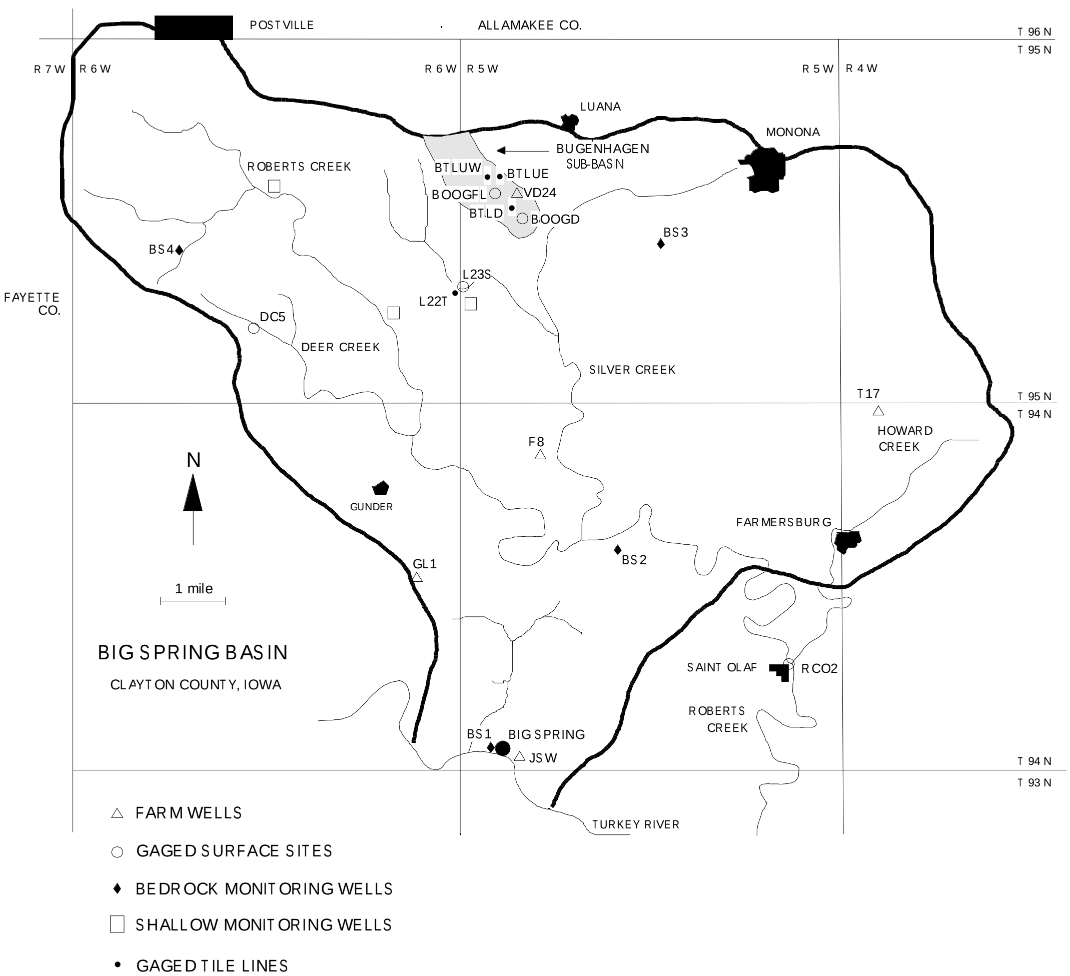
# GROUNDWATER MONITORING in the BIG SPRING BASIN 1992-1993: A Summary Review

**Geological Survey Bureau**
**Technical Information Series 34**




**Iowa Department of Natural Resources**
**Larry J. Wilson, Director**
**May 1995**

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A Report of The Big Spring Basin Demonstration Project

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# GROUNDWATER MONITORING in the BIG SPRING BASIN 1992-1993: A Summary Review

**Iowa Department of Natural Resources, Geological Survey Bureau**
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## ABSTRACT

The Big Spring basin is a 103 $mi^2$ groundwater basin in Clayton County, Iowa. Precipitation, groundwater discharge, and the concentrations and loads of various 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) 1992 and 1993. The cumulative annual discharge, and discharge as a percentage of precipitation during WYs 1992 and 1993 were the greatest recorded since monitoring began at Big Spring. While annual precipitation totals were similar to totals during WYs 1990 and 1991, annual discharge varied significantly. Antecedent conditions, including the volume of groundwater in storage within the basin, and increased groundwater levels and soil moisture, were factors causing greater recharge-discharge rates during WYs 1992 and 1993. Water years 1990 and 1991 followed the driest consecutive two-year period in the state's history, but WYs 1990 and 1991 were the two wettest consecutive years since monitoring began at Big Spring, providing very different antecedent conditions for WYs 1992 and 1993. Precipitation totals for the basin were 37.87 inches in WY 1990, 47.27 inches in WY 1991, 35.74 inches in WY 1992, and 46.47 inches in WY 1993. The WY 1992 and WY 1993 totals were 108% and 141% of the long-term average precipitation of 32.97 inches. The increased precipitation generated both runoff and infiltration recharge. Groundwater discharge from the basin to the Turkey River totaled 17,500 acre-feet (ac-ft) in WY 1990, 42,500 ac-ft in WY 1991, 37,278 ac-ft in WY 1992, and 58,186 ac-ft in WY 1993, which was the highest annual discharge measured during the WY 1982 through WY 1993 period of record at Big Spring. Discharge rates generally increased across the period, with a minimum monthly average of 31 cfs occurring in October 1991 and a maximum monthly average of 137 cfs in July 1993. Annual discharge of the Turkey River at Garber was 631,900 and 1,103,000 ac-ft, for WYs 1990 and 1991, and 1,101,000 and 2,103,000 ac-ft for WYs 1992 and 1993. Annual discharge from the Turkey River during WYs 1992 and 1993 was equivalent to 159% and 295% of the long-term average.

The annual flow-weighted (fw) mean nitrate concentration at Big Spring decreased from 56 mg/L in WY 1991, which was the highest recorded during the period of record, to 54 mg/L in WY 1992 and 51 mg/L in WY 1993. The total load of nitrate-nitrogen discharged by the groundwater system increased from 388,500 pounds in WY 1990 to 1,445,500 pounds in WY 1991, then decreased to 1,220,099 pounds in WY 1992. The annual nitrate-nitrogen discharge during WY 1993, 1,796,013 pounds, was the highest recorded since monitoring began at Big Spring. Nitrate concentrations were relatively stable across the period, remaining between 35 and 70 mg/L during WY 1992 and 15 and 70 mg/L during WY 1993. For the Turkey River, fw mean nitrate concentrations were 41 mg/L and 26 mg/L in WYs 1992 and 1993,

respectively. Total nitrate-nitrogen discharged by the river was about 27.2 million pounds in WY 1992 and 32.4 million pounds in WY 1993.

Atrazine is the most consistently detected herbicide in Big Spring groundwater. It was detected in all samples analyzed for pesticides during WY 1992, and in 96% of the samples analyzed in WY 1993. The WY 1991 annual fw mean atrazine concentration of 1.17 µg/L and annual atrazine load of 135 pounds were the greatest recorded during the period of monitoring at Big Spring. During WY 1992 the annual fw mean atrazine concentration and load decreased to 0.22 µg/L and 22.5 pounds, and during WY 1993 the fw mean and load increased to 0.27 µg/L and 42.0 pounds. Alachlor, cyanazine, and metolachlor were also detected at Big Spring and the Turkey River during the growing seasons of WYs 1992 and 1993. Significant decreases in annual fw mean atrazine concentrations and loads also occurred at the Turkey River from WY 1991 to WY 1992. The Turkey River discharged about 3,330 pounds of atrazine at a fw mean concentration of 1.11 µg/L during WY 1991, and about 739 pounds of atrazine at a fw mean concentration of 0.25 µg/L in WY 1992. During WY 1993 the annual fw mean atrazine concentration and load increased to 0.59 µg/L and 3,386 pounds.

Analysis of annual data for WYs 1982 through 1993 indicates that while fw mean nitrate concentrations and loads generally parallel changes in discharge, fw mean atrazine concentrations and loads do not. Relatively high concentrations and loads of atrazine have occurred during some years with low groundwater discharge and low concentrations and loads of atrazine have occurred during some years with high groundwater discharge. The climatic variations and resulting hydrologic conditions exhibited in the Big Spring basin during WYs 1982 through 1993 have led to variations in discharge rates and contaminant concentrations and loads ranging by factors from two to ten during the period of record. Extreme climatic variations complicate the interpretation of changes in water quality related to landuse and management changes and illustrate the need for detailed, long-term monitoring of nonpoint-source contamination.

## INTRODUCTION

The groundwater discharge and water quality of the 103 $mi^2$ Big Spring groundwater basin have been monitored continuously at Big Spring since November 1981. The basin is located within the Paleozoic Plateau landform region in Clayton County, northeast Iowa (Hallberg et al., 1984b; Prior, 1991). The bedrock units in the basin are Silurian and Ordovician strata and include the carbonate rocks of the Galena Group and the shales and silty-carbonate rocks of the Maquoketa Formation (Hallberg et al., 1983; Rowden and Libra, 1990). The Galena Group forms the bedrock aquifer that is the main groundwater source in the basin. Big Spring discharges near the base of the Galena aquifer in the valley of the Turkey River.

Landuse within the basin is essentially all agricultural, with no major industrial or urban areas, landfills, commercial feedlots or other point sources to significantly affect groundwater quality. These conditions, along with distribution structures at the Big Spring Fish Hatchery that allow accurate gaging of Big Spring's discharge, afford unambiguous study of the agricultural ecosystem within the basin.

The geographic extent of the groundwater basin was delineated in previous investigations by the Iowa Department of Natural Resources, Geological Survey Bureau and cooperating agencies. Previous reports have documented the magnitude of groundwater contamination related to agricultural practices, identified hydrogeologic settings susceptible to contamination from agricultural use, and provided insights into the mechanisms that deliver agricultural chemicals to groundwater. The hydrologic and water-quality monitoring of Big Spring and the Turkey River for water years (WYs; October 1 through September 30) 1982 through 1991 have been reviewed by Hallberg and others (1983, 1984a, 1985, 1987, 1989), Libra and others (1986, 1987, 1991), and Rowden and others (1993). Data from several monitoring sites within the basin for WYs 1988 through 1990 are presented in Kalkhoff (1989), Rowden and Libra (1990), Kalkhoff and Kuzniar (1991), and Kalkhoff and others (1992). Monitoring data from three surface water sub-basin sites, BOOGD, L23S and RC02, during WYs 1986 through 1992 are presented in Rowden and others (1995). Reviews of rainfall monitoring for pesticides are discussed in Nations (1990), Nations and Hallberg (1992), Goolsby and others (1990), and Capel (1990). The design and implementation of the network of monitoring stations used to quantify changes in water quality in the basin are described in Littke and Hallberg (1991).

This report summarizes the hydrologic and water-quality monitoring data from Big Spring and the Turkey River for WYs 1992 and 1993. Analytical methods and landuse are reviewed in Hallberg and others (1989). The interpretation of data presented in this report requires analyses of data from the network of monitoring sites throughout the basin. The hydrologic and water-quality data from tile lines, wells, and surface-water sites within the Big Spring basin and included sub-basins are being addressed in subsequent reports.

## HYDROLOGIC AND WATER QUALITY MONITORING

The groundwater discharge from the Big Spring basin to the Turkey River is a function of recharge within the basin, and is controlled by the amount, timing, and intensity of precipitation and snowmelt, along with antecedent conditions. These factors exert a major influence on the transport, concentrations, and loads of agriculturally-related contaminants. This section will discuss the monitoring of precipitation, discharge, and water quality at Big Spring, and some aspects of the discharge and water-quality record for the Turkey River. The Turkey River is a high baseflow stream, deriving a significant portion of its discharge from influent groundwater. The data from the Turkey River provides a regional perspective for the hydrologic and water-quality monitoring at Big Spring. All references to the Turkey River, or Turkey River basin, refer to the 1,545 $mi^2$ basin above Garber, Iowa, located about 15 miles downstream from Big Spring. Discharge records for the Turkey River at Garber are continuous since 1933 and are available for all but seven years since WY 1914. Discharge data for the Turkey River and Big Spring were supplied by the U.S. Geological Survey (USGS), Water Resources Division, Iowa City, Iowa.

The Big Spring hydrologic system receives both infiltration and runoff recharge, which have unique chemical signatures (Hallberg et al., 1983, 1984a). These signatures can be tracked through the hydrologic system, from the soil zone beneath individual fields to the basin water outlets (Hallberg et al., 1984a). Infiltration recharge is enriched in nitrate and other chemicals that are mobile in soil, relative to runoff recharge, particularly runoff derived from snowmelt. Runoff recharge has lower concentrations of such compounds, but is enriched in herbicides and other chemicals with low soil mobility. Typically Big Spring yields groundwater delivered through infiltration, but following significant precipitation or snowmelt, sinkholes within the basin may direct surface runoff into the aquifer, mixing it with the groundwater. As this runoff recharge moves through the groundwater system and discharges from Big Spring, relatively low nitrate and high herbicide concentrations occur during peak discharge periods. This is typically followed by higher nitrate and lower herbicide concentrations as the associated infiltration recharge moves through the hydrologic system.

During prolonged recession periods, nitrate and herbicide (particularly atrazine) concentrations generally show a slow, steady decline. This decline likely occurs as an increasing percentage of the discharge is relatively older groundwater from the less transmissive parts of the flow system (Hallberg et al., 1984a). In general, low discharge periods are accompanied by low contaminant concentrations, yielding small total contaminant loads. Concentrations are generally higher during periods of higher discharge, yielding greater loads, related to both the increased volume of water and greater concentrations.

The Big Spring basin monitoring network is designed in a nested fashion, allowing water and chemical responses to recharge events to be tracked through the hydrologic system, from the soil zone beneath individual fields to the basin water outlets (Hallberg et al., 1984a). The design also allows integration and comparison of water-quality responses at different scales to assess effects of landuse and landscape-ecosystem processes. Infiltrating recharge water from individual field sites delivers high concentrations of nitrate to shallow groundwater, and this shallow groundwater transports the nitrate laterally to streams and downward to the Galena aquifer and Big Spring. Although the discharge and chemical responses are not as great or immediate at the largest scales monitored, they clearly occur and the nested monitoring design allows the pulse to be followed back through the hydrologic system. The water quality of the Big Spring and Turkey River basins is an integration of the management practices on all of the individual parcels of land they contain.

## Precipitation

Precipitation data for WYs 1982-1988 were calculated using data from the Elkader, Waukon, and Fayette 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). Beginning in WY 1985, this data has also been used to calculate basin precipitation. 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 were calculated with data from the two USGS stations and the NADP station at the hatchery. Precipitation data for WY 1993 were calculated with data from the Elkader, Waukon, and Fayette weather stations. Precipitation for the Turkey River drainage basin, which includes a larger area, is estimated using averages for the state's northeast climatic division (IDALS, SCO). The mean annual WY precipitation for the basin area is 32.97 inches, and references to normal precipitation are based on the period 1951-1980.

Monthly precipitation and departures from normal for WYs 1982 through 1993 are shown in Figure 1, and are tabulated for WYs 1992 and 1993 in Table 1. The twelve-year period of record was

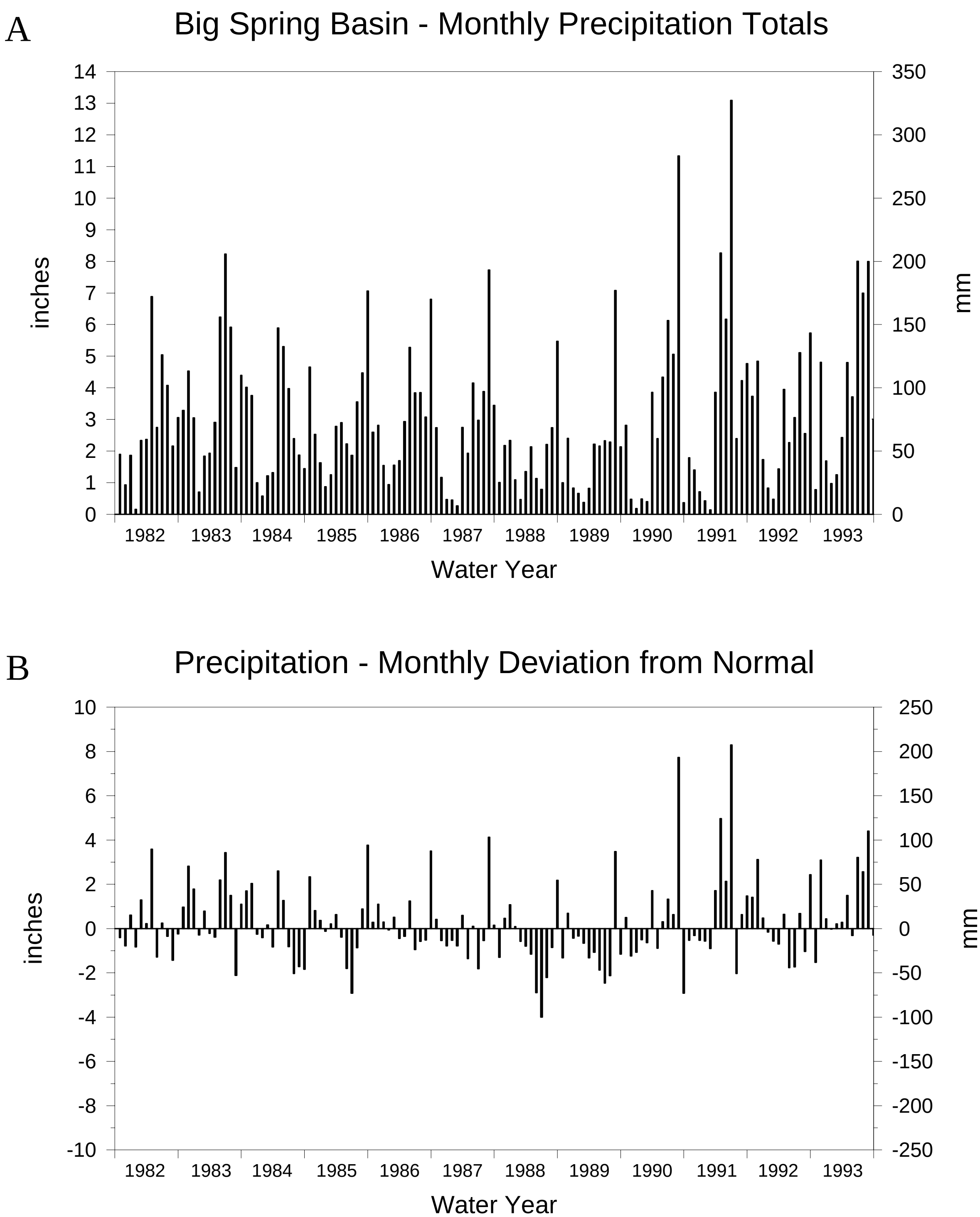


**Figure 1**. A) Monthly precipitation totals and B) departure from normal for the Big Spring basin, WYs 1982-1993 (Iowa Dept. of Ag. and Land Stewardship, State Climatology Office).

