SHALLOW GROUNDWATER AND SURFACE WATER MONITORING of the SILVER CREEK SUB-BASIN within the BIG SPRING BASIN 1986–1995: A Summary Review

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Iowa Department of Natural Resources Larry J. Wilson, Director March 1998

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A Report of The Big Spring Basin Demonstration Project

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ABSTRACT

The 4.39 mi² Silver Creek sub-basin is located in the north-central portion of the 103 mi² Big Spring groundwater basin in Clayton County, Iowa. Precipitation, surface water and groundwater discharge, and the concentrations and loads of various chemicals have been monitored within and around the Big Spring basin since 1981. This report summarizes the results of monitoring at sub-basin tile-line site L22T (85 acres) and surface-water site L23S (4.39 mi², or 2,810 acres) during water years (WYs) 1986-1995. During this period, precipitation has varied from 22.94 inches in WY 1988 to 47.27 inches in WY 1991. The driest consecutive two-year period in the state's history, WYs 1988 and 1989, preceded the wettest consecutive two-year period since monitoring began in WY 1981. Annual basin precipitation increased from 22.94 inches in WY 1988 and 24.32 inches in WY 1989 to 37.87 inches in WY 1990 and 47.27 inches in WY 1991. The precipitation total for WY 1992 was 35.74 inches. Water Year 1993 had the second-greatest annual precipitation total during WYs 1981-1995 at 46.47 inches, or 141% of the long-term average. The annual precipitation for WY 1994 was 30.42 inches, or 92% of normal, and precipitation for WY 1995 was 29.28 inches, or 89% of normal. The WY 1988 and 1989 totals were 70% and 74%, and the WY 1990 and 1991 totals were 115% and 143% of the long-term average precipitation of 32.97 inches. The increased precipitation during WYs 1990-1993 generated both runoff and infiltration recharge. During WY 1993, annual groundwater discharge totaled 188.7 acrefeet (ac-ft) at L22T, 58,186 ac-ft at Big Spring, and 5,720 ac-ft at L23S. These were the highest annual discharges for L22T and L23S during WYs 1986-1995, and for Big Spring during WYs 1982-1995. The lowest annual discharge from L22T, 13.8 ac-ft, occurred in WY 1990. The lowest annual discharges for Big Spring and L23S, 12,672 ac-ft and 552 acft, occurred in WY 1989.

The lowest annual flow-weighted (fw) mean nitrate-N concentrations and nitrate-N loads for L22T and L23S during WYs 1986-1995, and for Big Spring and the Turkey River during WYs 1982-1995, occurred in WY 1989. Annual fw means and loads were 15.0 mg/L and 622 pounds for L22T; 2.0 mg/L and 2,998 pounds for L23S; 5.7 mg/L and 195,000 pounds for Big Spring; and 2.6 mg/L and 1.6 million pounds for the Turkey River. The highest annual fw mean nitrate-N concentrations occurred in WY 1991, and greatest nitrate-N loads occurred in WY 1993. The fw mean for L22T was 31.3 mg/L for both WYs 1990 and 1991. For WY 1991, the annual fw mean for L23S was 12.0 mg/L, 12.5 mg/L for Big Spring and 9.9 mg/L for the Turkey River. The annual nitrate-N loads for L22T, 138,951 pounds for L23S, 1,796,013 pounds for Big Spring, and 32.4 million pounds for the Turkey River.

Atrazine is the most consistently detected herbicide in the Big Spring basin. During WYs

1982-1995, atrazine was detected in 83% of the samples from L22T, 68% of the samples from L23S, and 95% of the samples from Big Spring. The highest annual fw mean atrazine concentration for L22T, 0.40 μ g/L, and L23S, 6.75 μ g/L, occurred in WY 1989. The highest annual fw mean for Big Spring, 1.17 µg/L, occurred in WY 1991. The greatest annual atrazine loads, 0.063 pounds for L22T, 22.5 pounds for L23S, and 135 pounds for Big Spring, all occurred in WY 1991. For L22T, the lowest annual fw mean, 0.10 µg/L, occurred in WYs 1993 and 1994, and the smallest annual atrazine load, 0.013 pounds, occurred in 1987. For L23S, the lowest fw mean atrazine concentration, $0.09 \,\mu$ g/L, occurred in WY 1995, and the smallest atrazine load, 0.40 pounds, occurred in WY 1987. At Big Spring, the lowest annual fw mean atrazine concentration, $0.12 \mu g/L$, was recorded in WY 1995, and the smallest annual atrazine load, 9.2 pounds, was recorded in WY 1988. During WYs 1986-1995 annual fw mean atrazine concentrations for the Turkey River varied from $1.90 \ \mu g/L$ in WY 1990 to 0.25 µg/L in WY 1992, and atrazine loads varied from 407 pounds in WY 1988 to 3,386 pounds in WY 1993. Alachlor, cyanazine, and metolachlor were also detected at many monitoring sites within the Big Spring basin and in the Turkey River during WYs 1982-1995.

Basin monitoring during WYs 1982-1995 indicates that while fw mean nitrate concentrations and loads generally parallel changes in annual groundwater and surface-water discharge, fw mean atrazine concentrations and loads do not. Relatively high concentrations and loads of atrazine have occurred during some years with low groundwater and surfacewater discharge and low concentrations and loads have occurred during some years with high groundwater and surface-water discharge. During WYs 1988-1989 annual groundwater and surface-water discharge and annual fw mean nitrate concentrations and loads decreased to the lowest levels during the period of monitoring, while annual fw mean atrazine concentrations and loads increased significantly. From WY 1989 to WY 1991, annual groundwater and surface-water discharge increased, and fw nitrate concentrations and atrazine loads increased to record levels, while fw atrazine concentrations declined at L22T and L23S, and increased at Big Spring. From WY 1992 to WY 1993, annual discharges and nitrate-N loads increased to record levels, and annual atrazine loads increased, but remained relatively low, while fw nitrate concentrations decreased slightly at all three sites. Flow-weighted atrazine concentrations decreased slightly at L22T, and increased slightly at L23S and Big Spring. The interpretation of these water-quality changes is complicated by climatic variations, subsequent storage effects, and system time lags. Water Year 1993 was the first year of monitoring at Big Spring that annual fw mean nitrate concentration decreased while annual discharge increased. This decline in fw mean nitrate concentration may be due to increased leaching of nitrate-N during WYs 1990-1992, or it is possible that the gradual reductions in nitrogen fertilizer applied within the basin are beginning to affect changes in the water quality of Big Spring. Five years of data collection and analysis were necessary 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. 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. Climatic variations, storage effects and time-lags complicate the interpretation of changes in water quality related to landuse changes, and illustrate the need for detailed, longterm monitoring of nonpoint-source contamination. Therefore, before declines in fw mean nitrate-N and atrazine concentrations and loads can be attributed to improved management and source reduction, overall system variations must be considered.

INTRODUCTION

The groundwater discharge and water quality of the 103 mi² 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; Fig.1). The basin topography varies from moderately rolling in the northern half of the area, to steeply sloping near the Turkey River Valley in the southern portion of the area (Fig. 2). Total relief in the basin is approximately 420 feet, with as much as 320 feet of relief occurring along the Turkey River Valley in the southwest corner of the basin (Hallberg et al., 1983). 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 bedrock is mantled by thin Quaternary deposits, but is frequently exposed along small valleys in the basin. High on the landscape, Pre-Illinoian till and glacial-fluvial deposits are preserved. The uplands and hillslopes are draped by loess, and loamy alluvial deposits occur in the stream valleys and drainageways. The Galena Group forms the bedrock aquifer that is the main groundwater source in the basin. Over 85% of the groundwater discharged from the basin exits through Big Spring near the base of the Galena aquifer in the Turkey River Valley. Surface water is discharged by various streams, primarily Roberts Creek, which accounts for 65% of the basin's surface drainage area and 75-80% of the surfacewater flow leaving the basin.

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.

During the past decade, typically 50% of the basin has been in row crops, 42% in cover crops, and 5% in forest. The remainder of the basin is



Figure 1. Map showing the location of the Big Spring basin.

comprised of small urban areas, homesteads, quarries, and roads. Up until 1986, approximately 99% of the row crop acreage was in corn. Since then, there have been small increases in the amount of soybeans and sorghum grown in the area. The cover crops grown within the basin include hay, oats, and pasture, and occasionally small amounts of wheat. Landuse was interpreted from aerial photos, U.S. Department of Agriculture-Farm Service Agency (USDA-FSA) records, staff field notes, and landowner surveys.

The geographic extent of the groundwater basin was delineated in previous investigations by the Iowa Department of Natural Resources, Geological Survey Bureau (GSB) 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. As an outgrowth of research in the basin, a multiagency group initiated the Big Spring Basin Demonstration Project (BSBDP) in 1986. This effort involved integrating public education, on-farm research, and demonstration projects that stressed the environmental and economic benefits of pru-



Figure 2. Map of the Big Spring basin showing the location of some monitoring sites. The locations of monitoring sites L22T and L23S are shown in bold.

dent chemical management. The project involved various scales of monitoring to evaluate the environmental effects of farm management practices that improve efficiency and profitability, while reducing soil erosion, and chemical and nutrient contamination of surface water and groundwater.

The hydrologic and water-quality monitoring of Big Spring and the Turkey River for water years (WYs; October 1 through September 30) 19821995 have been reviewed by Hallberg and others (1983, 1984a, 1985, 1987, 1989, 1993), Libra and others (1986, 1987, 1991), Rowden and others (1993, 1995b), and Liu and others (1997). 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 1986-1992 are presented in Rowden and others (1995a). Reviews of rainfall monitoring for pesticides are discussed in Nations (1990) and Nations and Hallberg (1992). 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 sub-basin tileline site L22T (85 acres) and surface-water site L23S (4.39 mi²) during water years 1986 through 1995. Analytical methods and landuse are reviewed in Hallberg and others (1989). The interpretation of data presented in this report requires analysis of data from the network of monitoring sites throughout the basin. The hydrologic and water-quality data from other tile lines, wells, and surface-water sites within the Big Spring basin and included sub-basins are being addressed in subsequent reports.

Physiography and Groundwater in the Basin

The Big Spring basin includes most of the surface-drainage basin of Roberts Creek (Fig. 2). On the north and west, the groundwater-basin divide is nearly coincident with the surface-drainage divide, including the Roberts Creek system and a small unnamed creek which empties into the Turkey River near Big Spring (Fig. 2). On the east side of the basin, the groundwater divide cuts across the surface-drainage basins of Howard and Roberts creeks, and the basin of Bloody Run Creek, which lies to the east. Groundwater flows from the divide toward Big Spring, and discharges from the Galena aquifer through a narrow region to the Turkey River, with the major portion concentrated at Big Spring.

The relationship between the surface-water system and the groundwater system within the Big Spring basin is complex. In their headwaters, most of the streams are recharged by shallow-groundwater flow from local seeps and tile-lines, or diffuse groundwater flow from the Maquoketa Formation, Galena Group, and/or Quaternary deposits. In the central and eastern portions of the basin, the streams and their alluvial valleys are perched above the Galena potentiometric surface. Here streams lose surface water to the groundwater system through intermittent runoff into sinkholes, and as diffuse seepage in some perennial streams. As the streams leave the basin, in the St. Olaf area (Fig. 2), they receive discharge from the Galena aquifer, and again become gaining streams.

Most streams maintain perennial flows through portions of the basin that appear to be losing reaches. This is possible when sustained recharge, provided by shallow groundwater (including tile drainage) in the streams' headwaters, is greater than the rate of leakage into the groundwater system downstream. The upper portions of the alluvial deposits and large areas of the streambeds are fine-textured, silty deposits, which provide slow percolation, effectively retarding losses or leakage through the streambed.

Much of the well-integrated, dendritic drainage network developed in the Big Spring basin is controlled by bedrock, especially the second order and larger valleys in the eastern two-thirds of the basin. Many valleys in this area appear to follow major joint trends. Several small blind valleys in this area disrupt the integrated drainage network and lead to the development of hollows which discharge entirely into sinkholes, entering the groundwater system of the Galena aquifer. However, infiltration rates through the soil and rock are relatively high in this area and runoff is infrequent. The majority of the sinkholes are filled with soil and Quaternary deposits. As a consequence, the water that runs off into them must infiltrate through a mantle of silty to loamy sediment. The sinkhole basins occupy a total drainage area of 11.5 mi2, or 11% of the groundwater basin.

HYDROLOGIC AND WATER QUALITY MONITORING

The discharge of groundwater and surface water in the study area is a function of recharge within the Big Spring basin, and is controlled by the amount, timing, and intensity of precipitation and snowmelt. Climatic variations, along with antecedent conditions, exert a major control on the transport, concentrations, and loads of agriculturally related contaminants. This report will discuss the monitoring of precipitation, discharge, and water quality at tile-line site L22T and surface-water site L23S, and some aspects of the discharge and water-quality record for Big Spring (BSP) and the Turkey River (TR01). The Turkey River is a high baseflow stream, deriving a significant part of its discharge from influent groundwater. Therefore, data from the Turkey River provide a regional perspective for the hydrologic and water-quality monitoring at Big Spring and other sites within the basin. All references to discharge for the Turkey River or Turkey River basin refer to the 1,545 mi² basin above Garber, Iowa. Discharge data for L22T was collected by the GSB, and discharge data for L23S, TR01, and BSP were supplied by the U.S. Geological Survey, Water Resources Division, (USGS, WRD) Iowa City, Iowa. Discharge data for the Turkey River are monitored at a USGS gaging station at Garber, while water quality samples are collected from the Turkey River near the Big Spring Fish Hatchery at site TR01. Discharge records from the Turkey River at Garber are available since WY 1914 for all but seven years and are continuous since WY 1933.

The Big Spring hydrologic system receives both infiltration and runoff recharge that have unique chemical signatures (Hallberg et al., 1983, 1984a; Libra et al., 1986, 1987, 1991; Rowden et al., 1993, 1995a, 1995b; Liu et al., 1997). 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; Libra et al., 1986, 1987, 1991; Littke and Hallberg, 1991; Rowden et al., 1993, 1995a, 1995b; Liu et al., 1997). Infiltration recharge is enriched in nitrate and other chemicals that are soluble and mobile in soil, relative to runoff recharge. Runoff recharge has lower concentrations of such compounds, but is enriched in herbicides and other chemicals with low solubility and soil mobility (e.g., greater adsorption). Typically Big Spring yields groundwater, 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 flow periods. This is typically followed by higher nitrate and lower herbicide concentrations as the associated infiltration recharge moves through the system.

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

Monitoring Site Descriptions

A network of over 50 sites in the Big Spring basin has been routinely monitored for water quality. Precipitation, surface water, and groundwater from tile lines, shallow piezometers, bedrock wells and springs were included in the network (Fig. 2). The development of monitoring sites within the basin was a cooperative effort. Staff from the USGS (in Iowa City) designed, constructed, and maintained stream gaging stations at surface-water sites RC02, L23S, BOOGD, TR01, and a gaging station at BSP, and also cooperated in waterquality monitoring. Tile-monitoring installations (BTLUE, BTLUW, L22T, and BTLD) and a surface-water flume (BOOGFL) were designed and constructed under the direction of Dr. James Baker, Department of Agricultural Engineering, Iowa State University, Agriculture and Home Economics Experiment Station. The USGS discontinued monitoring at BOOGD at the end of WY 1992, and monitoring by the USGS at BSP was discontinued at the end of WY 1995. All monitoring at BTLUE and BTLUW was discontinued at the end of WY 1995 and at BTLD at the end of WY 1994. Presently USGS staff maintain sites RCO2, L23S, and TR01, and GSB staff continue to maintain site L22T, and have maintained site BSP since the beginning of WY 1996.

Site L23S monitors the surface-water discharge

from the 4.39 mi² watershed of the west branch of Silver Creek (Fig. 2). The site is equipped with a standard USGS gaging station, with continuous discharge records since May 13, 1986. Tile line L22T is located 60 feet west of L23S, on the south bank of Silver Creek. The 5-inch tile has no surface intakes and is installed approximately 6 feet deep in alluvium mapped as Otter and Worthen soils in the 36-acre field immediately above L22T. The site monitors the groundwater discharge from approximately 85 acres, with continuous discharge records since October 1, 1986. The field immediately above L22T has been cropped to corn during most of the years it has been monitored. Site L22T is the only monitored tile line within the Big Spring basin that has flowed continuously since monitoring began in WY 1987. Workers that installed the tile suggested the presence of a spring or seep near the upper extent of the tile, based on the amount of water they encountered, but the presence of a spring or seep was never documented. Originally, the 36-acre drainage area of the field above L22T was used to compute discharge as a percentage of precipitation and loads of nitrogen and atrazine in pounds per acre for the site. During some years, the discharge as a percentage of precipitation was unreasonably great compared to data from other monitoring sites within the Big Spring basin. To obtain a more reasonable drainage area for L22T, a linear regression was used. Figure 3 shows a cross plot of annual discharge in acre-feet (ac-ft) and millions of cubic meters (mcm) for L22T versus L23S. The slope of the line is described by the equation y = 28.6x + 374.6. Solving the equation for x = the drainage area for L22T, by using y = the 2,810-acre drainage area of L23S, produces a drainage area of 85 acres for L22T. This area extends well beyond the boundaries of the field immediately above L22T, but comparisons of the discharge as a percentage of precipitation with data from other monitoring sites within the basin suggest that 85 acres is a more reasonable drainage area than 36 acres. Consideration of the topography surrounding L22T also suggests that the larger drainage area is more realistic. It is probably incorrect to assume that the drainage area of a tile line remains constant through time. The area drained probably changes along with fluctuations in



Figure 3. Cross plot and linear regression of annual groundwater discharge from L22T versus annual surface-water discharge from L23S for WYs 1987-1995 (ac-ft=acre-feet).

the shallow water table, changes in the characteristics of the materials drained that are caused by climatic factors, and changes in landuse.

The Big Spring basin monitoring network was designed in a nested fashion. The design allows 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; Littke and Hallberg, 1991). Instrumentation at various sites added significant detail to monitoring. The smallest sites instrumented were individual fields or landuse tracts (5 to 40 acres) with known management. From individual field sites, the nested monitoring design follows the natural hierarchy of the drainage system. Watersheds of increasing size were monitored, up to the main surface-water and groundwater outlets for the basin at RC02 and Big Spring. The design 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 are clearly apparent 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 of all 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, supplemented by observations within the 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 BOOGD and RC02. Basin precipitation for WYs 1989-1992 was calculated with data from the two USGS stations and the NADP station at the hatchery. Precipitation for WY 1993 was calculated with data from the Elkader, Fayette, and Waukon weather stations and the NADP station at the hatchery (Rowden et al., 1995b). In January 1991, a weather station was established in Postville, a town closer to the Big Spring basin than Waukon. Basin precipitation for WYs 1994 and 1995 was calculated based on data from the NADP station at the Big Spring hatchery and the IDALS stations in Elkader, Fayette, and Postville. 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 used for the basin area is 32.97 inches, and references to normal precipitation are based on the period 1951-1980. This time period average is used rather than the newer 1961-1990 average used by IDALS, SCO, in order to compare more recent data with older data, which used the older average.

Monthly precipitation and departures from normal for WYs 1982 through 1995 are shown in Figure 4. The period of record has been characterized by extreme 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. 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 24.32 inches for WY 1989. 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, August or September were the wettest months (Hallberg et al., 1989). Previous reports (Hallberg et al., 1983, 1984a, 1989) have indicated that March through June are typically 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 after 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 4.9 inches above the long-term average. Monthly precipitation was above normal from May through August. The wettest months were August (11.33 inches) and June (6.13 inches), and the driest months were December (0.19 inches) and September (0.37 inches). Precipitation during August was 7.73 inches above normal, and precipitation during September was 2.93 inches below normal. The greatest rainfall occurred on August 24 (1.82 inches) and 25 (1.74 inches).

Water Year 1991 had the highest mean annual precipitation during WYs 1982-1992. Precipitation for the water year was 14.3 inches above the long-term average, or 143% of normal. Precipitation was 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 (13.09 inches) occurred in June, and the largest single rainfall event (local reports of 11 to 13 inches near Monona, Iowa) occurred on June 14. Precipitation during June was 8.29 inches above normal, and precipitation during July was 2.04 inches below normal.

Precipitation during WY 1992 was 2.8 inches above the long-term average, and rainfall was more evenly distributed than during WYs 1990 and 1991, with no large single rainfall or runoff events. Precipitation was above normal during October, November and September, and below normal during May, June, and August.

Water Year 1993 had the second-greatest annual precipitation during WYs 1982-1995. 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.

Precipitation was slightly below normal during WYs 1994 and 1995. The annual precipitation for WY 1994 was 30.42 inches, or 92% of normal, and precipitation for WY 1995 was 29.28 inches, or 89% of normal. During WY 1994, rainfall totals were far above average for January and June, above average during February, July, and September, and below average during the remainder of the year. The driest month of the water year was March, with only 0.14 inches of precipitation, or 7% of the monthly normal. In WY 1995, monthly rainfall totals were above average for November, March, April and August, and below average during January, February, June, July, and September. February was the driest month of WY 1995 with only 0.03 inches of precipitation, or 3% of the monthly normal.

The changes in the distribution patterns of precipitation during WYs 1982-1995 were significant, particularly from WY 1988 through WY 1993. 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 wet growing season. Water Year 1994 had a dry growing season until June, and the WY 1995 growing season was wet until June. 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 1986

Discharge Monitoring

Table 1 summarizes the discharge, water quality and chemical-load data for surface-water site L23S, and Figure 4 shows atrazine and nitrate concentrations for sites L23S and L22T, and daily surface-water discharge for L23S for WY 1986. Continuous records of daily discharge data for site L23S began May 13, 1986 and for site L22T, discharge data began October 1, 1986. Since the discharge data from site L23S is incomplete, data in Table 1 is computed for a partial water year.

The annual precipitation for WY 1986 was 36.96 inches, or four inches above the long-term average. For the period May 13 through September 30, precipitation was 22.43 inches, or 61% of the year's total (Rowden et al., 1995a). Precipitation was below normal during March, April, June,

Table 1. Annual summary of water and chemical discharge for L23S for partial WY 1986;05/13/86-09/30/86. (Discharge data are from the U.S. Geological Survey, W.R.D., IA Dist.)

DISCHARGE - Partial Water Year

Total

acre-feet	398
millions cf	17
millions cm	0.49
Average	
cfs	1.3
cms	0.04
mg/d	0.87
gpm	601

PRECIPITATION AND DISCHARGE

Partial Water Year

Precipitation	22.43 inches (570 mm)
Discharge	1.70 inches (43.2 mm)
Discharge as %	
of precipitation	7.6%

NITRATE DISCHARGE - Partial Water Year

Concentration - mg/L		As NO ₃	As NO ₃ -N
Flow-weighted mean		36.1	8.0
Mean of analyses		27.9	6.2
	NO ₃ -N o	utput	Total N output
lbs - N	,	687	10,355
kg - N		940	4,680
lbs - N/acre		3.1	3.7

ATRAZINE DISCHARGE - Partial Water Year

Concentration - µg/L

Flow-weighted mean	0.30
Mean of analyses	0.11
Total output	
lbs	0.33
g	148

July, and August, above normal during May, and much higher than normal during September. Although the discharge hydrograph for L23S is incomplete (Fig. 5), the discharge record from Big Spring for WY 1986 was dominated by a very large event that occurred in March, and accounted for 19% of the spring's annual discharge (Hallberg et al., 1989). In March, snowmelt accompanied by significant, intense rains generated the greatest instantaneous discharge (in excess of 360 cubic feet per second [cfs]) observed at Big Spring during WYs 1984-1986 (Hallberg et al., 1989). Infiltration recharge associated with the event sustained increased discharge at Big Spring through April. Recharge during the remainder of the water year was minor. All surface-water sites exhibited gradually declining flow rates, until late September, when rainfall generated both runoff and infiltration recharge as evidenced by the rapid increase and decrease in discharge, followed by a sustained increase in discharge into the beginning of WY 1987 (Rowden et al., 1995a).

The discharge from L23S from May 13 through September 30 was 398 acre feet (ac-ft), at an average daily discharge rate of 1.3 cfs (Table 1; Rowden et al., 1995a). The discharge was equivalent to 7.6% of the total precipitation during the period. At Big Spring the annual discharge was 30,290 ac-ft, or 15% of the annual precipitation, at an average daily discharge rate of 42.0 cfs (Hallberg et al., 1989). The annual discharge from the Turkey River at Garber (TR01) was 920,600 ac-ft, or 28% of the annual precipitation, at an average discharge rate of 1,272 cfs (Hallberg et al., 1989). Discharge from TR01 was equivalent to 138% of the longterm (1951-1980) average.

Nitrate Monitoring

Table 1 summarizes annual nitrate data for L23S, and Figure 5 summarizes the nitrate analyses for L22T and L23S for WY 1986. During WY 1986, nitrate samples were taken at most sites on a monthly basis.

Table 1 summarizes the nitrate and nitratenitrogen monitoring at L23S from May 13 through September 30 of WY 1986. During the period, eleven samples were analyzed for nitrate, and four





Figure 4. A) Monthly precipitation totals and B) departure from normal for the Big Spring basin, WYs 1982-1995 (Iowa Dept. of Ag. and Land Stewardship, State Climatology Office).



Figure 5. A) Atrazine and B) nitrate concentrations, and C) groundwater and surface-water discharge (Q) at L22T and L23S for WY 1986. (Discharge data for L23S are from the U.S. Geological Survey, W.R.D., IA Dist.)

samples were analyzed for the full nitrogen series (N-series; nitrate- plus ammonia- and organic-N). The flow-weighted (fw; mean concentration per unit volume of discharge) mean nitrate concentration for the water year was 36.1 mg/L (8.0 mg/L as NO₃-N; Rowden et al., 1995a). A total of 10,355 pounds of nitrogen were discharged by surface water from the sub-basin during the water year; of this total, 8,687 pounds, or 84%, was in the form of nitrate. Within the 4.39 mi² drainage area of L23S, the total nitrate-nitrogen output was equivalent to 3.1 lbs-N/acre and the total nitrogen output was 3.7 lbs-N/acre.

Near the beginning of WY 1986, nitrate concentrations at L23S were 34 mg/L (7.6 mg/L as NO₃-N; Fig. 5). Concentrations increased to 69 mg/L (15.3 mg/L as NO₃-N) in late November, then declined to 37 mg/L (8.2 mg/L as NO₃-N) in late January following snowmelt. Nitrate concentrations increased to 46 mg/L (10.2 mg/L as NO₃-N) in late March. Following snowmelt and rainfall in March, both discharge and nitrate concentrations declined through August. Rainfall in late September generated recharge, and nitrate concentrations increased to 39 mg/L (8.7 mg/L as NO₃-N), four days after peak discharge occurred.

The greatest monthly fw mean nitrate concentration, 42.8 mg/L (9.5 mg/L as NO₃-N), occurred during May, and the lowest monthly fw mean, 28.2 mg/L (6.3 mg/L as NO₃-N), occurred during August as discharge continued to recede. May also had the highest monthly nitrate-nitrogen discharge, 2,878 pounds, and the highest monthly surfacewater discharge, 111 ac-ft, accounting for 33% of the total nitrate-nitrogen output and 28% of the total surface-water discharge during the five-month period.

At site L22T, twelve samples were analyzed for nitrate, and seven samples were analyzed for Nseries. Nitrate concentrations for L22T showed trends similar to L23S, although concentrations at L22T were greater, except for one sample taken in November (Fig. 5). Concentrations increased from 57 mg/L (12.7 mg/L as NO₃-N) in mid-October to 67 mg/L (14.9 mg/L as NO₃-N) in November. In February nitrate concentrations declined to 61 mg/L (13.6 mg/L as NO₃-N). Concentrations rose to 69 mg/L (15.3 mg/L as NO₃-N) in early May, then declined slightly to $65 \text{ mg/L}(14.4 \text{ mg/L} \text{ as NO}_3\text{-N})$ in June. From June, nitrate concentrations increased, reaching $100 \text{ mg/L}(22.2 \text{ mg/L} \text{ as NO}_3\text{-N})$ in late September, four days after the recharge event on September 21.

At Big Spring, the fw mean nitrate concentration for the water year was 43.0 mg/L (9.7 mg/L as NO₃-N; Hallberg et al., 1989). A total of 839,790 pounds of nitrogen were discharged, and of this total, 790,454 pounds, or 94%, was in the form of nitrate. Within the 103 mi² drainage area of Big Spring, the total nitrogen output was equivalent to 12.7 lbs-N/acre and the total nitrate-nitrogen output was 12.0 lbs-N/acre. The highest monthly fw mean, 48 mg/L (10.7 mg/L as NO₃-N), occurred in April, and the greatest monthly nitrate-nitrogen discharge, 165,000 pounds, occurred in March accounting for 21% of the annual total.

The fw mean nitrate concentration for the Turkey River during WY 1986 was 28.0 mg/L (6.2 mg/L as NO₃-N; Hallberg et al., 1989). A total of 14,306,000 pounds of nitrogen were discharged during the water year. Within the 1,545 mi² drainage area of TR01, the total nitrogen output was equivalent to 14.5 lbs-N/acre. The greatest monthly nitrate-nitrogen discharge, 3,800,000 pounds, occurred in March, and accounted for 27% of the annual discharge.

Pesticide Monitoring

Table 1 summarizes annual atrazine data for L23S, and Figure 5 summarizes the atrazine analyses for L22T and L23S for WY 1986 (Tables 24 and 25 summarize the maximum concentrations and percentage of pesticides detected in samples on an annual basis for sites L22T and L23S for WYs 1986-1995). Samples for pesticide analyses were taken at most sites on a monthly basis during the water year.

During the water year, eight samples from L23S were analyzed for pesticides. Seven, or 88%, of the samples collected contained detectable levels of atrazine. The total atrazine discharge from L23S was 0.33 pounds, at a fw mean concentration of 0.30 μ g/L (Table 1; Rowden et al., 1995a).

Atrazine concentrations declined from $0.21 \,\mu\text{g}/$ L in November to $0.10 \,\mu\text{g}/L$ in January and late February (Fig. 5). Atrazine concentrations increased to 0.60 μ g/L following runoff in March. Concentrations reached non-detectable levels in late August as discharge continued to recede. Rainfall in September generated runoff and atrazine concentrations increased to 0.26 μ g/L.

Monthly fw mean atrazine concentrations decreased from $0.36 \mu g/L$ in May to $0.10 \mu g/L$ in August, then increased to $0.53 \mu g/L$ during September. The smallest monthly atrazine output, 5.1 grams, occurred during August, and the greatest monthly output, 69 grams, occurred during September. September accounted for 47% of the atrazine output during the five-month period.

Other pesticides detected at L23S during the water year include alachlor in three, or 38%, of the samples collected, and metolachlor in one, or 13%, of the samples collected. The greatest concentrations of pesticides detected during the water year included atrazine at 0.60 µg/L, alachlor at 0.31 μ g/L, and metolachlor at 0.60 μ g/L. The maximum concentration detected for atrazine occurred in March, and the maximum detections for alachlorand metolachlor occurred in June. Alachlor was detected in March, June, and September, and metolachlor was detected only during June. Atrazine and alachlor were detected in samples collected several weeks, and in some cases months, prior to chemical applications for the 1986 growing season.

During WY 1986, 11 samples from L22T were analyzed for pesticides. All of the samples collected contained detectable levels of atrazine (>0.10 µg/L). Atrazine concentrations at L22T showed the same seasonal trends as site L23S, although concentrations from L22T were generally higher at the beginning of the water year, lower through the spring, then higher during the last three months of WY 1986. Concentrations decreased from 0.27 µg/L in mid-October to 0.10 µg/L in late February. Atrazine concentrations increased to 0.22 µg/L in late March, then decreased to 0.15 µg/L on May 1st. Atrazine concentrations decreased from 0.17 µg/L in June to 0.13 µg/L on

July 15th. One day later, concentrations increased to $0.20 \,\mu$ g/L. A week after minor precipitation in August, the atrazine concentration was $0.21 \,\mu$ g/L. Near the end of the water year atrazine concentrations increased to $0.69 \,\mu$ g/L, four days after a large precipitation event.

