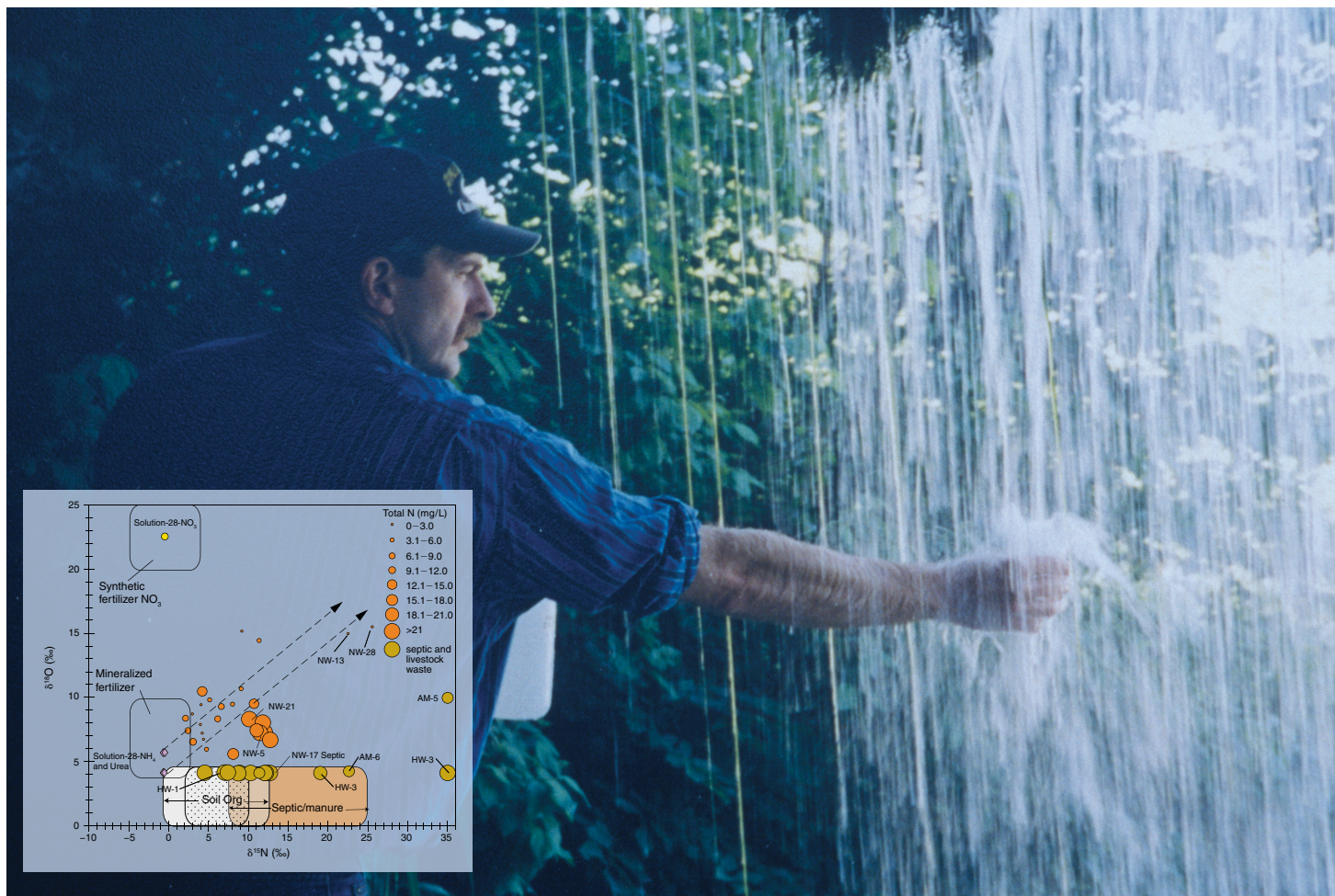# Groundwater Quality of Springs and Wells of the Sinkhole Plain in Southwestern Illinois: Determination of the Dominant Sources of Nitrate

K.C. Hackley, S.V. Panno, H.-H. Hwang, and W.R. Kelly

Illinois Department of **Natural Resources**

ISGS Illinois State Geological Survey

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Front Cover:
Keith Hackley is shown here collecting a water sample from Falling Springs near Dupo, Illinois. The sampling location is on a ledge several meters below the mouth of Falling Springs cave and about 20 m above the base of the bluff. (Photograph by S.V. Panno.) The inset figure is of the nitrogen and oxygen isostope composition of NO_3^- of well water and end-member samples.

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Contents

Tables

Figures

Abstract

About half the residents living in the area of southwestern Illinois known as the sinkhole plain obtain their potable water from the region's shallow karst aquifer. Previous work has shown that the groundwater from approximately 18% of the wells in the sinkhole plain has nitrate concentrations in excess of the U.S. Environmental Protection Agency's drinking water standard of 10 mg of N/L of water. The nitrate concentrations in water samples collected from approximately 50% of the wells and from all of the springs in the sinkhole plain area are greater than background concentrations, suggesting that sources other than naturally occurring organic matter in soil have contributed additional nitrate to groundwater in the shallow karst aquifer. This investigation characterized the geochemistry of the groundwater to determine which source of nitrogen in the sinkhole plain is the major contributor to the anomalous concentration of nitrate observed in the shallow karst aquifer.

Considering the dominance of agriculture and the expansion of urban development in the study area, sources of excessive nitrate and groundwater contamination include agrichemical, livestock, and sewage waste. Water samples from 10 karst springs and 17 wells were collected during different seasons and analyzed for chemical, isotopic, and bacterial characteristics. The samples from each spring were a representative composite of the shallow water recharging the associated watershed. Samples from the wells reflect individual points within the watersheds and were more susceptible to influence from local environments, including anthropogenic activities.

Chemical characteristics and the isotopic composition of some of the dissolved constituents varied seasonally in the samples of spring water, attesting to the rapid infiltration of surface and soil water into the karst aquifer. Bacteria concentrations in the springs and most of the wells were greater than those allowed by county and state regulations for drinking water. Nitrate concentrations in the springs covered a fairly narrow range, from 1.7 to 7.5 mg of N/L. In the wells, nitrate concentrations varied greatly, ranging from less than the detection limit (<0.2 mg of N/L) to 81 mg of N/L.

The isotopic data for the dissolved nitrate (NO_3^-) from the springs and wells were useful in distinguishing NO_3^- sources. The nitrogen and oxygen isotope composition ($\delta^{15}N$ and $\delta^{18}O$) of the NO_3^- ranged from 2.2 to 25.9 per mil (‰) and 5.1 to 21.9‰, respectively. These isotopic results suggest that the NO_3^- sources in spring water were dominated by fertilizer nitrogen and soil organic nitrogen that mixed with NO_3^- having an enriched ^{18}O signature.

The isotopic results for the wells indicate that the largest NO_3^- concentrations (between 13 and 80 mg of N/L) originated primarily from septic and livestock wastes. The isotopic results for most of the wells with NO_3^- concentrations between 2 and 12 mg of N/L indicate that nitrogen fertilizer was the dominant NO_3^- source.

The combined chemical, bacterial, and isotopic analyses of springs and individual wells provided independent evidence concerning the major susceptibility of the karst aquifer to surface contamination and helped to differentiate the sources of NO_3^- in the groundwater. Although many livestock facilities and septic systems were present in individual watersheds, the typical isotopic characteristics of NO_3^- originating from such point sources were overwhelmed by the constant input of nonpoint source nitrogen for the composite samples of spring water. However, results from groundwater samples from several residential wells did show the impact of point sources in NO_3^- contamination on a local scale.

Introduction

Nitrate (NO_3^-) is among the leading pollutants of rivers, lakes, estuaries, and groundwater (Parry 1998). In drinking water, NO_3^- in excess of 10 mg of N/L may be toxic to infants and may be responsible for an increased occurrence of stomach cancer in adults (O'Riordan and Bentham 1993). Nearly half of the residents living in the karst regions of St. Clair, Monroe, and Randolph Counties in southwestern Illinois use the shallow karst aquifer of Illinois' sinkhole plain (Figure 1) as their potable water source. Nitrate concentrations in excess of the U.S. Environmental Protection Agency's (USEPA) 1992 drinking water standard of 10 mg of N/L have been found in more than 18% of the wells in the sinkhole plain, even though these are bedrock wells ranging in depth from 20 to over 100 m (Panno et al. 1996). In addition, groundwater samples from 52% of the drilled wells in this area exceed a preliminary threshold concentration of 1.4 mg of N/L (Panno et al. 1996). Subsequent work by these authors yielded a revised threshold concentration of 2.5 mg of N/L for spring water and 2.1 mg of N/L for well water (Panno et al. 2006).

Nitrate and other nutrients enter surface streams in the Midwest via drainage tiles, groundwater discharge, springs, and surface runoff to ultimately discharge into the Mississippi River. Recent studies in the vicinity of the Mississippi Delta have suggested that nutrient-rich water from the Mississippi River may contribute to a 15,500-km^2 hypoxia zone in the Gulf of Mexico, resulting in the death of marine life (Rabalais et al. 1996). The determination of the NO_3^- sources in groundwater, then, is an important first step in the process of improving the groundwater quality within the karst aquifers of Illinois' sinkhole plain and perhaps reducing the amount of NO_3^- discharging to water bodies downstream.

In the southwestern sinkhole plain of Illinois, agriculture is the dominant land use, and the number of private septic systems is increasing because of urban development. The numerous sinkholes and associated macropores in the relatively thin soil overlying the karstified limestone are conducive to
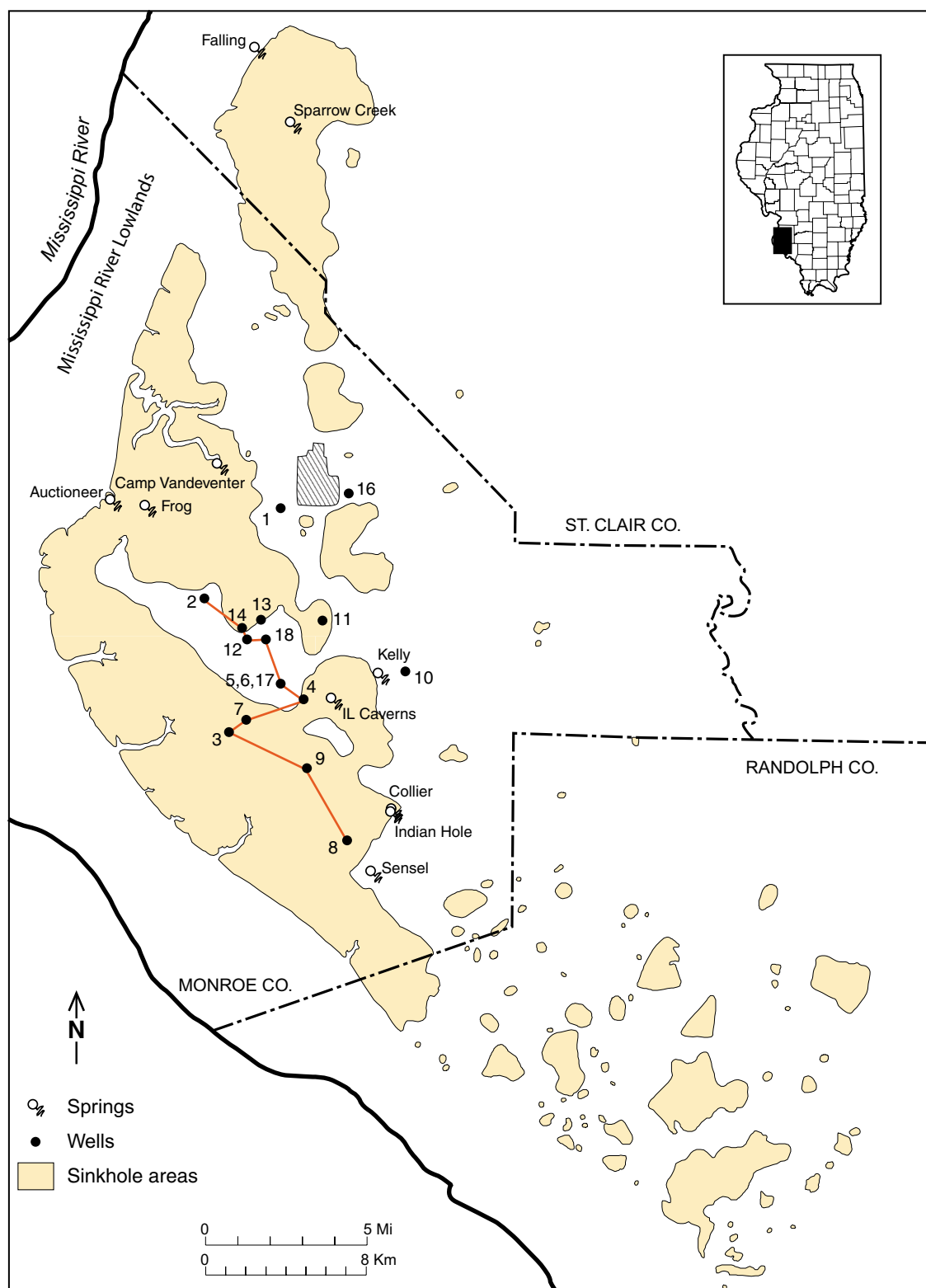
Figure 1 Map of the study area showing karst terrane (sinkhole areas) and the location of springs and wells sampled during this investigation (modified from Panno et al. 2001).

rapid influx of surface and soil water that potentially carries agrichemicals (fertilizers and pesticides), livestock waste, and septic effluent directly into the shallow karst aquifer. This influx has resulted in contamination of the karst aquifer in southwestern Illinois, which feeds springs, streams, and residential wells in the region (Panno et al. 1996). The dominance of agricultural land use and the strong correlation of NO_3^- and atrazine in spring water following springtime planting (Panno et al. 1996) suggest that agricultural sources of NO_3^- are probably considerable. Land use in the sinkhole plain is predominantly row crops and, to a lesser extent, livestock; 86% of the land surface in Monroe County is used for agricultural purposes (Southwestern Illinois Metropolitan and Regulatory Planning Commission, unpublished report 1977).

The objectives of this investigation were (1) to characterize the quality and general geochemistry of the groundwater in the karst aquifer of the sinkhole plain region in southwestern Illinois and (2) to determine the dominant source of anomalously large concentrations of NO_3^- in groundwater. The overall quality and geochemical characteristics of the karst groundwater were examined using chemical, isotopic, and bacterial analyses. Analyses of nitrogen and oxygen isotopes were used to determine the major sources of NO_3^- in groundwater. Analyses of the stable isotopes of the NO_3^- ion have been shown to be effective for identifying the dominant sources of NO_3^- in groundwater and to determine whether denitrification has occurred (Heaton 1986, Mariotti et al. 1988, Böttcher et al. 1990, Wassenaar 1995, Aravena and Robertson 1998, Mengis et al. 1999). Most applications using nitrogen and oxygen isotopes of NO_3^- in surface water and associated groundwater have been limited to relatively small geographic areas, such as small single watersheds, contamination plumes, or the edges of a cultivated field. This present study seasonally sampled springs that were discharge points from 10- to 100-km² watersheds to obtain samples that represented composite compositions

of the groundwater basins. These results were compared with specific well sites distributed throughout the watersheds. This research extends the work by Panno et al. (2001).

Study Area Description

Geology and Basin Hydrology

The study area was located on the western margin of the Illinois Basin known as the Illinois sinkhole plain (Figure 1). Area bedrock consists of Mississippian limestone, sandstone, and shale that lie at or near the surface and dip gently to the east, toward the center of the Illinois Basin. Much of the area is characterized by karst topography and has approximately 10,000 sinkholes (Panno 1996). Numerous large springs and the longest caves in the state are found in this region. The majority of caves and sinkholes occur in the calcite-rich Mississippian age Ste. Genevieve and St. Louis Limestones (Panno et al. 1997a). The upland area (about two-thirds of Monroe County) is, for the most part, covered with Illinoian glacial till and/or residuum overlain by a relatively thick layer of windblown Wisconsin age loess (Piskin and Bergstrom 1975). The loess is typically less than 15 m thick but can be 20 m or more thick. The unconsolidated loess is easily eroded, forming steep-sided sinkholes and associated gullies.

Data from drillers' logs indicate that the water table is closest to the surface (approximately within 3 to 6 m) beneath the covered karst region and becomes much deeper (approximately 25 to 38 m) in karst topography. The term "covered karst" refers to areas of the sinkhole plain that are underlain with karstified limestone but contain no sinkholes in the overlying fine-grained terrane. Where the water table is above the soil-bedrock interface, as much as 40% of the weight of the sediment may be supported by the buoyant force of water (Crawford et al. 1989). When the water table is lowered, buoyant support is lost, intergranular pressure increases, and water drains from the loess, increasing stress on the unconsolidated sedi-

ments (Freeze and Cherry 1979). As a result, sediment spalls and caves into crevices in bedrock, and sinkholes develop (Crawford et al. 1989). Consequently, water is quickly drained from the surface through sinkholes, solution-enlarged fissures, and cave systems.

The springs selected for groundwater sampling are the discharge points of groundwater basins and represent a composite of the groundwater flowing within each basin (Quinlan 1990). Thus, the inputs from surface sources via sinkholes, macropores, and soil water are averaged across the whole watershed. Wells, however, receive water from small areas of a groundwater basin and are more apt to be influenced by the local surface environment. Many residents depend on well water as their major potable water source, and the wells in this region have a wide range of NO_3^- concentrations. The wells chosen for sampling varied in depth, allowing comparison of the water quality of shallow and deep groundwater samples.

Land Use

Agriculture is the dominant land use throughout the study area (Panno et al. 1996). The 10 springs sampled are discharge points for 10 individual groundwater basins within the sinkhole plain (Figure 1; Table 1). Livestock commonly graze in the groundwater basins drained by Kelly and Frog Springs, and row crops dominate land use in the other groundwater basins. Livestock are also present, but to a lesser extent, in the drainage basins of Collier, Indian Hole, and Sensel Springs. Increased urban development of land in the groundwater basins of Falling, Sparrow Creek, Camp Vandeventer, and Auctioneer Springs during the past several years has probably resulted in additional input of septic effluent to these basins.

Nine of the springs are discharge points of branchwork-type caves in the limestone bedrock and drain the karst terrane. Sensel Spring discharges from the same host rock but drains an area of mantled karstified

bedrock (Figure 1; Table 1). Kelly Spring is also unique in that its catchment includes both a surface stream and a cave system. The upper half of Kelly Spring's watershed is drained by a surface stream, Dry Run Creek, that intersects Kruegers Dry Run Cave upon entering the karst terrane and flows underground for the other half of its catchment area prior to exiting at Kelly Spring.

Background

Potential Nitrogen Sources

Nitrate is very mobile in the natural environment (Hem 1985). The major mechanism for mobilizing NO_3^- from field soils in humid climates, such as Illinois, is through leaching during rain events (Tisdale et al. 1993). The background concentrations of NO_3^- in the shallow karst aquifer of the sinkhole plain ranges from 0.4 to 2.5 mg of N/L for springs and 0.1 to 2.1 mg N/L for wells (Panno et al. 2006); 2.5 mg N/L should be used as an upper bound for background concentrations in the sinkhole plain. However, as stated earlier, most of the springs and wells sampled in the sinkhole plain area contain NO_3^- concentrations that are considerably larger than the background concentrations. Probable NO_3^- sources in the sinkhole plain include soil organic matter, nitrogen fertilizers, livestock wastes, and septic systems. Although the nitrogen of most fertilizers and septic effluent is in the reduced form, as ammonium or organic nitrogen, aerobic microbes in the upper soil zone are capable of quickly oxidizing this nitrogen to NO_3^- through nitrification.

The annual application of nitrogen fertilizers (primarily anhydrous ammonia and urea) ranges from about 120 to 150 lbs/acre (135 to 168 kg/ha) for corn and about 80 to 100 lbs/acre (90 to 112 kg/ha) for wheat and other grains (P. Kremmell, personal communication 1998). Anhydrous ammonia and urea are usually applied in the early spring for corn, and ammonium nitrate and urea are used in the late winter (February and March) for wheat.

The water samples from springs were analyzed for atrazine because atrazine is considered representative of herbicides used in the study area (Panno et al. 1996) and is applied during the spring at approximately 1.0 to 1.5 lbs/acre (1.12 to 1.68 kg/ha) (P. Kremmell, personal communications 1997). Panno et al. (1996) concluded that the largest concentrations of agrichemicals entered groundwater via runoff into sinkholes during and immediately following spring planting. Thus, atrazine could be considered an indirect indicator for the source of some of the NO_3^- present in the shallow karst aquifer.

The effluent of septic systems may contribute substantially to local sources of NO_3^- in groundwater. Earlier work by Panno et al. (2007) found that total dissolved N, as NO_3^- and/or ammonia (NH_4^+), in effluent discharging from 22 septic systems ranged from 2.85 to 67 mg of N/L (mean and median, 24 mg of N/L). Livestock businesses in the area are generally small, and contamination from those operations is probably limited to individual wells or localized portions of groundwater basins.

Table 1 Spring locations, descriptions of their groundwater basins, and land use within the groundwater basins in the study area.[1]

Spring	Location[2]	Groundwater basin description	Land use
Falling	15/01N/10W	Resurgence of a small cave and waterfall	Row crops, housing development
Sparrow Creek	36/01N/10W	Resurgence for Stemler/Sparrow Creek Cave	Row crops, housing development
Collier	16/04S/09W	Resurgence for a large, suspected cave	Row crops, livestock
Indian Hole	16/04S/09W	Resurgence for Fogelpole Cave	Row crops, livestock
Sensel	29/04S/09W	Karst spring draining a covered karst area	Row crops, livestock
Illinois Caverns	31/03S/09W	Cave stream at cave entrance	Row crops, village
Kelly	29/03S/09W	Resurgence of Krueger's Dry Run Cave	Row crops, livestock, forest
Camp Vandeventer	21/02S/10W	Resurgence of a small cave	Row crops, housing development
Auctioneer	36/02S/11W	Resurgence of a small cave/waterfall	Row crops, housing development
Frog	31/02S/10W	Resurgence of Frog Cave	Row crops, livestock

[1]The boundaries of the groundwater basins were estimated from work by Panno and Weibel (1999) and Aley and Aley (1998, unpublished report). Springs are described by Webb et al. (1994) and Panno et al. (1996, 1998a, 1998b, 1999). Caves described as "small" refer to those thought to be dominated by passages less than 1 m in height.

[2]Location is reported as section, township, and range.

Stable Isotopes

The stable isotopes of an element have the same number of protons and the same electron configuration but a different number of neutrons in the nuclei of their atoms. Thus, the isotopes of a particular element have similar chemical behavior but slightly different atomic masses. The differences in atomic mass cause the isotopes to react at slightly different rates during physiochemical and biochemical processes. Such processes could involve changes in phase (e.g., evaporation), chemical reactions (e.g., precipitation of minerals), or biological activity (e.g., biologically mediated reactions such as denitrification). Thus, the concentration of isotopes that naturally occur in coexisting chemical phases or in reacting chemical compounds can be different. In general, lighter isotopes have slightly faster reaction rates and tend to concentrate in main reaction products

Table 2 Isotopic natural abundance of nitrogen, oxygen, carbon, hydrogen, and sulfur in the study area.[1]

Isotope	Abundance (%)
^{14}N	99.64
^{15}N	0.36
^{16}O	99.76
^{17}O	0.04
^{18}O	0.2
^{12}C	98.89
^{13}C	1.11
^{14}C	10^{-10} ($t_{1/2}$ = 5,730 years)[2]
^1H	99.984
D or ^2H	0.015
^3H	10^{-14} to 10^{-16} ($t_{1/2}$ = 12.33 years)[3]
^{32}S	95.02
^{33}S	0.75
^{34}S	4.21
^{35}S	$<10^{-11}$ ($t_{1/2}$ = 87.2 days)
^{36}S	0.02

[1] Hoefs (1980), Fritz and Fontes (1980), and Coplen (1993).

