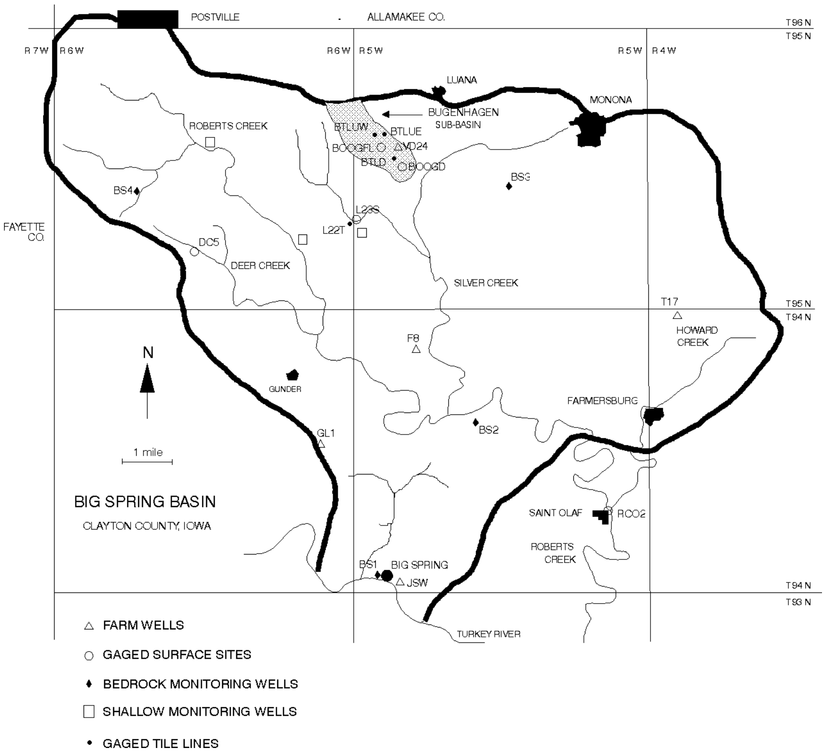
GROUNDWATER MONITORING in the BIG SPRING BASIN 1994-1995: A Summary Review

Geological Survey Bureau
Technical Information Series 37



Iowa Department of Natural Resources
Larry J. Wilson, Director
March 1997

GROUNDWATER MONITORING in the BIG SPRING BASIN 1994 - 1995:

A Summary Review

Geological Survey Bureau
Technical Information Series 37

A Report of The Big Spring Basin Demonstration Project

Prepared by

Huaibao Liu, R.D. Rowden, R.D. Libra

Energy and Geological Resources Division
Geological Survey Bureau

The Big Spring Basin Demonstration Project of the Iowa Department of Natural Resources is supported, in part, through the Iowa Groundwater Protection Act and Petroleum Violation Escrow accounts, and other sponsoring agencies: the U.S. Environmental Protection Agency, Region VII, Kansas City, Nonpoint Source Programs; the U.S. Department of Agriculture, Natural Resources Conservation Service; the Iowa State University Extension Service; the University of Iowa Hygienic Laboratory; and the Iowa Department of Agriculture and Land Stewardship, Division of Soil Conservation.

March 1997

Iowa Department of Natural Resources
Larry J. Wilson, Director

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

GROUNDWATER MONITORING in the BIG SPRING BASIN
1994-1995:
A Summary Review

Iowa Department of Natural Resources, Geological Survey Bureau
Technical Information Series 37, 1997, 45p.

Huaibao Liu, R.D. Rowden, R.D. Libra

ABSTRACT

The Big Spring basin is a 267 km^2 (103 mi^2) groundwater basin in Clayton County, northeast Iowa. Precipitation, groundwater and surface-water discharge, and the concentrations and loads of various agricultural chemicals have been monitored within and around the basin since 1981. This report summarizes the results of monitoring at Big Spring and the Turkey River during water years (WYs) 1994 and 1995.

After the wet period of WYs 1990 through 1993, WYs 1994 and 1995 were relatively dry. The annual precipitation totals for the basin were 30.42 inches in WY 1994 and 29.28 inches in WY 1995, about 92% and 89% of the long-term average precipitation of 32.97 inches. The annual groundwater discharge from Big Spring was 31,266 acre-feet (ac-ft), with an average discharge rate of 43.2 cubic feet per second (cfs), in WY 1994, and 30,013 ac-ft, with an average rate of 41.5 cfs, in WY 1995. These annual discharges were about half of the highest discharge value, 58,186 ac-ft, recorded in WY 1993, but were close to the average annual discharge, 31,987 ac-ft, during WYs 1982 through 1995. While annual precipitation totals in the Big Spring basin were lower than normal, the discharge as a percent of precipitation, 18.7% for both WYs 1994 and 1995, was the fifth greatest rate since WY 1983. The non-linear relationship between recharge and discharge at Big Spring is affected by antecedent conditions of groundwater in storage and soil moisture within the basin. Annual discharge of the Turkey River at Garber was 719,000 ac-ft for WY 1994 and 729,000 ac-ft for WY 1995. The annual discharges for WYs 1994 and 1995 were 100.7% and 102.1%, respectively, of the long-term average, 714,200 ac-ft, for WYs 1913 through 1995.

The annual flow-weighted (fw) mean nitrate concentration at Big Spring continued to decrease from 56 mg/L (12.4 mg/L as NO_3-N) in WY 1991, which was the highest concentration during the period of record, to 47 mg/L (10.4 mg/L as NO_3-N) in WY 1994 and 45 mg/L (10.1 mg/L as NO_3-N) in WY 1995. The total load of nitrate-nitrogen discharged by the groundwater system was 888,518 pounds in WY 1994 and 822,569 pounds in WY 1995. These annual nitrate-nitrogen loads were only about half of the total load, 1,796,013 pounds, of WY 1993, which was the highest recorded since monitoring began at Big Spring. For the Turkey River, fw mean nitrate concentrations were 23 mg/L (5.1 mg/L as NO_3-N) in WY 1994 and 30 mg/L (6.7 mg/L as NO_3-N) in WY 1995. Total nitrate-nitrogen discharged by the river was about 9.9 million pounds and 13.3 million pounds in WYs 1994 and 1995, respectively. These loads were significantly less than the highest annual nitrate-nitrogen load, 32.4 million pounds, recorded at the Turkey River in WY 1993. The decreases in nitrate-nitrogen fw mean concentrations and loads likely resulted from several factors, including

lower precipitation and discharge during the two-year period, antecedent hydrologic and climatic conditions, as well as the cumulative effects of reduced nitrogen applications.

Atrazine was detected in 94% and 75% of the samples analyzed for pesticides from Big Spring groundwater in WYs 1994 and 1995, respectively. The annual fw mean atrazine concentration declined from 0.27 µg/L in WY 1993 to 0.21 µg/L in WY 1994, and the annual atrazine load declined from 42.0 pounds in WY 1993 to 17.8 pounds in WY 1994. In WY 1995, the annual fw mean atrazine concentration at Big Spring, 0.12 µg/L, was the lowest recorded since the monitoring project started. The annual atrazine load in WY 1995, 9.8 pounds, was the second lowest to date. The lowest annual atrazine load, 9.2 pounds, was recorded in WY 1988. The highest annual fw mean atrazine concentration, 1.17 µg/L, and the greatest annual atrazine load, 135 pounds, were recorded in WY 1991. The concentrations of other common herbicides detected in Big Spring groundwater also remained at low levels during WYs 1994 and 1995. For the Turkey River, the annual fw mean atrazine concentration for WY 1994 was 0.41 µg/L and the annual atrazine load was 803 pounds. In WY 1995, the fw mean concentration was 0.42 µg/L and the load was 841 pounds. These values were also significantly lower than the highest fw mean atrazine concentration, 1.90 µg/L, recorded in WY 1990, and the greatest annual atrazine load, 3,386 pounds, recorded in WY 1993. Unlike the fluctuations of the annual nitrate concentrations and loads, it has been found that the annual concentrations and loads of atrazine do not correlate to discharge. The reasons for this are not clear. To better understand the transport and degradation mechanisms of agricultural contaminants, and to maintain a record of surface- and groundwater quality, continued monitoring in the Big Spring area is needed.

INTRODUCTION

The Big Spring basin is a 267 km^2 (103 mi^2) groundwater basin located in Clayton County, northeast Iowa. The land use, hydrology, and water quality of the basin have been extensively studied by the Iowa Department of Natural Resources, Geological Survey Bureau (GSB) since 1981. A network of sites, including groundwater, surface water, tile lines, and springs, was established by GSB and cooperating agencies to monitor water quality.

The Big Spring basin is located in the Paleozoic Plateau landform region (Prior, 1991). The bedrock in this area is Ordovician and Silurian carbonate strata. The main aquifer is the Ordovician Galena Group, with an average thickness of 67 m (220 ft) in the study area. The Galena aquifer is recharged by both infiltration and runoff recharge into sinkholes in this area. Sinkholes are widely distributed in the eastern portion of the basin, and occupy about 11% of the Big Spring groundwater basin (Hallberg et al., 1983; Rowden and Libra, 1990; Rowden et al., 1995a, b). The Big Spring is located near the base of the Galena aquifer. Over 85% of the groundwater that exits the basin to the Turkey River is discharged through Big Spring. The groundwater discharge from Big Spring is used to rear trout at a state-owned fish hatchery. The water distribution system at the hatchery greatly facilitates groundwater discharge monitoring.

Land use within the basin is essentially agricultural. Forty to fifty percent of the basin is annually cropped to corn, typically in rotation with alfalfa. Small- to moderate-sized hog and dairy operations are common. There are no significant industrial or urban contamination sources, such as large livestock feedlots, factories, or landfills. Therefore, agriculture is the main factor impacting the groundwater quality within the basin.

Many articles and reports about water quality in the Big Spring basin have been published since the early 1980's. Summary reviews of monitoring within the basin include: Hallberg and others (1984a) for Water Year 1983 (WY; A water year is a 12-month period, from October 1 through September 30, designated by the calendar year in which it ends.), Hallberg and others (1989) for WYs 1984-1987, Libra and others (1991) for WYs 1988-1989, Rowden and others (1993a) for WYs 1990-1991, and Rowden and others (1995b) for WYs 1992-1993. A summary review of surface water monitoring in the Big Spring basin for WYs 1986 through 1992 is reported by Rowden and others (1995a). Other water quality reviews for the basin include Hallberg and others (1984b, 1985, 1987). The design and implementation of monitoring sites for the Big Spring project were described by Littke and Hallberg (1991) and Libra and others (1992). Groundwater monitoring wells in the Big Spring area and related data were described by Rowden and Libra (1990). Big Spring hydrologic monitoring data were also presented by Kalkhoff (1989), Kalkhoff and Kuzniar (1991, 1994), Kalkhoff and others (1992). Some other publications related to the study of the basin include Libra and others (1986, 1987), Nations (1990), Goolsby and others (1990), Capel (1990), Nations and Hallberg (1992), Rowden and others (1993b), Seigley and others (1993), Hallberg and others (1993), Rowden (1995), Kalkhoff and Schaap (1996), and Rowden and Libra (1996).

In addition to the monitoring, the Big Spring basin is the site of extensive education and demonstration activities that are designed to improve the environmental and economic performance of agriculture. These activities were conducted under the auspices of the Big Spring Basin Demonstration Project (1986-1992) and continue as part of the Northeast Iowa Demonstration Project, under the direction of Iowa State University Extension Service.

This report is a part of the continuing summary review of the Big Spring project. It will focus on the groundwater monitoring data and water quality of Big Spring and the Turkey River for WYs 1994 and 1995. This report will also summarize the distribution and concentrations of agricultural chemicals, particularly nitrate and common pesticides. Hydrologic and water quality data from tile lines, wells, and other surface water sites within the basin will be addressed in subsequent reports. Analytical methods and processes are the same as in previous reports, which were reviewed in Hallberg and others (1989).

HYDROLOGIC AND WATER QUALITY MONITORING

The discharge of Big Spring responds to recharge within the 267 km^2 (103 mi^2) groundwater basin and is controlled by the amount, timing, and intensity of precipitation and snowmelt. Climatic variations, along with antecedent conditions, exert a major control on the transport, concentrations, and loads of agriculturally-related contaminants. The Turkey River is a high baseflow stream, deriving a significant part of its discharge from influent groundwater. As defined, the Turkey River basin contains 4,002 km^2 (1,545 mi^2). Data from the Turkey River provide a regional perspective for the hydrologic and water quality monitoring at Big Spring.

Groundwater discharge from the Big Spring basin to the Turkey River has been monitored at Big Spring since 1981. Discharge of the Turkey River is gaged at Garber, Iowa, which is about 15 miles (24 km) downstream from Big Spring. Gaging of stream discharge for the Turkey River began in WY 1914 and has been continuous since 1933. Discharge data for the Turkey River and Big Spring for WYs 1994 and 1995 were supplied by the Water Resources Division of the U.S. Geological Survey (USGS), Iowa District (May et al., 1995, 1996). Samples for water-quality analyses were collected at Big Spring and the Turkey River near the Big Spring Fish Hatchery.

Precipitation

Monthly precipitation and departures from normal for WYs 1982 through 1995 are shown in Figure 1. Precipitation data for WYs 1982-1988 were calculated using data from the Elkader, Fayette, and Waukon weather stations, which form a triangle around the Big Spring basin. These data and daily minimum/maximum temperature data are supplied by the Iowa Department of Agriculture and Land Stewardship, State Climatology Office (IDALS, SCO). Precipitation has been recorded at the Big Spring Fish Hatchery since August 1984 as part of the National Atmospheric Deposition Program (NADP). These data have also been used to calculate basin precipitation since WY 1985. In the summer of 1988, the USGS installed rain gages at two surface-water gaging stations within the basin. Basin precipitation for WYs 1989 through 1992 was calculated with data from the two USGS stations and the NADP station at the hatchery. Precipitation for WY 1993 was calculated with data from the Elkader, Fayette, and Waukon weather stations and the NADP station at the hatchery (Rowden et al., 1995b). In January 1991, IDALS installed a weather station in Postville, which is much closer to the Big Spring basin than Waukon. Therefore, basin precipitation for WYs 1994 and 1995 was calculated based on data from the NADP station at the Big Spring Fish Hatchery and the IDALS stations in Elkader, Fayette, and Postville. To be able to compare annual precipitation within the Big Spring basin, the mean annual precipitation for the period 1951-1980, 32.97 inches, is used, and references to normal precipitation are based on this period. This average is slightly different from the updated normal precipitation used by IDALS, SCO based on the period of 1961-1990. Precipitation for the Turkey River drainage basin is estimated using averages for the state's northeast climatic division (IDALS, SCO).

As shown in Figure 1, the fourteen-year period of record (WYs 1982 through 1995) in the Big Spring basin was characterized by significant climatic variability. The two driest consecutive years in Iowa's recorded history were WYs 1988 and 1989, with total annual precipitation of 22.94 and 24.32 inches, respectively. These were 10.03 and 8.65 inches below normal, or 70% and 74% of the long-term average precipitation. These two dry years were followed by two wet years. In WY 1990, the total annual precipitation, 37.87 inches, was 4.90 inches above normal, and 115% of the long-term average precipitation. Water Year 1991 was the wettest year since the Big Spring project's inception. The annual precipitation, 47.28 inches, was 14.29 inches above normal, and 143% of the long-term average. The annual precipitation for WY 1992, 35.74 inches, was close to the long-term average precipitation (32.97 inches). Water Year 1993 was another wet year after WY 1991. The annual precipitation, 46.47 inches, was 13.50 inches

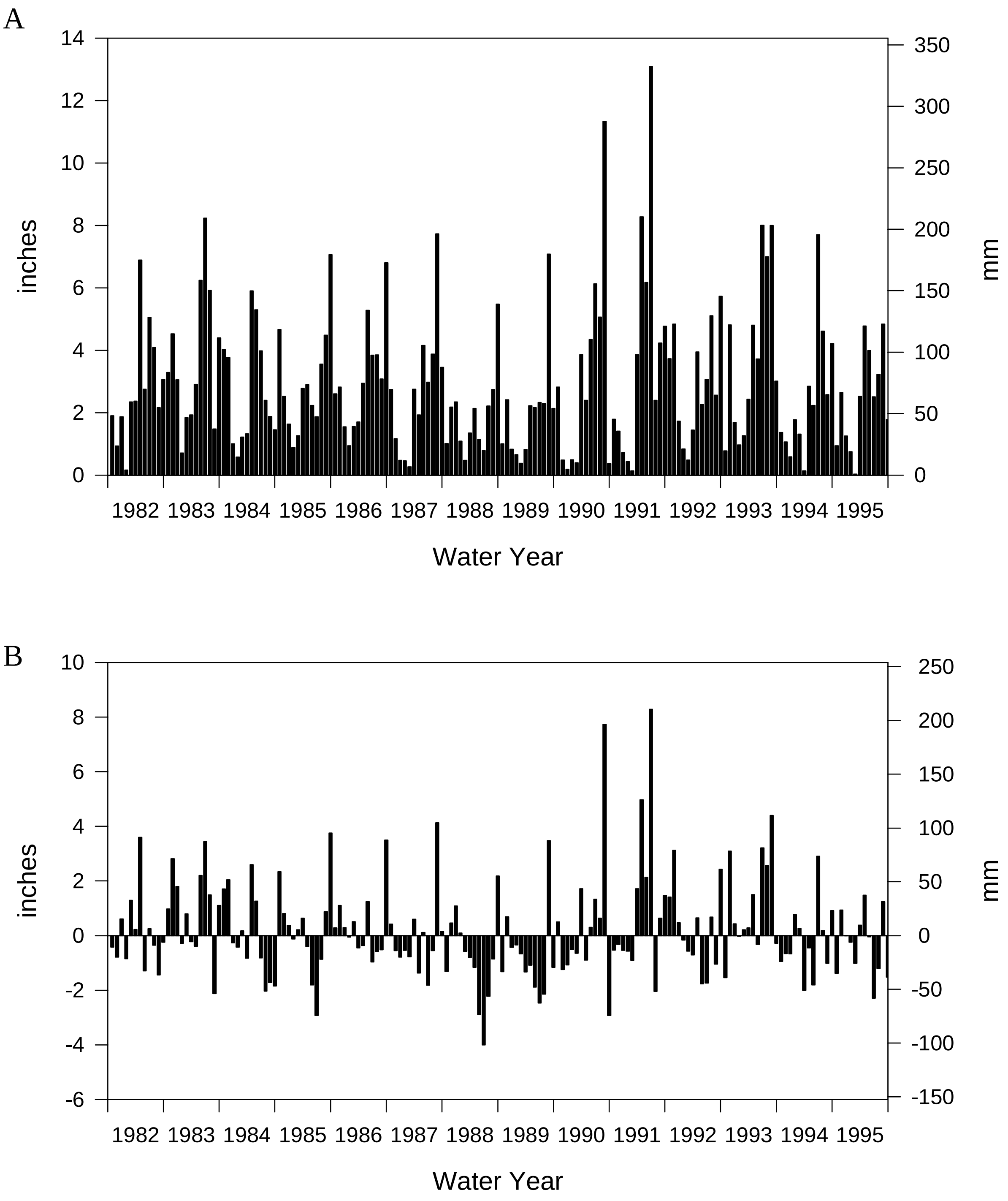


Figure 1. A) Monthly precipitation totals and B) departure from normal for the Big Spring basin, WYs 1982-1995 (Iowa Dept. of Ag. and Land Stewardship, State Climatology Office).

Table 1. Monthly precipitation and departure from normal, Big Spring basin; WYs 1994-1995.