The only other pesticide detected at L22T during the water year was alachlor in two, or 18%, of the samples collected. The highest concentrations of pesticides detected during the water year included atrazine at 0.69 μ g/L and alachlor at 0.13 μ g/L. The greatest concentration detected for atrazine occurred in September, and the greatest concentration detected for alachlor occurred in March. Alachlor was also detected at L22T in September.

At Big Spring, 29 pounds of atrazine were discharged during WY 1986, at a fw mean concentration of $0.35 \mu g/L$ (Hallberg et al., 1989). The largest monthly atrazine discharge, 6.9 pounds, occurred in March and accounted for 24% of the annual discharge.

The annual fw mean atrazine concentration for the Turkey River was $0.60 \mu g/L$ and the annual atrazine discharge was 1,407 pounds (Hallberg et al., 1989). The largest monthly atrazine discharge from TR01, 343 pounds, occurred in May and accounted for 24% of the annual discharge.

Water Year 1987

Discharge Monitoring

Tables 2 and 3 and Figure 6 summarize the discharge, water-quality and chemical-load data for sites L22T and L23S during WY 1987. In Figure 6, note the increase in scale on the nitrate plot relative to WY 1986.

Although the annual precipitation of 31.98 inches was only an inch below normal, the distribution of precipitation along with antecedent conditions led to limited groundwater recharge during WY 1987. From WYs 1984 through 1987, precipitation was below normal from March through June. This had a cumulative effect, decreasing groundwater and **Table 2.** Annual summary of water and chemicaldischarge for L22T for WY 1987.

DISCHARGE	
Total	
acre-feet millions cf millions cm Average	22.8 0.99 0.028
cfs cms mg/d gpm	0.032 0.001 0.020 14.4

PRECIPITATION AND DISCHARGE

31.98 inches (812 mm)
3.21 inches (81.5 mm)
10%

NITRATE DISCHARGE

Concentration	- mg/L	As NO ₃	As NO ₃ -N
Flow-weighted mean		70.5	15.7
Mean of analyses		73.9	16.4
	NO ₃ -N o	utput	Total N output
lbs - N	970		988
kg - N	440		448
lbs - N/acre	11.4		11.6

ATRAZINE DISCHARGE

Concentration - µg/L	
Flow-weighted mean	0.21
Mean of analyses	0.36
Total output	
lbs	0.013
g	5.98

surface-water recharge within the Big Spring basin. During WY 1987, precipitation totals were below normal during the growing season and greater than normal during the fall. Approximately 7.7 inches, or 24% of the annual precipitation occurred during August, with the remainder of the water year being more than 5.0 inches, or 16%, below normal.

The annual discharge for L22T during the water year was 22.8 ac-ft, at an average daily discharge rate of 0.032 cfs (Table 2). Discharge during the water year was equivalent to 10% of the annual precipitation. The annual discharge for L23S was 1,220 ac-ft, at an average daily rate of 1.7 cfs (Table 5; Rowden et al., 1995a). The discharge was equivalent to 16% of the annual precipitation. At Big Spring the annual discharge was 25,554 acft, or 14%, of the annual precipitation, at an average daily discharge rate of 35.4 cfs (Hallberg et al., 1989). Total discharge from the Turkey River at Garber (TR01) was 700,100 ac-ft, at an average discharge rate of 967 cfs (Hallberg et al., 1989). Annual discharge from TR01 was equivalent to 27% of the annual precipitation and 106% of the long-term average.

The hydrographs for WY 1987 show minor recharge in October, followed by steady discharge until mid-February (Fig. 6). Snowmelt and rainfall in February, early March and late April generated runoff and minor recharge, sustaining increased discharge at L22T and L23S. From April through July, general recession at the sites was punctuated by minor runoff and infiltration recharge. In August and late September, intense rainfalls generated the largest runoff events of the water year.

Nitrate Monitoring

Tables 2 and 3 and Figure 6 summarize the nitrate analyses from L22T and L23S during WY 1987. Beginning in March for L22T and in May for L23S, the sampling interval for nitrate, N-series, and pesticides was increased from monthly to weekly, increasing the resolution of monitoring data.

During the water year, fifty-one samples from L22T were analyzed for nitrate, and thirty-nine samples were analyzed for N-series. The annual

Table 3. Annual summary of water and chemical discharge for L23S for WY 1987. (Discharge data are from the U.S. Geological Survey, W.R.D., IA Dist.)

DISCHARGE

Total

acre-feet	1,220
millions cf	53
millions cm	1.5
Average	
cfs	1.7
cms	0.05
mg/d	1.1
gpm	763

PRECIPITATION AND DISCHARGE

Precipitation	31.98 inches (812 mm)
Discharge	5.21 inches (132 mm)
Discharge as %	
of precipitation	16%

NITRATE DISCHARGE

Concentration	- mg/L	As NO	As NO ₃ -N
Flow-weighted mean Mean of analyses		38.3 37.7	8.5 8.4
	NO ₃ -N o	utput	Total N output
lbs - N kg - N lbs - N/acre	27,1 12,7		38,303 17,370 13.6

ATRAZINE DISCHARGE

Concentration - µg/L		
Flow-weighted mean Mean of analyses	0.12 0.02	
Total output		
lbs kg	0.40 0.18	

fw mean nitrate concentration was 70.5 mg/L (15.7 mg/L as NO₃-N; Table 2). A total of 988 pounds of nitrogen were discharged along with the ground-water from L22T during the water year; of this total, 970 pounds, or 98%, was in the form of nitrate. Within the drainage area of L22T, the total nitrate-nitrogen output was equivalent to 11.4 lbs-N/acre and the total nitrogen output was 11.6 lbs-N/acre.

Near the beginning of WY 1987 nitrate concentrations at L22T were 73 mg/L (16.2 mg/L as NO₃-N; Fig. 6). Concentrations declined to 58 mg/L (12.9 mg/L as NO₃-N) in November, then increased to 72.0 mg/L (16.0 mg/L as NO₃-N) following minor runoff recharge from snowmelt in December. Nitrate concentrations declined to 60.0 mg/L (13.3 mg/L as NO₃-N) in late January, then increased slightly to 63 mg/L (14.0 mg/L as NO₃-N) in late February. From the end of February to mid-April, nitrate concentrations showed a general increase, as discharge generally increased. The highest nitrate concentration sampled at L22T during the water year, 105 mg/L (23.3 mg/L as NO₃-N), was collected on April 21, two days before the largest discharge event of the month. From April through July, both nitrate and discharge declined. The smallest concentration sampled from L22T during WY 1987, 44 mg/L (9.8 mg/L as NO₃-N), occurred on August 12, one day before the greatest daily discharge (0.23 ac-ft) of the water year. During the remainder of the water year, peaks in nitrate concentrations followed peaks in discharge. The nitrate concentration increased to 99 mg/L (22.0 mg/L as NO₃-N) on August 15, dropped to 75.0 mg/L (16.7 mg/L as NO₃-N) on August 16, then increased again to 95 mg/L (21.1 mg/L as NO₃-N) on August 18. Concentrations declined along with discharge until reaching 63 mg/ L (14.0 mg/L as NO₃-N) on September 16, then increased to 86 mg/L (19.1 mg/L as NO₃-N) on September 21, following a discharge event the 17th.

Monthly fw mean nitrate concentrations varied from 60.5 mg/L (13.4 mg/L as NO₃-N) in February to 82.1 mg/L (18.3 mg/L as NO₃-N) in April. Monthly nitrate-nitrogen output and monthly groundwater discharge varied from 117 pounds and 2.35 ac-ft in April, to 61.2 pounds and 1.59 ac-ft in July. April accounted for 18% of the annual nitrate-



Figure 6. A) Atrazine and B) nitrate concentrations, and C) groundwater and surface-water discharge (Q) at L22T and L23S for WY 1987 (note the increase in scale on the nitrate plot relative to WY 1986). (Discharge data for L23S are from the U.S. Geological Survey, W.R.D., IA Dist.)

nitrogen output and 16% of the annual surfacewater discharge.

During WY 1987, thirty-two samples from L23S were analyzed for nitrate, and twenty-one samples were analyzed for N-series. The annual fw mean nitrate concentration for L23S was 38.3 mg/L (8.5 mg/L as NO₃-N; Table 3; Rowden et al., 1995a). The total nitrate-nitrogen output for the water year was 27,177 pounds, or 9.7 lbs-N/acre, and the total nitrogen output (including organic- and ammonia-nitrogen) was 38,303 pounds, or 13.6 lbs-N/acre within the L23S drainage area.

From the beginning of the water year through the first week of February, surface-water discharge at L23S remained nearly constant. Nitrate concentrations decreased from 40 mg/L (8.9 mg/L as NO₃-N) in October to 30 mg/L (6.7 mg/L as NO₃-N) in November, then increased to 43 mg/L (9.6 mg/L as NO₃-N) in December before declining to 29 mg/L (6.4 mg/L as NO₃-N) in mid-February. Snowmelt in late February generated minor recharge and nitrate concentrations increased to 37 mg/L (8.2 mg/L as NO₃-N). From late February until mid-April, nitrate concentrations generally increased. The highest nitrate concentration reported from L23S during the water year, 55 mg/L (12.2 mg/L as NO₃-N), was sampled in late April, five days after the maximum daily discharge for the month occurred. From April through July, minor recharge had little effect on receding discharge and nitrate concentrations declined. Rainfall in August and September generated both runoff and infiltration recharge, which were followed by increases in nitrate concentrations in the first post-event samples. Concentrations then decreased in the weeks following, as discharge receded.

Flow-weighted mean nitrate concentrations from L23S varied from 45.5 mg/L (10.1 mg/L as NO₃-N) in May to 25.2 mg/L (5.6 mg/L as NO₃-N) in July. Although monthly fw mean concentrations were nearly constant, variations in monthly surface-water discharge caused large variations in total monthly nitrate-nitrogen output. Monthly nitrate-nitrogen output varied from 1,054 pounds in No-vember to 4,471 pounds in May. The nitrate-nitrogen output during May was equivalent to 16% of the annual total and the nitrate-nitrogen output

during November was equivalent to 4% of the annual total.

Previous monitoring of both surface water and groundwater in the Big Spring basin has shown that during peak discharge, much of the discharge is composed of runoff, containing low concentrations of nitrate-nitrogen (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. Conversely, pesticides and products associated with soils (sediment) and runoff, such as organicnitrogen and ammonia-nitrogen, and insoluble products such as potassium, phosphate, and iron increase during peak runoff and decrease during baseflow dominated periods. During prolonged recession periods, both nitrate and pesticide concentrations typically show a slow, steady decline.

At Big Spring, the annual fw mean nitrate concentration for WY 1987 was 41.0 mg/L (9.1 mg/L as NO₃-N; Hallberg et al., 1989). A total of 649,413 pounds of nitrogen were discharged, and of this total, 628,614 pounds, or 97%, was in the form of nitrate. Within the 103 mi² drainage area of Big Spring, the total nitrogen output was equivalent to 9.9 lbs-N/acre and the total nitrate-nitrogen output was 9.5 lbs-N/acre. The relatively constant discharge and nitrate concentrations during the water year resulted in fairly constant monthly nitratenitrogen loads. Flow-weighted mean monthly nitrate concentrations varied from 34.0 mg/L (7.6 mg/L as NO₃-N) in February to 46 mg/L (10.2 mg/ L as NO₃-N) in September. Monthly nitratenitrogen discharge varied from 38,000 pounds in February to 64,000 pounds in May.

A total of 11,100,000 pounds of nitrate-nitrogen were discharged by the Turkey River at a fw mean concentration 26.0 mg/L (5.8 mg/L as NO₃-N) during the water year (Hallberg et al., 1989). Within the 1,545 mi² drainage area of TR01, the total nitrate-nitrogen output was equivalent to 11.2 lbs-N/acre. Monthly fw mean nitrate concentrations varied from 31.0 mg/L (6.9 mg/L as NO₃-N) in March to 14.0 mg/L (3.1 mg/L as NO₃-N) in July. The greatest monthly nitrate-nitrogen discharge, 2,500,000 pounds, occurred in October, accounting for 23% of the annual discharge. The smallest monthly discharge, 249,000 pounds, occurred during July.

Pesticide Monitoring

Tables 2 and 3 and Figure 6 summarize the results of pesticide monitoring at L22T and L23S during WY 1987.

Fifty-one samples from L22T were analyzed for pesticides during WY 1987. Forty-eight samples, or 94%, contained detectable levels of atrazine (>0.10 µg/L). Occasionally the University Hygienic Laboratory changes detection limits, as on May 27 when the detection limit was $0.14 \mu g/L$, and August 18 when the detection limit was $0.40 \,\mu g/L$. During the water year a total of 0.013 pounds of atrazine were discharged, at a fw mean concentration of 0.21 μ g/L. Atrazine concentrations were stable from October through most of May, ranging from 0.24 μ g/L in October to 0.16 μ g/L in March (Fig. 6). Concentrations decreased to $0.11 \,\mu$ g/L on May 11, increased to 0.14 μ g/L a week later, then were below a $0.14 \,\mu g/L$ detection limit on May 27. The lowest concentration from L22T during the water year was a sample taken on June 15 that was below the 0.10 µg/L detection limit. Atrazine concentrations increased to 0.33 µg/L on July 7 then declined to 0.10 μ g/L near the end of the month. The highest atrazine concentration reported during the water year, 3.40 µg/L, was sampled August 14, one day after the greatest daily discharge of the water year occurred. Atrazine concentrations decreased to $0.16 \,\mu g/L$ near the end of the month, and remained below 0.18 µg/L through the end of the water year.

Monthly fw mean atrazine concentrations at L22T ranged from 0.14 μ g/L in May and June to 0.50 μ g/L in August. Monthly fw means remained below 0.20 μ g/L during all months except October, December, April, and August. The smallest monthly atrazine output, 0.30 grams, occurred in June, and the greatest monthly atrazine output, 1.42 grams, occurred in August. August accounted for 36% of the annual atrazine output and 16% of the annual surface-water discharge.

Other pesticides detected at L22T during the water year include cyanazine in 2, or 4%, of the samples collected, and alachlor in 1, or 2%, of the

samples collected. Propachlor was analyzed for, in four samples and was detected in all four. The greatest concentrations of pesticides detected during the water year included atrazine at 3.40 μ g/L, propachlor at 1.70 μ g/L, alachlor at 0.48 μ g/L, and cyanazine at 0.25 μ g/L. All maximum concentrations and detections occurred in August. Atrazine was the only pesticide detected at L22T during the water year in months other than August.

During WY 1987, twenty-one samples from L23S were analyzed for pesticides. Fifteen, or 71%, of the samples collected contained detectable levels of atrazine (>0.10 µg/L; Rowden et al., 1995a). The annual fw mean atrazine concentration was 0.12 µg/L, and the annual atrazine discharge was 0.4 pounds. Atrazine concentrations at L23S declined from 0.12 µg/L in early October to non-detectable levels in mid-November (Fig. 6). Atrazine concentrations were below the detection limit during November, December, January, and March. The highest atrazine concentration during the water year, 0.68 μ g/L, occurred May 19, the day with the largest daily rainfall accumulation during the month. The next highest concentration, 0.58 µg/L, occurred in June following rainfall. Atrazine concentrations decreased to non-detectable levels in early July, then increased to $0.26 \,\mu g/$ L in mid-August, five days after the largest discharge event of the water year, which occurred August 20. During the remainder of the water year atrazine concentrations remained near 0.1 µg/L.

Monthly fw mean atrazine concentrations from L23S varied from non-detectable levels in December, January and March to $0.35 \mu g/L$ in May. May also had the greatest monthly atrazine output, 70 grams, and the second-highest surface-water discharge, 163 ac-ft, which accounted for 39% of the annual atrazine output and 13% of the annual discharge.

Other pesticides detected at L23S during the water year include cyanazine in four, or 19%, of the samples collected, and alachlor in one, or 5%, of the samples collected. The maximum concentrations of pesticides detected at L23S during the water year include atrazine at 0.68 μ g/L, cyanazine at 0.19 μ g/L, and alachlor at 0.12 μ g/L. All maximum concentrations were detected during May. Cyanazine was detected during May and June, and

Table 4. Annual summary of water and chemicaldischarge for L22T for WY 1988.

DISCHARGE	
Total	
acre-feet millions cf millions cm Average	34.9 1.5 0.043
cfs cms mg/d gpm	0.048 0.001 0.031 21.5

PRECIPITATION AND DISCHARGE

2.94 inches (583 mm)
4.93 inches (125 mm)
1%

NITRATE DISCHARGE

Concentration	- mg/L	As NO $_3$	As NO ₃ -N
Flow-weighted mean		72.9	16.2
Mean of analyses		73.0	16.2
	NO ₃ -N o	utput	Fotal N output
lbs - N	1,539		1,621
kg - N	698		735
lbs - N/acre	18.1		19.1

ATRAZINE DISCHARGE

Concentration - µg/L	
Flow-weighted mean	0.19
Mean of analyses	0.22
Total output	
lbs	0.018
g	8.15

...

alachlor was detected only during May. Atrazine was not detected in samples collected in November, December, January, and March.

At Big Spring, 17.6 pounds of atrazine were discharged during the water year, at a fw mean concentration of 0.25 μ g/L (Hallberg et al., 1989). As was the case with discharge and nitrate concentrations, atrazine concentrations were relatively stable, leading to fairly constant monthly means and loads. Monthly fw means and loads varied from 0.16 μ g/L and 0.8 pounds in January to 0.38 μ g/L and 2.2 pounds in August. The monthly atrazine discharge during October was also 2.2 pounds, and the monthly fw mean, 0.34 μ g/L, was the second highest during the water year.

The annual fw mean atrazine concentration for the Turkey River was 0.47 μ g/L, and the annual atrazine discharge was 891 pounds (Hallberg et al., 1989). The greatest monthly atrazine discharge from TR01, 312 pounds, occurred in October and accounted for 35% of the annual discharge. The smallest monthly atrazine discharge, 23 pounds, occurred in January. Monthly fw mean atrazine concentrations varied from 1.16 μ g/L in June to 0.23 μ g/L in February.

Water Year 1988

Discharge Monitoring

Tables 4 and 5 and Figure 7 summarize the discharge, water quality and chemical-load data for tile-line site L22T and surface-water site L23S during WY 1988.

The annual precipitation during WY 1988 was 22.94 inches, or 10.03 inches below normal for the Big Spring basin. During the March through June period, months important for groundwater recharge, precipitation was 8.87 inches below normal. The extremely dry antecedent conditions that began in WY 1987 continued through WY 1988, severely limiting groundwater recharge and surface-water runoff within the basin.

The hydrographs reflect the lack of significant recharge from snowmelt and rainfall during WY 1988 (Fig. 7). From October through January, precipitation occurred, but intensity and amounts of rainfall were too low to generate significant recharge. Snowmelt in early February, combined with minor precipitation, generated runoff, but streams returned to baseflow conditions within a few days. The most significant recharge of the water year occurred in early March and was associated with snowmelt rather than rainfall. Precipitation in late March and early April generated runoff and minor infiltration recharge that sustained increased discharge temporarily, but in a matter of days, discharge rapidly receded. Following minor runoff in May, discharge continued to decline until late September. The most intense rainfall during the water year occurred in late September, but the associated runoff and infiltration recharge were limited.

The discharge from site L22T during the water year was 34.9 ac-ft, and the average daily discharge rate was 0.048 cfs (Table 4; Rowden et al., 1995a). The annual discharge was equivalent to 21% of the annual precipitation. At site L23S, the annual discharge for WY 1988 was 1,150 ac-ft, at an average daily discharge of 1.6 cfs (Table 5; Rowden et al., 1995a). The annual discharge was equal to 21% of the annual precipitation. At Big Spring the annual discharge for WY 1988 was 26,008 ac-ft, or 20.5%, of the annual precipitation, at an average daily discharge rate of 35.8 cfs (Libra et al., 1991). Total discharge from the Turkey River at Garber (TR01) was 436,100 ac-ft, at an average discharge rate of 601 cfs (Libra et al., 1991). Annual discharge from TR01 was equivalent to 23% of the annual precipitation and 65% of the long-term annual discharge average.

Nitrate Monitoring

Tables 4 and 5 and Figure 7 summarize the nitrate analyses from L22T and L23S for Water Year 1988.

During the water year, eighty-two samples from L22T were analyzed for nitrate, and fifty-six samples were analyzed for N-series. The annual fw mean nitrate concentration was 72.9 mg/L (16.2 mg/L as NO₃-N; Rowden et al., 1995a). The total nitrate-nitrogen output during the water year was 1,539 pounds, and the total nitrogen output (nitrateplus organic- and ammonia-nitrogen) was 1,621 pounds. Within the 85-acre drainage area of L22T, **Table 5.** Annual summary of water and chemical discharge for L23S for WY 1988. (Discharge data are from the U.S. Geological Survey, W.R.D., IA Dist.)

DISCHARGE

Total	
acre-feet	1,150
millions cf	50
millions cm	1.4
Average	
cfs	1.6
cms	0.04
mg/d	1.0
gpm	709

PRECIPITATION AND DISCHARGE

Precipitation	22.94 inches (583 mm)
Discharge	4.91 inches (125 mm)
Discharge as % of precipitation	21%

NITRATE DISCHARGE

Concentration	- mg/L	As NO	As NO ₃ -N
Flow-weighted r		43.0	9.6
Mean of analyse		37.6	8.4
	NO ₃ -N o	utput	Total N output
lbs - N	29,885		35,891
kg - N	13,553		16,277
lbs - N/acre	10.6		12.8

ATRAZINE DISCHARGE

Concentration - µg/L

Flow-weighted mean	0.24
Mean of analyses	0.35
Total output	
lbs	0.76
kg	0.34



Figure 7. A) Atrazine and B) nitrate concentrations, and C) groundwater and surface-water discharge (Q) at L22T and L23S for WY 1988. (Discharge data for L23S are from the U.S. Geological Survey, W.R.D., IA Dist.)

the total nitrate-nitrogen output was equivalent to 18.1 lbs-N/acre and the total nitrogen output was 19.1 lbs-N/acre.

Nitrate concentrations declined from 70 mg/L (15.6 mg/L as NO₃-N) in early October to 64 mg/ L (14.2 mg/L as NO₃-N) in mid-November, then increased to 88 mg/L (19.6 mg/L as NO₃-N) one day later following precipitation (Fig. 7). Concentrations declined to $71 \text{ mg/L} (15.8 \text{ mg/L} as \text{ NO}_3\text{-N})$ as discharge receded then increased to 102 mg/L (22.7 mg/L as NO₃-N) on November 28, following precipitation. Following the event, both discharge and nitrate concentrations decreased, and on December 8 the nitrate concentration was 68 mg/L (15.1 mg/L as NO₃-N). Nitrate concentrations increased to 78 mg/L (17.3 mg/L as NO₃-N) on December 16, as discharge continued to decline from December 9. From mid-December through mid-January nitrate levels declined, then increased to 88 mg/L (19.6 mg/L as NO₃-N) on February 1, as discharge at L22T remained relatively constant. Snowmelt generated runoff at L23S on February 3, but had no effect on groundwater discharge at L22T. This lack of a recharge response at L22T is probably due to the ground still being frozen above the tile line. During February, nitrate concentrations declined, as daily discharge remained constant at 0.025 cfs. On February 29, snowmelt generated significant recharge at both L22T and L23S, and the nitrate concentration at L22T declined to 54 mg/L (12.0 mg/L as NO₃-N) during the first day of increasing discharge. From late February to mid-August, declining discharge was punctuated by minor precipitation in March, April, and May, and from late February to early April, nitrate concentrations fluctuated and trended upward until peaking for the water year at 110 mg/L (24.4 mg/ L as NO₃-N) on April 3. After peaking, nitrate concentrations declined to 70 mg/L (15.6 mg/L as NO₃-N) near the end of April, then increased to 79 mg/L (17.6 mg/L as NO₃-N) on May 9 as discharge remained steady. Nitrate concentrations fluctuated between 62 mg/L (13.8 mg/L as NO₃-N) and 69 mg/L (15.3 mg/L as NO₃-N) until September 22, when concentrations increased to 82 mg/L (18.2 mg/L as NO₃-N) as discharge receded following precipitation. Near the end of the water year, the nitrate concentration of L22T was 64 mg/L (14.2

mg/L as NO₃-N).

A number of nitrate and atrazine samples were taken at L22T during runoff generated by snowmelt on February 29 and March 1 and 2 (Figure 8). As previously mentioned, runoff recharge, particularly snowmelt, usually has lower concentrations of nitrate and other chemicals that are mobile in the soil, yet is enriched in herbicides and other chemicals with low soil mobility. During a runoff event, relatively low nitrate and high herbicide concentrations occur during peak discharge. Higher nitrate and lower herbicide concentrations typically follow this as the associated infiltration recharge moves through the system as the discharge recedes. Since L22T is a tile line, with no surface-water intakes, it does not receive direct surface-water runoff, and can be used as a reasonable indicator of the quality of infiltrating groundwater of the shallow flow system within the basin. Dye tracing at L22T has shown that water from the land surface reaches the tile line much faster than can be attributed to infiltration through the soil (Libra et al., 1992). This more rapid transport of water to the tile line is facilitated by macropores, root casts, and desiccation cracks. These features allow runoff to enter the tile line, and in turn allow dilution of nitrate concentrations, and high concentrations of chemicals with low soil mobility, such as atrazine, to occur during recharge events. During normal infiltrating conditions, nitrate concentrations from L22T are generally greater than nitrate concentrations from surface-water sites, and atrazine concentrations from L22T are generally lower than atrazine concentrations from surface-water sites.

Prior to the snowmelt, the nitrate concentration at L22T was 68 mg/L (15.1 mg/L as NO₃-N; Fig. 8). The nitrate concentration decreased to 52 mg/ L (11.6 mg/L as NO₃-N) on March 1 at 13:20 and discharge decreased to 0.275 cfs, 13 hours after a peak discharge of 0.321 cfs. At 15:00, the nitrate concentration increased to 83 mg/L (18.4 mg/L as NO₃-N) and discharge remained at 0.275 cfs. By 18:00, the nitrate concentration was 52 mg/L (11.6 mg/L as NO₃-N), and the discharge was 0.30 cfs. On March 2 at 15:00, the nitrate concentration had increased to 83 mg/L (18.4 mg/L as NO₃-N) and the discharge had decreased to 0.280 cfs from a peak discharge of 0.306 cfs at 00:30. By 17:45, the



Figure 8. Groundwater discharge and nitrate-nitrogen and atrazine concentrations at L22T for the period 02/23/ 88-03/23/88, WY 1988.

nitrate concentration was 62 mg/L (13.8 mg/L as NO₃-N) and the discharge was 0.290 cfs. During the following days, the nitrate concentration increased to 74 mg/L (16.4 mg/L as NO₃-N) as discharge receded. The nitrate concentration decreased to 67 mg/L (14.9 mg/L as NO₃-N) on March 7 at 17:00, 23 hours after a peak discharge of 0.337 cfs that occurred on March 6. The nitrate concentration increased to 76 mg/L (16.9 mg/L as NO₃-N) on March 10, then remained above 73 mg/L (16.2 mg/L as NO₃-N) during the next two weeks as discharge receded.

The greatest monthly fw mean nitrate concentration from L22T, 82.9 mg/L (18.4 mg/L as NO₃-N), occurred during April, and the lowest monthly fw mean nitrate concentration, 64.2 mg/L (14.3 mg/L as NO₃-N), occurred during July. Large variations in groundwater discharge caused variations in monthly nitrate output. Monthly nitrate output varied from 396 pounds in March to 54.1 pounds in September. March accounted for 26% of the annual nitrate output and 25% of the annual groundwater discharge. July accounted for 3.5% of the annual nitrate output and 8% of the annual groundwater discharge. September had the smallest monthly groundwater discharge, accounting for 4% of the annual discharge.

During the water year, fifty-three samples from L23S were analyzed for nitrate, and twenty-eight samples were analyzed for N-series. Two samples, taken August 1 and August 15, were below the 1.0 mg/L detection limit for nitrate. The annual fw mean nitrate concentration was 43 mg/L (9.6 mg/L as NO₃-N; Table 5; Rowden et al., 1995a). The annual nitrate-nitrogen output was 29,885 pounds, and the annual nitrogen output (nitrate- plus organic-and ammonia-nitrogen) was 35,891 pounds. Within the drainage area of L23S, these outputs were equivalent to 10.6 lbs-N/acre of nitrate-nitrogen.

Nitrate concentrations at L23S fluctuated between 49 mg/L (10.9 mg/L as NO₃-N) in early October to 36 mg/L (8.0 mg/L as NO₃-N) in November and December and 52 mg/L (11.6 mg/ L as NO₃-N) in mid-February (Fig. 7). Samples taken at L23S during runoff in late February and early March showed trends similar to samples taken from other surface-water sites in the basin. Nitrate concentrations decreased during peak discharge, then increased as discharge receded. Concentrations increased from 13 mg/L (2.9 mg/L as NO₃-N) on February 29 at 15:45 to 24 mg/L (5.3 mg/L as NO₃-N) at 23:10, then increased to 30 mg/ L on March 1 at 13:30, before decreasing to 14 mg/ L (3.1 mg/L as NO₃-N) at 18:10. Nitrate concentrations increased to 50 mg/L (11.1 mg/L as NO3-N) on March 3 as mean daily discharge decreased from 26 cfs on March 1 to 7.4 cfs on March 3. The greatest nitrate concentration sampled at L23S during the water year, 65 mg/L (14.4 mg/L as NO₃-N), occurred in early April following minor recharge in late March. From April, nitrate concentrations declined, reaching non-detectable concentrations (<1.0 mg/L) twice in August. Rainfall in August and September had little impact on the generally declining discharge, but caused nitrate concentrations to fluctuate between less than 1 mg/ L (0.2 mg/L as NO₃-N) in early August and 33 mg/ L (7.3 mg/L as NO₃-N) in early September. The nitrate concentration was 24 mg/L (5.3 mg/L as NO₃-N) near the end of the water year.

Monthly fw mean nitrate concentrations at L23S varied from 58.5 mg/L (13.0 mg/L as NO₃-N) in April to 13.9 mg/L (3.1 mg/L as NO₃-N) in August. Variations in monthly fw nitrate concentrations and in monthly discharge were characterized by wide variations in monthly nitrogen output. The greatest monthly nitrogen output, 10,759 pounds, occurred in March and the smallest monthly output, 107 pounds, occurred in August. Monthly discharge varied from 433 ac-ft, or 38% of the annual discharge in March to 11 ac-ft, or 1% of the annual discharge in August.

At Big Spring, the annual fw mean nitrate concentration for the water year was 43 mg/L (9.5 mg/L as NO₃-N; Libra et al., 1991). A total of 700,617 pounds of nitrogen were discharged, and of this total, 672,023 pounds, or 96%, was in the form of nitrate. Within the 103 mi² drainage area of Big Spring, the total nitrogen output was equivalent to 10.6 lbs-N/acre and the total nitrate-nitrogen output was 10.2 lbs-N/acre. Monthly fw mean nitrate concentrations varied from 47 mg/L (10.4 mg/L as NO₃-N) in October to 34 mg/L (7.7 mg/L as NO₃-N) in September. Monthly nitrate-nitrogen loads and groundwater discharge varied from 86,000 pounds and 3,383 ac-ft in March, to 25,000 pounds

and 1,206 ac-ft in September. March accounted for 13% of the nitrate-nitrogen and 13% of the groundwater discharged during WY 1988.