**Table 1.** Monthly precipitation and departure from normal; Big Spring basin, water years 1992-1993.

| Water Year 1992 | Basin precip inches | Departure from normal inches | % of normal | Water Year 1993 | Basin precip inches | Departure from normal inches | % of normal |
|---|---|---|---|---|---|---|---|
| Oct-91 | 3.73 | 1.41 | 161 | Oct-92 | 0.78 | -1.54 | 34 |
| Nov-91 | 4.84 | 3.12 | 281 | Nov-92 | 4.81 | 3.09 | 280 |
| Dec-91 | 1.73 | 0.47 | 137 | Dec-92 | 1.69 | 0.43 | 134 |
| Jan-92 | 0.84 | -0.16 | 84 | Jan-93 | 0.97 | -0.03 | 97 |
| Feb-92 | 0.48 | -0.57 | 46 | Feb-93 | 1.26 | 0.21 | 120 |
| Mar-92 | 1.44 | -0.71 | 67 | Mar-93 | 2.43 | 0.28 | 113 |
| Apr-92 | 3.95 | 0.65 | 120 | Apr-93 | 4.80 | 1.50 | 145 |
| May-92 | 2.27 | -1.77 | 56 | May-93 | 3.72 | -0.32 | 92 |
| Jun-92 | 3.06 | -1.74 | 64 | Jun-93 | 8.01 | 3.21 | 167 |
| Jul-92 | 5.11 | 0.68 | 115 | Jul-93 | 6.99 | 2.56 | 158 |
| Aug-92 | 2.56 | -1.04 | 71 | Aug-93 | 8.00 | 4.40 | 222 |
| Sep-92 | 5.73 | 2.43 | 174 | Sep-93 | 3.01 | -0.29 | 91 |
| TOTAL | 35.74 | 2.77 | 108 | TOTAL | 46.47 | 13.50 | 141 |

characterized by significant climatic variability. The two driest consecutive years in Iowa's recorded history, WYs 1988 and 1989, preceded the two wettest consecutive water years since the Big Spring project's inception, WYs 1990 and 1991. Above average precipitation continued during WYs 1992 and 1993. Water Year 1993 was characterized by episodes of major flooding across the upper Midwest.

Mean annual precipitation increased from 33.56 inches in WY 1982 to 44.53 inches during WY 1983. Water years 1984, 1985, 1986, and 1987 had annual totals of 32.81, 35.84, 36.96, and 31.98 inches, respectively. Although the annual totals for WYs 1984 through 1987 were near normal, precipitation during June and July of these years was below normal. In general, precipitation amounts were lower than normal during the growing season, and greater than normal during the fall of these years. This trend continued throughout WYs 1988 and 1989. Basin precipitation for WY 1988 was 22.94 inches and for WY 1989, 24.32 inches. These annual totals were 70% and 74% of the long-term normal, respectively.

June has typically been the wettest month in the Big Spring basin (4.80 inches for 1951-1980). However, for WYs 1985-1989, either August or September have been the wettest months (Hallberg et al., 1989, Libra et al., 1991). Previous reports (Hallberg et al., 1983, 1984a, 1989, Libra et al., 1991) have indicated that the March through June period has typically been marked by low evapotranspiration and wet antecedent conditions, which are important for groundwater recharge. Precipitation during these months was below normal during WYs 1984 through 1987, and far below normal during WYs 1988 and 1989.

While there was timely precipitation for crops in WYs 1986 and 1987, the timing and intensity of rainfall was such that almost no runoff occurred, and recharge of any kind was limited following snowmelt in March of WY 1986. Baseflow conditions prevailed for nearly 18 months, depleting groundwater storage in the Galena aquifer during WYs 1987 through 1989.

Precipitation patterns began changing during the spring of WY 1990. Annual precipitation was 37.87 inches or 4.9 inches above the long-term average. Monthly precipitation was above normal from May through August. The wettest months during WY 1990 were August and June, and the driest months were December and September. The two largest single rainfall events during WY 1990 occurred on August 24 (1.82 inches) and 25 (1.74

inches). The events were relatively widespread and caused extensive flooding throughout the Turkey River valley.

Water Year 1991 had the greatest mean annual precipitation during WYs 1982-1993. Precipitation for the water year was 47.28 inches or 143% of the long-term average. Rainfall totals were slightly below normal from October through February, far below normal during July, and far above average from March through June. The greatest monthly accumulation of precipitation occurred in June, and the largest single rainfall event (local reports of 11 to 13 inches in the northern portion of the basin) occurred on June 14, causing flash flooding throughout the Big Spring study area.

The annual precipitation for WY 1992 was 35.74 inches, or 2.77 inches above the long-term average (Table 1). Precipitation during the water year was more evenly distributed than during WYs 1990 and 1991, with no large single rainfall or flooding events. Rainfall amounts were well above average at the beginning of the water year in October and November, and also near the end of the water year in September. Precipitation was below normal from January through March, and again in May, June and August. The driest month was February (0.48 inches) and the wettest month was September (5.73 inches).

Water Year 1993 had the second-greatest annual precipitation during the WY 1982-1993 period of record at Big Spring. The mean annual precipitation was 46.47 inches or 141% of the long-term average. Rainfall totals were below normal during October, January, May, and September, and well above normal in November, and from June through August. Approximately half of the annual precipitation occurred during the June through August period. October was the driest month of the water year, with 0.78 inches of precipitation, and June and August were the wettest months, with 8.01 and 8.00 inches of precipitation, respectively.

The change in the distribution patterns of precipitation from WYs 1988 and 1989 to WYs 1992 and 1993 was rather dramatic. WYs 1985 through 1989 were characterized by dry growing seasons and wet falls. During WYs 1990 and 1991 rainfall totals were below normal from October through February, and above normal from March through September. Water Year 1992 had a very dry growing season, and WY 1993 had a relatively wet growing season. The timing, intensity, and distribution of rainfall, along with antecedent conditions, all affect the resultant recharge to the soil-groundwater system, and the concentrations of agricultural contaminants transported by surface water and groundwater.

## Water Year 1992

### *Discharge Monitoring*

Tables 2 through 8 and Figures 2 through 5 summarize the discharge, climatic, water quality, and chemical loading data for Big Spring and the Turkey River at Garber during WY 1992.

Groundwater discharge from the Big Spring basin was 37,287 acre-feet (ac-ft), at an average daily discharge rate of 51.4 cubic feet per second (cfs). The annual discharge was equivalent to about 19% of the annual precipitation (Table 2). The annual discharge for the Turkey River was about 1,101,000 ac-ft, at an average daily discharge rate of 1,517 cfs (Table 3). Surface-water discharge accounted for about 37% of the annual precipitation, and was equal to about 108% of the long-term average annual discharge.

Figure 2 shows the discharge hydrograph and water temperature for Big Spring, along with daily basin precipitation and maximum/minimum air temperatures from the Elkader weather observation station. Snowmelt events are indicated by sharp drops in Big Spring water temperature. Periods when discharge rapidly increases and then rapidly decreases are the result of significant surface-water runoff recharge to sinkholes. This runoff occurs in small (<2 $mi^2$, with most <1 $mi^2$), generally ephemeral headwater drainage basins, and is short-term in nature. After such events, the discharge often remains at higher levels than previous to the event, and then very slowly decreases. This sustained increase in discharge indicates that significant infiltration occurred, delivering influent water to the more transmissive parts of the groundwater system, such as conduits or solutionally enlarged fractures

**Table 2.** Annual summary of groundwater and chemical discharge from the Big Spring basin to the Turkey River for Water Year 1992. (Discharge data are from the U.S. Geological Survey, Water Resources Division.)

| | | |
|---|---|---|
| **DISCHARGE** | | |
| **Total** | | |
| acre-feet | 37,278 | |
| millions cf | 1,624 | |
| millions cm | 46.0 | |
| **Average** | | |
| cfs | 51.4 | |
| cms | 1.45 | |
| mg/d | 33.2 | |
| gpm | 23,068 | |
| **PRECIPITATION AND DISCHARGE** | | |
| Precipitation | 35.74 inches (908 mm) | |
| Discharge | 6.79 inches (172 mm) | |
| Discharge as % of precipitation | 19% | |
| **NITRATE DISCHARGE** | | |
| **Concentration - mg/L** | **As $NO_3$** | **As $NO_3$-N** |
| Flow-weighted mean | 54.2 | 12.0 |
| Mean of analyses | 53.7 | 11.9 |
| | **$NO_3$-N output** | **Total N output** |
| lbs - N | 1,220,099 | 1,257,410 |
| kg - N | 553,333 | 570,254 |
| lbs - N/acre | 18.5 | 19.1 |
| **ATRAZINE DISCHARGE** | | |
| **Concentration - µg/L** | | |
| Flow-weighted mean | 0.22 | |
| Mean of analyses | 0.22 | |
| **Total output** | | |
| lbs | 22.5 | |
| kg | 10.2 | |

or bedding planes (Hallberg et al., 1989). During prolonged periods with insignificant recharge, the discharge from Big Spring consists of water from the less transmissive parts of the hydrologic system. This type of discharge is expressed on the hydrograph as long, nearly flat lines, indicating a very gradual decline in flow rates. Figure 3 shows the discharge hydrograph for Big Spring, along with plots of nitrate and atrazine concentrations for WY 1992.

The hydrograph shows discharge generally increasing through mid-December as above average precipitation during the first three months of the water year generated both runoff- and infiltration recharge. The largest single rainfall event occurred in early November. Mean daily discharge increased from 24 cfs to 109 cfs from early October through mid-December. From December, discharge generally decreased through mid February. The largest runoff event of the water year occurred on April 21, and was associated with snowmelt. Daily discharge receded from 246 cfs to pre-event levels of about 40 cfs by the end of May. During the remainder of the water year a number of minor precipitation events occurred, but had little effect on the slowly declining flow rates. Mean daily discharge receded from 39 cfs in late May to 23 cfs in late August. Discharge increased to 63 cfs in mid-September following the second largest single precipitation event of the water year, then receded to 37 cfs near the end of the water year.

Table 4 summarizes the discharge data for Big Spring on a monthly basis. The greatest monthly discharge, 4,674 ac-ft, occurred in December at an average daily rate of 76 cfs. The smallest monthly discharge, 1,892 ac-ft, occurred during October at an average rate of 31 cfs. Monthly discharge remained above 2,300 ac-ft during all other months except August. For the Turkey River at Garber, December and August were the highest- and lowest-flow months, with 171,800 ac-ft of surface water discharged, at an average daily discharge rate of 2,794 cfs in December, and 16,593 ac-ft discharged at an average daily rate of 535 cfs in August.

### *Nitrate Monitoring*

Tables 2 and 5 summarize the nitrate monitoring at Big Spring for WY 1992. During the water year, 116 samples were analyzed for nitrate and 64 samples were analyzed for the full nitrogen series (N-series; nitrate- plus ammonia- and organic-N). The flow-weighted (fw) mean nitrate concentration (mean concentration per unit volume of discharge) for the water year was 54.2 mg/L (12.0 mg/L as $NO_3$-N). A total of 1.26 million pounds of nitrogen (nitrate- plus ammonia-, and organic-N) were discharged by groundwater from the basin during the water year; of this total, 1.22 million pounds, or 97% of the nitrogen discharged, were in the form of nitrate.

Figure 3 shows the discharge hydrograph and a plot of nitrate concentrations for Big Spring during WY 1992. During October, both discharge and nitrate concentrations remained relatively low. Beginning in late October, precipitation events generated infiltration recharge, and nitrate concentrations increased in early November and remained relatively high during the remainder of the water year. Nitrate concentrations increased from 42 mg/L (9.3 mg/L as $NO_3$-N) in late October to 67 mg/L (14.9 mg/L as $NO_3$-N) in early November as discharge receded from the first significant discharge event of the water year. Concentrations declined during a small event later in November, then increased to the greatest concentration sampled during the water year, 69 mg/L (15.3 mg/L as $NO_3$-N), in mid-December. From December, concentrations generally declined, remaining above 50 mg/L (11.1 mg/L as $NO_3$-N) through mid-February as a number of minor precipitation events provided infiltration recharge and sustained small increases in discharge. During March, nitrate concentrations increased to 53 mg/L (11.8 mg/L as $NO_3$-N), then decreased to the lowest concentration sampled during the water year, 37 mg/L (8.2 mg/L as $NO_3$-N), as discharge generally receded. Nitrate concentrations decreased to 43 mg/L (9.6 mg/L as $NO_3$-N) during a large runoff event in April, then increased to 64 mg/L (14.2 mg/L as $NO_3$-N) five days later. Following the event, discharge and nitrate concentrations both slowly declined through mid-July. During the remainder of the water year, nitrate concentrations remained near 50 mg/L (11.1 mg/L as $NO_3$-N), increasing to 59 mg/L (13.1 mg/L as

**Table 3.** Annual summary of water and chemical discharge for the Turkey River at Garber for Water Year 1992. (Discharge data are from the U.S. Geological Survey, Water Resources Division.)

