9 and 2.10). During this study, the water levels in most wells varied 4 to 6 feet, but several wells (6S, 8S, & 8D) varied more than 10

feet. The water levels in most wells moved in unison and were highest in most wells in spring 2002. The lowest water levels were generally observed in fall 2001 or fall/winter 2002. The high water levels were likely in response to the normal precipitation in water year 2002, while precipitation in water years 2000, 2001 and 2003 was below normal. Groundwater levels in the shallow wells (Figure 2.11) and deep wells (Figure 2.12) follow the general surface topography. These contour plots from March 2003 (Figures 2.11 and 2.12) are typical of other dates.

Vertical hydraulic gradients are used to define the direction of vertical groundwater flow. Downward groundwater flow is denoted by positive vertical gradients, while upward flow is denoted by negative gradients (Table 2.4). The median vertical hydraulic gradient was negative for the four lowland well nests (1 S&D, 4 S&D, 7 S&D, 9 S&D), but positive for well nests in other areas of the watershed. In addition, the median vertical hydraulic gradient between the shallow wells and surface water was negative. In three lowland well nests instrumented with pressure transducers (1 S&D, 4 S&D, 9 S&D), the vertical gradient was negative 82%, 70%, and 82% of the time, over the course of the study for well nests 1, 4, and 9, respectively. The vertical gradient in these wells generally ranged from -0.1 to 0.1 for the period monitored. In an upland well nest (wells 10 S&D), the vertical gradient was always positive, usually within the range of 1.05 to 1.55. Finally, the shallow groundwater in this watershed will recharge two deeper aquifers, the Glasford sands and the Mahomet aquifer, as indicated by the positive median gradients between wells 1 D&G and between 1 D&M (Table 2.4).

The vertical gradients generally varied by position in the watershed. In the upland wells, the gradients between the water levels in the shallow and deep wells were generally positive or downward, but some vertical gradients varied between positive and negative. In the lowlands, most well nests generally had negative or upward gradients. The gradients between shallow groundwater and surface water (Big Ditch) were generally negative, which means that groundwater discharged to Big Ditch throughout most of the year. These data indicate that groundwater flowed downward in the uplands and upward in the lowland, eventually discharging to Big Ditch. Shallow groundwater also recharged the deeper aquifers (Glasford and Mahomet sands).
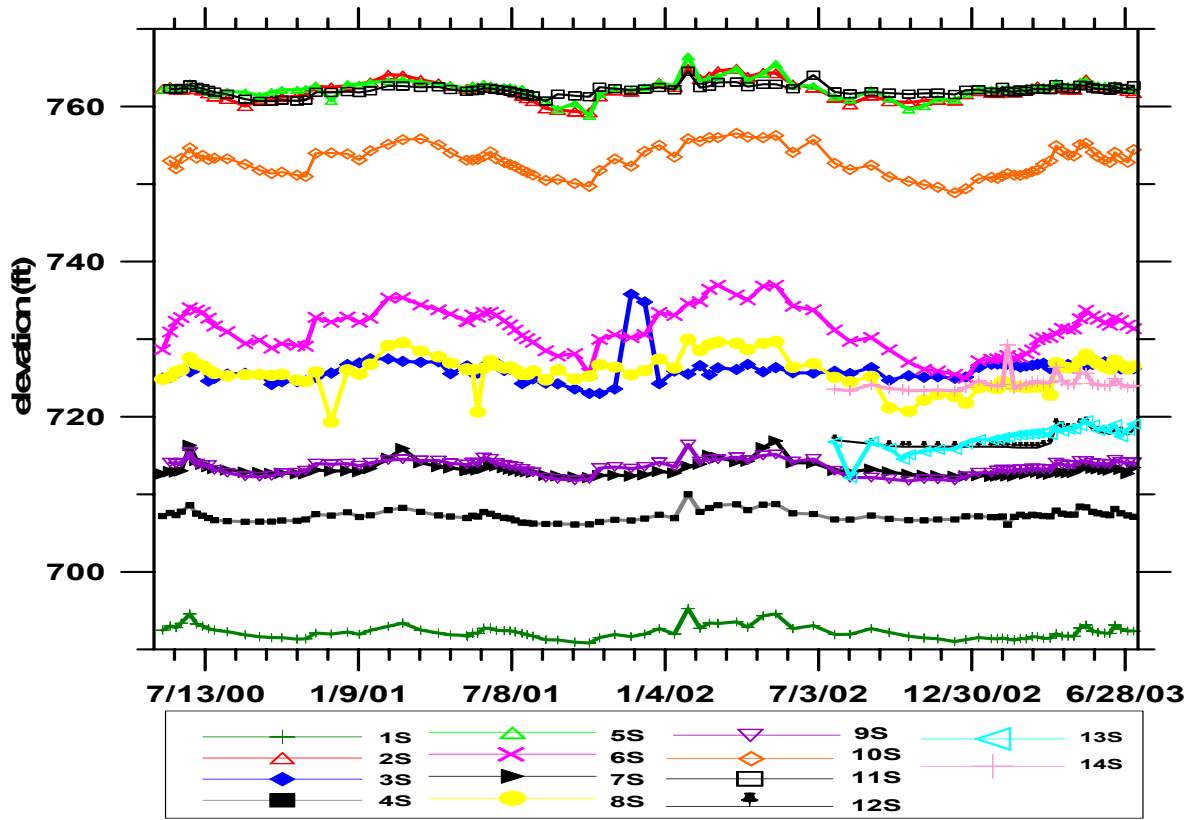
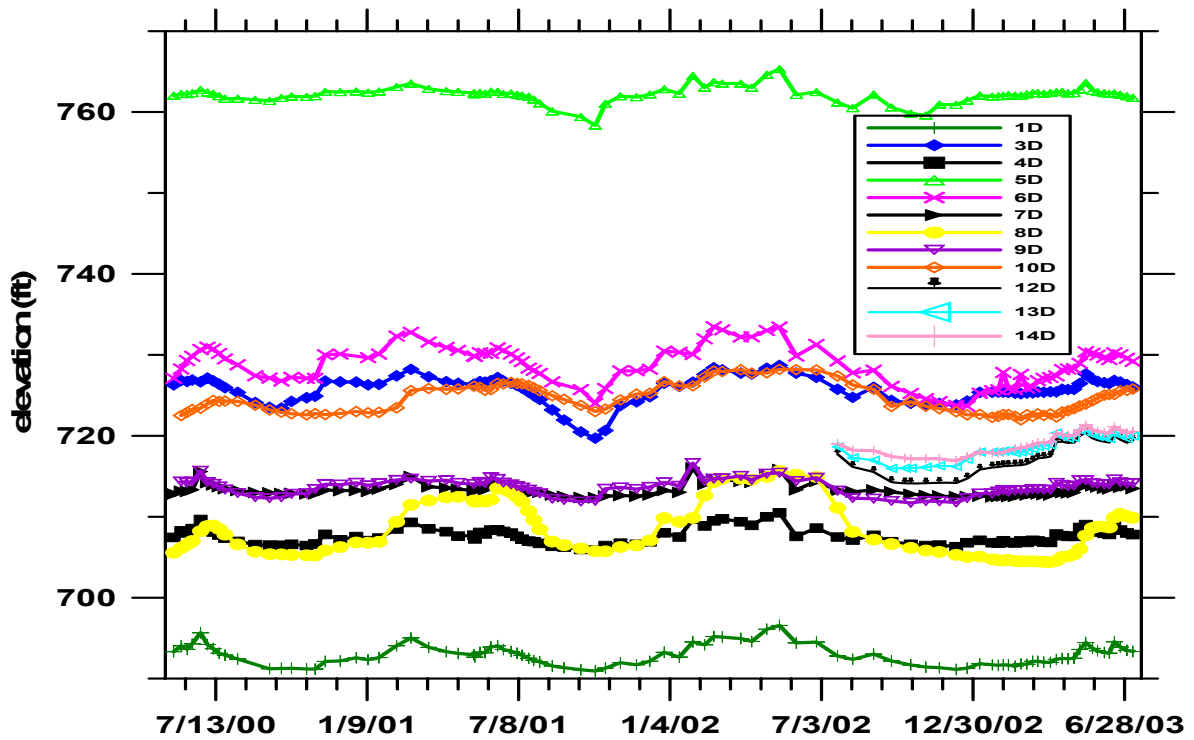Figure 2.9 Elevation of the water levels in shallow wells

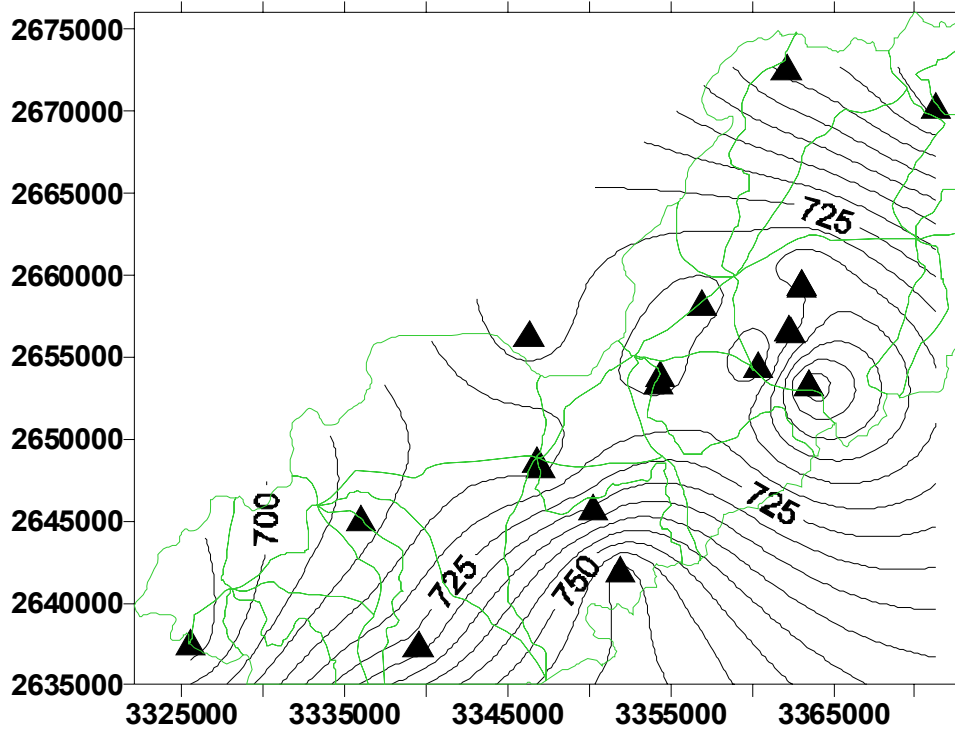Figure 2.10 Elevation of the water levels in deep wells

Figure 2.11 Contour map of water levels in surface water and the shallow wells over subwatershed boundaries (green lines). Data for March 17, 2003. (Data locations are marked with a triangle and are plotted using Lambert feet coordinates.)
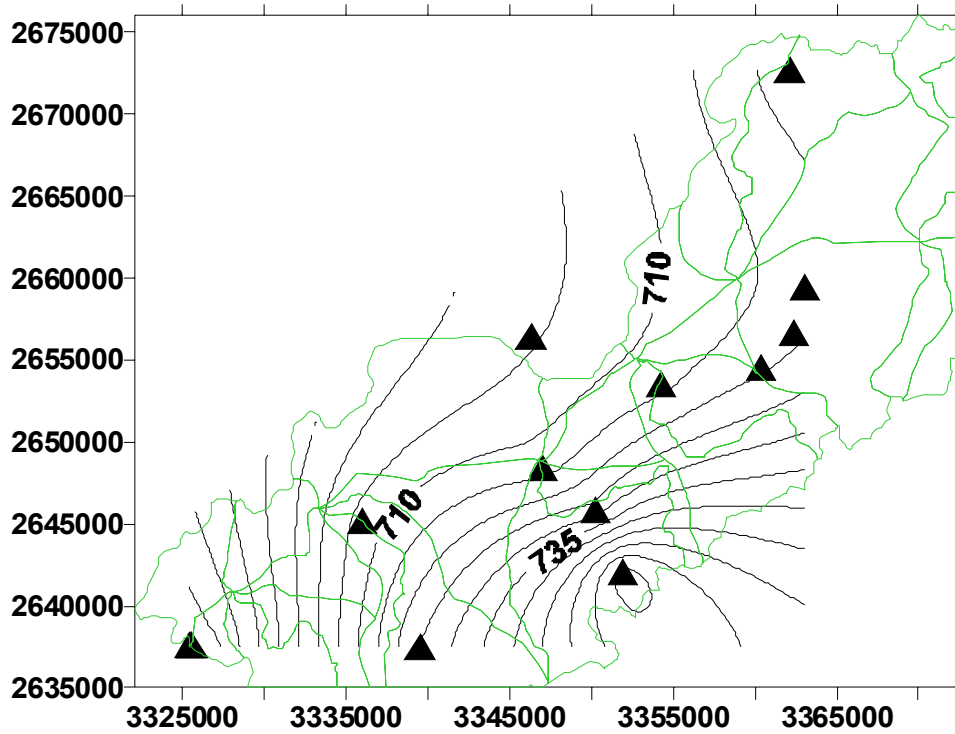

Figure 2.12 Contour map of water levels in the deep wells over subwatershed boundaries (green lines). Data for March 17, 2003. (Data locations are marked with a triangle and are plotted using Lambert feet coordinates.)

Table 2.4 Summary of hydraulic gradients between wells and between wells and surface water

Locations	Data record	Vertical Hydraulic Gradient		
		Minimum	Median	Maximum
1 S&D	May-00 to July-03	-0.12	-0.036	0.043
1 D&G	Mar-02 to July-03	0.18	0.19	0.20
1 D&M	Mar-01 to July-03	0.082	0.093	0.11
1 G&M	Mar-02 to July-03	-0.027	-0.004	0.026
sw & 1S	June-00 to July-03	-0.54	-0.37	-0.082
3 S&D	May-00 to July-03	-0.15	0.007	0.16
4 S&D	May-00 to July-03	-0.13	-0.031	0.034
sw & 4S	June-00 to July-03	-0.16	-0.053	0.039
5 S&D	May-00 to July-03	-0.14	0.020	0.16
6 S&D	May-00 to July-03	-0.018	0.16	0.29
7 S&D	May-00 to July-03	-0.18	-0.012	0.077
sw & 7S	June-00 to July-03	-0.58	-0.16	0.002
8 S&D	May-00 to July-03	0.29	0.59	0.73
9 S&D	May-00 to July-03	-0.030	-0.008	0.004
sw & 9S	June-00 to July-03	-0.32	-0.21	0.12
10 S&D	May-00 to July-03	1.20	1.35	1.55

2.4.3 Estimation of Hydraulic Conductivity

Slug tests are an easy way to estimate hydraulic conductivity (K) in a single well. Based on slug tests, the median hydraulic conductivity (Table 2.5) was estimated to be 2.9×10^{-4} cm/sec for the shallow wells and 4.3×10^{-4} cm/sec for the deep wells. The range of hydraulic conductivities was one order of magnitude greater for the deep wells than for the shallow wells, because the deep wells had a higher maximum K. The deep wells likely had a higher maximum K than the shallow wells because these deep wells were completed in sand and gravel lenses.

Table 2.5 Hydraulic conductivity based on slug testing

Well type	# of wells	median K (cm/sec)	minimum K (cm/sec)	maximum K (cm/sec)
shallow wells[1]	11	2.9×10^{-4}	5.3×10^{-5}	4.4×10^{-3}
deep wells	9	4.3×10^{-4}	4.8×10^{-5}	5.9×10^{-2}

1: wells 1 through 11 were tested.

2.5 Groundwater Flow Modeling

A model of shallow groundwater and surface water flow, at steady state, was developed for the watershed to better understand groundwater flow in the watershed and to define the hydraulic characteristics of the watershed (e.g., hydraulic conductivity and recharge). This flow model was based on analytical element modeling as described by Haitjema (1995). Steady-state flow might best approximate the flow in the watershed during late summer and early fall (i.e., during base flow conditions). During base flow conditions, the water table is below the tiles so the tiles are not flowing. Surface water flow within the Big Ditch watershed was measured in November 2001
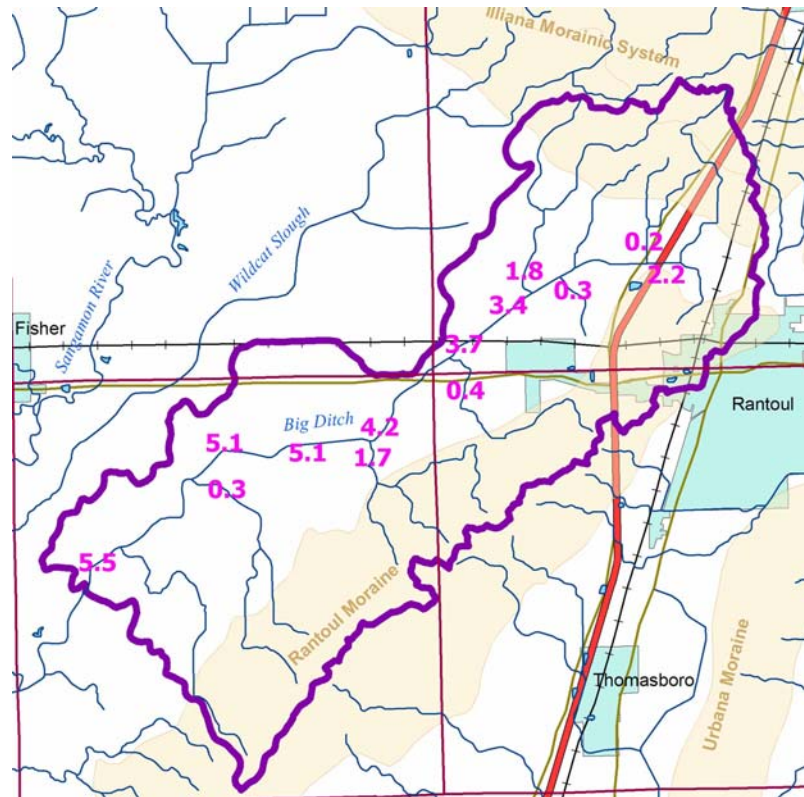
Figure 2.13 Surface water flow in the Big Ditch watershed, November 2001. Flow is given in cfs. Flow in tributaries is 0 unless otherwise noted.

(Figure 2.13). On this date, surface water flow was primarily from groundwater discharge to the stream, as no flow from tile drains was observed. These data show that groundwater discharge to surface water is not uniform across the watershed. In November 2001, 5.5 cfs was flowing from the outlet and 2.2 cfs was flowing at the northeastern end of the watershed. The flow at the northeastern end of the watershed includes storm water discharge routed through a closed wastewater treatment plant. The sum of the flows from the tributaries exceeds the flow out of the watershed, which indicates that some sections of Big Ditch are losing water, apparently in the downstream portion of Big Ditch. Surface water flow for April 2003 for Big Ditch and at some locations in the adjacent Wildcat Slough (Figure 2.14) was also measured when no water was discharging from tile drains. These flow data were quite valuable for modeling shallow groundwater flow for this study.

To simulate the flow of shallow groundwater and surface water of the Big Ditch watershed with GFLOW, the hydraulic conductivity was set at 37.5 ft/day or 0.013 cm/sec, aquifer thickness at 15 ft, and recharge over the modeled area at 0.0004 ft/day or 1.8 inches/year (case 1, Table 2.6). In addition, the recharge was increased in two areas– along the uplands near well 5 (additional recharge is 0.0002 ft/day) and around well 11 (additional recharge is 0.0009 ft/day). These areas are marked with black polygons in Figure 2.15. To calibrate the model, water levels in 11 shallow wells and stream flow at the outlet of the watershed (near well 1) from November 2001 (5.5 cfs) were used. Heads for Big Ditch, Wildcat Slough, Sangamon River, and other streams were determined from USGS 7.5 minute topographic maps. All streams were input as far field features except Big Ditch which was input as a near field feature.
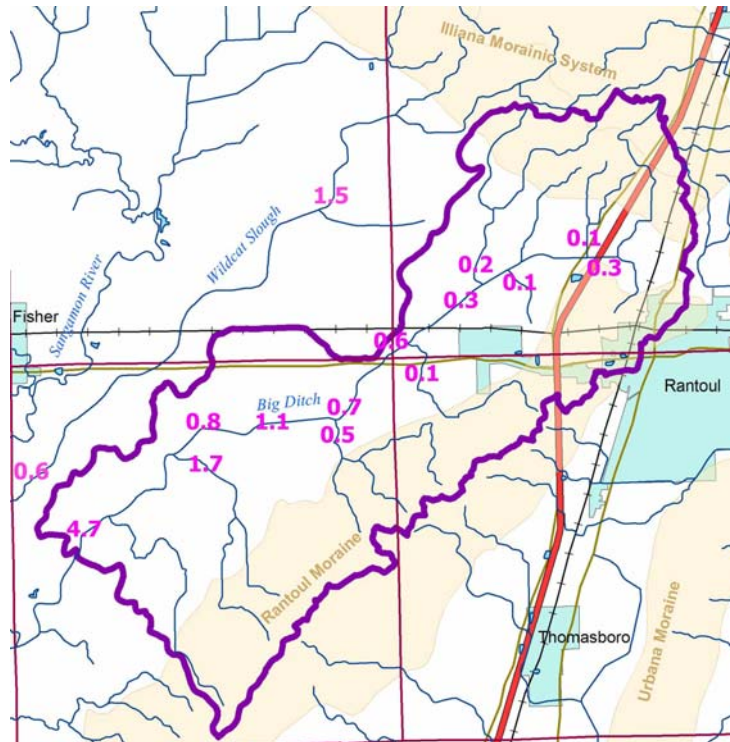
24

Figure 2.14 Surface water flow in the Big Ditch and surrounding watersheds, April 2003. Flow is given in cfs. Flow in tributaries is 0 unless otherwise noted.

GFLOW determines the head across the aquifer and stream flow in near field streams. GFLOW results for the input described above (case 1) are shown in Figure 2.15. Triangles are used to represent the difference between the modeled and input heads. Upward pointing triangles indicate that the modeled heads are higher than the input heads, while downward pointing triangles indicate that the modeled heads are lower than the input heads. The triangle size increases as the difference between the modeled and input heads increases. The heads in the aquifer are contoured and shown as dashed lines. Groundwater flows perpendicular to the head contours.

2.5.1 Modeling Results
The model results show generally good agreement between the modeled and input heads (Figure 2.15). The difference between the modeled and input heads ranged from -6.0 to 7.7 feet, with an average difference of 1.4 feet (case 1, Table 2.6). The stream flow by well 1 was determined to be 5.8 cfs by GFLOW, which is very close to the measured flow of 5.5 cfs. These heads show that steady-state groundwater flow is generally perpendicular to Big Ditch south of Big Ditch and is toward Big Ditch, Wildcat Creek, and even the Sangamon River north of Big Ditch.
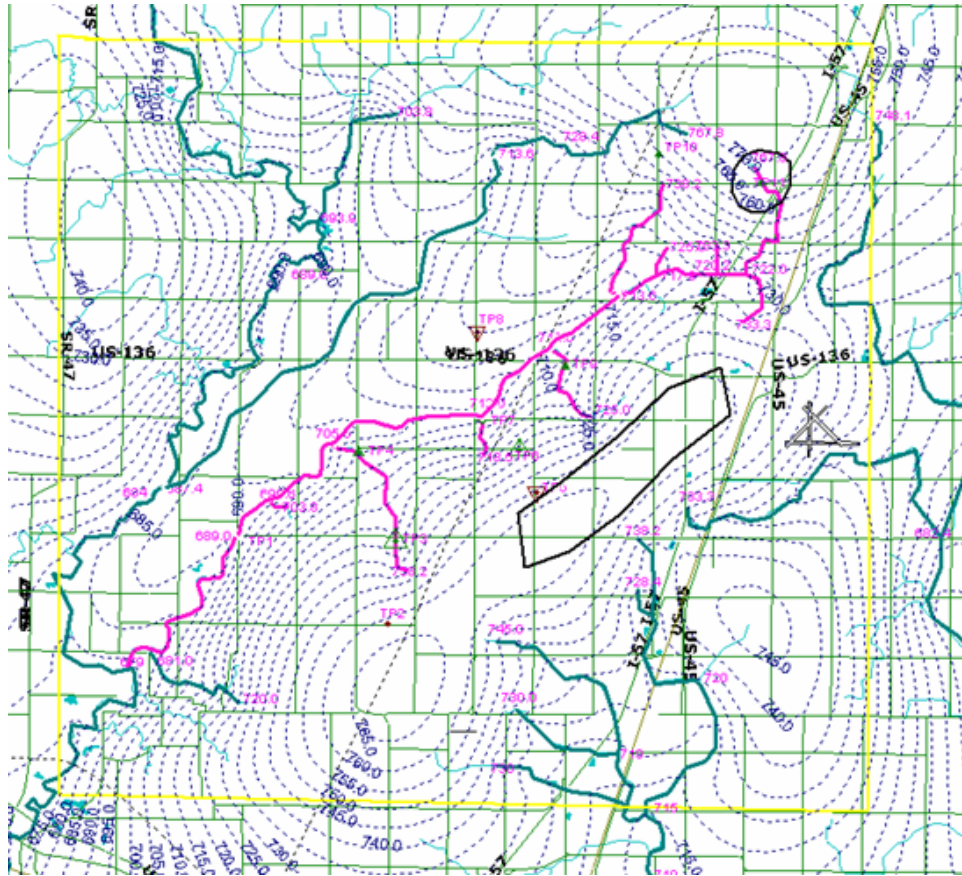
Figure 2.15 GFLOW modeling results for the Big Ditch watershed, case 1

Table 2.6 GFLOW input and output for the Big Ditch watershed

Case #	Input Data								Output		
	Entire domain			Uplands by Well 5		Well 11			Head difference		
	K	r	b	K	r	K	r	Q @ well 1	min	max	mean
	ft/day	ft/day	ft	ft/day	ft/day	ft/day	ft/day	cfs	ft	ft	ft
1	37.5	0.0004	15	37.5	0.0002	55	0.0009	5.8	-6.0	7.7	1.4
2	37.5	0.0006	15	37.5	0.0002	55	0.0009	8.6	0.5	19.0	6.2
3	37.5	0.0002	15	37.5	0.0002	55	0.0009	3.1	-20.3	7.3	-4.4
4	18.75	0.0004	30	18.75	0.0002	55	0.0009	5.8	-6.0	7.7	1.4
5	375.	0.004	15	37.5	0.0002	55	0.0009	55.	-9.5	7.7	0.9
6	3.75	0.00004	15	37.5	0.0002	55	0.0009	0.92	-5.2	29.0	6.2

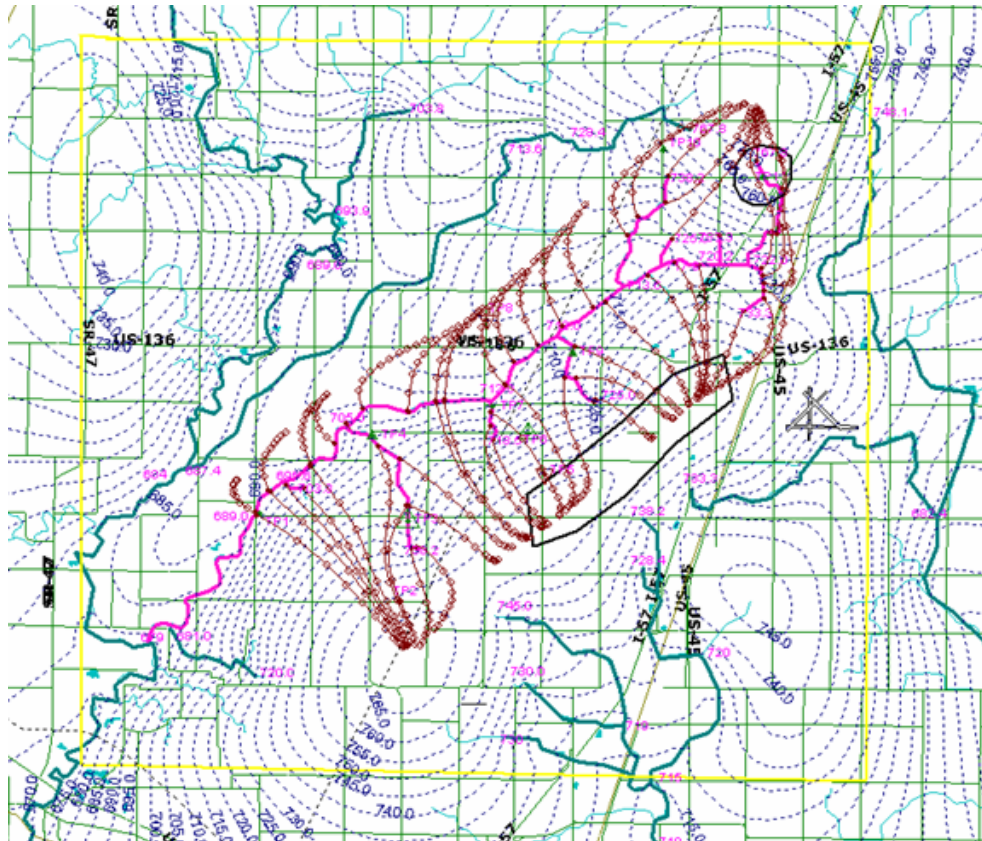For all cases, base elevation of aquifer was set at 660 feet and porosity at 0.20.

Figure 2.16 GFLOW modeling results showing particle tracking

Stream flow at the outlet near well 1 was a significant parameter for developing a realistic model for the watershed. Stream flow varied linearly with the recharge rate (cases 1, 2 & 3, Table 2.6). For example, increasing the recharge rate 50% produced a 50% increase in stream flow at well 1 and also increased groundwater levels. Using cases 1, 2, 3, and other unreported cases, the stream flow at well 1 was linearly related to areal recharge as follows:

$$Q= 13777r + 0.4155$$

where   Q= stream flow at well 1 (cfs)
                     r= areal recharge (ft/day)

For constant values of transmissivity (transmissivity is the product of hydraulic conductivity and aquifer thickness) (cases 1 & 4), no changes in stream flow or water levels in wells were observed. When the ratio of recharge over hydraulic conductivity was held constant (cases 1, 5 & 6), water levels in wells and stream flow changed significantly. Stream flow is known to be a sensitive parameter for defining steady-state groundwater flow (Mitchell-Bruker and Haitjema, 1996).

GFLOW allows a modeler to trace particles through the flow system. Particles were added to locations along Big Ditch and traced backwards. For case 1, these particles were added to the base of the aquifer and traced for 100 years (Figure 2.16). The particle traces show the relative speed of steady-state groundwater flow in the shallow groundwater of the watershed. This modeling shows

that a portion of the groundwater moving through the watershed to Big Ditch has a long residence time, ranging from decades to 100 years. Using Figure 2.16, the "groundwater watershed" was determined to be 40 square miles, which is approximately the same size as the actual Big Ditch watershed (i.e., the watershed defined by surface water flow). The watersheds defined by surface water and shallow groundwater generally coincide, probably because the watershed is also located at the upper end of the regional watershed. Winter et al. (2003) noted that surface water and groundwater watersheds generally do not coincide, except for situations similar to the Big Ditch watershed.

2.5.2 Modeling Discussion
The hydraulic conductivity was determined by model calibration to be 37.5 ft/day, which is much greater than the values determined by slug tests. Slug tests in the shallow wells yielded values of hydraulic conductivity ranging from 0.15 to 13 ft/day with a median of 0.82 ft/day. This difference between the modeled and slug test K was also noted by Haitjema (1992) for a model of shallow groundwater flow in central Indiana. In our case, a higher value of K for the model may reflect flow through macropores, such as dessication cracks, root channels, worm holes, etc., that are prominent in the shallow geologic materials. This increase in hydraulic conductivity at larger scales is known as the scale effect (Desbarats, 1992) and has been attributed to geologic heterogeneity and the type of flow (radial vs unidirectional flow) (Rovey, 1998).

Inherent in the modeling conducted here was the assumption that all groundwater flows through the surficial aquifer. That is, all the water that infiltrates moves through the shallow geologic materials and discharges to the stream. However, from the vertical hydraulic gradients, we know that the shallow aquifer will recharge the deeper aquifer. One way to explain this apparent anomaly is to consider two components of infiltration—one component of the total infiltration moves through the shallow geologic materials and another component recharges the deeper aquifer. With GFLOW, we only accounted for the portion of the infiltration that flows through the shallow materials.

Using a groundwater flow model, we estimated recharge for the watershed at 1.8 in/year. This value is less than half of the range of 3.9 to 4.9 in/yr estimated for the Upper Sangamon River watershed (Arnold et al., 2000). Arnold et al. (2000) used the SWAT model to estimate water balances for 131 watersheds in the Upper Mississippi River basin based on soils, hydrology, agronomic and long-term weather data. SWAT was calibrated based on average precipitation. Our model was calibrated for conditions after two years of below average precipitation, so our recharge estimate seems reasonable.

3. GROUNDWATER CHEMISTRY OF THE BIG DITCH WATERSHED

The primary focus of our sampling was to determine the spatial and temporal distribution of nitrogen and phosphorus. A limited number of samples were collected and analyzed for other analytes to help us better understand the N chemistry within the watershed. These analytes included selected anions and cations, CFCs, and other parameters to define the relative age of groundwater and to define the redox conditions.

3.1 Methods

Analytical methods for nitrate (NO_3-N) and ammonium (NH_4-N) have been developed and validated. No analytical method is available for organic nitrogen (Org-N), because it is comprised of many compounds. In the total Kjeldahl nitrogen (TKN) method, the amino sugars, amino acids, peptides, and proteins that comprise Org-N in a water sample are hydrolyzed to produce NH_3. TKN, therefore, includes Org-N and NH_4-N. Org-N is calculated by subtracting NH_4-N from TKN (Clesceri et al., 1998).

3.1.1 Sampling Methods

Each well had a dedicated sampling tube (3/8 in. O.D., 1/4 in. I.D. polyethylene) that reached from the top of the well casing to the bottom of the screen. The tubes were installed in all wells at sites 1-3, 5-8, 10, and 11 and left in place. For sites 4 and 9, dedicated tubes were used only when samples were collected because of the size of the pressure transducers installed in these wells. A peristaltic pump was used to collect water samples from all wells except well 10D. The water level in that well was too low to use a peristaltic pump, so a submersible pump was used.

Before sampling a well, the water level was measured as described in Section 2.2.4. The peristaltic pump was then attached to the tubing and to a flow cell containing probes for temperature (T), specific conductance (SpC), pH, oxidation-reduction potential (ORP), and dissolved oxygen (DO) (Hydrolab MiniSonde®, Austin, TX). The well was purged (pumped) at a flow rate of approximately 250 mL/min while monitoring the various measurements. Purging continued until the measurements stabilized or a minimum of 5 minutes. During a typical well purge, these measurements varied as shown in Figure 3.1. The conductivity and dissolved oxygen measurements were unstable initially because the cell had not yet filled with water. After stabilization, the measurements were recorded. The pump was detached from the flow cell and attached to a 0.45 μm filter (Groundwater Capsule®, Gelman, Ann Arbor, MI) for sample collection.

All samples were filtered to avoid collecting particulate or colloidal material that would normally be immobile in the subsurface flow system but may be mobilized by the high flow rate in the vicinity of the well screen caused by pumping. After allowing roughly 100 mL to flow through the filter to waste, separate samples were collected for nitrate, ammonia/TKN/total P, and total organic carbon (TOC). The container materials and preservatives are given in Table 3.1.

Grab samples were collected from surface water and tiles. Specific conductance and temperature were usually monitored using an Orion meter (model 115) prior to collection of grab samples.
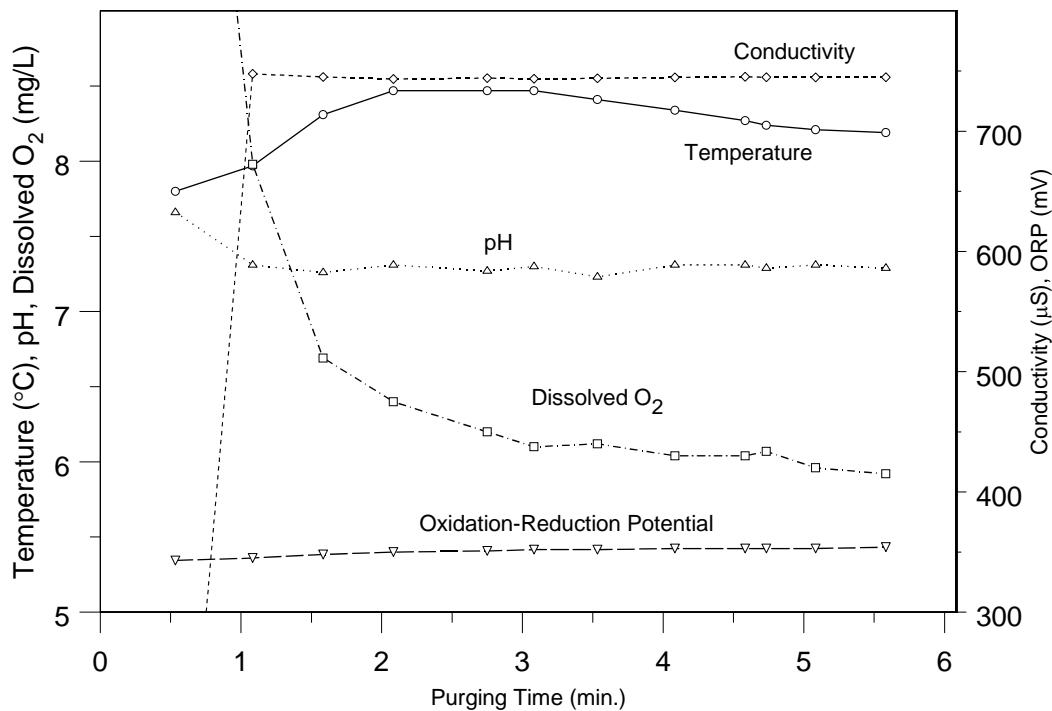
Figure 3.1 Typical variation of temperature, conductivity, pH, oxidation-reduction potential, and dissolved oxygen with purging time from well 8S on February 20, 2002.

Table 3.1 Container materials and analyte preservatives

Analyte	Material	Preservative
Nitrate	HDPE[1]	None
TKN, NH_4^+-N, Total P	HDPE	0.2% H_2SO_4[2]
TOC	Glass	0.2% H_2SO_4

Notes: 1= High-density polyethylene
        2= % by volume

There were some exceptions to the sampling procedure described above. For part of each year, wells 1S and 4S were pumped dry within 5 minutes. When this happened, the last measurements were recorded and the sampling apparatus was moved to the deep well for sampling while the water level in the shallow well was allowed to recover. After purging and sampling the deep well, the sampling apparatus was moved back to the shallow well and samples were collected. The water level in well 3S recovered too slowly to allow sample collection after it was pumped dry. After several sampling events, it became apparent at which water levels it was possible to purge and sample this well. For lower water levels, water samples were collected without purging. The

submersible pump used to sample well 10D had a fixed speed and it pumped the well dry in less than 2 minutes. The water level in this well recovered very slowly. Therefore, after the first sampling event, water samples were collected from this well without purging. Because of the difficulty in sampling well 10D, no samples were collected from it after October 16, 2001.

Duplicate samples were collected from one well per day. One set of blank samples was collected per day by pumping deionized water through the filter. Duplicate and blank samples were submitted as regular samples. After sample collection, the water samples were stored on ice in a cooler for transport to the laboratory.

All wells were sampled quarterly in calendar years 2000 (CY00), CY01, and CY03. The wells with the highest total N concentrations were sampled at least bimonthly in CY01. The wells nearest the ditch (1, 3, 4, 7, 9, and 11) were sampled at least bimonthly in CY02 and CY03.

