2005

Changes in Groundwater Quality in a Conduit-Flow-Dominated Karst Aquifer as a Result of Best Management Practices

James C. Currens

University of Kentucky, currens@uky.edu

Right click to open a feedback form in a new tab to let us know how this document benefits you.

Follow this and additional works at: https://uknowledge.uky.edu/kgs_ri

Part of the Environmental Monitoring Commons, Hydrology Commons, and the Natural Resources Management and Policy Commons

CHANGES IN GROUNDWATER QUALITY
in a Conduit-Flow-Dominated Karst Aquifer
as a Result of
BEST MANAGEMENT PRACTICES

James C. Currens

Changes in Groundwater Quality in a Conduit-Flow-Dominated Karst Aquifer as a Result of Best Management Practices

James C. Currens

Technical Level

General	Intermediate	Technical

Cover photograph by James C. Currens. KGS staff member Steven Webb is beginning work to collect water samples and service the water-quality monitoring equipment during a high-flow event at Pleasant Grove Spring.

Contents

Contents
(continued)

Figures

Figures
(continued)

Figures
(continued)

Tables

Our Mission

Our mission is to increase knowledge and understanding of the mineral, energy, and water resources, geologic hazards, and geology of Kentucky for the benefit of the Commonwealth and Nation.

Earth Resources—Our Common Wealth

www.uky.edu/kgs

Changes in Groundwater Quality in a Conduit-Flow-Dominated Karst Aquifer as a Result of Best Management Practices

James C. Currens

Abstract

Water quality in the Pleasant Grove Spring karst groundwater basin was monitored to determine the effectiveness of best management practices (BMP's) implemented through the U.S. Department of Agriculture's Water Quality Incentive Program (WQIP). The project was divided into three phases. Phase I, beginning in August 1990, was the initial reconnaissance of the hydrogeology and water quality of the basin. Phase II, beginning in October 1993, monitored the water quality for 1 year prior to BMP implementation. This phase was followed by a 1-year interim extension, which continued the monitoring. Phase III monitored the water quality during and following BMP implementation. The findings of phases I and II, along with extensive descriptions of the hydrogeology and groundwater quality, were reported in Currens (1999). This report covers the specific findings of the interim extension and phase III (October 1994–October 1998). It also summarizes the overall findings of the project and evaluates the outcome of the BMP's, which began in 1995.

Pleasant Grove Spring discharges runoff from a 4,069-hectare (10,054-acre) karst groundwater basin in southern Logan County, southwestern Kentucky. The basin is characterized by mature karst topography developed on Mississippian carbonates mantled with residuum. Sinkholes and sinking streams dominate the landscape, and perennial surface-flowing streams occur only in the headwaters of the basin. Most of the area of the basin (about 90 percent) is used for agriculture. The principal crop grown is corn in rotation with winter wheat and soybeans. Other row crops include tobacco and other small grains. Livestock are dairy and beef cattle and swine. Over 68 percent of the area of the watershed was enrolled in the WQIP.

Analysis of samples collected since October 1994 at seven locations in the basin indicated the principal contaminants of probable agricultural origin were herbicides, nitrate-nitrogen, suspended sediment, orthophosphate, and bacteria (as was the case during the first two phases of the project). The maximum nitrate-nitrogen concentration measured in the basin between 1994 and 1998 was 13.1 mg/L, at Leslie Page karst window, and the average concentration was 5.05 mg/L. The maximum orthophosphate concentration was 1.4 mg/L, at Pleasant Grove Spring, and the median was 0.17 mg/L. The total suspended solids maximum was 3,267 mg/L, and the median concentration was 53 mg/L. The maximum triazine concentration measured by enzyme-linked immunosorbent assay (ELISA) was 393.0 μg/L, at Leslie Page karst window; median concentration was 1.15 μg/L. Maximum bacteria counts were 200,000 fecal coliform colony-forming units per 100 mL (col/100 mL) and 810,000 fecal streptococci col/100 mL; medians were 400 col/100 mL and 640 col/100 mL, respectively.

Water quality at Pleasant Grove Spring was monitored from May 1992 through the end of the project in October 1998. The maximum nitrate-nitrogen concentration measured at the spring was 8.11 mg/L, and the concentration never exceeded the maximum contaminant level (MCL) of 10 mg/L; average concentration was 4.8 mg/L. The maximum orthophosphate concentration was 1.4 mg/L and the median was 0.53 mg/L. The total suspended solids maximum was 3,073 mg/L, and median was 55 mg/L. The maximum triazine concentration (ELISA) was 62.2 μg/L. Triazine concentrations briefly exceed MCL's during the spring each year. Peak concentrations of the other three frequently analyzed pesticides (alachlor, metolachlor, and carbofuran) were 12.0, 29.6, and 7.4 μg/L, respectively—the highest measured in the basin. Median concentrations of these pesti-

cides, however, are near detection limits. Fecal coliform and fecal streptococci bacteria are always present at Pleasant Grove Spring, and counts occasionally exceed drinking-water supply limits (2,000 col/100 mL). Maximum bacteria counts were 60,000 col/100 mL of fecal coliform and 200,000 col/100 mL of fecal streptococci.

The quality of groundwater discharging at Pleasant Grove Spring before and after BMP implementation was evaluated by comparing the annual mass flux of nitrate-nitrogen, total suspended solids, and triazines (atrazine-equivalent). Annual descriptive statistics were compared for orthophosphate and bacteria, as well as for the other contaminants. The flux and annual statistics of nitrate-nitrogen were little changed over the course of the BMP program. Atrazine-equivalent flux and triazine geometric averages indicated an increase. Total suspended solids concentrations decreased slightly, whereas orthophosphate increased slightly. Fecal streptococci counts improved, but the improvement was not statistically significant.

The comparison of the pre- and post-BMP monitoring indicates that the WQIP was only partly successful. Although the program was fully implemented, the types of BMP's funded and the rules for BMP participation resulted in less-effective BMP's being chosen by producers. Future BMP programs for the protection of groundwater in karst aquifers should limit BMP's to the installation of buffer strips around sinkholes, the exclusion of livestock from streams, and the removal of certain land from agricultural production.

Introduction

Karst aquifers in Kentucky provide groundwater to countless wells and springs used by individual households. Large springs are the source for a number of public water-supply systems. Furthermore, the flow of streams in karst areas is maintained during dry months by discharge from karst springs, and many Kentucky cities obtain their water from spring-fed streams and rivers. Because replacing these water sources would be impractical, if not impossible, protecting the quality of groundwater in karst aquifers is vital for human health and economic development of Kentucky.

Karst terrane forms on limestone or other soluble rock, and is characterized by sinkholes, sinking streams, caves, and springs. The water-bearing zones of karst aquifers are the solution-enlarged joints, bedding planes, conduits, and caves in the otherwise relatively impermeable bedrock. Recharge into the aquifer is both from seepage through the soil overlying the bedrock and from direct run-in from the land surface through sinkholes and sinking streams (with no filtration). Because recharge to karst aquifers is rapid and largely unfiltered, groundwater can be easily contaminated. When a karst terrane is subjected to intensive land use, the potential for groundwater contamination from any human activities that produce waterborne pollution, including agriculture, is significant.

Reducing the potential for nonpoint-source pollution of karst aquifers from agriculture is important be-

cause some of the most productive agricultural lands in Kentucky are in the karst regions of the state. The farms located in the 35 counties that are predominantly of karst terrane produce over 50 percent of the annual agricultural receipts in Kentucky (Kentucky Agricultural Statistics Service, 1998). Logan County is one of these counties, and typically is among the top 10 agriculture-producing counties in the state. The karst landscape in the southern half of Logan County is mostly gently rolling with thick, fertile soils. Large crops of corn, wheat, soybean, and tobacco are grown, and significant numbers of cattle and swine are raised.

Purpose

The U.S. Department of Agriculture (USDA) has long recognized the need to conserve natural resources (Bennett and Chapline, 1928), and has developed, along with other farming-related institutions, best management practices (BMP's) intended to minimize soil loss and protect water quality. The purpose of this project was to test whether a financial incentive program intended to encourage farmers to use BMP's designed to protect groundwater would reduce nonpoint-source pollution of groundwater in a karst aquifer. The financial incentive was administered through the Water Quality Incentive Program (WQIP), which was in effect during the mid-1990's. The WQIP paid farmers to adopt BMP's that had been shown, at field and farm scales, to protect water quality.

This project was divided into three phases. During phase I (August 1990–October 1993), reconnaissance and mapping of the karst groundwater basin was conducted. Phase II (October 1993–October 1994) continued reconnaissance field work and began the first full year of pre-BMP water-quality monitoring. The results of phases I and II, field reconnaissance and early water-quality monitoring through October 1994, are reported in Currens (1999); this publication also contains extensive descriptions of the methodologies used and the basin hydrogeology. An interim phase (October 1994–October 1995) followed phase II because of a delay in funding of phase III. This report covers specific results from the interim phase and field work and water-quality monitoring results during the post-BMP period of phase III from October 1995 through October 1998. It summarizes the overall findings of the entire project from its initial inception in August 1990 through its conclusion in October 1998.

Study Area Description
Geographic Location

The Pleasant Grove Spring karst groundwater basin is located in the Pennyroyal Plateau physiographic region in Logan County, southwestern Kentucky (Fig. 1). The spring is 14.5 km (9 mi) south of the county seat, Russellville. The study area includes parts of the Russellville, Dennis, Dot, and Adairville 7.5-minute quadrangles. As determined by groundwater dye tracing, the total surface catchment area of the groundwater basin is 4,069 hectares (10,054 acres).

