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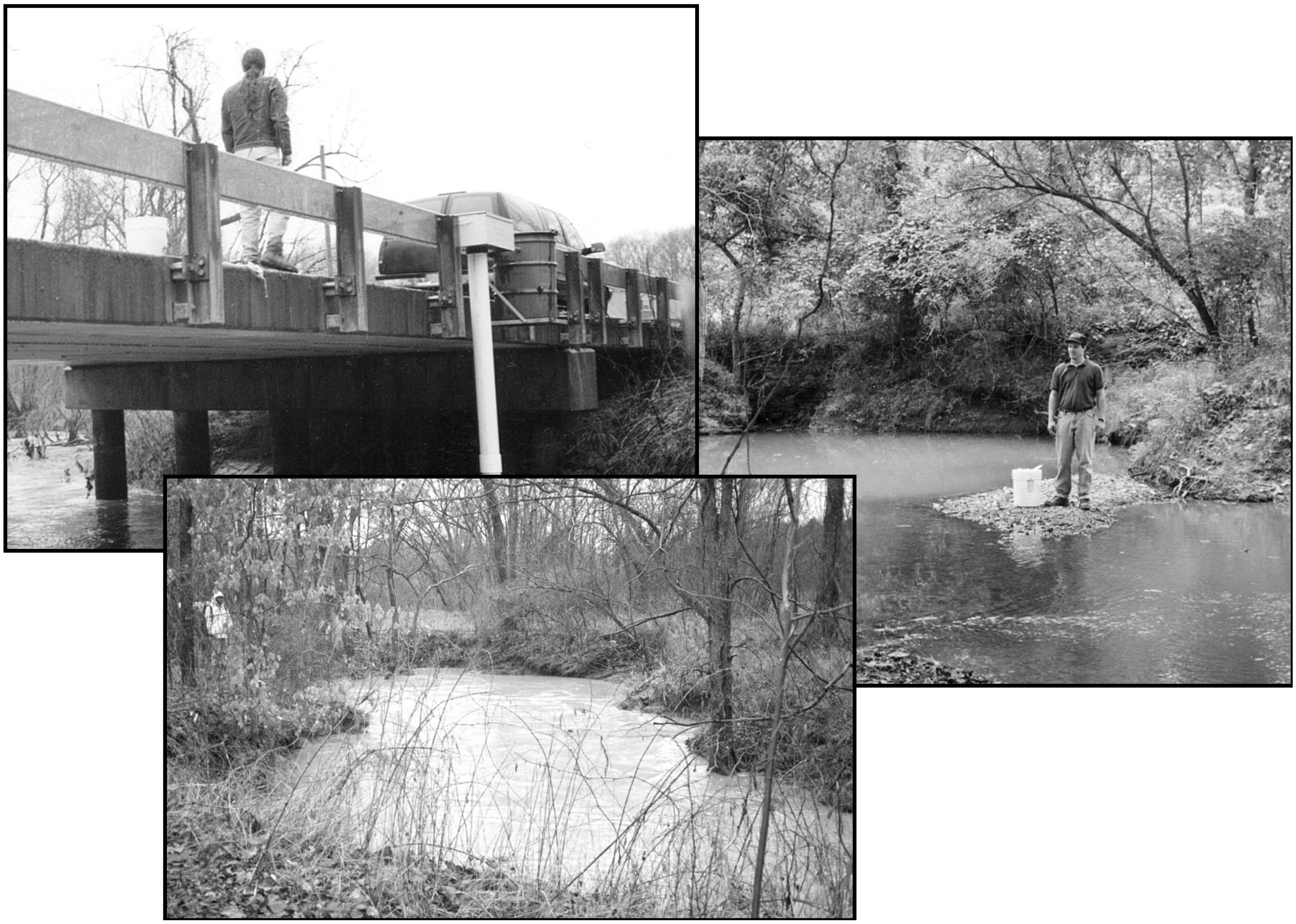

Environmental Geology 156 2003

Rod R. Blagojevich, Governor

Department of Natural Resources
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ILLINOIS STATE GEOLOGICAL SURVEY
William W. Shilts, Chief

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Cover: *(Upper left) The stream monitoring and water sampling system on the South Fork Creek bridge. (Lower left) Collier Spring under flood conditions. (Center right) Collier Spring, a circular feature and the headwaters of South Fork Creek, is also the resurgence of a cave or conduit system that, at some point, flows beneath Fogelpole Cave.*

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Contents

Tables

Figures

Abstract

In a karst area, leaching and runoff of agrichemicals and animal waste from land dominated by row crops and livestock can rapidly contaminate groundwater with nitrogen (N), phosphorous (P), pesticides, bacteria, and soil. Discharge of contaminated groundwater from groundwater basins can contribute to the degradation of water quality in surface streams and, ultimately, coastal areas. To understand the possible extent of contamination in one karst region, we monitored two groundwater basins in Illinois' sinkhole plain from October 1996 to August 1998 during a period of average precipitation. We examined the character and degree of bacterial contamination, the mass of atrazine on suspended solids, and the soil erosion rates of two karst springs and their spring-fed stream.

The two karst springs—Collier and Indian Hole Springs—drain relatively large groundwater basins (approximately 19.9 km^2 [7.68 mi^2] and 17.8 km^2 [6.87 mi^2], respectively) in southwestern Illinois' sinkhole plain. The springs are located 400 m (1,300 ft) from each other and form the headwaters of the South Fork of Horse Creek. Groundwater was monitored as it discharged from Collier and Indian Hole Springs and at a monitoring station (a bridge) downstream of the springs. Water quality analyses and stream discharge measurements were used to calculate the total quantity of selected agrichemicals (NO_3^--N, PO_4^{3-}, and herbicides) (mass loading) being carried out of the groundwater basins to surface streams.

The NO_3^--N concentrations in water samples ranged from 1.08 to 6.08 mg/L; median concentration was 3.48 mg/L. Atrazine and alachlor concentrations ranged from <0.01 to 34.0 µg/L and <0.01 to 0.98 µg/L, respectively; median concentrations were 0.52 and 0.12 µg/L, respectively, for all sites. The two groundwater basins discharged approximately 100,000 kg/yr (220,000 lb/yr) of N as NO_3^--N, 39 kg/yr (86 lb/yr) of atrazine, and 2.8 kg/yr (6.2 lb/yr) of alachlor. These values represent a 21 to 31% loss of fertilizer N, a 3.8 to 5.8% loss of applied atrazine, and a 0.05 to 0.08% loss of applied alachlor. The loss of atrazine adsorbed onto the suspended solid fraction was low relative to the mass of atrazine in solution and amounted to only about 2 kg/yr (4 lb yr) or 5.1% of the total mass of atrazine discharging from the groundwater basins. Phosphate concentrations in water were typically less than 0.01 mg/L, suggesting that the loss of dissolved P was insignificant.

Bacteria identified in the spring water included 17 genera and species present in millions of colony-forming units/100 mL of water. *Klebsiella pneumoniae*, *Pseudomonas* spp., *Escherichia coli*, and *Bacillus* spp. predominated.

The soil erosion rate in the study area, based on the suspended solids load in the stream at the bridge (10^8 kg/yr or 2.2 × 10^8 lb/yr), was estimated to be approximately 0.15 cm/yr (0.06 in/yr)—or about twice the rate of soil losses in the rest of Illinois.

Introduction

Loss of agricultural chemicals from leaching and runoff from croplands and animal waste from livestock grazing areas can load streams and shallow groundwater with nitrogen (N), phosphorous (P), pesticides, and bacteria. The contamination of groundwater and surface water with nitrogenous compounds went from a local problem in the early 1970s, to a regional problem in the 1990s (Heathwaite et al. 1993), and is now becoming a problem worldwide (Hallberg and Keeney 1993, Rabalais et al. 1996, Diaz 2001). Because of the intensive agricultural activities in Illinois and the portion of the central and midwestern United States drained by the Mississippi River, N contamination of groundwater and surface water has become a widespread problem (Schock et al. 1992, Kolpin et al. 1998, Groschen et al. 2000, Randall and Mulla 2001). For example, some scientists have attributed the hypoxic zone in the Gulf of Mexico to excessive algal growth brought on by nutrients delivered by the Mississippi River (Rabalais et al. 2001, Goolsby et al. 2001). In addition, human health problems are associated with coliform bacteria (Craun 1979), NO_3^- (O'Riordan and Bentham 1993), and pesticides (Kelce et al. 1995). Pesticides have also been linked to environmental problems associated with endocrine disruption and the feminization of aquatic organisms, leading to reproductive problems (Colborn et al. 1993, Kelce et al. 1995, McLachlan and Arnold 1996). The herbicides atrazine and alachlor are examined in this investigation. Soil cultivation can accelerate soil erosion and lead to transport of sediments with elevated concentrations of these contaminants into surface streams and, in karst areas, into the groundwater system.

Septic systems (N, phosphate, and bacteria) and atmospheric deposition (N) are also potential sources of stream pollution. Discharge of their contaminants to surface streams, in many cases via groundwater, can degrade the water quality of higher-order streams and other bodies of water fed by these streams (Rabalais et al. 1996).

Karst regions of the world are especially susceptible to groundwater contamination from fertilizer N, associated agrichemicals, and other surface-borne sources of N (e.g., Feth 1966, Hallberg 1986, White 1988, Pasquarell and Boyer,1995). In the central United States, water quality problems have been observed in springs and wells in the karst region of southwestern Illinois (Panno et al. 1994, 1996), northeastern Iowa (Rowden et al. 1993), and Kentucky (Currens 1999, Ryan and Meiman 1996). Although several investigators have measured dissolved constituents in karst hydrologic systems during flooding (e.g., Ryan and Meiman 1996), only a few researchers have conducted such studies on a scale wide enough to encompass the groundwater basin (Rowden et al. 1993, Currens 1999).

Karst regions, such as the "sinkhole plain" in Monroe, Randolph, and St. Clair Counties in southwestern Illinois (fig. 1), are distinguished by numerous sinkholes, disappearing or losing streams, large springs, and caves (Panno 1996, Weibel and Panno 1997). Water quality in these regions has long been known to be highly susceptible to contamination from surface activities. Because of the rapid movement of water and suspended sediment into subsurface cave and conduit systems in this region, the amount of time available for purifying reactions—such as adsorption, degradation, and filtration in the subsurface—and the opportunities for exposure to them are limited (White 1988). The contamination potential is especially acute during flood events, when large volumes of water carrying large loads of suspended sediment that have eroded from cropland soil and other sources are rapidly flushed through karst aquifers.

Further, new sinkholes may develop, and existing ones may expand, during and following heavy rains. The extent and effects of erosion in the sinkhole plain are reflected in complaints of water quality degradation by owners of private wells in karst aquifers. Complaints about high concentrations of suspended sediment in well water commonly are received by the Monroe-Randolph Bi-County Health Department in Waterloo, Illinois, following intense rainfall and related flooding events (J. Bade, personal communication 1994). Much of the suspended sediment in floodwaters of the sinkhole plain results from erosion of topsoil and surficial deposits (predominantly glacial till), which, in this agricultural region, could contain adsorbed pesticides. Desorption of pesticides during sediment transport or following deposition could cause elevated concentrations of agrichemicals in surface streams.

Panno et al. (1994, 1996) initially investigated the problems associated with groundwater contamination in the karst regions of southwestern Illinois. Groundwater samples from over 30 domestic wells and 10 springs in Monroe and Randolph Counties were found to contain large concentrations of agrichemicals during and just after spring planting. For example, in 1994, floodwaters issuing from a spring that drained a groundwater basin in the sinkhole plain dominated by row crops were sampled following the first significant rainfall after planting. Concentrations of the herbicides atrazine and alachlor in the water samples were as high as 97 and 16 μg/L, respectively. However, atrazine and alachlor concentrations in all well-water samples from the same area were always below the U.S. Environmental Protection Agency's (USEPA) maximum contaminant levels (MCL) of 3 and 2 μg/L (USEPA 1992), respectively.

For this investigation, the areas selected for monitoring were the Collier Spring and Fogelpole Cave groundwater basins and their discharge points. These groundwater basins were chosen because their land use is dominated by agriculture (predominantly croplands), and the terrain is intensely karstified. We hypothesized that the results from this investigation could represent a worst-case scenario for the loss of applied fertilizer N to a watershed. The basins were delineated via dye-tracing techniques (Aley et al. 2000) and are underlain, in part, by Fogelpole Cave, a bedding-plane–controlled, branchwork-type cave (Panno et al. 1998a) with over 22.5 km (14 mi) of mapped passages (Paul Wightman, personal communication 1997), and what appears to be an equally long but inaccessible cave (Panno et al. 1998a, Aley et al. 2000). Drainage from the basins exits through two springs (Collier and Indian Hole) that form the headwaters of the South Fork of Horse Creek (locally and herein referred to as South Fork Creek) (fig. 1). A monitoring site was located 2.4 km (1.5 mi) downstream from the two springs along South Fork Creek. The stream drains into Horse Creek, which, in turn, drains into the Kaskaskia River, which discharges to the Mississippi River. A bridge spanning South Fork Creek was the site of much of our monitoring effort.

Objectives

The primary objective of this investigation was to determine the mass loading of selected agrichemicals and the character and degree of bacterial contamination of the springs and a spring-fed stream discharging from the two groundwater basins. Because the two groundwater basins are intensely karstified and land use within the basins is dominated by agriculture, we hypothesized that discharge from these basins might represent a worst-case scenario for the loss of applied agrichemicals to a surface stream.

The secondary objective was to estimate the rate of soil erosion and the potential for the transport of pesticides adsorbed on suspended solids out of the basins. Erosion is severe in many places in the sinkhole plain because of the open conduits and cultivation practices. We hypothesized that the amount of sediment discharging from these groundwater basins could constitute a worst-case scenario for soil erosion in an intensively cultivated karst area.

Geology and Basin Hydrology

Monroe County is on the western margin of the Illinois Basin where bedrock dips gently to the east toward the center of the basin. Here, beds of Mississippian age limestone, sandstone, and shale lie at or near the surface. In the western part of the county, where calcite-rich limestone beds lie at or near land surface, karstification is a dominant process. This region is referred to as the sinkhole plain because of its high density of sinkholes. Approximately 10,000 sinkholes, numerous large springs, and the longest caves in the state are found here (Panno 1996). Glacial drift and other materials that overlie the bedrock in the upland areas of Monroe County are relatively thin (typically less than 15 m (50 ft)), and bedrock exposures are common (Piskin and Bergstrom 1975). The upland area (about two-thirds of Monroe County) is, for the most part, covered with Illinoian glacial till and/or residuum that is overlain by a layer of loess (windblown silt). Loess and till are easily eroded and form steep-sided sinkholes and associated gullies (Hansel and Johnson 1996).

The chemical composition of groundwater and surface water in the sinkhole plain (wells, cave streams, springs, and surface streams) is characterized as a Ca^{2+}-HCO_3^- –type water, which is typical of waters in contact with limestone (Panno et al. 1996). The majority of caves and sinkholes in the sinkhole plain occur in the calcite-rich, Mississippian age Ste. Genevieve and St. Louis Limestones and in the overlying sediments, respectively (Panno et al. 1997a). Structures in the vicinity of the study area include the northwest-southeast–trending Valmeyer Anticline and Monroe City Syncline (Weller and Weller 1939, Nelson 1995). These structures and local bedrock topography played major roles in the formation of Fogelpole Cave, the Fogelpole Cave groundwater basin, adjacent large caves and their groundwater basins, and associated karst terrane in this area (Panno and Weibel 1999). Fogelpole Cave—the longest known cave in Illinois—lies on the northeast limb of the Valmeyer Anticline, and its directional trend parallels the axis of the anticline.

Panno and Weibel (1999) mapped the approximate boundaries of the groundwater basins of the four largest known cave systems in the sinkhole plain using sinkhole distribution, water table elevation, and bedrock topography. This initial mapping showed that the boundaries of the two groundwater basins discussed herein lie parallel to and just to the northeast of the axis of the Valmeyer Anticline. Both basins are bounded on the northeast by the Illinois Caverns and Kruegers Dry Run Cave groundwater basins, lie within the Horse Creek Watershed, and terminate at two large springs, Indian Hole and Collier. Further work by Aley et al. (2000) refined the basin boundaries through the use of tracer dyes. The refined basin boundaries showed that the Collier Spring groundwater basin lies, in part, to the south of the Fogelpole groundwater basin and that the two groundwater basins had a shared recharge area (fig. 1).

Methods

Groundwater Basins

The study area consists of two groundwater basins: (1) the Fogelpole Cave groundwater basin that is drained by Fogelpole Cave, which, in turn, feeds Indian Hole Spring, and (2) the Collier Spring groundwater basin is drained by a separate conduit system, which, in turn, feeds Collier Spring (Panno et al. 1998a, Aley et al. 2000). The two

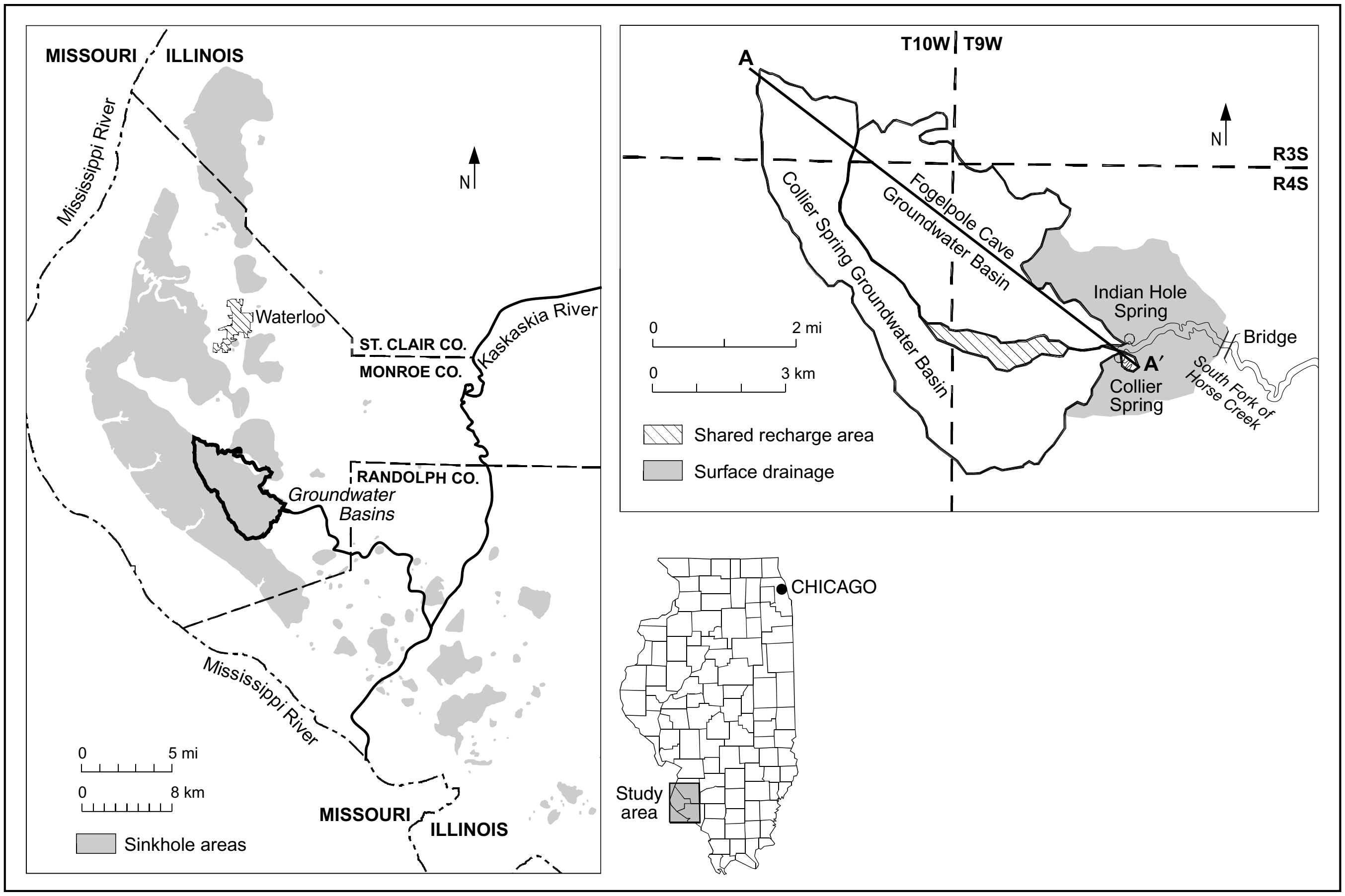

Figure 1 Karst terrane of southwestern Illinois' sinkhole plain (left) showing sinkhole areas, sinkhole density, and location of the Collier Spring and Fogelpole Cave groundwater basins. The boundaries of the groundwater basin, sampling sites, and line of cross-section A–A′ (fig. 9) are shown on the right (modified from Panno et al. 1999, Aley et al. 2000).

basins have mostly distinct drainage areas and relatively small areas with shared drainage (Aley et al. 2000; fig. 1, table 1).

The areas of the two groundwater basins are similar, and land use is predominantly agriculture. The total area for the two groundwater basins that feed the stream is 37.7 km^2 (14.6 mi^2). Additional drainage area to the stream (the area drained between the springs and the bridge) must be considered when interpreting data from water samples collected at the bridge, which lies 2.4 km (1.5 mi) downstream from the springs. That area is approximately 10.9 km^2 (4.2 mi^2) and increases the total area to 48.6 km^2 (18.8 mi^2). Detailed examination of the land use in the basins shows that it is dominated by row crops and grasslands (table 2). Crops include milo, alfalfa, soybeans, wheat, corn, and barley. Herbicides, predominantly atrazine and alachlor, typically are applied in April and May; the application of the herbicide alachlor has decreased significantly since the initiation of this investigation, and its use is being phased out. Nitrogen fertilizer is applied once or twice per year, usually in the spring and fall (Panno et al. 1996). Potassium and phosphate fertilizers are applied as needed (P. Kremmell, U.S. Department of Agriculture [USDA], personal communication 1998).

The average precipitation for the study area, measured at Red Bud, Illinois (located about 10 km [6.2 mi] east of the study area), was 107 cm (42 in) for 1990–2000. The average precipitation during 1996 to 1998 was 103 cm (41 in) (J. Angel, State Climatologist, personal communications). Thus, the period during which we conducted our investigation had average precipitation and should have yielded representative loadings of agrichemicals in the springs and stream, as well as erosion rates.

Table 1 The drainage areas of the Fogelpole Cave and Collier Spring groundwater basins as determined from maps by Aley et al. (2000) and using GIS techniques.

	Area of each drainage[1]		Total area	
Groundwater basin	(km^2)	(mi^2)	(km^2)	(mi^2)
Fogelpole Cave (FC)	16.9	6.52	17.8[2]	6.87
Collier Spring (CS)	19.2	7.41	19.9[2]	7.68
Shared (FC and CS)	1.44	0.56		
Shared (FC and IC[3])[4]	0.27	0.10		
Total area of basins	37.7	14.6	37.7	14.6
Surface drainage	10.9	4.2	10.9[5]	4.2
Total area of study			48.6	18.8

[1] Area of each drainage is the area that constitutes a single groundwater basin, component of that basin, or separate surface drainage; total area is the area that constitutes a single groundwater basin plus any areas that make up two or more groundwater basins (overlapping basinal areas) and surface drainage between the springs and the bridge.

[2] Includes shared areas of different groundwater basins. One half of each shared basin was added to the FC and CS groundwater basins.

[3] IC, Illinois Caverns groundwater basin.

[4] Because the area is shared by Illinois Caverns, only half of this area was used to calculate total area.

[5] Includes the area of surface drainage between the springs and the bridge.

Bridge Site South Fork Creek is fed by Collier and Indian Hole Springs. However, during flooding, overland flow between the springs and the bridge enters South Fork Creek via ephemeral streams that only flow during and immediately following major rainfall events. Discharge at the bridge was determined to be about 125 L/s (2,000 gpm) under base flow conditions. Under high flow conditions, discharge measurements at the bridge were as high as 44,000 L/s (700,000 gpm) (fig. 2; table A1). Discharge and stage data (fig. 3) were fitted to a polynomial equation, which yielded the following relationship:

$$Q = 43.86(stage) + 0.4088(stage^2). \tag{1}$$

where Q is discharge in thousands of liters per second, and stage is given in centimeters ($r^2 = 0.99$). Stage measurements at the bridge site were converted to discharge measurements using this rating curve (fig. 3).