Water Year 1994	Basin precip inches	Departure from normal inches	% of normal	Water Year 1995	Basin precip inches	Departure from normal inches	% of normal
Oct-93	1.37	-0.95	59%	Oct-94	0.94	-1.38	41%
Nov-93	1.06	-0.66	62%	Nov-94	2.65	0.93	154%
Dec-93	0.59	-0.67	47%	Dec-94	1.25	-0.01	99%
Jan-94	1.77	0.77	177%	Jan-95	0.75	-0.25	75%
Feb-94	1.31	0.26	125%	Feb-95	0.03	-1.02	3%
Mar-94	0.14	-2.01	7%	Mar-95	2.53	0.38	118%
Apr-94	2.85	-0.45	86%	Apr-95	4.78	1.48	145%
May-94	2.23	-1.81	55%	May-95	3.99	-0.05	99%
Jun-94	7.70	2.90	160%	Jun-95	2.51	-2.29	52%
Jul-94	4.61	0.18	104%	Jul-95	3.23	-1.20	73%
Aug-94	2.58	-1.02	72%	Aug-95	4.84	1.24	134%
Sep-94	4.21	0.91	128%	Sep-95	1.78	-1.52	54%
TOTAL	30.42	-2.55	92%	TOTAL	29.28	-3.69	89%

above normal, or 141% of the long-term average. In WY 1993, most rainfall events occurred during the June through August period, and major flooding occurred throughout much of central and eastern Iowa, including the Big Spring basin.

Table 1 shows the monthly precipitation and departure from normal for WYs 1994 and 1995 for the Big Spring basin. Following the wet WY 1993, WYs 1994 and 1995 were relatively dry. The annual precipitation for WY 1994, 30.42 inches, was 2.55 inches below normal, or 92% of the long-term average. For WY 1995, the annual precipitation, 29.28 inches, was 3.69 inches below normal, or 89% of the long-term average. The annual precipitation for WY 1995 was the third lowest since the Big Spring project started in WY 1982.

The monthly precipitation totals in the Big Spring basin for WYs 1994 and 1995 showed large deviations from normal. During WY 1994, the precipitation totals for January, February, June, and September were considerably higher than normal. The monthly precipitation for June, 7.70 inches, was 2.90 inches above normal, or 160% of the long-term average precipitation. In WY 1995, the monthly precipitation totals for November, March, April, and August were significantly greater than normal. The wettest month of the water year was August, with 4.84 inches of precipitation or 134% of the long-term average precipitation. April had 4.78 inches of precipitation, which was 1.48 inches above normal or 145% of the long-term average precipitation. The precipitation totals for some months during the two-year period were significantly lower than normal. The driest month of WY 1994 was March, with 0.14 inches of precipitation or 7% of normal. For WY 1995, February was the driest month, with 0.03 inches of precipitation or 3% of normal. Based on the long-term average precipitation, June, with an average precipitation of 4.80 inches for 1951-1980, has typically been the wettest month in the Big Spring basin. In WY 1995, precipitation in June was only 2.51 inches, which was 2.29 inches below normal or 52% of the long-term monthly average.

Previous reports have indicated that the March through June period is typically marked by low evapotranspiration and wet antecedent conditions, and is important for groundwater recharge in the Big Spring area (Hallberg et al., 1983, 1984a, 1989; Libra et al., 1991; Rowden et al., 1993a, 1995b). Although the precipitation totals for June, 1994 and April, 1995 were significantly higher than normal, the average precipitation for the March through June periods was below normal (1.37 inches below normal for WY 1994 and 0.48 inches below normal for WY 1995) due to the low precipitation during the remaining months of the period.

Water Year 1994

Discharge Monitoring

Tables 2 through 8 and figures 2 through 6 summarize the discharge, climatic, water quality, and chemical loading data for Big Spring and the Turkey River at Garber during WY 1994.

Annual groundwater discharge at Big Spring for WY 1994 was 31,266 acre-feet (ac-ft), at an average daily discharge rate of 43.2 cubic feet per second (cfs; Table 2). The annual discharge was equivalent to 18.7% of the annual precipitation, which was 30.42 inches for the Big Spring basin. The annual discharge for the Turkey River at Garber was about 719,000 ac-ft, at an average daily discharge rate of 993 cfs for WY 1994 (Table 3). Surface-water discharge accounted for 28% of the annual precipitation in the Turkey River basin, and was equal to 101% of the long-term average annual discharge.

Figure 2 shows the discharge hydrograph (A) and water temperature (B) for Big Spring, along with daily precipitation of the Big Spring basin (C) and daily maximum/minimum air temperatures recorded at the Elkader weather observation station (D). The Big Spring groundwater temperature record for WY 1994 begins on March 28. It is incomplete because of equipment failures. The discharge hydrograph consists of several peaks and relatively flat lines between the peaks. The narrow shape of these peaks indicates a rapid increase and decrease in discharge. Based on previous reports (e.g., Rowden et al., 1995b), rapid changes in discharge at Big Spring usually result from snowmelt and/or precipitation-generated surface-water runoff recharge to sinkholes. Discharge changes caused by snowmelt are indicated by sharp drops in Big Spring's water temperature. Surface-water runoff in the basin is generally ephemeral in nature. After the rapid changes, the discharge often remains at higher levels than pre-

Table 2. Annual summary of groundwater and chemical discharge from the Big Spring basin to the Turkey River for WY 1994. (Discharge data are from the U.S. Geological Survey, Water Resources Division.)

DISCHARGE		
Total		
acre-feet	31,266	
millions cf	1,360	
millions cm	38.6	
Average		
cfs	43.2	
cms	1.22	
mg/d	27.9	
gpm	19,382	
PRECIPITATION AND DISCHARGE		
Precipitation	30.42 inches (773 mm)	
Discharge	5.69 inches (145 mm)	
Discharge as % of precipitation	18.7%	
NITRATE DISCHARGE		
Concentration - mg/L	**As NO_3**	**As NO_3-N**
Flow-weighted mean	47.0	10.4
Mean of analyses	47.3	10.5
	NO_3-N output	**Total N output**
lbs - N	888,518	911,133
kg - N	402,956	413,212
lbs - N/acre	13.5	13.8
ATRAZINE DISCHARGE		
Concentration - µg/L		
Flow-weighted mean	0.21	
Mean of analyses	0.18	
Total output		
lbs	17.8	
kg	8.1	

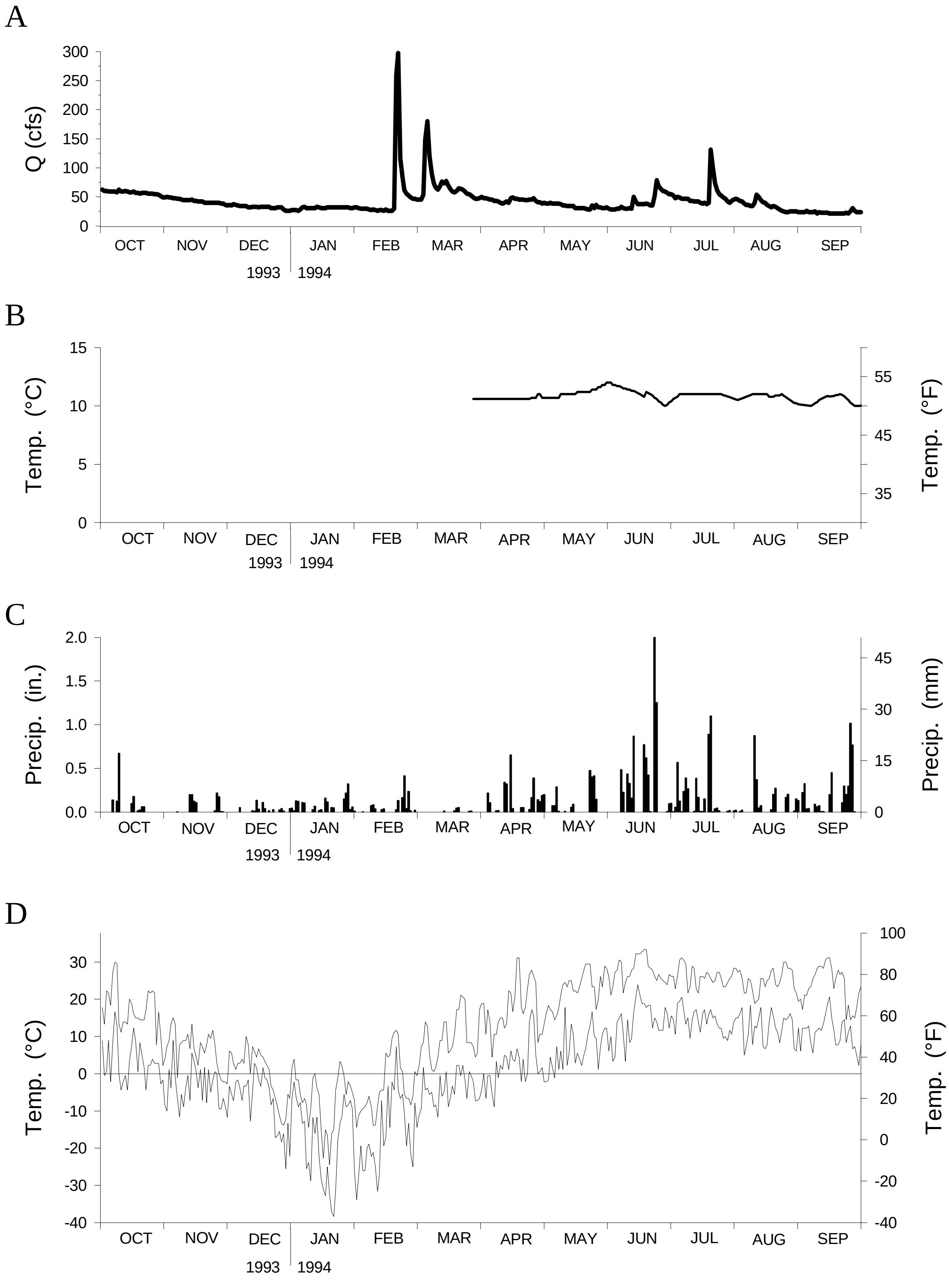


Figure 2. A) Groundwater discharge, B) groundwater temperature and C) daily precipitation for the Big Spring basin; and D) maximum-minimum temperatures for Elkader, IA (Iowa Dept. of Ag. and Land Stewardship, State Climatology Office), for WY 1994.

vious to the event, and then slowly declines to pre-event levels. During prolonged periods with insignificant recharge, the discharge from Big Spring is usually expressed on the hydrograph as long, nearly flat lines, indicating a very gradual decline in flow rates.

During WY 1994 at Big Spring, only a few days had average daily discharges of more than 100 cfs. The greatest daily discharges from Big Spring, 260 cfs and 298 cfs, occurred on February 19 and 20, respectively. Discharge decreased to 116 cfs on February 21, and then gradually declined to 45 cfs in the following days. The period with the next largest daily discharges, 149 cfs, 180 cfs, and 120 cfs, occurred during March 5, 6, and 7, respectively. The period with the third largest set of daily discharges at Big Spring, 131 cfs and 102 cfs, occurred on July 20 and 21, respectively. During all of these events, the discharge increased rapidly, and then gradually decreased to pre-event levels within a few days. Since there was no significant precipitation during late February and early March, and the discharge events coincided with rising regional air temperatures, the two largest discharges at Big Spring resulted from snowmelt. The discharge event in late July followed two days of relatively heavy rainfall, 0.89 inches on July 19 and 1.1 inches on July 20.

As mentioned before, the wettest month of WY 1994 was June, when 7.7 inches of precipitation fell. The greatest rainfalls of the water year occurred on June 23 and 24, and totalled 2.01 and 1.26 inches, respectively. Antecedent conditions in the basin were not conducive to significant runoff at this time. Although the events generated the second greatest daily discharge of the water year for the Turkey River on June 24 (4,720 cfs; Fig. 4), the discharge at Big Spring, 79 cfs, was only the 11th largest daily discharge during WY 1994. A number of minor precipitation events occurred during the remainder of the water year; they had little effect on discharge rates.

Three recession periods can be recognized on the discharge hydrograph. The first occurred from October, 1993 through mid-February, 1994, with daily discharge declining from 60 cfs to 26 cfs. The second occurred from mid-March through mid-June. Daily discharge declined from 78 cfs on

Table 3. Annual summary of water and chemical discharge for the Turkey River at Garber for WY 1994. (Discharge data are from the U.S. Geological Survey, Water Resources Division.)

DISCHARGE		
Total		
acre-feet	719,000	
millions cf	31,320	
millions cm	887	
Average		
cfs	993	
cms	28.1	
mg/d	642	
gpm	445,658	
PRECIPITATION AND DISCHARGE		
Precipitation	31.20 inches (792mm)	
Discharge	8.73 inches (222mm)	
Discharge as % of precipitation	28.0%	
NITRATE DISCHARGE		
Concentration - mg/L	**As NO_3**	**As NO_3-N**
Flow-weighted mean	22.8	5.1
Mean of analyses	23.2	5.2
	NO_3-N output	**Total N output**
lbs - N	9,903,478	10,581,755
kg - N	4,491,373	4,798,982
lbs - N/acre	10.0	10.7
ATRAZINE DISCHARGE		
Concentration - μg/L		
Flow-weighted mean	0.41	
Mean of analyses	0.31	
Total output		
lbs	803	
kg	364	

Table 4. Monthly summary of groundwater discharge from the Big Spring basin for WY 1994.

	1993			1994								
	Oct	Nov	Dec	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep
TOTAL MONTHLY DISCHARGE												
Acre-feet	3,525	2,557	1,987	1,910	3,127	4,254	2,645	2,100	2,464	3,161	2,143	1,396
Cubic feet (millions)	154	111	87	83	136	185	115	92	107	138	93	61
Gallons (millions)	1,149	833	648	622	1,019	1,386	862	684	803	1,030	698	455
Cubic meters (millions)	4.3	3.2	2.4	2.4	3.9	5.2	3.3	2.6	3.0	3.9	2.6	1.7
AVERAGE DISCHARGE												
cfs	57	43	32	31	56	69	45	34	41	51	35	23
cms	1.6	1.2	0.9	0.9	1.6	2.0	1.3	1.0	1.2	1.5	1.0	0.7
mg/d	37	28	21	20	36	45	29	22	27	33	22	15
MAXIMUM												
cfs	63	50	38	33	298	180	50	40	79	131	54	31
cms	1.8	1.4	1.1	0.9	8.4	5.1	1.4	1.1	2.2	3.7	1.5	0.9
MINIMUM												
cfs	49	35	26	26	26	46	39	29	29	38	24	22
cms	1.4	1.0	0.7	0.7	0.7	1.3	1.1	0.8	0.8	1.1	0.7	0.6

March 15 to 30 cfs on June 12. The third recession period occurred from late August through September, with daily discharges remaining below 30 cfs. The lowest daily discharges at Big Spring during WY 1994 occurred in September and were about 22 cfs.

Table 4 summarizes the discharge data on a monthly basis for Big Spring in WY 1994. The greatest monthly discharge, 4,254 ac-ft, occurred in March at an average daily discharge rate of 69 cfs. The smallest monthly discharge, 1,396 ac-ft, was in September, a month with the third highest monthly precipitation (4.21 inches, and 128% of normal) of the water year. The average daily discharge for September was 23 cfs. Other months with a total discharge of less than 2,000 ac-ft were December, 1993 (1,987 ac-ft) and January, 1994 (1,910 ac-ft).

For the Turkey River at Garber, the largest monthly discharge during WY 1994, 126,500 ac-ft, also occurred in March. The smallest monthly surface-water discharge, 26,830 ac-ft, occurred in January. The September discharge for the Turkey River at Garber was 37,860 ac-ft, at an average daily discharge rate of 636 cfs, which was 200 cfs higher than the daily discharge rate for January.

Nitrate Monitoring

Tables 2 and 5 summarize the nitrate monitoring at Big Spring for WY 1994. In previous water years, samples for both nitrate and full nitrogen series (N-series; including nitrate-N, ammonia-N, and organic-N) analyses were collected weekly from Big Spring. Beginning in WY 1994, the

Table 5. Monthly summary of nitrate-N discharged in groundwater from the Big Spring basin to the Turkey River; WY 1994.

	1993			1994								
	Oct	Nov	Dec	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep
Flow weighted mean NO_3 concentration, in mg/L;	55	53	54	46	35	40	47	47	51	46	51	44
as NO_3-N	12.3	11.7	12.0	10.3	7.9	8.9	10.5	10.5	11.4	10.3	11.3	9.7
Mean of NO_3 analyses, in mg/L;	60	54	54	46	44	41	47	47	43	37	49	44
as NO_3-N	13.3	12.0	12.0	10.3	9.9	9.2	10.4	10.4	9.6	8.3	11.0	9.7
Total monthly NO_3-N output, thousands lbs	117	81	65	53	67	103	75	60	76	88	66	37
Total monthly NO_3-N output, thousands kg	53	37	29	24	30	47	34	27	35	40	30	17

sampling schedule was changed due to budget constraints. Six samples collected from Big Spring in October, November, and June were analyzed for nitrate, eight samples collected in October through early January were analyzed for the full nitrogen series, and forty-four samples collected through the water year were analyzed for partial nitrogen series (nitrate-N and ammonia-N). In previous years, the total nitrogen outputs for Big Spring and the Turkey River were calculated by adding the total nitrate-nitrogen output to the total ammonia- and organic-nitrogen outputs, and the daily fw mean and mean of analyses for nitrate concentrations were estimated and computed based on weekly nitrate data. Since the replacement of full N-series analysis with partial N-series analysis, the total nitrogen output from Big Spring for WY 1994 was calculated by adding the total nitrate-nitrogen output to total ammonia- and organic-nitrogen outputs for the period with full N-series analysis, and was calculated for the remainder of the water year by adding the total nitrate-nitrogen output to the total ammonia-nitrogen output. The daily mean concentration of nitrate in WY 1994 was estimated and computed by the same procedure for those days with nitrate data. For the remaining days, the daily concentration of nitrate was estimated and computed based on partial N-series data by multiplying the nitrate-N analysis by 4.5. Since only six samples from Big Spring were analyzed for nitrate in WY 1994, the annual and monthly means of analyses for nitrate concentrations were derived by multiplying the nitrate-N concentrations from partial N-series analysis by 4.5. For the Turkey River, all samples were analyzed only for partial N-series and nitrate during WY 1994. The total nitrogen output was calculated by adding the total nitrate-nitrogen to the total ammonia-nitrogen.