**DISCHARGE**

| | |
|---|---|
| **Total** | |
| acre-feet | 1,101,000 |
| millions cf | 47,960 |
| millions cm | 1,358 |
| **Average** | |
| cfs | 1,517 |
| cms | 43.0 |
| mg/d | 980 |
| gpm | 680,830 |

**PRECIPITATION AND DISCHARGE**

| | |
|---|---|
| Precipitation | 35.74 inches (908mm) |
| Discharge | 13.37 inches (340mm) |
| Discharge as % of precipitation | 37% |

**NITRATE DISCHARGE**

| Concentration - mg/L | As $NO_3$ | As $NO_3$-N |
|---|---|---|
| Flow-weighted mean | 41.0 | 9.1 |
| Mean of analyses | 41.1 | 9.1 |

| | $NO_3$-N output | Total N output |
|---|---|---|
| lbs - N | 27,244,063 | 29,644,014 |
| kg - N | 12,355,584 | 13,443,997 |
| lbs - N/acre | 27.6 | 30.0 |

**ATRAZINE DISCHARGE**

| | |
|---|---|
| **Concentration - µg/L** | |
| Flow-weighted mean | 0.25 |
| Mean of analyses | 0.27 |
| **Total output** | |
| lbs | 739 |
| kg | 335 |

**Table 4.** Monthly summary of groundwater discharge from the Big Spring basin for Water Year 1992.

| | 1991 Oct | Nov | Dec | 1992 Jan | Feb | Mar | Apr | May | Jun | Jul | Aug | Sep |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **TOTAL MONTHLY DISCHARGE** | | | | | | | | | | | | |
| Acre-feet | 1,892 | 4,537 | 4,674 | 3,306 | 2,645 | 2,759 | 4,663 | 3,443 | 2,451 | 2,337 | 1,915 | 2,656 |
| Cubic feet (millions) | 82 | 198 | 204 | 144 | 115 | 120 | 203 | 150 | 107 | 102 | 83 | 116 |
| Gallons (millions) | 617 | 1,479 | 1,523 | 1,077 | 862 | 899 | 1,520 | 1,122 | 799 | 762 | 624 | 866 |
| Cubic meters (millions) | 2.3 | 5.6 | 5.8 | 4.1 | 3.3 | 3.4 | 5.7 | 4.2 | 3.0 | 2.9 | 2.4 | 3.3 |
| **AVERAGE DISCHARGE** | | | | | | | | | | | | |
| cfs | 31 | 76 | 76 | 54 | 46 | 45 | 78 | 56 | 41 | 38 | 31 | 45 |
| cms | 0.9 | 2.2 | 2.2 | 1.5 | 1.3 | 1.3 | 2.2 | 1.6 | 1.2 | 1.1 | 0.9 | 1.3 |
| mg/d | 20 | 49 | 49 | 35 | 30 | 29 | 51 | 36 | 27 | 25 | 20 | 29 |
| **MAXIMUM** | | | | | | | | | | | | |
| cfs | 40 | 137 | 124 | 106 | 82 | 56 | 280 | 87 | 46 | 47 | 36 | 72 |
| cms | 1.1 | 3.9 | 3.5 | 3.0 | 2.3 | 1.6 | 7.9 | 2.5 | 1.3 | 1.3 | 1.0 | 2.0 |
| **MINIMUM** | | | | | | | | | | | | |
| cfs | 27 | 60 | 56 | 42 | 33 | 38 | 39 | 44 | 38 | 33 | 26 | 27 |
| cms | 0.8 | 1.7 | 1.6 | 1.2 | 0.9 | 1.1 | 1.1 | 1.2 | 1.1 | 0.9 | 0.7 | 0.8 |

**Table 5.** Monthly summary of nitrate-N discharged in groundwater from the Big Spring basin to the Turkey River; Water Year 1992.

| | 1991 Oct | Nov | Dec | 1992 Jan | Feb | Mar | Apr | May | Jun | Jul | Aug | Sep |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Flow weighted mean NO3 concentration, in mg/L; | 44 | 58 | 63 | 55 | 49 | 47 | 52 | 60 | 53 | 50 | 52 | 53 |
| as NO3-N | 9.8 | 13.0 | 14.1 | 12.3 | 10.9 | 10.4 | 11.5 | 13.2 | 11.9 | 11.2 | 11.5 | 11.7 |
| Mean of NO3 analyses, in mg/L; | 44 | 62 | 64 | 56 | 51 | 47 | 53 | 58 | 53 | 51 | 51 | 55 |
| as NO3-N | 9.7 | 13.8 | 14.3 | 12.4 | 11.3 | 10.5 | 11.7 | 12.9 | 11.7 | 11.2 | 11.4 | 12.2 |
| Total monthly NO3-N output, thousands lbs | 51 | 160 | 179 | 111 | 78 | 78 | 146 | 124 | 79 | 71 | 60 | 82 |
| Total monthly NO3-N output, thousands kg | 23 | 73 | 81 | 50 | 36 | 35 | 66 | 56 | 36 | 32 | 27 | 37 |

**Table 6.** Monthly summary of nitrate-N discharged for the Turkey River at Garber; Water Year 1992.

| | 1991 Oct | Nov | Dec | 1992 Jan | Feb | Mar | Apr | May | Jun | Jul | Aug | Sep |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Flow weighted mean NO3 concentration, in mg/L; | 33 | 42 | 50 | 49 | 35 | 36 | 39 | 38 | 42 | 39 | 39 | 36 |
| as NO3-N | 7.3 | 9.4 | 11.1 | 10.9 | 7.8 | 8.0 | 8.7 | 8.4 | 9.3 | 8.7 | 8.7 | 8.0 |
| Mean of NO3 analyses, in mg/L; | 33 | 49 | 51 | 52 | 37 | 39 | 39 | 37 | 42 | 38 | 39 | 37 |
| as NO3-N | 7.2 | 10.8 | 11.4 | 11.5 | 8.1 | 8.6 | 8.6 | 8.2 | 9.4 | 8.5 | 8.7 | 8.2 |
| Total monthly NO3-N output, thousands lbs | 745 | 3,469 | 5,913 | 2,472 | 1,801 | 2,933 | 4,026 | 2,009 | 1,279 | 1,265 | 777 | 1,275 |
| Total monthly NO3-N output, thousands kg | 338 | 1,573 | 2,355 | 1,121 | 817 | 1,330 | 1,826 | 911 | 580 | 574 | 353 | 578 |

**Table 7.** Monthly summary of atrazine discharged in groundwater from the Big Spring basin to the Turkey River; Water Year 1992.

| | 1991 Oct | Nov | Dec | 1992 Jan | Feb | Mar | Apr | May | Jun | Jul | Aug | Sep |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Flow-weighted mean atrazine concentration, in µg/L | 0.21 | 0.30 | 0.22 | 0.19 | 0.19 | 0.16 | 0.17 | 0.25 | 0.29 | 0.30 | 0.20 | 0.18 |
| Mean of atrazine analyses, in µg/L | 0.21 | 0.31 | 0.21 | 0.17 | 0.18 | 0.16 | 0.15 | 0.25 | 0.32 | 0.29 | 0.20 | 0.18 |
| Total monthly atrazine output, lbs | 1.1 | 3.8 | 2.8 | 1.7 | 1.4 | 1.2 | 2.1 | 2.3 | 1.9 | 1.9 | 1.1 | 1.3 |
| Total monthly atrazine output, grams | 491 | 1,700 | 1,281 | 763 | 633 | 534 | 952 | 1,059 | 878 | 860 | 481 | 580 |

**Table 8.** Monthly summary of atrazine discharged for the Turkey River at Garber; Water Year 1992.

| | 1991 Oct | Nov | Dec | 1992 Jan | Feb | Mar | Apr | May | Jun | Jul | Aug | Sep |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Flow-weighted mean atrazine concentration, in µg/L | 0.29 | 0.31 | 0.23 | 0.18 | 0.22 | 0.17 | 0.21 | 0.18 | 0.31 | 0.51 | 0.30 | 0.32 |
| Mean of atrazine analyses, in µg/L | 0.39 | 0.22 | 0.17 | 0.21 | 0.21 | 0.12 | 0.17 | 0.28 | 0.43 | 0.66 | 0.20 | 0.21 |
| Total monthly atrazine output, lbs | 29.1 | 114 | 106 | 41.9 | 50.8 | 62.5 | 96.5 | 42.9 | 43.0 | 74.2 | 27.0 | 51.1 |
| Total monthly atrazine output, kg | 13.2 | 51.6 | 48.3 | 19.0 | 23.1 | 28.4 | 43.8 | 19.4 | 19.5 | 33.7 | 12.2 | 23.2 |

$NO_3$-N) in late September as discharge receded from a small event earlier in the month. Comparison of the nitrate plot with the hydrograph shows peaks in nitrate concentrations closely following peaks in discharge. In addition, both discharge rates and nitrate concentrations showed increases during November and December, as relatively nitrate-rich groundwater recharged the aquifer. From late April through June, discharge rates and nitrate concentrations showed slow, steady declines as an increasing percentage of the discharge was being supplied by the less transmissive areas of the basin's hydrologic system.

Previous monitoring of both surface water and groundwater in the Big Spring basin has shown that often during peak discharge events, much of the discharge is composed of runoff, containing low concentrations of nitrate-nitrogen and relatively high concentrations of pesticides, particularly atrazine (Hallberg et al., 1983, 1984a, 1985, 1987, 1989). Following peak discharge, as the percentage of infiltration recharge comprising the discharge increases, the nitrate-nitrogen concentration generally increases, then again decreases as the discharge continues to recede. The concentrations of pesticides and products associated with soils (sediment) and runoff, such as organic-nitrogen and ammonium-nitrogen, and insoluble products such as potassium, phosphate and iron generally increase during peak runoff and decrease as discharge recedes. During prolonged recession periods, both nitrate and pesticide concentrations generally show a slow, steady decline.

Table 5 summarizes fw mean nitrate concentrations and nitrate-N loads for Big Spring on a monthly basis for WY 1992. The highest monthly fw mean, 63 mg/L (14.1 mg/L as $NO_3$-N), and greatest monthly N-load, about 179,000 pounds, occurred in December. The lowest monthly fw mean, 44 mg/L (9.8 mg/L as $NO_3$-N), and smallest N-load, 51,000 pounds, occurred during October. December accounted for 12.5% of the annual groundwater discharge and 14.7% of the annual nitrate-N load. Monthly fw mean nitrate concentrations exceeded the 45 mg/L (10 mg/L as $NO_3$-N) drinking water standard for nitrate during all months except October. The monthly fw mean nitrate concentration for December, 63 mg/L (14.1 mg/L as $NO_3$-N), was the third-highest recorded at Big Spring during WYs 1983-1993. The highest

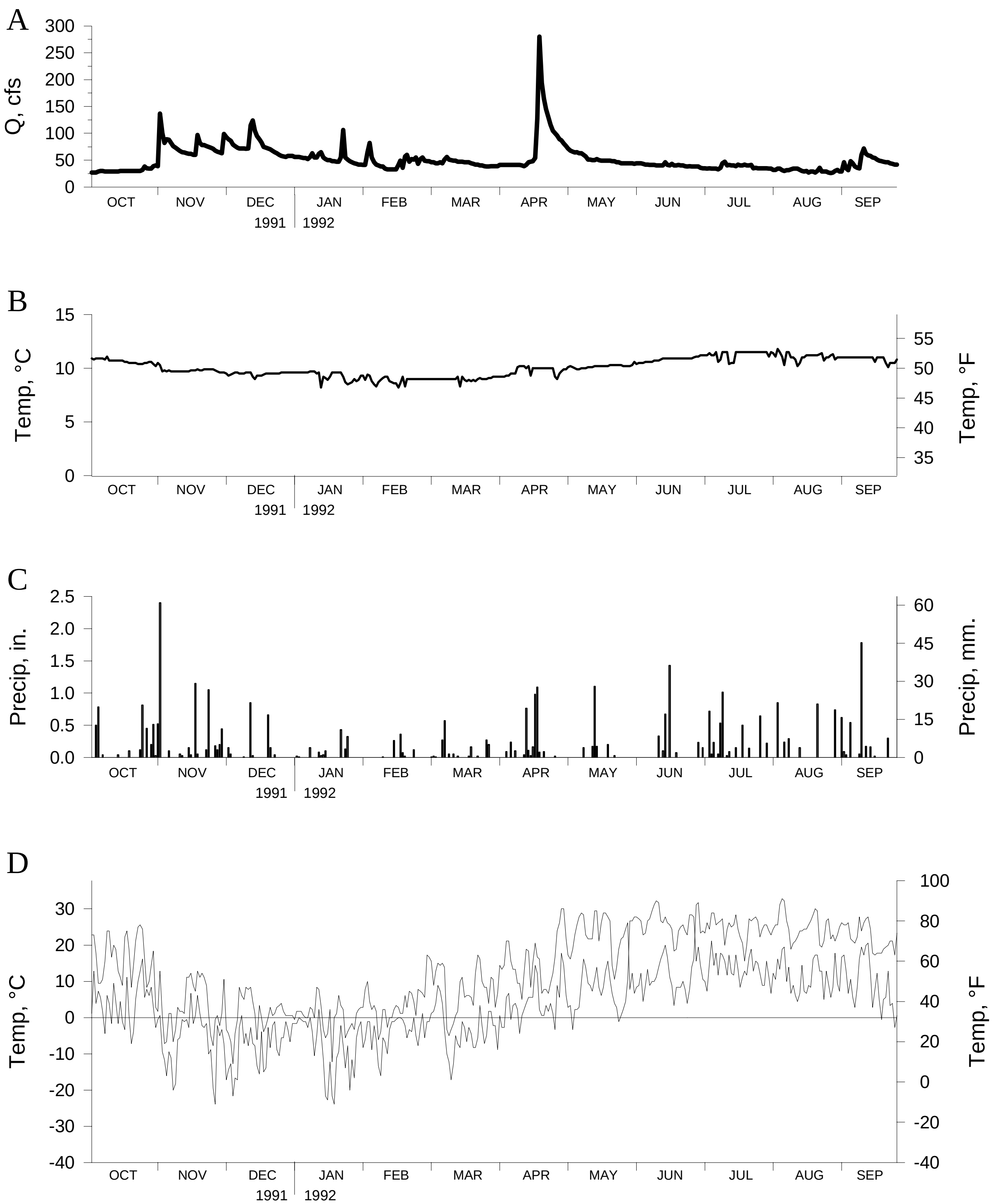


**Figure 2**. A) Groundwater discharge, B) groundwater temperature and C) daily precipitation for the Big Spring basin; and D) maximum-minimum temperatures for Elkader, IA (Iowa Dept. of Ag. and Land Stewardship, State Climatology Office), for WY 1992.

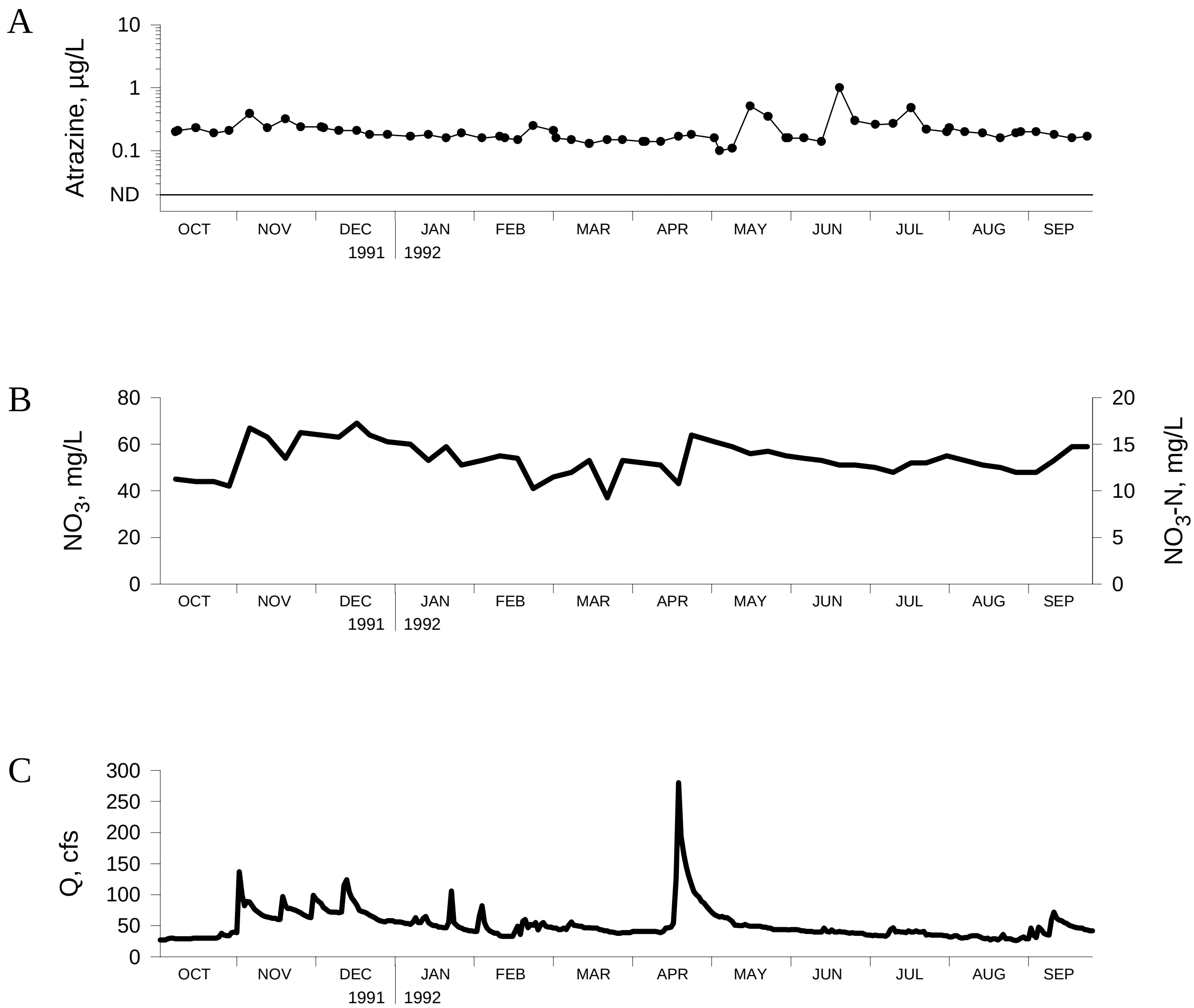


**Figure 3**. A) Atrazine and B) nitrate concentrations; and C) groundwater discharge at Big Spring for WY 1992.

monthly fw mean nitrate concentrations previously recorded were 70 mg/L (15.5 mg/L as $NO_3$-N) in April, 64 mg/L (14.1 mg/L as $NO_3$-N) in May, and 64 mg/L (14.2 mg/L as $NO_3$-N) in June of WY 1991 (Rowden et al., 1993).

Figure 4 and Tables 3 and 6 summarize nitrate concentrations and loads for the Turkey River basin for WY 1992. During the water year, 64 samples were analyzed for nitrate, and 12 samples were analyzed for the full nitrogen series (nitrate- plus ammonia- and organic-N). A total of 29.6 million pounds of nitrogen were discharged by the Turkey River during the water year; of this total, about 27.2 million pounds, or 92% of the nitrogen discharged, were in the form of nitrate. The annual fw mean nitrate concentration for WY 1992, 41.0 mg/L (9.1 mg/L as $NO_3$-N), was the second-greatest recorded during WYs 1984-1992 at the Turkey River. The greatest annual fw mean nitrate concentration during the period, 44.4 mg/L (9.9 mg/L as $NO_3$-N), occurred in WY 1991 (Rowden et al., 1993).