The groundwater basin is roughly bounded on the east by U.S. 431 (Plate 1). Ky. 96 traverses the basin from north to south along the western third of the basin. Mortimer Road connects from Ky. 96 east to U.S. 431 and approximates the southern boundary of the basin. Pleasant Grove Spring discharges to Pleasant Grove Creek, which flows 2.4 km (1.5 mi) to its confluence with the Red River, a major tributary of the Cumberland River. For this study, the previously unnamed surface-flowing reaches upstream from major swallow holes (immediately north of Campground Road) to the northwest corner of the basin are collectively called upper Pleasant Grove Creek.

Geology and Hydrogeology

The drainage basin of Pleasant Grove Spring lies entirely within the Pennyroyal Plateau, which is developed on thick, pure carbonates of Late Mississippian age. The geology of the area was mapped by Rainey (1965), Shawe (1966a, b), and Miller (1968). Only two mappable units, the St. Louis Limestone and the overlying Ste. Genevieve Limestone, crop out at the surface in the basin. The strata dip gently to the northwest at 11 m/km (60 ft/mi) into the Illinois structural basin. The headwaters area of the groundwater basin is underlain by the Ste. Genevieve Limestone, and the downstream areas are underlain by the St. Louis Limestone. A prominent horizon of bedded chert at the top of the St. Louis Limestone has a significant influence on karst development and thus the hydrogeology. This unit is probably the stratigraphic equivalent of the Lost River Chert (Garland R. Dever Jr., Kentucky Geological Survey, oral communication, 1994). Pleasant Grove Spring discharges from the St. Louis Limestone. Previous hydrogeologic investigations in the area are by Brown and Lambert (1962), Van Couvering (1962), and Currens (1999).

The groundwater basin is a shallow, unconfined carbonate aquifer (Currens, 1999) and can be divided into two areas with differing flow regimes, based on groundwater flow velocities. Although two groundwater flow regimes are recognized, both are karstic, and flow is turbulent through a tributary network of conduits and caves. The northern, headwaters half of the basin is characterized by a slow-flow regime (diffuse karst flow of Shuster and White [1971]), whereas the southern, downstream half is predominantly a fast-flow regime (conduit flow) (Plate 1). The gradient of the potentiometric surface in the headwaters area is uniformly gentle, and flow velocities are relatively slow (0.002 m/s [0.005 ft/s]), probably because conduit development is locally restricted by a bedded chert unit (Currens, 1999). The depth to groundwater is shallow in the headwaters area of the basin and indicates significant groundwater is stored in joints and bedding planes in this area. Throughout the basin an unquantified, but probably significant, volume of water is stored in the epikarst, consisting of the near-surface weathered bedrock and overlying soil. In the downstream area of the basin, quantitative groundwater dye traces (discussed later) show that flow in the conduits is fast and may exceed 0.10 m/s (0.39 ft/s) during high flow. Water flowing in upper Pleasant Grove Creek persists at the surface through most of the year, gradually ceasing headward as drought periods lengthen. Flow in the southern end of the basin is underground except during extreme high flow. The intake capacity of George Delaney swallow hole is exceeded during floods, and water flows south in a normally dry channel to Johnson swallow hole. Under exceptional flood conditions, discharge also exceeds the intake capacity of Johnson swallow hole and flows overland to a confluence with Pleasant Grove Creek, downstream of Pleasant Grove Spring, and out of the groundwater basin. Thus, Pleasant Grove Spring is an alluviated, underflow spring (Worthington, 1991) discharging from a totally submerged cave.
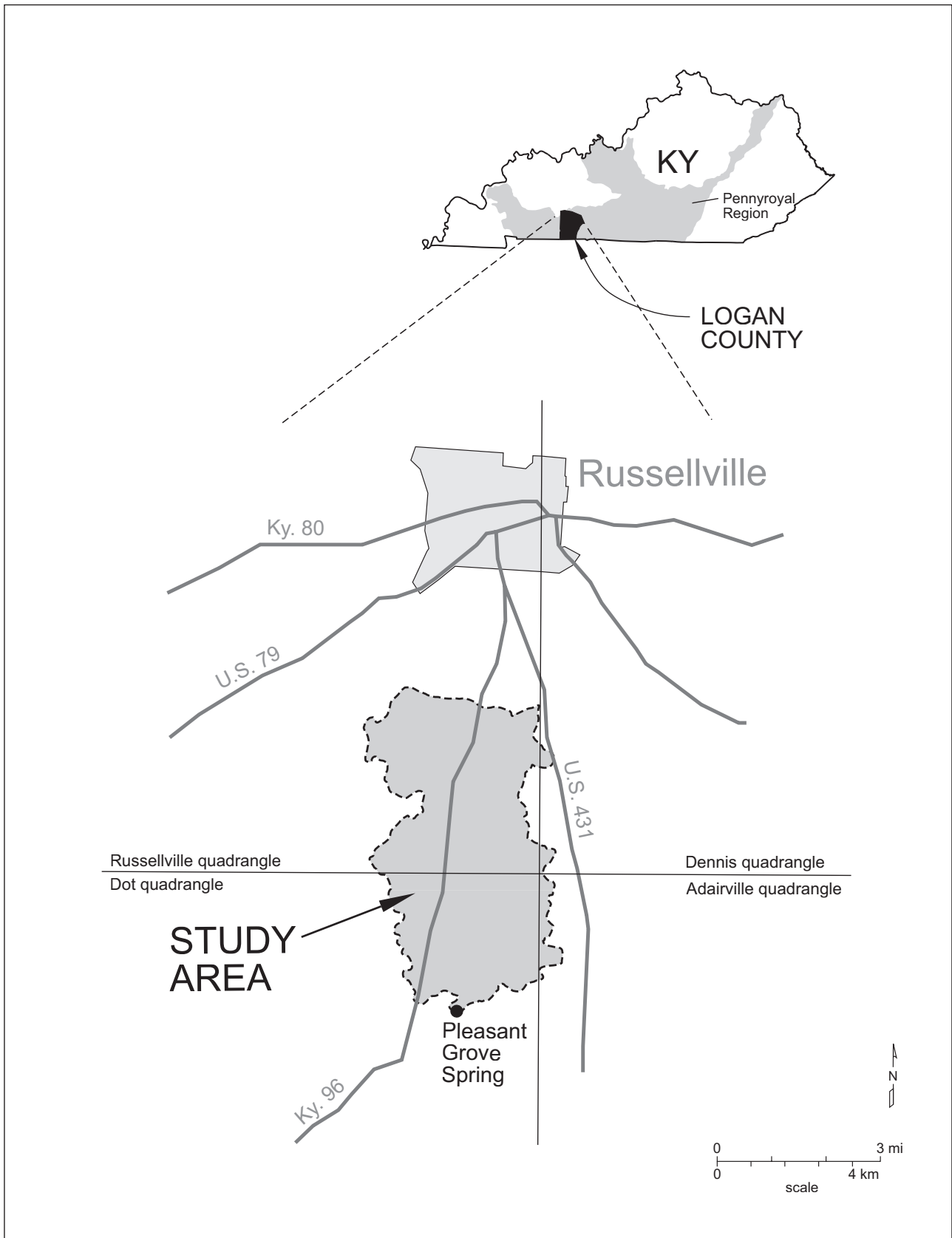
Figure 1. Location of the Pleasant Grove Spring karst groundwater basin.

Soils

The soils in the basin are silt loams derived from loess and limestone residuum, which are classified in the Pembroke-Crider association (Dye and others, 1975). The Pembroke and Crider occur on nearly level ridgetops to gentle slopes. Both soils are described as having a high natural fertility. The soils are moderately permeable, well drained, and have deep root zones with loamy or clayey subsoils. The soils are deep to very deep and have a thickness as great as 2 m (76 in.) to the base of the subsoil. Six auger holes drilled by KGS in the vicinity of Leslie Page karst window, in the central part of the watershed, ranged in depth from 1.5 to 5.8 m (5 to 19 ft), but none encountered bedrock.

Land Use

The Pleasant Grove Spring watershed was chosen as the study area in May of 1989 because of the presence of several karst features that would facilitate access to groundwater and the general absence of nonagricultural land use. The only nonagricultural business in the watershed is a tractor and automobile repair garage. There is no urban development in the basin. The largest residential community is Oakville in the northeastern quadrant of the study area, which consists of about 30 scattered houses and mobile homes. Other residential development is limited to farmsteads. Only one State highway, which has only infrequent industrial traffic, and no rail lines cross the basin. There is no history of significant petroleum production or other mineral resource extraction in the basin.

Approximately 70 percent of the basin area is row crop, largely in the northern two-thirds of the study area (Currens, 1999). Another 20 percent is hay fields and pasture. The predominant agricultural production system is no-till corn on a 2-year rotation with winter wheat and soybeans. Large fields of wheat, oats, rye, soybean, alfalfa, corn, milo, hay, and tobacco are grown. Livestock production in the basin is mostly beef and dairy cattle, with some swine. Almost all of the row crops are cultivated using conservation tillage, although some conventional tillage was still practiced at the beginning of the project.

Previous Research

The literature on the occurrence of pesticides, nitrate, and other agriculturally derived contaminants in groundwater in general, as well as karst-specific studies, through the early 1990's was reviewed at length by Currens (1999).

Movement of pesticides deep into the soil, and by inference eventually into groundwater, has been documented for decades (Lichtenstein, 1958; Johnston and others, 1967; Dao and others, 1979; Smith and others, 1988; Wartenberg, 1988; Honeycutt and Schabacker, 1994). The detection of pesticides in groundwater became more common and a matter of public concern in the 1980's (Garner and others, 1986; Ritter, 1986; U.S. Environmental Protection Agency, 1986; Gish and others, 1990). Pesticides had been found in groundwater in 40 states by 1988, although mostly in concentrations below health limits (Williams and others, 1988).