3.1.2 Analytical Methods

Each sample was tracked on a chain of custody form. The samples and tracking form were relinquished to the analytical laboratory immediately upon return from the field. Samples for nitrate determination were analyzed within 48 hours, usually within 24 hours. All samples were stored at 4°C until they were analyzed. Most analyses were performed by chemists in the ISWS Analytical Chemistry and Technology Unit. The analytical methods used to determine the nutrients (N & P) in this study are presented in Table 3.2.

Table 3.2 Analytical methods to determine the nutrients N, P and TOC

Analyte	Method	Reference
Nitrate	Anion Chromatography	USEPA method 300.0, rev. 2.1[1]
Ammonia	Automated Colorimetry	USEPA method 350.1, rev. 2.0[1]
Total Kjeldahl Nitrogen	NaOH digestion, Automated Colorimetry	USEPA method 351.2, rev. 2.0[1]
Total Phosphorus	NaOH digestion, Automated Colorimetry	USEPA method 365.2[1]
Total Organic Carbon	Persulfate oxidation, Infrared Spectrometry	USEPA method 415.2[2]

1: USEPA (1993)
2: USEPA (1983)

A limited number of water samples were collected and analyzed for anions and cations by the ISGS Geochemistry Laboratory. Anions were determined using a Dionex DX-120 Ion Chromatograph with Ionpac AG14 Guard Column, Ionpac AS14 Analytical Column, and ASRS-ULTRA (4 mm) suppressor module. Analytes were measured with a CDM-3 conductivity detector cell with a DS4 detection stabilizer. The eluent was 3.5mM sodium carbonate and 1.0 mM sodium bicarbonate. The following were approximate retention times in minutes: fluoride, 2.9; chloride, 4.0; bromide, 5.6; nitrate, 6.4; phosphate, 8.0; and sulfate, 9.5. Instrument operation and data collection were controlled using PeakNet 5.01 software. A calibration check standard and blank were run with each analysis set.

Cations were determined by ISGS geochemists with a Thermo Jarrell-Ash Model ICAP 61e inductively coupled plasma spectrometer. The list of elements and their wavelengths in nanometers are: Ca(393.3, 317.9), Fe(259.9, 271.4), K(766.4), Mg(279.5, 383.2), Na(588.9, 330.2), and Si(288.1). Instrument operation, interelement interference correction, background correction, and data collection were controlled using ThermoSPEC/AE 6.20 software. Blanks, calibration check standards, and reference standards were run with each analysis set.

3.2 Description of Groundwater Chemistry of the Watershed-- Nitrogen

The following section compares temporal variations of total N in the wells. Section 3.2.2 describes the concentrations of NH_4-N, Org-N, and NO_3-N in the Big Ditch wells starting with site 11, the site farthest upstream, and working downstream (counting down the site numbers) to site 1, the site near the watershed outlet (Figure 2.1). For each site, the concentration data are displayed in a box-and-whisker plot that summarizes all concentrations and an area plot that shows how the concentrations varied temporally. The uncertainty of Org-N concentrations is reported in section 3.2.3.

3.2.1 Total Nitrogen

The temporal variations in total N in the wells located near the ditch are shown in Figure 3.2. It is expected that these wells reflect the composition of groundwater flowing into the ditch. The open symbols are for the shallow wells and the filled symbols are for the deep wells. Well 3S consistently had 6 to 11 mg/L total N. Well 9D consistently had 1 to 3 mg/L, well 11 often 2 to 6 mg/L, and well 9S sometimes had 1 to 2 mg/L. Otherwise, the rest of the wells near the ditch usually had less than 1 mg/L total N.

The temporal variations in total N in the upland wells, i.e., those wells located at least 100 m from the ditch or its tributaries, are shown in Figure 3.3. The total N in well 6S increased from approximately 4 mg/L in May 2000 to approximately 19 mg/L in summer 2001 and then fluctuated between 16 and 24 mg/L. The total N in well 6D was approximately 4 mg/L in one sample collected in summer 2001 but otherwise was always less than 2 mg/L. Total N in well 5S seemed to vary seasonally, with maxima in the summer and fall of 2000 and 2001 and brief minima in the late winter/early spring of 2001 and 2002. No samples from these wells were analyzed for most of 2002. Total N in well 8S was less than 1 mg/L through October 2001 and above 3 mg/L thereafter.

The total N concentrations in all shallow wells are compared in Figure 3.4. Wells 3S and 6S were the only shallow wells with consistently high total N concentrations. The total N in wells 5S, 8S, 9S, and 11S were above 3 mg/L at times. Wells 1S, 2S, 4S, and 7S were almost always below 1 mg/L. Six wells (1S, 5S, 6S, 7S, 8S & 11S) had peak total N concentrations in water year 2002, which was the only year of normal precipitation and was preceded by 2 years of below normal precipitation. This pattern of N flux has been observed by other researchers (e.g., Goolsby et al., 2001).
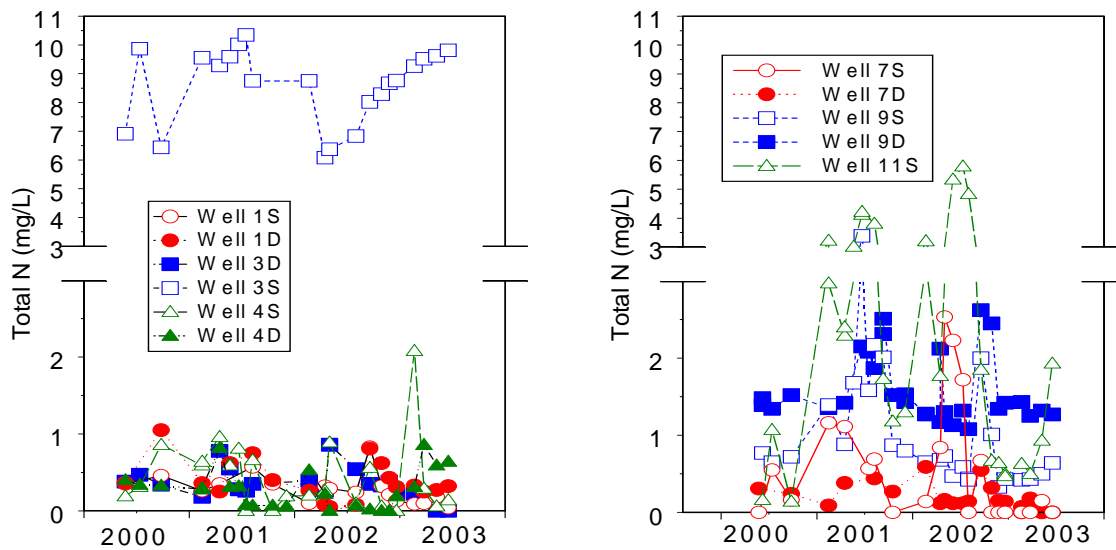
Figure 3.2 Temporal variation of total N concentrations in wells located near the Big Ditch
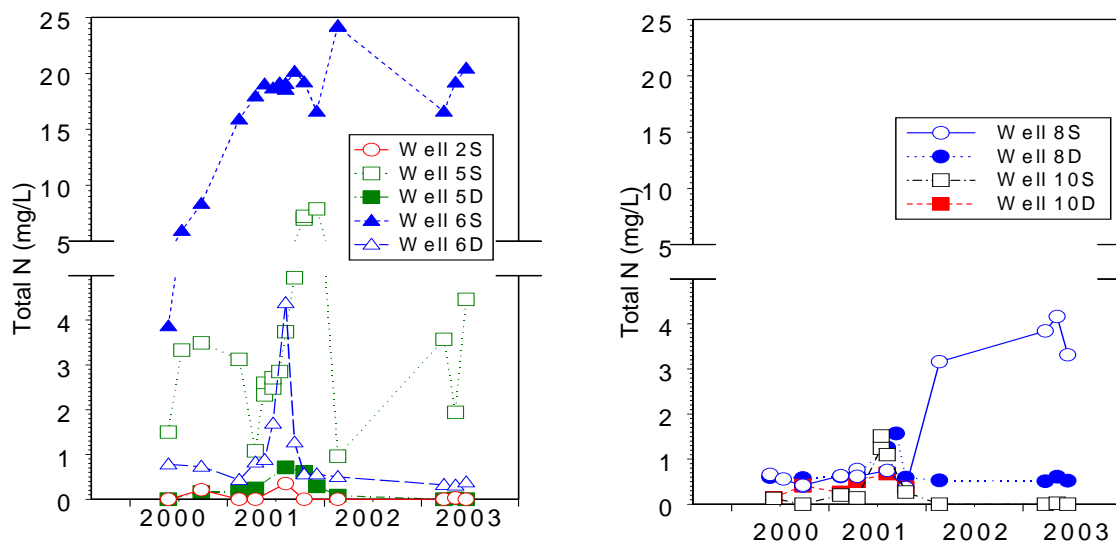

Figure 3.3 Temporal variations of total N concentrations in upland wells
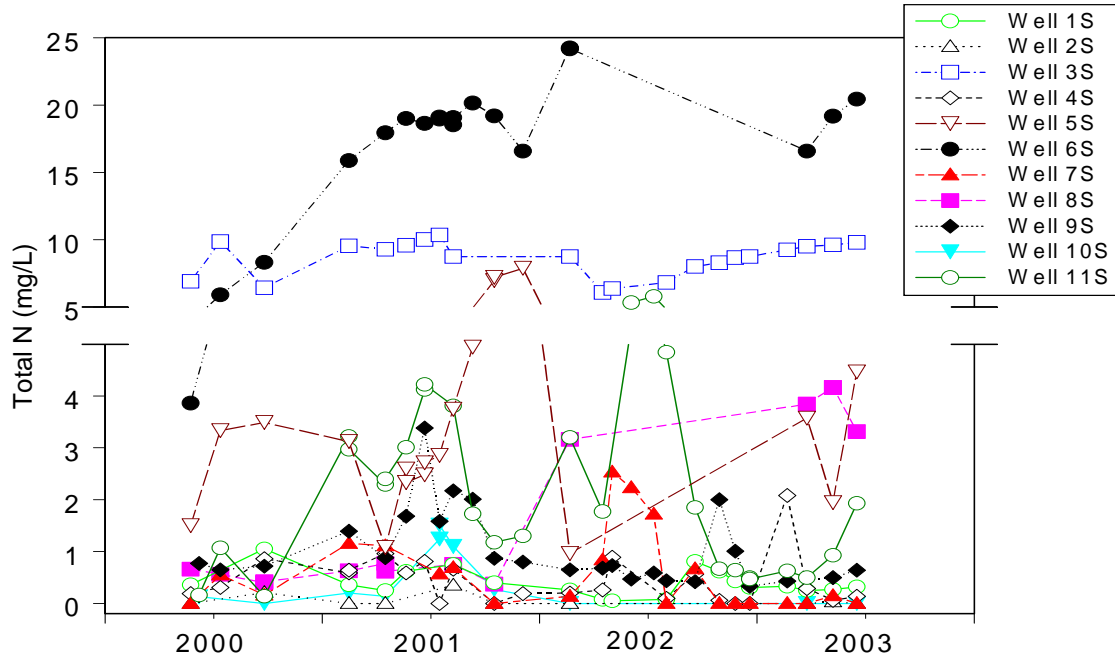
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Figure 3.4 Comparison of total N concentrations in all shallow wells

Descriptive statistics for the N species in the shallow and deep wells are given in Tables 3.3 through 3.5. Overall, N concentrations tended to be low in the groundwater. Only 6 of the 20 wells (5 shallow wells & 1 deep well) had total N concentrations that consistently exceeded 1 mg/L. Nitrate comprised almost 100% of the N in the two wells (3S and 6S) with the highest total N concentrations (median total N = 8 and 18 mg/L). In the other 18 wells, organic N generally comprised 10 to 40% of the total N. Nitrate was rarely detected in the deep wells, while ammonia was rarely detected in the shallow wells. These N concentrations are consistent with the nitrate-N concentrations reported for shallow (10 to 15 ft) and deep wells (>15 feet) in the Walnut Creek watershed, an agricultural watershed in northern Iowa (Cambardella et al., 1999). In the Walnut Creek watershed, samples from shallow wells had a median nitrate-N concentration of 1.8 mg/L and exceeded 10 mg/L in 16% of samples over a 6-year period, while samples from deep wells had a median nitrate-N concentration of 1.1 mg/L and exceeded 10 mg/L in 4% of samples. Nitrate-N was not expected in deep groundwater of the Walnut Creek watershed because it was considered geochemically unstable (Eidem et al., 1999).

Table 3.3 Descriptive statistics for N species at sites 1 through 5

	Well 1D			Well 1S			Well 2S		
	NH4-N	NO3-N	TKN	NH4-N	NO3-N	TKN	NH4-N	NO3-N	TKN
Samples		20			20			10	
Nondetects	1	13	7	2	13	10	9	10	8
Minimum	0.00	0.00	0.15	0.00	0.00	0.00	0.00	0.00	0.00
25%	0.07	0.00	0.27	0.05	0.00	0.00	0.00	0.00	0.00
Median	0.25	0.00	0.32	0.08	0.00	0.07	0.00	0.00	0.00
75%	0.30	0.20	0.43	0.12	0.08	0.28	0.00	0.00	0.00
Maximum	0.40	0.28	0.57	0.23	0.26	1.05	0.03	0.00	0.35
Range	0.40	0.28	0.42	0.23	0.26	1.05	0.03	0.00	0.35
Mean	0.20	0.07	0.35	0.09	0.04	0.21	0.00	0.00	0.06
StDev	0.12	0.11	0.13	0.05	0.07	0.30	0.01	0.00	0.12

	Well 3D			Well 3S			Well 4D		
	NH4-N	NO3-N	TKN	NH4-N	NO3-N	TKN	NH4-N	NO3-N	TKN
Samples		21			22			21	
Nondetects	4	7	11	17	0	16	11	8	12
Minimum	0.00	0.00	0.00	0.00	5.26	0.00	0.00	0.00	0.00
25%	0.05	0.00	0.00	0.00	7.06	0.00	0.00	0.00	0.00
Median	0.19	0.11	0.00	0.00	8.76	0.00	0.00	0.07	0.00
75%	0.26	0.21	0.28	0.00	9.50	0.11	0.09	0.09	0.23
Maximum	0.36	0.38	0.59	0.65	10.10	0.52	0.26	0.16	0.70
Range	0.36	0.38	0.59	0.65	4.84	0.52	0.26	0.16	0.70
Mean	0.16	0.13	0.17	0.04	8.35	0.07	0.06	0.06	0.14
StDev	0.12	0.13	0.21	0.14	1.44	0.13	0.09	0.05	0.19

	Well 4S			Well 5D			Well 5S		
	NH4-N	NO3-N	TKN	NH4-N	NO3-N	TKN	NH4-N	NO3-N	TKN
Samples		25			12			16	
Nondetects	11	8	12	7	7	1	13	0	0
Minimum	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.86	0.14
25%	0.00	0.00	0.00	0.00	0.00	0.00	0.00	1.91	0.22
Median	0.00	0.07	0.14	0.00	0.00	0.00	0.00	3.08	0.27
75%	0.04	0.22	0.32	0.06	0.07	0.17	0.00	3.69	0.60
Maximum	0.49	2.08	1.16	0.18	0.61	0.65	0.24	7.88	0.89
Range	0.49	2.08	1.16	0.18	0.61	0.65	0.24	7.02	0.76
Mean	0.04	0.24	0.24	0.04	0.08	0.11	0.02	3.26	0.41
StDev	0.10	0.46	0.31	0.07	0.17	0.19	0.06	1.90	0.24

Table 3.4 Descriptive statistics for N species at sites 6 through 9

	Well 6D			Well 6S			Well 7D		
	NH4-N	NO3-N	TKN	NH4-N	NO3-N	TKN	NH4-N	NO3-N	TKN
Samples	15			17			20		
Nondetects	5	1	3	15	0	12	8	12	10
Minimum	0.00	0.00	0.00	0.00	3.86	0.19	0.00	0.00	0.14
25%	0.00	0.24	0.07	0.00	16.58	0.24	0.00	0.00	0.17
Median	0.14	0.29	0.43	0.00	18.40	0.27	0.07	0.00	0.25
75%	0.35	0.46	0.61	0.00	19.19	0.30	0.14	0.08	0.30
Maximum	0.57	3.63	1.04	0.04	24.24	0.71	0.20	0.59	0.44
Range	0.57	3.63	1.04	0.04	20.38	0.52	0.20	0.59	0.30
Mean	0.19	0.55	0.39	0.00	16.81	0.34	0.07	0.06	0.25
StDev	0.19	0.88	0.37	0.01	5.65	0.21	0.07	0.13	0.10

	Well 7S			Well 8D			Well 8S		
	NH4-N	NO3-N	TKN	NH4-N	NO3-N	TKN	NH4-N	NO3-N	TKN
Samples	22			11			11		
Nondetects	8	12	10	0	11	0	9	0	2
Minimum	0.00	0.00	0.13	0.35	0.00	0.50	0.00	0.37	0.12
25%	0.00	0.00	0.23	0.47	0.00	0.52	0.00	0.39	0.19
Median	0.00	0.00	0.24	0.50	0.00	0.60	0.00	0.51	0.24
75%	0.00	0.72	0.50	0.53	0.00	0.64	0.00	2.82	0.26
Maximum	0.02	2.53	0.69	0.64	0.00	1.57	0.14	3.97	0.84
Range	0.02	2.53	0.56	0.29	0.00	1.07	0.14	3.60	0.72
Mean	0.00	0.45	0.35	0.50	0.00	0.72	0.01	1.50	0.30
StDev	0.01	0.77	0.22	0.07	0.00	0.35	0.04	1.54	0.21

	Well 9D			Well 9S		
	NH4-N	NO3-N	TKN	NH4-N	NO3-N	TKN
Samples	25			26		
Nondetects	0	25	0	0	8	0
Minimum	0.98	0.00	0.97	0.10	0.00	0.33
25%	1.08	0.00	1.27	0.17	0.00	0.36
Median	1.14	0.00	1.35	0.36	0.09	0.58
75%	1.19	0.00	1.51	0.48	0.14	0.76
Maximum	1.35	0.00	2.31	1.18	0.89	3.11
Range	0.37	0.00	1.33	1.07	0.89	2.78
Mean	1.14	0.00	1.46	0.39	0.14	0.82
StDev	0.10	0.00	0.32	0.26	0.20	0.68

Table 3.5 Descriptive statistics of N species at sites 10 and 11

	Well 10D			Well 10S			Well 11S		
	NH4-N	NO3-N	TKN	NH4-N	NO3-N	TKN	NH4-N	NO3-N	TKN
Samples	7			11			24		
Nondetects	4	5	0	7	10	3	22	2	11
Minimum	0.00	0.00	0.14	0.00	0.00	0.13	0.00	0.00	0.13
25%	0.00	0.00	0.22	0.00	0.00	0.19	0.00	0.64	0.22
Median	0.00	0.00	0.26	0.00	0.00	0.22	0.00	1.21	0.22
75%	0.11	0.07	0.39	0.09	0.00	0.48	0.00	3.05	0.30
Maximum	0.19	0.32	0.55	0.40	0.09	1.15	0.38	5.80	0.72
Range	0.19	0.32	0.41	0.40	0.09	1.02	0.38	5.80	0.59
Mean	0.06	0.06	0.31	0.08	0.01	0.43	0.02	1.96	0.29
StDev	0.08	0.12	0.14	0.15	0.03	0.43	0.08	1.69	0.19

3.2.2 Nitrogen Species

The concentrations of NH_4-N, Org-N, and NO_3-N in the groundwater samples from well 11S are summarized in Figure 3.5, which is a box and whisker plot. For each plot, the top and bottom of the rectangle (box) show the 75th and 25th percentiles while the line with a solid dot indicates the median concentration. The lines extending from the top and bottom of the box (whiskers) indicate the maximum and minimum concentrations.   The y-axis is split because some wells had high concentrations of some N species, while most other wells had low concentrations. Nitrate was the predominant N species, with a median concentration of approximately 1 mg/L as N. The median concentrations of NH_4-N and Org-N were below the detection limits and these species were only detected in a few samples.

Figure 3.6, an area graph, shows how the concentrations of the N species in well 11S varied over time. The concentrations of NH_4-N, Org-N, and NO_3-N are shown in dark, medium, and light shading. The N species concentrations are stacked with NH_4-N on the bottom, Org-N in the middle, and NO_3-N on top of Org-N. The line along the top of NO_3-N is the sum of the NH_4-N, Org-N, and NO_3-N concentrations, i.e., the total dissolved N concentration. The series of vertical dashes in the middle of the graph show when samples were collected. The date listed on the x-axis shows July 1st for the given year. As for the box plots, the area plots all have the same y-axis for ease of comparison, which has been split to show low and high concentrations. The maximum NO_3-N and total N concentrations were found in the summer of 2000 and 2001 with peak values from 4 to 5 mg/L as N. The minimum values of 0.5 to 1.2 mg/L were found in the winter.

The NH_4-N and NO_3-N concentrations in both wells at site 10 were quite low, with median values
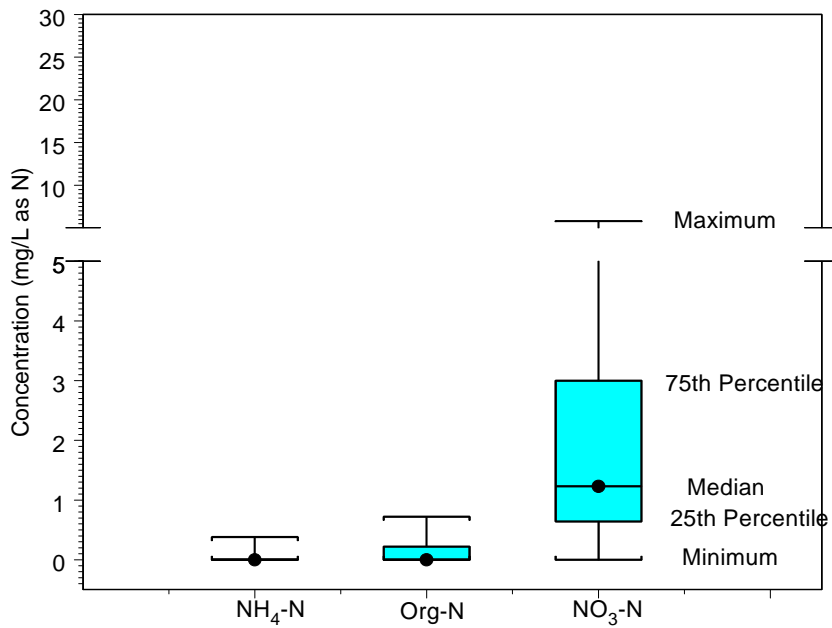
Figure 3.5 Summary of N species concentrations in well 11S
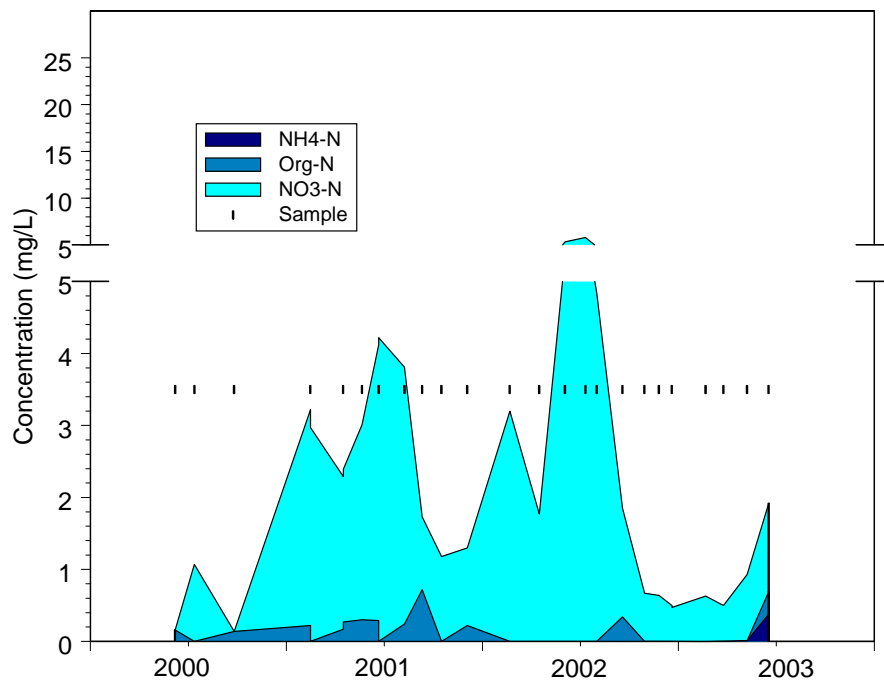

Figure 3.6 Temporal variation of N species concentrations in well 11S (For the x-axis, the date denotes July 1 of the given year.)

below the detection limits and maximum values of 0.4 mg/L or less (Figure 3.7). Org-N concentrations were only slightly higher. There was a spike in both NH_4-N and Org-N in well 10S in summer 2001, with the total N reaching about 1.3 mg/L (Figure 3.8). All N species were undetectable in nearly all samples from well 10S in 2002 and 2003. The Org-N concentration in samples from well 10D was nearly constant at 0.2 to 0.3 mg/L, while the NH_4-N and NO_3-N concentrations varied from below detection to 0.2 mg/L.

NH_4-N and Org-N were the predominant N species in both wells at site 9 (Figure 3.9). The concentrations of NH_4-N and Org-N were generally higher in well 9D than in 9S. NO_3-N was undetectable in all samples from well 9D and most from 9S. NH_4-N and Org-N spiked in both wells at site 9 in the summer of 2001 and summer-fall of 2002 (Figure 3.10).

Nitrate was the predominant N species in well 8S, while Org-N was often found at low concentrations, and NH_4-N was usually undetectable (Figure 3.11). Nitrate was undetectable in all samples from well 8D. The concentrations of all N species were usually below 1 mg/L in both wells, although NO_3-N concentrations in well 8S were occasionally as high as 4 mg/L. NO_3-N concentrations in well 8S were sharply higher in 2002 than in 2000 and 2001 (Figure 3.12). The NH_4-N concentration was practically constant in well 8D. Org-N values were near or below the detection limit, except for a spike in Org-N in well 8D in summer 2001. The median values of all three N species in well 7S and those of Org-N and NO_3-N in well 7D were below the detection limits, although NO_3-N concentrations in well 7S were occasionally as high as 2 mg/L (Figure 3.13). The highest total N concentrations in well 7S occurred in the spring of 2001 and 2002 when nitrate was the predominant N species (Figure 3.14). No temporal trends are apparent in the data for well 7D.

The predominant N species in well 6S was nitrate, while the median values of NH_4-N and Org-N were below the detection limits (Figure 3.15). Well 6S had the highest total N concentrations measured in the project, with a median value of approximately 19 mg/L. In well 6D, all three N species occurred in roughly equal concentration ranges. The NO_3-N concentration in well 6S increased from the beginning of the project to spring 2002 and then fluctuated above and below 20 mg/L (Figure 3.16). The only samples with detectable Org-N were collected from the fall 2001 through spring 2002. Total N concentrations in that well were essentially constant, except for a spike in NO_3-N in well 6D in summer 2001.

The surficial soils in this watershed are similar in texture (mostly silt loams and silty clay loams, see Table 2.2 and Figure 2.6) and have sufficient organic matter (2 to 7% by weight) to support denitrification. However, soil drainage may contribute to the high nitrate-N concentrations observed in well 6S. The predominant soil around well 6S is a well drained soil, while most soils in the watershed are somewhat poorly to poorly drained.

The predominant N species in well 5S, like well 6S, was nitrate (Figure 3.17). The minimum NO_3-N concentration was greater than all but the maximum Org-N concentration. The median values of NH_4-N in well 5S and all three N species in well 5D were below detection. Except for samples
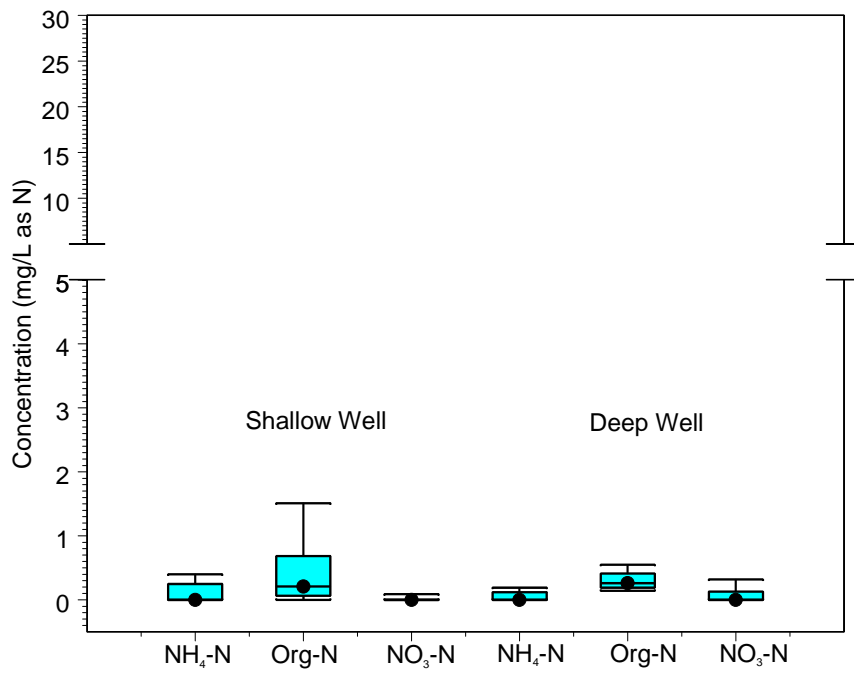
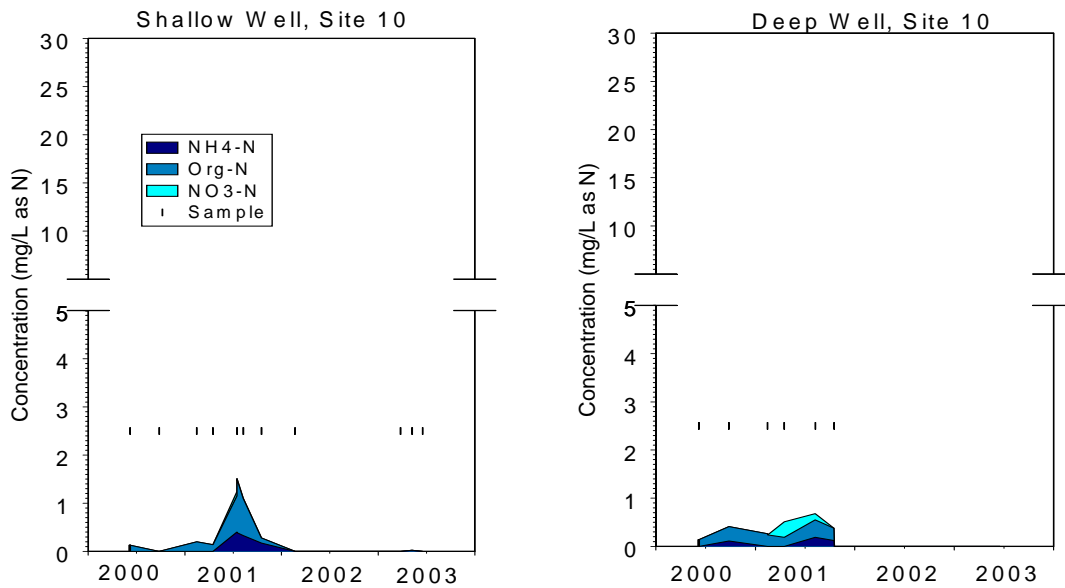Figure 3.7 Summary of N species concentrations in wells 10S and 10D

Figure 3.8 Temporal variation of N species concentrations in wells 10S and 10D
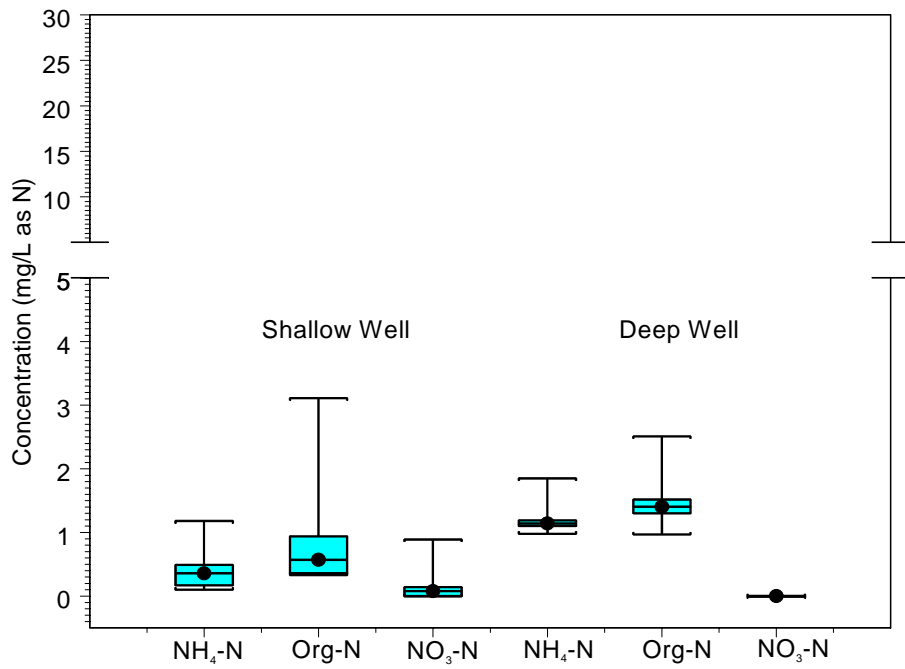
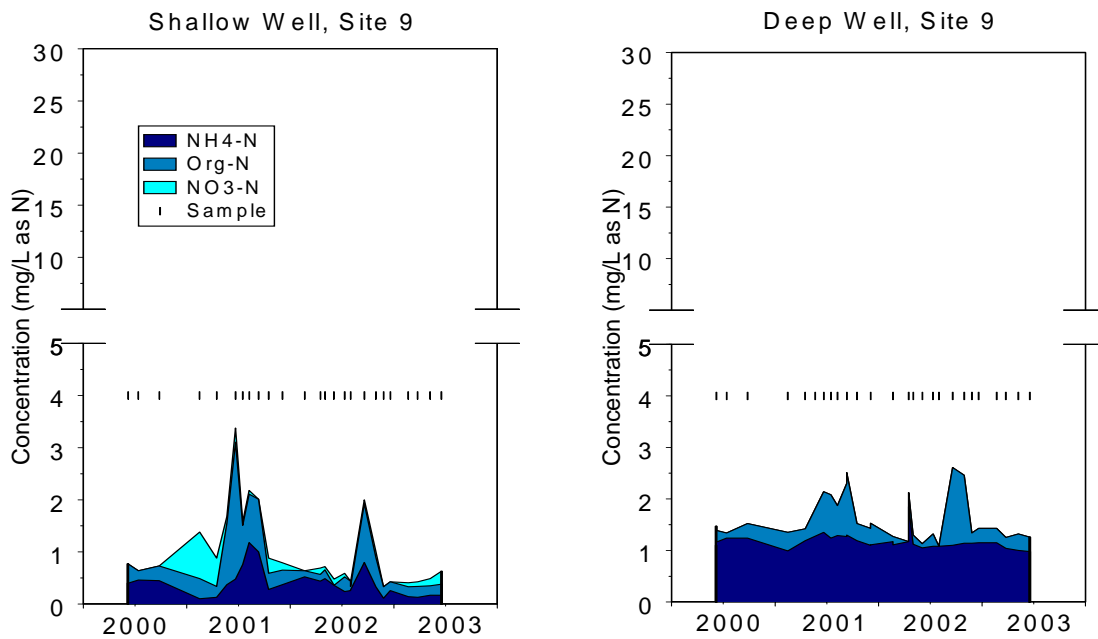Figure 3.9 Summary of N species concentrations for wells 9S and 9D

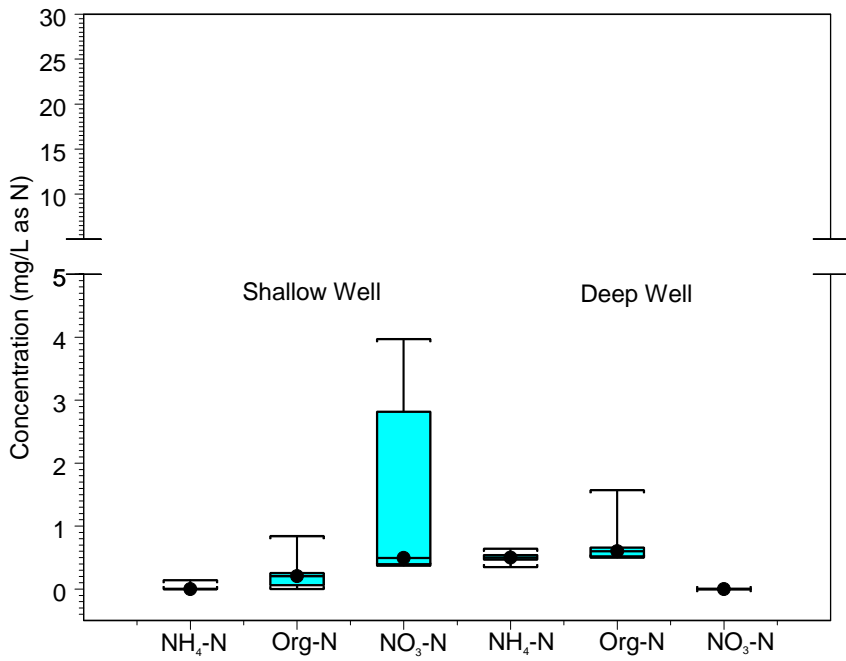Figure 3.10 Temporal variation of N species concentrations in wells 9S and 9D

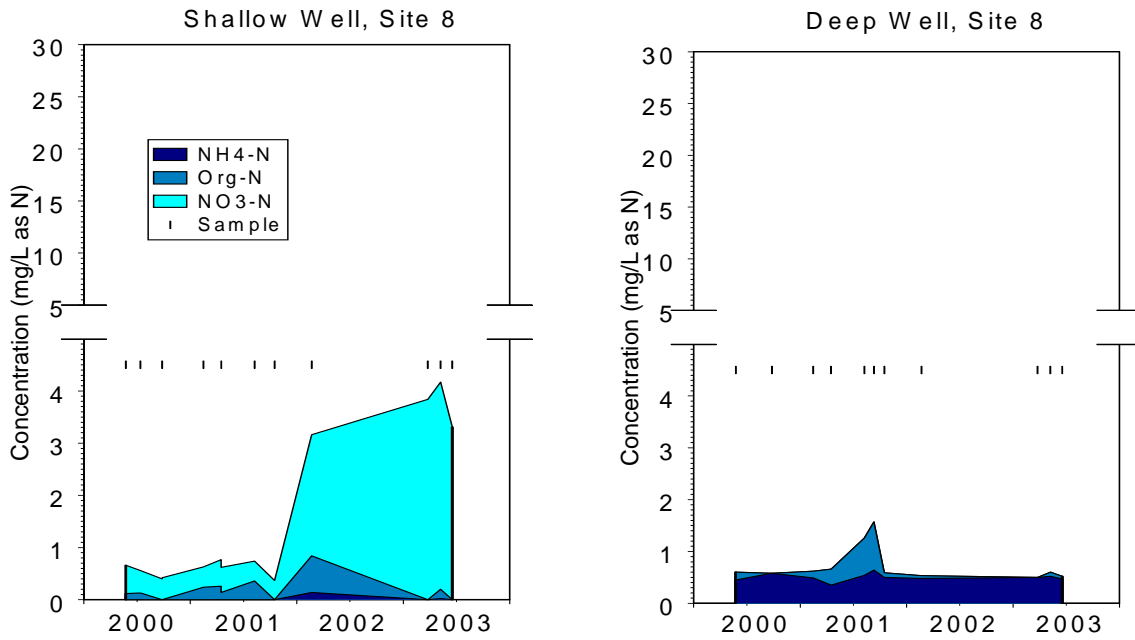Figure 3.11 Summary of N species concentrations for wells 8S and 8D