[2] $t_{1/2}$, radioactive half-life.

[3] Lucas and Unterweger (2000).

relative to the heavier isotopes. The overall natural abundance of the isotopes of elements used in this study are listed in Table 2.

Because differences in isotopic abundance of an element from one substance to another are small, concentrations are expressed in delta (δ) notation. The δ-value of an isotope in a sample is the per mil (‰, parts per thousand) difference in the ratio of the less abundant isotope to the most abundant isotope relative to the same ratio in a known standard. This relationship is represented by the following equation:

$$\delta X = \left[\frac{R_{sample} - R_{standard}}{R_{standard}} \right] 10^3 \qquad [1]$$

where δX stands for the isotope of interest (e.g., $\delta^{18}O$ or $\delta^{15}N$), and R is the ratio of the less abundant isotope relative to the most abundant isotope (e.g., $^{18}O/^{16}O$ or $^{15}N/^{14}N$). The isotopic results of this study are reported against reference standards. The reference standards used for $\delta^{15}N$ is nitrogen in air; for isotopic oxygen and deuterium ($\delta^{18}O$ and δD), Vienna-Standard Mean Ocean Water (V-SMOW); for isotopic carbon ($\delta^{13}C$), Vienna PeeDee Belemnite (VPDB); and for isotopic sulfur ($\delta^{34}S$), Canyon Diablo Troilite (CDT).

$\delta^{15}N$ and $\delta^{18}O$ of NO_3^- Generally, different sources of NO_3^- have different $\delta^{15}N$ values. The $\delta^{15}N$ value for fertilizers is about 0 ± 4‰ (Heaton 1986, Gormly and Spalding 1979). The $\delta^{15}N$ values for NO_3^- from animal waste and septic systems commonly range from +8 to +22‰ (Heaton 1986). The $\delta^{15}N$ of NO_3^- from soil organic matter varies considerably but is generally between +2 and +10‰ for most soils (Feigin et al. 1974, Heaton 1986, Mariotti et al. 1988, Shearer and Kohl 1988, Fogg et al. 1998, Kendall 1998). Although the $\delta^{15}N$ of the individual sources of NO_3^- (the end members) may initially be different, certain geochemical processes, such as denitrification (the reduction of NO_3^- to nitrogen gas, N_2), cause isotope fractionation to alter the isotopic composition of the NO_3^-. During microbial

denitrification, the lighter isotope (^{14}N) is preferentially partitioned to the reduced N_2 gas. The heavier isotope (^{15}N) becomes enriched in the remaining NO_3^-. Thus, as denitrification occurs, the isotopic composition of the remaining NO_3^- changes, and it becomes difficult to distinguish its source using only $\delta^{15}N$ values. To help resolve this problem, $\delta^{18}O$ value of the NO_3^- was also analyzed.

The $\delta^{18}O$ of NO_3^- varies depending on the source of oxygen in the NO_3^- and geochemical processes such as denitrification. In some cases, such as with synthetic nitrate fertilizer, the source of oxygen is completely atmospheric; in other cases, such as with nitrification of ammonium in groundwater, the source of oxygen is a combination of groundwater oxygen and atmospheric oxygen. During nitrification, it is generally thought that approximately two-thirds of the oxygen in NO_3^- is from groundwater ($\delta^{18}O$ values of groundwater are usually negative and vary depending on geographic location), and one-third is from the atmosphere ($\delta^{18}O$ is approximately +23.5‰) (Amberger and Schmidt 1987, Böttcher et al. 1990, Kendall 1998). However, recent studies (Mayer et al. 2001, Burns and Kendall 2002) indicate this suggested distribution may be an oversimplification for predicting the $\delta^{18}O$ of NO_3^- during nitrification. Based on incubation experiments and measurements of NO_3^- from forest soils, those studies found that the $\delta^{18}O$ was greater than expected, suggesting that perhaps the contribution of atmospheric oxygen might sometimes be greater than one-third. Mayer et al. (2001) suggested that in some environments, such as those with low pH, which they observed in forest soils, a different bacterial process dominates the nitrification reaction and utilizes a greater amount of atmospheric oxygen. There is also the possibility that the $\delta^{18}O$ of the soil water at some locations might be enriched in ^{18}O from respiratory isotope fractionation and/or evaporative effects within the soil zone (Kendall 1998, Burns and Kendall 2002). Thus, the isotopically heavier soil water would contribute oxygen to NO_3^- with greater $\delta^{18}O$ values than

expected from local groundwater isotope values.

The $\delta^{18}O$ values are usually fairly low for NO_3^- in shallow groundwater in agricultural settings, and many of the larger values in these areas are attributed to denitrification or fast throughput of NO_3^- fertilizers (Aravena et al. 1993, Mengis et al. 2001, Beaumont 2003). The lower $\delta^{18}O$ values of the NO_3^- in those studies are consistent with the nitrification process that purports two-thirds oxygen from groundwater and one-third from atmospheric oxygen. However, there is always a range of values that probably reflect the variable $\delta^{18}O$ of the soil water and influences from some of the processes just discussed. It appears that the environmental setting and climatic conditions affect the initial $\delta^{18}O$ value of NO_3^- during nitrification of reduced N sources. Our study samples are primarily from agricultural settings. In order to estimate initial $\delta^{18}O$ values of NO_3^- for nitrification of reduced nitrogen sources, we have assumed that the nitrification process that dominates in the study area uses two-thirds water and one-third atmospheric contribution. The range of $\delta^{18}O$ of NO_3^- from the nitrification reaction will, of course, vary depending on the $\delta^{18}O$ of the shallow groundwater that comes in contact with the nitrifying bacteria.

The other process that strongly affects the $\delta^{18}O$ value of NO_3^- is denitrification. Denitrification fractionates the oxygen isotopes, causing the residual NO_3^- to become more enriched in ^{18}O. Although the fractionation factor for both $\delta^{15}N$ and $\delta^{18}O$ exhibits a range of values depending on local conditions and rates of reactions, when compared with each other, the $\delta^{15}N$ and $\delta^{18}O$ isotopes fractionate at a relatively constant ratio during denitrification (Kendall 1998). Thus, using both $\delta^{15}N$ and $\delta^{18}O$ measurements helps to determine the major sources of NO_3^- and indicates whether denitrification has occurred in the groundwater system. A 1:2.1 relationship between $\delta^{18}O$ and $\delta^{15}N$ of NO_3^- has been observed (Böttcher et al. 1990, Aravena and Robertson 1998) in detailed groundwater studies involving NO_3^-

attenuation at sites in Germany and in Ontario, Canada. A strong correlation between decreasing NO_3^- concentration and increasing $\delta^{15}N$ and $\delta^{18}O$ values was observed in both studies. In a recent study by Mengis et al. (1999), a similar linear relationship was observed between the $\delta^{18}O$ and the $\delta^{15}N$ of the NO_3^-; however, correlation was poor between decreasing NO_3^- concentrations and increasing isotopic composition of NO_3^-. This poor correlation was explained by variable inputs of NO_3^- into the groundwater caused by crop rotation of the cultivated field, riparian buffer zone, and mixing with local, deeper groundwater. Thus, denitrification may be identified in a groundwater system by using $\delta^{15}N$ and $\delta^{18}O$ of the dissolved NO_3^- even though decreases in NO_3^- concentration may not be strongly correlated with increasing isotopic values.

δD and $\delta^{18}O$ of Water The δD and $\delta^{18}O$ isotopes in precipitation from around the world follow a consistent relationship that is characteristic of latitude and climatic conditions (Craig 1961, Dansgaard 1964). This relationship results in a straight line referred to as the "global meteoric water line" (GMWL):

$$\delta D = 8(\delta^{18}O) + 10. \qquad [2]$$

The $\delta^{18}O$ and δD values are generally not altered in meteoric water after it enters the soil zone and infiltrates to the shallow groundwater (Fontes 1980). However, under certain conditions, noticeable deviations from the GMWL are caused by physical and chemical processes that affect the isotopic composition of the water subsequent to precipitation; examples are evaporation and geothermal water-rock interactions (Coplen 1993, Fontes 1980). The conservative nature of $\delta^{18}O$ and δD in low-temperature environments allows these isotopes to be used in leakage or mixing studies between reservoirs of water that are isotopically distinct. Furthermore, in nitrate studies, the $\delta^{18}O$ of groundwater should be determined in order to estimate the $\delta^{18}O$ of NO_3^- produced

from nitrification of reduced nitrogen in the soil zone. This process for estimating $\delta^{18}O$ of the NO_3^- produced from nitrification was described in the previous section.

$\delta^{13}C$ in Groundwater The carbon isotope ($\delta^{13}C$) of dissolved inorganic carbon (DIC) in groundwater is useful in determining the geochemical evolution of the groundwater because of the differences in isotopic composition of the major sources of carbon and the fractionation of its isotopes caused by certain geochemical reactions. The $\delta^{13}C$ of DIC in shallow groundwater is initially dependent on several factors, including the isotopic composition of the soil CO_2, the input of carbon from dissolution of carbonate minerals as groundwater percolates into the subsurface, and whether the dissolution of carbonate minerals has occurred in isolation relative to soil CO_2.

The partial pressure of CO_2 in soil is usually 10 to 100 times that of atmospheric CO_2 and comes primarily from root respiration and decomposition of organic debris (Mora et al. 1993, Clark and Fritz 1997). Thus, the $\delta^{13}C$ of soil CO_2 and, hence, DIC of the recharging groundwater depend on the vegetation growing in the region. The $\delta^{13}C$ of plant carbon depends on the photosynthetic pathway of the plants. The majority of plants, including agricultural crops such as wheat and soybeans, utilize the Calvin cycle (C_3), a photosynthetic pathway that results in low $\delta^{13}C$ values averaging –27‰. Some grasses, including corn, utilize the Hatch-Slack pathway (C_4), which results in $\delta^{13}C$ values averaging –12‰. Normally, there is a combination of C_3 and C_4 plants, resulting in soil CO_2 $\delta^{13}C$ values between –12 and –27‰ (Clark and Fritz 1997). Another possible source of organic carbon in soils of agricultural areas is organic fertilizers, such as urea, which has very low $\delta^{13}C$ composition, near –50‰ (Zlotnick 1992). The actual isotopic composition of soil CO_2 is usually more enriched in ^{13}C than the overall composition of the vegetation rate because of a 4.4‰ fractionation caused by diffusion of CO_2 through the soil to the atmosphere (Cerling et

al. 1991). Measured $\delta^{13}C$ values of soil CO_2 in east-central and south-central Illinois ranged from –16.7 to –22.4‰ (Hackley and Liu, unpublished data).

The $\delta^{13}C$ of DIC for shallow groundwater in recharge areas is initially quite negative (isotopically light) because most of the DIC is from soil CO_2, which has been dissolved into the soil water and carried down into the subsurface with groundwater flow. As the water percolates into the ground, rocks containing inorganic carbon, such as limestone and dolomite, dissolve and add to the DIC pool. Carbonate minerals usually have isotopically heavier $\delta^{13}C$ values than do plants. The $\delta^{13}C$ of most marine carbonates is close to 0‰ (Anderson and Arthur 1983). The final $\delta^{13}C$ of the DIC depends on the type of system in which carbonate dissolution occurs (Mook 1980, Clark and Fritz 1997). If dissolution is completely open to exchange between soil CO_2 and DIC, then the isotopic composition of the DIC is controlled by the reservoir of soil CO_2. However, if the dissolution of carbonate occurs under conditions closed to exchange between DIC and soil CO_2 (i.e., in the saturated zone), then the $\delta^{13}C$ of the DIC becomes an intermediate value between the two end members: soil CO_2 and carbonate carbon. Typically, the DIC of groundwater for temperate areas with C_3 plants dominating has a $\delta^{13}C$ value between –10 to –13‰ (i.e., between the average soil CO_2 and average carbonate mineral compositions).

$\delta^{34}S$ in Groundwater   Sulfate in groundwater is generally derived from the dissolution of sulfate minerals, such as gypsum, and/or the oxidation of reduced sulfide minerals, such as pyrite. In some cases, sulfide oxidation may be associated with denitrification (Kelly 1997, Kölle et al. 1985). The $\delta^{34}S$ of sulfate from gypsum evaporite deposits is usually considerably different from that of sulfate from the oxidization of sedimentary sulfide minerals. $\delta^{34}S$ values from evaporite deposits are generally about +20‰ but vary with age (Holser and Kaplan 1966, Nielsen 1976, Claypool et al. 1980). The $\delta^{34}S$ values of reduced sulfides in sediments and sedimen-

tary rocks vary widely, mostly in the general range of –50 to +10‰ (Kaplan 1983, Canfield and Teske 1996). Typically, however, sedimentary sulfides usually have values ranging from –10 to –30‰ (Hoefs 1980). The isotopic composition of sulfur in dissolved sulfate helps to delineate the source of sulfate in the groundwater and to indicate whether the concentration changes within an aquifer are the result of microbial sulfate reduction reactions or the mixing of waters with different amounts of sulfate.

Methodology

Water Sampling

Groundwater samples were collected from 10 springs and 17 wells in the Illinois' sinkhole plain during different seasons of the year. Several samples of individual NO_3^- sources (end-member samples) were also collected including Solution-28 (a nitrogen fertilizer in solution form, containing 30% urea and 40% ammonium nitrate), urea (a nitrogen fertilizer in solid pellet form), livestock waste (hog waste), monitoring wells contaminated by hog waste, septic effluent, water from field runoff, and atmospheric NO_3^- from precipitation. Water samples from the springs were collected during six consecutive seasons: fall (November) 1998, winter (February/March) 1999, spring (May) 1999, summer (August) 1999, fall (November) 1999, and winter (March) 2000. During the 1999 winter sampling event, two separate collection trips were made to the springs. Samples collected during the initial trip, the third week of February, included only nine springs and were used for chemical analyses, for $\delta^{18}O$ and δD of the water and $\delta^{13}C$ of the DIC. The samples for nitrogen and oxygen isotopes of the dissolved NO_3^- and $\delta^{34}S$ of sulfate were collected 2 weeks later, in March. The second trip was needed because of a complication with the preservative used for the NO_3^- isotope samples from the initial sampling. During this resampling trip, samples for chemical and isotopic analyses were collected from Frog Spring. No precipitation fell during the interval between the two sampling trips. Field

conditions at the springs, such as discharge and NO_3^- concentrations, were essentially the same. Thus, the chemical and isotopic data for the water samples collected from springs during winter 1999 are presented together as one sampling event. Samples collected from Falling Springs were generally taken from the top and bottom of the falls. Falling Springs discharges from the middle of a cliff and spills over and through a large tufa deposit, forming a stream at the base of the cliff.

Water samples from the wells were collected during spring (May) 1999 and fall (November) 1999. Well water was sampled from residential homes through outside spigots to avoid the effects of water softeners, as outside spigots are not normally connected to residential water softener systems.

Samples of aeration-type septic system effluent were collected at the discharge end of the overflow pipe or directly from the final septic chamber. Samples were collected in large 2.3-L glass containers and filtered in the laboratory using a high-capacity filter and peristaltic pump. The hog waste samples were taken directly from waste pits at active hog operations. Two hog waste samples and hog waste-contaminated monitoring wells were collected in south-central Illinois and included here as examples of the chemical and isotope compositions from large hog waste facilities.

All water, septic, and waste samples were analyzed in the field for temperature, pH, redox potential (Eh), and specific conductance. Field measurements for pH and specific conductance were made using meters that allowed temperature compensation. All instruments were calibrated using appropriate standards. Groundwater samples were collected in accordance with field techniques described by Wood (1981) and Panno et al. (1996).

Groundwater samples were collected from the springs and wells for cation, anion, dissolved organic carbon (DOC), atrazine, bacteria, and the stable isotope analyses, including nitrogen, oxygen, hydrogen, carbon, and sulfur isotopes. Samples col-

lected for cations, anions, DOC, and stable isotopes were filtered through 0.45-μm membranes and stored in polyethylene bottles. Samples analyzed for cations were acidified in the field with ultrapure nitric acid to pH <2.0. Separate samples were collected for ammonium analyses from the septic systems and hog waste pit. Most groundwater samples were not analyzed for ammonium because of its very low concentration in the springs (Panno et al. 1998a, 2005). Groundwater samples for nitrogen and oxygen isotopic analyses of dissolved NO_3^- were collected in 2-L bottles and were preserved with hydrochloric acid to a pH <2 or with the addition of several drops of mercuric chloride solution. Samples for tritium (^3H) analysis were collected in 500-ml polyethylene bottles. Atrazine samples were unfiltered and were collected in precleaned, 1-L glass bottles. Bacterial samples also were unfiltered and were collected in two sterilized 120-ml bottles. All samples were transported in ice-filled coolers to the appropriate laboratories and kept refrigerated at approximately 4°C until analyses were completed.

Analytical Techniques

Cation concentrations in the water samples were determined as described by Panno et al. (1996) using a Model 1100 Thermo-Jarrell Ash Inductively Coupled Argon Plasma Spectrometer (ICAP). Instrument control, automatic background correction, and spectral interference corrections were performed using a DEC Micro PDP 11/23 computer. Solution concentrations of anions were determined using a Dionex 211i ion chromatograph, following USEPA Method 300 (O'Dell et al. 1984). All water chemistry data were evaluated with the Geochemist's Workbench (Bethke 1994) reaction model to determine saturation states.

Dissolved organic carbon was determined by difference (total carbon minus inorganic carbon) (Greenburg et al. 1987). In summary, total carbon was determined by completely combusting an aliquot of filtered water sample on a heated coil (950°C) and

measuring the amount of CO_2 driven off by a CO_2 coulometer. The DIC was determined by using a weak solution of nitric acid on an aliquot of filtered water and measuring the amount of the CO_2 released with a coulometer (ASTM 1994).

Atrazine and bacteria were analyzed by the Illinois Department of Agriculture's Animal Disease Laboratory in Centralia, Illinois. Atrazine samples were analyzed using gas chromatography and mass spectrometry techniques (U.S. Environmental Protection Agency 1982). Bacterial samples were analyzed within 24 hr of collection for total coliforms, fecal coliforms, and total bacteria using standard methods to isolate and identify bacterial colonies present (Clesceri et al. 1989). Concentrations of bacteria are reported as colony-forming units (cfu) per 100 ml of water. Bacterial species were identified and listed from most dominant to least. The dominance of each bacterial species was summarized using ranking (arithmetic mean) and prevalence (percentage) of each species in water samples (Panno et al. 1997b). Bacteria were ranked from 1 (most dominant) to 15 (least dominant) for all water samples collected during each sampling period. The ranks for each bacterium were added, and mean ranking was determined (e.g., the lowest mean ranking is the most abundant); non-detections were given the highest rank for this calculation.

Tritium (^3H) was analyzed using electrolytic enrichment (Ostlund and Dorsey 1977) and liquid scintillation counting. The electrolytic enrichment process basically consisted of distillation, electrolysis, and purification of enriched samples. The results are reported in tritium units (TU). One TU is defined as one ^3H atom per 10^{18} hydrogen atoms. The precision for the analyses in this study is 0.25 TU.

Nitrogen and oxygen isotopic analyses of NO_3^- in water samples were conducted using methods similar to those described by Silva et al. (1994, 2000) and Wassenaar (1995) with the modifications of Hwang et al. (1999). The samples were first boiled under acidification to remove bicarbonate

(HCO_3^-) and dissolved CO_2. The DOC and sulfate (SO_4^{2-}) ions also were removed to minimize contamination of the $\delta^{18}O$ by oxygen in the SO_4^{2-} ions and the dissolved organic matter and to help eliminate anionic interference during the ion-exchange step for NO_3^- extraction. The dissolved organic matter was removed using a silicalite molecular sieve, and SO_4^{2-} ions were removed by precipitation as barium sulfate ($BaSO_4$). After removal of HCO_3^-, SO_4^{2-}, and DOC, the NO_3^- was extracted using an anion-exchange column packed with BioRad AG 1-X8 resin (Silva et al. 2000). Nitrate collected on the anion-exchange column was eluted with hydrogen bromide (HBr) solution (Hwang et al. 1999) and converted to silver nitrate ($AgNO_3$) by adding silver oxide (AgO_2). The $AgNO_3$ was precipitated by freeze-drying the sample in a vacuum system. The dried $AgNO_3$ was converted to CO_2 and N_2 for $\delta^{18}O$ and $\delta^{15}N$ analysis, respectively, by sealed quartz-tube combustion techniques with and without graphite as described by Silva et al. (2000) and Hwang et al. (1999). The standard deviation for $\delta^{15}N$ was less than or equal to ±0.4‰: the mean value was ±0.1‰. We discovered a problem part way through the study involving the use of quartz wool with the combustion procedure for determining $\delta^{18}O$ of NO_3^-. Many of the samples for which extra $AgNO_3$ remained were reanalyzed, changing the $\delta^{18}O$ values an average of 1.4‰. For those samples that could not be rerun, a correction factor was applied. The standard deviation of $\delta^{18}O_{NO3}$ for the reanalyzed samples was less than or equal to ±0.9‰; the mean was ±0.3‰. For those mathematically corrected samples, the standard deviation for $\delta^{18}O$ was ±1.7‰.

Recently, Révész and Bohlke (2002) published a new method for determining the $\delta^{18}O$ of NO_3 that does not employ any quartz tubing but instead uses a graphite tube and high temperature conversion elemental analysis (TCEA) technique. In order to compare the $\delta^{18}O_{NO3}$ values reported here using quartz-tube combustions to $\delta^{18}O_{NO3}$ values determined by the newly developed (TCEA) method, the following equation can be used:

Y = 1.284X – 3.3. The equation is based on a comparison of our analyses of the National Institute of Standards and Technology (NIST) nitrate standards (IAEA-N3 and USGS-34 and -35) with $\delta^{18}O$ values reported by Bohlke et al., (2003). However, most of the data for $\delta^{18}O$ of nitrate in the published literature have been prepared using sealed quartz-tube combustion techniques, so, for this publication, we have reported the quartz-tube combustion $\delta^{18}O$ values.

The $\delta^{18}O$ of the water samples was determined using the CO_2-H_2O equilibration method as originally described by Epstein and Mayeda (1953) with modifications of Hackley et al. (1999). The δD of water was determined using the zinc-reduction method (Coleman et al. 1982, Vennemann and O'Neil 1993) with modifications described by Hackley et al. (1999). The $\delta^{13}C$ of DIC was determined by the gas evolution technique in a manner similar to that described by Atekwana and Krishnamurthy (1998). Instead of 85% phosphoric

acid, we used 2 g of crystalline ortho-phosphoric acid (99%) that was placed into vials that were then sealed with a septum and evacuated. Approximately 10 ml of the water sample was injected into the vials, and the CO_2 released at room temperature was extracted from the vial and purified cryogenically as described by Atekwana and Krishnamurthy (1998).

The purified gases (N_2, CO_2, H_2, and SO_2) were analyzed on an isotope ratio mass spectrometer. Analytical reproducibility for δD, $\delta^{18}O$, $\delta^{13}C$, and $\delta^{34}S$ is equal to or less than $\pm 1.0‰$, $\pm 0.1‰$, $\pm 0.15‰$, and $\pm 0.3‰$, respectively.

Results and Discussion

End-Member Samples: Chemical Composition

As expected, the results of some field parameters and chemical analyses (Tables 3 and 4) for the different end-member sources of NO_3^- were anoma-

lous compared with values for natural groundwater composition. For example, values for specific conductance, chloride, sodium, nitrogen, and bicarbonate for most of the septic samples and the livestock (hog) waste samples were considerably greater than typical values for shallow groundwater chemistry.

Specific conductance is a relative measure of the dissolved ions in solution and gives a quick indication in the field of whether the chemical composition of the water has an anomalously large concentration of dissolved ions. The specific conductance of the septic system effluents and the livestock waste was high compared with that of the spring-water samples, which were typically between 400 and 800 micro-Siemens (μS)/cm. The specific conductivities for the septic systems ranged between 819 and 1,983 μS/cm. The specific conductivity for the hog waste samples ranged from 11,400 to 38,200 μS/cm (Table 3).

