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Diversity of Aquatic Macroinvertebrates at Two Karst Springs in the Sinkhole Plain of Monroe County, Illinois: Effects of Water Quality and Hydrology

Final Report

Illinois Wildlife Preservation Fund
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ABSTRACT

Water samples were collected and discharge measurements were made on a weekly basis from May through December 1998 at two karst springs in the sinkhole plain of Monroe County, Illinois. Samples of surface runoff water were also collected at two sinkholes in the recharge area of one of the springs during the same period of time. Spring-water samples were analyzed for nitrate-N and atrazine to establish the agrichemical environments at the springs and their relationships with the spring hydrographs. The influence of chemical environment on diversity of aquatic macroinvertebrates, which is markedly different at the two springs, was then examined.

Except during storm events the concentration of nitrate-N is relatively constant with time in the waters at both springs, but the nitrate-N level at Auctioneer Spring, characterized by relatively low taxa richness, is significantly greater than at Camp Vandeventer Spring. Low nitrate-N concentrations in the surface runoff samples suggest that consistently much higher levels in the spring waters are provided from groundwater reservoirs in the spring systems that were established by soil water percolating downward from the fields.

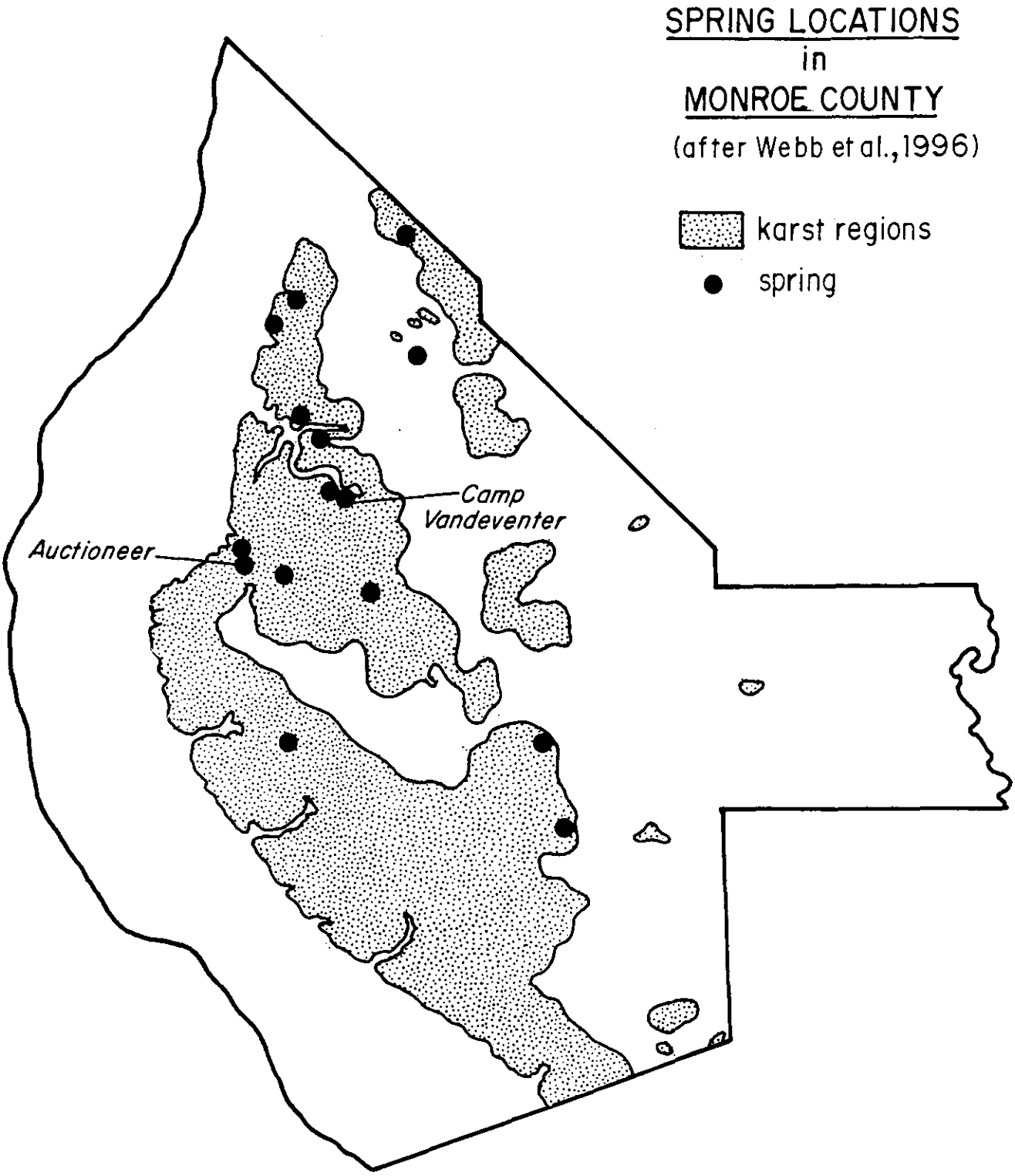
The atrazine chemographs at the springs are marked by consistently low background levels of about 1 ppb atrazine, with superimposed pulses of very high atrazine concentration that occur shortly after the planting season and during storm events. In the former case atrazine has been leached from the fields and transported in solution by surface runoff to the sinkholes, an interpretation supported by analyses of runoff waters. The latter case involves mobilization of atrazine adsorbed on soil and sediments that are taken into suspension by storm runoff. Biodiversity of aquatic macroinvertebrates at springs may be influenced by sudden changes in the chemical environment, such as the pulses of high atrazine concentration observed in the spring chemographs.

INTRODUCTION

Springs and their associated outflow brooks provide a unique habitat for endemic and rare species of aquatic animals and plants because they usually have a nearly constant physical and chemical environment (e.g., Glazier, 1991). Until recently, little research had been done on springs with regard to taxa richness and endemism within the chemical setting. Although the occurrence of springs in Illinois had been documented, baseline information on their fauna, flora, water quality, and hydrogeology was virtually nonexistent circa 1990. A program designed to develop such a baseline of data was initiated in 1991 by the Illinois Natural History Survey and the Illinois State Geological Survey. As a part of that program, Webb et al. (1996) studied the biodiversity, hydrogeology, and water quality of ten karst springs in the sinkhole plain of Monroe and St. Clair counties in southwestern Illinois. Locations of many of the springs involved in the study, including the two that are the subject of this report, are shown in Figure 1.

One of the primary objectives of the research of Webb et al. (1996) was to compare the information gathered from the karst springs with similar data from seven springs located in the Shawnee Hills of southern Illinois (Webb et al., 1992) that had been studied because they are not near areas of intensive agriculture and showed only minimal effects of agricultural contamination. These springs provide a baseline for evaluating the effects of agrichemicals on biodiversity at other springs. The karst springs, on the other hand, are located in counties where land use is predominantly agricultural and where there is rapid communication between surface runoff water and the shallow karst aquifer. A "worst case" situation was anticipated, in which spring contamination by nitrate-nitrogen and herbicides would adversely affect the diversity of aquatic macroinvertebrates. Contrary to expectations, Webb et al. (1996) found that the karst springs support a moderate diversity of aquatic macroinvertebrates, as great as the diversity at the Shawnee Hills springs, even though water quality was found to be significantly degraded. Among the ten karst springs, biodiversity appeared to be more closely related to the composition of the bottom

FIGURE 1


SPRING LOCATIONS
in
MONROE COUNTY
(after Webb et al., 1996)
karst regions
spring
Camp
Vandeventer
Auctioneer

sediments than to the levels of contamination. Springs with bottom sediments of fine silt or sand showed less biodiversity than springs with coarse gravel and cobble in the bottom sediments (Illinois Groundwater Consortium, 1995/96).

Water-quality data reported by Webb et al. (1996) are based on just four samples collected at each of the springs, on a seasonal basis, between November 1994 and August 1995. Concentration levels of agrichemicals such as nitrate-nitrogen and herbicides vary with hydrologic conditions, so that concentration data based on four samples collected in a twelve-month period may not adequately reflect the long-term water quality at a spring. Furthermore, additional water-quality parameters such as the mass loads of chemical species may be more important than concentration levels in affecting the diversity of aquatic macroinvertebrates at a spring. Taxa richness at the ten karst springs studied by Webb et al. (1996) ranged from 18 to 82. Given this range of biodiversity, a more comprehensive study of water quality and hydrology at these springs seems warranted in order to examine the potential relationship between macroinvertebrate diversity and water quality more thoroughly.

Two of the karst springs studied by Webb et al. (1996), Auctioneer and Camp Vandeventer (Figure 1), are the subjects of the M.S. thesis research of Mark Abendroth, a graduate student in the Environmental Sciences Program at Southern Illinois University Edwardsville (SIUE). His research primarily involves the hydrogeology of these springs; he is determining the residence times of groundwater in the spring reservoirs through measurements of the isotopic composition of oxygen in the spring waters. As reported in Webb et al. (1996), the taxa richness values for Auctioneer and Camp Vandeventer springs (20 and 64, respectively) are quite different and near the extremes of values found in their study. Two recent reports (Odemerho et al., 1998; Calero, 1999) provide data which suggest that a correlation between biodiversity and water quality may exist at these two springs. Both reports involved water-quality measurements at numerous springs in Monroe County, which were sampled on an infrequent basis. Auctioneer Spring, with low reported taxa richness, invariably showed significantly greater concentrations of nitrate-nitrogen

and atrazine in its waters than those found in samples from Camp Vandeventer Spring, which has a much higher taxa richness.

The Illinois Wildlife Preservation Fund provided a grant that has allowed Mark Abendroth to extend his thesis research to include analyses of water samples from Auctioneer and Camp Vandeventer springs for nitrate-nitrogen and atrazine, in order to examine the potential relationship between aquatic macroinvertebrate diversity and water quality in a comprehensive manner. Water samples for the analyses have been collected at the two springs on a weekly basis for a period of eight months in order to monitor water quality on a long-term basis. Simultaneous measurements of discharge in the two springbrooks provide data for examination of the relationships between water quality and hydrologic conditions as well as calculations of agrichemical mass loads at the two springs. Runoff collectors were installed at each of two sinkholes that are hydraulically connected to Auctioneer Spring. Samples of runoff water from agricultural fields into the two sinkholes were collected and analyzed for nitrate-nitrogen and atrazine to monitor likely sources of the agrichemicals found in the discharge of Auctioneer Spring. This report presents the data and interpretations resulting from Mark Abendroth's research that was supported by the Illinois Wildlife Preservation Fund.

FIELD AND LABORATORY PROCEDURES

Auctioneer Spring is located in the uppermost part of Trout Hollow, just south of Trout Camp Road (Figure 2). Water at the springhead has been described as the resurgence of a small cave, one that is dominated by passages less than one meter in height (Panno et al., 1999). The opening of Auctioneer Cave is formed on a vertical limestone face, 2.4 to 4.6 m above the springbrook (Webb et al., 1996). The branchwork-type cave and conduit system is controlled by bedding planes and joints in limestone and dolomite of the Salem Limestone of Mississippian age. The substrate at the springhead consists of limestone bedrock, whereas Auctioneer springbrook is characterized by cobble riffles, small pools, sand and gravel riffles, and bedrock outcrops (Webb

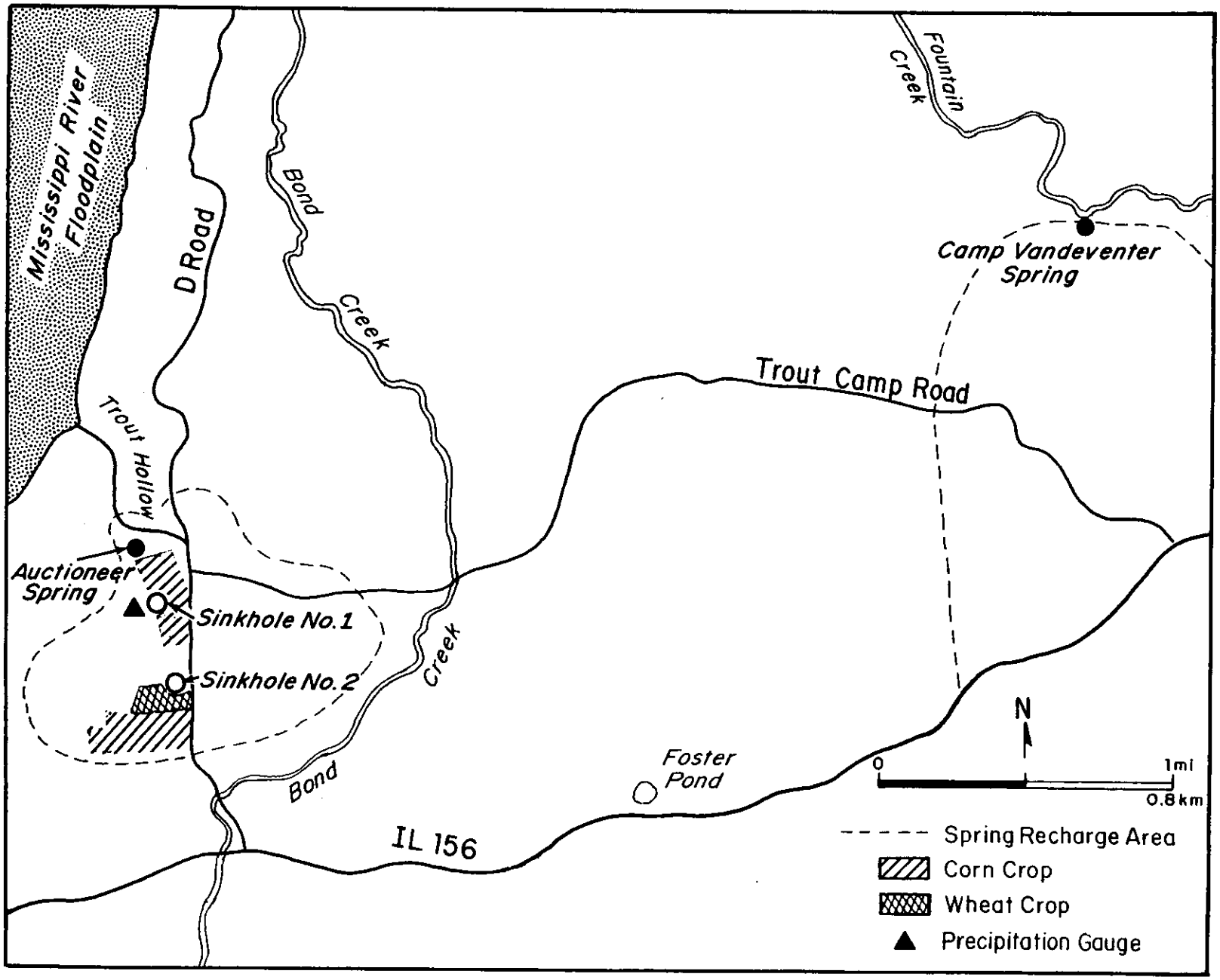

Mississippi River Floodplain
D Road
Bond Creek
Fountain Creek
Camp Vandeventer Spring
Trout Camp Road
Trout Hollow
Auctioneer Spring
Sinkhole No. 1
Sinkhole No. 2
Bond Creek
Foster Pond
IL 156
N
0
1mi
0.8km
Spring Recharge Area
Corn Crop
Wheat Crop
Precipitation Gauge

FIGURE 2

et al., 1996). The springbrook flows to the north and, after passing under Trout Camp Road, it merges with a drainage channel that carries runoff down Trout Hollow to the Mississippi River floodplain (Figure 2). Discharge from Auctioneer Spring measured during the course of this study ranged from 0.56 to 9.6 L/s.

Camp Vandeventer Spring (Figure 2) represents the resurgence of another small branchwork-type cave located at the base of a bluff, 12 to 14 m high, in the upper St. Louis Limestone of Mississippian age. Discharge from the springhead moves outward into a retention pool formed by a poured concrete wall, then through a small spillway to the springbrook, which then flows 30.5 m to Fountain Creek (Webb et al., 1996). The substrate at the springhead consists of coarse sand and gravel and a few large limestone blocks. The springbrook is characterized by sand, gravel, cobble, and limestone blocks. Discharge from Camp Vandeventer Spring measured during the course of this study ranged from 33.4 to greater than 210 L/s.

Grab samples of spring water were collected at both springheads on a weekly basis, from May through December 1998. A sample for herbicide analysis was taken directly into a 473-mL amber glass jar. The jar was filled to approximately 60 percent volume in order to provide space for expansion when the sample was transferred to a freezer for long-term storage. A sample for nitrate-N analysis was passed through a 0.45 μm filter into a 30-mL polypropylene bottle. Both samples were placed in an ice chest for transport to a laboratory at SIUE, where the sample for herbicide analysis was stored in a freezer and the sample for nitrate-N analysis was stored in a refrigerator.

The field parameters pH, temperature, and specific electrical conductance were measured at the springhead when the samples were collected. The pH of a water sample was monitored with a Hach EC 10 portable pH/mV/Temperature meter, Model 500050, provided with a standard gel-filled combination electrode, Model 50200. An automatic temperature compensation refers the pH values to 25°C. The temperature and specific electrical conductance were measured using a hand-held conductivity meter with incorporated temperature sensor, Cole-Parmer Model 19820. The

specific electrical conductance measurements were obtained with automatic temperature compensation so that the recorded values have been referred to 25°C.

At a location near Auctioneer Spring, precipitation was collected in a 1-L plastic bottle that was buried in the ground as deep as its shoulder. A plastic funnel, 9.9 cm in diameter, was sealed in a hole drilled into the cap of the bottle. Water that had accumulated in the bottle was removed each week; its volume was measured and converted to cm of rainfall. Experiments showed that burial of the plastic bottle prevented evaporation of any rainfall that accumulated during the intervals between collections.

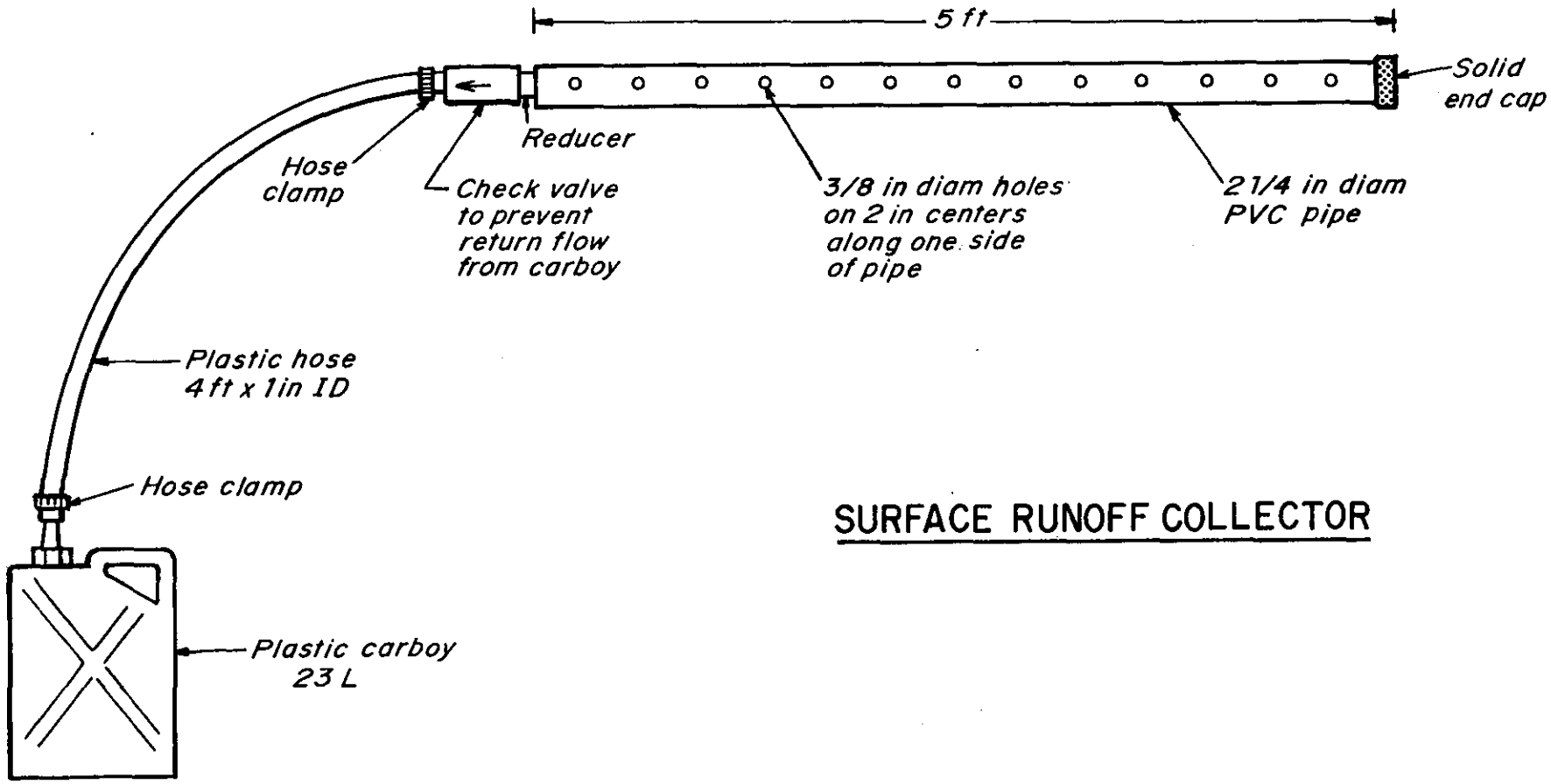
In conjunction with sample collection, spring discharge measurements were made at the two sites beginning in May and extending through December 1998. The velocity-area method was employed, utilizing determinations of the flow-velocity of the outflow stream and the cross-sectional area of flow. Flow velocity was measured with a Global flow meter and cross-sectional area was measured with a steel tape. Discharge was determined by the product of the two measurements. At Auctioneer Spring, characterized by low discharge and a rough, irregular springbrook, discharge was measured in the springbrook at a point approximately 50 m downstream from the springhead. At Camp Vandeventer Spring, the small spillway in the concrete wall that forms the retention pool provided an ideal cross section for discharge measurements under base-flow conditions. Roughly ten percent of the flow was channeled around the wall through bedrock fractures, but this discharge component could be accurately determined with a second measurement where it joined the springbrook just beyond the wall. Following large precipitation events spring discharge could not be gauged because water from the retention pool flowed over the entire length of the concrete wall. On one occasion flow was confined to the spillway but at the level of the top of the retention wall. This provided a measurement of minimum discharge under high-flow conditions, which is 210 L/s.