Indian Hole Spring Indian Hole Spring drains the Fogelpole Cave groundwater basin. The spring is a rel-

Table 2 Land use in the Collier Spring and Fogelpole Cave groundwater (GW) basins and the total area of those groundwater basins plus the area drained between the springs and the South Fork Creek bridge.[1]

	Total area			GW basins		
Land use categories	(ha)	(acres)	(%)	(ha)	(acres)	(%)
Row Crops[2]	1,214	3,000	25.0	1,214	3,000	32.2
Forest/Woodlands	1,794	4,433	36.9	1,059	2,617	28.1
Grasslands (e.g., pasture)	1,127	2,785	23.2	814	2,011	21.6
Small Grains	589	1,455	12.1	589	1,455	15.6
Wetlands and Water	115	284	2.36	73.3	181	2.0
Urban Build-up (e.g., pavement)	22.5	55.6	0.46	19.1	47.2	0.5
Total	4,862	12,014	100	3,768	9,311	100

[1] Land use is based on a database developed by the Illinois Department of Natural Resources (1996) and the Illinois Natural History Survey (2000). The database described the land use in 1996 and 1997, and there were no major changes to land use during this investigation.

[2] Corn and soybeans (row crops) usually are rotated annually. Acreage was assumed to contain 50% corn and 50% soybeans each year.

atively small, shallow pool; its water flows up through solutionally sculpted limestone at the head of a blind valley (box canyon) leading to South Fork Creek (fig. 4). The results of dye-tracing experiments in Fogelpole Cave indicate that Indian Hole Spring is the resurgence of Fogelpole Cave (Wightman 1967, Aley and Aley 1998). Discharge from this spring under base flow conditions was approximately 95 L/s (1,500 gpm). Indian Hole Spring is separated by a low ridge from a larger blind valley containing a circular, water-filled sinkhole most often referred to as "Indian Hole" (fig. 5). Dye-tracing experiments showed that the two features are hydraulically connected (Aley and Aley 1998). The Indian Hole sinkhole flows only during and immediately following significant rainfall events, but when it does flow, it pirates most of Fogelpole Cave's discharge from Indian Hole Spring (fig. 6). During one of these pirating events (February 17, 1998), discharge from the sinkhole and spring was measured at 8,200 L/s (130,000 gpm) (table A2). During that event, the water sample was collected from the Indian Hole sinkhole because of accessibility problems associated with flooding; all other samples were collected from Indian Hole Spring.

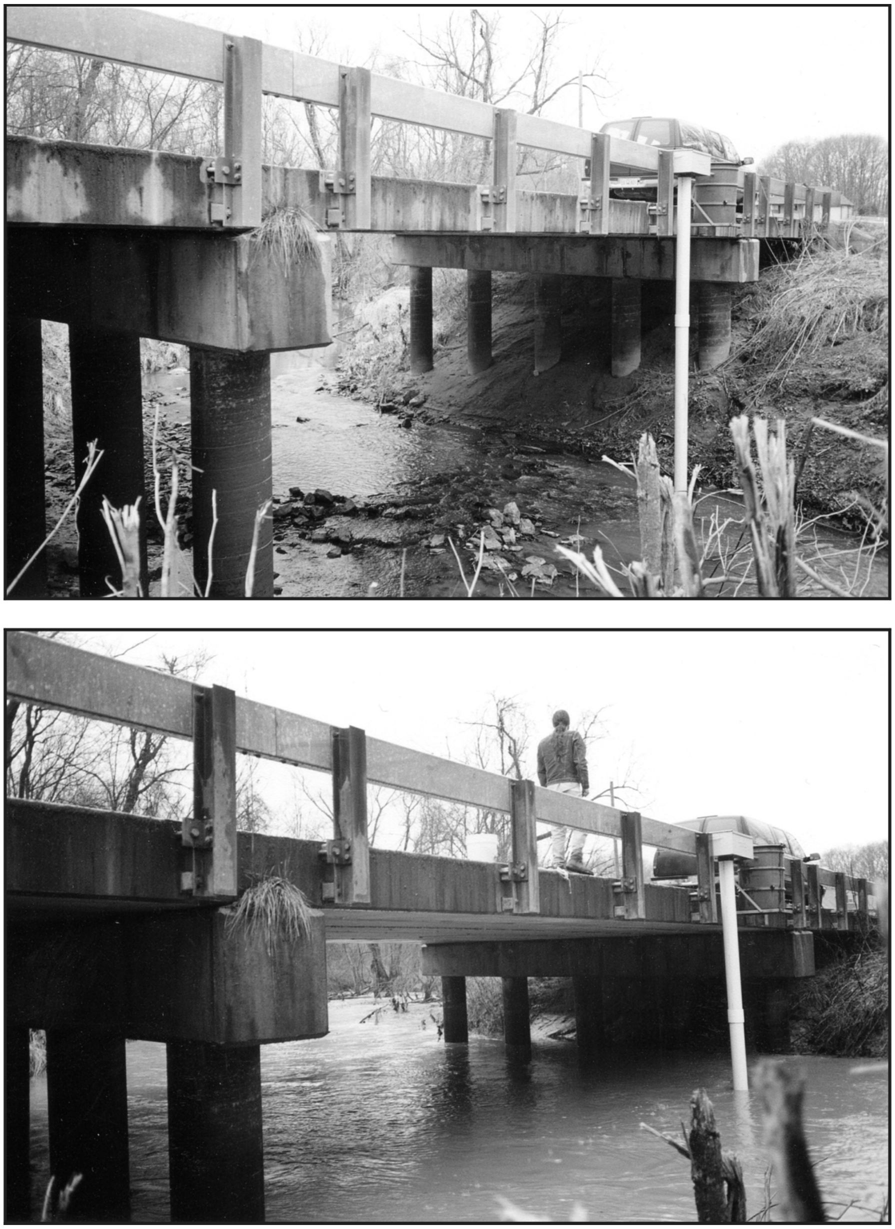

Figure 2 The bridge monitoring site at base flow (top) and flood stage (bottom). The box, pipe, and 55-gal drum mounted to the side of the bridge (on the right) contain a data logger, electrodes, and an ISCO automatic water sampler, respectively.

Collier Spring The Collier Spring groundwater basin discharges at Collier Spring located about 400 m (1,300 ft) from Indian Hole Spring. Water from this spring flows upward from a circular pool bounded by limestone bedrock at the head of a blind valley and forms the headwaters of South Fork Creek (figs. 4 and 7). Discharge from Collier Spring under base flow conditions was estimated to be about 80 L/s (1,300 gpm; fig. 8, top) and under high flow conditions was about 10,000 L/s (160,000 gpm) (fig. 8, bottom; table A3). A single dye-tracing experiment, conducted in a sinkhole in the northwestern half of the groundwater basin, resulted in the discharge of dye from Collier Spring. The dye was not detected in any of the passages of Fogelpole Cave (Aley and Aley 1998). On the basis of the dye-tracing experiments, cave maps, the geology and geomorphology of the study area, and the chemical compositions of water issuing from the two springs, Panno et al. (1999) suggested the existence of a second cave and/or conduit system that passes beneath Fogelpole Cave at some point(s). Because of the predominance of bedding-plane–controlled caves in this region (Panno et al. 1997a), the second cave, if it exists, should have a morphology similar to that of Fogelpole Cave. Panno and Weibel (1999) suggested that the two groundwater basins are separated by bedrock high to the northwest, which also controls the elevation of the surface topography. The configuration of the bedrock surface suggested that bedrock topography focused recharge to bedrock (fig. 9), thereby controlling the initiation of at least Fogelpole Cave (Panno and Weibel 1999).

Sampling

Water quality and water discharge at the South Fork Creek bridge and at Collier and Indian Hole Springs were monitored and sampled once every 2 to 3 weeks from October 1996 until August 1998. Spring discharge and stream flow rates were measured, and all water samples were analyzed in the field for temperature, pH, redox potential, and specific conductance. Field measurements of pH and specific conductance were made using calibrated, temperature-compensated meters. All water samples were collected in accordance with field techniques described by Wood (1981).

Continuous monitoring at the bridge site (fig. 1), which began in March 1997 and extended until August 1998, used an ISCO 3700™ automatic water sampler; commercially available field-durable electrodes and meters for pH, temperature, and specific conductance; and a pressure transducer for stream stage—all connected to a data logging device. During periods of high rainfall, the automatic sampler was used to sample stream water at the bridge (daily samples were a composite of 4 samples per day at 6-hour intervals). Readings from the electrodes were recorded electronically by the data logger on an hourly basis. All electrodes were calibrated every 2 to 3 weeks. The data logger and sampler were secured in tamper-resistant containers on the bridge, and the probes were encased within a secured perforated pipe that extended into the stream.

Rainfall was monitored with a recording, tipping-bucket rain gage. The rain gage was built in-house using a microprocessor-based, low-power data logger that counted tips from the tipping bucket; the log interval was once per hour. Data were stored with a time stamp in non-volatile memory (EEprom) and downloaded to a laptop computer in the field.

A rating curve for South Fork Creek was prepared by directly measuring discharge with a Global Water propeller-type flow meter and staff gauge using standard methods (Rantz et al.1982a, 1982b). Velocity was integrated across the depth of the stream by moving the propeller up and down through the entire water column for 30 seconds (per manufacturer's recommendations); the meter yielded an average velocity for that time period. Measurements were taken every 0.3 m (1 ft) along transects perpendicular to the stream banks across the width of the stream; discharge was calculated using the equation

$$Q = \sum_{i=1}^{n} v_i d_i w_i. \qquad (2)$$

where Q is the stream discharge, v is the velocity of the stream for each segment in meters per second, d is the depth of stream for each segment in meters, w is the width of each segment in meters, and n is the number of stream segments. The results were converted from cubic meters per second to liters per second. A total of 19 discharge measurements were collected for each spring and at the bridge under various flow conditions (fig. 3).

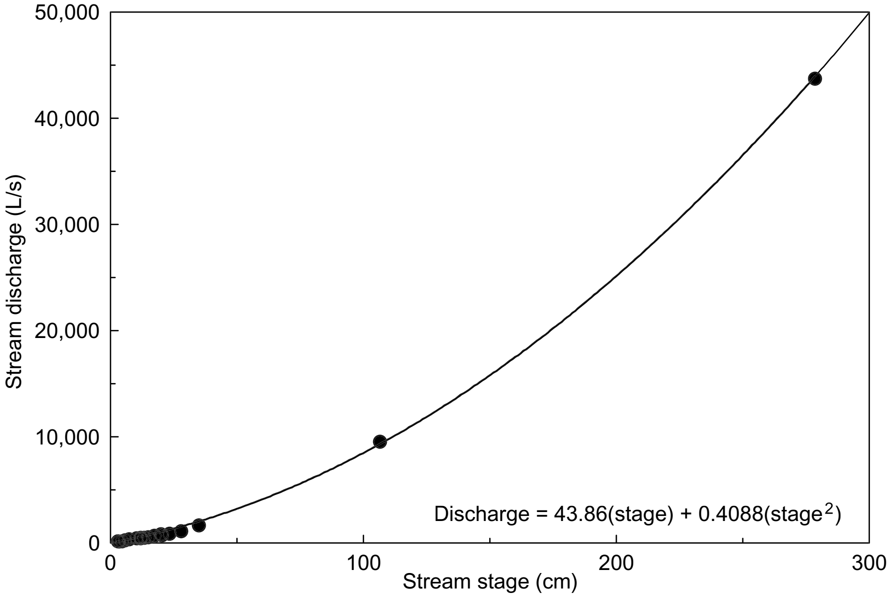

Figure 3 Stream discharge versus stream stage for South Fork Creek at the bridge site. ($r^2 = 0.99$).

Grab-type water samples also were collected every 2 to 3 weeks from the bridge site and from Collier and Indian Hole Springs. Spring samples and field measurements were collected as close to the mouth of the springs as possible; stream samples at the bridge were collected from midstream locations. Daily composite samples (4 samples; collected every 6 hours) were collected using the ISCO sampler during the spring months (from April through June in1997 and 1998). A total of 46 samples was selected, based on rainfall events in the area, and analyzed for NO_3^-, atrazine, and alachlor.

Analyses

All water samples except the ISCO samples were analyzed for cations, anions, alachlor, atrazine, bacteria, and suspended solids. A subset of samples was analyzed for dissolved organic carbon (DOC). Samples to be analyzed for cations, anions, and DOC were filtered through 0.45-µm membranes and stored in 60-mL polyethylene bottles. Samples to be analyzed for cations were acidified in the field with ultra-pure nitric acid to pH <2.0. Samples to be analyzed for herbicides were not filtered; they were stored in 60-mL, precleaned amber glass bottles. Samples to be analyzed for bacteria were not filtered; they were stored in sterile, 250-mL plastic bottles. All samples were transported to the laboratory in ice-filled coolers and they were kept refrigerated at approximately 4°C until analyses were completed. Samples to be analyzed for herbicides were filtered in the laboratory.

Concentrations of cations in water samples were determined with a Thermo-Jarrell Ash Model ICAP 61e Inductively Coupled Argon Plasma Spectrometer. Instrument operation, inter-element interference correction, background correction, and data collection were controlled using ThermoSPEC/AE 6.20 software.

Figure 4 Indian Hole Spring (top) is located at the head of a blind valley and is the resurgence of Fogelpole Cave. Collier Spring (bottom) is a circular feature and the headwaters of South Fork Creek. It is also the resurgence of a cave or conduit system that, at some point, flows beneath Fogelpole Cave.

Blanks, calibration check standards, and reference standards were analyzed with each sample set. Solution concentrations of anions were determined using a Dionex 211i ion chromatograph with Ionpac AG14 Guard Column, Ionpac AS14 Analytical Column, and Anion Self-regenerating Suppresor-11 (4 mm) following USEPA Method 300.0 (Pfaff 1993). Analytes were measured using a CDM-3 conductivity detector cell with a DS4 detection stabilizer. The eluent was prepared with 3.5 mm of sodium carbonate and 1.0 mm of sodium bicarbonate. Instrument operations and data collection were controlled using PACNET 5.01 software. A calibration check standard and blank sample were run with each sample set.

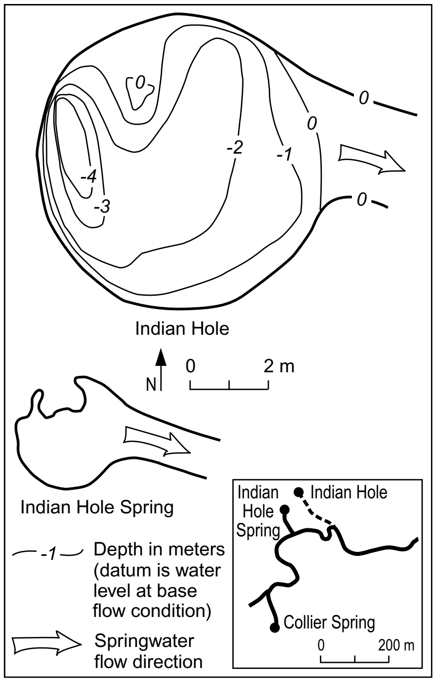

Figure 5 Contour map of Indian Hole (top) and Indian Hole Spring (bottom). Datum is water level under base flow conditions. The two features are hydraulically connected, and Indian Hole flows only during periods of flooding when it pirates water from Indian Hole Spring. The deepest part of Indian Hole is a fissure from which water discharges during high-water conditions.

The DOC in water samples was determined by difference (total carbon minus inorganic carbon) in accordance with methods described by Greenberg et al. (1992). Total carbon was determined by injecting a filtered water sample onto a heated coil (950°C) and completely combusting the sample. The mass of CO_2 driven off was determined using standard techniques. Inorganic carbon was determined by injecting the filtered sample into a weak solution of nitric acid and collecting and measuring the mass of the CO_2 driven off using an infrared analyzer (ASTM 1994).

Water chemistry data were evaluated with the chemical reaction models NETPATH (Plummer et al. 1994) and *The Geochemist's Workbench™, Version 2.0* (Bethke 1994), to determine the saturation states of all water samples. Concentrations for total dissolved solids (TDS) were calculated for water samples using the relationship

Figure 6 Indian Hole (top) does not flow under base flow conditions but pirates water from Indian Hole Spring during periods of flooding (bottom).

$$\mathit{TDS}\ (mg/L) = 0.55 \times \text{specific conductance}\ (\mu S/cm), \qquad (3)$$

which is appropriate for Ca^{2+}-HCO_3^--type groundwater (from Clark and Fritz 1997).

Samples collected for bacterial analysis were analyzed within 24 hours of collection for total coliforms, fecal coliforms, and total aerobic bacteria. Bacterial densities were determined at the Illinois Department of Agriculture's Animal Disease Laboratory, Centralia, Illinois, using standard methods to isolate and identify bacterial colonies (Clesceri et al. 1989). Data on the dominance of each bacterial species were summarized using mean ranking coupled with the percentage of each species found to be present in water samples (Panno et al. 1997b).

Water samples were analyzed for atrazine and alachlor using enzyme-linked immunosorbent assays (ELISA) to detect pesticide metabolites (breakdown products) and the pesticide of interest. The technique is sensitive (cross-reactive) to large concentrations of other triazines in groundwater (e.g., cyanazine). For simplicity, atrazine and alachlor are used throughout the text to describe the results, but metabolites (which are breakdown products) are commonly found in greater concentrations than their parent compounds in surface and groundwater (Kolpin et al. 1998, Groschen et al. 2000). The ELISA technique yields data that correlate well with samples analyzed using gas chromatography-mass spectrometry techniques (Thurman et al. 1990).

To determine suspended solids, which were used for determining erosion rates, water samples were collected biweekly in 100-mL bottles by grab sampling. Samples were analyzed using standard methods (Greenberg et al. 1992). The detection limit for suspended solids was 25 mg/L and, as such, yielded censored data, which resulted in additional uncertainty in the erosion rate estimates. Erosion rates were calculated by determining the relationship between specific conductance and suspended solids and then using that relationship to convert specific conductance into mass of suspended solids per volume of water discharging from the groundwater basin. This technique was used because there was no discernible relationship between stage and suspended solids and because continuous data were available for specific conductance at the bridge site. Although stage and suspended solids are well correlated (see Results and Discussion), the erosion rate should be considered semiquantitative because of the uncertainty associated with the technique and the estimates.

Because of its relatively low concentration, the suspended solid fraction in the water at the bridge site was difficult to collect in sufficient quantity for pesticide analysis, even during flooding. However, the plastic pipe that housed the electrodes used for continual monitoring of field parameters was perforated with small holes about 1 cm (0.4 in) in diameter. The plastic pipe fortuitously served as a low-energy environment that allowed sediment deposition between samplings. The sediment was brought to the surface as it lay on top of the plastic block that

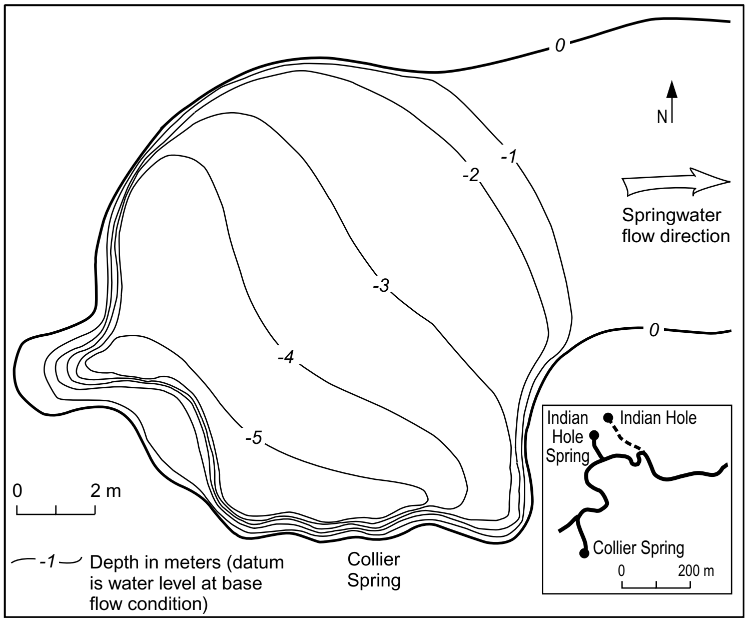

Figure 7 Contour map of Collier Spring. Datum is water level under base flow conditions. The deepest part of the spring is a fissure from which water discharges.

held the electrodes and was collected in a plastic, partially filled 19-L (5 gal) bucket of stream water. The bucket was sealed with a plastic sheet and stored at room temperature (25°C) until it was filtered, dried, and analyzed. The mixture of water and solids was vigorously stirred in the laboratory and filtered through a 35-mm diameter, 0.45-µm Millipore filter. The filter was placed under a constant vacuum of –5 psi (–34kPa) for about 24 hours. The filtrate was transferred to a watch glass and allowed to air dry for at least 24 hours. The dried samples were lightly pulverized. A 10-g (0.35-oz) portion of the dried, pulverized sample was added to a 3:1 (vol/vol) mixture of methanol and water. The mixture was shaken vigorously on a reciprocating shaker at 200 cycles/minute for 30 minutes and then allowed to sit for 24 hours. The sample was shaken again for 30 minutes and allowed to sit for 15 minutes prior to extracting a subsample for analysis (unpublished method developed by R.E. Hughes 1999). The standard ELISA technique for atrazine analysis was used (Thurman et al. 1990).

Many different methods have been used for estimating loads of chemicals in streams (Godfrey et al. 1995). The major limitation has been infrequent water sampling for the compound of interest. Although stream stage can be measured easily on a relatively continuous basis, sampling and analytical constraints usually allow only infrequent measurement of chemical parameters. One relatively robust method for estimating chemical loads in water is the discharge ratio (Hartley and Ross 1954, Godfrey et al. 1995, Anisfeld et al. 1999):

$$L = (\bar{l}/\bar{q}) \times Q. \tag{4}$$

where L is the total load of a parameter for the period of measurement, $\bar{l}$ is the average daily load, $\bar{q}$ is the average daily discharge, and Q is the total discharge for the period of measurement. Discharge was measured hourly at the bridge from March 27, 1997, to August 18, 1998. Discharges ($\bar{q}$ and Q) were determined by converting the pressure transducer data, collected hourly, into liters per second using the rating curve and then summing the values over one day ($\bar{q}$) and then one year (Q). Daily chemical loads were determined for days on which grab samples were taken by multiplying the concentration of the constituent by the discharge for that day. The average daily load ($\bar{l}$) was then determined from these daily loads.

Samples were collected 37 times for analysis during the study period.

Because the parameters vary seasonally, we limited the data used in the load calculations to a one-year period (April 1, 1997, to March 31, 1998). Percentages of agrichemical losses were calculated from the approximated basin areas, land use data, and amount of agrichemicals applied in the region.

Results and Discussion

Chemical Composition of Surface Water and Groundwater

Spring-fed surface waters and groundwaters in the sinkhole plain and the Collier and Indian Hole Springs are Ca^{2+}-HCO_3^-–type waters owing to the calcite-rich Mississippian limestone bedrock that dominates the area (figs. 10 and 11). pH ranged from 6.6 to 8.2; median value was 7.6 (fig. 12). Measurements of redox potential at the springs were comparable with those of surface water at the bridge. This result is indicative of water in contact with the atmosphere and reflects the short travel times within the shallow karst aquifer. The pH values and temperature of stream water at the bridge were typically higher during the warmer, drier months (fig. 12); the higher pH values are consistent with the greater input of groundwater and the lesser input of runoff. In addition, groundwater from the springs and surface water at the bridge were usually oversaturated with respect to calcite, dolomite, and quartz.

The oversaturation of spring water with calcite (fig. 13) generally suggests that diffuse flow is a significant component of the flow regime relative to the amount of conduit flow of groundwater through the larger cave passages. Diffuse flow allows more time for equilibration with the carbonate bedrock (Shuster and White 1972). However, this oversaturation also could be due to degassing of CO_2 from water at the springs or to low pCO_2 concentrations because of the rapid transit of recharge water through the unsaturated zone of the soil and bedrock (Lopez-Chicano et al. 2001). During periods of high flow rates, saturation indices of the waters tended

Figure 8 Collier Spring under base flow conditions (top) and under flood conditions (bottom).

to decrease, reflecting increased contributions from conduit flow. The saturation indices (SI) for calcite were typically greater (more supersaturated) for stream water (relative to spring water) during the warmer months. This increase may be due, in part, to the warmer stream waters and probably to outgassing of CO_2 from the water prior to reaching the bridge; both factors are consistent with the higher pH values found in the samples obtained at the bridge. The chemical compositions of the spring and surface waters at the bridge and at Indian Hole and Collier Springs are summarized in table 3.