Compared with the samples of spring

Table 3 Field parameters and total alkalinity of samples analyzed for end-member sources of NO_3^-.

Date sampled	Sample[1]	Sample description	Temp. (°C)	pH	Eh[2] (mV)	Sp. Cond. (µS/cm)	Tot. Alk. (mg of CO_3/L)
Septic effluence							
09/18/96	96-42	Septic	25.6	6.9	253	1,031	327
09/18/96	96-44	Septic	20.0	7.3	324	1,225	346
09/18/96	96-47	Septic	24.6	6.9	349	819	117
09/18/96	96-49	Septic	23.7	6.6	602	1,148	118
09/18/96	96-56	Septic	28.0	6.5	−11	1,983	368
11/18/99	NW-17-septic	Septic	12.0	8.6	365	1,723	385
03/21/01	SS-1	Septic	10.0	7.5	321	1,840	402
03/21/01	SS-2	Septic	12.8	7.5	355	1,246	513
03/21/01	SS-3	Septic	9.2	7.5	51	1,699	501
Animal waste							
03/21/01	HW1	Hog waste	--	6.8	--	29,130	8,210
03/21/01	HW2	Hog waste	--	8.0	--	11,400	4,300
03/21/01	HW3	Hog waste	--	7.8	--	38,200	14,370
03/21/01	Am5	Hog waste[3]	10.1	6.6	−242	2,240	574
03/21/01	Am6	Hog waste[3]	11.1	7.1	−228	1,616	697
Fertilizers							
03/21/01	Soln-28	Soln-28 - NH_3	--	--	--	--	--
03/21/01	Soln-28	Soln-28 - NO_3	--	--	--	--	--
03/21/01	Urea	Urea					
Field runoff							
05/14/99	Runoff	Field water	19.4	9.2	--	231	97

[1]HW2 (HW E458-01), HW3 (HW E254-01), Am5 (HW A 467-02), and Am6 (HW A 469-02) from south-central Illinois.

[2] Temp., temperature; Eh, redox potential, calibrated with Zobell solution; Sp. Cond., specific conductivity; Tot. Alk., total alkalinity; Soln, solution; --, not determined.

[3]Contaminated groundwater.

Table 4 Chemical composition (mg/L) of samples analyzed for end-member sources of NO_3^-.[1]

Sample	Ca^{2+}	Mg^{2+}	Na^+	K^+	NH_4-N	HCO_3^-	Cl^-	SO_4^{2-}	NO_3-N	SiO_2	Al	B	Ba
Septic effluent													
96-42	66.8	25.6	88.9	17	34.6	399	69.1	95.1	1.66	12.9	<0.02	1.15	0.06
96-44	69.1	24.5	115	17	36.5	422	84.3	130	0.53	16.6	<0.02	0.70	0.02
96-47	68.1	26	70.1	16	0.14	143	63.2	76.9	25.9	14.8	<0.02	0.18	0.05
96-49	118	24.3	77.4	28	0.09	144	147	84.1	25.4	9.6	<0.02	1.73	0.05
96-56	65.6	23.6	225	33	21.2	449	312	91.7	0.83	7.9	0.12	0.33	0.10
NW17-septic	59.5	6.48	80.2	345	--[1]	470	91.7	59.0	70.1	29.5	0.03	0.13	0.04
SS-1	84.0	18.6	416	11	16.9	490	504	51.6	<0.1	20.4	<0.3	0.97	0.10
SS-2	33.0	10.1	224	12	34.8	626	91.0	38.5	<0.02	23.5	<0.3	0.05	0.03
S-3	64.5	23.2	262	22	45.6	611	253	73.4	0.26	13.2	<0.3	0.77	0.03
Animal waste													
HW1	343	70.2	493	2,760	3,670	10,010	900	797	<0.25	68.5	<0.3	3.90	0.04
HW2	34.0	3.1	348	2,010	323	5,243	794	1.9	<0.1	33.4	--	2.43	0.023
HW3	26.0	0.9	1,190	4,950	1,806	17,520	1,980	47	<0.2	50.1	--	5.11	0.031
Am5	275	117	70	2	<0.01	700	280	52	12.7	11.1	--	0.03	0.199
Am6	116	84	113	23	13.4	850	171	23	0.05	21.2	--	0.15	0.417
Runoff	36.5	2.28	0.70	14	--	118	15.0	14.0	0.52	0.4	0.145	0.02	0.03

[1]--, not determined.

water, the septic systems and hog wastes had anomalous concentrations of several chemical constituents including chloride, sodium, potassium, and total nitrogen (as NO_3^- or ammonium). The hog wastes also had high concentrations of bicarbonate (Table 4). Of these ions, chloride is an important constituent to monitor because it is one of the most conservative ions in groundwater; that is, it does not tend to react or exchange with other minerals or ions as groundwater flows through the subsurface environment. Many other ions have the tendency to react with the surrounding environment and are not as dependable as tracers. Decreases in chloride concentrations from point sources such as septic systems or feedlots are primarily the result of dilution when the contaminated waste water mixes with groundwater.

End-Member Samples: Isotopic Composition

The end-member samples were measured primarily for their $\delta^{15}N$ composition; however, a few of the samples were measured for some other common stable isotopes (Table 5). The $\delta^{15}N$ values for the ammonium and NO_3^- of the septic system and hog waste samples ranged from +4.7 to +35‰. Three values were lower than the range typically observed in the literature for septic and manure waste (+8 to +22‰). The first five septic samples listed in Table 5 were collected prior to this study, and, thus, no $\delta^{18}O$ values were available for the dissolved NO_3^-. However, because those septic systems were collected from the sinkhole plain area, we have included the $\delta^{15}N$ results here. The field runoff sample had enough sulfate for $\delta^{34}S$ analysis and could be used as an end member for cultivated field sulfate.

Spring Samples: Chemical Composition

Overall, the general chemical composition of the spring-water samples (Tables 6 and 7) was typical of shallow groundwater in contact with carbonate bedrock. Some of the parameters measured for these samples showed seasonal variations; other parameters were typical of soil-water or surface-water chemistry.

Groundwater samples from the springs were Ca^{2+}- HCO_3^--type water and were supersaturated to slightly undersaturated with respect to calcite, aragonite, and dolomite. All of the samples from springs were supersaturated with respect to quartz. Saturation indices with respect to a particular mineral are a reflection of rock-water interactions as the groundwater passes through the soil zone, epikarst, and bedrock formations. The saturation indices for calcite indicate that the water discharging from the springs ranged from very supersaturated to slightly undersaturated conditions (Figure 2). Falling Springs and Auctioneer Spring had the greatest degree of calcite saturation and also had large tufa deposits associated with them. The waters discharging from these two springs have vertical drops 4 to 20 m, causing considerable agitation, which contributes to the degassing of CO_2 and the concomitant precipitation of calcite at the springs (e.g., Hubbard and Herman 1991). Sensel Spring had the most undersaturated water with respect to calcite. Most of Sensel Spring's discharge is from soil water that enters the limestone bedrock just before discharging to a spring house. The undersaturated conditions at this spring suggest there was minimal time for the water to become saturated with respect to calcite.

The pH values for the springs ranged from 6.7 to 8.2. Most of the spring samples had values greater than pH 7.5 (Table 6). The greater pH values reflect the buffering effects of the carbonate bedrock. Groundwater from

Br⁻	F⁻	Fe	Mn	Sr²⁺	Zn
0.1	--[1]	<0.05	<0.01	0.28	0.10
0.08	--	<0.05	<0.01	0.21	0.04
0.06	--	<0.05	<0.01	0.25	0.09
--	--	<0.05	<0.01	0.28	0.06
0.07	--	1.12	0.1	0.29	0.46
0.47	0.2	0.01	<0.01	0.14	0.02
0.09	0.4	0.11	0.03	0.22	0.02
0.09	0.3	0.17	0.04	0.07	0.01
<0.05	1	0.45	0.53	0.14	0.01
<0.6	<1.2	5.7	1.10	0.82	0.06
0.823	<0.5	0.30	0.036	0.087	--
1.413	<1	2.06	0.011	0.073	--
0.360	0.1	0.01	0.537	0.349	--
0.216	0.2	0.06	0.062	0.471	-
<0.18	0.52	0.03	0.01	0.06	<0.01

Table 5 Isotopic data of samples that were analyzed for end-member sources of NO_3^-.

Sample	$\delta^{15}N_{NH4}$ (‰)	$\delta^{15}N_{NO3}$ (‰)	$\delta^{18}O_{NO3}$ (‰)	$\delta^{18}O$ (‰)	δD (‰)	$\delta^{13}C$ (‰)	$\delta^{34}S$ (‰)
Septic effluent							
96-42	4.7	--[1]	--	--	--	--	--
96-44	7.7	--	--	--	--	--	--
96-47	--	9.1	--	--	--	--	--
96-49	--	10.5	--	--	--	--	--
96-56	12.1	--	--	--	--	--	--
NW-17-septic		12.7	4.1	--	--	--	--
SS-1	11.6	--	--	−4.64	−33.3	−13.7	--
SS-2	8.9	--	--	−4.22	−31.3	−10.8	--
SS-3	12.2	--	--	−7.38	−54.2	−8.6	--
Animal waste							
HW1	7.1	--	--	−2.90	--	7.9	3.1
HW2	35.0	--	--	1.10	−5.30	25.8	--
HW3	18.8	--	--	−0.07	−2.20	37.1	--
Am5	--	35.1	10.3	−4.96	−36.2	6.96	--
Am6	23.0	--	--	−5.78	−38.5	11.4	--
Fertilizer							
Solution-28	−0.6		--	--	--	--	--
Solution-28	--	−0.3	22.4	--	--	--	--
Urea	−0.4[2]		--	--	--	−47.8	--
Runoff		16.4	15.2	−5.69	−40.1	−10.8	2.7
Rainwater							
RWA-99	--	4.8	32.5	--	--	--	--
RWAU-99	--	-2.5	23.1	--	--	--	--
RWJN-00	--	-0.8	23.8	--	--	--	--
RWJY2k	--	-3.3	42.9	--	--	--	--

[1]--, not determined.

[2]Organic nitrogen.

Sensel Spring usually had the lowest pH. This lower pH probably reflects a major influence of soil water (more dissolved CO_2) and minimal contact with the limestone bedrock prior to discharging at the surface.

The temperature of the water discharging from springs can be indicative of the seasons and the openness of the flow system. For example, the largest variability in water temperature was measured at Kelly Spring, followed by Indian Hole Spring (Figure 3). Such results reflect a more open conduit system for these springs relative to the others. As mentioned previously, the water discharging at Kelly Spring flows on the surface for half of its watershed before plunging into a sinkhole and entering Krueger's Dry Run Cave. The difference in temperature between top and bottom samples from Falling Springs illustrates how quickly exposure to surface conditions (openness) can affect the measured water temperature. Sensel Spring had the most consistent water temperature (13.9 to 14.2°C) measured during the different seasons. The constant temperatures at Sensel Spring suggest that this flow system, through the sediments covering the limestone bedrock, was more consistent and less open to rapid surface influx than were those of the other springs sampled.

Specific conductance ranged from 386 to 823 µS/cm for the springs. The most consistent values were observed at Sensel Spring, followed by Frog Spring. In general, the data collected during this investigation agreed with previous data from the sinkhole plain area, which indicated that specific conductance is a rough measure of the total alkalinity of Ca^{2+}- HCO_3^--type groundwater (Panno et al. 1996). Specific conductance and alkalinity were also directly proportional to the Na^+, Ca^{2+}, Mg^{2+}, SO_4^{2-}, and Cl^- concentrations, which are usually a function of inputs from limestone and accessory minerals within the rock formation through which groundwater flows.

The oxidation/reduction potential of the water ranged from +336 to +513 mV. These Eh values indicate that the spring water was exposed to atmospheric oxygen along its flow path (generally through air-filled caves or conduits). The lowest Eh values, indicating the most reducing conditions for each spring, were usually measured during the summer sampling event, possibly reflecting the greater biological activity during the warmer season. The largest Eh values, indicating the most oxidizing conditions, were primarily measured during spring and could reflect the influx of more oxygenated water as recharge is usually greatest for this area during spring (Panno et al. 1998b).

Chloride (Cl^-) concentrations for the spring water ranged from 6.5 to 24.7 mg/L. The greatest concentrations were consistently observed in Sparrow Creek, Illinois Caverns, and Kelly and Frog Springs. Potential sources for Cl^- include agrichemicals (potash or potassium chloride), road salt,

animal waste, septic effluent, and natural sources (minerals and upwelling saline groundwater). The springtime sampling event had the highest Cl^- concentrations (Table 7). Springtime recharge could have brought in a greater amount of anthropogenic sources of Cl^-, possibly related to agrichemicals, livestock, septic effluent, and road salt. The fall and winter sampling events generally had the lowest Cl^- concentrations.

The Na^+ and Cl^- concentrations were positively correlated, but plotted below (toward greater Na^+ concentrations) the stoichiometric line showing a 1:1 relationship (Figure 4). This shift toward higher Na^+ concentrations suggested that cation exchange (Na^+ with Ca^{2+} and Mg^{2+}) probably played a role in the chemical makeup of the spring waters. The samples from Kelly Spring showed even greater Na^+ enrichment than the other springs. The reason for the distinctly different plot of the Kelly Spring samples for these ions was unclear.

The fluoride (F^-) concentration for the springs ranged from approximately 0.1 to 0.35 mg/L and followed a seasonal trend; concentrations were greatest during spring and summer (Figure 5). Because phosphatic fertilizers are used throughout Illinois (Hamamo et al. 1995) and are derived from carbonate-fluorapatite, this F^- enrichment possibly was a consequence of cropland drainage after spring fertilizer application (Aswathanarayana et al. 1985).

Sulfate (SO_4^{2-}) concentrations ranged from 17.5 to 93.5 mg/L. When the SO_4^{2-} concentrations were plotted against Ca^{2+}, the data for several of the springs clustered. A few of the springs showed a somewhat linear relationship, and data for one spring, Kelly, were clustered differently from the others (Figure 6). Such results probably reflect a variety of inputs to the groundwater system in the sinkhole plain. Sources for SO_4^{2-} include the dissolution of gypsum ($CaSO_4 \cdot 2H_2O$) and anhydrite ($CaSO_4$) and the oxidation of pyrite (FeS_2) from the St. Louis Limestone; agricultural sulfate minerals such as $(NH_4)2SO_4$, $MgSO_4$, and $CaSO_4$; and $CuSO_4$ added to sinkhole ponds (farm ponds) to control algal growth. Gypsum and anhydrite have been found in cores that intersected the northern half of the St. Louis Limestone formation in southern Illinois (Saxby and Lamar 1957). Although only "small" occurrences of these evaporites have been identified in cores from boreholes located in St. Clair County (Saxby and Lamar 1957), their presence could explain the elevated concentrations of SO_4^{2-} in samples from Falling and Sparrow Creek Springs and their slightly differ-ent trend in Figure 6. Pyrite nodules and pyrite crystal clusters are also present near the top of the St. Louis Limestone along discrete bedding planes (Z. Lasemi, ISGS, personal communications 1999); once oxidized, pyrite could contribute SO_4^{2-} to infiltrating water.

The DOC in water samples from the springs in the sinkhole plain ranged from 1.7 to 13.8 mg/L. These concentrations are generally higher than those typical for groundwater, which

Table 6 Field parameters and total alkalinity for water samples collected from springs in the study area.

Sample	Date sampled	Spring	Temp. (°C)	pH	Eh[1] (mV)	Sp. Cond. (µS/cm)	Tot. Alk. (mg CaCO$_3$/L)
Fall 1998							
IG-1T	11/19	Falling, top	12.6	8.1	496	766	321
IG-1B	11/19	Falling, bottom	12.8	8.1	475	770	323
IG-2	11/19	Sparrow Creek	13.5	7.3	506	624	243
IG-3	11/19	Collier	13.7	7.3	448	471	200
IG-4	11/19	Indian Hole	13.9	7.2	455	481	182
IG-5	11/19	Sensel	14.0	6.9	460	611	272
IG-6	11/19	Illinois Caverns	13.3	8.2	485	554	229
IG-7	11/19	Kelly	12.8	8.0	472	663	245
IG-8	11/19	Camp Vandeventer	13.6	8.0	483	543	238
IG-9	11/19	Auctioneer	12.7	8.1	460	591	279
Winter 1999							
IG-1AT	03/04	Falling, top	--[2]	--	--	--	323
IG-1AB	03/04	Falling, bottom	11.6	7.8	451	688	304
IG-2A	02/19	Sparrow Creek	12.0	7.3	462	572	219
IG-3A	02/19	Collier	12.4	7.4	436	521	228
IG-4A	02/19	Indian Hole	11.2	7.7	450	467	186
IG-5A	02/19	Sensel	14.0	6.8	476	605	273
IG-6A	02/19	Illinois Caverns	12.3	7.9	456	535	209
IG-7A	02/19	Kelly	9.1	7.8	481	616	213
IG-8A	02/19	Camp Vandeventer	11.8	7.8	461	476	200
IG-9A	02/19	Auctioneer	11.9	7.8	438	547	254
IG-10A	03/04	Frog	12.3	7.7	--	620	253
Spring 1999							
IG-1BT	05/18	Falling, top	13.0	7.9	--	814	364
IG-1BB	05/18	Falling, bottom	13.2	8.0	476	806	351
IG-2B	05/18	Sparrow Creek	13.3	7.0	456	734	287
IG-3B	05/18	Collier	13.6	7.2	513	523	237
IG-4B	05/18	Indian Hole	13.9	7.6	508	527	233
IG-5B	05/18	Sensel	14.0	7.8	508	604	290
IG-6B	05/18	Illinois Caverns	13.5	7.7	492	573	240
IG-7B	05/18	Kelly	14.4	7.6	492	694	246
IG-8B	05/18	Camp Vandeventer	13.5	7.5	430	588	267
IG-9B	05/18	Auctioneer	13.2	7.7	467	626	314
IG-10B	05/18	Frog	13.3	7.2	485	650	288

(continued)

usually contains less than 2 mg/L of DOC (Drever 1997). Falling, Sparrow Creek, Collier, Indian Hole, and Kelly Springs contained consistently greater DOC for each sampling event than did the remaining springs (Table 7). The DOC concentrations for all springs were more consistent with the DOC concentrations detected in surface water samples (2 to 15 mg/L) (Degens 1982) than those in groundwater samples. The DOC in groundwater is usually derived from the organic-rich layer in soils (Drever 1997) and plays an important role in

NO_3^- reduction as an electron donor (Appelo and Postma 1994). High DOC concentrations could be associated with agricultural activities (Cane and Clark 1999), septic systems (Clark and Fritz 1997), or both. Many of the springs sampled for this study are resurgent cave streams that receive surface runoff through sinkholes and associated macropores of the karst terrane, and the chemical composition of the springs would be expected to have some characteristics similar to those of surface streams.

Nitrate-N concentrations for the springs ranged from 1.74 to 7.48 mg of N/L. These concentrations are less than 10 mg of N/L, the USEPA's (1992) regulatory standard for drinking water, but typically greater than 2 mg of N/L, the threshold for background NO_3^- concentrations (Panno et al. 2003). Thus, one or more of the sources discussed previously have contributed NO_3^- to the flow system. The NO_3^- concentrations for the different springs tended to cluster and are without a consistent seasonal trend (Figure 7).

Atrazine typically was detected during the springtime and summer sampling events. During the fall and winter sampling events, atrazine was usually less than detection limits (Table 7). Because atrazine is applied only during the spring, it follows that a portion of it was mobilized and rapidly incorporated into the shallow karst aquifer during rainfall events, as has been observed by Panno et al. (1996). These results attest to the rapid influx of surface water into the shallow groundwater of a karst system.

Spring Samples: Bacterial Composition

Bacterial colonies present in water samples from the springs included coliforms, fecal coliforms, fecal enterococci, and bacteria common to soil and aqueous environments. The bacterial counts were usually greater than 3×10^6 cfu for total aerobic bacteria, from 1 to more than 4,800 cfu for total coliforms, from 0 to more than 2,400 cfu for fecal coliforms (FC), and from 0 to more than 4,800 for fecal enterococci (Table 8). Many of the species are opportunistic pathogens and are typical of those found in springs throughout the sinkhole plain (Panno et al. 1996). For comparison, Illinois water quality regulations require that waters suitable for "primary contact" (intimate contact with water such as swimming) must not exceed 200 cfu FC for a geometric mean of a minimum of five samples collected during a period of 30 days or less between May and October. Ten percent of the samples cannot exceed

Table 6 *(continued)* Field parameters and total alkalinity for water samples collected from springs in the study area.

Sample	Date sampled	Spring	Temp.[1] (°C)	pH	Eh (mV)	Sp. Cond. (µS/cm)	Tot. Alk. (mg CaCO$_3$/L)
Summer 1999							
IG-1CT	08/23	Falling, top	14.2	7.9	383	823	367
IG-1CB	08/23	Falling, bottom	15.0	8.1	336	802	365
IG-2C	08/24	Sparrow Creek	13.5	7.0	414	733	295
IG-3C	08/24	Collier	14.8	7.1	418	506	229
IG-4C	08/24	Indian Hole	16.1	7.2	438	438	190
IG-5C	08/24	Sensel	13.9	7.0	452	610	280
IG-6C	08/24	Illinois Caverns	13.4	7.5	421	577	239
IG-7C	08/24	Kelly	15.2	7.6	425	694	262
IG-8C	08/24	Camp Vandeventer	14.2	7.6	420	622	282
IG-9C	08/24	Auctioneer	13.9	8.0	379	628	295
IG-10C	08/24	Frog	13.9	7.2	432	647	283
Fall 1999							
IG-1DT	11/17	Falling, top	12.1	8.1	421	770	357
IG-1DB	11/17	Falling, bottom	11.4	8.2	392	745	318
IG-2D	11/17	Sparrow Creek	12.4	7.3	425	754	320
IG-3D	11/17	Collier	13.4	7.4	405	620	301
IG-4D	11/17	Indian Hole	13.4	7.2	463	629	271
IG-5D	11/17	Sensel	14.2	6.9	485	587	279
IG-6D	11/17	Illinois Caverns	13.2	8.2	442	525	221
IG-7D	11/17	Kelly	13.3	8.1	451	730	289
IG-8D	11/17	Camp Vandeventer	13.4	7.9	443	452	198
IG-9D	11/17	Auctioneer	12.7	8.0	410	575	272
IG-10D	11/17	Frog	13.2	7.5	442	638	288
Winter 2000							
IG-1ET	03/07	Falling, top	12.8	8.0	459	710	326
IG-1EB	03/07	Falling, bottom	12.6	8.1	450	700	332
IG-2E	03/07	Sparrow Creek	13.1	7.3	455	555	201
IG-3E	03/07	Collier	12.9	7.1	444	386	156
IG-4E	03/07	Indian Hole	12.4	7.2	464	478	191
IG-5E	03/07	Sensel	14.1	6.7	486	597	282
IG-6E	03/07	Illinois Caverns	13.1	7.9	472	555	237
IG-7E	03/07	Kelly	11.8	7.8	468	777	221
IG-8E	03/07	Camp Vandeventer	13.2	8.0	452	555	248
IG-9E	03/07	Auctioneer	12.9	7.9	449	563	269
IG-10E	03/07	Frog	13.1	7.6	508	635	285

[1]Temp., temperature; Eh, redox potential; Sp. Cond., specific conductivity; Tot. Alk., total alkalinity.

[2]--, not determined.

Table 7 Chemical results (mg/L) for water samples collected from springs in the study area.