The presence of pesticides and other agriculturally derived nonpoint-source pollutants in the groundwater of karst aquifers also began to be studied in the 1980's. The most widely cited study was conducted in Iowa; it investigated the water quality of the Big Spring karst groundwater basin in the Galena aquifer (Hallberg and others, 1983, 1984; Libra and others, 1984, 1986; Libra, 1987). The Galena aquifer is overlain by Pleistocene glacial outwash and till (Hallberg and others, 1983) and therefore has a significant diffuse-flow component characterized by few direct inflows and long residence time. Nitrate-nitrogen concentrations were typically under 45 mg/L but occasionally exceeded 70 mg/L. Concentrations of atrazine seldom exceeded 0.85 µg/L, but peaked at 5.1 µg/L during one spring storm. Investigation through the 1996–97 water year (Rowden and others, 1999) has shown that nitrate concentrations generally decrease and triazine concentrations generally increase with discharge. Furthermore, they reported that correlating nitrate and triazine flow-weighted averages with changes in chemical uses or weather conditions has proved difficult.

Hippe and others (1994) studied two karst springs in Pennsylvania and found only low concentrations of herbicides and nitrate, no springtime pesticide pulse, and little difference in atrazine or nitrate between springs overlain by agricultural and residential land uses. They collected single grab samples during a few storms.

More recent work has been completed in southeastern West Virginia by Boyer and Pasquarell (1994, 1996) and Pasquarell and Boyer (1995, 1996). They found a strong positive linear relationship between nitrate concentrations and percentage of the groundwater basin area used for agriculture. Furthermore, the occurrence of atrazine coincided with spring application season, and the counts of fecal coliform bacteria found in springs increased with percentage of land in agricultural production. Boyer and Pasquarell (1994) found average fecal coliform counts of less than 1 colony-forming unit per 100 mL (col/100 mL) in a spring draining a pristine karst basin.

Panno and others (1998) monitored the Fogelpole Cave groundwater basin in southwestern Illinois, an area principally used for agriculture. They found that

triazines and sediment increased in response to spring storms during the application period and that nitrate-nitrogen becomes elevated in the winter and peaks during the spring. High bacteria counts occur during high-flow events, but are attributed to human waste.

Two significant studies in Kentucky have monitored karst springs for agricultural nonpoint-source pollution. Felton (1991) monitored Garretts Spring in east-central Woodford County, which drains the Sinking Creek Basin of Woodford and Jessamine Counties of the Inner Bluegrass Region. He found that nitrate concentrations varied seasonally and were highest during wet winter months, but pesticide concentrations were low throughout the year. Agriculture conducted in the basin is primarily livestock (thoroughbred horses), with relatively few acres in row crops, and suburban development is the next major land use. Ryan and Meiman (1996) identified discrete periods of high-flow events when waters containing higher suspended sediment and bacteria counts (1,400 col/100 mL) arrived from agricultural lands bordering Mammoth Cave National Park. Groundwater dye traces from the suspected source areas were conducted simultaneously with the storm to identify the source of the sediment and bacteria. In contrast, samples collected at Buffalo Creek Spring, also within the park and draining a forested and pristine karst basin, had a low average fecal coliform bacteria count of 85 col/100 mL (Joe Meiman, National Park Service, oral communication, 1994).

In an earlier report on the Pleasant Grove Spring project, for the period from August 1990 through October 1994, Currens (1999) stated that significant contaminants in the basin are herbicides (specifically, atrazine), bacteria, and sediment. Nitrate-nitrogen was the most widespread, persistent contaminant in the basin. Concentrations averaged 52 mg/L basinwide and generally did not exceed U.S. EPA maximum contaminant levels (MCL's), but were above concentrations expected in an unpopulated setting. Atrazine was consistently detected in low concentrations, and other pesticides were occasionally detected. Concentrations of triazines (including atrazine) and alachlor exceeded drinking-water MCL's during springtime flooding. Maximum concentrations of triazines, carbofuran, metolachlor, and alachlor in samples from Pleasant Grove Spring were 44.0, 7.4, 9.6, and 6.1 µg/L, respectively. Bacteria counts always exceeded standards for drinking water, and occasionally exceeded standards for drinking-water sources. Basinwide, samples averaged 465 col/100 mL of fecal coliform and 1,891 col/100 mL of fecal streptococci; maximum counts were 14,000 and 24,000 col/100 mL, respectively. A biological assessment showed an adverse impact on aquatic biota downstream, probably caused by sedi-

mentation. Several sites upgradient of Pleasant Grove Spring were also sampled, with similar results.

Currens (1999) estimated the mass flux of an atrazine-equivalent triazine (atrazine and other related chemicals) and nitrate for water years 1992–93 and 1993–94. The flow-weighted concentration of nitrate remained nearly constant at between 5.0 and 5.7 mg/L while the total annual flux increased from 51 metric tons (56 tons) to 184 metric tons (202 tons), probably because of dry conditions in 1992–93. The atrazine-equivalent flow-weighted concentration decreased from 4.91 µg/L to 0.97 µg/L (total annual flux of 50 kg down to 31 kg). The sediment flux was not estimated in the 1999 report because of poor turbidity records for the early period of monitoring. Minor revisions of all flux values reported in 1999 have been made in this report to reflect improved stage-discharge rating curves.

In 1990 the University of Kentucky College of Agriculture was charged and funded by the Kentucky legislature to assess the impact of agricultural practices in Kentucky on water quality (Kentucky Senate Bill SB-271). As part of this work, a site in Logan County was sampled concurrently with this project from the fall of 1990 through October 1993 (Haszler, 1994?). The sample location is not described or named in the report, but rather identified as Spring-711. I have firsthand knowledge, however, that the location is The Canyon karst window in the Pleasant Grove Spring groundwater basin. Samples were collected monthly from September 1990 through August 1993. The College of Agriculture determined physical parameters and analyzed samples for nitrate-nitrogen, triazines and alachlor (by ELISA), and fecal coliform, fecal streptococci, and salmonella bacteria.

The College of Agriculture report does not summarize the data from Spring-711 or draw conclusions about this specific site. Haszler (1994?) found, however, that nitrate-nitrogen varied little, from 3 to 5 mg/L. Pesticides peaked during the spring, when the maximum concentration detected was 15 µg/L of triazines. Bacteria counts varied from zero to several thousand colonies per 100 mL. These data are not used in this evaluation of the effectiveness of the best management practices because of differences in sampling protocol, analytical methods, and quality assurance/quality control practices.

A summary of the statewide findings of the College of Agriculture is reported in Taraba and others (1995) and concludes that statewide there was little correlation between agricultural activity and the occurrence of nitrate, herbicides, and bacteria in groundwater for various groundwater flow regimes. The flow regime they called "shallow, rapid circulation groundwater zone," also called karst, was the exception; it positively correlated with agricultural activity. Nitrate-nitrogen

concentrations above natural levels were found to be positively associated with the percentage of land in row crop and domestic animal activity and tobacco stalk disposal. Herbicide occurrence was noted to be seasonal and positively associated with the percentage of land in row crop. They also noted that only a small percentage of samples contained concentrations of triazines that exceeded the MCL for atrazine. High bacteria populations were associated with the presence of domestic animals.

Methodology
Project Design

The approach used to judge the effectiveness of best management practices was to characterize the quality of water discharged from Pleasant Grove Spring before and after BMP implementation. Specifically, the mass flux of waterborne constituents discharged was estimated, and the totals for each water year compared. The implementation of BMP's was initially planned to be through established USDA programs and by USDA staff, but with emphasis on the Pleasant Grove Spring Basin. Coincidentally, a major grant was awarded by the USDA through the Water Quality Incentive Program to the Logan County office of the Natural Resources Conservation Service to implement BMP's in the drainage basin of Pleasant Grove Spring. Included in WQIP, but not the KGS monitoring program, were an annual detailed inventory of crop acreage, a livestock census, and one-on-one attempts to influence farmers to participate in any BMP program. As a condition of receiving WQIP money, farmers were required to report chemical usage to the NRCS for 1996, 1997, and 1998.

Monitoring Strategy

The strategy was to focus intensive monitoring on the most important contaminants at the principal discharge point (Pleasant Grove Spring) while conducting less-intensive monitoring at upgradient sites. Four principal contaminants of likely agricultural origin were identified during reconnaissance of the basin: atrazine, nitrate, suspended sediment, and bacteria from animal waste. In addition, orthophosphate was later identified as a pollutant. Arithmetic averages, geometric averages, medians, and total flux were calculated for each year of monitoring at Pleasant Grove Spring for triazines, nitrate, and suspended solids. Arithmetic averages, geometric averages, and medians were calculated for bacteria and orthophosphate. The population of pre-BMP annual values was then compared to post-BMP values using various statistical tests.