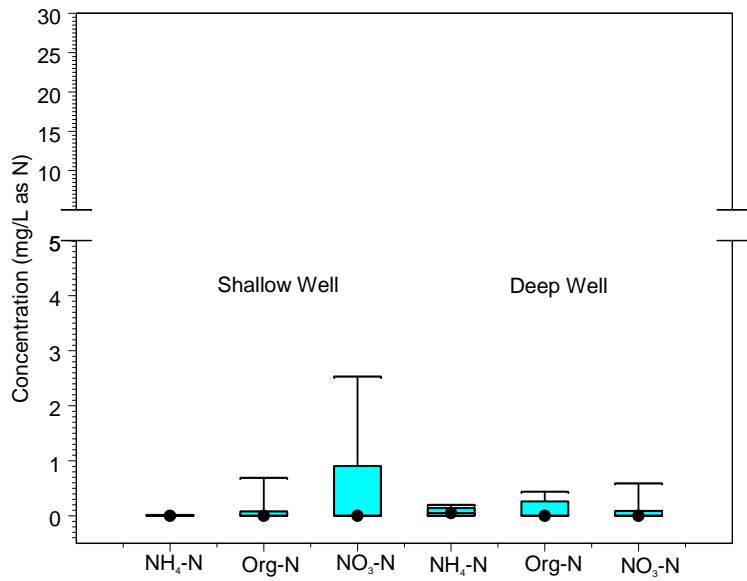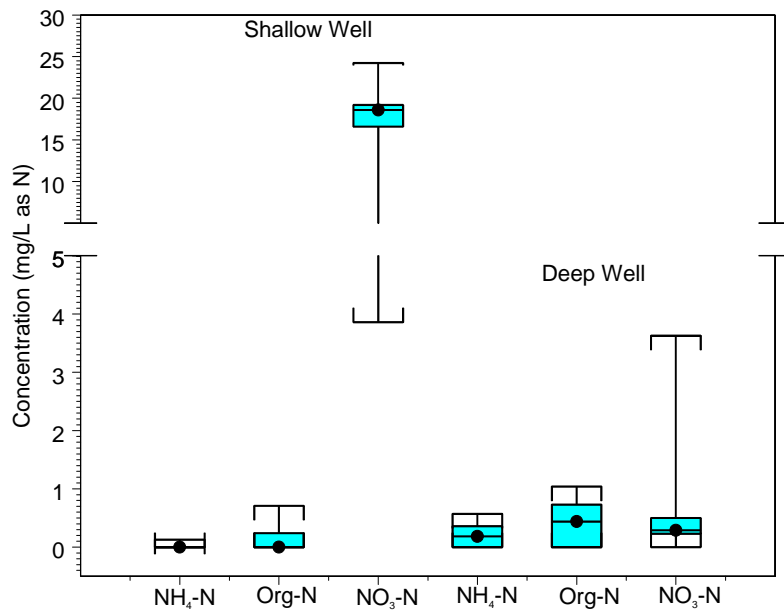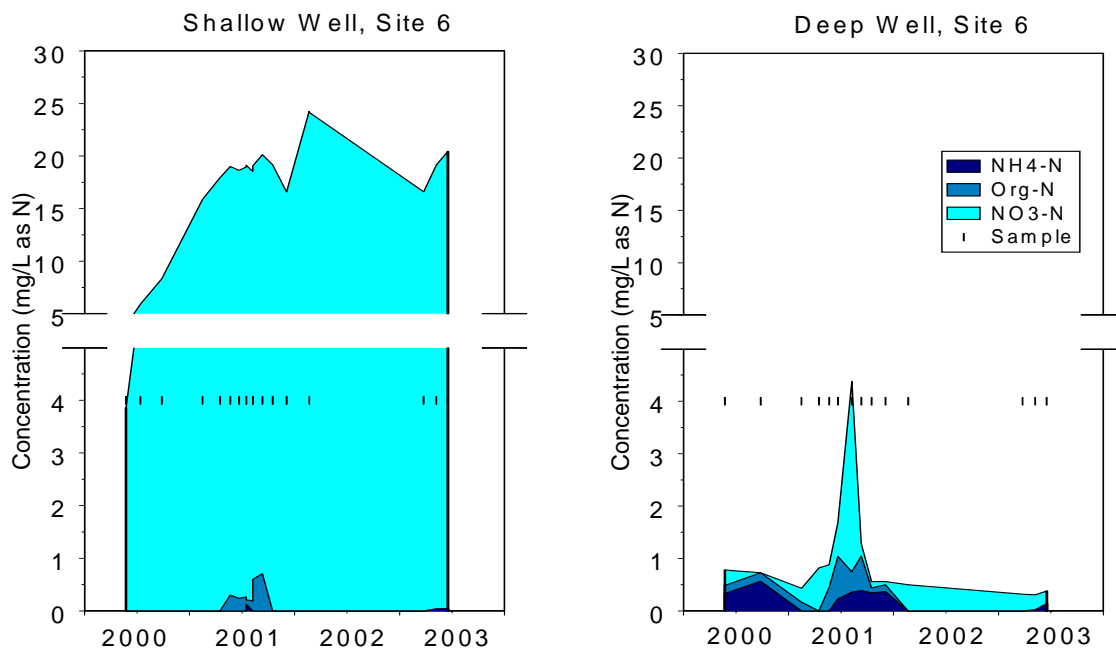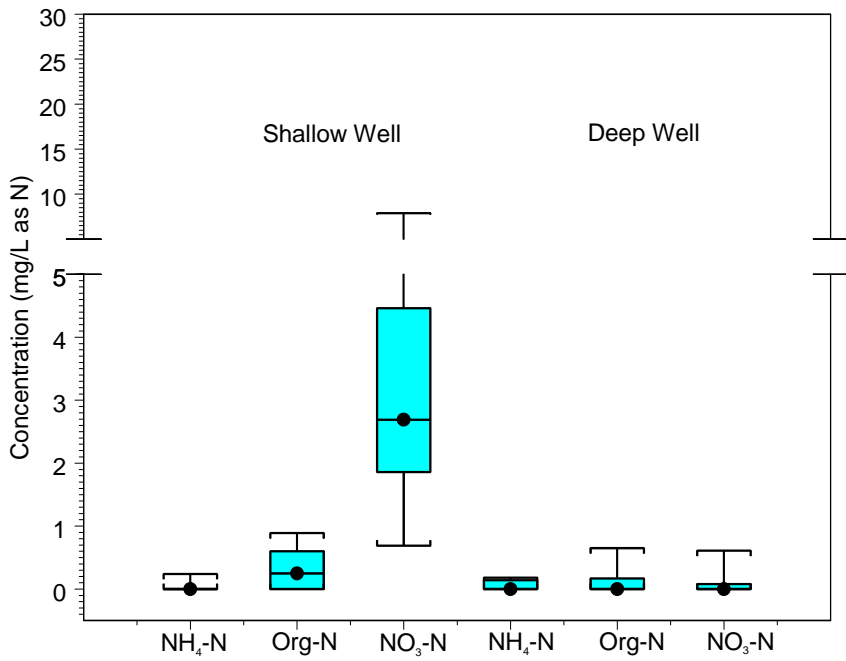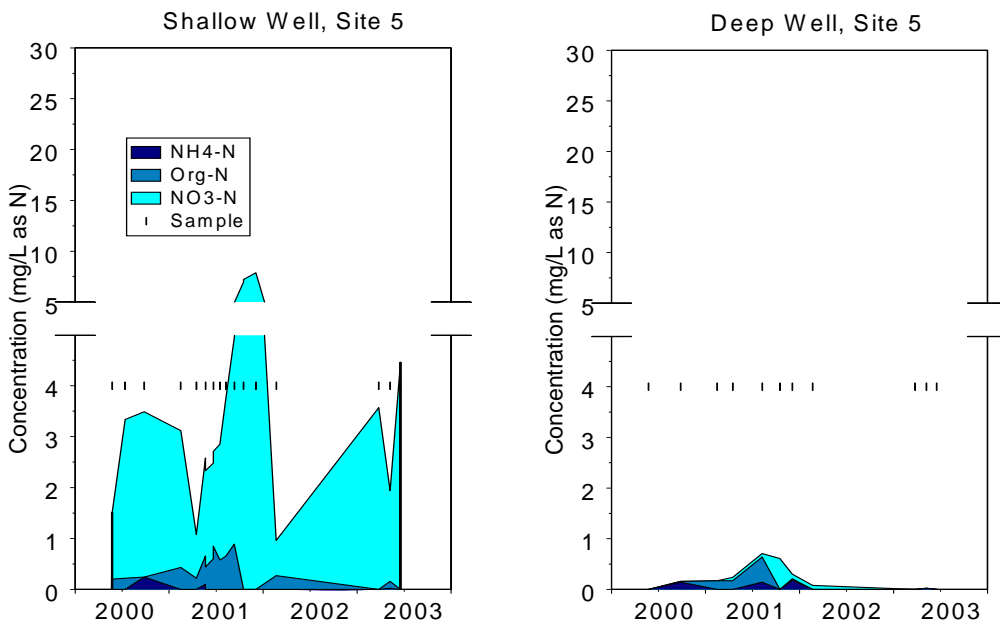Figure 3.12 Temporal variation of N species in wells 8S and 8D

Figure 3.13 Summary of N species concentrations in wells 7S and 7D
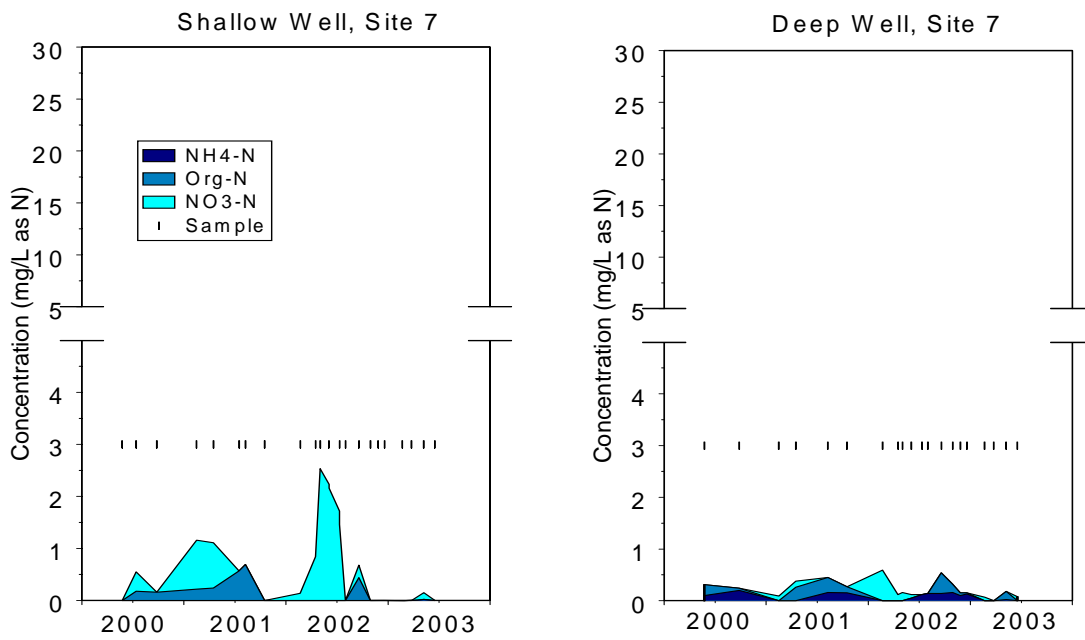
Figure 3.14 Temporal variation of N species in wells 7S and 7D

Figure 3.15 Summary of N species concentrations in wells 6S and 6D

Figure 3.16 Temporal variation of N species concentrations in wells 6S and 6D

Figure 3.17 Summary of N species concentrations in wells 5S and 5D

Figure 3.18 Temporal variation of N species concentrations in wells 5S and 5D

collected in spring 2001 and winter 2002, the NO_3-N and total N concentrations in well 5S fluctuated between 2.5 and 5 mg/L (Figure 3.18). The maximum total N concentration occurred in the summer and fall 2001. During this period, the predominant N species was Org-N in 5D samples and NO_3-N in 5S samples.

The concentrations of all three N species in both wells at site 4 were low in most samples, with median concentrations between the detection limits and ~0.1 mg/L (Figure 3.19). Org-N and NO_3-N concentrations as high as 1 mg/L and 2 mg/L, respectively, were found in a few samples. NH_4-N, Org-N, and NO_3-N were the predominant N species in well 4S at different times (Figure 3.20). There were no obvious temporal patterns in either N speciation or total N. The total N concentration in well 4D generally declined from the beginning of the project to the end, although minor spikes in Org-N and total N were observed in the summers of 2001 and 2002.

Nitrate was the dominant N species in well 3S (Figure 3.21). The median Org-N and NH_4-N concentrations in this well were both below the detection limits. In well 3D, the NH_4-N, Org-N, and NO_3-N values were all in roughly the same low range. No temporal trends in NO_3-N or total N were apparent in well 3S data (Figure 3.22). In well 3D, the highest concentrations of all three N species occurred in the summer and fall of 2000, 2001, and 2002.

All three N species were almost always undetectable in samples from well 2S (Figure 3.23). The only samples in which Org-N was detected were collected in the summer/fall of 2000 and 2001 and spring of 2002 (Figure 3.24).

All three N species concentrations were below 0.4 mg/L in almost all samples from wells 1S and 1D. The median NO_3-N values for both wells were both below the detection limit (Figure 3.25). One sample from well 1S had an Org-N concentration of approximately 1 mg/L. The predominant N species in well 1S was usually NH_4-N with maximum concentrations in the summer and fall of 2000, 2001, and 2002 and minimum concentrations in the spring (Figure 3.26). The predominant N species in well 1D was usually Org-N. The maximum Org-N concentrations were found in summer and fall of 2000 and 2001 and in spring 2002.

The nitrate-N and TKN concentrations in well 1S were similar to those concentrations in the Big Ditch during periods of low flow, but not during other times (Figure 3.27).
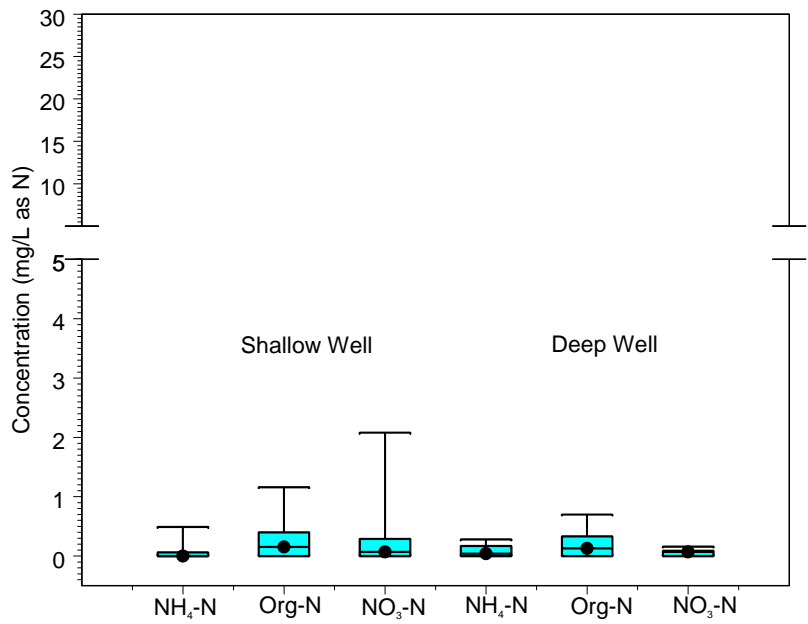
Figure 3.19 Summary of N species concentrations in wells 4S and 4D
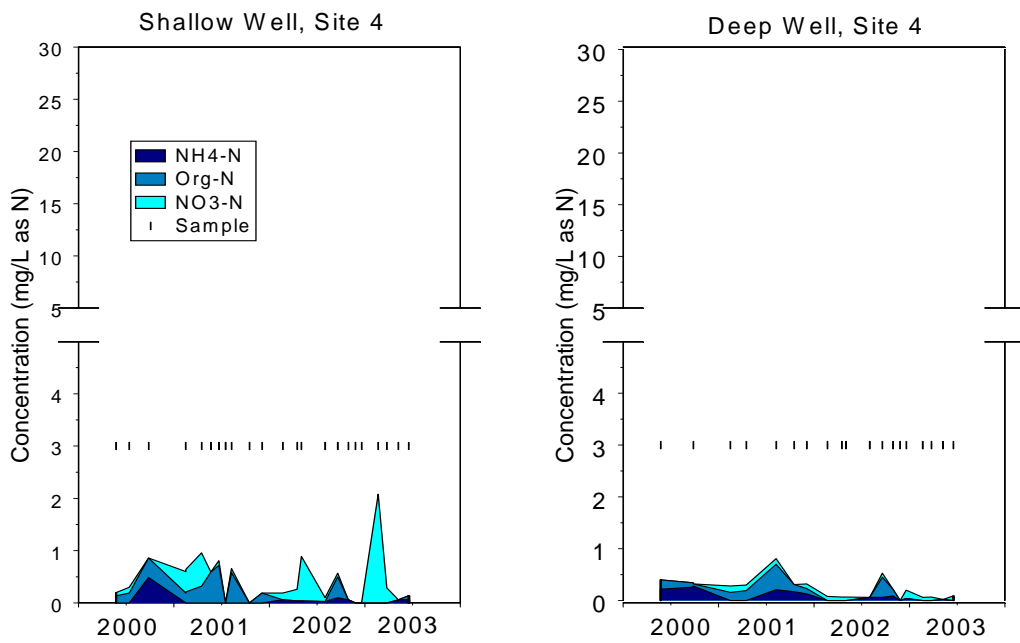

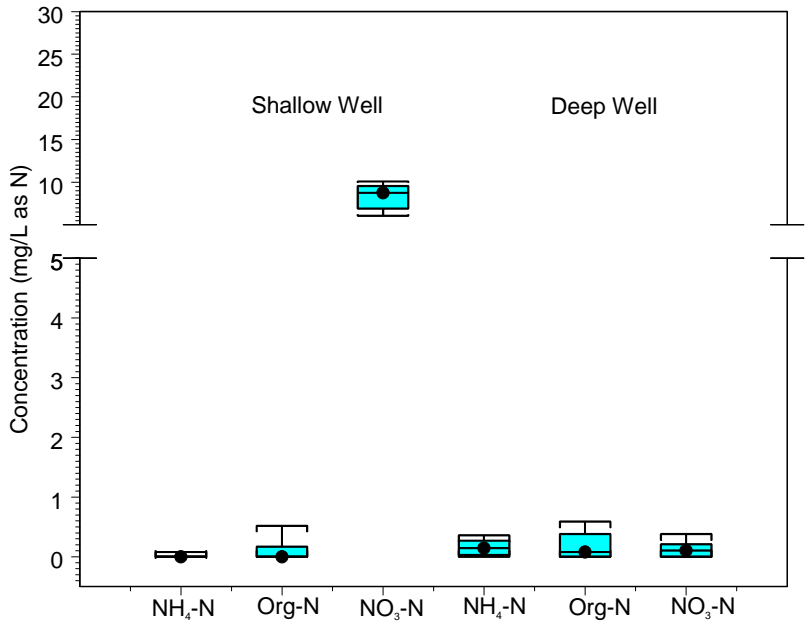Figure 3.19 Temporal variation of N species concentrations in wells 4S and 4D

Figure 3.20 Summary of N species concentrations in wells 3S and 3D
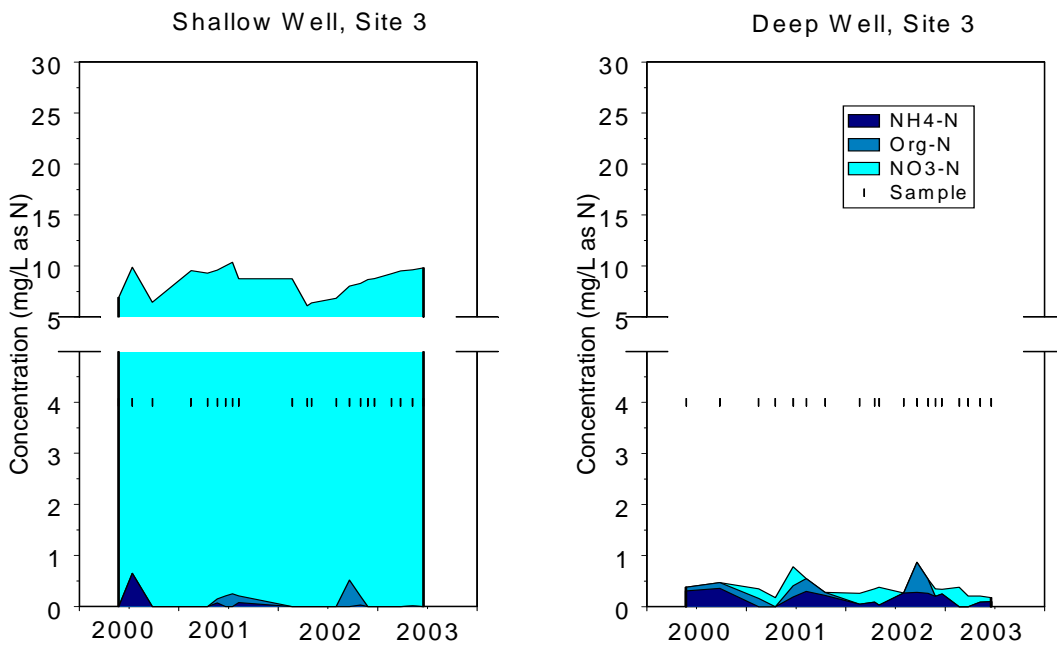

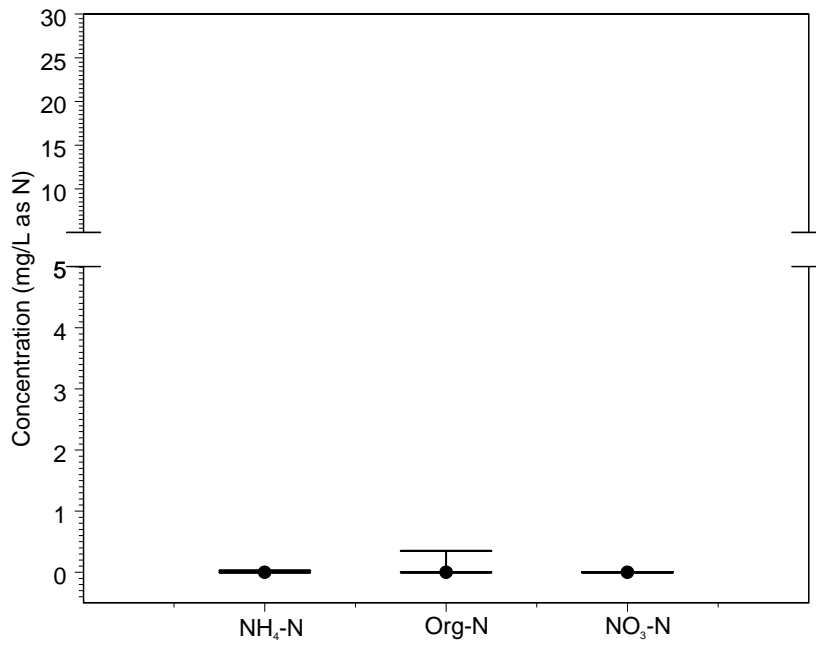Figure 3.21 Temporal variation of N species concentrations in wells 3S and 3D

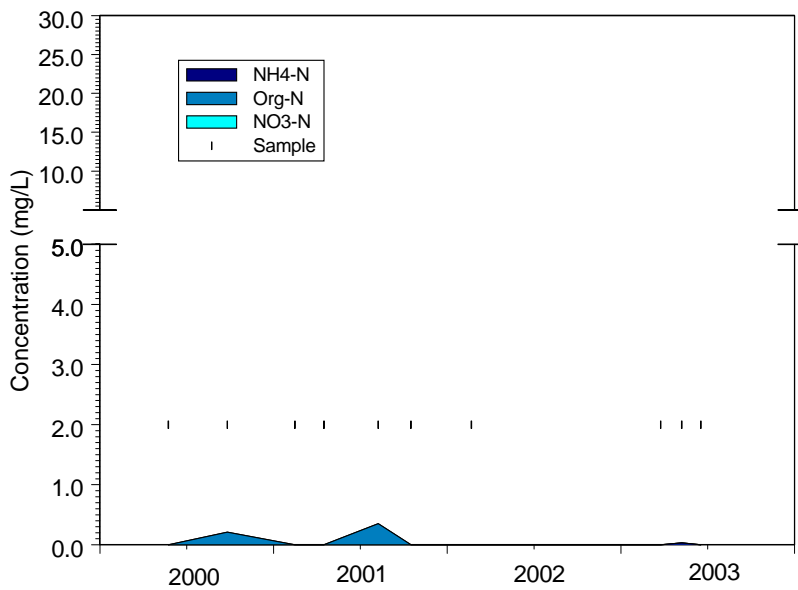Figure 3.22 Summary of N species concentrations in well 2S

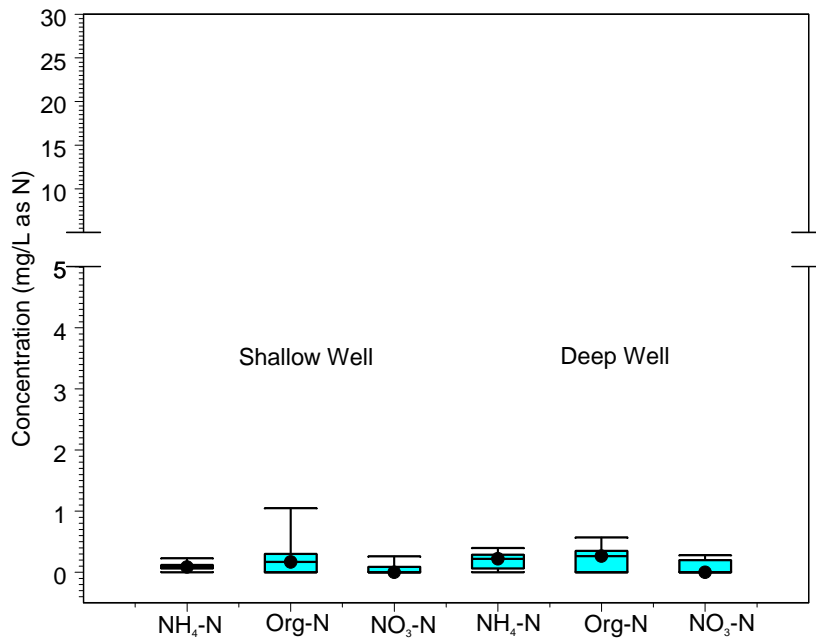Figure 3.23 Temporal variation of N species concentrations in well 2S

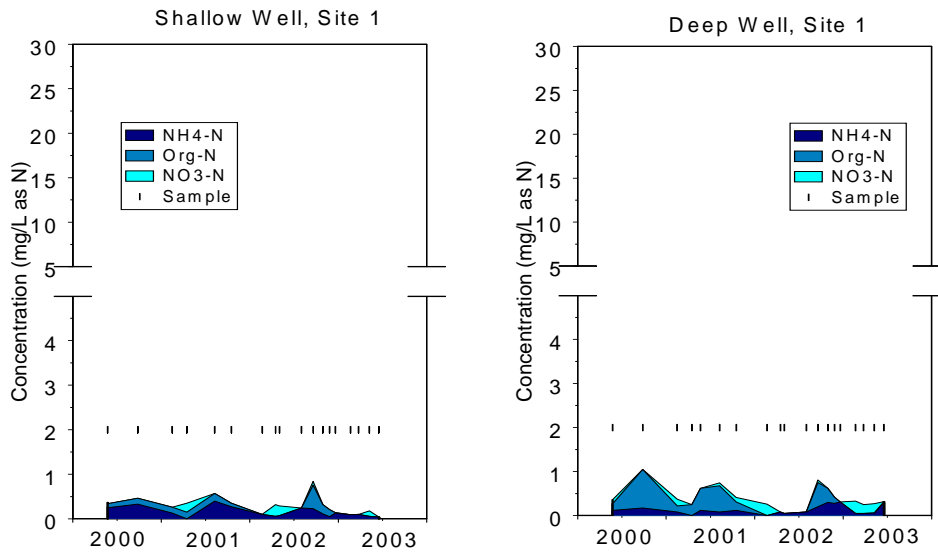Figure 3.24 Summary of N species concentrations in wells 1S and 1D

Figure 3.25 Temporal variation of N species concentrations in wells 1S and 1D
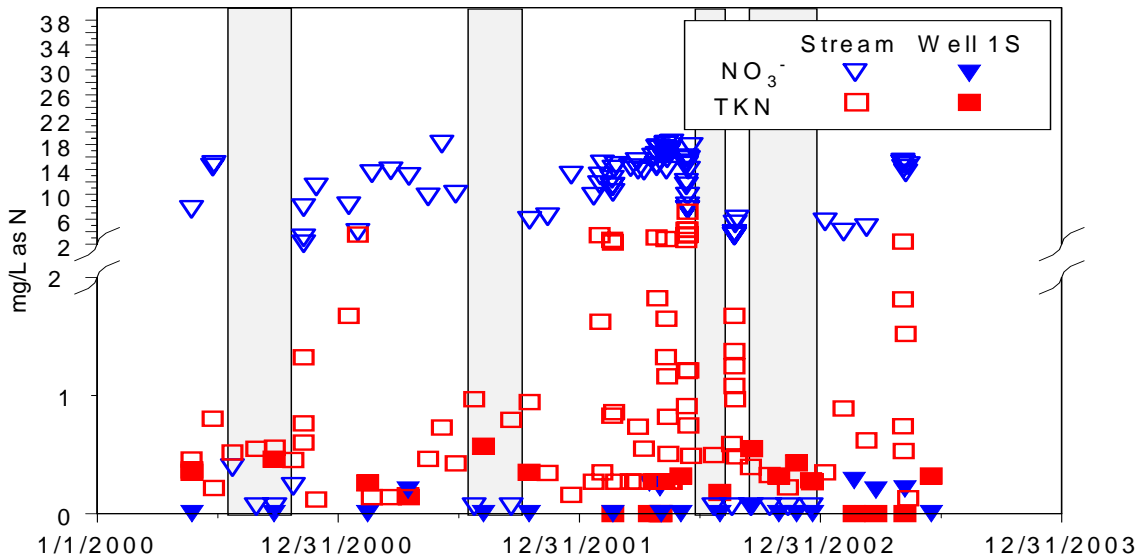
Figure 3.27 Nitrate-N and TKN in well 1S and Big Ditch. Periods of low flow are shown by the grey boxes. Concentrations of nitrate-N and TKN in well 1S and Big Ditch were similar during low flow conditions.

3.2.3 Estimation of Uncertainty of Organic N Concentrations

Org-N is operationally defined as the difference between TKN and NH_4-N. Therefore, the uncertainty in Org-N is a combination of the uncertainties in both NH_4-N and TKN. The uncertainty of an analysis can be estimated from duplicate determinations (Taylor, 1987) and pooling several duplicates gives a more reliable estimate of the analytical uncertainty than just one set of duplicates if the data are normally distributed (Minkkinen, 1986). Altogether, 32 sets of duplicate samples were collected. For the uncertainty estimate, only duplicates for which at least one sample had a detectable amount of either NH_4-N or TKN were considered. For this analysis, 14 such duplicates were used for NH_4-N and 22 duplicates for TKN. The pooled relative standard deviations (standard deviation divided by the mean) were 0.14 for NH_4-N and 0.19 for TKN. Because Org-N is simply the difference between TKN and NH_4-N, the uncertainty in Org-N is the root mean square of the uncertainties in TKN and NH_4-N using Equation 3.1, where $\sigma(x)$ and $\sigma(x)/x$ stand for the standard deviation and relative standard deviation of x, where x is either TKN, NH_4-N, or Org-N (Bevington, 1969).

$$\frac{\sigma(Org-N)}{Org-N} = \sqrt{\left(\frac{\sigma(TKN)}{TKN}\right)^2 + \left(\frac{\sigma(NH_4-N)}{NH_4-N}\right)^2} \qquad \text{Equation 3.1}$$

Substituting the estimated relative standard deviations for TKN and NH_4-N into equation 3.1 gives an estimate of the relative standard deviation in Org-N of approximately 0.24 (24%). For water samples with undetectable NH_4-N, the relative standard deviation of Org-N is the same as for TKN (19%). By using data from duplicate samples, rather than duplicate analyses of single samples, this

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estimate includes the uncertainties of both analysis and sampling. Equation 3.1 is strictly applicable only if uncertainties in TKN and NH4-N are normally distributed (Bevington, 1969).

3.3 Phosphorus

The total P concentration was below the detection limit of 0.08 mg/L in all samples from the May 2000 samples except one sample from well 9D which had 0.2 mg/L. Similarly, in March 2001, total P was undetectable (<0.03 mg/L) in all samples but those from wells 8D, 8S, and 9D. Total P analyses were discontinued after March 2001 because of these low concentrations.

3.4 Organic Carbon

The nonvolatile organic carbon (NVOC) concentrations in samples from sites 1 through 8, 10 and 11 varied over a fairly narrow range, from 0.5 to 2 mg/L, while concentrations from the site 9 wells generally ranged between 2 and 3 mg/L (Figure 3.28). For sites 1, 5, 7, and 8, the NVOC concentrations in the shallow well were significantly higher than in the deep well. That is, the first quartile for the shallow wells was greater than the third quartile for the deep wells. On the other hand, NVOC at sites 3, 4, 6, and 9, was about the same in the shallow and deep wells. Recharging groundwater dissolves organic matter in the soil zone, thus shallow groundwater may have high NVOC concentrations. However, organic matter can be mineralized (converted to CO_2) in the subsurface, meaning deeper groundwater may be depleted of organic matter. Deep groundwater may have high NVOC concentrations if: mineralization has not occurred; an organic source exits at depth; or rapid recharge, possibly via macropores, transported organic matter through the shallow geologic materials. An organic-rich paleosol was found at site 9 and may explain the high NVOC values at this site. Well 10D was not plotted because proper purging of this well was not feasible. Less than half (43%) of all samples analyzed for NVOC had detectable Org-N; however, over 80% of the 9S and 9D samples had detectable Org-N. There was no apparent correlation between NVOC and Org-N (Figure 3.29).
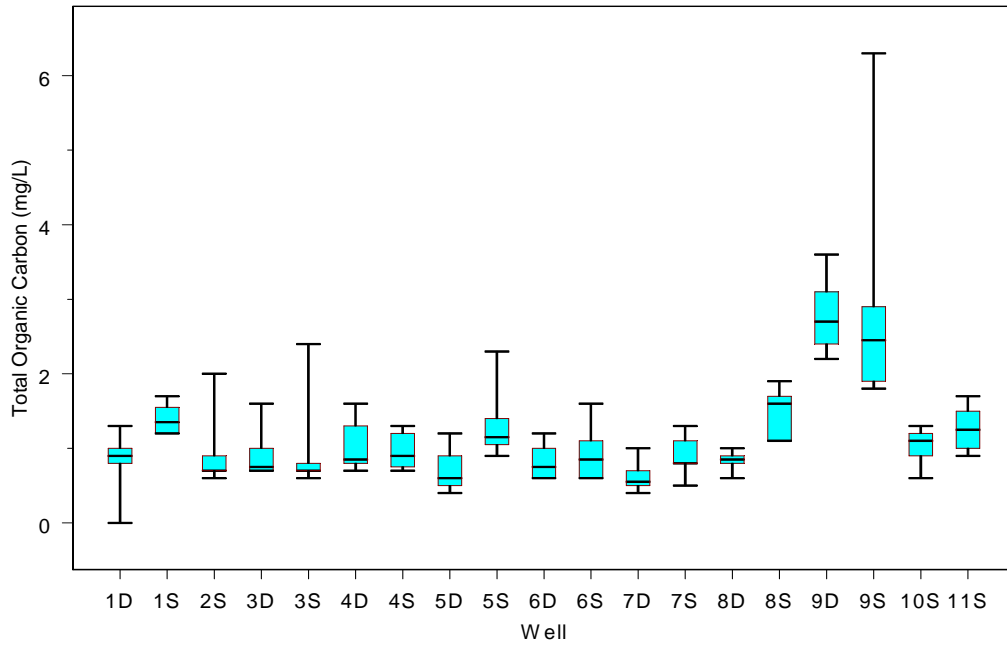
Figure 3.28 Box and whisker plot of nonvolatile organic carbon concentrations in the shallow (S) and deep (D) wells
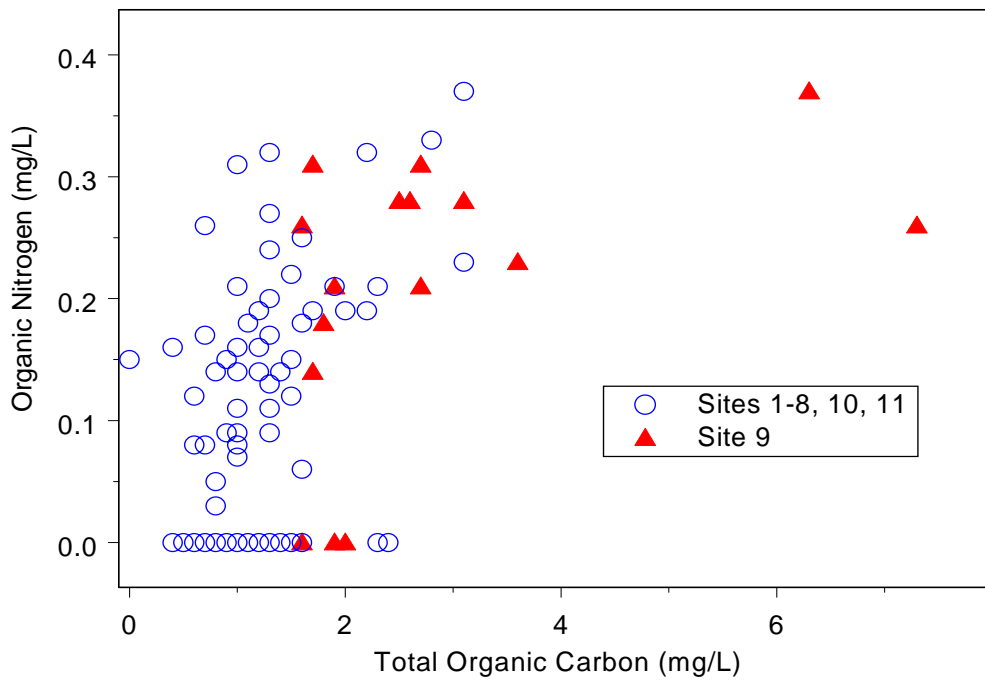

Figure 3.29 Organic nitrogen vs nonvolatile organic carbon

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3.5 Other Geochemical Data
Water quality data can help define the relative residence time of water in the subsurface and help define the general redox conditions of groundwater. Most of these water quality data were collected as part of special sampling efforts to gain insight into mass transport within the watershed.

3.5.1 Water Quality to Define the Relative Residence Time
On March 26, 2003, samples were collected from the shallow wells (13 samples), tile drains (4 samples), and surface water (8 samples). On this day, discharge at the outlet of Big Ditch was approximately 2.8 cfs. Despite low flow in the Big Ditch, we observed water flowing from drain tiles and shallow groundwater seeping into the surface water. Water samples were collected from all shallow wells except well 12S, which was dry.

Cation concentrations can provide information about the relative residence time of water in the subsurface. Concentrations of calcium (Ca), potassium (K), magnesium (Mg), sodium (Na), silica (Si) and other ions can increase as water flows through and weathers soil and geologic materials containing these cations (Puckett et al., 2002). These cations have been used in mixing models to define the components of stream flow in watersheds (e.g., Hyer et al., 2001). Similar to cation concentrations, specific conductance can provide information about the relative residence time of water in the subsurface (Keefer et al., 1996). In this watershed, sources of water for the stream flow include runoff, soil water (water from the water table to the tile drain), tile water, shallow groundwater, and deep groundwater. In addition, iron concentrations were determined for deep wells on a limited number of sampling trips. The median Fe concentrations for the deep wells will be discussed later in this section.