Sample	Ca²⁺	Mg²⁺	Na⁺	K⁺	HCO₃	Cl⁻	SO₄²⁻	NO₃⁻-N	SiO₂	Al	B	Ba	F⁻
Fall 1998													
IG-1T	119	28.7	20.9	<1	392	12.3	77.2	3.47	30.6	0.04	0.03	0.10	0.17
IG-1B	118	28.6	20.9	<1	394	12.4	73.8	3.50	30.4	0.03	0.05	0.09	0.17
IG-2	93.3	17.1	21.9	5	296	17.0	52.5	3.64	22.7	0.05	0.03	0.09	0.13
IG-3	75.1	10.5	15.0	4	244	9.9	21.8	3.98	19.1	0.04	<0.01	0.10	0.11
IG-4	68.9	12.4	21.0	4	222	11.9	38.2	4.25	16.0	0.04	<0.01	0.09	0.12
IG-5	105	11.0	26.6	<1	332	8.9	28.1	5.16	32.9	<0.02	<0.01	0.07	0.09
IG-6	91.7	11.1	22.3	<1	279	15.2	25.4	6.65	21.4	0.03	<0.01	0.08	0.08
IG-7	80.9	20.4	45.4	5	299	20.5	69.4	4.68	14.8	0.03	0.03	0.09	0.13
IG-8	83.4	14.4	21.5	2	290	12.2	31.7	2.86	19.5	0.05	<0.01	0.08	0.1
IG-9	105	13.9	16.4	<1	340	8.2	22.0	5.12	33.8	<0.02	0.02	0.08	0.13
Winter 1999													
IG-1AT	113	26.5	20.2	3	394	11.3	60.8	2.89	30.0	0.02	0.02	0.09	0.22
IG-1AB	111	26.1	19.9	3	371	11.3	57.6	2.86	29.5	0.04	0.03	0.09	0.22
IG-2A	98.7	16.6	22.3	<1	267	15.4	54.9	3.56	23.7	<0.01	<0.02	0.09	0.18
IG-3A	99.7	10.6	17.3	<1	278	8.4	26.6	3.50	24.4	<0.01	<0.02	0.10	0.13
IG-4A	79.3	12.3	21.6	<1	227	9.7	38.5	2.76	17.7	<0.01	<0.02	0.09	<0.10
IG-5A	123	12.6	26.9	<1	333	9.0	27.9	4.88	36.6	<0.01	<0.02	0.08	<0.10
IG-6A	96.3	11.4	23.0	<1	255	16.1	27.5	7.08	22.7	<0.01	<0.02	0.09	0.11
IG-7A	88.7	20.9	42.6	<1	260	19.6	76.2	3.60	16.0	<0.01	<0.02	0.09	<0.10
IG-8A	83.3	13.2	19.3	<1	244	10.7	28.7	2.97	19.3	<0.01	<0.02	0.09	0.11
IG-9A	106	13.2	14.0	<1	310	7.8	22.2	4.36	32.1	<0.01	<0.02	0.09	0.18
IG-10A	94.7	13.6	25.4	2.5	309	16.5	50.7	7.48	21.8	<0.01	<0.01	0.08	0.17
Spring 1999													
IG-1BT	130	32.6	23.6	<1	444	17.5	73.4	3.07	27.0	<0.02	<0.02	0.10	0.35
IG-1BB	128	32.6	23.6	<1	428	17.5	73.2	3.00	27.0	<0.02	0.05	0.10	0.35
IG-2B	113	20.9	29.4	3	351	24.7	67.6	4.83	21.6	<0.02	0.04	0.08	0.31
IG-3B	91.4	10.2	16.4	<1	289	13.6	27.8	3.91	19.1	<0.02	0.04	0.10	0.26
IG-4B	83.0	13.0	21.9	2.5	285	14.2	37.4	2.84	14.8	<0.02	0.025	0.09	0.28
IG-5B	106	10.9	25.2	<1	354	12.9	28.5	4.61	27.6	<0.02	<0.02	0.07	0.23
IG-6B	95.4	11.1	24.0	<1	293	19.3	28.0	6.46	18.3	<0.02	<0.02	0.09	0.23
IG-7B	87.6	24.7	40.6	3	300	20.2	93.5	4.00	12.5	<0.02	<0.02	0.09	0.28
IG-8B	93.5	15.8	23.5	<1	326	16.4	35.0	2.89	17.4	<0.02	<0.02	0.09	0.26
IG-9B	113	14.1	16.7	<1	384	13.1	26.9	4.92	29.3	<0.02	<0.02	0.08	0.33
IG-10B	106	14.3	24.9	<1	351	19.5	33.5	5.51	21.6	<0.02	<0.02	0.08	0.31
Summer 1999													
IG-1CT	125	32.9	22.0	<1	447	13.9	68.0	3.29	26.7	<0.02	0.02	0.11	0.32
IG-1CB	121	32.3	21.7	<1	445	13.8	67.9	3.20	26.5	<0.02	<0.02	0.10	0.34
IG-2C	114	21.8	25.6	<1	360	18.7	58.8	--	22.7	0.04	<0.02	0.10	0.27
IG-3C	85.4	10.3	13.3	<1	280	13.4	19.8	3.44	17.8	<0.02	0.02	0.12	0.23
IG-4C	65.4	11.2	16.0	<1	232	10.1	25.7	2.28	10.9	<0.02	<0.02	0.10	0.26
IG-5C	103	10.8	25.1	<1	341	11.2	26.1	4.67	27.8	<0.02	<0.02	0.07	0.21
IG-6C	91.6	11.0	22.4	<1	292	17.5	23.9	6.23	17.8	<0.02	<0.02	0.09	0.22
IG-7C	86.1	21.9	41.9	<1	320	20.3	65.2	4.66	13.5	<0.02	<0.02	0.11	0.31
IG-8C	96.8	16.7	23.7	<1	344	14.6	31.6	2.87	18.8	<0.02	<0.02	0.10	0.26
IG-9C	111	14.2	17.1	<1	360	11.6	22.6	5.48	29.7	<0.02	<0.02	0.09	0.31
IG-10C	109	14.1	22.7	<1	345	16.0	26.8	6.03	23.1	<0.02	<0.02	0.09	0.31
Fall 1999													
IG-1DT	113	31.2	17.4	2	436	10.1	67.1	3.07	24.4	0.04	<0.02	0.08	0.25
IG-1DB	111	31.5	18.5	3	388	10.2	66.7	3.06	24.6	0.03	<0.02	0.08	0.24
IG-2D	110	21.7	22.0	3	390	17.6	60.8	4.12	20.7	0.04	0.02	0.07	0.22
IG-3D	97.6	13.5	16.8	3	367	9.3	20.7	3.60	18.1	<0.02	<0.02	0.09	0.19
IG-4D	81.7	18.3	24.4	2	331	12.3	46.6	2.80	14.3	<0.02	<0.02	0.09	0.23
IG-5D	95.2	9.68	18.9	<1	340	7.3	20.8	4.20	25.0	<0.02	<0.02	0.05	0.11
IG-6D	79.1	10.1	17.3	3	270	14.7	19.1	6.00	16.3	<0.02	<0.02	0.06	0.12
IG-7D	84.3	22.8	36.4	4	353	19.3	73.4	3.30	12.2	0.03	<0.02	0.07	0.18
IG-8D	64.1	11.8	13.1	4	242	8.6	25.1	1.74	12.6	0.03	0.02	0.06	0.19
IG-9D	92.6	13.3	14.4	2	332	7.9	18.2	5.55	27.2	<0.02	<0.02	0.06	0.22
IG-10D	99.5	13.0	18.9	3	351	12.7	23.3	5.57	20.5	<0.02	<0.02	0.06	0.22
Winter 2000													
IG-1ET	112	29.5	19.9	<2	398	11.9	53.4	2.95	24.2	0.02	0.04	0.09	0.26
IG-1EB	111	29.5	20.1	<2	405	11.9	53.3	2.83	24.2	0.04	0.04	0.09	0.29
IG-2E	74.5	16.2	21.6	7	245	17.6	39.1	3.27	15.9	0.02	0.03	0.08	0.24
IG-3E	60.1	10.0	12.8	4	190	6.5	20.3	4.39	14.8	0.06	0.01	0.08	0.17
IG-4E	67.6	13.9	22.9	<2	233	9.4	32.2	3.86	12.3	0.02	<0.01	0.08	0.21
IG-5E	103	10.9	26.2	<2	344	7.6	20.5	4.27	28.2	0.02	<0.01	0.07	0.12
IG-6E	91.7	12.0	23.4	<2	289	14.2	18.7	6.21	18.4	0.03	<0.01	0.08	0.12
IG-7E	76.0	21.6	48.7	3	270	22.6	76.9	5.07	8.9	0.03	<0.01	0.08	0.19
IG-8E	86.8	16.8	23.3	<2	303	12.5	28.3	2.41	16.5	0.02	<0.01	0.08	0.17
IG-9E	99.8	15.8	17.9	<2	328	8.3	17.5	5.07	29.7	0.02	<0.01	0.08	0.23
IG-10E	108	15.8	24.8	<2	348	15.0	22.8	4.78	22.0	0.02	<0.01	0.08	0.24

[1]DOC, dissolved organic carbon.

[2]--, not determined.

| Fe	Mn	Sr²⁺	Zn	DOC[1]	Atrazine (µg/L)
<0.01	0.01	0.22	<0.01	12.3	--[2]
<0.01	0.01	0.22	<0.01	13.8	<0.10
0.03	0.05	0.21	<0.01	11.0	<0.10
0.02	<0.01	0.19	<0.01	11.1	<0.10
0.03	0.05	0.19	<0.01	11.2	<0.10
<0.01	<0.01	0.16	<0.01	8.8	<0.10
<0.01	<0.01	0.18	<0.01	7.7	<0.10
0.01	0.01	0.20	<0.01	12.0	<0.10
<0.01	0.02	0.19	<0.01	10.8	<0.10
<0.01	0.02	0.18	<0.01	9.3	<0.10
<0.01	0.04	0.22	<0.01	11.2	--
<0.01	0.04	0.22	<0.01	11.1	<0.10
<0.01	0.05	0.20	<0.01	11.1	<0.10
<0.01	0.02	0.20	<0.01	10.9	<0.10
<0.01	0.04	0.19	<0.01	9.9	<0.10
<0.01	<0.01	0.17	<0.01	11.9	<0.10
<0.01	0.02	0.18	<0.01	7.0	<0.10
<0.01	0.01	0.21	<0.01	13.1	<0.10
<0.01	0.01	0.18	<0.01	10.3	<0.10
<0.01	0.14	0.19	<0.01	11.1	<0.10
<0.01	0.01	0.19	0.02	9.6	--
<0.01	0.02	0.23	<0.01	--	--
<0.01	0.01	0.23	<0.01	7.4	0.16
<0.01	0.03	0.22	<0.01	6.7	12.1
<0.01	0.02	0.19	<0.01	6.5	5.21
<0.01	0.07	0.20	<0.01	6.9	1.09
<0.01	<0.01	0.15	<0.01	4.2	0.11
<0.01	0.01	0.18	<0.01	3.3	0.19
<0.01	0.01	0.22	<0.01	5.6	3.2
<0.01	0.02	0.19	<0.01	4.9	0.21
<0.01	0.02	0.18	<0.01	3.5	<0.10
<0.01	0.02	0.10	<0.03	5.0	0.1
<0.01	0.01	0.22	<0.01	9.5	0.23
<0.01	0.01	0.22	<0.01	7.2	--
<0.01	0.05	0.23	<0.01	9.1	0.14
<0.01	0.03	0.21	<0.01	7.8	1.4
<0.01	0.14	0.18	<0.01	7.6	1.76
<0.01	<0.01	0.15	<0.01	6.5	0.12
<0.01	<0.01	0.18	<0.01	4.5	0.11
<0.01	0.03	0.22	<0.01	7.1	<0.10
<0.01	0.02	0.22	<0.01	6.1	0.1
<0.01	0.01	0.19	<0.01	6.0	<0.10
<0.01	0.01	0.2	<0.01	5.2	0.19
<0.01	0.01	0.19	<0.01	5.0	<0.10
<0.01	<0.01	0.20	<0.01	5.9	<0.10
<0.01	0.02	0.20	<0.01	5.0	<0.10
<0.01	0.02	0.21	<0.01	4.4	<0.10
<0.01	0.03	0.23	<0.01	3.5	0.14
<0.01	<0.01	0.13	<0.01	3.4	<0.10
<0.01	<0.01	0.14	<0.01	2.1	<0.10
<0.01	0.01	0.18	<0.01	4.3	0.11
<0.01	0.03	0.14	<0.01	7.0	<0.10
<0.01	<0.01	0.14	<0.01	2.1	<0.10
<0.01	0.01	0.16	<0.01	1.7	<0.10
0.02	0.014	0.223	<0.001	8.1	<0.10
<0.01	0.014	0.223	<0.001	9.8	<0.10
0.02	0.005	0.179	<0.001	12.0	<0.10
0.05	0.006	0.169	0.003	11.2	<0.10
0.02	0.019	0.197	<0.001	11.4	<0.10
<0.01	<0.001	0.154	0.003	6.9	<0.10
<0.01	<0.001	0.190	<0.001	5.9	<0.10
0.03	0.003	0.196	<0.001	10.9	<0.10
<0.01	0.007	0.207	<0.001	8.8	<0.10
<0.01	0.004	0.180	<0.001	6.7	<0.10
<0.01	0.005	0.198	0.005	6.6	<0.10
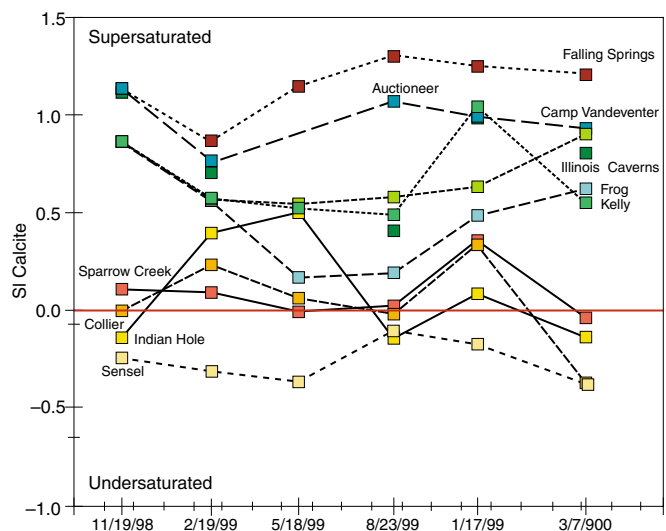
Figure 2 Saturation indices for each spring sampled from fall 1998 through winter 2000. The zero line marks the boundary between undersaturation and supersaturation (modified from Panno et al., 2001).
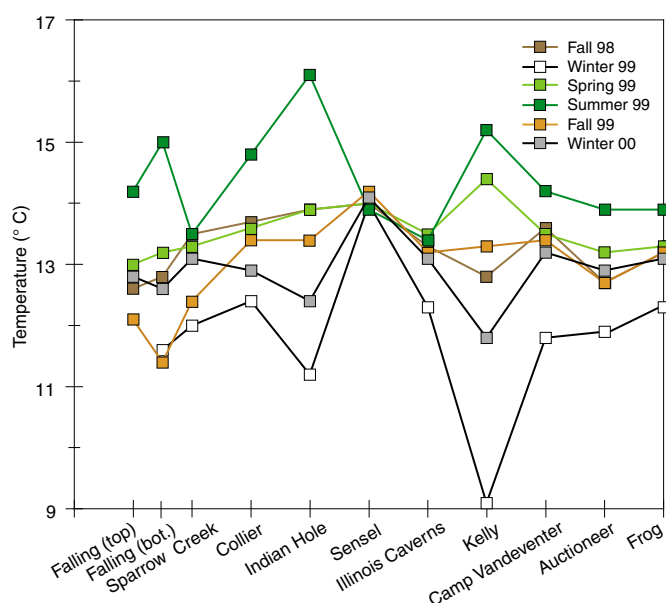

Figure 3 Temperature of each spring sampled for six consecutive seasons.

400 cfu FC/100 mL (Illinois Environmental Protection Agency, Illinois Pollution Control Board 1999).

The quality of the water flowing through the karst aquifers of southwestern Illinois is similar to that of springs and caves in other karst environments. For 19 samples collected in 1990 and 1991 from Buffalo Creek Spring, which drains a pristine groundwater basin populated only by wildlife near Mammoth Cave in Kentucky, the mean was 67 cfu FC/L, and the maximum was about 300 cfu FC/L (Meiman 1993). Given that 1 g of feces contains tens of millions to tens of billions of FC bacteria (Feachem et al. 1983), their presence in spring water, as noted by Meiman (1993), was expected. As a comparison, weekly water samples from two springs
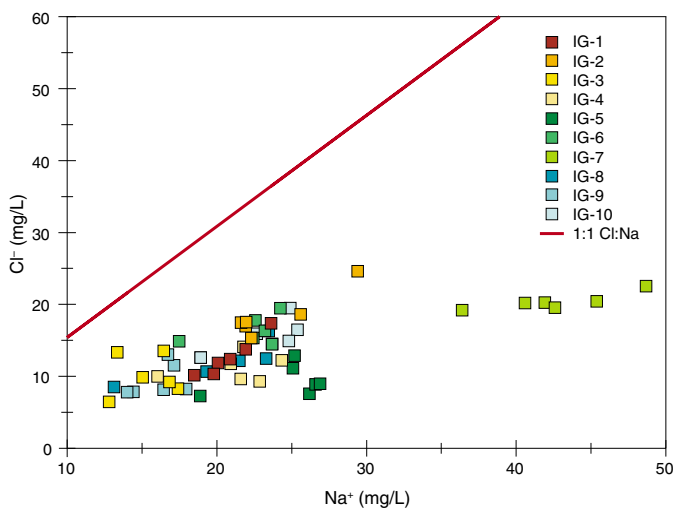
Figure 4 Chloride and sodium concentrations of all spring samples showing trends and distinct differences among the individual springs. Kelly Spring (IG-7) is well separated from the other springs.
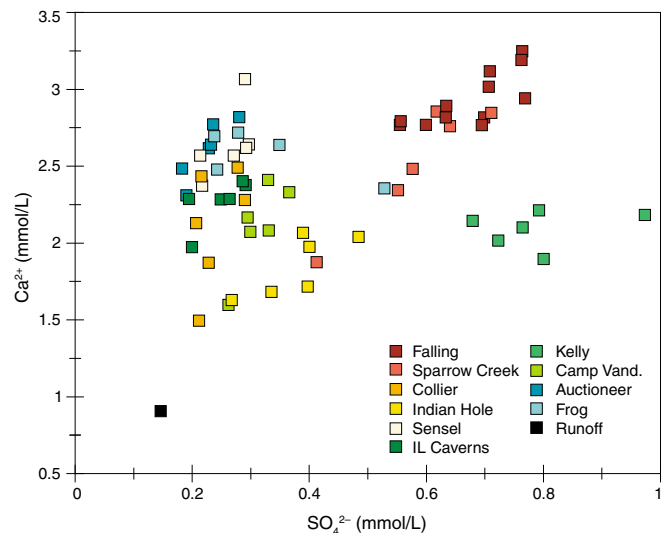

Figure 6 Calcium and sulfate concentrations for spring samples and runoff. Kelly Spring, Sparrow Creek, and Falling Springs show larger sulfate concentrations than do the rest of the springs.
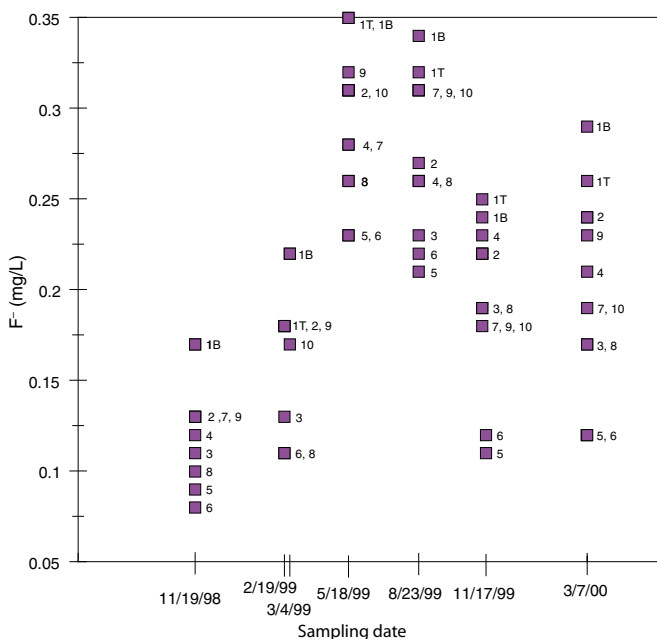

Figure 5 Seasonal variation of fluoride in spring samples. Note increase in fluoride for spring and summer sampling events. Springs are identified according to numbers in Table 7 (1 and 1.5 refer to Falling Springs, top and bottom).
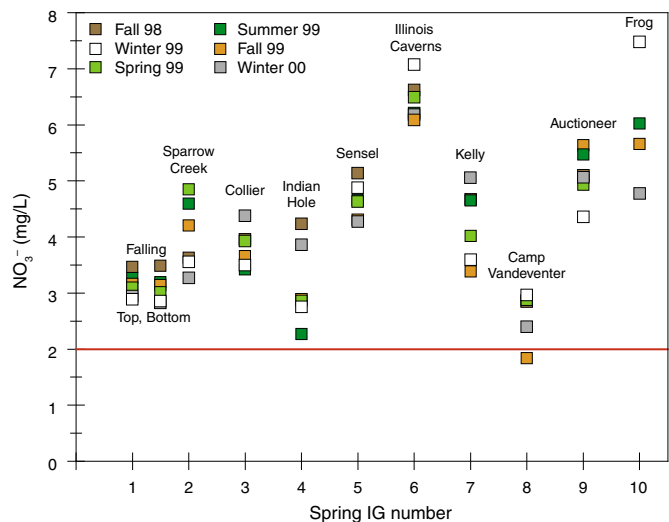

Figure 7 Nitrate concentrations of the spring samples over six consecutive seasons. The upper boundary for background concentration of NO_3^-, about 2.0 mg of N/L (Panno et al. 2003), is shown by the horizontal line.

that drain groundwater basins used for animal grazing in West Virginia yielded 0 to 1,434 cfu FC/L; mean concentrations were 101 and 139 cfu FC/L (Pasquarell and Boyer 1995). In a similar setting in Kentucky, flood pulses in springs have been shown to contain a short-term increase in FC and associated turbidity (Ryan and Meiman 1996). The effects of flooding on the water quality of springs in the present study are apparent in the elevation of FC, fecal streptococci (FS), and fecal enterococci concentrations during the spring and early fall when abundant rainfall and surface runoff (into sinkholes) are most prevalent.

Except for Sensel Spring, the bacterial species isolated from the spring samples in the study area were almost identical and included between 10 and 15 genera and species (Table 9). The four most dominant bacteria, *Bacillus* spp., *Pseudomonas* spp., *Klebsiella pneumoniae*, and *Serratia* spp., were typically present in over 90% of the spring samples. These bacteria are ubiquitous in the natural environment. *Bacillus* spp. and *Pseudomonas* spp. are especially associated with the soil zone and are classified as opportunistic pathogens by Geldreich (1996). Also present in about 90% of the spring samples, but ranking lower, were *Enterococcus faecium, Enterococcus faecalis,* and *Escherichia coli*. These three enteric species (associated with fecal materials) suggest the influence of livestock (animal) waste and possibly private septic systems. Ranked lower but present in some of the springs were *Aeromonas hydrophila, Citrobacter* spp., and, to a lesser extent, *Providencia stuartii* and *Proteus* spp. *Aeromonas hydrophila* is commonly associated with cold-blooded vertebrates (e.g., amphibians) (Freeman 1985). Panno et al. (1999) frequently found *Aeromonas hydrophila* in cave water and suggested that the species is an indicator of conduit systems of the sinkhole plain. These systems are typically greater than 1 cm in width and even larger in height, contain an air-water interface, are connected to the surface at some point, and are large enough to provide amphibian habitats.