In addition to Pleasant Grove Spring (Plate 1), several upstream sites were monitored to identify the general source area of any pollutants found at Pleasant Grove Spring. Water-level gaging stations were placed at four locations: two on upper Pleasant Grove Creek, at George Delaney swallow hole and at the box culvert where Johnson-Young Road crosses the creek, and two more at Spring Valley karst window and Leslie Page karst window. The water-level recorders at Leslie Page karst window and the station at upper Pleasant Grove Creek were installed in April and June of 1993. During the reconnaissance period, samples were also collected at Shackelford Spring, Thad Flowers blue hole, The Canyon karst window, and Joe Harper water well (an estavelle lined with masonry and formerly used as a hand-dug water well). Monitoring at Spring Valley karst window, Shackelford Spring, and Thad Flowers blue hole was discontinued for logistical, budgetary, and hydrologic reasons in October 1994. The water-level recorder at Spring Valley karst window was decommissioned in October 1997. For a complete description of the Spring Valley karst window, Shackelford Spring, and Thad Flowers blue hole sites, and for analytical data from these sites, see Currens (1999). An additional site, Miller School House well, was added in 1994. This abandoned, drilled domestic well is just inside the eastern mapped drainage boundary of Pleasant Grove Spring, near the community of Oakville. It was used as a control since the well is upgradient of most agricultural activity.

Constituents Analyzed

The constituents determined for a sample were contingent upon the data needs at each site under various flow conditions. Three constituent lists were grouped into the following analysis suites. The comprehensive suite included determinations of major and minor ions, orthophosphate, chloride, sulfate, bicarbonate, nitrate, pesticides by gas chromatograph (GC), four pesticides (triazines, metolachlor, alachlor, and carbofuran) by enzyme-linked immunosorbent assay (ELISA), and total and dissolved solids. Ammonia, nitrite, and organic nitrogen were deleted from the comprehensive suite at the end of the 1990–91 water year because the concentrations of these constituents measured in reconnaissance samples were very low. Because the groundwater in the basin is generally well oxygenated (Pleasant Grove Spring is typically over 70 percent oxygen saturated), reduced ionic species are normally very low in concentration. Additional opportunistic samples for GC analysis of pesticides were collected as conditions warranted. The second constituent suite, event samples, was analyzed for total suspended solids, total dissolved solids, nitrate, and four pesticides (by

ELISA). These samples were collected at Pleasant Grove Spring by ISCO 3700[1] automatic samplers. Samples were also collected at Leslie Page karst window by automatic sampler, but total dissolved solids content was omitted from the constituent suite. The third suite, the base-flow constituent suite, included nitrate and the four pesticides (by ELISA). It was used for dipped samples, most commonly collected during base flow and for quality-control samples.

Analytical Methods

The laboratory and field methods used in this study are described in detail in Currens (1999). All major-ion and pesticide analyses were performed at the Kentucky Geological Survey's water-quality laboratory. Cations were determined on an inductively coupled plasma spectrometer, and anions were determined on an ion chromatograph. Total alkalinity was determined in the laboratory with an autotitrator for comprehensive samples and was also determined monthly in the field with a Hach digital titrator field kit. Pesticide analyses were made on a gas chromatograph using EPA methods 507 and 508 or by enzyme-linked immunosorbent assay. The Ogden Environmental Laboratory at Western Kentucky University in Bowling Green determined bacteria counts by multiple-tube fermentation and most-probable-number statistical estimation until May 1992, when the laboratory changed to membrane filter techniques (EPA methods 9222D and 9230B). Nitrogen isotopes ($^{15}N/^{14}N$) were analyzed by Global Geochemistry Corporation, Canoga Park, Calif., on a gas chromatograph mass spectrometer.

Quantification of ELISA

Analysis of pesticides by enzyme-linked immunosorbent assay was chosen because the number of analyses needed for mass-flux estimation by gas chromatograph was cost-prohibitive and logistically impractical. The validity of quantifying pesticide concentrations with ELISA was evaluated by analyzing split samples by GC and ELISA for triazines, alachlor, and metolachlor, but a GC method was not available for carbofuran. The ELISA method for triazines detects atrazine, cyanazine, simazine, and their degradation products, but is most sensitive to atrazine. The ELISA triazines versus GC atrazine correlation had an r^2 of 0.95, and ELISA versus GC metolachlor had an r^2 of 0.80; both were at the 95 percent confidence level. Alachlor determined by ELISA had a poor correlation coefficient

with alachlor determined by GC. This evaluation and a complete discussion of the ELISA methods may be found in Currens (1999).

Sampling Protocol

Water samples were collected using field protocols and quality-control practices of the U.S. Geological Survey (1982) and the U.S. Environmental Protection Agency (1983). Samples collected by dipping were with the mouth of the bottle facing upstream (ASTM D3370), and all containers were new and prewashed or sterilized. Intermediate containers were not used for samples collected manually. All other sampling equipment was cleaned in compliance with EPA method 507 (revision 2.0, paragraph 4.1.1) (U.S. EPA, 1989). The equipment was washed with tap water and laboratory detergent, rinsed with tap water, rinsed three times with distilled water, and final-rinsed with reagent-grade acetone instead of oven drying. Samples from Miller School House well were collected with a bailer decontaminated as described above. Samples from other wells were collected at the nearest tap to the well. Samples for bacteria counts were collected only by dipping. The samples for dissolved constituents (major and minor ions, a limited number of pesticide samples) were collected with a peristaltic pump directly from the rise pool of the spring. Water was pumped through a stainless steel and Teflon filter stand equipped with 0.45 μm cellulose acetate filters and Teflon tubing. The stand and tubing were assembled and sealed immediately after cleaning for transport to the field. Samples for nitrogen isotope ($^{15}N/^{14}N$) analysis were collected by dipping the cubitainers. The samples were preserved with metallic silver, and shipped in ice chests within 24 hours via overnight express for analysis by Global Geochemistry Corp., Canoga Park, Calif. Conductivity, pH, and temperature were measured in the field for samples collected at the beginning of the month and biweekly (every other week). See Appendix B of Currens (1999) for a detailed listing of sample containers, preservation methods, and holding times.

High-flow event samples were collected directly from the rise pool of the spring or stream channel by an ISCO 3700 or 2900 automatic sampler. The automatic sampler intake hoses and its sample containers were decontaminated before each field deployment according to EPA method 507. The intake tubing and screen were assembled and sealed for transport immediately after cleaning. An equipment blank was collected when each automatic sampler was installed; then the intake hose was purged with water from the sample site and the hose was left empty. A water-presence sensor activated the sampling machines. When activated, the sampler

---

[1]The use of manufacture and trademark names does not constitute an endorsement of the product by KGS or the University of Kentucky; they are included for reference only.

was programmed to fill and purge the intake lines three times before filling the sample container.

Duplicate samples for suspended sediment analysis were collected using an integrated depth sampler and methods recommended by the U.S. Geological Survey (Guy and Norman, 1970) at Pleasant Grove Spring. The standard-method duplicates were collected during high-flow events and synchronously with samples collected by automatic sampler and turbidity observations.

Rain samples were collected for pesticide and nitrate analysis with a ring stand supporting glass funnels deployed away from trees and buildings. An 8-in.-diameter glass funnel emptied into a 4-in.-diameter funnel covered with a stainless-steel screen. The spout of the smaller funnel fit tightly into the mouth of a sample bottle. All rain-collection equipment was decontaminated before each deployment using EPA method 507.

Sampling Schedule

A strict interval was not used for sample collection because of logistical and budgetary constraints. Previous studies of karst springs, however, have shown that the concentration of waterborne constituents changes rapidly during high-flow events (Ashton, 1966; Meiman, 1985; Quinlan and Alexander, 1987; White, 1988; Ford and Williams, 1989). Accordingly, sample collection was planned to be frequent at Pleasant Grove Spring during storms, in order to precisely represent the rapidly changing conditions during high flow, and less frequent during base flow. Apart from high-flow events, the sampling frequency at Pleasant Grove Spring was monthly through the reconnaissance phase

(spring of 1992) and approximately biweekly thereafter (Table 1). The base-flow analysis suite was determined on the biweekly samples through the spring of 1995. Comprehensive-analysis samples were collected quarterly at Pleasant Grove Spring. For high-flow events, an attempt was made to collect a suite of samples by automatic sampler for every storm causing a rise in stage of 3 cm (0.1 ft) or greater at Pleasant Grove Spring from mid-March to July. Because some high-flow events were missed, beginning in early 1995 a second automatic sampler was deployed during the spring. This machine collected samples daily as a supplement to the high-flow samples. If no storm occurred, every other day a sample was submitted for analysis. If the high-flow sampler failed to collect one or more samples during an event, the missed samples were replaced with the next available sample from the set collected daily. Also, beginning in 1995, all samples analyzed for total suspended solids were collected through the automatic samplers. Between funded phases (September 1994–March 1995), sampling frequency was reduced to minimize cost. For further discussion of the sampling schedule, see Currens (1997).

Leslie Page karst window was sampled monthly in the summer, fall, and winter using the base-flow analysis suite and every other week during the spring through 1995 and at least every other week year-round thereafter. During the spring, an ISCO model 2900 automatic sampler was deployed. Stage response at Leslie Page karst window was frequently so minor that water failed to reach the actuator of the automatic sampler, and some storms were not sampled. The automatic sampler was reprogrammed to collect samples every 24 hours

Table 1. Summary of sample collecting frequency at the monitoring sites in the Pleasant Grove Spring groundwater basin.

Site	Topical	Quarterly	Monthly	Biweekly	Daily	Every Other Day	Quasi-Hourly*
Pleasant Grove Spring	B, Bact., NI	C		B, Bact.	E	E	E
Leslie Page karst window	NI	C		B, Bact.	B	E	E
George Delaney swallow hole	E		B, Bact.	B			
Upper Pleasant Grove Creek	B						
The Canyon karst window			B, Bact.	B			
Joe Harper water well	B						
Miller School House well	B, C, Bact.						
Rainwater samples	B/GC						

*	Varies from 20-minute to 4-hour intervals
C	Comprehensive constituent list
E	High-flow event constituent list
B	Base-flow constituent list
B/GC	Base-flow constituent list and pesticides determined by GC
NI	Nitrogen isotopes
Bact.	Fecal coliform and fecal streptococci

during the spring of 1995. The collection frequency of the sampler was increased to every 12 hours in March of 1996; this schedule was maintained through the end of the project. Unless a storm had occurred, samples were submitted every other day during the planting season. If a high-flow event had occurred, every sample collected during the event was submitted for analysis.