During WY 1994, 911 thousand pounds of nitrogen (nitrate-, ammonia-, and organic-N) were discharged by groundwater from the Big Spring basin. Of this, 889 thousand pounds, or 97%, were in the form of nitrate-nitrogen. That amount is equivalent to 13.5 pounds of nitrate-nitrogen per acre (lbs-N/acre) for the basin. The flow-weighted (fw) mean nitrate concentration (mean concentration per unit volume of discharge) for the water year was 47 mg/L (milligrams per liter), or

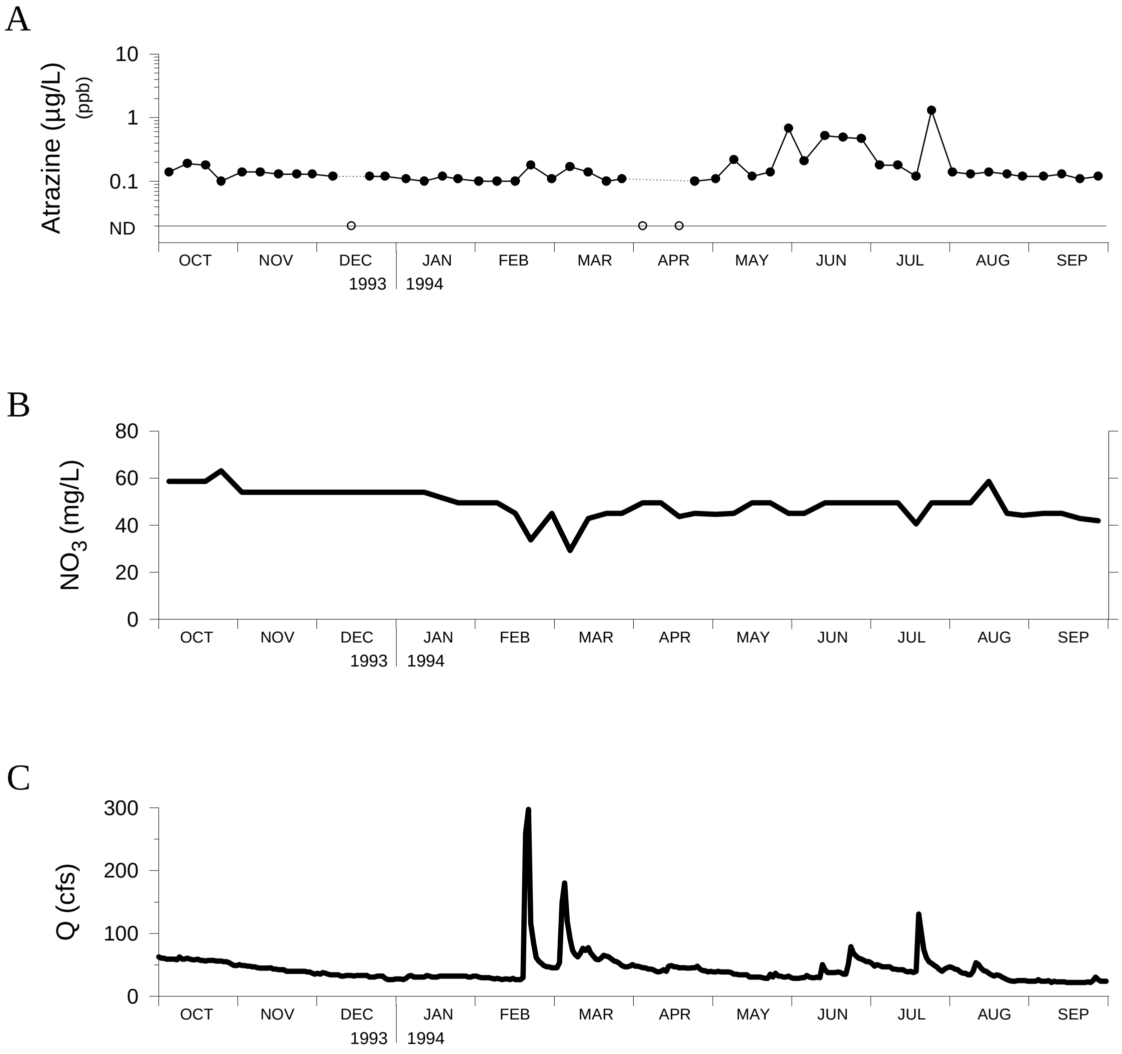


Figure 3. A) Atrazine and B) nitrate concentrations; and C) groundwater discharge at Big Spring for WY 1994.

10.4 mg/L as NO_3-N. Water Year 1994 was the first year that the annual total nitrate-nitrogen load was less than one million pounds from the Big Spring basin since WY 1990, and was the first year that the fw mean nitrate concentration was below 50 mg/L since WY 1991.

Figure 3 shows the discharge hydrograph (C) and the nitrate concentrations (B) for Big Spring during WY 1994. Nitrate concentrations were relatively high at the beginning of the water year, with a concentration of 59 mg/L (13.0 mg/L as NO_3-N). By late October, the nitrate concentration increased to 63 mg/L (14.0 mg/L as NO_3-N), the highest concentration recorded during the water year. From early November to mid-January, the nitrate concentration remained at 54 mg/L (12.0 mg/L as NO_3-N). Following gradually decreasing discharge, the concentration declined to 45 mg/L (10.0 mg/L as NO_3-N) in mid-February. As mentioned before, the two greatest discharge events of the water year at Big Spring occurred from late February to early March due to snowmelt. The greatest daily discharge, 298 cfs, occurred on February 20. The nitrate concentration on February 21 decreased to 34 mg/L (7.5 mg/L as NO_3-N), and then increased to 45 mg/L (10.0 mg/L as NO_3-

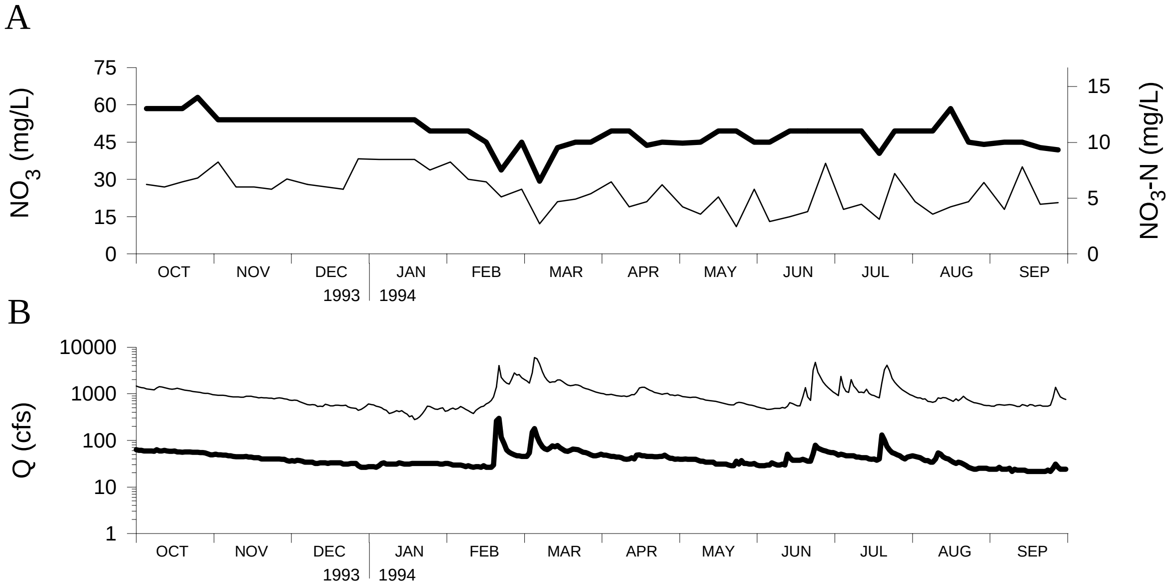


Figure 4. A) Nitrate concentrations and B) discharge hydrographs for Big Spring (bold lines) and the Turkey River at Garber (lighter lines) for WY 1994. (Turkey River discharge data are from the U.S. Geological Survey, W.R.D., IA Dist.)

N) one week later. The lowest nitrate concentration recorded at Big Spring during the water year, 29 mg/L (6.5 mg/L as NO_3-N), occurred on March 8, following the second greatest discharge event which occurred from March 5 through March 7. One week later, the nitrate concentration increased to 43 mg/L (9.5 mg/L as NO_3-N), and then increased to 50 mg/L (11.0 mg/L as NO_3-N) by mid-April. During the remainder of the water year, nitrate concentrations fluctuated between 40 and 50 mg/L, except in mid-August when the nitrate concentration increased to 59 mg/L (13.0 mg/L as NO_3-N).

Although several precipitation and discharge events occurred during June and July, they did not significantly affect the nitrate concentrations at Big Spring. From mid-August to the end of the water year, nitrate concentrations gradually decreased to 42 mg/L (9.3 mg/L as NO_3-N). Based upon previous reports, high nitrate concentrations usually occur a few days after discharge peaks. During WY 1994, nitrate concentrations usually decreased during significant discharge events, then increased back to the pre-event levels, but did not show significant concentration peaks. The two greatest nitrate concentrations, 63 mg/L on October 25 and 59 mg/L on August 16, did not result from increased discharge events.

Table 5 summarizes the nitrate data for Big Spring during WY 1994 on a monthly basis. The highest monthly fw mean nitrate concentration, 55 mg/L (12.3 mg/L as NO_3-N), and the greatest monthly nitrate-N output, 117,000 pounds, occurred in October. The lowest monthly fw mean nitrate concentration, 35 mg/L (7.9 mg/L as NO_3-N), occurred in February, while the lowest monthly nitrate-N output, 37,000 pounds, occurred in September. October accounted for 11.3% of the annual groundwater discharge from Big Spring, and 13.2% of the annual nitrate-N load, while February accounted for 10% of the annual discharge and 7.5% of the annual nitrate-N load. The monthly fw mean nitrate concentration was below the 45 mg/L (10.0 mg/L as NO_3-N) drinking water standard for nitrate in February, March, and September during WY 1994.

Figure 4 and tables 3 and 6 summarize the surface-water discharge, and nitrate concentra-

Table 6. Monthly summary of nitrate-N discharged for the Turkey River at Garber; WY 1994.

	1993 Oct	Nov	Dec	1994 Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep
Flow-weighted mean NO_3 concentration, in mg/L;	29	29	31	37	25	19	23	18	17	18	20	23
as NO_3-N	6.5	6.4	6.8	8.1	5.7	4.2	5.1	4.0	3.7	4.1	4.5	5.1
Mean of NO_3 analyses, in mg/L;	28	29	27	25	32	23	23	17	15	17	19	24
as NO_3-N	6.2	6.5	6.0	5.6	7.1	5.1	5.1	3.8	3.3	3.9	4.3	5.4
Total monthly NO_3-N output, thousands lbs	1,318	878	651	584	981	1,449	851	468	638	1,017	548	521
Total monthly NO_3-N output, thousands kg	598	398	295	265	445	657	386	212	289	461	249	236

tions and loads for the Turkey River for WY 1994. During the water year, thirty-seven samples were analyzed for nitrate, and thirteen samples were analyzed for partial nitrogen series (nitrate-N and ammonia-N). A total of 10.6 million pounds of nitrogen were discharged by the Turkey River. Of that, 9.9 million pounds, or 94% of the total nitrogen discharged, were in the form of nitrate. This is equivalent to 10.0 lbs-N/acre for the Turkey River basin above Garber. Since organic-nitrogen was not analyzed for or used to calculate the total nitrogen output for WY 1994, the total nitrogen discharge for the Turkey River may be lower than previous water year totals, and the nitrate-N accounts for a higher percentage of the total nitrogen discharge. The greatest total nitrogen discharge to date from the Turkey River, 44.3 million pounds, was recorded in WY 1993 (Rowden et al., 1995b). The annual fw mean nitrate concentration for WY 1994, 22.8 mg/L (5.1 mg/L as NO_3-N), was the third-lowest at the Turkey River during the period of WYs 1984-1994. The lowest annual fw mean concentration for nitrate, 11.9 mg/L (2.6 mg/L as NO_3-N), was recorded during WY 1989 (Libra et al., 1991), and the second-lowest, 16 mg/L (3.6 mg/L as NO_3-N), occurred in WY 1985 (Hallberg et al., 1989).

Figure 4 shows the hydrographs and nitrate data for Big Spring and the Turkey River at Garber. The hydrographs are on a logarithmic scale. The trends in both discharge and nitrate concentrations were similar for Big Spring and the Turkey River, except for the responses to the precipitation events which occurred in late June. As mentioned above, the greatest precipitation events of the water year which occurred on June 23 and 24, with a total of 3.27 inches of rainfall, did not generate significant groundwater discharge or nitrate fluctuation at Big Spring. At the Turkey River, however, the events generated the second-greatest daily discharge of the water year, 4,720 cfs, on June 24. The greatest daily discharge, 5,920 cfs, occurred on March 6 due to snowmelt. The nitrate concentration of the Turkey River increased from 17 mg/L (3.8 mg/L as NO_3-N) on June 21 to 37 mg/L (8.1 mg/L as NO_3-N) on June 28, and then decreased to 18 mg/L (4.0 mg/L as NO_3-N) on July 5. These short-term changes in nitrate concentrations were generated

Table 7. Monthly summary of atrazine discharged in groundwater from the Big Spring basin to the Turkey River; WY 1994.

	1993			1994								
	Oct	Nov	Dec	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep
Flow-weighted mean atrazine concentration, in μg/L	0.15	0.13	0.09	0.11	0.20	0.15	0.04	0.21	0.44	0.62	0.14	0.12
Mean of atrazine analyses, in μg/L	0.15	0.13	0.09	0.11	0.12	0.13	0.03	0.25	0.42	0.45	0.13	0.12
Total monthly atrazine output, lbs	1.4	0.93	0.51	0.57	1.7	1.7	0.25	1.2	2.9	5.3	0.80	0.46
Total monthly atrazine output, grams	644	422	232	260	778	771	115	539	1,329	2,403	364	207

by changes in the recharge mechanisms which discussed earlier: decreasing nitrate concentrations for a short period (several days, at most) during runoff recharge periods, followed by increasing nitrate concentrations during the infiltration recharge periods that follow (Hallberg et al., 1984a; Libra et al., 1984; Baker and Johnson, 1981; Hallberg et al., 1989; Libra et al., 1991; Rowden et al., 1993a, Rowden et al., 1995b; Rowden, 1995). Most other discharge and nitrate concentration trends for both Big Spring and the Turkey River also followed the changes in recharge mechanisms. Differences in detail occur because of the size difference between the systems, the larger proportion of surface runoff water in the Turkey River, and in-stream processes that affect surface water (see Hallberg et al., 1983, 1984a).

Nitrate concentrations from the Turkey River gradually increased from 28 mg/L (6.2 mg/L as NO_3-N) in October to 37 mg/L (8.2 mg/L as NO_3-N) in early November. The concentrations then decreased to 27 mg/L (6.0 mg/L as NO_3-N) and remained at the relatively low concentration until late December. On December 27, the nitrate concentration peaked for the water year at 38 mg/L (8.5 mg/L as NO_3-N). Nitrate concentrations remained relatively high through January, and then gradually declined to 12 mg/L (2.7 mg/L as NO_3-N) on March 8th because of increased discharge from snowmelt. For the remainder of the water year, nitrate concentrations generally fluctuated around 20 mg/L, with some short-term concentration and discharge peaks caused by precipitation events. The lowest nitrate concentration analyzed in the water year, 11 mg/L (2.4 mg/L as NO_3-N), was sampled on May 24. In general, nitrate concentrations from the Turkey River were relatively high during the first four months of the water year. Concentrations then decreased as did discharge, from February through May. After a series of recharge events in June and July, discharge and nitrate concentrations both declined through the remainder of the water year.

The monthly fw mean nitrate concentrations and loads from the Turkey River are shown in Table 6. All monthly fw mean concentrations for nitrate remained well below the 45 mg/L (10 mg/L as NO_3-N) drinking water standard for nitrate

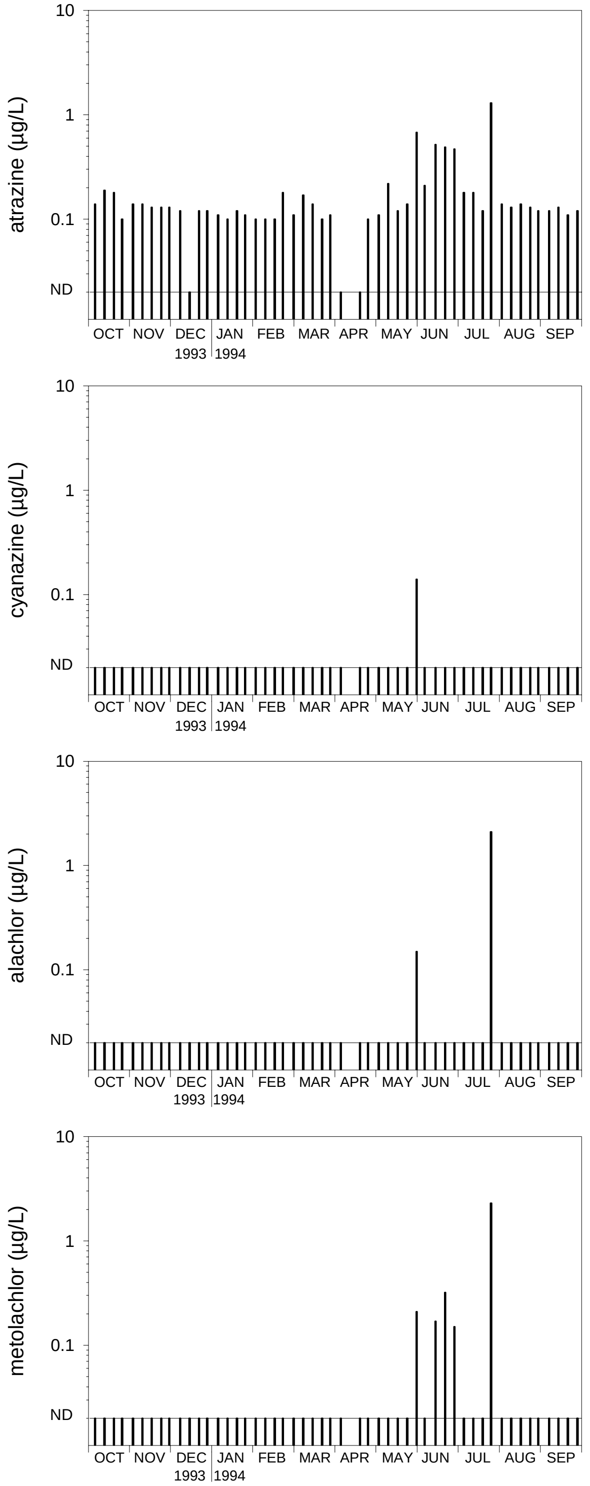


Figure 5. Bar graphs of pesticide concentrations at Big Spring for WY 1994. ND represents not detected.

during WY 1994. The highest monthly fw mean nitrate concentration, 37 mg/L (8.1 mg/L as NO_3-N), occurred in January. The fw mean nitrate concentrations for all other months except December were lower than 30 mg/L. The lowest monthly fw mean nitrate concentration, 17 mg/L (3.7 mg/L as NO_3-N), occurred in June. Three other months with fw mean nitrate concentrations less than 20 mg/L were March (19 mg/L), May (18 mg/L), and July (18 mg/L). The greatest monthly N-load, 1,449 thousand pounds, occurred in March, and the smallest N-load, 468 thousand pounds, occurred in May. March accounted for 17.6% of the annual surface-water discharge and 14.6% of the annual nitrate-N load, while January accounted for 3.7% of the annual surface-water discharge and 5.9% of the annual nitrate-N load.

Pesticide Monitoring

Figures 3, 5, and 6 and tables 2 and 7 summarize the results of pesticide monitoring at Big Spring for WY 1994. Fifty-one samples from Big Spring were analyzed for pesticides during the water year. A total of 17.8 pounds of atrazine were discharged from Big Spring at annual fw mean concentration of 0.21 µg/L (micrograms per liter). This was the third-lowest annual atrazine load and the second-lowest annual fw mean concentration observed during WYs 1983-1994. The two water years with lower annual atrazine loads were 1987 (17.6 pounds) and 1988 (9.2 pounds). The smallest annual fw mean atrazine concentration, 0.13 µg/L, also occurred in WY 1988 (Libra et al., 1991).