The groundwater flow system in the shallow karst aquifer within a portion of the Monroe County sinkhole plain has been mapped through the use of fluorescent tracer dyes (Aley and Aley, 1998). Recharge areas for numerous karst springs were delineated from the results of dye traces

that involve dye introduction at sinkholes and monitoring for tracer recovery at various springs. The recharge area for the Auctioneer Spring Complex (Figure 2), generally located southeast of the spring, is 0.67 square mile (1.7 km^2). For the Camp Vandeventer Spring Complex the recharge area, located to the south of the spring, could be determined only to be greater than 0.88 square mile (>2.3 km^2) because the southern boundary was outside the area studied by Aley and Aley (1998).

Surface runoff collectors, designed and constructed by Mark Abendroth (Figure 3), were installed at each of two sinkholes located within the recharge area of Auctioneer Spring (Figure 2). Sinkhole No. 1, located 50 ft (15 m) northeast of a sinkhole that yielded a positive tracer test to Auctioneer Spring, was chosen because surface runoff from a large agricultural field flows into it. Sinkhole No. 1 is approximately 1100 ft (335 m) south-southeast of Auctioneer Spring (Figure 2); the adjacent agricultural field to the east was planted in corn during the summer of 1998. Sinkhole No. 2, approximately 2600 ft (790 m) south-southeast of Auctioneer Spring, was the site of a positive tracer test to the spring (Aley and Aley, 1998). Surface runoff from an agricultural field to the south, which was partially planted in wheat during the spring of 1998 and partially planted in corn during the summer, flows into this sinkhole. The runoff collectors were installed in major drainage channels at the perimeters of the sinkholes. Samples of runoff water that had accumulated in the collectors were taken for herbicide and nitrate-N analyses at two-week intervals from May through December 1998.

Herbicides were separated from aliquants of water samples collected at the springs and in the runoff collectors by liquid-liquid extraction into pesticide-grade hexanes. After volume reduction to 2 mL and transfer to auto-sampler vials, the samples were stored in a freezer prior to analysis for herbicide concentration levels in a gas chromatograph. Results reported are limited to atrazine, which was the only herbicide detected with any frequency in the samples. Samples were analyzed on the gas chromatograph in two batches, each of which involved a different detection limit (0.6 ppb and 1.4 ppb) for the atrazine data that were obtained.



SURFACE RUNOFF COLLECTOR

FIGURE 3

Aliquants of water samples collected at the springs and in the runoff collectors were analyzed for nitrate-N by the cadmium reduction method. In the presence of cadmium, nitrate is reduced to nitrite. This method uses Cd granules treated with copper sulfate and packed in a glass chromatography column. The nitrite produced by passing a water sample through the column is diazotized with sulfanilamide. This is followed by coupling with N-(1-naphthyl)-ethylenediamine to form a highly colored azo dye. The intensity of the developed color is measured on a spectrophotometer at 540 nm. The concentration of nitrate in the water sample is then read from a standard curve by plotting absorbances of various prepared standards against their nitrate-N concentrations.

RESULTS

All data obtained in the field are recorded in Table 1. Snow and icy conditions in late December 1998 limited access to the springs and reduced the amount of field data collected in the last week of the study period. Water temperature at Camp Vandeventer Spring was slightly higher than at Auctioneer Spring throughout the study (Figure 4) and fluctuated to a somewhat greater degree as a function of time. Nevertheless, temporal variations at the two springs were generally sympathetic. Significantly higher than normal temperatures were recorded under storm-flow conditions that occurred on 6/20/98 and on 8/8/98 (Figure 4), indicating that at least some of the discharge had moved more rapidly through the spring systems. The pH of Auctioneer Spring water was quite consistent at about 8.0 during the study (Figure 5a); pH at Camp Vandeventer Spring was equally steady at a slightly lower value of about 7.7, with the exception of an excursion to low values on November 7 and 14 (Figure 5b) when the pH meter was behaving erratically.

Although discharge measured at Camp Vandeventer Spring was generally more than an order of magnitude greater than the flow at Auctioneer Spring, temporal variations at the two springs through the period of study were sympathetic (Figure 6). There were two intervals of high-flow conditions, which crested between June 20 and 27 and between August 1 and 15, respectively

Table 1
Field Measurements

1998 Date	Precip. (cm)	Auctioneer Spring (S4) Discharge (cfs)	Specific Conductance (µs/cm)	Temp (°C)	pH	Camp Vandeventer Spring (S6) Discharge (cfs)	Specific Conductance (µs/cm)	Temp (°C)	pH	Surface Runoff 1998 Collection Period	Sinkhole No.1 sample volume (mL)	Sinkhole No. 2 sample volume (mL)
5/3	no sample	no sample	no sample	no sample	7.98	no sample	no sample	no sample	7.28	5/3-5/16	70	20
5/9	no sample	no sample	546	12.9	7.97	no sample	503	13.2	7.86			
5/16	no sample	no sample	540	13.1	7.97	no sample	527	13.3	7.96	5/16-5/23	75	23000
5/23	2.14	0.13	548	13.6	8.10	1.94	567	13.2	7.94	5/23-5/31	0.0	23400
5/31	2.35	0.10	550	13.8	8.09	2.00	549	13.5	7.97	5/31-6/13	18930	23200
6/6	no collect	no collect	no collect	no collect	no collect	no collect	no collect	no collect	no collect			
6/13	9.85	0.15	484	13.6	8.07	2.97	438	14.4	7.92	6/13-6/27	15000	23350
6/20	7.92	0.34	260	15.8	7.57	>7.43	142	17.4	7.33			
6/27	1.61	0.29	510	13.8	8.05	4.00	411	15.5	7.86	6/27-7/11	8550	23250
7/3	3.73	0.15	501	14.0	8.48	3.25	412	15.9	7.79			
7/11	7.98	0.17	497	13.7	8.04	4.05	391	17.1	7.66	7/11-7/25	15950	25
7/18	0.09	0.16	481	13.9	7.99	3.15	452	15.7	7.84			
7/25	2.55	0.13	483	13.5	7.94	3.73	303	16.5	8.18	7/25-8/8	no sample	1250
8/1	7.72	0.20	462	14.2	7.99	7.43	182	19.2	7.37			
8/8	7.85	0.27	459	14.7	7.81	>7.43	189	20.3	7.35	8/8-8/22	1300	5730
8/15	0.48	0.27	487	13.8	7.93	4.16	385	17.3	7.56			
8/22	2.04	0.25	475	13.8	7.90	2.59	406	16.7	7.66	8/22-9/12	0.0	0.0
8/29	0.00	0.20	465	13.9	7.75	2.28	489	15.5	7.55			
9/5	no collect	no collect	no collect	no collect	no collect	no collect	no collect	no collect	no collect			
9/12	0.27	0.14	468	13.5	7.94	1.83	499	14.6	7.77	9/12-9/26	0.0	500
9/19	2.30	0.11	470	13.6	8.00	1.80	496	14.5	7.5			
9/26	0.31	0.08	469	13.8	8.13	1.72	502	14.4	7.71	9/26-10/10	1950	21000
10/3	0.00	0.12	475	13.4	7.96	1.58	506	14.2	7.58			
10/10	4.68	0.09	465	12.7	8.06	1.18	469	14.0	7.76	10/10-10/25	2500	4000
10/17	1.60	0.08	464	13.4	7.91	1.94	499	14.1	7.82			
10/25	1.44	0.04	451	12.7	8.27	1.24	480	13.8	8.04	10/25-11/7	2000	18400
10/31	0.48	0.04	468	12.6	8.09	1.18	487	13.8	7.98			
11/7	4.21	0.05	447	11.8	7.92	1.68	350	13.2	4.19	11/7-11/21	2200	3000
11/14	1.29	0.06	469	12.6	8.11	1.66	339	13.3	5.78			
11/21	1.00	0.06	464	11.5	7.89	1.19	442	12.8	8.03	11/21-12/5	16150	3500
11/28	0.00	0.04	486	13.1	8.13	1.21	475	13.4	7.97			
12/5	2.16	0.04	394	13.6	7.79	1.62	428	13.7	7.75	12/5-12/19	150	750
12/12	0.45	0.03	442	11.7	8.29	1.26	403	12.9	8.21			
12/19	0.70	0.02	440	11.6	8.24	1.22	432	12.9	8.3	12/19-1/1/99	910	1500
12/26	0.76	0.04	406	10.3	8.07	no sample	390	12.6	8.26			
1/1	0.00	no sample	449	8.1	8.21	no sample	no sample	no sample	no sample			

Figure 4

Temporal Variation in Water Temperature at Auctioneer Spring (S4) and Camp Vandeventer Spring (S6)

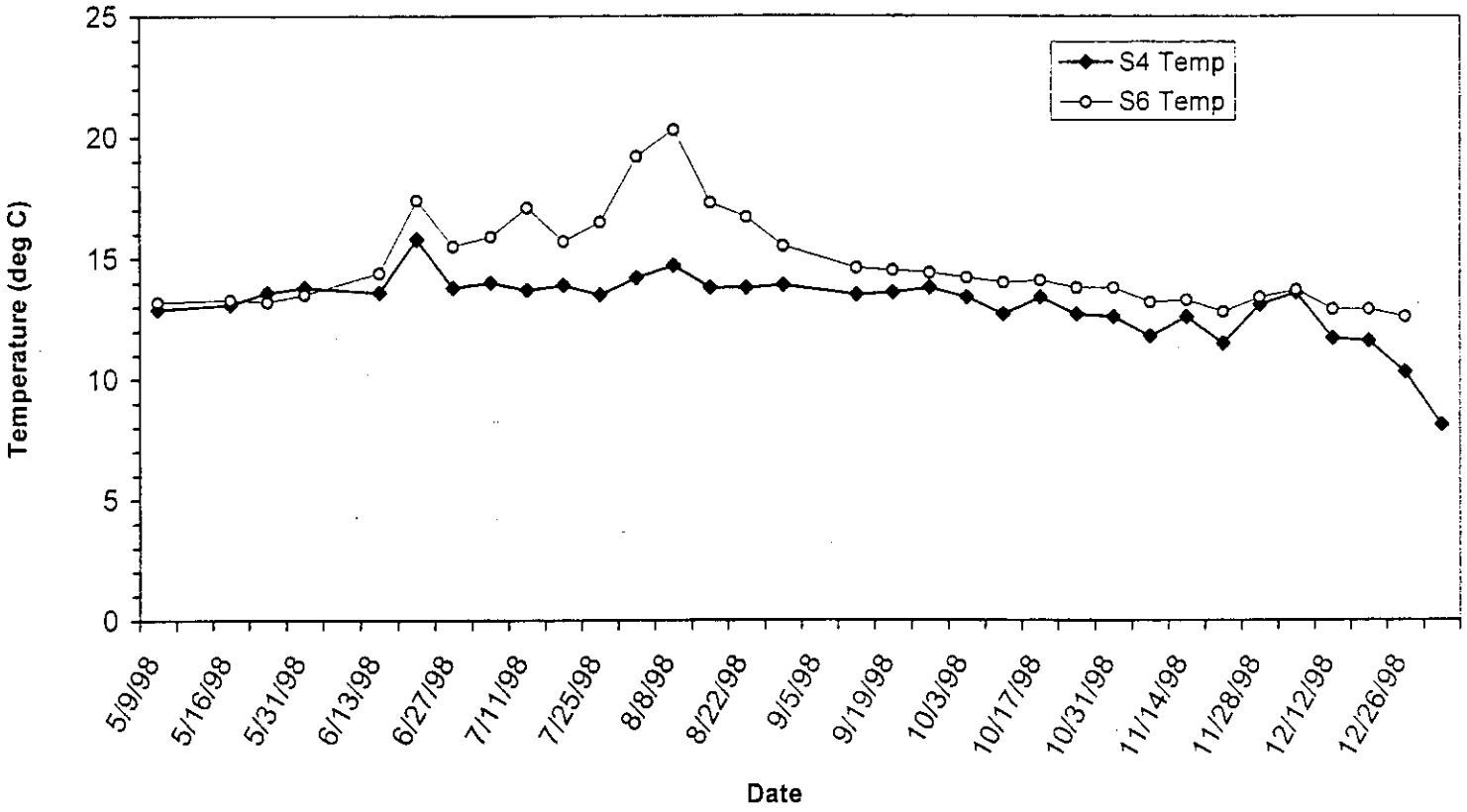
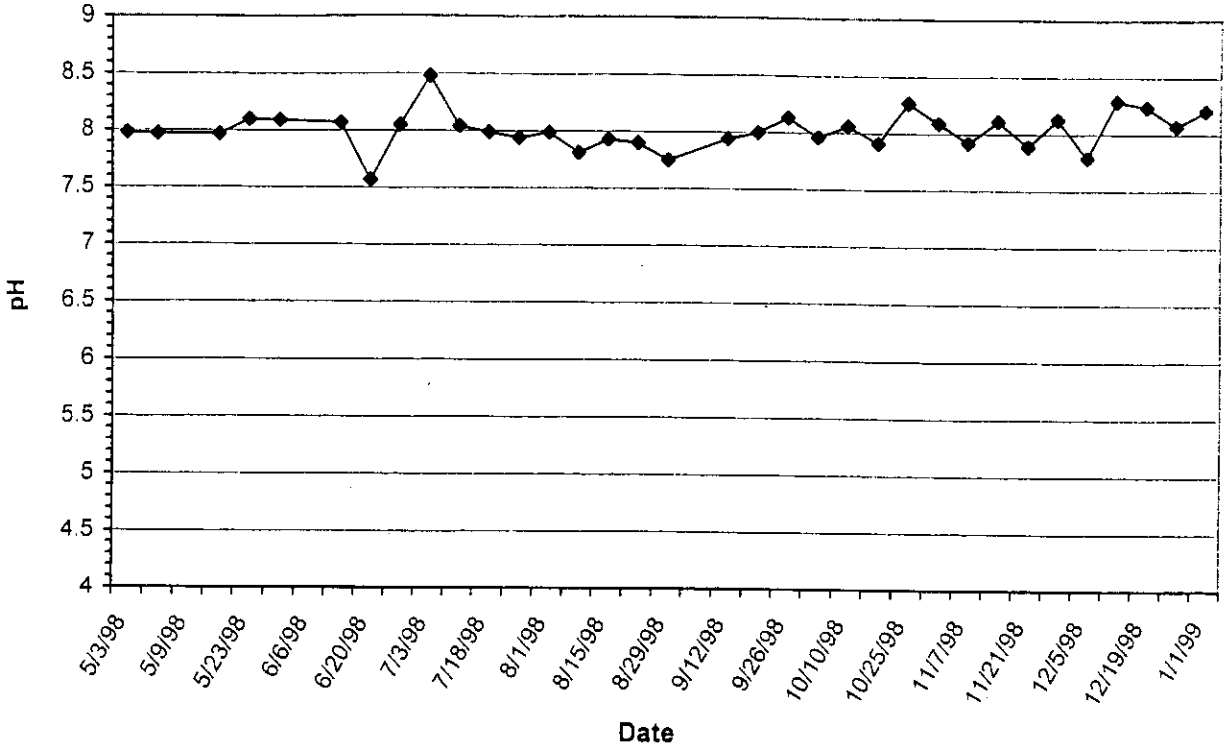


Figure 5

(a) Temporal Variation in pH at Auctioneer Spring (S4)



(b) Temporal Variation in pH at Camp Vandeventer Spring (S6)

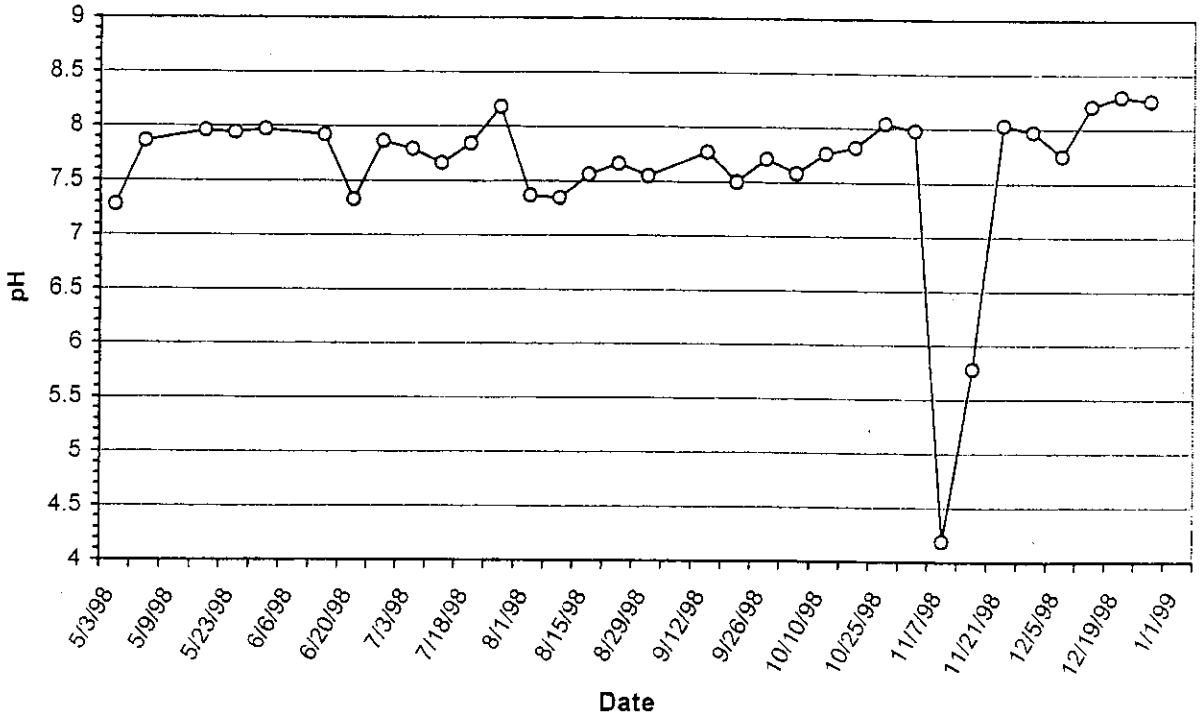
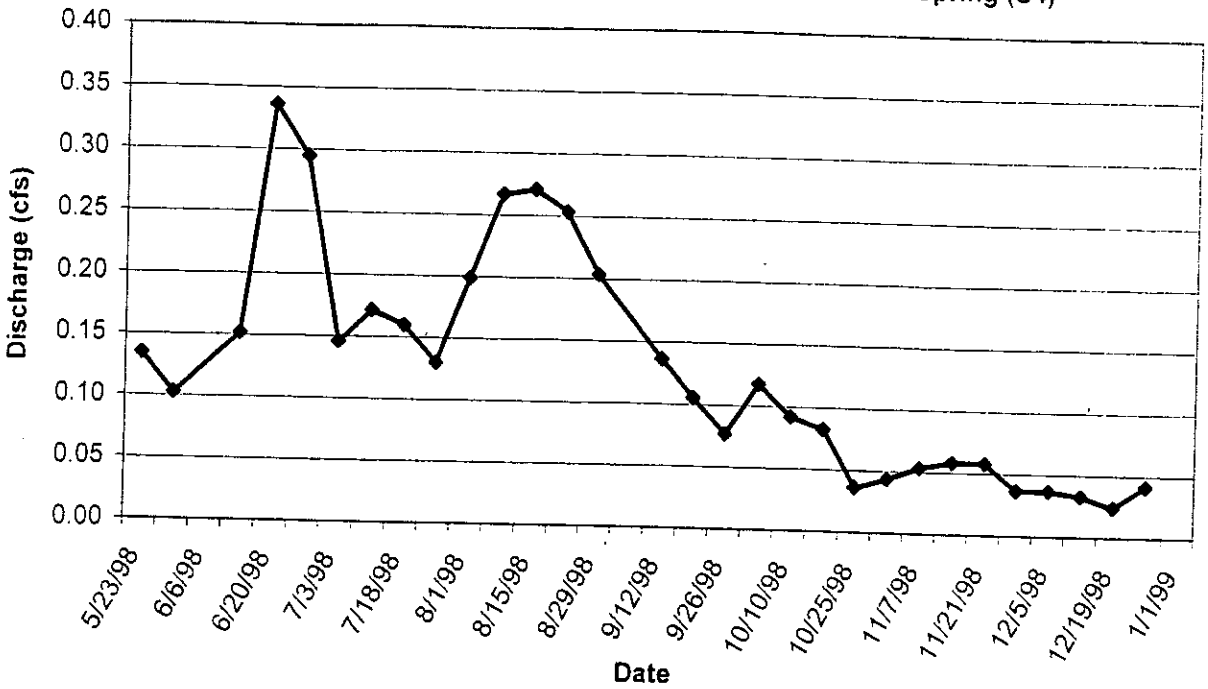
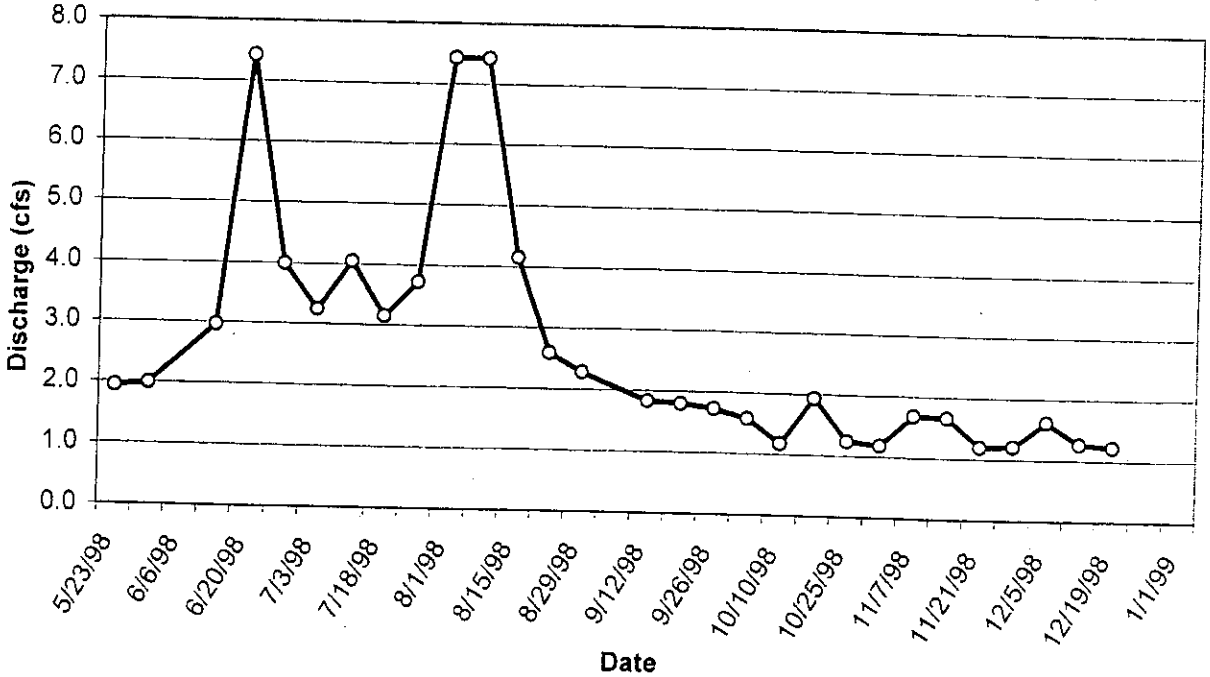