The Canyon karst window and George Delaney swallow hole were sampled manually monthly to biweekly using the base-flow suite. Flow in upper Pleasant Grove Creek would commonly cease at George Delaney swallow hole in midsummer or early fall; when this occurred, samples were collected at the upper Pleasant Grove Creek station. When The Canyon karst window was flooded, and flowing water was inaccessible, a sample was collected at Joe Harper water well. Sampling at The Canyon karst window began early in 1992, then was suspended until the spring of 1995; it resumed and continued without interruption through October 1998. The upper Pleasant Grove Creek station is upstream of George Delaney swallow hole on upper Pleasant Grove Creek. Dye tracing has demonstrated that Joe Harper water well is 300 m (1,000 ft) upstream of The Canyon karst window. Some special-case samples were also collected at George Delaney swallow hole by automatic sampler in the spring of 1997 and 1998.

Samples for bacteria count were collected monthly to biweekly at Pleasant Grove Spring and Leslie Page karst window, and monthly at The Canyon karst window (replaced by Joe Harper water well when The Canyon karst window was flooded) and George Delaney swallow hole (replaced by upper Pleasant Grove Creek station when dry). Sampling for bacteria was discontinued in June 1992, resumed in early 1994, and continued through October 1998. In addition, three attempts with varying degrees of success to manually collect sets of bacteria samples were made at Pleasant Grove Spring during high-flow events. Analyses of bacteria and orthophosphate were not performed on samples collected by automatic sampler because samples had to be left in the field for periods exceeding the holding time for orthophosphate, and the bacteria counts could be cross-contaminated by the adhesion of cells to the intake lines.

Topical samples were collected from Miller School House well and a few other domestic water wells; topical rainwater samples were also collected. Most of the samples were analyzed for the base-flow constituent list, but one comprehensive sample was collected. Samples for nitrogen isotope ($^{15}N/^{14}N$) analysis were collected at Pleasant Grove Spring and Leslie Page karst window in May and October of 1996 and January of 1997. Rainwater samples were collected during the planting season in 1995, 1996, and 1997, and were analyzed for

pesticides (by ELISA) and for nitrate. Duplicate samples for suspended sediment were collected during some high-flow events synchronously with samples collected by automatic sampler. A few duplicate samples for total and dissolved (unfiltered and filtered) pesticides were collected during the spring.

Monitoring Equipment

Installation of monitoring equipment at Pleasant Grove Spring was completed June 3, 1992. A Yellow Springs Instruments (YSI) model 3800 water-quality logger continuously recorded water temperature, pH, conductivity, dissolved oxygen, turbidity, and barometric pressure on 10-minute intervals. The YSI also recorded a point discharge velocity from a Marsh-McBirney 201-D water flow meter. A Telog water level recorder (model 2109) independently recorded the stage. The monitoring equipment at each of the upstream sites consisted of a staff gage and Telog model 2109e water-level recorder mounted in a stilling well constructed of PVC plastic with intake pipe and screen extending into the channel. All Telog data loggers were battery-powered. Stage determined by water-level recorder was checked monthly against a staff gage, and the water-level recorder was recalibrated when drift exceeded 3 cm (0.1 ft). The ISCO automatic water sampler, the Marsh-McBirney flow meter, and the YSI 3800 water-quality logger at Pleasant Grove Spring were supplied with line power, and the YSI and the Marsh-McBirney had battery backup. Samples for two high-flow events were missed in the spring of 1993 because power fluctuations caused by thunderstorms initiated sampling by the ISCO, which resulted in the bottles being full when a genuine event occurred later. A lightning strike from another storm on April 10, 1994, caused a loss of line power, which also resulted in lost samples. Beginning in April 1994, the ISCO automatic samplers were converted to battery power from April through October. Other battery-powered ISCO samplers were temporarily installed at George Delaney swallow hole and Leslie Page karst window as needed.

A simple weather station was installed at Pleasant Grove Spring. A Telog model 2107 pulse recorder recorded from a Rain Wise tipping bucket gage, and a Telog model 2103 ambient temperature recorder recorded the air temperature. A nonrecording rain gage was used as a check on the tipping bucket. Both loggers recorded at 10-minute intervals and were synchronized with the water-level recorders. The data-logger records were interrupted at various times during the project. The outages were mostly caused by pressure sensor failure, but were also caused by battery failure, electrical damage from lightning, damage from rain leaking into enclosures, and programming errors.

A second nonrecording rain gage was installed at the Leslie Page residence at the corner of Ky. 96 (Orndorff Mill Road) and Joe Harper Road. This location was near the center of the groundwater basin and approximately 3.7 km (12,000 ft) due north of Pleasant Grove Spring. Mr. Page read the rain gage each morning, and the records were retrieved periodically by KGS staff. The data were used to verify heavier precipitation in the upstream end of the basin caused by summer thunderstorms, and as a further check on the Pleasant Grove Spring rain gage.

Validity of Fecal Coliform/Fecal Streptococci Ratios

Geldreich and Kenner (1969) recommended using the count of fecal coliform colony-forming units divided by the count of fecal streptococci colony-forming units (FC/FS ratio) as an indicator of the source of fecal contamination. They suggested that a ratio less than 0.7 strongly indicates animal waste, whereas ratios over 4.0 indicate human waste. Ratios between 0.7 and 4.0 are ambiguous, but the greater the ratio, the more likely a human source.

The use of FC/FS ratios as an indicator of contamination origin is no longer recommended by the American Water Works Association (1992) because fecal streptococci die rapidly in treated water. Because fecal streptococci die in significant numbers within 24 hours of being excreted, skewed ratios occur in treated water, and false positives occur with some incubation techniques. The ratios are used in this study because groundwater flow rates in the basin are relatively fast, particularly during high flow, minimizing die-off of streptococci after they enter the water. Furthermore, all samples were of untreated water, which reduced the possibility of skewed ratios, and the Ogden lab used m-enterococcus agar, not the KF agar suspected of causing false positives (Rose Huellett, oral communication, 1995).

Quality Control/Quality Assurance

Conductivity and pH meters were checked for proper operation before each field trip. Meters were calibrated or compared with standards at the beginning of each sampling day. Permanently installed water-quality meters were calibrated monthly. The Marsh-McBirney flow meters are factory calibrated, and the calibration cannot be adjusted in the field. All monitoring equipment was cleaned and checked monthly to ensure proper operation. The turbidity probe was cleaned every field trip, at least every other week, beginning in May 1995.

Quality-control samples included equipment blanks, trip blanks, and field blanks (see Appendix A for more details). The KGS laboratory analyzed pesticides in replicate as part of its internal quality-assurance protocol. Duplicate samples for pesticide analysis (by ELISA) and nitrate were collected from Pleasant Grove Spring monthly beginning in 1994. Cross-plots of duplicate samples for nitrate, triazines, and metolachlor (by ELISA), with correlation coefficients, are shown in Figures 2 through 4. The correlation coefficients of these relationships are high (r^2=0.90 or higher) and are statistically significant at the 95 percent confidence level, which demonstrates acceptable reproducibility of sampling and laboratory technique. The number of duplicates for alachlor and carbofuran with concentrations above the minimum detection limits (four of 84 samples) was insufficient to allow calculation of meaningful correlations. In addition, nine duplicate samples were left in the sample tub of the automatic samplers for 14 to 16 days while the primary samples were submitted for analysis as soon as possible. The purpose of the delayed analysis of the duplicates was to determine any effect on nitrate-nitrogen and triazine concentration caused by leaving the ISCO-collected samples in the unrefrigerated machines. There was no significant difference between the concentrations measured in the delayed duplicates versus the initial samples (Fig. 5).