Comparison of the hydrographs and nitrate plots for Big Spring and the Turkey River shows similar seasonal trends in both discharge and nitrate

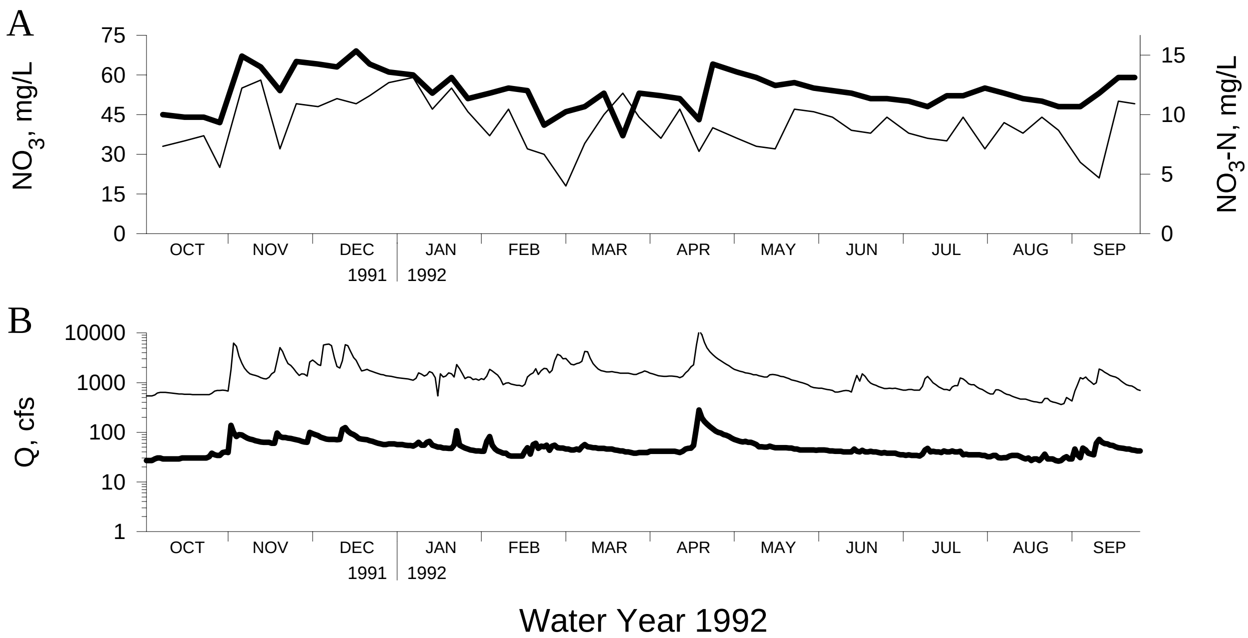


**Figure 4**. A) Nitrate concentrations and B) discharge hydrographs for Big Spring (bold lines) and the Turkey River (lighter lines) at Garber for WY 1992. (Turkey River discharge data are from the U.S. Geological Survey, W.R.D., IA Dist.)

concentrations. Differences in detail occur because of the size difference between the systems, the larger proportion of surface runoff water in the Turkey River, in-stream processes that affect surface water, and the greater frequency of sampling at Big Spring.

Nitrate concentrations from the Turkey River generally increased from the beginning of the water year through December. Concentrations were diluted during minor runoff events in late October and mid-November. Nitrate concentrations peaked at 59 mg/L (13.1 mg/L as $NO_3$-N) in early January, then declined to the lowest concentration sampled during the water year, 18 mg/L (4.0 mg/L as $NO_3$-N), in early March following minor runoff. Later in March, concentrations increased to 53 mg/L (11.8 mg/L as $NO_3$-N) as discharge declined, then concentrations generally declined through mid-May. Nitrate concentrations increased to 47 mg/L (10.4 mg/L as $NO_3$-N) near the end of May as the proportion of groundwater baseflow constituting the discharge increased. Precipitation events during the remainder of the water year caused minor fluctuations in both nitrate concentrations and discharge. In September, nitrate concentrations generally decreased during peak discharge events and increased as discharge receded. As with Big Spring, nitrate concentrations from the Turkey River generally increased following infiltration recharge early in the water year, then generally decreased along with discharge during the latter half of the water year.

Monthly fw mean nitrate concentrations and loads from the Turkey River showed trends similar to Big Spring. The highest monthly fw mean, 50 mg/L (11.1 mg/L as $NO_3$-N), and greatest monthly N-load, about 5.9 million pounds, occurred in December (Table 6). The lowest monthly fw mean, 33 mg/L (7.3 mg/L as $NO_3$-N), and smallest N-load, 745,000 pounds, occurred during October. The highest monthly fw mean nitrate concentration previously recorded for the Turkey River, 50 mg/L (11.0 mg/L as $NO_3$-N), occurred in May of WY 1990 (Rowden et al., 1993). December accounted for approximately 15.6% of the annual surface-water discharge and 21.7% of the annual nitrate-N load.

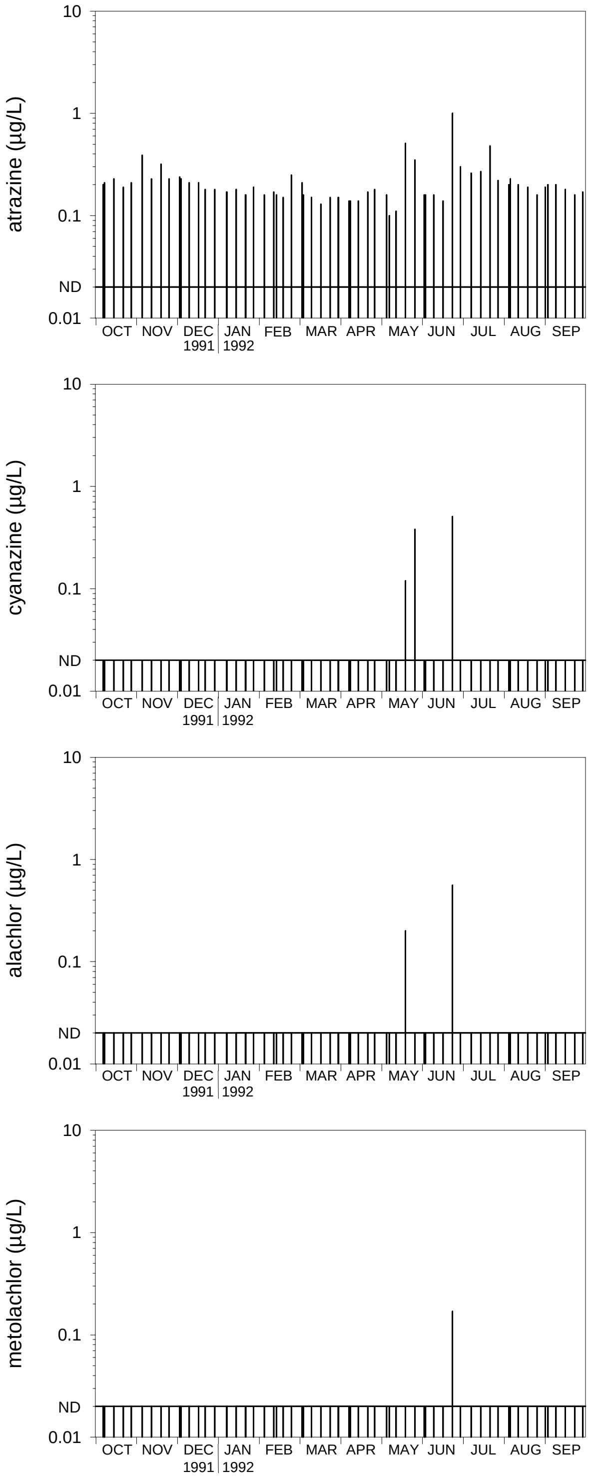


**Figure 5**. Bar graphs of pesticide concentrations at Big Spring for WY 1992. ND represents not detected.

### *Pesticide Monitoring*

Figures 3 and 5 and Tables 2 and 7 summarize the results of pesticide monitoring at Big Spring for WY 1992. Sixty-four samples from Big Spring were analyzed for pesticides. *All* samples contained detectable levels of atrazine (>0.10 µg/L). A total of 22.5 pounds of atrazine were discharged at a fw mean concentration of 0.22 µg/L. This was the fourth-lowest annual atrazine load and the third-lowest annual fw mean atrazine concentration observed during WYs 1982-1993. The lowest annual fw mean atrazine concentration and smallest annual atrazine load, 0.13 µg/L and 9.2 pounds, occurred in WY 1988 (Libra et al., 1991). The highest annual fw mean atrazine concentration and greatest annual atrazine load recorded at Big Spring, 1.17 µg/L and 135 pounds, occurred during WY 1991 (Rowden et al., 1993). Figure 3 shows atrazine concentrations and the discharge hydrograph from Big Spring. Atrazine concentrations were relatively stable during the first seven months of the water year, generally decreasing from 0.39 µg/L in November to the lowest concentration sampled during the water year, 0.10 µg/L, in early May. Increases in atrazine concentrations during May, June and July were associated with runoff recharge following precipitation events. These precipitation events did not substantially increase groundwater discharge, but may have increased the percentage of runoff- versus infiltration recharge composing the discharge. Concentrations increased to 0.51 µg/L later in May, then decreased to 0.14 µg/L in mid-June. The highest atrazine concentration during the water year, 1.00 µg/L, occurred on June 23. Atrazine concentrations decreased to 0.21 µg/L in early July, then increased to 0.48 µg/L later in the month. Concentrations remained above 0.15 µg/L during the remainder of the water year.

Table 7 summarizes fw mean atrazine concentrations and loads on a monthly basis for WY 1992. Monthly fw mean atrazine concentrations and loads were relatively stable, remaining between 0.30 µg/L and 0.16 µg/L during the water year. November had the highest monthly fw mean and load at 0.30 µg/L, and 3.8 pounds. March had the lowest monthly fw mean atrazine concentration at 0.16 µg/

L, and October and August had the lowest monthly atrazine loads at approximately 1.1 pounds.

Figure 5 summarizes detections and concentrations of atrazine, cyanazine, alachlor, and metolachlor for the water year (a list of pesticides that were included in the routine analyses, but not detected at Big Spring are included in Table 16). The occurrence of non-detections of atrazine or other pesticides is indicated by concentration bars ending at "ND." All samples collected contained detectable levels of atrazine (the detection limit for pesticides is usually 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). Three samples, or 4.7% of those collected from Big Spring, contained detectable levels of cyanazine; two, or 3.1% contained detectable levels of alachlor; and one, or 1.6% contained detectable levels of metolachlor. The highest concentration of pesticides detected during the water year included atrazine at 1.00 µg/L; alachlor at 0.56 µg/L; cyanazine at 0.51 µg/L; and metolachlor at 0.17 µg/L. All maximum pesticide detections occurred June 23. Cyanazine and alachlor were detected during May and June, and metolachlor was detected during June only.

Tables 3 and 8 summarize the atrazine data for the Turkey River for WY 1992. During the water year, twelve samples from the Turkey River were analyzed for pesticides. An estimated 739 pounds of atrazine were discharged, at a fw mean concentration of 0.25 µg/L. This was the third-smallest annual atrazine load, and the lowest annual fw mean atrazine concentration observed at the Turkey River during the WY 1986-1993 period of record. As with Big Spring, monthly fw mean atrazine concentrations and loads were relatively stable during the water year. Monthly fw mean concentrations remained above 0.20 µg/L during all months except January, March and May. Monthly concentrations ranged between 0.17 µg/L in March and 0.51 µg/L during July. Atrazine loading was greatest in November (114 pounds) and smallest in August (27 pounds). November accounted for about 15% of the annual atrazine load and about 12% of the annual surface-water discharge. All samples collected from the Turkey River during the water year contained detectable levels of atrazine. The only other pesticide detected during the water year was cyanazine. It was detected in one, or about 8% of the samples collected. The highest concentration of pesticides detected during the water year included atrazine at 0.66 µg/L and cyanazine at 0.21 µg/L. The maximum detection for atrazine occurred July 27 and the only detection of cyanazine occurred May 26.

## Water Year 1993

### *Discharge Monitoring*

Tables 9 through 15 and Figures 6 through 9 summarize the discharge, climatic, water quality, and chemical loading data for Big Spring and the Turkey River for WY 1993. The annual groundwater discharge from the Big Spring basin was 58,186 ac-ft, at an average daily discharge rate of 80.4 cfs. Groundwater discharge was equivalent to about 23% of precipitation during the water year (table 9). The annual discharge and discharge as a percent of precipitation for WY 1993 were the greatest recorded during WYs 1982-1993. The annual precipitation, 46.47 inches, was the second-highest recorded during the twelve-year period. The annual precipitation during WY 1991, 47.28 inches, was slightly higher.

The annual discharge from the Turkey River at Garber was 2,103,000 ac-ft, at an average discharge rate of 2,905 cfs (table 10). Surface-water discharge was equal to about 55% of the annual precipitation, and was approximately three times the long-term average. The annual discharge and discharge as a percent of precipitation for the Turkey River during WY 1993 were the highest recorded during the WY 1913-1993 period of record at Garber.

Figure 6 shows the discharge hydrograph for Big Spring, along with basin precipitation and daily maximum/minimum air temperatures from the Elkader weather observation station for WY 1993. Figure 7 also shows the hydrograph, along with nitrate and atrazine concentrations. Mean daily discharge declined from 41 cfs at the beginning of WY 1993 to 29 cfs in mid-November. Precipitation

**Table 9.** Annual summary of groundwater and chemical discharge from the Big Spring basin to the Turkey River for Water Year 1993. (Discharge data are from the U.S. Geological Survey, Water Resources Division.)

| | | |
|---|---|---|
| **DISCHARGE** | | |
| **Total** | | |
| acre-feet | 58,186 | |
| millions cf | 2,535 | |
| millions cm | 71.7 | |
| **Average** | | |
| cfs | 80.4 | |
| cms | 2.28 | |
| mg/d | 52.0 | |
| gpm | 36,084 | |
| **PRECIPITATION AND DISCHARGE** | | |
| Precipitation | 46.47 inches (1,180 mm) | |
| Discharge | 10.59 inches (269 mm) | |
| Discharge as % of precipitation | 23% | |
| **NITRATE DISCHARGE** | | |
| **Concentration - mg/L** | **As $NO_3$** | **As $NO_3$-N** |
| Flow-weighted mean | 51.1 | 11.4 |
| Mean of analyses | 54.0 | 12.0 |
| | **$NO_3$-N output** | **Total N output** |
| lbs - N | 1,796,013 | 1,916,838 |
| kg - N | 814,518 | 869,314 |
| lbs - N/acre | 27.2 | 29.1 |
| **ATRAZINE DISCHARGE** | | |
| **Concentration - µg/L** | | |
| Flow-weighted mean | 0.27 | |
| Mean of analyses | 0.23 | |
| **Total output** | | |
| lbs | 42.0 | |
| kg | 19.1 | |

in November generated infiltration recharge, and discharge increased to 96 cfs on November 21. Discharge then generally declined to 34 cfs in early March. Later in March, small amounts of rainfall generated minor runoff and infiltration recharge, and snowmelt at the end of the month generated the largest runoff event of WY 1993, and the greatest mean daily discharge observed at Big Spring during the period of record. The peak mean daily discharge for WY 1993, 474 cfs, occurred on March 31. The greatest daily discharge previously recorded was 420 cfs, on June 15 of WY 1991 (Rowden et al., 1993). Numerous precipitation events in April, June, July and August generated significant runoff and infiltration recharge. During May, precipitation was below normal and discharge declined from 190 cfs to 49 cfs in early June. Significant runoff events in late June, mid-July and late August, were followed by quickly receding discharge. From late August, discharge declined to about 60 cfs near the end of the water year. The sustained, general increase in mean daily discharge during the latter half of the water year indicates a net increase in overall storage in the basin's hydrologic system.

Table 11 summarizes discharge data from Big Spring for WY 1993 on a monthly basis. During the water year, all months except October, November and February had monthly discharges exceeding 3,000 ac-ft. The greatest monthly discharge measured at Big Spring during the period of record, 8,436 ac-ft, occurred in July, at an average discharge rate of 137 cfs. Previously, the greatest monthly discharge from Big Spring was 8,413 ac-ft, recorded in June of WY 1990, at an average rate of 141 cfs (Rowden et al., 1993). The groundwater discharge during July of WY 1993 accounted for about 14.5% of the annual total. The smallest monthly discharge from Big Spring during WY 1993, 2,075 ac-ft, occurred in October at an average daily rate of 34 cfs. July and October were also the greatest and smallest discharge months for the Turkey River during WY 1993. In July, 354,900 ac-ft of surface water were discharged at an average daily rate of 5,772 cfs. During October, 33,270 ac-ft of surface water were discharged at an average rate of 541 cfs.