Figure 6

(a) Temporal Variation in Discharge at Auctioneer Spring (S4)



(b) Temporal Variation in Discharge at Camp Vandeventer Spring (S6)



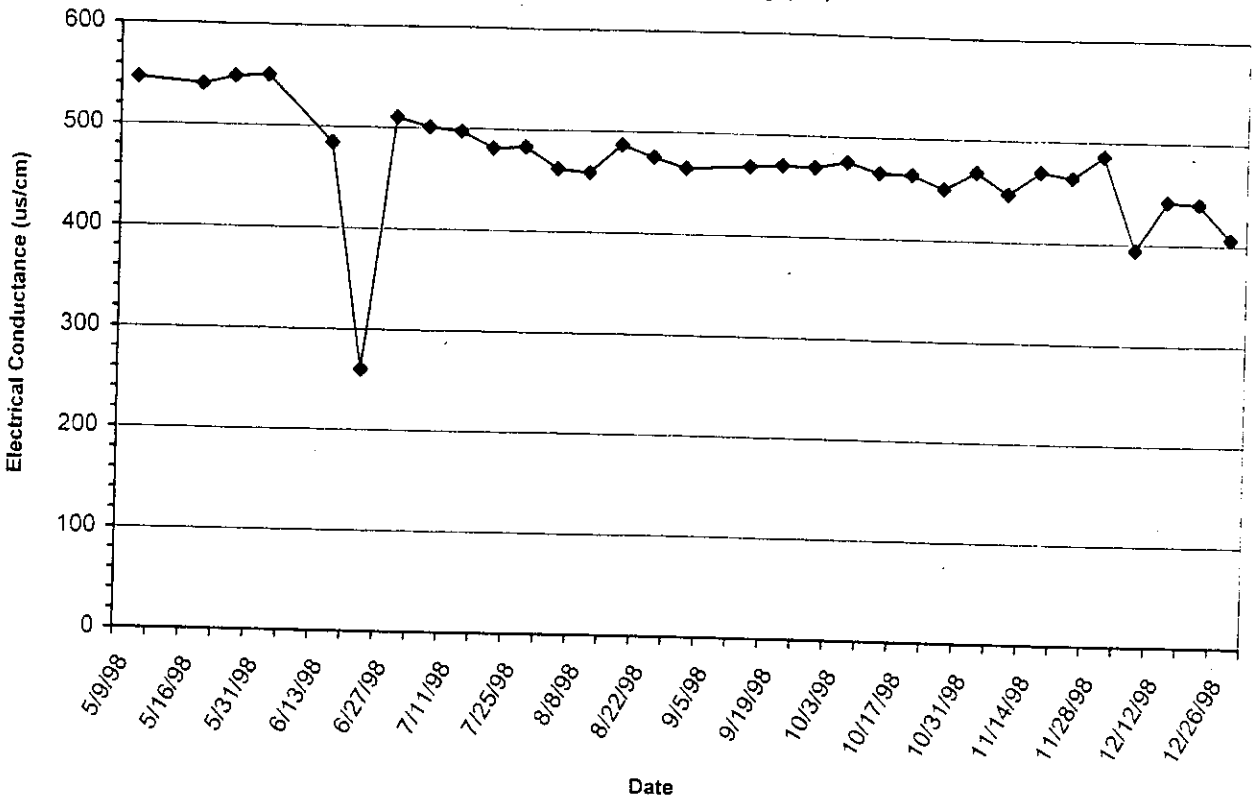
(Table 1 and Figure 6). It should be noted that discharges reported at Camp Vandeventer Spring for June 20 and August 8 are minimum values, as the flow was over the top of the concrete wall that forms the retention pool at the springhead. The storm events shown in Figure 6 are correlated with periods of high precipitation recorded near Auctioneer Spring (Table 1). The two storm events are superimposed on normal patterns of base-flow recession in the two spring hydrographs (Figure 6). They account for depressions in the temporal trends of specific electrical conductance at the two springs (Figure 7), although the second storm event had just a minor effect at Auctioneer Spring. Specific electrical conductance reflects the total concentration of dissolved ionic species in the spring water. Both springs show a background level under base-flow conditions of approximately 500 μ S/cm (Figure 7).

Analytical data for atrazine and nitrate-N in water samples from springs and runoff collectors are presented in Table 2. Nitrate-N was detected in all spring-water samples that have been analyzed. In no case did the concentration exceed the USEPA regulatory standard for drinking water of 10 ppm nitrate-N (USEPA, 1992). Spring-water samples with detectable atrazine are relatively few because of the high analytical detection limits involved, and for the most part were collected early in the study period, shortly after herbicides were applied to the fields in April and May. Seasonal occurrences of herbicides in spring waters of the sinkhole plain have been reported by numerous workers (e.g., Panno et al., 1996).

When atrazine concentration is plotted versus nitrate-N in waters from each of the springs (Figure 8) there is no indication of a covariant relationship in either case. Under high-flow conditions surface runoff into the sinkholes tends to mobilize atrazine from sediments but it also dilutes the concentration of nitrate-N, which has no association with the sediments. Thus nitrate-N is expected to show negative covariance with discharge at the springs. At Auctioneer Spring the nitrate-N concentration level remains essentially constant until a discharge of 0.30 cfs is reached and then it declines sharply (Figure 9a). At Camp Vandeventer Spring there is an overall negative covariant trend (Figure 9b), but the decline in nitrate-N with discharge is significant only above 4.0 cfs. These discharge values may represent threshold levels at each spring, above which additional

Figure 7

(a) Temporal Variation in Specific Electrical Conductance at Auctioneer Spring (S4)



(b) Temporal Variation in Specific Electrical Conductance at Camp Vandeventer Spring (S6)

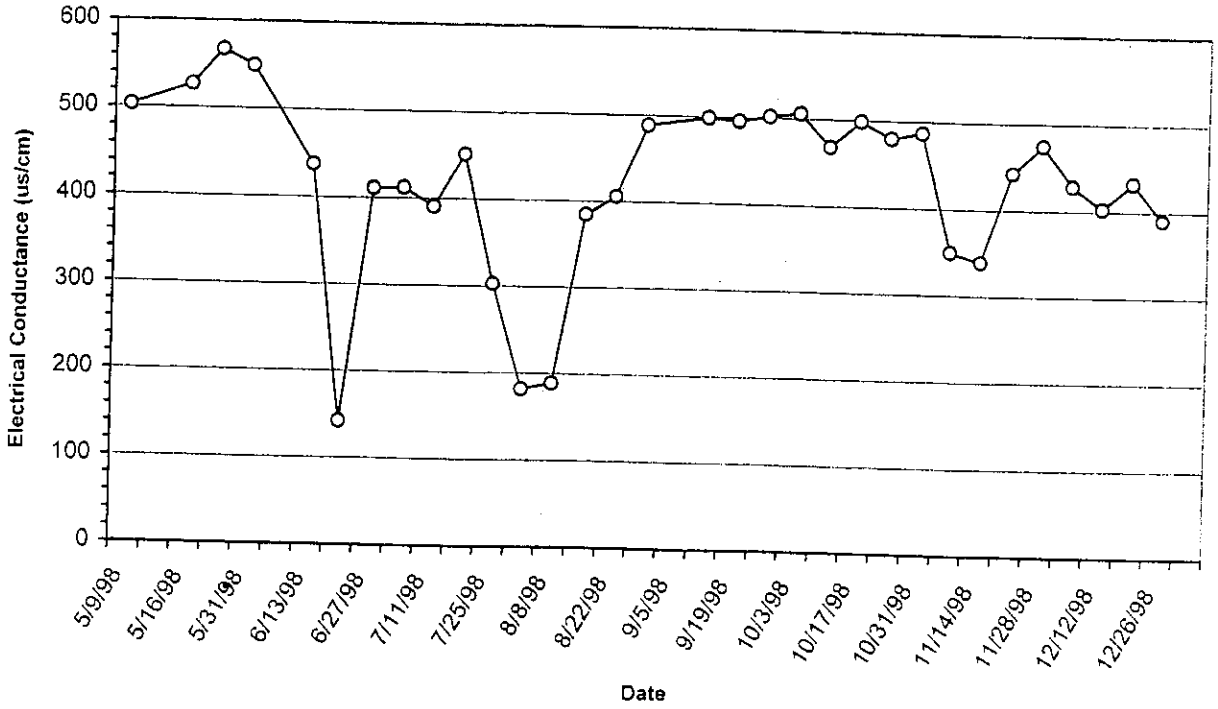


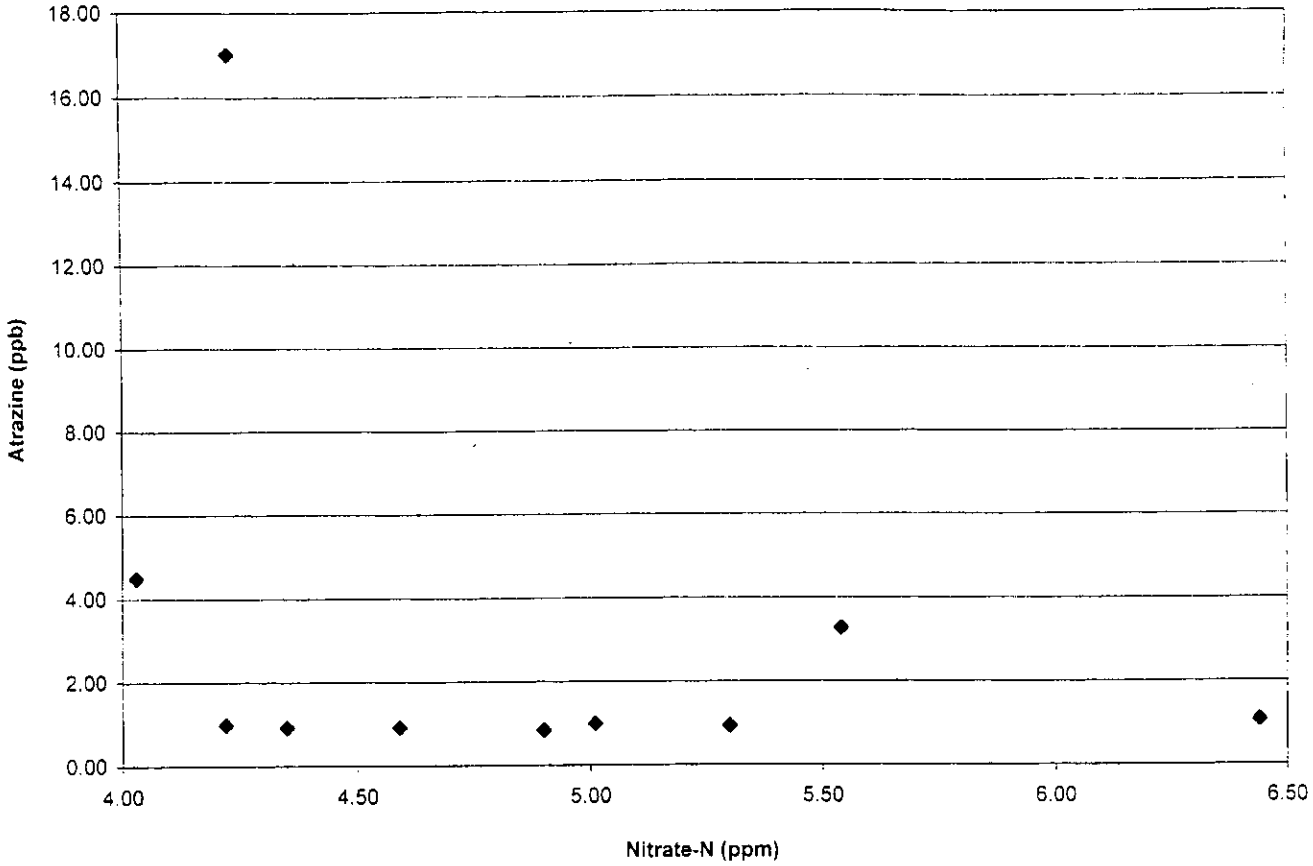
Table 2
Analytical Data

1998 Sample Date	Springs: Auctioneer Spring (S4) Nitrate-N (ppm)	Auctioneer Spring (S4) Atrazine (ppb)	Camp Vandeventer Spring (S6) Nitrate-N (ppm)	Camp Vandeventer Spring (S6) Atrazine (ppb)
5/3	4.23	17.01	2.30	1.17
5/9	3.51	<1.4	2.90	<1.4
5/16	4.03	4.49	2.15	0.85
5/23	4.99	<1.4	3.40	<0.6
5/31	5.54	3.27	3.63	0.95
6/6	no collect	no collect	no collect	no collect
6/13	6.44	1.07	4.81	<1.4
6/20	2.05	no anal.	0.76	no anal.
6/27	4.35	0.92	2.52	2.12
7/3	5.04	<1.4	2.67	<1.4
7/11	4.22	<1.4	2.13	1.63
7/18	4.59	0.90	2.90	1.43
7/25	4.90	0.83	1.45	8.37
8/1	5.30	0.93	0.80	no anal.
8/8	4.53	<0.6	0.75	0.90
8/15	4.38	<1.4	2.11	0.78
8/22	4.22	0.98	2.48	<1.4
8/29	4.44	<1.4	3.16	<1.4
9/5	no collect	no collect	no collect	no collect
9/12	4.81	<0.6	3.58	<1.4
9/19	4.91	<0.6	3.30	<0.6
9/26	5.33	<0.6	3.54	0.89
10/3	5.01	0.99	3.24	<0.6
10/10	4.61	<0.6	2.78	<1.4
10/17	4.73	<0.6	2.87	<0.6
10/25	4.73	<0.6	2.79	<0.6
10/31	4.73	<0.6	2.59	<0.6
11/7	4.33	<0.6	2.41	<0.6
11/14	4.35	<0.6	1.81	0.74
11/21	4.40	<1.4	2.39	0.96
11/28	4.63	<0.6	2.44	<0.6
12/5	4.27	<1.4	2.57	<1.4
12/12	4.83	<1.4	2.41	<1.4
12/19	4.76	<1.4	2.30	<1.4
12/26	4.96	<1.4	2.63	<1.4
1/1	5.04	<1.4	no collect	<1.4

1998 Collection Period	Surface Runoff: Sinkhole No. 1 Runoff Nitrate-N (ppm)	Sinkhole No. 1 Runoff Atrazine (ppb)	Sinkhole No. 2 Runoff Nitrate-N (ppm)	Sinkhole No. 2 Runoff Atrazine (ppb)
5/3-5/16	no sample	no sample	no sample	<1.4
5/16-5/23	no sample	<1.4	0.13	3.78
5/23-5/31	no sample	no sample	1.78	2.26
5/31-6/13	31.29	7.65	0.04	5.90
6/13-6/27	1.99	<1.4	0.01	<1.4
6/27-7/11	0.13	<1.4	0.09	<1.4
7/11-7/25	0.63	2.01	no sample	<1.4
7/25-8/8	no sample	no sample	0.18	<0.6
8/8-8/22	1.09	<1.4	0.14	<1.4
8/22-9/12	no sample	no sample	no sample	no sample
9/12-9/26	no sample	no sample	0.69	no anal.
9/26-10/10	6.60	<0.6	0.16	<1.4
10/10-10/25	1.44	<1.4	0.06	<0.6
10/25-11/7	1.06	<0.6	2.14	0.95
11/7-11/21	0.73	<0.6	no anal.	<0.6
11/21-12/5	0.03	<1.4	0.07	<1.4
12/5-12/19	no sample	<1.4	0.36	no anal.
12/19-1/1/99	0.07	<1.4	0.41	no anal.