Figure 3 shows atrazine concentrations (A) and the discharge hydrograph (C) for Big Spring. Atrazine concentrations were 0.14 µg/L in early October, and increased to 0.19 µg/L one week later. Then, concentrations slowly declined to 0.10 µg/L by mid-February. Corresponding to the discharge peaks that resulted from snowmelt in late February and early March, the atrazine concentrations increased to 0.18 µg/L on February 21 and 0.17 µg/L on March 8. During the water year, the late March to early May period contained the lowest atrazine concentrations. Atrazine concentrations remained around 0.10 µg/L during the period, and were below detectable levels (<0.10 µg/L) twice in

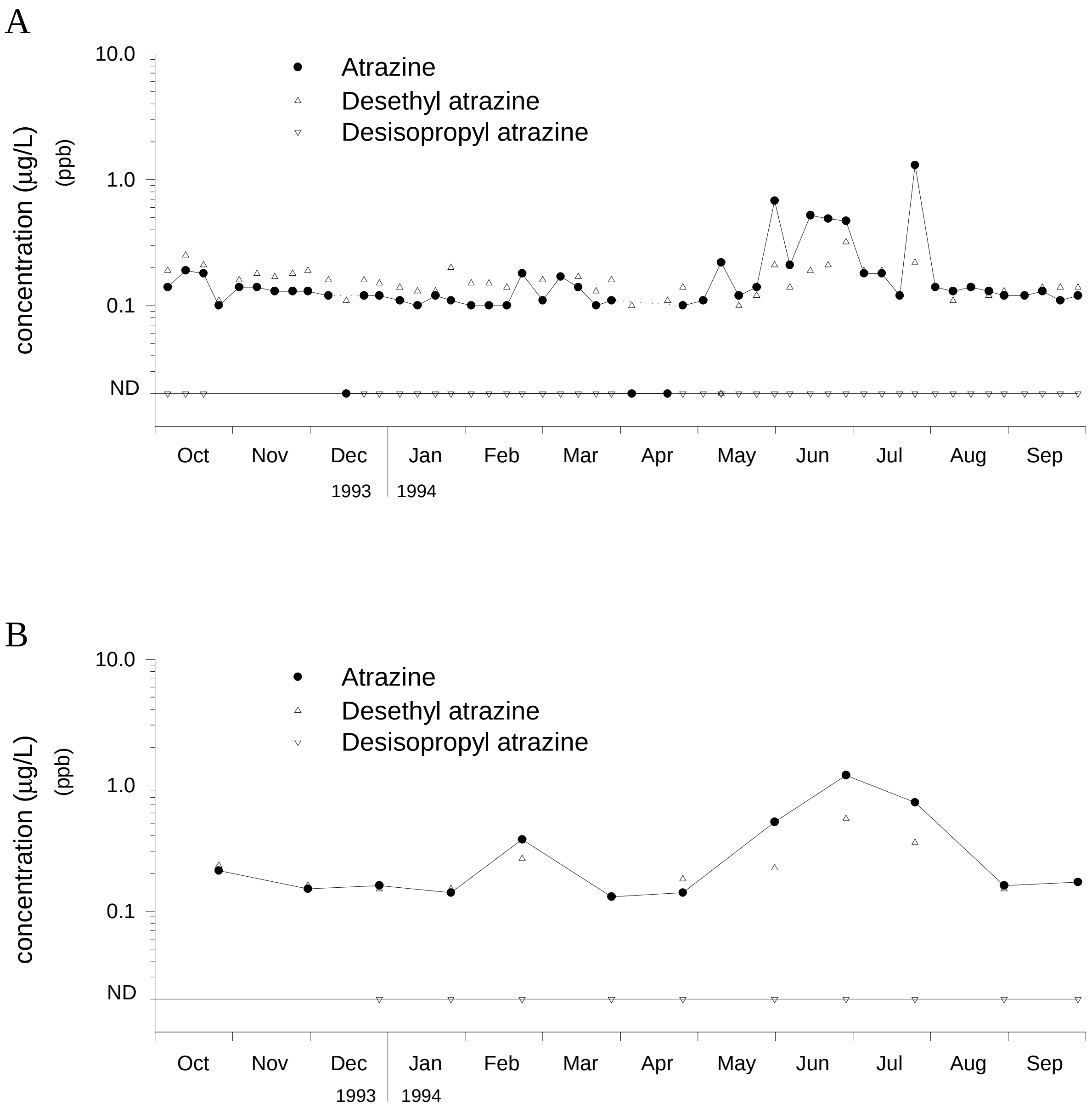


Figure 6. A) Atrazine, desethyl atrazine and desisopropyl atrazine concentrations for Big Spring and B) the Turkey River at Garber for WY 1994. ND represents not detected.

April. The mid-May to late July period had relatively high atrazine concentrations. Most samples collected in this period contained atrazine concentrations greater than 0.20 µg/L, and the greatest concentration of the water year, 1.30 µg/L, occurred on July 25. During the remainder of the water year, atrazine concentrations from Big Spring were relatively low, and gradually decreased from 0.14 µg/L in early August to 0.11 µg/L in late September.

Table 8. Monthly summary of atrazine discharged for the Turkey River at Garber; WY 1994.

	1993			1994								
	Oct	Nov	Dec	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep
Flow-weighted mean atrazine concentration, in µg/L	0.24	0.18	0.15	0.15	0.28	0.26	0.12	0.32	1.25	1.02	0.18	0.16
Mean of atrazine analyses, in µg/L	0.21	0.15	0.16	0.07	0.37	0.13	0.14	0.51	1.20	0.73	0.16	0.17
Total monthly atrazine output, lbs	49.2	24.4	14.4	11.1	49.0	88.6	20.3	38.3	216	254	21.5	16.4
Total monthly atrazine output, kg	22.3	11.1	6.5	5.0	22.2	40.2	9.2	17.3	98.1	115.0	9.7	7.4

Table 7 summarizes fw mean atrazine concentrations and loads at Big Spring on a monthly basis for WY 1994. During the water year, the greatest monthly fw mean atrazine concentration, 0.62 µg/L, and the largest monthly atrazine load, 5.3 pounds, occurred in July. April had the lowest monthly fw mean atrazine concentration at 0.04 µg/L, which is the lowest monthly fw mean atrazine concentration for Big Spring since WY 1984. The previous low, 0.06 µg/L, occurred in November and August of WY 1988 (Libra et al., 1991). The smallest monthly atrazine load for WY 1994, 0.25 pounds, also occurred in April, and was the second-smallest monthly atrazine load since WY 1984. The smallest monthly atrazine load, 0.20 pounds, was recorded in August of WY 1988 and December of WY 1989 (Libra et al., 1991).

Figure 5 summarizes the detection and concentrations of atrazine, cyanazine, alachlor, and metolachlor on a logarithmic scale. The occurrence of non-detection of pesticides is indicated by concentration bars ending at "ND". The detection criterion for pesticides is 0.10 µg/L, although the detection limit may be increased to 0.20 µg/L, depending on the quantity of water sampled and lab variations. Among the fifty-one samples collected from Big Spring during the water year, forty-eight samples, or 94%, contained detectable levels of atrazine; one sample, or 2%, contained detectable levels of cyanazine; two samples, or 4%, contained detectable levels of alachlor; and five samples, or 10%, contained detectable levels of metolachlor. The only sample that contained detectable cyanazine, at 0.14 µg/L, was collected on May 31. The greatest concentrations of atrazine (1.30 µg/L), alachlor (2.10 µg/L) and metolachlor (2.30 µg/L) were detected from the sample collected on July 25. All of the samples with detectable levels of cyanazine, alachlor, and metolachlor were collected from mid-May to late July, the period with the greatest atrazine concentrations.

The atrazine data for the Turkey River in WY 1994 are summarized in Figure 6 (B) and tables 3 and 8. During the water year, twelve samples from the Turkey River were analyzed for pesticides. A total of 803 pounds of atrazine, at annual fw mean concentration of 0.41 µg/L, was discharged by the river. This was the fourth-smallest annual atrazine load, and the third-lowest annual fw mean atrazine concentration observed at the Turkey River during the WY 1986-1994 period of record. The smallest annual atrazine load, 407.1 pounds, was recorded in

WY 1988 (Libra et al., 1991), and the lowest annual fw mean concentration of atrazine, 0.25 µg/L, occurred during WY 1992 (Rowden et al., 1995b).

Table 8 summarizes the fw mean atrazine concentrations and loads on a monthly basis for the Turkey River for WY 1994. The greatest monthly fw mean atrazine concentration, 1.25 µg/L, occurred in June, and the greatest monthly atrazine load, 254 pounds, occurred in July. July accounted for 31.6% of the annual atrazine load and 12.7% of the annual surface-water discharge. The lowest monthly fw mean atrazine concentration, 0.12 µg/L, was recorded in April, and the smallest monthly atrazine load, 11.1 pounds, occurred in January. The lowest monthly fw mean atrazine concentration during the water year, 0.12 µg/L, was the sixth-lowest for the Turkey River since WY 1986. All other monthly concentrations lower than 0.12 µg/L occurred in WYs 1988 and 1989 (Libra et al., 1991).

All 12 samples collected from the Turkey River during WY 1994 contained detectable levels of atrazine. Concentrations ranged from 0.13 µg/L to 1.20 µg/L. The sample with the greatest atrazine concentration, 1.20 µg/L, was collected on June 28. The sample with the lowest atrazine concentration, 0.13 µg/L, was collected on March 28. Of the 12 samples, two samples, or 17%, contained detectable levels of cyanazine; two samples (also 17%) contained detectable levels of alachlor; and four samples, or 33%, contained detectable levels of metolachlor.

Other pesticides analyzed for at both Big Spring and the Turkey River during the water year included fonofos, butylate, trifluralin, metribuzin, acetochlor, and the atrazine metabolites desethyl atrazine and desisopropyl atrazine. Three samples from Big Spring collected in October were analyzed for fonofos. None of the samples contained detectable levels (0.10 µg/L) of fonofos. Butylate, trifluralin, and metribuzin were analyzed through the water year. All samples analyzed were below detectable concentrations (0.10 µg/L). Acetochlor was added to the list of analytes in late August, 1994. By the end of the water year, six samples from Big Spring and two samples from the Turkey River were analyzed; none contained detectable concentration of acetochlor.

Forty-three samples from Big Spring and ten samples from the Turkey River were analyzed for desisopropyl atrazine. None of these samples contained detectable concentrations of desisopropyl atrazine. Fifty-one samples collected from Big Spring in WY 1994 were analyzed for desethyl atrazine. Fifty, or 98%, contained detectable concentrations of desethyl atrazine. The sample with the greatest desethyl atrazine concentration, 0.32 µg/L, was collected on June 28. The only sample with no detection of desethyl atrazine concentration was collected on May 10. All twelve samples collected from the Turkey River during WY 1994 contained detectable levels of desethyl atrazine. The greatest desethyl atrazine concentration sampled at the Turkey River, 0.54 µg/L, also occurred on June 28.

Both desethyl atrazine and desisopropyl atrazine are metabolites of atrazine. Research has shown that desethyl atrazine is the more stable and dominant initial degradation product. Atrazine can be degraded by either biotic or abiotic processes. Kolpin and Kalkhoff (1993) studied the concentrations of atrazine, desethyl atrazine, and desisopropyl atrazine in surface water of Roberts Creek in the Big Spring basin and suggested that abiotic degradation processes may be occurring in the stream. Figure 6 shows a plot of atrazine, desethyl atrazine, and desisopropyl atrazine for both Big Spring and the Turkey River during WY 1994. Two aspects of this plot may provide some insights about atrazine degradation. First, the concentration trends for desethyl atrazine were very similar to atrazine, indicating atrazine degradation processes occurred in the study area. Second, the atrazine degradation probably resulted from abiotic activity since desethyl atrazine occurred in both groundwater at Big Spring and surface water of the Turkey River. Figure 6 also indicates that atrazine and desethyl atrazine concentrations were similar, except during rainfall-generated runoff periods in late summer, when atrazine concentrations were notably higher.

Table 9. Annual summary of groundwater and chemical discharge from the Big Spring basin to the Turkey River for WY 1995. (Discharge data are from the U.S. Geological Survey, Water Resources Division.)

DISCHARGE	
Total	
acre-feet	30,013
millions cf	1,306
millions cm	37.0
Average	
cfs	41.5
cms	1.17
mg/d	26.8
gpm	18,605

PRECIPITATION AND DISCHARGE	
Precipitation	29.28 inches (744 mm)
Discharge	5.46 inches (139 mm)
Discharge as % of precipitation	18.7%

NITRATE DISCHARGE

Concentration - mg/L	**As NO_3**	**As NO_3-N**
Flow-weighted mean	45.3	10.1
Mean of analyses	44.4	9.9
	NO_3-N output	**Total N output**
lbs - N	822,569	826,212
kg - N	373,047	374,699
lbs - N/acre	12.5	12.5

ATRAZINE DISCHARGE	
Concentration - μg/L	
Flow-weighted mean	0.12
Mean of analyses	0.11
Total output	
lbs	9.8
kg	4.4

Water Year 1995

Discharge Monitoring

Tables 9 through 15 and figures 7 through 11 summarize the discharge, climatic, water quality, and chemical loading data for Big Spring and the Turkey River for WY 1995.

The annual groundwater discharge from the Big Spring basin was 30,013 ac-ft, at an average daily discharge rate of 41.5 cfs. This is 52% of the greatest annual discharge from the basin, 58,186 ac-ft, recorded in WY 1993. The annual precipitation in the basin for WY 1995, 29.28 inches (744 mm), was the third lowest annual precipitation since the monitoring project began in WY 1982. The groundwater discharge was equivalent to 18.7% of precipitation during the water year, the same discharge/precipitation ratio as was recorded in WY 1994.

Figure 7 shows the discharge hydrograph (A) and water temperature (B) for Big Spring, along with daily precipitation in the basin (C) and daily maximum/minimum air temperature (D) recorded by the Elkader weather observation station for WY 1995. Figure 8 shows the discharge hydrograph (C), along with nitrate (B) and atrazine (A) concentrations in the Big Spring groundwater. During WY 1995, mean daily discharge from Big Spring remained below 25 cfs from October through mid-November. Responding to precipitation on November 20 (0.48 inches) and 21 (0.67 inches), discharge rose to 35 cfs on November 22 and to 40 cfs on November 23, then declined to below 25 cfs in late November. This low groundwater discharge continued through most of February, appearing as a flat line on the hydrograph. Two discharge peaks occurred in late February and mid-March, respectively. The daily discharge was 52 cfs on February 20 and 83 cfs on March 11. February was the driest month of the water year, with monthly precipitation of only 0.03 inches (1.05 mm). The discharge peaks that occurred in February and March resulted from snowmelt. Although maximum air temperatures remained above 60°F in the area during mid-March, discharge at Big Spring declined through early April since all the snow had melted. After several rainfalls in early April, including the

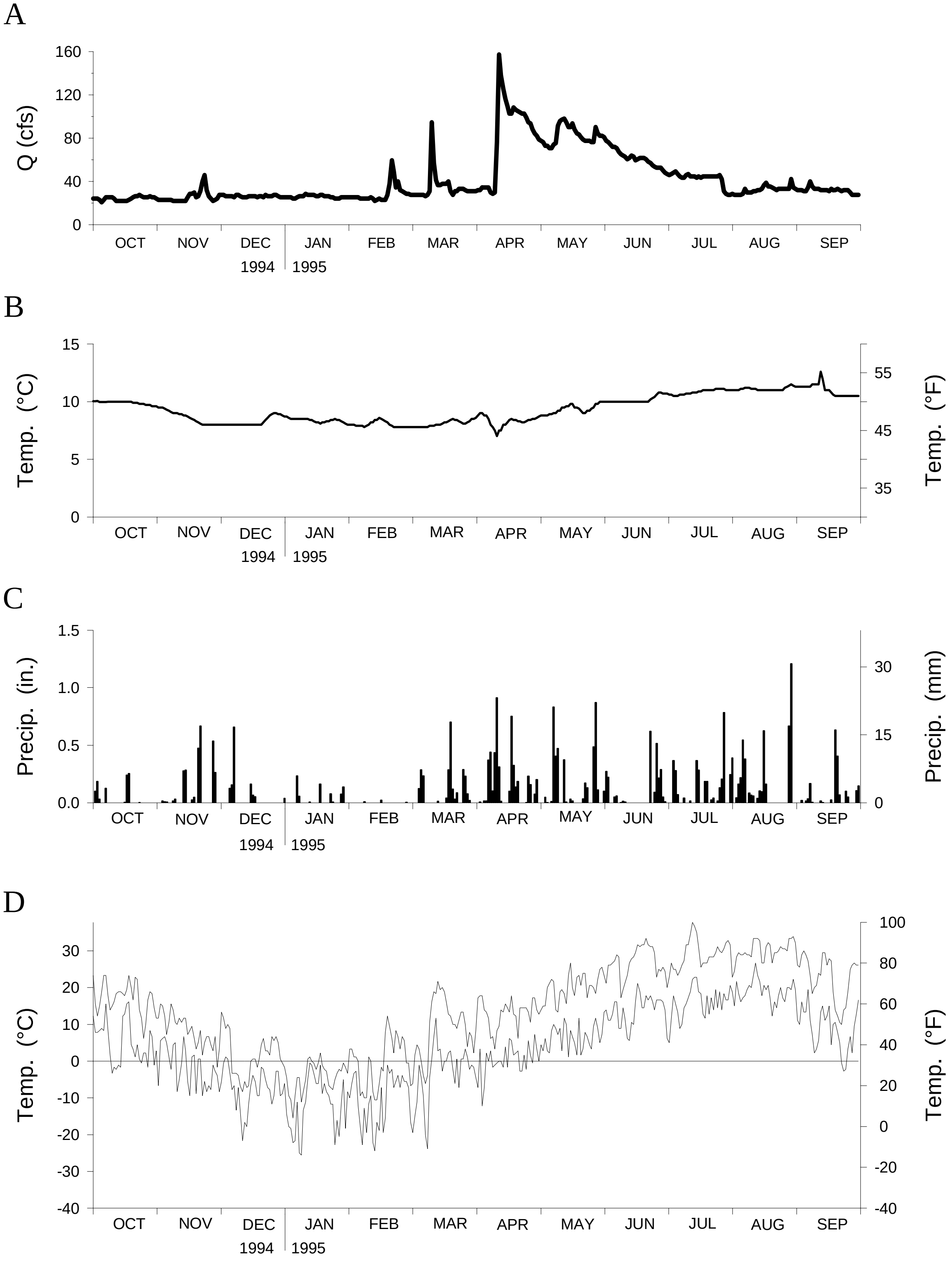


Figure 7. A) Groundwater discharge, B) groundwater temperature and C) daily precipitation for the Big Spring basin; and D) maximum-minimum temperatures for Elkader, IA (Iowa Dept. of Ag. and Land Stewardship, State Climatology Office), for WY 1995.

Table 10. Monthly summary of groundwater discharge from the Big Spring basin for WY 1995.

	1994 Oct	Nov	Dec	1995 Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep
TOTAL MONTHLY DISCHARGE												
Acre-feet	1,480	1,525	1,609	1,584	1,593	2,120	4,797	5,077	3,720	2,636	1,984	1,889
Cubic feet (millions)	64	66	70	69	69	92	209	221	162	115	86	82
Gallons (millions)	482	497	524	516	519	691	1,563	1,655	1,212	859	647	616
Cubic meters (millions)	1.8	1.9	2.0	2.0	2.0	2.6	5.9	6.3	4.6	3.3	2.4	2.3
AVERAGE DISCHARGE												
cfs	24	26	26	26	29	34	81	83	63	43	32	32
cms	0.7	0.7	0.7	0.7	0.8	1.0	2.3	2.3	1.8	1.2	0.9	0.9
mg/d	16	17	17	17	19	22	52	53	40	28	21	21
MAXIMUM												
cfs	27	46	27	29	59	95	157	98	81	49	42	40
cms	0.8	1.3	0.8	0.8	1.7	2.7	4.5	2.8	2.3	1.4	1.2	1.1
MINIMUM												
cfs	21	22	25	24	22	26	29	71	48	27	27	27
cms	0.6	0.6	0.7	0.7	0.6	0.7	0.8	2.0	1.4	0.8	0.8	0.8

second largest precipitation event of the water year (0.91 inches on April 11), Big Spring's daily discharge increased to 138 cfs on April 12. This was the highest average daily discharge in WY 1995. The daily discharge remained above 100 cfs through April 15, and then gradually declined to 60 cfs by early May. Precipitation was above normal in the basin from early May through mid-May, and included the water year's fourth greatest rainfall, 0.83 inches on May 8. Responding to precipitation, discharge at Big Spring rose to 86 cfs on May 13. On May 28, the third greatest daily precipitation of WY 1995, 0.87 inches, occurred in the basin, and caused the last discharge peak (79 cfs) on the Big Spring hydrograph. After this, discharge at Big Spring declined to 25 cfs in late July, and remained relatively low through the rest of the water year. The water year's greatest daily precipitation, 1.21 inches, occurred on August 30. However, it did not cause significant runoff in this area. Average discharge at Big Spring on that day was 37 cfs.