The Ca, Mg, and Si concentrations are generally highest in the shallow wells and lowest in the surface water samples (Table 3.6 and Figure 3.30). These data indicate that the water from the shallow wells and tile drains can have comparable residence times in the subsurface and that the stream water included a significant component of shallow groundwater on March 26, 2003. Because of the low concentrations of Ca, Mg, and Si in the stream water, it appears that soil water is a major component of the stream water. The K and Na concentrations are comparable for the three sample types—tile, shallow wells, and surface water. The uniform concentration of K and Na may reflect the presence of these ions in surficially applied fertilizers (K) and road salt (Na). The spatial distribution of the Ca, Mg, Na, and Si concentrations in the shallow well samples was fairly uniform (Figure 3.31), being slightly lower in wells 8S and 11S and slightly higher in well 10S. The higher concentrations in well 10S may reflect the influence of irrigation water applied to the fields surrounding 10S. The irrigation well near well 10S pumps water from the Mahomet aquifer. The order of cation concentrations (Ca > Mg > Na > K) in Big Ditch surface water matches those reported by Gburek and Folmar (1999) for base flow in an agricultural watershed in Pennsylvania.

Table 3.6 Selected water quality data for samples collected on March 26, 2003

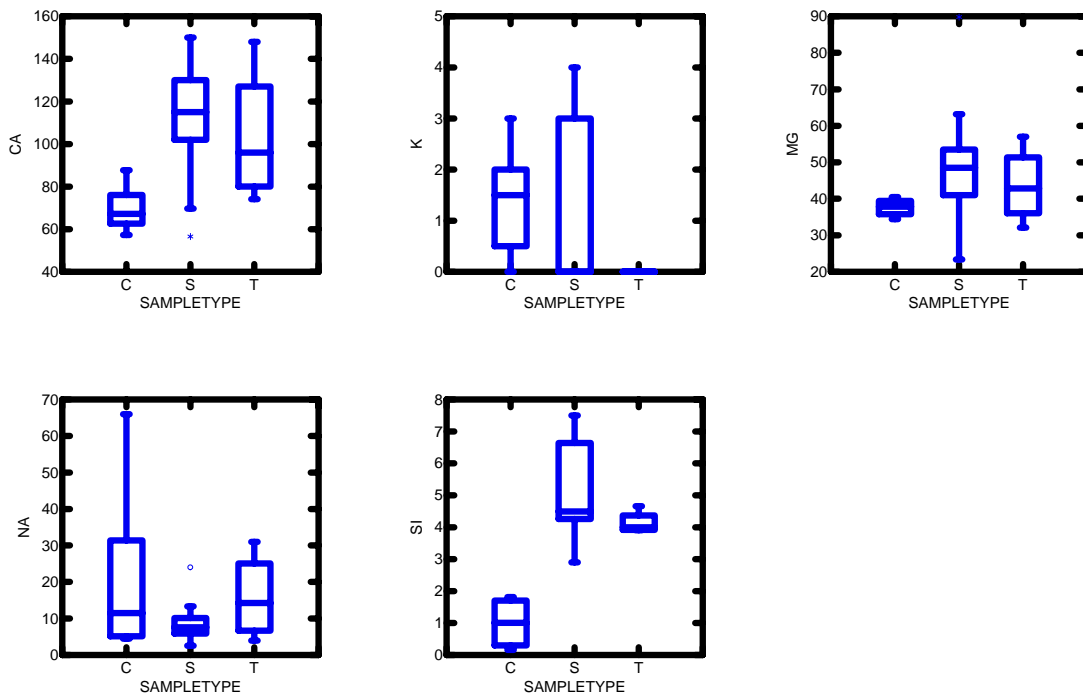|	Median Concentration (mg/L)			
	Surface Water	Tiles	Shallow Wells	Deep Wells
Ca	67.2	96.0	115	NA
Fe	0.0	0.0	0.0	0.75
K	1.5	0.0	0.0	NA
Mg	37.9	42.9	48.5	NA
Na	11.5	14.3	7.6	NA
Si	1.0	4.0	4.5	NA

NA= not analyzed

Figure 3.30 Concentrations of selected cations (Ca, K, Mg, Na & Si) for samples collected on March 26, 2003 for creek (C), shallow well (S) and tile (T) samples. Concentrations are mg/L.
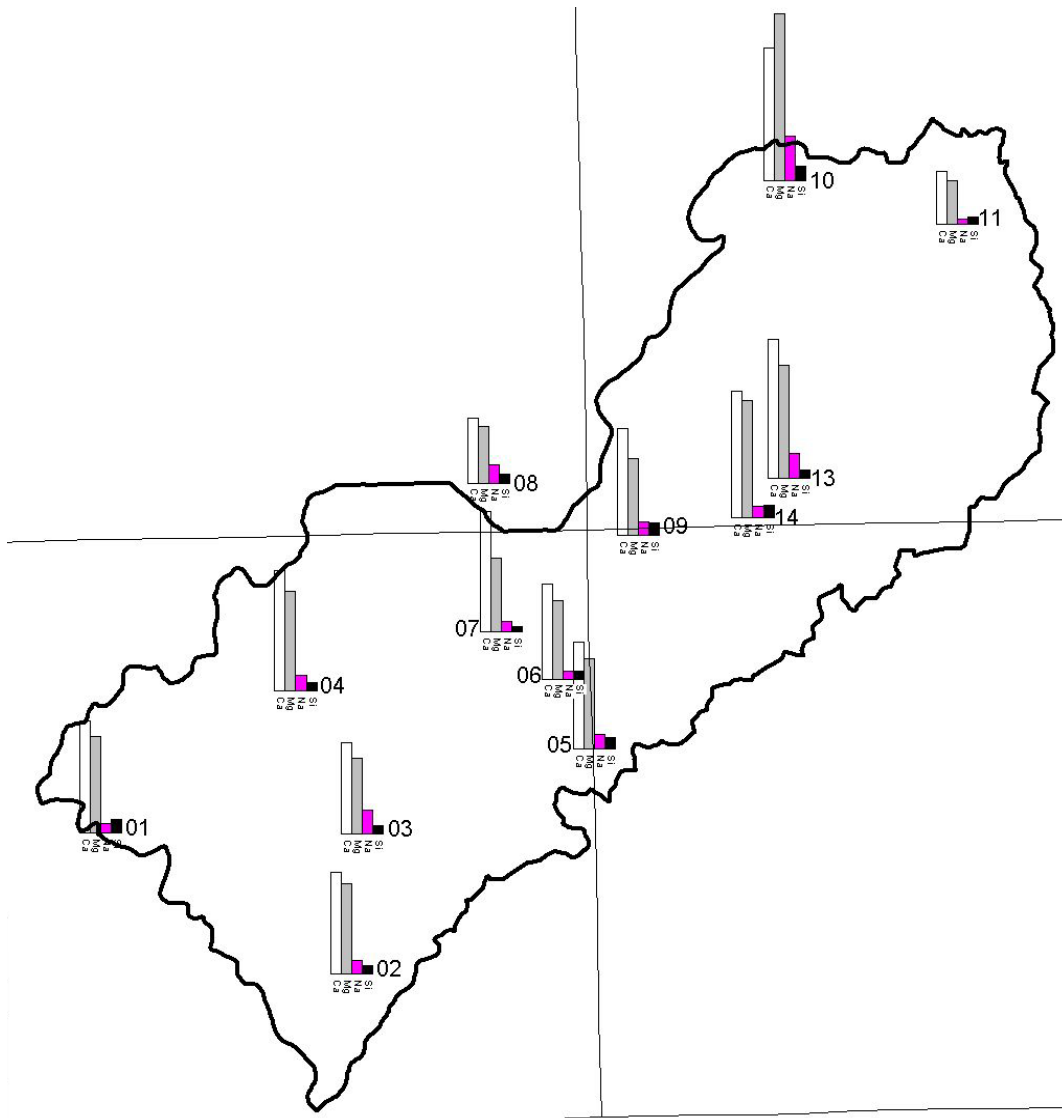
Figure 3.31 Spatial distribution of the concentrations of selected cations in the shallow wells
(bar charts: left to right: calcium, magnesium, sodium, and silica)

Specific conductance (SpC) of the water samples varied by sample type and location and over time.
Specific conductance data were collected for creek and tile samples on March 23, 2003, while the
samples from the shallow and deep wells were collected from May 2000 through June 2003. The
median value of specific conductance was greatest for the tile samples and lowest for the deep wells
(Table 3.7 and Figure 3.32).

Table 3.7 Specific conductance values by sample type

Sample type	Specific Conductance (S/cm)		
	Median	Minimum	Maximum
Creek	858	566	1070
Tiles	1120	851	1540
Shallow wells[1]	782	574	1300
Deep wells[1]	686	587	964

1: median values from approximately 15 samples are reported
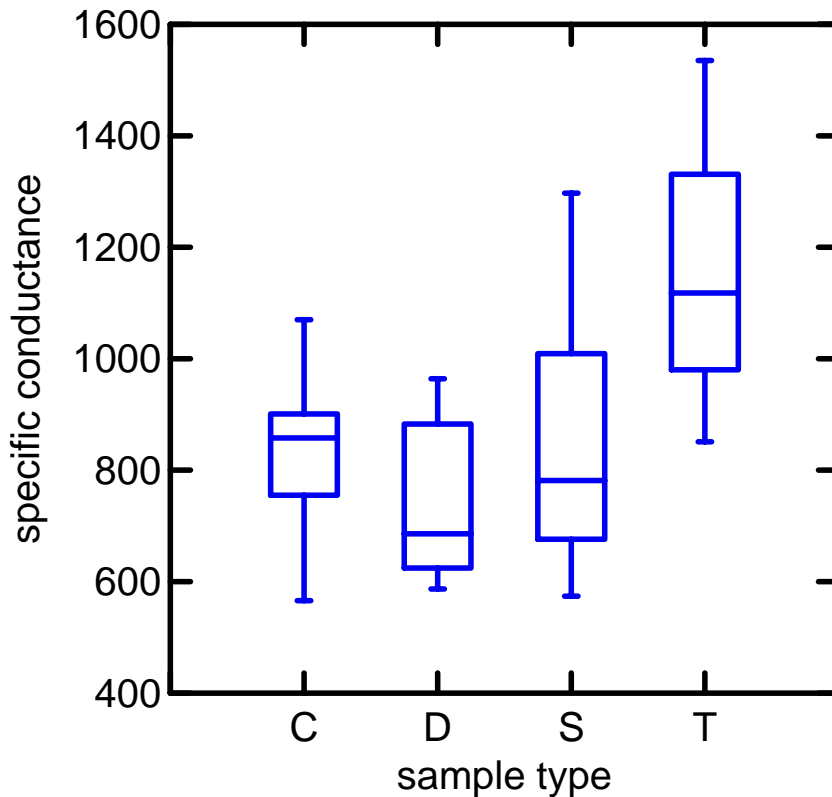

Figure 3.32 Box plots of specific conductance (µS/cm) by sample type (C= creek, D= deep well, S= shallow well, and T= tile)

Figure 3.33 shows time series plots of SpC values for the shallow wells. Wells 1S through 7S behaved similarly. The SpC values for these wells usually ranged from 500 to 1250 µS/cm. In 2001, the SpC values for these wells all had a maximum in April, a minimum in June, and a maximum in August. They followed a similar pattern in 2002 with a maximum in February, a minimum from April through May, and a maximum in July. Wells 9S and 10S had the highest SpC values for nearly every sampling event. Well 10S also followed the max-min-max pattern in 2002. Well 10S is the only well located near an irrigation well and the higher SpC values in 10S may reflect the influence of irrigation with water from the Mahomet aquifer. Well 11S usually had one of the lowest SpC values for each sampling event.
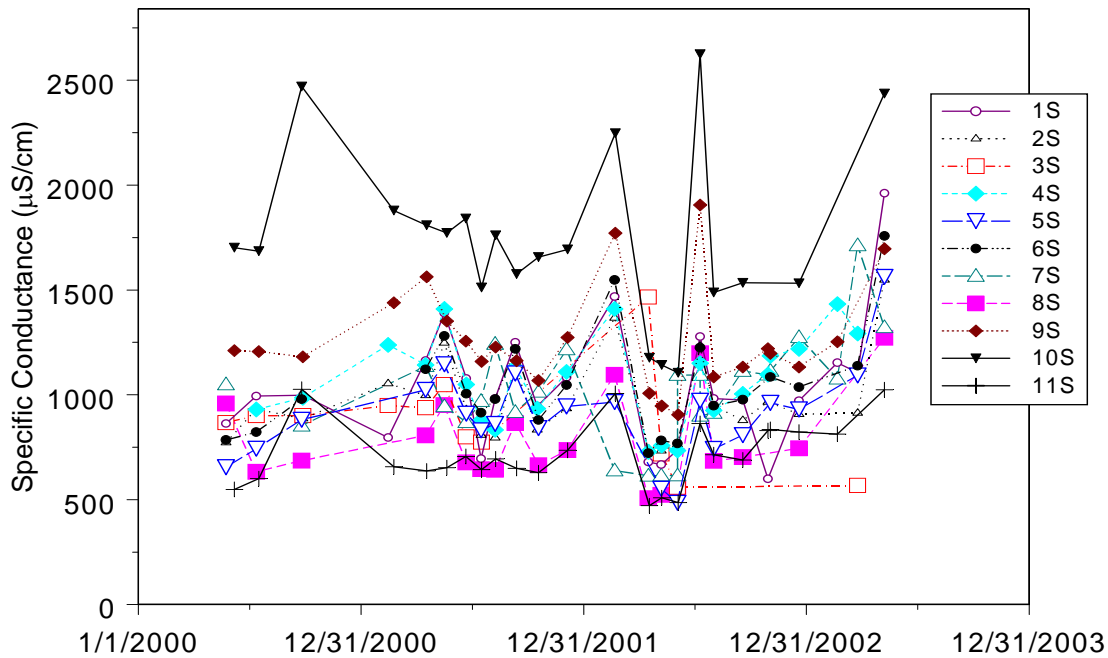
Figure 3.33 Specific conductance in the shallow wells. All values adjusted to 25º C.

Figure 3.34 shows time series plots of SpC values for the deep wells. All deep wells followed the same max-min-max SpC pattern as the shallow wells in 2002 and all deep wells but 1D followed the pattern in 2001. The variations in SpC may have been related to physical processes, such as groundwater recharge and biogeochemical process, such as microbial respiration, nitrification, and denitrification. The most common fertilizer in the Big Ditch watershed is anhydrous ammonia. When ammonia dissolves in water it raises the pH (equation 3.2).

$$NH_3 + H_2O = NH_4^+ + OH^-$$
Equation 3.2

This is accompanied by $CaCO_3$ precipitation (equation 3.3).

$$Ca^{2+} + HCO_3^- + OH^- = CaCO_3 + H_2O$$
Equation 3.3

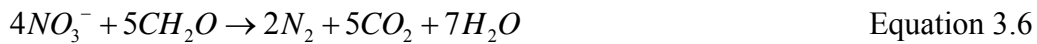The net result is to decrease the ionic content of the water. Nitrification (equation 3.4) is a microbially mediated process that transforms ammonium ion to nitrate ion and produces H^+ ions. Clearly, nitrification can only occur under aerobic conditions. Nitrification proceeds through several steps. Equation 3.4 shows the overall process.
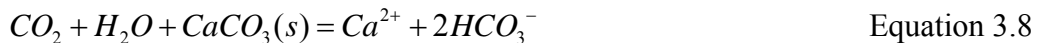
$$NH_4^+ + O_2 \rightarrow NO_3^- + 2H^+$$
Equation 3.4

Respiration (equation 3.5) also occurs under aerobic conditions. In equation 3.5, CH_2O stands for biodegradable organic matter (carbohydrate).

$$CH_2O + O_2 \rightarrow CO_2 + H_2O \qquad \qquad \text{Equation 3.5}$$

Nitrate ion can be transformed to nitrogen gas by denitrification, another microbial process. Denitrification occurs under anaerobic conditions. Denitrification consists of several intermediate steps. Equation 3.6 shows the overall process.

$$4NO_3^- + 5CH_2O \rightarrow 2N_2 + 5CO_2 + 7H_2O \qquad \qquad \text{Equation 3.6}$$

The H^+ or CO_2 produced by nitrification, respiration, and denitrification can react with $CaCO_3$ (equations 3.7 and 3.8). The net result is to increase the ionic content of the groundwater.

$$H^+ + CaCO_3(s) = Ca^{2+} + HCO_3^- \qquad \qquad \text{Equation 3.7}$$

$$CO_2 + H_2O + CaCO_3(s) = Ca^{2+} + 2HCO_3^- \qquad \qquad \text{Equation 3.8}$$

The temporal and spatial variability of specific conductance is illustrated in Figures 3.33 and 3.34, which shows the SpC data collected during the project. In both the shallow and deep wells, SpC remains fairly constant from May 2000 through December 2001, then it increases during
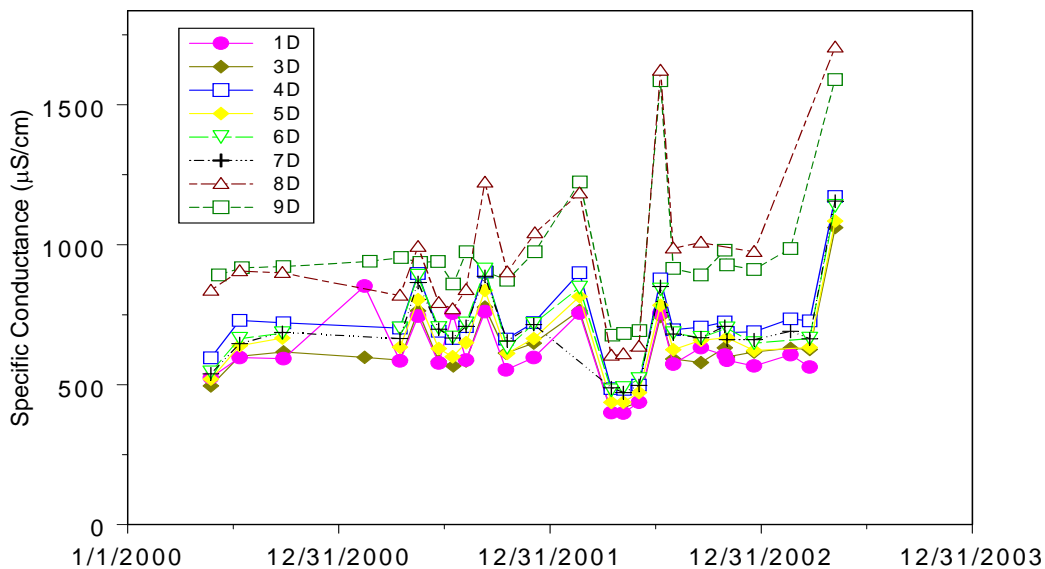

Figure 3.34 Specific conductance in the deep wells. All values adjusted to 25º C.

early 2001, drops in spring 2002, rises in late summer 2002, and returns to more typical values in the fall 2002. High SpC values seem to correspond to low groundwater levels, while low SpC values seem to correspond to high groundwater levels (see Figure 2.7 and 2.8). The water levels in the Big Ditch wells changed more dramatically in 2002 than in 2001. The SpC of most shallow wells was similar, while the SpC in wells 9S and 10S were consistently higher. For the deep wells, the SpC values of wells 8D and 9D were consistently higher than the other wells. The temporal trends observed in the shallow wells were also observed in the deep wells, which are screened at depths ranging from 25 to 43 feet. This pattern in SpC for the deeper wells is consistent with the downward hydraulic gradients during wet periods such as May 2002.

Water samples from selected wells (wells 1D, 7S, 7D, 8S and 8D) were analyzed for chlorofluorocarbons in November and December 2001. The sampling and analytical methods were described by Wright (2002). Using concentrations of CFC-12, recharge can be estimated from the measured CFC-12 concentration in the sample and known atmospheric CFC-12 concentrations, assuming that the precipitation was in equilibrium with the atmosphere at the time of recharge. The method allows one to date recharge to the early 1940s (Plummer et al., 1993); however, we chose to limit the oldest interpretation to the mid-1960s (reported as <1965). These samples (Table 3.8) suggest that the water in wells 7S and 8S was recharged in 1975 and 1984, while water in wells 1D, 7D, and 8D was recharged in the late 1960s or earlier (Van der Hoven and Wright, 2002).

Table 3.8 CFC-12 data for selected wells in the Big Ditch watershed (from Van der Hoven and Wright, 2002)

Well (screen depth)	Sample Date	CFC-12 (pmoles/kg)	Recharge Year	Mean Recharge Year
1D (30 ft)	11/29/01	0.58	1967	1968
		0.55	1967	
		0.82	1970	
1G (165 ft)	12/6/01	0.45	1965	<1965
		0.53	1967	
		0.51	1966	
1M (339 ft)	12/6/01	0.06	1951	<1965
		0.16	1958	
		0.39	1964	
7S (15 ft)	12/6/01	1.39	1975	1975
		1.46	1975	
		1.48	1975	
7D (28 ft)	12/6/01	0.36	1964	<1965
		0.53	1967	
		0.23	1961	
8S (15 ft)	12/6/01	2.48	1983	1984
		2.56	1984	
8D (45 ft)	12/6/01	0.15	1957	<1965
		0.34	1963	
		0.28	1962	

Recharge to wells completed in the deeper Glasford sand (1G) and the Mahomet sand (1M) also predated the mid-1960s. These data help show the relative difference in ages of the water in geologic materials of different depths.

3.5.2 Water Quality to Define Redox Conditions

The general reduction-oxidation (redox) condition of water can be characterized in several ways including by measurement of the amount of dissolved oxygen (DO), the oxygen-reduction potential (ORP), and the concentration of cations sensitive to the redox state such as iron (Fe) and manganese (Mn) (e.g., Puckett et al., 2002).

When groundwater samples were collected, ORP and DO were generally measured using specific electrodes. The DO readings for well 10D are not shown because the well generally was pumped dry before the readings stabilized. The median DO level in all deep wells was less than 1 mg/L (Figure 3.35). In other words, the deep layers were probably anoxic most of the time. For sites 1-8 and 11, most DO measurements in the shallow wells were above 1.5 mg/L, so the shallow groundwater was usually oxic and always oxic at sites 3, 5, and 8. At site 9, the shallow and the deep well were almost always anoxic, probably due to the higher organic carbon concentrations (Figure 3.28). The difference between the DO in the shallow and deep wells is probably due to the longer residence time of groundwater sampled in the deep wells, which allows more time for the oxygen to be consumed by microbial respiration. The DO concentrations are generally consistent with the ORP measurements (Figure 3.36), with higher measurements in the shallow wells than in the deep wells.
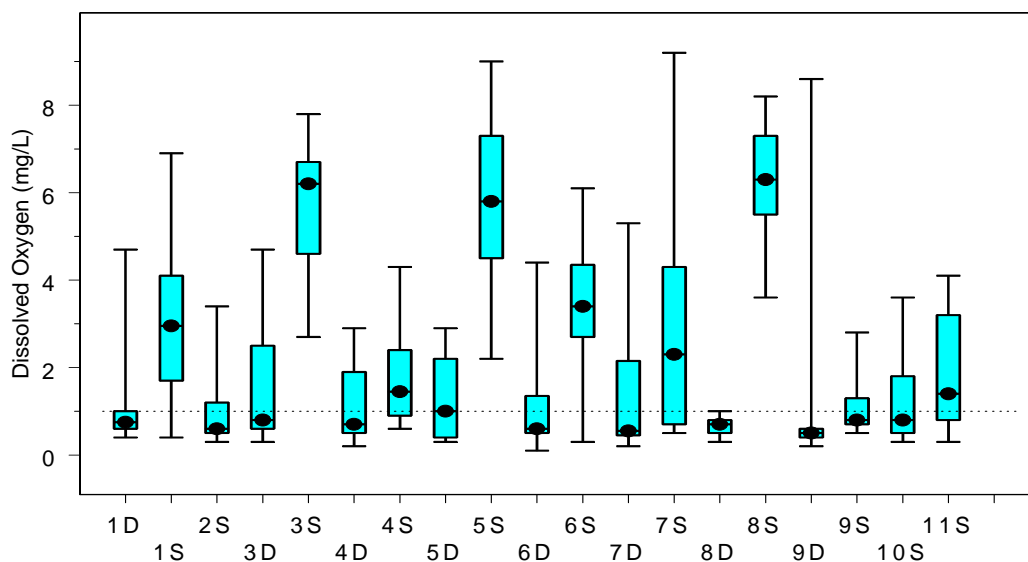

Figure 3.35 Box plots of all dissolved oxygen measurements. The dotted line shows the level below which the measurements were assumed to be unreliable (see discussion of Fe data).
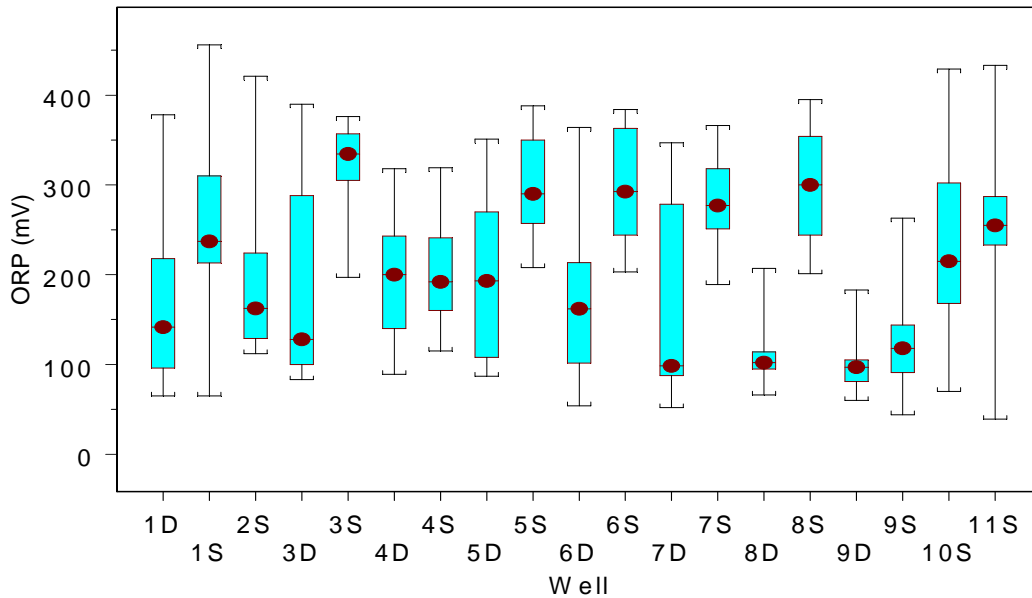
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Figure 3.36 Box plots of all ORP measurements.

The DO concentrations and water levels changed roughly in unison in well 7S (Figure 3.37). The highest levels were measured in the spring, then decreased through the summer and fall. This pattern was observed in 2000, 2001, and 2002. Water levels were not measured in 2003. These DO and water level data likely indicate that oxygen-rich precipitation infiltrates and recharges shallow groundwater in the early spring. After recharge, the water level declines as ET increases, recharge decreases and groundwater flows toward the ditch. As groundwater flows through the subsurface, oxygen is consumed by microbial respiration and other processes.

The ORP measurements were generally consistent with the DO and iron concentrations. All ORP measurements for the shallow wells were above 200 mV, while most of the measurements for the deep wells were below 100 mV. This is consistent with more-oxidizing conditions in the shallow layer than the deep layer. For example, most ORP measurements were less than 100 mV in wells 7D and 7S for DO values less than 1 mg/L, the limit of reliable measurements (Figure 3.38). On the other hand, for DO values greater than 1.5 mg/L, the ORP values in wells 7S and 7D were greater than 200 mV. For most samples with detectable iron, the ORP values were less than 100 mV (Figure 3.39). However, the ORP values were greater than 150 mV for most samples without detectable iron.
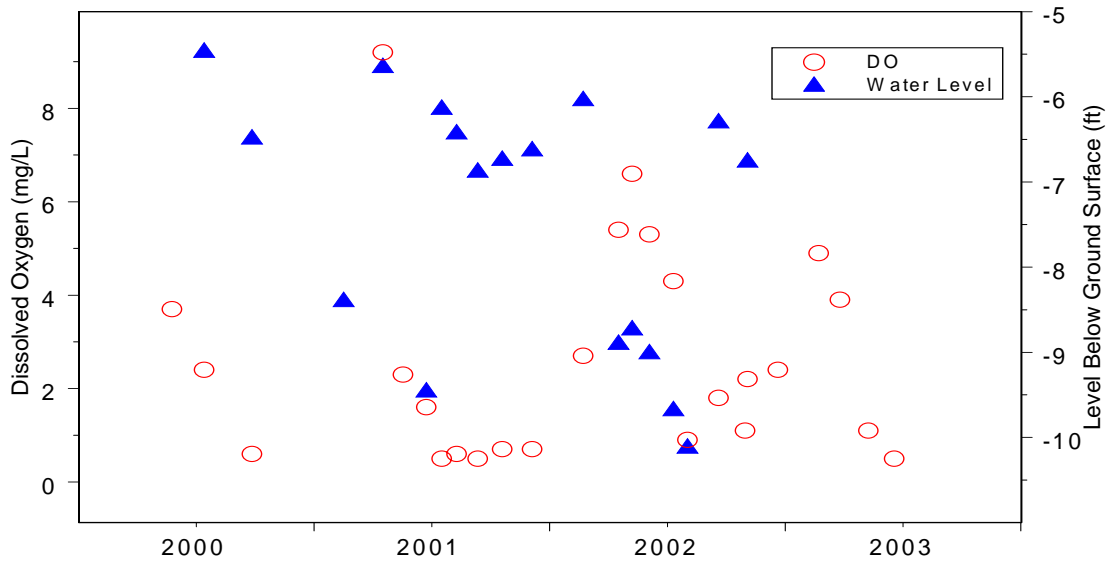
Figure 3.37 Dissolved oxygen concentrations and water levels in well 7S
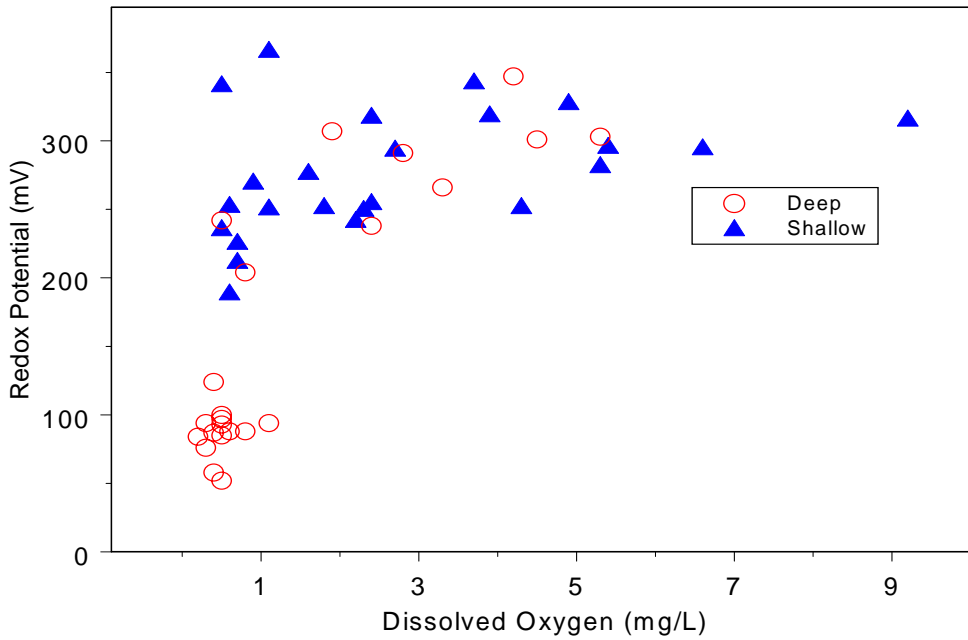

Figure 3.38 Oxidation-reduction potential vs dissolved oxygen measurements for wells 7D and 7S
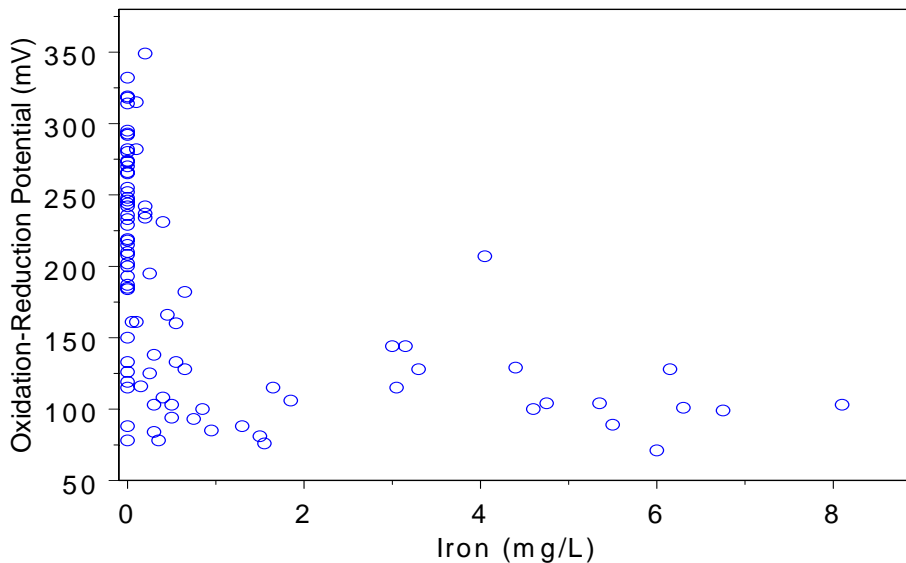
Figure 3.39 Oxidation-reduction potential vs iron concentration.

Because iron and manganese are usually detected only in anoxic groundwater, these cations provide valuable data to check ORP and DO values, which can be somewhat unreliable. All groundwater samples collected in June, July, August, and September 2002 were also analyzed for iron. All soluble iron was assumed to be in the ferrous form because ferric hydroxide has a very low solubility. For DO concentrations greater than ~2 mg/L, only one sample had more than ~0.1 mg/L Fe (Figure 3.40). However, for DO concentration less than 1 mg/L, many samples had Fe concentrations greater than 1 mg/L. Ferrous iron and oxygen react fairly rapidly at neutral pH values (Stumm and Morgan, 1996). For example, for 5.6 mg/L Fe and 0.3 mg/L O_2 the half-life of Fe^{2+} is ~30 minutes, which is much shorter than the residence time of shallow groundwater. Therefore, oxygen and iron are not expected to both be detectable in groundwater. This may mean that our DO measurements were unreliable below ~1 mg/L and possibly below ~1.5 mg/L. Although there was one outlier, we feel our DO measurements of 1.5 mg/L and above were reliable.

Samples collected on March 26, 2003 were analyzed for cations including iron and manganese. These samples show that ORP and DO were much lower in the deep wells than the shallow wells (Figure 3.41), as would be expected. The Fe concentrations were higher in the deeper wells than the shallow wells (Figure 3.42). The Fe concentrations in the creek and tile samples were ≤0.03 mg/L. The spatial distributions of Fe and Mn concentrations generally showed the highest concentrations in the shallow wells were in the lowland settings (1S, 4S and 9S) (Figure 3.43).
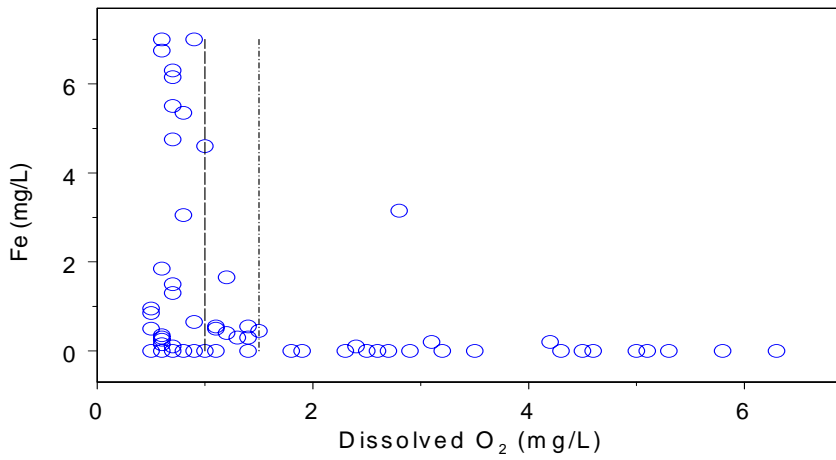
Figure 3.40 Dissolved oxygen vs iron concentrations in groundwater samples collected from June through September, 2002.
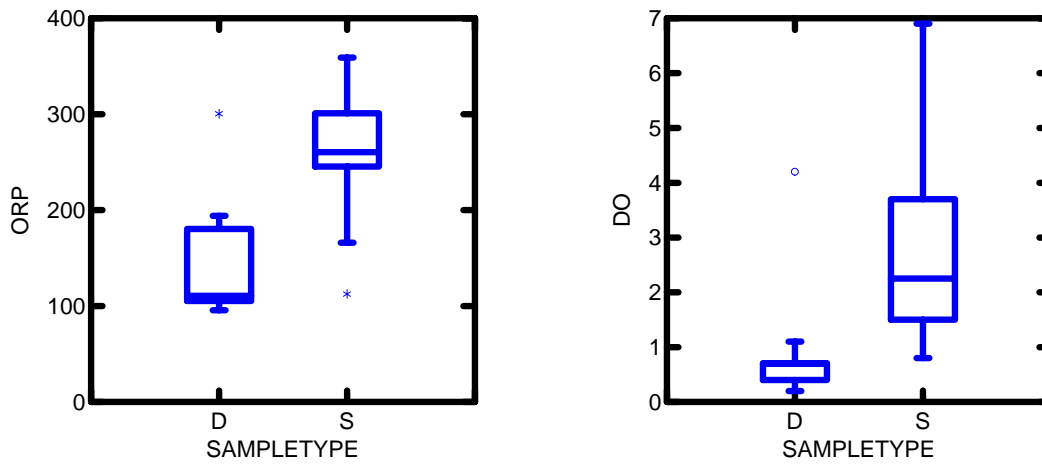
Figure 3.41 ORP (mV) and DO (mg/L) values for samples collected on March 26, 2003 in deep (D) & shallow (S) wells
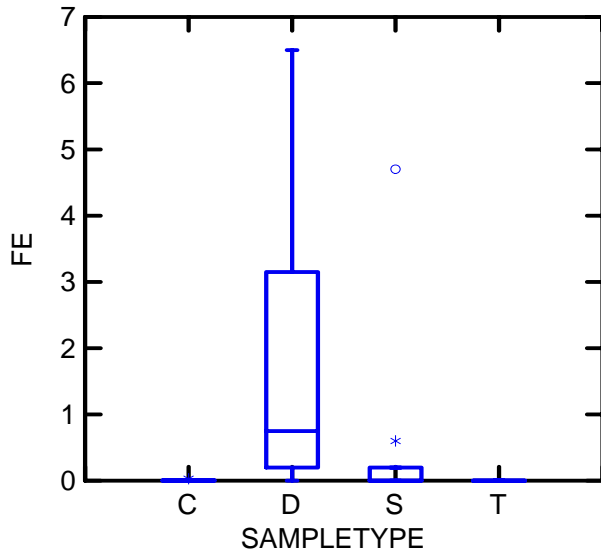
Figure 3.42 Iron concentrations (mg/L) in the water samples from the creek (C), deep wells (D), shallow wells (S) & tiles (T)
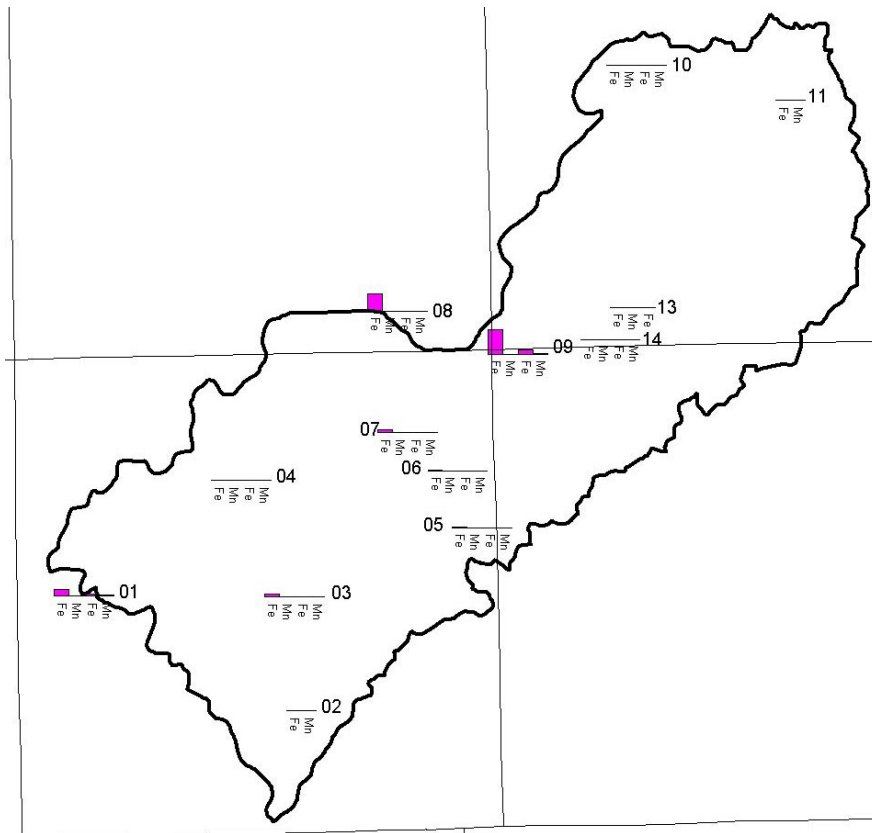
Figure 3.43 Spatial distribution of Fe and Mn concentrations in shallow (right set of bars) and deep wells (left set of bars)

4. ISOTOPIC ASSESSMENT OF NITROGEN DYNAMICS IN SHALLOW GROUNDWATER

The goal of this part of the study was to use natural variations in the isotope ratios of nitrogen ($^{15}N/^{14}N$) and oxygen ($^{18}O/^{16}O$) as indicators of the extent to which nitrate had been removed from soil water and shallow groundwater by denitrification. Tritium was also measured in selected samples to help estimate relative groundwater age.