A total of 6,248,173 pounds of nitrate-nitrogen were discharged by the Turkey River at a fw mean concentration of 23 mg/L (5.1 mg/L as NO₃-N) during the water year (Libra et al., 1991). Of this total, 6,052,690 pounds, or 97%, was in the form of nitrate. Within the 1,545 mi² drainage area of TR01, the total nitrogen output was equivalent to 6.3 lbs-N/acre, and the total nitrate-nitrogen output was equivalent to 6.1 lbs-N/acre. Monthly fw mean nitrate concentrations varied from 29 mg/L $(6.5 \text{ mg/L} \text{ as NO}_3\text{-N})$ in January to 4 mg/L (0.9 mg/L as NO₃-N) in August. The greatest monthly nitrate-nitrogen discharge, 1,446,000 pounds, and surface-water discharge, 90,400 ac-ft, occurred in March, accounting for 24% of the annual nitratenitrogen discharge and 21% of the annual surfacewater discharge. The smallest monthly nitratenitrogen load, 27,000 pounds, occurred in August, and accounted for 0.4% of the annual nitratenitrogen discharge. The smallest monthly surfacewater discharge, 10,740 ac-ft, occurred in September, and represented 2.5% of the annual surfacewater discharge.

Pesticide Monitoring

Tables 4 and 5 and Figure 7 summarize the results of pesticide monitoring at sites L22T and L23S during WY 1988.

Sixty-seven samples from L22T were analyzed for pesticides during WY 1988. Fifty samples, or 75%, contained detectable levels of atrazine (>0.10 μ g/L). The fw mean atrazine concentration for WY 1988 was 0.19 μ g/L and the total atrazine output was 0.018 pounds.

From the beginning of the water year until the end of February, atrazine concentrations fluctuated between non-detectable levels and $0.14 \mu g/L$, except for on November 28 when concentrations increased to 0.25 $\mu g/L$ during minor runoff. As previously discussed, in late February and early March, snowmelt generated runoff and both atrazine and nitrate concentrations showed significant short-term fluctuations (figs. 7 and 8). As ground-

water discharge increased from 0.025 cfs on February 24 to a peak of 0.321 cfs at 00:18 on March 1, atrazine concentrations increased from nondetectable levels on February 24 to 0.69 µg/L on March 1 at 13:20. Atrazine concentrations decreased to below the 0.10 µg/L detection limit on March 3, as the groundwater discharge receded to 0.222 cfs. Atrazine concentrations increased to $0.38 \,\mu\text{g/L}$ on March 7 as discharge receded from another event that peaked at 0.337 cfs at 24:00 on March 6. As discharge continued to recede, atrazine concentrations decreased to 0.33 µg/L on March 8 at 15:00, then increased to 0.60 μ g/L by 24:00 on March 9. Atrazine concentrations continued to decrease to $0.44 \,\mu$ g/L on March 12, then to non-detectable levels ($<0.10 \,\mu g/L$) on March 15 as discharge continued to recede. Six days later the atrazine concentration increased to 0.13 µg/L as the groundwater discharge decreased to 0.213 cfs. Atrazine concentrations decreased slightly then increased to 0.52 µg/L on March 25, as discharge receded from an event that occurred late on March 24. From March through August, atrazine concentrations showed an increasing trend, fluctuating between non-detectable levels and 0.22 µg/L. In September, precipitation occurred, and atrazine concentrations increased from 0.19 µg/L on September 6 to the greatest concentration recorded during the water year, 1.80 µg/L, on September 27.

Monthly fw mean atrazine concentrations at L22T remained below 0.20 μ g/L for most of the water year, except during February, March, and September. Monthly concentrations ranged from 0.03 μ g/L in November to 0.35 μ g/L in March. Monthly atrazine output varied from 0.06 grams in November to 3.76 grams in May. The increased atrazine output during May was more a function of the timing of chemical application than event related. While May accounted for 46% of the annual atrazine output, only 12% of the annual groundwater total was discharged during May.

The only other pesticides detected at L22T during the water year were alachlor in three, or 5%, of the samples collected, and cyanazine in two, or 3%, of the samples collected. The highest concentrations of pesticides detected during the water year included atrazine at 1.80 μ g/L, alachlor at 2.00 μ g/L, and cyanazine at 0.72 μ g/L. The maximum

concentration detected for atrazine occurred in September, the maximum for alachlor occurred in March, and the maximum concentration for cyanazine occurred in August. Atrazine was detected during every month of the water year, alachlor was detected in November, March, and August, and cyanazine was detected in August and September.

During WY 1988, thirty samples from L23S were analyzed for pesticides. Twelve, or 40%, of the samples collected contained detectable levels of atrazine (>0.10 μ g/L). The annual fw mean atrazine concentration was 0.24 μ g/L, and the total atrazine output was 0.76 pounds (Rowden et al., 1995a).

The atrazine plot for L23S shows concentrations generally lower than concentrations from L22T. This may be due in part to fewer samples collected at L23S during recharge events than were taken at L22T (Fig. 7). The lack of significant recharge during most of the water year was reflected by low atrazine concentrations, especially during the first seven months of the water year. Atrazine concentrations were below the detection limit (<0.10 µg/L) in samples collected from October through most of February. Concentrations increased to 0.36 µg/L in late February following snowmelt. As discharge receded, atrazine concentrations fluctuated between 0.24 µg/L and nondetectable levels through February. All samples collected from mid-March through early May were below the 0.10 μ g/L detection limit for atrazine. The highest atrazine concentration reported during WY 1988, 8.4 µg/L, was sampled May 9, following precipitation. As discharge receded, atrazine concentrations declined to non-detectable levels in mid-July. Concentrations increased to 0.12 µg/L following rainfall in August, then decreased to nondetectable levels prior to the intense rainfall that occurred near the end of the water year.

Monthly fw mean atrazine concentrations from L23S varied from non-detectable levels during much of the water year to $1.96 \mu g/L$ in May. The greatest monthly atrazine output, 246 grams, occurred during May and accounted for 72% of the annual atrazine output.

Other pesticides detected at L23S during the water year include cyanazine, alachlor, and

metolachlor in two, or 7%, of the samples collected. The highest concentrations of pesticides detected during the water year included atrazine at 8.40 μ g/L, alachlor at 4.50 μ g/L, cyanazine at 1.90 μ g/L, and metolachlor at 0.21 μ g/L. All maximum detections, except for metolachlor, occurred May 9. The highest concentration of metolachlor occurred February 29. Alachlor was detected during May and August, cyanazine twice in May, and metolachlor was detected in February and May.

At Big Spring, 9.2 pounds of atrazine were discharged during the water year, at a fw mean concentration of $0.13 \,\mu$ g/L (Libra et al., 1991). This was the smallest annual load and lowest annual fw mean atrazine concentration observed at Big Spring during WYs 1982-1992. Monthly fw mean atrazine concentrations varied from 0.22 μ g/L in May to 0.06 μ g/L in November and August. The monthly atrazine discharge was greatest in March, at 1.7 pounds, and smallest in August, at 0.2 pounds.

The annual fw mean atrazine concentration for the Turkey River was 0.34 μ g/L, and the annual atrazine discharge totaled 407 pounds (Libra et al., 1991). The largest monthly atrazine discharge, 234 pounds, and the highest monthly fw mean atrazine concentration, 1.99 μ g/L, occurred in May and accounted for 57% of the annual atrazine discharge. The smallest monthly atrazine discharge, 1.1 pounds, and the lowest monthly fw mean, 0.02 μ g/L, occurred in November.

Water Year 1989

Discharge Monitoring

Tables 6 and 7 and Figure 9 summarize the discharge, water quality and chemical-load data for sites L22T and L23S for WY 1989. In Figure 9, note the increase in scale on the atrazine and nitrate plots, and the lower origin on the discharge axis of the discharge plot relative to WY 1988.

As previously mentioned, WYs 1988 and 1989 were the two driest consecutive years in Iowa's recorded history. State-wide, average precipitation was more than 18 inches below normal. Precipitation in the Big Spring area was 10 inches below normal during WY 1988 and 8.7 inches below normal during WY 1989. **Table 6.** Annual summary of water and chemicaldischarge for L22T for WY 1989.

DISCHARGE		
Total		
acre-feet millions cf millions cm Average	15.3 0.67 0.019	
cfs cms mg/d gpm	0.021 0.001 0.014 9.4	

PRECIPITATION AND DISCHARGE

Precipitation	24.32 inches (618 mm)
Discharge	2.16 inches (54.9 mm)
Discharge as % of precipitation	8.9%

NITRATE DISCHARGE

Concentration -	mg/L	As NO ₃	As NO ₃ -N
Flow-weighted m		67.3	15.0
Mean of analyse		69.7	15.5
NO ₃ -N output Total N output			Total N output
lbs - N	-	22	634
kg - N		82	287
lbs - N/acre		7.3	7.5

ATRAZINE DISCHARGE

Concentration - µg/L

Flow-weighted mean	0.40
Mean of analyses	0.73
Total output	
lbs	0.017
g	7.55

Table 7. Annual summary of water and chemicaldischarge for L23S for WY 1989. (Discharge dataare from the U.S. Geological Survey, W.R.D., IADist.)

DISCHARGE

Total

acre-feet	552
millions cf	24
millions cm	0.68
Average	
cfs	0.76
cms	0.02
mg/d	0.49
gpm	341

PRECIPITATION AND DISCHARGE

Precipitation	24.32 inches (617 mm)
Discharge	2.36 inches (59.9 mm)
Discharge as % of precipitation	10%

NITRATE DISCHARGE

Concentratio	n - mg/L	As NO ₃	As NO ₃ -N
Flow-weighted		9.0	2.0
Mean of analy		23.0	5.1
	NO ₃ -N o	utput To	otal N output
lbs - N	,	998	19,813
kg - N		360	8,988
lbs-N/acre		1.1	7.1

ATRAZINE DISCHARGE

Concentration - µg/L			
Flow-weighted mean	6.75		
Mean of analyses	5.43		
Total output			
lbs	10.1		
kg	4.6		

The hydrographs reflect the continuation of drought conditions that prevailed during WY 1988 (Fig. 9). Rainfall occurred throughout the water year, generating minor runoff, but intensity and accumulation of rainfall were too low to generate significant groundwater recharge. Precipitation was 0.7 inches above normal during November and 3.5 inches above normal in August. Precipitation was below normal during all other months of the water year. August was the only month during the water year with a monthly precipitation total greater than 2.5 inches. Almost 2 inches of precipitation fell November 18th, but recharge was minimal and discharge returned to baseflow conditions within two days. The most significant runoff of the water year occurred in late January, early February and mid-March and was associated with snowmelt rather than rainfall. The amount of recharge associated with the snowmelt was limited and discharge returned to pre-event levels within five days in February and within four weeks in March. The discharge from March 10 through March 15 accounted for only 2.2% of the annual discharge at L22T, but accounted for 55% of the annual discharge at L23S, and 48% of the annual discharge from Roberts Creek, the main surface-water discharge point from the Big Spring basin (Rowden et al, 1995a). During the remainder of the water year, declining discharge was punctuated by minor recharge. Intense rainfall in August and September generated minor runoff, but the associated infiltration recharge was limited.

The annual groundwater discharge from L22T was 15.3 ac-ft, and the average daily rate was 0.021 cfs. The annual flow was equivalent to 8.9% of the precipitation during the water year (Table 6). At site L23S, the annual discharge for WY 1989 was 552 ac-ft, at an average daily rate of 0.76 cfs (Table 7; Rowden et al., 1995a). The annual flow from L23S was equivalent to 10% of the precipitation during the water year. The discharge and the equivalent percentage of precipitation discharged during WY 1989 were the lowest recorded at all surface-water sites during WYs 1986-1995 (Rowden et al, 1995a). The annual groundwater flow and the discharge as a percentage of precipitation from L22T were the second lowest recorded during WYs 1987-1995.


Figure 9. A) Atrazine and B) nitrate concentrations, and C) groundwater and surface-water discharge (Q) at L22T and L23S for WY 1989 (note the increase in scale on the atrazine and nitrate plots, and the lower origin on the discharge axis of the discharge plot relative to WY 1988). (Discharge data for L23S are from the U.S. Geological Survey, W.R.D., IA Dist.)

Annual groundwater flow from Big Spring was 12,672 ac-ft at an average rate of 17.6 cfs (Libra et al., 1991). The discharge was equivalent to 9% of the precipitation during the water year. The annual discharge, and percent of precipitation discharged from Big Spring during WY 1989 were the lowest recorded during WYs 1982-1995.

The annual surface-water discharge from the Turkey River was 220,700 ac-ft, or 11% of the annual precipitation, at an average rate of 305 cfs (Libra et al., 1991). The annual flow was only 32% of the long-term (1951-1980) average. The discharge from TR01 during WY 1989 was the fourth lowest during this entire period of record.

The prolonged recession period, combined with the large proportion of annual discharge composed of runoff recharge from snowmelt with very low nitrate concentrations and relatively high atrazine concentrations, led to low annual fw mean nitrate concentrations and loads, and high annual fw mean atrazine concentrations and loads.

Nitrate Monitoring

Tables 6 and 7 and Figure 9 summarize the nitrate analyses from L22T and L23S for WY 1989.

During the water year, seventy-two samples from L22T were analyzed for nitrate, and fifty-one samples were analyzed for N-series. The annual fw mean nitrate concentration was 67.3 mg/L (15.0 mg/L as NO₃-N). The total nitrate-nitrogen output for the water year was 622 pounds, and the total nitrogen output (nitrate- plus organic- and ammonia-nitrogen) was 634 pounds. Within the 85-acre drainage area of L22T, these outputs were equivalent to 7.3 lbs-N/acre for total nitrate-nitrogen and 7.5 lbs-N/acre for total nitrogen. The annual fw mean nitrate concentration and nitrogen discharge from L22T during WY 1989 were the lowest recorded during WYs 1987-1995.

Nitrate concentrations were very stable during the water year, remaining between 60 mg/L (13.3 mg/L as NO₃-N) and 67 mg/L (14.9 mg/L as NO₃-N), except during recharge events in March, April, August, and September (Fig. 9). On March 14, the nitrate concentration declined to 36 mg/L (8.0 mg/ L as NO₃-N) at 18:00 as discharge peaked at 0.05

cfs following snowmelt. On April 23, the nitrate concentration increased to 113 mg/L (25.1 mg/L as NO₃-N) at 15:00, following a peak discharge of 0.128 cfs that occurred at 11:30. Nitrate concentrations decreased to 70 mg/L (15.6 mg/L as NO3-N) as groundwater discharge receded to 0.036 cfs by April 24. During an event that began on August 31, the nitrate concentration rose to 136 mg/L(30.2)mg/L as NO₃-N) as the discharge increased to 0.137 cfs. By 02:00 the following morning, the groundwater discharge was 0.237 cfs, and the nitrate concentration was 201 mg/L (44.7 mg/L as NO₃-N). Groundwater discharge peaked at 0.321 cfs at 14:20 that afternoon, and by 08:00 the following morning, the discharge was 0.036 cfs. Five days later, on September 6, the groundwater discharge was 0.015 cfs, and the nitrate concentration declined to 65 mg/L (14.4 mg/L as NO_3 -N).

During the first ten months of the water year, monthly fw mean nitrate concentrations remained between 61.3 mg/L (13.6 mg/L as NO₃-N), recorded in March, and 67.6 mg/L (15.0 mg/L as NO₃-N), recorded in April. The greatest monthly fw mean concentration during the water year, 96.5 mg/L (21.5 mg/L as NO₃-N), occurred in September. The greatest monthly nitrate-nitrogen output, 79.5 pounds, occurred during April, and the smallest monthly output, 28.1 pounds, occurred in June. April accounted for 13% of the annual nitratenitrogen load, and 13% of the annual discharge at L22T.

During WY 1989, forty-four samples from L23S were analyzed for nitrate, and sixteen samples were analyzed for N-series. The annual fw mean nitrate concentration was 9 mg/L (2.0 mg/L as NO₃-N; Rowden et al., 1995a). The total nitrate-nitrogen output for the water year was 2,998 pounds, and the total nitrogen output (nitrate- plus organic- and ammonia-nitrogen) was 19,813 pounds. Within the drainage area of L23S, the total nitrate-nitrogen output was equivalent to 1.1 lbs-N/acre, and the total nitrogen output was equal to 7.1 lbs-N/acre.

From the beginning of the water year through mid-January, nitrate concentrations increased, fluctuating between 21 mg/L (4.7 mg/L as NO₃-N) in mid-October and 46 mg/L (10.2 mg/L as NO₃-N) in mid-December (Fig. 9). Nitrate concentrations

decreased to 3.5 mg/L (0.8 mg/L as NO₃-N) in late January during peak runoff from snowmelt. From January, nitrate concentrations increased to 43 mg/ L (9.6 mg/L as NO₃-N) on March 7, just prior to snowmelt. Two days later, nitrate concentrations had declined to 11 mg/L (2.4 mg/L as NO₃-N). As discharge receded in March, nitrate concentrations increased to 27 mg/L (6.0 mg/L as NO₃-N). Concentrations decreased to 4 mg/L (0.9 mg/L as NO₃-N) following precipitation in late April and early May. Nitrate concentrations increased to 25 mg/L (5.6 mg/L as NO₃-N) at the end of May. During the remainder of the water year, nitrate concentrations fluctuated between $7 \text{ mg/L} (1.6 \text{ mg/L as NO}_3\text{-N})$ in mid-July during precipitation and 19 mg/L (4.2 mg/ L as NO₃-N) in late July and early August during extremely low flow conditions.

Monthly fw mean nitrate concentrations from L23S remained below 40 mg/L (8.9 mg/L as NO₃-N), varying from 36.9 mg/L (8.2 mg/L as NO₃-N) in December to 3.0 mg/L (0.7 mg/L as NO₃-N) in March. Variations in monthly fw mean nitrate concentrations were buffered by variations in total monthly discharge during much of the water year. January and March had the greatest monthly discharges during the water year, at 116 ac-ft and 319 ac-ft, and low monthly fw mean nitrate concentrations, at 12.9 mg/L (2.9 mg/L as NO₃-N) and 3 mg/ L (0.7 mg/L as NO₃-N). March accounted for 58% of the annual surface-water discharge and 19% of the annual nitrate-nitrogen output. The largest monthly nitrate-nitrogen output, 907 pounds, occurred during January, and accounted for 30% of the annual nitrate-nitrogen discharge.

The annual fw mean nitrate concentration for Big Spring during WY 1989 was 25 mg/L (5.7 mg/ L as NO₃-N; Libra et al., 1991). A total of 242,245 pounds of nitrogen were discharged, and of this total, 194,928 pounds, or 80%, was in the form of nitrate. Within the 103 mi² drainage area of Big Spring, the total nitrogen output was equivalent to 3.7 lbs-N/acre and the total nitrate-nitrogen output was 3.0 lbs-N/acre. The annual fw mean nitrate concentration and total nitrate-nitrogen output were the lowest recorded during WYs 1982-1992. Flowweighted mean monthly nitrate concentrations varied from 33 mg/L (7.2 mg/L as NO₃-N) in October to 18 mg/L (4.0 mg/L as NO₃-N) in February. Monthly nitrate-nitrogen discharge varied from 10,000 pounds in February to 24,000 pounds in March. The greatest monthly nitrate-nitrogen discharge during WY 1989 was less than the smallest monthly discharge (25,000 pounds in September) in WY 1988.

A total of 3,853,485 pounds of nitrogen were discharged by the Turkey River in WY 1989 (Libra et al., 1991). Of this total, 1,580,050 pounds, or 41%, was discharged in the form of nitrate at a fw mean concentration of 11.9 mg/L (2.6 mg/L as NO₃-N). Within the 1,545 mi² drainage area of TR01, the total nitrogen output was equivalent to 3.9 lbs-N/acre, and the total nitrate-nitrogen output equaled 1.6 lbs-N/acre. Nitrate concentrations from the Turkey River were more variable than concentrations from Big Spring during the water year. Monthly fw mean nitrate concentrations varied from 19 mg/L (4.2 mg/L as NO₃-N) in December to 5 mg/L (1.2 mg/L as NO₃-N) in July. The greatest monthly nitrate-nitrogen discharge, 398,000 pounds, occurred in March, accounting for 25% of the annual discharge, and the smallest monthly discharge, 26,000 pounds, occurred during July.

Pesticide Monitoring

Tables 6 and 7 and Figure 9 summarize the results of pesticide monitoring at sites L22T and L23S during WY 1989.

Fifty-nine samples from L22T were analyzed for pesticides during WY 1989. All samples contained detectable levels of atrazine (>0.10 μ g/L). The annual fw mean atrazine concentration was 0.40 μ g/L and the annual atrazine output was 0.017 pounds. Although the annual fw mean atrazine concentration for WY 1989 was the highest recorded during WYs 1987-1995, the annual atrazine discharge was the third smallest during the period of record.

As was the case with nitrate concentrations, atrazine concentrations at L22T were stable during the water year, except during recharge events. Atrazine concentrations remained between 0.14 μ g/L and 0.22 μ g/L from the beginning of the water year until January 30, when concentrations increased to 2.00 μ g/L as discharge peaked at 0.067

cfs during snowmelt. Concentrations declined to 0.20 µg/L as discharge receded to 0.021 cfs on February 6. In mid-March, atrazine concentrations increased to 8.50 µg/L, as discharge peaked at 0.050 cfs during snowmelt. Atrazine concentrations declined along with discharge through March then increased along with discharge to $0.27 \,\mu$ g/L on April 23. Concentrations decreased to 0.11 µg/L on April 26 as discharge receded. From late April through mid-August, atrazine concentrations fluctuated between 0.17 µg/L and 0.30 µg/L. On August 22 concentrations increased to $0.64 \,\mu$ g/L as groundwater discharge increased from 0.013 cfs to 0.087 cfs. Concentrations declined, then increased to 0.40 µg/L during a smaller event on August 23. Discharge increased from 0.13 cfs on August 31, to 0.237 cfs at 02:00 on September 1, and atrazine concentrations increased to 0.94 µg/L, prior to discharge peaking at 0.321 cfs at 14:20. Atrazine concentrations declined to 0.10 µg/L on September 26, which was the lowest concentration recorded during WY 1989.

Monthly fw mean atrazine concentrations at L22T varied from 0.18 μ g/L during the months of November, December, and May to 1.54 μ g/L in March. Monthly atrazine output varied from 2.64 grams in March, the month with the greatest groundwater discharge, to 0.17 grams during June, the month with the lowest groundwater discharge. March accounted for 35% of the annual atrazine output and 13% of the annual groundwater discharge.

Other pesticides detected at L22T during the water year include alachlor in four, or 7%, of the samples collected, cyanazine in four, or 7%, metolachlor in one, or 2%, and metribuzin in one, or 2%, of the samples collected. The highest concentrations of pesticides detected during the water year included atrazine at 8.50 µg/L, cyanazine at 0.71 µg/L, alachlor at 0.70 µg/L, metolachlor at 0.24 μ g/L, and metribuzin at 0.21 μ g/L. The maximum detection for atrazine occurred on March 14, for cyanazine and metribuzin the maximum detection was on August 22, and for metolachlor the maximum occurred on July 18. Cyanazine was also detected during the months of July and September, and alachlor was also detected in January and March.

During WY 1989, sixteen samples from L23S were analyzed for pesticides. Ten, or 63%, of the samples collected contained detectable levels of atrazine (>0.10 μ g/L). The annual fw mean atrazine concentration for L23S was 6.75 μ g/L, and the annual atrazine output was 10.1 pounds (Rowden et al., 1995a). The fw mean atrazine concentration for L23S during WY 1989 was the highest recorded during the period of record, and was probably, in part, due to a very high concentration (68.00 μ g/L) sampled during runoff on May 31.

At L23S, atrazine concentrations were below detectable limits from the beginning of the water year through most of January (Fig. 9). In late January, concentrations increased to 4.30 µg/L during runoff from snowmelt, then decreased to less than detectable concentrations by mid-February. Atrazine concentrations increased to 3.50 µg/ L in March, two days after peak runoff following snowmelt. Near the end of April, atrazine concentrations had declined to 0.17 µg/L. In May, atrazine concentrations increased to 68.00 µg/L following minor precipitation. This was the highest atrazine concentration sampled at the surface-water sites during WY 1989 (Rowden et al, 1995a). Atrazine concentrations decreased to 1.50 µg/L in July, then to 0.15 µg/L in early August as discharge continued to recede. Following minor rainfall in August, concentrations increased to 1.50 µg/L, then decreased to non-detectable levels a week later. Rainfall generated runoff on August 22 and atrazine concentrations increased to 5.70 µg/L on August 23. Near the end of the month, atrazine concentrations were 2.60 µg/L following minor precipitation.

Monthly fw mean atrazine concentrations from L23S varied from non-detectable levels during the first three months of the water year to 9.84 μ g/L in March. March accounted for 3.9 kilograms, or 84% of the annual atrazine output and 58% of the annual surface-water discharge.

Other pesticides detected at L23S during the water year include cyanazine in seven, or 44%, of the samples collected, alachlor in two, or 13%, metolachlor in two, or 13%, and metribuzin in one, or 6%, of the samples collected. The highest concentrations of pesticides detected during the water year included atrazine at $68.00 \mu g/L$, alachlor

Table 8. Annual summary of water and chemicaldischarge for L22T for WY 1990.

DISCHARGE	
Total	
acre-feet millions cf millions cm	13.8 0.60 0.017
Average cfs cms mg/d gpm	0.019 0.001 0.012 8.5

PRECIPITATION AND DISCHARGE

Precipitation	37.87 inches (962 mm)
Discharge	1.95 inches (49.5 mm)
Discharge as %	
of precipitation	5.1%

NITRATE DISCHARGE

Concentration -	mg/L As NO	As NO ₃ -N
Flow-weighted me Mean of analyses		31.3 26.3
N	O ₃ -N output	Total N output
lbs - N kg - N lbs - N/acre	1,171 531 13.8	1,183 536 13.9

ATRAZINE DISCHARGE

Concentration - µg/L	
Flow-weighted mean	0.37
Mean of analyses	0.40
Total output	
lbs	0.014
g	6.33

at $38.00 \ \mu g/L$, cyanazine at $22.00 \ \mu g/L$, metolachlor at $4.20 \ \mu g/L$, and metribuzin at $0.13 \ \mu g/L$. All maximum detections occurred May 31. Cyanazine was detected during March, April, May, July, and August; alachlor was detected in May and August; metolachlor was detected in May and July; and metribuzin was detected during May only.

During WY 1989, 21.2 pounds of atrazine were discharged from Big Spring, at a fw mean concentration of $0.61 \mu g/L$ (Libra et al., 1991). Monthly fw mean atrazine concentrations and loads varied from $1.68 \mu g/L$ and 8.7 pounds in March, to $0.08 \mu g/L$ and 0.2 pounds in December.

The annual fw mean atrazine concentration for the Turkey River was 0.95 μ g/L and the annual atrazine discharge totaled 571 pounds (Libra et al., 1991). The highest monthly fw mean atrazine concentration, 1.88 μ g/L, occurred during May, and the lowest fw mean, 0.04 μ g/L, occurred in December. The largest monthly atrazine discharge, 246 pounds, occurred in March, accounting for 43% of the annual discharge, and the smallest monthly discharge, 1.2 pounds, occurred during December.

Water Year 1990

Discharge Monitoring

Tables 8 and 9 and Figure 10 summarize the discharge, water quality and chemical-load data for sites L22T and L23S during WY 1990. In Figure 10, note the increase in scale on the nitrate plot and the lower origin on the discharge axis of the discharge plot relative to WY 1989.

Water Year 1990 followed the two driest consecutive years in Iowa's recorded history. In the Big Spring area, precipitation during the water year was 37.87 inches, or five inches above the longterm average for northeast Iowa. The greatest monthly accumulation of rainfall occurred during August. The largest single rainfall occurred August 25, following two days of widespread rainfall, and caused extensive flooding throughout the Turkey River Valley.

The hydrographs for L22T and L23S show the continuation of the drought conditions that prevailed during WYs 1988 and 1989. Extremely lowflow conditions persisted during the first four months **Table 9.** Annual summary of water and chemical discharge for L23S for WY 1990. (Discharge data are from the U.S. Geological Survey, W.R.D., IA Dist.)

DISCHARGE

Total

acre-feet	982
millions cf	43
millions cm	1.2
Average	
cfs	1.4
cms	0.04
mg/d	0.88
gpm	610

PRECIPITATION AND DISCHARGE

Precipitation	37.87 inches (962 mm)
Discharge	4.19 inches (106 mm)
Discharge as % of precipitation	11%

NITRATE DISCHARGE

Concentration	i - mg/L	As NO ₃	As NO ₃ -N
Flow-weighted		25.4	5.6
Mean of analys		34.9	7.8
	NO ₃ -N o	output	Total N output
lbs - N	15,034		65,047
kg - N	6,818		29,500
lbs-N/acre	5.4		23.2

ATRAZINE DISCHARGE

Concentration - µg/L		
Flow-weighted mean Mean of analyses	6.52 1.14	
Total output		
lbs kg	17.4 7.9	

of the water year. Precipitation in March generated runoff, but very little infiltration recharge, and surface-water discharge quickly returned to base levels. Rainfall in May, June, and July generated minor runoff and provided enough infiltration recharge to sustain discharge.

The overall increase in precipitation during the latter part of the water year caused large increases in both runoff and infiltration recharge, which in turn caused large increases in discharge and the output of both nitrogen and pesticides.

From the beginning of the water year through December, the mean daily discharge at L22T remained below 0.01 cfs except during a few recharge events (Fig. 10). From January through February 27, daily discharge remained below 0.003 cfs, except during an event on February 5. Snowmelt in early March and precipitation in the spring and summer months generated both runoff and infiltration recharge, and discharge increased from late February through most of August. The monthly precipitation during September was only 0.37 inches, or 2.93 inches below normal. The lack of recharge during September led to rapidly receding discharge at all sites within the Big Spring basin. The annual groundwater discharge from L22T for WY 1990 was 13.8 ac-ft, at an average daily discharge rate of 0.019 cfs (Table 8). The annual surface-water discharge was equivalent to 5.1% of the annual precipitation during the water year. This was the lowest annual discharge, and discharge as a percent of precipitation, recorded at L22T during WYs 1987-1995. The annual discharge from L23S during the water year was 982 ac-ft and the average daily discharge was 1.4 cfs (Table 9; Rowden et al., 1995a). The annual discharge from L23S was equivalent to 11% of the precipitation during the water year.

At Big Spring the annual discharge during WY 1990 was 17,476 ac-ft, or 8% of the annual precipitation, and the average daily discharge rate was 24.1 cfs (Rowden et al., 1993). This is the secondlowest annual discharge, and the lowest percent of precipitation discharged during WYs 1982-1992. The annual surface-water discharge from the Turkey River was 631,900 ac-ft, at an average discharge rate of 873 cfs (Rowden et al., 1993). Annual discharge from TR01 equaled 20% of the



Figure 10. A) Atrazine and B) nitrate concentrations, and C) groundwater and surface-water discharge (Q) at L22T and L23S for WY 1990 (note the increase in scale on the nitrate plot, and the lower origin on the discharge axis of the discharge plot relative to WY 1989). (Discharge data for L23S are from the U.S. Geological Survey, W.R.D., IA Dist.)

annual precipitation and 93% of the long-term discharge average.

Although the annual basin precipitation was five inches above the long-term average, the amount of runoff, annual discharge, and discharge as a percent of precipitation were relatively low throughout the basin during the water year. A large percentage of the precipitation likely replenished soil moisture and infiltrated the less transmissive parts of the basin's hydrologic system that had been depleted during WYs 1988 and 1989.