Table 10 summarizes the groundwater discharge data from Big Spring for WY 1995 on a monthly basis. Although May had near normal precipitation (3.99 inches), Big Spring had its greatest monthly discharge, 5,077 ac-ft, during this month, at an average daily discharge rate of 83 cfs. The discharge for May accounted for 16.9% of the annual discharge. August had the greatest monthly precipitation, 4.84 inches, in the Big Spring basin in WY 1995. But the monthly discharge during August, 1,984 ac-ft, was significantly less than monthly discharges for March through July. This may have resulted from evapotranspiration during the growing season. The smallest monthly discharge from Big Spring, 1,480 ac-ft, occurred in October, at an average daily discharge rate of 24 cfs. All months except March through July had monthly discharges less than 2,000 ac-ft during WY 1995.

For the Turkey River at Garber, the discharge hydrograph was very similar to Big Spring during WY 1995 (Fig. 9B). The annual surface water discharge from the Turkey River at Garber was about 729,000 ac-ft, at an average daily discharge of 1,007 cfs (Table 11). This amount is slightly greater than WY 1994, and equates to 35% of the greatest annual discharge recorded in WY 1993 (Rowden et al., 1995). The annual precipitation in the basin was 30 inches (764 mm). Surface-water discharge was equal to 29.4% of the annual precipitation, and was 102% of the long-term average annual discharge. On a monthly basis, April had the greatest total discharge, 147,500 ac-ft, at a mean daily discharge rate of 2,478 cfs. The smallest monthly discharge, 23,230 ac-ft, occurred in February, with an average daily discharge rate of 418 cfs. The maximum daily discharge of the Turkey River at Garber, 4,850 cfs, occurred on April 13, which resulted from frequent precipitation events in the Turkey River basin. The minimum daily discharge, 280 cfs, occurred on January 24.

Nitrate Monitoring

During Water Year 1995, fifty-two samples of Big Spring groundwater were analyzed for partial nitrogen series (nitrate-N and ammonia-N). Since nitrate samples were not taken at Big Spring during WY 1995, the daily nitrate concentration was estimated and computed based on weekly nitrate-N concentration data. Both the fw mean and mean of analyses for nitrate concentrations were derived by multiplying the nitrate-N concentrations by 4.5. Beginning in WY 1995, the total nitrogen output from Big Spring was calculated by adding the total nitrate-N output to the total ammonia-N output; organic-N was not included. For the Turkey River, only nitrate samples were collected during WY 1995. Thus, both organic- and ammonia-N can not be calculated for the annual total nitrogen output from the Turkey River for this water year.

Table 11. Annual summary of water and chemical discharge for the Turkey River at Garber for WY 1995. (Discharge data are from the U.S. Geological Survey, Water Resources Division.)

DISCHARGE		
Total		
acre-feet	729,000	
millions cf	31,712	
millions cm	899	
Average		
cfs	1,007	
cms	28.5	
mg/d	651	
gpm	451,928	
PRECIPITATION AND DISCHARGE		
Precipitation	30.07 inches (764 mm)	
Discharge	8.85 inches (225 mm)	
Discharge as % of precipitation	29.4%	
NITRATE DISCHARGE		
Concentration - mg/L	**As NO_3**	**As NO_3-N**
Flow-weighted mean	30.1	6.7
Mean of analyses	28.8	6.4
	NO_3-N output	**Total N output**
lbs - N	13,253,486	NA
kg - N	6,010,651	NA
lbs - N/acre	13.4	NA
ATRAZINE DISCHARGE		
Concentration - μg/L		
Flow-weighted mean	0.42	
Mean of analyses	0.43	
Total output		
lbs	841	
kg	382	

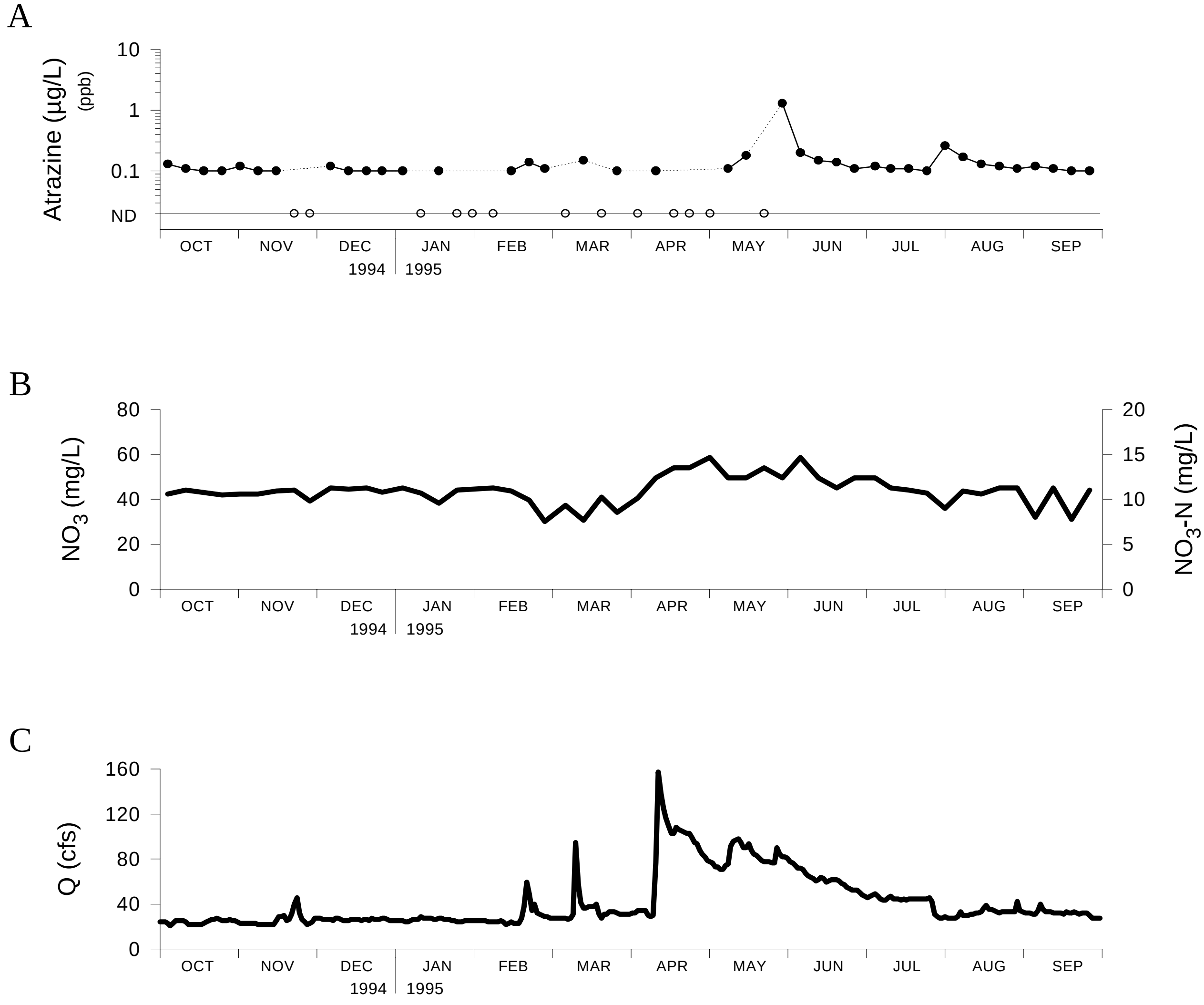


Figure 8. A) Atrazine and B) nitrate concentrations; and C) groundwater discharge at Big Spring for WY 1995.

Annual nitrate discharge from Big Spring is summarized in Table 9. A total of 826,212 pounds of nitrogen were discharged from the basin. Of this, 822,569 pounds, or 99.6%, of the nitrogen discharged were in the form of nitrate. The amount is equivalent to 12.5 lbs-N/acre for the basin and is the smallest annual nitrate-nitrogen discharge from Big Spring since WY 1991. The annual fw mean nitrate concentration for WY 1995 was 45.3 mg/L (10.1 mg/L as NO_3-N). The annual mean concentration of analyses for nitrate was 44.4 mg/L (9.9 mg/L as NO_3-N) for the water year. At Big Spring, all of the annual mean concentrations of analyses for nitrate were below the 45 mg/L (10.0 mg/L as NO_3-N) drinking water standard from WY 1982 through WY 1990 except for WY 1983. During WY 1991, the annual mean concentration of analyses for nitrate increased to 49.1 mg/L (10.9 mg/L as NO_3-N), and continued to increase to 54.0 mg/L (12.0 mg/L as NO_3-N) in WY 1993. The concentration declined to 47.3 mg/L (10.5 mg/L as NO_3-N) in WY 1994. The 44.4 mg/L (9.9 mg/L as NO_3-N) concentration for WY 1995 was the lowest annual mean concentration of analyses for nitrate since WY 1991.

Figure 8 shows the discharge hydrograph (C)

Table 12. Monthly summary of nitrate-N discharged in groundwater from the Big Spring basin to the Turkey River; WY 1995.

	1994			1995								
	Oct	Nov	Dec	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep
Flow weighted mean NO_3 concentration, in mg/L;	43	42	44	42	41	33	49	52	50	45	43	39
as NO_3-N	9.5	9.4	9.8	9.4	9.0	7.3	10.8	11.5	11.2	10.0	9.5	8.6
Mean of NO_3 analyses, in mg/L;	34	42	44	56	40	36	50	52	51	45	42	38
as NO_3-N	7.5	9.4	9.9	12.4	8.8	8.0	11.0	11.6	11.3	10.1	9.4	8.5
Total monthly NO_3-N output, thousands lbs	38	39	43	41	39	42	141	159	113	72	51	44
Total monthly NO_3-N output, thousands kg	17	18	20	18	18	19	64	72	51	33	23	20

and the nitrate concentrations (B) for Big Spring groundwater during WY 1995. Nitrate concentrations were relatively stable during the first five months of the water year, with concentrations remaining around 45 mg/L (10.0 mg/L as NO_3-N). On February 27, nitrate concentration declined to the lowest level, 30 mg/L (6.7 mg/L as NO_3-N), for WY 1995. The low nitrate concentrations continued through early April. From mid-April through early July, nitrate concentrations at Big Spring increased and remained above 45 mg/L (10.0 mg/L as NO_3-N). The highest concentration recorded during the water year, 59 mg/L (13.0 mg/L as NO_3-N), occurred on May 2 and June 6. During the remainder of the water year, nitrate concentrations declined, with most concentrations below 45 mg/L (10.0 mg/L as NO_3-N).

Table 12 summarizes the nitrate data for Big Spring during WY 1995 on a monthly basis. Monthly fw mean nitrate concentrations exceeded the 45 mg/L (10.0 mg/L as NO_3-N) drinking water standard for nitrate from April through June. The highest monthly fw mean nitrate concentration during the water year, 52 mg/L (11.5 mg/L as NO_3-N), occurred in May. The lowest monthly fw mean nitrate concentration, 33 mg/L (7.3 mg/L as NO_3-N), occurred in March. Three months, April, May, and June, had total monthly nitrate-N outputs of more than 100,000 pounds. The month with the greatest nitrate-N output, 159,000 pounds, was May, the month with the greatest groundwater discharge. The lowest monthly nitrate-N output, 38,000 pounds, occurred in October, the month with the smallest monthly groundwater discharge during the water year. May accounted for 19.3% of the annual nitrate-N load and 16.9% of the annual groundwater discharge at Big Spring.

For the Turkey River, fifty-two samples were analyzed for nitrate during Water Year 1995. Annual nitrate discharge from the Turkey River at Garber is summarized in Table 11. A total of 13,253,486 pounds of nitrate-nitrogen were discharged by the river. This amount is equivalent to 13.4 lbs-N/acre for the Turkey River basin, and is the second smallest annual nitrate-nitrogen discharge from the Turkey River since WY 1991. The annual fw mean nitrate concentration was 30.1 mg/L (6.7 mg/L as NO_3-N), and the annual mean of

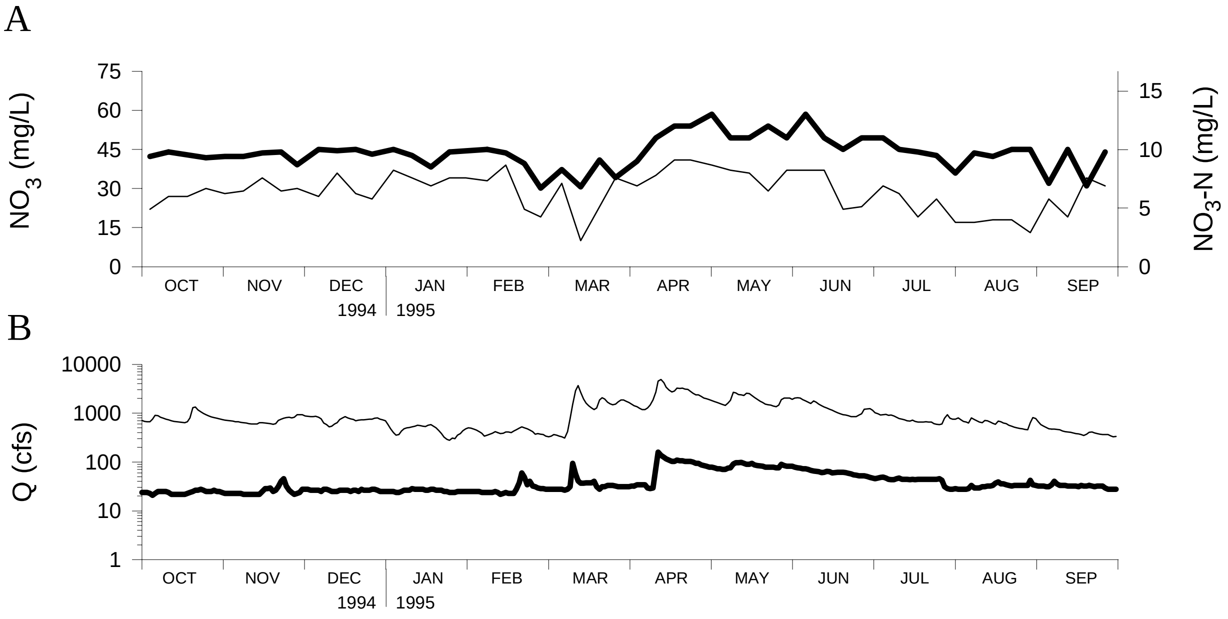


Figure 9. A) Nitrate concentrations and B) discharge hydrographs for Big Spring (bold lines) and the Turkey River at Garber (lighter lines) for WY 1995. (Turkey River discharge data are from the U.S. Geological Survey, W.R.D., IA Dist.)

analyses was 28.8 mg/L (6.4 mg/L as NO_3-N) for WY 1995.

The lighter line of Figure 9 (A) shows nitrate concentrations for the Turkey River during Water Year 1995. The concentration trends were similar to those of the Big Spring groundwater shown by the bold line of Figure 9 (A). From October through December, nitrate concentrations in the Turkey River were relatively low, with most concentrations below 30 mg/L (6.7 mg/L as NO_3-N). Nitrate concentrations increased from early January through mid-February, and rose to 39 mg/L (8.7 mg/L as NO_3-N) on February 14. Responding to discharge variations, nitrate concentrations fluctuated significantly from late February to late April. On March 14, the concentration decreased to 10 mg/L (2.2 mg/L as NO_3-N), which was the lowest concentration recorded from the Turkey River during WY 1995. This occurred one day after a relatively high discharge peak, 3,640 cfs, of the Turkey River. Following this, nitrate concentrations increased gradually. The highest nitrate concentration recorded during the water year, 41 mg/L (9.1 mg/L as NO_3-N), occurred on April 18 and 24, a few days after the largest daily discharge, 4,850 cfs, of the water year. After the peaks, the nitrate concentration of the Turkey River slowly declined to 13 mg/L (2.9 mg/L as NO_3-N) by the end of August. In September, the nitrate concentration increased again, but remained below 35 mg/L (7.8 mg/L as NO_3-N).

The monthly summary of nitrate-N discharge for the Turkey River in WY 1995 is shown in Table 13. All monthly fw means of nitrate were below the 45 mg/L (10.0 mg/L as NO_3-N) drinking water standard for nitrate during WY 1995. The greatest monthly fw mean nitrate concentration, 36 mg/L (8.1 mg/L as NO_3-N), and the greatest monthly nitrate-N output, 3.25 million pounds, occurred in April. April accounted for 20.2% of the annual surface-water discharge and 24.5% of the annual nitrate-N output. The lowest monthly fw mean nitrate concentration, 17 mg/L (3.7 mg/L as NO_3-N), occurred in August, and September recorded the smallest monthly total nitrate-N output, 395,000 pounds, for the Turkey River in WY 1995.

Table 13. Monthly summary of nitrate-N discharged for the Turkey River at Garber; WY 1995.

	1994			1995								
	Oct	Nov	Dec	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep
Flow-weighted mean NO_3 concentration, in mg/L;	25	30	30	34	30	23	36	35	32	25	17	26
as NO_3-N	5.7	6.7	6.6	7.6	6.8	5.1	8.1	7.7	7.0	5.5	3.7	5.8
Mean of NO_3 analyses, in mg/L;	27	30	29	34	28	25	37	36	30	26	17	28
as NO_3-N	5.9	6.7	6.5	7.6	6.3	5.5	8.2	7.9	6.6	5.8	3.7	6.1
Total monthly NO_3-N output, thousands lbs	773	758	813	570	427	1,182	3,250	2,454	1,525	710	399	395
Total monthly NO_3-N output, thousands kg	350	344	369	258	194	536	1,474	1,113	691	322	181	179

Pesticide Monitoring

Pesticide monitoring results at Big Spring for WY 1995 are summarized in figures 8(A) and 10 and tables 9 and 14. Fifty-two samples from Big Spring groundwater were analyzed for pesticides during WY 1995. A total of 9.8 pounds of atrazine were discharged by Big Spring groundwater during this water year. This was the second-lowest annual atrazine load since WY 1982. The lowest annual atrazine load, 9.2 pounds, occurred in WY 1988 (Libra et al., 1991). The annual fw mean atrazine concentration was 0.12 μg/L for WY 1995. This was the smallest annual fw mean atrazine concentration observed since the monitoring began in WY 1982.

Figure 8(A) shows atrazine concentration trends at Big Spring during WY 1995. The atrazine concentration was 0.13 μg/L in early October, and declined to 0.10 μg/L two weeks later. The relatively low concentrations continued through mid-February. Responding to discharge events from snowmelt in late February and mid-March, the atrazine concentration increased to 0.14 μg/L on February 21 and 0.15 μg/L on March 14. From late March through early May, atrazine concentrations remained low at Big Spring. Most atrazine concentrations were below detectable levels (< 0.10 μg/L) during this period, even though the greatest groundwater discharge of the water year occurred at Big Spring in mid-April. Following this, atrazine concentrations at Big Spring increased. From mid-May through September, all samples, except the one collected on May 23, contained detectable atrazine concentrations. The greatest atrazine concentration of the water year, 1.30 μg/L, occurred on May 30. The second-greatest atrazine concentration, 0.26 μg/L, occurred on August 1. By the end of the water year, atrazine concentrations at Big Spring decreased to 0.10 μg/L again.