Field blanks and equipment blanks were also collected. All blanks used triple-distilled water as sample water and were commonly generated in the spring when
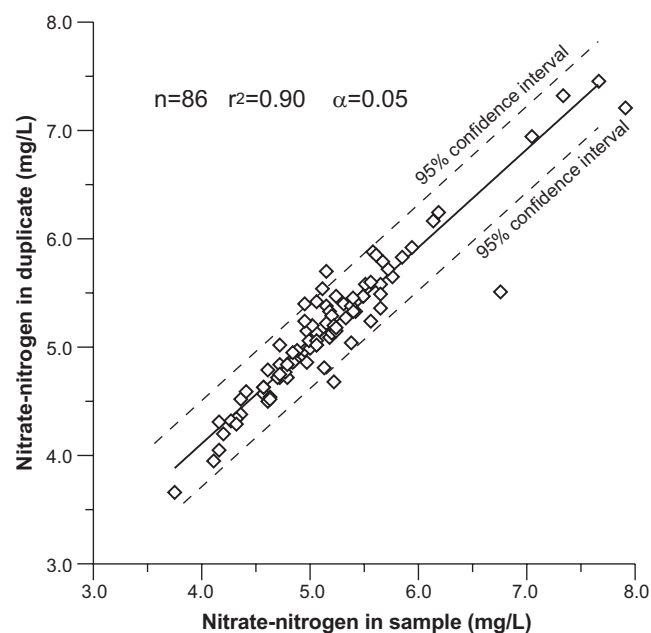
Figure 2. Cross-plot of nitrate-nitrogen determined for samples and duplicates collected at Pleasant Grove Spring between December 1993 and September 1998.
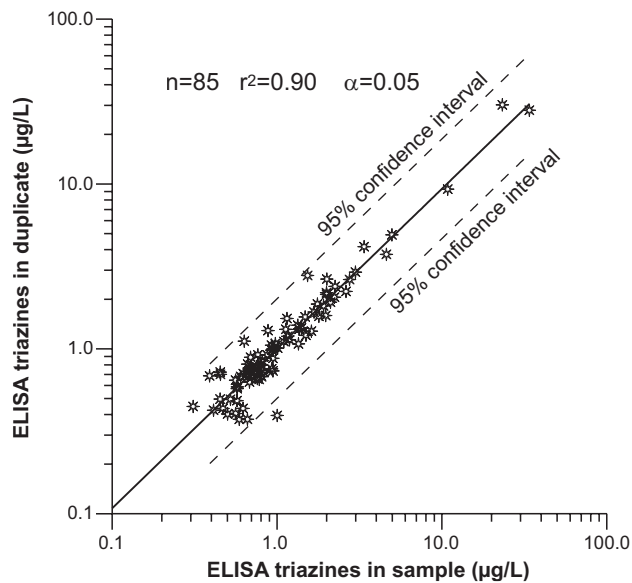
Figure 3. Cross-plot of triazines determined by ELISA for samples and duplicates collected at Pleasant Grove Spring between December 1993 and September 1998.
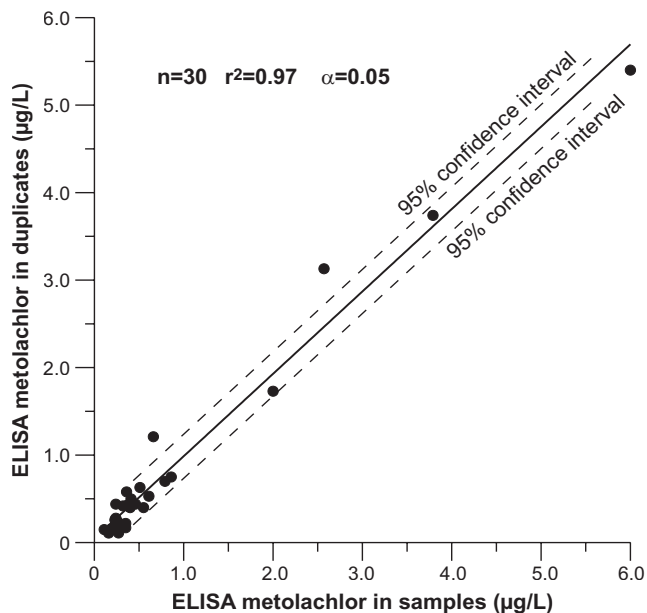
Figure 4. Metolachlor determined by ELISA for samples cross-plotted against duplicates collected at Pleasant Grove Spring between December 1993 and September 1998.

Figure 5. Cross-plot of triazines (ELISA) and nitrate-nitrogen determined for samples and duplicates collected at Pleasant Grove Spring, June 1996 through April 1997. Duplicate was held under field conditions for 14 to 16 days.

Of 30 blanks collected, one nitrate-nitrogen analysis of an equipment blank was as high as 1.13 mg/L and all others were 0.52 mg/L or less. The average nitrate-nitrogen concentration was 0.14 mg/L. Twenty-seven of 30 triazine concentrations were less than the detection limit, and the maximum concentration determined was 0.60 µg/L.

Groundwater Tracing

Extensive qualitative groundwater dye tracing was conducted during the early phases of the project to delineate the base boundary of Pleasant Grove Spring (Currens, 1999). One recent qualitative dye tracing conducted from the vicinity of Oakville verified the previously established groundwater basin boundary. An attempt was made to delineate the boundary of the sub-basin drained by the spring in Leslie Page karst window, but there were no natural features into which dye could be injected, so epikarstic dye injection points (EDIPS of Aley, 1997) were drilled. In this case, the injection points were holes drilled by a handheld, gasoline-powered auger into the soil as deep as the equipment would allow. Most holes were about 3 m (10 ft) deep, and the maximum was 5.8 m (19 ft) deep. The holes were then filled with water and the level observed to determine if significant flow into the epikarst occurred. No traces were attempted because none of the five holes had an adequate rate of inflow.

contamination of samples and equipment by pesticides was the most likely. Field blanks were generated by pouring distilled water into a sample container under field conditions. Equipment blanks were generated by passing distilled water through an intake hose, or over other equipment, and into a sample bottle. The detection limit for nitrate-nitrogen is 0.002 mg/L and the detection limit for triazines (by ELISA) is 0.06 µg/L.

Groundwater traces conducted since 1994 have been primarily quantitative, for determining travel times from George Delaney swallow hole and Leslie Page karst window to Pleasant Grove Spring. These traces were conducted with sodium fluorescein or precisely measured amounts of rhodamine WT. Water samples were collected at Pleasant Grove Spring with automatic samplers over the period during which dye would be expected to arrive. The sampling machines were variously programmed to collect samples at 10- to 60-minute intervals. The samples were transported to Lexington in an ice chest for later analysis on a Turner Designs model 10 filter fluorometer. The fluorometer was calibrated with serial dilutions prepared from the same shipment of rhodamine dye used for the tracing. Rhodamine dye concentrations were determined to the nearest 0.1 µg/L, but fluorescein was determined semiquantitatively. The first arrival of dye and time of travel of the plume were determined from the dye concentration curves.

Development of Discharge Rating Curve

The continuous discharge record at the five water-level recorder stations was calculated from the stage record by using algorithms determined for stage-discharge rating curves developed empirically for each station. Existing channel conditions controlled the stage-discharge relationship at all sites, except at Leslie Page karst window, where a broad-crested weir was installed (see below). All discharge measurements were made using a Marsh-McBirney 2000 magnetic water-flow meter by the partial-sections method (Buchanan and Somers, 1976) from a boat or by wading. Stage-discharge graphs were plotted and stage-discharge relationships were calculated in English units because the available field equipment was so graduated. The discharge hydrograph was converted to metric units for flux calculations. Discharge measurements continued to be made late into the project at upper Pleasant Grove Creek station, Leslie Page karst window, and other sites because of changing channel conditions and because positioning field crews in advance of storms and simultaneously making measurements at multiple sites was difficult. All discharge results presented in this report were calculated using the latest stage-discharge rating, as applicable.

Of critical importance to determining the mass flux discharging from the basin was accounting for overland flow bypassing Pleasant Grove Spring. During extreme high flow, water overflows Johnson swallow hole, flows through a box culvert under Ky. 96, then flows overland to Pleasant Grove Creek downstream of the spring. Flow through the culvert is of both short duration and very high velocity, making the measurement of discharge difficult. Initially, several flow measurements were made at alternative cross sections downstream of the box culvert, but the locations proved unsatisfactory because of poor channel definition. The box culvert was then reconsidered. After several attempts, a set of rising-limb measurements and several falling-limb measurements was obtained. A peak discharge estimate was also made by indirect methods. The discharge data were used to develop a rating curve for the box culvert, and the overflow discharge was subsequently added to high-flow discharge at Pleasant Grove Spring. A new, two-function rating curve was developed using the base-flow segment of the old Pleasant Grove Spring rating curve and the new high-flow segment.

The Leslie Page karst window gaging station was originally installed in April 1993 with the intake screen of the stilling well imbedded in the stream bed. By the fall of 1995, erosion of the stream channel left the intake screen well above the bottom and resulted in flow occurring beneath the water intake and below zero stage. The erosion was probably because the channel reestablished its preagriculture grade in response to the reduction of sediment load from surrounding fields as a result of conservation tillage practices. The channel erosion problem was overcome by installing a broad-crested weir just downstream of the stilling well at the beginning of the 1995–96 water year. A new series of discharge measurements was then made. Discharge prior to October 1995 is estimated with the earlier stage-discharge relationship, and later discharge with the discharge rating for the weir. The discharge rating curve for Leslie Page karst window is complex, because backflooding occurs at the swallow hole. A second rating curve was developed for backflooded conditions. Because of the limited number of flow measurements at Leslie Page karst window, the stage at which backflooding occurred was assumed to be the same for both the rising and falling limbs of the hydrograph. Also, the water-level data lo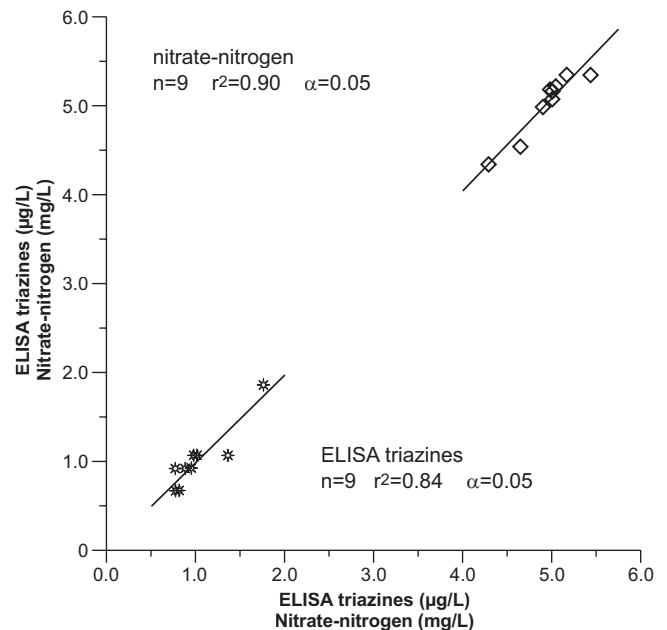gger at Leslie Page karst window failed twice during the late spring and late summer of 1995, resulting in an incomplete stage record. Fortunately, stage data for previous years indicated that flow at Leslie Page karst window is relatively constant, and few storms occurred during the periods the instrument was being repaired. The missing stage record was replaced with frequent staff gage readings and discharge measurements made at every opportunity.