## *Nitrate Monitoring*

During WY 1993, 104 samples of Big Spring groundwater were analyzed for nitrate and 52 samples were analyzed for the full nitrogen series. Table 9 summarizes nitrate and nitrate-nitrogen data for the water year. A total of 1.9 million pounds of nitrogen were discharged by groundwater from the basin. Of this total, 1.8 million pounds, or 94% of the nitrogen discharged, were in the form of nitrate. The flow-weighted mean nitrate concentration for the water year was 51.1 mg/L (11.4 mg/L as $NO_3$-N). The annual nitrate-N discharge for WY 1993 was the greatest documented during the WY 1982 through WY 1993 period of record at Big Spring. The annual fw mean nitrate concentration was the third-greatest during the period of record, following 56.4 mg/L in WY 1991 (Rowden et al., 1993) and 54.2 mg/L in WY 1992.

Figure 7 is a plot of nitrate concentrations at Big Spring for WY 1993. Nitrate concentrations remained above 50 mg/L (11.1 mg/L as $NO_3$-N) during the water year, except during runoff periods in March, April and August. The highest concentration during the water year, 65 mg/L (14.4 mg/L as $NO_3$-N), occurred near the end of November following minor infiltration recharge. Groundwater discharge and nitrate concentrations both generally declined from November through February. During March, concentrations decreased to 31 mg/L (6.9 mg/L as $NO_3$-N) during a minor snowmelt event, then increased to 43 mg/L (9.6 mg/L as $NO_3$-N) one week later. The lowest concentration during the water year, 19 mg/L (4.2 mg/L as $NO_3$-N), occurred during a major snowmelt event. Nitrate concentrations increased to 48 mg/L (10.7 mg/L as $NO_3$-N) in early April as discharge receded from a large runoff event at the end of March. Nitrate concentrations generally increased from April through mid-July. Concentrations decreased to 39 mg/L (8.7 mg/L as $NO_3$-N) following a runoff event in August, then increased to 58 mg/L (12.9 mg/L as $NO_3$-N) as discharge continued to recede. During the remainder of the water year discharge and nitrate concentrations both slowly declined.

Table 12 summarizes the nitrate data for Big Spring during WY 1993 on a monthly basis.

**Table 10.** Annual summary of water and chemical discharge for the Turkey River at Garber for Water Year 1993. (Discharge data are from the U.S. Geological Survey, Water Resources Division.)

| | | |
|---|---|---|
| **DISCHARGE** | | |
| **Total** | | |
| acre-feet | 2,103,000 | |
| millions cf | 91,607 | |
| millions cm | 2,593 | |
| **Average** | | |
| cfs | 2,905 | |
| cms | 82.3 | |
| mg/d | 1,878 | |
| gpm | 1,303,764 | |
| **PRECIPITATION AND DISCHARGE** | | |
| Precipitation | 46.47 inches (1,180mm) | |
| Discharge | 25.53 inches (648mm) | |
| Discharge as % of precipitation | 55% | |
| **NITRATE DISCHARGE** | | |
| **Concentration - mg/L** | **As $NO_3$** | **As $NO_3$-N** |
| Flow-weighted mean | 25.6 | 5.7 |
| Mean of analyses | 31.0 | 6.9 |
| | **$NO_3$-N output** | **Total N output** |
| lbs - N | 32,447,979 | 44,290,241 |
| kg - N | 14,715,637 | 20,086,277 |
| lbs - N/acre | 32.8 | 44.8 |
| **ATRAZINE DISCHARGE** | | |
| **Concentration - µg/L** | | |
| Flow-weighted mean | 0.59 | |
| Mean of analyses | 0.30 | |
| **Total output** | | |
| lbs | 3,386 | |
| kg | 1,535 | |

**Table 11.** Monthly summary of groundwater discharge from the Big Spring basin for Water Year 1993.

| | 1992 Oct | Nov | Dec | 1993 Jan | Feb | Mar | Apr | May | Jun | Jul | Aug | Sep |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **TOTAL MONTHLY DISCHARGE** | | | | | | | | | | | | |
| Acre-feet | 2,075 | 2,633 | 3,614 | 3,146 | 2,143 | 6,851 | 7,991 | 6,145 | 4,845 | 8,436 | 5,723 | 4,583 |
| Cubic feet (millions) | 90 | 115 | 157 | 137 | 93 | 298 | 348 | 268 | 211 | 367 | 249 | 200 |
| Gallons (millions) | 676 | 858 | 1,178 | 1,025 | 698 | 2,233 | 2,604 | 2,003 | 1,579 | 2,749 | 1,865 | 1,494 |
| Cubic meters (millions) | 2.6 | 3.2 | 4.5 | 3.9 | 2.6 | 8.4 | 9.9 | 7.6 | 6.0 | 10.4 | 7.1 | 5.7 |
| **AVERAGE DISCHARGE** | | | | | | | | | | | | |
| cfs | 34 | 44 | 59 | 51 | 39 | 111 | 135 | 100 | 82 | 137 | 93 | 77 |
| cms | 1.0 | 1.2 | 1.7 | 1.4 | 1.1 | 3.1 | 3.8 | 2.8 | 2.3 | 3.9 | 2.6 | 2.2 |
| mg/d | 22 | 28 | 38 | 33 | 25 | 72 | 87 | 65 | 53 | 89 | 60 | 50 |
| **MAXIMUM** | | | | | | | | | | | | |
| cfs | 41 | 96 | 74 | 64 | 44 | 474 | 227 | 190 | 280 | 375 | 215 | 99 |
| cms | 1.2 | 2.7 | 2.1 | 1.8 | 1.2 | 13.4 | 6.4 | 5.4 | 7.9 | 10.6 | 6.1 | 2.8 |
| **MINIMUM** | | | | | | | | | | | | |
| cfs | 27 | 27 | 48 | 43 | 34 | 34 | 91 | 54 | 49 | 88 | 50 | 60 |
| cms | 0.8 | 0.8 | 1.4 | 1.2 | 1.0 | 1.0 | 2.6 | 1.5 | 1.4 | 2.5 | 1.4 | 1.7 |

**Table 12.** Monthly summary of nitrate-N discharged in groundwater from the Big Spring basin to the Turkey River; Water Year 1993.

| | 1992 Oct | Nov | Dec | 1993 Jan | Feb | Mar | Apr | May | Jun | Jul | Aug | Sep |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Flow-weighted mean NO3 concentration, in mg/L; | 53 | 55 | 61 | 58 | 53 | 28 | 49 | 54 | 55 | 56 | 50 | 57 |
| as NO3-N | 11.9 | 12.2 | 13.7 | 13.0 | 11.7 | 6.2 | 10.8 | 12.0 | 12.3 | 12.5 | 11.1 | 12.7 |
| Mean of NO3 analyses, in mg/L; | 53 | 58 | 61 | 58 | 53 | 37 | 53 | 54 | 56 | 60 | 53 | 57 |
| as NO3-N | 11.8 | 12.9 | 13.6 | 12.9 | 11.8 | 8.2 | 11.8 | 12.0 | 12.4 | 13.3 | 11.8 | 12.7 |
| Total monthly NO3-N output, thousands lbs | 67 | 88 | 134 | 111 | 68 | 115 | 236 | 202 | 162 | 288 | 172 | 154 |
| Total monthly NO3-N output, thousands kg | 30 | 40 | 61 | 50 | 31 | 52 | 107 | 91 | 73 | 131 | 78 | 70 |

**Table 13.** Monthly summary of nitrate-N discharge for the Turkey River at Garber; Water Year 1993.

| | 1992 Oct | Nov | Dec | 1993 Jan | Feb | Mar | Apr | May | Jun | Jul | Aug | Sep |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Flow-weighted mean NO3 concentration, in mg/L; | 35 | 35 | 36 | 36 | 36 | 13 | 24 | 30 | 30 | 30 | 16 | 29 |
| as NO3-N | 7.8 | 7.8 | 7.9 | 8.0 | 8.0 | 2.9 | 5.4 | 6.6 | 6.7 | 6.6 | 3.5 | 6.4 |
| Mean of NO3 analyses, in mg/L; | 32 | 41 | 38 | 37 | 36 | 21 | 29 | 29 | 33 | 31 | 19 | 29 |
| as NO3-N | 7.1 | 9.1 | 8.4 | 8.2 | 8.0 | 4.7 | 6.4 | 6.4 | 7.3 | 6.9 | 4.2 | 6.4 |
| Total monthly NO3-N output, thousands lbs | 706 | 1,955 | 1,694 | 990 | 698 | 1,813 | 5,559 | 3,516 | 4,007 | 6,419 | 3,020 | 2,069 |
| Total monthly NO3-N output, thousands kg | 320 | 887 | 768 | 449 | 317 | 822 | 2,521 | 1,595 | 1,817 | 2,911 | 1,370 | 938 |

**Table 14.** Monthly summary of atrazine discharged in groundwater from the Big Spring basin to the Turkey River; Water Year 1993.

| | 1992 Oct | Nov | Dec | 1993 Jan | Feb | Mar | Apr | May | Jun | Jul | Aug | Sep |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Flow-weighted mean atrazine concentration, in µg/L | 0.15 | 0.15 | 0.13 | 0.07 | 0.12 | 0.22 | 0.15 | 0.14 | 0.69 | 0.56 | 0.23 | 0.16 |
| Mean of atrazine analyses, in µg/L | 0.15 | 0.14 | 0.10 | 0.06 | 0.12 | 0.15 | 0.15 | 0.15 | 0.82 | 0.38 | 0.23 | 0.16 |
| Total monthly atrazine output, lbs | 0.9 | 1.1 | 1.3 | 0.6 | 0.7 | 4.2 | 3.3 | 2.4 | 9.1 | 12.9 | 3.6 | 2.0 |
| Total monthly atrazine output, grams | 389 | 489 | 581 | 265 | 324 | 1,885 | 1,487 | 1,096 | 4,119 | 5,868 | 1,647 | 906 |

**Table 15.** Monthly summary of atrazine discharge for the Turkey River at Garber; Water Year 1993.

| | 1992 Oct | Nov | Dec | 1993 Jan | Feb | Mar | Apr | May | Jun | Jul | Aug | Sep |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Flow-weighted mean atrazine concentration, in µg/L | 0.18 | 0.26 | 0.15 | 0.12 | 0.13 | 0.26 | 0.29 | 0.24 | 0.91 | 1.58 | 0.59 | 0.28 |
| Mean of atrazine analyses, in µg/L | 0.16 | 0.17 | 0.12 | 0.13 | 0.11 | 0.25 | 0.15 | 0.17 | 1.10 | 0.66 | 0.28 | 0.28 |
| Total monthly atrazine output, lbs | 16.6 | 64.1 | 32.3 | 15.1 | 11.0 | 160 | 296 | 126 | 545 | 1,524 | 505 | 90.6 |
| Total monthly atrazine output, kg | 7.5 | 29.1 | 14.6 | 6.8 | 5.0 | 72.5 | 134 | 57.4 | 247 | 691 | 229 | 41.1 |

Monthly fw mean nitrate concentrations exceeded the 45 mg/L (10 mg/L as $NO_3$-N) drinking water standard for nitrate during all months except March. The highest monthly fw mean nitrate concentration during the water year, 61 mg/L (13.7 as $NO_3$-N), occurred in December and the lowest monthly fw mean, 28 mg/L (6.2 as $NO_3$-N), occurred in March. Monthly nitrate-N discharge varied from 67,000 pounds in October, the month with the smallest groundwater discharge, to 288,000 pounds in July, the month with the greatest groundwater discharge. July accounted for about 16% of the annual nitrate-N load and about 14.5% of the annual discharge. The monthly nitrate-N discharge for July was the second-greatest recorded during WYs 1983-1993 at Big Spring. The greatest monthly nitrate-N discharge recorded at Big Spring was 326,000 pounds in June of WY 1991 (Rowden et al., 1993).

During WY 1993, 64 samples from the Turkey River were analyzed for nitrate and 12 samples were analyzed for the full nitrogen series. During the water year, a total of 44.3 million pounds of nitrogen were discharged at a fw mean concentration of 25.6 mg/L (5.7 mg/L as $NO_3$-N; Table 10). About 32.4 million pounds, or 73% of the nitrogen discharged, were in the form of nitrate. The annual nitrate-N discharge from the Turkey River for WY 1993 was the highest documented during WYs 1984-1993. Figure 8 shows a plot of nitrate concentrations for the Turkey River and Big Spring; their discharge hydrographs are also shown. Nitrate concentrations from the Turkey River showed the same general trends as Big Spring during the water year. Concentrations peaked at 48 mg/L (10.7 mg/L as $NO_3$-N) in mid-November, then generally declined to 31 mg/L (6.9 mg/L as $NO_3$-N) in mid-February as surface-water discharge generally receded. Nitrate concentrations increased to 47 mg/L (10.4 mg/L as $NO_3$-N) later in February following a slight increase in discharge. Precipitation events in March generated runoff, and nitrate concentrations declined to 8 mg/L (1.8 mg/L as $NO_3$-N), the lowest value recorded during the water year. From March, nitrate concentrations generally increased, reaching 37 mg/L (8.2 mg/L as $NO_3$-N) in late June. Fluctuations in nitrate concentrations, similar to those at Big Spring, continued to occur during the remainder of the water year. Concentrations declined to 24 mg/L (5.3 mg/L as $NO_3$-N) during a runoff event in mid-July, then

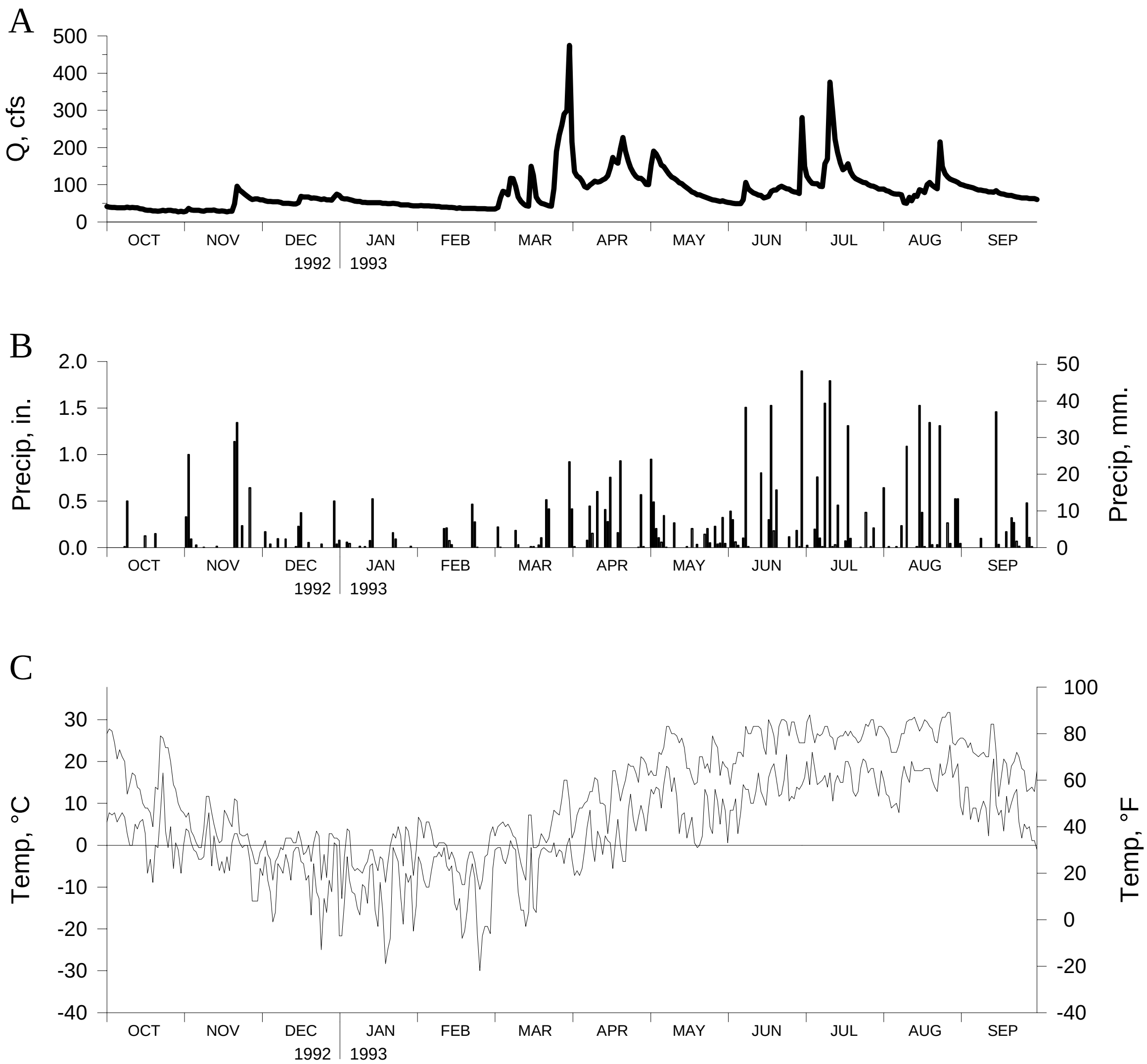


**Figure 6**. A) Groundwater discharge and B) daily precipitation for the Big Spring basin; and C) maximum-minimum temperatures for Elkader, IA (Iowa Dept. of Ag. and Land Stewardship, State Climatology Office), for WY 1993.

increased to 36 mg/L (8.0 mg/L as $NO_3$-N) two weeks later as discharge receded. From July, nitrate concentrations generally decreased, and were diluted to 9 mg/L (2.0 mg/L as $NO_3$-N) during a runoff event in mid-August. Nitrate concentrations increased to 31 mg/L (6.9 mg/L as $NO_3$-N) in September and remained above 25 mg/L (5.6 mg/L as $NO_3$-N) during the remainder of the water year as discharge continued to recede.