Table 14 summarizes fw mean atrazine concentrations and loads at Big Spring on a monthly basis. The monthly fw mean atrazine concentrations were relatively low compared with previous years. Concentrations were below 0.10 μg/L

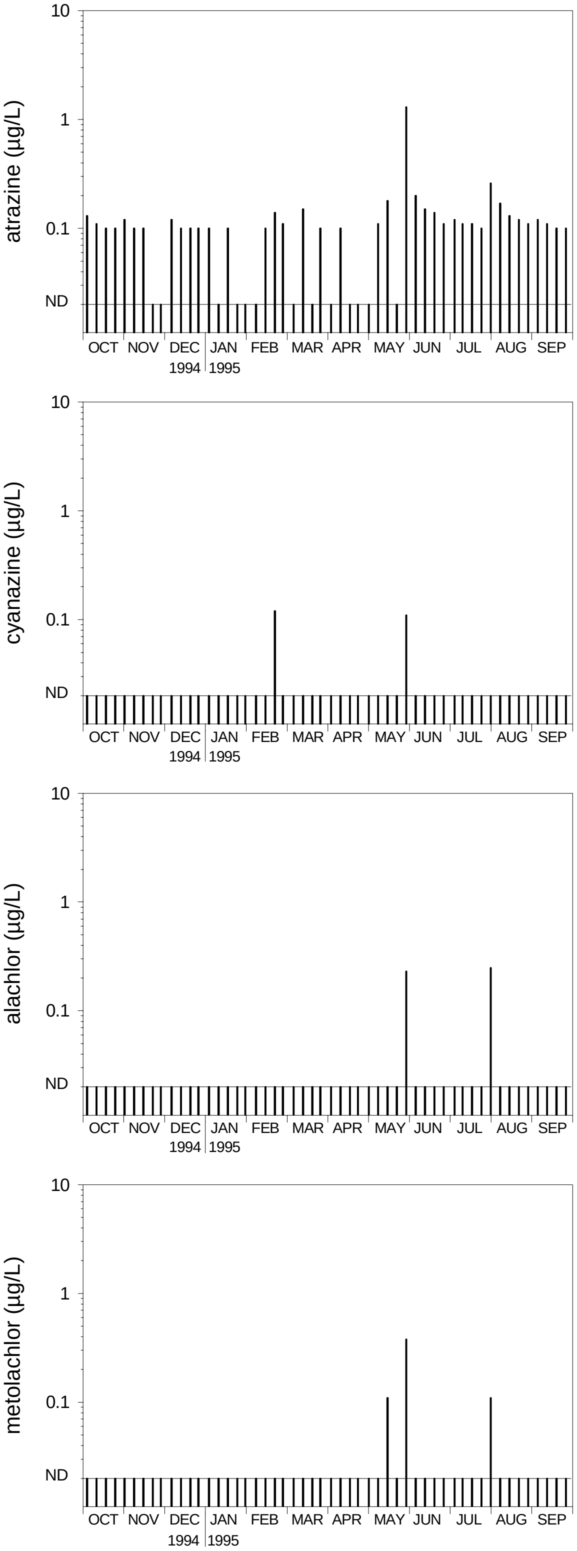


Figure 10. Bar graphs of pesticide concentrations at Big Spring for WY 1995. ND represents not detected.

during November, and from January through April. The smallest monthly fw mean atrazine concentration, 0.04 µg/L, occurred in January and April. This equaled the previous lowest monthly fw mean atrazine concentration, which occurred in April of 1994. All monthly atrazine loads, except for May and June, were less than 1.0 pound during WY 1995. January had the smallest monthly atrazine load, 0.17 pound. This was the lowest monthly atrazine load at Big Spring since WY 1984. The greatest fw mean atrazine concentration, 0.22 µg/L, occurred in June. June was the only month with a fw mean atrazine concentration higher than 0.20 µg/L during WY 1995. May had the greatest monthly atrazine load, 2.6 pounds, during the water year.

Figure 10 summarizes the detections and concentrations of atrazine, cyanazine, alachlor, and metolachlor on a logarithmic scale. Among the fifty-two samples collected from Big Spring during the water year, thirty-nine samples, or 75%, contained detectable levels of atrazine ($\geq$ 0.10 µg/L). Two samples, or 3.8%, had detectable levels of cyanazine. Those were collected on February 21 (0.12 µg/L) and May 30 (0.11 µg/L), respectively. Alachlor was also detected in two samples during the water year: one was collected on May 30 (0.23 µg/L) and the other was collected on August 1 (0.25 µg/L). Three samples, or 5.8%, contained detectable levels of metolachlor. They were collected on May 16 (0.11 µg/L), May 30 (0.38 µg/L), and August 1 (0.11 µg/L).

Figure 11 (B) and Tables 11 and 15 summarize atrazine data from the Turkey River in WY 1995. During the water year, twelve samples from the river were analyzed for pesticides. An estimated 841 pounds of atrazine, at an annual fw mean concentration of 0.42 µg/L, were discharged by the river in WY 1995. Although the fw mean concentrations and loads for atrazine were slightly higher than those recorded in WY 1994, both were still relatively low historically. Table 15 summarizes the atrazine concentrations and loads on a monthly basis for the Turkey River in WY 1995. The highest monthly fw mean atrazine concentration, 1.62 µg/L, and the greatest monthly atrazine load, 351 pounds, occurred in June. June accounted for 42% of the annual atrazine load and 11% of the

Table 14. Monthly summary of atrazine discharged in groundwater from the Big Spring basin to the Turkey River; WY 1995.

	1994 Oct	Nov	Dec	1995 Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep
Flow-weighted mean atrazine concentration, in µg/L	0.11	0.06	0.10	0.04	0.08	0.09	0.04	0.19	0.22	0.11	0.15	0.11
Mean of atrazine analyses, in µg/L	0.11	0.06	0.11	0.04	0.09	0.06	0.03	0.32	0.15	0.11	0.16	0.11
Total monthly atrazine output, lbs	0.45	0.26	0.45	0.17	0.35	0.54	0.56	2.6	2.2	0.81	0.80	0.55
Total monthly atrazine output, grams	202	119	203	75	161	245	252	1,188	993	367	363	252

annual surface-water discharge. April accounted for more than 20% of the annual surface-water discharge and only 6% of the annual atrazine load. The lowest monthly fw mean atrazine concentration, 0.11 µg/L, occurred in December, and the lowest monthly atrazine load, 7.8 pounds, occurred in February. The fw mean atrazine concentration for December was the fifth-lowest monthly atrazine concentration from the Turkey River since WY 1986. Four other months with fw mean atrazine concentrations less than 0.10 µg/L were recorded in WYs 1988 and 1989 (Libra et al., 1991).

All of the twelve samples collected from the Turkey River in WY 1995 contained detectable levels of atrazine. The concentrations varied from 0.10 µg/L to 2.40 µg/L. The sample with the highest atrazine concentration, 2.40 µg/L, was collected on May 30. The sample with the second-highest atrazine concentration, 1.40 µg/L, was collected on June 27. Two samples, or 17%, contained detectable concentrations of cyanazine and alachlor; these samples were also collected on May 30 and June 27. The cyanazine concentrations were 1.0 µg/L and 0.13 µg/L, and the alachlor concentrations were 0.41 µg/L and 0.14 µg/L, respectively. Three samples, or 25%, contained detectable levels of metolachlor. They were collected on February 27 (0.67 µg/L), May 30 (0.38 µg/L), and June 27 (0.18 µg/L).

Other pesticides analyzed for at Big Spring and the Turkey River in WY 1995 include acetochlor, butylate, trifluralin, metribuzin, desethyl atrazine, and desisopropyl atrazine. All samples collected from both Big Spring and the Turkey River were below detectable concentrations (<0.10 µg/L) for butylate, trifluralin, and metribuzin. One sample, or 2%, collected from Big Spring on May 30 contained acetochlor at a concentration of 0.60 µg/L. Two samples, or 17%, collected from the Turkey River on May 30 and June 27, contained acetochlor at concentrations of 1.30 µg/L and 0.38 µg/L, respectively. The concentrations of desethyl atrazine and desisopropyl atrazine are shown on Figure 11. The concentrations of desisopropyl atrazine were below detectable levels for all the samples collected from both Big Spring and the Turkey River. Forty-six samples, or 89%, from Big Spring contained detectable levels (≥0.10 µg/L) of desethyl atrazine. The highest desethyl atrazine concentration, 0.18

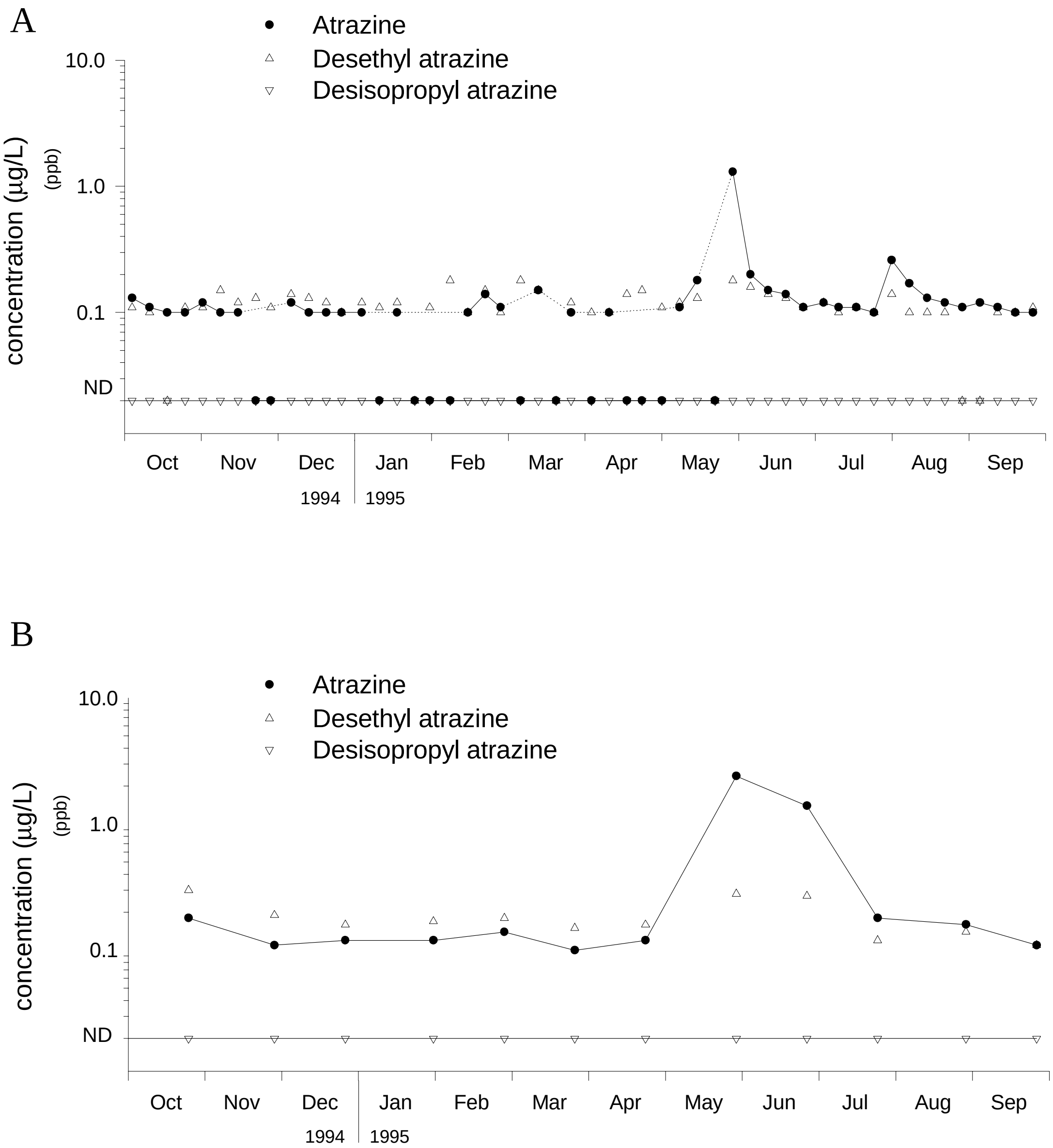


Figure 11. A) Atrazine, desethyl atrazine and desisopropyl atrazine concentrations Big Spring and B) the Turkey River at Garber for WY 1995. ND represents not detected.

µg/L, occurred on February 7, March 7, and May 30. All twelve samples collected from the Turkey River had detectable concentrations of desethyl atrazine. Concentrations ranged from 0.11 µg/L to 0.30 µg/L. The sample with the greatest concentration of desethyl atrazine, 0.30 µg/L, was collected on October 25. Two other samples from the Turkey River with desethyl atrazine concentrations greater than 0.20 µg/L were collected on May 30 (0.28 µg/L) and June 27 (0.27 µg/L).

DISCUSSION

It has been recognized that groundwater discharge and water quality in a given basin can be affected by many factors, such as precipitation volume and pattern, groundwater storage, and

Table 15. Monthly summary of atrazine discharged for the Turkey River at Garber; WY 1995.

	1994 Oct	Nov	Dec	1995 Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep
Flow-weighted mean atrazine concentration, in µg/L	0.17	0.13	0.11	0.12	0.12	0.13	0.12	0.75	1.62	0.59	0.17	0.12
Mean of atrazine analyses, in µg/L	0.18	0.11	0.12	0.12	0.14	0.10	0.12	2.4	1.4	0.18	0.16	0.11
Total monthly atrazine output, lbs	23.8	14.7	13.9	9.1	7.8	30.1	50.2	238	351	76.9	18.5	8.0
Total monthly atrazine output, kg	10.8	6.7	6.3	4.1	3.6	13.6	22.7	108	159	34.9	8.4	3.6

biotic/abiotic degradation. For the Big Spring basin, previous studies have shown that precipitation volumes and patterns have varied significantly through the years (e.g., Rowden et al., 1995a, b). Following WY 1993, the second-wettest year since WY 1982, WYs 1994 and 1995 were relatively dry. Precipitation was 30.42 inches for WY 1994 and 29.28 inches for WY 1995 (Table 1), and these totals were 92% and 89% of the normal annual precipitation of 32.97 inches, respectively. As a result, the two-year period became the second-driest period after the driest period of WYs 1988 and 1989 since the monitoring project started. Because most precipitation during WYs 1994 and 1995 occurred in growing seasons with high evapotranspiration rate, most rainfall events did not result in significant runoff in the basin except in mid-April of 1995. Snowmelt in the early spring played a major role in generating discharge events at Big Spring in February and early March for both WYs 1994 and 1995.

Although WYs 1994 and 1995 were relatively dry, annual groundwater discharges from Big Spring were near the annual average, 31,897 ac-ft, for the period of record. Annual discharges at Big spring for WYs 1994 and 1995 were not only greater than the annual discharges of the driest WYs 1988 and 1989, but also greater than the annual discharges for WYs 1985, 1986, 1987, and 1990, when the annual precipitation totals were significantly greater than those of WYs 1994 and 1995 (Fig. 12). Water years 1994 and 1995 were not the only years that the volumes of annual discharge from Big Spring did not coincide with the volumes of annual precipitation within the basin. Water Year 1990, for example, had 37.87 inches of rainfall, which was 115% of normal precipitation, but the annual groundwater discharge from Big Spring, 17,476 ac-ft, accounted for only 55% of the annual average. The driest WY 1988 had an annual precipitation of 22.94 inches, but the annual discharge at Big Spring for this water year was 26,008 ac-ft. The discharge/precipitation ratio was also relatively high during WYs 1994 and 1995. Discharge as a percentage of precipitation was 18.7% in the Big Spring basin for both WYs 1994 and 1995. This represented the fifth greatest discharge/precipitation ratio since WY 1983. Previous studies have indicated that the non-linear relationship between recharge-discharge rates is, in part, the result of antecedent conditions. Because WYs 1990 through 1993 were very wet, groundwater stored in the

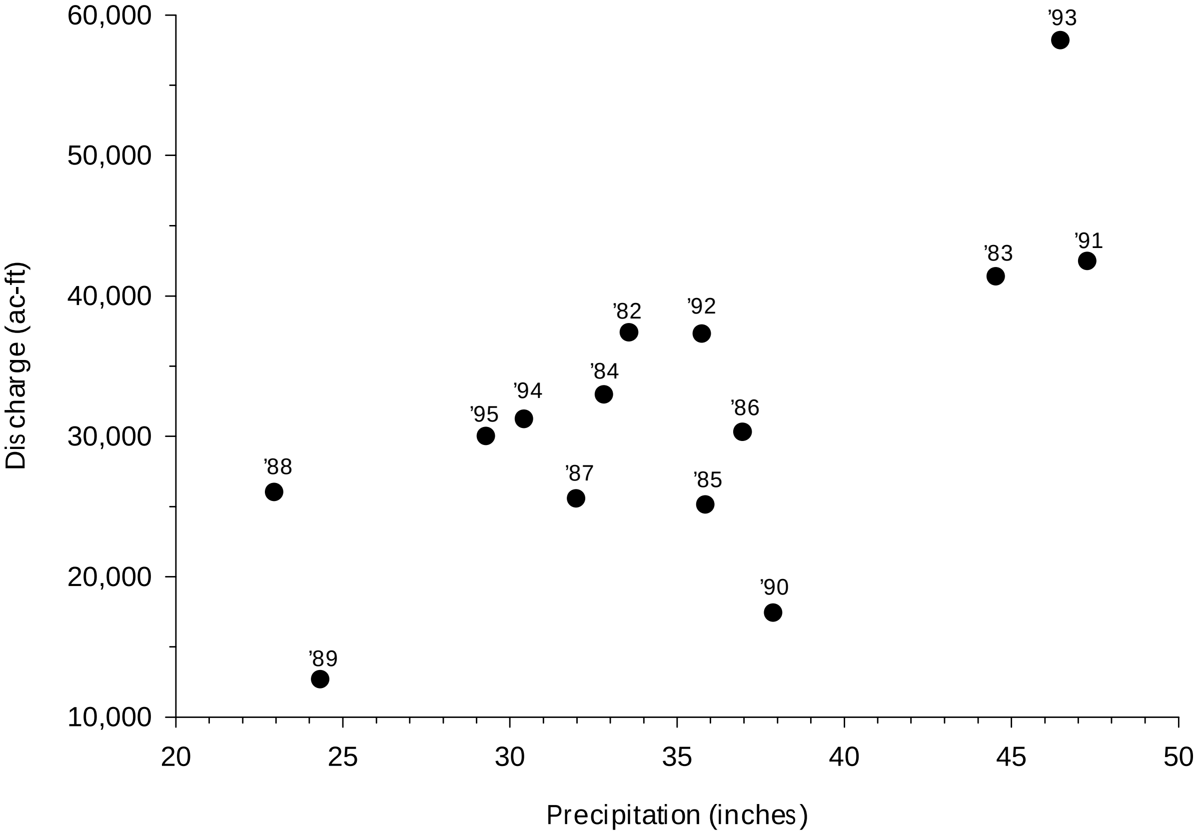


Figure 12. Annual basin precipitation versus annual groundwater discharge from Big Spring.

basin during this wet period may have provided a significant discharge source during the relatively dry WYs 1994 and 1995. Therefore, besides the timing, intensity, and distribution of rainfall, the recharge-discharge rates are also affected by soil moisture conditions within the basin.

Variations of precipitation and groundwater discharge affect water quality. Figure 13 and tables 16 through 18 summarize the annual precipitation, groundwater discharge, and the concentrations and loads of nitrate and atrazine for the Big Spring basin from WY 1982 through 1995. The annual nitrate-N load was 888,518 pounds for WY 1994 and 822,569 pounds for WY 1995. These annual loads are significantly lower than the highest annual nitrate-N load, 1,796,013 pounds, recorded in WY 1993 (Rowden et al., 1995b). The annual fw mean nitrate concentrations were 47.0 mg/L (10.4 mg/L as NO_3-N) for WY 1994 and 45.3 mg/L (10.1 mg/L as NO_3-N) for WY 1995. The highest annual fw mean nitrate concentration in Big Spring groundwater, 56.4 mg/L (12.5 mg/L as NO_3-N), was observed in WY 1991 (Rowden et al., 1993a). Since then, nitrate concentrations have continued to decline at Big Spring.