The stage-discharge relationship at upper Pleasant Grove Creek station also changed during the project. Beavers constructed a dam across upper Pleasant Grove Creek 200 m (660 ft) downstream of the upper Pleasant Grove Creek gaging station in August 1994. The property owner removed the dam and channelized the stream in October 1997. Thus, three stage-discharge

relationships were used to estimate discharge at upper Pleasant Grove Creek station.

The inflow from upper Pleasant Grove Creek into George Delaney swallow hole was also problematic. The George Delaney swallow hole station was chosen because it is closest to the point where flow goes underground during median and high flow. The site is occasionally dry between July and November, and flow stopped at George Delaney swallow hole approximately 4 percent of the time during the 5 years it was monitored.

When flow into George Delaney swallow hole ceased, inflow continued into swallow holes between it and the upper Pleasant Grove Creek station at Johnson-Young Road. The gaps in the stage record at George Delaney swallow hole under-represented the remaining flow sinking upstream. Therefore, an algorithm was written to shift the discharge calculations and flux estimation to the upper Pleasant Grove Creek gaging station when inflow into George Delaney swallow hole ceased. The mass flux was calculated for a composite of the two stage monitoring stations and represents the surface-flowing stream reach of upper Pleasant Grove Creek between those two stations. Where the abbreviation "PGCK" is used for upper Pleasant Grove Creek, either in the text or in the figures, the values represented (typically discharge or flux) were developed from both stations.

Calculation of Mass Flux

Pesticides and Nitrate-Nitrogen. Mass flux, or flow loading, is the quantity of a constituent moving past a water-quality monitoring station at a spring or stream during a specific interval. Mass flux was calculated for Pleasant Grove Spring, upper Pleasant Grove Creek (George Delaney swallow hole and upper Pleasant Grove Creek stations), and Leslie Page karst window. Flux was estimated by multiplying the discharge during each 10-minute interval by the most recently determined concentration for that constituent. The annual mass flux was calculated by summing the 10-minute intervals for the entire water year. All flux calculations presented in this report are based on the revised stage-discharge rating curves. The annual flux was estimated at Pleasant Grove Spring for nitrate-nitrogen, atrazine-equivalent triazines, metolachlor, carbofuran, and total suspended solids. The concentrations of triazines and metolachlor were standardized to GC-equivalent atrazine and GC metolachlor, respectively, before mass flux was calculated. The ELISA carbofuran concentration was used directly because its relationship to GC equivalent is unknown. The nitrate-nitrogen concentration was used without adjustment. The flux of alachlor was not estimated because of the poor correlation between GC and

ELISA for this constituent. The mass flux of orthophosphate and bacteria were not calculated because samples were not collected frequently enough. The calculations were performed using algorithms programmed in Digital DataTrieve. For additional discussion, see Currens (1999).

Samples were not collected during some high-flow events because of various mechanical failures, human errors, and budget limitations. It is known, for example, that samples were missed during the peak concentration of triazines at Pleasant Grove Spring in May 1998. This results in a lower mass flux for high-flow concentrated constituents. Similarly, a higher mass flux for an event results when a triazine peak has been detected but further samples are not collected until after flow recession.

The magnitude of the over- or under-representation of the flux is unquantifiable for most individual events. It was possible, however, to examine the general effect of missed water samples during high flow on the mass-flux calculations, using events that have a complete sample set and also by using events that can be augmented with other data. The event sampler at Pleasant Grove Spring failed to activate during the May 1997 high-flow event, but samples from the daily automatic sampler bracketing the high flow were submitted for analysis. Furthermore, an automatic sampler had been deployed at George Delaney swallow hole and collected nine samples distributed over the event. The triazine and nitrate-nitrogen analyses for the George Delaney swallow hole samples were extrapolated to Pleasant Grove Spring in accordance with travel times determined from dye traces and concentrations proportioned in accordance with observed discharge. The mass flux at Pleasant Grove Spring was recalculated using the daily analyses from Pleasant Grove Spring and the extrapolated analyses from George Delaney swallow hole. The Pleasant Grove Spring atrazine-equivalent flux using the extrapolated data was 86 percent of the flux based on the daily analyses alone. Using the daily analyses from Pleasant Grove Spring, the flux at Pleasant Grove Spring was 6.85 kg versus 6.12 kg at George Delaney swallow hole (using nine analyses) for the same 7-day interval.

Another high-flow event for which sampling frequency was analyzed was that of May 7–10, 1996 (Currens, 1997). Twenty-seven samples covered the entire high-flow hydrograph of this event; most samples were concentrated during the early part of the event, as planned. The analytical data set was reconfigured into bihourly (every other hour; 11 samples) and daily (four samples) analysis sets to mimic the effect of missed samples. The mass flux of atrazine-equivalent for the daily analysis set was 85 percent of the flux computed

for the complete analysis set, and the mass flux of at-razine-equivalent for the bihourly analysis set was 124 percent of the flux for the complete analysis set. The nitrate-nitrogen flux was 92 percent and 100 percent for the daily and bihourly data sets, respectively. No attempt was made to estimate the comparative accuracy of the suspended sediment flux for these events because the availability of turbidity data minimizes the consequences of missed samples for that constituent.

Based on the above evaluation of partially sampled high-flow events during the spring, the accuracy of the annual mass flux of atrazine-equivalent is believed to be no worse than plus or minus 15 percent, and the accuracy for nitrate-nitrogen is within plus or minus 8 percent. When the data for the entire year are considered, the accuracy of the annual mass flux for atrazine-equivalent and nitrate-nitrogen is thought to be better than these ranges, because the relatively constant concentrations of both nitrate-nitrogen and triazines during base flow makes calculation of the estimated flux more reliable.

Total Suspended Solids. Flux for total suspended solids was not estimated in the reconnaissance report (Currens, 1999) because the data-logger record was interrupted and because the turbidity probe was occasionally fouled. There were two causes of fouling. As delivered by the manufacturer, the probe had an infrared reflection cone mounted below the probe optics, so as to form a cup when the instrument was deployed. The continuous discharge of suspended sediment, even the low concentrations during base flow, quickly filled the cone when the instrument was deployed. This resulted in a constant turbidity reading at the maximum end of the range of the instrument (approximately 1,100 nephelometric turbidity units [NTU's]). At the manufacturer's recommendation, the reflection cone was removed. A series of turbidity standard dilutions was used to make comparative readings with the cone off and with the cone on. A quadratic curve was fitted to the results, and values above 46.26 NTU's were found to be unaffected by the removal of the reflective cone (Fig. 6). The second cause of the fouling of the probe was the growth of a biological film (bacteria slime?) over the probe's optics, which caused a gradually increasing apparent turbidity. After the optics were cleaned, the biofilm growth was initially slow, but continued at an exponentially increasing rate, which accelerated following high-flow events. The problem was further complicated by the partial removal of the growth by random grazing of aquatic snails. Beginning in late 1993, a policy of cleaning the probe whenever the site was visited reduced the length of periods affected by the biofilm and the magnitude of induced error.

To salvage the turbidity data, the record for the entire monitoring period from October 1992 through October 1998 was examined. Written records had been kept of when the probe was cleaned, and suspended-sediment analyses were also available for comparison. When turbidity data were thought to be anomalously high, the monitoring record was further examined to determine if precipitation, increased stage, or if other indicators of high flow had occurred. When no flow-related cause of the increased turbidity could be found, the turbidity data were interpolated between readings known to be nominal. A simple base-e exponential decay function was used to interpolate the data for segments of record where biofilm growth was evident (Fig. 7). Because of the highly variable length of time for periods of biofilm growth, the value of the exponent needed to reduce high readings to the normally low target value also varied. The interpolation fit was selected by inspection, and the choice of exponent was by trial and error. Generally, the exponent used was between –0.01 and –0.1.