The highest monthly fw mean nitrate concentration from the Turkey River, 36 mg/L (8.0 mg/L as $NO_3$-N), occurred in December, January and February. The lowest monthly fw mean, 13 mg/L (2.9 mg/L as $NO_3$-N), occurred in March (Table 13). Monthly fw mean nitrate concentrations remained above 20 mg/L (4.4 mg/L as $NO_3$-N), except during March and August. Monthly nitrate-N loading from the Turkey River was greatest in July and lowest in February. The monthly nitrate-N discharge varied from 6.4 million pounds in July,

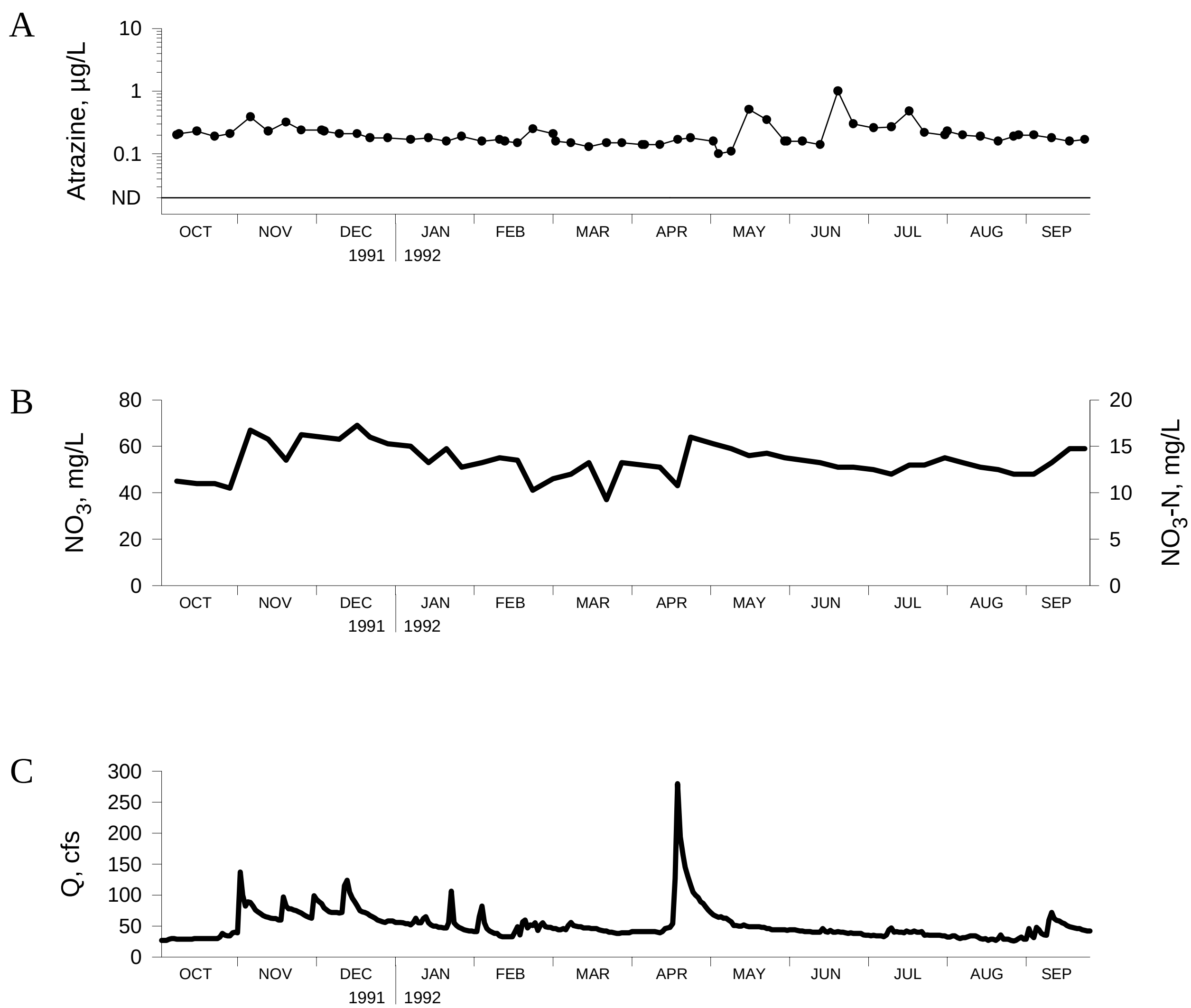


**Figure 7**. A) Atrazine and B) nitrate concentrations; and C) groundwater discharge at Big Spring for WY 1993.

which accounted for about 20% of the annual nitrate-N load, to 698,000 pounds in February. The monthly nitrate-N discharge during July was the third-greatest recorded during WYs 1984-1993. The greatest monthly nitrate-N discharges previously recorded from the Turkey River were 7.5 million pounds in June, and 7.4 million pounds in April, of WY 1991 (Rowden et al., 1993).

***Pesticide Monitoring***

Figures 7 and 9 and Tables 9 and 14 summarize the results of pesticide monitoring at Big Spring for WY 1993. Forty-two pounds of atrazine were discharged by groundwater at a fw mean concentration of 0.27 µg/L. This was the fourth-lowest annual fw mean atrazine concentration observed at Big Spring during WYs 1982-1993. Fifty-two samples of Big Spring groundwater were analyzed for pesticides during the water year. Forty-nine, or 94%, of the samples contained detectable levels of atrazine (>0.10 µg/L).

Atrazine concentrations remained below 0.20 µg/L during the first eight months of the water year

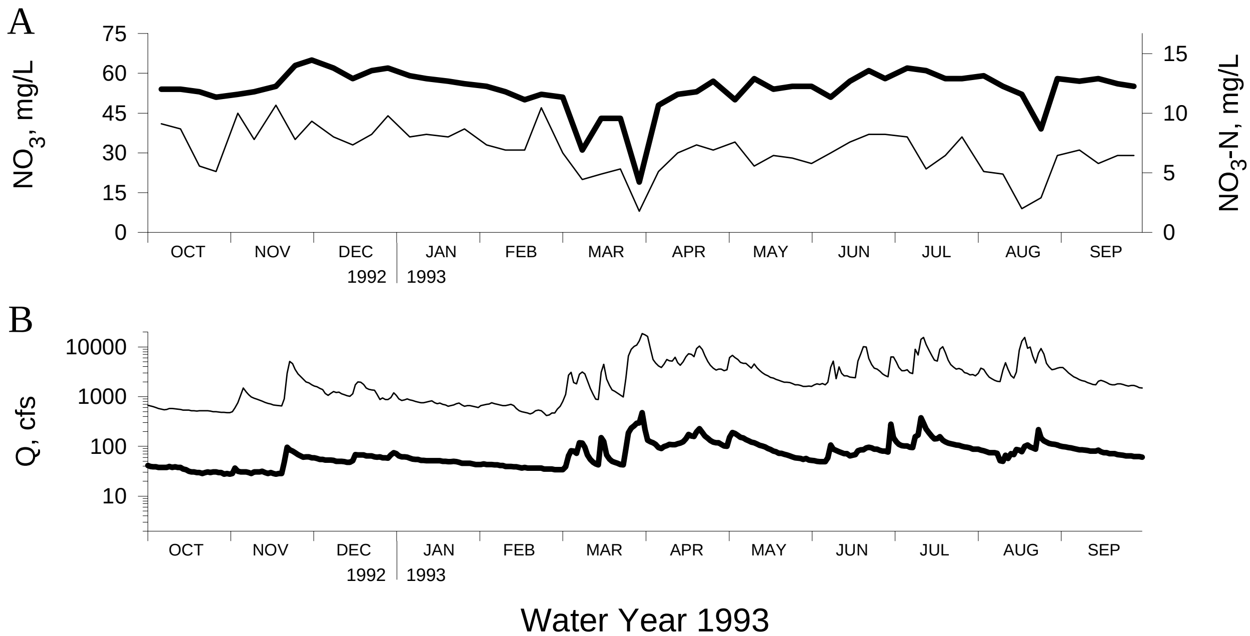


**Figure 8**. A) Nitrate concentrations and B) discharge hydrographs for Big Spring (bold lines) and the Turkey River (lighter lines) at Garber for WY 1993. (Turkey River discharge data are from the U.S. Geological Survey, W.R.D., IA Dist.)

(Fig. 7). Concentrations declined to non-detectable levels (<0.10 µg/L) once in December and twice during January. Atrazine concentrations increased to 2.50 µg/L during a minor runoff event in early June, then decreased to 0.30 µg/L one week later. Concentrations reached 0.75 µg/L in mid-June, two days after another larger runoff event. During the remainder of the water year, atrazine concentrations generally declined, increasing slightly during runoff events in July and August. Atrazine concentrations were 0.12 µg/L near the end of the water year.

Table 14 summarizes the atrazine data for Big Spring on a monthly basis. Monthly fw mean atrazine concentrations varied from 0.07 µg/L in January to 0.69 µg/L in June. The greatest monthly atrazine load occurred during July, when 12.9 pounds of atrazine were discharged, and the lowest monthly atrazine discharge, 0.6 pounds, occurred in January. Atrazine discharge during July accounted for about 31% of the annual total at Big Spring.

Figure 9 is a bar plot of atrazine, cyanazine, alachlor, and metolachlor concentrations for WY 1993. Atrazine was detected in forty-nine, or 94% of the samples; cyanazine was detected in four samples, or 8% of those collected; metolachlor in three, or 6%; and alachlor was detected in two, or 4% of the samples. The highest concentration of pesticides detected during the water year included atrazine at 2.50 µg/L; cyanazine at 1.90 µg/L; alachlor at 1.50 µg/L; and metolachlor at 0.86 µg/L. All maximum detections occurred June 8. Cyanazine was detected during June, July and August; metolachlor was detected in May and June; and alachlor was detected only during June.

Tables 10 and 15 summarize the results of atrazine monitoring for the Turkey River during WY 1993. The annual atrazine discharge was 3,386 pounds, and the annual fw mean concentration was 0.59 µg/L. The annual atrazine discharge from the Turkey River during WY 1993 exceeded all previous annual atrazine loads during WYs 1986-1993. The second-greatest annual atrazine discharge, 3,325 pounds, occurred during WY 1991 (Rowden et al., 1993). Although the annual

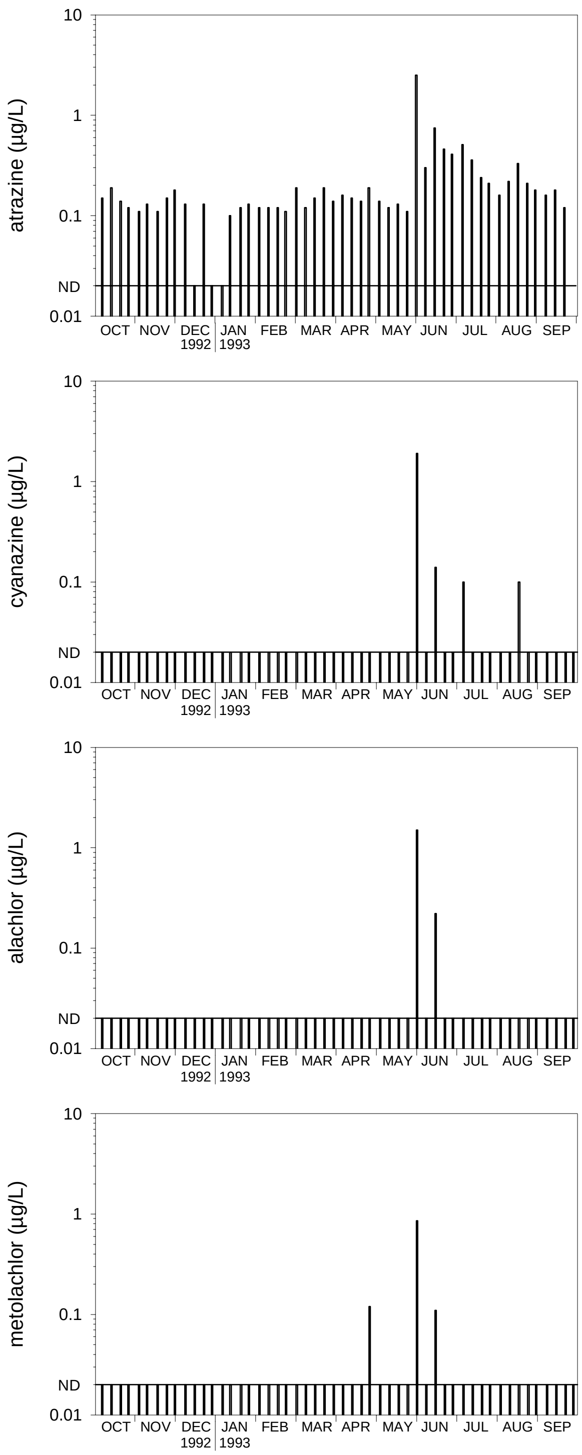


**Figure 9**. Bar graphs of pesticide concentrations at Big Spring for WY 1993. ND represents not detected.

atrazine discharge from the Turkey River for WY 1993 was the greatest recorded during WYs 1986-1993, the annual fw mean atrazine concentration was about average for the period of record. The highest monthly fw mean atrazine concentration and greatest discharge during the water year, 1.58 µg/L and 1,524 pounds, occurred during July, the month with the greatest surface-water discharge. The lowest monthly fw mean atrazine concentration, 0.12 µg/L, occurred in January. The smallest monthly atrazine load, 11 pounds, occurred in February. July accounted for about 45% of the annual atrazine load and about 17% of the annual surface-water discharge. The monthly atrazine discharge for July of WY 1993, 1,524 pounds, was the second-greatest recorded during WYs 1986-1993. The greatest monthly atrazine discharge previously recorded from the Turkey River, 2,102 pounds, occurred during June of WY 1991 (Rowden et al., 1993).

Twelve samples from the Turkey River were analyzed for pesticides during the water year. All samples contained detectable levels of atrazine (>0.10 µg/L). Three samples, or 25% of those collected contained detectable levels of metolachlor; two, or 17% contained alachlor; and one, or 8% of the samples contained detectable levels of cyanazine. The highest concentration of pesticides detected during the water year included atrazine at 1.10 µg/L; metolachlor at 0.19 µg/L; cyanazine at 0.18 µg/L; and alachlor at 0.10 µg/L. Metolachlor was detected during March, June and July; alachlor was detected in May and June; and cyanazine was detected during June only. All maximum detections occurred June 28.

## DISCUSSION

Relating watershed-scale water quality to differences in landuse and management between watersheds, or within a watershed over time, requires consideration of many complex processes. The timing, intensity, and distribution of rainfall, along with antecedent conditions, all affect the resultant runoff and recharge to the surface-water and soil-groundwater systems, and the concentrations of agricultural contaminants transported by these systems. Other factors that complicate the analysis of water-quality changes within watersheds include landuse changes, changes in input rates of fertilizers and pesticides, mineralization of organic material into nitrogen, in-stream biological processing, losing stream effects, subsequent storage or carry-over effects, and system time lags, particularly at the watershed scale.

The cumulative annual discharge and discharge as a percentage of precipitation during WYs 1992 and 1993 were the greatest recorded since monitoring began at Big Spring. While annual precipitation totals were similar to totals during WYs 1990 and 1991, annual discharge totals increased significantly. Antecedent conditions, including the volume of groundwater in storage within the basin and increased groundwater levels and soil moisture, were factors causing greater recharge-discharge rates during WYs 1992 and 1993. Water years 1990 and 1991 were the two wettest consecutive years since monitoring began at Big Spring, but they followed the driest consecutive two-year period in the state's history.

The volume and distribution patterns of rainfall have varied significantly from WY 1988 to WY 1993. Precipitation totals for the basin were about 70% of the long-term average of 32.97 inches during WYs 1988 and 1989. Annual precipitation increased to 37.87 inches in WY 1990 and 47.27 inches during WY 1991, then decreased to 35.74 inches in WY 1992, and increased to 46.47 inches in WY 1993. The WY 1992 and WY 1993 totals were 108% and 141% of the long-term average for the basin. Water Years 1985 through 1989 were characterized by dry growing seasons and wet falls and WYs 1990 and 1991 had below normal rainfall from October through February, and above normal rainfall from March through September. Water Year 1992 had a very dry growing season and WY 1993 had a relatively wet growing season. Monitoring during the past four years has shown the effects of increases in precipitation and resultant recharge on the Big Spring basin's hydrologic system, and on the transport of contaminants within the system, following both the drought conditions of WYs 1988 and 1989 and the wet conditions of WYs 1990 and 1991.