4.1 Background

Denitrification occurs in a multi-step process in which NO_3^- is reduced to N_2 with various intermediate compounds such as NO_2^-, NO, and N_2O (Stumm and Morgan, 1996). Abiotic reduction, although thermodynamically favored in many natural systems, is generally insignificant due to extremely slow reaction rates (Postma et al., 1991). Microbially mediated reduction of NO_3^- is kinetically viable on a practical time scale and is generally the method of NO_3^- decomposition in natural systems. A generalized half-cell reaction for biotic reduction is:

$$2NO_3^- + 12H^+ + 10e^- \rightarrow N_2 + 6\,H_2O \qquad \text{Equation 4.1}$$

Potential electron (e^-) donors to the reaction include organic matter (Trudell et al., 1986) and FeS_2 (Kölle et al., 1987).

In general, NO_3^- concentration changes are an inadequate tool for determining rates and extent of denitrification in the subsurface because dilution may reduce the concentration of NO_3^- independently of actual loss through denitrification. Similarly, a concentration drop caused by advection of a nitrate-rich groundwater pulse through an observation point may give the appearance of denitrification without any actual loss of NO_3^- to the system.

Isotopic fractionation associated with microbial denitrification provides a method to quantify NO_3^- losses due to denitrification independently of dilution and advection effects. Microbial preference for denitrification of ^{14}N-bearing NO_3^- leads to the enrichment of ^{15}N-bearing NO_3^- in the residual unreacted fraction (Mariotti et al., 1981). Similarly, the residual NO_3^- is enriched with respect to $^{18}O/^{16}O$ as denitrification proceeds. The isotopic ratios in the residual fraction increase in a regular manner and thus if initial ratios are known, percent loss of NO_3^- can be calculated. Several studies have examined NO_3^- contamination of aquifers in this context (Mariotti et al., 1981 & 1988; Böttcher et al., 1990; Fujikawa and Hendry, 1991; McMahon and Böhlke, 1996).

4.2 Methods
4.2.1 Sampling Methods

Prior to sampling wells, 1 to 3 well-volumes were purged using a 12V Whale[tm] purging pump. Due to low well yields, purging 3 well-volumes was not always possible. In all cases, however, the pump allowed for complete removal of water in the well prior to sampling. All samples were collected in plastic containers and kept on ice in the field. To prevent microbial growth, all nitrate samples were processed on the same day as collected. H_2O oxygen isotope analysis samples were refrigerated up to one month. Tile drain samples were collected in HDPE containers by allowing the drain discharge to flow directly into the sampling bottle. Sampling dates were chosen for times when tile

drains were likely to be flowing, i.e. following precipitation events. Tile drains were generally not flowing during summer months.

4.2.2 Isotope Ratio Measurement Methods

All isotope ratio analyses are reported in delta notation to facilitate analysis and display of the very small variations in the ratios that were observed and were resolved given the very high precision typical for these analyses. The $\delta^{18}O$ value represents variation of measured $^{18}O/^{16}O$ ratios in parts per thousand (‰, or per mil), with the zero point on the $\delta^{18}O$ scale set equal to the $^{18}O/^{16}O$ ratio of the seawater reference standard, standard mean ocean water (SMOW). The mathematical definition is:

$$\delta^{18}O = (\frac{R_{meas.} - R_{std.}}{R_{std.}}) \times 1000$$

where $R_{meas.}$ and $R_{std.}$ are the $^{18}O/^{16}O$ ratios of the measured sample and the seawater reference standard, respectively. $\delta^{15}N$ is calculated the same way as $\delta^{18}O$. The reference standard for $\delta^{15}N$ is Air nitrogen.

Measurements of the $\delta^{18}O$ in water were made on a set of groundwater samples using a $CO_2–H_2O$ equilibration method described originally in Epstein and Mayeda (1953), with modifications described in Hackley et al. (1999). Tritium analyses were performed using the electrolytic enrichment process (Ostlund and Dorsey, 1977) and the liquid scintillation counting method. Nitrate concentrations were determined with a Dionex DX20 ion chromatograph. Concentrations are reported in milligrams per liter of NO_3^- as nitrogen (mg-N/L).

Isotopic analyses of N and O were performed using published methods (Silva et al., 1994; 2000; Wassenaar, 1995) with some modification (Hwang et al., 1999; Panno el al., 2001). Nitrate samples were first passed through a 0.45 μm filter to remove particulate matter. Samples were acidified to pH 4 and boiled to remove bicarbonate. $Ba(OH)_2$ was added in excess to the boiling sample to remove SO_4^{-2}. Boiling continued for 1 hour and was followed by an overnight standing period to obtain complete precipitation of $BaSO_4$. Samples were again filtered at 0.45 μm to remove the precipitate. If Cl^- was present in concentrations greater than 100 mg/L, Ag_2O was added to form AgCl, which was also removed by filtration. After removal of SO_4^{-2} and excess Cl^-, samples were passed through a cation exchange column using BioRad AG-50W resin to remove excess cations. Samples were then passed through a 0.8 cm x 4.0 cm AG1-X8 anion exchange resin column to collect NO_3^-. The column was rinsed with approximately 30 mL of deionized water to remove residual sample water. NO_3^- was then eluted from the column by flushing with 10 mL of 1 M HBr solution. Ag_2O was added in excess to precipitate Br^- and Cl^- and the solution was refiltered at 0.45 μm. Samples were freeze-dried overnight to produce solid $AgNO_3$.

The $\delta^{15}N$ of the $AgNO_3$ was measured with methods from Kendall and Grimm (1990). Conversion of $AgNO_3$ to N_2 for $\delta^{15}N$ measurement was accomplished by loading 6-12 mg of $AgNO_3$ into quartz glass tubing with 1.0 g CaO, 0.5 g CuO, 5 to 10 flakes of Ag, and a copper turning plug. Tubes were evacuated, sealed, heated for 2 hours at 850º C, cooled at a rate of 1º C per minute to 600º C, and then cooled to room temperature. Conversion of the O in the $AgNO_3$ to CO_2 for $\delta^{18}O$ measurements was accomplished by adding carbon as graphite into a quartz tube. Six mg of $AgNO_3$ and 1.5 mg of graphite (a 4:1 $AgNO_3$:graphite ratio) were generally used. The tube was heated to 100º C in a

vacuum oven overnight to remove air moisture. The tube was then evacuated, sealed, combusted for 1 hour at 650º C, cooled and baked at 600º C for 10 hours, and then cooled to room temperature at a rate of 1º C per minute. After combustion, the resultant CO_2 was extracted cryogenically. $\delta^{18}O$ and $\delta^{15}N$ ratios were measured on a Finnigan Mat Delta E dual gas inlet mass spectrometer. All $\delta^{18}O$ values reported are relative to SMOW (standard mean ocean water) and $\delta^{15}N$ values reported are relative to $N_{2(Air)}$.

4.2.3 Known Systematic Error in $\delta^{18}O$ Measurements

Révész and Böhlke (2002) reported an error with a method similar to the graphite reduction reaction for conversion of the O in $AgNO_3$ to CO_2 for $\delta^{18}O$ measurements described above. The oxygen in CO_2 is contaminated during combustion, likely due to interaction with oxygen contained in the glass of the combustion tube. These errors are highly systematic and do not affect interpretation at all. However, as future analyses in this region may use a corrected technique, we report a correction equation as follows:

$$\delta^{18}O = 1.245(\delta^{18}O_{(Graphite)} - 3.6‰)$$

The relationship between the two methods is shown in Figure 4.1. Due to the consistency of our data, any error is likely to be systematic, correctable, and unlikely to influence conclusions greatly.
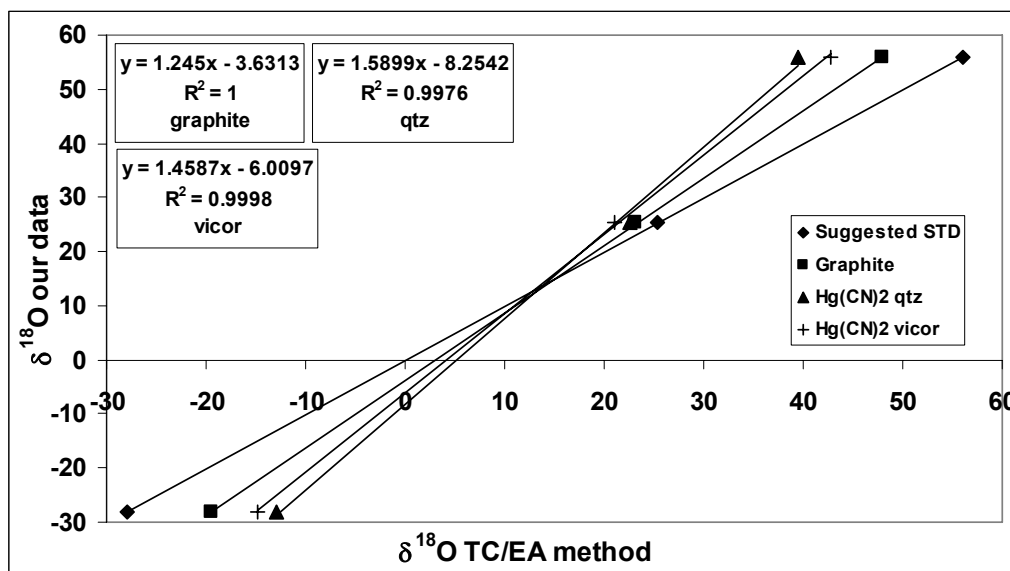
Figure 4.1 Potential errors in ^{18}O-NO_3 measurement for different sealed-tube combustion techniques relative to the on-line TC/EA method modified from Révész and Böhlke (2002). $\delta^{18}O$ measurements are given relative to Vienna Standard Mean Ocean Water (VSMOW). Diamonds represent TC/EA measurement of standard. Squares represent a correction line for graphite reduction method. Triangles represent $Hg(CN)_2$ reduction method using quartz tubing. Crosses represent $Hg(CN)_2$ reduction method using vycor tubing.

Furthermore, the $\delta^{18}O$ data reported are close to the junction of graphite correction line and the standard TC/EA line, meaning the absolute error was small in most cases. The lowest reported $\delta^{18}O$ value of 3.1‰ would require a correction of -2.7‰ with the correction dropping to -0.2‰ for the

highest $\delta^{18}O$ value of 13.8‰. For these reasons, we proceeded to interpret the data without correcting for this known error.

4.3 Results
Water samples were collected from several tile drains and several monitoring wells. The analytical data for tile drain samples are listed in Table 4.1 and the groundwater samples in Table 4.2. Monitoring tiles drains was the primary responsibility of another research group in the Water Quality Strategic Research Initiative; however, we also sampled tile drains. Tile drains provide an aggregate sample of soil water, commonly from a depth of 0 to 3.5 to 4 feet. For our samples, the tile drains were numbered according to their proximity to one of our monitoring wells. For example, tile drain 3 was located near well 3S.

Table 4.1 Nitrate-nitrogen and isotopic results for the tile drain samples

Sampling date	Nitrate-N concentration (mg/L)	δN^{15}-NO$_3$ (‰)	δO^{18}- NO$_3$ (‰)
Tile drain 3			
March 2001	12.01	5.90	5.28
April 2001	11.93	7.00	8.12
May 2001	14.72	3.56	6.86
June 2001	14.43	11.36	9.99
February 2002	13.52	5.84	7.18
March 2002	15.56	4.63	5.72
April 2002	15.62	5.01	5.48
May 2002	26.11	1.20	6.19
June 2002	26.86	7.39	8.15
Tile drain 6			
January 2002	13.88	6.96	6.87
February 2002	16.66	5.61	7.96
March 2002	18.12	4.66	6.18
April 2002	18.50	4.48	5.52
May 2002	18.98	4.44	5.96
June 2002	19.78	6.25	6.59
Tile drain 9A			
March 2001	No data	1.90	5.32
April 2001	12.10	8.40	5.20
May 2001	13.62	7.98	6.23
March 2002	14.42	3.01	4.10
April 2002	16.54	6.17	3.89
May 2002	33.11	4.35	3.60
Tile drain 9B			
March 2001	no data	2.20	3.09
April 2001	14.28	2.20	6.76
May 2001	17.81	3.52	3.92
June 2001	18.56	3.36	4.84
March 2002	17.10	4.18	5.26
April 2002	17.11	4.86	6.37
May 2002	16.51	4.22	5.37
June 2002	17.74	6.19	5.58
Tile drain 11			
March 2001	19.84	4.50	5.84
April 2001	17.78	7.37	9.07
May 2001	16.91	7.37	5.95
June 2001	22.01	5.88	5.78
October 2001	19.01	4.31	8.20

Table 4.2 Nitrate-nitrogen and isotopic results for the groundwater samples

Sampling date	Nitrate-N concentration (mg/L)	δN^{15}-NO_3 (‰)	δO^{18}- NO_3 (‰)	δO^{18}- H_2O (‰)
Well 3S				
July 2001	9.55	14.07	8.92	-5.70
January 2002	7.68	15.71	9.66	-6.79
February 2002	9.57	14.99	10.39	-6.99
March 2002	9.14	14.01	9.61	-7.03
April 2002	8.49	14.35	9.93	-7.23
May 2002	6.02	13.03	9.93	-6.53
June 2002	5.95	13.90	8.61	-7.21
Well 5S				
April 2001	1.30	no data	no data	no data
May 2001	2.19	11.90	13.68	no data
July 2001	2.21	13.18	14.15	-6.72
August 2001	3.20	13.49	10.60	-6.40
September 2001	4.14	13.41	11.74	-6.93
October 2001	6.65	12.79	9.59	-6.57
December 2001	7.36	12.92	10.85	-7.04
January 2002	7.19	10.52	9.41	-6.40
February 2002	2.66	9.65	9.38	-6.92
Well 6S				
April 2001	18.96	2.70	10.30	no data
May 2001	19.49	2.40	5.20	no data
July 2001	20.06	3.27	5.79	-7.03
August 2001	19.46	3.84	4.59	-7.54
September 2001	19.39	3.80	5.24	-7.24
October 2001	20.29	4.08	4.61	-7.25
December 2001	17.31	5.08	5.83	-7.31
January 2002	23.70	4.22	2.10	-6.89
February 2002	29.51	4.18	6.74	-7.20
March 2002	30.60	4.08	6.01	-7.35
April 2002	34.31	4.05	6.09	-7.10
May 2002	29.47	3.15	4.22	-7.10
June 2002	30.75	3.12	4.10	-7.25
Well 11S				
May 2001	2.35	16.00	10.08	no data
July 2001	2.39	17.50	12.96	-8.19
August 2001	1.69	36.91	13.81	-8.46
September 2001	0.90	no data	no data	-8.51
October 2001	1.09	15.56	8.20	-7.79
December 2001	0.90	25.24	10.34	-8.05
January 2002	1.26	20.53	11.20	-6.76
February 2002	3.07	5.86	6.12	-8.04

Sampling date	Nitrate-N concentration (mg/L)	δN^{15}-NO_3 (‰)	δO^{18}- NO_3 (‰)	δO^{18}- H_2O (‰)
March 2002	2.58	4.84	4.81	-7.90
April 2002	1.52	8.55	8.41	-8.26
May 2002	2.97	8.43	5.86	-8.21
June 2002	6.55	12.35	10.21	-7.80

4.3.1 Tritium and δ^{18}O in Water

Wells 5S and 6S had tritium values of 8.61 and 8.02 TU, respectively (Table 4.3). Wells 1D and 3D had tritium values of 1.04 and 0.10 TU, respectively. The δ^{18}O-H_2O data for wells 3S, 5S, 6S, and 11S showed little variation (< 2.1‰) over the sampling period (Figure 4.2). These four wells had δ^{18}O values that were principally in the -6.5 to -8.0‰ range with no significant variation despite significant seasonal changes in the δ^{18}O of the precipitation. This indicates that the residence time of the water in the shallow groundwater zone is certainly greater than two months, and probably greater than several months (see 4.4 Discussion).

Table 4.3 Tritium concentrations for groundwater samples

Well	Tritium Concentration (TU[1])
1D	1.04 ± 0.25
3D	0.10 ± 0.25
5S	8.61 ± 0.27
6S	8.02 ± 0.35

1: TU is tritium unit, which is defined as 1 tritium atom in 10^{18} hydrogen atoms
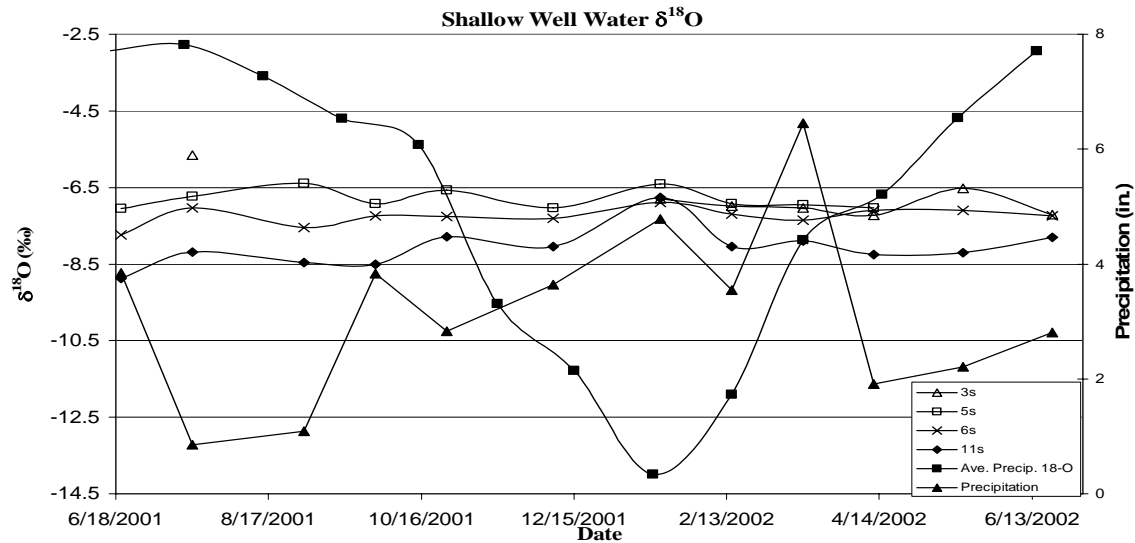
Shallow Well Water δ¹⁸O

Figure 4.2 $\delta^{18}O$ values of groundwater and precipitation.   Triangles represent amount of precipitation during the sampling period (National Climatic Data Center, 2002). Squares represent 20-year average (1960 and 1980) $\delta^{18}O\text{-}H_2O$ for precipitation in Illinois (Hackley, personal communication).

4.3.2 Nitrate-Nitrogen Concentration

Nitrate-nitrogen concentrations and isotopic analysis with respect to time are plotted as a pair of graphs for samples from the tile drains (Figure 4.3) and the wells (Figure 4.4). Nitrate-nitrogen concentrations in the tile drain samples ranged between 12.1 to 33.1 mg/L with an average value of 17.5 mg/L. Some tile drains showed no trends, while others had higher $NO_3\text{-}N$ concentrations in 2002 than 2001.
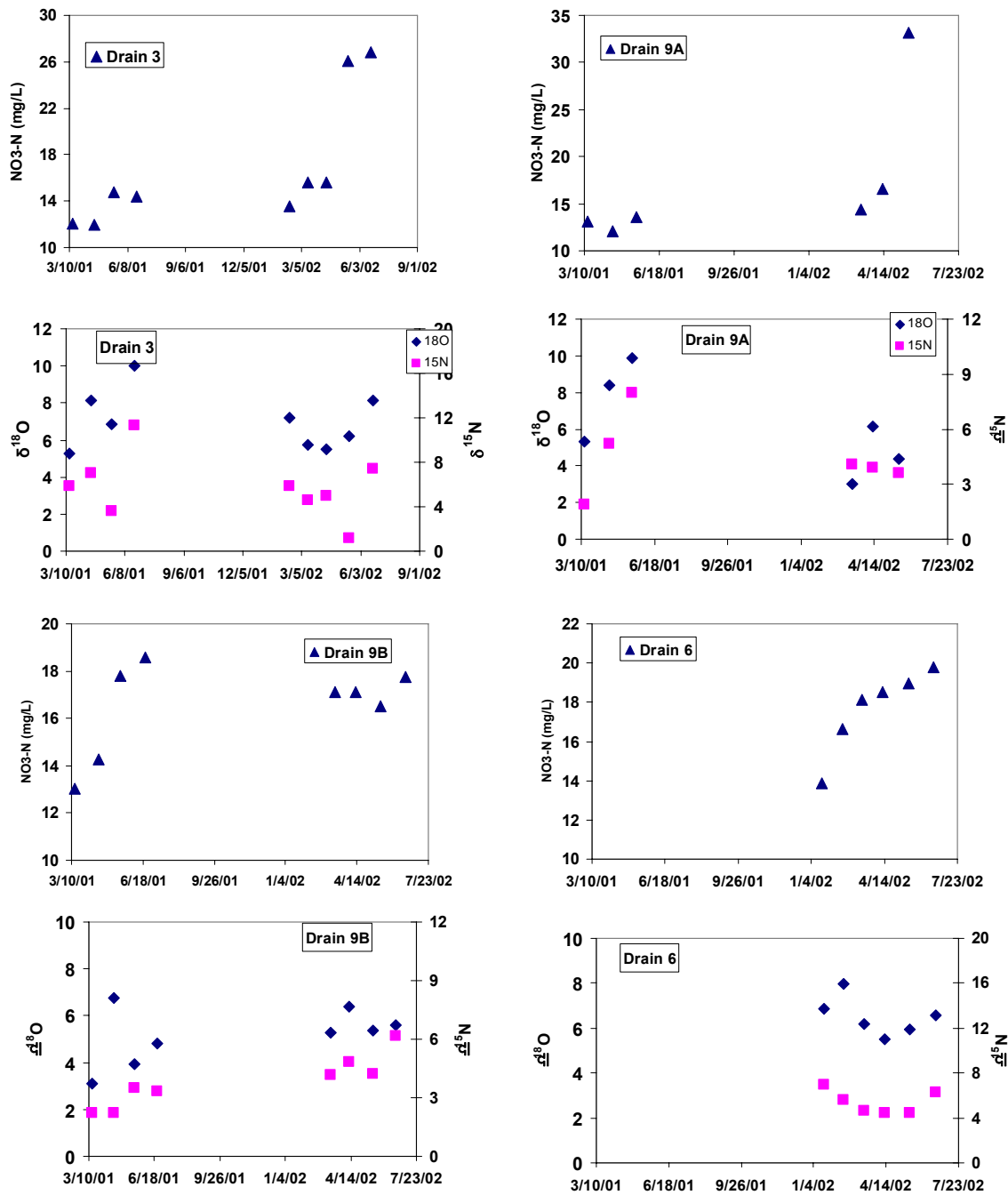
Figure 4.3 Temporal trends of NO₃-N concentration and δ¹⁵N or δ¹⁸O values in the drains. Concentrations are given in mg/L of NO₃-N. Isotopic data is given in per mil. In the isotopic graphs, diamonds represent $\delta^{18}O$, while squares represent $\delta^{15}N$ ratios.
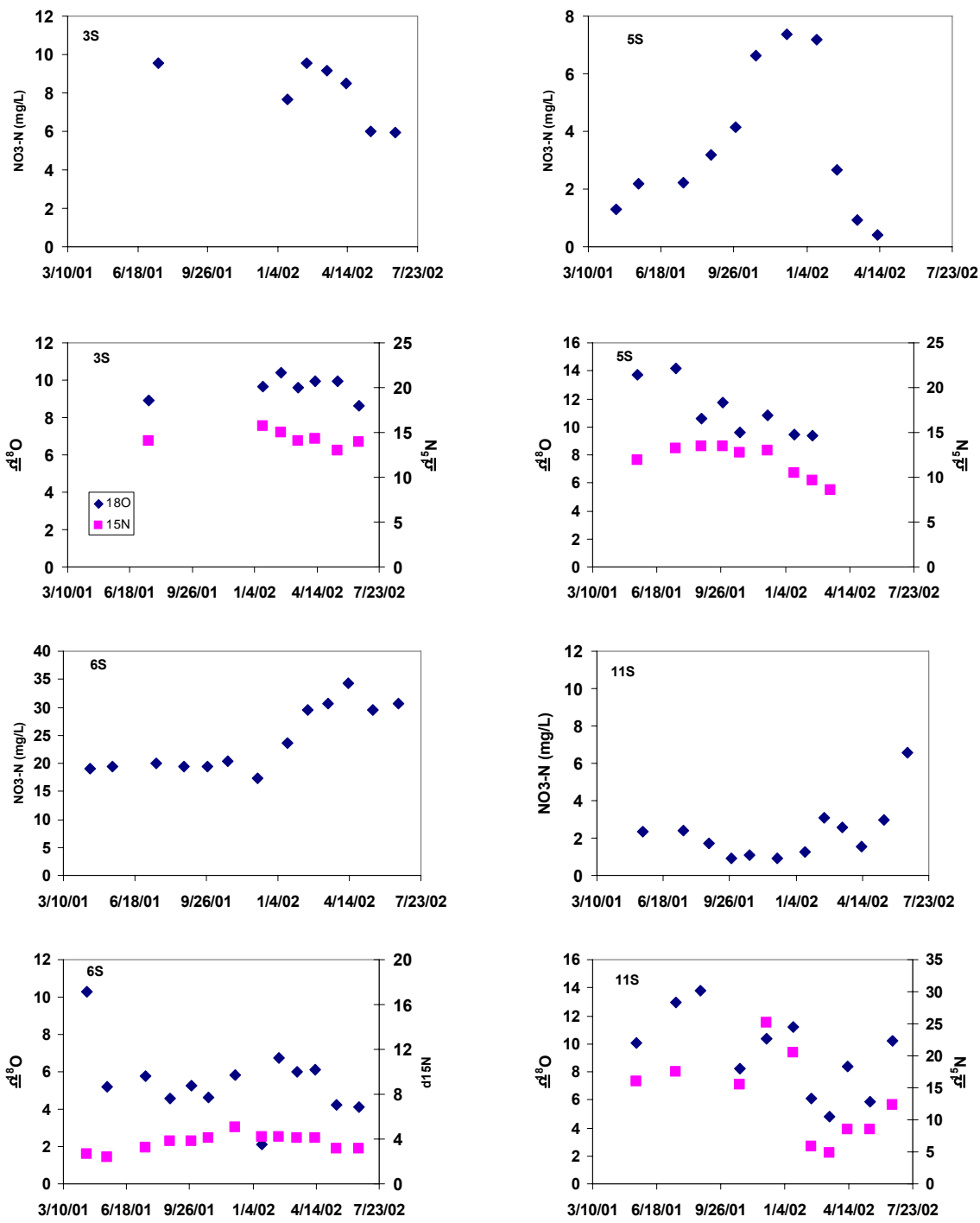
Figure 4.4 Temporal trends of NO$_3$-N concentration and δ^{15}N or δ^{18}O values in shallow wells. Concentrations are given in mg/L of NO$_3$-N. Isotopic data are given as per mil values. In the isotopic graphs, diamonds represent δ^{18}O values and squares represent δ^{15}N values.

Four of eleven shallow monitoring wells (3, 5, 6, and 11) contained NO_3-N concentrations that exceeded 1 mg/L consistently, allowing for isotopic analysis. The other seven shallow wells had concentrations that were consistently below 1 mg/L indicating that fertilizer-derived nitrate was either completely denitrified or somehow nonexistent in overlying soils. The low NO_3-N concentrations in these seven wells, combined with low water yields, made them sampling for isotopic analysis impractical. Also, because the nitrate-nitrogen concentrations in the deep wells rarely exceeded 1 mg/L; these wells also were not sampled for isotopic analysis.

The NO_3-N concentration in well 3S was relatively constant, varying between 5.9 and 9.5 mg-N/L, indicating the nitrate flux near this well is near steady state. The NO_3^--N concentration in well 5S varied widely from 0.4 to 7.4 mg-N/L. The concentration increased steadily throughout 2001, representing influx of NO_3^--N from a fertilization event, and decreased dramatically during 2002, either due to denitrification or advection/dilution. Well 6S showed steady concentrations of NO_3-N during 2001 then increasing concentrations in 2002, presumably from the influx of NO_3-N from fertilization. Concentration values were relatively high in this well, ranging from 17.3 to 34.3 mg-N/L. With the exception of one month, these values are greater than concentration values seen in the tile drains. A wide range of NO_3-N concentrations were observed in well 11S, fluctuating between 0.9 and 6.5 mg-N/L. The concentrations of NO_3-N dropped initially in 2001, remained stable for a period, increased in January and February 2002, dropped again and then increased in May and June. The general upward trend in concentration during 2002 likely represents influx of NO_3^- from a fertilization event.

4.3.3 Effects of Denitrification on δ^{15}N and δ^{18}O of Nitrate

Denitrification causes both the δ^{15}N (Marriotti et al., 1981) and δ^{18}O (Olleros, 1983; Böttcher et al., 1990) values of the residual NO_3^- to increase. A simplified Rayleigh equation (Mariotti et al. 1981) was used to describe the relationship between N and O isotopic ratios in residual nitrate:

$$\delta_s = \delta_{s,o} + \varepsilon * \ln f \qquad\qquad \text{Equation 4.2}$$

where: δ_s = Delta value of the nitrate (‰)
$\delta_{s,o}$ = Initial delta value in the nitrate (‰)
ε = Enrichment factor (‰; a negative number)
f = Fraction of the unreacted residual nitrate:

$$f = N_s/N_{s,o} \qquad\qquad \text{Equation 4.3}$$

N_s = Nitrate concentration (mg/L)
$N_{s,o}$ = Initial nitrate concentration (mg/L)

Solving for f in Equation 4.2 yields:
$$f = \exp[(\delta_s - \delta_{s,o})/ \varepsilon] \qquad\qquad \text{Equation 4.4}$$

Thus, as denitrification proceeds, the ^{15}N/^{14}N ratio of the residual fraction of NO_3^- increases. This relationship can be used to calculate f, and thus the degree of denitrification, if the δ^{15}N or δ^{18}O values of the initial nitrate source and reacted nitrate are known and epsilon can be estimated.

Epsilon is a variable that depends on the conditions in the soil or aquifer (Hübner, 1986), and reported values range from -15.0‰ to -4.0‰ (see 4.4 Discussion).

4.3.4 $\delta^{15}N$ and $\delta^{18}O$ of Nitrate: Tile drains

The $\delta^{15}N$ and $\delta^{18}O$ values for the nitrate from the tile drains, shown in Figure 4.5 and Table 4.1, ranged from +1.2 to +11.4 and +3.6 to +9.8 ‰, respectively. The majority of these values fall within ranges expected for nitrified (microbially oxidized) anhydrous ammonia after either direct nitrification or mineralization reactions with organic matter (Figure 4.5, see Discussion). A few samples have delta values that are greater than those expected for nitrified ammonia, which indicates denitrification has occurred. During 2001, nitrate-nitrogen in tile drains 3, 9A, and 9B all show increasing isotopic ratios. In early 2002, tile drains 3, 9A, and 6 show decreasing isotopic values indicative of an influx of new NO_3^- from fertilization followed by increasing ratio. Simultaneously increasing isotopic ratios taken with combined ratios outside of expected ranges are suggestive of small amounts of denitrification occurring in the shallow soil zone.
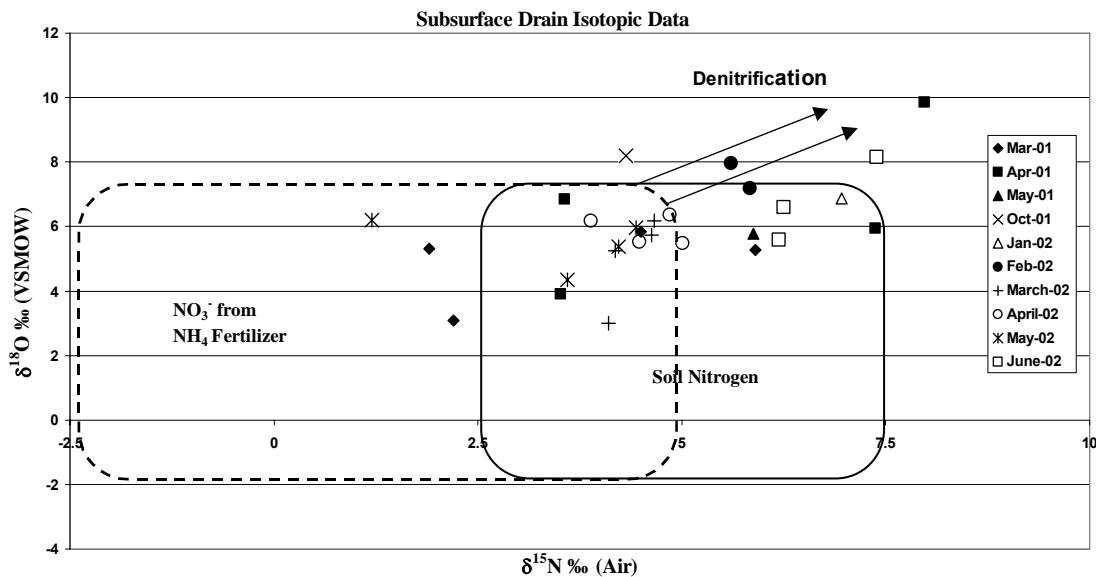

Figure 4.5 Distribution of $\delta^{15}N$ and $\delta^{18}O$ ratios in tile drain samples. Boundaries modified from Kendall (1998).

4.3.5 Nitrate $\delta^{15}N$ and $\delta^{18}O$: Groundwater

$\delta^{15}N$ and $\delta^{18}O$ values from the sampled shallow wells vary widely between wells. Time series values are shown in Figure 4.4. In wells 3S, 5S, and 11S, $\delta^{15}N$ and $\delta^{18}O$ ratios are consistently higher than those in the drains (Figure 4.3), indicating denitrification has occurred. Figure 4.6 shows the relationship between NO_3-N concentrations and $\delta^{15}N$ values in both tile drains and wells. Well 6S has $\delta^{15}N$ values similar to those of the tile drains, suggesting that denitrification in groundwater is limited at this site. Wells 3S and 5S shows $\delta^{15}N$ ratios that are relatively constant over the sampling period indicating that the amount of denitrification occurring upgradient of the well is stable. Well 11S has widely variable $\delta^{15}N$ ratios signifying variable denitrification rates and/or mixing of different NO_3^- sources.
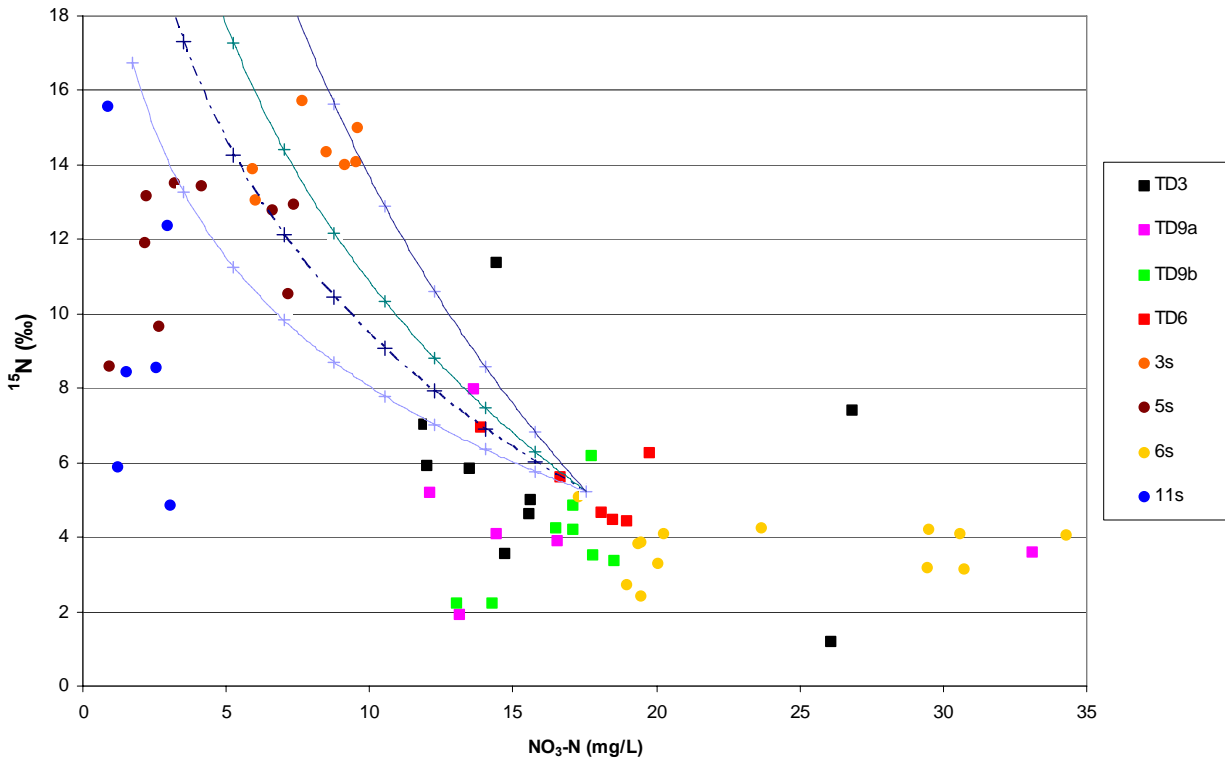
Figure 4.6 Concentration of NO_3-N versus $\delta^{15}N$ ratios. Drains show high concentrations and low isotopic ratios. As denitrification proceeds, concentrations should drop while isotopic ratios increase. Lines give concentration versus $\delta^{15}N$ relationships for $\varepsilon = -5$ (left), -7.5, -10, and -15 (right).