Table 8 Bacterial analyses for water samples collected from springs in the study area.[1]

Sample	Spring	Total aerobic colonies (cfu /L)[1]	Total coliforms (cfu/L)	Fecal coliforms (cfu/L)	Fecal enterococci (cfu/L)
Fall 1998					
IG-1T	Falling, top	--[2]	--	--	--
IG-1B	Falling, bottom	$>3 \times 10^6$	>2,419	49	60
IG-2	Sparrow Creek	$>3 \times 10^6$	>2,419	108	104
IG-3	Collier	$>3 \times 10^6$	>2,419	68	136
IG-4	Indian Hole	$>3 \times 10^6$	>2,419	73	126
IG-5	Sensel	600	1	0	0
IG-6	Illinois Caverns	9×10^5	>2,419	59	108
IG-7	Kelly	$>3 \times 10^6$	>2,419	86	290
IG-8	Camp Vandeventer	$>3 \times 10^6$	>2,419	223	143
IG-9	Auctioneer	$>3 \times 10^6$	>2,419	68	116
Winter 1999					
IG-1AB	Falling, bottom	$>3 \times 10^6$	3,466	40	36
IG-2A	Sparrow Creek	$>3 \times 10^6$	>4,800	108	1,540
IG-3A	Collier	$>3 \times 10^6$	3,106	192	722
IG-4A	Indian Hole	$>3 \times 10^6$	2,600	86	278
IG-5A	Sensel	34	4	0	0
IG-6A	Illinois Caverns	$>3 \times 10^6$	3,106	156	114
IG-7A	Kelly	$>3 \times 10^6$	3,106	96	1,374
IG-8A	Camp Vandeventer	$>3 \times 10^6$	3,972	172	222
IG-9A	Auctioneer	$>3 \times 10^6$	1,842	220	104
IG-10A	Frog	--	--	--	--
Spring 1999					
IG-1BT	Falling, top				
IG-1BB	Falling, bottom	$>3 \times 10^6$	2,600	86	72
IG-2B	Sparrow Creek	$>3 \times 10^6$	>4,800	570	208
IG-3B	Collier	$>3 \times 10^6$	>4,800	182	1,096
IG-4B	Indian Hole	$>3 \times 10^6$	>4,800	110	552
IG-5B	Sensel	1,200	86	2	10
IG-6B	Illinois Caverns	$>29 \times 10^3$	1,960	130	210
IG-7B	Kelly	$>3 \times 10^6$	>4,800	230	922
IG-8B	Camp Vandeventer	$>3 \times 10^6$	2,240	186	160
IG-9B	Auctioneer	$>3 \times 10^6$	1,454	17	334
IG-10B	Frog	$>3 \times 10^6$	>4,800	192	216
Summer 1999					
IG-1CT	Falling, top	27,000	3,466	12	62
IG-1CB	Falling, bottom	22,000	1,226	8	14
IG-2C	Sparrow Creek	49,000	1,226	32	94
IG-3C	Collier	78,000	4,838	50	368
IG-4C	Indian Hole	79,000	4,800	56	146
IG-5C	Sensel	900	40	0	4
IG-6C	Illinois Caverns	63,000	4,838	110	400
IG-7C	Kelly	71,000	>4,800	94	922
IG-8C	Camp Vandeventer	97,000	>4,800	304	536
IG-9C	Auctioneer	95,000	>4,800	100	518
IG-10C	Frog	89,000	4,800	168	280
Fall 1999					
IG-1DT	Falling, top	17,000	870	14	42
IG-1DB	Falling, bottom	1,430	390	8	30
IG-2D	Sparrow Creek	4,700	976	62	278
IG-3D	Collier	27,000	1,842	626	644
IG-4D	Indian Hole	1,600	476	2	62
IG-5D	Sensel	340	6	0	4
IG-6D	Illinois Caverns	7,600	582	66	88
IG-7D	Kelly	14,000	616	100	324
IG-8D	Camp Vandeventer	$>3 \times 10^6$	>4,838	394	>4,838
IG-9D	Auctioneer	45,000	2,600	1,632	>4,838
IG-10D	Frog	120,000	3,106	2,406	>4,838
Winter 2000					
IG-1ET	Falling, top	5,300	976	20	118
IG-1EB	Falling, bottom	4,100	1,034	8	145
IG-2E	Sparrow Creek	4,900	282	20	48
IG-3E	Collier	1,300	220	40	540
IG-4E	Indian Hole	2,300	570	12	66
IG-5E	Sensel	400	14	0	16
IG-6E	Illinois Caverns	1,100	154	2	80
IG-7E	Kelly	6,500	870	18	22
IG-8E	Camp Vandeventer	14,000	1,034	40	128
IG-9E	Auctioneer	5,700	1,226	10	140
IG-10E	Frog	6,300	2,240	10	140

[1] cfu, colony-forming units.

[2] --, not detected.

Table 9 Bacteria (genera and species) present in springs in the study area, percentage of time the bacteria were detected in samples, and ranking based on their dominance in the groundwater samples.[1]

Rank	November 1998	February 1999	May 1999	August 1999	November 1999	March 2000
1	*Bacillus* 100	*Bacillus* 100	*Pseudomonas* 91	*Pseudomonas* 100	*Pseudomonas* 100	*Bacillus* 100
2	*Pseudomonas* 100	*Pseudomonas* 100	*Bacillus* 91	*Bacillus* 91	*K. pneumoniae* 100	*Pseudomonas* 100
3	*Klebsiella pneumoniae* 100	*K. pneumoniae* 89	*K. pneumoniae* 82	*K. pneumoniae* 100	*Serratia* 91	*E. aerogenes* 82
4	*Serratia* 89	*Serratia* 89	*Serratia* 82	*Serratia* 91	*Enterobacter* 91	*E. faecium* 100
5	*Escherichia coli* 89	*A. hydrophila* 89	*A. hydrophila* 82	*Citrobacter* 82	*E. faecium* 91	*K. pneumoniae* 63
6	*Aeromonas hydrophila* 78	*E. coli* 89	*E. faecium* 91	*E. faecium* 91	*E. faecalis* 91	*E. coli* 91
7	*Enterococcus faecium* 89	*E. faecium* 89	*C. freundii* 54	*E. faecalis* 91	*Citrobacter* 64	*Citrobacter* 54
8	*Enterococcus faecalis* 89	*P. mirabilis* 56	*E. coli* 82	*Staphylococcus* 100	*Bacillus* 91	*E. faecalis* 27
9	*Staphylococcus* 67	*Citrobacter freundii* 33	*Enterobacter cloacae* 27	*E. coli* 73	*A. hydrophila* 45	*Serratia* 18
10	*Providencia stuartii* 22	*E. faecalis* 56	*E. faecalis* 45	*Micrococcus* 9	*E. coli* 36	*P. mirabilis* 9
11	*Proteus mirabilis* 11	*Staphylococcus aureus* 56	*P. mirabilis* 45	*Enterococcus* 9	*P. mirabilis* 18	
12			*Enterobacter aerogenes* 18	*P. mirabilis* 9		
13			*Enterococcus avium* 18			
14			*S. aureus* 54			
15			*P. stuartii* 9			

[1]Rank was based on the bacteria that were most dominant in the water samples. Dominance was based on the largest concentration to smallest concentration of bacteria genera and species present in the water samples. The number below each genera is the percent of time they were detected in the samples.

Spring Samples: Isotopic Composition

As with several of the chemical constituents, some isotopic characteristics showed seasonal variations for the water samples from springs. The isotopic results (Table 10) help to improve our understanding of the geochemical evolution of the groundwater in the sinkhole plain and to delineate the origin of the NO_3^- in the spring water samples.

$\delta^{15}N$ and $\delta^{18}O$ of NO_3^- The $\delta^{15}N$ and $\delta^{18}O$ of the NO_3^- from the springs ranged from +3.2 to +12.5‰ and from +5.1 to +21.9‰, respectively. Many of the $\delta^{15}N$ and $\delta^{18}O$ data appeared to be positively correlated (Figure 8). Figure 8 illustrates the typical areas for different NO_3^- sources (Kendall et al. 1995, Clark and Fritz 1997, Mengis et al. 2001). The range of $\delta^{18}O$ values for the NO_3^- domains originating from the reduced N sources (reduced fertilizer, soil organic matter, and manure and sewage) were estimated based on the assumption that the nitrification process for these soils derives one-third of the oxygen from the atmosphere and two-thirds from the surrounding water. The lowest isotopic values for the NO_3^- from the spring samples clustered near the area typically observed for NO_3^- originating primarily from mineralized fertilizer nitrogen. Values for most of the spring 1999 and winter 2000 samples plotted very close to the mineralized fertilizer domain. The isotopic values for most of the summer, fall, and winter 1999 samples are more positive. Many of the samples had isotopic values that generally followed the denitrification trend (arrows, Figure 8). When comparing $\delta^{15}N$ and NO_3^- concentrations, the trend for most of the data follows a negative slope, which would be expected with denitrification processes (Figure 9). However, there also appears to be a major mixing component involved, as indicated by the spread of data points shown in Figure 8 and the small correlation coefficient in Figure 9; however, the correlation is also weak when $\delta^{15}N$ is plotted versus the $1/[NO_3]$ and versus $\ln([NO_3])$. Both of those relationships have been used in the literature (Mariotti et al. 1988) to help determine whether NO_3^- concentration and $\delta^{15}N$ variability was due to mixing or denitrification processes, respectively.

Typically, a plot of $\delta^{15}N$ vs. $1/[NO_3]$ should yield a straight line for mixtures of two sources, whereas a plot of $\delta^{15}N$ versus $\ln([NO_3])$ will yield a linear correlation for denitrification. Thus, these types of plots did not help differentiate between denitrification and mixing.

We did not have $\delta^{18}O$ and $\delta^{15}N$ values for mineralized nitrogen fertilizer in the soil zone for the study area. However, we measured the $\delta^{15}N$ for three fertilizers commonly used in the sinkhole plain. The mean $\delta^{15}N$ value for these fertilizers was –0.44‰ (Table 5), which is within the range of literature values described for fertilizer nitrogen (Kendall 1998). The $\delta^{18}O$ of NO_3^- produced from reduced nitrogen, such as ammonium, can be estimated using the two-thirds groundwater–one-third atmospheric O_2 assumption of Böttcher et al. (1990). The average $\delta^{18}O$ of the groundwater sampled from the springs is –5.5‰, and the average $\delta^{18}O$ for atmospheric oxygen is about +23.5‰ (Amberger and Schmidt 1987, Clark and Fritz 1997). Thus, the $\delta^{18}O$ of NO_3^- from NH_4 would have a value of approximately +4.2‰ for the sinkhole plain area. This value is in very good agreement with the NO_3^- measured from a septic system, which had enough NO_3^- for us to analyze $\delta^{18}O$ (Table 5). However, when fertilizer application for the area is considered, approximately 85% of nitrogen is applied as reduced nitrogen and 15% as ammonium nitrate (Paul Kremmell, personal communication 1999). Because half of the nitrogen of ammonium nitrate is synthetic NO_3^-, which typically has a $\delta^{18}O$ value of about +22‰, we added a 7.5% contribution of this isotopically heavy NO_3^- to estimate the range of $\delta^{18}O$ composition (+4 to +5.7‰) for the fertilizer-derived end member (Figure 8). Assuming the diamond symbols within the mineralized fertilizer domain of Figure 8 represent the average isotopic values for NO_3^- in the upper soil zone, the data suggest that a considerable degree of denitrification occurred within the soil zone, epikarst, and shallow karst aquifer of the study area. The DOC

concentrations in the water samples from springs were certainly high enough to support the denitrification process.

Several of the water samples from springs had considerably greater $\delta^{18}O$ values of NO_3^- than would be expected from denitrification alone, and these values plot well above the denitrification trajectories shown in Figure 8. The greater $\delta^{18}O$ values suggest that (1) these samples contained a source of NO_3^- that had more of the heavy oxygen isotope (^{18}O), such as atmospheric NO_3^-; (2) during the nitrification process, a greater amount of atmospheric oxygen contributed to the NO_3^- oxygen; or (3) the $\delta^{18}O$ of the soil zone water was greater due to evapotranspiration effects (Mayer et al. 2001, Burns and Kendall 2002). The most positive $\delta^{18}O$ values for NO_3^- were observed for the winter and summer samples. These samples also had relatively small amounts of NO_3^-, making them more susceptible to influences of isotopically heavier NO_3^-. The source of the more positive $\delta^{18}O$ values may have been the NO_3^- of ammonium nitrate fertilizer or possibly atmospheric NO_3^-, which has very positive $\delta^{18}O$ values. Atmospheric NO_3^- can have $\delta^{18}O$ values ranging from +20 to +75‰ in precipitation (Kendall et al. 1995) and can affect the NO_3^- leaching through soils (Durka et al. 1994, Campbell et al. 2002). The average NO_3^--N concentration in precipitation for this area is about 0.3 ± 0.15 mg/L (National Atmospheric Deposition Program 1998). Four precipitation samples, collected at Illinois Caverns in Monroe County, contained enough NO_3^- to allow $\delta^{15}N$ and $\delta^{18}O$ analyses. The $\delta^{18}O$ of the NO_3^- ranged from 23.1 to 42.9‰ (precipitation included in Figure 10), which agrees with $\delta^{18}O$ values of atmospheric NO_3^- reported in the literature. As demonstrated by Mengis et al. (2001), however, the impact of larger $\delta^{18}O$ values from nitrate fertilizer, and probably atmospheric NO_3^-, is typically not observed. Rapid consumption and/or transformation of NO_3^- to organic nitrogen within the soil zone and reoxidation back to NO_3^- resets the $\delta^{18}O$ value. Additionally, we would expect that the greater $\delta^{18}O$

Table 10 Isotopic results by season for water samples collected from springs in the study area.

Sample	Spring	$\delta^{15}N_{NO3}$ (‰)	$\delta^{18}O_{NO3}$ (‰)	$\delta^{18}O$ (‰)	δD (‰)	$\delta^{13}C$ (‰)	$\delta^{34}S$ (‰)	Tritium (TU)[1]
Fall 1998								
IG-1T	Falling, top	6.8	8.2	−6.30	−39.2	−12.0	0.2	--[2]
IG-1B	Falling, bottom	--	--	−6.42	−41.2	−11.8	0.1	--
IG-2	Sparrow Creek	6.5	8.1	−5.68	−38.3	−12.1	−1.6	--
IG-3	Collier	5.4	13.2	−5.38	−33.7	−11.9	0.7	--
IG-4	Indian Hole	5.8	10.5	−5.32	−34.0	−12.0	−2.1	--
IG-5	Sensel	6.0	11.5	−6.74	−45.3	−13.9	1.9	--
IG-6	Illinois Caverns	5.6	5.6	−6.24	−44.1	−10.0	2.0	--
IG-7	Kelly	7.7	7.4	−5.80	−37.9	−10.7	−4.9	--
IG-8	Camp Vandeventer	7.6	14.8	−5.10	−36.2	−11.1	−1.4	--
IG-9	Auctioneer	5.7	8.1	−6.05	−39.2	−10.9	2.1	--
Winter 1999								
IG-1AT	Falling, top	3.2	7.7[3]	--	--	--	0.5	--
IG-1AB	Falling, bottom	6.0	13.4[3]	−6.41	−39.4	−12.4	0.9	6.5
IG-2A	Sparrow Creek	6.2	9.3[3]	−6.00	−39.3	−11.9	−1.2	7.9
IG-3A	Collier	6.4	10.1[3]	−6.06	−40.2	−11.5	0.4	4.7
IG-4A	Indian Hole	9.0	21.9[3]	−5.91	−38.0	−11.1	−2.0	5.6
IG-5A	Sensel	7.6	8.2[3]	−6.33	−39.7	−13.9	2.0	6.8
IG-6A	Illinois Caverns	10.5	10.1[3]	−6.33	−40.4	−10.6	2.2	5.7
IG-7A	Kelly	12.5	13.2[3]	−6.06	−37.7	−11.0	−4.2	5.4
IG-8A	Camp Vendeventer	7.5	7.8[3]	−5.47	−36.5	−11.1	−0.9	5.5
IG-9A	Auctioneer	8.4	11.9[3]	−6.20	−41.7	−11.1	2.3	5.8
IG-10A	Frog	4.6	10.7[3]	--	--	--	0.5	6.8
Spring 1999								
IG-1BT	Falling, top	--	--	−5.97	−39.6	−12.9	0.5	--
IG-1BB	Falling, bottom	5.7	7.2[3]	−6.15	−40.2	−12.6	0.8	6.2
IG-2B	Sparrow Creek	3.7	7.5[3]	−5.81	−39.6	−12.3	−2.4	5.9
IG-3B	Collier	4.5	6.9[3]	−5.87	−38.7	−12.0	0.6	5.8
IG-4B	Indian Hole	6.2	8.6[3]	−5.24	−33.8	−13.0	−1.6	5.8
IG-5B	Sensel	4.2	5.6	−6.08	−40.1	−13.6	2.1	6.3
IG-6B	Illinois Caverns	3.4	6.5[3]	−6.05	−37.1	−11.6	2.1	5.4
IG-7B	Kelly	5.5	11.8[3]	−5.29	−34.5	−12.3	−7.0	5.9
IG-8B	Camp Vendeventer	5.4	8.7[3]	−4.78	−35.6	−12.1	−1.8	5.6
IG-9B	Auctioneer	3.5	5.5	−6.06	−40.8	−11.8	2.2	5.6
IG-10B	Frog	4.8	6.7[3]	−5.98	−39.2	−12.1	0.9	5.5
Summer 1999								
IG-1CT	Falling, top	--	--	−6.18	−40.2	−13.1	0.4	--
IG-1CB	Falling, bottom	5.7	8.2	−6.06	−41.1	−12.5	0.4	7.1
IG-2C	Sparrow Creek	7.0	7.9[3]	−5.50	--	−13.2	−2.9	5.2
IG-3C	Collier	7.5	17.6	−4.21	−30.9	−13.7	0.2	5.8
IG-4C	Indian Hole	9.0	20.1[3]	−2.57	−24.3	−13.1	−3.2	5.7
IG-5C	Sensel	4.8	--	−5.56	−40.0	−13.6	2.0	6.5
IG-6C	Illinois Caverns	3.9	7.1[3]	−5.25	−39.2	−12.5	1.9	4.9
IG-7C	Kelly	7.3	8.0[3]	−3.60	−32.1	−12.0	−6.5	5.6
IG-8C	Camp Vandeventer	7.0	--	−4.34	−32.2	−13.5	−2.9	5.3
IG-9C	Auctioneer	4.3	--	−6.03	−40.2	−11.8	1.8	5.1
IG-10C	Frog	5.6	8.8[3]	−5.07	−37.7	−13.1	0.8	5.5
Fall 1999								
IG-1DT	Falling, top	6.9	9.5	−5.93	−40.2	−11.7	--	5.9
IG-1DB	Falling, bottom	7.5	7.6[3]	−5.96	−39.9	−11.4	--	5.7
IG-2D	Sparrow Creek	6.7	10.1	−5.28	−37.9	−12.0	--	7.8
IG-3D	Collier	7.2	6.8[3]	−4.81	−35.4	−12.2	--	4.8
IG-4D	Indian Hole	9.7	9.9[3]	−4.76	−36.6	−10.9	--	5.8
IG-5D	Sensel	5.2	8.3	−5.69	−39.6	−13.4	--	6.6
IG-6D	Illinois Caverns	4.6	7.2	−5.99	−36.8	−9.3	2.1	4.9
IG-7D	Kelly	8.4	10.2	−4.62	−34.5	−10.7	−6.4	4.6
IG-8D	Camp Vandeventer	7.4	12.0	−0.54	−16.4	−11.5	−1.4	--

(continued)

Sample	Spring	$\delta^{15}N_{NO3}$ (‰)	$\delta^{18}O_{NO3}$ (‰)	$\delta^{18}O$ (‰)	δD (‰)	$\delta^{13}C$ (‰)	$\delta^{34}S$ (‰)	Tritium (TU)[1]
IG-9D	Auctioneer	5.0	11.3	−5.76	−40.4	−10.5	1.6	5.0
IG-10D	Frog	6.1	7.1	−5.89	−38.5	−11.9	0.3	5.5
Winter 2000								
IG-1ET	Falling, top	7.4	7.2[3]	−5.86	−38.9	−11.4	−3.1	--
IG-1EB	Falling, bottom	8.0	7.5[3]	−5.84	−37.7	−11.4	−1.3	5.5
IG-2E	Sparrow Creek	7.1	8.3	−5.84	−37.5	−9.9	−3.3	4.7
IG-3E	Collier	3.5	7.8	−5.70	−37.6	−6.6	1.8	--
IG-4E	Indian Hole	4.6	6.9	−5.52	−37.8	−10.5	−2.4	4.0
IG-5E	Sensel	4.8	5.1	−5.92	−37.6	−13.5	--	4.7
IG-6E	Illinois Caverns	4.2	5.2	−6.14	−38.7	−9.4	--	3.9
IG-7E	Kelly	6.9	7.6[3]	−5.85	−38.8	−10.6	2.5	--
IG-8E	Camp Vandeventer	7.1	7.1[3]	−4.47	−33.1	−9.5	0.5	--
IG-9E	Auctioneer	4.1	6.7[3]	−5.88	−39.2	−10.0	--	4.8
IG-10E	Frog	5.8	5.2	−5.48	−37.6	−10.8	--	4.5

[1]TU, tritium units.

[2]--, not determined.

[3]Standard deviation, 1.7.

value from nitrate fertilizer would have been incorporated into the overall background value for mineralized nitrate fertilizer. However, this type of fertilizer is only applied during winter months for the winter wheat crops. Thus, plant uptake during winter would be low, and rapid throughput of the $\delta^{18}O$-enriched NO_3^- may occur during large precipitation events or snow melts as observed by Mengis et al. (2001) on experimental plots. This scenario, plus the possibility of atmospheric NO_3^- contribution, may help explain some of the isotopically heavy $\delta^{18}O$ values for NO_3^- during some of the winter sampling events. However, isotopically heavy $\delta^{18}O$ values also were observed during summer and fall sampling events, which were several months after nitrate fertilizer application, and during extensive biological activity.

Perhaps some of the elevated $\delta^{18}O$ values, especially those from the summer and fall sampling events, reflect the influence of ^{18}O enrichment of soil water by evaporation or evapotranspiration during nitrification (e.g., Burns and Kendall 2002, Mayer et al. 2001). Two of the summer samples from springs that had relatively large $\delta^{18}O$ values for NO_3^- also had more positive $\delta^{18}O$ values for water (Figure 11). However, this relationship obviously needs to be investigated
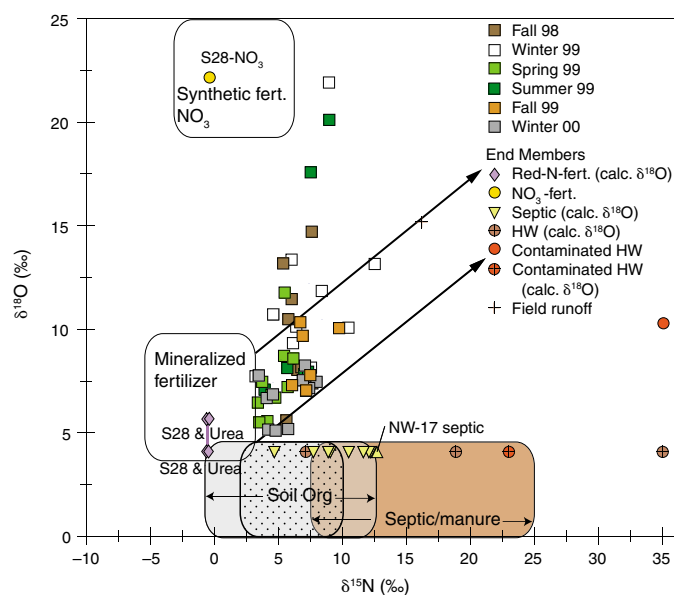

Figure 8 Isotopic composition of NO_3^- from springs and end-member samples including fertilizers (fert.), septic systems, and livestock waste. The $\delta^{18}O$ values were calculated (calc.) for the NO_3^- that would be produced from reduced nitrogen sources, such as most fertilizers (urea and NH_3), hog waste (HW), and most septic effluent (see text for details). The arrows represent the typical trend expected for denitrification and bracket the main cluster of samples that appear to follow the denitrification trend. Isotopic ranges characteristic of different sources are also shown (general domains taken from Kendall et al. 1995, Clark and Fritz 1997, Mengis et al. 2001). S28, Solution-28. Stippled area indicates most typical $\delta^{15}N$ values for soil organic nitrogen.
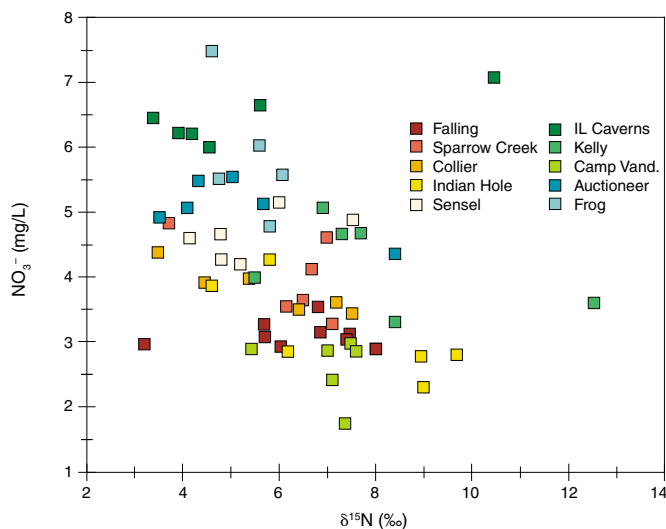
Figure 9 Nitrate concentrations versus $\delta^{15}N$ values for the springs. Slope for most of the samples is generally negative ($r^2 = -0.4$, excluding three outliers).