Previous computations of total nitrogen discharged from Big Spring included nitrate-, ammonia-, and organic-nitrogen. The nitrate-nitrogen usually accounted for more than 90% of total-nitrogen load in the Big Spring basin. Table 16 summarizes annual loads of nitrate-, ammonia-, and organic-nitrogen in the Big Spring basin from WY 1986 through 1994. Prior to WY 1986, ammonia-N and organic-N were not analyzed frequently enough to calculate their annual loads. Due to budget constraints, organic-N was omitted from the analysis list in WY 1995. The nitrogen analyses show that the total annual ammonia-N discharged from Big Spring groundwater varied between 3.6 thousand pounds and 32.9 thousand pounds, with an average of 11.5 thousand pounds. Water Year 1995 had the smallest annual ammonia-N load, at 3.6 thousand pounds. The annual loads for organic-N varied from 5.9 thousand pounds to 106.4 thousand pounds, with an average of 40.4 thousand pounds. Water Year 1994 had the smallest organic-N load, at 5.9 thousand pounds, which accounted for the lowest organic-N component, 0.65%, of the annual total-N load. The annual nitrate-N load has had a very wide range, from 195.3 thousand pounds in WY 1989 to 1.8 million pounds in WY 1993. The annual nitrate-N load was 888.5 thousand pounds for WY 1994, and 822.6 thousand pounds for WY 1995, which were close to the average annual nitrate-N load of 884.7 thousand pounds. Total-N (nitrate-, ammonia-, plus organic-N) load varied between 242.7 thousand pounds in WY 1989 and 1.9 million pounds in WY 1993, with an average of 944.3 thousand pounds. The total-N load was 911.1 thousand pounds in WY 1994. For WY 1995, the total nitrate-N and ammonia-N loads were 826.2 thousand pounds. If the 40.4 thousand pounds of average annual organic-N load were added, the total-N load for WY 1995 would still be less than the average of 944.3 thousand pounds.

From WY 1989 through 1993, the annual groundwater discharge at Big Spring continued to increase. The increased volume of discharge may have leached out the nitrate that likely accumulated in the soil during the preceding years. In addition, the changes in practices of basin farmers brought about by the Big Spring and the Northeast Iowa Demonstration projects have helped reduce nitrogen application rates from 174 lbs-N/acre in 1981 to 115 lbs-N/acre in 1993. The gradual reduction of nitrogen fertilizer applications within the basin is probably also a factor influencing the regional water quality. However, this factor cannot be separated, at this time, from the variations in concentrations that annual differences in recharge rates have caused. Previous studies (e.g., Hallberg et al., 1983, 1984a, 1989; Libra et al., 1986, 1987, 1991; Rowden et al., 1993a, 1995b) have shown that the nitrate concentrations and loads from Big Spring groundwater are related to recharge/dis-

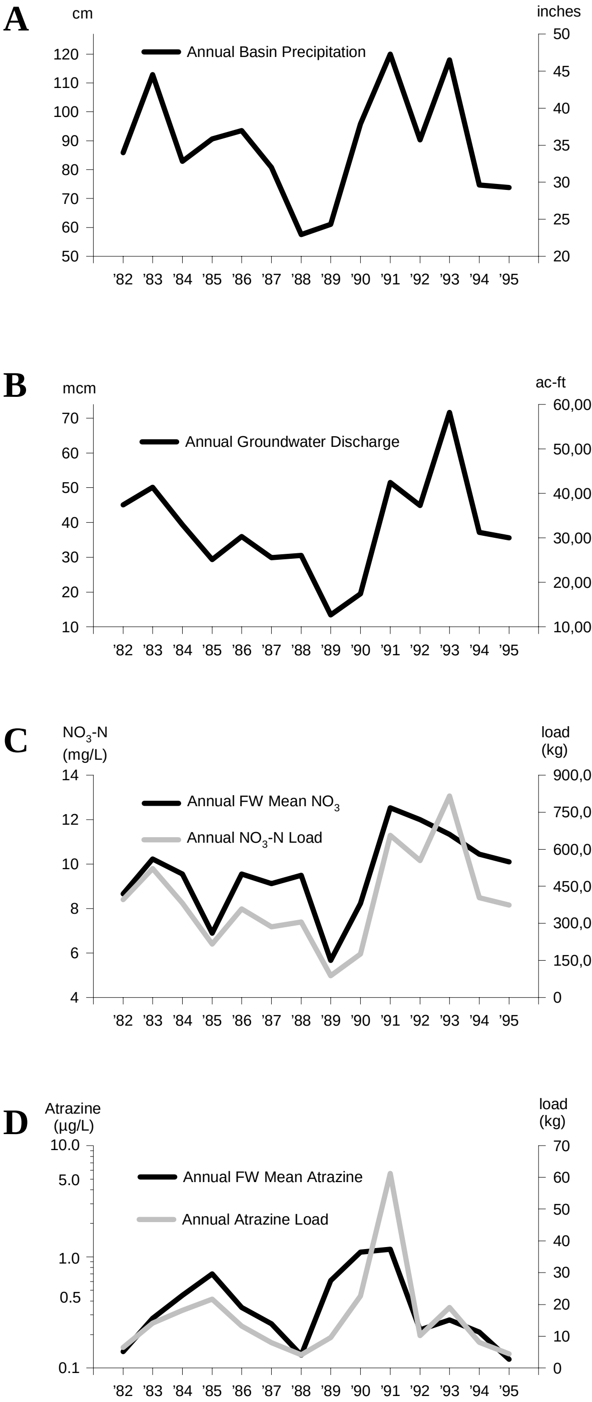


Figure 13. Summary of annual A) basin precipitation, B) groundwater discharge, C) flow-weighted mean NO_3 concentrations and NO_3-N loads, and D) atrazine concentrations and loads from Big Spring groundwater.

Table 16. Water year summary data for nitrogen discharged from the Big Spring basin to the Turkey River.

	Water Year										
	86	87	88	89	90	91	92	93	94	95	Average
Flow-weighted mean concentration, mg/L:											
as nitrate (NO_3)	43	41	43	25	37	56	54	51	47	45	44.2
as nitrate-N (NO_3-N)	9.7	9.1	9.5	5.7	8.2	12.5	12	11.4	10.4	10.1	9.86
ammonia-N	0.1	0.1	0.1	0.6	0.1	0.1	0.1	0.2	0.2	0.04	0.16
organic-N	0.5	0.2	0.3	0.8	0.6	0.9	0.3	0.6	0.1	***	0.48**
Nitrogen load:											
total-N (1,000 lbs)	837.9	651.6	699.4	242.7	420.3	1,561.5	1,257.4	1,916.8	911.1	826.2***	944.3**
as nitrate-N (1,000 lbs)	788.6	630.7	670.9	195.3	388.5	1,445.5	1,220.1	1,796.0	888.5	822.6	884.7
% of total-N	94.1	96.8	95.9	80.5	92.4	92.6	97.0	93.7	97.5	99.6***	93.4**
as ammonia-N (1,000 lbs)	6.4	7.5	8.2	19.3	5.5	9.5	5.2	32.9	16.7	3.6	11.5
% of total-N	0.76	1.14	1.17	7.95	1.30	0.61	0.42	1.72	1.83	0.44	1.88**
as organic-N (1,000 lbs)	42.9	13.4	20.3	28.0	26.4	106.4	32.1	87.9	5.9	***	40.4**
% of total-N	5.12	2.05	2.91	11.55	6.27	6.82	2.55	4.59	0.65	***	4.72**

* Prior to WY 1986 ammonia-N and organic-N were not analyzed frequently enough to calculate annual flow-weighted means.

** Does not include WY 1995 data.

*** Organic-N was not analyzed for WY 1995.

charge mechanisms. In general, low discharge periods are accompanied by low concentrations, yielding small total loads. Concentrations are generally higher during periods of greater discharge, yielding greater loads. This relationship works well for total-N loads as well as for the major nitrogen component nitrate-N, but ammonia-N and organic-N do not seem to show the relationship. Water Year 1989 had the smallest groundwater discharge at Big Spring, but ammonia- and organic-N accounted for the highest component percentages, 7.95% and 11.55%, of the total-N, respectively, during the WY 1986-1995 period.

Of the common pesticides, atrazine was the most frequently detected in the Big Spring basin. Flow-weighted mean atrazine concentrations and loads reached record highs, 1.17 μg/L and 135 pounds, in WY 1991 (Rowden et al., 1993a). Since then, atrazine concentrations and loads have gradually declined at Big Spring, and these declines continued in WYs 1994 and 1995. During WY 1995, the annual fw mean atrazine for Big Spring reached its lowest concentration, 0.12 μg/L. The annual atrazine output for WY 1995, 9.8 pounds, was the second-lowest, and only slightly higher than the lowest level (9.2 pounds) recorded in WY 1988 (Libra et al., 1991). Previous reports have recognized that groundwater discharge events are an important factor affecting atrazine concentrations at Big Spring temporarily, which means atrazine concentration peaks usually accompany groundwater discharge events. For longer time periods, however, atrazine concentrations and loads do not seem related to groundwater discharge changes. This was evidenced again by the annual atrazine data from WYs 1994 and 1995. Annual atrazine concentrations and loads were very low during the two water years, while groundwater discharges at Big Spring were higher than annual discharges in the later 1980's .

Rowden and others (1995b) discussed possible factors affecting atrazine concentrations and loads in detail, including regional herbicide applications, sampling timing bias, atrazine in-stream degradation, and antecedent conditions. Extensive educational programs aimed at reducing the inputs of agricultural chemicals should play an important role in the continued reduction of atrazine concentrations and loads in the Big Spring basin. Although it is difficult to obtain accurate estimates of atrazine use within the basin because its application to crops is usually not uniform, farm surveys have shown that atrazine application rates have been reduced from about 2 pounds per acre in the early 1980's to less than 1.5 pounds per acre by 1990 (Rowden et al., 1995b). Sampling times and frequency also affect annual atrazine concentrations and loads. Based on previous studies, high atrazine concentrations usually accompany significant runoff events. Because peak runoff is temporary, atrazine concentrations decrease as discharge recedes. Therefore, accurate atrazine concentrations, as well as accurate annual atrazine loads, are dependent on both scheduled routine samples and specific event samples. The collection of only routine samples may reduce the annual averages of the fw mean atrazine concentrations and loads.

Although many authors have devoted their efforts to the transport and degradation of atrazine, the migration mechanisms of atrazine are not clearly understood. Based on the data from Big Spring, annual atrazine concentrations seem to display patterns on a long time scale. From WY 1982 through 1995, atrazine concentrations and loads at Big Spring showed two low-high-low cycles; these cycles occurred independent of discharge volumes (Fig. 13D). The first low-high-low cycle occurred during WYs 1982-1988, when the annual fw mean atrazine concentration gradually increased from 0.31 µg/L in WY 1982 to 0.70 µg/L in WY 1985, and the annual atrazine load increased from 14.2 pounds to 47.6 pounds. After that, the fw mean atrazine concentration gradually declined to 0.13 µg/L and the annual atrazine load declined to 9.2 pounds in WY 1988. The next low-high-low cycle included WYs 1988-1995. During this period, the fw mean atrazine concentration changed from 0.13 µg/L in WY 1988 to 1.17 µg/L in WY 1991, and the annual atrazine load increased from 9.2 pounds to 135 pounds. The period of WY 1991 to WY 1995 represented a declining trend of the second low-high-low cycle. During this period, the fw mean atrazine concentration decreased from its record high of 1.17 µg/L to a record low of 0.12 µg/L, and the annual atrazine load decreased from 135 pounds in WY 1991 to 9.8 pounds in WY 1995. During this declining period, the atrazine concentration and load were slightly higher in WY 1993 than in WY 1992. This may have resulted from the record high groundwater discharge in WY 1993. In brief, the data from the Big Spring monitoring project show that atrazine concentrations and loads are independent of long-term discharge volumes, but may have periodic accumulating-releasing trends. If the atrazine transport trends represent a pattern, the period for accumulation or release is about 3-4 years, and the low-high-low cycle is about 6-7 years. The mechanism of the transport pattern, however, remains unknown. It is also unclear whether the current low level of atrazine concentrations will continue or increase again in the future.

Rowden and others (1995b) suggested that instream degradation of atrazine is likely a significant factor affecting atrazine concentrations and loads at Big Spring and the Turkey River. Degradation of atrazine has been studied by several authors, and it is recognized that atrazine can be degraded by either biotic or abiotic processes (e.g., Kolpin and Kalkhoff, 1993). The abiotic degradation of atrazine forms an initial degradation product of hydroxy atrazine, while biotic degradation of atrazine produces either desethyl atrazine or desisopropyl atrazine. Kolpin and Kalkhoff (1993) studied the biotic degradation of atrazine along the Roberts Creek in the Big Spring basin. They determined that the two biotic atrazine degradation products were constant or even decreasing downstream. This suggests that abiotic degradation processes may be occurring in the stream. Remaining questions include what the biotic and abiotic degradation rates are, and what the atrazine degradation rate is within the basin.

Pesticide samples collected for the Big Spring project have been analyzed for desethyl atrazine and desisopropyl atrazine since 1993. Rowden and others (1995b) reported that desethyl atrazine was detected more often than desisopropyl atrazine, and that desethyl atrazine and atrazine usually show similar trends in concentration in Big Spring and the Turkey River. These observations are supported by the data collected during WYs 1994 and 1995 (Figs. 6, 11). During these two water years, none of the samples collected from Big Spring or the Turkey River contained detectable concentrations of desisopropyl atrazine, while all of the samples from the Turkey River and about 90% of the samples from Big Spring contained detectable concentrations of desethyl atrazine, and usually at concentrations greater than atrazine. The concentrations of desethyl atrazine were usually higher during May through July for the Turkey River and other surface-water sites. For groundwater of Big Spring and other groundwater monitory sites in the basin, desethyl atrazine concentrations did not show seasonal variations, but varied with discharge fluctuations. This may result from the differences in biotic degradation processes and/or degradation rates between groundwater and surface water. Since high concentrations of desethyl atrazine were detected from both surface water and groundwater in the Big Spring area, desethyl atrazine may also be produced by abiotic degradation.

Desisopropyl atrazine is rarely detected in the basin's hydrologic system. During WYs 1994 and 1995, 160 groundwater samples from Big Spring and farm wells, 172 tile-line samples, and 177 surface-water samples were analyzed for metabolites of atrazine. Of the 172 tile-line samples, only one contained detectable desisopropyl atrazine at a concentration of 0.1 μg/L. Of the 177 surface-water samples, only four samples contained detectable concentrations of desisopropyl atrazine. None of the samples from Big Spring or farm wells contained detectable concentrations of desisopropyl atrazine.

Acetochlor was added to the pesticide analysis list for the Big Spring project in August, 1994. Since then, one, or 1.7% of 58 samples from Big Spring, and two, or 14.3% of 14 samples from the Turkey River, contained detectable acetochlor (≥ 0.1 μg/L). The sample from Big Spring was collected on May 30, 1995, and the two samples from the Turkey River were collected on May 30 and June 27, 1995. Based on these data, it is still too early to reveal the distribution trend of acetochlor.

In brief, the relationship between nitrogen concentrations and loads and groundwater discharges has been well-documented based on monitoring results from the Big Spring project since 1981. However, the concentrations and loads of pesticides, their relationship with groundwater recharge and discharge, their degradation and transport mechanisms, as well as possible factors affecting their concentrations and loads, still remain as questions to be solved in the future.

OVERVIEW OF MONITORING RESULTS FOR WYs 1982 THROUGH 1995

Figure 13 shows the annual precipitation, groundwater discharges, fw mean nitrate concentrations and nitrogen loads, and fw mean atrazine concentrations and loads from WYs 1982 through 1995. The data is summarized in Table 18. Table 17 summarizes the annual percentage of detection and maximum concentrations for pesticides in Big Spring groundwater.

As discussed before, discharge is related to both precipitation amounts and antecedent soil-moisture conditions. From WY 1982 through 1995, the annual precipitation in the Big Spring basin has ranged from 22.94 inches (WY 1988) to 47.28 inches (WY 1991), and annual groundwater discharge has varied from 12,672 ac-ft (WY 1989) to 58,186 ac-ft (WY 1993). Discharge as a percentage of precipitation has ranged from 8% (WY 1990) to 23% (WY 1993) and averaged 16.4%. After the wet period of WYs 1990 through 1993, WYs 1994 and 1995 were relatively dry years in the Big Spring basin. The annual precipitation for WYs 1994 and 1995, 30.42 inches and 29.28 inches, respectively, was only slightly higher than the driest two water years, 1988 and 1989, since the monitoring began. Because of the low precipitation, the annual groundwater discharge from Big Spring declined from 58,186 ac-ft in WY 1993 to 31,266 ac-ft in WY 1994 and to 30,013 ac-ft in WY 1995. The hydrographs show only few significant rainfall-related runoff events. However, discharge as a percentage of precipitation, 18.7%, for both WYs 1994 and 1995, was higher than average.

The annual fw mean nitrate concentrations and total nitrogen loads corresponded with groundwater discharge changes during the monitoring period.

Table 17. Summary of annual % of detections and maximum concentrations for pesticides in groundwater at Big Spring.

	Water Year														
	82	83	84	85	86	87	88	89	90	91	92	93	94	95	
Pesticide common chemical name	% detections maximum concentrations, µg/L														% detections (total record)
Herbicides															
atrazine	100%	100%	100%	100%	99%	100%	75%	88%	100%	100%	100%	94%	94%	75%	95%
	2.50	5.10	10.00	6.10	1.40	0.70	0.40	3.30	8.20	16.00	1.00	2.50	1.30	1.30	
acetochlor	na	na	na	na	na	na	na	na	na	na	na	na	nd	2%	<2%
	na	na	na	na	na	na	na	na	na	na	na	na	nd	0.60	
alachlor	16%	28%	23%	14%	7%	2%	nd	18%	18%	18%	3%	4%	4%	4%	11%
	0.20	0.60	4.00	5.00	0.70	0.10	nd	0.20	0.90	5.50	0.56	1.50	2.10	0.25	
butylate	na	na	na	na	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	0%
	na	na	na	na	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	
cyanazine	32%	26%	21%	15%	3%	5%	3%	31%	35%	13%	5%	8%	2%	4%	14%
	0.70	1.20	1.70	4.60	0.10	0.10	1.00	3.00	0.90	2.60	0.51	1.90	0.14	0.12	
metolachlor	na	4%	17%	4%	4%	nd	nd	6%	8%	4%	2%	6%	10%	6%	5%
	na	0.60	4.50	4.60	0.60	nd	nd	0.20	0.60	2.20	0.17	0.86	2.30	0.38	
metribuzin	na	na	na	1%	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	<1%
	na	na	na	3.60	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	
trifluralin	na	na	na	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	0%
	na	na	na	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	
Insecticides															
fonofos	na	1%	8%	nd	nd	nd	nd	nd	nd	nd	nd	nd	na	na	<1%
	na	0.10	0.30	nd	nd	nd	nd	nd	nd	nd	nd	nd	na	na	

na- not analyzed; nd- not detected

Acetochlor has been an analyte since August, 1994.