Nitrate Monitoring

Tables 8 and 9 and Figure 10 summarize the nitrate analyses from L22T and L23S during WY 1990.

During the water year, ninety samples from L22T were analyzed for nitrate, and sixty-two samples were analyzed for N-series. The annual fw mean nitrate concentration was 140.8 mg/L (31.3 mg/L as NO₃-N). The total nitrate-nitrogen output for the water year was 1,171 pounds, and the total nitrogen output (nitrate- plus organic- and ammonia-nitrogen) was 1,183 pounds. Within the drainage area of L22T these outputs were equivalent to 13.8 lbs-N/acre for total nitrate-nitrogen and 13.9 lbs-N/acre for total nitrogen.

During the first five months of the water year, nitrate concentrations at L22T were relatively constant, except during a recharge event on October 30. Concentrations ranged between 74 mg/L (16.4 mg/L as NO₃-N) on October 16, to 49 mg/L (10.9 mg/L as NO₃-N) of February 5. Concentrations then increased to 129 mg/L (28.7 mg/L as NO₃-N) as discharge increased from 0.005 cfs to 0.028 cfs during the event near the end of October. On March 14 at 17:30, concentrations increased to 196 mg/L (43.6 mg/L as NO₃-N) as discharge was receding from a peak of 0.119 cfs at 17:00. The nitrate concentration declined to 82 mg/L (18.2 mg/ L as NO₃-N) on March 19, then to 65 mg/L (14.4 mg/L as NO₃-N) on May 8. During the last five months of the water year, large short-term fluctuations in nitrate concentrations occurred during recharge events. The nitrate concentration increased to 301 mg/L (66.9 mg/L as NO₃-N) during events on May 19 and June 22. Peak nitrate concentrations occurred within minutes following peak groundwater discharge. From July through mid-August nitrate concentrations remained between 110 mg/ L (24.4 mg/L as NO₃-N) and 72 mg/L (16.0 mg/ L as NO₃-N). Nitrate concentrations increased to 229 mg/L (50.9 mg/L as NO₃-N) on August 24, then declined along with discharge through the remainder of the water year.

Monthly fw mean nitrate concentrations at L22T ranged between 56.8 mg/L (12.6 mg/L as NO₃-N) in February and 180.3 mg/L (40.1 mg/L as NO₃-N) in July. August had the greatest monthly nitrate-nitrogen output of 527 pounds, and the greatest monthly groundwater discharge at 4.9 ac-ft. August accounted for 45% of the annual nitrate-nitrogen output and 36% of the annual groundwater discharge at L22T.

During WY 1990, forty-six samples from L23S were analyzed for nitrate, and thirty-one samples were analyzed for N-series. The annual fw mean nitrate concentration was 25.4 mg/L (5.6 mg/L as NO₃-N; Rowden et al., 1995a). The total nitrate-nitrogen output for the water year was 15,034 pounds, or 5.4 lbs-N/acre, and the total nitrogen output (nitrate- plus organic- and ammonia-nitrogen) was 65,047 pounds, or 23.2 lbs-N/acre, within the L23S drainage area.

Nitrate concentrations from L23S followed the same general trends as concentrations from L22T, but showed a much smaller range of fluctuation. During the first five months of WY 1990, nitrate concentrations remained between 37 mg/L (8.2 mg/L as NO₃-N) in late October and 6 mg/L (1.3 mg/L as NO₃-N) in late February (Fig. 10). Precipitation in mid-March generated runoff and minor infiltration recharge, and nitrate concentrations increased from 7 mg/L (1.6 mg/L as NO₃-N) to 30 mg/L (6.7 mg/L as NO₃-N). Following the events, discharge remained steady, and nitrate concentrations declined to 8 mg/L (1.8 mg/L as NO₃-N) in early May. Later in May, nitrate concentrations increased to 78 mg/L (17.3 mg/L as NO₃-N) following minor precipitation. The highest nitrate concentration sampled at L23S during the water year, 106 mg/L (23.6 mg/L as NO₃-N), was sampled in mid-June, one day after a runoff event. Increases in precipitation during the latter part of WY 1990 led to increased infiltration recharge and elevated nitrate concentrations from June through September. During August, nitrate concentrations increased to 104 mg/L (23.1 mg/L as NO₃-N), two days after the greatest runoff during the water year. Concentrations then decreased, along with discharge, throughout the remainder of the water year.

The lowest fw mean nitrate concentration from L23S, 3.5 mg/L (0.8 mg/L as NO₃-N), occurred during March, when snowmelt constituted a large percentage of the discharge. The highest monthly fw mean, 57 mg/L (12.7 mg/L as NO₃-N), occurred during June, when an increased percentage of discharge was being supplied by infiltration recharge. Forty percent of the annual nitrate-nitrogen, or 6,033 pounds, was discharged during August, the month that had the greatest monthly surface-water discharge, which accounted for 42% of the annual total.

The annual fw mean nitrate concentration for Big Spring during WY 1990 was 37 mg/L (8.2 mg/ L as NO₃-N; Rowden, et al., 1993). A total of 420,294 pounds of nitrogen were discharged, and of this total, 388,479 pounds, or 92%, was in the form of nitrate. Within the 103 mi² drainage area of Big Spring, the total nitrogen output was equivalent to 6.4 lbs-N/acre, and the total nitrate-nitrogen output was 5.9 lbs-N/acre. Monthly fw mean nitrate concentrations varied from 19 mg/L (4.1 mg/L as NO₃-N) in February to 52 mg/L (11.6 mg/L as NO₃-N) in September. Monthly fw means remained below 30 mg/L (6.7 mg/L as NO₃-N) from October through April and above the 45 mg/L (10.0 mg/L as NO₃-N) drinking water standard from June through September. The greatest monthly nitrate-nitrogen load and groundwater discharge, 70,000 pounds and 2,542 ac-ft, occurred in August. The smallest monthly nitrate-nitrogen load, 11,000 pounds, occurred during November and December, months with the second lowest and lowest groundwater discharge, respectively. The nitratenitrogen discharge from Big Spring during these two months was the lowest recorded during WYs 1982-1992.

A total of 16,724,530 pounds of nitrogen were discharged by the Turkey River in WY 1990 (Rowden, et al., 1993). Of this total, 11,649,897 pounds, or 70%, was discharged in the form of

nitrate at a fw mean concentration of 30.5 mg/L (6.8 mg/L as NO₃-N). Within the $1,545 \text{ mi}^2$ drainage area of TR01, the total nitrogen output was equivalent to 16.9 lbs-N/acre, and the total nitrate-nitrogen output equaled 11.8 lbs-N/acre. Monthly fw mean nitrate concentrations varied from 11 mg/L (2.4 mg/L as NO₃-N) in October to 50 mg/L (11.0 mg/L as NO₃-N) in May. The highest monthly fw mean nitrate concentration previously recorded for the Turkey River was 34 mg/L (7.6 mg/L as NO₃-N), occurring in November and December of WY 1986. The greatest monthly nitrate-nitrogen discharge, 3,578,000 pounds, or 31% of the annual discharge, occurred in August, the month with the highest surfacewater discharge. The smallest monthly nitratenitrogen discharge, 66,000 pounds, occurred during October, and represented less than 0.6% of the annual discharge.

Pesticide Monitoring

Tables 8 and 9 and Figure 10 summarize the results of pesticide monitoring at sites L22T and L23S during WY 1990.

Seventy-eight samples from L22T were analyzed for pesticides during WY 1990. Seventy-four, or 95%, of the samples contained detectable levels of atrazine (>0.10 μ g/L). The annual fw mean atrazine concentration was 0.37 μ g/L, and the annual atrazine output was 0.014 pounds.

From the beginning of the water year, atrazine concentrations remained between 0.15 µg/L and 0.25 µg/L until October 31 when concentrations decreased to 0.10 μ g/L after a recharge event on October 30 (Fig. 10). Concentrations remained near 0.17 µg/L from November through December, decreasing temporarily to non-detectable levels (<0.10 µg/L) on November 27. In mid-January, atrazine concentrations decreased to 0.10 µg/L, then increased to 0.30 µg/L on February 5, during snowmelt. Concentrations then decreased to 0.13 μ g/L, then increased to 1.90 μ g/L during recharge on March 11. Afterward, atrazine concentrations remained near 0.10 µg/L through early May, decreasing to non-detectable levels on March 19, April 16, and May 14. The greatest atrazine concentration recorded at L22T during the water year, $8.20 \mu g/L$, was sampled during runoff on May 19. During the remainder of the water year, atrazine concentrations remained above detection limits, increasing during runoff, then decreasing, and gradually increasing until the next event.

Monthly fw mean atrazine concentrations at L22T varied from $0.07 \,\mu$ g/L in June to $0.98 \,\mu$ g/L in May. The greatest monthly atrazine output, 2.14 grams, and the greatest monthly surface-water discharge, 4.9 ac-ft, occurred during August and accounted for 34% of the annual atrazine discharge and 36% of the annual discharge.

The only other pesticide detected at L22T during WY 1990 was cyanazine in three, or 4%, of the samples collected. The greatest concentrations of pesticides detected during the water year included atrazine at 8.20 μ g/L and cyanazine at 0.24 μ g/L. The maximum detection for atrazine occurred on May 19, and the maximum detection for cyanazine was also detected once in October.

During WY 1990, thirty-one samples from L23S were analyzed for pesticides. Twenty-nine, or 94%, of the samples collected contained detectable levels of atrazine (> $0.10 \mu g/L$). The annual atrazine output from L23S was 17.4 pounds, at an annual fw mean concentration of 6.52 $\mu g/L$ (Rowden et al., 1995a).

Atrazine concentrations at L23S increased from non-detectable levels in early October to 2.90 μ g/L in mid-February, then declined to 0.36 μ g/L in late February. Concentrations increased to 3.50 μ g/L following runoff in March, then declined to 0.18 μ g/ L in late April. In May, atrazine concentrations increased to 1.10 μ g/L following minor precipitation, then declined to 0.37 μ g/L near the end of the month. The greatest atrazine concentration reported from L23S, 16.0 μ g/L, was sampled June 14, one day after runoff. During the remainder of the water year, atrazine concentrations declined.

Monthly fw mean atrazine concentrations at L23S varied from $0.14 \mu g/L$ in October to $9.14 \mu g/L$ in August. August had the highest monthly atrazine output, 4.7 kilograms, and the highest monthly surface-water discharge, 413 ac-ft, which accounted for 59% of the annual atrazine output and 42% of the surface-water discharge.

Table 10. Annual summary of water and chemicaldischarge for L22T for WY 1991.

DISCHARGE			
Total			
acre-feet millions cf millions cm Average	79.2 3.4 0.098		
cfs cms mg/d gpm	0.11 0.003 0.071 48.9		

PRECIPITATION AND DISCHARGE

Precipitation	47.27 inches (1,201 mm)
Discharge	11.18 inches (284 mm)
Discharge as % of precipitation	24%

NITRATE DISCHARGE

Concentration -	· mg/L	As NO3	As NO ₃ -N
Flow-weighted n		140.8	31.3
Mean of analyse		114.6	25.5
	NO ₃ -N ou	utput	Total N output
lbs - N	6,735		6,811
kg - N	3,054		3,088
lbs - N/acre	79.2		80.1

ATRAZINE DISCHARGE

Concentration - µg/L

Flow-weighted mean	0.29
Mean of analyses	0.26
Total output	
lbs	0.063
g	28.6

Other pesticides detected at L23S during the water year include cyanazine and alachlor in four, or 13%, and metolachlor in three, or 10%, of the samples collected. The highest concentrations of pesticides detected during the water year included atrazine at 16.00 μ g/L, metolachlor at 1.90 μ g/L, alachlor at 1.40 μ g/L, and cyanazine at 0.57 μ g/L. All maximum detections occurred June 14. Cyanazine was detected during February, May, and June, alachlor was detected in November, May, and June, and metolachlor was detected in April and June.

During the water year, 50 pounds of atrazine were discharged from Big Spring, at a fw mean concentration of 1.06 μ g/L (Rowden et al., 1993). This was the highest annual fw mean atrazine concentration and annual load observed at Big Spring during WYs 1982-1990. Monthly fw mean atrazine concentrations and loads varied from 2.38 μ g/L and 14.9 pounds in June, to 0.16 μ g/L and 0.3 pounds in December.

The annual fw mean atrazine concentration for the Turkey River was 1.90 μ g/L and the annual atrazine discharge totaled 3,259 pounds (Rowden et al., 1993). The highest monthly fw mean atrazine concentration, 4.88 μ g/L, occurred in June, and the lowest fw mean, 0.14 μ g/L, occurred in December. The greatest monthly atrazine discharge, 1,236 pounds, occurred in August, accounting for 38% of the annual discharge, and the smallest monthly discharge, 2.4 pounds, occurred in December.

Water Year 1991

Discharge Monitoring

Tables 10 and 11 and Figure 11 summarize the discharge, water quality and chemical-load data for sites L22T and L23S for WY 1991 (note the decrease in scale on the atrazine and nitrate plots, and the different origin on the discharge plot relative to WY 1990).

Basin precipitation during the water year was 47.27 inches, or 143% of the long-term average. This was the greatest annual precipitation recorded in the Big Spring basin during WYs 1982-1995 (Liu et al., 1997). Precipitation was slightly below

Table 11. Annual summary of water and chemicaldischarge for L23S for WY 1991. (Discharge dataare from the U.S. Geological Survey, W.R.D., IADist.)

DISCHARGE

Total

acre-feet	3,594
millions cf	156
millions cm	4.4
Average	
cfs	4.9
cms	0.14
mg/d	3.2
gpm	2,230

PRECIPITATION AND DISCHARGE

Precipitation	47.27 inches (1,201 mm)
Discharge	15.36 inches (390 mm)
Discharge as % of precipitation	32%

NITRATE DISCHARGE

Concentration	- mg/L	As NO	As NO ₃ -N
Flow-weighted Mean of analys		53.9 55.1	12.0 12.3
	NO ₃ -N ou	utput	Total N output
lbs - N kg - N lbs - N/acre	117,1 53,1		174,304 79,050 62.0

ATRAZINE DISCHARGE

Concentration - µg/L

Flow-weighted mean	2.30
Mean of analyses	0.24
Total output	
lbs	22.5
kg	10.2



Figure 11. A) Atrazine and B) nitrate concentrations, and C) groundwater and surface-water discharge (Q) at L22T and L23S for WY 1991 (note the decrease in scale on the atrazine and nitrate plots, and the slightly different origin on the discharge plot relative to WY 1990). (Discharge data for L23S are from the U.S. Geological Survey, W.R.D., IA Dist.)

normal from October through February, far below normal in July, and far above normal from March through June. The greatest monthly accumulation of rainfall, 13.09 inches, occurred during June and the largest single rainfall (local reports of 11 to 13 inches near Monona, Iowa) occurred on June 14, causing extensive flooding throughout the Big Spring area.

The groundwater discharge from L22T during WY 1991 was 79.2 ac-ft, and the average daily discharge was 0.11 cfs (Table 10). The annual discharge was equivalent to 24% of the annual precipitation. At L23S, the annual discharge for the water year was 3,594 ac-ft, at an average daily rate of 4.9 cfs (Table 11; Rowden et al., 1995a). The annual discharge from L23S was equal to 32% of the annual precipitation.

At Big Spring, the annual groundwater discharge was 42,481 ac-ft, or 16% of the annual precipitation, at an average flow rate of 59 cfs (Rowden et al., 1993). The annual discharge from the Turkey River was 1,103,000 ac-ft, at an average rate of 1,524 cfs (Rowden et al., 1993). The discharge accounted for 28% of the precipitation and was 160% of the long-term discharge average. The greatest instantaneous discharge recorded during WYs 1914-1995 at Garber, 49,900 cfs, occurred on June 15, 1991. The groundwater and surface-water discharge from all sites within the basin increased significantly during the springmonths of WY 1991 (Rowden et al., 1995a).

During the first five months of the water year, the mean daily discharge at L22T remained below 0.015 cfs, and the mean daily discharge at L23S continued to recede from the last major runoff event in WY 1990 (Fig. 11). Discharge at L23S remained relatively steady from October through February, ranging from 0.88 cfs in early October to 0.22 cfs in early December. Snowmelt and small amounts of rainfall in late February and March generated minor runoff and infiltration recharge, and discharge at all sites within the basin increased significantly. Above average rainfall during April, May, and June generated increased runoff and infiltration recharge. Mean daily discharge at all sites peaked in mid-June following intense rains and then receded through August. Precipitation in mid-September generated minor runoff, followed by

receding discharge during the remainder of the water year. The peak daily discharges recorded in mid-June were the greatest observed at the surface-water sites during WYs 1986-1995 and at Big Spring during WYs 1982-1995 (Liu et al., 1997). 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.

Nitrate Monitoring

Tables 10 and 11 and Figure 11 summarize the nitrate analyses from L22T and L23S during WY 1991.

During the water year, sixty-six samples from L22T were analyzed for nitrate, and sixty-two samples were analyzed for N-series. The annual fw mean nitrate concentration, 140.8 mg/L (31.3 mg/L as NO₃-N), was the same as the annual fw mean for WY 1990, and was the greatest recorded during WYs 1987-1995. The annual nitrate-nitrogen output for the water year was 6,735 pounds, and the total nitrogen output was 6,811 pounds. Within the drainage area of L22T these outputs were equivalent to 79.2 lbs-N/acre for total nitrate-nitrogen.

The nitrate plots for L22T and L23S show the same general trends as the hydrographs for the two sites. During the first five months of the water year, concentrations ranged from 62 mg/L (13.8 mg/L as NO₃-N) to 69 mg/L (15.3 mg/L as NO₃-N) at L22T, and from 43 mg/L (9.6 mg/L as NO₃-N) to 30 mg/ L (6.7 mg/L as NO₃-N) at L23S. Nitrate concentrations increased along with discharge during most of March. At L22T, concentrations peaked at 213 mg/L (47.3 mg/L as NO₃-N) at 11:30 as discharge was receding from a peak of 0.957 cfs at 06:00, on the morning of March 27. Concentrations declined to 118 mg/L (26.2 mg/L as NO₃-N) on April 8 as discharge increased. Nitrate concentrations increased to 202 mg/L (44.9 mg/L as NO₃-N) on April 14 at 05:00, prior to discharge peaking at 0.388 cfs at 11:00. From mid-April through June, nitrate concentrations showed a declining trend, decreasing to 129 mg/L (28.7 mg/L as NO₃-N) on June 10. Concentrations decreased from 155 mg/L (34.4 mg/L as NO₃-N) on June 17 to 78 mg/L (17.3 mg/ L as NO_3 -N) on July 8. During the rest of the water year nitrate concentrations at L22T remained near 70 mg/L (15.6 mg/L as NO_3 -N).

At L22T the greatest monthly fw mean nitrate concentration, 163 mg/L (36.3 mg/L as NO₃-N), occurred during April, and the lowest monthly fw mean, 63.7 mg/L (14.2 mg/L as NO₃-N), occurred during February. The greatest monthly nitrate output, 2,168 pounds, and greatest monthly groundwater discharge, 24.4 ac-ft, occurred during June, and accounted for 32% of the annual nitrate-nitrogen output and 31% of the annual groundwater discharge at L22T.

During WY 1991, forty-eight samples from L23S were analyzed for nitrate, and thirty samples were analyzed for N-series. The annual fw mean nitrate concentration was 53.9 mg/L (12.0 mg/L as NO₃-N), the annual nitrate-nitrogen output for the water year was 117,164 pounds, or 41.7 lbs-N/ acre, and the total nitrogen output was 174,304 pounds, or 62.0 lbs-N/acre (Rowden et al., 1995a). The annual fw mean nitrate concentration for WY 1991 was the greatest recorded at L23S during WYs 1986-1995.

Nitrate concentrations from L23S showed the same general trends as concentrations from L22T during the water year, remaining lower during the first five months of the water year, then increasing from March through most of June, and then decreasing through early September. The lowest concentration during the water year, 27 mg/L (6.0 mg/L as NO₃-N), occurred in March during minor runoff, and the highest concentration, 126 mg/L (28.0 mg/L as NO₃-N), occurred June 17, two days after the largest runoff event during the period of record.

The lowest monthly fw mean nitrate concentration from L23S, 31.1 mg/L (6.9 mg/L as NO₃-N), occurred during December, and the highest monthly fw mean, 81.0 mg/L (18.0 mg/L as NO₃-N), occurred during April, when an increased percentage of discharge was being supplied by infiltration recharge. Fifty-three percent of the annual surface-water discharge, and 44%, or 51,157 pounds of the annual nitrate-nitrogen, were discharged during June.

The annual fw mean nitrate concentration for Big Spring during WY 1991 was 56.4 mg/L (12.5 mg/L as NO₃-N; Rowden et al., 1993). A total of 1,561,450 pounds of nitrogen were discharged, and of this total, 1,445,506 pounds, or 93%, was in the form of nitrate. Within the 103 mi² drainage area of Big Spring, the total nitrogen output was equivalent to 23.7 lbs-N/acre and the total nitrate-nitrogen output was 21.9 lbs-N/acre. The annual fw mean nitrate concentration and total nitrate-nitrogen output were the highest recorded during the WY 1982-1992 period of record.

The highest monthly fw mean nitrate concentrations from Big Spring during WYs 1982-1991 occurred in April, May, June, and July of WY 1991. Concentrations decreased from 70 mg/L in April to $61 \text{ mg/L in July} (15.5 \text{ mg/L to } 13.6 \text{ as } \text{NO}_3\text{-N})$. The highest monthly fw mean nitrate concentrations previously recorded were 54 mg/L in April and 56 mg/L in July, of WY 1983. The lowest monthly fw mean nitrate concentration during the water year, 30 mg/L (6.7 mg/L as NO₃-N), occurred in January and February. Monthly nitrate-nitrogen loads varied from 15,000 pounds in January, the month with the lowest groundwater discharge, to 326,000 pounds in June, the month with the greatest groundwater discharge. The monthly nitrate-nitrogen discharges during April, May, June, and July were the highest recorded during WYs 1982-1991.

A total of 34,244,926 pounds of nitrogen were discharged by the Turkey River during WY 1991 (Rowden et al., 1993). Of this total, 29,591,638 pounds, or 86%, was discharged in the form of nitrate, at a fw mean concentration of 44.4 mg/L (9.9 mg/L as NO₃-N). Within the 1,545 mi² drainage area of TR01, the total nitrogen output was equivalent to 34.6 lbs-N/acre, and the total nitrate-nitrogen output equaled 29.9 lbs-N/acre. Monthly fw mean nitrate concentrations varied from 22 mg/L (5.0 mg/L as NO₃-N) in January to 49 mg/L (10.9 mg/L as NO₃-N) in March. Monthly nitrate-nitrogen discharge varied from 198,000 pounds in January to 7,505,000 pounds in June, which accounted for 25% of the annual total for WY 1991. The monthly nitrate-nitrogen discharge remained well above 4 million pounds from March through June. Previously, the greatest monthly nitrate-N discharge was 3.8 million pounds in March of WY 1986.

Pesticide Monitoring

Tables 10 and 11 and Figure 11 summarize the results of pesticide monitoring at L22T and L23S for WY 1991.

Sixty-three samples from L22T were analyzed for pesticides during WY 1991. Fifty-five, or 87%, of the samples collected contained detectable levels of atrazine (>0.10 μ g/L). The annual fw mean atrazine concentration was 0.29 μ g/L, and the annual atrazine output was 0.063 pounds. The annual atrazine output during WY 1991 was the greatest recorded at L22T during WYs 1987-1995.

Atrazine concentrations from L22T and L23S showed trends similar to nitrate concentrations during the water year. Concentrations at L22T were steady during the first five months of the water year, ranging from $0.22 \,\mu$ g/L on October 1, to below the detection limit of 0.10 µg/L on December 19. From March through early June, atrazine concentrations showed greater fluctuations: increasing during recharge events, declining below detectable concentrations (<0.10 μ g/L) in some samples collected in March, April, and May, and peaking at 1.40 μ /L on May 10 and May 29. Atrazine concentrations probably reached greater concentrations on June 15, but the automatic sampler was inundated during the major event and failed to function. During July and August, concentrations ranged from $0.11 \,\mu\text{g/L}$ to $0.21 \,\mu\text{g/L}$. Atrazine concentrations increased to 1.00 µg/L on September 12, during the last precipitation event of the water year, and then decreased to 0.12 μ g/L before increasing to $0.17 \,\mu$ g/L on September 30.

Monthly fw mean atrazine concentrations at L22T varied from 0.05 μ g/L in December to 0.91 μ g/L in June. The greatest monthly atrazine output during the period of monitoring, 16.3 grams, also occurred during June, and accounted for 57% of the annual atrazine discharge.

Other pesticides detected at L22T during WY 1991 include alachlor in five, or 8%, and cyanazine in one, or 2%, of the samples collected. The highest concentrations of pesticides detected during the water year included atrazine at 1.40 μ g/L and cyanazine at 0.19 μ g/L. The maximum detections for atrazine occurred on May 29 and 30, and for alachlor, on September 12. The only detection of

cyanazine occurred on June 4. Alachlor was detected once in June and four times in September.

During WY 1991, thirty samples from L23S were analyzed for pesticides. Twenty-five, or 83%, of the samples collected contained detectable levels of atrazine (> $0.10 \mu g/L$). The annual atrazine output from L23S was 22.5 pounds, at an annual fw mean concentration of 2.30 $\mu g/L$ (Rowden et al., 1995a). The annual atrazine output for the water year was the greatest recorded at L23S during WYs 1986-1995.

Atrazine concentrations from L23S showed similar seasonal trends as concentrations from L22T, being lower during the first five months of the year, increasing through spring, then decreasing through the summer. From the beginning of the water year, concentrations decreased from 0.14 μ g/L to 0.10 μ g/L at the end of October. In November, concentrations increased to $0.12 \,\mu g/L$, then declined to non-detectable levels in mid-December. Atrazine concentrations remained below the detection limit until mid-March. From March through May, runoff events led to a general increase in atrazine concentrations. Atrazine concentrations increased to 0.71 µg/L during an event in mid-May, then declined to 0.29 µg/L a week later as discharge receded. The greatest atrazine concentration from L23S, 1.80 µg/L, was sampled two days after the major runoff even that occurred June 15. During the remainder of the water year, concentrations generally declined to 0.20 µg/L in September.

At other surface-water sites within the basin and at Big Spring, the greatest atrazine concentrations of the water year also occurred during the large event in mid-June (Rowden et al., 1995a). Sites L22T and L23S were not sampled during the event, so the maximum concentrations at these sites for the water year were much lower than the maximums from other sites in the basin. Estimates of atrazine concentrations during the event were based on concentrations from other sites, and as a result, the annual fw mean atrazine concentration for L23S exceeded the maximum concentration detected during the water year.

Monthly fw mean atrazine concentrations from L23S varied from 0.06 μ g/L in December to 3.91 μ g/L in June. June had the greatest monthly

atrazine output, 9.3 kilograms, and the greatest monthly surface-water discharge, 1,920 ac-ft, during the period of record. These monthly totals accounted for 91% of the annual atrazine output and 53% of the annual surface-water discharge.

Other pesticides detected at L23S during the water year include cyanazine in four, or 13%, alachlor in four, or 13%, and metolachlor in two, or 7%, of the samples collected. The greatest concentrations of pesticides detected during the water year included atrazine at 1.80 μ g/L, cyanazine at 0.74 μ g/L, metolachlor at 0.56 μ g/L, and alachlor at 0.32 μ g/L. The maximum detections for atrazine, metolachlor, and alachlor occurred June 17, and for cyanazine the maximum detection occurred April 9. Alachlor was detected during January, May, and June; cyanazine was detected in April, May and June; and metolachlor was detected in May and June.

At Big Spring, 135 pounds of atrazine were discharged during the water year at a fw mean concentration of $1.17 \mu g/L$ (Rowden et al., 1993). Monthly fw mean concentrations varied from $3.32 \mu g/L$ in June to $0.16 \mu g/L$ in February. The greatest monthly atrazine loads occurred during June, when 76.0 pounds of atrazine were discharged, and the smallest monthly atrazine discharge, 0.4 pounds, occurred in February. Atrazine discharge during June accounted for 56% of the annual total. The monthly fw means and loads registered during May and June of WY 1991 exceeded all previous monthly fw means and loads from Big Spring during WYs 1982-1992.

The atrazine discharge from the Turkey River during the water year was 3,325 pounds, at a fw mean concentration of 1.11 μ g/L (Rowden et al., 1993). The highest monthly fw mean atrazine concentration and discharge occurred in June, at 2.94 μ g/L, and 2,102 pounds, while the lowest occurred during January, at 0.21 μ g/L, and 8.5 pounds. Over 63% of the annual atrazine output occurred during June.

The annual fw mean atrazine concentrations and loads observed at Big Spring and the Turkey River at Garber during WY 1991 exceeded all previous annual fw means and loads registered during WYs 1986 through 1992.

Water Year 1992

Discharge Monitoring

Tables 12 and 13 and Figure 12 summarize the discharge, water quality and chemical-load data for sites L22T and L23S for WY 1992. In Figure 12, note the decrease in scale on the nitrate plot and the change in the origin on the discharge plot relative to WY 1991.

Water Year 1992 followed the two wettest consecutive water years during WYs 1982-1995. Precipitation during the water year was 35.74 inches, or 2.8 inches, above the long-term average. Rainfall was more evenly distributed than during WYs 1990 and 1991, with no large single rainfall or runoff events. Precipitation was above average during October, November, and September, and below average during May, June, and August.

Above average precipitation during October and November, combined with the recharge that occurred during WY 1991, led to sustained increases in discharge at groundwater and surfacewater sites throughout the basin during November and December. Discharge generally receded from December through most of February, with minor snowmelt and precipitation generating little runoff. Snowmelt and precipitation later in February generated enough recharge to sustain discharge for a few weeks, and then discharge continued to recede through most of April. The second largest event of the water year occurred in mid-April, followed by general recession through mid-June. During July, precipitation led to small increases in discharge, followed by generally receding discharge through August. Above average precipitation during September led to increases in discharge early in the month, followed by general recession during the remainder of the water year.

The annual groundwater discharge from site L22T during the water year was 103.5 ac-ft and the average daily discharge was 0.14 cfs (Table 12). The annual discharge from L22T was equivalent to 41% of the annual precipitation. At L23S, the annual discharge during WY 1992 was 3,980 ac-ft, and the average daily discharge was 5.5 cfs (Table 13; Rowden et al., 1995a). The annual discharge from L23S was equal to 48% of the annual precipitation.

Table 12. Annual summary of water and chemicaldischarge for L22T for WY 1992.

DISCHARGE			
Total			
acre-feet millions cf millions cm	103.5 4.5 0.13		
Average			
cfs cms mg/d gpm	0.14 0.004 0.092 64.2		

PRECIPITATION AND DISCHARGE

35.74 inches (908 mm)
14.61 inches (371 mm)
41%

NITRATE DISCHARGE

Concentratio	n - mg/L	As NO3	As NO ₃ -N
Flow-weighted		83.3	18.5
Mean of analy		80.5	17.9
	NO ₃ -N o	utput	Total N output
lbs - N	,	213	5,292
kg - N		364	2,400
lbs - N/acre		61.3	62.3

ATRAZINE DISCHARGE

Concentration - µg/L	
Flow-weighted mean	0.11
Mean of analyses	0.11
Total output	
lbs	0.032
g	14.6

At Big Spring the annual discharge during WY 1992 was 37,278 ac-ft, or 19% of the annual precipitation, and the average daily discharge rate was 51.4 cfs (Rowden et al., 1995b). The annual surface-water discharge from the Turkey River was 1,101,000 ac-ft, at an average discharge rate of 1,517 cfs (Rowden et al., 1995b). Annual discharge from TR01 was equivalent to 37% of the annual precipitation and 162% of the long-term discharge average.