4.4 Discussion

4.4.1 Tritium and $\delta^{18}O$-H_2O

The tritium values for groundwater samples are compared with values of precipitation measured over the last 50 years (Figure 4.7). Tritium values for wells 5S and 6S, 8.61 and 8.02 TU respectively, correspond to values for groundwater infiltrating at any time over the last 20 years. The tritium value for well 3D, 0.1 TU, is indistinguishable from zero given the uncertainty for the measurement method and thus may be considered "tritium dead" (over 55 years in age). The tritium value for well 1D, 1.04 TU, corresponds to an approximate age or time of recharge in the early 1950s. Because widespread fertilization in the area did not begin until the late 1950s it is almost certain that neither deep well ever contained large amounts of NO_3^-.

Two possible interpretations exist for the distribution of $\delta^{18}O$-H_2O in the shallow wells: 1) Recharge of the wells is occurring mainly during one period of the year, or 2) Mixing of at least 1 year's worth of waters over the flow path. The weighted average $\delta^{18}O$-H_2O value of precipitation during the sampling period is −6.4‰, assuming precipitation $\delta^{18}O$-H_2O values are equal to the 30 year average (Hackley et al., 1996). Removing data from June, July and August, when evapotranspiration and
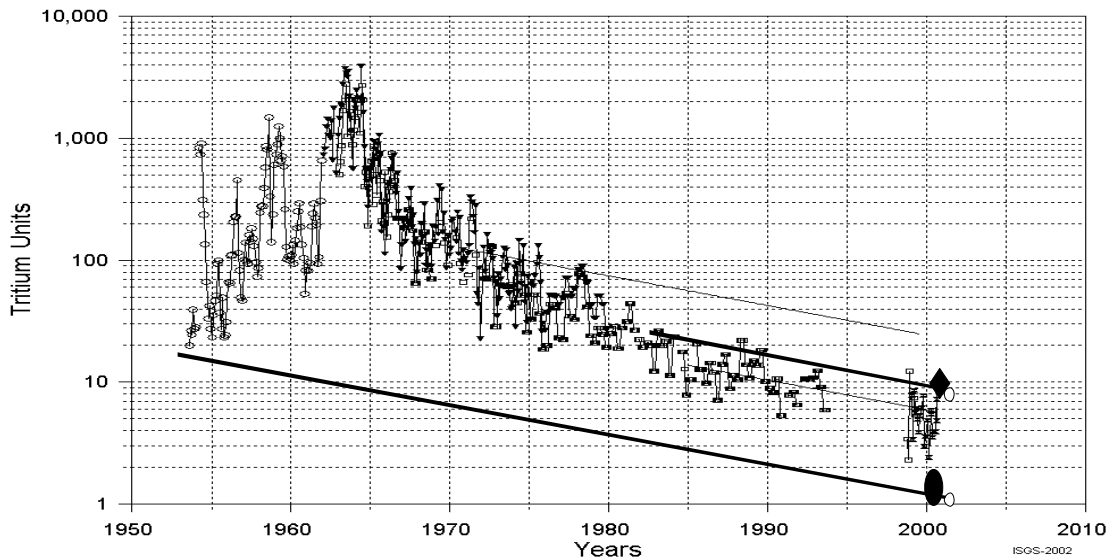
Figure 4.7 Tritium values for precipitation in Illinois and Canada over the last 50 years. Squares represent St Louis, MO, triangles represent Chicago, IL, open circles represent Ottawa, ON, stars represent Waterloo, ON. The diamond represents shallow well tritium values. The oval represents the tritium value for well 1D.

water uptake by plants are likely to significantly lower recharge rates, as evidenced by lack of flowing tile drains, the weighted average $\delta^{18}O$ value of precipitation becomes $-7.5‰$. These values bracket the observed data for wells 3S, 5S, and 6S reasonably well and with the lack of wide variations in the observed data suggest that the sand layers sampled by the shallow wells contain a well-mixed combination of water recharged mainly between September and May. Slightly lighter isotopic values seen in well 11S ($\sim1‰$) could indicate less evaporation is taking place in its area due to different soil type or flow regime. Evaporation favors the preferential removal of ^{16}O-bearing water leaving the residual water enriched in ^{18}O. Most importantly, we conclude that water in the shallow wells cannot have a subsurface residence time of less than 6 months. If this were the case, we would expect to see summer and winter excursions in the oxygen isotopes as shown in Figure 4.2.

In addition, the oxygen isotope data indicated that the shallow wells do not have any significant recent recharge. These data are consistent with the relative groundwater ages estimated by other techniques. The approximate age of the groundwater samples from the shallow and deep wells, as measured by tritium, are consistent with those estimated by CFC dating, which were discussed in Section 3.5.1.

4.4.2 Initial $\delta^{15}N$ Values for NO_3^-

The type of fertilizer used defines the initial $\delta^{15}N$ value of nitrate. Anhydrous ammonia, the primary fertilizer used in the study area, may have $\delta^{15}N$ ratios ranging from -2.7 to $+1.6‰$ (Hübner, 1986). Because fertilizer reacts in the soil after its application, measurement of the fertilizer $\delta^{15}N$ cannot be taken as the initial $\delta^{15}N$ value of nitrate. Nitrification of ammonia by bacteria can alter the $\delta^{15}N$ ratio by ±2-3‰ (Shearer and Kohl, 1986). Volatilization of ammonia after application can increase $\delta^{15}N$ in the residual fraction by 2-3‰ (Kreitler, 1975). Mineralization reactions, the production of

ammonia from organic matter, can affect $\delta^{15}N$ ratios by $\pm 1‰$ (He et al., 1999). Finally sorption of NH_4^+ to clays may fractionate nitrogen isotopes to varying extents dependent on ammonia concentrations and the type of clay minerals present (Karamanos and Rennie, 1978).

Uncertainties in initial $\delta^{15}N$ values of fertilizers from field to field coupled with variable extents of post-fertilization fractionation caused by heterogeneous conditions within individual fields contribute to uncertainty in choosing initial values for nitrate *a priori*. Consequently, estimates of denitrification in tile drain water based on the $\delta^{15}N$ values are highly uncertain. Given our current lack of knowledge about the processes affecting the initial $\delta^{15}N$ values, it is conceivable that the entire range of values observed in the tile drains results from processes other than denitrification. Simultaneous changes in $\delta^{15}N$ and $\delta^{18}O$ during the sampling period are, however, difficult to reconcile with other processes that are likely to affect isotopic ratios indicating denitrification is the most likely explanation for our observations.

Choosing an initial value for denitrification in the sub-drain zone is less complicated. Aside from minor effects associated with plant uptake, once NO_3^- is formed, denitrification becomes the primary method by which $\delta^{15}N$ and $\delta^{18}O$ ratios may be altered. Once NO_3^- moves below the drains, its $\delta^{15}N$ and $\delta^{18}O$ ratios are unlikely to be changed by any processes other than denitrification. For this reason, the average $\delta^{15}N$ value for the tile drains ($+6.1‰ \pm 2.2‰$) was taken to be the starting value for the groundwater nitrate.

4.4.3 Estimates of Initial $\delta^{18}O$ Values of Nitrate

Initial $\delta^{18}O$ values of nitrate are a result of the nitrification process, in which two oxygen atoms from H_2O and one from atmospheric O_2 ($+22‰$) are used to create nitrate (Kroopnick and Craig, 1972). The $\delta^{18}O$ value of the precipitation water donating oxygen to nitrification will change depending upon the season in which the fertilizer was applied (Figure 4.5). In addition, heterogeneous conditions within the agricultural fields, such as different evaporation rates, which leave residual water enriched with respect to ^{18}O, may influence the initial $\delta^{18}O$ ratio of the water. For these reasons, estimates of initial $\delta^{18}O$ values of the nitrate that reaches the tile drains involve rather large uncertainties. Groundwater beneath the tile drains, however, should have an initial $\delta^{18}O$-NO_3 value similar to that seen in tile drains. For this reason, the average drain value for $\delta^{18}O$, $5.2‰ \pm 1.6‰$, was taken to be the initial value for the saturated zone.

4.4.4 Estimates of Epsilon Values

Measured and calculated values of ε, the per mil N isotope fractionation for denitrification, range from $-40‰$ in desert environments to $-5‰$ in laboratory studies (Hübner, 1986; Mariotti et al., 1988; Böttcher et al., 1990). Mariotti et al. (1988) correlated the rate of denitrification to changing ε values. Slower denitrification rates correspond to larger ε values due to increasing microbial selectivity for ^{14}N and ^{16}O. Low NO_3-N concentrations at 7 of 11 shallow wells and large concentration drops, relative to tile drain waters, at 3 of the remaining 4 wells are indicative of high rates of denitrification compared to oligotrophic (low dissolved carbon/high dissolved oxygen) aquifers. On the other hand, flow path time scales of months to years imply that denitrification rates are slow compared to laboratory studies. Assuming constant nitrate input across the watershed, the varying NO_3-N concentrations found in shallow groundwater indicate that denitrification rates also

are variable in the watershed. Accordingly, it is impossible to determine ε precisely for this study, thus we interpreted the data using a range of ε values.

Denitrification calculations were done for three ε values which could be representative of field conditions: -5‰, -10‰, and -15‰. Corresponding epsilon values for oxygen fractionation have been established in the literature and are very nearly one half the epsilon values for nitrogen fractionation (Olleros, 1983; Böttcher et al., 1990; Voerkelius and Schmidt, 1990). Differences in error or uncertainty during measurement of $\delta^{18}O$ ratios via the HgCN reduction method reported by Révész and Böhlke (2002) and measured error for using graphite reduction in our study (Figure 4.1) will change this relationship somewhat. To correct for this difference, the averaged value for the epsilon vycor and quartz methods reported by Révész and Böhlke (2002) was used to calculate a corrected $\varepsilon_{nitrogen}/\varepsilon_{oxygen}$ ratio of 2.45 for the carbon reduction method. Epsilon values for oxygen isotopes were thus set at 2.04‰, 3.08‰, and 6.21‰ for calculations in which $\varepsilon_{nitrogen}$ values were -5‰, -10‰, and -15‰, respectively.

4.4.5 Drain $\delta^{15}N$ and $\delta^{18}O$: Evidence for Denitrification

While most of the $\delta^{15}N$ and $\delta^{18}O$ ratios of the nitrate in tile drain samples are in the expected range for nitrified anhydrous ammonia or soil nitrogen, increasing ratios through time are suggestive of denitrification (Figure 4.3). The trend of greater ratios with time is seen in 2001 and is repeated in 2002, when after a decrease in isotopic ratios due to the influx of new nitrate, both $\delta^{15}N$ and $\delta^{18}O$ ratios in tile drains 3, 9B, and 6 increased over time.

The observed changes in the nitrate concentrations in tile drain samples would appear to not match these conclusions, because concentrations increased even as the isotopic ratios increased. However, the anomaly is likely an artifact of the increased mobility of NO_3^- as soil temperatures rise during spring. As the soil temperature rises and water begins to move in the system, leaching of NO_3^- to the tile drains begins. Warmer temperatures also allow for microbial growth in the shallow soil zone, increasing the amount of NO_3^- consumed. Furthermore large amounts of spring precipitation can saturate the soil column, isolating it from contact with the atmosphere and encouraging the anaerobic conditions required for denitrification. Thus, the absolute concentrations of NO_3^- may increase during the year, but the fraction of the concentration increase representing the NO_3^- that was not denitrified may decrease.

4.4.6 Estimates of Initial Well NO_3^- Concentration

Exact initial concentrations of NO_3-N also are difficult to estimate due to variations in fertilizer application rates between fields, the inhomogeneous conditions within fields, and an unknown amount of N released from soil organic matter. While the nitrate concentrations observed in the tile drains could serve as a proxy for the initial concentration of nitrate entering the saturated zone, some problems exist. Tile drains are not always proximal to wells and often drain more than one field, meaning that nitrate concentrations could be an average concentration between a field that was recently fertilized and one that was not. In addition, tile drain coverage in the fields is not uniform, meaning some fields are better drained than others. NO_3^- is likely to be more leached from well-drained areas, and thus water recharged in these areas may exhibit a greater temporal variation than water recharged in poorly drained areas. For these reasons, a non-concentration based method was adopted for calculation of amounts of denitrification occurring between the drains and wells.

Calculated denitrification extents are given as a ratio of the observed concentration over the initial concentration.

4.4.7 Denitrification Estimates

The concentration and isotope data indicated little or no denitrification had occurred in well 6S. One possible explanation is a grove of nearby trees (<20 feet), the roots of which may either be providing a fast flow path to the well or allowing for the shallow water to remain oxygenated and preventing denitrification. The location of well 6S in an upland setting may also explain the limited observed denitrification. Tesoriero et al. (2000) noted that upland areas had lower rates of denitrification than lowland areas.

Calculated percentages of denitrification over time (i.e., the percentage of nitrate originally present that has been lost) for wells 3S, 5S, and 11S are shown in Figure 4.8. Denitrification estimates derived from $\delta^{18}O$ match those derived from $\delta^{15}N$ reasonably well for all three wells. The averaged $\delta^{18}O$-based calculations differ from the averaged $\delta^{15}N$-based calculations, by 2.6%, -16%, and 17% for wells 3S, 5S, and 11S. These differences are likely due to uncertainty in the initial $\delta^{15}N$ and $\delta^{18}O$ values combined with the uncertainty in the 2.45:1 ratio between ε values.

Comparison of calculated denitrification percentages (f) to measured concentrations of NO_3^- (N_s) in the shallow wells using equation 4.3 provides a method to judge whether the chosen ε values were reasonable. Knowing f and N_s allows the initial NO_3-N concentration to be estimated. In wells 3S and 5S, an epsilon value of -5‰ for ^{15}N calculations corresponds to initial NO_3-N concentrations averaging 50.4 and 18.5 mg/L, respectively. An epsilon value of -2.04‰ for ^{18}O calculations in wells 3S and 5S corresponds to average initial NO_3-N concentrations of 46.1 and 52.3 mg/L, respectively. The average nitrate concentration in all drains was 17.1 mg/L and less than 30 mg/L with the exception of a single sample. Epsilon values of -5‰ for ^{15}N and -2.04‰ for ^{18}O calculations are thus unreasonable due to the large initial NO_3^- concentrations needed to accommodate observed isotopic fractionations. For this reason, results for $\varepsilon_{Nitrogen}$ and ε_{Oxygen} of -5‰ and -2.04‰ are likely not relevant and will not be discussed further.

Calculated percentages of denitrification for well 3S using either $\delta^{15}N$ or $\delta^{18}O$ remain relatively constant throughout the sampling period, ranging on average between 56% and 63% for an epsilon value of -10‰. The NO_3-N concentration in well 3S is similarly constant throughout the sampling period. Assuming water was constantly entering the volume sampled by well 3S, this suggests that denitrification is near steady state, with a rough balance between new nitrate entering and existing nitrate being removed by denitrification. The amount of nitrate recharging to the well and the removal rate via denitrification are thus likely to be reasonably constant.

Calculated percentages in well 5S also remain constant throughout much of the sampling period, ranging on average between 37 and 55% for an epsilon value of -10‰. This contrasts sharply with the concentrations, which show a seven-fold increase during 2001, followed by a decrease back to values similar to those seen at the beginning of sampling. Neither isotopic ratio is enriched during the associated concentration drop in early 2002, suggesting that enhanced denitrification is not responsible for the concentration change. Stability of $\delta^{15}N$ and $\delta^{18}O$ ratios in well 5S also suggests that NO_3 is being denitrified at a relatively constant rate along flow paths to the well.
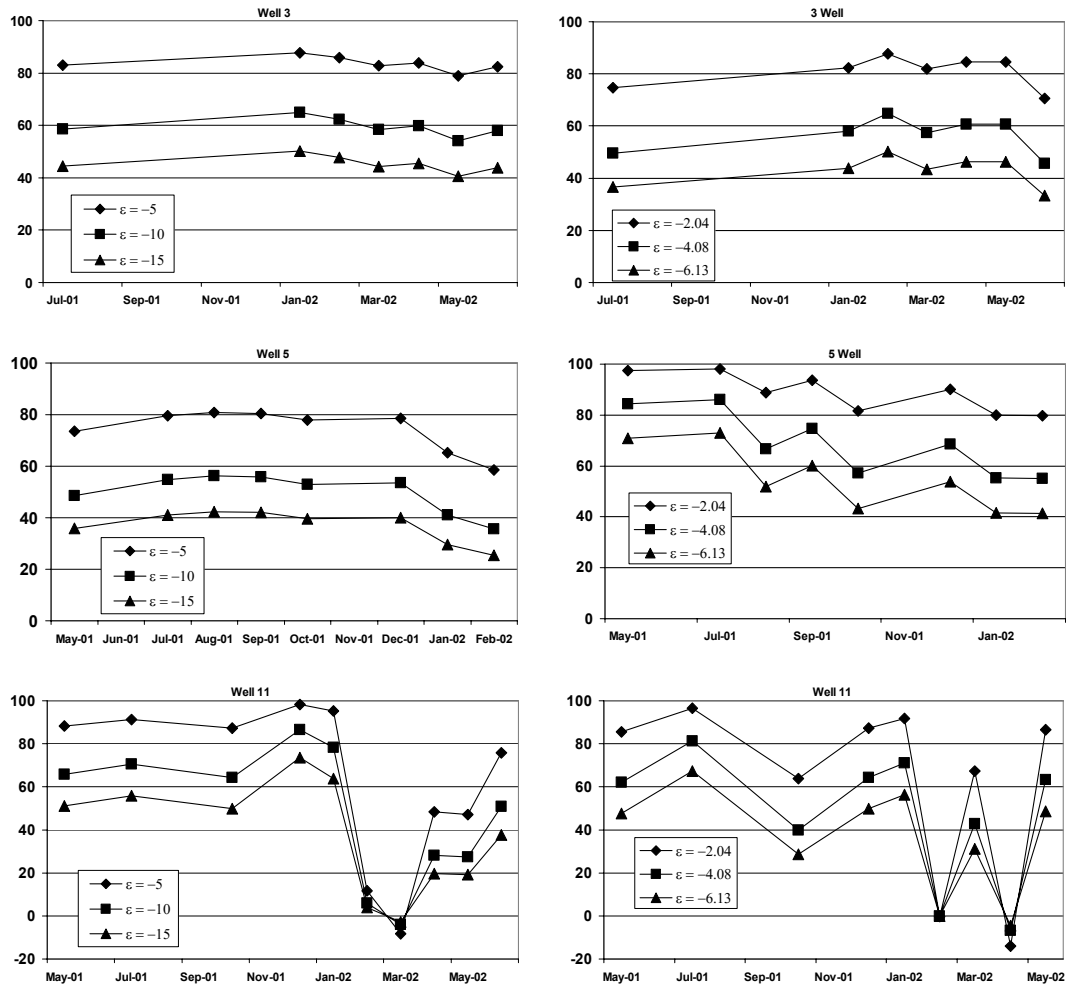
Figure 4.8 Estimated percentages of original nitrate removed by denitrification using nitrogen isotope data (left side plots) and oxygen isotope data (right side plots).

Calculated denitrification percentages in well 11S show a wide range of variability (0 to 85%) for an epsilon value of -10‰ during the sampling period. During 2001, low concentrations of nitrate-nitrogen coupled with high $\delta^{15}N$ and $\delta^{18}O$ ratios suggest an initial large abundance of nitrate has been removed by denitrification. Decreasing $\delta^{15}N$ and $\delta^{18}O$ ratios and increasing concentrations in February and March 2002 suggest influx of fresh NO_3^- into the well. This mixing of nitrate sources has the effect of reducing the calculated denitrification rate. Increasing $\delta^{15}N$ and $\delta^{18}O$ ratios after March 2002 indicate denitrification rates over the length of the flow path increase even as NO_3-N concentrations increase.

4.4.8 Dissolved Gases of Limited Applicability in Shallow Groundwater

Dissolved N_2 concentrations and isotopic composition have been used in several studies (Vogel et al., 1981; Wilson et al., 1990; Böhlke and Denver, 1995; McMahon and Böhlke, 1996) to estimate the extent of denitrification in agricultural settings. Preliminary sampling of dissolved N_2 concentrations in the Big Ditch watershed indicated that water in the shallow wells did not contain N_2 concentrations in large excess of that expected for equilibrium with atmospheric N_2. If the average NO_3-N concentration observed in the tile drains (17 mg/L) were completely denitrified, the

amount of dissolved N_2 present in the shallow groundwater would roughly double. The pressure needed to keep that amount of N_2 dissolved would also double from an original value equal to the partial pressure of nitrogen in the atmosphere of 0.789 atm to 1.56 atm. The new pressure is equal to that exerted by 16 m of water. At most, the shallow wells in the watershed have 3 m of water above them and thus it is probable that N_2 formed by denitrification in the shallow soil zone resulted in at least partial exsolution of gas from the water. This pattern is likely to be reproduced in similar glacially dominated geological regimes where denitrification rates are high relative to recharge rates.

4.5 Conclusions

The suite of geochemical data collected in this project suggests that denitrification is a major sink for nitrate in a flat, glacial till-dominated, agricultural watershed containing subsurface tile drains. Tritium and $\delta^{18}O$-H_2O values associated with shallow groundwater show that water was recharged months to years before reaching shallow monitoring wells and was derived primarily from precipitation in the spring and fall. $\delta^{15}N$ and $\delta^{18}O$ data from the tile drain samples, which define the top of the saturated zone, showed evidence for minor denitrification in some cases. However, the initial $\delta^{15}N$ and $\delta^{18}O$ values of the nitrate, which came from injected anhydrous ammonia fertilizer, are uncertain, and could vary in space and time due to various chemical and biological reactions.

The shallow groundwater system in the watershed is a sink for nitrate. Using the $\delta^{15}N$ and $\delta^{18}O$ values in the tile drains as initial values for recharged groundwater, we calculated the percent denitrification for several time points. Results derived from nitrogen isotopes were largely consistent with those derived from oxygen isotopes and provided strong evidence that microbial denitrification was the cause of decreases in nitrate concentration. In three of four shallow wells analyzed, isotopic data indicated that denitrification was responsible for losses of nitrate between 30 to 80%. Seven shallow wells with nitrate concentrations too low for isotopic analysis likely underwent near complete denitrification, or never had significant amounts of nitrate present. The former conclusion seems probable due to the consistently high nitrate concentrations measured in tile drain waters that approximate an initial recharge value for shallow wells. In general, this distribution is likely to be repeated in other till-dominated watersheds in the American Midwest.

Slow infiltration rates and long residence times allow for microbial denitrification to proceed to completion. Poor surface drainage in such watersheds also necessitates the emplacement of tile drainage, that provides a fast path for nitrate transfer to surface waters. Denitrification in the shallow soil zone may play a significant role in reducing the flux of nitrogen from fields to surface waters. Difficulties in assessing initial $\delta^{15}N$ and $\delta^{18}O$ ratios of NO_3^-, as well as assigning a value to ε that would be consistent over the entire range of the watershed make calculations of denitrification with precisions less than $\pm 15\%$ difficult. Increasing accuracy, decreasing sample size, and speed of analysis due to the recent development of on-line isotopic analysis techniques are likely to aid in future investigations of these issues. Nonetheless, the $\delta^{15}N$ and $\delta^{18}O$ ratios of dissolved NO_3^- clearly indicate the rapid removal of NO_3^- in shallow saturated zones in our study area.

5. THE MICROBIAL DENITRIFYING ACTIVITY IN THE GROUNDWATER OF THE BIG DITCH WATERSHED

5.1 Background

Many factors affect the extent of nitrate contamination in groundwater: nitrogen loading, land use, soil drainage characteristics, irrigation, and biogeochemical transformations (Figure 1.1) (Nolan and Stoner, 2000). Under aerobic conditions, the main source of nitrate is ammonium oxidation by the microbially-mediated process nitrification. Because nitrate is stable under aerobic conditions, it may persist in groundwater for decades (Nolan and Stoner, 2000). Nitrate can be attenuated in groundwater under anaerobic conditions through denitrification. Denitrifying microorganisms reduce nitrate to nitrogen gas, which is released to the atmosphere and therefore serves as an inert nitrogen sink. The denitrification pathway of nitrate to nitrogen gas involves the following series of reduction reactions: $NO_3^-{\rightarrow}NO_2^-{\rightarrow}NO{\rightarrow}N_2O{\rightarrow}N_2$ (Tiedje, 1994). Some bacteria only reduce nitrate to nitrite or grow by dissimilatory reduction of nitrate to ammonia. These two alternate pathways result in nitrogen not being removed from the groundwater. In the absence of denitrification, nitrite and ammonia may persist and continue to contaminate groundwater. The significance of these alternative pathways is usually low in oligotrophic (low carbon) groundwater ecosystems, where denitrification predominates (Tiedje, 1994). Most denitrifying bacteria are facultative, heterotrophic anaerobes and therefore denitrification can only occur in the absence of significant dissolved oxygen (DO) (Korom, 1992). Because organic carbon is required for heterotrophic growth, the amount of dissolved organic carbon (DOC) in the sediment is an important factor in determining the extent of denitrification in groundwater.

Because the fate and attenuation of nitrate in groundwater is not well characterized in Illinois, the purpose of this study was to quantify the activity of denitrifying microorganisms in the shallow groundwater of a tile-drained, agricultural watershed (the Big Ditch watershed) and to determine their capacity to remove nitrate in shallow groundwater. Denitrifying activity by microorganisms in the watershed was analyzed using three experimental approaches. First, denitrifying microorganisms in the sediment were enumerated using conventional approaches. Second, the rate of denitrification was measured using the denitrification enzyme assay (DEA) for several sediment and water samples from different areas of the watershed. Third, *in situ* nitrate reduction rates were determined directly using the push-pull method (Haggerty et al., 1998; Istok et al., 1997). A push-pull test involves the injection and subsequent extraction of a test solution containing both a reacting and a non-reacting tracer into and out of a monitoring well. The extracted water samples can be analyzed for the reactant and tracer concentrations to construct and compare breakthrough curves. Differences in the tracer and reactant breakthrough curves can be used to determine first or pseudo-first-order reaction rate coefficients using a mathematical analysis originally described by Haggerty et al. (1998). Several different sites across the watershed were sampled to determine the extent of spatial variability of denitrification activity in the aquifer.

5.2 Material and Methods
5.2.1 Water Chemistry

The well water was sampled and tested for DO, nonvolatile organic carbon (NVOC), and nitrate-N at various times throughout the year. The DO was measured while pumping using a membrane electrode, and after the readings stabilized, filtered water samples were collected. The samples were

then analyzed for NVOC and nitrate. Nitrate was determined using ion chromatography and NVOC was measured using persulfate-ultraviolet oxidation (Standard Methods 16th ed., 1985).

5.2.2 Sample Collection

Water samples were collected in July 2000 and December 2000 from all wells except 8D and 10D, which had too little water for collection. Water was pumped from each well using a peristaltic pump. Wells were flushed for 5 minutes, and then 250 to 500 mL was collected depending on the well's ability to produce water. These samples were then refrigerated at 10° C until the enumeration and rate tests were completed. Enumeration was completed within 48 hours, while the rate tests were completed within 1 week.

Samples of geologic materials were taken from different depths at each site to determine the horizontal and vertical variability of denitrification rates in the watershed. Samples were taken in two sets. In April 2000, the initial set of sediment samples were collected as boreholes for the monitoring wells were drilled using a hollow stem auger drill rig. In September 2000, the second set of samples was collected using a Geoprobe rig at six sites for a more detailed vertical profile. To prevent contamination, the sediment samples were taken from the center of the core retrieved from drilling at each site. Aseptic technique was used when collecting the samples to prevent cross-contamination. The samples were stored at 4° C for up to 3 months until the analyses were completed. Most probable number (MPN) analyses were started within 1 week of sample collection.

5.2.3 Nitrate Reduction Rate Determination

To determine the rate of nitrate reduction in water samples, the change in concentration of nitrate was measured. A 120 mL water sample was added to an anaerobic, 160-mL serum bottle and then spiked with 1 mM each of nitrate, glucose, and acetate. One 1mM of nitrate is equivalent to 14 mg/L NO_3-N. Liquid samples were taken periodically over a 1-week period and analyzed for nitrate and nitrite. The nitrate and nitrite concentrations of the liquid samples were analyzed using an HPLC.

5.2.4 Denitrification Rate Determination

The denitrification rate in sediments was measured by using a modification of the standard soil denitrification enzyme activity (DEA) assay (Tiedje, 1994). In this assay, 160-mL serum bottles were filled with 10 grams of sediment and phosphate buffer for a total volume of 100 mL. The headspace in these bottles was 60 mL of 90% nitrogen gas and 10% acetylene (added as an inhibitor of N_2O reduction). Samples were incubated at 25° C. The starting nitrate concentration was 2mM. In order to determine the effect of available carbon, the DEA was determined by measuring the N_2O production rate from soil samples with four different carbon amendments: no carbon, 0.2 mM, 2 mM, 8 mM, and 20 mM. The carbon source, acetate and glucose, were added in equimolar amounts. Chloramphenical, an antibiotic typically used to inhibit new growth in DEA analysis, was not used because it has been shown to underestimate the actual denitrification rates (Pell et al., 1996) and because N_2O production was undetectable when it was used in this study. Instead of the usual 2-hour DEA test used for surface soils, headspace gas samples were taken at different intervals depending on the rate of N_2O production and the carbon amendments applied: 3 to 4 days (2, 8, and 20 mM C), 1 week (0.2 mM C), and 8 weeks (no carbon). The rate was determined using the maximum slope of a linear fit line on a graph of mM N_2O produced versus time for each sample.

5.2.5 Pore Water Analysis

The pore water in the sediment samples collected with the Geoprobe was analyzed for nitrate and nitrite. The pore water was extracted by using a 1 g sample of sediment and adding 1 mL of distilled-deionized water. The samples were then mixed completely and allowed to equilibrate for 45 minutes. After the samples were filtered, the water was analyzed for nitrate and nitrite by HPLC. The concentration of nitrate was determined by using the moisture content of the soil to determine the volume of water that was extracted and then using that volume to determine the amount of dilution that occurred when 1 mL of distilled-deionized water was added.

5.2.6 Enumeration

The sediment and water samples were enumerated using a modified MPN method for denitrifying microorganisms (Tiedje, 1994). For three-tube MPN determinations, R2A broth media was used with 0.5 mM nitrate. The samples were incubated for 2 weeks and then the number of positive and negative tubes were counted for each sample. Positive tubes were determined by using a diphenylamine indicator test, which detects residual nitrate or nitrite (Tiedje, 1994). Plate counts on R2A agar plates with 0.5 mM nitrate were also used for selected samples from wells 1, 7, and 9 to enumerate the number of nitrate-reducing microorganisms. The plates were inoculated with the same dilutions as the MPN tests, incubated for 2 weeks in an anaerobic chamber ($T \approx 22°$ C), and then the number of colony forming units were counted.

5.2.7 Push-Pull Testing

Six push-pull tests were conducted to determine *in situ* nitrate reduction rates in shallow and deep groundwater at well 1 (Table 5.1, McDonald, 2003). The push-pull test is a cost effective method to estimate *in situ* reaction rates and can be conducted on a much more representative sample of the actual subsurface conditions than can be accurately reproduced under laboratory conditions. It involves the injection and extraction from the same well of a test solution containing both a reacting and a conservative or non-reacting tracer. The conservative tracer is used to quantify solute losses due to physical processes such as advection, dispersion and diffusion occurring during the test (Istok et al., 1997). The reactant is used to quantify the microbial activities. The test solution used in these experiments consisted of local groundwater spiked with approximately 10 mg/L NO_3^- as N (reactant) and 100 mg/L Br^- as a conservative tracer. The injection (push) phase involves the injection of the test solution into a single monitoring well, followed by the injection of a chaser solution. The chaser solution consisted of distilled, deionized (DDI) water, and was used to push the test solution out of the well casing and into the subsurface. A resting phase between the injection and extraction phases was used in every test conducted. No pumping occurred in this phase to allow time for nitrate reduction to occur. Resting phase length was based on the rate of the microbial reaction in the subsurface. After the resting phase, the groundwater with bromide and nitrate was extracted from

Table 5.1 Dates and locations of push-pull tests conducted

Test Name	Test Date	Well	Screened Depth Below Surface	Water Table Depth Below Well Casing
Big Ditch – Test 1	8/6-7/2002	1D	8.20 – 9.72 m	3.75 m
Big Ditch – Test 2	9/24-25/2002	1D	8.20 – 9.72 m	3.90 m
Big Ditch – Test 3	11/7-8/2002	1D	8.20 – 9.72 m	3.96 m
Big Ditch – Test 4	3/14/2003	1S	3.05 – 4.57 m	3.99 m
Big Ditch – Test 5	4/15/2003	1S	3.05 – 4.57 m	3.93 m
Big Ditch – Test 6	5/3/2003	1S	3.05 – 4.57 m	3.99 m

the same monitoring well during the extraction (pull) phase. By collecting samples during the extraction phase at timed intervals, bromide and nitrate breakthrough curves could be constructed.

Push-pull tests were conducted only at Site 1. The wells at site 1 were drilled with an approximately 178 mm diameter auger. The wells were constructed of schedule 40 PVC pipe with a 60 mm diameter and had a screen length of 1.52 meters. Well 1S was screened at a depth of 3.05 to 4.57 meters below the ground surface, with the well casing extending 0.72 meters above the ground surface. Well 1D was screened at a depth of 8.20 to 9.72 meters below the ground surface with the well casing extending 0.69 meters above the ground surface.

For each of the push-pull tests, all water pumped out of the well, except water samples, was collected in large plastic pull-out jugs to conduct a mass recovery analysis on the total bromide and nitrate extracted from the well. At the conclusion of each test, samples were taken from each pull-out jug. The concentrations of the solutions in these jugs were measured by ion chromatography. The mass of bromide and nitrate summed from all containers collected during the extraction phase divided by the mass injected in the test solution yielded a mass recovery percentage for each test.

Microbial nitrate reduction rates were first determined in the deeper well, well 1D, in the late summer of 2002. The groundwater used to make the test solution was pumped from well 8D in the Big Ditch watershed, because it was known to be able to produce substantial volumes of water geochemically similar to well 1D water. Twenty liters of groundwater were brought back to the laboratory, mixed with the 100x NO_3^- and Br^- concentrate to make the test solution and stored at 4° C. The test solution was degassed by bubbling nitrogen (N_2) gas through the solution until the measured dissolved oxygen (DO) level was under 1 mg/L. A chaser solution of DDI water was also degassed with N_2 gas until the measured DO was less than 1 mg/L and brought to the well.

The initial water level in well 1D was 3.75 meters below the top of the well casing. A volume of 15 L of groundwater was pumped out of the well, and the well was allowed to recover to its initial water level. Samples from this groundwater and the initial test solution were taken for later analysis. The volumes of test and chaser solutions used were 15 L and 5 L, respectively. The chaser solution was injected immediately after the test solution. All injections occurred through plastic tubing that ended 9.14 meters below the ground surface. A resting time of 25.8 hours was used for this test.

Initially, the pump was set to remove water at 500 mL/min; however, the extracted water started to turn noticeably turbid after the first eight samples. After this, the pump rate was reduced to about 260 mL/min. Samples were taken after each liter extracted for the first 20 samples and then every 2 liters for the next 15 samples. The volume of water extracted and stored in pull-out jugs for this test reached 48 L. These jugs were sampled for mass recovery of nitrate before leaving the site.

A second test at well 1D was conducted in the fall 2002. Procedures similar to those used in the first test were followed with two exceptions. The test and chaser solution volumes were increased to 20 L and 7.5 L, respectively, to increase the volume of the subsurface tested in the study. Also, an additional tracer of chloride (Cl^-) at a concentration of 50 mg/L Cl^- as NaCl was added to the chaser solution to help determine if the test and chaser solutions were mixing during the push-pull test. The extraction pump was set at 260 mL/min to avoid the turbidity issues encountered in the first test. A resting time of 22.6 hours was used for this test and a total of 56 L of water were collected in pull-out containers during the extraction phase for later mass recovery analysis. A third push-pull test was conducted in the late fall of 2002. This test was conducted in a similar manner to the second test with three important changes. To avoid shocking the well or unnecessarily increasing dispersion in the groundwater flow immediately before the push-pull test, only a 10 mL sample for background nitrate analysis was removed from the well prior to injecting the test solution. Due to the lack of significant nitrate reduction occurring in the first two tests, a dose of an organic carbon electron donor in the form of Na-acetate (8 mg/L or ~0.1 mM) was added to the test solution. This concentration of acetate should theoretically allow for about 20% of the nitrate in the test solution to be reduced, based on the stoichiometry of acetate oxidation coupled to complete nitrate reduction to nitrogen gas. The resting time was shortened to 18.09 hours in hopes of increasing the mass recovery. A total of 56 L of water was collected in the pull-out containers during the extraction phase for later mass recovery analysis.

Using well 1S, the shallow groundwater was tested in the spring 2003 to determine if there were inherent differences in the nitrate reduction rate between the shallow and deep groundwater. The bottom of the tubing used for injection and extraction was 4.57 meters below the top of the well casing, with the water table was at 3.99 meters below the top of the casing prior to the start of the test. A 10 mL sample of water for background nitrate analysis was removed from the well prior to the test solution injection. The test solution volume of 20 L was pumped into the well at roughly 300 mL/min, followed immediately by the chaser solution injection of 7.5 L. The well was left overnight for a resting time of 18.5 hours. For the extraction phase, the pumping rate was set to the same flow rate used in the deeper well, 250 mL/min; however, this extraction rate was higher than the well recovery rate and thus was reduced to 90 mL/min after the removal of five samples spaced 1 L apart. The remainder of the extraction took place with a mixture of water and air coming up the extraction tubing, because the water level remained at the same level as the bottom of the tubing. A

total of 33 L was extracted for later mass recovery analysis for this test, with samples taken every liter for the first 21 samples and after every two liters for the remaining 6 samples.

Because the shallow well behaved quite differently from the deep well with regards to pumping rates and resting time, modifications were required in order to obtain reliable results. The second well 1S test was thus conducted with a few changes to account for the different behavior of this shallow well. First, the test and chaser solution volumes were reduced to 15 L and 5 L, respectively, to adjust for the smaller volume of water in the well. Secondly, the resting time was reduced to 0.97 hours. Finally, the extraction rate was reduced to 90 mL/min in order to prevent the extraction problems encountered in the previous test. A total of 28.3 L was extracted during this test for later mass recovery analysis.

The third test in well 1S used the same procedure as the second push-pull test, except that the well was allowed to recover between the test solution injection and the chaser solution injection. This additional recovery time was included to minimize the mixing of the chaser and test solutions observed in the previous test. After the chaser solution was injected, the well was allowed to recover to its initial level with a resting time of 0.57 hours after the chaser solution injection stopped.

5.2.8 Chemical Analysis

Liquid nitrate and nitrite concentrations where determined using a Waters 486 Tunable Absorbance Detector (λ 210 nm) High Performance Liquid Chromatograph with a Partisil SAX 10 micron column. The headspace samples for the DEA assay were analyzed for the N_2O concentration using a Varian 3800 Gas Chromatograph equipped with a Thermal Conductivity Detector (TCD) and Poropak Q column.

For the push-pull tests, all samples were about 10 mL each and stored in 15 mL capped plastic vials. Upon taking each sample, it was shaken to aerate and inhibit anaerobic denitrifying activity, and put on ice for transportation back to the laboratory. Prior to analysis, each sample was filtered through a 0.45 m nylon filter and placed into a fresh plastic capped vial. One milliliter of sample was diluted with 4 mL DDI water, placed into a 5 mL polyvial, and fit with a filter cap manufactured by Dionex for ion chromatography analysis. The extracted water samples were analyzed for NO_3^-, Br^- and Cl^- concentrations using ion chromatography on a Dionex model DX-300 ion chromatograph (IC) with a self-regenerating suppressor. The IC used a Dionex anion column IonPac AS-9 with an IonPac AG-9 guard column running under Dionex AI-450 software. The remaining samples were frozen for possible future analysis.