The specific conductance of these waters is controlled by the dissolution of limestone (calcite) and, to a lesser extent, dolomite. As such, specific conductance can be used as a fairly accurate means of calculating the alkalinity of groundwater in the karst aquifer. Alkalinity for the Ca^{2+}-HCO_3^-–type spring-fed surface and groundwater in the sinkhole plain was calculated by linear regression using the equation

$$A = 0.48[SpC - ([NO_3^-] + [SO_4^{2-}] + [Cl^-])] - 22.8 \tag{5}$$

where A is alkalinity in milligrams per liter of $CaCO_3$; SpC is specific conductance in micro-Siemens per centimeter; and concentrations of NO_3^- (as N), SO_4^{2-}, and Cl^- are in milligrams per liter. Equation 5 was developed from 118 analyses of groundwater (springs and wells) samples from the sinkhole plain ($r^2 = 0.97$) where alkalinity was measured in the field using a standard titration method (fig. 14). A similar equation was developed by Panno et al. (1996) from the same database using only specific conductance, but the correlation coefficient was lower ($r^2 = 0.91$):

$$A = 0.42(SpC) - 15. \tag{6}$$

Specific conductance also correlates well with selected cations and anions and may be used to approximate Na^+, Ca^{2+}, Mg^{2+}, SO_4^{2-}, and, to a lesser extent, Cl^- (table 4, equations 7 to 18; fig. 15). The source of these ions in water samples collected from Collier and Indian Hole Springs and at the bridge probably is dominated by the dissolution of the surrounding rocks; Ca^{2+} and Mg^{2+} are particularly associated with the dissolution of calcite, high-Mg calcite, and dolomite. There appear to be several sources of SO_4^{2-} in spring water that potentially include fertilizer, the oxidation of organic matter from field soils, the oxidation of pyrite in bedrock, and the dissolution of gypsum in bedrock (Panno et al. 2001; Hackley et al. 2001; Hackley, unpublished data). The relationship between Ca^{2+} and SO_4^{2-} in spring waters is very close (for Collier and Indian Hole Springs, $r^2 = 0.72$ and $r^2 = 0.81$, respectively). The regression lines for these samples suggest that the ions are influenced, in part, by two distinct sources (fig. 16).

Sodium correlates well with SO_4^{2-} ($r^2 = 0.75$ for all water samples collected; not shown) and, to a lesser extent, with Cl^-. This correlation is probably related to the dissolution of limestone, dolomite,

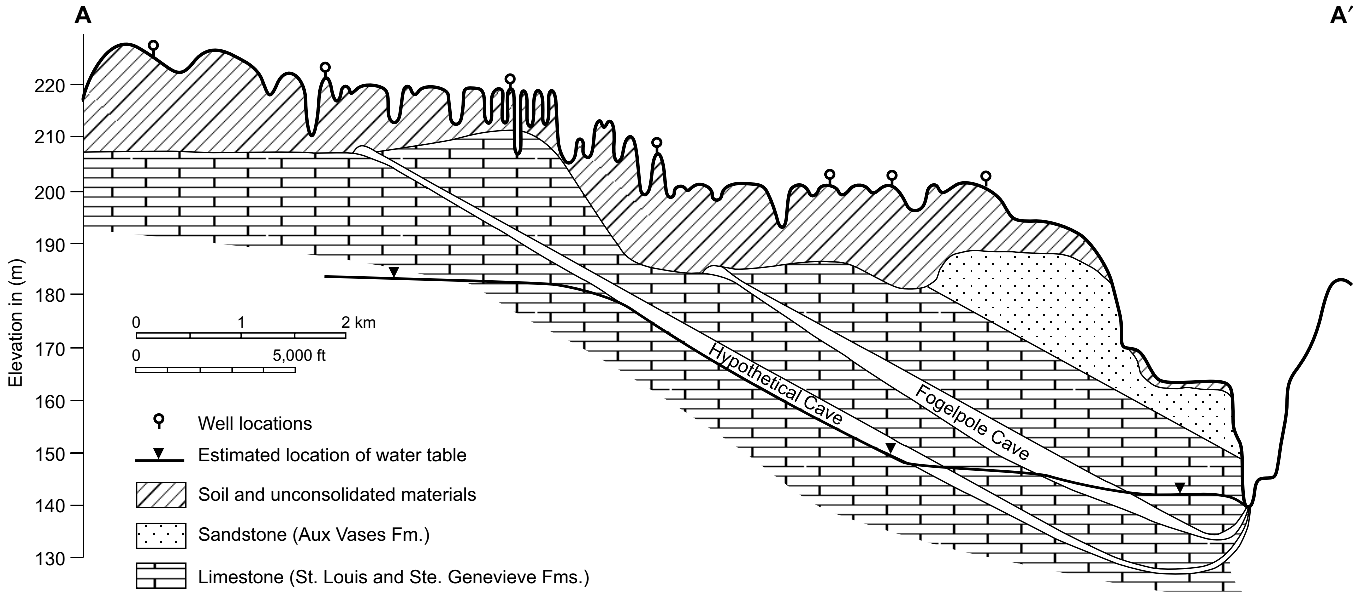

Figure 9 Cross section A–A′ (see fig. 1) showing a schematic for the approximate location of the two separate systems that drain the groundwater basin and associated bedrock controls (modified from Panno et al. 1999). Vertical exaggeration, 50×.

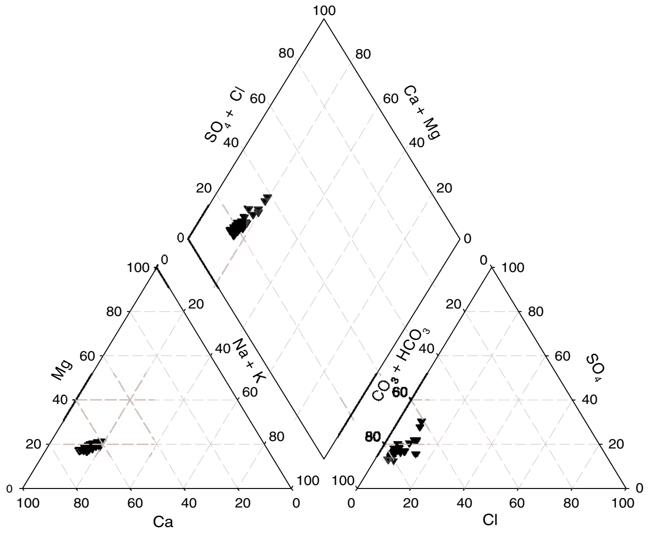

Figure 10 Trilinear diagram showing the chemical composition of groundwater from Indian Hole Spring.

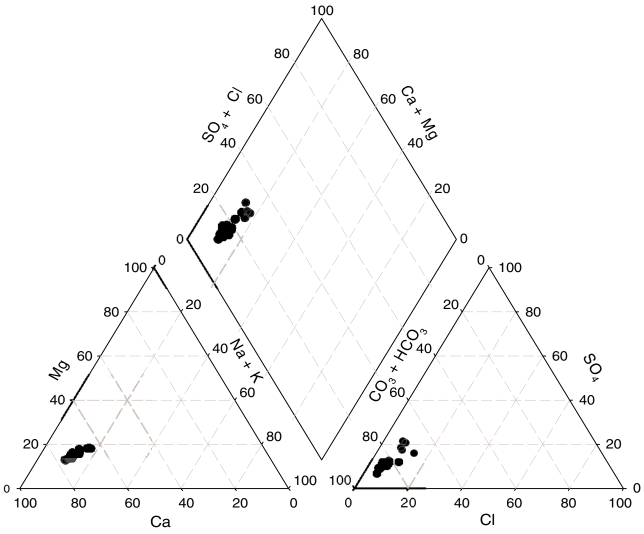

Figure 11 Trilinear diagram showing the chemical composition of groundwater from Collier Spring.

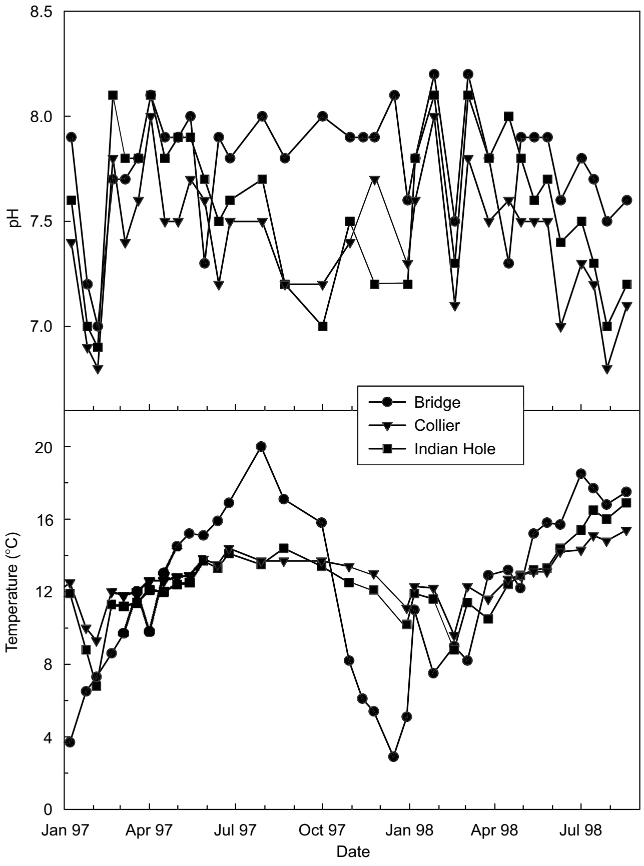

Figure 12 Changes in pH and temperature of groundwater (Collier Springs and Indian Hole Springs) and stream water (bridge site) during the sampling period. Stream water at the bridge site typically had a higher pH (top) than the spring water. Water temperatures (bottom) at the bridge site showed a greater seasonal variability than the spring water.

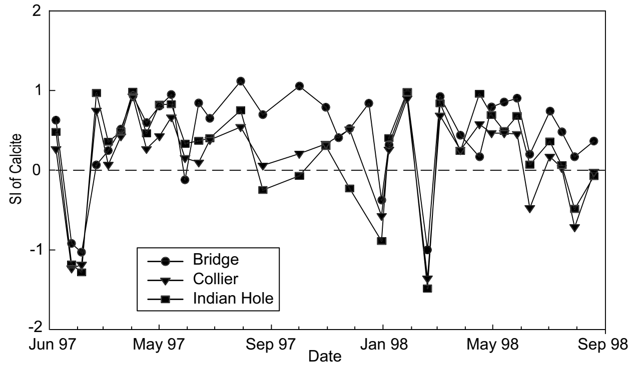

Figure 13 Spring and stream water were typically oversaturated with respect to calcite. Samples showing undersaturation (a saturation index [SI] < 0) were collected during and following significant rainfall events. Stream water generally had a greater saturation index during the warmer months.

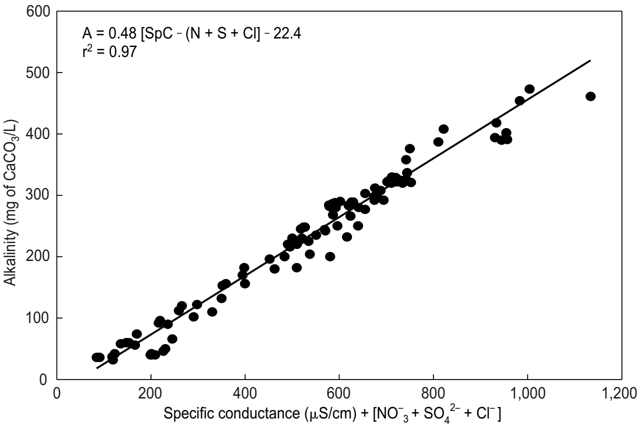

Figure 14 Relationship between laboratory-measured alkalinity and specific conductance plus anion concentrations used to calculate alkalinity for this investigation. NO_3^- is as N.

and minerals therein and the concomitant leaching and cation exchange within shale partings.

Indian Hole and Collier Springs

The geology, hydrogeology, and land use of the groundwater basins that feed Indian Hole and Collier Springs are essentially identical. Geologic mapping (Panno and Weibel 1999) and results of discharge measurements and dye tracing (Aley et al. 2000) show that each spring originates from adjacent and similarly sized basins within the same geologic strata, and each is recharged by surface runoff and subsurface seepage from areas with similar soils and land use. Because of their proximity to each other, both basins are affected by the same weather patterns. Because of those similarities, the geochemical characteristics of groundwater discharging from Indian Hole and from Collier Springs have only subtle differences. Specifically, groundwater from Indian Hole Spring, relative to groundwater from Collier Spring, is colder in the winter, spring, and fall and warmer in the summer. The temperature difference is consistent with the hypothesis of Panno and Weibel (1999) that groundwater issuing from Indian Hole Spring is more rapidly affected by surface conditions and discharges from a somewhat shallower conduit system. That is, the conduit system feeding Collier Spring is better protected from seasonal surface temperature changes than the Fogelpole Cave system that feeds Indian Hole Spring. As expected, surface water at the bridge showed a much greater range of water temperatures than did the springs (tables 3, A1, A2, and A3).

The chemical compositions of groundwater samples from Indian Hole and Collier Springs were only slightly different; for example, the specific conductances values fell directly on or close to a 1:1 line; $r^2 = 0.89$ (fig. 15). Further, compositional differences are statistically significant ($P < 0.05$) for only a few components. Indian Hole Spring groundwater was consistently lower in SiO_2 (fig. 17) and higher in Mg^{2+}, SO_4^{2-}, and Br^- (table 3) than was Collier Spring groundwater. Sources of SiO_2 in the strata include chert-rich zones of the St. Louis Limestone and relatively thin beds of shale in underlying formations. Given that the initial concentration of SiO_2 in rainwater is generally at or near zero (Laudon and Slaymaker 1997) and that the SiO_2 content of Collier Spring is greater than that of Indian Hole Spring (table 3), it follows that groundwater from Collier Spring probably had been in contact with bedrock longer than

Table 3 Field parameters, ions, bacterial indicators, and herbicides for Collier and Indian Hole Springs and the bridge across the South Fork of Horse Creek.[1,2]

	Collier	Indian Hole	Bridge
Temperature			
Median	12.8	12.4	12.2
Range	(7.80–15.4)	(6.20–16.9)	(2.90–20.0)
pH			
Median	7.4	7.6	7.8
Range	(6.8–8.0)	(6.6–8.1)	(7.0–8.2)
Eh (mV)			
Median	484	495	428
Range	(147–620)	(118–712)	(95–585)
SpC (µS/cm)			
Median	548	488	477
Range	(138–683)	(118–712)	(129–669)
T. Alk. (mg/L $CaCO_3$)			
Median	221	192	179
Range	(27–288)	(16–295)	(23–286)
Na^+ (mg/L)			
Median	15.8	20.2	16.1
Range	(2.69–22.4)	(3.00–27.9)	(2.60–27.7)
K^+ (mg/L)			
Median	2	2	2
Range	(<1–5)	(<1–5)	(1–8)
Ca^{2+} (mg/L)			
Median	88.9	73.1	77.1
Range	(18.1–117)	(14.1–114)	(16.3–111)
Mg^{2+} (mg/L)			
Median	10.2	12.3	10.6
Range	(3.07–13.9)	(3.00–18.8)	(3.18–15.8)
SiO_2 (mg/L)			
Median	21.3	16.7	17.4
Range	(9.26–26.4)	(8.34–20.9)	(9.28–22.3)
HCO_3^-			
Median	269	228	218
Range	(32–351)	(19–356)	(28–349)
NO_3^--N			
Median	3.92	3.29	3.16
Range	(1.19–5.00)	(1.12–6.08)	(1.08–4.95)
PO_4^{3-}-P			
Median	ND	ND	<0.01
Range			(<0.01–0.24)
SO_4^{2-} (mg/L)			
Median	24.5	38.0	28.5
Range	(10.2–32.1)	(11.2–55.8)	(11.1–40.8)
Cl^- (mg/L)			
Median	9.34	10.3	9.74
Range	(3.16–13.0)	(2.77–23.3)	(3.56–15.1)
Br^- (mg/L)			
Median	0.05	0.08	0.06
Range	(<0.10–0.14)	(<0.10–0.59)	(<0.01–0.15)
Fe (mg/L)			
Median	<0.01	<0.01	<0.01
Range	(<0.01–0.31)	(<0.01–0.34)	(<0.01–0.36)
Mn (mg/L)			
Median	0.02	0.02	0.14
Range	(<0.01–0.06)	(<0.01–0.09)	(0.06–0.34)
TC (cfu/100 mL)			
Median	>4,000	>4,000	>4,000
Range	(432–4,000)	(648–4,000)	(1,632–>4,000)
FC (cfu/100 mL)			
Median	262	176	517
Range	(20–>4,000)	(15–>4,000)	(40–>4,000)
FE (cfu/100 mL)			
Median	1,034	294	1,034
Range	(12–>4,000)	(21–>4,000)	(55–>4,000)
TA (cfu /100 mL)			
Median	$>3 \times 10^6$	$>3 \times 10^6$	$>3 \times 10^6$
Range	$>3 \times 10^6$	$>3 \times 10^6$	$>3 \times 10^6$
Alachlor (µg/L)			
Median	0.16	0.11	0.14
Range	(<0.01–0.98)	(<0.01–0.92)	(<0.01–0.66)
Atrazine (µg/L)			
Median	0.44	0.50	0.48
Range	(<0.01–13.4)	(<0.01–16.1)	(<0.01–21.8)

[1] Samples were collected about every 2 weeks from October 1996 through August 1998. n = 37.

[2] Eh, redox potential; SpC, specific conductivity; T. Alk., total alkalinity; TC, total coliform; FC, fecal coliforms; FE, fecal enterococci; TA, total aerobic bacteria; AL, alachlor; AT, atrazine; ND, no data.

that from Indian Hole Spring, suggesting that Collier Spring lies deeper in the bedrock than does Indian Hole Spring. The higher Mg^{2+} concentrations in water from Indian Hole Spring water (fig. 18) suggest that Fogelpole Cave intersects a bed or beds of dolomite that occur in the St. Louis Limestone (Willman et al. 1975). Scanlan (1989) used the Ca/Mg molar ratio to differentiate between subtypes of groundwater. Ratios greater than 0.17 define a Ca/Mg water subtype, whereas ratios less than 0.17 define a Ca subtype. The range and median molar ratios for groundwater from Collier and Indian Hole Springs were calculated from Ca and Mg concentrations given in tables A1 and A2. Values are 0.16 to 0.28 (median = 0.20) and 0.24 to 0.35 (median = 0.28), respectively, showing distinct differences. Even though some of the Collier Spring samples fell into the Ca subtype, most of the groundwater samples from both springs fell into the Ca/Mg subtype.

The source or sources of the higher Br^- in Indian Hole Spring and its significance are not clear from the available data. The elevated Br^- concentrations of Indian Hole Spring were not correlated with increases in Cl^- concentrations, as would be expected if saline water from a deeper source was mixing with the spring water somewhere in the conduit system. The Na^+ and Cl^- concentrations were greater, and the range of values was broader, for samples from Indian Hole Spring than for samples from Collier Spring. Given the relatively limited number of sources for these ions in the groundwater basin, the Na^+ and Cl^- sources may include livestock wastes, septic effluent, road salt, and agrichemicals entering the shallower Fogelpole Cave system and discharging from Indian Hole Spring.

Sulfate concentrations in water from Indian Hole Spring were typically 25% higher than in water from Collier Spring and showed distinct differences when plotted against Ca^{2+} (fig. 16). Sulfur isotopes ($\delta^{34}S$) in spring water from Indian Hole and Collier Springs were –2.8 and +0.8 parts per thousand (ppt) (± 0.3 ppt), respectively (Panno et al. 1998b). These isotopically light values are consistent with a $\delta^{34}S$ value for a sample collected from a seep in Illinois Caverns just to the north (–11.9

Table 4 Relationships between specific conductance (SpC) and major ions and suspended solids (SS) using simple linear regression (n = 37).

Spring[1]	Equation	r^2	Equation
Collier	$Na^+ = 0.0371(SpC) - 3.34$	0.93	7
Indian Hole	$Na^+ = 0.0461(SpC) - 3.21$	0.94	8
Collier	$Ca^{2+} = 0.187(SpC) - 9.63$	0.96	9
Indian Hole	$Ca^{2+} = 0.165(SpC) - 9.70$	0.97	10
Collier	$Mg^{2+} = 0.0194(SpC) - 0.316$	0.92	11
Indian Hole	$Mg^{2+} = 0.0270(SpC) - 0.904$	0.96	12
Collier	$SO_4^{2-} = 0.0319(SpC) + 8.13$	0.70	13
Indian Hole	$SO_4^{2-} = 0.0699(SpC) + 3.15$	0.82	14
Collier	$Cl^- = 0.0106(SpC) + 3.90$	0.45	15
Indian Hole	$Cl^- = 0.0156(SpC) + 2.78$	0.48	16
Collier and Indian Hole	$SpC_{Ind.Hole} = 1.03(SpC_{Collier}) - 18.4$	0.89	17
Suspended solids	$\text{Log } SS = -0.0034(SpC) + 3.34$	0.71	18

[1] All water samples and measurements were taken at Collier and Indian Hole Springs.

ppt). Isotopically light $\delta^{34}S$ values usually reflect the input of S from the oxidation of pyrite. The isotopic composition of S derived exclusively from the dissolution of gypsum or other evaporite minerals has a lower limit of +10 ppt (Holser and Kaplan 1966), whereas the $\delta^{34}S$ values for organic S derived from the degradation of plant debris range from 0 to +12 ppt (Hackley and Anderson 1986). Although the S isotopic data are not definitive, the intermediate $\delta^{34}S$ values for groundwater from the springs suggest that the SO_4^{2-} comes from a mixture of end-member waters from the two sources. Differences between the $\delta^{34}S$ values of the spring water relative to the cave seep could be the result of differences in the relative proportions of end-member waters. This interpretation is consistent with findings by Panno et al. (2000, 2001) and Hackley et al. (2001) for groundwater samples from 10 springs (including Indian Hole and Collier) distributed across the sinkhole plain. However, the input of sulfate from agrichemicals cannot be ruled out and currently is being investigated by the authors.

South Fork Creek Bridge As expected from discharge measurements, the composition of water flowing under the South Fork Creek bridge was a slightly modified amalgam of Indian Hole and Collier Spring groundwaters (tables 3, A1, A2, and A3). Dark coatings assumed to be Mn oxide and Fe oxyhydroxide cover the rocks and concrete pylons beneath the bridge. Similar coatings were not observed on rocks upstream or downstream of the bridge. The coating on the pylons extends 3 to 4 m (10 to 13 ft) above the stream bottom and is consistent with the seasonally high Mn concentration in water samples taken at the bridge. Manganese concentrations in the spring waters ranged from < 0.01 to 0.09 mg/L; concentrations of Mn at the bridge ranged from 0.06 to 0.34 mg/L. The seasonal high occurred during May (fig. 19), which is the opposite of the results found by Shiller (1997) for the Mississippi River, where the Mn concentrations were lowest during spring. The source of the elevated Mn concentrations at the bridge was unclear, but further evaluation was beyond the scope of this investigation.

Agrichemicals Agriculture (cropland and livestock pasture) is the predominant land use in the Collier Spring and Fogelpole Cave groundwater basins (table 2). The presence of agrichemicals in spring and surface waters discharging from these basins (tables A1, A2, A3, and A4) was expected based on previous work in the area (Panno et al. 1996). Agrichemicals in water samples collected from the two springs and from the stream at the bridge site included NO_3^-, PO_4^{3-} (present in detectable concentrations at the bridge only), K^+, alachlor, and atrazine.

Nitrate Nitrogen is a major pollutant in rivers (Parry 1998). Leaching of NO_3^- from nitrogenous compounds applied to field or cropland soils in humid climates is a major mechanism for the removal of N from soils (Tisdale et al. 1993), because NO_3^- is extremely soluble in water and is a highly mobile anion in the natural environment (Hem 1989). Nitrogen is applied to croplands in the study area (primarily as either anhydrous ammonia or urea) at an annual rate of 90 to 112 kg/ha (80 to 100 lb/acre) for wheat and other small grains and 135 to 168 kg/ha (120 to 150 lb/acre) for corn (P. Kremmell, personal communication 1998). The total mass of N applied to row crops in the groundwater basins and watershed just upstream of the bridge ranged from 135,000 to 168,000 kg/yr (298,000 to 370,000 lb/yr). This range assumes that the corn and soybean crops are each 50% of the total row crop area (P. Kremmell, USDA, personal communication 1998), adding the mass applied to wheat and small grains, and based on the area in table 2. Other potential sources in the study area include livestock waste, septic effluent, fixed N from legumes (soybeans and alfalfa), anthropogenic airborne sources (combustion products and volatilized NH_3 from fertilizers and animal waste), and natural background (soil organic matter and natural atmospheric sources).