Nitrate Monitoring

Tables 12 through 13 and Figure 12 summarize the nitrate analyses from L22T and L23S during WY 1992.

During the water year, sixty-two samples from L22T were analyzed for nitrate, and sixty samples were analyzed for N-series. The annual fw mean nitrate concentration was 83.3 mg/L (18.5 mg/L as NO -N). The annual nitrate-nitrogen output for the water year was 5,213 pounds, and the annual nitrogen output (nitrate- plus organic-, and ammonia-nitrogen) was 5,292 pounds. Within the 85-acre drainage area of L22T these outputs were equivalent to 61.3 lbs-N/acre for nitrate-nitrogen and 62.3 lbs-N/acre for total nitrogen.

The overall increase in infiltration recharge during WY 1992 led to higher nitrate concentrations at most monitoring sites throughout the water year. Nitrate concentrations at L22T and L23S showed the same seasonal trends as discharge for the sites. Nitrate concentrations at L22T increased from 76 mg/L (16.9 mg/L as NO₃-N) in late October to the highest concentration recorded during the water year, 120 mg/L (26.7 mg/L as NO₃-N) in late November, as discharge increased. Nitrate concentrations decreased to 80 mg/L (17.8 mg/L as NO₃-N) in early January, then increased to 99 mg/L (22.0 mg/L as NO₃-N) following runoff. Concentrations then decreased as discharge receded. Nitrate concentrations were diluted to 49 mg/L (10.9 mg/L as NO₃-N) in mid-February and 51 mg/L (11.3 mg/L as NO₃-N) later in the month during snowmelt. Concentrations increased to 83 mg/L (18.4 mg/L as NO3-N) in March, then generally decreased through mid-April. Nitrate concentrations increased to 99 mg/L (22.0 mg/L as NO3**Table 13.** Annual summary of water and chemicaldischarge for L23S for WY 1992. (Discharge dataare from the U.S. Geological Survey, W.R.D., IADist.)

DISCHARGE

Total

acre-feet	3,980
millions cf	173
millions cm	4.9
Average	
cfs	5.5
cms	0.16
mg/d	3.5
gpm	2,459

PRECIPITATION AND DISCHARGE

Precipitation	35.74 inches (908 mm)
Discharge	17.00 inches (432 mm)
Discharge as % of precipitation	48%

NITRATE DISCHARGE

Concentration	- mg/L	As NO ₃	As NO ₃ -N
Flow-weighted Mean of analys		51.5 52.5	11.4 11.7
	NO ₃ -N o	utput	Total N output
lbs - N kg - N lbs - N/acre	123,9 56,0		143,301 64,990 51.0

ATRAZINE DISCHARGE

Concentration - μg/L			
Flow-weighted mean	0.26		
Mean of analyses	0.20		
Total output			
lbs	2.9		
kg	1.3		

N) on April 26 as discharge was receding from a recharge event that occurred on April 20. Concentrations declined through May, and were stable from June through August. Concentrations dropped to $55 \text{ mg/L} (12.2 \text{ mg/L as NO}_3\text{-N})$ in early September as discharge was increasing during an event, then increased to 77 mg/L (17.1 mg/L as NO}_3\text{-N}) two weeks later as discharge declined.

Monthly fw mean nitrate concentrations at L22T were consistently high during the water year. The smallest monthly fw mean concentration, 74 mg/L (16.4 mg/L as NO₃-N), occurred during February, March, June, and July. The greatest monthly fw mean, 107 mg/L (23.9 mg/L as NO₃-N), occurred during December. March, the month with one of the smallest monthly fw means, had the greatest monthly nitrate output, 719 pounds, and the greatest monthly groundwater discharge, 16.0 ac-ft. These totals accounted for 14% of the annual nitrate-nitrogen output and 16% of the annual groundwater discharge at L22T.

During WY 1992, fifty-one samples from L23S were analyzed for nitrate, and twenty samples were analyzed for N-series. The annual fw mean nitrate concentration was 51.5 mg/L (11.4 mg/L as NO₃-N; Rowden et al., 1995a). The total nitratenitrogen output for the water year was 123,530 pounds, which is equivalent to 44.0 lbs-N/acre, and the total nitrogen output (nitrate- plus organic- and ammonia-nitrogen) was 143,301 pounds, or 51.0 lbs-N/acre, within the L23S drainage area. The annual nitrate-nitrogen discharge during WY 1992 was the second greatest recorded at L23S during WYs 1986-1995.

The nitrate plot for L23S shows the same general trends as concentrations from L22T during the water year, with concentrations from L22T as in previous years. Nitrate concentrations increased from 47 mg/L (10.4 mg/L as NO₃-N) in early October to 67 mg/L (14.9 mg/L as NO₃-N) in November following infiltration recharge from precipitation. Concentrations remained steady through December, then declined during January and February. The lowest concentration sampled during the water year, 35 mg/L (7.8 mg/L as NO₃-N) occurred in February during snowmelt, and the highest concentration, 69 mg/L (15.3 mg/L as NO₃-N)



Figure 12. A) Atrazine and B) nitrate concentrations, and C) groundwater and surface-water discharge (Q) at L22T and L23S for WY 1992 (note the decrease in scale on the nitrate plot and the change in the origin on the discharge plot relative to WY 1991). (Discharge data for L23S are from the U.S. Geological Survey, W.R.D., IA Dist.)

N), occurred in April following runoff. Nitrate concentrations declined from April through mid-June, then increased temporarily following minor discharge events later in June, July, and August. Concentrations increased slightly in September following runoff.

The greatest monthly fw mean nitrate concentration at L23S, 61.7 mg/L (13.7 mg/L as NO₃-N), occurred during December, and the lowest monthly mean, 37.9 mg/L (8.4 mg/L as NO₃-N), occurred during February, when an increased percentage of discharge was being supplied by snowmelt. December had the greatest monthly nitrate-nitrogen output, 21,418 pounds, which accounted for 17% of the annual total, and the second-greatest monthly discharge, 574 ac-ft, which accounted for 14% of the annual discharge.

The annual fw mean nitrate concentration for Big Spring during WY 1992 was 54.2 mg/L (12.0 mg/L as NO₃-N; Rowden et al., 1995b). A total of 1,257,410 pounds of nitrogen were discharged, and of this total, 1,220,099 pounds, or 97%, was in the form of nitrate. Within the 103 mi² drainage area of Big Spring, the total nitrogen output was equivalent to 19.1 lbs-N/acre, and the total nitrate-nitrogen output was 18.5 lbs-N/acre. The annual fw mean nitrate concentration and total nitrate-nitrogen output were the second greatest recorded during WYs 1982-1992.

The greatest monthly fw mean nitrate concentration and load, 63.0 mg/L (14.1 mg/L as NO₃-N) and 179,000 pounds, occurred during December, and the smallest monthly fw mean and load, 44.0 mg/L (9.8 mg/L as NO₃-N) and 51,000 pounds, occurred in October.

A total of 29,644,014 pounds of nitrogen were discharged by the Turkey River during WY 1992 (Rowden et al., 1995b). Of this total, 27,244,063 pounds, or 92%, was discharged in the form of nitrate at a fw mean concentration of 41.0 mg/L (9.1 mg/L as NO₃-N). Within the 1,545 mi² drainage area of TR01, the total nitrogen output was equivalent to 30.0 lbs-N/acre, and the total nitrate-nitrogen output equaled 27.6 lbs-N/acre. Monthly fw mean nitrate concentrations and loads varied from 33.0 mg/L (7.3 mg/L as NO₃-N) and 745,000 pounds in October to 50.0 mg/L (11.1 mg/ L as NO₃-N) and 5,913,000 pounds in December. The monthly nitrate-nitrogen discharge remained above 1 million pounds during all months except October and August.

Pesticide Monitoring

Tables 12 and 13 and Figure 12 summarize the results of pesticide monitoring at sites L22T and L23S during WY 1992.

Sixty-seven samples from L22T were analyzed for pesticides during WY 1992. Fifty-three, or 79%, of the samples contained detectable levels of atrazine (>0.10 μ g/L). The annual fw mean atrazine concentration was 0.11 μ g/L, and the annual atrazine output was 0.032 pounds (Table 12).

Atrazine concentrations were stable at both L22T and L23S during the water year. Concentrations at L22T increased from 0.15 μ g/L at the beginning of the water year to 0.30 μ g/L on November 1, as discharge peaked at 0.957 cfs (Fig. 12). From December through July, atrazine concentrations at L22T ranged from 0.10 μ g/L to 0.22 μ g/L, declining to non-detectable levels (<0.10 μ g/L) in December, March, April, May, and July. The greatest concentration sampled at L22T during the water year, 0.40 μ g/L, occurred on August 7 during low-flow conditions. During the remainder of the water year atrazine concentrations remained around 0.12 μ g/L, decreasing to non-detectable concentrations (<0.10 μ g/L) in mid-September.

The smallest monthly fw mean atrazine concentration at L22T, $0.05 \mu g/L$, occurred in December and May, and the greatest monthly mean, $0.20 \mu g/L$, occurred during February. May had the smallest monthly atrazine output, 0.46 grams, and February had the greatest monthly atrazine discharge, $2.57 \mu g/L$, which accounted for 18% of the annual atrazine discharge.

The only other pesticide detected at L22T during WY 1992 was alachlor, which was detected in six, or 10%, of the samples collected. The greatest concentrations of pesticides detected during the water year included atrazine at 0.40 μ g/L and alachlor at 2.00 μ g/L. The maximum detection for atrazine occurred on August 7, and for alachlor the maximum occurred on November 1. Alachlor was detected twice in November and December, once in June, and once in September.

At L23S, twenty samples were analyzed for pesticides during WY 1992. All samples analyzed contained detectable levels of atrazine (>0.10 μ g/L). The annual atrazine output from L23S was 2.9 pounds at a fw mean concentration of 0.26 μ g/L (Table 13; Rowden et al., 1995a).

Atrazine concentrations from L23S showed trends similar to concentrations from L22T, although samples from L23S remained above the detection limit throughout the water year. Atrazine concentrations from L23S remained low throughout the water year, ranging from $0.10 \,\mu$ g/L to 0.21µg/L, except for one sample taken in July. Concentrations decreased from 0.19 µg/L in late October to 0.13 μ g/L in late November, then increased to 0.20 µg/L in mid-December. Concentrations declined to 0.10 µg/L on February 11 then increased to 0.20 µg/L during runoff one week later. Atrazine concentrations decreased as discharge receded through March. Following the large runoff event in April, discharge remained relatively steady through May, and atrazine concentrations increased to 0.21 µg/L. From May through June, both discharge and atrazine concentrations decreased. Atrazine concentrations reached 1.20 µg/L during runoff in mid-July, then declined during the remainder of the year.

Monthly fw mean atrazine concentrations from L23S varied from 0.63 μ g/L in November to 0.14 μ g/L during January, March and August. November had the greatest monthly atrazine output, 515 grams, and the greatest monthly surface-water discharge, 662 ac-ft, which accounted for 40% of the annual atrazine output and 17% of the surface-water discharge.

Other pesticides detected at L23S during the water year include cyanazine in two, or 10%, alachlor in two, or 10%, and metolachlor in one, or 5%, of the samples collected. The greatest concentrations of pesticides detected during the water year included atrazine at 1.20 μ g/L, metolachlor at 0.50 μ g/L, cyanazine at 0.28 μ g/L, and alachlor at 0.13 μ g/L. All maximum detections occurred July 14. Cyanazine and alachlor were also detected during May.

During WY 1992, 22.5 pounds of atrazine were discharged from Big Spring, at a fw mean concentration of 0.22 μ g/L (Rowden et al., 1995b). This was the third lowest annual fw mean atrazine

concentration observed at Big Spring during WYs 1982-1992. Monthly fw mean atrazine concentrations varied from 0.30 μ g/L during November and July, to 0.16 μ g/L in March. The greatest monthly atrazine discharge, 3.8 pounds, occurred in November, and the smallest monthly atrazine discharge, 1.1 pounds, occurred during October and August.

The annual fw mean atrazine concentration for the Turkey River, was 0.25 μ g/L and the annual atrazine discharge totaled 739 pounds (Rowden et al., 1995b). The highest monthly fw mean atrazine concentration, 0.51 μ g/L, occurred in July, and the lowest fw mean, 0.17 μ g/L, occurred in March. The greatest monthly atrazine discharge, 113.9 pounds, occurred in November, accounting for 15% of the annual discharge, and the smallest monthly discharge, 27 pounds, occurred during August.

Water Year 1993

Discharge Monitoring

Tables 14 and 15 and Figure 13 summarize the discharge, water quality and chemical-load data for sites L22T and L23S for WY 1993. In Figure 13, note the decrease in scale on the nitrate plot relative to WY 1992.

Water Year 1993 had the second-greatest annual basin precipitation during WYs 1982-1995. Precipitation during the water year was 46.47 inches, or 141% of the long-term average. Monthly 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.

The annual groundwater discharge from site L22T during the water year was 188.7 ac-ft and the average daily discharge was 0.26 cfs (Table 14). The annual discharge from L22T was equivalent to 57% of the annual precipitation. At L23S, the annual discharge during WY 1993 was 5,720 ac-ft, and the average daily discharge was 7.9 cfs (Table 15). The annual discharge from L23S was equal to 53% of the annual precipitation. The annual disc

Table 14. Annual summary of water and chemicaldischarge for L22T for WY 1993.

DISCHARGE	
Total	
acre-feet millions cf millions cm Average	188.7 8.2 0.23
cfs cms mg/d gpm	0.26 0.007 0.17 117.1

PRECIPITATION AND DISCHARGE

Precipitation	46.47 inches (1,180 mm)
Discharge	26.64 inches (677 mm)
Discharge as %	
of precipitation	57%

NITRATE DISCHARGE

Concentration - mg	/L As NO ₃	As NO ₃ -N
Flow-weighted mear Mean of analyses	n 79.8 78.5	17.7 17.5
NO ₃ -N output		otal N output
lbs - N	9,103	9,408
kg - N	4,128	4,266
lbs - N/acre	107	111

ATRAZINE DISCHARGE

Concentration - µg/L		
Flow-weighted mean	0.10	
Mean of analyses	0.12	
Total output		
lbs	0.053	
g	24.2	

charge, and discharge as a percent of annual precipitation during WY 1993 were the greatest recorded at L22T and L23S during WYs 1986-1995.

The hydrographs for WY 1993 show significant recharge occurring in November followed by generally receding discharge through much of February. Snowmelt at the end of March generated the largest runoff event of the water year, with a mean daily discharge of 86 cfs at L23S on March 31. Precipitation in April, June, July, and August generated significant runoff and infiltration recharge. During May, precipitation was below normal, and discharge declined from 14 cfs to 5.5 cfs at L23S, and from 0.48 cfs to 0.22 cfs at L22T from May 2 to June 6. Significant runoff in late June, mid-July and late August, was followed by quickly receding discharge. From late August, discharge declined to 2.4 cfs at L23S and 0.24 cfs at L22T near the end of the water year.

At Big Spring the annual discharge during WY 1993 was 58,186 ac-ft, or 23% of the annual precipitation, and the average daily discharge rate was 80.4 cfs (Rowden et al., 1995b). The annual surface-water discharge from the Turkey River was 2,103,000 ac-ft, at an average discharge rate of 2,905 cfs (Rowden et al., 1995b). Annual discharge from TR01 was equivalent to 55% of the annual precipitation and 295% of the long-term discharge average. The annual discharge, and discharge as a percent of annual precipitation during WY 1993 were the greatest recorded at Big Spring and the Turkey River during WYs 1982-1995. The sustained, general increase in mean daily discharge at monitoring sites within the basin during the latter half of the water year indicates a net increase in overall storage in the Big Spring basin's hydrologic system. It is probable that some of the groundwater and chemicals transported by the groundwater during the water year accumulated prior to WY 1993.

Nitrate Monitoring

Tables 14 through 15 and Figure 13 summarize the nitrate analyses from L22T and L23S during WY 1993.

During the water year, fifty-seven samples

Table 15. Annual summary of water and chemical discharge for L23S for WY 1993. (Discharge data are from the U.S. Geological Survey, W.R.D., IA Dist.)

DISCHARGE

Total

acre-feet	5,720
millions cf	249
millions cm	7.1
Average	
cfs	7.9
cms	0.22
mg/d	5.1
gpm	3,546

PRECIPITATION AND DISCHARGE

Precipitation	46.47 inches (1,180 mm)
Discharge	24.43 inches (621 mm)
Discharge as % of precipitation	53%

NITRATE DISCHARGE

Concentration	n - mg/L	As NO	As NO ₃ -N
Flow-weighted Mean of analys		40.2 49.6	8.9 11.0
	NO ₃ -N o	utput	Total N output
lbs - N kg - N lbs - N/acre	138,9 63,0		179,947 81,609 64.0

ATRAZINE DISCHARGE

Concentration - µg/L		
Flow-weighted mean	0.40	
Mean of analyses	0.15	
Total output		
lbs	6.2	
kg	2.8	

from L22T were analyzed for nitrate, and fifty-five samples were analyzed for N-series. The annual fw mean nitrate concentration was 79.8 mg/L (17.7 mg/L as NO₃-N). The annual nitrate-nitrogen output for the water year was 9,103 pounds, and the annual nitrogen output (nitrate- plus organic-, and ammonia-nitrogen) was 9,408 pounds. Within the 85-acre drainage area of L22T, these outputs were equivalent to 107 lbs-N/acre for nitrate-nitrogen and 111 lbs-N/acre for total nitrogen. The annual nitrate-nitrogen discharges from L22T and L23S during WY 1993 were the greatest recorded during WYs 1986-1995.

Nitrate concentrations at L22T and L23S showed an increasing trend during the water year, except during periods of runoff when concentrations were temporarily diluted. At L22T, nitrate concentrations decreased from 76 mg/L (16.9 mg/ Las NO₃-N) on November 17 to 49 mg/L (10.9 mg/ L as NO₃-N) on November 20, as discharge increased from 0.213 cfs to 0.482 cfs. On November 24, concentrations had increased to 77 mg/L (17.1 mg/L as NO₃-N) as discharge receded to 0.263 cfs. Nitrate concentrations increased to 89 mg/L (19.8 mg/L as NO₃-N) in late February, then decreased to the lowest level recorded during the water year, 26 mg/L (5.8 mg/L as NO₃-N) on March 23, following a series of runoff events. From March, nitrate concentrations increased, reaching 95 mg/L (21.1 mg/L as NO₃-N) on June 1, as discharge continued to recede through May. During the remainder of the water year, nitrate concentrations decreased during peak discharge, and increased as discharge was receding, ranging from 96 mg/L (21.3 mg/L as NO₃-N) on August 3, to 78 mg/L (17.3 mg/L as NO₃-N) on August 24. Near the end of the water year, the nitrate concentration of L22T was 90 mg/L (20.0 mg/L as NO₃-N).

The smallest monthly fw mean nitrate concentration from L22T, 43 mg/L (9.6 mg/L as NO₃-N), occurred during March, and the greatest monthly fw mean, 89 mg/L (19.8 mg/L as NO₃-N), occurred in June. The smallest monthly nitrate output, 258 pounds, and the second-smallest monthly groundwater discharge, 5.8 ac-ft, occurred during October. The greatest monthly output, 1,512 pounds, and greatest monthly groundwater discharge, 29.2 ac-ft, occurred in July. These totals accounted for



Figure 13. A) Atrazine and B) nitrate concentrations, and C) groundwater and surface-water discharge (Q) at L22T and L23S for WY 1993 (note the decrease in scale on the nitrate plot relative to WY 1992). (Discharge data for L23S are from the U.S. Geological Survey, W.R.D., IA Dist.)

17% of the annual nitrate-nitrogen output and 15% of the annual groundwater discharge at L22T during WY 1993.

During WY 1993, fifty samples from L23S were analyzed for nitrate, and thirteen samples were analyzed for N-series. The annual fw mean nitrate concentration was 40.2 mg/L (8.9 mg/L as NO₃-N; Table 15). The annual nitrate-nitrogen output for the water year was 138,951 pounds, which is equivalent to 49.5 lbs-N/acre, and the total nitrogen output (nitrate- plus organic- and ammonia-nitrogen) was 179,947 pounds, or 64.0 lbs-N/acre, within 4.39 mi² drainage area of L23S.

The nitrate plot for L23S shows some of the same general trends as concentrations from L22T during the water year, with concentrations from L23S gradually declining from January and being diluted during runoff in March, then increasing through most of June. Nitrate concentrations decreased from 47 mg/L (10.4 mg/L as NO₃-N) on March 2 to 6 mg/L (1.3 mg/L as NO₃-N) on March 16, as surface-water discharge increased from 2.0 cfs to 39.0 cfs. Concentrations increased to 51 mg/ L (11.3 mg/L as NO₃-N) in mid-April, then decreased to 40 mg/L (8.9 mg/L as NO₃-N), one week later during additional runoff. From late April through June, concentrations remained relatively steady, reaching the greatest concentration recorded during the water year, 64 mg/L (14.2 mg/L as NO₃-N), on June 22 as discharge was receding from an event on June 17. From July through the remainder of the water year, nitrate concentrations generally declined, reaching 36 mg/L (8.0 mg/L as NO₃-N) during minor runoff in mid-September. Concentrations increased to 47 mg/L(10.4 mg/L as)NO₃-N) near the end of the water year, as discharge receded.

The greatest monthly fw mean nitrate concentration at L23S, 56.3 mg/L (12.5 mg/L as NO₃-N), occurred during January, and the smallest monthly mean, 7.6 mg/L (1.7 mg/L as NO₃-N), occurred during March, when an increased percentage of discharge was being supplied by snowmelt. July had the greatest monthly nitrate-nitrogen output, 24,113 pounds, which accounted for 17% of the annual total output, and the second-greatest monthly discharge, 862 ac-ft, which accounted for 15% of the annual surface-water discharge. The annual fw mean nitrate concentration for Big Spring for WY 1993 was 51.1 mg/L (11.4 mg/ L as NO₃-N; Rowden et al., 1995b). A total of 1,916,838 pounds of nitrogen were discharged, and of this total, 1,796,013 pounds, or 94%, was in the form of nitrate. Within the 103 mi² drainage area of Big Spring, the total nitrogen output was equivalent to 29.1 lbs-N/acre and the total nitrate-nitrogen output was 27.2 lbs-N/acre.

Monthly fw mean nitrate concentrations from Big Spring exceeded the 45 mg/L (10 mg/L as NO₃-N) drinking water standard for nitrate during all months of WY 1993 except March. The greatest monthly fw mean nitrate concentration during the water year, 61 mg/L (13.7 as NO₃-N), occurred in December and the smallest monthly fw mean, 28 mg/L (6.2 as NO₃-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 16% of the annual nitrate-N load and 14.5% of the annual discharge. The monthly nitrate-N discharge for July was the second greatest recorded during WYs 1983-1995 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).

A total of 44,290,241 pounds of nitrogen were discharged by the Turkey River during WY 1993 (Rowden et al., 1995b). Of this total, 32,447,979 pounds, or 73%, was discharged in the form of nitrate at a fw mean concentration of 25.6 mg/L (5.7 mg/L as NO₃-N). Within the 1,545 mi² drainage area of TR01, the total nitrogen output was equivalent to 44.8 lbs-N/acre, and the total nitrate-N output equaled 32.8 lbs-N/acre.

The greatest monthly fw mean nitrate concentration from the Turkey River, 36 mg/L (8.0 mg/L as NO₃-N), occurred in December, January, and February. The smallest monthly fw mean, 13 mg/ L(2.9 mg/L as NO₃-N), occurred in March. Monthly nitrate-N discharge from the Turkey River varied from 6.4 million pounds in July, which accounted for 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 1984-1995. 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., 1995b).

Pesticide Monitoring

Tables 14 and 15 and Figure 13 summarize the results of pesticide monitoring at sites L22T and L23S during WY 1993. As a cost savings measure, pesticide samples at L23S were taken monthly, rather than bi-weekly during WY 1993. Beginning in January of WY 1993, two degradation products, or metabolites of atrazine, desethylatrazine and deisopropylatrazine, were added to the list of analytes for the pesticide samples taken in the Big Spring basin.

Sixty samples from L22T were analyzed for pesticides during WY 1993. Thirty-six, or 60%, of the samples contained detectable levels of atrazine (>0.10 μ g/L). The annual fw mean atrazine concentration was 0.10 μ g/L and the annual atrazine output was 0.053 pounds (Table 14). The annual fw mean atrazine concentration for L22T during WY 1993 was the lowest recorded during WYs 1987-1993.

Atrazine concentrations remained low at both L22T and L23S during the first five months of the water year. Concentrations at L22T ranged from 0.15 µg/L on November 20 to non-detectable concentrations (< 0.10 µg/L) in late November, December, and most of January. Concentrations increased to 0.25 µg/L on March 29 following snowmelt earlier in the month. Atrazine concentrations decreased to non-detectable levels during most of April, and then increased to 0.63 µg/L during runoff on June 8. One week later, atrazine concentrations were again below the 0.10 μ g/L detection limit. Concentrations increased back to 0.63 μ g/L during another event on June 30. The highest atrazine concentration recorded at L22T during the water year, 0.73 µg/L, occurred July 10, prior to groundwater peaking at 0.82 cfs on July 11. During the remainder of the water year atrazine concentrations remained lower, ranging from 0.21 µg/L on July 13 to non-detectable concentrations (<0.10 µg/L) in late July, early August, and mid- and late September.

The smallest monthly fw mean atrazine concentration at L22T, 0 μ g/L, and smallest monthly atrazine output, 0 pounds, occurred in December. There may actually have been some atrazine discharged during the month, but since all the samples taken during the month were below the detection limit of 0.10 μ g/L, the estimates were kept to zero. The greatest monthly fw mean atrazine concentration, 0.21 μ g/L, and the greatest monthly atrazine output, 7.53 grams, occurred during July, and accounted for 38% of the annual atrazine discharge.

Other pesticides detected at L22T during WY 1993 include desethylatrazine in twenty-one, or 49%, and deisopropylatrazine in six, or 14%, of the samples that were analyzed for metabolites. Metolachlor was detected in four, or 7%, and alachlor was detected in one, or 2%, of the samples collected. The greatest concentrations of pesticides detected during the water year include atrazine at 0.73 μ g/L, desethylatrazine at 0.41 μ g/L, deisopropylatrazine at 0.38 µg/L, metolachlor at $0.35 \,\mu\text{g/L}$, and alachlor at $0.35 \,\mu\text{g/L}$. The maximum detection for atrazine, desethylatrazine and deisopropylatrazine occurred on July 10, for metolachlor the maximum occurred on June 30, and for alachlor the maximum detection occurred on November 1. Metolachlor was detected once in June and three times in July.

At L23S, thirteen samples were analyzed for pesticides during WY 1993. Eight, or 62%, of the samples analyzed contained detectable levels of atrazine (>0.10 μ g/L). The annual atrazine output from L23S was 6.2 pounds, at a fw mean concentration of 0.40 μ g/L (Table 15).

Atrazine concentrations from L23S showed trends similar to concentrations from L22T, remaining below the $0.10 \mu g/L$ detection limit from October through February, increasing during runoff in March, May, June, and July, and then declining from July through the remainder of the water year. The greatest atrazine concentration sampled at L23S during the water year, $0.48 \mu g/L$, occurred on June 28 as discharge was receding from runoff on June 17.

Monthly fw mean atrazine concentrations and monthly output from L23S varied from $0 \mu g/L$ and 0 grams in January and February, to $0.87 \mu g/L$ and 861 grams during June. As mentioned, there may have been some atrazine discharged during January and February, but since the monthly samples taken during the two months were below the detection limit of $0.10 \,\mu$ g/L, the estimates were kept to zero. The surface-water discharge during June accounted for 14% of the annual total, and the atrazine output for June accounted for 31% of the annual total.

Other pesticides detected at L23S during the water year include desethylatrazine in three, or 27%, and deisopropylatrazine in one, or 10%, of the samples that were analyzed for metabolites, alachlor in two, or 15%, and metolachlor in one, or 8%, of the samples collected. The greatest concentration of pesticides detected during the water year include alachlor at 0.81 µg/L, atrazine at 0.48 µg/L, metolachlor at 0.22 µg/L, desethylatrazine at 0.22 μ g/L, and deisopropylatrazine at 0.12 μ g/L. The maximum detections for both atrazine metabolites occurred July 26, for alachlor the maximum occurred May 24, and for metolachlor the maximum occurred June 28. Desethylatrazine was detected in July, August and September, and alachlor was also detected June 28.

During WY 1993, 42.0 pounds of atrazine were discharged from Big Spring, at a fw mean concentration of $0.27 \,\mu$ g/L (Rowden et al., 1995b). Monthly fw mean atrazine concentrations varied from 0.07 μ g/L during January, to 0.69 μ g/L in June. The greatest monthly atrazine discharge, 12.9 pounds, and the greatest monthly groundwater discharge, 8,436 ac-ft, occurred in July and the smallest monthly atrazine discharge, 0.6 pounds, occurred during January. The atrazine discharge during July accounted for 31%, and the groundwater discharge accounted for 14.5%, of the annual totals at Big Spring.

The annual fw mean atrazine concentration for the Turkey River was 0.59 μ g/L and the annual atrazine discharge totaled 3,386 pounds (Rowden et al., 1995b). The annual atrazine load discharged by the Turkey River during WY 1993 was the greatest recorded during WYs 1986-1995. The greatest monthly fw mean atrazine concentration, 1.58 μ g/L, occurred in July, and the smallest fw mean, 0.12 μ g/L, occurred in January. The greatest monthly atrazine discharge, 1,524 pounds, occurred in July, accounting for 45% of the annual discharge, and the smallest monthly discharge, 11 pounds, occurred during February. The monthly atrazine discharge for July was the second greatest recorded during WYs 1986-1995. The greatest monthly atrazine discharge previously recorded from the Turkey River, 2,102 pounds, occurred during June of WY 1991 (Rowden et al., 1993).

Water Year 1994

Discharge Monitoring

Tables 16 and 17 and Figure 14 summarize the discharge, water quality and chemical-load data for sites L22T and L23S for WY 1994. In Figure 14, note the increase in scale on the nitrate plot relative to WY 1993.

Water Year 1994 had the fourth-lowest annual basin precipitation during WYs 1982-1995. The annual precipitation for WY 1994 was 30.42 inches, or 92% of normal. During WY 1994, rainfall totals were far above average for January and June, above average during February, July, and September, and below average during the remainder of the year. The driest month of the water year was March, with only 0.14 inches of precipitation, or 7% of the monthly normal.

The annual groundwater discharge from site L22T during the water year was 88.9 ac-ft, and the average daily discharge was 0.12 cfs (Table 16). The annual discharge from L22T was equivalent to 41% of the annual precipitation. At L23S, the annual discharge during WY 1994 was 1,590 ac-ft, and the average daily discharge was 2.2 cfs (Table 17). The annual discharge from L23S was equal to 22% of the annual precipitation.

The hydrographs for WY 1994 show discharge generally receding, especially during the first four months of the water year. From the beginning of the water year through February 10, mean daily discharge at L23S declined from 2.9 cfs to 0.90 cfs, and at L22T daily discharge decreased from 0.263 cfs to 0.102 cfs. The two largest discharge events of the water year occurred on February 19 and March 5, and were associated with snowmelt. The greatest daily discharge recorded at L22T during WY 1994 was 0.568 cfs on February 19, and the greatest daily discharge from L23S during the

Table 16. Annual summary of water and chemicaldischarge for L22T for WY 1994.