The dissolved oxygen of the degassed solutions was measured using a YSI model 57 dissolved oxygen meter coupled to a YSI model 5239 dissolved oxygen probe. A GeoPump 2 peristaltic pump was used to inject and extract the groundwater from the monitoring wells. A water level indicator (Slope Indicator Company model S1453) was used to monitor the water level in the wells.

5.3 Results
5.3.1 Water Quality

To determine the variables that affected the microbial denitrification rate, several water characteristics were analyzed. The median NVOC concentration varied from 0.5 mg/L (0.042 mM) to 2.0 mg/L (0.17 mM) in most wells, and was approximately 2.5 mg/L (0.21 mM) for wells at site 9. The NVOC was considered to be the biologically-available carbon for each site. For the wells in the Big Ditch watershed, the median nitrate-N concentration ranged from 0.0 mg/L (0.0 mM) to 18.4 mg/L (1.5 mM), with all of the deeper wells at or below the detection limit. The nitrate concentration tended to be higher in the wells that had a higher DO and a lower NVOC concentration. The DO concentration also tended to be higher in the shallow wells than the deeper wells.
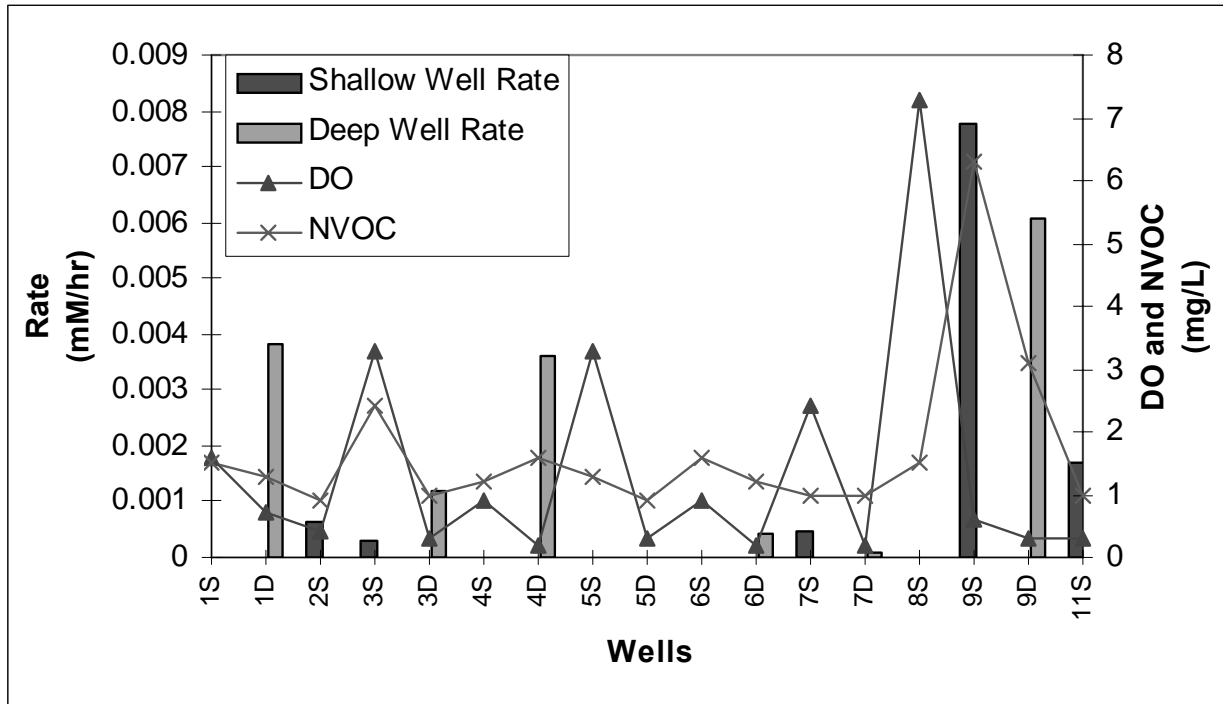
5.3.2 Nitrate Reduction Rate Analysis

Nitrate reduction rates for groundwater samples were measured to determine the differences in microbial denitrification activity across the watershed. Nitrate reduction rates were determined for the water samples because in oligotrophic environments they should approximate the denitrification rates and are easier to measure. The nitrate reduction rates in water tended to be lower in the wells with high DO and higher in the wells that had higher amounts of available carbon to promote denitrification (Figure 5.1). Higher denitrification rates tended to occur in the deeper wells, which showed lower amounts of nitrate when analyzed. The highest rates occurred at sites 1, 4, and 9 in July and at sites 6, 7, and 9 in December. Overall the rates were higher in December than in July with the average shallow well rate being 0.0011 mM/h in July and 0.0017 mM/h in December. Deep well rates averaged 0.0022 mM/h in July and 0.0029 mM/h in December.

The denitrification rates of sediment samples from several different depths were analyzed using four different carbon amendments to determine the effect of available carbon on the denitrification rates. The rates increased with the amount of carbon in the sample, which is what was expected because the denitrifying microorganisms require carbon for growth (Table 5.2, Figure 5.2). Figure 5.2 shows the range of denitrification rates that could be expected from the carbon concentrations present in the Big Ditch Watershed. Figure 5.3 shows that in general there is a trend for lower rates to occur as the depth increases. The exception is site 9, which had a higher NVOC concentration.

All samples were evaluated using the 2 mM C concentration, which although an order of magnitude higher than the natural concentration of carbon in the aquifer, was the most suitable for determining reliable DEA analyses. The rates of denitrification in the sediment samples tended to be higher at sites with more NVOC and low DO levels in the groundwater (Figure 5.4). The highest denitrification rate measured was at site 9, which was consistent with the nitrate reduction rates for the water samples.
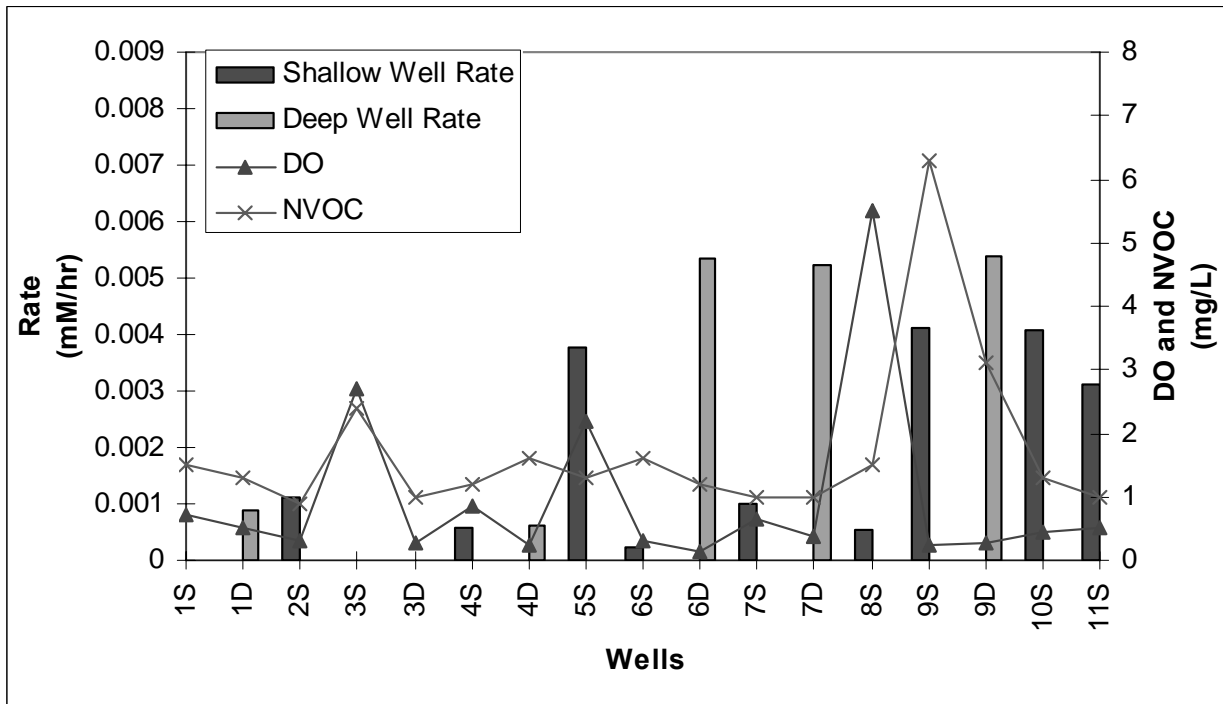
a) July 2000

b) December 2000

Figure 5.1 Nitrate reduction rates for water samples collected in July and December 2000 compared to available carbon and dissolved oxygen.

Table 5.2 Range of denitrification rates in sediments amended with different carbon concentrations

Carbon concentration (mM C)	Range of rates (mg N/kg-day)	Average rate (mg N/kg-day)
No Carbon Added	0 to 0.103	0.0312 ± 0.00107
0.2	0.275 to 1.37	0.82 ± 0.0199
2	12.2 to 162	48.4 ± 0.384
8	14.3 to 217	133 ± 1.17
20	11.7 to 338	194 ± 3.11
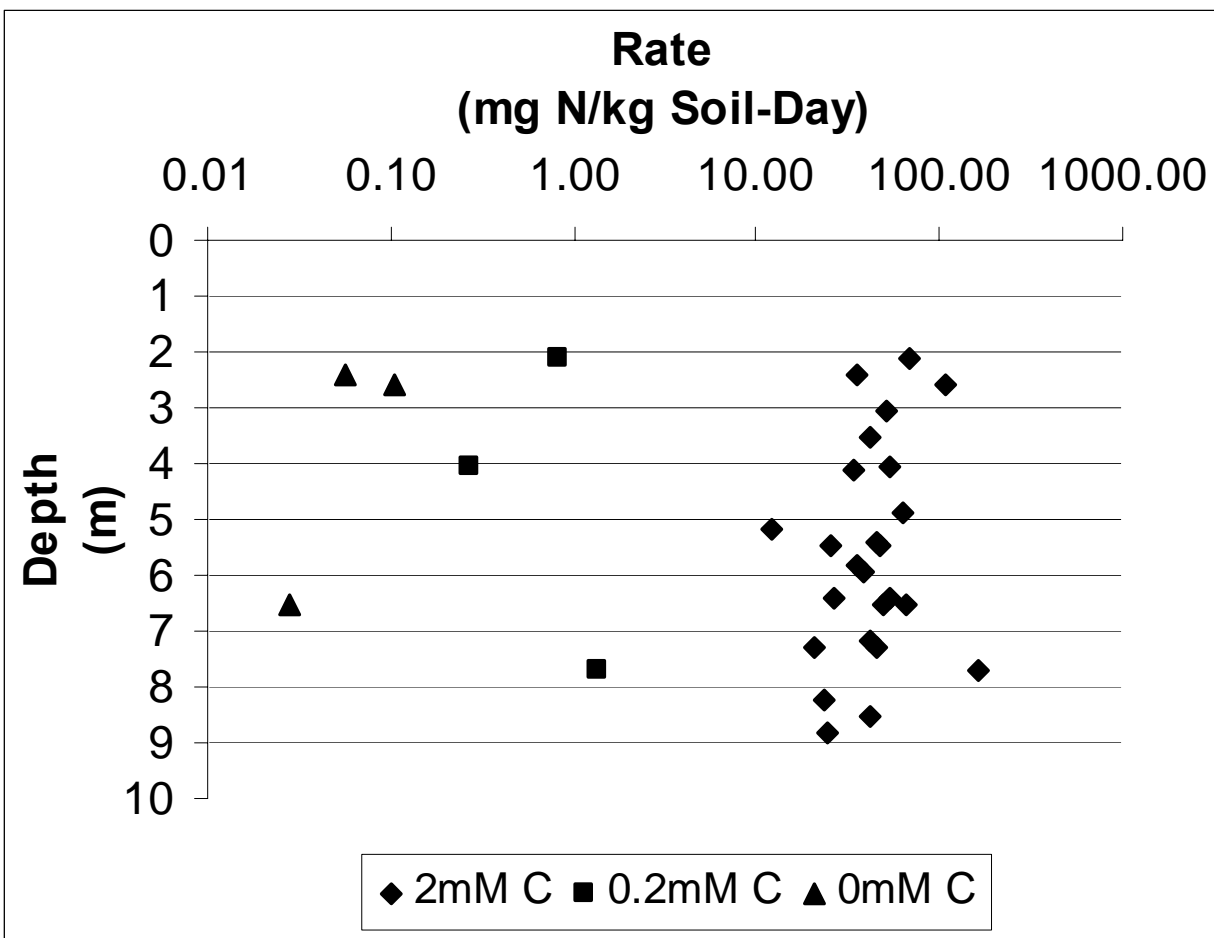
Figure 5.2 Range of denitrification rates in sediments for 0 mM C, 0.2 mM C and 2 mM C amendments compared with depth.
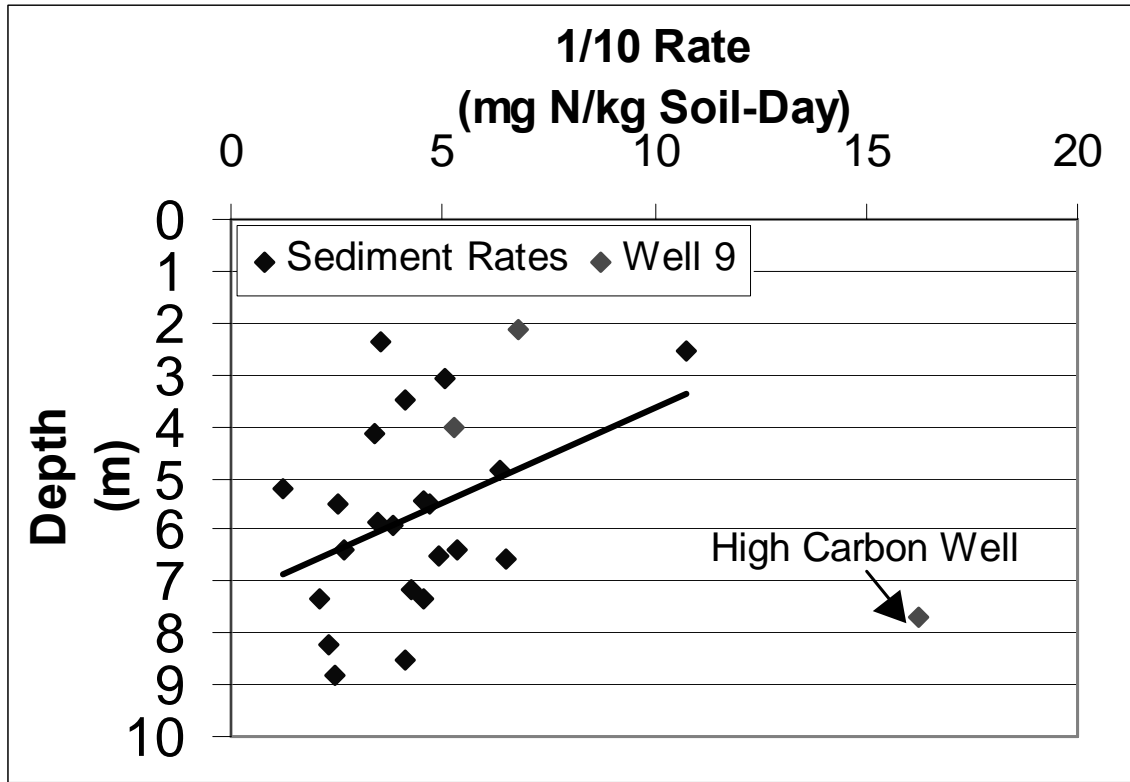
Figure 5.3 Denitrification rates compared with depth of sample amended with 2 mM C
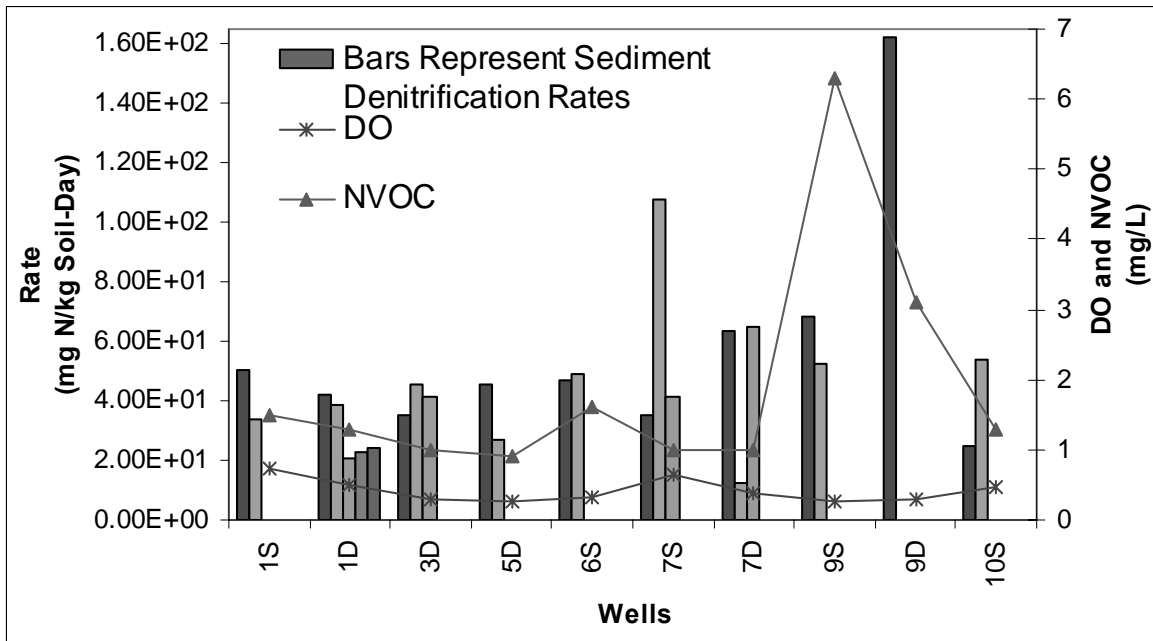

Figure 5.4 Denitrification rates for sediment samples that correlate with the screened depth of the shallow and deep wells at each site. All rates were measured using 2 mM C. Sediment denitrification rates were analyzed at several depths and are represented by different bars on the figure. Each bar is a different depth with the lowest depth on the left.

5.3.3 Enumeration of Denitrifiers and Pore Water Analysis

Pore water nitrate concentrations and the number of denitrifiers were measured at several depths to determine the vertical variability in the cores. The relationship between the number of denitrifying microorganisms enumerated and depth of sample and pore water nitrate concentrations is shown in Figure 5.5. The number of microorganisms was quite variable, both with depth and between wells. This variability is also apparent in the pore water nitrate concentrations, which approach a maximum concentration of 30 mg/L. The extent of variability of MPNs and the nitrate concentration appears to be related to the type of geologic material at the different sample depths. The number of microorganisms tended to be higher in the water-bearing sandy sediments than in the fine-grained glacial tills. Samples with higher MPNs tended to have lower pore water nitrate concentrations as can be seen at sites 3, 7, and 9. This might be expected because in the presence of denitrifying bacteria, the nitrate will become depleted. Sites 3 and 7 have an order of magnitude lower MPNs than the other core samples, approximately 10^5 versus 10^6 cells/g sediment. At site 6, an organic rich layer was found at a depth of 1.5 m, which correlated to a paleosol. This core layer had a high number of denitrifying microorganisms as expected.
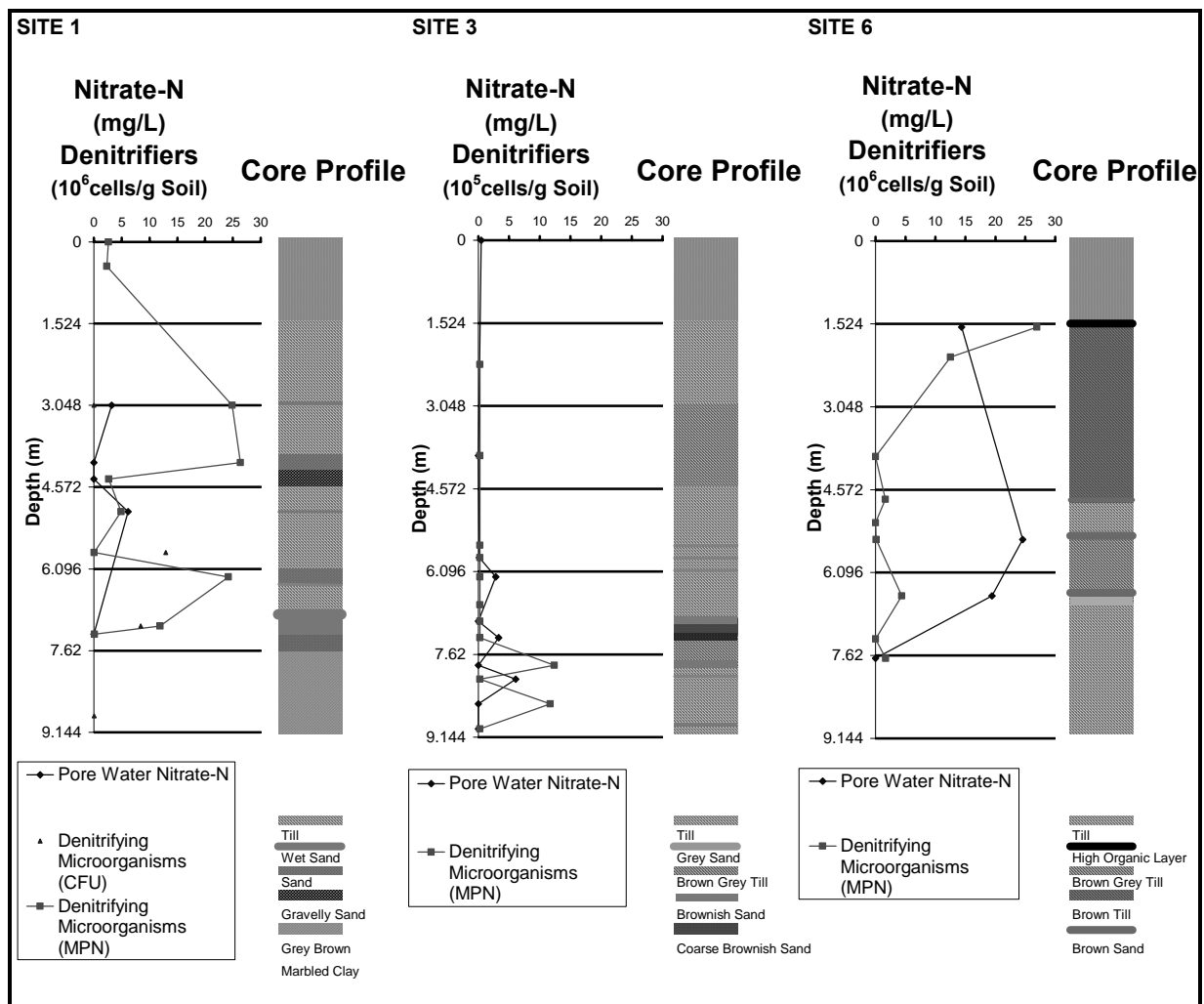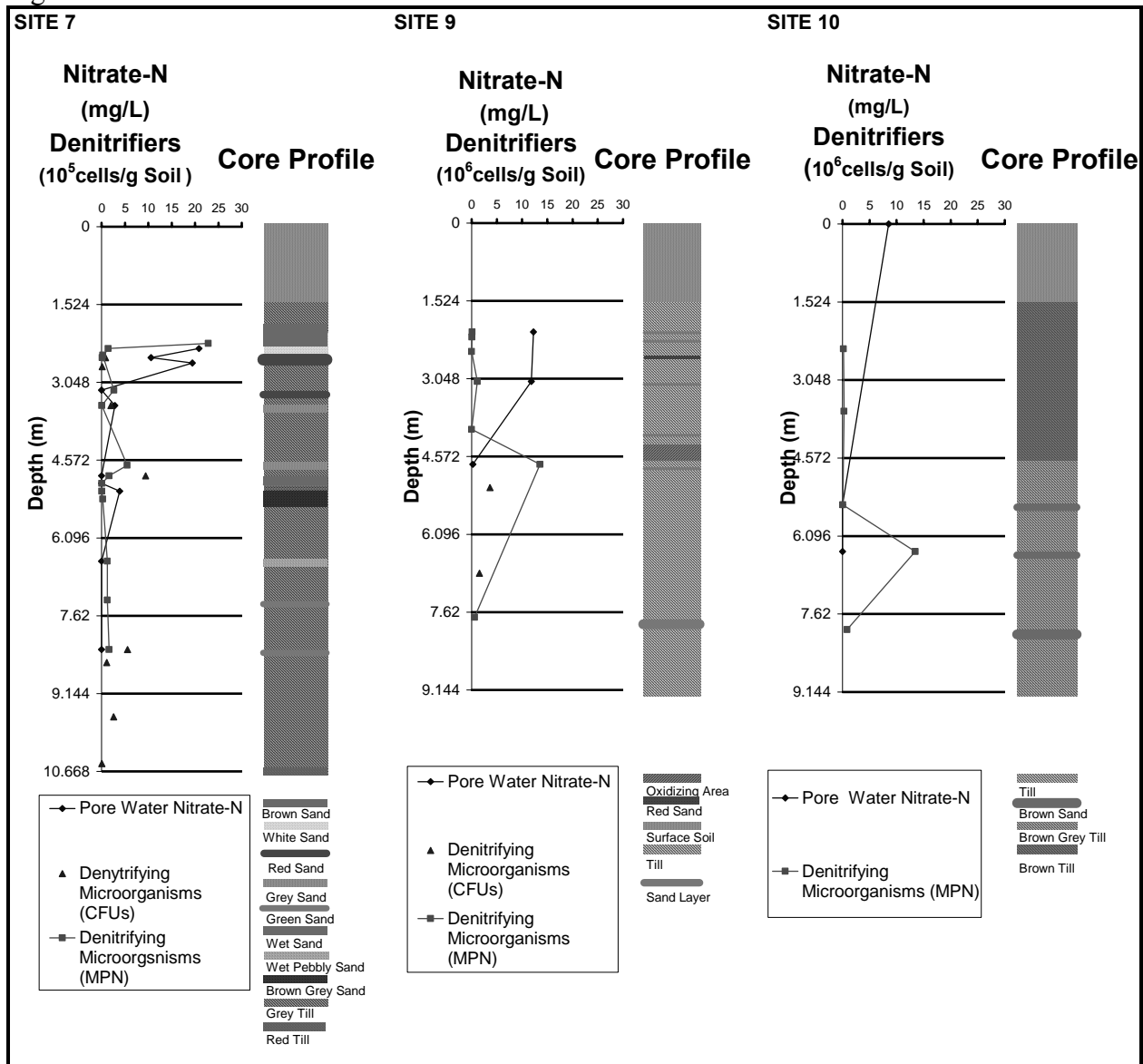
Figure 5.5A

Figure 5.5B

Figure 5.5 Comparison of core profile and depth with pore water nitrate-N and number of denitrifiers for sites 1, 3, and 6 (a) and sites 7, 9 and 10 (b).

5.3.4 Push-Pull Tests

The bromide and nitrate breakthrough curves from the first push-pull test at well 1D show that the normalized bromide concentration peaked at about 0.80 (Figure 5.6). Despite increasing the resting time to 25.8 hours, a large portion of the plot shows the normalized nitrate data overlapping the bromide tracer data, so a first-order nitrate reduction rate could not be estimated. This relative increase of nitrate in the test may have been due to groundwater originating in different subsurface layers that had a higher background nitrate concentration than was measured during the initial sampling, influencing this test over the longer resting time. The mass recovery from this test for bromide and nitrate were 55% and 48%, respectively. Based on this mass recovery analysis, a zero-order rate estimation was calculated (0.00352 mM NO_3^-/hr).
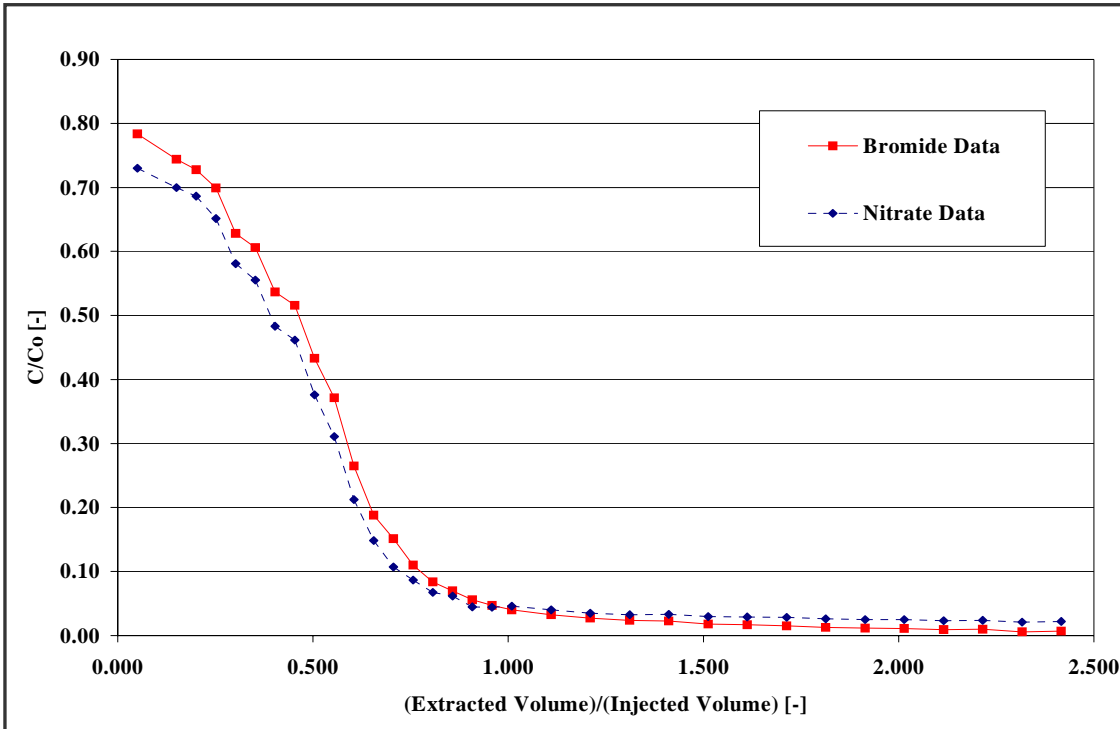
Figure 5.6 Nitrate and bromide breakthrough curves for the first push-pull test at well 1D

A chloride tracer was added to the chaser solution in all subsequent Big Ditch tests to help determine if the test and chaser solutions were mixing during the test. The chloride breakthrough curve is expected to peak prior to the bromide curve, since the chaser was the last solution injected into the well. A minimal overlap of these curves would demonstrate that very little mixing of chaser and test solution had occurred.

The second test at well 1D was done with an adjustment in the resting time to 22.60 hours and the test and chaser solution volumes were increased to ensure that the test solution was forced into the subsurface. The bromide and nitrate breakthrough curves showed the normalized bromide peak only reached about 0.25 with nitrate surpassing the bromide concentration during latter parts of the extraction phase (data not shown). The mass recovery achieved during this test was only 24% and 21% of the original bromide and nitrate in the test solution, respectively. An increase in the hydraulic gradient, increased dispersion or unexpected heterogeneity in the subsurface may have led to the lower tracer recovery during this test. Based on these results, it appeared that the push-pull test was not likely to produce usable data for analysis and determination of first-order rate constants. By using the overall mass recovery data, however, a zero-order reaction rate of 0.00395 mM NO_3^-/hr was calculated for this test. Test and chaser solution volumes remained at 20 L and 7.5 L, respectively, for the final test conducted at well 1D. The resting time was decreased to 18 hours in an attempt to obtain a higher recovery of the test solution. In order to ensure that enough of the nitrate would be able to react during this shorter resting time to show a significant difference between the bromide and the tracer curves, an additional carbon source (acetate) was added to the test solution as an electron donor. Thus, the reaction rate obtained provided the nitrate reduction potential of the subsurface assuming that the availability of an organic carbon source was limiting

the extent of denitrification. The breakthrough curves for nitrate and bromide for this carbon-augmented test showed significant nitrate reduction with a total mass recovery of bromide and nitrate of 41% and 26%, respectively (Figure 5.7). The normalized bromide concentration peak reached 0.38 for this test, above the 0.24 threshold. A linear regression provided an estimated first-order nitrate reduction rate coefficient of -0.0109 hr^{-1} (Figure 5.8).
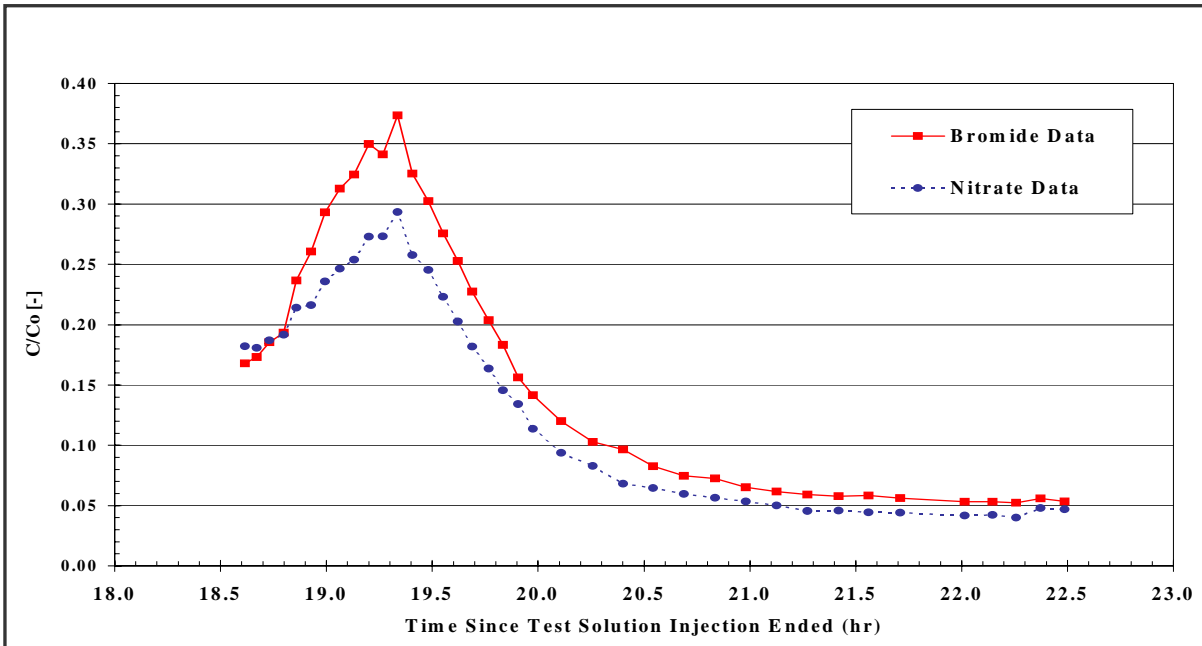

Figure 5.7 Nitrate and bromide breakthrough curves for the carbon augmented third test at well 1D

After estimating a first-order nitrate reduction rate in the deep aquifer, the push-pull tests were applied to the shallow aquifer (well 1S). As in the last test at well 1D, a carbon-augmented test solution volume of 20 L and a chaser solution volume of 7.5 L were used with a resting time of 18.5 hours. The bromide and nitrate breakthrough curves exhibited unusual characteristics for this test (Figure 5.9). Both the bromide and nitrate concentrations quickly dropped in the first few samples, then leveled off for the rest of the test, with no asymmetric tailing in the breakthrough curves for this test. During the extraction phase of this test, the recharge rate for well 1S was much slower than expected. Thus, water was pumped from the surface of the lowered water table for the majority of the test. The well continued to recharge at a rate slower than could be feasibly pumped, and the pump continued to extract water mixed with air.
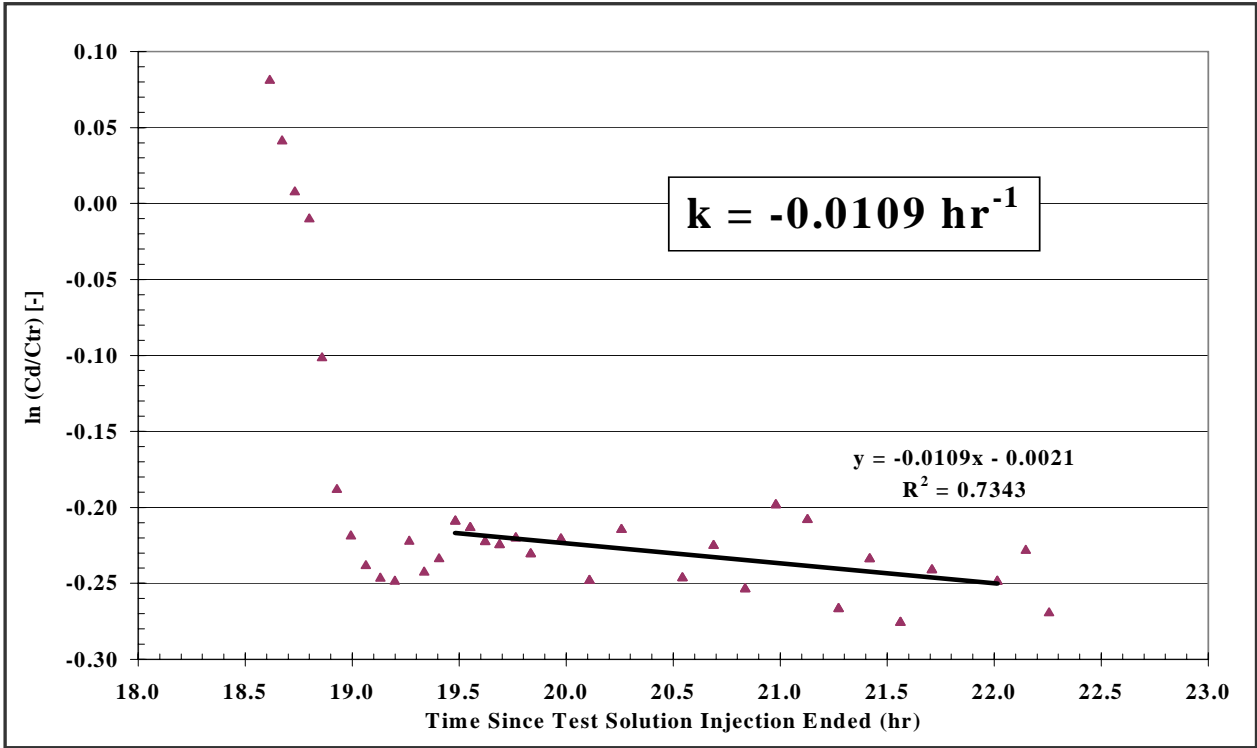
Figure 5.8   Determination of first-order nitrate reduction rate coefficient, k, for the carbon augmented third push-pull test at well 1D
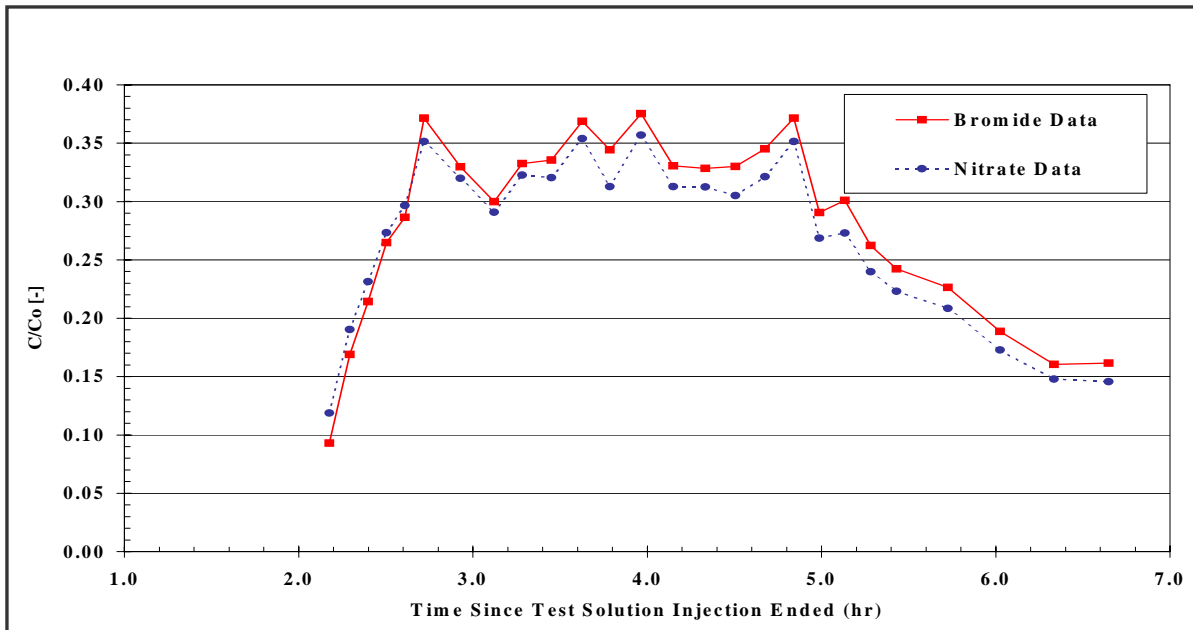

Figure 5.9 Nitrate and bromide breakthrough curves for the carbon augmented first test at well 1S
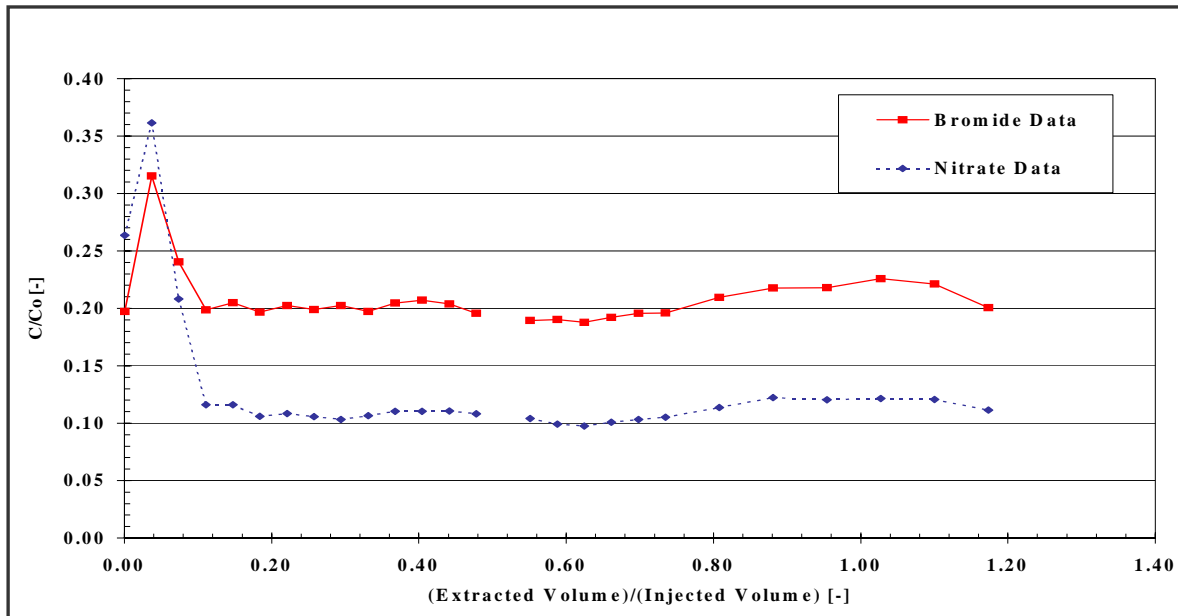
Figure 5.10 Nitrate and bromide breakthrough curves for the carbon-augmented second test at well 1S

Well 1S has unique subsurface characteristics with a highly permeable sand lens sitting within the screened depth of the well right above the water table at the time of this test (Shiffer, 2001). The test solution may have filled up the previously unsaturated sand layer during the injection phase because the test solution was pumped into the well casing more quickly than it entered the subsurface, thus creating a pressure head. Typically the water level approached the top of the casing during injection. As the well recovered during the resting phase, the water remained within this sand lens, slowing the flow of solution back into the well. However, during the extraction phase, the well was pumped out too quickly, and the water table was brought below its normal position. This allowed the test solution contained in the sand lens to trickle back into the well and mix with other groundwater during the extraction phase, leading to the unique breakthrough curve shape. A first-order rate was not attainable due to the unusual shape of the breakthrough curve. The total mass recoveries of bromide and nitrate were 33% and 20%, respectively. This gave a zero-order reaction rate of 0.00386 mM NO_3^-/hr and is the same order of magnitude as other zero-order nitrate reduction rates estimated for the deep well.