The sustained, slowly declining discharge during WYs 1988, 1989 and the first few months of WY 1990 was relatively slow-moving groundwater that flows from storage in the less transmissive parts of the basin's hydrologic system (Libra et al., 1991; Rowden et al., 1993). As discharge continued to slowly decline during the first few months of WY 1990, nitrate concentrations remained at the low levels of about 25 mg/L (5.6 mg/L as $NO_3$-N) seen during WY 1989 (Libra et al., 1991; Rowden et al., 1993). During the latter half of WY 1990 as infiltration recharge occurred and discharge began increasing, nitrate concentrations showed a generally increasing trend, and concentrations remained between about 40 mg/L (8.9 mg/L as $NO_3$-N) and 65 mg/L (14.4 mg/L as $NO_3$-N) through the end of the water year. During WY 1991, nitrate concentrations decreased very slowly from about 40 mg/L (8.9 mg/L as $NO_3$-N) at the beginning of the water year to about 30 mg/L (6.7 mg/L as $NO_3$-N) in late February as discharge slowly declined. Significant infiltration recharge occurred from March through June, and nitrate concentrations remained above 60 mg/L (13.3 mg/L as $NO_3$-N) from April through June. Discharge generally receded from June through September, and nitrate concentrations generally declined to about 40 mg/L (8.9 mg/L as $NO_3$-N) near the end of the water year. In WY 1992, nitrate concentrations increased as infiltration recharge occurred in November, and concentrations remained relatively high through WY 1993, except during periods of significant surface-water influx. These changes in nitrate concentrations may be the result of several factors. Typically, a large part of Big Spring's discharge is relatively recent, nitrate-rich recharge water. During the drought conditions of WYs 1988 and 1989 recharge was limited and a large proportion of the discharge was relatively older water from the less transmissive parts of the groundwater system. A portion of this water may have infiltrated the land surface prior to the major increases in nitrogen fertilizer applications of the 1960s and 1970s, and therefore has relatively low nitrate concentrations (Hallberg et al., 1983, 1984a).

Denitrification and in-stream nitrogen uptake may also influence nitrate concentrations at Big Spring, especially during low-flow periods. Denitrification within some of the less transmissive parts of the basin's hydrologic system, and leakage of surface water from streams into the groundwater within the basin may result in lower nitrate concentrations. Denitrification and nitrogen uptake by aquatic vegetation are significant in-stream processes within the basin, particularly under low flow, high temperature conditions (Crumpton and Isenhart, 1987; Isenhart and Crumpton, 1989; Seigley et al., 1993; Rowden et al., 1995). The portion of Big Spring's discharge that may be supplied by leakage from streams under very low-flow conditions would also contribute to low nitrate concentrations, at least during warm-weather periods. Conversely, during higher discharge periods the effects of denitrification and in-stream nitrogen uptake are less pronounced since a larger portion of the discharge is recent, nitrate-rich groundwater.

The Roberts Creek watershed (70.7 $mi^2$) located within the Big Spring basin, and the watersheds of Bloody Run (37.6 $mi^2$), and Sny Magill (35.6 $mi^2$) are contiguous and share a similar hydrologic framework which allows comparison of surface-water data to understand the relationships between landuse, management practices, and water quality (Seigley et al., 1993). Comparison of these watersheds provides insights on nitrogen cycling in the groundwater and surface-water systems as it relates to landuse differences, in-stream biological processing, seasonal variations, and the size of the watersheds sampled. The watersheds differ in landuse and this difference affects nitrogen loading within the watersheds. Within all three watersheds there are no significant urban or industrial nitrogen sources, and the watersheds are dominated by agricultural activity. Corn accounts for over 95% of the row-cropped areas in these watersheds, with about 50% grown as continuous corn, and the remainder grown in rotation with alfalfa and oats. Over 80% of the farms in the watersheds have livestock, involving dairy or beef cattle, and/or swine, so manure is utilized as a nutrient source. Although there are many sources of nitrogen within these watersheds, the greatest nitrogen input is from fertilizer applied to corn. Therefore, the proportion of land area in corn production within these watersheds directly affects the nitrate concentrations and nitrogen loads in the surface water and groundwater. Comparison of the water quality of the streams within these watersheds is instructive. During WY 1991, 53% of the Roberts Creek watershed was in row-crop and the stream had an annual mean nitrate concentration of 36 mg/L (8 mg/L as $NO_3$-N). In comparison, Bloody Run watershed had 39% of its area in corn with an annual mean of 18 mg/L (4 mg/L as $NO_3$-N), and Sny Magill had 26% of the watershed in row-crop production and an annual mean nitrate concentration of 9 mg/L (2 mg/L as $NO_3$-N). The comparison of annual nitrogen loading within these watersheds is complicated by variations in fertilizer-application rates and changes in the land area used for corn production.

In the Roberts Creek, Sny Magill, and Bloody Run watersheds, nitrate-nitrogen concentrations tend to decline downstream (Seigley et al., 1993). Within the Roberts Creek watershed, landuse and loading factors show little change downstream and there are no significant changes in landuse sources that might dilute nitrate-nitrogen. In the central and eastern portion of the Big Spring basin, Roberts Creek loses water through its bed to groundwater. Without other influences nitrate-nitrogen should remain constant. The downstream decline in nitrate-nitrogen can be related to in-stream biological processing (Crumpton and Isenhart, 1987; Isenhart and Crumpton, 1989; Bachmann et al., 1990). Studies suggest that the depletion of nitrate in these stream systems is facilitated by bacterial denitrification in the anaerobic stream-sediment interface and algal assimilation of nitrate and ammonium (Isenhart and Crumpton, 1989). Data from Roberts Creek indicate that the rate and mass of in-stream nitrate removal reaches a maximum during summer low flow, high temperature periods when groundwater inputs are at a minimum. The seasonal variations are related to seasonal discharge patterns that affect residence time of the water and $NO_3$-N, as well as temperature.

In-stream processing contributes to significant variability of nitrate concentrations in surface water. During cool seasons nitrate concentrations from RC02 tend to parallel concentrations at Big Spring. During warm seasons, concentrations at RC02 tend to be much lower than the integrated groundwater concentrations from Big Spring because of the in-stream processing. Similar trends occur at other surface-water sites within the basin, but at watershed scales much greater than Roberts Creek, an equilibrium pattern appears to be reached. In similar monitoring from the Turkey River, little downstream difference in nitrate concentrations has been apparent, although similar seasonal trends in concentrations occur (Hallberg et al., 1983, 1984a, 1985, 1987, 1989; Libra et al., 1986, 1987, 1991; Rowden et al., 1993). The spatial and temporal variability of nitrate concentrations in surface water must be considered when comparing water-quality data from different monitoring sites and in defining the scale of watershed comparisons that are feasible. Subsequent reports will incorporate monitoring data from streams, tile lines, and wells to further evaluate the effects of denitrification and in-stream nitrogen processing. When trying to assess nitrogen balances on a watershed scale, in-stream nitrate losses, nitrate losses from streambed denitrification, and uptake by aquatic plants must be considered (e.g., Bachmann et al., 1990; Isenhart and Crumpton, 1989).

Previous reports (Hallberg et al., 1983, 1984a, 1985, 1987, 1989; Libra et al., 1986, 1987, 1991; Rowden et al., 1993, 1995) have shown that increases in annual discharge have generally been accompanied by increases in annual fw mean nitrate concentrations and nitrate loads (Fig 10). Annual fw mean atrazine concentrations and loads have shown no consistent relationship to annual discharge, although atrazine concentrations tend to increase with increasing recharge, particularly runoff recharge, on a short-term basis. In WY 1989, during the drought, groundwater discharge and annual fw mean nitrate concentrations declined to the lowest values recorded during the period of record at Big Spring. During WY 1991, groundwater discharge increased significantly and annual fw mean nitrate and atrazine concentrations increased to the highest values recorded during the period of record. From WY 1991 to WY 1992 annual groundwater discharge and annual fw mean nitrate concentrations and loads decreased slightly, while annual fw mean atrazine concentrations and loads decreased substantially. During WY 1993, the

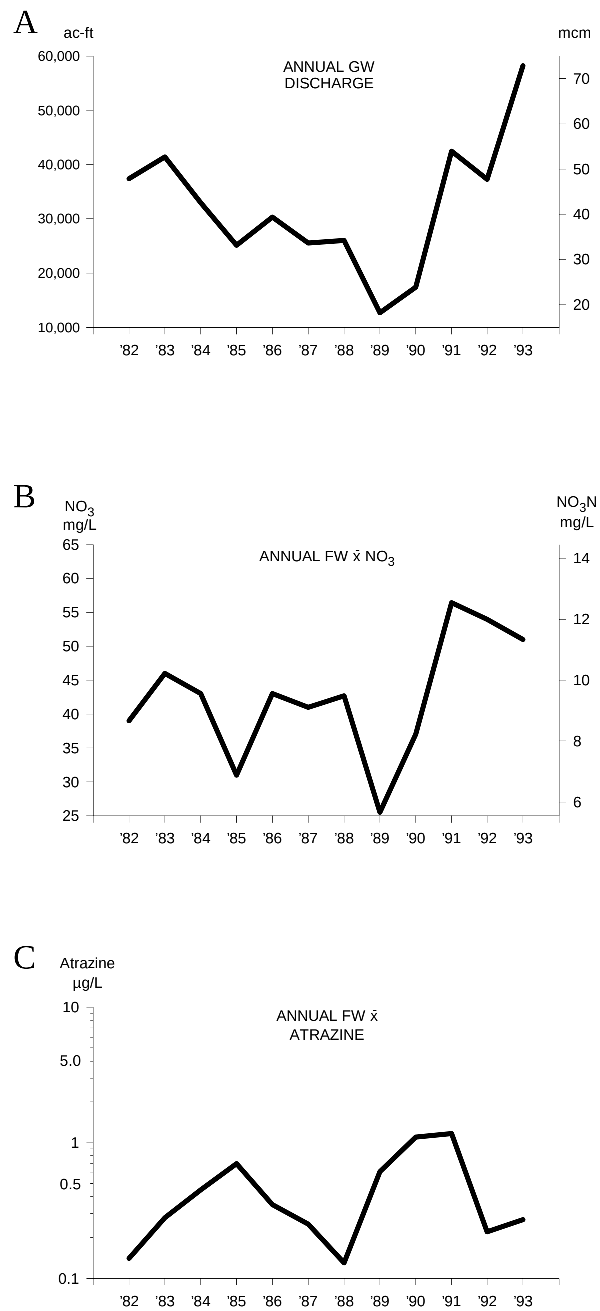


**Figure 10**. Summary of annual A) basin precipitation, B) groundwater discharge, C) flow-weighted mean $NO_3$ and D) atrazine concentrations from Big Spring groundwater.

annual groundwater and nitrate-N discharge both increased to the highest values recorded, as the annual fw mean nitrate concentration decreased slightly. At the same time, the annual fw mean atrazine concentration increased slightly, and the atrazine load increased significantly.

The annual data from WYs 1991, 1992 and 1993 show a general relationship between groundwater discharge and fw mean nitrate concentrations and loads. Relative to WY 1991, WY 1992 had 25% less precipitation, 12% less groundwater discharge, a 4% lower fw mean nitrate concentration, a 16% smaller nitrate load, an 82% lower fw mean atrazine concentration, and an 83% smaller atrazine load. Relative to WY 1991, WY 1993 had 2% less precipitation, 37% greater groundwater discharge, a 9% lower fw mean nitrate concentration, a 24% greater nitrate load, a 78% lower fw mean atrazine concentration and a 69% smaller atrazine load. While the decreases in the annual fw mean nitrate concentrations and loads from WY 1991 to WY 1992 were proportional to the decrease in discharge, the decreases in the annual fw mean atrazine concentrations and loads were much greater. From WY 1992 to WY 1993, precipitation increased 30%, discharge increased 56%, fw mean nitrate decreased 6%, but the nitrate load increased 47%. At the same time, the fw mean atrazine concentration and load increased 2% and 87% respectively. The increases in annual nitrate and atrazine loads from WY 1992 to 1993 were more a function of the increase in discharge than the change in fw mean nitrate and atrazine concentrations. These data show a relationship between precipitation, groundwater discharge, and fw mean nitrate concentrations and loads, and a lack of any clear relationship between annual fw mean atrazine concentration and groundwater discharge. These data also show a time lag, over the long-term, between changes in precipitation and changes in groundwater discharge as storage in the Galena aquifer is slowly replenished. During WY 1992, the decrease in groundwater discharge was about half as great as the decrease in precipitation, and during WY 1993 the increase in discharge was about twice as great as the increase in precipitation. The timing, intensity, and distribution of rainfall all affect the resultant recharge to the soil-groundwater system, and therefore affect long-term trends in the transport of agricultural contaminants.

The decrease in annual fw mean nitrate concentration, as discharge increased from WY 1992 to WY 1993 was unusual, and may be the result of several factors. A number of large runoff events occurred during the latter half of WY 1993. Nitrate concentrations typically decrease during runoff events and increase as the discharge is receding. If a greater than normal proportion of the annual discharge is composed of runoff, this would lower the annual fw mean nitrate concentration. In addition, the greater than normal precipitation during WY 1991, and the significant infiltration recharge during the first half of WY 1992, would have led to increased leaching, leaving a smaller than normal mass of nitrate in storage in the soil system available for transport to the hydrologic system during WY 1993. It is also possible that the gradual reductions in nitrogen fertilizer applied within the basin are beginning to affect changes in the water quality of Big Spring. It required five years of data collection and analysis to establish the water-quality significance of input changes from the Payment-In-Kind set-aside program in 1983, when the basin area used for corn production was reduced by about 33% relative to 1982 (Hallberg et al., 1993). It will take additional years of monitoring and analysis to fully ascertain the changes in water quality caused by smaller magnitude landuse changes and gradual improvements in nitrogen management within the basin. Subsequent years of monitoring will be required to put WY 1993 in perspective, relative to changes in hydrologic conditions and landuse.

Reductions in atrazine use within the basin have been difficult to document because its application to crops is generally not as uniform as the application of nitrogen. Farm surveys conducted in the basin have shown that some changes and reductions in atrazine use have occurred. Application rates have declined from about 2 lbs/acre in the early 1980's to less than 1.5 lbs/acre by 1990 (George Hallberg, personal communication). This change has partly been accomplished by using atrazine mixed (either premixed or tank mixed) with various other herbicides. While the average rate of atrazine used per acre has decreased, the number of acres treated with compounds that contain atrazine have increased. While the surveys suggest a decrease in the total mass of atrazine applied, it is probably not as great as suggested from the rate reductions because of the increased proportion of acres treated. The reduction in total loading may, however, contribute to a decline in atrazine concentrations in the basin.

The decreases in atrazine concentrations and loads from WYs 1990 and 1991 to WYs 1992 and 1993 are probably also in part related to changes in the timing and intensity of precipitation, and in the relative proportion of infiltration- versus runoff recharge composing Big Spring's discharge. Pesticide degradation rates vary with environmental factors, such as soil moisture. The low soil moisture conditions during WYs 1988 and 1989 may have inhibited hydrolysis and microbial activity, which are important degradation processes (USEPA, 1986). The dry conditions may also have left a greater than normal mass of herbicide available for mobilization and transport during WYs 1990 and 1991. The higher soil moisture conditions during WYs 1990 and 1991 may have enhanced hydrolysis and microbial activity, and left a smaller than normal mass of herbicide available for mobilization and transport to groundwater during WYs 1992 and 1993. The large proportion of infiltration recharge in early WY 1992 and the generally receding discharge later during the growing season would also have contributed to low fw mean atrazine concentrations and loads. In WY 1993, a number of significant runoff events occurred during the growing season. At the same time, atrazine concentrations remained relatively low, leading to a significant increase in atrazine load, but only a minor increase in fw mean atrazine concentration from WY 1992.

The in-stream degradation of atrazine by biotic and/or abiotic processing is likely also a significant factor affecting atrazine concentrations and loads at Big Spring and the Turkey River. Atrazine can be degraded by biotic or abiotic processes (Goswami and Green, 1971; Paris et al., 1973; Wehtje et al., 1983). During biotic degradation of atrazine, N-dealkylation of the atrazine structure initially produces either desethylatrazine or deisopropylatrazine (Paris et al., 1973). Various research has shown desethylatrazine to be the more stable initial biotic degradation product (metabolite; Adams and Thurman, 1991; Geller, 1980). The abiotic degradation of atrazine forms an initial degradation product of hydroxyatrazine through hydrolysis of the atrazine structure (Pape and Zabik, 1970). Koplin and Kalkhoff (1993) documented a general decrease in atrazine concentration between water entering and exiting a 7-mile, loosing reach of Roberts Creek during four of seven sampling periods. During the same four periods, the concentrations of the two biotic atrazine degradation products were constant or decreasing downstream. The lack of an inverse relation between the concentrations of atrazine and the biotic degradation products suggests that abiotic degradation processes may be occurring in the stream. Other possible explanations for the lack of an inverse relation between atrazine and its biotic metabolites include the rapid transformation of metabolites to the next degradation product, and/or that aquatic plants are removing atrazine from the stream through uptake and internal degradation or temporary storage within the plants.