DISCHARGE	
Total	
acre-feet millions cf millions cm Average	88.9 3.9 0.11
cfs cms mg/d gpm	0.12 0.003 0.08 55.2

PRECIPITATION AND DISCHARGE

Precipitation	30.42 inches (773 mm)
Discharge	12.55 inches (319 mm)
Discharge as %	
of precipitation	41%

NITRATE DISCHARGE

Concentration	i - mg/L	As NO3	As NO ₃ -N
Flow-weighted Mean of analys		94.5 96.4	21.0 21.4
	NO ₃ -N o	utput	Total N output
lbs - N kg - N lbs - N/acre	5,0 2,3)74 801 59.7	5,110 2,318 60.1

ATRAZINE DISCHARGE

Concentration - μg/L			
Flow-weighted mean	0.10		
Mean of analyses	0.12		
Total output			
lbs	0.024		
g	11.0		

water year was 52 cfs on March 5. At L23S, surface water discharge increased during April and June, and decreased from mid-August through mid-September. The lowest mean daily discharge at L23S during WY 1994, 0.71 cfs, occurred September 20, prior to the last significant runoff during the water year which occurred on September 25. At L22T, groundwater discharge receded the entire year, increasing only temporarily during recharge events. The lowest daily discharge recorded at L22T during the water year, 0.05 cfs, occurred September 20-23.

At Big Spring the annual discharge during WY 1994 was 31,266 ac-ft, or 19% of the annual precipitation, and the average daily discharge rate was 43.2 cfs (Liu et al., 1997). The annual surfacewater discharge from the Turkey River was 719,000 ac-ft, at an average discharge rate of 993 cfs (Liu et al., 1997). Annual discharge from TR01 was equivalent to 28% of the annual precipitation and 101% of the long-term discharge average. The sustained, general decrease in mean daily discharge at monitoring sites within the basin during the water year indicates a net decrease in overall storage in the Big Spring basin's hydrologic system.

Nitrate Monitoring

Tables 16 and 17 and Figure 14 summarize the nitrate analyses from L22T and L23S during WY 1994.

As a way to lower operational costs, beginning in WY 1994 at L22T, weekly nitrate sampling was discontinued, and partial nitrogen-series samples (nitrate- and ammonia-nitrogen) were collected, rather than full nitrogen-series samples (nitrateplus organic-, and ammonia-nitrogen) on a weekly basis. The nitrate plot for L22T for WY 1994 uses the nitrate-nitrogen values from weekly partial Nseries, multiplied by 4.5. The estimates for nitratenitrogen for L22T and total nitrogen loads for L22T and L23S for WY 1994 are also based on the nitrate-nitrogen data from the weekly partial Nseries samples. As a result, the annual total nitrogen loads for L22T and L23S are somewhat smaller than if full N-series samples were used, since the annual loads are lacking the organicnitrogen component of the total nitrogen. During the water year, five samples from L22T were analyzed for nitrate, and fifty-five samples were analyzed for partial N-series. The annual fw mean nitrate concentration was 94.5 mg/L (21.0 mg/L as NO₃-N). The annual nitrate-nitrogen output for the water year was 5,074 pounds, and the annual total nitrogen output (nitrate- and ammonia-nitrogen) was 5,110 pounds. Within the 85-acre drainage area of L22T these outputs were equivalent to 59.7 lbs-N/acre for nitrate-nitrogen and 60.1 lbs-N/acre for total nitrogen.

Nitrate concentrations at L22T and L23S were relatively steady during the water year, with L23S showing less fluctuation than L22T. At L22T, nitrate concentrations decreased from 108 mg/L (24.0 mg/L as NO₃-N) on October 5 to 99 mg/L (22.0 mg/L as NO₃-N) on October 12.

From mid-October to mid-February, nitrate concentrations remained between 95 mg/L (21.0 mg/L as NO₃-N) and 108 mg/L (24.0 mg/L as NO₃-N) as groundwater discharge receded. Nitrate concentrations were diluted to the lowest concentration recorded during the water year, 43 mg/L (9.5 mg/L as NO₃-N), during the largest recharge event of the water year on February 19. Concentrations increased to 95 mg/L (21.0 mg/L as NO3-N) on March 1, then decreased to 77 mg/L (17.0 mg/L as NO₃-N) one week later, as discharge was receding from the second-largest event of the water year at L22T which occurred on March 5. From March, nitrate concentrations increased, reaching 135 mg/L (30.0 mg/L as NO₃-N) on May 10, as discharge continued to recede from mid-April. During the remainder of the water year, nitrate concentrations tended to decrease during peak discharge, and increase as discharge receded, ranging from 113 mg/L (25.0 mg/L as NO₃-N) on June 13, to 72 mg/L (16.0 mg/L as NO₃-N) on July 20 and September 27.

The monthly fw mean nitrate concentrations for L22T during WY 1994 remained above 80 mg/L (17.8 mg/L as NO₃-N) during the entire year. The smallest monthly fw mean nitrate concentration from L22T during WY 1994, 81 mg/L (17.9 mg/L as NO₃-N), occurred during March, and the greatest monthly fw mean, 104 mg/L (23.1 mg/L as NO₃-N), occurred in January. The greatest monthly nitrate output, 768 pounds, and greatest monthly

Table 17. Annual summary of water and chemicaldischarge for L23S for WY 1994. (Discharge dataare from the U.S. Geological Survey, W.R.D., IADist.)

DISCHARGE

Total

acre-feet	1,590
millions cf	69
millions cm	2.0
Average	
cfs	2.2
cms	0.062
mg/d	1.4
gpm	987

PRECIPITATION AND DISCHARGE

Precipitation	30.42 inches (773 mm)
Discharge	6.79 inches (172 mm)
Discharge as % of precipitation	22%

NITRATE DISCHARGE

Concentration	- mg/L	As NO3	As NO ₃ -N
Flow-weighted		41.0	9.1
Mean of analys		43.7	9.7
	NO ₃ -N o	utput	Total N output
lbs - N	39,358		43,761
kg - N	17,849		19,846
lbs - N/acre	14.0		15.6

ATRAZINE DISCHARGE

Concentration - µg/L

Flow-weighted mean	0.14
Mean of analyses	0.05
Total output	
lbs	0.59
g	269



Figure 14. A) Atrazine and B) nitrate concentrations, and C) groundwater and surface-water discharge (Q) at L22T and L23S for WY 1994 (note the increase in scale on the nitrate plot relative to WY 1993). (Discharge data for L23S are from the U.S. Geological Survey, W.R.D., IA Dist.)

groundwater discharge, 13.4 ac-ft, occurred during October, and the smallest monthly output, 230 pounds, and smallest monthly groundwater discharge, 4.3 ac-ft, occurred in September. The greatest monthly output and discharge totals accounted for 15% of the annual nitrate-nitrogen output and 15% of the annual groundwater discharge at L22T during WY 1994.

During WY 1994, thirty-nine samples from L23S were analyzed for nitrate, and thirteen samples were analyzed for partial N-series. The annual fw mean nitrate concentration was 41.0 mg/L (9.1 mg/ L as NO₃-N; Table 17). The annual nitrate-nitrogen output for the water year was 39,358 pounds, which is equivalent to 14.0 lbs-N/acre, and the total nitrogen output (nitrate- and ammonia-nitrogen) was 43,761 pounds, or 15.6 lbs-N/acre, for the 4.39 mi² drainage area of L23S.

The nitrate plot for L23S shows very steady concentrations throughout the water year, except for one sample taken in March and one sample taken in September. During the first five months of the water year nitrate concentrations ranged from 54 mg/L (12.0 mg/L as NO₃-N) on October 19 to 44 mg/L (9.8 mg/L as NO₃-N) on December 21. Concentrations increased to 63 mg/L (14.0 mg/L as NO₃-N) on March 8 as discharge continued to recede from runoff that occurred on March 5.

From March through May, nitrate concentrations remained low compared to concentrations prior to the large runoff event. Concentrations remained below 40 mg/L (8.9 mg/L as NO₃-N) until June 6. Concentrations increased to 49 mg/L (10.9 mg/L as NO₃-N) on June 14, then remained above 41 mg/L (9.1 mg/L as NO₃-N) through September 6. Nitrate concentrations decreased to 17 mg/L (3.8 mg/L as NO₃-N) on September 13 as groundwater discharge continued to slowly recede from late August. This decrease is difficult to explain, since there was no precipitation or significant change in discharge on or prior to September 13. One week later the nitrate concentration at L23S was 36 mg/L (8.0 mg/L as NO₃-N).

The greatest monthly fw mean nitrate concentration at L23S during WY 1994, 51.5 mg/L (11.4 mg/L as NO₃-N), and the greatest monthly nitratenitrogen discharge, 5,356 pounds, occurred during October. The smallest monthly fw mean, 30.0 mg/ L (6.7 mg/L as NO₃-N), occurred during March, when an increased percentage of discharge was being supplied by snowmelt. The smallest monthly nitrogen output, 1,149 pounds, occurred during September, the month with the smallest groundwater discharge. The nitrate-nitrogen output during October accounted for 14% of the annual output.

The annual fw mean nitrate concentration for Big Spring for WY 1994 was 47.0 mg/L (10.4 mg/ L as NO₃-N; Liu et al., 1997). A total of 911,133 pounds of nitrogen were discharged, and of this total, 888,518 pounds, or 98%, was in the form of nitrate. Within the 103 mi² drainage area of Big Spring, the total nitrogen output was equivalent to 13.8 lbs-N/acre and the total nitrate-nitrogen output was 13.5 lbs-N/acre.

The greatest monthly fw mean nitrate concentration at Big Spring, 55 mg/L (12.3 mg/L as NO₃-N), and the greatest monthly nitrate-nitrogen output, 117,000 pounds, occurred in October (Liu et al., 1997). The smallest monthly fw mean, 35 mg/L (7.9 mg/L as NO₃-N), occurred in February, and the smallest monthly load, 37,000 pounds, occurred in September. October accounted for 11% of the annual groundwater discharge from Big Spring, and 13% of the annual nitrate-nitrogen load. February accounted for 10% of the annual discharge and 7.5% of the annual nitrate-nitrogen load.

A total of 10,581,755 pounds of nitrogen were discharged by the Turkey River during WY 1994 (Liu et al., 1997). Of this total, 9,903,478 pounds, or 94%, was discharged in the form of nitrate at a fw mean concentration of 22.8 mg/L (5.1 mg/L as NO₃-N). Within the 1,545 mi² drainage area of TR01, the total nitrogen output was equivalent to 10.7 lbs-N/acre, and the total nitrate-nitrogen output equaled 10.0 lbs-N/acre.

The greatest monthly fw mean nitrate concentration at the Turkey River, 37 mg/L (8.1 mg/L as NO₃-N), occurred in January, and the smallest monthly fw mean, 17 mg/L (3.7 mg/L as NO₃-N), occurred in June (Liu et al., 1997). The greatest monthly nitrate-nitrogen load, 1.449 million pounds, occurred in March, and the smallest load, 468,000 pounds, occurred in May. March accounted for 18% of the annual surface-water discharge and 15% of the annual nitrate-nitrogen load, and January accounted for 4% of the annual surface-water discharge and 6% of the annual nitrate-nitrogen load.

Pesticide Monitoring

Tables 16 and 17 and Figure 14 summarize the results of pesticide monitoring at sites L22T and L23S during WY 1994. As a cost savings measure, pesticide samples at L23S were taken monthly, rather than bi-weekly during WY 1994. Beginning in August of WY 1994, acetochlor was added to the list of analytes for the pesticide samples taken in the Big Spring basin.

Fifty-four samples from L22T were analyzed for pesticides during WY 1994. Forty-one, or 76%, of the samples contained detectable levels of atrazine (>0.10 μ g/L). The annual fw mean atrazine concentration was 0.10 μ g/L, and the annual atrazine output was 0.024 pounds (Table 16). The annual fw mean atrazine concentrations for L22T during WYs 1993 and 1994 were the lowest recorded during WYs 1987-1995.

Atrazine concentrations remained low at both L22T and L23S during the water year, particularly from March through May. Concentrations at L22T ranged from 0.13 µg/L to non-detectable concentrations ($<0.10 \,\mu$ g/L) during the water year, except for June 14, June 28, and July 20. Atrazine concentrations at L22T remained below the 0.10 μ g/L detection limit during March and most of May. On June 14, the concentration increased to $0.24 \,\mu\text{g}/$ L as discharge receded from recharge that occurred on June 13. The atrazine concentration increased to $0.16 \,\mu\text{g/L}$ on June 28, as discharge was receding from an event that occurred on June 23. The greatest atrazine concentration recorded during WY 1994, 1.98 µg/L, occurred on July 20 during minor recharge. During the remainder of the water year atrazine concentrations at L22T remained below 0.13 μ g/L.

The smallest monthly fw mean atrazine concentration at L22T, $0.04 \mu g/L$, and smallest monthly atrazine output, 0.33 grams, occurred in May. The greatest monthly fw mean atrazine concentration, $0.28 \mu g/L$, and the greatest monthly atrazine output, 1.7 grams, occurred during July, and accounted for 15% of the annual atrazine discharge.

The only other pesticide detected at L22T

during WY 1994 was desethylatrazine in fortynine, or 94%, of the samples that were analyzed for metabolites. The greatest concentrations of pesticides detected during the water year include atrazine at 1.98 μ g/L and desethylatrazine at 0.30 μ g/L. The maximum detection for atrazine occurred July 20 and the maximum for desethylatrazine occurred October 12.

At L23S, twelve samples were analyzed for pesticides during WY 1994. Four, or 33%, of the samples analyzed contained detectable levels of atrazine (>0.10 μ g/L). The annual atrazine output from L23S was 0.59 pounds, at a fw mean concentration of 0.14 μ g/L (Table 17). The annual fw mean atrazine concentration for WY 1994 was the third lowest, and the percent of atrazine detections was the second lowest recorded during WYs 1986-1995.

Atrazine concentrations from L23S remained low during WY 1994, as did concentrations from L22T. Concentrations remained below the $0.10 \,\mu g/$ L detection limit from October through January, increasing to 0.16 µg/L on February 21, then decreasing below the detection limit in March and April. The concentration increased to $0.16 \,\mu$ g/L on May 31, then decreased to 0.13 μ g/L in June and 0.10 µg/L in July. Atrazine concentrations remained below the 0.10 µg/L detection limit during August and September. Monthly fw mean atrazine concentrations and monthly output from L23S varied from 0 µg/L and 0 grams in November, December, and January, to 0.29 µg/L and 98 grams during March, the month with the greatest surface-water discharge during the water year. There may have been some atrazine discharged during the November through January period, but since the monthly samples taken during the period were below the detection limit of $0.10 \,\mu$ g/L, the estimates were kept to zero. During March, the surface-water discharge accounted for 17% of the annual total, and the atrazine output accounted for 36% of the annual total.

Other pesticides detected at L23S during the water year include desethylatrazine in ten, or 83%, of the samples that were analyzed for metabolites and metolachlor in one, or 8%, of the samples collected. The greatest concentrations of pesticides detected during the water year include

desethylatrazine at 0.19 μ g/L, atrazine at 0.16 μ g/L, and metolachlor at 0.15 μ g/L. The maximum detections for atrazine occurred February 21 and May 31, for desethylatrazine on February 21, and for metolachlor the maximum occurred April 25.

During WY 1994, 17.8 pounds of atrazine were discharged from Big Spring, at a fw mean concentration of $0.21 \mu g/L$ (Liu et al., 1997).

Monthly fw mean atrazine concentrations and loads at Big Spring varied from 0.62 μ g/L and 5.3 pounds during July, to 0.04 μ g/L and 0.25 pounds in April (Liu et al., 1997). The fw mean atrazine concentration for April was the lowest recorded at Big Spring since the previous low of 0.06 μ g/L, recorded in November and August of WY 1988 (Libra et al., 1991). The monthly atrazine load for April was the second smallest recorded since the previous low of 0.20 pounds, recorded in August of WY 1988 and December of WY 1989. The atrazine output during March accounted for 30% of the annual atrazine output from Big Spring.

The annual fw mean atrazine concentration for the Turkey River for WY 1994, was 0.41 μ g/L and the annual atrazine discharge totaled 803 pounds (Liu et al., 1997). The annual fw mean atrazine concentration for the Turkey River for WY 1994 was the third lowest recorded during WYs 1986-1995. The lowest annual atrazine fw mean from the Turkey River, 0.25 μ g/L, occurred during WY 1992.

Monthly fw mean atrazine concentrations at the Turkey River varied from $1.25 \,\mu$ g/L in June, to $0.12 \,\mu$ g/L in April, and monthly atrazine loads varied from 254 pounds during July, to 11 pounds during January (Liu et al., 1997). The monthly atrazine output for July accounted for 32% of the annual atrazine discharge.

Water Year 1995

Discharge Monitoring

Tables 18 and 19 and Figure 15 summarize the discharge, water quality and chemical-load data for sites L22T and L23S for WY 1995. In Figure 15, note the decrease in scale on both the atrazine and nitrate plots relative to WY 1994.

Water Year 1995 had the third-lowest annual

Table 18. Annual summary of water and chemicaldischarge for L22T for WY 1995.

DISCHARGE	
Total	
acre-feet millions cf millions cm Average	55.7 2.4 0.069
cfs cms mg/d gpm	0.077 0.002 0.050 34.6

PRECIPITATION AND DISCHARGE

Precipitation	29.28 inches (744 mm)
Discharge	7.86 inches (200 mm)
Discharge as % of precipitation	27%

NITRATE DISCHARGE

Concentration -	mg/L	As NO $_3$	As NO ₃ -N
Flow-weighted m Mean of analyses		80.2 81.7	17.8 18.2
١	NO ₃ -N ou	tput	Total N output
lbs - N	2,700		n/a
kg - N	1,2	25	n/a
lbs - N/acre	;	31.8	n/a

ATRAZINE DISCHARGE

Concentration - µg/L

Flow-weighted mean	0.17
Mean of analyses	0.12
Total output	

lbs	0.026
g	11.8

Table 19. Annual summary of water and chemical discharge for L23S for WY 1995. (Discharge data are from the U.S. Geological Survey, W.R.D., IA Dist.)

DISCHARGE

Total

acre-feet	1,870
millions cf	81
millions cm	2.3
Average	
cfs	2.6
cms	0.073
mg/d	1.7
gpm	1,158

PRECIPITATION AND DISCHARGE

Precipitation	29.28 inches (744 mm)
Discharge	7.99 inches (203 mm)
Discharge as %	
of precipitation	27%

NITRATE DISCHARGE

Concentration -	mg/L	As NO ₃	As NO ₃ -N
Flow-weighted m Mean of analyse		45.6 n/a	10.1 n/a
I	NO ₃ -N oi	utput	Total N output
lbs - N kg - N lbs - N/acre	51,6 23,4		53,967 24,475 19.2

ATRAZINE DISCHARGE

Concentration - µg/L		
Flow-weighted mean Mean of analyses	0.09 0.08	
Total output		
lbs	0.46	
g	210	

basin precipitation during WYs 1982-1995. The annual precipitation for WY 1995 was 29.28 inches, or 89% of normal. During the water year, monthly rainfall totals were above average for November, March, April, and August, and below average during October, January, February, June, July, and September. February was the driest month of WY 1995 with only 0.03 inches of precipitation, or 3% of the monthly normal.

The annual groundwater discharge from L22T during WY 1995 was 55.7 ac-ft and the average daily discharge was 0.077 cfs (Table 18). The annual discharge from L22T was equivalent to 27% of the annual precipitation. For L23S, the annual discharge during WY 1995 was 1,870 ac-ft, and the average daily discharge was 2.6 cfs (Table 19). The annual discharge from L23S was equal to 27% of the annual precipitation.

The hydrographs for WY 1995 show groundwater discharge receding at L22T and surfacewater discharge remaining steady through mid-February. Discharge increased at both sites through early June, then generally receded through the remainder of the water year. From the beginning of the water year through February 17, mean daily discharge at L22T declined from 0.080 cfs to 0.025 cfs. At L23S, daily discharge ranged from 2.5 cfs on November 21 to 0.60 cfs on January 9. The greatest mean daily discharge at L22T during the water year, 0.520 cfs, occurred on May 28, and at L23S, the greatest daily discharge during WY 1995 was 23.0 cfs, on April 12. Following the peaks in daily discharge, groundwater discharge at L22T receded to 0.056 cfs, and surface-water discharge from L23S declined to 0.86 cfs at the end of the water year.

At Big Spring the annual discharge during WY 1995 was 30,013 ac-ft, or 19% of the annual precipitation, and the average daily discharge rate was 41.5 cfs (Liu et al., 1997). The greatest monthly groundwater discharge at Big Spring, 5,077 ac-ft, occurred in May and accounted for 17% of the annual discharge. The smallest monthly discharge during the water year, 1,480 ac-ft, occurred in October.

The annual surface-water discharge from the Turkey River was 729,000 ac-ft, at an average discharge rate of 1,007 cfs (Liu et al., 1997). The



Figure 15. A) Atrazine and B) nitrate concentrations, and C) groundwater and surface-water discharge (Q) at L22T and L23S for WY 1995 (note the decrease in scale on both the atrazine and nitrate plots relative to WY 1994). (Discharge data for L23S are from the U.S. Geological Survey, W.R.D., IA Dist.)

greatest monthly surface-water discharge at the Turkey River, 147,500 ac-ft, occurred in April and accounted for 20% of the annual discharge. The smallest monthly discharge during the water year, 23,230 ac-ft, occurred in February. The annual discharge from the Turkey River was equivalent to 29% of the annual precipitation and 102% of the long-term discharge average.

The annual groundwater discharge from L22T and Big Spring decreased from WY 1994 to WY 1995. The annual surface-water discharge from L23S and other surface-water sites in basin increased during WY 1995, in spite of WY 1995 having slightly less annual precipitation than WY 1994. The increases in annual surface-water discharge from WY 1994 to WY 1995 are probably related to the timing and intensity of precipitation. Water Year 1994 had a dry growing season until June, and the WY 1995 growing season was wet until June.

Nitrate Monitoring

Tables 18 through 19 and Figure 15 summarize the nitrate analyses from L22T and L23S during WY 1995.

To lower costs, weekly partial N-series sampling at L22T was discontinued and replaced with weekly nitrate sampling during WY 1995. As a result, total nitrogen output (nitrate- and ammonianitrogen) from L22T could not be calculated for WY 1995. At L23S, weekly nitrate sampling was discontinued and replaced with weekly partial Nseries sampling. The nitrate plot for L23S for WY 1995 uses the nitrate-nitrogen values from weekly partial N-series, multiplied by 4.5. The estimates for nitrate-nitrogen loads for L23S for WY 1995 are also based on the nitrate-nitrogen data from the weekly partial N-series samples.

During the water year, fifty-one samples from L22T were analyzed for nitrate. The annual fw mean nitrate concentration was 80.2 mg/L (17.8 mg/L as NO₃-N). The annual nitrate-nitrogen output for the water year was 2,700 pounds. Within the 85-acre drainage area of L22T this output was equivalent to 31.8 lbs-N/acre.

Nitrate concentrations at L22T and L23S were low, compared to concentrations during WY 1994.

Concentrations fluctuated at both sites throughout the water year, but did not show as much range in concentrations as in some previous years. At L22T, nitrate concentrations remained in the mideighties from the beginning of the water year through mid-November. Concentrations decreased to 71 mg/L (15.8 mg/L as NO₃-N) on November 22 following minor recharge on November 21, and decreased to 70 mg/L (15.6 mg/L as NO₃-N) during another minor event on November 28. During December and January, nitrate concentrations returned to the mid-eighties.

From February through mid-April, nitrate concentrations showed a declining trend, during a series of runoff events. From April 18 to May 30, the concentration increased from 65 mg/L (14.4 mg/L as NO₃-N) to 101 mg/L (22.4 mg/L as NO₃-N) as groundwater discharge increased. During the remainder of the water year, nitrate concentrations generally declined along with discharge. The nitrate concentration reached the lowest level recorded during the water year, 64 mg/L (14.2 mg/L as NO₃-N), on August 15 as groundwater discharge receded. One week later the concentration was 84 mg/L (18.7 mg/L as NO₃-N), and during the rest of the year, concentrations ranged from 79 mg/ L (17.6 mg/L as NO₃-N) to 83 mg/L (18.4 mg/L as NO₃-N).

The smallest monthly fw mean nitrate concentration from L22T during WY 1995, 67 mg/L (14.9 mg/L as NO₃-N), occurred during March, and the greatest monthly fw mean, 92 mg/L (20.4 mg/L as NO₃-N), occurred in June. The greatest monthly nitrate output, 450 pounds, and greatest monthly groundwater discharge, 9.0 ac-ft, occurred during May, and the smallest monthly output, 122 pounds, and smallest monthly groundwater discharge, 2.6 ac-ft, occurred in February. The monthly nitrate output and groundwater discharge during May accounted for 17% of the annual nitrate-nitrogen output and 16% of the annual groundwater discharge at L22T during WY 1995.

During WY 1995, fifty-two samples from L23S were analyzed for partial N-series. The annual fw mean nitrate concentration was 45.6 mg/L (10.1 mg/L as NO₃-N; Table 19). The annual nitratenitrogen output for the water year was 51,621 pounds, which is equivalent to 18.4 lbs-N/acre, and
the total nitrogen output (nitrate- and ammonianitrogen) was 53,967 pounds, or 19.2 lbs-N/acre, within the 4.39 mi² drainage area of L23S.

The nitrate plot for L23S shows basic similarities to the plot for L22T, as nitrate concentrations declined from February through most of April, increased through late May, then decreased through the remainder of the water year.

During the first six months of the water year nitrate concentrations at L23S ranged from 54 mg/ L (12.0 mg/L as NO₃-N) on January 3 to 26 mg/L (5.8 mg/L as NO₃-N) on March 27. The concentration peaked at 81 mg/L (18.0 mg/L as NO₃-N) on May 30 as discharge receded from an event that began on May 28 and peaked on May 29. The nitrate concentration declined to 32 mg/L (7.1 mg/ L as NO₃-N) on July 25, as surface-water discharge receded. The concentration decreased to 28 mg/L (6.2 mg/L as NO₃-N) on August 1, as discharge receded from an event on July 27. The concentration increased to 36 mg/L (7.9 mg/L as NO₃-N) on August 22, then decreased to the lowest concentration recorded during the water year, 24 mg/L (5.3 mg/L as NO₃-N), during runoff on August 29. During September, concentrations ranged from 29 mg/L (6.5 mg/L as NO₃-N) on September 5, to 39 mg/L (8.7 mg/L as NO₃-N) on September 12.

The greatest monthly fw mean nitrate concentration at L23S during WY 1995, 66.2 mg/L (14.7 mg/L as NO₃-N), occurred during June, and the smallest monthly mean, 30.1 mg/L (6.7 mg/L as NO₃-N), occurred during March, when an increased percentage of discharge was being supplied by snowmelt. The greatest monthly nitratenitrogen output from L23S during WY 1995, 14,097 pounds, and the greatest monthly groundwater discharge, 514 ac-ft, occurred during April. The smallest monthly nitrogen output, 1,207 pounds, and the smallest monthly discharge, 52.5 ac-ft, occurred during October. The nitrate-nitrogen output during April accounted for 27% of the annual output, and the monthly groundwater discharge accounted for 28% of the annual discharge for WY 1995.

The annual fw mean nitrate concentration for Big Spring for WY 1995 was 45.3 mg/L (10.1 mg/ L as NO₃-N; Liu et al., 1997). A total of 826,212 pounds of nitrate- and ammonia-nitrogen were discharged, and of this total, 822,569 pounds, or 99.6%, was in the form of nitrate. For WY 1995, the annual total nitrogen load for Big Spring does not include organic-nitrogen, since full N-series sampling was replaced by partial N-series sampling as a way to reduce project costs. Within the 103 mi² drainage area of Big Spring, the total nitrogen output and total nitrate-nitrogen output were both 12.5 lbs-N/acre.

The greatest monthly fw mean nitrate concentration at Big Spring, 52 mg/L (11.5 mg/L as NO₃-N), the greatest monthly nitrate-nitrogen output, 159,000 pounds, and the greatest monthly discharge, 5,077 ac-ft, occurred in May (Liu et al., 1997). The smallest monthly fw mean, 33 mg/L (7.3 mg/L as NO₃-N), occurred in March, and the smallest monthly load, 38,000 pounds, occurred in October, the month with the smallest groundwater discharge. May accounted for 19% of the annual nitrate-nitrogen load, and 17% of the annual groundwater discharge from Big Spring.

To reduce monitoring costs, N-series sampling was discontinued at the Turkey River in WY 1995. As a result, total nitrogen loads were not calculated for the Turkey River for WY 1995. During WY 1995, a total of 13,253,486 pounds of nitratenitrogen were discharged by the Turkey River at a fw mean concentration of 30.1 mg/L (6.7 mg/L as NO₃-N; Liu et al., 1997). Within the 1,545 mi² drainage area of TR01, the annual nitrate-nitrogen output was equivalent to 13.4 lbs-N/acre.

The greatest monthly fw mean nitrate concentration at the Turkey River during WY 1995, 36 mg/ L (8.1 mg/L as NO₃-N), and greatest monthly nitrogen load, 3.25 million pounds, occurred in April (Liu et al., 1997). The smallest monthly fw mean, 17 mg/L (3.8 mg/L as NO₃-N), occurred in August, and the smallest monthly nitrogen load, 395,000 pounds, occurred in September. April accounted for 20% of the annual surface-water discharge and 25% of the annual nitrate-nitrogen load, and August accounted for 5% of the annual surface-water discharge and 3% of the annual nitrate-nitrogen load.

Pesticide Monitoring

Tables 18 and 19 and Figure 15 summarize the results of pesticide monitoring at sites L22T and L23S during WY 1995. For WY 1995 pesticide samples at L23S were taken monthly, and pesticide samples from L22T were taken weekly.

Fifty samples from L22T were analyzed for pesticides during WY 1995. Thirty-six, or 72%, of the samples contained detectable levels of atrazine (>0.10 μ g/L). The annual fw mean atrazine concentration was 0.17 μ g/L, and the annual atrazine output was 0.026 pounds (Table 18).

Atrazine concentrations remained low at both L22T and L23S during most of the water year. Concentrations at L22T ranged from 0.13 µg/L to non-detectable concentrations ($< 0.10 \,\mu g/L$) during the first seven months of the water year. From late April, the atrazine concentration remained below the 0.10 µg/L detection limit until May 23 when the concentration increased to 0.38 µg/L as discharge was receding from an event that occurred on May 17. The greatest concentration recorded at L22T during WY 1995, 0.90 µg/L, occurred on May 30, as discharge was receding from the largest event of the water year which occurred on May 28. During the remainder of the water year atrazine concentrations at L22T remained above the 0.10 µg/L detection limit, declining along with discharge to $0.12 \mu g/L$ near the end of September.

The smallest monthly fw mean atrazine concentration at L22T, $0.04 \mu g/L$, occurred in December, and the smallest monthly atrazine output, 0.18grams, occurred in January. The greatest monthly fw mean atrazine concentration, $0.43 \mu g/L$, greatest monthly atrazine output, 4.7 grams, and the greatest monthly groundwater discharge, 9.0 ac-ft, occurred during May, and accounted for 40% of the annual atrazine discharge and 16% of the annual groundwater discharge.

The only other pesticides detected at L22T during WY 1995 were the atrazine metabolites. Desethylatrazine was detected in forty-nine, or 98%, and deisopropylatrazine was detected in one, or 2%, of the samples that were analyzed for metabolites. The greatest concentrations of pesticides detected during the water year include atrazine at $0.90 \mu g/L$, desethylatrazine at $0.27 \mu g/L$, and

deisopropylatrazine at 0.10μ g/L. The maximum detection for atrazine occurred May 30, the maximum for desethylatrazine occurred February 7, and the only detection of deisopropylatrazine occurred on June 6.