Figure 8

(a) Atrazine vs Nitrate-N at Auctioneer Spring (S4)



(b) Atrazine vs Nitrate-N at Camp Vandeventer Spring (S6)

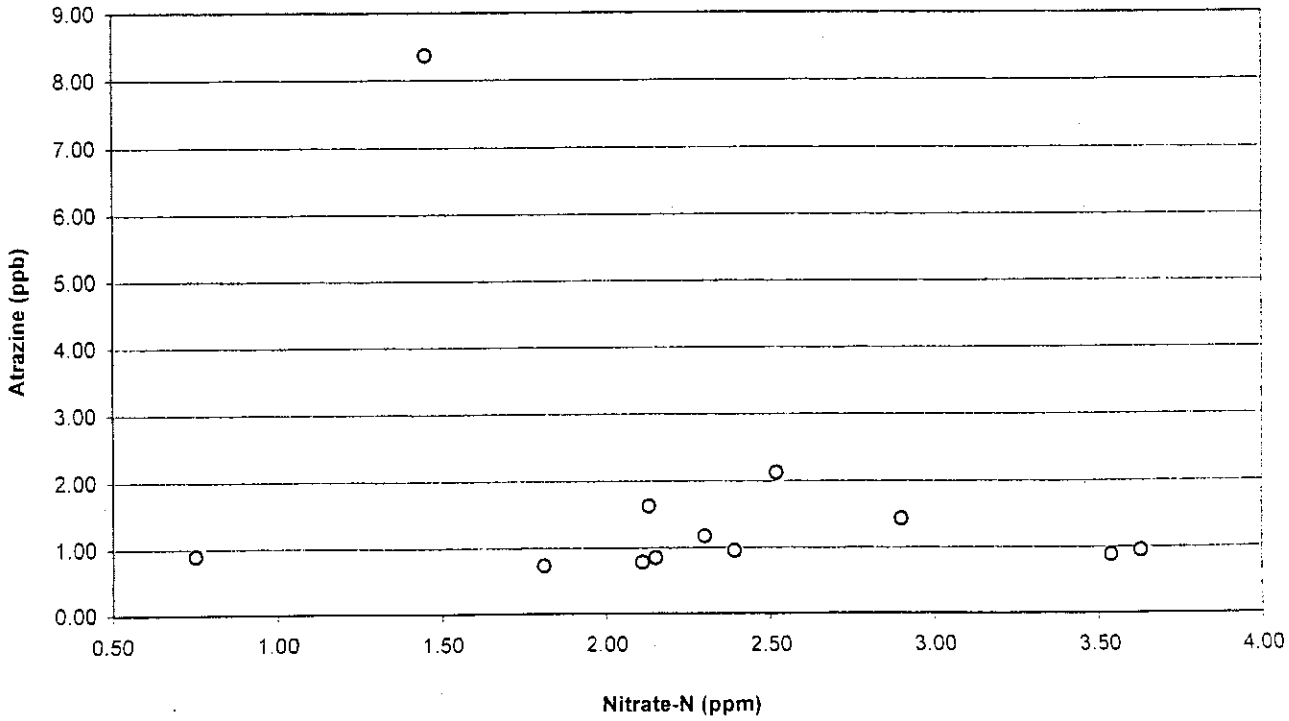
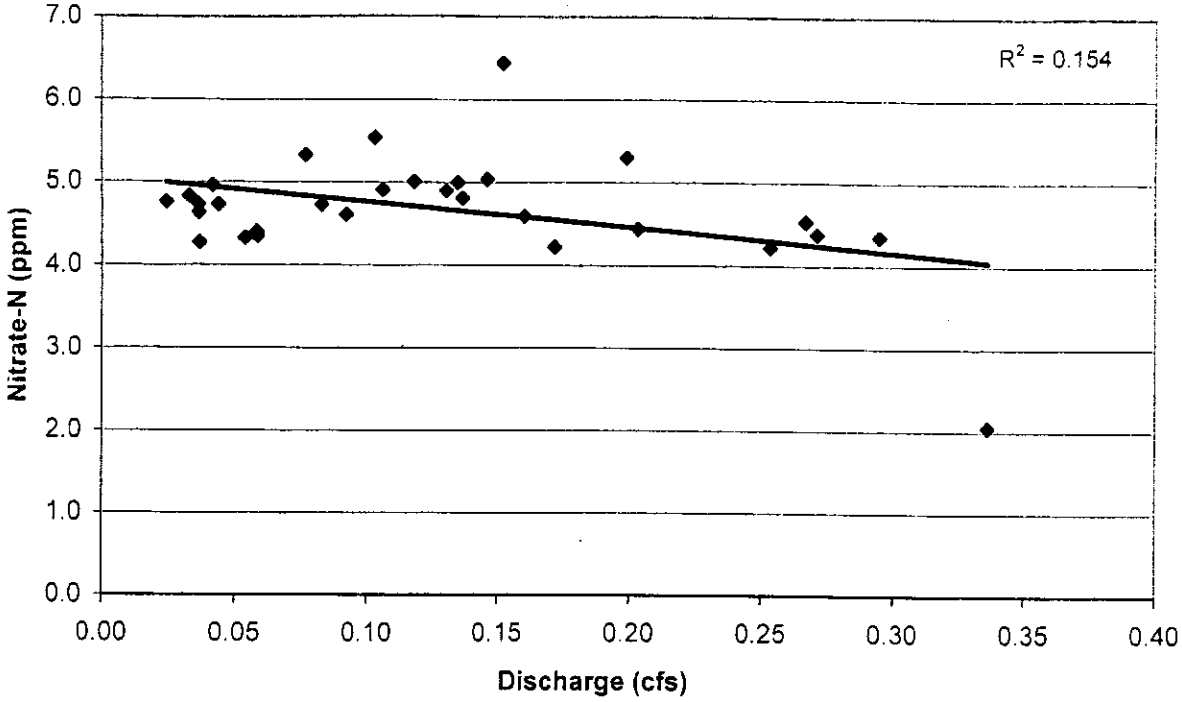
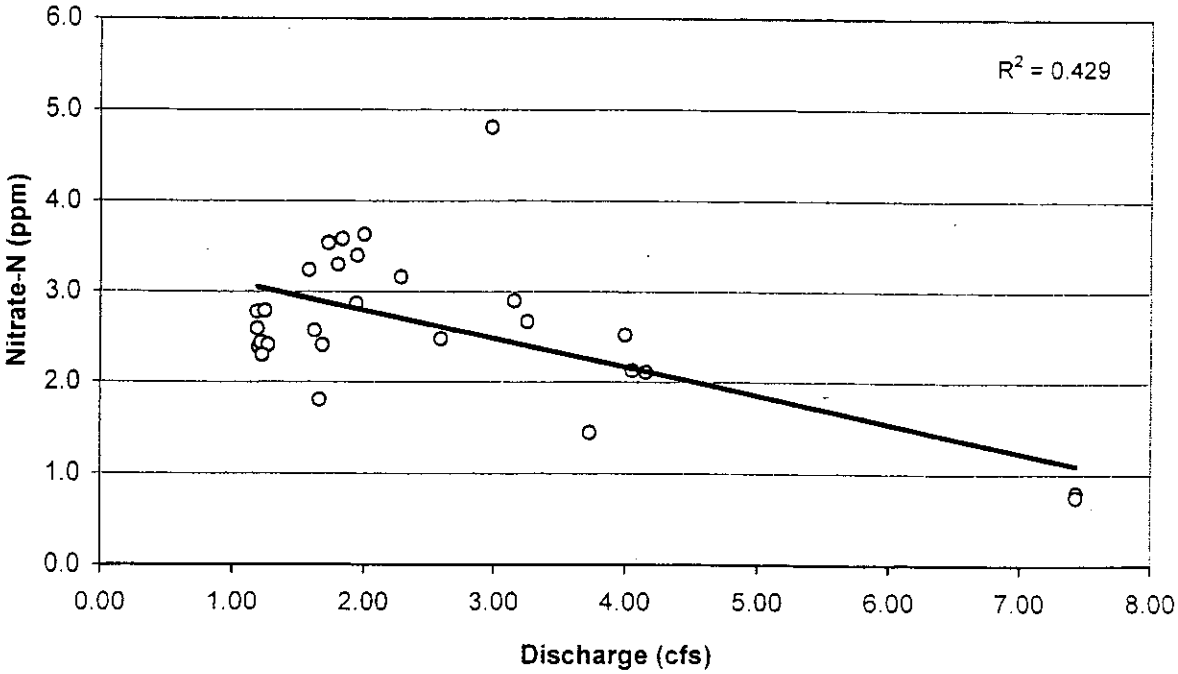


Figure 9

(a) Nitrate-N vs Discharge at Auctioneer Spring (S4)



(b) Nitrate-N vs Discharge at Camp Vandeventer Spring (S6)



karst conduits in the spring systems become activated under relatively high-flow conditions. Below these discharge levels nitrate-N concentrations remain relatively constant as water moves continuously through conduits and/or smaller openings that are active under base-flow conditions of the spring hydrographs (Figure 6). This interpretation is consistent with the temporal trends in temperature and specific electrical conductance at Auctioneer Spring (Figures 4 and 7a), in which the second storm event in the spring hydrograph (Figure 6a) did not significantly affect these parameters in the spring water. This storm event produced a maximum discharge of only 0.27 cfs at the spring.

Nitrate-N concentrations in runoff waters collected at the sinkholes are, with two exceptions, significantly lower than the concentration levels found in Auctioneer Spring waters (Table 2). Excess nitrate-N in the soils tends to percolate downward to the water table; it is so soluble that little is lost in direct surface runoff (Logan, 1995). Detectable levels of atrazine in water samples from the runoff collectors (Table 2) are generally confined to the early portion of the study period, just after herbicide application to the fields. Concentration levels for the most part exceed the USEPA Maximum Contaminant Level (MCL) of 3.0 ppb for drinking water (USEPA, 1992), and are comparable to the levels observed in Auctioneer Spring waters in the same time interval. An isolated occurrence of detectable atrazine in runoff water at Sinkhole No. 2 in late October-early November (Table 2) is correlated with heavy precipitation that fell during this time period (Table 1).

DISCUSSION

The premise of this study is that although a significant difference in biodiversity level (taxa richness) exists between Auctioneer and Camp Vandeventer springs (Webb et al., 1996), investigations of water quality and hydrology at the two springs have not been sufficiently comprehensive to evaluate the importance of these factors in controlling the observed levels of biodiversity. Previous investigations of hydrology and/or water quality at these springs have been based on data gathered at bimonthly or quarterly intervals. Ideally, automatic water samplers and

stream stage recorders should be installed in both springbrooks to provide continuous records of water quality and discharge over an extended period of time. But the equipment is expensive and difficult to maintain, and such an investigation requires a high level of funding. The procedure employed in this study represents a compromise; water samples were collected and discharge and other field parameters were measured at both springs on a weekly basis for a period of eight months. Thus reasonably detailed spring hydrographs have been established (Figure 6) that show two major storm events superimposed on base-flow recession. Concentrations of the agrichemicals nitrate-N and atrazine have been obtained for water samples collected under variable hydrologic conditions at both springs. These data can be evaluated for relationships between water quality, hydrology, and biodiversity.

Both water temperature (Figure 4) and pH (Figure 5) were nearly identical at Auctioneer and Camp Vandeventer springs throughout the course of the study, and both parameters showed little temporal variability. It is unlikely that either of these water-quality parameters is related to the different levels of biodiversity observed by Webb et al. (1996) at the two springs.

Nitrate-N at the Springs

Temporal variations in nitrate-N concentrations at Auctioneer and Camp Vandeventer springs are illustrated in Figure 10. It is clear that nitrate-N levels in the spring waters are influenced by hydrologic conditions. The two major storm events that appear on the spring hydrographs (Figure 6) are correlated with significant reductions in nitrate-N concentrations in the spring waters (Figure 11). The second storm event has a less pronounced effect at Auctioneer Spring than at Camp Vandeventer Spring. It is important to observe, however, that the depressions in nitrate-N levels were immediately preceded by significant increases in nitrate-N concentrations in the waters discharging from the springs. For example, the first storm hydrograph is just beginning to rise on 6/13/98 at both springs (Figure 11), but the nitrate-N levels in the spring waters peak sharply on that date. The week leading up to June 13 was marked by a large amount of rainfall (Table 1). The second storm hydrograph is beginning to rise on 7/18/98 at Camp Vandeventer Spring and on

Figure 10

Temporal Variations in Nitrate-N Concentrations at Auctioneer Spring (S4) and Camp Vandeventer Spring (S6)

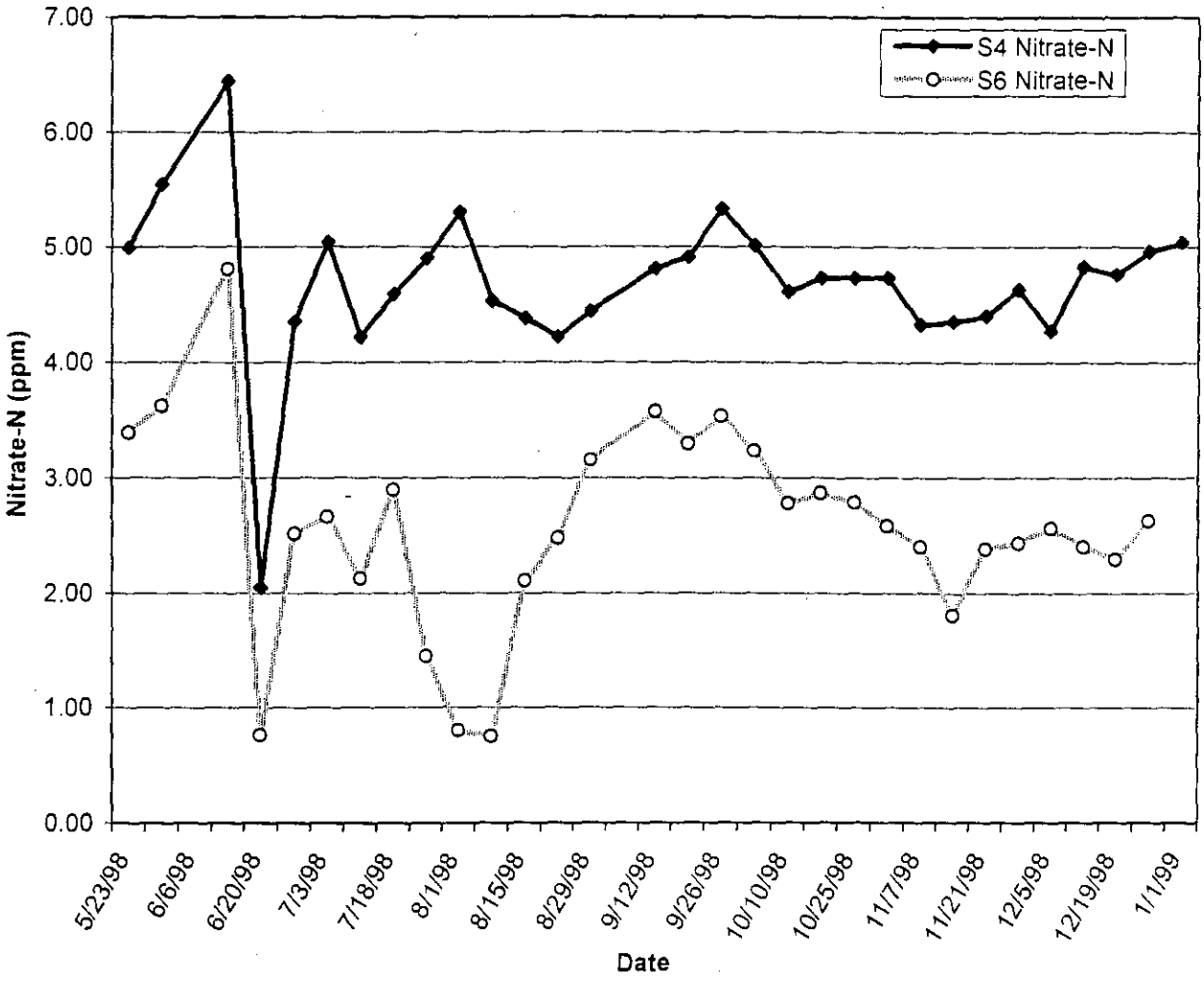
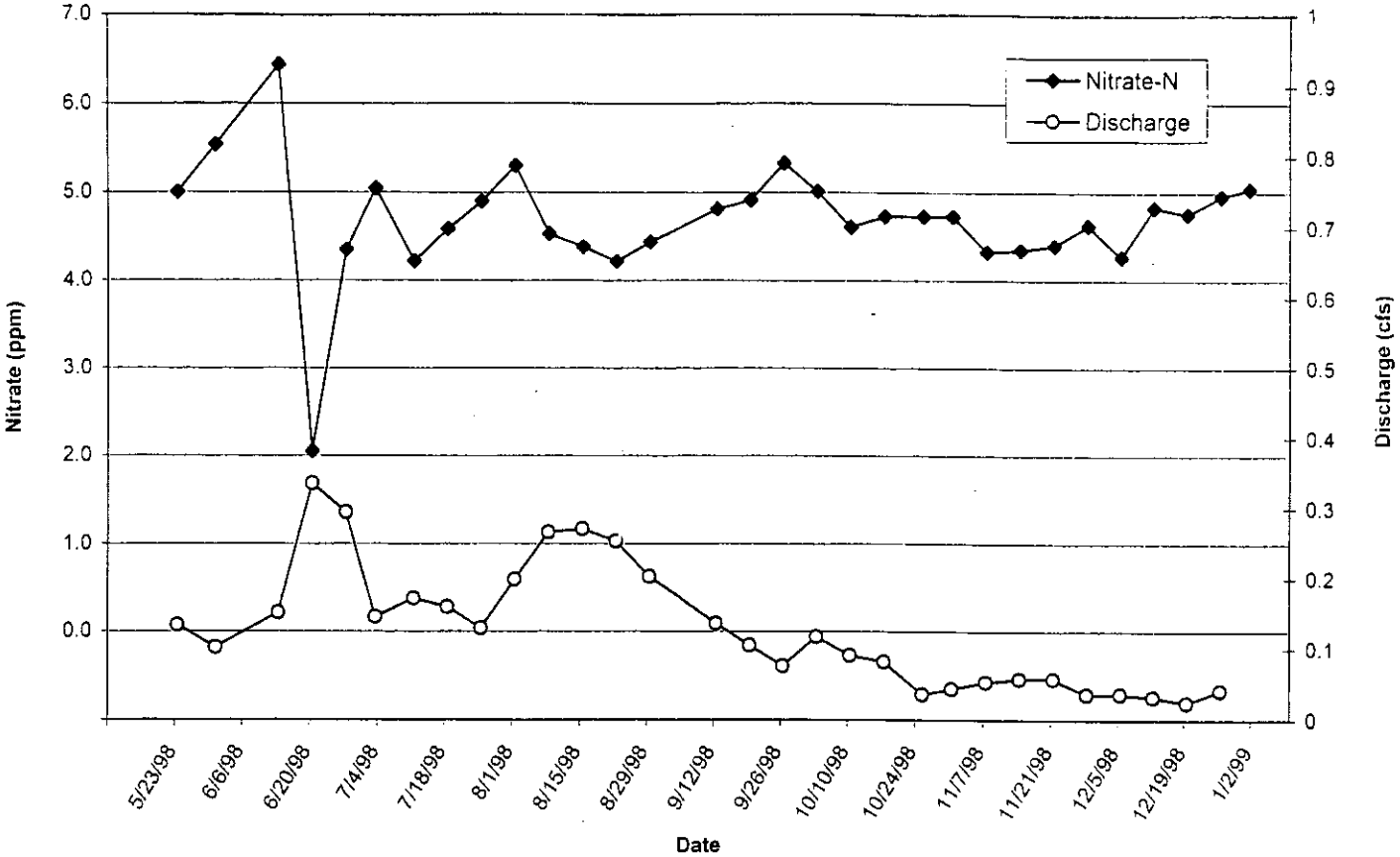
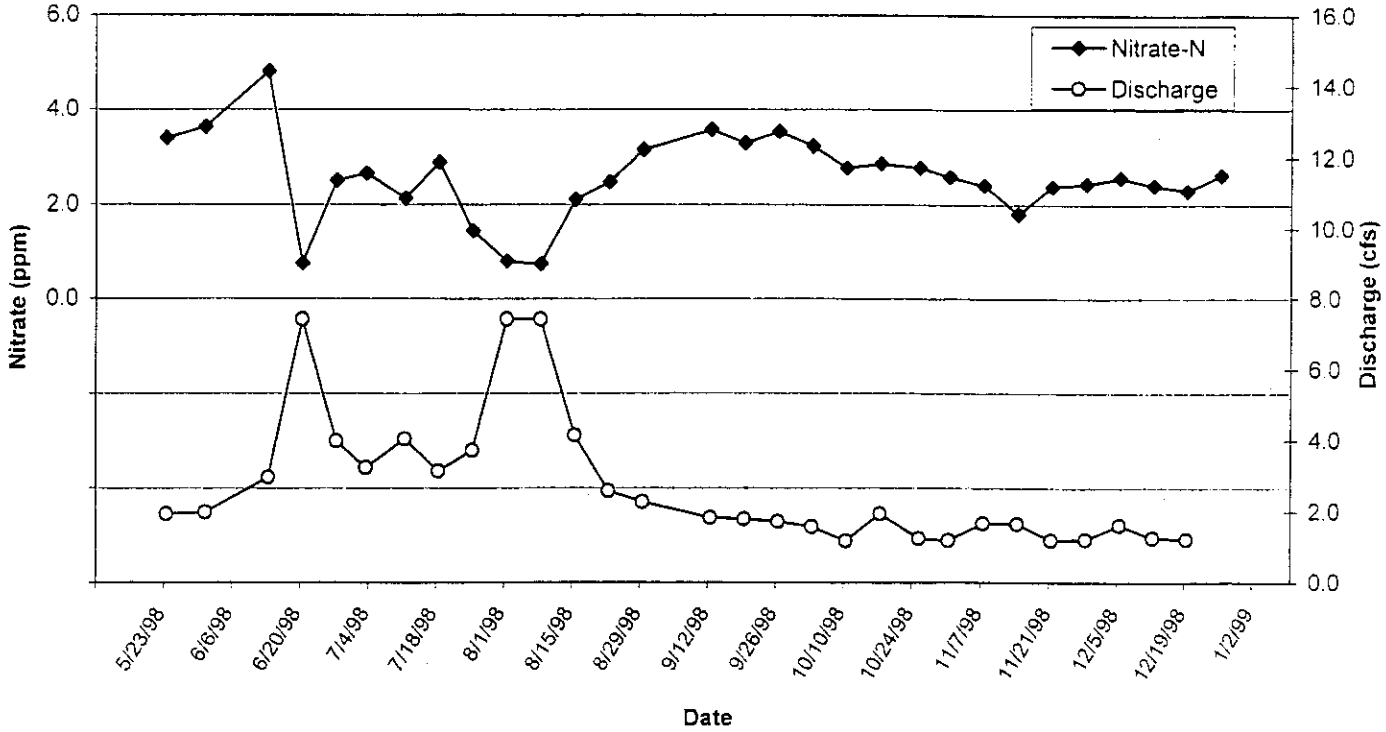


Figure 11

(a) Temporal Variations in Nitrate-N and Discharge at Auctioneer Spring (S4)



(b) Temporal Variations in Nitrate-N and Discharge at Camp Vandeventer Spring (S6)



7/25/98 at Auctioneer Spring (Figure 11), and the nitrate-N levels in the spring waters rise sharply on or just after those dates. These peaks in nitrate-N concentrations in the spring waters at the beginning of a storm event may represent initial discharges from karst conduits in the spring systems that are activated only under high-flow conditions. They correlate with the onset of increases in water temperature at the springs (Figure 4), which suggest activation of more direct flow channels in the spring systems.