The degradation rate of atrazine, as determined from its half-life, varied throughout the study, with the maximum degradation rate (minimum half-life) occurring during the July sampling period (Koplin and Kalkhoff, 1993). Since both biotic and abiotic degradation processes would likely exhibit similar trends, with the seasonal increase and subsequent decrease of water temperature and photosynthesis affecting the rate of biotic degradation, and the seasonal increase and subsequent decrease of daylight hours affecting the rate of photolytic degradation, the seasonal trend in atrazine degradation rate provides no indication as to the type of atrazine degradation that is occurring. Koplin and Kalkhoff (1993) found no significant correlation between atrazine half-life and water temperature, but did find a significant inverse relation with daily hours of sunlight during each sampling period. The results suggest that sunlight is an important factor in atrazine degradation in streams and that photolytic degradation may be occurring.

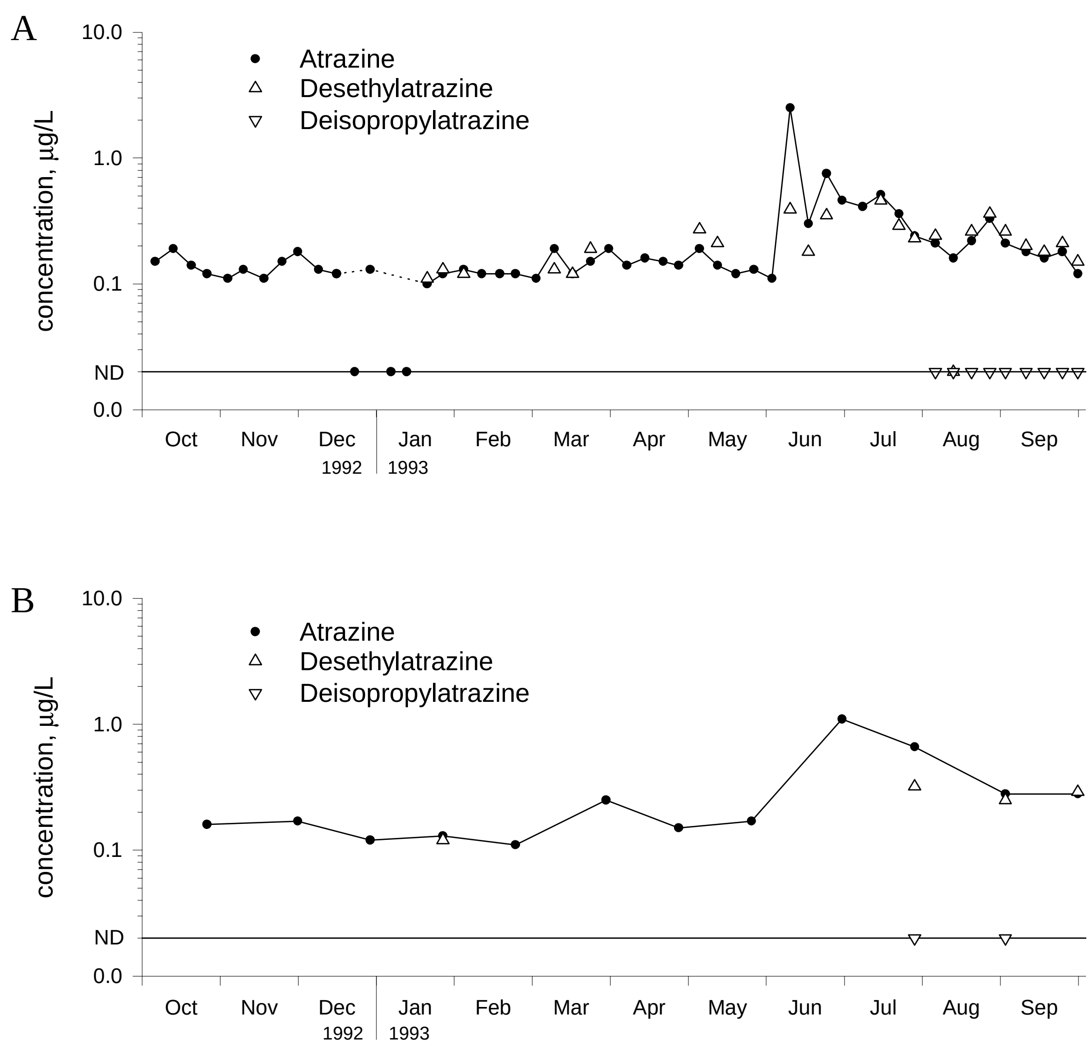


**Figure 11**. A) Atrazine, desethylatrazine and deisopropylatrazine concentrations for Big Spring and B) atrazine, desethylatrazine and deisopropylatrazine concentrations for the Turkey River at Garber for WY 1993. ND represents not detected.

In laboratory experiments, Goldberg and others (1991) found that atrazine degraded by indirect photolysis and that the rate of photolytic degradation increased with increasing nitrate concentrations in the water. The nitrate ions produce hydroxyl radicals in water, in the presence of sunlight that attack the atrazine structure to form hydroxyatrazine, which initiates the abiotic degradation chain for atrazine. Koplin and Kalkhoff (1993) found no significant relation between atrazine half-life and the average nitrate concentration in the study reach. They reasoned that the strong seasonal pattern in atrazine half-life likely masks any potential relation between nitrate concentration in the water and the rate of atrazine degradation.

Since January 1993, the pesticide samples collected for the Big Spring Project have been analyzed for desethylatrazine and deisopropylatrazine (Fig. 11). The large number of detections (>0.10 µg/L) of desethylatrazine, along with the absence of detections of deisopropylatrazine during the monitoring period at Big Spring, the Turkey River, and other sites, support research that has shown desethylatrazine to be the more stable initial biotic degradation product (Adams and Thurman, 1991; Geller, 1980). The pesticide analyses from Big Spring and the Turkey River show similar atrazine and desethylatrazine concentrations, generally increasing and decreasing simultaneously. As with atrazine, desethylatrazine concentrations generally increase during runoff periods and decrease during prolonged recession periods. Both desethylatrazine and deisopropylatrazine have been detected in monitoring sites along Roberts and Silver creeks, and in tile line monitoring sites within the basin. Preliminary data show desethylatrazine being detected more often than deisopropylatrazine, and usually at higher concentrations at most monitoring sites. Near the basin's surface water outlet at RC02, atrazine typically showed the greatest concentrations, followed by desethylatrazine, then deisopropylatrazine concentrations. At tile line monitoring sites desethylatrazine often showed the greatest concentrations, followed by atrazine, then deisopropylatrazine concentrations. Most detections of deisopropylatrazine occurred during June through August, which may support the inference that the amount of sunlight is an important factor in atrazine degradation.

It is likely that atrazine degradation is occurring in other midwestern streams. Documentation of this degradation may be difficult, because unlike the study section of Roberts Creek, most streams have groundwater and/or surface-water sources contributing to streamflow (Koplin and Kalkhoff, 1993). The amount of atrazine in Big Spring and the Turkey River is affected by the degradation of atrazine occurring in the streams within their watersheds. Research examining relations between atrazine, hydroxyatrazine, desethylatrazine, and deisopropylatrazine in both water and suspended sediment is needed to verify the occurrence of biotic and abiotic degradation of atrazine in streams.

Ongoing analysis of data from the nested monitoring network of streams, tile lines, and wells within the Big Spring basin adds significant detail to observations from Big Spring and the Turkey River. Over time, these combined analyses will refine the assessment of water-quality changes resulting from improvements in farm management.

## OVERVIEW OF MONITORING RESULTS FOR WYs 1982 THROUGH 1993

The cumulative annual discharge, and discharge as a percentage of precipitation during WYs 1992 and 1993 were the greatest recorded since monitoring began at Big Spring. While annual precipitation totals were similar to totals during the previous two-year period, annual discharge increased significantly. WYs 1990 and 1991 followed the driest consecutive two-year period in the state's history and WYs 1992 and 1993 followed the wettest consecutive two-year period since the project's inception. Precipitation patterns changed significantly from WYs 1988 and 1989 to WYs 1992 and 1993. The increased precipitation generated both runoff and infiltration recharge. Discharge rates decreased slightly from WY 1991 to 1992, then increased to record levels during WY 1993 as the net increase in overall storage within the basin's hydrologic system that began in WY 1990 continued.

Figure 10 and Tables 16 and 17 summarize the results of hydrologic and water-quality monitoring at Big Spring for WYs 1982 through 1993. During the period, annual precipitation has varied from 22.9 inches for WY 1988 to 47.3 inches for WY 1991. Annual groundwater discharge has ranged between 12,700 ac-ft during WY 1989 and 58,186 ac-ft in WY 1993. The lowest annual fw mean and nitrate-N load, 25 mg/L and 194,928 pounds, occurred in WY 1989. The highest annual fw mean nitrate concentration, 56 mg/L, occurred in WY 1991, and the greatest nitrate-N load, 1,796,013 pounds, was discharged during WY 1993. The lowest annual atrazine load and fw mean occurred during WY 1988, when only 9.2 pounds of atrazine were discharged, at a fw mean concentration of 0.13 µg/L. The highest annual fw mean atrazine concentration, 1.17 µg/L, and the greatest annual atrazine load, 135 pounds, occurred during WY 1991. Maximum atrazine concentrations from Big

**Table 16.** 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 | |
| Pesticide common chemical name | % detections maximum concentrations, ug/L | | | | | | | | | | | | % detections (total record) |
| Herbicides | | | | | | | | | | | | | |
| atrazine | 100% | 100% | 100% | 100% | 99% | 100% | 75% | 88% | 100% | 100% | 100% | 94% | 96% |
| | 2.5 | 5.1 | 10.0 | 6.1 | 1.4 | 0.7 | 0.4 | 3.3 | 8.2 | 16.0 | 1.0 | 2.5 | |
| alachlor | 16% | 28% | 23% | 14% | 7% | 2% | nd | 18% | 18% | 18% | 3% | 4% | 13% |
| | 0.2 | 0.6 | 4.0 | 5.0 | 0.7 | 0.1 | nd | 0.2 | 0.9 | 5.5 | 0.6 | 1.5 | |
| cyanazine | 32% | 26% | 21% | 15% | 3% | 5% | 3% | 31% | 35% | 13% | 5% | 8% | 16% |
| | 0.7 | 1.2 | 1.7 | 4.6 | 0.1 | 0.1 | 1.0 | 3.0 | 0.9 | 2.6 | 0.5 | 1.9 | |
| metolachlor | na | 4% | 17% | 4% | 4% | nd | nd | 6% | 8% | 4% | 2% | 6% | 5% |
| | na | 0.6 | 4.5 | 4.6 | 0.6 | nd | nd | 0.2 | 0.6 | 2.2 | 0.2 | 0.9 | |
| metribuzin | na | na | na | 1% | nd | nd | nd | nd | nd | nd | nd | nd | <1% |
| | na | na | na | 3.6 | nd | nd | nd | nd | nd | nd | nd | nd | |
| 2,4-D | na | na | na | 1% | nd | na | na | na | na | na | na | na | <1% |
| | na | na | na | 0.2 | nd | na | na | na | na | na | na | na | |
| Insecticides | | | | | | | | | | | | | |
| fonofos | na | 1% | 8% | nd | nd | nd | nd | nd | nd | nd | nd | nd | <1% |
| | na | 0.1 | 0.3 | nd | nd | nd | nd | nd | nd | nd | nd | nd | |

na- not analyzed; nd- not detected

The following compounds were not detected: butylate, pendimethalin, trifluralin, chlorpyrifos, diazinon, ethoprop, malathion, parathion, phorate, and terbufos; 2,4,5-T, 2,4,5-TP, acifluorfen, chloramben, and dicamba.

**Table 17.** 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 |
| 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 |
| 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 |
| 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 |
| 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 |
| Nitrogen discharged with groundwater: | | | | | | | | | | | | |
| flow-wtd mean concentration, mg/L | | | | | | | | | | | | |
| as nitrate (NO3) | 39 | 46 | 43 | 31 | 43 | 41 | 43 | 25 | 37 | 56 | 54 | 51 |
| as nitrate-N (NO3-N) | 8.8 | 10.3 | 9.7 | 7.0 | 9.7 | 9.1 | 9.5 | 5.7 | 8.2 | 12.5 | 12 | 11.4 |
| ammonia-N* | * | * | * | * | 0.1 | 0.1 | 0.1 | 0.6 | 0.1 | 0.1 | 0.1 | 0.2 |
| organic-N* | * | * | * | * | 0.5 | 0.2 | 0.3 | 0.8 | 0.6 | 0.9 | 0.3 | 0.6 |
| 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 |
| lbs-N/acre | 13.2 | 17.4 | 12.8 | 7.2 | 12.1 | 9.6 | 10.2 | 3.0 | 5.9 | 21.9 | 18.5 | 27.2 |
| (for total basin area) | | | | | | | | | | | | |
| Atrazine discharged with groundwater: | | | | | | | | | | | | |
| flow-wtd mean concentration, | | | | | | | | | | | | |
| atrazine, ug/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 |
| 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 |

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

Spring varied from 0.40 µg/L during WY 1988 to 16.00 µg/L in WY 1991. The variability of climatic and hydrologic conditions within the Big Spring basin, along with variations in annual fw mean nitrate and atrazine concentrations and loads by factors ranging from two to ten over relatively short time periods, underscores the need for long-term, nonpoint-source monitoring to evaluate the impact of agricultural practices on surface-water and groundwater quality at larger watershed scales.

As discussed in previous reports (Libra et al., 1986, and 1991; Hallberg et al., 1989; Rowden et al., 1993; Rowden et al., 1995), annual fw mean nitrate concentrations tend to parallel annual groundwater discharge, or flux through the hydrologic system. Higher nitrate concentrations have generally occurred during years with greater groundwater discharge. Annual fw mean atrazine concentrations, and the frequency and magnitude of detections of other herbicides, have not paralleled annual discharge. On a short-term basis, atrazine concentrations tend to increase during runoff recharge events. Relatively high fw mean atrazine concentrations have occurred during some years with low groundwater discharge and low fw mean atrazine concentrations have occurred during some years with high groundwater discharge, for reasons that are currently unclear. While annual groundwater discharge and fw mean nitrate concentrations decreased from WY 1983 to WY 1985 and from WY 1988 to WY 1989, annual fw mean atrazine concentrations and loads increased (Fig. 10). The second highest annual fw mean atrazine concentration, 1.10 µg/L, and the second greatest atrazine load, 49.9 pounds, occurred during WY 1990, a year with the second lowest annual groundwater discharge, 17,476 ac-ft, during the period of record. Water Year 1993 had the highest annual groundwater and nitrate-N discharge, and the third highest annual fw mean nitrate concentration, while having the fourth lowest annual fw mean atrazine concentration during the period of record. Retardation of atrazine transport to and through the groundwater system, and annual changes in the mass of atrazine present on the land surface, are likely important factors influencing annual fw mean atrazine concentrations and loads. While the mass of atrazine present is largely a function of the amount applied in a given year, climatic factors may significantly vary degradation rates, leaving a larger percentage of the amount applied available for transport. The low soil moisture from the drought conditions during WYs 1988 and 1989 may have inhibited hydrolysis and microbial activity, important to degradation processes and left a greater than normal mass of herbicide available for mobilization and transport to groundwater during WYs 1990 and 1991. Conversely, the cumulative increase in soil moisture during WYs 1992 and 1993 may have enhanced herbicide degradation processes, leaving a lower than normal mass of herbicide available for transport. The increased runoff during WYs 1990 and 1991 probably removed a greater than normal mass of herbicide, leaving less available for mobilization and transport to groundwater during WYs 1992 and 1993.

The large decreases in annual fw mean atrazine concentrations and loads from WYs 1990 and 1991 to WYs 1992 and 1993 are also, in part, related to the timing of precipitation and runoff events, and the distribution of atrazine concentrations during the water years. Precipitation events during WYs 1990 and 1991 were less evenly distributed than during WYs 1992 and 1993. Atrazine concentrations were greater than 1.00 µg/L during most of January through March, and June and July of WY 1990. During WY 1991 atrazine concentrations were relatively high during May and June. These high atrazine concentrations, combined with numerous runoff events, led to high fw mean atrazine concentrations and loads. During WYs 1992 and 1993, atrazine concentrations remained relatively low. The short lived increases in concentrations that did occur, were usually not coincident with runoff events and as a result fw means and loads remained low.

## SUMMARY

The variable climatic and resulting hydrologic conditions exhibited in the Big Spring basin during the period of record complicate interpretation of changes in water quality and illustrate the need for detailed, long-term monitoring projects for the understanding of nonpoint-source contamination. The gradual reductions in nitrogen fertilizer and in the use of herbicides, such as atrazine, resulting from improved management practices may not result in pronounced water-quality changes, but they will be detectable over time. At larger scale watersheds such as Big Spring, many landuse and management practices are integrated, and water-quality responses are dampened and complicated by climatic variations, storage effects, and biochemical processing in both surface-water and groundwater systems. Policy makers and planners must be aware of the time lag involved at these larger watershed scales and make appropriate commitments to long-term support.

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