At L23S, eleven samples were analyzed for pesticides during WY 1995. Two, or 18%, of the samples contained detectable levels of atrazine (>0.10 μ g/L). The annual atrazine output from L23S was 0.46 pounds, at a fw mean concentration of 0.09 μ g/L (Table 19). The fw mean atrazine concentration and percent of atrazine detections for WY 1995 were the lowest recorded at L23S during WYs 1986-1995.

Atrazine concentrations from L23S remained below the 0.10 μ g/L detection limit during WY 1995, except on May 30 and August 29. The concentration increased to 0.73 μ g/L on May 30, as discharge receded from an event on May 29. The only other atrazine detection during the water year, 0.14 μ g/L, occurred in late August during runoff.

Monthly fw mean atrazine concentrations and monthly output from L23S varied from 0 μ g/L and 0 grams in October, December, and January, to 0.23 μ g/L in February, and 57 grams during May. There may have been some atrazine discharged during October, and the December through January period, but since the monthly samples taken during the period were below the detection limit of 0.10 μ g/L, the estimates were kept to zero. During May, monthly surface-water discharge accounted for 18% of the annual discharge, and the monthly atrazine output accounted for 27% of the annual atrazine discharge.

Other pesticides detected at L23S during the water year include desethylatrazine in four, or 36%, of the samples that were analyzed for metabolites, and acetochlor and metolachlor in one, or 9%, of the samples collected. The greatest concentrations of pesticides detected during the water year include atrazine at $0.73 \mu g/L$, desethylatrazine at $0.20 \mu g/L$, acetochlor at $0.38 \mu g/L$, and metolachlor at $0.22 \mu g/L$. All maximum detections occurred May 30.

During WY 1995, 9.8 pounds of atrazine were discharged from Big Spring, at a fw mean concentration of $0.12 \mu g/L$ (Liu et al., 1997). The annual fw mean atrazine concentration and load from Big Spring for WY 1995 were the lowest annual fw

mean atrazine concentration and the second-smallest annual atrazine load recorded during WYs 1982-1995.

Monthly fw mean atrazine concentrations at Big Spring varied from 0.04 μ g/L during January and April, to 0.22 μ g/L in June (Liu et al., 1997). Monthly atrazine loads varied from 0.17 pounds in January, to 2.6 pounds in May. The fw mean atrazine concentration for January and April equaled the previous monthly low since 1984, which occurred in April of WY 1994. The atrazine output during May accounted for 27% of the annual atrazine output from Big Spring.

The annual fw mean atrazine concentration for the Turkey River for WY 1995 was $0.42 \mu g/L$, and the annual atrazine discharge was 841 pounds (Liu et al., 1997).

The greatest monthly fw mean atrazine concentration and monthly atrazine load for the Turkey River during WY 1995, 1.62 μ g/L and 351 pounds, occurred in June. The smallest monthly atrazine concentration, 0.11 μ g/L, occurred in December, and the smallest monthly atrazine load, 7.8 pounds, occurred during February (Liu et al., 1997). The monthly atrazine output for June accounted for 42% of the annual atrazine discharge from the Turkey River.

DISCUSSION

Relating water quality changes to changes in landuse and management within a watershed over time requires consideration of many factors. The timing, intensity, and distribution of rainfall, along with antecedent conditions, all affect the resultant runoff and recharge to the surface-water and soilgroundwater systems, and the concentrations of agricultural contaminants transported by these systems. Other factors that complicate the analysis of water-quality changes within a watershed 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 carryover effects, and system time lags, particularly at the watershed scale.

Corn accounts for over 95% of the row-cropped areas in the Big Spring study area, with 50% grown

as continuous corn, and the remainder grown in rotation with alfalfa and oats. Over 80% of the farms in the study area have livestock, including dairy or beef cattle, and/or swine, so manure is utilized as a nutrient source. Although there are many sources of nitrogen within the study area, the greatest nitrogen input is from fertilizer applied to corn. Therefore, the proportion of land area in corn production within a watershed directly affects the nitrate concentrations and nitrogen loads in the surface water and groundwater.

Comparison of the water quality of Roberts Creek watershed (70.7 mi²) within the Big Spring basin with the water quality of the watersheds of Bloody Run (37.6 mi²) and Sny Magill (35.6 mi²) which are contiguous with the study area, and have a similar hydrologic setting is instructive (Seigley et al., 1993; Rowden et al., 1995a). During WY 1991, 53% of the Roberts Creek watershed was in rowcrop and the stream had an annual mean nitrate concentration of 36 mg/L (8 mg/L as NO₃-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 NO₃-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 NO₃-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.

Significant, but gradual improvements in nitrogen management have been made within the Big Spring basin through the Big Spring Basin Demonstration Project. From 1981 to 1993, the average rates of fertilizer used on all corn within the basin have been reduced from 174 lbs/acre to 115 lbs/ acre, reducing nitrogen loading by 34% with no apparent yield losses. Since these changes in nitrogen management have been gradual and incremental, the resulting changes in water quality within the basin will also be gradual. It will take time to accurately define these changes, even under ideal circumstances.

The application of pesticides to crops within the Big Spring basin is not as uniform as the application of nitrogen, hence accurately documenting reductions in pesticide usage in the basin has not been possible. Surveys conducted in the basin have shown that some changes and reductions in atrazine use have occurred. Application rates have declined from approximately 2 lbs/acre in the early 1980's to less than 1.5 lbs/acre by 1990 (George Hallberg, personal communication). This change has partially 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 numbers of acres treated with compounds that contain atrazine have increased. While farm 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 mineralization of organic matter, either naturally occurring or later added to soils, is a source of nitrogen that is poorly understood, but should be considered when trying to assess nitrogen balances on a watershed scale. As organic matter is transformed into nitrogen in the soil, the amount of fertilizer nitrogen needed by crops decreases. Rates of mineralization vary with climatedependent factors such as temperature, soil moisture, and groundwater flux through the soil.

Nitrate-nitrogen concentrations tend to decline downstream within Roberts Creek, Bloody Run, and Sny Magill watersheds (Seigley et al., 1993). In watersheds within the Big Spring basin, 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, creeks loose water through their beds 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 instream 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 NO₃-N, as well as temperature.

In-stream processing contributes to the variability of nitrate concentrations at surface water sites within the Big Spring basin. During cool seasons, nitrate concentrations from Roberts Creek tend to parallel concentrations at Big Spring. During warm seasons, concentrations tend to be much lower than the integrated groundwater concentrations from Big Spring because of the in-stream processing. Similar trends occur at L23S, 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, 1995a, 1995b; Liu et al., 1997). The spatial and temporal variability of nitrate concentrations in surface water must be considered when comparing surface-water data from different monitoring sites and in defining the scale of watershed comparisons that are feasible.

The Big Spring basin hydrologic system receives both infiltration and runoff recharge, which have unique chemical signatures (Hallberg et al., 1983, 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. As runoff recharge moves through a stream, relatively low nitrate and high herbicide concentrations occur during peak flow periods. This is typically followed by higher nitrate and lower herbicide concentrations as the associated infiltration recharge moves through the system. During prolonged recession periods, nitrate and herbicide (particularly atrazine) concentrations often show a slow, steady decline. Low discharge periods often 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 volumes of water and greater contaminant concentrations.

Monitoring during WYs 1986 through 1995 showed the effects of significant variations in precipitation and resultant recharge on the discharge and water quality of sites L22T and L23S. The change in precipitation patterns from WYs 1988 and 1989 to WYs 1990 and 1991 was dramatic. Annual precipitation increased from 30% below the long-term average during WYs 1988 and 1989 to 115% of the long-term average in WY 1990 and 143% of the long-term average in WY 1991. Above average precipitation continued during WYs 1992 and 1993 with annual precipitation totals of 108% and 141% of normal, respectively. Water Year 1993 was characterized by episodes of major flooding across the upper Midwest. Annual precipitation decreased to 92% of normal in WY 1994 and continued to decrease to 89% of normal during WY 1995.

WYs 1985-1989 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 wet growing season. Water Year 1994 had a dry growing season until June, and the WY 1995 growing season was wet until June.

Water years 1988 and 1989 were the two driest consecutive years in Iowa's recorded history. From a crop production standpoint, WY 1988 was considered a drought year, however, from a hydrologic standpoint the drought began much earlier. 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. Recharge of any kind was limited after snowmelt in March of WY 1986. Baseflow conditions prevailed for nearly 18 months, depleting groundwater storage during WYs 1987 and 1988.

Previous reports (Hallberg et al., 1983, 1984a, 1989) have indicated that March through June are typically marked by low evapotranspiration and wet antecedent conditions, which are important for groundwater recharge. Precipitation during this period was 8.87 inches below normal in WY 1988 and 6.76 inches below normal in WY 1989. These periods were also characterized by small rainfalls;

no daily rainfall exceeded one inch. The wettest months of WY 1988 and WY 1989 were September (5.48 inches) and August (7.08 inches), respectively. Less than 3 inches of precipitation occurred during any other month. June has typically been the wettest month in the Big Spring basin, 4.80 inches, for 1951-1980. However, during WYs 1985-1989, either August or September was the wettest month (Hallberg et al., 1989). Climatic variations were probably the greatest factor affecting nitrate and atrazine concentrations and loads at L22T and L23S during the monitoring period.

Figures 16 and 17 show monthly mean nitrate and atrazine concentrations for sites L22T, L23S, and Big Spring (BSP) for WYs 1982-1995. Monthly mean concentrations were used to remove some of the sampling bias and make monitoring results from the three sites more comparable. Computed mean monthly atrazine concentrations of <0.10 µg/L are shown as non-detections (ND), even if some samples taken during the month were above detectable concentrations. Figure 18 shows mean daily surface-water discharge for L23S for partial WY 1986 through WY 1995, and mean daily groundwater discharge for L22T for WYs 1987-1995, and for BSP for WYs 1982-1995. Figure 19 shows annual basin precipitation, groundwater and surface-water discharge, flow-weighted (fw) mean NO₃-N concentrations and loads, and fw mean atrazine concentrations and loads for Big Spring and for L22T and L23S. Since these data are from monitoring actual farm operations, interpretation of water quality changes at these sites is not as straightforward as with data from controlled experimental farm operations.

Interpretation of the water quality of these sites is complicated by changes in landuse and cropping patterns over the period of monitoring. Rotational sequences have been disrupted by changes in ownership, changing farm programs (from PIK to CRP, etc.), and implementation of conservation BMP projects.

Table 20 shows crops, crop yields, pesticides applied, fertilizer-nitrogen application rates, and total pounds of nitrogen applied for the 36-acre field immediately above L22T during WY 1987 and WYs 1990-1995. Comparison of annual changes in corn acreage and nitrogen and atrazine applied



Figure 16. Monthly mean nitrate concentrations at L22T, L23S and Big Spring (BSP) for WYs 1982-1995.

within the field with annual fw mean nitrate and atrazine concentrations and loads from L22T during the entire WY 1987-1995 period is not possible because fertilizer and pesticide application rates were not available for WYs 1988 and 1989.

The upland and bottom within the field are nearly equal in area at approximately 18 acres each. Since the field constitutes 42% of the 85acre drainage area of L22T, and only 1.3% of the 4.39 mi² drainage area of L23S, the effects of management practices within the field on the water quality of L22T should be discernible, but the effects of the management practices on the water quality of L23S can probably not be ascertained. The entire field was planted to corn during 1987, 1990, 1991, 1993, and 1995. In 1992, corn was grown in the upland and soybeans were grown on the bottom, and during 1994, soybeans were grown in the upland and corn was planted on the bottom (Table 20). Fertilizer-nitrogen application rates for

corn within the 36-acre field varied from 177 pounds of nitrogen per acre (lbs N/ac) during 1990 and 1991, to 0 lbs N/ac during 1992 (Table 20). Crop yields for corn ranged from 170 bushels per acre (bu/ac) in 1990 to 128 bu/ac in 1993, when frequent rains lowered yields within the Big Spring basin and across Iowa. Within the Big Spring basin, from 1981 to 1993, the average rates of fertilizer used on all corn were reduced from 174 lbs N/ac to 115 lbs N/ac. From 1987, the average rates of fertilizer used on all corn in the basin declined from 149 lbs N/ac to 123 lbs N/ac in 1990, 117 lbs N/ac in 1991 and 1992, and 115 lbs N/ac in 1993. From 1981-1993, the average yield for continuous corn grown in the basin ranged from 79 bu/ac in 1988 to 165 bu/ac in 1992. The second lowest average yield within the basin, 110 bu/ac, occurred in 1993.

Comparisons of annual changes in the amount of nitrogen applied within the field above L22T with annual fw mean nitrate-nitrogen concentrations



Figure 17. Monthly mean atrazine concentrations at L22T, L23S and Big Spring (BSP) for WYs 1982-1995.

and loads from L22T suggest some possible relationships between the implementation of the landuse changes and water quality responses at L22T. The comparisons also show that time lags and climatic effects are involved between the implementation of landuse changes and water quality responses. This is supported by monitoring data from tile-line sites BTLUE and BTLUW within the 1,105-acre Bugenhagen sub-basin, located 1.5 miles northeast of L22T (Fig. 2). Corn acreage and total nitrogen applied within the field drained by L22T were greatest in WYs 1990 and 1991, and smallest during WY 1992. The greatest annual fw mean nitrate concentrations for L22T also occurred during WYs 1990 and 1991, while the smallest fw mean nitrate concentration occurred in WY 1989. The greatest annual nitrate-nitrogen load from L22T occurred during WY 1993, and the smallest nitrate-nitrogen load occurred in WY 1989. The greatest annual fw mean nitrate concentrations for L23S and Big Spring also occurred in WY 1991, and the smallest fw means also occurred in WY 1989, but both sites had low annual fw mean nitrate concentrations in WY 1990. Like L22T, the greatest annual nitratenitrogen loads from L23S and Big Spring occurred during WY 1993, and the smallest loads occurred in WY 1989.

Within the 366-acre upper Bugenhagen subbasin, corn acreage and total fertilizer use were smallest during WY 1987 and greatest during WY 1991. Like L22T, L23S and Big Spring, annual fw mean nitrate concentrations and nitrate-nitrogen loads from the tile lines in the upper sub-basin were smallest in WY 1989, and annual fw mean nitrate concentrations were greatest in WY 1991. The annual nitrate-nitrogen load from BTLUE, the tile draining 250 acres of the east side of the upper subbasin, was greatest in WY 1991, while the nitratenitrogen load from BTLUW, the tile draining 116 acres of the west side of the upper sub-basin, was



Figure 18. Mean daily groundwater discharge for L22T for WYs 1987-1995 and for Big Spring (BSP) for WYs 1982-1995, and mean daily surface-water discharge for L23S for partial Water Year 1986 through WY 1995. (Discharge data for L23S are from the U.S. Geological Survey, W.R.D., IA Dist.)

greatest in WY 1993.

Atrazine was not used in the field above L22T during WYs 1991-1994, and annual fw mean atrazine concentrations declined during this period. At L23S and Big Spring, fw mean atrazine concentrations declined in WY 1992, increased in WY 1993, then declined again in WY 1994. Annual atrazine loads for all three sites were greatest during WY 1991, while the smallest atrazine loads for L22T and L23S occurred in WY 1987, and the smallest atrazine load for Big Spring occurred in WY 1988.

Within the upper Bugenhagen sub-basin, atrazine use was greatest in WY 1989, and smallest in WYs 1991 and 1994 when no atrazine was used. The greatest annual fw mean atrazine concentration for BTLUE occurred in WY 1989 and the greatest annual fw mean atrazine concentration for BTLUW occurred in WY 1990. The smallest annual fw mean atrazine concentration for BTLUE occurred in WYs 1994 and 1995 and the smallest annual mean for BTLUW occurred in WYs 1988 and 1994. The smallest atrazine load for BTLUE occurred in WY 1987 and the smallest atrazine load for BTLUW occurred in WYs 1988 and 1994. Like L22T, L23S, and Big Spring, the greatest annual atrazine loads from BTLUE and BTLUW occurred in WY 1991, even though no atrazine was used in the upper sub-basin during the water year.

The annual data from L22T, L23S, Big Spring, and the Bugenhagen tile lines shows that climatic factors and resulting hydrologic conditions can overshadow changes in water quality brought about by changes in landuse and agrichemical application rates, even at small watershed scales. Large year**Table 20.** Crops, crop yields, pesticides applied, fertilizer-nitrogen application rates, and total pounds of nitrogen applied for the 36-acre field immediately above monitoring site L22T. Also shown are the annual fw mean NO_3 -N concentrations and NO_3 -N loads for site L22T. Fertilizer and pesticide application rates were not available for WYs 1988 and 1989.

Crop Year	• •		Pesticides Applied	Nitrogen Applied lbs N/Ac	Applied Nitrogen Total Ibs	L22T FW Mean NO ₃ -N mg/L	L22T NO ₃ -N Load lbs	
1987	Corn	150	alachlor, atrazine, cyanazine, terbufos	170	6,120	15.7	970	
1990	Corn	170	alachlor, atrazine, fonofos	177	6,372	31.3	1,171	
1991	Corn	160	pendimethalin, fonofos	177	6,372	31.3	6,735	
1992	Corn on top	145	alachlor, metribuzin,	0	0	18.5	5,213	
	Beans on bottom	40	bentazon	0	0			
1993	Corn	128*	cyanazine	140 following corn 100 following beans	2,520 1,800	17.7	9,103	
1994	Beans on Top	60	glyphosate, command**,	0	0			
	Corn on bottom	155	cyanazine, alachlor	140	2,520	21.0	5,074	
1995	Corn	140	atrazine, pendimethalin, permit***	100 following beans 135 following corn	1,800 2,430	17.8	2,700	

* frequent rains lowered yields in the basin and across lowa

**Clomazone 2-(2-Chlorophenyl)methyl-4, 4-dimethyl-3isoxazolidinone

*** Methyl 5-{[(4, 6-dimethoxy-2-pyrimidinyl) amino] carbonylaminosulfonyl}-3-chloro-1-methyl-1-H-pyrazole-4-carboxylate

to-year variations in recharge can obscure relationships between landuse changes within the subbasins and water quality responses at the basin monitoring sites.

Monthly mean nitrate concentrations from L22T were significantly greater than concentrations from sites L23S and Big Spring during the WY 1982-1995 period of record (Fig. 16). This is to be expected, since the entire area above L22T is usually planted to fertilized corn, and without surface-water intakes, the tile effluent is usually composed of infiltration recharge.

Monthly nitrate concentrations from L22T, L23S, and Big Spring generally declined from WY

1983 through the first quarter of WY 1985 and again through the drought during WYs 1988 and 1989. Monthly mean atrazine concentrations did not show trends as consistent as nitrate concentrations, although there were no monthly means below the 0.10μ g/L detection limit at any of the monitoring sites during WYs 1982-1984 (Fig. 17). In WY 1989, monthly atrazine concentrations generally increased as groundwater and surface-water discharge declined, and during WYs 1990 and 1991, monthly nitrate and atrazine concentrations increased as groundwater and surface-water discharge increased due to above normal precipitation (figs. 16-18). The lack of monthly mean atrazine non-detections at L22T and L23S during WYs 1982-1984 may be, in part, due to sampling bias since only fifteen samples were taken at L22T, and only six samples were taken at L23S during the WY 1982-1984 period.

On an annual basis, discharge and fw mean NO_{3-N} concentrations and loads at Big Spring declined from WY 1983-1985 as annual fw mean atrazine concentrations and loads increased (Fig. 19). In 1983, the Payment-In-Kind set-aside program reduced the area used for corn production in the Big Spring basin by 33% relative to 1982. This reduction in the land area used for corn production led to a 40% reduction in nitrogen use in the basin. Statistical analysis of discharge and nitrate concentrations at Big Spring suggests that the decline in nitrate concentrations in 1985 was related to the reduction in nitrogen inputs in 1983 (Hallberg et al., 1993). Annual discharge and fw mean NO_{3-N} concentrations and loads from L22T, L23S, and Big Spring also declined from WY 1988 to WY 1989, as annual fw mean atrazine concentrations increased at all three sites. During the same period, annual atrazine loads increased at L23S and Big Spring, but decreased slightly at L22T. During WYs 1990 and 1991, annual fw mean NO_{3-N} concentrations and loads increased significantly at L22T, L23S, and Big Spring, as fw mean atrazine concentrations decreased at L22T and L23S, but increased at Big Spring. Annual atrazine loads at L23S and Big Spring increased during WY 1990 and increased to record levels in WY 1991. At L22T annual atrazine loads decreased slightly during WY 1990, then increased to record levels in WY 1991.

The high monthly nitrate and atrazine concentrations during WYs 1990 and 1991 were associated with runoff and infiltration recharge events. The significant increases in nitrate concentrations usually occurred following discharge peaks, as an increasing percentage of the discharge is composed of infiltration recharge. Large increases in atrazine concentrations generally occurred during discharge peaks when a greater proportion of the discharge is composed of runoff recharge. Although L22T has no surface-water intakes, surface-water runoff does enter the tile line during significant recharge events through macropores, desiccation cracks, and root casts. The rapid movement of surface-applied water into L22T was documented by dye tracing above the tile line (Libra et al., 1992).

During WY 1992, annual precipitation decreased to 108% of normal and annual discharge decreased at Big Spring, while increasing slightly at L22T and L23S. Monthly mean nitrate concentrations from L22T and L23S decreased through February, increased through spring, then decreased through the summer. Annual fw mean NO₃.N concentrations and loads decreased at L22T and Big Spring, and at L23S, the annual fw mean nitrate concentration also decreased, but the annual nitrate-nitrogen load increased slightly. All monitoring sites showed significant decreases in annual fw mean atrazine concentrations and loads during WY 1992.

During WY 1993, the annual precipitation increased to 141% of normal and led to the greatest groundwater and surface-water discharges recorded since monitoring began at all three sites. Monthly mean nitrate concentrations increased during WY 1993, but showed large decreases at all sites in March, due to dilution from snowmelt generated recharge. On an annual basis, fw mean nitrate concentrations decreased slightly from WY 1992, and nitrate-nitrogen loads increased to record levels at all monitoring sites. Annual atrazine loads increased significantly at all monitoring sites as annual fw mean atrazine concentrations increased at L23S and Big Spring, and decreased to the lowest annual fw mean atrazine concentration recorded at L22T since monitoring began. Annual precipitation decreased to 92% of normal in WY 1994, and decreased further, to 89% of normal in WY 1995. Monthly mean nitrate concentrations for the most part declined, along with discharge, through WY 1994, showing the largest decreases in February and March, due to dilution from snowmelt derived recharge. During WY 1995, discharge declined through mid-February, increased through mid-April, then again declined through the end of the water year. Monthly mean nitrate concentrations increased in December and January, decreased through March, increased again through June, then decreased through August before increasing slightly in September.

Previous reports (Hallberg et al., 1983, 1984a, 1985, 1987, 1989; Libra et al., 1986, 1987, 1991;



Figure 19. Summary of annual A) basin precipitation, B) groundwater discharge, C) flow-weighted mean NO_3 -N concentrations and NO_3 -N loads, and D) atrazine concentrations and loads from Big Spring, and annual E) groundwater and surface-water discharge, F) flow-weighted mean NO_3 -N concentrations and NO_3 -N loads, and G) atrazine concentrations and loads from L22T and L23S.

Rowden et al., 1993, 1995a, 1995b; Liu et al., 1997) have shown that increases and decreases in annual discharge at Big Spring and other sites within the study area have been accompanied by increases and decreases in annual fw mean NO3-N concentrations and nitrate-nitrogen loads (Fig. 19). Annual fw mean atrazine concentrations and loads have shown no consistent relationship to annual groundwater or surface-water discharge, although atrazine concentrations and loads tend to increase with increasing runoff on a short-term basis. Similar seasonal trends and short- and long-term changes in nitrate and atrazine concentrations occur at most monitoring sites within the Big Spring basin. From WY 1988 to WY 1989, annual surface-water and groundwater discharge and annual fw mean nitrate concentrations and nitrate-nitrogen loads from most sites in the basin declined to the lowest values recorded during the period of monitoring, while annual fw mean atrazine concentrations increased significantly. Unlike Big Spring and L23S, the lowest annual groundwater discharge from L22T occurred in WY 1990, rather than WY 1989. From WY 1989 to WY 1991, significant increases in groundwater and surface-water discharge generated large increases in annual nitrate-nitrogen loads, and annual fw mean nitrate concentrations increased to the greatest values recorded during the period of record for the monitoring sites. The annual fw mean atrazine concentration increased at Big Spring, but decreased at L22T and L23S from WY 1989 to WY 1991. Annual atrazine loads from Big Spring and L23S increased from WY 1989 to WY 1991, but decreased slightly at L22T in WY 1990, before increasing significantly in WY 1991. The greatest annual atrazine loads from all three monitoring sites during the period of monitoring occurred in WY 1991. From WY 1991 to WY 1992, annual groundwater and surface-water discharge, and annual fw mean NO₃₋N concentrations and loads from most monitoring sites showed minor decreases while annual fw mean atrazine concentrations and loads decreased significantly. The largest decrease in annual fw mean nitrate concentrations, as well as the smallest decrease in annual fw mean atrazine concentrations, occurred at L22T.

Comparison of the annual data during WYs 1988-1995 from Big Spring and L23S shows a

general relationship between annual discharge and annual fw mean NO_{3-N} concentrations and loads, and little relationship between annual discharge and annual atrazine concentrations and loads. Atrazine loads do increase on a short-term basis during runoff events as the proportion of runoff composing the discharge increases. At Big Spring, WY 1989 had 6% more precipitation, 51% less groundwater discharge, a 42% lower fw mean nitrate concentration, a 71% smaller nitrate-nitrogen load, a 369% higher fw mean atrazine concentration, and a 130% greater atrazine load than WY 1988. At L23S, surface-water discharge decreased 52%, fw mean nitrate decreased 79%, the nitrate-nitrogen load decreased 90%, fw mean atrazine concentration increased 2,713%, and the atrazine load increased 1,229%. Relative to WY 1988, WY 1990 had 65% more precipitation, and Big Spring had a 33% decrease in groundwater discharge, a 14% lower fw mean nitrate concentration, a 42% smaller nitrate-nitrogen load, a 715% higher fw mean atrazine concentration, and a 443% greater atrazine load. At L23S discharge decreased 15%, fw mean nitrate decreased 42%, the nitrate-nitrogen load decreased 50%, fw mean atrazine concentration increased 2,617%, and the atrazine load increased 2,189%. Although the changes in discharge and fw mean NO₃-N concentrations and loads are greater, and the changes in fw atrazine concentrations and loads are much greater at L23S, they are proportional to the changes at Big Spring. At both sites changes in fw mean NO₃-N concentrations and loads more closely resemble changes in annual discharge.

Increases in atrazine loading during WYs 1990 and 1991 can be partially attributed to very large runoff events in March and August of WY 1990 and June of WY 1991. At Big Spring, March accounted for 13% of the annual groundwater discharge and 28% of the annual atrazine load. August of WY 1990 accounted for 15% of the annual groundwater discharge and 9% of the annual atrazine load at Big Spring. At L23S, 21% of the annual surface-water discharge and 24% of the annual discharge and 59% of the annual atrazine load occurred in March, and 42% of the annual discharge and 59% of the annual atrazine load occurred in August. During WY 1991, June accounted for 20% of the annual discharge and 56% of the annual atrazine load at Big Spring, and 54% of the annual discharge and 91% of the annual atrazine load at L23S.

During WY 1992, the annual precipitation was 32% lower than during WY 1991 and rainfall was more evenly distributed with no large runoff events. At Big Spring, WY 1992 had 14% less groundwater discharge, a 4% lower fw mean nitrate concentration, a 19% reduction in nitrate-nitrogen load, a 445% lower fw mean atrazine concentration, and a 500% reduction in atrazine load when compared to WY 1991. At L23S, surface-water discharge increased 11%, the fw mean nitrate concentration decreased 4%, the nitrate-nitrogen load increased 5%, the fw mean atrazine concentration decreased 752%, and the atrazine load decreased 676%. As in previous years, the changes in annual fw mean NO_{3-N} concentrations and loads are much more proportional to the changes in annual discharge than the changes in fw mean atrazine concentrations and loads.

The increases in NO₃-N concentrations and loads during WYs 1990 and 1991 may be the result of several factors. The effects of denitrification and nitrogen uptake by aquatic vegetation were probably less pronounced under the higher-flow conditions of WYs 1990 and 1991. In addition, the below normal precipitation and lack of recharge during WYs 1988 and 1989 would have led to less leaching. This may have left a greater than normal mass of nitrate in storage in the soil system available for transport to the hydrologic system by the increased recharge during WYs 1990 and 1991. Decreased crop uptake of nitrogen related to decreased yields during the drought also may have contributed to increased nitrate storage during the drought.

The increases in atrazine concentrations and loads during WYs 1990 and 1991 are probably also in part related to the drought. 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 ofherbicide available for mobilization and transport to groundwater during WYs 1990 and 1991.

The small decreases in annual fw mean nitrate concentrations during WY 1992 are probably related to decreased groundwater flux during the period. The increased infiltration and leaching of nitrogen during WY 1991 may also have left a smaller than normal mass of nitrate in storage in the soil system available for transport during WY 1992. The large decreases in annual atrazine concentrations and loads during WY 1992 are probably related to decreases in the proportion of runoff contributing to the annual groundwater and surface-water discharge during the water year. The increased runoff during WYs 1990 and 1991 probably removed a greater than normal mass of herbicide, leaving less available for mobilization and transport during WY 1992. The cumulative increase in soil moisture during WYs 1990 and 1991 may also have enhanced pesticide degradation processes, leaving a lower than normal mass of herbicide available for transport in WY 1992.

In WY 1993, annual basin precipitation increased 30% relative to WY 1992. At Big Spring, annual groundwater discharge increased 56%, annual fw mean nitrate decreased 6%, the annual nitrate-nitrogen load increased 47%, the fw mean atrazine concentration increased 2%, and the annual atrazine load increased 87%. At L23S, surface-water discharge increased 44%, the fw mean nitrate concentration decreased 23%, the nitratenitrogen load increased 12%, the fw mean atrazine concentration increased 48%, and the atrazine load increased 114%. At L22T, groundwater discharge increased 82%, the fw mean nitrate concentration decreased 4%, the nitrate-nitrogen load increased 75%, the fw mean atrazine concentration decreased 9%, and the atrazine load increased 66%. The increases in annual NO₃₋N and atrazine loads from WY 1992 to WY 1993 were more related to the increase in groundwater and surface-water discharge than to the change in annual fw mean nitrate and atrazine concentrations.

The decrease in annual fw mean nitrate concentrations, as annual groundwater and surfacewater discharge increased from WY 1992 to WY 1993, was unusual and may be related to several factors. A number of large runoff events occurred during the latter half of WY 1993. Nitrate concentrations typically decrease during runoff and increase as 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, above normal precipitation during WY 1991, and increased infiltration 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 the Big Spring basin. 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 33% relative to 1982 (Hallberg et al., 1993).

Annual basin precipitation decreased 35% from WY 1993 to WY 1994 and declined 4% from WY 1994 to WY 1995. At Big Spring, annual groundwater discharge decreased 46% in WY 1994 and 4% in WY 1995. The annual fw mean nitrate concentration at Big Spring decreased 8% in WY 1994 and 4% in WY 1995, and the annual nitratenitrogen load decreased 51% during WY 1994 and 7% during WY 1995. The fw mean atrazine concentration decreased 22% in WY 1994 and 43% in WY 1995, and the annual atrazine load decreased 58% in WY 1994 and 45% in WY 1995. At L23S, surface-water discharge decreased 72% in WY 1994 and increased 18% in WY 1995. The fw mean nitrate concentration at L23S increased 3% in WY 1994 and 12% in WY 1995, and the nitrate-nitrogen load decreased 72% in WY 1994 and increased 31% in WY 1995. The fw mean atrazine concentration decreased 65% during WY 1994 and 36% during WY 1995, and the atrazine load decreased 90% in WY 1994 and 20% in WY 1995. At L22T, groundwater discharge decreased 53% in WY 1994 and 37% in WY 1995, the fw mean nitrate concentration increased 19% in WY 1994 and decreased 16% in WY 1995, and the nitrate-nitrogen load decreased 44% in WY 1994 and 47% in WY 1995. The fw mean atrazine concentration for L22T remained at 0.10 µg/L during WYs 1993 and 1994, then increased 70% in

WY 1995, and the atrazine load decreased 55% during WY 1994 and increased 8% in WY 1995.