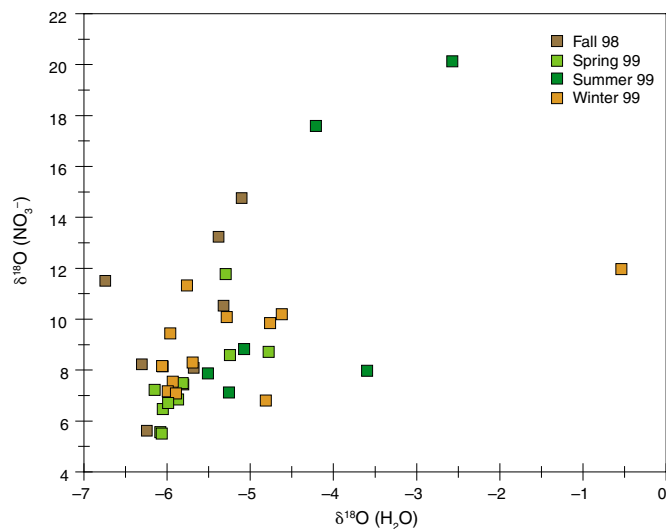**Figure 11** $\delta^{18}O$ of NO_3^- and $\delta^{18}O$ of water samples collected from springs during four seasons in the study area.
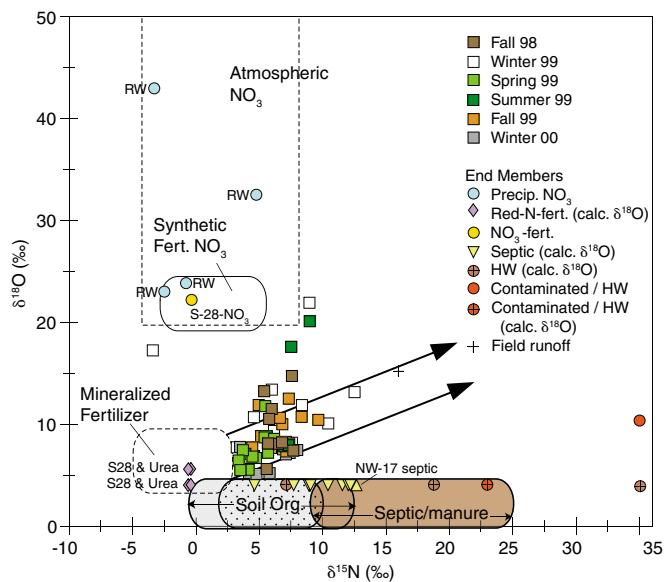

Figure 10 $\delta^{18}O$ and $\delta^{15}N$ of NO_3^- from springs showing isotopic values of samples from precipitation collected in the study area. The dashed domain for isotopic range characteristic of precipitation NO_3^- extends to larger $\delta^{18}O$ values than shown here (Kendall et al. 1995). Precip., precipitation; fert., fertilizers; calc., calculated; HW, hog waste.
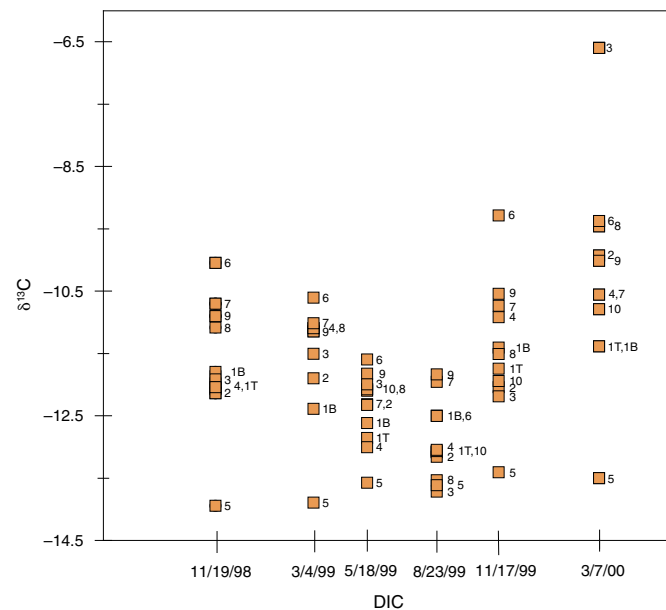
Figure 12 $\delta^{13}C$ of dissolved inorganic carbon (DIC) in spring water samples from six sampling dates in the study area.

in more detail because two other samples from different springs did not have such large $\delta^{18}O$ for the NO_3^-, although they did have relatively enriched ^{18}O water values. There is also the possibility that atmospheric oxygen contributes more than one-third of the oxygen for the nitrification process (Mayer et al. 2001) within some of the watersheds in this study area.

The more negative $\delta^{18}O$ values observed in the winter 2000 samples from Frog and Sensel Springs and Illinois Caverns suggested some NO_3^- contribution from livestock and/or septic waste. This source is supported by the range of $\delta^{15}N$ values obtained for septic and hog waste samples and the measured $\delta^{18}O$ value for one of the septic effluent samples containing enough NO_3^- to allow analysis of oxygen isotopes. Furthermore, some of the land near Frog and Sensel Springs is used for raising livestock, and a small village is located just up-gradient of Illinois Caverns. The more negative $\delta^{18}O$ values for these specific samples may indicate a greater soil organic nitrogen contribution at the time of sampling. In general, livestock and septic effluents likely play a minor role as a source of NO_3^- in most of the spring water of the sinkhole plain (Figures 8 and 10). This conclusion is supported by the mass loading calculations of Panno et al. (2003).

$\delta^{13}C$ of DIC   The $\delta^{13}C$ values of the DIC for the spring water ranged from −6.6 to −13.9‰, which probably reflects the amount of water-rock interaction that occurred in the sub-surface after infiltration of ground-water from the soil zone. Springtime water samples with the most negative $\delta^{13}C$ values suggest a greater contribution of soil zone water; those samples with more positive $\delta^{13}C$ values suggest more water-rock interaction, especially the dissolution of limestone. A plot of $\delta^{13}C$ values and sampling dates (Figure 12) shows that $\delta^{13}C$ values tended to be more negative during the spring and summer (May and August) than during the fall and winter (November and March). This seasonal trend coincides with greater biological activity in the soil during the growth periods of the spring and

summer than during dormant peri-ods of fall and winter. Greater bio-logical activity in the soil zone would increase the concentration of soil CO_2 and amount of soil CO_2 dissolved in the infiltrating groundwater. The seasonal fluctuations of $\delta^{13}C$ values observed in the waters from springs supports earlier suggestions that infil-tration of surficial water into much of the shallow karst aquifer was typi-cally quite rapid. The $\delta^{13}C$ values for one of the springs, Sensel Spring, did not follow the same seasonal trend observed for the other springs. The consistently more negative $\delta^{13}C$ values for Sensel Spring suggest that its dis-charge water comes primarily from the soil zone. These isotope results support the chemical results showing lower pH and undersaturation with respect to calcite. The more negative $\delta^{13}C$ values indicate that the water discharging from Sensel Spring was relatively more open to exchange with soil CO_2 than was water from the rest of the springs sampled in this study.

δD and $\delta^{18}O$ of Water   Data for δD and $\delta^{18}O$ cluster near the GMWL (Figure 13). The isotopic composition of water from summer and fall sam-pling events plot along a trajectory representative of evaporation, indi-cating that considerable evaporation occurred at the land surface prior to water infiltration into the subsurface in some of the watersheds. Most of the samples collected during spring plotted on or very close to the GMWL. Seasonal detection of evaporational effects in the groundwater discharging from the springs was another indica-tion of rapid influx of surface water to the karst aquifer of the sinkhole plain.

$\delta^{34}S$ of Sulfate   The $\delta^{34}S$ values for the springs ranged from −6 to +2.5‰. Because no strong correlation between the sulfur isotope data and NO_3^- concentrations was observed, pyrite oxidation probably did not play a major role in NO_3^- reduction in the sinkhole plain karst environment. The correlation between sulfate concen-trations and $\delta^{34}S$ values was negative ($r^2 = −0.65$) for most of the springs sampled. The sulfur isotope data from Falling Springs were unique. For most of the springs, the samples with greater sulfate concentrations gener-

ally had more negative $\delta^{34}S$ values, suggesting that pyrite oxidation contributed sulfate to these samples. However, many of the springs had $\delta^{34}S$ values ranging between −1 to +2.2‰, which were similar to the +2.7‰ for the $\delta^{34}S$ measured from the water runoff end member sampled from a cornfield in the study area (Table 5). The origin of the sulfate in the runoff sample was assumed to be from fertil-izer application and the oxidation of organic matter in the upper horizons of the soil zone. Freney and Williams (1983) indicated that sulfur in the upper horizons of well-drained aer-ated soils occurs primarily as organic sulfur from plant debris, and much of the inorganic sulfate in the lower horizons of these soils is a result of mineralization of the organic sulfur. The typical range of $\delta^{34}S$ for terrestrial primary plant sulfur is about 0 to +12‰, as measured from low-sulfur coals and freshwater peat deposits throughout the world (summarized by Hackley and Anderson 1986). The lower end of this range is also similar to that observed for most of the spring waters. The $\delta^{34}S$ values for several of the springs suggested that much of the sulfate was the result of fertilizer sulfate and the oxidation of organic sulfur from the soil zone. The distri-bution of $\delta^{34}S$ values observed in the springs can be explained by sulfate from the upper soil zone that had more positive $\delta^{34}S$ values mixing with sulfate that had more negative $\delta^{34}S$ values caused by pyrite oxidation as the groundwater percolated deeper into the sediments and bedrock units (Figure 14).

Well Samples: Chemical Composition

The variation in chemical composi-tion observed for the well samples (Tables 11 and 12) reflected the impact of local conditions (e.g., back-ground, point and non-point source contamination) on groundwater chemistry. The chemical character-istics of some of the well samples were similar to the spring samples, but samples from other wells showed the influence of local, anthropogenic inputs.

Groundwater samples from the wells were mostly undersaturated or near equilibrium with respect to calcite (Figure 15). The saturation indices for the well samples were noticeably different from those for the water samples from springs; spring water samples were predominantly super-saturated with respect to calcite.

The pH for the samples from 16 wells ranged from 6.7 to 7.2 (Table 11). The variation was small when compared with that for the spring samples, and no major trends were observed for depth or season. The pH of the well samples was similar to that of Sensel Spring, which primarily drained the soil zone above the limestone bedrock. The lower pH values and under-saturated calcite conditions for many of the well samples indicate that the water flowing into these wells had not been buffered by the limestone bedrock to the same degree as most of the spring water had. The water flowing into most of the wells prob-ably travels quickly from the soil zone through fractures and fissures in the bedrock to the well screen because most of the wells are cased only from 1 to 4 m below the top of limestone bedrock (Panno et al. 1996). Pumping

the wells would decrease water level and draw water in through the most permeable zone near the top of the bedrock where the limestone is most weathered and contains dissolution-enlarged fissures and fractures in the top 10 to 15 m (Panno et al. 1996).

The temperature for most of the well samples was consistent and ranged from 14.1 to 15.8°C. Two wells had temperatures that fell outside this range. Sample NW-16 from well 15 ran through the residential water softener and was slightly warmer. Sample NW-42 from well 17 reflected the cold season (winter) because of a long dis-tribution pipe buried just below the land surface from the well head to the outside spigot.

The range of the Eh measurements for most of the well samples fell between +334 and +529 mV, which was similar to the range for the samples of spring water, indicating a similar exposure to atmospheric oxygen along its flow path.

The specific conductance for the wells ranged from 539 to 1,718 µS/cm. The values were generally greatest for the shallower wells (Figure 16) and for wells located on property with

livestock facilities. The high specific conductance observed for site NW-16 was because the water had passed through a residential water softener, as reflected by the anomalously large Na^+ and Cl^- concentrations (Table 12).

The range of Cl^- concentrations for the wells was much greater than that for the springs. The Cl^- ranged from 3.1 to 127 mg/L for the wells; concentrations were greatest for the shallower wells and for those sites in close proximity to livestock areas. Like the spring water samples, the Na^+ and Cl^- concentrations for the water samples from wells are correlated roughly along the 1:1 stoichiometric line, although Na^+ concentrations tend to be greater (Figure 17). This positive shift of Na^+ concentrations was also observed in the data for water samples from springs and sug-gests that ion exchange (with Ca^{2+}) probably plays a role in the chemical makeup of the karst aquifer system. Greater Na^+ concentrations could also come from weathering of sodium silicate minerals and anthropogenic sources such as septic systems, live-stock waste, and fertilizers such as $NaNO_3$. Many residential homes have water softeners, which would increase
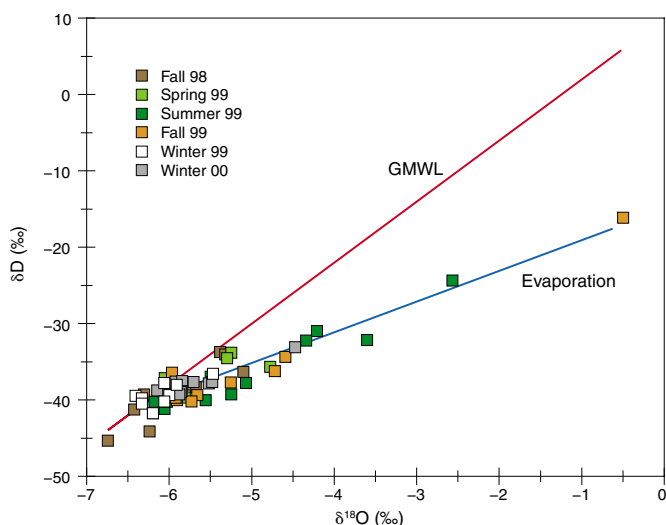

Figure 13 Isotopic composition (δD and $\delta^{18}O$) of the springs in relation to the global meteoric water line (GMWL) and along a trajectory typical of evaporation.
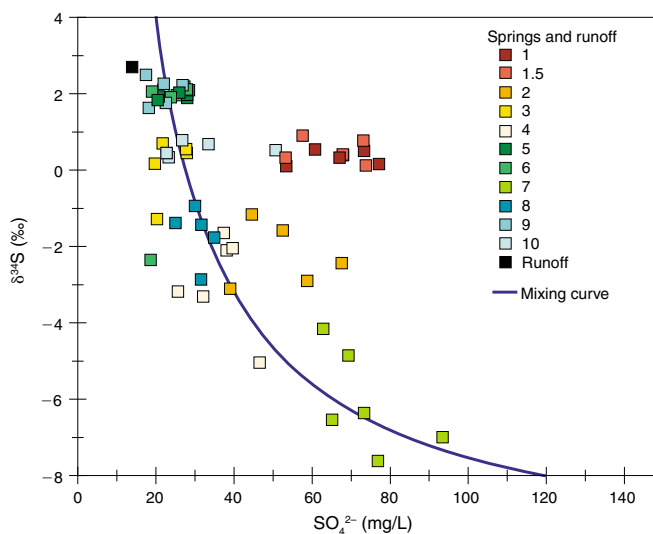

Figure 14 $\delta^{34}S$ versus SO_4^{2-} concentration of runoff and spring samples. Spring samples are identified by number. A mixing curve is included to show the trend for mixing sulfate containing more positive $\delta^{34}S$ values with sulfate containing more negative $\delta^{34}S$ values. The mixing curve was generated using end-member sulfate concentrations of 20 and 120 mg/L and $\delta^{34}S$ values of +4‰ and −8‰, respectively.

the Na⁺ concentration in septic discharge. Although sample NW-16 was not septic discharge, its increased Na⁺ concentration shows the effect of water softeners (Figure 17).

The DOC concentrations for the samples from wells were somewhat less than for the water samples from springs, but usually larger relative to typical groundwater, which contains less than 2 mg of DOC /L (Drever 1997). The DOC in water samples from the wells, excluding NW-16, ranged from less than the detection limit to 5.8 mg/L. Sample NW-16 had 9.9 mg of DOC/L but was contaminated with a high concentration of Cl⁻, which could have interfered with DOC analyses. As with the springs, the elevated concentrations of DOC may have been associated with agricultural activities and/or septic systems.

There are two types of wells in southwestern Illinois, bored wells and drilled wells. Bored wells are dug completely within and open to the soil zone to depths of 6 to 10 m. Drilled wells are typically cased only through the soil zone and about a meter into bedrock, allowing soil water and very shallow groundwater to seep into the open borehole and contaminate the well, regardless of whether deep or shallow (Panno et al. 1996).

Nitrate concentrations for well samples ranged from less than the detection limit (<0.02 mg of N/L) to 80.9 mg of N/L. Five of 17 wells contained concentrations greater than the USEPA (1992) regulatory standard for drinking water. The shallower wells consistently had the highest NO_3^- concentrations (Figure 18). The shallow wells were all located in the covered karst region where the water table was higher (above the soil-bedrock interface) than in the karst topography (below the soil-bedrock interface). A cross section connecting many of the sampled wells shows the effects of the karst terrain on the local hydrology and the distribution and stratification of NO_3^- in the karst aquifer of the region (Figure 19). Generally, most wells drilled into the covered karst region of the sinkhole plain contained significant NO_3^- concentrations, regardless of depth (Table 13; Figure 19).

In contrast to the samples from the covered karst region, groundwater

Table 11 Field parameters and total alkalinity for water samples from wells in the study area.

Sample	Well	Date sampled	Well depth (m)	Temp.[1] (°C)	pH	Eh (mV)	Specific conductivity (µS/cm)	Total alkalinity (mg CaCO₃/L)
NW-1	1	05/14/99	93	14.6	6.9	795	866	314
NW-2	2	05/14/99	170	15.3	7.2	529	616	251
NW-3	3	05/14/99	61	14.4	7.0	469	602	325
NW-4	4	05/14/99	17	14.1	6.9	494	810	334
NW-5	5	05/14/99	6	15.8	6.7	504	1,595	386
NW-7	7	05/19/99	95	15.5	7.0	453	588	311
NW-8	8	05/19/99	--[2]	15.3	7.1	432	578	291
NW-9	9	05/19/99	73	15.1	6.7	485	1,122	385
NW-10	10	05/19/99	105	14.8	6.9	423	753	320
NW-11	11	05/19/99	33	14.8	6.8	448	586	226
NW-12	12	05/19/99	13	15.4	7.0	467	844	290
NW-13	13	05/19/99	89	15.4	7.1	420	702	346
NW-14	14	05/19/99	10	15.1	7.0	494	1,064	352
NW-15	14	07/06/99	--	--	--	--	--	--
NW-16	15	07/06/99	154	16.6	7.0	415	1,378	468
NW-17	1	11/18/99	93	14.7	6.8	409	804	315
NW-18	2	11/18/99	170	15.2	7.1	430	618	277
NW-19	3	11/18/99	61	15.0	7.0	465	594	323
NW-20	4	11/18/99	17	14.8	6.9	463	796	336
NW-21	5	11/18/99	6	15.8	6.9	432	1,718	410
NW-21D	6	11/18/99	37	15.2	6.9	144	776	413
NW-22	8	11/18/99	--	14.9	6.9	450	591	315
NW-23	9	11/17/99	73	14.5	6.8	--	929	412
NW-24	10	11/17/99	105	14.4	7.1	334	730	313
NW-25	11	11/18/99	33	14.5	6.9	429	539	219
NW-26	12	11/18/99	13	15.2	6.8	417	894	304
NW-27	14	11/18/99	10	15.6	6.9	396	1,232	410
NW-28	13	11/18/99	89	14.7	7.0	407	676	347
NW-40	16	03/21/01	69	14.7	7.0	281	748	361
NW-42	17	03/21/01	108	8.3	7.1	422	831	372

[1]Temp., temperature; Eh, redox potential.

[2]--, not determined.

Table 12 Chemical data for water samples from wells in the study area.