The effects of storm events on nitrate-N concentrations at the springs are superimposed on relatively constant nitrate-N levels in the spring waters under low-flow conditions (Figure 11), which may reflect the dominance of diffuse groundwater flow in the spring systems under such conditions. This effect is underscored in the fall and winter, when the spring systems are undergoing base-flow recession. Excluding the effects of storm events, the nitrate-N concentration in Auctioneer Spring waters is relatively uniform at 4.5 - 5.0 ppm, whereas at Camp Vandeventer Spring the nitrate-N level is fairly steady at 2.5 - 3.0 ppm (Figure 11). Thus Auctioneer Spring waters are characterized by a significantly larger concentration of nitrate-N, which may be a factor that contributes to the markedly lower level of biodiversity observed at that spring.

The mean nitrate-N concentration for samples collected at Auctioneer Spring during this study is 4.6 ppm, whereas Camp Vandeventer Spring waters yield a mean nitrate-N concentration of 2.6 ppm. These values are consistent with data reported by other workers. For samples collected under base-flow conditions in November 1998, Panno et al. (1999) reported nitrate-N concentrations of 5.1 ppm at Auctioneer Spring and 2.9 ppm at Camp Vandeventer Spring. In a study involving nine samples collected under both high- and low-flow conditions at each spring during a twelve-month interval between August 1996 and July 1997, mean nitrate-N at Auctioneer Spring was 7.3 ppm whereas at Camp Vandeventer Spring it was 3.3 ppm (Odemerho et al., 1998). Webb et al. (1996) collected samples at both springs under various hydrologic conditions, on a quarterly basis between November 1994 and August 1995. They reported mean nitrate-N concentrations of 4.0 ppm at Auctioneer Spring and 2.9 ppm at Camp Vandeventer Spring. A total of five samples was collected from each spring under base-flow conditions between May and

October 1995 by Calero (1999). Nitrate-N analyses yielded mean values of 4.1 ppm at Auctioneer Spring and 3.1 ppm at Camp Vandeventer Spring.

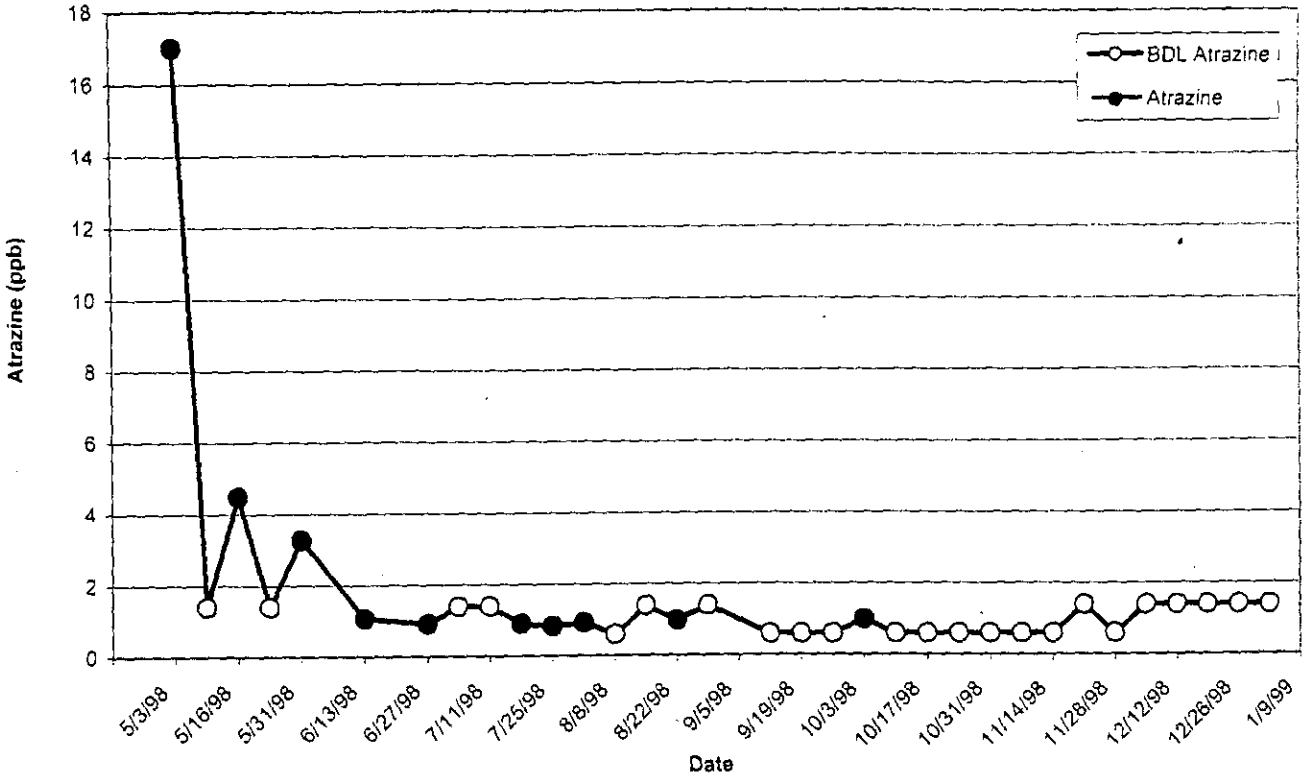
Atrazine at the Springs

Temporal variations in atrazine concentrations at Auctioneer and Camp Vandeventer springs are shown in Figure 12. Atrazine was detected in only ten water samples collected at Auctioneer Spring; these show a sharp decline in concentration level after herbicide application to the fields in April and May (Figure 12a). Atrazine concentrations in Auctioneer Spring waters during May exceeded the USEPA MCL of 3.0 ppb for drinking water and are comparable to the concentrations in runoff waters at the two sinkholes during the same time period (Table 2). This atrazine was probably dissolved in runoff waters and moved quickly from the fields through the sinkholes to the springhead. Following this initial pulse, atrazine in the runoff samples declined to very low or undetectable concentrations by mid-June. Thereafter, atrazine when detected in water at the springhead was at a concentration of about 1 ppb, just above the analytical detection limit (Figure 12a). The interval of time during which this atrazine level was observed, June 13 through October 3, corresponds with the interval during which the two prominent storm events occurred on the Auctioneer Spring hydrograph (Figure 13a). The atrazine in the spring waters may have been removed from sediments that became suspended in surface runoff and carried into the sinkholes. Atrazine was not detected in samples collected after base-flow recession began in the Auctioneer Spring system in early October (Figure 13a).

At Camp Vandeventer Spring an initial pulse of high atrazine concentrations was not observed in the spring waters (Figure 12b). When detected during May, atrazine was at a level of about 1 ppb. The difference between this observation and the temporal variation observed at Auctioneer Spring during May could be the result of greater discharge at Camp Vandeventer Spring under low-flow conditions, which could dilute the atrazine present. During the interval of the two major storm events at Camp Vandeventer Spring, June 13 to August 22, significant increases were observed in the atrazine concentrations in the spring water (Figure 13b). This is undoubtedly due

Figure 12

(a) Temporal Variation in Atrazine Concentration at Auctioneer Spring (S4)



(b) Temporal Variation in Atrazine Concentration at Camp Vandeventer Spring (S6)

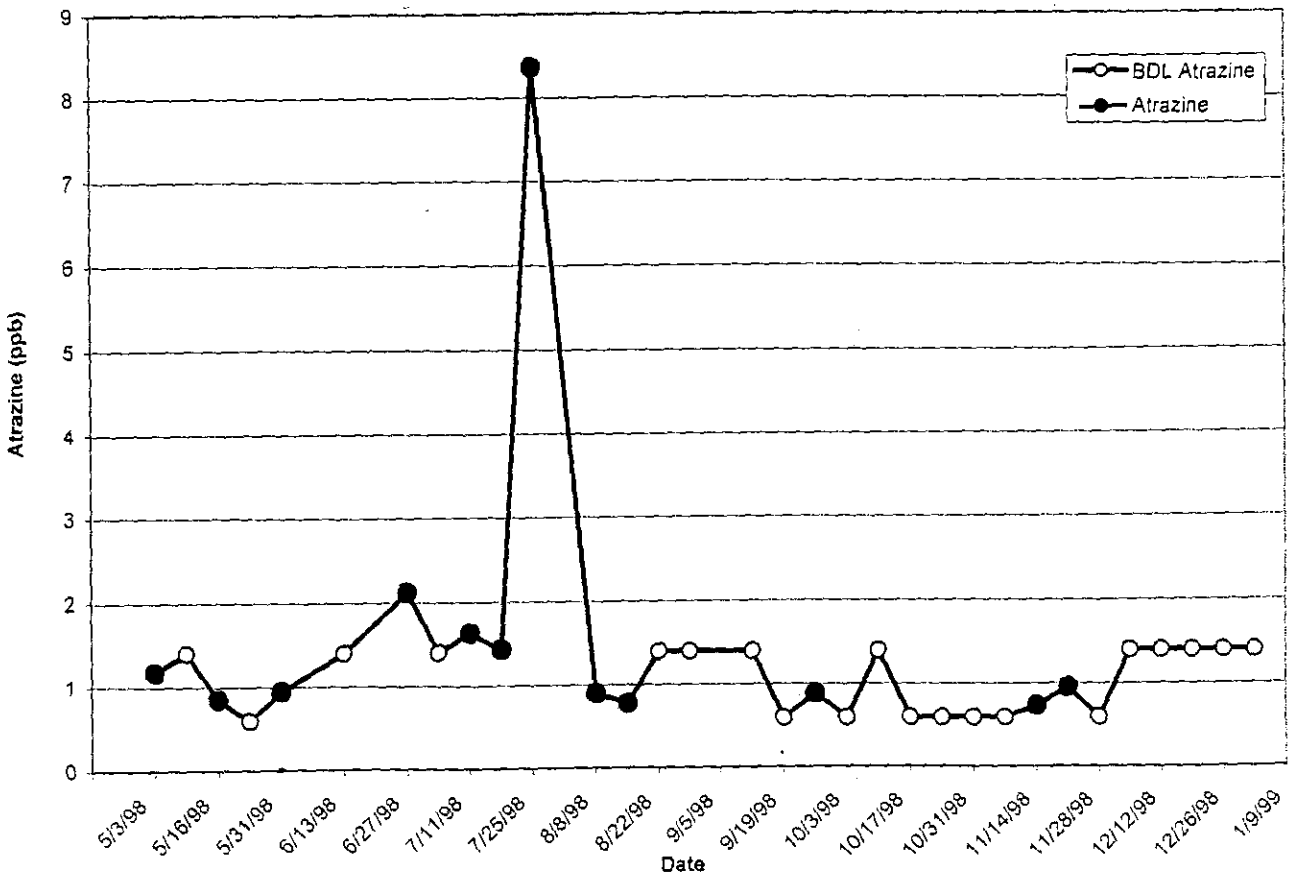
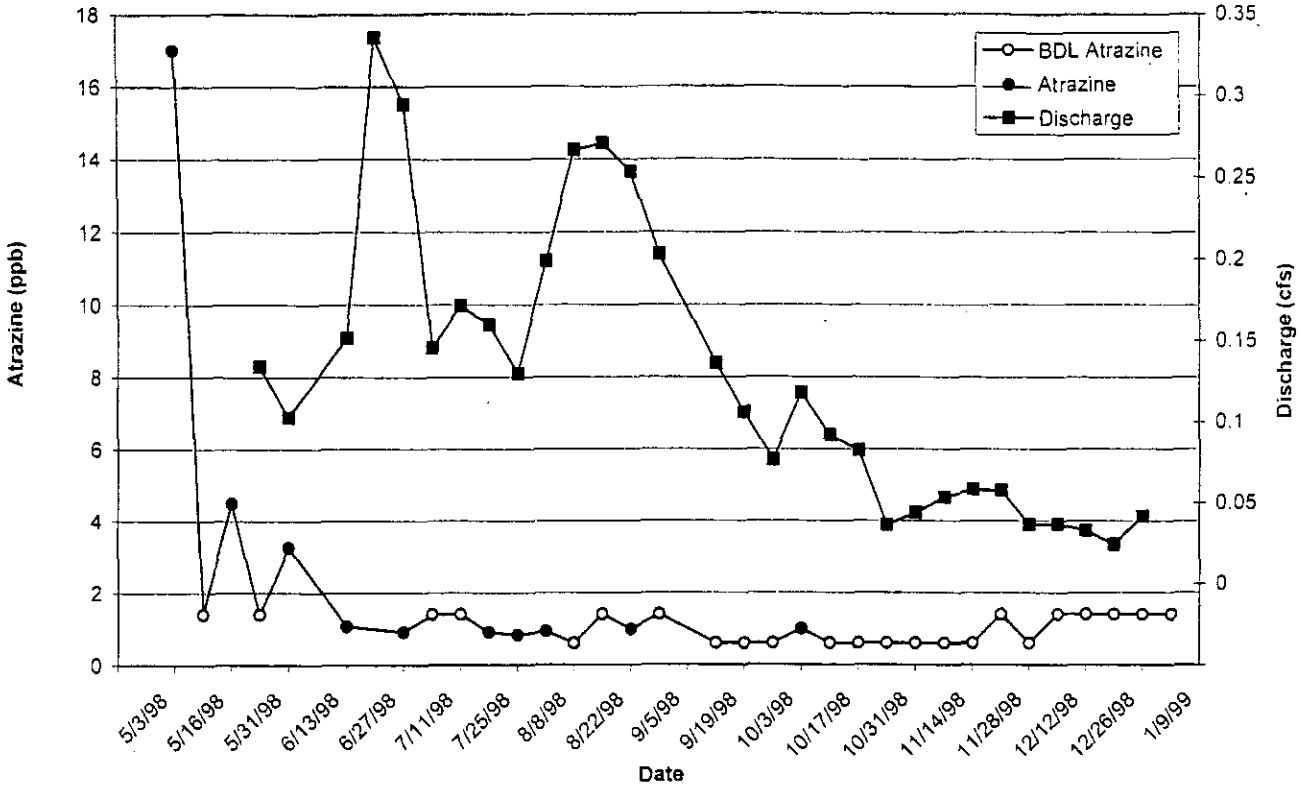
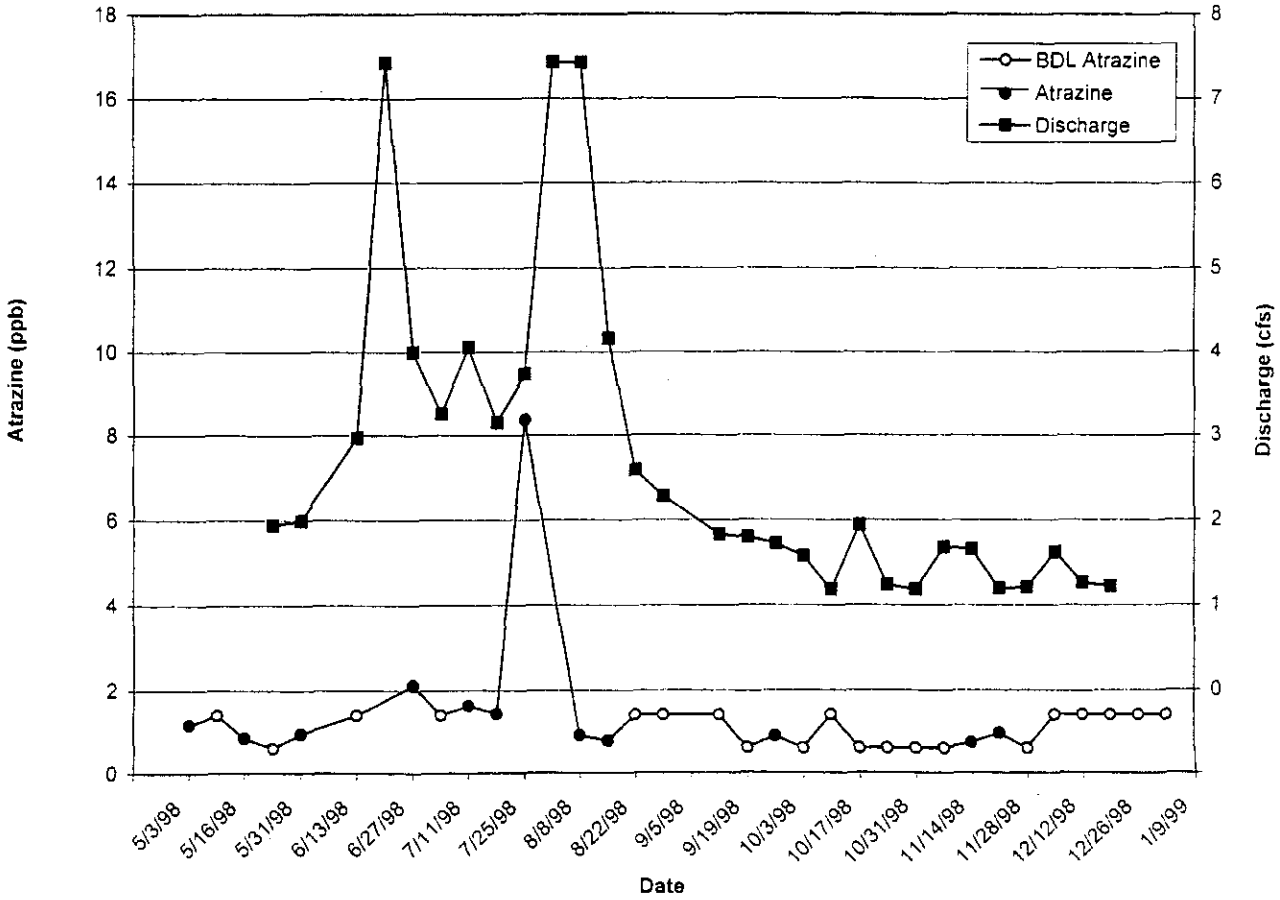


Figure 13

(a) Temporal Variations in Atrazine Concentration and Discharge at Auctioneer Spring (S4)



(b) Temporal Variations in Atrazine Concentration and Discharge at Camp Vandeventer Spring (S6)



to mobilization of sediments in runoff waters and subsequent removal of atrazine from them. After base-flow recession began at Camp Vandeventer Spring atrazine was occasionally detected in the spring water at a level of about 1 ppb (Figure 13b). Concentration levels of nitrate-N and atrazine in water samples show antithetical patterns during storm events at Auctioneer Spring and at Camp Vandeventer Spring (Figures 11 and 13) due to the difference in behavior of the two chemical species in the natural environment.

Atrazine concentration levels observed at Auctioneer and Camp Vandeventer springs during the period of this research are comparable with those reported in other studies that involved either or both of the springs. Camp Vandeventer Spring water was sampled ten times on a monthly basis under a range of hydrologic conditions by Panno et al. (1996), who found a mean atrazine concentration of 3.0 ppb and individual values ranging from below detection limit to 15.2 ppb. Odemerho et al. (1998) collected a total of nine samples from each of the two springs during a 12-month interval, under various hydrologic conditions. They reported mean atrazine concentrations of 0.75 ppb for Auctioneer Spring waters and 1.0 ppb for the samples from Camp Vandeventer Spring. Webb et al. (1996) collected four samples at each of the two springs under variable hydrologic conditions, on a quarterly basis over a 12-month period of time. These workers found mean atrazine concentrations of 0.27 ppb at Auctioneer Spring and 1.16 ppb at Camp Vandeventer Spring. Calculations of mean atrazine levels at the two springs from data gathered in this study are limited by the high analytical detection limits (0.6 ppb and 1.4 ppb) and the preponderance of samples in which atrazine was not detected. If the samples that contained no detectable atrazine are assigned zero values, the mean atrazine level at Auctioneer Spring is 0.95 ppb and at Camp Vandeventer Spring it is 0.65 ppb. Thus the water discharged at Auctioneer Spring, where there is a much lower level of biodiversity, on average contains a somewhat higher concentration of atrazine. Perhaps the aquatic macroinvertebrates are more sensitive to pulses of spring water with extremely high concentrations of atrazine, such as those that occured at Auctioneer Spring just after herbicide application in April and May or during major storm events at Camp Vandeventer Spring

(Figure 13). At such times the atrazine level can be several times greater than the USEPA MCL for drinking water.