The annual groundwater and surface-water discharges during WYs 1994 and 1995 were relatively high, given the amount of precipitation that occurred during the period. The discharges were probably sustained by groundwater recharge from storage that accumulated during WYs 1990-1993. Surface-water discharges from L23S, Roberts Creek, and the Turkey River increased from WY 1994 to WY 1995, as groundwater discharges decreased from both L23S and Big Spring. The increase in annual surface-water discharge as annual precipitation and annual groundwater discharge were decreasing is probably related to the timing and intensity of precipitation, as well as soil conditions and evapotranspiration rates of crops grown in and near the basin. Water Year 1994 had a dry growing season until June, and the WY 1995 growing season was wet until June. Much of the precipitation falling after crops were up in WY 1994 probably infiltrated the soil and were utilized by the crops, rather than running off into the streams. Much of the precipitation during WY 1995 occurred from February through May. During some of this period, the ground may have been frozen, leading to increased runoff, and there would have been less uptake of soil moisture from crops.

Hydrologic conditions during WY 1994 were similar to WY 1992 in that both years followed very wet years. The decreases in annual fw mean nitrate concentrations during WYs 1994 and 1995 are probably related to decreased groundwater flux during the period. The increased infiltration and leaching of nitrogen during WY 1993 probably also have left a smaller than normal mass of nitrate in storage in the soil system available for transport during WYs 1994 and 1995. The decreases in annual atrazine concentrations and loads during WYs 1994 and 1995 are probably related to decreases in the proportion of runoff contributing to the annual groundwater and surface-water discharge during the water years. The increased runoff during WY 1993 may have removed a greater than normal mass of herbicide, leaving less available for mobilization and transport during WYs 1994 and 1995. The cumulative increase in soil moisture during WYs 1990-1993 may also have enhanced pesticide degradation processes, leaving a lower than normal mass of herbicide available for transport in WYs 1994 and 1995. 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.

During WYs 1982-1995, monthly mean nitrate concentrations were greatest at L22T, followed by concentrations from Big Spring, then L23S (Fig. 16). Monthly mean atrazine concentrations were more variable, but generally lowest at L22T. The greater nitrate concentrations and lower atrazine concentrations at L22T are partially due to the greater percentage of infiltration recharge constituting the tile effluent. Infiltration recharge is enriched in nitrate and other chemicals that are soluble and mobile in soil, relative to runoff recharge. Runoff recharge has lower concentrations of such compounds, but is enriched in herbicides and other chemicals with low solubility and soil mobility (e.g., greater adsorption). The surface water discharge from L23S and the groundwater discharge from Big Spring contain a greater percentage of runoff recharge than the discharge from L22T. The greater nitrate concentrations at L22T may also result from the greater percentage of land cropped to corn within the drainage area of L22T, relative to the areas cropped to corn within the drainage areas of L23S and Big Spring.

A general decrease in nitrate concentrations at increasingly larger watershed scales has been documented within the Big Spring basin and is probably related in part to in-stream denitrification and nitrogen uptake by aquatic vegetation (Rowden et al., 1995a). In addition, in the smaller streams, the influence of nitrate-rich tile effluent may be more pronounced, constituting a larger percentage of the total surface-water discharge. The variability of atrazine concentrations is probably related to variations in the concentrations of atrazine applied and in the percentage of area within each subbasin where atrazine is used. The relatively high concentrations of atrazine that persist year-round at many surface-water sites within the basin suggest that instream biological processing is not as effective on atrazine as it is on nitrate.

The data from WYs 1986-1995 show a relationship between groundwater and surface-water discharge, and fw mean NO3-N concentrations and loads, and a lack of any clear relationship between annual discharge and annual fw mean atrazine concentrations and loads when runoff inputs are minimal. The data also show time lags between increases in precipitation and increases in groundwater and surface-water discharge, as storage within the Big Spring basin is slowly replenished. The parallel responses in water-quality changes over time of the various scale watersheds within the basin and the groundwater at Big Spring illustrate that hydrologic and chemical responses to recharge events can be tracked from smaller scale monitoring sites through the larger groundwater and surface-water systems. The water quality of these smaller watersheds, and ultimately at Big Spring, is an integration of the management practices of all the individual parcels of land they contain. Water-quality improvements caused by changes in agricultural practices require longer periods of time to become apparent at increasingly larger watershed scales.

OVERVIEW OF MONITORING RESULTS FOR WYs 1986 THROUGH 1995

Figure 19 and tables 21 through 23 summarize the results of hydrologic and water-quality monitoring at L22T for WYs 1987-1995, at L23S for partial WY 1986 through WY 1995, and at Big Spring for WYs 1982-1995. Data for the partial WY 1986 begins on May 13 for site L23S. During the period, annual precipitation varied from 22.9 inches in WY 1988 to 47.3 inches during WY 1991. Annual surface water and groundwater discharges for L23S and Big Spring were smallest during WY 1989 (552 ac-ft at L23S and 12,700 ac-ft at Big Spring), and greatest for all three sites during WY 1993 (5,720 ac-ft at L23S; 188.7 ac-ft at L22T; and 58,186 ac-ft at Big Spring). The smallest annual groundwater discharge from L22T, 13.8 ac-ft, occurred during WY 1990. The smallest annual fw mean nitrate concentrations and smallest nitrate-N loads from the sites occurred during WY 1989 and the greatest annual fw mean nitrate concentrations

				Water Yea	ar				
	87	88	89	90	91	92	93	94	95
Precipitation:									
water inches	32.0	22.9	24.3	37.9	47.3	35.7	46.5	30.4	29.3
Groundwater discharge (Q):									
mean Q, cfs	0.032	0.048	0.021	0.019	0.109	0.143	0.261	0.123	0.077
total Q, inches	3.2	4.9	2.2	2.0	11.2	14.6	26.6	12.6	7.9
acre-feet	22.8	34.9	15.3	13.8	79.2	103.5	188.7	88.9	55.7
Nitrogen discharged with groundwater: flow-wtd mean concentration, mg/L									
as nitrate (NO ₃)	71	73	67	141	141	83	80	95	80
as nitrate-N (NO ₃ -N)	15.7	16.2	15.0	31.3	31.3	18.5	17.7	21.0	17.8
ammonia-N organic-N	0.1 0.2	0.1 0.7	0.1 0.2	<0.1 0.3	<0.1 0.3	0.1 0.2	0.2 0.4	0.1 <0.1	n/a n/a
-	0.2	0.7	0.2	0.0	0.0	0.2	0.4	50.1	n/u
nitrogen load: (nitrate-N + nitrite-N)									
(Initiale-IN + Initiale-IN)	970	1,539	622	1,171	6,735	5,213	9,103	5,074	2,700
lbs-N/acre	11.4	18.1	7.3	13.8	79.2	61.3	107.1	59.7	31.8
(for sub-basin area)									
Atrazine discharged with groundwater:									
flow-wtd mean concentration,									
atrazine, µg/L	0.21	0.19	0.40	0.37	0.29	0.11	0.10	0.10	0.17
atrazine load:									
lbs - atrazine	0.013	0.018	0.017	0.014	0.063	0.032	0.053	0.024	0.026

Table 21. Water year summary data for groundwater discharge from L22T.

					Water Ye	ar				
	86*	87	88	89	90	91	92	93	94	95
Precipitation:										
water inches	22.4	32.0	22.9	24.3	37.9	47.3	35.7	46.5	30.4	29.3
Surface-water discharge (Q):									
mean Q, cfs	1.3	1.7	1.6	0.8	1.4	4.9	5.5	7.9	2.2	2.6
total Q, inches	1.7	5.2	4.9	2.4	4.2	15.4	17.0	24.4	6.8	8.0
acre-feet	398	1,220	1,150	552	982	3,594	3,980	5,720	1,590	1,870
Nitrogen discharged with su flow-wtd mean concentrat		:								
as nitrate (NO₃)	36	38	43	9	25	54	52	40	41	46
				-						
as nitrate-N (NO3-N)	8.0	8.5	9.6	2.0	5.6	12.0	11.4	8.9	9.1	10.1
ammonia-N	0.1	0.1	0.1	2.4	1.2	0.1	0.1	0.1	1.0	0.4
organic-N	0.2	0.5	0.3	0.1	2.9	1.3	0.3	1.8	n/a	n/a
nitrogen load:										
(nitrate-N + nitrite-N)	0.007	07 477	00.005	0.000	45.004	447 404	400 500	100.054	00.050	54.00
lbs-N lbs-N/acre	8,687 3.1	27,177 9.7	29,885 10.6	2,998 1.1	15,034 5.4	117,164 41.7	123,530 44.0	138,951 49.5	39,358 14.0	51,62 18.4
(for sub-basin area)	3.1	9.7	10.6	1.1	5.4	41.7	44.0	49.5	14.0	10.4
Atrazine discharged with su	rface water:									
flow-wtd mean concentrat										
atrazine, µg/L	0.30	0.12	0.24	6.75	6.52	2.30	0.26	0.40	0.14	0.09
atrazine load:										
lbs - atrazine	0.33	0.40	0.76	10.1	17.4	22.5	2.9	6.2	0.59	0.47

Table 22. Water year summary data for surface-water discharge from L23S.

* Partial water year

					Wat	ter Year								
	82	83	84	85	86	87	88	89	90	91	92	93	94	95
Precipitation:														
water inches	34.0	44.5	32.8	35.8	36.7	32.0	22.9	24.3	37.9	47.3	35.7	46.5	30.4	29
Groundwater discharge (Q) to the	Furkey Riv	er:												
mean Q, cfs	51.4	56.9	45.3	35.2	42.0	35.4	35.8	17.6	24.1	58.7	51.4	80.4	43.2	41
total Q, inches	6.8	7.5	5.9	4.6	5.5	4.6	4.7	2.3	3.2	7.7	6.8	10.6	5.7	5.
acre-feet, 1000s	37.4	41.4	32.7	25.1	30.3	25.5	26.0	12.7	17.5	42.5	37.3	58.2	31.3	30
Nitrogen discharged with groundwa	iter:													
flow-wtd mean concentration, mg	/L													
as nitrate (NO ₃)	39	46	43	31	43	41	43	25	37	56	54	51	47	4
as nitrate-N (NO ₃ -N)	8.8	10.3	9.7	7.0	9.7	9.1	9.5	5.7	8.2	12.5	12	11.4	10.4	10
ammonia-N*	*	*	*	*	0.1	0.1	0.1	0.6	0.1	0.1	0.1	0.2	0.2	<0
organic-N*	*	*	*	*	0.5	0.2	0.3	0.8	0.6	0.9	0.3	0.6	0.1	*
nitrogen load:														
(nitrate-N + nitrite-N)														
1,000s lbs-N	873.0	1,150	843.4	476.8	796.8	636.1	672.0	194.9	388.5	1,446	1,220	1,796	888.5	82
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	13.5	12
(for total basin area)														
trazine discharged with groundwa	ter:													
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	0.21	0.1
atrazine load;														
lbs - atrazine	14.2	31.2	40.0	47.6	29.0	17.6	9.2	21.2	50.0	135.0	22.5	42.0	17.8	9.

Table 23. Water year summary data for groundwater discharge from the Big Spring basin to the Turkey River.

** In WY 1995, organic-N was omitted from the list of analyses.

occurred during WY 1991. The annual fw mean nitrate concentration for L22T was unchanged from WY 1990 to WY 1991. The greatest nitrate-N loads from the sites were discharged during WY 1993. From WY 1989 to WY 1991, annual fw mean nitrate concentrations ranged from 67 to 141 mg/L (15.0 to 31.3 mg/L as NO₃-N) at L22T, 9 to 54 mg/L (2.0 to 12.0 mg/L as NO₃-N) at L23S, and 25 to 56 mg/L (5.6 to 12.4 mg/L as NO₃-N) at Big Spring. Annual nitrate-N loads from WY 1989 to WY 1993 varied between 622 and 9,103 pounds at L22T; 2,998 and 138,951 pounds at L23S; and 195,000 and 1,796,000 pounds at Big Spring. The smallest annual fw mean atrazine concentration for L22T, 0.10 μ g/L, occurred during WYs 1993 and 1994. The smallest annual fw mean atrazine concentration for L23S, 0.09 μ g/L, and Big Spring, 0.12 μ g/L, occurred during WY 1995. The smallest annual atrazine loads for L22T, 0.013 pounds, and L23S, 0.40 pounds, were discharged during WY 1987. For Big Spring the smallest atrazine load, 9.2 pounds, occurred in WY 1988. The greatest annual

fw mean atrazine concentration for L22T, 0.40 μ g/ L, and L23S, 6.75 μ g/L, occurred in WY 1989. For Big Spring, the greatest annual fw mean atrazine concentration, 1.17 μ g/L, occurred during WY 1991. The greatest annual atrazine loads from L22T, L23S, and Big Spring, 0.063 pounds, 22.5 pounds, and 135 pounds were discharged during WY 1991.

Tables 24 through 26 summarize the annual percentage of detections and maximum concentrations for pesticides for L22T, L23S, and Big Spring for WYs 1982-1995. The greatest percentage of atrazine detections for the entire WY 1982-1995 period, 95%, occurred at Big Spring, followed by 83% at L22T, and 70% at L23S. Atrazine was detected in all samples collected from all three sites during WYs 1982-1984. Atrazine was also detected in all samples collected at L22T during WYs 1986 and 1989, all samples collected at L23S during WYs 1985 and 1992, and all samples collected at Big Spring during WYs 1985, 1987, and WYs 1990-1992. The lowest annual percentage of detections at L22T, 60%, occurred in WY 1993. At L23S the lowest percentage of detections, 18%, occurred during WY 1995, and at Big Spring the lowest annual percentage of detections, 75%, occurred in WYs 1988 and 1995. At L22T maximum atrazine concentrations analyzed varied from 0.35 µg/L in WY 1984 to 8.50 µg/L in WY 1989. At L23S, maximum atrazine concentrations varied from 0.16 μ g/L in WY 1994 to 68.00 μ g/L in WY 1989, and at Big Spring, maximum atrazine concentrations varied from 0.40 µg/L in WY 1988 to 16.00 µg/L in WY 1991.

As discussed in previous reports (Libra et al., 1986, and 1991; Hallberg et al., 1989; Rowden et al., 1993, 1995a, and 1995b; Liu et al., 1997), annual fw mean nitrate concentrations tend to parallel annual groundwater discharge, or flux through the hydrologic system. Higher nitrate concentrations and greater nitrate-nitrogen loads occur during years with greater groundwater and surface-water discharge. Annual fw mean atrazine concentrations, and the frequency and magnitude of detections of other herbicides do not tend to parallel annual discharge. Relatively high fw mean atrazine concentrations have occurred during some years with low groundwater discharge, for reasons that

are currently unclear. At Big Spring, annual groundwater discharge and fw mean nitrate concentrations decreased from WY 1983 to WY 1985 and from WY 1988 to WY 1989, while annual fw mean atrazine concentrations and loads increased from WY 1982 to WY 1985 and from WY 1988 to WY 1991. At L22T and L23S, annual groundwater and surface-water discharge decreased from WY 1988 to WY 1989, and annual fw mean NO3-N concentrations and loads decreased to the smallest values recorded, as fw mean atrazine concentrations increased to the greatest values recorded. The greatest annual atrazine loads were discharged from all three sites during WY 1991, a year with the second-greatest annual discharge from Big Spring, the third-greatest discharge from L23S, and the fourth-greatest annual discharge from L22T. The greatest annual nitrate-nitrogen loads, as well as the greatest annual groundwater and surface-water discharge from all three sites occurred in WY 1993.

The decrease in annual fw mean nitrate concentrations, as annual groundwater and surfacewater discharge increased from WY 1992 to WY 1993, was unusual and may be related to a greater than normal proportion of the annual discharge during WY 1993 being composed of runoff. In addition, above normal precipitation during WY 1991, and increased infiltration 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 the Big Spring basin.

Retardation of atrazine transport to and through the Big Spring basin's groundwater system, and annual changes in the mass of atrazine present on the land surface, are likely important factors affecting 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. The low soil moisture from the drought conditions during WYs 1988 and 1989 may have inhibited hydrolysis and microbial activity, important to degradation pro-

							Water `	Year							
	82	83	84	85	86	87	88	89	90	91	92	93	94	95	
Pesticide														·	
common chemical						% dete	ections								% detections
name					maximu	im conc	entratio	ns, µg/L							(total record)
Herbicides															
atrazine	100%	100%	100%	75%	100%	94%	75%	100%	95%	87%	79%	60%	76%	72%	83%
	1.40	1.20	0.35	2.70	0.69	3.40	1.80	8.50	8.20	1.40	0.40	0.73	1.98	0.90	
acetochlor	na	na	na	na	na	na	na	na	na	na	na	na	nd	nd	0%
	na	na	na	na	na	na	na	na	na	na	na	na	nd	nd	
alachlor	100%*	100%*	nd	8%	18%	2%	5%	7%	nd	8%	10%	2%	nd	nd	4%
	0.16	0.12	nd	4.20	0.13	0.48	2.00	0.70	nd	2.30	2.00	0.10	nd	nd	
butylate	na	na	na	na	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	0%
	na	na	na	na	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	
cyanazine	na	100%*	nd	8%	nd	4%	3%	7%	4%	2%	nd	nd	nd	nd	3%
	na	0.11	nd	5.30	nd	0.25	0.72	0.71	0.24	0.19	nd	nd	nd	nd	
metolachlor	na	na	nd	100%*	nd	nd	nd	2%	nd	nd	nd	7%	nd	nd	1%
	na	na	nd	5.70	nd	nd	nd	0.24	nd	nd	nd	0.35	nd	nd	
metribuzin	na	na	na	100%*	nd	nd	nd	2%	nd	nd	nd	nd	nd	nd	<1%
	na	na	na	1.90	nd	nd	nd	0.21	nd	nd	nd	nd	nd	nd	
trifluralin	na	na	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	0%
	na	na	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	
Atrazine metabolites															
desethyl atrazine	na	na	na	na	na	na	na	na	na	na	na	49%	94%	98%	80%
2	na	na	na	na	na	na	na	na	na	na	na	0.41	0.30	0.27	
desisopropyl atrazine	na	na	na	na	na	na	na	na	na	na	na	14%	nd	2%	5%
	na	na	na	na	na	na	na	na	na	na	na	0.38	nd	0.10	
Insecticides															
fonofos	na	na	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	na	0%
	na	na	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	na	576

Table 24. Summary of annual % of detections and maximum concentrations for pesticides in groundwater at L22T.

na- not analyzed; nd- not detected; * only one analysis

Desethyl atrazine and desisopropyl atrazine have been analytes since Janruary, 1993. Acetochlor has been an analyte since August, 1994.

				Water Year													
	82	83	84	85	86	87	88	89	90	91	92	93	94	95			
Pesticide																	
common chemical						% det	ections								% detections		
name					maxim	um conc	entratio	ns, µg/L							(total record)		
Herbicides																	
atrazine	100%	100%	100%*	100%	88%	71%	40%	63%	94%	83%	100%	62%	33%	18%	70%		
	0.82	0.93	0.60	2.40	0.60	0.68	8.40	68.00	16.00	1.80	1.20	0.48	0.16	0.73			
acetochlor	na	na	na	na	na	na	na	na	na	na	na	na	nd	9%	8%		
	na	na	na	na	na	na	na	na	na	na	na	na	nd	0.38			
alachlor	100%*	na	nd	25%	38%	5%	7%	13%	13%	13%	10%	15%	nd	nd	11%		
	0.15	na	nd	0.20	0.31	0.12	4.50	38.00	1.40	0.32	0.13	0.81	nd	nd			
butylate	na	na	na	na	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	0%		
	na	na	na	na	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd			
cyanazine	na	100%*	nd	25%	nd	19%	7%	44%	13%	13%	10%	nd	nd	nd	13%		
	na	0.10	nd	0.35	nd	0.19	1.90	22.00	0.57	0.74	0.28	nd	nd	nd			
metolachlor	na	na	na	na	13%	nd	7%	13%	10%	10%	5%	8%	8%	9%	8%		
	na	na	na	na	0.60	nd	0.21	4.20	1.90	0.56	0.50	0.22	0.15	0.22			
metribuzin	na	na	na	na	nd	nd	nd	6%	nd	nd	nd	nd	nd	nd	<1%		
	na	na	na	na	nd	nd	nd	0.13	nd	nd	nd	nd	nd	nd			
trifluralin	na	na	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	0%		
	na	na	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd			
Atrazine metabolites																	
desethyl atrazine	na	na	na	na	na	na	na	na	na	na	na	27%	83%	36%	49%		
	na	na	na	na	na	na	na	na	na	na	na	0.22	0.19	0.20			
desisopropyl atrazine	na	na	na	na	na	na	na	na	na	na	na	10%	nd	nd	3%		
1 17 11 11	na	na	na	na	na	na	na	na	na	na	na	0.12	nd	nd			
Insecticides																	
fonofos	na	na	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	na	na	0%		
10110103	iid	110	nu	nu	nu	nu	nu	nu	nu	nu	nu	nu	iia	na	078		

 Table 25.
 Summary of annual % of detections and maximum concentrations for pesticides in surface water at L23S.

na- not analyzed; nd- not detected; * only one analysis

Desethyl atrazine and desisopropyl atrazine have been analytes since Janruary, 1993. Acetochlor has been an analyte since August, 1994.

							Water `	Year							
	82	83	84	85	86	87	88	89	90	91	92	93	94	95	
Pesticide															
common chemical						% dete	ections								% detections
name					maxim	um conc	entratio	ns, µg/L							(total record)
Herbicides															
atrazine	100%	100%	100%	100%	99%	100%	75%	88%	100%	100%	100%	94%	94%	75%	95%
	2.50	5.10	10.00	6.10	1.40	0.70	0.40	3.30	8.20	16.00	1.00	2.50	1.30	1.30	
acetochlor	na	na	na	na	na	na	na	na	na	na	na	na	nd	2%	<2%
	na	na	na	na	na	na	na	na	na	na	na	na	nd	0.60	
alachlor	16%	28%	23%	14%	7%	2%	nd	18%	18%	18%	3%	4%	4%	4%	11%
	0.20	0.60	4.00	5.00	0.70	0.10	nd	0.20	0.90	5.50	0.56	1.50	2.10	0.25	
butylate	na	na	na	na	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	0%
	na	na	na	na	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	
cyanazine	32%	26%	21%	15%	3%	5%	3%	31%	35%	13%	5%	8%	2%	4%	14%
	0.70	1.20	1.70	4.60	0.10	0.10	1.00	3.00	0.90	2.60	0.51	1.90	0.14	0.12	
metolachlor	na	4%	17%	4%	4%	nd	nd	6%	8%	4%	2%	6%	10%	6%	5%
	na	0.60	4.50	4.60	0.60	nd	nd	0.20	0.60	2.20	0.17	0.86	2.30	0.38	
metribuzin	na	na	na	1%	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	<1%
	na	na	na	3.60	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	
trifluralin	na	na	na	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	0%
	na	na	na	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	
Atrazine metabolites															
desethyl atrazine	na	na	na	na	na	na	na	na	na	na	na	96%	98%	88%	94%
	na	na	na	na	na	na	na	na	na	na	na	0.46	0.32	0.18	
desisopropyl atrazine	na	na	na	na	na	na	na	na	na	na	na	nd	nd	nd	0%
	na	na	na	na	na	na	na	na	na	na	na	nd	nd	nd	
Insecticides															
fonofos	na	1%	8%	nd	nd	nd	nd	nd	nd	nd	nd	nd	na	na	<1%
	na	0.10	0.30	nd	nd	nd	nd	nd	nd	nd	nd	nd	na	na	,0

Table 26. Summary of annual % of detections and maximum concentrations for pesticides in groundwater at Big

 Spring.

na- not analyzed; nd- not detected

Desethyl atrazine and desisopropyl atrazine have been analytes since Janruary, 1993. Acetochlor has been an analyte since August, 1994.

cesses and left a greater than normal mass of herbicide available for mobilization and transport to groundwater during WYs 1990 and 1991. The large decrease in fw mean atrazine concentrations and loads during WY 1992 may be related to the lack of large runoff events during the year and the great losses that occurred during WYs 1990 and 1991. This may have left a smaller than normal mass of herbicide available for mobilization and transport.

The variability of these annual parameters over relatively short periods of time underscores the need for long-term monitoring of nonpoint-source contamination, especially at increasingly larger watershed scales.

SUMMARY

Water years 1982-1995 were characterized by extreme climatic variability. The driest consecutive two-year period in the state's history, WYs 1988 and 1989, preceded the two wettest consecutive years during the WY 1982-1995 period of monitoring within the Big Spring basin. The change in distribution patterns of precipitation during WYs 1988-1995 was also a significant factor. Water years 1985-1989 were characterized by dry growing seasons and wet falls. During WYs 1990 and 1991, rainfall amounts were below normal from October through February and above normal from March through September. The annual precipitation during WY 1992 was more evenly distributed than during WYs 1990 and 1991, with no large single rainfall or runoff events. Water Year 1992 had a very dry growing season, and WY 1993 had a wet growing season. Water Year 1994 had a dry growing season until June, and the WY 1995 growing season was wet until June. The increased precipitation generated both runoff and infiltration recharge, and discharge rates increased from WY 1989 to WY 1991 and from WY 1992 to WY 1993, as a net increase in overall storage within the basin's hydrologic system occurred.

Since the 36-acre field immediately above site L22T constitutes 42% of the 85-acre drainage area of L22T, and only 1.3% of the 4.39 mi² drainage area of L23S, the effects of management practices within the field on the water quality of L22T should

be discernible, but the effects of the management practices on the water quality of L23S can probably not be ascertained. Comparison of annual changes in corn acreage and nitrogen and atrazine applied within the field above L22T with annual fw mean NO₃.N and atrazine concentrations and loads from L22T during the entire WY 1987-1995 period was not possible since fertilizer and pesticide application rates were not available for WYs 1988 and 1989.

The annual data from L22T did suggest some possible relationships between the implementation of landuse changes in the field above L22T and water quality responses at L22T, and showed that time lags and climatic effects are involved between the implementation of landuse changes and water quality responses. This is supported by monitoring data from tile-line sites within the 1,105-acre Bugenhagen sub-basin (Fig. 2). Corn acreage and total nitrogen applied within the field above L22T were greatest in WYs 1990 and 1991, and smallest during WY 1992. The greatest annual fw mean nitrate concentrations for L22T also occurred during WYs 1990 and 1991, while the smallest fw mean nitrate concentration occurred in WY 1989. The greatest annual nitrate-nitrogen load from L22T occurred during WY 1993, and the smallest nitrate-nitrogen load occurred in WY 1989. The greatest annual fw mean nitrate concentrations for L23S and Big Spring also occurred in WY 1991, and the smallest fw means also occurred in WY 1989, but both sites had relatively low annual fw mean nitrate concentrations in WY 1990. Like L22T, the greatest annual nitrate-nitrogen loads from L23S and Big Spring occurred during WY 1993, and the smallest loads occurred in WY 1989.

Within the 366-acre upper Bugenhagen subbasin, corn acreage and total fertilizer use were smallest during WY 1987 and greatest during WY 1991. Like L22T, L23S, and Big Spring, the annual fw mean nitrate concentrations and nitrate-nitrogen loads from the tile lines in the upper sub-basin were smallest in WY 1989, and annual fw mean nitrate concentrations were greatest in WY 1991. The annual nitrate-nitrogen load from the tile draining the east side of the upper sub-basin was greatest in WY 1991, while the nitrate-nitrogen load from the tile draining the west side of the upper sub-basin was greatest in WY 1993.

The greatest annual fw mean atrazine concentrations for L22T and L23S occurred in WY 1989, and the greatest annual fw mean atrazine concentration for Big Spring occurred in WY 1991. The smallest annual fw mean atrazine concentration for L22T occurred during WYs 1993 and 1994, and the smallest fw mean for L23S occurred in WY 1987. The smallest annual fw mean atrazine concentration for Big Spring occurred in WY 1995. Atrazine was not used in the field above L22T during WYs 1991-1994 and annual fw mean atrazine concentrations declined during this period. At L23S and Big Spring, fw mean atrazine concentrations declined in WY 1992, increased in WY 1993, then declined again in WY 1994. Annual atrazine loads for all three sites were greatest during WY 1991, while the smallest atrazine loads for L22T and L23S occurred in WY 1987, and the smallest atrazine load for Big Spring occurred in WY 1988.

Within the upper Bugenhagen sub-basin, atrazine use was greatest in WY 1989 and smallest in WYs 1991 and 1994 when no atrazine was used. The greatest annual fw mean atrazine concentration for the east tile occurred in WY 1989 and the greatest fw mean atrazine concentration for the west tile occurred in WY 1990. The smallest atrazine mean for the east tile occurred in WYs 1994 and 1995 and the smallest mean for the west tile occurred in WYs 1988 and 1994. The smallest atrazine load for the east tile occurred in WY 1987 and the smallest atrazine load for the west tile occurred in WYs 1988 and 1994. Like L22T, L23S, and Big Spring, the greatest annual atrazine loads from the east and west tiles occurred in WY 1991, even though no atrazine was used in the upper subbasin during the water year.

The similarity of annual data from L22T, L23S, Big Spring, and the Bugenhagen tile lines show that climatic factors and resulting hydrologic conditions can overshadow annual changes in water quality brought about by changes in landuse and agrichemical application rates, even at small watershed scales. Large variations in recharge make it difficult to document relationships between landuse changes within the sub-basins and the water quality responses at the basin monitoring sites.

Analysis of annual groundwater and surfacewater data from sites L22T and L23S for WYs 1987-1995 supports observations from Big Spring indicating that annual fw mean NO₃.N concentrations and loads generally parallel discharge, and annual fw mean atrazine concentrations and loads do not. Relatively high concentrations and loads of atrazine have occurred during some years with low groundwater and surface-water discharge. The variable climatic and hydrologic conditions within the Big Spring basin during the monitoring period complicate the interpretation of changes in water quality brought about by landuse changes and illustrates the need for detailed, long-term monitoring of nonpoint-source contamination.

The similarity of annual data from watersheds of different scales, with different landuse practices, demonstrates that climatic factors can obscure the relationships between landuse changes and water quality responses at a variety of scales. The pronounced short-term changes in nitrate and atrazine concentrations are responses to significant recharge. The concentration changes at the larger watershed scales are not as great or immediate as changes at smaller scale monitoring sites, although they clearly occur. The nested monitoring network within the Big Spring basin allows tracking of water and chemical responses to recharge events as they are propagated through the hydrologic system from the soil profile beneath individual fields to the basin water outlets (Hallberg et al., 1984a). This allows the integration and comparison of various watershed scales to assess the effects of different landuse and landscape-ecosystem processes. Within 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. The nested monitoring network affords detailed observation of these watershed systems at a variety of scales. Responses to changes in management practices can be tracked at these various scales, and a detailed record of the chemical flux through the basin can be established. 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 waterquality changes in the short-term, but they will be

detectable over time. Policy makers and planners must be aware of the time lags involved at these larger watershed scales and make appropriate commitments to long-term support of monitoring and implementation projects. Ongoing analysis of monitoring data from streams, springs, tile lines and wells, over time, will provide a better understanding of water-quality improvements resulting from changes in agricultural practices.

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

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