The median concentrations and range of NO_3^--N for water samples from Collier Spring, Indian Hole Spring, and the bridge were 3.92 mg/L (1.19 to 5.00 mg/L), 3.29 mg/L (1.12 to 6.08 mg/L), and 3.16 mg/L (1.08 to 4.98 mg/L), respectively (table 3). For comparison, in the Sangamon River, which drains an area dominated by tile-drained row crops in central Illinois, NO_3^--N concentrations near Decatur, Illinois, ranged from near 0 mg/L in late summer and early fall to 16.4 mg/L in May 1997 (Keefer and Demissie 1999). Nitrate concentrations and loading of Collier and Indian Hole Springs and South Fork Creek tended to become elevated in the early part of the year following rainfall events in mid-February and reached maximum

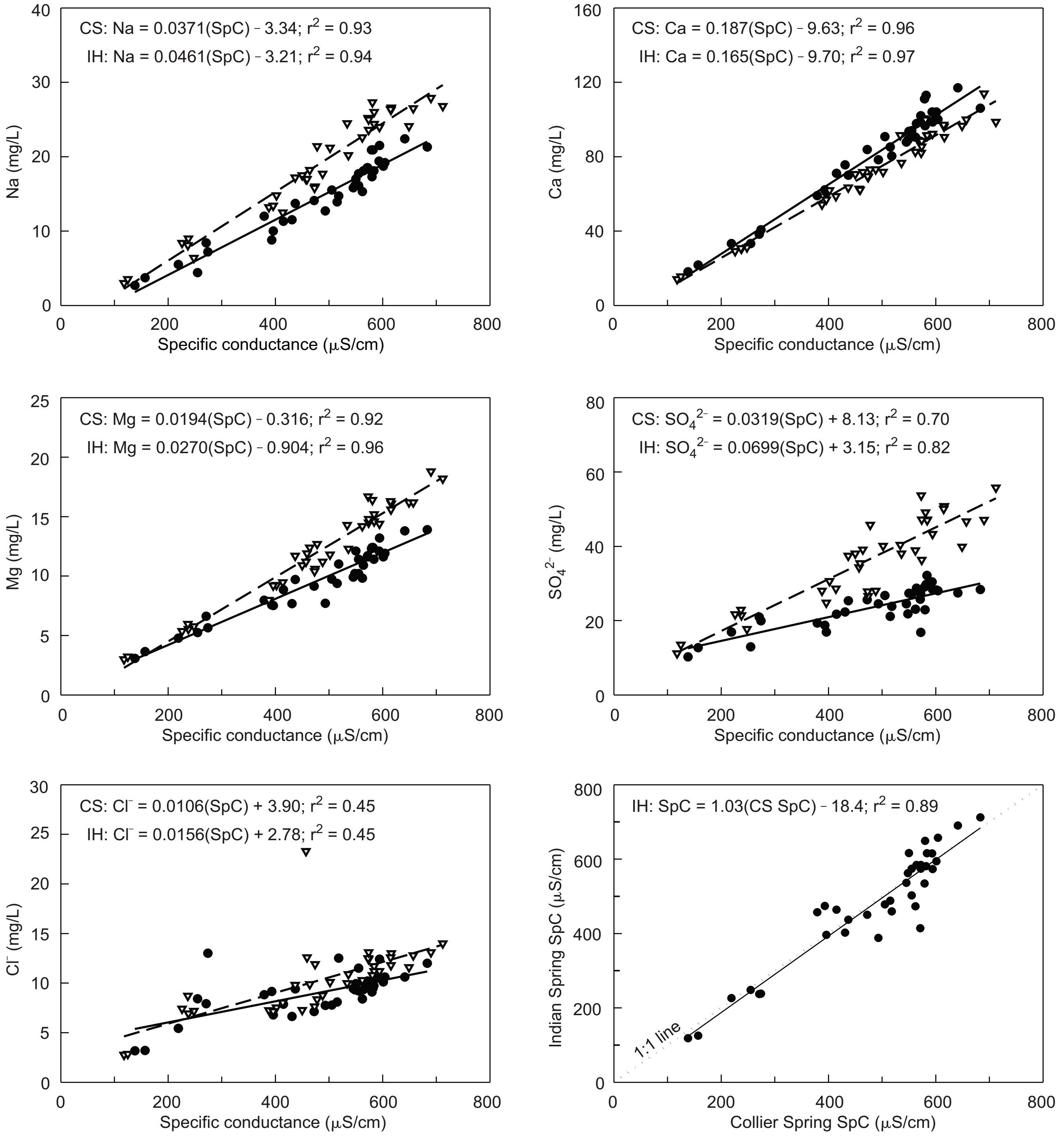

Figure 15 Relationships between Na^+, Ca^{2+}, Mg^{2+}, SO_4^{2-}, Cl^-, and specific conductance for all samples collected and the relationship between specific conductance measured at Indian Hole (IH; dashed line) and Collier Springs (CS; solid line).

loading levels in the late spring during and following planting (figs. 20 and 21). The NO_3^- likely was derived from NO_3^--enriched soil water flushed from the soil by rain pulses (Lakey and Krothe 1996). Although the maximum NO_3^--N concentrations in the study area fell well below the USEPA's regulatory standard for drinking water of 10 mg/L (USEPA 1992), concentrations seldom fell below the 1.9 mg/L threshold for background. In this publication, background refers to a range of concentrations that were derived from natural sources, airborne sources (both natural and anthropogenic), and soil organic matter from all sources.

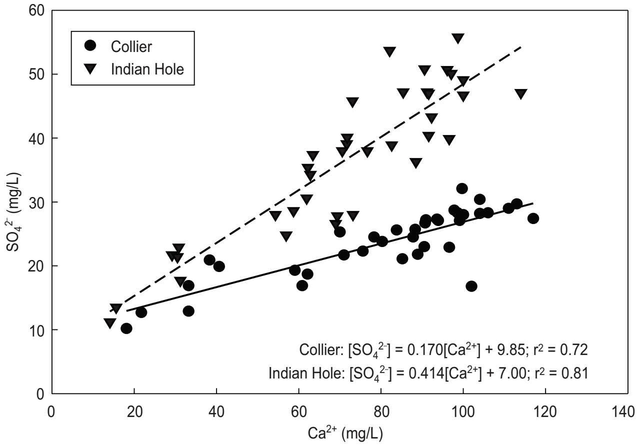

Figure 16 Relationships between Ca^{2+} and SO_4^{2-} concentrations for all samples collected at Indian Hole (dashed line) and Collier Springs (solid line). The data form two distinct trends, suggesting two distinctly different sources.

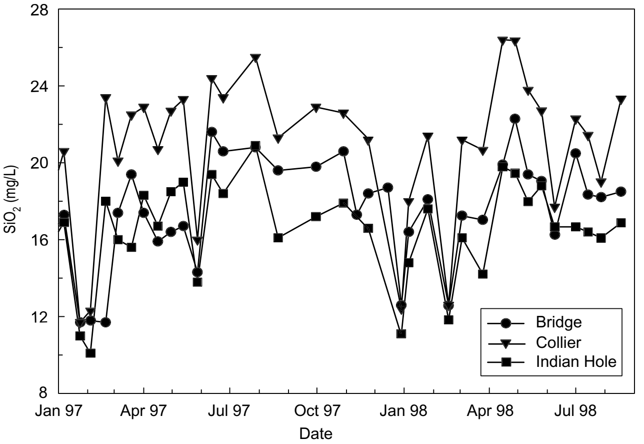

Figure 17 Temporal changes in silica concentrations in water samples from all sites over the sampling period reveals that groundwater from Collier Spring had a higher concentration of silica than did Indian Hole Spring.

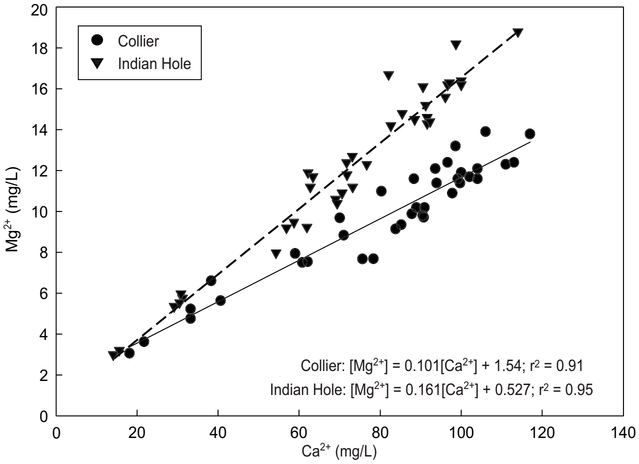

Figure 18 Calcium versus Mg^{2+} concentrations in water samples from Indian Hole (dashed line) and Collier Springs (solid line) showing two distinct trends.

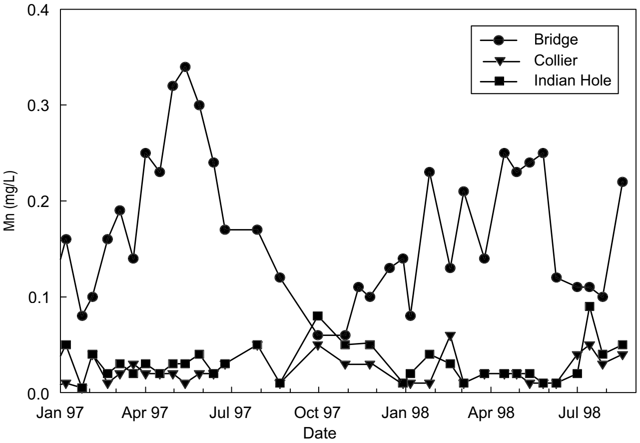

Figure 19 Temporal changes in Mn concentrations in spring and surface water samples showing seasonally elevated concentrations of Mn at the bridge site during spring.

Atmospheric deposition is a potentially significant contributor of N to groundwater and surface water in this area, both as ammonium (NH_4^+) and NO_3^- (figs. A1 and A2). The seasonality of the data (fig. A3) presented by the National Atmospheric Deposition Program (NADP) (1998) suggests that a significant percentage of the N is derived from fertilizers applied during the spring. The Clean Air Status and Trends Network (CASTNet)/NADP station closest to the study area is in Alhambra, Illinois, about 80 km to the north. In 1997 and 1998, the average annual atmospheric deposition of inorganic N (wet and dry) at Alhambra was 8.5 kg/ha (4.6 lb/acre) (USEPA 2001); deposition in the basins of approximately 32,000 kg (71,000 lb) of N/yr and for the entire area was approximately 41,000 kg (90,000 lb) of N/yr. Organic N is not measured at NADP sites but may be a significant component of atmospheric N (Scudlark et al. 1998). Conversely, a significant percentage of the atmospheric N within the basins may be derived from fertilizers applied during the spring; thus, there may be some overlap between atmospheric N and the fertilizer N values (NADP 2000). Other potential atmospheric sources of N include industrial waste gases (Tisdale et al. 1993) and other combustion-related sources (e.g., automobile exhaust), such as those from the St. Louis area, located about 48 km (30 mi) to the northwest.

Because of their relatively low concentrations in spring and surface water, ammonium concentrations in the water samples were not determined. For example, NH_4^+ concentrations in samples from nearby Kelly Spring during and following a rainstorm immediately after application of anhydrous ammonia to the croplands should represent a "worst-case scenario" for NH_4^+ contamination (table A5). Kelly Spring is located 3 km (2 mi) north of the study area and is the discharge point for the Krueger Dry Run Cave groundwater basin. Because of the nature of this rain event, and because the maximum NH_4^+-N concentration in this spring was 0.56 mg/L and normal concentrations were ≤0.10 mg/L, we

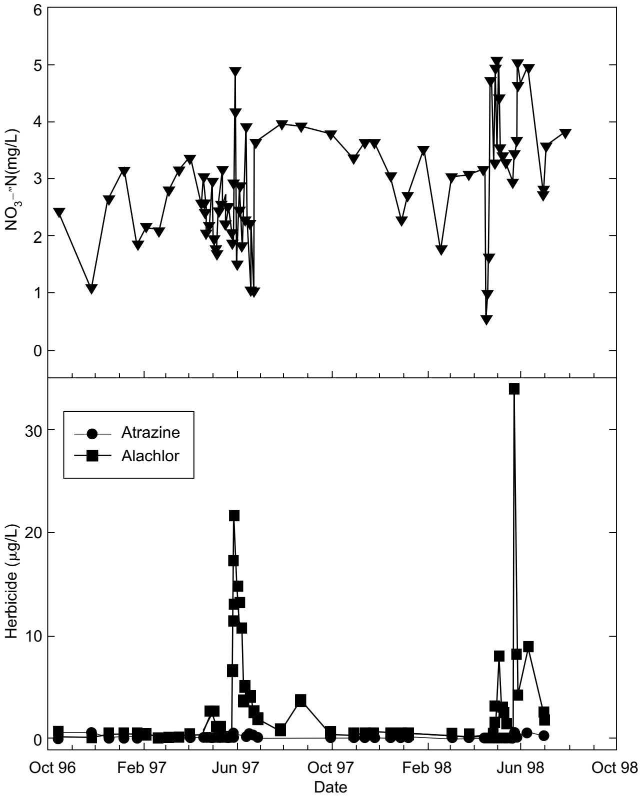

Figure 20 Seasonal trends in nitrate and herbicide concentrations in water samples collected at the bridge site.

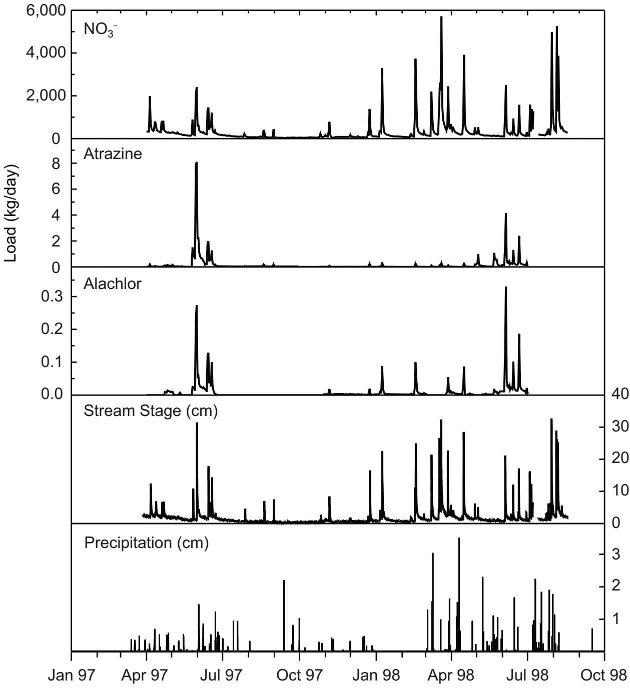

Figure 21 Loading of nitrate, atrazine, and alachlor; stream stage; and precipitation.

reasoned that NH_4^+ would not contribute significantly to the total N discharging from the groundwater basins. The lower NH_4^+ values found are similar to background for stream water in pristine watersheds in the United States (0.1 mg/L) (USGS 2002). At this concentration, the total mass of NH_4^+ discharging at the bridge was estimated to be about 3,220 kg (7,100 lb) of N/yr.

Loehr (1974) determined that the rate of nitrogen loading per hectare of land receiving manure was between 4 and 13 kg (9 to 29 lb) of N/yr. A per-head estimate was not possible because of the uncertainty associated with the number of cows per hectare in the pastures in the groundwater basins. Using Loehr's estimates, the mass of N on land receiving manure from cattle ranged from 3,260 to 10,600 kg (7,190 to 23,400 lb) of N/yr in the groundwater basins and 4,510 to 14,700 kg (1,940 to 32,400 lb) of N/yr at the bridge. Thus, N loading by cattle in the Collier Spring and Fogelpole Cave groundwater basins could contribute a maximum of 10,600 kg/yr (23,400 lb) at the springs, assuming that all N produced enters groundwater as NO_3^-. However, this value is certainly a gross overestimate. The actual mass would be much lower because of the likelihood of volatilization of NH_3, uptake by vegetation, conversion to soil organic matter, and denitrification of NO_3^- in the soil zone. Isotopic analyses of the spring waters suggested that livestock manure was not a significant source of NO_3^- (Panno et al. 2001).

Private septic systems also are a source of N in the sinkhole plain. Septic effluent, containing concentrations ranging from 2.9 to 67 mg of N/L (median = 24 mg of N/L; n = 19) from NH_4^+ and NO_3^- (Panno et al., 2002), is discharged onto or into the ground and directly into sinkholes in many places. There are approximately 154 houses within the Collier Spring and Fogelpole Cave groundwater basins (determined from USGS topographic maps updated in 1993). If it is assumed that the average household is three people and that each person uses about 380 L (100 gal) of water/day (USEPA 2000), the annual N mass from septic systems (predominantly from human waste) would be approximately 1,600 kg (3,500 lb), distributed uniformly over time, for all households. Again, the actual N mass reaching the aquifer would be lower because of the likelihood of uptake by vegetation and denitrification of NO_3^- in the soil zone. Thus, the sum of animal waste and septic effluent represents a minor contribution to the total N mass in the study area, which is less than 4% of the amount of N applied as fertilizer.

Finally, there was a net loss of NO_3^- from the springs to the bridge (table 3, fig. 22). The average concentration of NO_3^--N in water samples from Indian Hole and Collier Springs (at a 1:1 ratio) was significantly different (P = 0.024; by Student's *t*-test)from the average concentration of NO_3^--N in water samples from the bridge site. Because the flow path to the bridge from the spring is 2.4 km (1.5 mi), biological uptake of NO_3^- by benthic algae and planktonic materials could reasonably account for the loss (e.g., Burt et al. 1993). We speculate that biological uptake, possibly coupled with denitrification of water

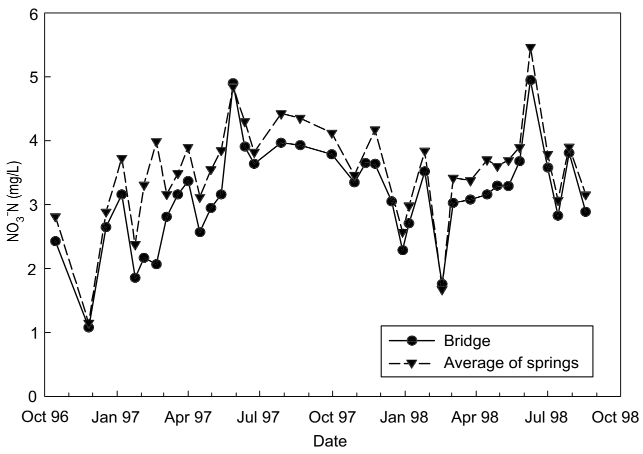

Figure 22 Nitrate concentrations in combined spring water (1:1 ratio) and in stream water at the bridge site. The consistently lower concentration of the stream water supports the loss of NO_3^- compared with those concentrations found in stream water at the bridge site.

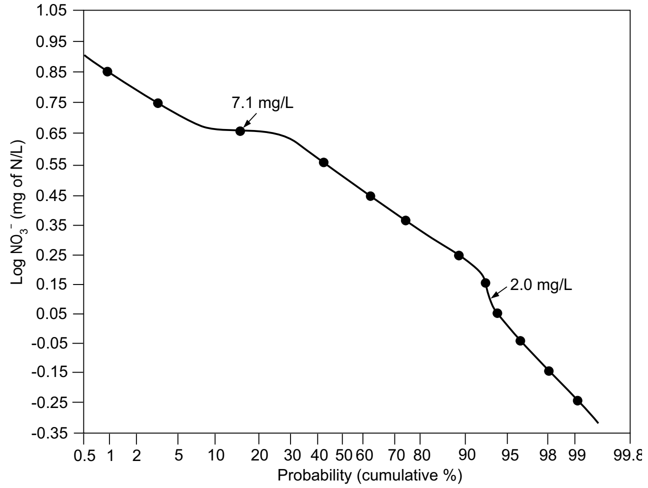

Figure 23 Cumulative probability plot of NO_3^- concentrations in water samples from springs, caves, and spring-fed surface water from southwestern Illinois. Threshold concentrations are 2.0 and 7.1 mg of N/L (n = 219).

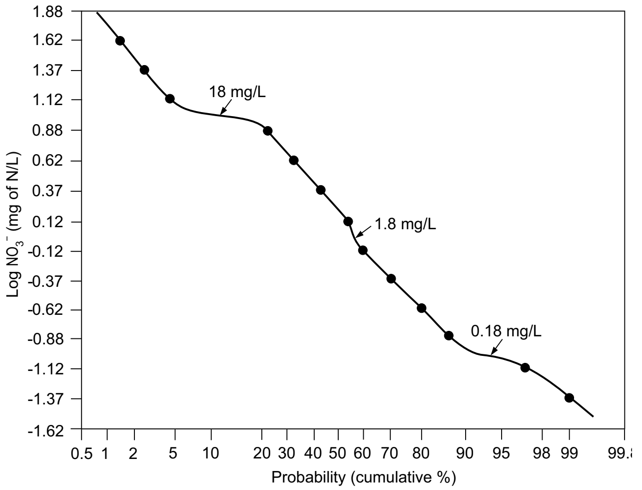

Figure 24 Cumulative probability plot of NO_3^- concentrations in water samples from drilled and dug wells in southwestern Illinois. Threshold concentrations are 0.18, 1.8, and 18 mg of N/L (n = 76).

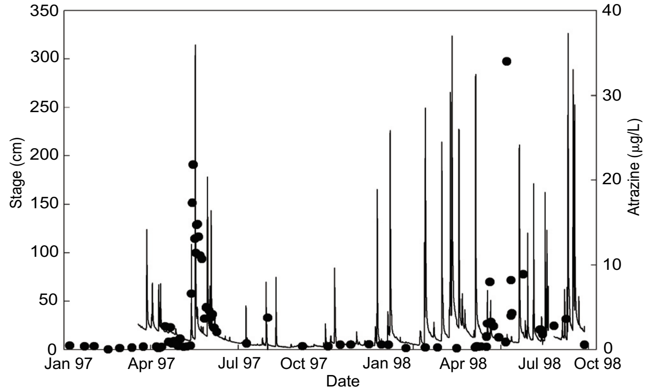

Figure 25 Atrazine concentrations (dots) in surface water at the South Fork Creek bridge and stream stage (lines) during the sampling period. The close relationship between periods of high stage and elevated atrazine concentrations in May and June reflect the loss of this pesticide during and following rainfall events subsequent to field application.

between the springs and the bridge site during the warmest months of the year, probably caused the decreased NO_3^--N concentrations in water samples collected at the bridge site.

The sources of NO_3^--N in water samples from Collier and Indian Hole Springs and eight other large springs in the sinkhole plain, determined using the isotopes of NO_3^-, ($\delta^{18}O$ vs $\delta^{15}N$), were found to be dominated by N fertilizers and soil organic matter (Panno et al. 2001; Hackley et al. 2001; Hackley, unpublished data). Samples collected for those studies over six consecutive seasons also showed the effects of atmospheric contributions when NO_3^--N concentrations approached background concentrations.

Nitrate Background The technique used for calculating background concentrations of NO_3^--N was borrowed from the field of mineral exploration where geochemical indicators are used to locate mineral deposits. Indicators, such as metal concentrations in rock, soil, or water, are divided into two categories, background and anomalies, and are separated by a threshold concentration. Tens to hundreds of samples are collected and analyzed for an indicator element or ion. The data are then plotted on a cumulative probability plot, which groups the data into various populations (if there is more than one) (Sinclair 1974). The inflection points along the plots indicate the threshold between two or more populations. In this context, background is used as the baseline concentration; anything above the threshold concentration is interpreted as an anomaly and is indicative of the presence or influence of a mineral deposit.