Runoff at the Sinkholes

Concentrations of nitrate-N and atrazine in surface runoff waters collected at two sinkholes that are hydraulically connected to Auctioneer Spring (Table 2) provide insight into the sources of these chemical species that contribute to their concentration levels in water discharging from the spring. Precipitation in the vicinity of the sinkholes and spring (Table 1) was monitored at a site located approximately 450 feet (140 m) west of Sinkhole No. 1 (Figure 2). Temporal variations of biweekly precipitation during the period of study correlate well with temporal variations in discharge measured at the spring (Figure 14). Biweekly precipitation totals are utilized because runoff water samples taken at the sinkholes represent two-week periods of accumulation in the collectors (Table 2).

Temporal variations of nitrate-N concentrations in biweekly runoff at the sinkholes (Figure 15) show an exceptionally high concentration level of about 31 ppm in the first sample collected at Sinkhole No. 1 in early June, shortly after fertilizer application to the fields (Figure 15a). Thereafter, nitrate-N concentrations declined sharply to values less than 2 ppm, with one exception (10/10/98). After the initial pulse of nitrate-N in runoff, precipitation events (Figure 15c) apparently did not mobilize significant amounts of nitrate-N from the adjacent corn field. At Sinkhole No. 2, concentration levels of nitrate-N in runoff never exceeded about 2 ppm and generally were below 1 ppm (Figure 15b). Thus beginning shortly after the planting season, nitrate-N levels in surface runoff to the sinkholes were generally well below the concentration levels observed in water discharging from Auctioneer Spring except during major storm events (Figure 16). Only the anomalously high nitrate-N concentration observed at the spring on 6/13/98 (Figure 16c), which correlates with the exceptionally high level found at Sinkhole No. 1 on the same date, can be largely attributed to a surface-runoff source. This occurrence probably represents discharge through more direct karst conduits in the spring system that are activated

Figure 14

Temporal Variations in Biweekly Precipitation at Sinkholes and Discharge at Auctioneer Spring (S4)

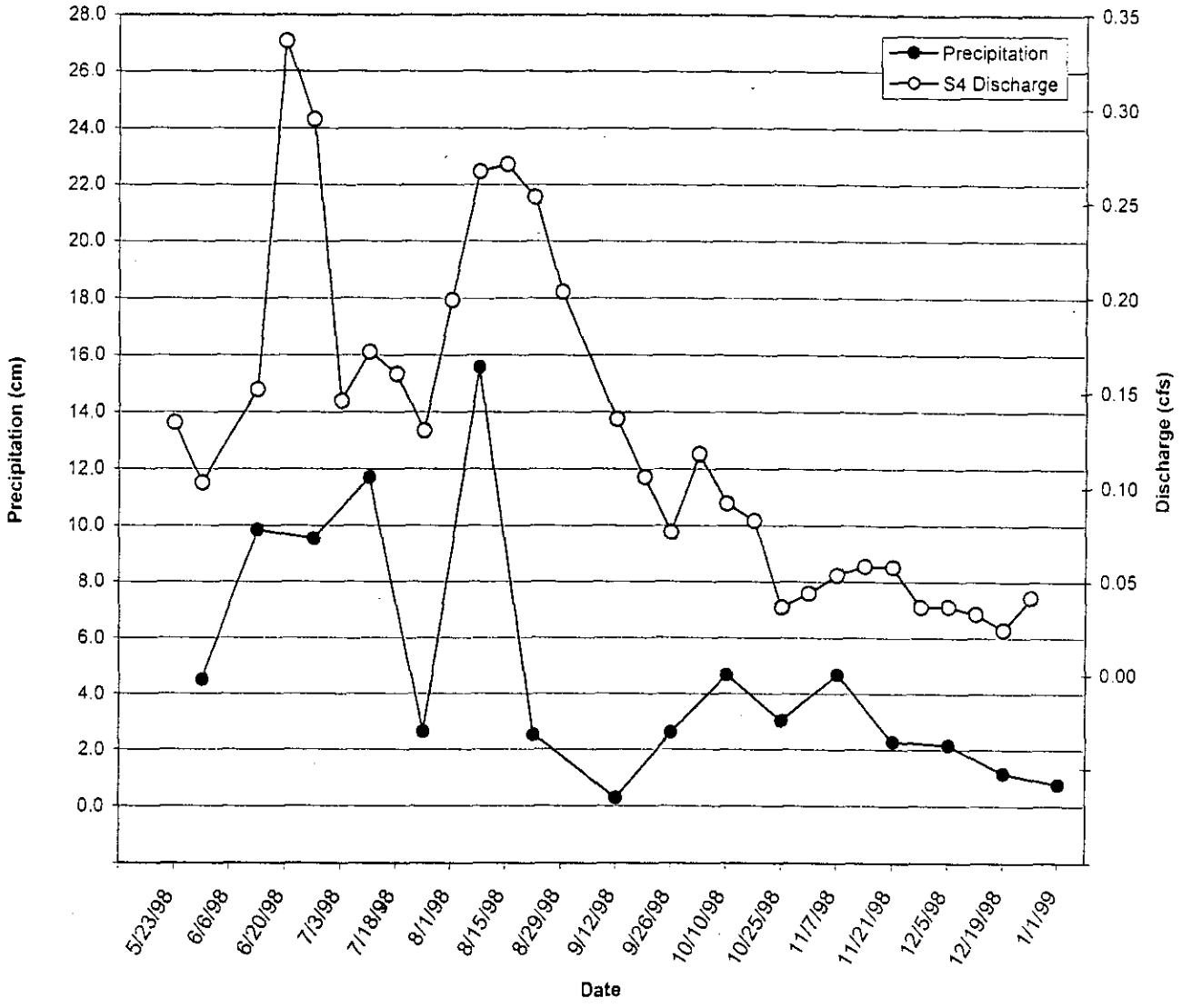
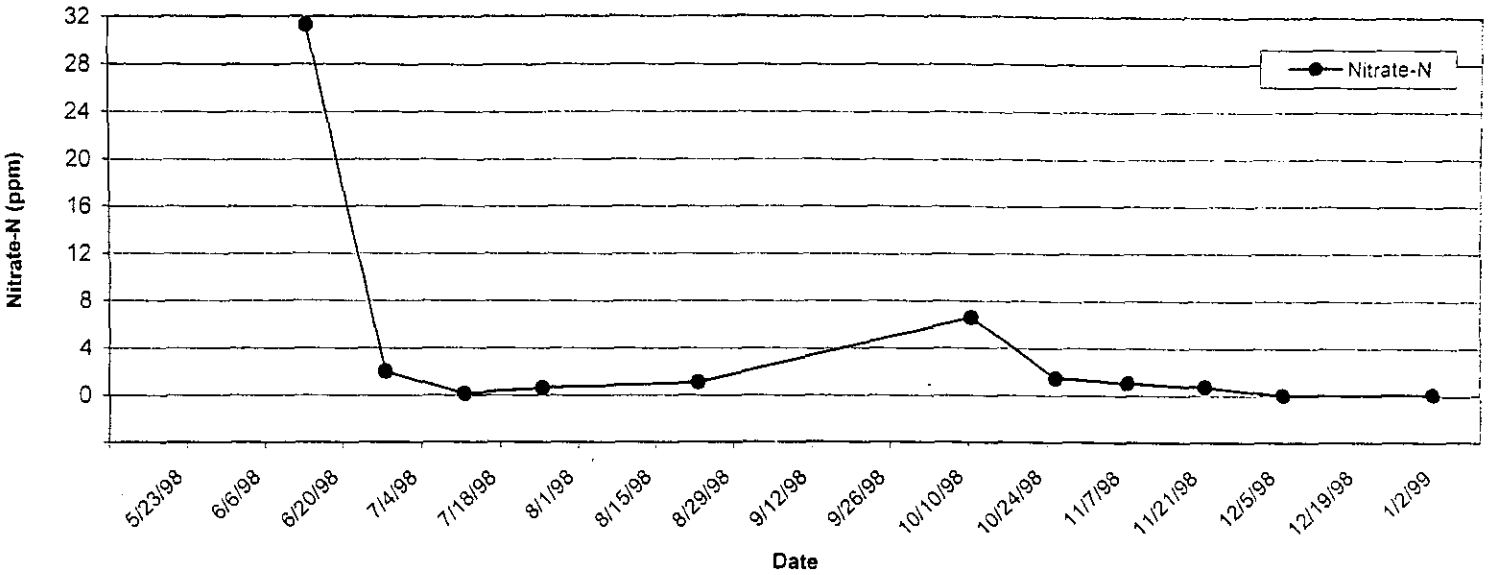
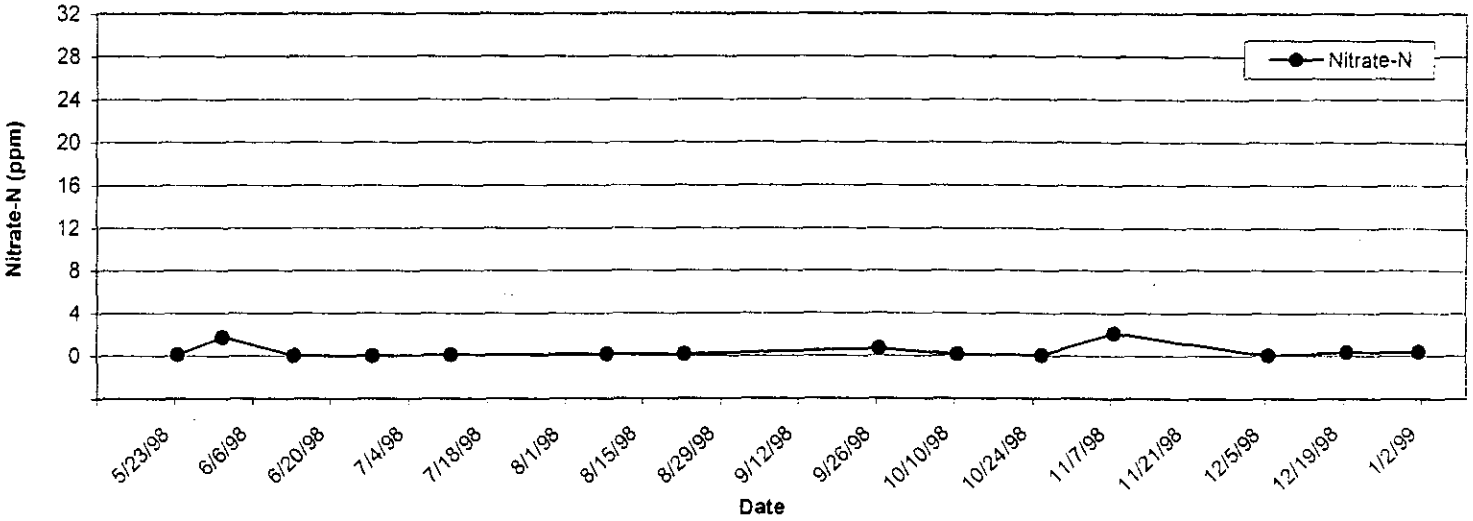


Figure 15

(a) Temporal Variation in Nitrate-N at Sinkhole No. 1



(b) Temporal Variation in Nitrate-N at Sinkhole No. 2



(c) Temporal Variation in Biweekly Precipitation at Sinkholes

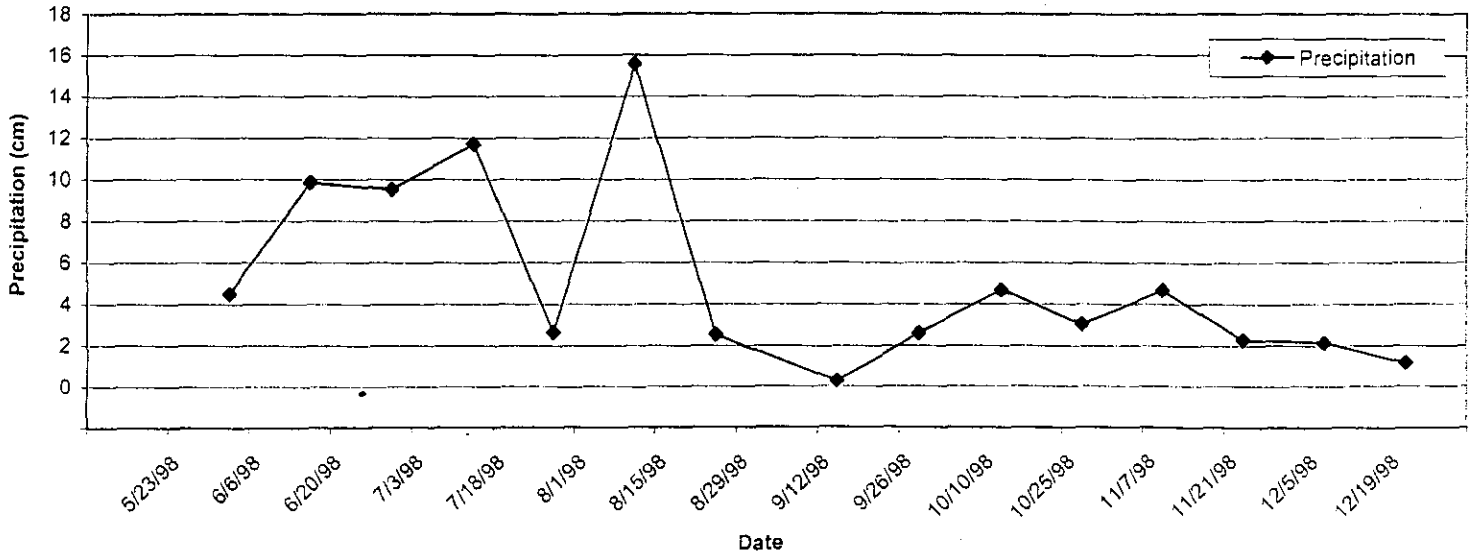
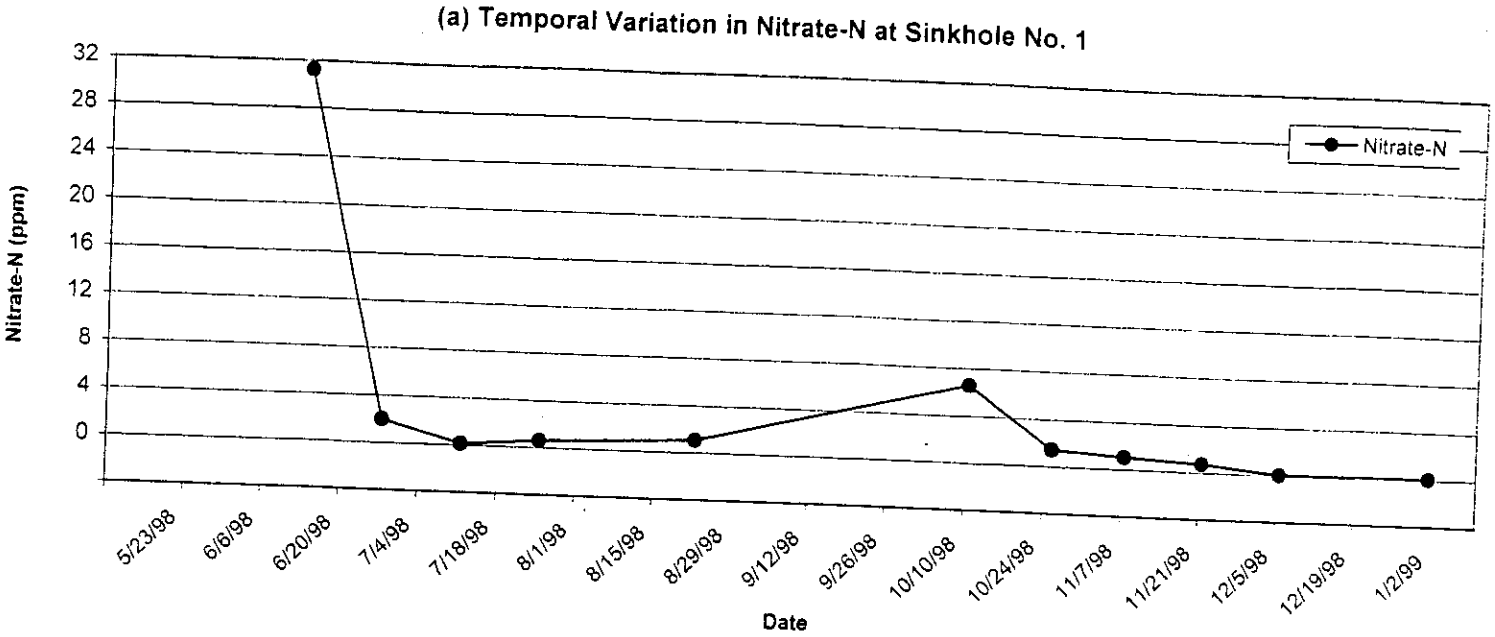
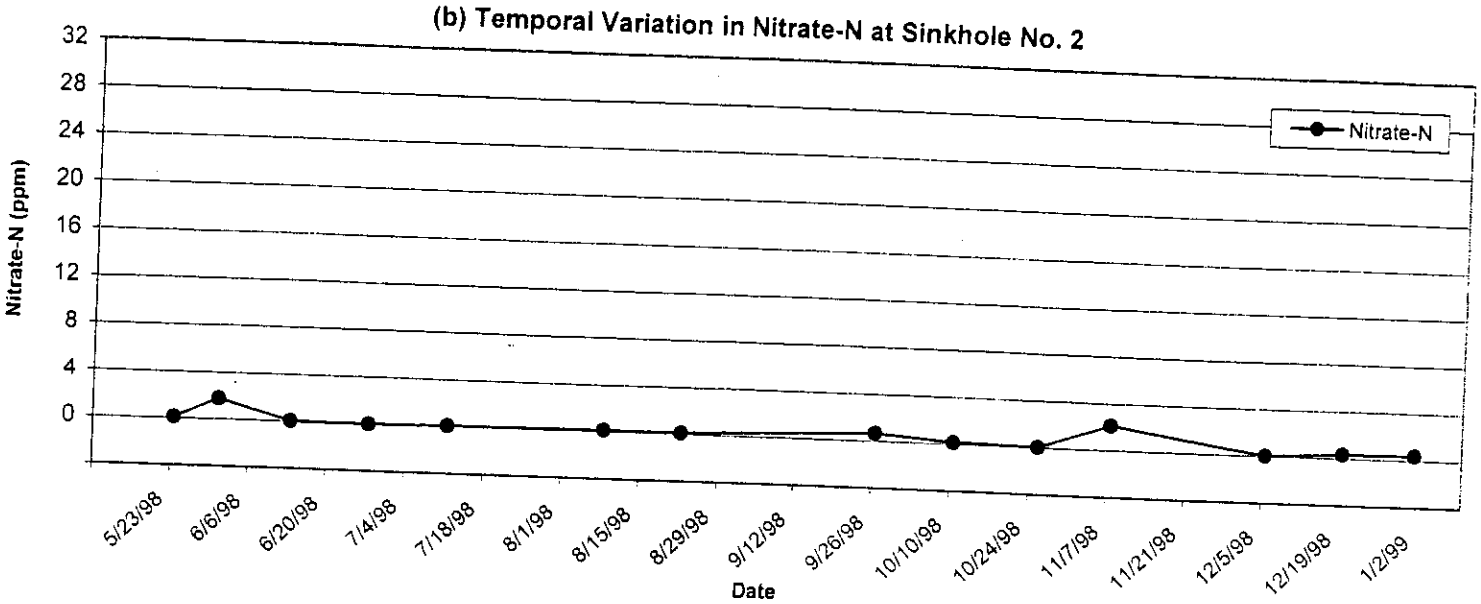
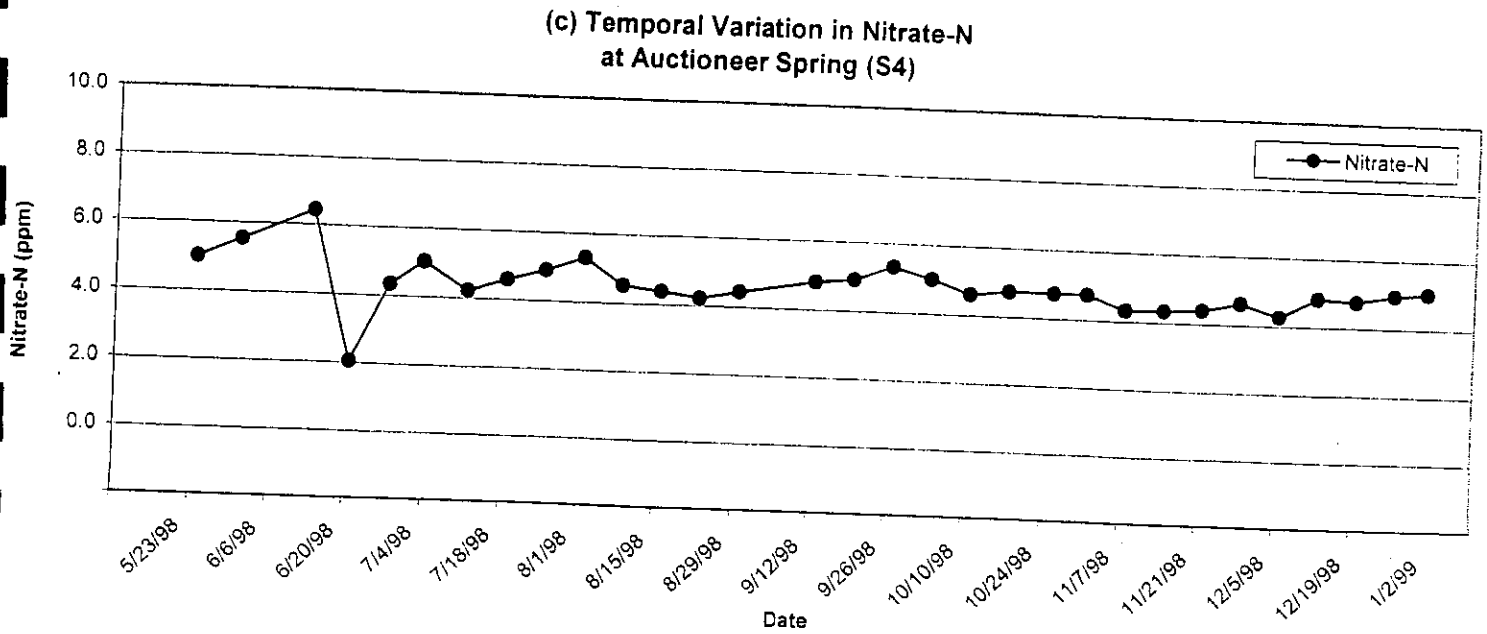