The fw mean nitrate concentrations varied from 25.0 mg/L (5.7 mg/L as NO_3-N) in WY 1989 to 56.4 mg/L (12.5 mg/L as NO_3-N) in WY 1991, and the total nitrogen loads varied from 242 thousand pounds (WY 1989) to 1.9 million pounds (WY 1993). From WY 1991, fw mean nitrate concentrations continually decreased at Big Spring. This may be in part related to decreased nitrogen applications following the extensive public education in the basin. Based on data since WY 1986, ammonia-nitrogen loads from Big Spring have varied from 3.6 thousand pounds (WY 1995) to 32.9 thousand pounds (WY 1993) and averaged 11.5 thousand pounds. Organic-nitrogen was removed from the nitrogen analysis list in WY 1995. From WY 1986 to WY 1994, organic-nitrogen loads ranged from 5.9 thousand pounds (WY 1994) to 106.4 thousand pounds (WY 1991) and averaged 40.4 thousand pounds.

Of the common pesticides, atrazine was the

Table 18. Water year summary data for groundwater discharge from the Big Spring basin to the Turkey River.

	Water Year													
	82	83	84	85	86	87	88	89	90	91	92	93	94	95
Precipitation:														
water inches	34.0	44.5	32.8	35.8	36.7	32.0	22.9	24.3	37.9	47.3	35.7	46.5	30.4	29.3
Groundwater discharge (Q) to the Turkey River:														
mean Q, cfs	51.4	56.9	45.3	35.2	42.0	35.4	35.8	17.6	24.1	58.7	51.4	80.4	43.2	41.5
total Q, inches	6.8	7.5	5.9	4.6	5.5	4.6	4.7	2.3	3.2	7.7	6.8	10.6	5.7	5.5
acre-feet, 1000s	37.4	41.4	32.7	25.1	30.3	25.5	26.0	12.7	17.5	42.5	37.3	58.2	31.3	30.0
Nitrogen discharged with groundwater: flow-wtd mean concentration, mg/L														
as nitrate (NO_3)	39	46	43	31	43	41	43	25	37	56	54	51	47	45
as nitrate-N (NO_3-N)	8.8	10.3	9.7	7.0	9.7	9.1	9.5	5.7	8.2	12.5	12	11.4	10.4	10.1
ammonia-N*	*	*	*	*	0.1	0.1	0.1	0.6	0.1	0.1	0.1	0.2	0.2	<0.1
organic-N*	*	*	*	*	0.5	0.2	0.3	0.8	0.6	0.9	0.3	0.6	0.1	**
nitrogen load: (nitrate-N + nitrite-N)														
1,000s lbs-N	873.0	1,150	843.4	476.8	796.8	636.1	672.0	194.9	388.5	1,446	1,220	1,796	888.5	822.6
lbs-N/acre (for total basin area)	13.2	17.4	12.8	7.2	12.1	9.6	10.2	3.0	5.9	21.9	18.5	27.2	13.5	12.5
Atrazine discharged with groundwater: flow-wtd mean concentration,														
atrazine, μg/L	0.31	0.28	0.45	0.70	0.35	0.25	0.13	0.61	1.06	1.17	0.22	0.27	0.21	0.12
atrazine load;														
lbs - atrazine	14.2	31.2	40.0	47.6	29.0	17.6	9.2	21.2	50.0	135.0	22.5	42.0	17.8	9.8

* Prior to WY 1986 ammonia-N and organic-N were not analyzed frequently enough to calculate annual flow-weighted means.

** In WY 1995, organic-N was omitted from analysis list.

most frequently detected, followed by cyanazine, alachlor, and metolachlor. Butylate and trifluralin have never been detected in Big Spring groundwater. Metribuzin detections are rare, and it has not been detected since WY 1986. Acetochlor was added to the analysis list in August of 1994 and was detected in Big Spring groundwater in May and in the Turkey River samples in May and June of 1995.

Atrazine was detected in 95% of Big Spring groundwater samples since monitoring began in WY 1982. Atrazine annual fw mean concentrations have varied between 0.12 µg/L (WY 1995) and 1.17 μg/L (WY 1991), and annual atrazine loads have varied from 9.2 pounds (WY 1988) to 135 pounds (WY 1991). The highest atrazine concentration detected, 16.0 μg/L, was sampled in mid-June, 1991 (Rowden et al., 1993a). Both annual atrazine concentrations and loads declined rapidly from the peaks in WY 1991 to an annual load of 22.5 pounds, with a fw mean concentration of 0.22 μg/L in WY 1992. After small increases in WY 1993, the annual atrazine fw mean concentrations and loads declined again in WY 1994. In WY 1995, the fw mean atrazine concentration reached the lowest level recorded, 0.12 μg/L, and the annual load decreased to 9.8 pounds, which was also close to the smallest annual load, 9.2 pounds, recorded in WY 1988 (Libra, et al., 1991).

Annual fw mean atrazine concentrations and loads, and the frequency and magnitude of detections of other herbicides, do not fluctuate with annual precipitation changes or with groundwater discharge changes. Relatively high annual fw mean atrazine concentrations and loads have occurred with high annual discharges such as WY 1991, and with low annual discharges such as WY 1985. Many factors, including annual application rates and degradation processes, can affect pesticide concentrations and loads. Atrazine transport mechanisms should be studied in greater detail in the future. Based on the monitoring results at Big Spring, atrazine concentrations and loads have increased or declined every 3-4 years, with a low-high-low cycle in 6-7 years. If these trends are influenced by transport and degradation mechanisms, annual atrazine concentrations and loads may increase at Big Spring in the next few years.

SUMMARY

Water years 1994 and 1995 were relatively dry compared to the early 1990's. During the two-year period, snowmelt played an important role in generating runoff events in the Big Spring basin. Following the relatively low precipitation, groundwater discharge, nitrate concentrations, and nitrogen loads all decreased at Big Spring during both water years. The annual mean of analyses concentration for nitrate declined from 54.0 mg/L (12.0 mg/L as NO_3-N) in WY 1993 to 47.3 mg/L (10.5 mg/L as NO_3-N) in WY 1994, and to 44.4 mg/L (9.9 mg/L as NO_3-N) in WY 1995. The fw mean nitrate concentrations for Big Spring groundwater have declined since WY 1991, and the concentrations from WYs 1994 and 1995 represent a continuation of this trend. The fw mean nitrate concentration was 47.0 mg/L (10.4 mg/L as NO_3-N) in WY 1994 and 45.3 mg/L (10.1 mg/L as NO_3-N) in WY 1995. Both the annual mean of analyses and fw mean concentrations for nitrate for WY 1995 represent the lowest levels since WY 1991. The annual nitrate-N load was 888,518 pounds for WY 1994 and 822,569 pounds for WY 1995. Both years represent the first time since WY 1991 that the annual nitrate-N load for Big Spring has been less than one million pounds.

The concentrations and loads of atrazine and other herbicides were also low in Big Spring groundwater and the Turkey River surface water during WYs 1994 and 1995. The annual fw mean atrazine concentration for Big Spring declined to the lowest level to date, 0.12 μg/L, in WY 1995.

A long-term monitoring project is required to detect improvements in water quality at the watershed scale. Factors affecting water quality are multiple and complex, and improvements are gradual. Certain questions related to nonpoint-source contamination, such as atrazine transport and degradation mechanisms, remain to be answered by future studies.

ACKNOWLEDGEMENTS

The Big Spring Basin Demonstration Project of the Iowa Department of Natural Resources (IDNR) has been supported in part through the Groundwater Protection Act and the Petroleum Violation Escrow accounts, and other sponsoring agencies: the U.S. Department of Agriculture; Natural Resources Conservation Service; the U.S. Environmental Protection Agency, Region VII, Kansas City, Nonpoint Source Programs; the Iowa State University Extension Service; and the University of Iowa Hygienic Laboratory.

Other demonstration projects within the basin have been supported through special cost-share funds provided by the U.S. Department of Agriculture-Farm Services Agency (USDA-FSA) and the Iowa Department of Agriculture and Land Stewardship. The USDA-Natural Resources Conservation Service (NRCS) provides technical assistance in implementing soil and water conservation practices used by the farmers. Thanks to Dave Gibney, District Conservationist, USDA-NRCS, Clayton County, and Frank Phippen, USDA-FSA, Clayton County. The Iowa State University (ISU) Extension Service provides special consultation and assistance to farmers in planning and applying improved nutrient and pesticide management. John Rodecap, Kevin Kuhn, and Nick Rolling with the Northeast Iowa Demonstration Project, and Jim Hosch from the Clayton County Extension Service, work very hard to maintain local coordination. Special thanks go to Roger Koster who retired from the Clayton County Extension Service, Charles Wittman, Northeast Iowa Demonstration Project (NEIDP), and Kathie Bentley who left the NEIDP.

The development of monitoring sites within the Big Spring basin has been a cooperative effort. The USGS, Water Resources Division designed, constructed and maintains the stream gaging stations and also cooperates in water-quality monitoring. Tile monitoring sites and a surface-water flume site were designed and constructed by Dr. James Baker, Department of Agricultural Engineering, ISU, Agriculture and Home Economics Experiment Station. Other cooperating agencies include the departments of Agronomy and Botany, ISU, and the University of Iowa Hygienic Laboratory.

Individuals who were instrumental in maintaining the coordination of inter-agency activities include: Dr. Gerald Miller, ISU, Extension Service; Julie Elfving, U.S. Environmental Protection Agency; Rick Kelley, Nancy Hall, and Lynn Hudachek, University of Iowa Hygienic Laboratory; Dan Lindquist and James Gulliford, Division of Soil Conservation, Iowa Department of Agriculture and Land Stewardship; Ubbo Agena, IDNR; and Roger Link and Lyle Asell, USDA-NRCS.

Special thanks go to Dr. George Hallberg, University of Iowa Hygienic Laboratory, for his many years of efforts in the design, establishment, and research of the Big Spring Basin Demonstration Project.

A number of Geological Survey Bureau staff have been involved with the Big Spring Demonstration Project at one time or another. Much of the information contained in this report is a result of their combined efforts. John Littke made significant contributions to the monitoring network design and made improvements at many of the monitoring sites. John

Schmidt developed the programming used to operate and maintain the Big Spring data base. Many thanks to the Hydrogeology and Environmental Studies Section staff for doing field work in a variety of climatic conditions. Pat Lohmann provided assistance with graphic arts and formatting of this report. Thanks also to Lynette Seigley for proofreading this report and part of the field sampling and to E. Arthur Bettis III for reviewing this report.

Many thanks to Jerry Spykerman and his staff at the IDNR Big Spring Fish Hatchery for allowing us access to their facilities over the years.

The farmers and families living in the Big Spring study area have been instrumental in the demonstration projects. They have often been the key workers in many of the demonstrations, and hopefully are the main benefactors of improvements in farm management. The level of support, hospitality, and enthusiasm provided by the local residents has been unparalleled. Many thanks to the families that have allowed us to install and access monitoring sites on their property.

Huaibao Liu extends his special thanks to Robert Rowden, Robert Libra, and John Schmidt for their assistance in familiarizing him to the Big Spring project, field facilities, and Big Spring database.

There have been a very large number of people who have contributed to this project over the years. Many thanks to all of those who have helped.

REFERENCES

Baker, J.L., and Johnson, H.P., 1981, Nitrate-nitrogen in tile drainage as affected by fertilization: Jour. Environ. Qual., v. 10, p. 519-522.

Capel, P.D., 1990, Atmospheric deposition of herbicides in the mid-continental United States (abs): Eos, Trans. AGU, v. 71, no. 43, p. 1329.

Goolsby, D.A., Thurman, E.M., Pomes, M.L., and Majure, J.J., 1990, Herbicides in atmospheric wet deposition-preliminary results: National Atmospheric Deposition Program Technical Committee Meeting Abstracts of Papers, NADP/NTN Coordination Office, Colorado State University, Fort Collins, CO, p. 7.

Hallberg, G.R., Hoyer, B.E., Bettis, E.A., III, and Libra, R.D., 1983, Hydrogeology, water quality, and land management in the Big Spring basin, Clayton County, Iowa: Iowa Geological Survey, Open File Report 83-3, 191 p.

Hallberg, G.R., Libra, R.D., Bettis, E.A. III, and Hoyer, B.E., 1984a, Hydrologic and water-quality investigations in the Big Spring basin, Clayton County, Iowa: 1983 Water-Year: Iowa Geological Survey, Open File Report 84-4, 231 p.

Hallberg, G.R., Prior, J.C., and Bettis, E.A., III, 1984b, Geologic overview of the Paleozoic Plateau Region of northeastern Iowa: Proceedings Iowa Academy of Science v. 91, p. 3-11.

Hallberg, G.R., Libra, R.D., and Hoyer, B.E., 1985, Nonpoint source contamination of groundwater in karst-carbonate aquifers in Iowa, *in* Perspectives on Nonpoint Source Pollution: Washington, D.C., United States Environmental Protection Agency, Environmental Protection Agency 440/5 85-001, p. 109-114.

Hallberg, G.R., Libra, R.D., Long, K.R., and Splinter, R.C., 1987, Pesticides, groundwater, and rural drinking water quality in Iowa, *in* Pesticides and Groundwater: A Health Concern for the Midwest: Navarre, MN, The Freshwater Foundation and the USEPA, p. 83-104.

Hallberg, G.R., Libra, R.D., Quade, D.J., Littke, J., and Nations, B., 1989, Groundwater monitoring in the Big Spring basin 1984-1987: a summary review: Iowa Department of Natural Resources, Geological Survey Bureau, Technical Information Series 16, 68 p.

Hallberg, G.R., Libra, R.D., Zhi-jun Liu, Rowden, R.D., and Rex, K.D., 1993, Watershed-scale water-quality response to changes in landuse and nitrogen management: Proceedings, Agricultural Research to Protect Water Quality, Soil and Water Conservation Society, Ankeny, IA, p. 80-84.

Kalkhoff, S.J., 1989, Hydrologic data for the Big Spring Basin, Clayton County, Iowa, Water Year 1988: U.S. Geological Survey Open-File Report 89-230, 44 p.

Kalkhoff, S.J., and Kuzniar, R.L., 1991, Hydrologic data for the Big Spring Basin, Clayton County, Iowa, Water Year 1989: U.S. Geological Survey Open-File Report 91-63, 66 p.

Kalkhoff, S.J., and Kuzniar, R.L., 1994, Hydrologic data for the Big Spring Basin, Clayton County, Iowa, Water Year 1991: U.S. Geological Survey Open-File Report 94-56, 87 p.

Kalkhoff, S.J., Kuzniar, R.L., Kolpin, D.L., and Harvey, C.A., 1992, Hydrologic data for the Big Spring

Basin, Clayton County, Iowa, Water Year 1990: U.S. Geological Survey Open-File Report 92-67, 80 p.

Kalkhoff, S.J., and Schaap, B.D., 1996, Agricultural chemicals in ground and surface water in a small watershed in Claton County, Iowa, 1988-91: U.S. Geological Survey Water-Resources Investigation Report 95-4158, 38 p.

Kolpin, D.W., and Kalkhoff, S.J., 1993, Atrazine degradation in a small stream in Iowa: Environmental Science and Technology, v. 27, no. 1, p. 134-139.

Libra, R.D., Hallberg, G.R., Ressmeyer, G.R., and Hoyer, B.E., 1984, Groundwater quality and hydrogeology of Devonian-Carbonate aquifers in Floyd and Mitchell Counties, Iowa: Iowa Geological Survey, Open File Report 84-2, 106 p.

Libra, R.D., Hallberg, G.R., Hoyer, B.E., and Johnson, L.G., 1986, Agricultural impacts on groundwater quality: the Big Spring Basin study *in* Agricultural Impacts on Ground Water: National Water Well Association, Worthington, OH, p. 253-273.

Libra, R.D., Hallberg, G.R., and Hoyer, B.E., 1987, Impacts of agricultural chemicals on groundwater quality in Iowa, *in* Fairchild, D.M. (ed.): Ground Water Quality and Agricultural Practices, Chelsea, MI, Lewis Publ. Inc., p. 185-217.

Libra, R.D., Hallberg, G.R., Littke, J.P., Nations, B.K., Quade, D.J., and Rowden, R.D., 1991, Groundwater monitoring in the Big Spring basin 1988-1989: a summary review: Iowa Department of Natural Resources, Geological Survey Bureau, Technical Information Series 21, 29 p.

Libra, R.D., Hallberg, G.R., Rowden, R.D., Bettis, E.A., III, Kalkhoff, S.J., and Baker, D.G., 1992, Environmental geology of the Big Spring groundwater basin, northeast Iowa: Iowa Department of Natural Resources, Geological Survey Bureau, Guidebook Series no. 15, 51 p.

Littke, J.P., and Hallberg, G.R., 1991, Big Spring basin water-quality monitoring program; design and implementation: Iowa Department of Natural Resources, Geological Survey Bureau, Open-File Report 91-1, 19 p.

May, J.E., Sneck-Fahrer, D., Gorman, J.G., Goodrich, R.D., Nations, B.K., and Miller, V.E., 1995, Water resources data, Iowa, Water Year 1994: U.S. Geological Survey Water-Data Report IA-94-1, 370 p.

May, J.E., Gorman, J.G., Goodrich, R.D., Bobier, M.W., and Miller, V.E., 1996, Water resources data, Iowa, Water Year 1995: U.S. Geological Survey Water-Data Report IA-95-1, 387 p.

Nations, B.K., 1990, Pesticides in Iowa precipitation: National Atmospheric Deposition Program Technical Committee Meeting Abstracts of Papers, NADP/NTN Coordination Office, Colorado State University, Fort Collins, CO, p. 7.

Nations, B.K., and Hallberg, G.R., 1992, Pesticides in Iowa precipitation: Journal of Environmental Quality, v. 21, no. 3, July-September, p. 486-492.

Prior, J.C., 1991, Landforms of Iowa: University of Iowa Press, Iowa City, IA, 153 p.

Rowden, R.D., 1995, Temporal trends in groundwater quality of the Big Spring basin 1982-1994: Proceedings, 40th Annual Midwest Ground Water Conference, Abstracts of Papers, October 16-18, 1995, Columbia, MO, p. 50.

Rowden, R.D., and Libra, R.D., 1990, Hydrogeologic observations from bedrock monitoring well nests in the Big Spring basin: Iowa Department of Natural Resources, Geological Survey Bureau, Open-File Report 90-1, 27 p.

Rowden, R.D., Libra, R.D., Hallberg, G.R., and Nations, B.K., 1993a, Groundwater monitoring in the Big Spring basin 1990-1991: a summary review: Iowa Department of Natural Resources, Geological Survey Bureau, Technical Information Series 27, 36 p.

Rowden, R.D., Hallberg, G.R. and Libra, R.D., 1993b, Temporal trends in groundwater quality of the Big Spring basin 1982-1992: Proceedings, 38th Annual Midwest Ground Water Conference, Abstracts of Papers, October 6-8, 1993 Champaign, IL, p. 23.

Rowden, R.D., Libra, R.D., and Hallberg, G.R., 1995a, Surface water monitoring in the Big Spring basin 1986-1992: a summary review: Iowa Department of Natural Resources, Geological Survey Bureau, Technical Information Series 33, 109 p.

Rowden, R.D., Libra, R.D., Hallberg, G.R., and Nations, B.K., 1995b, Groundwater monitoring in the Big Spring basin 1992-1993: a summary review: Iowa Department of Natural Resources, Geological Survey Bureau, Technical Information Series 34, 43 p.

Rowden, R.D., and Libra, R.D., 1996, Groundwater quality and agriculture: results from the Big Spring basin: Proceedings, Agriculture and Environment; Building Local Partnerships, January 16-18, 1996 Ames, IA, p. 5-39 to 5-50.

Seigley, L.S., Hallberg, G.R., Rowden, R.D., Libra, R.D., Giglierano, J.D., Quade, D.J., and Mann, K. 1993, Agricultural landuse and nitrate cycling in surface water in northeast Iowa: Proceedings, Agricultural Research to Protect Water Quality, Soil and Water Conservation Society, Ankeny, IA, p. 85-88.