Adapting this technique to groundwater contamination problems, the threshold between background and anomalous concentrations for NO_3^--N was identified. Because of the ubiquitous nature of NO_3^- in the environment from a variety of human-related sources, background could not be defined as being derived from only natural sources (e.g., natural atmospheric sources, wildlife, and degradation of naturally derived soil organic matter). Background now includes these natural sources, plus soil organic matter from the residue from fertilized and unfertilized crops, products of combustion (e.g., from nearby St. Louis and East St. Louis), and evaporation of NH_3 from fertilizer and livestock waste. These sources typically provide slow but constant inputs of N into the karst aquifer. Anomalies are defined as NO_3^- derived from human-related sources that include N fertilizers, livestock waste, and septic effluent, all of which are subject to rapid influx into the karst aquifer.

The threshold concentration was calculated using two cumulative probability plots, one with 219 spring samples from 19 springs, caves, and spring-fed streams (fig. 23), and one with 76 from 15 wells (fig. 24). All samples were collected in the sinkhole plain of southwestern Illinois by Panno et al. (1996). The threshold between water contaminated with N fertilizer and background, for the spring water and water-well sample plots, was 2.0 and 1.8 mg/L, respectively. Above this concentration, altrazine and alachlor are detected in spring water samples. Spring water samples revealed the presence of three populations (fig. 23). The third population had NO_3^--N concentrations of $\geq$7.1 mg/L and was interpreted as containing NO_3^- from livestock and/or septic effluent in addition to N fertilizer. The water-well samples revealed four populations (fig. 24): a livestock/septic system component for samples $\geq$18 mg/L and another at 0.18 mg/L. Interpretation of the latter threshold is uncertain, but is probably related to reduction of NO_3^- within the aquifer.

On the basis of these plots, 1.9 mg/L was chosen as the threshold for NO_3^--N concentrations between background values and concentrations in samples affected by the addition of N fertilizers. This threshold is slightly larger than the 1.4-mg/L background determined by Panno et al. (1996) who used about half as many data for their calculation. The 1.9-mg/L threshold falls within the range determined by Chapelle (1993) who found that it was unusual for groundwater in a pristine flow system to have more than 1 to 2 mg/L NO_3^--N. The threshold is also consistent with background values determined by the USGS for shallow groundwater (2.0 mg/L) (USGS 2002) and is about three times that of the background for NO_3^--N in streams in the United States (0.6 mg/L). Our background value for wells in the study area (1.8 mg/L) is almost identical to that of the USGS value for shallow groundwater (2.0 mg/L) (USGS 2002). Because the springs and streams in this study are fed directly by conduits, there is no riparian zone where denitrification can remove NO_3^-. Background concentrations for their shallow groundwater are similar to those for the springs and streams of this investigation.

Phosphate Phosphate is used as a soil amendment in the study area at the recommended average annual rate of about 67 kg of P/ha (60 lb/acre)(Anderson et al. 1989; P. Kremmell, personal communication 2001). The application rate may vary depending on crop type and expected yield. Other potential sources of PO_4^{3-}-P include effluent from private septic systems (in concentrations as high as 9.0 mg/L [Panno et al. 2002]), livestock, and natural sources (e.g., waterfowl and bats). Concentrations of PO_4^{3-}-P in stream water samples rarely exceeded the detection limit of 0.01 mg/L throughout the year (tables 3, A1, A2, and A3). These low concentrations were expected because PO_4^{3-} is readily adsorbed in the soil zone by metal oxyhydroxides that have a positive surface charge under pH ranges typical for the study area (Hem 1989, Goldberg and Sposito 1984). In addition, phosphate-bearing minerals precipitate within the soil zone on the surfaces of calcium carbonate when concentrations of applied inorganic P are relatively high. In contrast, organic P (i.e., animal wastes) is more mobile than inorganic P in the soil zone (Tisdale et al. 1993) and may enter a conduit of the shallow karst aquifer. Once in stream water, PO_4^{3-} can be readily taken up by aquatic vegetation (Hem 1989). Goolsby et al. (1999) determined that >75% of P in the entire Mississippi River basin and >90% for some of the Mississippi River subbasins were in particulate form. Thus, dissolved PO_4^{3-} would not be expected to be present in significant concentrations in spring or surface water in the study area.

Because only 11% of our water samples contained measurable concentrations of PO_4^{3-}-P (all occurring in early 1997), the mass loading of PO_4^{3-}-P could not be calculated. On the basis of low detection rates, the loading of PO_4^{3-}-P in the Collier Spring and Fogelpole Cave groundwater basins as a dissolved phase does not significantly contribute to the aquatic environment. However, the presence of PO_4^{3-} as a component sorbed onto inorganic and organic suspended solids may be significant (e.g., Goolsby et al. 1999).

Pesticides The herbicides atrazine and alachlor were chosen because they were the dominant row crop herbicides used in southwestern Illinois at the time of this investigation (Panno et al. 1996). However, recent modifications to herbicide formulations now include less alachlor (P. Kremmell, personal communication 1998). Atrazine is the most environmentally persistent pesticide in the midcontinental United States (Goolsby 1991); as such, atrazine was assumed to be representative of pesticide contamination in the study area. Because pesticides are not naturally occurring, and because no pesticide dealerships are located within the groundwater basins, detections were assumed to be due to herbicide application to croplands. Atrazine and alachlor are pre-emergence and early post-emergence pesticides and are used primarily on corn; alachlor is also used on soybeans. They are applied as commercially available, premixed herbicides. Premixed herbicides are used to control a wider variety of species of annual grasses and broadleaf weeds and to reduce carryover and crop injury (Anderson et al. 1989). At the time of this investigation, atrazine and alachlor were applied in the spring at rates of 1.1 to 1.7 kg/ha (1.0 to 1.5 lb/acre) and 2.7 to 4.4 kg/ha (2.4 to 3.9 lb/acre), respectively (P. Kremmell, personal communication 1997).

Concentrations of atrazine in all water samples were typically above detection limits (0.1 µg/L); the median concentration for all sites was 0.52 µg/L (tables A1, A2, A3). Concentrations of alachlor were lower: the median concentration for all sites was 0.12 µg/L. Elevated concentrations of pesticides were expected during periods of storm runoff in the spring and early summer and following application of pesticides to fields (e.g., Thurman et al. 1992, Kimbrough and Litke 1996). Relatively large concentrations of atrazine, as great as 34 µg/L, were detected in water samples following the first significant rainfall after local crops were planted and pesticides were applied (fig. 25). Alachlor appeared to be more erratic during the fall and the beginning of 1997; however, the maximum concentration for alachlor was only 0.98 µg/L. Concentrations of atrazine in water samples from the study area were similar to those from other karst springs in the sinkhole plain (as reported by Panno et al. 1996), and concentrations of alachlor were typically much lower than those of atrazine.

Mass Loading Calculations—Stream Flow To calculate the total mass loading of selected agrichemicals in groundwater issuing from Collier and Indian Hole Springs, we initially calculated the total volume of water that flowed under the bridge at our sampling site during a one-year period. The techniques used, described in the Methods section (equations 2 and 4), yielded a total water volume of 3.22×10^{10} L/yr flowing out of the groundwater basins and to the bridge. The total volume of water that fell on the groundwater basins and on the total study area including that between the springs and the bridge (given an average precipitation of 103 cm/yr) was 3.88×10^{10} L/yr and 5.00×10^{10} L/yr, respectively. The difference represents a 36% loss from the total recharge within the study area, probably from evaporation and evapotranspiration.

Mass Loading Calculations—Agrichemicals Sampling data for NO_3^--N and pesticides were used to calculate an average daily concentration and a mass for agrichemicals (equation 4). Approximately 90,000 kg/yr (198,000 lb/yr) of NO_3^--N, 39 kg/yr (86 lb/yr) of atrazine, and 2.8 kg/yr (6.2 lb/yr) of alachlor were discharged from the 48.6 km^2 (18.8 mi^2) recharge area (the two groundwater basins and the surface drainage area from the springs to the bridge) during the monitoring period between 1996 and 1998**.** Using the median concentration of NO_3^--N in groundwater that discharged from the springs, we calculated that a somewhat greater mass of approximately 100,000 kg/yr (220,000 lb/yr) should have passed under the bridge. That is, the mass of NO_3^--N discharging from Indian Hole and Collier Springs, calculated from their median concentration (3.60 mg/L), was greater than that measured at the bridge (3.16 mg/L). This difference reflects the loss of NO_3^--N between the springs and the bridge that was discussed earlier. We chose to use the median concentration of NO_3^--N discharging from the springs for our mass balance calculations because it yielded a mass loading that eliminated the effects of the surface-water processes reducing the concentration of NO_3^--N in the spring water as it flowed to the bridge. Thus, the calculated mass of NO_3^--N was consistent with that discharging from the springs. The median concentrations of pesticides discharging from the springs were the same as those at the bridge.

Based on previous research on Collier and Indian Hole Springs and on other springs in the sinkhole plain (Panno et al. 2001; Hackley et al. 2001; Hackley, unpublished data), a significant portion of the NO_3^- in groundwater discharging from these springs was assumed to be N fertilizers. Taking into consideration the local application rate for these chemicals and the area of land used for corn and grains, we estimated that between 135,000 and 168,000 kg of N/yr (298,000 and 370,000 lb of N/yr) was applied to the croplands in the study area. The total mass of N from background (1.9 mg/L for NO_3^--N) was 53,000 kg/yr (117,000 lb/yr), which was assumed to be from all atmospheric sources and leaching of soil organic matter from both fertilized and unfertilized soils. The remaining 47,000 kg/yr (104,000 lb/yr) of NO_3^--N was assumed to be derived from N fertilizer and animal waste (livestock and septic effluent). Subtracting the N derived from livestock and septic effluent (12,220 kg/yr [26,950 lb/yr]), the final mass of N fertilizer is approximately 34,780 kg/yr [76,690 lb/yr] and represents a 21 to 31% loss of N applied to the croplands of the study area. This value is slightly greater than an estimate by Howarth et al. (1996) of 20 to 25% of agricultural N lost (regionally to globally) to coastal areas.

The total annual NO_3^--N losses from the groundwater basins represent about 27 kg of NO_3^--N/ha (24 lb/acre); slightly less than 50% of the land use is row-crop agriculture. This loss level is similar to annual NO_3^--N losses from other karst basins in Iowa and Kentucky. The Big Spring Basin in Iowa lost between 2.7 and 24.2 kg of NO_3^--N/ha (2.4 and 21 lb/acre) annually, averaging 11.8 kg of NO_3^--N/ha (10 lb/acre) per year over a 12-year period (Liu et al. 1997). The Big Spring Basin also has 50% of its land use as row-crop agriculture. The Pleasant Grove Spring Basin in Kentucky had an annual loss of 12.6 to 45.1 kg of NO_3^--N/ha (11 to 40 lb/acre) (Currens 1999). That basin had a somewhat greater agricultural land use: 70% was in row crops. Non-karst basins in Illinois had similar losses: 8 to 44 kg of NO_3^--N/ha (7.1 to 391 lb/acre) annually for the Lake Decatur watershed (Keefer and Demissie 1999) and 20 to 46 kg of NO_3^--N/ha (18 to 41 lb/acre) annually for the upper Embarras River watershed (David et al. 1997). Both of these watersheds are drained by tiles, and 90% of land use was row-crop agriculture. Thus, the susceptibility of NO_3^--N loss from the study area appears to be similar to that of other karst and tile-drained areas of the central United States.

The total applied atrazine and alachlor ranged from 670 to 1,030 kg/yr (1,480 to 2,270 lb/yr) and 3,280 to 5,340 kg/yr (7,230 to 11,780 lb/yr), respectively. These numbers are based on the median concentrations of the two herbicides and the area used for row-crop agriculture (table 2). Corn and soybeans received most of the application (Kolpin 1997). The amount of applied herbicides lost from the groundwater basins ranged from 3.8 to 5.8% of the applied atrazine and 0.05 to 0.08% of the applied alachlor, representing an annual loss of 3.28 g/ha (0.02 lb/acre) of atrazine and 0.74 g/ha (0.004 lb/acre)of alachlor basin wide. Atrazine loss for other karst basins ranged from 0.31 to 4.5 g/ha (0.002 to 0.02 lb/acre) from the Big Spring Basin (Liu et al. 1997) and 7.6 to 12.3 g/ha (0.04 to 0.07 lb/acre) from the Pleasant Grove Spring Basin in Kentucky (Currens 1999). As with NO$_3^-$, atrazine losses from the study area were similar.

Water-borne Bacteria Bacterial colonies present in water samples from Collier and Indian Hole Springs and at the bridge included coliforms, fecal coliforms, fecal enterococci, and soil bacteria. The bacterial counts were >3,000,000 colony-forming units (cfu)/100 mL of water for total aerobic bacteria, typically >4,000 cfu/100 mL of water for coliform bacteria, and about 15 cfu/ml to >4,000 cfu/100 mL of water for fecal coliform and fecal streptococci (tables 3 and A6). Many of the species isolated from the spring water are opportunistic pathogens that are typical of those found in other springs throughout the sinkhole plain (Panno et al. 1996). For comparison, Illinois water quality regulations require that fecal coliforms present in waters suitable for "primary contact" (intimate contact with water such as swimming) must not exceed 200 cfu/100 mL 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 400 cfu/100 mL (Illinois Environmental Protection Agency, Illinois Pollution Control Board 1999). If the latter limit can be applied to our samples (approximately two samples per 30-day period were collected), then the water in Collier Spring, Indian Hole Spring, and at the bridge site exceeded the state limit for fecal coliforms 46%, 31%, and 60% of the time, respectively. Fortunately, the springs and stream are probably rarely used for swimming.

The bacterial species isolated from water samples collected from the two springs and the stream at the bridge were almost identical and included 17 species. Some of the bacterial species showed seasonal variation in their relative abundance. Based on their mean rankings, the four bacterial species most commonly present in the spring waters included *K. pneumoniae*, *Pseudomonas* spp., *E. coli*, and *Bacillus* spp.; these species were present almost 100% of the time (table 5). Mean ranking is simply the arithmetic mean of the most dominant bacterial species or genera (rank of 1) to the least dominant (rank of 17) for all water samples at each sampling site. The mean ranks were calculated by summing the scores (1 being most dominant) for each bacterial genus or species for all the samples at particular sampling site. A score one higher than the highest score was used for water samples with no detection; finally, the sum of the scores was divided by the total number of samples collected at each site.

Pseudomonas spp. and *K. pneumoniae* are widely distributed in soil and water, and the latter is commonly found in the intestinal tracts of animals (including humans). *Escherichia coli* is a fecal coliform bacteria that thrives in the intestines of warm-blooded animals.

Table 5 Bacterial species isolated from water samples collected from Indian Hole and Collier Springs and the bridge site from January 1997 to August 1998.

	Indian Hole		Collier		Bridge	
Bacterial species	Mean ranking	Percent present	Mean ranking	Percent present	Mean ranking	Percent present
Klebsiella pneumoniae	2.1	100	2.1	100	2.1	100
Pseudomonas spp.	2.8	100	2.8	100	3	97
Escherichia coli	4.3	97	4.1	100	4	97
Bacillus spp.	4.9	97	4.8	94	5.3	92
Serratia spp.	5.7	85	5.5	83	5.2	89
Enterococcus faecalis	7.6	82	7.1	91	6.9	94
Enterococcus faecium	7.5	85	7.3	88	6.4	94
Aeromonas hydrophila	8.3	61	9.3	55	10	36
Pseudomonas aeruginosa	9.5	33	10.3	24	10.3	44
Staphylococcus spp.	10.9	39	10.3	45	11.6	2.8
Staphylococcus aureus	11.2	30	10.9	39	9.4	53
Proteus mirabilis	11.5	24	10.1	42	10	36
Proventia stuartii	11.9	21	11.8	18	11.5	14
Micrococcus spp.	12.6	9.1	12.9	3	11.8	8.3
Enterococcus spp.	12.6	6.1	12.1	15	11.3	14
Staphylococcus saprophyticus	12.7	6.1	12.9	3	11.8	8.3
Flavobacterium spp.	12.7	3	ND	ND	ND	ND
Enterococcus cloacae	ND[1]	ND	12.3	9.1	11.7	5.6
Citrobacter freundii	ND	ND	ND	ND	11.3	14
Flavobacter spp.	ND	ND	ND	ND	11.8	5.6

[1] ND, Not detected.

Both *K. pneumoniae* and *E. coli* are classified as opportunistic pathogens (Geldreich 1996). Panno et al. (1997b) found that these three bacteria were the dominant species present in the effluent from 19 private aeration-type septic systems in the study area. *Pseudomonas*, *Bacillus*, and *Serratia* spp.—ranked 2, 4, and 5, respectively—are typically associated with soils and are ubiquitous in the environment. The *E. coli* was dominant over *Ent. faecalis* and *Ent. faecium* (ranked 6 and 7, respectively), but all three are enteric bacteria (associated with fecal materials) whose presence suggests the influence of private septic systems or livestock waste on the microflora of the springs. The abundance of *E. coli* indicates that the movement of these bacteria to the springs was relatively rapid, given the 15-day half life of *E. coli* once it is out of the host animal's body (Burks and Minnis 1994). *Aeromonas hydrophila* commonly is associated with cold-blooded vertebrates (e.g., amphibians) (Freeman 1985) and is frequently found in cave water (Panno et al. 1999). We suggest that the presence of *A. hydrophila* is an indicator of the relatively large conduit systems of the sinkhole plain and probably other karst regions in the central United States. Specifically, these systems are typically >1 cm (0.4 in) 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.

The bacterial composition and bacterial indicator counts for the stream water collected at the bridge site are similar to those of water samples collected at the spring heads, which indicates that the bacterial isolates are surviving, although not all are thriving, in the stream water after being discharged from the springs.

Dissolved Organic Carbon The DOC that is derived from soil is dominated by humic and fulvic acids, which are the products of bacterial degradation of vegetation (Clark and Fritz 1997). Concentrations of DOC in groundwater typically are greater in agricultural areas than in natural and urban areas (Cane and Clark 1999). The concentrations of DOC present in the water of the springs and at the bridge ranged from 11.5 to 16.0 mg/L; the median was 14.4 mg/L (tables A1, A2, and A3). These concentrations exceed the 1 to 2 mg/L and the 1 to 12 mg/L normally found in groundwater and surface streams, respectively (Drever 1997, Wassenaar et al. 1990), but are typical for springs throughout the sinkhole plain (Panno et al. 1999). We suggest that the relatively high concentrations of DOC result from periodic rapid infiltration of cropland runoff and the infiltration of soil water directly into the conduit systems of the shallow karst aquifer.

Soil Erosion Rate Most soils in the Collier Spring and Fogelpole Cave groundwater basins are predominantly in the Alford association. This soil association is described as "gently sloping to very steep, well-drained, moderately permeable, silty soil: formed in loess in areas of karst topography" with a moist bulk density of 1.25 to 1.50 g/cm^3 (U.S. Department of Agriculture 1987). Suspended solids in spring and surface water ranged from <25 mg/L to 1,860 mg/L; the median concentration was 34 mg/L. Concentrations of suspended solids were inversely proportional to specific conductance, and their semilogarithmic relationship is described by least squares equation 18 ($r^2 = 0.71$) in table 4 (fig. 26). Values below detection limits were censored; as a result, the calculated erosion rate should be considered as semi-quantitative. The relationship between suspended solids and specific conductance is a function of the close association of runoff (rainfall and snowmelt initially have specific conductance values in the tens of micro-Siemens per centimeter) with the entrainment of soil during the erosion process. However, there was no discernible relationship between suspended solids and discharge owing to the differences between surface streams and karst springs, their response to recharge events, and the timing of sampling. For example, the initial pulse of groundwater from Indian Hole Spring during a flood event contained suspended solids that were below detection limits at a flow rate of 904 L/s (14,330 gpm) (Table A2).

Using the data from the monitoring station at the bridge and the regression equation in table 4 that describes the relationship between suspended solids and specific conductance, the total annual mass of suspended solids measured at the bridge was approximately 100,000,000 kg (2.2 × 10^8 lb). Assuming a moist bulk density for the soil of 1.25 to 1.50 mg/cm^3 and a groundwater-surface water drainage area of 48.6 km^2 (18.8 mi^2), the annual erosion rate for both basins, including that portion between the springs and the bridge, was approximately 20.6 tonnes/ha (55.6 tons/acre) or 0.14 to 0.16 cm (about 0.06 in). This amount exceeds the Illinois Department of Agriculture's "tolerable soil loss level," which is equal to the amount of soil that is replaced by soil-forming processes. For most soils in Illinois, the tolerable soil loss level is defined as 3 to 5 tons/acre per year (1 to 2 tonnes/ha per year). About 86% of the land in Illinois meets the tolerable soil loss level, which is based on estimates using the revised universal soil loss equation (Illinois Department of Agriculture 2000). Erosion rates in the study area are about 8.4 tons/acre per year (3.1 tonnes/ha) and exceed the tolerable soil loss level by a factor of 1.7 to 2.8. Further, the erosion rate of the study area is almost an order of magnitude higher than the erosion rates of 0.02 to 0.04 cm/yr (0.01 to 0.02 in/yr) calculated by others for the karst Shenandoah region of Virginia (Kastning 1995).

Atrazine on Suspended Solids Eight samples of suspended solids were collected between January and July 1998 (table 6) using materials collected within the pipe that protected the electrodes. These data, although too few for mass loading calculations, showed the presence of atrazine adsorbed to three of the eight samples of fine-grained sediment. In addition, the highest concentrations occurred in January, February, and early July 1998, suggesting that the occurrence of the atrazine-bearing sediment in the stream may be out of phase with the occurrence of large concentrations of atrazine dissolved in water by up to 6 months. That is, atrazine may be stored in sediments within the cave systems, along the stream channel, or both, and not undergo degradation. However, based on our limited data, the mass of atrazine adsorbed onto the sediment suggests that the contributions of atrazine in suspended solids were very small relative to the dissolved phase. For example, if it is assumed that

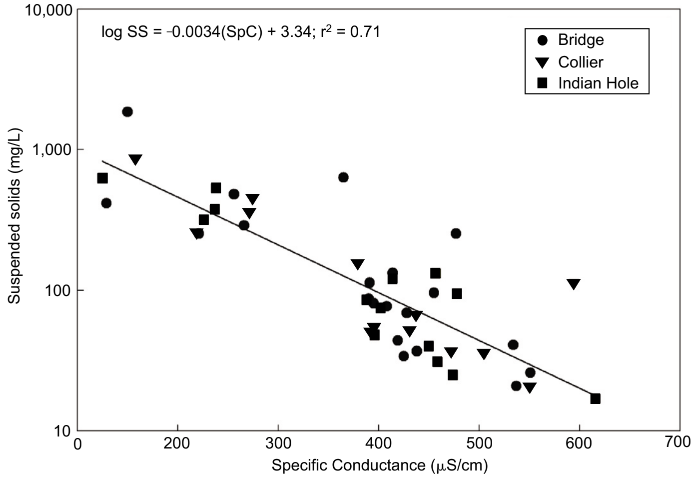

Figure 26 Relationship between specific conductance and the log of suspended solids. This relationship (table 4) shows that suspended solids could be estimated from specific conductance for this area (r^2 = 0.71).

Table 6 Atrazine in aqueous and solid phases in stream-water and sediment samples collected in 1998 at the bridge site.

	Atrazine[1]	
Date sampled	Aqueous (µg/L)	Solid (µg/kg)
01/06/98	0.33	28.0
02/17/98	0.24	18.0
05/12/98	1.42	<15.0
05/26/98	8.20	<15.0
06/09/98	8.90	<15.0
07/01/98	1.76	26.1
07/14/98	2.77	<15.0
07/28/98	3.61	<15.0

[1] Includes colloidally transported atrazine.

the mass of atrazine carried on the solid phases totaled 20 µg/L (an overestimate based on our limited data), this mass would add only about 2 kg/(4 lb/yr) of atrazine/yr to the total of 39 kg/yr (86 lb/yr) (about a 5.13% increase). These results agree with findings by Blum et al. (1993) and Seta and Karathanasis (1997), who found the solid phase transport of atrazine to be insignificant in nonkarst settings.

Summary and Conclusions

Because of the susceptibility of karst terrain to contamination of groundwater and surface water, the potential for the loss of applied agrichemicals to surface waterways in Illinois' sinkhole plain is often regarded as a worst-case situation for the state and the central and midwestern United States. In order to estimate the percentage of loss of agrichemicals from a row-crop–dominated area of the sinkhole plain, the water quality and agrichemical loading of the discharge from two groundwater basins were monitored for almost 2 years. The results provided the basis for estimates of the mass loading of nutrients and pesticides to surface water in a karst region that eventually discharges to the Mississippi River. From these estimates, we attempted to determine the dominant source of NO_3^- discharging from the groundwater basins and entering surface waters. A secondary objective was to estimate the erosion rate and the mass of pesticides associated with suspended sediments.