Figure 16


(a) Temporal Variation in Nitrate-N at Sinkhole No. 1
Nitrate-N (ppm)
32
28
24
20
16
12
8
4
0
Nitrate-N
5/23/98
6/6/98
6/20/98
7/4/98
7/18/98
8/1/98
8/15/98
8/29/98
9/12/98
9/26/98
10/10/98
10/24/98
11/7/98
11/21/98
12/5/98
12/19/98
1/2/99
Date


(b) Temporal Variation in Nitrate-N at Sinkhole No. 2
Nitrate-N (ppm)
32
28
24
20
16
12
8
4
0
Nitrate-N
5/23/98
6/6/98
6/20/98
7/4/98
7/18/98
8/1/98
8/15/98
8/29/98
9/12/98
9/26/98
10/10/98
10/24/98
11/7/98
11/21/98
12/5/98
12/19/98
1/2/99
Date


(c) Temporal Variation in Nitrate-N
at Auctioneer Spring (S4)
Nitrate-N (ppm)
10.0
8.0
6.0
4.0
2.0
0.0
Nitrate-N
5/23/98
6/6/98
6/20/98
7/4/98
7/18/98
8/1/98
8/15/98
8/29/98
9/12/98
9/26/98
10/10/98
10/24/98
11/7/98
11/21/98
12/5/98
12/19/98
1/2/99
Date

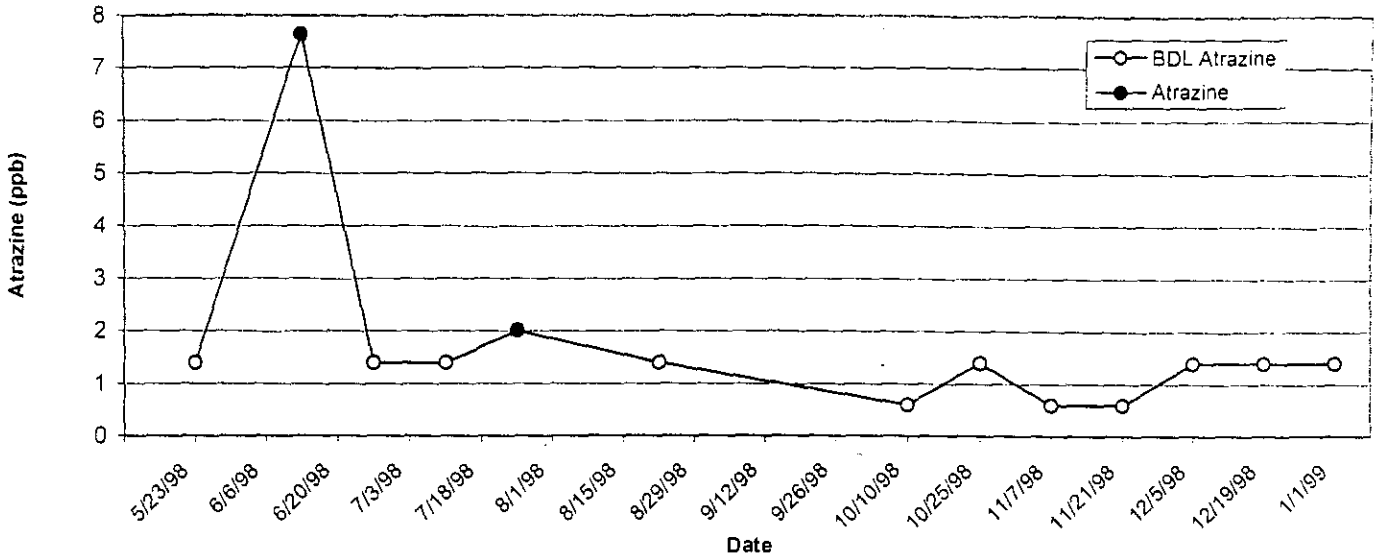
under high-flow conditions (Figure 11a). A similar effect was observed at Camp Vandeventer Spring on the same date (Figure 11b).

These observations, along with the relatively constant nitrate-N level of 4.5 - 5.0 ppm in Auctioneer Spring waters under low-flow conditions (Figure 16c), suggest that the major portion of nitrate-N discharged at the spring is moving by diffuse flow from a spring reservoir that has developed a constant level of nitrate-N through years of downward percolation of soil water from agricultural fields. Nitrate-N is so soluble that little is lost in direct surface runoff (Logan, 1995). After initial pulses of high nitrate-N from surface runoff following the planting season, nitrate-N in spring discharge is at a constant level that changes significantly only as a result of dilution under high-flow conditions (Figure 11a). The same interpretation can be applied to nitrate-N concentrations observed in the discharge at Camp Vandeventer Spring (Figure 11b), which show the same pattern of temporal variation.

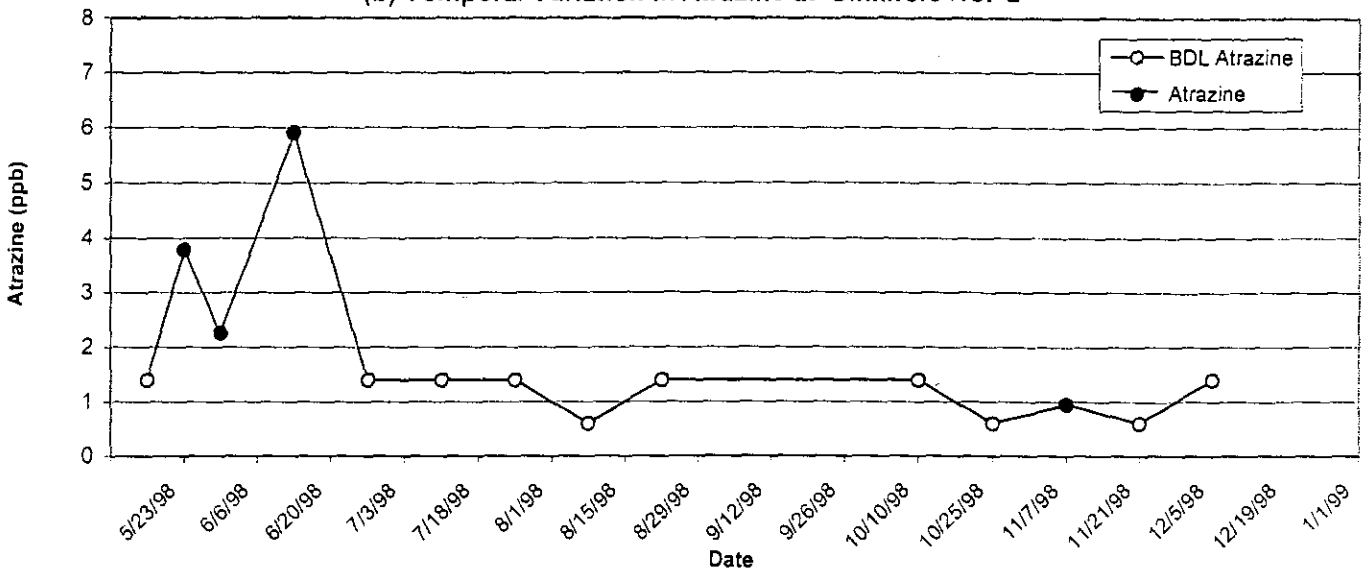
Atrazine concentrations in runoff waters at the sinkholes (Figure 17) show temporal behavior patterns similar to those of nitrate-N. Exceptionally high concentrations, well above the USEPA MCL of 3.0 ppb, were found in surface runoff during a short period of time (May and early June) just after pesticide application to the fields (Figures 17a and 17b). After these initial pulses, atrazine in runoff waters fell to concentrations at or below the analytical detection limit of about 1 ppb and remained at those levels throughout the remainder of the study period (through December) in spite of significant precipitation events (Figure 17c). Atrazine concentrations in the discharge at Auctioneer Spring (Figure 18c) showed a similar temporal pattern, never rising above 1 ppb after 5/31/98 and never rising above the detection limit after 10/3/98. Therefore the atrazine discharged at Auctioneer Spring, unlike the nitrate-N, can be largely attributed to a source in recent surface runoff rather than to slow release from storage in the spring reservoir. Atrazine is regarded as a seasonal surface-water contaminant because it degrades rapidly relative to water percolation from the surface to the water table (Logan, 1995). In karst terrains, however, there is rapid communication between surface waters and groundwaters through sinkholes and conduit flow, so that large atrazine concentrations are found in spring discharge on a seasonal basis before

Figure 17

(a) Temporal Variation in Atrazine at Sinkhole No. 1



(b) Temporal Variation in Atrazine at Sinkhole No. 2



(c) Temporal Variation in Biweekly Precipitation at Sinkholes

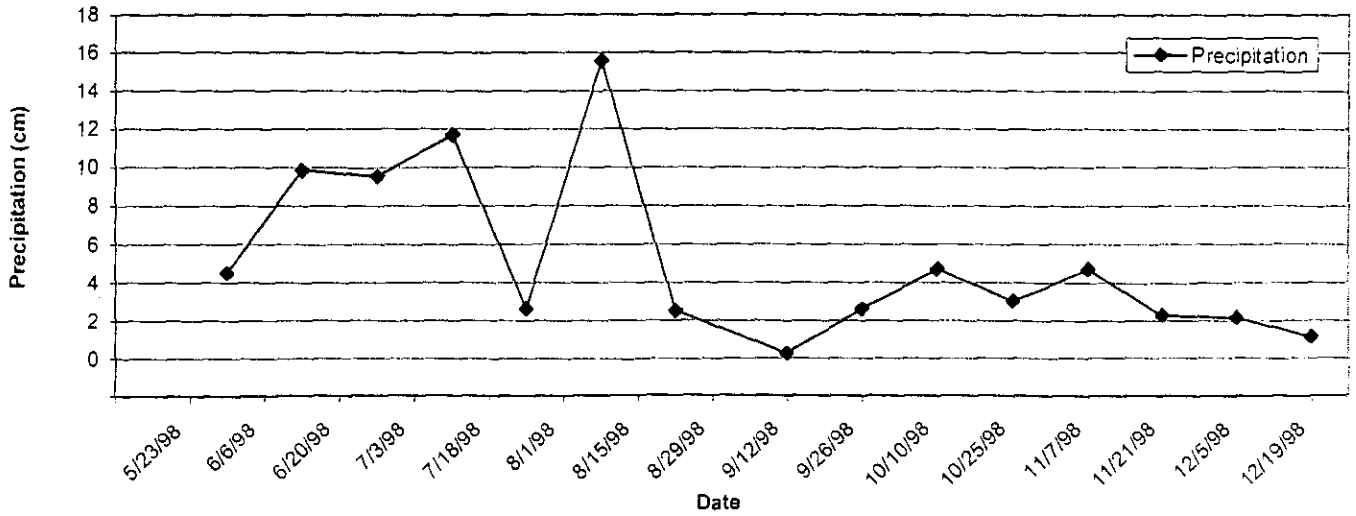
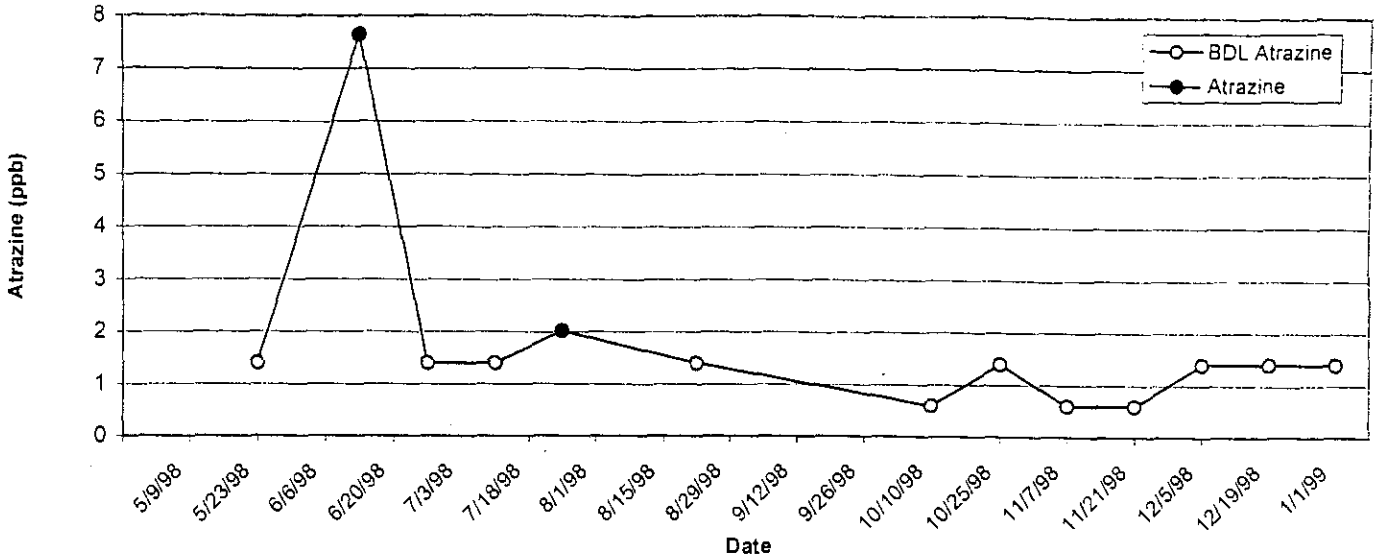
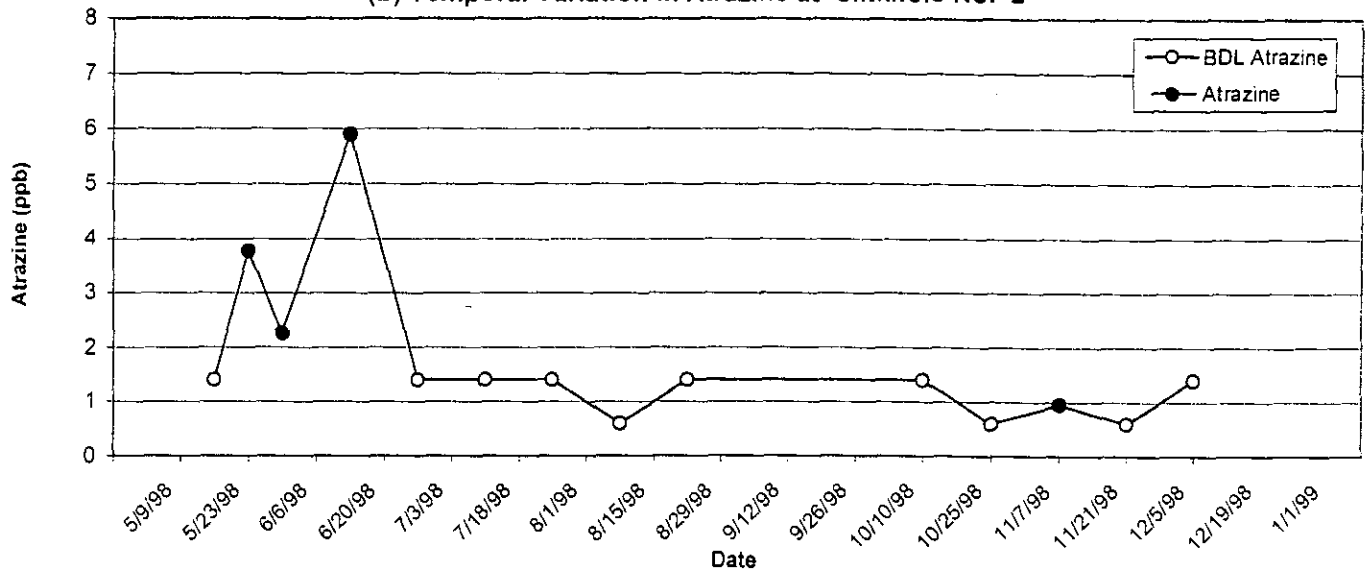


Figure 18

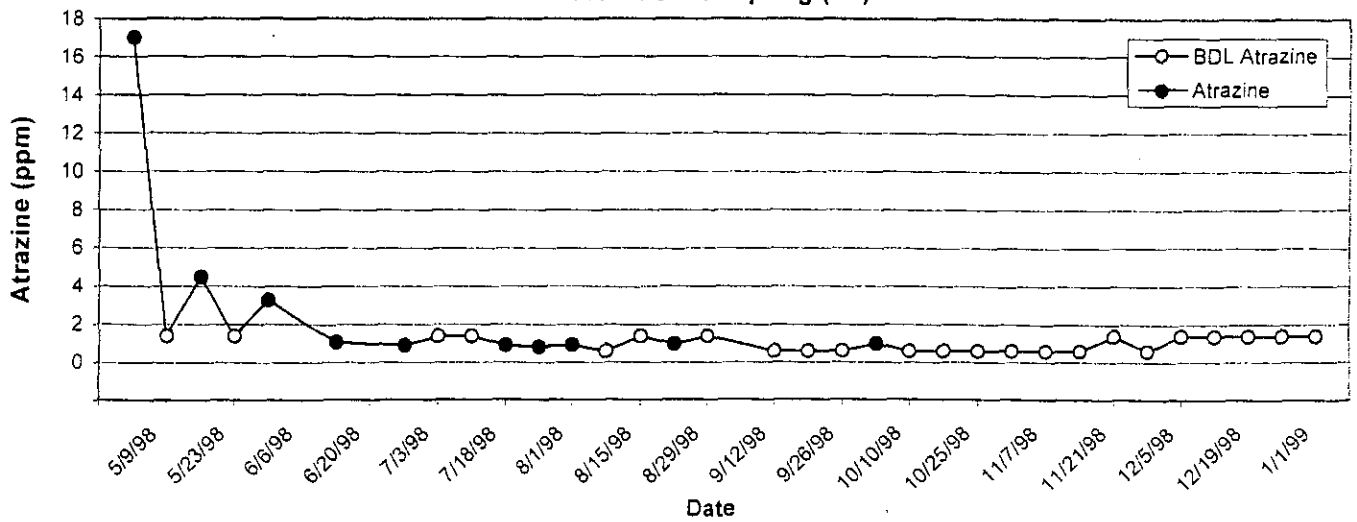
(a) Temporal Variation in Atrazine at Sinkhole No. 1



(b) Temporal Variation in Atrazine at Sinkhole No. 2



(c) Temporal Variation in Atrazine at Auctioneer Spring (S4)



degradation has occurred. At Camp Vandeventer Spring, pulses of elevated atrazine concentration were observed in July and August, well after the planting season. These pulses were associated with the two major storm events in the spring hydrograph (Figure 13b), and probably represent atrazine mobilization from large concentrations of suspended sediment that are typically found in the discharge of this large spring during such storm events.

Solute Mass Loads at the Springs

The mass load of a chemical species in a stream is determined from the product of the species concentration in the stream water and the stream discharge measured at a suitable transection. It represents the mass of the chemical species passing the transection per unit of time, and is commonly expressed in kilograms per day. Mass load is the best indicator of the impact of a contaminant source on the environment; it is an extensive parameter whereas species concentration is an intensive parameter.