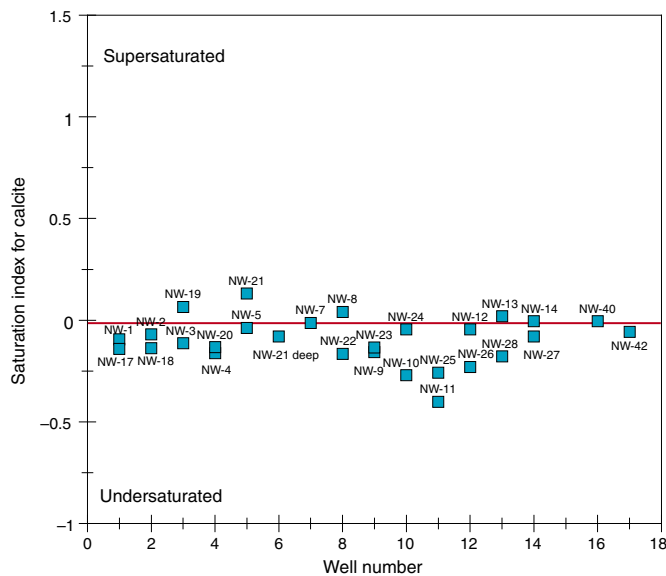| Sample	Ca²⁺	Mg²⁺	Na⁺	K⁺	NH₄-N	HCO₃⁻	Cl⁻	SO₄²⁻	NO₃-N	SiO₂	Al	Ba	Br⁻	F⁻	Fe	Mn	Sr²⁺	Zn	DOC	Atrazine (µg/L)
NW-1	127	15.6	52.6	<1	--[1]	383	47.5	54.8	7.43	20.7	<0.02	0.09	<0.18	0.25	<0.01	<0.01	0.19	<0.01	--	<0.10
NW-2	71.7	15.4	52.2	<1	--	306	14.5	42.4	7.61	15.7	<0.02	0.05	<0.18	0.34	<0.01	<0.01	0.18	<0.01	--	<0.10
NW-3	83.2	36.7	7.7	<1	--	397	9.0	20.2	1.99	13.5	<0.02	0.15	<0.18	0.65	<0.01	<0.01	0.35	<0.01	--	<0.10
NW-4	99.2	23.6	60.8	<1	--	407	26.6	36.7	12.5	16.2	<0.02	0.09	<0.18	0.31	<0.01	<0.01	0.19	<0.01	--	<0.10
NW-5	203	66.8	67.2	<1	--	470	120	53.9	57.8	23.3	<0.02	0.31	0.60	0.32	<0.01	<0.01	0.56	0.05	--	<0.10
NW-7	77.1	33.5	11.4	<1	--	380	8.7	20.7	1.63	13.8	<0.02	0.17	<0.18	0.58	<0.01	<0.01	0.25	0.02	5.2	<0.10
NW-8	104	13.4	13.2	<1	--	355	8.4	26.0	2.24	26.5	<0.02	0.05	<0.18	0.30	<0.01	<0.01	0.14	<0.01	5.8	<0.10
NW-9	145	39.7	52.9	<1	--	469	50.4	31.7	30.1	18.3	<0.02	0.12	0.30	0.29	<0.01	<0.01	0.23	0.05	3.1	0.14
NW-10	86.1	27.9	54.5	<1	--	391	10.5	73.6	4.88	12.3	<0.02	0.07	<0.18	0.31	<0.01	0.03	0.23	0.01	4.8	0.18
NW-11	105	7.35	19.4	<1	--	276	22.7	36.9	5.99	22.9	0.02	0.06	<0.18	0.19	<0.01	<0.01	0.19	0.01	2.8	<0.10
NW-12	100	19.4	68.2	<1	--	354	35.4	50.0	16.2	17.1	<0.02	0.11	0.24	0.29	<0.01	<0.01	0.19	0.03	1.9	<0.10
NW-13	69.3	43.3	39.1	<1	--	422	11.9	37.6	1.54	9.5	<0.02	0.15	<0.18	1.85	<0.01	<0.01	0.85	0.02	0.8	<0.10
NW-14	95	43.7	83.8	<1	--	430	41.7	64.0	24.6	18.7	<0.02	0.09	0.26	0.40	<0.01	0.01	0.24	<0.01	--	0.65
NW-15	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	1.2	--
NW-16	0.63	0.075	344	2	--	571	115	53.3	5.17	27.1	<0.02	<0.01	0.54	0.34	<0.01	<0.01	<0.01	<0.01	9.9	0.1
NW-17	128	15.5	43.9	2	--	384	38.5	46.1	5.78	21.0	0.03	0.09	<0.02	0.17	<0.01	<0.01	0.20	0.02	2.3	<0.1
NW-18	72.6	15.2	49.5	3	--	338	8.4	36.0	6.66	15.1	0.03	0.05	<0.02	0.23	<0.01	<0.01	0.16	<0.01	4.4	<0.1
NW-19	83.1	33.7	7.5	3	--	394	3.4	13.0	1.91	13.5	<0.02	0.13	<0.02	0.50	<0.01	<0.01	0.31	<0.01	5.3	<0.1
NW-20	95.9	21.5	58.4	3	--	410	21.5	29.8	12.0	15.6	<0.02	0.09	0.07	0.20	<0.01	<0.01	0.17	0.01	0.3	<0.1
NW-21	205	63.6	66.5	2	--	500	127	59.1	80.9	22.5	0.03	0.30	0.39	0.19	<0.01	0.01	0.53	0.13	1.3	<0.1
NW-21D	92.2	31.2	27.9	2	--	504	11.2	21.9	<0.02	12.6	<0.02	0.15	0.09	0.32	1.32	0.11	0.33	0.01	2.0	<0.1
NW-22	103	18.0	11.6	3	--	384	3.1	13.9	2.12	22.2	0.03	0.05	<0.02	0.24	<0.01	<0.01	0.16	<0.01	<0.2	<0.1
NW-23	127	31.7	44.7	2	--	503	32.6	13.7	15.4	18.1	0.04	0.09	0.14	0.20	<0.01	<0.01	0.20	0.05	5.7	<0.1
NW-24	80.7	24.4	48.1	2	--	382	3.7	64.0	3.39	11.7	<0.02	0.06	<0.02	0.20	<0.01	0.12	0.21	<0.01	0.7	<0.1
NW-25	98.8	5.73	17.3	2	--	267	14.7	23.2	5.27	22.7	<0.02	0.04	<0.02	0.09	<0.01	<0.01	0.17	<0.01	2.4	0.18
NW-26	107	19.8	64.6	2	--	371	38.4	44.6	21.4	16.6	<0.02	0.11	0.08	0.18	<0.01	<0.01	0.19	0.05	2.9	<0.1
NW-27	113	43.8	102	2	--	500	51.3	81.8	36.0	17.9	0.02	0.10	0.11	0.31	<0.01	<0.01	0.26	<0.01	2.9	<0.1
NW-28	63.5	38.1	33.3	2	--	423	5.7	31.3	0.72	8.7	<0.02	0.12	<0.02	1.82	<0.01	<0.01	0.80	0.02	0.9	<0.1
NW-40	102	28.0	51.7	<1	<0.01	440	31.8	24.4	0.71	16.9	<0.3	0.15	<0.05	0.50	0.27	0.05	0.26	0.06	--	--
NW-42	92.6	32.3	77.0	<1	<0.01	454	23.0	51.1	7.71	15.5	<0.3	0.14	0.09	0.30	1.15	0.09	0.24	0.08	--	--

[1]--, not determined.

Figure 15 Calcite saturation indices for wells sampled in the study area.
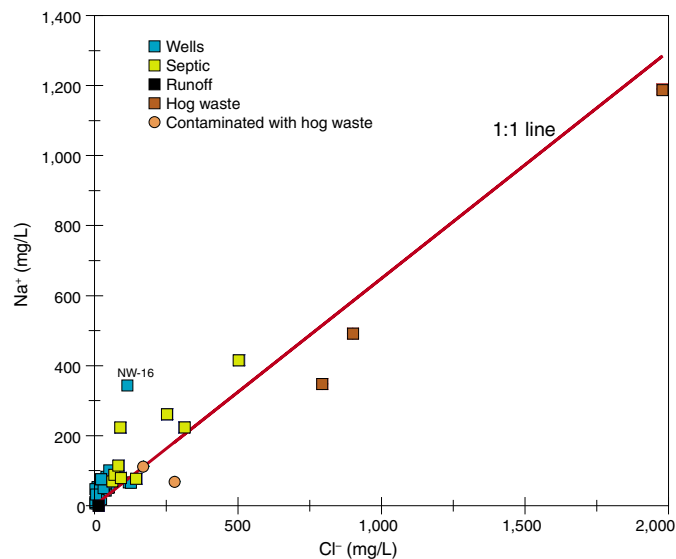

Figure 17 Sodium and chloride concentrations for the well-water samples, including the end-member samples of field runoff, septic systems, and hog waste (HW1).
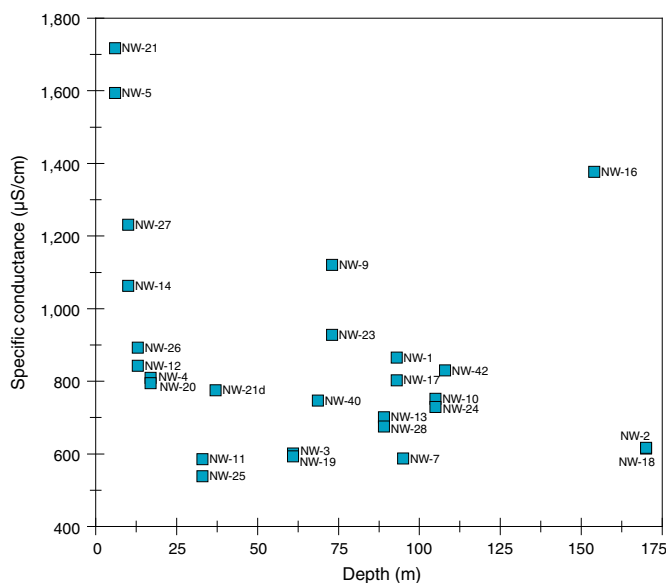

Figure 16 Specific conductance of the well water sampled in the study area. Note the generally larger values for the shallower wells.
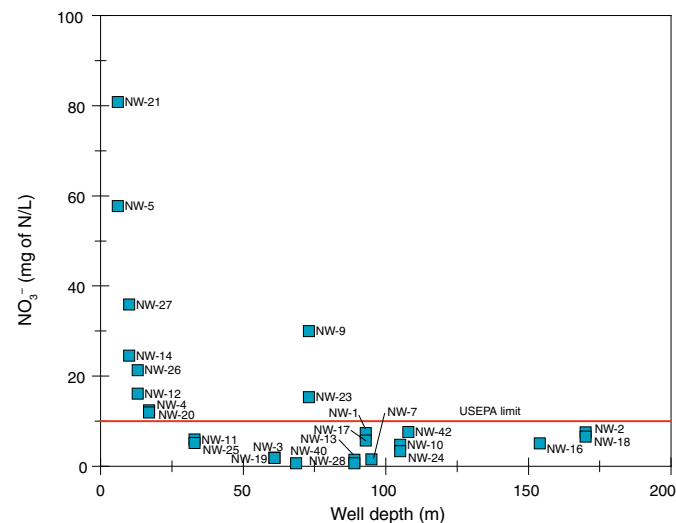

Figure 18 Nitrate concentration and well depth. Concentrations were largest for the most shallow wells. The USEPA (1992) regulatory limit (10 mg of N/L) is identified by the horizontal line.

Table 13 Descriptive statistics of NO_3^- concentrations for a limited number of water samples from wells from karst and covered karst regions and water samples from caves and springs of the sinkhole plain.

Parameter	Wells in karst terrane	Wells in covered karst terrane	Caves and springs in karst terrane
Samples, no.	9	7	62
Range, mg of N/L	1.63 to 30.5	<0.02 to 80.1	1.74 to 7.48
Median, mg of N/L	5.22	14.3	3.97
Mean, mg of N/L	6.75	22.6	4.19
Standard deviation, mg of N/L	7.44	24.7	1.27

sampled from wells drilled in karst regions had smaller NO_3^- concentrations that were similar to those from springs and caves. The largest NO_3^- concentration for the karst area was from sample NW-9 (30.1 mg of N/L). The reason for this anomalous concentration is probably that the well was drilled into a buried bedrock depression (Figure 19) where water seeping through the soil zone would be channeled into the depression. Because the bedrock surface is fractured, the NO_3^--enriched soil water could easily be funneled into the well.

Three wells drilled on one property (wells 5, 6, and 17) demonstrated how crevice-controlled groundwater flow can result in a broad range of NO_3^- concentrations because of variable amounts of input from surficial water sources. Nitrate concentrations in these three wells ranged from less than 0.02 to 80.9 mg of N/L. The shallowest well, well 5 (samples NW-5 and -21), was hand dug only 6 m into sediment. Well 6 (sample NW-21D) and well 17 (sample NW-42) were drilled into bedrock at a depth of 37 and 108 m, respectively (Figure

19). Wells 5 and 6 were close to hog-raising facilities. Well 17 was away from the hog facilities in the midst of row crops. Shallow well 5 had the greatest NO_3^- concentration, indicating the infiltration of animal waste. Medium-depth well 6 had the lowest NO_3^- concentration (<0.2 mg of N/L) and was apparently drilled into the bedrock where the crevices are more isolated from surface water infiltration. In fact, well 6 (NW-21D) was under reducing conditions and had a strong hydrogen sulfide (H_2S) odor (note low Eh, 144 mV). The residents using well 6 had problems with iron deposits at the well screen and in the house. The deepest well, well 17, had a NO_3^- concentration of 7.7 mg of N/L, which was much less than the shallow well but greater than the background concentrations for this region.

Of all wells sampled during this study, only 3 had NO_3^- concentrations that were less than the 2.1 mg of N/L threshold for background concentrations. Thus, most of the wells had been contaminated with NO_3^-. Wells with large NO_3^- concentrations also had large Cl^- concentrations, suggesting the source of these two ions was the same, probably livestock or septic waste. In order to show this relationship and include the end member sources, Cl^- concentrations were plotted against total inorganic nitrogen (NO_3^- plus NH_4^+) in Figure 20.

An overall evaluation of the major cations and anions in the well samples indicated that these were Ca^{2+}-HCO_3^- -type to mixed cation-HCO_3^- type waters (Figure 21). For a more direct comparison, spring water and samples of animal waste and septic systems have been included on the trilinear diagram (Figure 21). The septic and animal waste samples were included because their greater concentration of contaminants might be affecting the chemical composition of some of the wells. Most wastewater samples fell in the Na^+-Cl^-- to Na^+-HCO_3^- -type water regions of the trilinear diagram. It should be emphasized that ammonia—often a major component of the septic and animal waste samples—was not included in these trilinear plots. To compensate, total N was included by enlarging the
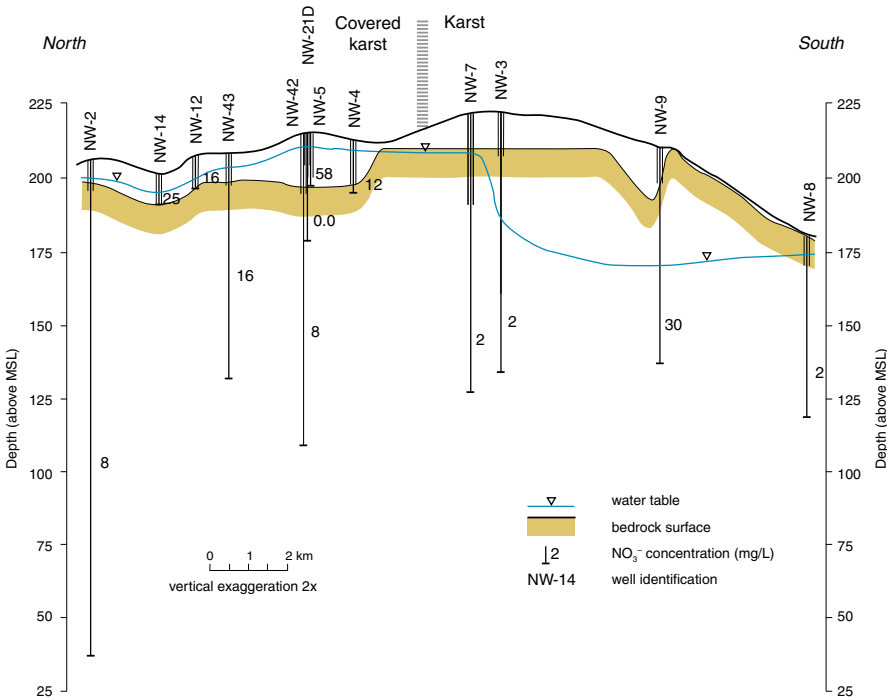

Figure 19 North-south cross section through many of the wells sampled, showing water table, topography of the bedrock surface, and NO_3^- concentrations for the wells of various depths.

diameter of the dots on the plot; the smallest and largest dots indicate the lowest and highest N concentrations, respectively. The samples with greater N concentrations typically fell to the right of the total group of samples on the cation, anion, and composite figures. The septic effluent and the hog waste samples showed distinct departures from the field defined by groundwater samples and springs in the composite diagram. However, the two water samples known to be contaminated with hog waste did plot with some of the wells in the sinkhole plain that showed elevated NO_3^- concentrations (Figure 21).

Compared with the water samples from springs, many of the well samples tended to have greater Mg^{2+}, Na^+, Cl^-, and NO_3^- concentrations. The higher Mg^{2+} concentrations were probably the result of greater dissolution of dolomite within the soil zone and/or within bedrock in the vicinity of some of the wells. Dolomite is known to occur as thin beds within the St. Louis Limestone (Willman et al. 1975, Panno et al. 1997a). Most of the well samples that had relatively large NO_3^- concentrations tended to plot toward the septic effluent and hog waste samples on the anion trilinear and composite diagram (Figure 21). The exceptions were samples NW-5 and NW-21, which had an unusually high Ca^{2+} content (Table 12).

In addition to the anomalously high Ca^{2+} concentrations, NW-5 and NW-21 also had the greatest NO_3^- and Mg^{2+} concentrations. The large amounts of Ca^{2+} and Mg^{2+} were probably a result of carbonate mineral dissolution caused by the acidic conditions associated with nitrification of ammonium as effluent from animal waste migrated into the soil zone:

Nitrification:

$$NH_4^+ + 2O_2 \rightleftharpoons NO_3^- + H_2O + 2H^+.$$

Calcite dissolution:

$$2CaCO_3 + 2H^+ \rightleftharpoons 2Ca^{2+} + 2HCO_3^-.$$

Dolomite dissolution:

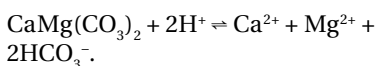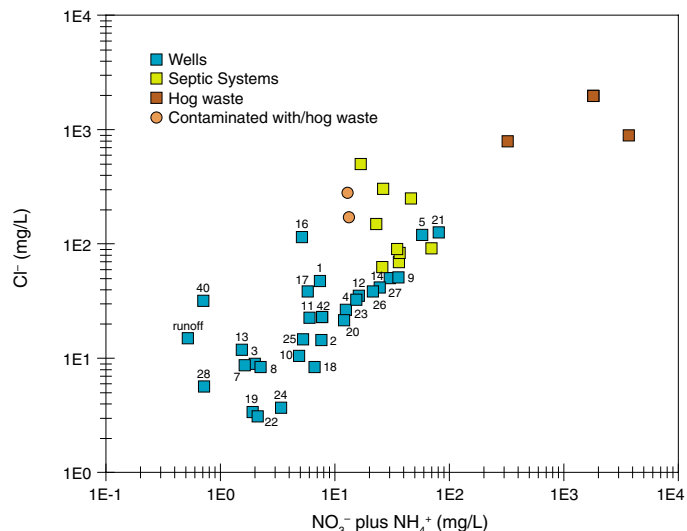$$CaMg(CO_3)_2 + 2H^+ \rightleftharpoons Ca^{2+} + Mg^{2+} + 2HCO_3^-.$$

Figure 20 Chloride and total inorganic nitrogen (NO_3^- plus NH_4) concentrations for the wells and end-member samples including field runoff, septic systems, and livestock waste. Numbers represent NW sample identification numbers in Table 12.
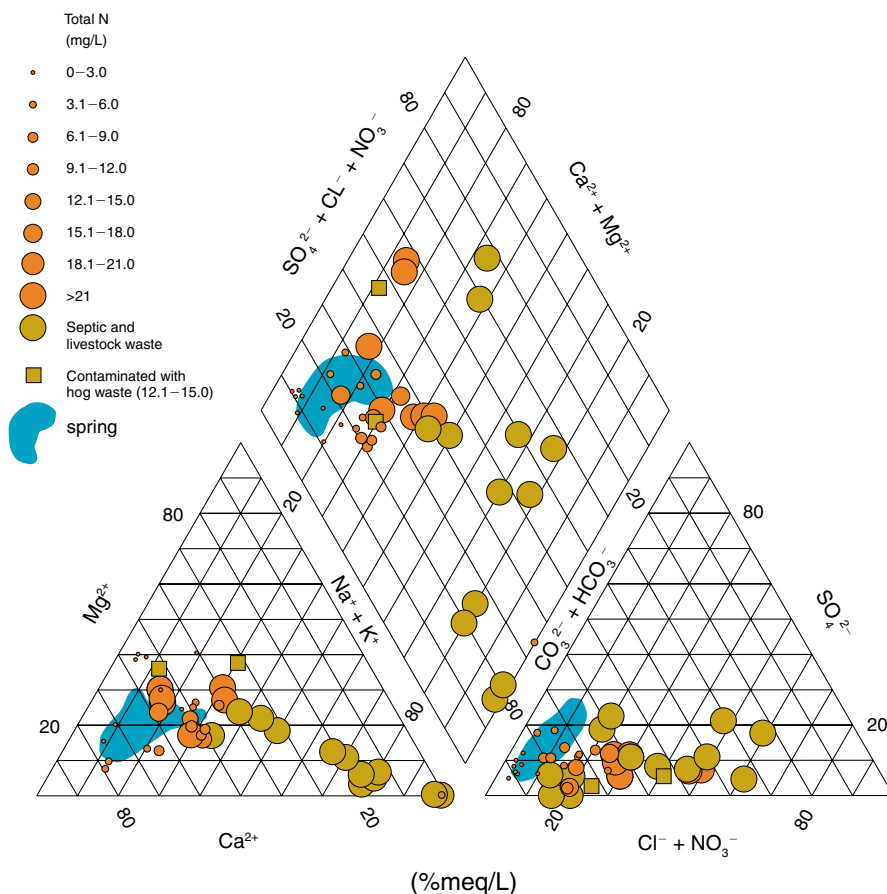

Figure 21 Trilinear diagram comparing the distribution of major cations and anions in the springs, wells, and end-member samples.

Table 14 Bacterial analyses for water samples collected from wells in the study area.

Sample	Well	Total aerobic colonies (cfu/L)	Total coliforms (cfu/L)	Fecal coliforms (cfu/L)	Fecal enterococci (cfu/L)
NW-1	1	230	0	0	0
NW-2	2	140	44	0	0
NW-3	3	260	12	0	0
NW-4	4	8,000	450	0	44
NW-5	5	14,000	3,466	0	198
NW-7	7	220	2	0	6
NW-8	8	32	0	0	0
NW-9	9	67	0	0	0
NW-10	10	190	4	0	0
NW-11	11	38	4	0	2
NW-12	12	2,700	1,840	2	110
NW-13	13	20	0	0	0
NW-14	14	3×10^6	870	46	192
NW-15	14	--[1]	--	--	--
NW-16	15	570	650	8	2
NW-17	1	490	0	0	0
NW-18	2	410	0	0	0
NW-19	3	106	0	0	0
NW-20	4	350	0	0	0
NW-21	5	2,200	1,732	0	120
NW-21D	6	120	4	0	10
NW-22	8	50	0	0	8
NW-23	9	88	0	0	0
NW-24	10	130	6	0	38
NW-25	11	204	0	0	0
NW-26	12	1,400	106	10	46
NW-27	14	430	112	0	28
NW-28	13	22	2	0	0
NW-40	16	--	--	--	--
NW-42	17	--	--	--	--

[1]--, not determined.

Samples NW-5 and NW-21 were collected from well 5 next to a hog waste facility. As shown in Table 4, hog waste samples had very high ammonium contents, even compared with the septic samples.

Well Samples: Bacterial Composition

Groundwater in wells in the sinkhole plain can be contaminated by a variety of bacterial genera and species similar to those found in the springs (Panno et al. 1996). County and state regulations for drinking water require fewer than 80 cfu/L for total coliforms and no fecal coliforms in private wells. Only 5 of the 15 wells consistently met these criteria (Table 14).

The two most dominant bacteria present in the well-water samples were *Pseudomonas* and *Bacillus* spp. (Table 15). *Pseudomonas* spp. were present in all but 1 of the 15 wells (92%). *Bacillus* spp. were present in all but 2 wells (86%). As with the spring water, these bacteria are associated with the natural flora present in the soil zone and aqueous environments.

Escherichia coli was present only in well 14 (NW-14), which also contained the greatest amount of aerobic bacteria counted. This result suggested rapid recharge to the well because the half-life of *E. coli* is about 15 hours after leaving the host animal (Burks and Minnis 1994). NW-14 was a dug well immediately adjacent to livestock grazing in a barnyard. The presence of more than 3×10^6 cfu of aerobic bacteria/L, 870 cfu of coliforms/L, 46 cfu of FC/L, and 192 cfu of fecal enterococci/L (Table 14) indicated

that animal waste was reaching this well. Wells 5 and 12, which were also dug wells located near livestock facilities, contained the next highest concentrations of aerobic and coliform bacteria, suggesting that the groundwater sampled by these wells was probably affected by animal waste effluent.

As with NO_3^-, the distribution of coliforms and fecal enterococci concentrations was stratified by depth (Figures 22 and 23). The shallowest wells had the greatest bacterial contamination. The most contaminated wells (wells 5, 12, and 14) were shallow wells where land use was dominated by livestock. Land use near well 4 was row crop agriculture; this well was drilled only a few meters into bedrock and was the shallowest of the bedrock wells. Groundwater from the deeper wells contained fewer FC and fecal enterococci, probably because these bacteria tend to die off rapidly after leaving the host animal.

In general, the bacterial content of the well samples reflected the susceptibility of the wells in a karst aquifer to surface activities and land use. This same well susceptibility was seen for NO_3^- and pesticides.