A monitoring station was set up just downstream of the two springs that drain the Collier Spring and Fogelpole Cave and/or conduit groundwater basins. The geology, results of ongoing work, previous tracer studies by others, and chemical compositions of the spring waters suggest that the springs discharge from two cave systems occupying adjacent and slightly overlapping geographic areas that are vertically separated where they overlap. Land use in the groundwater basins is mostly row-crop agriculture, which our investigation shows to have a negative impact on the water quality of the springs and stream.

Water-quality data and discharge measurements from the monitoring station allowed the annual mass loading of agrichemicals from the basin to be estimated. Using estimates of background NO_3^--N concentrations and results from NO_3^- isotope studies, the threshold for background concentrations for NO_3^--N was determined to be approximately 1.9 mg/L, and slightly over one third of the NO_3^--N discharging from the springs was N fertilizer. Using these estimates, we determined that approximately 100,000 kg/yr (220,000 lb/yr) of NO_3^--N, 39 kg/yr (86 lb/yr) of atrazine, and 2.8 kg/yr (6.2 lb/yr) of alachlor were discharged from the groundwater basins. These rates represent a 21 to 31% loss of applied N, a 3.8 to 5.8% loss of applied atrazine, and a 0.05 to 0.08% loss of applied alachlor. The loss of atrazine adsorbed to suspended solids was relatively low, amounting to only about 2 kg/yr (4 lb) (5.1% of the total lost atrazine). The loss of dissolved P from the Collier Spring and Fogelpole Cave groundwater basins was insignificant, and concentrations in the water rarely exceeded our detection limits of 0.01 mg/L.

Bacteria isolated from spring water samples included up to 17 species that were present in millions of colonies per 100 mL of water. These bacteria were dominated by *K. pneumoniae*, *Pseudomonas* spp., *E. coli,* and *Bacillus* spp., the first and third of which are fecal coliforms. The presence of *E. coli* and fecal enterococci (in 97 to 100% and 82 to 94% of the water samples, respectively) suggests the influence of private septic systems and/or livestock wastes within the basin.

Soil erosion rates for the Collier Spring and Fogelpole Cave groundwater basins were based on samples of suspended solids collected every 2 to 3 weeks from the two springs and at the bridge site over a 22-month period. Because of a strong correlation between the concentration of suspended solids and the specific conductance of spring and stream water (r^2 = 0.71), and because the specific conductance was continually monitored, we were able to estimate the annual erosion rate from the groundwater basins. The erosion rate for the Collier Spring and Fogelpole Cave groundwater basins was calculated to be approximately 0.15 cm/yr (0.06 in/yr), which is about twice the rate at which soil is being produced by natural soil-forming processes and about twice the rate of soil losses for most of Illinois.

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References

Aley, T., and C. Aley, 1998, Groundwater tracing and recharge area delineation study for two karst study areas in Monroe County, Illinois, Report to the Mississippi Karst Resource Planning Committee, Monroe County, Illinois: Protem, Missouri, Ozark Underground Laboratory.

Aley, T., P. Moss, and C. Aley, 2000, Delineation of recharge areas for four biologically significant cave systems in Monroe and St. Clair County, Report to the Illinois Nature Preserves Commission and the Monroe County Soil and Water Conservation District: Protem, Missouri, Ozark Underground Laboratory.

Anderson, C.D., et al., 1989, Illinois agronomy handbook: Champaign, Illinois, University of Illinois Cooperative Extension Service, Circular 1290, 116 p.

Anisfeld, S.C., T. Trexler, M. Steinhoff, G. Benoit and P. Barten, 1999, Analysis of temporal sampling requirements for determination of riverine nitrogen loads, American Geophysical Union 1999 Spring Meeting, Boston, June 1–4: Eos, v. 80, no. 17, p. S179.

ASTM (American Society for Testing and Materials), 1994, Standard test method for total and organic carbon in water by high temperature oxidation and coulometric detection, Annual Book of ASTM Standards, Section 11, Water and Environmental Technology, 11.02: Conshohocken, Pennsylvania, ASTM, p. 536.

Bethke, C.M., 1994, The Geochemist's Workbench™, version 2.0, hydrogeology program: Urbana, University of Illinois at Urbana-Champaign.

Blum, D.A., J.D. Carr, R.K. Davis, and D.T. Peterson, 1993, Atrazine in a stream-aquifer system—Transport of atrazine and its environmental impact near Ashland, Nebraska: Groundwater Monitoring & Remediation, v. 13, no. 2, p. 125–133.

Burks, B.D., and M.M. Minnis, 1994, Onsite wastewater treatment systems: Madison, Wisconsin, Hogarth House, Ltd., 248 p.

Burt, T.P., A.L. Heathwaite, and S.T. Trudgil, 1993, Nitrate—Processes, patterns and management: New York, John Wiley and Sons, 444 p.

Cane, G., and I.D. Clark, 1999, Tracing ground water recharge in an agricultural watershed with isotopes: Groundwater, v. 37, no. 1, p.133–139.

Chapelle, F.H., 1993, Ground-water microbiology and geochemistry: New York, John Wiley and Sons, Inc., 424 p.

Clark, I.D., and P. Fritz, 1997, Environmental isotopes in hydrogeology: New York, Lewis Publishers, 328 p.

Clesceri, L.S., A.E. Greenberg, and R.R. Trussel, 1989, Standard methods for the examination of water and wastewater (17th ed.): Washington, D.C., American Public Health Association.

Colborn, T., F.S. vom Saal, and A.M. Soto, 1993, Developmental effects of endocrine-distrupting chemicals in wildlife and humans: Environmental Health Perspectives, v. 101, no. 5, p. 378–384.

Craun, G.F., 1979, Waterborne disease—A status report emphasizing outbreaks in ground-water systems: Ground Water, v. 17, no. 2, p. 183–191.

Currens, J.C., 1999, Mass flux of agricultural nonpoint-source pollutants in a conduit-flow–dominated karst aquifer, Logan County, Kentucky: Lexington, Kentucky, Kentucky Geological Survey, Report of Investigations 1, Series XII, 151 p.

David, M.B., L.E. Gentry, D.A. Kovacic, and K.M. Smith, 1997, Nitrogen balance in and export from an agricultural watershed: Journal of Environmental Quality, v. 26, p. 1038– 1048.

Diaz, R.J., 2001, Overview of hypoxia around the world: Journal of Environmental Quality, v. 30, p. 275–281.

Drever, J.I., 1997, The geochemistry of natural waters: Surface and groundwater environments (3rd ed.): New Jersey, Prentice Hall, 436 p.

Feth, J.H., 1966, Nitrogen compounds in natural water—A review: Water Resources Research, v. 2, p. 41–58.

Freeman, B.A., 1985, Burrows textbook of microbiology, 22nd ed.: Philadelphia, Pennsylvania, W.B. Saunders, 1038 p.

Geldreich, E.E., 1996, Microbial quality of water supply in distribution systems, Boca Raton, Florida: CRC Press Inc., Lewis Publishers, 504 p.

Godfrey, J.T., G.D. Foster, and K.A. Lippa, 1995, Estimated annual loads of selected organic contaminants to Chesapeake Bay via major tributaries: Environmental Science and Technology, v. 29, no. 8, p. 2059–2064.

Goldberg, S., and G. Sposito, 1984, A chemical model of phosphate adsorption by soils: I. Reference oxide minerals: Soil Science of America Journal, v. 48, p. 772–778.

Goolsby, D.A., 1991, Agricultural chemicals in surface-water resources of the midcontinental United States, *in* D. Hamotharan, ed., Proceedings of the 27th Annual Conference on Water Management of River Systems and Symposium on Resource Development of the Lower Mississippi River, New Orleans: Bethesda, Maryland, American Water Resources Association, p. 373–374.

Goolsby, D.A., W.A. Battaglin, B.T. Aulenbach, and R.P. Hooper, 2001, Nitrogen input to the Gulf of Mexico: Journal of Environmental Quality, v. 30, p. 329–336.

Goolsby, D.A., W.A. Battaglin, G.B. Lawrence, R.S. Artz, B.T. Aulenbach, R.P. Hooper, D.R. Keeney, and G.J. Stensland, 1999, Flux and sources of nutrients in the Mississippi-Atchafalaya river basin, Topic 3 report for the Integrated Assessment of Hypoxia in the Gulf of Mexico, NOAA Coastal Program Decision Analysis, Series No. 17: Silver Spring, Maryland, NOAA Coastal Ocean Program.

Greenberg, A.E., L.S. Clesceri, and A.D. Eaton, 1992, Standard methods for the examination of water and wastewater (18th ed.): Washington, D.C., American Public Health Association, Methods 2540 D and 5310 B.

Groschen, G.E., M.A. Harris, R.B. King, P.J. Terrio, and K.L. Warner, 2000, Water quality in the lower Illinois River Basin, Illinois, 1995–98: Reston, Virginia, U.S. Geological Survey, Circular 1209, 36 p.

Hackley, K.C., and T.F. Anderson, 1986, Sulfur isotopic variation in low-sulfur coals from the Rocky Mountain region: Geochimica et Cosmochimica Acta, v. 50, p. 1703–1713.

Hackley, K.C., S.V. Panno, H.H. Hwang, and W.R. Kelly, 2001, Groundwater quality of springs and wells of the sinkhole plain in southwestern Illinois: Determination of the dominant sources of nitrate: Illinois State Geological Survey, Final Report to the Monroe County Soil and Water Conservation District, 75 p.

Hallberg, G.R., 1986. From hoes to herbicides—Agriculture and ground-water quality: Journal of Soil and Water Conservation, v. 41, p. 357–364.

Hallberg, G.R., and D.R. Keeney, 1993, Nitrate, *in* W.J. Alley, ed., Regional Ground-Water Quality: New York, Van Nostrand Reinhold, p. 297–322.

Hansel, A.K., and W.H. Johnson, 1996, Wedron and Mason Groups: Lithostratigraphic reclassification of deposits of the Wisconsin Episode, Lake Michigan Lobe area: Illinois State Geological Survey, Bulletin 104, 116 p.

Hartley, H.O., and A. Ross, 1954, Unbiased ratio estimators: Nature, v. 174, p. 270–271.

Heathwaite, A.L., T.P. Burt, and S.T. Trudgill, 1993, Overview—The nitrate issue, *in* T.P. Burt, A.L. Heathwaite, and S.T. Trudgill (eds.), Nitrate—Processes, patterns and management: New York, John Wiley and Sons, p. 3–21.

Hem, J.D., 1989, Study and interpretation of the chemical characteristics of natural water: Washington, D.C., U.S. Geological Survey, Water Supply Paper 2254, 3rd ed., 263 p.

Holser, W.T., and I.R. Kaplan, 1966, Isotope geochemistry of sedimentary sulfates: Chemical Geology, v. 1, p. 93–135.

Howarth, R.W., G. Billen, D. Swaney, A. Townsend, N. Jaworski, K. Lajtha, J.A. Downing, R. Elmgren, N. Caraco, T. Jordan, F. Berendse, J. Freney, V. Kudeyarcv, P. Murdoch, and Z. Zhao-Liang, 1996, Regional nitrogen budgets and riverine N& P fluxes for the drainages to the North Atlantic Oceans—Natural and human influences: Biogeochemistry, v. 35, p. 75–139.

Illinois Department of Agriculture, 2000, 2000 Illinois soil conservation transect summary: Springfield, Illinois, Illinois Department of Agriculture, 71 p.

Illinois Department of Natural Resources, 1996, Illinois land cover—An atlas: Springfield, Illinois, Illinois Department of Natural Resources, IDNR/EEA-96/05.

Illinois Environmental Protection Agency, Illinois Pollution Control Board, 1999, Title 35: Environmental Protection, Subtitle C: Water Pollution, Chapter I: Pollution Control Board, State of Illinois Rules and Regulations 302.209.

Illinois Natural History Survey, 2000, Illinois GAP project classification for Festus: Champaign, Illinois, Illinois Natural History Survey, 1:100,000 maps.

Kastning, E.H., III, 1995, Evolution of a karstic groundwater system, Cave Hill, Augusta County, Virginia—A multi-disciplinary study, *in* B.F. Beck (ed.), Proceedings of the Fifth Multidisciplinary Conference on Sinkholes and the Engineering and Environmental Impacts of Karst, Gatlinburg, Tennessee, April 2–5: Rotterdam/Brookfield, A.A. Balkema, p. 141–148.

Keefer, L., and M. Demissie, 1999, Watershed monitoring for the Lake Decatur Watershed: Champaign, Illinois, Illinois State Water Survey, Contract Report 637, 27 p.

Kelce, W.R., C.R. Stone, S.C. Laws, L.E. Gray, J.A. Kemppainen, and E.M. Wilson, 1995, Persistent DDT metabolite, p,p′-DDE is a potent androgen receptor antagonist: Nature, v. 375, p. 581–585.

Kimbrough, R.A., and D.W. Litke, 1996, Pesticides in streams draining agriculture and urban areas in Colorado: Environmental Science and Technology, v. 30, no. 3, p. 908–916.

Kolpin, D.W., 1997, Agricultural chemicals in groundwater of the midwestern United States: relations to land use: Journal of Environmental Quality, v. 27, p. 1025–1037.

Kolpin, D.W., E.M. Thurman, and S.M. Linhart,1998, The environmental occurrence of herbicides: The importance of degradates in ground water: Archives of Environmental Contaminants Toxicology, v. 35, p. 385–390.

Lakey, B., and N.C. Krothe, 1996, Stable isotopic variation of storm discharge from a perennial karst spring, Indiana: Water Resources Research, v. 32, no. 3, p. 721–731.

Laudon, H., and O. Slaymaker, 1997, Hydrograph separation using stable isotopes, silica and electrical conductivity—An alpine example: Journal of Hydrology, v. 201, p. 82–101.

Liu, H., R.D. Rowden, and R.D. Libra, 1997, Groundwater monitoring in the Big Spring Basin 1994–1995; A summary review: Iowa City, Iowa, Department of Natural Resources, Technical Information Series 37.

Loehr, R.C., 1974, Characteristics and comparative magnitude of non-point sources: Journal of Water Pollution Control Federation, v. 46, 1849–1872.

Lopez-Chicano, M.M., Boramama, A Vallejoy, and A. Pulido-Bosch, 2001, Factors which determine the hydrochemical behaviour of karstic springs; A case study from the Betic Cordilleras, Spain: Applied Geochemistry, v. 16, p. 1179–1192.

McLachlan, J.A., and S.F. Arnold, 1996, Environmental estrogens—Chemicals in the environment can mimic the effects of biological signaling molecules: American Scientist, v. 84, no. 5, p. 452–461.

National Atmospheric Deposition Program (NRSP-3)/National Trends Network, 1998, NADP Program Office: Champaign, Illinois, Illinois State Water Survey.

National Atmospheric Deposition Program, 2000, NADP Program Office: Champaign, Illinois, Illinois State Water Survey.

Nelson, W.J., 1995, Structural features in Illinois: Illinois State Geological Survey, Bulletin 100, 144 p.

O'Riordan, T., and G. Bentham, 1993, The politics of nitrate in the UK, *in* T.P. Burt, A.L. Heathwaite, and S.T. Trudgill (eds.), Nitrate—Processes, patterns and management: New York, John Wiley and Sons, p. 403–416.

Panno, S.V., 1996, Water quality in karst terrane: The Karst Window, v. 2, p. 2–4.

Panno, S.V., K.C. Hackley, H.-H. Hwang, and W.R. Kelly, 2000, Determination of the sources of nitrate contamination in karst springs using isotopic and chemical indicators, *in* Proceedings of the Tenth Annual Conference on Research on Agricultural Chemicals in Illinois Groundwater: Status and Future Directions X, Illinois Groundwater Consortium, Makanda, Illinois, April 13, p. 68–82.

Panno, S.V., K.C. Hackley, H.-H. Hwang, and W.R. Kelly, 2001, Determination of the sources of nitrate contamination in karst springs using isotopic and chemical indicators: Chemical Geology, v. 179, p. 113–128.

Panno, S.V., K.C. Hackley, W.R. Kelly, and H.-H. Hwang, H.H. 1999. Sources of nitrate contamination in karst springs using isotopic, chemical, and bacterial indicators—Preliminary results, *in* Proceedings of the Ninth Annual Conference on Research on Agricultural Chemicals in Illinois Groundwater: Status and Future Directions IX, Illinois Groundwater Consortium, Makanda, Illinois, April 1, p. 91–103.

Panno, S.V., K.C. Hackley, and C.P. Weibel, 1998b, The chemical composition of observation wells, springs and surface water at the City of Columbia Municipal Landfill: Illinois State Geological Survey, Report to the City of Columbia, 15 p.

Panno, S.V., W.R. Kelly, K.C. Hackley, and H.-H. Hwang, 2002, Distribution and sources of heterotrophic bacteria in wells, caves and springs of a karst aquifer in the midwestern U.S. *in* Proceedings of the KWI Symposium on Karst Frontiers: Florida and Related Environments, March 6–9, 2002, Gainesville, Florida: Charles Town, West Virginia, Karst Waters Institute, Special Publication 7, p. 92–94.

Panno, S.V., W.R. Kelly, C.P. Weibel, I.G. Krapac, and S.L. Sargent, 1998a, The effects of land use on water quality and agrichemical loading in the Fogelpole Cave groundwater basin, southwestern Illinois, *in* Proceedings of the Illinois Groundwater Consortium's Eighth Annual Conference, Research on Agricultural Chemicals in Illinois Groundwater, April 1–2, Makanda, Illinois, p. 215–233.

Panno, S.V., I.G. Krapac, C.P. Weibel, and J.D. Bade, 1996, Groundwater contamination in karst terrain of southwestern Illinois: Illinois State Geological Survey, Environmental Geology 151, 43 p.

Panno, S.V., E.C. Storment, C.P. Weibel, and I.G. Krapac, 1997b, Bacterial species isolated from groundwater from springs, caves and wells in southwestern Illinois' sinkhole plain and their potential sources, *in* Proceedings of the Annual Environmental Laboratories Seminar, October 2–3, Springfield, Illinois, p. 1–4.

Panno, S.V., and C.P. Weibel, 1999, Delineation and characterization of the groundwater basins of four cave systems of southwestern Illinois' sinkhole plain, in A.N. Palmer, M.V. Palmer and I.D. Sasowsky (eds.), Abstract *in* Karst Modeling: Symposium Proceedings, Charlottesville, Virginia, February 24–27, 1999, Karst Water Institute Special Publication 5, p. 244.

Panno, S.V., C.P. Weibel, D.A. Keefer, and I.G. Krapac, 1994, Mapping of karst areas in Illinois II: Agrichemical contamination in karst aquifers of southwestern Illinois, *in* Proceedings of the Fourth Annual Conference on Research on Agricultural Chemicals in Illinois Groundwater: Status and Future Directions IV. Illinois Groundwater Consortium, Makanda, Illinois, March 23–24, p. 99–109.

Panno, S.V., C.P. Weibel, and W. Li, 1997a, Karst regions of Illinois: Illinois State Geological Survey, Open File Series 1997-2, 43 p.

Parry, R., 1998, Agricultural phosphate and water quality—A U.S. Environmental Protection Agency perspective: Journal of Environmental Quality, v. 27, p. 258–261.

Pasquarell, G.C., and D.G. Boyer, 1995, Agricultural impacts on bacterial water quality in karst groundwater: Journal of Environmental Quality, v. 24, p, 959–969.

Pfaff, J.D., 1993, Method 300.0: Determination of inorganic anions in water by ion chromatography, revision 2.1: Cincinnati, Ohio, US Environmental Protection Agency, p. 30.

Piskin, K., and R.E. Bergstrom, 1975. Glacial drift in Illinois—Thickness and character: Illinois State Geological Survey, Circular 490.

Plummer, L.N., E.C. Prestemon, and D.L. Parkhurst, 1994, An interactive code (NETPATH) for modeling NET geochemical reactions along a flow PATH—Version 2.0, Water Resources Investigation Report 94-4169: Reston, Virginia, U.S. Geological Survey.

Rabalais, N.N., R.E. Turner, D. Justic, Q. Dortch, W.J. Wiseman Jr., and B.K. Sen Gupta, 1996, Nutrient changes in the Mississippi River and system responses on the adjacent continental shelf: Estuaries, v. 19, p. 286–407.

Rabalais, N.N., R.E. Turner, and W.J. Wiseman, Jr., 2001, Hypoxia in the Gulf of Mexico: Journal of Environmental Quality, v. 30, p. 320–329.

Randall, G.W., and D.J. Mulla, 2001, Nitrate nitrogen in surface waters as influenced by climatic conditions and agricultural practices: Journal of Environmental Quality, v. 30, p. 337–344.

Rantz, S.E., et al., 1982a, Measurement and computation of streamflow, volume 1, Measurement of stage and discharge: Reston, Virginia, U.S. Geological Survey, Water-Supply Paper 2175, p. 1–284.

Rantz, S.E., et al., 1982b, Measurement and computation of streamflow, volume 2, Computation of discharge: Reston, Virginia, U.S. Geological Survey, Water-Supply Paper 2175, p. 285–631.

Rowden, R.D., R.D. Libra, G.R. Hallberg, and B. Nations, 1993, Groundwater monitoring in the Big Spring Basin 1990–1991; A summary review: Iowa City, Iowa, Iowa Department of Natural Resources, Technical Information Series 27.

Ryan, M., and J. Meiman, 1996, An examination of short-term variations in water quality at a karst spring in Kentucky: Ground Water, v. 34, p. 23–30.

Scanlan, B.R., 1989, Physical controls on hydrochemical variability in the inner Bluegrass karst region of central Kentucky: Ground Water, v. 27, p. 639–646.

Schock, S.C., E. Mehnert, M.E. Caughey, G.B. Dreher, W.S. Dey, S. Wilson, C. Ray, S.-F.J. Chou, J. Valkenburg, J.M. Gosar, J.R. Karny, M.L. Barnhardt, W.F. Black, M.R. Brown, and V.J. Garcia, 1992, Pilot study: agricultural chemicals in rural, private wells in Illinois: Illinois State Geological Survey, Illinois State Water Survey, and Illinois Department of Agriculture, Cooperative Groundwater Report 14.

Scudlark, J.R., K.M. Russell, J.N. Galloway, T.M. Church, and W.C. Keene, 1998, Organic nitrogen in precipitation at the Mid-Atlantic U.S. coast–methods evaluation and preliminary measurements: Atmospheric Environment, v. 32, p.1719–1728.

Seta, A.K., and A.D. Karathanasis, 1997, Atrazine adsorption by soil colloids and co-transport through subsurface environments: Soil Science Society of America Journal, v. 61, p. 612–617.

Shiller, A.M., 1997, Dissolved trace elements in the Mississippi River: Seasonal, interannual, and decadal variability: Geochemica et Cosmochemica Acta, v. 61, p. 4321–4330.

Shuster, E.T., and W.B. White, 1972, Source areas and climatic effects in carbonate groundwaters determined by saturation indices and carbon dioxide pressures: Water Resources Research, v. 8, p. 1067–1073.

Sinclair, A.J., 1974, Selection of threshold values in geochemical data using probability graphs: Journal of Geochemical Exploration, v. 3, p.129–149.

Thurman, E.M., D.A. Goolsby, M.T. Meyer, M.S. Mills, M.L. Pomes, and D.W. Kolpin, 1992, A reconnaissance study of herbicides and their metabolites in surface water of the midwestern United States using immunoassay and gas chromatography/mass spectrometry: Environmental Science and Technology, v. 26, p. 2440–2447.

Thurman, E.M., M. Meyer, M. Pomes, C.A. Perry, and A.P. Schwab, 1990, Enzyme-linked immunosorbent assay compared with gas chromatography/mass spectrometry for the determination of triazine herbicides in water: Analytical Chemistry, v. 62, p. 2043–2048.

Tisdale, S.L., W.L. Nelson, J.D. Beaton, and J.L. Havlin, 1993, Soil fertility and fertilizers, 5th ed.: New York, Macmillan Publishing Company, 634 p.

U.S. Department of Agriculture, 1987, Soil survey of Monroe County, Illinois, National Cooperative Soil Survey: Washington, D.C., U.S. Department of Agriculture, Soil Conservation Service, in cooperation with the Illinois Agricultural Station, Washington, Soil Report 127, 174 p.

U.S. Environmental Protection Agency, 1992, SOCs and IOCs, Final Rule: Washington, D.C., USEPA Federal Regulation 56:20:3526.