The mass loads of nitrate-N and atrazine in Auctioneer and Camp Vandeventer springbrooks (Table 3) were calculated from values of springbrook discharge (Table 1) and species concentration in the spring waters (Table 2) determined on a weekly basis. Temporal variations in nitrate-N mass loads at Auctioneer and Camp Vandeventer springs are illustrated in Figure 19. The overall trends of mass load with time mirror the temporal variations in discharge at the two springs (Figure 6), showing long-term decline with base-flow recession; the nitrate-N mass load at Camp Vandeventer Spring is usually more than an order of magnitude greater than at Auctioneer Spring. The two major storm events on the spring hydrographs (Figure 6) are correlated with significant depressions in the temporal trend of nitrate-N mass load at Camp Vandeventer Spring (Figure 19), due to dilution of the nitrate-N concentrations in the spring waters (Figure 11b). This effect is not detectable at Auctioneer Spring, where discharge is more than an order of magnitude smaller. During the base-flow recession portions of the spring hydrographs that begin in early October (Figure 6), nitrate-N mass loads in the springbrooks continue to decline in concert with the hydrographs (Figure 19) but the nitrate-N concentrations in the spring waters remain at relatively

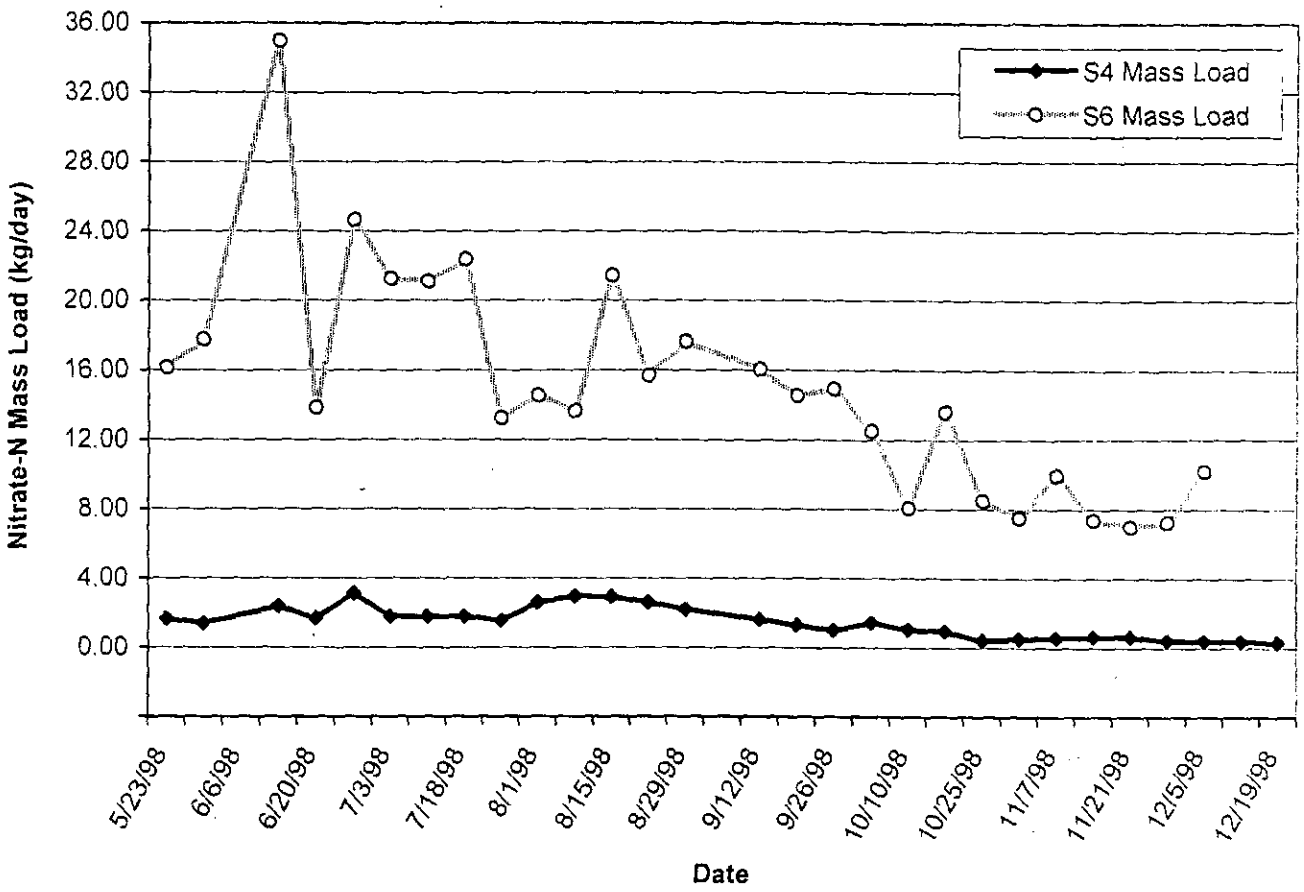
Table 3

Atrazine and Nitrate-N Mass Loads
at Auctioneer Spring and Camp Vandeventer Spring

	Auctioneer Spring (S4)		Camp Vandeventer Spring (S6)	
1998 Date	Nitrate-N (kg/day)	Atrazine (kg/day)	Nitrate-N (kg/day)	Atrazine (kg/day)
5/23	1.64		16.16	
5/31	1.39	0.00082	17.73	0.00463
6/6	no collect	no collect	no collect	no collect
6/13	2.39	0.00040	34.98	
6/20	1.69		13.82	
6/27	3.14	0.00066	24.64	0.02077
7/3	1.80		21.24	
7/11	1.77		21.12	0.01612
7/18	1.80	0.00035	22.35	0.01103
7/25	1.56	0.00026	13.23	0.07634
8/1	2.58	0.00045	14.55	
8/8	2.96		13.64	
8/15	2.90		21.45	0.00797
8/22	2.62	0.00061	15.70	
8/29	2.21		17.63	
9/5	no collect	no collect	no collect	no collect
9/12	1.60		16.03	
9/19	1.27		14.52	
9/26	1.00		14.93	0.00374
10/3	1.44	0.00029	12.50	
10/10	1.04		8.05	
10/17	0.95		13.62	
10/25	0.42		8.47	
10/31	0.51		7.50	
11/7	0.57		9.91	
11/14	0.62		7.35	0.00300
11/21	0.62		6.98	0.00280
11/28	0.41		7.23	
12/5	0.38		10.19	
12/12	0.39		7.46	
12/19	0.28		6.87	
12/26	0.50		no sample	no sample
1/1	no sample		no sample	no sample

Figure 19

Temporal Variations in Mass Loads of Nitrate-N at Auctioneer Spring (S4) and Camp Vandeventer Spring (S6)



constant levels (Figure 11). In spite of temporal perturbations in nitrate-N concentrations and mass loads imposed by storm events, these spring systems seem to contain groundwater reservoirs with constant nitrate-N concentrations. The mass loads of nitrate-N discharging from them fluctuate through the water year with their annual hydrographs.

Temporal variations in atrazine mass loads at Auctioneer and Camp Vandeventer springs are shown in Figure 20. During the period of study the atrazine mass load at Camp Vandeventer Spring was between five and 300 times greater than at Auctioneer Spring. Temporal mass-load variations and hydrographs at the two springs are illustrated in Figure 21; mass load at Auctioneer Spring is shown on an expanded scale. Notwithstanding the limited number of data points, there is a clear correlation between elevated atrazine mass loads and storm events on the spring hydrographs. Contrary to the behavior of nitrate-N, atrazine concentrations in the spring waters do not decrease during storm events (Figure 13) and the atrazine mass loads increase (Figure 21). Thus during storm conditions at these springs, both discharge and atrazine mass load increase. The high-flow conditions must activate another source of atrazine, which is likely found in sediments taken into suspension by surface runoff.

Although nitrate-N and atrazine mass loads at Auctioneer and Camp Vandeventer springs provide considerable additional insight into the nature of these spring systems, it is not likely that mass loads of chemical species have an influence on biodiversity at the springs. In general, nitrate-N and atrazine mass loads at Camp Vandeventer Spring are more than an order of magnitude greater than at Auctioneer Spring, yet Camp Vandeventer Spring is characterized by a significantly greater taxa richness. It would seem that aquatic macroinvertebrates would be sensitive to the concentration levels of agrichemicals (the intensive parameter) in the spring waters but not to the mass loads of these contaminants (the extensive parameter). From a chemical standpoint, whether a springbrook is large or small and the streamflow is high or low should not affect macroinvertebrates that are under the influence of their immediate surroundings.

Figure 20

Temporal Variations in Mass Loads of Atrazine at Auctioneer Spring (S4) and Camp Vandeventer Spring (S6)

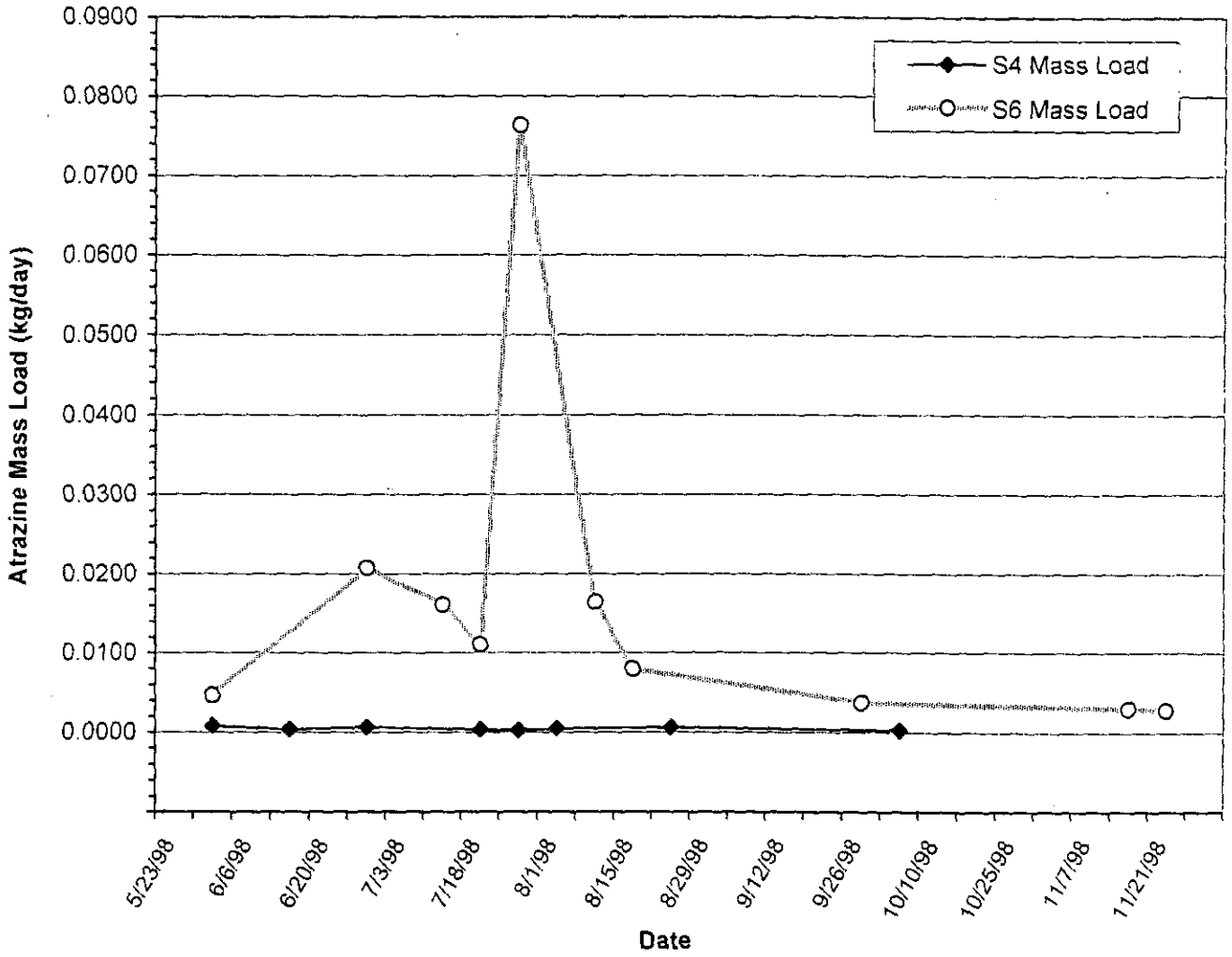
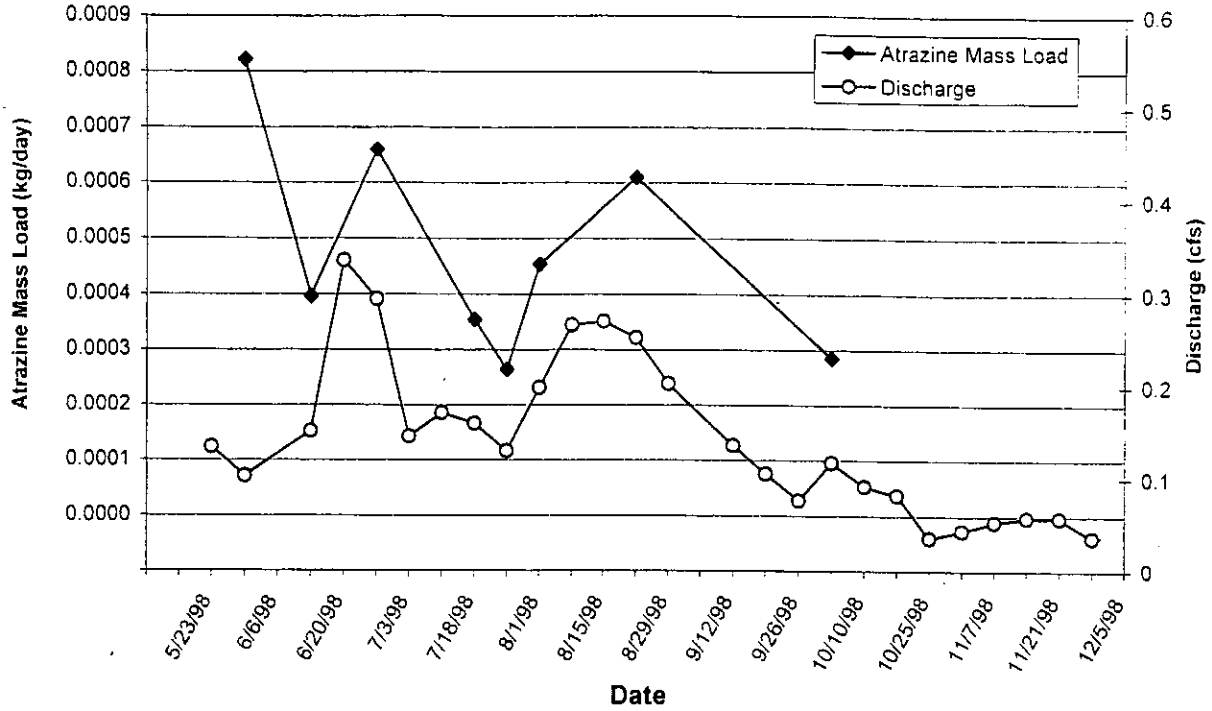
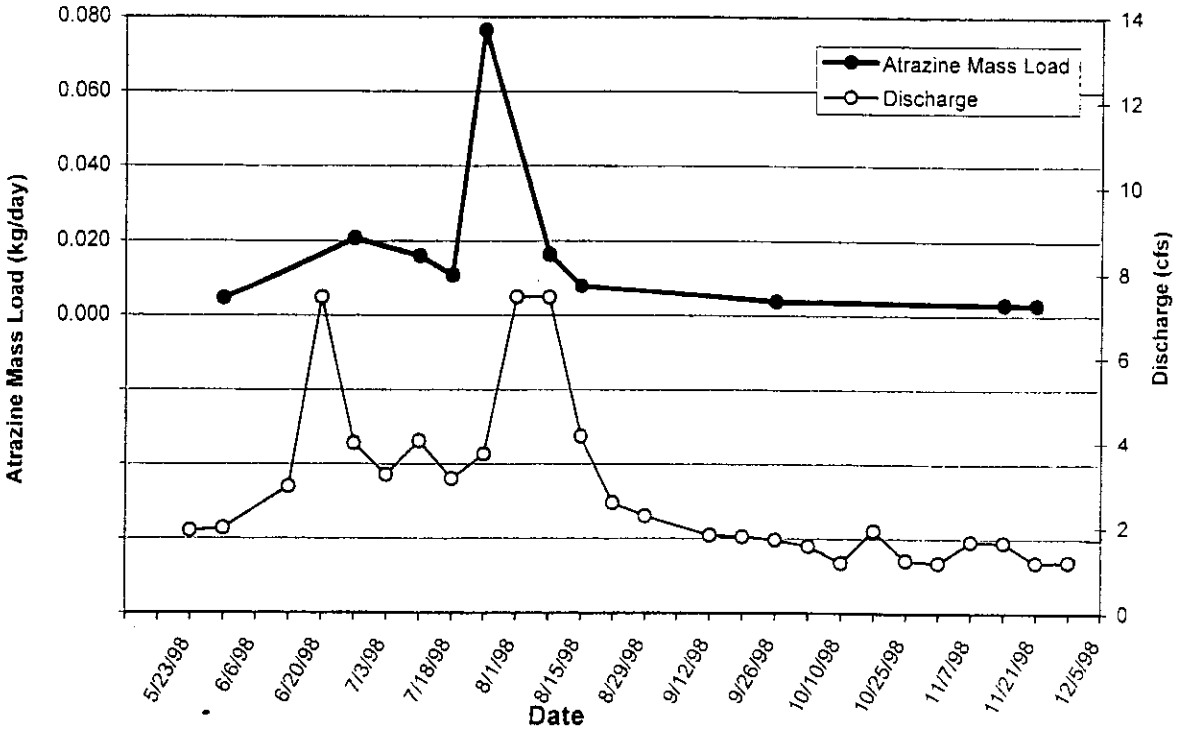


Figure 21

(a) Temporal Variations in Mass Load of Atrazine and Discharge at Auctioneer Spring (S4)



(b) Temporal Variations in Mass Load of Atrazine and Discharge at Camp Vandeventer Spring (S6)



CONCLUSIONS

Evaluation of the influence of chemical environment on the biodiversity of aquatic macroinvertebrates at karst springs requires a thorough study of water quality and hydrology over an extended period of time. Because of the complexity of spring systems in shallow karst aquifers, water quality is directly related to variable hydrologic conditions. A hydrograph for the spring system should be established over a major portion of the water year in order to understand the effects of all potential hydrologic conditions on water quality at the spring. Water samples should be collected on a frequent basis, at least once a week, to establish both the long- and short-term aspects of water quality and the chemical nature of the spring reservoir. Once the chemistry and hydrology of the spring system are understood the potential control of chemical environment on observed biodiversity can be examined.

This type of investigation, carried out at two karst springs in the sinkhole plain of Monroe County that exhibit very different levels of taxa richness, has shown that both of the agrichemicals nitrate-N and atrazine behave quite differently under variable hydrologic conditions. This dependence affects their long- and short-term concentration levels in the spring waters. The concentration of nitrate-N, a very soluble species that has little affinity for soil and sediment, declines under high-flow conditions but under base-flow conditions it remains essentially constant at a higher level. This chemical species seems to be moving by diffuse flow from spring reservoirs that have developed constant levels of nitrate-N through years of downward percolation of soil water from agricultural fields. Support for this interpretation is provided by analyses of surface runoff water samples, collected at two sinkholes that are hydraulically connected to one of the springs. After the planting season, runoff samples contain much lower nitrate-N concentrations than are observed at the spring. Auctioneer Spring water, with a low taxa richness of 20, is characterized by a significantly higher long-term nitrate-N concentration level (4.6 ppm) than water at Camp Vandeventer Spring (2.6 ppm), which has a much higher taxa richness of 64.

Atrazine is a commonly used herbicide that is water soluble but also adsorbs on soil and sediment. Under normal conditions it degrades before percolating soil water reaches the water

table, although in karst terrains there may be rapid transmission via sinkholes and other conduits. Thus atrazine migrates primarily in surface runoff, either in solution or attached to suspended material. Large atrazine concentrations were found in the sinkhole runoff collectors during May and June, just after herbicide application to the fields, and in Auctioneer Spring waters during the same time interval. After this initial pulse of dissolved atrazine, the concentration level in the spring water remained steady at about 1 ppb until it became undetectable during base-flow recession. At Camp Vandeventer Spring pulses of large atrazine concentrations in the water are correlated with storm events and are superimposed on a low background level of about 1 ppb. Under high-flow conditions atrazine is mobilized from soil and sediments that become suspended in surface runoff waters. Aquatic macroinvertebrates may be sensitive to sudden and large increases in atrazine concentration that occur in spring waters during the planting season and during storm events.

The mass loads of nitrate-N and atrazine in Camp Vandeventer springbrook are much greater than at Auctioneer springbrook, by at least an order of magnitude in each case. It is likely, however, that aquatic macroinvertebrates would be more sensitive to the concentration levels of these agrichemicals in the spring waters because the macroinvertebrates should be influenced only by their immediate chemical environments.

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