Well Samples: Isotopic Composition

$\delta^{15}N$ and $\delta^{18}O$ of NO_3^-   The $\delta^{15}N$ and $\delta^{18}O$ of the NO_3^- in well samples ranged from +2.2 to +25.9‰ and from +5.5 to +15.5‰, respectively (Table 16). When plotted, isotope data for most of the well samples containing ≤ 15 mg/L NO_3N tend to follow the denitrification trajectory (Figure 24). The lowest $\delta^{15}N$ and $\delta^{18}O$ values from the well samples plotted within the area typical of mineralized fertilizer nitrogen. None of the well samples showed the anomalously high $\delta^{18}O$ values for NO_3^- that were found in the spring samples. However, the isotopic composition of NO_3^- from several wells plotted below what would be expected for denitrification for this region, indicating that the NO_3^- from these samples was predominantly from septic and/or livestock waste. We were able to analyze one sample of
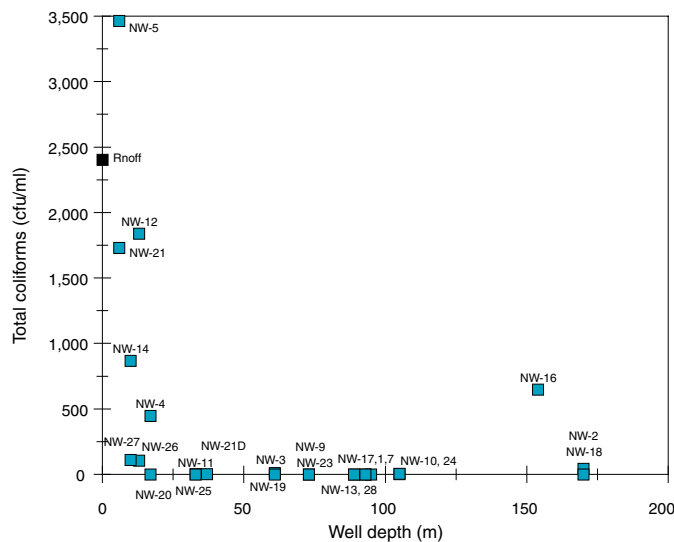
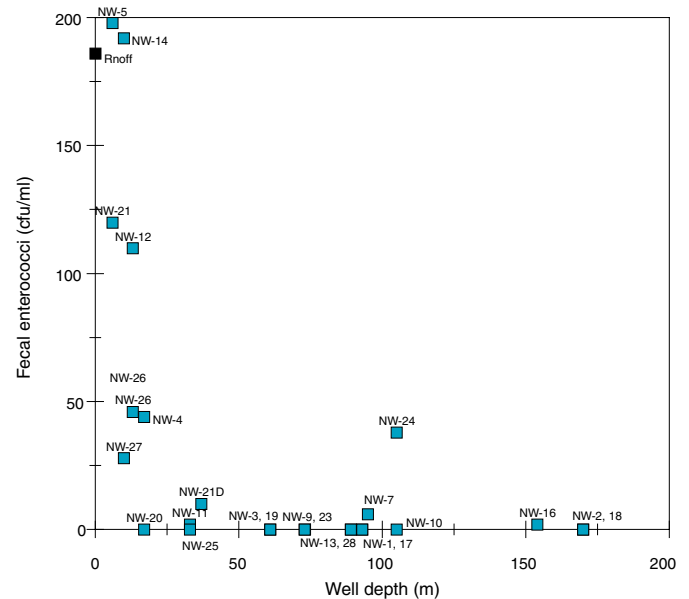**Figure 22** Bacterial analyses results for total coliforms by depth of wells sampled.

Figure 23 Bacterial analyses results for fecal enterococci by depth of wells sampled.

NO_3^- directly from the discharge point of a septic system (NW-17-septic) and two samples just down-gradient from a hog facility (NW-5, NW-21). Those samples gave a good indication of where NO_3^- influenced by septic and livestock waste would plot (Figure 24). Other samples that plotted in the same area as NW-17-septic, NW-5, and NW-21 were undoubtedly influenced by septic and/or livestock waste.

The septic and livestock waste samples contained very high concentrations of NO_3^- or ammonium compared with those of most well and spring samples. However, those well samples that showed isotopic evidence of septic and livestock contamination also contained greater concentrations of NO_3^- (Figure 24). Many of the septic and livestock waste samples

contained only ammonium, so a composite nitrogen concentration (NO_3^- plus NH_4) was used for this diagram. For those samples that contained ammonium only, the $\delta^{18}O$ value was calculated (applying the assumptions discussed earlier) and used to plot the data.

Two samples from well 13 (NW-13 and NW-28) had the highest $\delta^{15}N$ and $\delta^{18}O$ values for NO_3^- and low NO_3^- concentrations (0.7 and 1.5 mg/L). These results indicated that considerable denitrification had occurred in the groundwater at this site.

When plotted on a $\delta^{15}N$ vs. $\ln[NO_3^-N]$ (Figure 25), many of the well samples (particularly those affected by N fertilizers) follow a linear correlation ($r^2 = 0.89$) in which the isotopic com-

position increases with decreasing NO_3^-N concentration. As noted earlier, a linear correlation on this type of diagram indicates that NO_3 in the groundwater has undergone denitrification (Mariotti et al. 1988). Samples containing relatively large NO_3^-N concentrations (>15 mg/L) derived from animal waste and septic effluent plot along mixing lines to the right of the linear correlation. The small group of samples that plot to the left of the linear correlation have relatively low NO_3^-N concentrations and probably represent groundwater samples in which the NO_3 concentration have decreased due to mixing with water containing little NO_3^-N.

$\delta^{13}C$ of DIC and ^3H of Water The $\delta^{13}C$ values of the DIC for the wells ranged from –7.7 to –14.3‰ (Table 16), which was similar to the range for the springs. As with the spring water, the more negative $\delta^{13}C$ values for the well samples suggested that a considerable proportion of the water infiltrated rapidly from the soil zone. The less negative $\delta^{13}C$ values suggested that the groundwater had reacted with the rock to a greater degree after passing through the soil zone and, therefore, was probably older and had traveled a longer pathway before reaching the well. This interpretation is supported

Table 15 Bacteria (genera and species) present in water samples from wells and their ranking relative to their dominance in the groundwater samples.

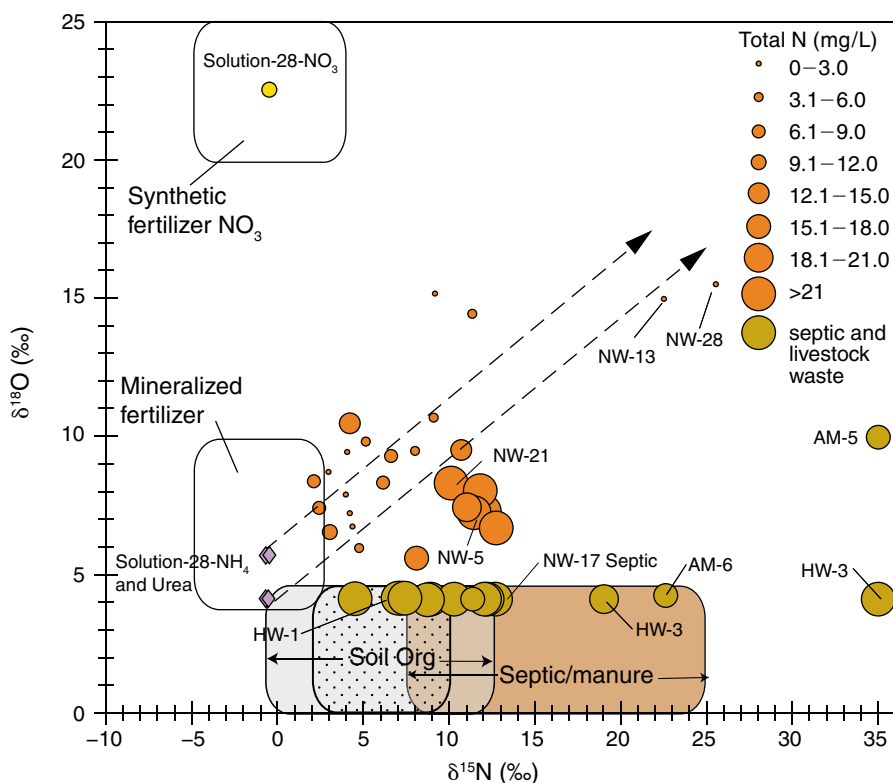| Genera and species	Relative rank	Percent present	Final rank
Pseudomonas spp.	2.0	92	1
Bacillus spp.	3.0	86	2
Klebsiella pneumoniae	4.9	57	3
Enterobacter aerogenes	6.3	36	4
Enterococcus faecium	6.8	36	5
Serratia spp.	6.9	21	6
Enterococcus faecalis	7.6	14	7
Escherichia coli	7.9	7.1	8

Figure 24 $\delta^{15}N$ and $\delta^{18}O$ of NO_3^- for the wells and end-member samples including fertilizers and septic and livestock waste. The relative nitrogen concentration (NO_3^- plus NH_4) is depicted by the size of the circles (mg of N/L). The $\delta^{18}O$ values for the fertilizer, the livestock waste, and most of the septic samples were calculated (except NW-17 and AM-5), as described in the text. Typical trends for denitrification are shown by the dashed arrows. Isotopic ranges characteristic of different sources are also shown (general domains taken from Kendall et al. 1995, Clark and Fritz 1997, Mengis et al. 2001). Stippled area indicates most typical $\delta^{15}N$ values for soil organic nitrogen.

by the correlation between $\delta^{13}C$ and ^3H observed for most of the wells (Figure 26). The samples with greater ^3H concentrations (5 to 6 TU) are indicative of younger water that very recently percolated into the subsurface sediments.

Most samples that had larger ^3H concentrations also had greater NO_3^- concentrations (Figure 27), which again suggested that the groundwater containing high NO_3^- concentrations was young water. However, the shallow well, well 5 (NW-21), did not follow this trend. Sample NW-21 had a small amount of ^3H, a large NO_3^- concentration, and a relatively low $\delta^{13}C$ value.

These results suggested mixing of young infiltrating water from the soil zone with older groundwater from the bedrock limestone. Panno et al. (1996) noted springs discharging through the loess deposits on this property. The spring water appears to originate from the bedrock limestone.

δD and δ^{18}O of Water The values for δD and $\delta^{18}O$ of the water from the wells were very similar to those values for the water samples from springs; most samples plotted near the GMWL (Figure 28). The isotopic composition of water from at least seven of the wells plotted along the same trajectory below the GMWL as several of

the water samples from springs. The trajectory of these samples follows the evaporation line, which indicates that considerable evaporation took place prior to infiltration into the subsurface in some of the watersheds of the sinkhole plain. The wells that followed the evaporation trajectory were located in the same watersheds as spring samples that plotted along the evaporation line. These results suggested a strong connection between the groundwater sampled by the wells and the crevice and conduit karst system supporting the springs.

δ^{34}S of Sulfate The range of $\delta^{34}S$ values was much larger for water from the wells than for water from the springs. The $\delta^{34}S$ of the well samples ranged from –13.6 to +3.8‰ (Table 16). Most of the groundwater sampled from the wells had $\delta^{34}S$ values greater than –1‰, which were similar to values for the spring water, suggesting that the source of the sulfate in many of the wells was the same as in the spring water. However, samples from 3 wells had significantly lower $\delta^{34}S$ values, indicating a different sulfate source than that for the spring water. The more negative $\delta^{34}S$ values for the sulfate in these 3 wells indicated oxidation of reduced sulfur. The source of the reduced sulfur may have been from pyrite in the bedrock or dissolved H_2S in the deeper groundwater. The sinkhole plain is known to have groundwater seeps containing H_2S (Panno et al. 2005). Some of the wells possibly were screened in an area where deeper groundwater containing H_2S mixed with younger recharge water containing dissolved oxygen that oxidized the sulfide sulfur to sulfate. Two of the 3 wells containing considerably negative $\delta^{34}S$ values also had relatively low ^3H concentrations, indicating an older groundwater component. Well 13 (NW-13 and NW-28) had a quite negative $\delta^{34}S$ rating, the most positive $\delta^{15}N$ and $\delta^{18}O$ values for NO_3^-, and very low NO_3^- concentrations, suggesting that perhaps reduced sulfates (pyrite) played a role in the denitrification process at this site.

Table 16 Isotopic data for water samples from wells in the study area.

Sample	Well	δ15N (‰)	δ18O_NO3 (‰)	δ18O (‰)	δD (‰)	δ13C (‰)	δ34S (‰)	Tritium (TU)[1]
NW-1	1	6.8	9.2[2]	−5.53	−37.3	−13.2	−0.6	--[3]
NW-2	2	2.2	8.3[2]	−5.93	−41.7	−13.2	1.2	--
NW-3	3	4.5	6.6[2]	−5.99	−41.5	−8.3	−7.7	2.6
NW-4	4	4.3	10.4[2]	−5.25	−35.4	−14.1	1.3	--
NW-5	5	11.7	7.1	−6.26	−42.3	−13.0	--	--
NW-7	7	4.1	9.4[2]	−6.21	−41.2	−8.9	−11.2	1.8
NW-8	8	4.1	7.8[2]	−5.87	−42.1	−11.8	3.8	6.1
NW-9	9	12.0	7.8	−3.85	−29.8	−12.1	1.6	6.1
NW-10	10	9.2	10.6[2]	−2.37	−25.4	−12.3	−4.7	5.4
NW-11	11	4.8	5.8	−6.10	−45.9	−11.9	1.9	5.6
NW-12	12	8.3	5.5	−5.87	−39	−13.8	1.4	6.9
NW-13	13	22.9	14.9[2]	−6.91	−38.9	−7.8	−13.4	2.2
NW-14	14							7.4
NW-15	14	12.9	6.7	−6.38	−45	−14.3	0.5	9.2
NW-16	15	9.0	--	−6.42	−43.9	−14.1	2.7	7.2
NW-17	1	8.2	9.4	−6.25	−41.8	−13.1	−10.0	5.9
NW-18	2	2.5	7.3[2]	−6.3	−42.6	−12.8	--	6.0
NW-19	3	4.3	7.1	−6.4	−42.0	−8.6	--	1.3
NW-20	4	3.1	6.4	−5.94	−40.8	−13.2	--	5.5
NW-21	5	10.3	8.3	−6.495	−42.4	−13.2	2.5	2.5
NW-21D	6	--	--	−6.24	−42.1	−11.6	−2.7	0.8
NW-22	8	2.9	8.6	−6.43	−40.4	−10.9	--	4.4
NW-23	9	10.9	9.5	−2.87	−25.6	−12.3	2.3	4.9
NW-24	10	11.6	14.4	−2.21	−23.0	−11.6	−5.4	5.0
NW-25	11	5.2	9.7[2]	−5.71	−38.5	−11.1	1.3	6.1
NW-26	12	11.2	7.3	−5.99	−42.7	−13.5	1.1	6.6
NW-27	14	12.3	7.2	−6.32	−40.2	−13.2	--	6.3
NW-28	13	25.9	15.5[2]	−6.74	−46.2	−7.7	−13.6	2.0
NW-40	16	9.4	15.1	−4.15	−31.1	−12.3	--	5.6
NW-42	17	6.3	8.2	−6.39	−41.2	−14.3	--	5.6

[1] TU, tritium units.

[2] Standard deviation, 1.7.

[3] --, not determined.

Figure 25 δ15N versus ln[NO3−N] of groundwater samples showing effects of denitrification and groundwater mixing. Samples affected by denitrification follow the diagonal trend, whereas groundwater samples for which nitrate is affected by mixing follow an arcuate or horizontal trend away from the denitrification line.
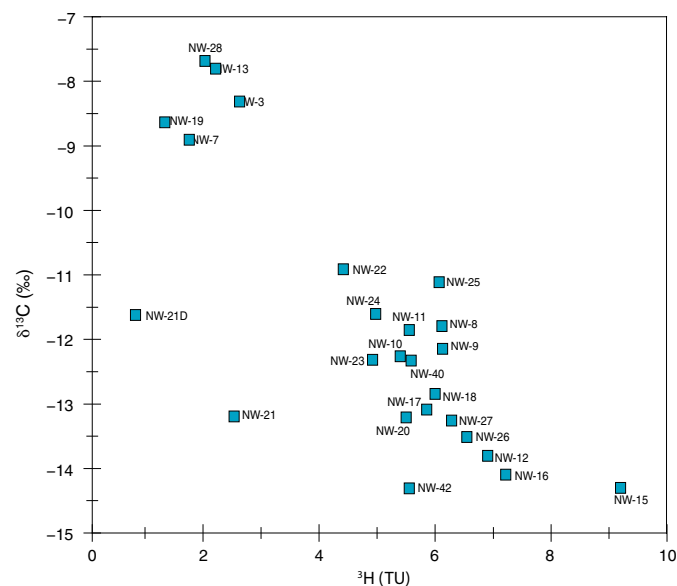

Figure 26 Correlation between δ13C of dissolved inorganic carbon and 3H for the wells, showing more negative δ13C values with greater tritium concentration. TU, tritium units.
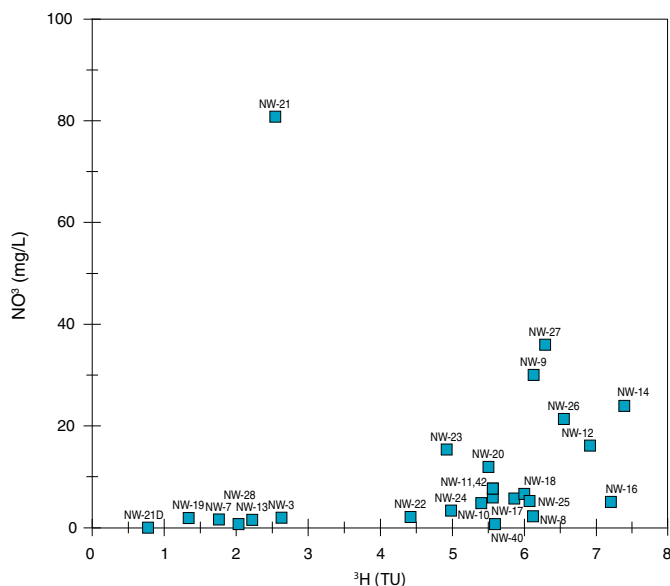
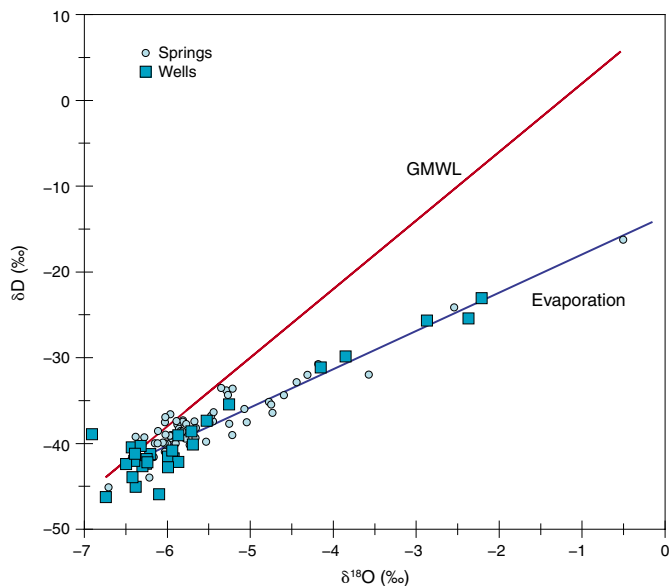**Figure 27** Nitrate concentration and ^{3}H values for wells sampled. TU, tritium units.

Figure 28 Isotopic composition (δD and $\delta^{18}O$) of groundwater sampled from wells. Water samples from springs are shown for comparison.

Summary and Conclusions

Seasonal variations in field and chemical measurements as well as isotopic results for the 10 springs sampled in the sinkhole plain of southwestern Illinois indicated that water from the surface and soil zone infiltrates quite rapidly into the shallow karst aquifer. Temperature, fluorite concentrations, and $\delta^{13}C$, $\delta^{18}O$, and δD results varied by season for most of the springs. Both ^{3}H and $\delta^{13}C$ of the DIC indicated that the karst aquifer was rapidly recharged with water from the soil zone that carried with it elevated amounts of NO_3^- and chloride derived from anthropogenic sources. The bacterial results also attested to the rapid infiltration of contaminants from the surface environment.

The NO_3^- concentrations in the springs, representative of the overall shallow karst groundwater system, were approximately 1.5 to nearly 4 times greater than the threshold background level of 2.5 mg of N/L. The isotopic data suggested that the sources of NO_3^- in the spring water were dominated by nitrogen fertilizers and soil organic matter and that livestock and septic effluent played a

very minor role. During the springtime, the isotopic values of NO_3^- in the water samples plotted close to values typically expected for NO_3^- originating from soil organic matter and nitrogen fertilizers, which are applied primarily in the early spring (late March and April). The $\delta^{18}O$ of the NO_3^- in several of the samples from the springs that contained relatively small NO_3^- concentrations appeared to have been influenced by NO_3^- sources containing isotopically heavy $\delta^{18}O$ values. Such sources may include NO_3^- fertilizers, atmospheric NO_3^-, or NO_3^- formed in the soil zone with greater than expected $\delta^{18}O$ values because of soil water enrichment from evapotranspiration or nitrification (Mayer et al. 2001, Burns and Kendall 2002). More detailed investigations are necessary to help determine which of these possible sources of ^{18}O-enriched NO_3^- is more responsible for the relatively large $\delta^{18}O$ values observed for some of the NO_3^- in shallow groundwater and streams in the study area.

Chemical, isotopic, and bacterial results indicated that many of the wells received a large portion of their water directly from the soil zone or from water originating close to the surface environment. Because most

of the wells in this region are usually cased only down to the top few feet of the bedrock, contaminated surface and soil water may easily flow through the crevices and conduits of the weathered zone near the top of the limestone bedrock and into the wells.

Five of the 17 wells sampled in this study had NO_3^- concentrations that were greater than the USEPA (1992) drinking water standard of 10 mg of N/L. Twelve of the well samples had NO_3^- concentrations that were greater than background concentrations. The greatest NO_3^- concentrations were detected in the shallow wells located in covered karst areas. However, one of the deeper wells (>70 m) contained relatively large NO_3^- concentrations, indicating that water from the surface may easily enter the deeper, uncased wells. The $\delta^{15}N$ and $\delta^{18}O$ data of the dissolved NO_3^- indicate that the source of NO_3^- in the wells containing the greatest NO_3^- concentrations (>15 mg of N/L) was predominantly from livestock and/or septic waste. These same wells also had large concentrations of chloride and considerable amounts of coliform bacteria, both of which are typical of animal waste. The isotopic composition of the NO_3^- in the wells with smaller NO_3^- con-

centrations (1.7 to 12 mg of N/L) indicated that the predominant source of NO_3^- was from nitrogen fertilizers, soil organic matter, or both.

The overall positive trend between $\delta^{15}N$ and $\delta^{18}O$ values, in both the spring and well samples, suggested the occurrence of denitrification within the soil zone, epikarst, and/or shallow karst hydrogeologic system. Microbial denitrification probably occurs primarily by oxidation of dissolved organic matter, considering concentrations of DOC in the samples were relatively large from both springs and wells. However, the very negative $\delta^{34}S$ values and positive $\delta^{15}N$ and $\delta^{18}O$ for one well suggest that sulfide (pyrite) oxidation could have also played a role in some cases for the denitrification process in this region.

This study demonstrated the usefulness of measuring the $\delta^{15}N$ and $\delta^{18}O$ of dissolved NO_3^- in water discharged from springs in a karst terrain to help determine the dominant sources of NO_3^- in shallow groundwater basins and the occurrence of denitrification. Measurements of $\delta^{15}N$ and $\delta^{18}O$ of NO_3^- in wells are useful for evaluating the impact of local land use practices on groundwater. The combination of chemical, isotopic, and bacterial analyses demonstrated the openness of the karst aquifer. Seasonal variations in the chemical and isotopic analyses illustrated how surface contaminants can quickly affect the quality of both shallow and deep wells in a karst environment.

Acknowledgments

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