U.S. Environmental Protection Agency, 2000, How much drinking water do we use in our homes?: Washington, D.C., Office of Groundwater and Drinking Water (www.epa.gov/safewater/wot/howmuch.html).

U.S. Environmental Protection Agency, 2001, Clean air status and trends network (CASTNET): Washington, D.C., Office of Air Quality Planning and Standards, USEPA (www.epa.gov/castnet).

U.S. Geological Survey, 2002, The quality of our nation's waters—Nutrients and pesticides: Reston, Virginia, U.S. Geological Survey, Circular 1225.

Wassenaar, L., R. Aravena, P. Fritz, and J. Barker, 1990, Isotopic composition (13C, 14C, 2H) and geochemistry of aquatic humic substances from groundwater: Organic Geochemistry, v. 15, p. 383–396.

Weibel, C.P., and S.V. Panno, 1997, Karst terrains and carbonate rocks of Illinois: Illinois State Geological Survey, Illinois Map 8, 1:500,000.

Weller, S., and J.M. Weller, 1939, Preliminary geological maps of the Pre-Pennsylvanian Formations in part of southwestern Illinois: Illinois State Geological Survey, Report of Investigations 59.

White, W.B., 1988, Geomorphology and hydrology of karst terrains: New York, Oxford University Press, 464 p.

Wightman, P., 1967, Monroe County's cellar, *in* H.R. Klein, ed., Arrowheads to Aerojets: Valmeyer, Illinois, Monroe County Historical Society, Myron Roever Associates, p. 71–73.

Willman, H.B., E. Atherton, T.C. Buschbach, C. Collinson, J.C. Frye, M.E. Hopkins, J.A. Lineback, and J.A. Simon, 1975, Handbook of Illinois Stratigraphy: Illinois State Geological Survey, Bulletin 95, 261 p.

Wood, W.W., 1981, Guidelines for collection and field analysis of groundwater samples for selected unstable constituents, *in* Techniques of water-resources investigations of the U.S. Geological Survey, Book 1, Ch. D2, Reston, Virginia, U.S. Geological Survey, p. 1–24.

Appendix

Table A1 Complete chemical data for the water samples collected from the South Fork Creek bridge site.[1,2] All data are reported in milligrams per liter unless otherwise indicated.

Date	Temp. (°C)	pH	Eh (mV)	SpC (µS/cm)	Na	K	Ca	Mg	SiO_2	HCO_3^-	NO_3^--N	SO_4^{2-}	PO_4^{3-}	Cl^-	Br^-	Fe	Mn	Alachlor (µg/L)	Atrazine (µg/L)	SS	DOC	Dis-charge (L/s)
10/15/96	7.4	7.14	ND	247	5.24	5.0	32.6	5.50	11.2	102	2.43	14.7	<0.01	7.71	<0.01	<0.009	0.06	0.66	0.18	215	ND	ND
11/26/96	5.8	7.11	ND	129	2.60	4.0	16.3	3.18	9.28	38.1	1.08	11.1	<0.01	4.38	<0.01	<0.009	0.11	0.54	0.18	415	ND	ND
12/18/96	3.7	7.99	419	408	13.2	4.0	66.3	10.0	15.8	188	2.65	28.5	0.12	8.50	<0.01	<0.009	0.09	<0.01	0.47	77	ND	ND
01/07/97	3.7	7.88	433	537	20.0	<0.6	90.2	13.7	17.3	257	3.16	35.8	<0.01	10.7	0.15	<0.009	0.16	0.14	0.48	21	ND	ND
01/24/97	6.5	7.15	490	221	6.90	4.0	34.3	5.69	11.7	85.3	1.86	20.0	0.09	6.03	<0.01	<0.009	0.08	0.15	0.37	253	ND	ND
02/04/97	7.3	7.02	432	256	7.90	3.0	36.0	5.72	11.8	106	2.17	19.3	0.08	6.09	<0.01	<0.009	0.10	0.43	0.39	481	ND	ND
02/20/97	8.6	7.66	416	365	14.0	8.0	48.3	8.64	11.7	162	2.07	24.7	0.24	13.3	0.07	<0.009	0.16	0.16	<0.01	631	ND	ND
03/05/97	9.7	7.72	402	391	11.7	3.0	64.7	8.09	17.4	181	2.81	24.8	<0.01	6.54	<0.01	0.03	0.19	0.21	0.16	113	ND	ND
03/19/97	12.0	7.76	422	455	16.6	2.0	77.1	10.6	19.4	214	3.16	31.9	<0.01	7.52	<0.01	0.07	0.14	0.22	0.21	96	ND	ND
04/01/97	9.8	8.11	351	545	20.3	2.0	91.4	12.3	17.4	263	3.37	34.7	<0.01	9.76	0.06	0.01	0.25	<0.01	0.34	<25	ND	ND
04/16/97	13.0	7.87	349	438	14.4	2.0	72.9	9.64	15.9	206	2.57	29.7	<0.01	6.81	0.07	0.03	0.23	<0.01	0.33	37	ND	ND
04/30/97	14.5	7.90	345	559	19.8	2.0	90.3	12.5	16.4	269	2.95	38.5	<0.01	10.1	0.06	0.01	0.32	0.16	0.89	<25	ND	ND
05/13/97	15.2	8.01	343	572	21.6	<0.6	96.4	13.7	16.7	277	3.16	37.7	<0.01	11.0	0.06	<0.009	0.34	<0.01	1.24	<25	ND	ND
05/28/97	15.1	7.31	428	414	13.2	<0.6	60.5	9.37	14.3	187	4.90	26.5	<0.01	15.1	0.05	0.11	0.30	0.54	21.8	133	ND	ND
06/12/97	15.9	7.85	512	555	20.1	2.0	93.5	12.9	21.6	272	3.91	29.1	<0.01	10.6	<0.01	<0.009	0.24	0.23	4.99	<25	ND	ND
06/24/97	16.9	7.84	334	509	16.1	<0.6	78.3	10.4	20.6	245	3.64	29.0	<0.01	9.49	0.06	0.01	0.17	<0.01	2.04	<25	ND	ND
07/28/97	20.0	8.03	484	625	22.4	<0.6	111	15.3	20.8	310	3.97	33.5	<0.01	11.1	0.07	<0.009	0.17	ND	0.72	<25	ND	ND
08/21/97	17.1	7.84	499	534	17.3	2.0	82.0	11.4	19.6	261	3.93	26.3	<0.01	9.74	0.05	0.02	0.12	ND	3.76	41	ND	ND
09/30/97	15.8	8.01	482	669	22.6	<0.6	102	15.1	19.8	333	3.79	35.5	<0.01	12.5	0.05	<0.009	0.06	<0.01	0.39	<25	ND	ND
10/29/97	8.2	7.88	425	623	27.7	4.0	99.0	15.8	20.6	303	3.35	40.8	<0.01	13.1	0.07	<0.009	0.06	<0.01	0.37	<25	16.0	ND
11/12/97	6.1	7.88	489	419	14.5	5.0	61.7	9.51	17.3	193	3.65	24.3	<0.01	13.5	0.04	0.05	0.11	0.19	0.57	44	15.8	164
11/24/97	5.4	7.93	399	476	15.0	2.0	71.8	11.1	18.4	226	3.64	25.8	<0.01	12.8	0.04	0.01	0.10	0.11	0.58	<25	15.3	115
12/15/97	2.9	8.14	298	574	21.5	4.0	86.5	14.5	18.7	279	3.05	34.7	<0.01	12.7	0.07	<0.009	0.13	0.10	0.62	<25	14.6	144
12/29/97	5.1	7.63	393	266	8.52	6.0	37.2	6.84	12.6	105	2.29	23.8	<0.01	13.0	0.05	0.15	0.14	<0.01	0.59	289	13.1	236
01/06/98	11.0	7.80	ND	390	13.2	5.0	58.9	9.58	16.4	176	2.71	28.4	<0.01	10.0	0.06	0.16	0.08	0.18	0.57	87	14.8	664
01/26/98	7.5	8.18	538	529	18.9	3.0	83.2	12.1	18.1	251	3.52	35.1	<0.01	13.8	0.08	<0.009	0.23	<0.01	0.16	<25	13.5	328
02/17/98	9.0	7.50	585	150	3.83	4.0	19.4	3.65	12.6	48.6	1.76	14.3	<0.01	3.56	<0.01	0.36	0.13	<0.01	0.24	1,860	13.6	43,727
03/03/98	8.2	8.22	468	506	17.0	<0.6	77.7	10.6	17.3	242	3.03	32.6	<0.01	9.32	0.06	<0.009	0.21	<0.01	0.23	<25	ND	452
03/25/98	12.9	7.79	443	428	11.9	3.0	63.4	7.67	17.0	202	3.08	25.8	<0.01	7.38	0.04	0.02	0.14	<0.01	0.14	69	12.1	1,645
04/15/98	13.2	7.32	444	543	20.9	2.0	99.3	13.1	19.9	262	3.16	34.7	<0.01	9.57	0.07	<0.009	0.25	0.15	0.23	<25	13.6	8,590
04/28/98	12.2	7.91	423	536	21.3	2.0	99.4	13.1	22.3	260	3.30	32.0	<0.01	9.63	0.07	<0.009	0.23	<0.01	0.31	<25	ND	720
05/12/98	15.2	7.90	431	579	19.9	<0.6	95.4	12.5	19.4	282	3.29	35.3	<0.01	10.6	0.07	<0.009	0.24	0.13	1.42	<25	14.4	518
05/26/98	15.8	7.87	281	611	21.4	2.0	98.8	13.5	19.1	301	3.68	34.2	<0.01	11.4	0.15	<0.009	0.25	0.17	8.20	<25	ND	447
06/09/98	15.7	7.60	95	395	10.6	3.0	59.3	8.54	16.3	182	4.95	20.8	<0.01	10.0	0.07	0.05	0.12	0.59	8.90	81	13.8	823
07/01/98	18.5	7.78	452	551	18.3	3.0	89.0	11.6	20.5	272	3.58	26.7	<0.01	9.37	0.07	<0.009	0.11	0.21	1.76	26	ND	497
07/14/98	17.7	7.66	534	475	14.0	2.0	75.2	9.57	18.3	231	2.83	22.2	<0.01	7.87	0.05	0.01	0.11	<0.01	2.77	<25	13.0	481
07/28/98	16.8	7.49	428	425	12.6	4.0	63.8	8.87	18.2	202	3.81	21.6	<0.01	7.31	0.03	0.01	0.10	<0.01	3.61	34	ND	459
08/18/98	17.5	7.56	485	477	13.5	2.0	73.6	9.29	18.5	232	2.89	23.2	<0.01	7.33	0.07	<0.009	0.22	ND	0.55	253	13.6	1,107

[1] Samples were collected about every 2 weeks from October 1996 through August 1998.

[2] Eh, redox potential; SpC, specific conductivity, SS, suspended solids; DOC, dissolved organic carbon; ND, no data.

Table A2 Complete chemical data for the water samples collected from Indian Hole Spring.[1,2] All data are reported in milligrams per liter unless otherwise indicated.

Date	Temp. (°C)	pH	Eh (mV)	SpC (μS/cm)	Na	K	Ca	Mg	SiO_2	HCO_3^-	NO_3^--N	SO_4^{2-}	PO_4^{3-}	Cl^-	Br^-	Fe	Mn	Alachlor (μg/L)	Atrazine (μg/L)	SS	DOC	Discharge (L/s)
09/03/96	14.1	7.30	ND	649	24.1	<0.6	96.6	16.2	17.6	320	4.03	39.9	<0.01	11.6	0.07	<0.009	0.02	ND	ND	ND	ND	ND
10/15/96	12.3	6.64	ND	248	6.39	4.0	31.2	5.77	11.2	101	3.25	17.7	<0.01	7.19	<0.01	<0.009	<0.009	0.52	<0.01	195	ND	ND
11/26/96	6.2	7.08	ND	118	3.00	4.0	14.1	3.00	8.34	32.5	1.12	11.2	<0.01	2.77	0.44	<0.009	0.07	0.92	<0.01	413	ND	ND
12/18/96	11.3	7.45	449	464	18.2	3.0	71.7	12.4	15.3	213	3.00	39.1	<0.01	9.89	0.15	<0.009	0.01	0.13	0.48	83	ND	ND
01/07/97	11.9	7.63	453	616	26.6	3.0	90.6	16.1	16.9	293	3.89	50.8	<0.01	13.0	0.18	<0.009	0.05	<0.01	0.52	17	ND	ND
01/24/97	8.8	7.03	469	226	8.40	4.0	29.2	5.36	11.0	86.1	2.39	21.7	<0.01	7.41	<0.01	<0.009	<0.009	0.10	0.53	316	ND	ND
02/04/97	6.8	6.90	429	238	9.00	2.0	30.5	5.54	10.1	93.7	2.12	21.4	<0.01	6.94	0.59	<0.009	0.04	0.17	0.57	532	ND	ND
02/20/97	11.3	8.06	414	584	26.0	<0.6	91.2	15.2	18.0	277	3.88	47.2	<0.01	11.7	0.09	<0.009	0.02	0.31	0.21	243	ND	ND
03/05/97	11.2	7.76	425	402	14.8	1.0	61.9	9.23	16.0	183	3.03	30.6	<0.01	7.54	0.36	0.13	0.03	0.25	0.14	75	ND	ND
03/19/97	11.4	7.80	393	478	21.4	2.0	73.1	12.7	15.6	218	3.35	45.8	<0.01	8.36	0.08	0.03	0.02	0.20	0.16	95	ND	ND
04/01/97	12.1	8.07	375	584	24.4	2.0	91.6	14.6	18.3	278	3.89	47.0	<0.01	11.2	0.08	<0.009	0.03	<0.01	0.29	<25	ND	ND
04/16/97	12.0	7.81	372	450	17.5	2.0	70.6	10.9	16.7	207	2.89	38.0	<0.01	7.27	0.51	0.08	0.02	<0.01	0.22	40	ND	ND
04/30/97	12.4	7.90	355	615	26.3	2.0	96.1	15.6	18.5	294	3.48	50.7	<0.01	11.8	0.07	<0.009	0.03	0.16	0.28	<25	ND	ND
05/13/97	12.5	7.94	429	615	26.4	<0.6	97.1	16.3	19.0	293	3.78	50.1	<0.01	12.6	0.08	<0.009	0.03	<0.01	<0.01	<25	ND	ND
05/28/97	13.7	7.68	518	457	17.0	<0.6	62.8	11.2	13.8	203	5.12	34.3	<0.01	23.3	0.07	0.04	0.04	0.43	16.1	132	ND	ND
06/12/97	13.3	7.50	556	574	23.6	<0.6	88.5	14.5	19.4	277	4.08	36.3	<0.01	12.4	<0.01	<0.009	0.02	0.11	4.74	<25	ND	ND
06/24/97	14.1	7.62	377	536	20.2	<0.6	76.7	12.3	18.4	255	3.45	38.0	<0.01	10.9	0.07	<0.009	0.03	0.13	2.21	<25	ND	ND
07/28/97	13.5	7.68	479	690	27.9	<0.6	114	18.8	20.9	338	4.31	47.1	<0.01	13.1	0.08	<0.009	0.05	ND	0.42	<25	ND	ND
08/21/97	14.4	7.21	498	414	12.5	4.0	58.7	9.47	16.1	191	4.20	28.6	<0.01	8.03	0.04	0.19	0.01	ND	6.90	122	ND	ND
09/30/97	13.4	7.00	460	712	26.8	2.0	98.7	18.2	17.2	346	3.78	55.8	<0.01	14.0	0.08	<0.009	0.08	<0.01	0.55	<25	ND	ND
10/29/97	12.5	7.49	488	573	25.2	4.0	82.1	16.7	17.9	267	2.95	53.7	<0.01	12.5	0.09	<0.009	0.05	0.13	1.89	<25	14.8	ND
11/24/97	12.1	7.19	398	459	17.0	3.0	62.2	11.9	16.6	210	4.23	35.4	<0.01	12.6	0.05	0.01	0.05	<0.01	0.63	31	14.4	92
12/29/97	10.2	7.19	431	237	8.10	5.0	30.8	5.97	11.1	90.9	2.59	22.9	<0.01	8.71	<0.01	0.05	<0.009	<0.01	0.92	376	14.7	143
01/06/98	11.9	7.76	ND	437	17.2	4.0	63.4	11.7	14.8	199	3.03	37.4	<0.01	9.81	0.08	0.10	0.02	0.10	0.33	ND	15.7	230
01/26/98	11.6	8.14	528	574	25.0	2.5	85.4	14.8	17.6	271	3.69	47.2	<0.01	13.1	0.09	0.01	0.04	<0.01	0.19	<25	ND	207
02/17/98	8.8	7.28	604	125	3.54	4.0	15.6	3.22	11.8	34.8	1.71	13.5	<0.01	2.85	<0.01	0.34	0.03	<0.01	0.33	625	ND	8,241
03/03/98	11.4	8.12	490	502	21.2	2.0	71.8	11.8	16.1	235	2.98	40.1	<0.01	10.1	0.06	<0.009	<0.009	<0.01	0.17	<25	ND	307
03/25/98	10.5	7.76	432	388	13.2	3.0	54.3	7.98	14.2	177	3.02	28.0	<0.01	7.26	0.04	<0.009	0.02	<0.01	0.14	86	ND	1,085
04/15/98	12.4	8.05	470	581	27.3	1.0	100	16.4	19.8	275	3.44	49.1	<0.01	10.8	0.07	<0.009	0.02	<0.01	0.26	<25	ND	904
04/28/98	12.9	7.84	459	534	24.5	3.0	91.6	14.3	19.5	253	3.13	40.4	<0.01	9.99	0.07	<0.009	0.02	<0.01	0.23	<25	ND	382
05/12/98	13.2	7.59	487	594	24.0	2.0	92.3	14.4	18.0	286	3.25	43.3	<0.01	11.2	0.08	<0.009	0.02	0.12	1.08	<25	ND	296
05/26/98	13.3	7.70	ND	657	26.5	<0.6	100	16.2	18.8	320	3.47	46.7	<0.01	12.8	0.12	<0.009	0.01	<0.01	1.25	<25	ND	ND
06/09/98	14.4	7.37	124	474	16.0	4.0	69.0	10.6	16.7	224	6.08	26.6	<0.01	11.9	0.08	0.02	<0.009	0.27	15.0	25	ND	438
07/01/98	15.4	7.46	430	562	22.6	2.0	82.6	14.2	16.7	270	3.29	38.9	<0.01	10.3	0.09	<0.009	0.02	0.17	2.77	<25	ND	150
07/14/98	16.5	7.34	ND	488	17.7	4.0	73.2	11.2	16.4	235	2.51	28.0	<0.01	8.77	0.07	0.02	0.09	<0.01	3.03	<25	ND	225
07/28/98	16.0	6.98	ND	396	13.4	3.0	56.9	9.20	16.1	184	2.81	24.8	<0.01	7.15	0.04	0.05	0.04	<0.01	7.40	48	ND	355
08/18/98	16.9	7.18	500	473	15.8	<0.6	69.4	10.4	16.9	227	2.50	27.8	<0.01	7.63	0.06	<0.009	0.05	ND	0.54	<25	ND	474

[1] Samples were collected about every 2 weeks from October 1996 through August 1998.

[2] Eh, redox potential; SpC, specific conductivity, SS, suspended solids; DOC, dissolved organic carbon; ND, no data.

Table A3 Complete chemical data for the water samples collected from Collier Spring.[1,2] All data are reported in milligrams per liter unless otherwise indicated.

Date	Temp. (°C)	pH	Eh (mV)	SpC (μS/cm)	Na	K	Ca	Mg	SiO_2	HCO_3^-	NO_3^--N	SO_4^{2-}	PO_4^{3-}	Cl^-	Br^-	Fe	Mn	Alachlor (μg/L)	Atrazine (μg/L)	SS	DOC	Discharge (L/s)
09/03/96	14.0	7.12	429	580	17.3	<0.6	96.6	12.4	21.2	291	3.89	22.9	<0.01	9.10	0.04	<0.009	0.03	ND	ND	ND	ND	ND
10/15/96	11.2	6.96	ND	255	4.41	5.0	33.2	5.23	11.6	108	2.38	12.9	<0.01	8.41	<0.01	<0.009	<0.009	0.72	0.24	133	ND	ND
11/26/96	7.8	6.97	ND	138	2.69	5.0	18.1	3.07	9.30	44.5	1.19	10.2	<0.01	3.16	<0.01	<0.009	0.03	0.45	0.44	353	ND	ND
12/18/96	11.7	7.40	512	415	11.3	3.0	71.0	8.84	17.4	196	2.78	21.7	<0.01	7.86	<0.01	<0.009	<0.009	0.19	0.52	90	ND	ND
01/07/97	12.5	7.41	451	550	17.0	2.0	93.6	12.1	20.6	270	3.57	27.3	<0.01	9.94	0.14	<0.009	0.01	0.18	0.43	21	ND	ND
01/24/97	10.0	6.93	514	219	5.50	4.0	33.2	4.76	11.7	86.0	2.37	16.9	<0.01	5.43	<0.01	<0.009	<0.009	0.16	0.43	256	ND	ND
02/04/97	9.3	6.77	425	274	7.20	3.0	40.6	5.64	12.3	111	4.50	19.9	<0.01	13.0	0.03	<0.009	0.04	0.18	0.29	452	ND	ND
02/20/97	12.0	7.80	424	572	18.3	<0.6	102	11.7	23.4	289	4.10	16.8	<0.01	9.58	0.07	<0.009	0.01	0.24	0.23	<25	ND	ND
03/05/97	11.8	7.44	451	431	11.5	<0.6	75.6	7.67	20.1	206	3.30	22.3	<0.01	6.63	<0.01	0.02	0.02	0.26	0.20	52	ND	ND
03/19/97	12.0	7.56	350	505	15.5	2.0	90.7	9.72	22.5	245	3.63	26.7	<0.01	7.77	0.07	0.01	0.03	0.17	<0.01	36	ND	ND
04/01/97	12.6	8.04	421	564	18.1	<0.6	97.8	10.9	22.9	278	3.91	28.7	<0.01	9.34	0.05	0.01	0.02	0.16	0.23	<25	ND	ND
04/16/97	12.6	7.53	429	472	14.1	2.0	83.8	9.14	20.7	227	3.35	25.6	<0.01	7.13	0.07	0.03	0.02	<0.01	0.19	37	ND	ND
04/30/97	12.8	7.50	404	584	18.1	2.0	99.7	11.4	22.7	287	3.63	32.1	<0.01	9.73	0.05	<0.009	0.02	0.17	1.14	<25	ND	ND
05/13/97	12.9	7.72	358	593	19.4	<0.6	104	12.1	23.3	293	3.92	30.4	<0.01	10.5	0.05	<0.009	0.01	<0.01	0.96	<25	ND	ND
05/28/97	13.8	7.58	533	379	12.0	3.0	59.0	7.95	16.0	175	4.57	19.3	<0.01	8.82	<0.01	0.04	0.02	0.67	13.4	156	ND	ND
06/12/97	13.5	7.19	544	572	18.5	<0.6	99.1	11.6	24.4	283	4.53	27.1	<0.01	10.2	<0.01	<0.009	0.02	0.39	4.99	<25	ND	ND
06/24/97	14.4	7.53	413	545	15.8	<0.6	87.8	9.89	23.4	269	4.20	24.5	<0.01	9.43	0.04	0.01	0.03	<0.01	1.90	<25	ND	ND
07/28/97	13.7	7.49	504	641	22.4	<0.6	117	13.8	25.5	322	4.54	27.4	<0.01	10.6	0.05	<0.009	0.05	ND	1.19	<25	ND	ND
08/21/97	13.7	7.20	539	571	18.5	<0.6	88.3	11.6	21.3	283	4.51	25.7	<0.01	10.2	0.05	0.02	0.01	ND	5.10	<25	ND	ND
09/30/97	13.7	7.17	496	683	21.3	<0.6	106	13.9	22.9	346	4.47	28.3	<0.01	12.0	0.04	<0.009	0.05	<0.01	0.31	<25	ND	ND
10/29/97	13.4	7.44	524	594	21.5	3.0	98.6	13.2	22.6	294	3.98	28.3	<0.01	12.4	0.04	<0.009	0.03	0.12	0.40	113	14.9	ND
11/24/97	13.0	7.67	374	518	14.7	<0.6	80.3	11.0	21.2	252	4.12	23.8	<0.01	12.5	0.04	<0.009	0.03	0.11	0.41	<25	14.2	82
12/29/97	11.1	7.32	484	271	8.39	5.0	38.3	6.61	12.4	112	2.56	20.9	<0.01	7.92	0.05	0.05	<0.009	0.16	0.47	359	11.5	151
01/06/98	12.3	7.63	ND	437	13.7	4.0	70.0	9.69	18.0	206	2.94	25.3	<0.01	9.40	0.06	0.07	0.01	0.12	0.36	67	15.2	274
01/26/98	12.2	7.98	525	555	17.7	1.0	93.9	11.4	21.4	272	4.00	27.1	<0.01	11.5	0.06	<0.009	0.01	<0.01	0.26	<25	ND	214
02/17/98	9.6	7.10	620	157	3.71	4.0	21.7	3.63	12.6	53.9	1.64	12.7	<0.01	3.20	<0.01	0.31	0.06	<0.01	0.20	862	ND	10,355
03/03/98	12.3	7.84	517	555	16.1	<0.6	90.9	10.2	21.2	273	3.86	27.2	<0.01	9.20	0.05	<0.009	0.01	<0.01	0.19	<25	ND	246
03/25/98	11.6	7.53	486	493	12.7	<0.6	78.3	7.69	20.7	240	3.74	24.5	<0.01	7.74	0.04	<0.009	0.02	<0.01	0.16	<25	ND	733
04/15/98	12.7	7.57	467	582	20.9	3.0	113	12.4	26.4	288	3.97	29.7	<0.01	9.48	0.05	<0.009	0.02	<0.01	0.16	<25	ND	743
04/28/98	12.9	7.51	462	579	20.9	2.0	111	12.3	26.4	286	4.08	29.0	<0.01	10.2	0.05	<0.009	0.02	<0.01	2.84	<25	ND	392
05/12/98	13.1	7.55	479	601	18.7	2.0	104	11.6	23.8	299	4.14	28.2	<0.01	10.1	0.06	<0.009	0.01	<0.01	1.22	<25	ND	289
05/26/98	13.1	7.48	486	604	19.2	2.0	100	11.9	22.7	301	4.33	28.0	<0.01	10.6	0.09	<0.009	0.01	0.26	12.5	<25	ND	ND
06/09/98	14.2	7.00	147	393	8.80	4.0	62.1	7.55	17.7	183	4.85	18.7	<0.01	9.15	<0.01	0.04	<0.009	0.98	3.18	50	ND	439
07/01/98	14.3	7.26	535	548	16.1	3.0	88.9	10.2	22.3	272	4.29	21.8	<0.01	9.31	0.06	<0.009	0.04	0.21	0.97	25	ND	300
07/14/98	15.1	7.17	564	515	13.9	2.0	85.2	9.36	21.4	254	3.63	21.1	<0.01	8.09	<0.01	<0.009	0.05	0.15	2.61	<25	ND	292
07/28/98	14.8	6.75	ND	396	10.0	4.0	60.8	7.51	19.0	187	5.00	16.9	<0.01	6.78	0.03	0.03	0.03	0.11	1.88	55	ND	179
08/18/98	15.4	7.11	514	562	15.3	<0.6	90.5	9.81	23.3	281	3.82	23.0	<0.01	8.39	0.06	<0.009	0.04	ND	0.74	<25	ND	534

[1] Samples were collected about every 2 weeks from October 1996 through August 1998.