Based on the results of the previous test of well 1S, it was apparent that the pumping rates and resting times would require adjustment for the second shallow well test. The resting time was drastically decreased to 0.97 hours to assure a better recovery for this well. The extraction rate remained less than 90 mL/min to avoid pumping the well dry. In order to allow for the test to be conducted within a day, the test and chaser solution volumes were also decreased to 15 L and 5 L, respectively. The total mass recoveries of bromide and nitrate were 59% and 57%, respectively. The breakthrough curves showed that the normalized bromide peak concentration reached about 0.60 (data not shown). It is believed that the chaser solution mixed with and diluted the test solution in the middle of this push-pull test. During the injection phase, the test solution was placed into the well and drained into the subsurface. At the end of the test solution injection, the chaser solution injection began; however, some of the remaining test solution was still present in the well casing. The chaser solution mixed with and diluted the test solution in the well casing. The first-order nitrate reduction rate coefficient was calculated to be -0.0284 hr^{-1}.

For the final test of well 1S, the test solution and chaser solution volumes and composition remained the same as in the previous test, but a shorter resting time of 0.57 hours was used to achieve higher mass recovery. A resting period of 1.2 hours between the test and chaser solution injection was allowed for the well to recover back to its equilibrium level to avoid the mixing of chaser and test solution that occurred in the second test. Total mass recoveries for bromide and nitrate of 49% and 46%, respectively, were achieved. The breakthrough curves show the normalized bromide peak reached of 0.36 (Figure 5.10). The first-order nitrate reduction rate coefficient calculated was -0.0197 hr^{-1} using 21 data points (Figure 5.11).

Figure 5.11 Determination of first-order nitrate reduction rate coefficient, k, in the carbon
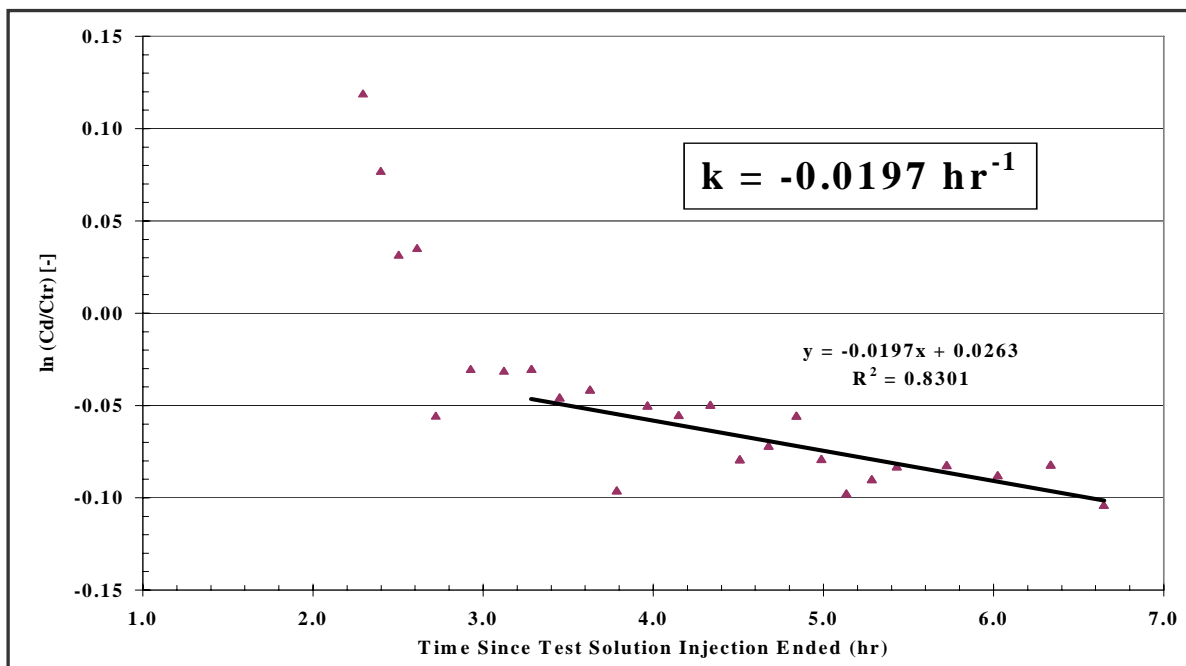
augmented, third push-pull test in well 1S

5.4 Discussion

In the Big Ditch watershed, push-pull tests were used successfully to obtain first-order nitrate reduction rate coefficients, however these only succeeded when carbon as acetate was used as an amendment for the test. This was not considered unusual, as it has been suggested previously that carbon is limiting for *in situ* denitrification activity in groundwater (Trundell et al., 1986). The first-order rate coefficient for the deep aquifer is 0.0109 hr^{-1} (Table 5.2). Using a typical nitrate concentration of 0.1 mM NO$_3^-$ found in the groundwater of the Big Ditch, this first-order reaction rate coefficient can be converted to an instantaneous rate of 0.00109 mM NO$_3^-$/hr (Table 5.3). In contrast, the shallow aquifer had a faster nitrate turnover capacity, with first-order nitrate reduction rate coefficients of 0.0284 hr^{-1} and 0.0197 hr^{-1}, respectively (Table 5.3). These rates convert to instantaneous rates of 0.00284 mM NO$_3^-$/hr and 0.00197 mM NO$_3^-$/hr, respectively (Table 5.3). These instantaneous rates for both shallow and deep wells agree well with rates measured in sediments from different wells, 0.275 mg-N/kg-d to 1.39 mg-N/kg-d (Table 5.3). They are also

similar to the zero-order rates estimated for the push-pull tests for which no first-order rate could be calculated (Table 5.4). They also are similar to the results of a denitrification study conducted by Starr and Gillham (1993) who found a rate of 0.57 mg-N/kg-d (Starr and Gillham, 1993). The most significant finding of the push-pull experiments is that the first-order nitrate reduction rate coefficients of the shallow well tended to be higher than those of the deep well. This could be due to the fact that the shallow wells are more often exposed to higher nitrate concentrations, increasing the number of denitrifying microorganisms, thus increasing the nitrate reduction rate. Although there appears to be a logical explanation, the results do not agree with the measurements of groundwater denitrification rates which appeared to be higher in the deeper aquifer (Figure 5.1). The data are in agreement with the measured sediment denitrification rates, which tended to decrease with depth (Figures 5.2 and 5.3).

Table 5.3 Big Ditch watershed nitrate reduction first-order reaction rate coefficient and instantaneous rate summary

Date of test	Well tested	First-order reaction rate coefficient (hr^{-1})	Instantaneous rate at 0.1 mM NO_3^-	
			(mM NO_3^-/hr)	(mg-N/L-d)
November 7-8, 2002	1D	0.0109	0.00109	0.366
April 15, 2003	1S	0.0284	0.00284	0.954
May 3, 2003	1S	0.0197	0.00197	0.662

Table 5.4 Big Ditch watershed zero-order nitrate reduction rates estimated from push-pull tests that did not yield first-order rate constants

Date of test	Well tested	Zero-order reaction rate	
		(mM NO_3^-/hr)	(mg-N/L-d)
August 6-7, 2002	1D	0.00352	1.18
September 24-25, 2002	1D	0.00395	1.33
March 14, 2002	1S	0.00386	1.30

According to the results of this study, the abundance and activity of denitrifiers in the groundwater are dependent on DO, and the available organic carbon. This is not surprising since studies of denitrification rates in aquifers have shown that carbon is commonly the limiting nutrient (Starr and Gillham, 1993). The average carbon concentration of 0.133 mM C in the aquifer is close to the 0.2 mM C amendment used for rate determinations of several samples; thus, the true in situ denitrification rates in the aquifer should be similar to the values determined by the DEA assay for these samples. Sediment denitrification rates and groundwater nitrate reduction rates were compared using a 2 mM C amendment, ten times the natural carbon loading (Figures 5.1 and Table 5.3). However, the actual rates in the aquifer will probably be 100 times less. This becomes apparent by showing the relationship between carbon amendment concentration and denitrification rates (Figure 5.12). As expected, the highest denitrification rates were found in the samples with the most available carbon. This is most apparent at site 9, which had the highest nitrate utilization rates in the sediment and groundwater tests and had the highest available carbon concentration while having a low DO. These conditions are optimal for denitrification.
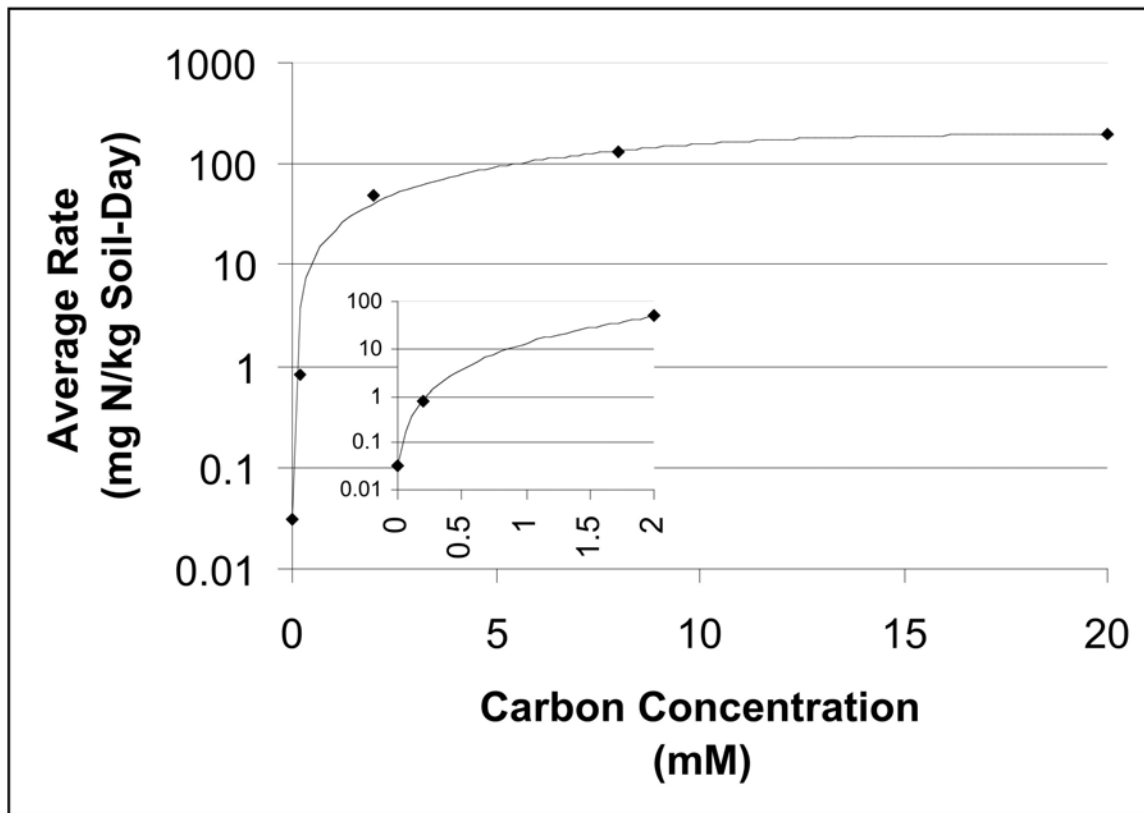
Figure 5.12 Plot of average denitrification rate versus carbon amendment concentration used

In a study of an aquifer with carbon concentrations similar to the Big Ditch, the in situ denitrification rates were $2.4x10^{-5}$ g N/L-h (Starr and Gillham, 1993). When approximately 2 mM of carbon as glucose were added to the aquifer, the in situ denitrification rate increased to $1.4x10^{-4}$ g N/L-h (Starr and Gillham, 1993). This glucose amended rate is similar to the average rate observed for the 2mM carbon amendments of $1.19x10^{-4} \pm 0.015x10^{-4}$ g N/L-h (48.4 ± 0.384 mg N/kg soil-day). Thus, it might be expected that because the available carbon concentrations in both aquifers are similar, the in situ rate of denitrification in the Big Ditch watershed would be similar to the initial in situ denitrification rate found by Starr and Gillham (1993). The rate of $1.77x10^{-6}$ g N/L-h (0.45 mg N/kg soil-day) predicted for 0.133 mM in Figure 5.12, however, is actually about 13 times less than the values they reported. This difference may be attributed to different aquifer materials at the sites tested. Cambardella et al. (1999) noted that different sub-soils generally have different denitrification rates. They found that in oxidized glacial till with low organic carbon and oxidized iron, denitrification rates ranged from 0.0233 to 0.0888 mg N/kg soil-day, while unoxidized glacial till with higher organic carbon had a rate of 0.262 mg N/kg soil-day. The highest rate, 0.495 mg N/kg soil-day, was found for an unoxidized loess, which also had the highest organic carbon content.

To estimate the denitrification potential within the shallow groundwater of the Big Ditch watershed, several assumptions were made (Table 5.5). Denitrification was assumed to occur in all of the water

bearing areas of the aquifer. The depth of the water bearing areas was assumed to be the screened area of the wells and an average value of 4.6 m (15 ft) was assumed, but it varied significantly throughout the watershed. Denitrification was also assumed to be occurring at the denitrification rate for the average carbon concentration of 0.133 mM (Figure 5.12). This denitrification rate was determined from Figure 5.12 and from the push-pull experiments. The nitrogen applied to the farmland was assumed to be 0.168 kg N/m^2 (150 lb/acre), the area of the watershed was approximately 9.85×10^7 m^2, and assuming that half of the watershed had a uniform nitrogen application, the total nitrogen applied to the watershed area was 8.3×10^9 g N/yr. The amount of nitrate that could affect the aquifer is significantly less than this because it is taken up by plants and is intercepted by tile drains. The potential denitrifying ability of the aquifer that was determined, however (Table 5.5) is great enough to remove 84% of the nitrogen applied to the land in one year. Thus, the subsurface capacity appears to be sufficient to denitrify all the nitrate that was not utilized by crops and bypassed the tile drains, i.e. the nitrate that entered the shallow groundwater.

Table 5.5 Nitrate removal potential for the shallow groundwater beneath the Big Ditch watershed

Time period	Nitrate removal potential[1]
1 week	1.3×10^8 g N
1 month	5.7×10^8 g N
1 year	7.0×10^9 g N

[1]Assumptions:
Denitrification rate $\approx 1.77 \times 10^{-6}$ g N/L-h (0.45 mg N/kg soil-day). Depth of the water bearing materials ≈ 4.6 m (15 ft). Watershed area $\approx 9.85 \times 10^7 \, m^2$ (~38 miles^2). Denitrification is assumed to occur in all of the water bearing areas of the aquifer.

The variability of denitrification rates and MPNs is significant both in vertical (depth of sample) and horizontal (between wells) space. The spatial variability could be related to the nature of the aquifer material. For example, some layers might be richer in organic carbon and other nutrients, leading to different microbial populations. This is supported by observations made with site 9 sediments, which appeared to have higher denitrification rates associated with higher NVOC concentrations. The number of microorganisms tends to be higher in sandy sediments than in the fine-grained glacial tills. This probably occurs because the sandy sediments represent areas of higher water flow and therefore have greater exposure to carbon and nutrients in the water. Pore water nitrate concentrations varied considerably between sites and with depth, and showed little relationship to the bulk groundwater nitrate concentration. Wells 3 and 6 had the highest nitrate concentrations in the bulk groundwater samples, but the concentration was less than 7 mg/L. In contrast, the nitrate concentrations in the pore water ranged from 0 to almost 30 mg/L. In some sediment layers, nitrate is present in the pore water, but little or no nitrate was detected in the bulk groundwater such as in Wells 7 and 9 (Figure 5.5B). The variability of nitrate concentrations in the different geologic materials could indicate that some areas have more water flow than others. There may also be some interactions between the sand layers. Although the denitrification rates also show significant variability with depth (Figure 5.3), there is a slight trend toward a decrease in denitrification rates

with depth, particularly evident for the 2 mM C amended samples. The spatial variability of denitrification rates and MPNs corresponds to different geological characteristics at each site. This correlation might be used to determine the groundwater denitrifying ability in different areas of the aquifer and to determine the attenuation of nitrate in the groundwater of the watershed.

The total amount of denitrification that occurs in the sediments and aquifer will probably be greater in the shallower wells that have low or no DO concentration and decrease in the deeper wells due to the higher carbon and nitrate concentrations in the shallower wells. The concentration of nitrate in the deeper wells are below the detection limit, so it seems likely that the nitrate applied to the surface of the watershed is being attenuated before it reaches the deeper aquifer, as found by Starr and Gillham (1993).

Single-well push-pull tests also provided a useful data for measuring *in situ* reaction rate coefficients, but should be used with care. Multiple tests at the same monitoring well may be required to establish the optimal operating conditions before reliable data can be obtained. Estimation of actual *in situ* nitrate reduction rates provided useful information regarding the fate of nitrogen in this agricultural watershed and contributed to the comprehensive nitrogen mass balance being conducted on the Big Ditch watershed.

More studies on the watershed need to be completed to improve the accuracy of *in situ* denitrification estimates. It might be best to combine the approach taken here with isotope methods. Also the spatial variability of denitrification, both horizontally and vertically, need to be better integrated to obtain a better estimate of the actual denitrification activity in the groundwater of the Big Ditch watershed. It is clear, however, that the attenuation capacity of the watershed is significant. The geological characteristics at all well locations, the variable DO concentration, and available carbon will need to be considered when determining the extent of denitrification activity that is occurring in the groundwater and sediments. Regardless of the geological characteristics and microbial population of the sediments, if there is not enough available carbon and there are significant amounts of DO, significant denitrification will not occur.

6. N Dynamics in the Shallow Groundwater of Big Ditch

The fate and transport of N through shallow geologic materials is a complex process. Modeling denitrification is difficult because it varies spatially as discussed previously. In addition, developing a numerical model to predict this transient behavior was the focus of another research team; thus, predicting the transient fate and transport of N in the shallow groundwater was beyond the scope of this project. Rather, we adopted a simple approach to estimate the steady-state dynamics of nitrogen in the shallow groundwater of a watershed. This approach did not account for the observed spatial variability, but assumed uniform geologic and hydrogeologic conditions can be used to describe the watershed. This simple approach was based on two widely known facts. First, N concentrations in very shallow groundwater (i.e., soil water within and below the root zone) are generally high, as shown by the N concentrations in tile drainage and soil pore water from this study and in the literature (e.g., Cambardella et al., 1999). Second, during base flow conditions (generally late summer and early fall), groundwater comprises all water in the stream, and N concentrations in the stream are generally zero (Figure 6.1). Within the Mississippi River Basin, similar seasonal variation in N concentrations have been observed (Goolsby et al., 2001). During base flow conditions, nitrate-N concentrations in Big Ditch were <0.06 mg/L and the stream flow varied from year to year (from 0.12 to 7 cfs). For this model, we assumed that high N concentrations that enter shallow groundwater and are reduced to zero by denitrification, before groundwater discharges to the stream. For the case of steady-state groundwater flow, the amount of N entering shallow groundwater and the amount denitrified were assumed to be equal and were estimated using the following relationship:

mass of N denitrified= (change in N) × (groundwater recharge) × (watershed area)

The change in N is defined as the difference in N concentration at the beginning and end of the flow path. The beginning of the flow path is the base of the root zone. We used the concentration of N in water from tile drains to estimate the N concentration at the base of the root zone. The end of the flow path is where groundwater discharges to the stream and the N concentration was assumed to be zero here. Groundwater recharge was determined by steady-state groundwater flow modeling described in Section 2.5. The watershed area was assumed to be 38.0 square miles.

As part of the larger effort, another research group monitored tile drains for this project, and monitored 11 tile drains in the Big Ditch and adjoining watersheds during water years (October through September) 1998, 1999, and 2000. For these three years, the flow-averaged N concentration of water discharging from tile drains was 16.6 mg/L for fields planted to corn and 12.3 mg/L for fields planted to soybeans (Mirek, 2001). For our calculations, we averaged these values for a mean N concentration of 14.5 mg/L. For water years 2001 and 2002, a subset of these tile drains was monitored. The average N concentrations, on a flow-weighted basis, were 8.7 and 17.9 mg/L for water years 2001 and 2002 (G. Collins and M. David, 2004, personal communication). To compute the range of N flux from the watershed for water years 1998 through 2000, the mean N concentration of water from tile drains was altered by 50% for a low concentration of 7.2 mg/L and a high concentration of 21.8 mg/L. These values are close to the median of the minimum and maximum monthly averages of 6.4 mg/L and 22.9 mg/L reported for the 11 tile drains for water years 1998
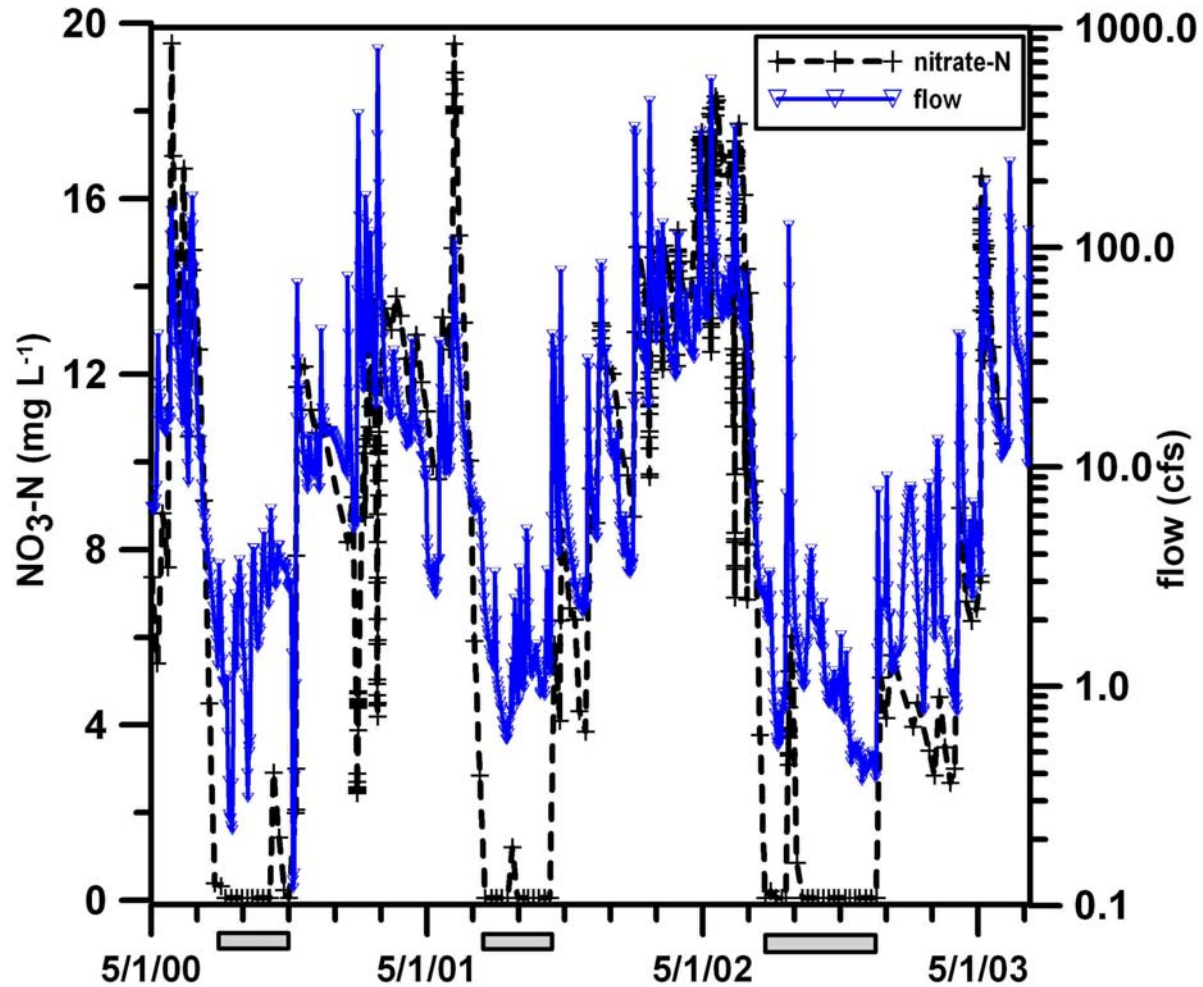
Figure 6.1 Nitrate-N and stream flow in Big Ditch at the watershed outlet (Keefer and Bauer, 2005). The bars on the x-axis show periods of base flow.

through 2000 (Mirek, 2001). Similar ranges for N concentrations were assumed for water years 2001 and 2002.

Groundwater recharge was determined using a steady-state groundwater flow model (see Section 2.5) by matching computer estimates of stream flow at the outlet and water levels in the 11 shallow wells with field data. Three values of recharge were used to develop a range of N flux from the watershed. For each of the three years we monitored, stream flow during base flow conditions (when N concentrations in the stream were at or near zero) was evaluated to determine the first quartile, median, and third quartile of stream flow. These values are reported in Tables 6.1 through 6.3. For the median values of stream flow, steady-state groundwater flow contributed 6.9% and 5.0% of the total stream flow for WY01 and WY02, respectively. For this steady-state flow model, groundwater recharge and groundwater discharge to the stream are equivalent. Thus, our model results indicate that steady-state groundwater recharge is the source of 5.0% to 6.9% of stream flow.

The estimated mass of N denitrified in the shallow groundwater (Tables 6.1 to 6.3) varied with groundwater recharge and the N concentration in tile drainage. The best estimate for the mass of N

denitrified in shallow groundwater was 2.3% of N applied for water year 2000, 1.2% of N applied for water year 2001, and 3.1% of N applied for water year 2002. Water years 2000 and 2001 were dry years, while water year 2002 was a wet year. Higher N flux during a wet year following a dry year has been noted by others (e.g., Goolsby et al., 2001) because N is thought to be stored in the soil during the dry year, then flushed from the soil during the wet year. Over the course of the three years monitored, the estimated mass of N denitrified in shallow groundwater ranged from 0.3% to 6.4% of applied N, so these estimates vary considerably. The N exported from the watershed via surface water was estimated to be equivalent to 12.5% of applied N in 2000, 13.1% in 2001, and 11.3% in 2002 (Keefer and Bauer, 2005). Our estimates of N denitrified in shallow ground water represent 9% to 27% of the estimated N exported from the watershed via surface water.

However, these estimates should be considered minimal values, because this simple model only accounts for steady-state groundwater flow and ignores transient flow. Thus, any additional N transported by transient groundwater flow, such as flow from precipitation events (e.g., Cey et al., 1998), is not included in the estimates in Tables 6.1 through 6.3. However, we have some isotopic data that shows that transient groundwater remains in the subsurface long enough to allow for partial and possibly complete denitrification.

Previous studies support the expectation that our values underestimate the amount of N denitrified in the shallow groundwater. For common grain-production systems, nitrate leaching below the root zones was found to range from 10 to 30% of applied N (Meisinger and Delgado, 2002). For a coarse-grained, outwash aquifer in Minnesota, 49% of the nitrogen fertilizer applied was transported past the root zone and 22% of the nitrogen fertilizer applied was denitrified (Puckett et al., 1999).

Table 6.1 Estimates of N denitrified in shallow groundwater for water year 2000

Base recharge (ft/day) Discharge @ well 1 (cfs)	Change in N (mg/L)	N denitrified	
		N mass (g/yr)	% of N applied*
r= 0.0000473 Q= 1.07	7.2	5.5×10^6	0.7
	14.5	1.1×10^7	1.3
	21.8	1.7×10^7	2.0
r=0.0000994 Q= 1.79	7.2	9.6×10^6	1.2
	14.5	**1.9×10^7**	**2.3**
	21.8	2.9×10^7	3.5
r= 0.000175 Q= 2.83	7.2	1.6×10^7	1.9
	14.5	3.1×10^7	3.8
	21.8	4.7×10^7	5.7

*Assumed 150 lbs/acre (168 kg/ha) of N fertilizer was applied on 50% of the watershed.

Table 6.2 Estimates of N denitrified in shallow groundwater for water year 2001

Base recharge (ft/day) Discharge @ well 1 (cfs)	Change in N (mg/L)	N denitrified	
		N mass (g/yr)	% of N applied*
r= 0.0000319 Q= 0.86	4.4	$2.6x10^6$	0.3
	8.7	$5.2x10^6$	0.6
	13.1	$7.7x10^6$	0.9
r= 0.0000787 Q= 1.50	4.4	$4.8x10^6$	0.6
	8.7	**$9.6x10^6$**	**1.2**
	13.1	$1.4x10^7$	1.7
r= 0.000151 Q= 2.50	4.4	$8.3x10^6$	1.0
	8.7	$1.7x10^7$	2.0
	13.1	$2.5x10^7$	3.0

*Assumed 150 lbs/acre (168 kg/ha) of N fertilizer was applied on 50% of the watershed.

Table 6.3 Estimates of N denitrified in shallow groundwater for water year 2002

Base recharge (ft/day) Discharge @ well 1 (cfs)	Change in N (mg/L)	N denitrified	
		N mass (g/yr)	% of N applied*
r= 0.0000433 Q= 1.01	9.0	$6.4x10^6$	0.78
	17.9	$1.3x10^7$	1.6
	26.9	$1.9x10^7$	2.3
r= 0.000108 Q= 1.90	9.0	$1.3x10^7$	1.5
	17.9	**$2.6x10^7$**	**3.1**
	26.9	$3.8x10^7$	4.6
r= 0.000158 Q= 2.59	9.0	$1.8x10^7$	2.1
	17.9	$3.5x10^7$	4.3
	26.9	$5.3x10^7$	6.4

*Assumed 150 lbs/acre (168 kg/ha) of N fertilizer was applied on 50% of the watershed.

7. SUMMARY & RECOMMENDATIONS

Mass balances for nitrogen and phosphorus were conducted in a tile-drained, agricultural watershed by a multidisciplinary team. Our efforts focused on the shallow groundwater, while cooperating researchers studied N and P fluxes for crops, soils, surface water, and atmospheric deposition. The overall mass balance was conducted under the Water Quality Strategic Research Initiative and was sponsored by the Illinois Council on Food and Agricultural Research. In this report, we summarized the groundwater research conducted for the mass balances of the nutrients, N and P. In a future report, we will help to develop the comprehensive mass balances for N and P and assist other researchers in compiling a report regarding the flux of nutrients through the watershed.

This mass balance study was conducted in the Big Ditch watershed of northern Champaign County. The Big Ditch watershed covers 38 squares miles and is part of the Sangamon River watershed. The shallow geologic materials beneath this watershed were deposited during the Wisconsin Episode and modern times and consist of thin loess overlying clayey glacial tills interbedded with sorted sediments (sand and silt). Monitoring wells were installed to monitor the water table at 11 sites and to monitor the deeper sand-and-gravel layers at 9 of these sites. These monitoring well nests were located near the stream and in upland areas. An analytical, steady state, groundwater flow model was developed and calibrated using stream flow data and water levels in 11 shallow wells. Use of stream flow at the watershed outlet and water level data allowed us to achieve very good model calibration. The main result from the groundwater flow model was an estimate of the steady-state groundwater recharge for the watershed, which was used to estimate N flux through the watershed.

Groundwater samples were collected on 28 occasions from May 2000 through June 2003. Overall, N concentrations in the groundwater tended to be low. Only 6 of the 20 wells (5 shallow & 1 deep) had total N concentrations that consistently exceeded 1 mg/L. Nitrate comprised almost 100% of the N in the two wells with the highest total N concentrations (median total N = 8 and 18 mg/L). In the other 18 wells, organic N generally comprised 10 to 40% of the total N. Nitrate was rarely detected in the deep wells, and ammonia was rarely detected in the shallow wells. These N concentrations are consistent with those observed in an Iowa agricultural watershed (Cambardella et al., 1999).

Nitrogen concentrations in samples from the shallow wells varied over time. Maximum N concentrations were generally observed in 2002, a year with normal precipitation that followed two dry years. Precipitation measured at Fisher and Urbana was below average from 1998 to 2003 except the water year 2002, which had normal precipitation. This type of temporal change in N concentrations has been observed by other researchers (e.g., Goolsby et al., 2001).

Denitrification in the subsurface appears to be a significant N sink. Stable isotope ratios for the O and N in nitrate from shallow groundwater samples revealed enrichment of the heavy isotopes relative to the initial values inferred from tile drain samples. These enrichments suggested that denitrification in shallow groundwater was generally greater than 50% complete, but varied from 0% to 98% complete across the watershed. Denitrifying bacteria varied in abundance by a factor of 10 in water-bearing layers throughout the watershed, but are considered sufficiently abundant to denitrify a significant amount of N. Denitrification rates were determined by laboratory and field experiments and were dependent on the availability of biodegradable organic carbon. Denitrification rates averaged 0.82 mg N/kg-d when amended with 0.2 mM carbon as acetate (2.4 mg/L as C).

To estimate the dynamics of nitrogen in the shallow subsurface, we adopted a simple approach. We assumed that N concentrations in very shallow groundwater (i.e., soil water within and below the root zone) are generally high, as shown by the N concentrations in tile drainage and soil pore water. These high N concentrations entering shallow groundwater are reduced to zero (by denitrification) by the end of the flow path, where groundwater discharges to the stream. At base flow, when groundwater comprises all water in the stream, N concentrations in the stream are essentially zero. During base flow conditions, nitrate-N concentrations in Big Ditch were <0.06 mg/L and the stream flow varied from year to year (from 0.12 to 40 cfs). To estimate steady-state groundwater recharge, stream flow was assumed to vary from 0.9 to 10 cfs. Groundwater recharge was determined by steady-state groundwater flow modeling. Using this approach, the estimates of mass of N denitrified were equivalent to 0.3 to 6.4% of the N applied, with the best estimates being 2.3% of N applied for water year 2000, 1.2% of N applied for water year 2001, and 3.1% of N applied for water year 2002. Our estimates of N denitrified in shallow ground water represent 9% to 27% of the estimated N exported from the watershed via surface water. However, these estimates should be considered minimum values because our approach does not account for transient flow. Additional N transported by transient groundwater flow, such as groundwater flow following precipitation events, probably remains in the subsurface long enough to be partially, and possibly completely, denitrified.

7.1 Recommendations

To estimate the fate and transport of nutrients in the shallow groundwater of an agricultural watershed, one must know the flux of water and the concentration of nutrients in the water throughout the watershed. Our estimates could be improved if the following recommendations were implemented.

1) Rather than use a steady-state estimate of groundwater flow, a transient groundwater flow model could be used to estimate water flow through the watershed. Flow through tile drains should also be included in the flow model.
2) Collect more data on nutrient concentrations. Water should be sampled on a regular interval (perhaps monthly) and episodically such as following significant precipitation events and winter/spring thaws.
3) Additional research should be conducted to better understand the variability of nutrients in the subsurface. For example, denitrification is controlled by the availability of organic carbon (electron donor). Thus, the distribution of the organic carbon in the subsurface should be characterized when attempting to estimate N flux through the subsurface.
4) Increase the number of monitoring wells in the watershed. Additional wells are needed on the north side of Big Ditch to improve the spatial resolution of the groundwater flow data and near Big Ditch where groundwater discharges to the stream to improve the vertical resolution of the groundwater flow data.

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