[2] Eh, redox potential; SpC, specific conductivity, SS, suspended solids; DOC, dissolved organic carbon; ND, no data.

Table A4 Nitrate and herbicide samples collected at the bridge site using the automated ISCO sampler.

Date	NO_3^--N (mg/L)	Alachlor (μg/L)	Atrazine (μg/L)
04/18/97	3.04	<0.01	0.16
04/19/97	3.02	<0.01	0.16
04/20/97	2.58	<0.01	0.22
04/21/97	2.42	<0.01	0.23
04/22/97	2.06	<0.01	0.32
04/26/97	2.19	0.24	2.72
05/02/97	1.94	0.16	2.60
05/04/97	1.76	<0.01	0.69
05/06/97	1.69	<0.01	0.95
05/09/97	2.44	<0.01	0.65
05/11/97	2.56	0.17	0.41
05/17/97	2.20	<0.01	0.31
05/21/97	2.51	<0.01	0.36
05/25/97	2.05	<0.01	0.46
05/26/97	1.87	0.11	6.60
05/27/97	2.92	0.50	17.3
05/30/97	4.17	ND[1]	13.1
05/31/97	1.51	ND	11.4
06/01/97	1.49	ND	14.7
06/02/97	2.90	ND	14.8
06/03/97	2.45	ND	13.3
06/05/97	2.89	ND	11.1
06/07/97	1.82	ND	10.7
06/10/97	2.27	ND	3.65
06/15/97	2.17	0.40	4.66
06/17/97	2.23	0.22	4.12
06/18/97	1.06	0.30	3.83
06/19/97	1.05	0.35	4.19
06/21/97	1.02	0.11	2.54
04/17/98	0.54	<0.01	0.33
04/18/98	0.98	<0.01	0.37
04/20/98	1.64	<0.01	0.33
04/23/98	4.73	0.10	0.35
04/29/98	4.95	<0.01	1.52
04/30/98	5.08	<0.01	3.06
05/03/98	4.41	<0.01	8.00
05/04/98	3.54	<0.01	3.27
05/07/98	3.40	<0.01	2.73
05/21/98	2.93	<0.01	0.88
05/22/98	3.44	0.59	34.0
05/27/98	5.04	0.12	4.01
05/28/98	4.64	0.30	4.30
06/29/98	2.72	0.24	2.31
06/30/98	2.81	0.34	2.31

[1] ND, not determined.

Table A5 Ammonium, nitrate, and herbicide concentrations in spring water samples from Kelly Spring, southwestern Illinois, collected at the peak of flooding just after a 5.0-cm rainfall event.[1]

Time from start of storm (min)	NH_4^+-N (mg/L)	NO_3^--N (mg/L)	Alachlor (µg/L)	Atrazine (µg/L)	Cyanazine (µg/L)
Prestorm[2]	0.23	1.12	8.30	10.9	0.29
360	0.50	6.47	10.8	97.5	0.52
420	0.56	6.97	13.4	72.0	0.46
480	0.53	7.19	16.2	97.0	0.54
540	0.56	7.36	12.8	71.5	0.49
600	0.53	7.01	13.7	71.0	0.49
660	0.53	6.81	15.3	67.0	0.66
720	0.51	6.79	15.6	66.5	0.47
1,850	0.22	5.55	12.9	75.0	0.47
3,340	0.12	5.20	11.1	69.5	0.41
6,130	0.11	4.89	8.30	48.0	0.33
10,330	0.07	4.59	2.85	26.4	0.30

[1] This event was the first rainfall immediately following the application of agrichemicals to the groundwater basin feeding Kelly Spring on June 2, 1994.

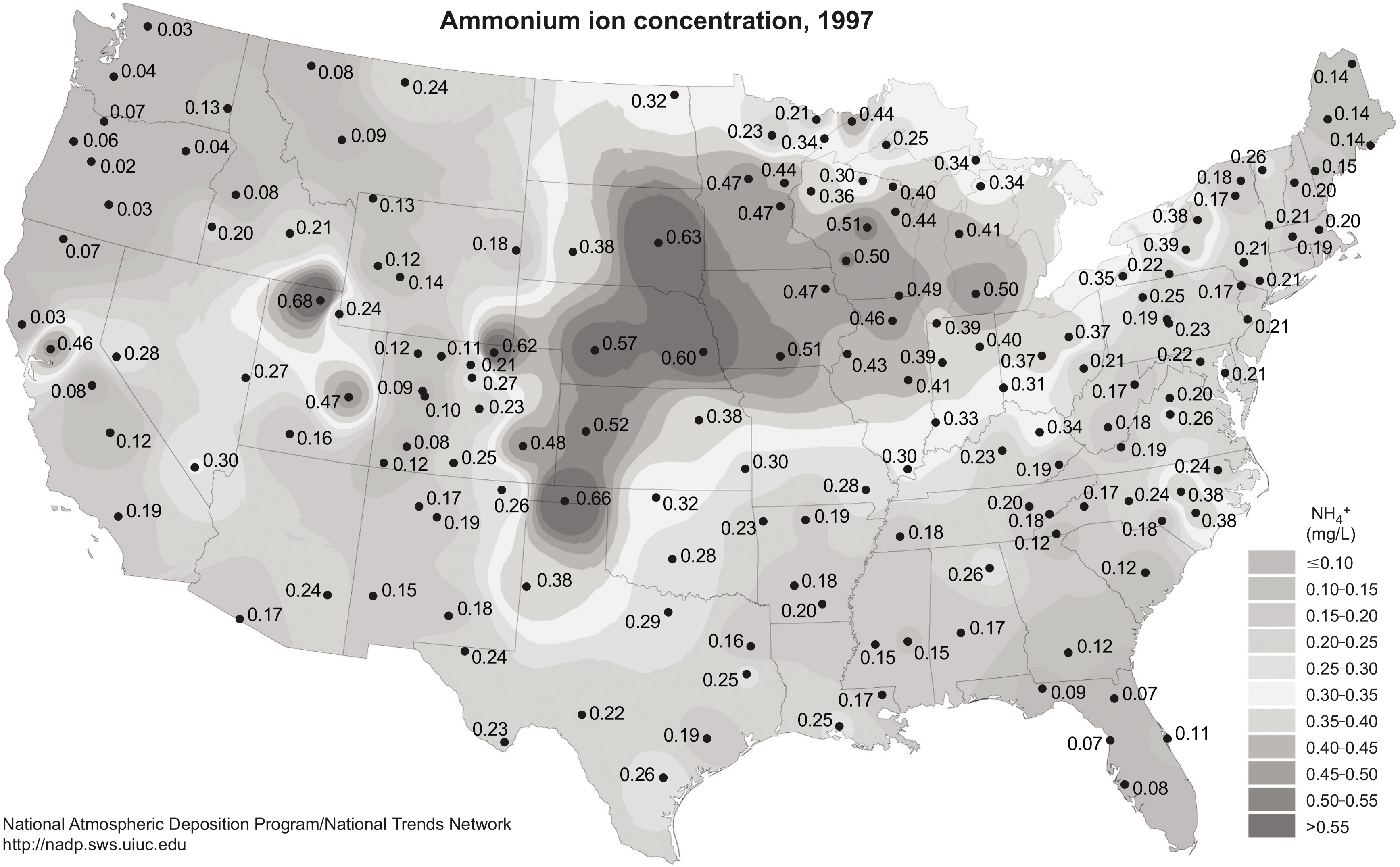
[2] Prestorm water sample from Kelly Spring collected during base flow conditions on May 2, 1994.

Table A6 Bacterial data for Collier and Indian Hole Springs and the South Fork Creek bridge site.[1,2]

	Collier Spring				Indian Hole Spring				Bridge			
Date sampled	Coliforms	FC	FE	Colonies	Coliforms	FC	FE	Colonies	Coliforms	FC	FE	Colonies
09/03/96	1,460	60	320	$>3.0 \times 10^5$	2,400	40	70	$>3.0 \times 10^5$	ND[2]	ND	ND	ND
10/15/96	>4,000	224	1,450	$>3.0 \times 10^5$	>4,000	522	>4,000	$>3.0 \times 10^5$	>4,000	580	1,840	$>3.0 \times 10^5$
11/26/96	>4,000	>4,000	>4,000	$>3.0 \times 10^6$	>4,000	>4,000	>4,000	$>3.0 \times 10^6$	>4,000	>4,000	>4,000	$>3.0 \times 10^6$
12/18/96	>4,000	1,034	>4,000	$>3.0 \times 10^5$	>4,000	126	>4,000	$>3.0 \times 10^5$	>4,000	730	>4,000	$>3.0 \times 10^5$
01/07/97	432	20	20	$>3.0 \times 10^5$	688	18	30	$>3.0 \times 10^5$	1,632	74	90	$>3.0 \times 10^5$
01/24/97	>2,419	488	>2,419	$>3.0 \times 10^5$	>2,419	727	>2,419	$>3.0 \times 10^5$	>2,419	517	>2,419	$>3.0 \times 10^5$
02/04/97	>4,000	1,374	>4,000	$>3.0 \times 10^5$	>4,000	614	>4,000	$>3.0 \times 10^5$	>4,000	870	>4,000	$>3.0 \times 10^5$
02/20/97	>2,419	186	>2,419	$>3.0 \times 10^5$	>2,419	52	>2,419	$>3.0 \times 10^5$	>2,419	>2,419	>2,419	$>3.0 \times 10^5$
03/05/97	>4,000	>4,000	102	$>3.0 \times 10^5$	>4,000	3,960	154	$>3.0 \times 10^5$	>4,000	>4,000	162	$>3.0 \times 10^5$
03/19/97	>4,000	196	288	$>3.0 \times 10^5$	>4,000	616	1,034	$>3.0 \times 10^5$	>4,000	334	388	$>3.0 \times 10^5$
04/01/97	>2,419	114	133	$>3.0 \times 10^5$	1,553	15	21	$>3.0 \times 10^5$	>2,419	126	55	$>3.0 \times 10^5$
04/16/97	>4,000	242	688	$>3.0 \times 10^5$	>4,000	120	262	$>3.0 \times 10^5$	>4,000	208	330	$>3.0 \times 10^5$
04/30/97	>4,000	62	90	$>3.0 \times 10^5$	>4,000	70	68	$>3.0 \times 10^5$	>4,000	64	162	$>3.0 \times 10^5$
05/13/97	2,914	372	576	$>3.0 \times 10^5$	2,914	96	154	$>3.0 \times 10^5$	2,914	372	576	$>3.0 \times 10^5$
05/28/97	>4,000	1,733	>4,000	$>3.0 \times 10^5$	>4,000	1,200	>4,000	$>3.0 \times 10^5$	>4,000	1,300	>4,000	$>3.0 \times 10^5$
06/12/97	>4,000	730	2,092	$>3.0 \times 10^5$	>4,000	96	294	$>3.0 \times 10^5$	>4,000	336	1,034	$>3.0 \times 10^5$
06/24/97	4,350	180	2,610	$>3.0 \times 10^5$	3,650	230	390	$>3.0 \times 10^5$	19,860	350	810	$>3.0 \times 10^5$
07/28/97	>2,419	46	122	$>3.0 \times 10^5$	>2,419	37	244	$>3.0 \times 10^5$	>2,419	866	>2,419	$>3.0 \times 10^5$
08/21/97	>4,000	1,632	>4,000	$>3.0 \times 10^6$	>4,000	3,466	>4,000	$>3.0 \times 10^6$	>4,000	>4,000	>4,000	$>3.0 \times 10^6$
09/30/97	648	23	45	$>3.0 \times 10^6$	648	18	29	$>3.0 \times 10^6$	>2,419	248	866	$>3.0 \times 10^6$
10/29/97	>4,000	688	>4,000	$>3.0 \times 10^6$	>4,000	314	>4,000	$>3.0 \times 10^6$	>4,000	1,300	976	$>3.0 \times 10^6$
11/12/97	ND	ND	ND	ND	ND	ND	ND	ND	>4,000	132	584	$>3.0 \times 10^5$
11/24/97	3,970	20	12	$>3.0 \times 10^6$	>4,000	16	40	$>3.0 \times 10^6$	>4,000	40	202	$>3.0 \times 10^6$
12/15/97	ND	ND	ND	ND	ND	ND	ND	ND	>4,000	76	62	$>3.0 \times 10^6$
12/29/97	>4,000	1,034	1,160	$>3.0 \times 10^6$	>4,000	>2,406	>4,000	$>3.0 \times 10^6$	>4,000	>2,406	>4,000	$>3.0 \times 10^6$
01/06/98	>4,000	262	>4,000	$>3.0 \times 10^6$	>4,000	176	1,540	$>3.0 \times 10^6$	>4,000	372	2,828	$>3.0 \times 10^6$
01/26/98	3,106	34	62	$>3.0 \times 10^6$	870	24	24	$>3.0 \times 10^6$	>4,000	1,732	346	$>3.0 \times 10^6$
02/17/98	>4,000	3,462	>4,000	$>3.0 \times 10^6$	>4,000	2,600	>4,000	$>3.0 \times 10^6$	>4,000	3,972	>4,000	$>3.0 \times 10^6$
03/03/98	4,230	152	198	$>3.0 \times 10^6$	3,962	92	116	$>3.0.\times 10^6$	>4,000	110	100	$>3.0 \times 10^6$
03/25/98	>4,000	36	108	$>3.0 \times 10^6$	>4,000	56	146	$>3.0 \times 10^6$	>4,000	48	96	$>3.0 \times 10^6$
04/15/98	>4,838	496	412	$>3.0 \times 10^6$	3,972	116	614	$>3.0 \times 10^6$	>4,838	614	2,238	$>3.0 \times 10^6$
04/28/98	>4,000	118	108	$>3.0 \times 10^6$	870	16	24	4.8×10^5	>4,000	296	274	$>3.0 \times 10^6$
05/12/98	>4,000	46	174	7.6×10^4	1,960	48	54	4.7×10^4	>4,000	108	278	1.8×10^5
05/26/98	>4,838	1,732	870	$>3.0 \times 10^6$	2,238	190	72	$>3.0 \times 10^6$	>4,838	1,226	730	$>3.0 \times 10^6$
06/09/98	>4,000	324	3,972	$>3.0 \times 10^6$	>4,000	300	270	$>3.0 \times 10^6$	>4,000	2,092	>4,000	$>3.0 \times 10^6$
07/01/98	>4,000	1,120	>4,000	$>3.0 \times 10^6$	>4,000	517	>4,000	$>3.0 \times 10^6$	>4,000	438	>4,000	$>3.0 \times 10^6$
07/14/98	>4,000	284	1,373	$>3.0 \times 10^6$	>4,000	228	922	$>3.0 \times 10^6$	>4,000	262	>4,000	$>3.0 \times 10^6$
07/28/98	>4,000	>4,000	3,972	$>3.0 \times 10^6$	>4,000	>4,000	1,732	$>3.0 \times 10^6$	>4,000	>4,000	>2,406	$>3.0 \times 10^6$
08/18/98	>4,000	176	1,034	$>3.0 \times 10^6$	>4,000	198	288	$>3.0 \times 10^6$	>4,000	>4,000	>4,000	$>3.0 \times 10^6$

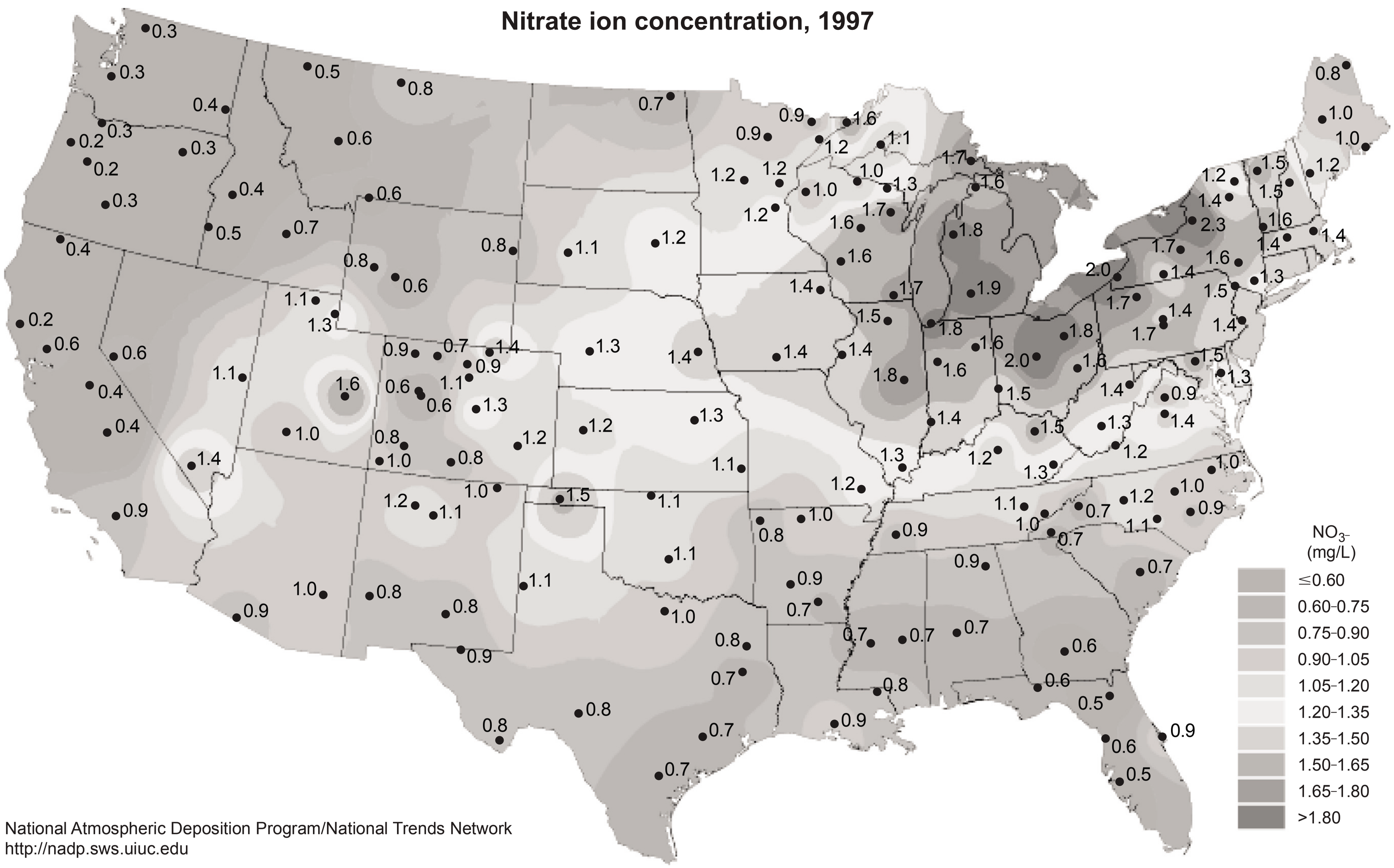
[1] All data are reported in colony-forming units per milliliter.

[2] FC, fecal coliforms; FE, fecal enterococci; ND, not determined.



National Atmospheric Deposition Program/National Trends Network
http://nadp.sws.uiuc.edu

Figure A1 Mean ammonium concentrations (wet deposition) across the United States in 1997 showing industrial and agricultural input (National Atmospheric Deposition Program 2000).



Nitrate ion concentration, 1997

National Atmospheric Deposition Program/National Trends Network
http://nadp.sws.uiuc.edu

Figure A2 Mean nitrate concentrations (wet deposition) across the United States in 1997 showing industrial and agricultural input (National Atmospheric Deposition Program 2000).

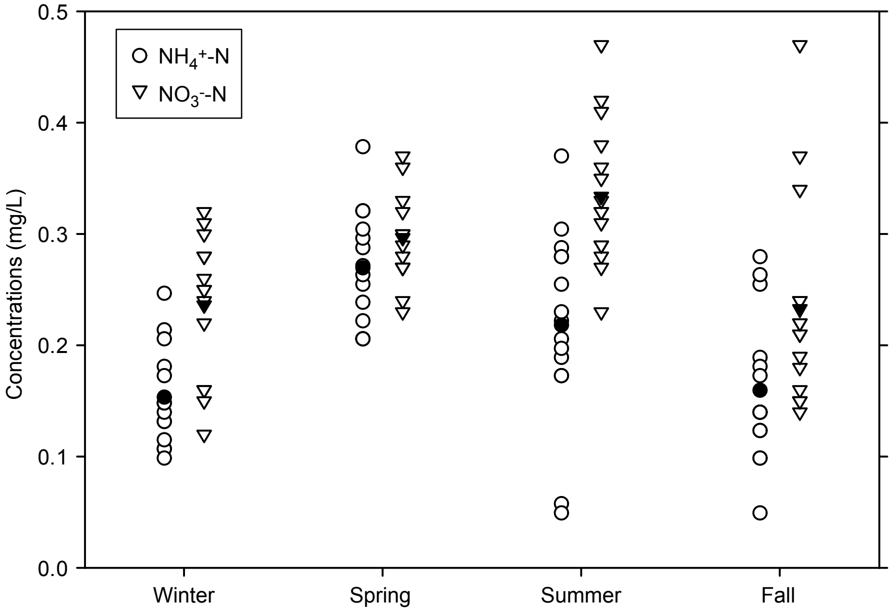


Figure A3 Nitrate and ammonium concentrations in rainfall samples collected at the NADP sampling site nearest the study area from 1979 through 1993 showing a seasonal trend with the highest concentrations during the spring and summer

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