Although the interpolation process significantly reduced the erroneously high turbidity values, the annual mass flux of suspended sediment calculated with these data is still thought to slightly exceed what would have been determined if no fouling had occurred. This is because events recorded with a clean turbidity probe showed rapid decrease in turbidity with diminished flow, rather than the gradual decrease generated by the
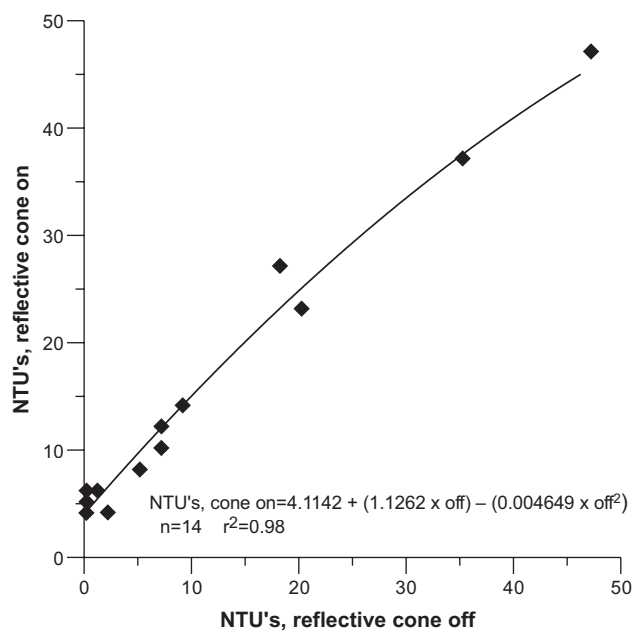
Figure 6. Turbidity probe observations plotted with the instrument's reflective cone off versus with the reflective cone installed, and to which a polynomial regression is fitted. The two observation methods produce equivalent readings above 46.26 NTU's.
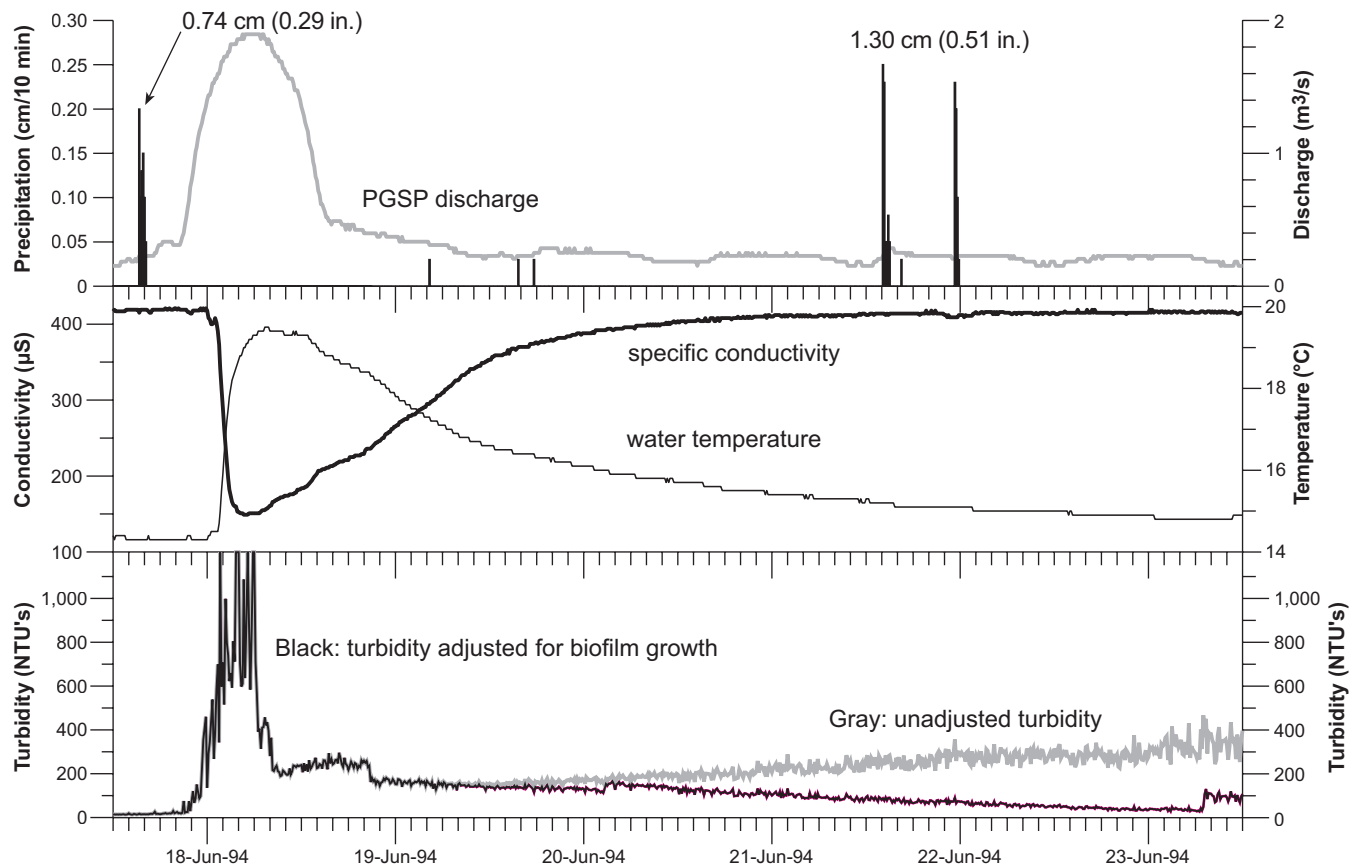
Figure 7. An example of the rise in turbidity readings caused by growth of a biological film on submerged equipment following high-flow events. Graphs are for the June 1994 event at Pleasant Grove Spring.

exponential decay interpolation. Conversely, turbidites determined during high-flow events were commonly more accurate (biofilm growth became significant after the high-flow period ended) and were accompanied by suspended sediment samples. Furthermore, the interpolated data have a relatively low contribution to flux, because the preponderance of sediment flux occurs during storms, and the parts of the record requiring interpolation were generally for base-flow periods. This reduces the significance of any error introduced by the interpolation.

The suspended sediment mass flux was calculated in the following manner. The adjusted turbidity data, and the analyses of suspended sediment from samples collected by automatic sampler, were independently regressed on suspended-sediment concentrations from samples collected by standard methods (Fig. 8). The prevailing standardized suspended-sediment concentration was preferentially calculated from the samples collected by automatic sampler. When a sample had not been collected during the increment being evaluated, the turbidity-derived concentration was used. Turbidity data that were missing because the data logger was

$sample = 2.1729 \times cone\text{-}on\ turbidity - 9.2707$
$n = 11 \qquad r^2 = 0.86 \qquad \alpha = 0.05$
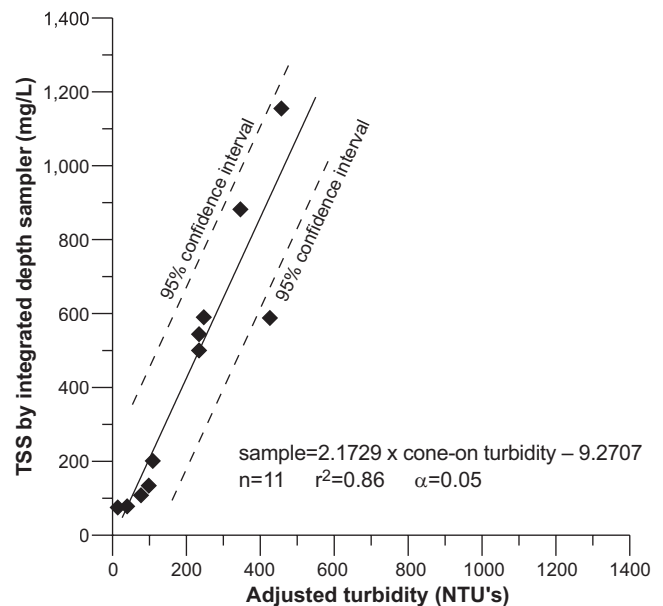
Figure 8. Plot of total suspended solids as determined in samples collected with an integrated depth sampler versus adjusted turbidity.

halted during calibration or were otherwise lost were not estimated; rather, the most recent total suspended solids analysis was substituted. Increments in which no suspended sediment concentration could be estimated were rare, but when they occurred, the concentration was assumed to be zero. The normalized suspended sediment concentration was then multiplied by the discharge, and each 10-minute incremental flux was summed for the year. The revised algorithms were used to calculate the suspended-sediment annual flux for the 1992–93 through 1997–98 water years.

Biological Inventory of Pleasant Grove Creek

Two biological inventories of Pleasant Grove Creek were conducted (before and after BMP implementation) in the reaches immediately downstream of Pleasant Grove Spring as a bioassay confirmation of the water-quality monitoring. The surveys were conducted by Kentucky Division of Water staff in April 1994 and 1998 (Sampson, 1995; McMurray, 1999). The two surveys used the same methodology; however, water flow was significantly higher in 1994. Fish were collected by seining for 1 hour. Macroinvertebrates were collected with three 1-minute, 10-foot traveling kicknet traverses. Samples were picked and preserved in the field, and taxa were determined both in the field and at Division of Water facilities. Pre- and post-BMP metrics were then computed and compared.

Implementation of the Water Quality Incentive Program

The financial incentives for the adoption of best management practices were funded through the Water Quality Incentive Program and administered by the USDA. The Pleasant Grove Spring Basin program was funded February 10, 1995, and enrollment of producers began in the spring of 1995. Enrollment in WQIP was permitted through December 1996, and incentive payments lasted no more than 5 years, but were typically 1 to 3 years. By the fall of 1995, most BMP's were implemented in the field, and the post-BMP period is defined as beginning October 1, 1995. Approximately 90 percent of the agricultural producers operating in the basin participated, which resulted in 68 percent of the watershed being under some BMP.

The list of BMP's allowed in the WQIP that were relevant to the karst setting of Logan County and eligible for cost-share support was short (Table 2) (U.S. EPA, 1993). Producers were allowed to choose BMP's they would participate in, except for the chemical application record-keeping, which was required of all participants. The most popular BMP was conservation cover. The least popular was increased use of buffer strips. WQIP money was not available for animal manure management, but exclusion of animals from streams was allowed. In addition, one animal waste-handling facility was constructed in the basin under another program. Compliance of the producers with their contracts was very high. There were a few nonparticipating farmers, and although the relative impact their farms had on the water quality is unknown, the area involved was comparatively small. One dairy farm is known to have runoff from a pasture adjacent to the milking parlor and tributary to upper Pleasant Grove Creek (Fig. 9), but the quality of the runoff was not determined.

Modern agricultural practices require the use of large amounts of herbicides, insecticides, and fertilizers (Fig. 10). No-till cropping, a method of eliminating the competition of noncrop plants by using herbicides such as atrazine instead of plowing, is perhaps the most effective technique used by farmers to minimize soil erosion. An average of 41 metric tons of atrazine alone is sold in Logan County annually (Ernest Collins, Kentucky Division of Pesticides, personal communication, 1999). Other pesticides with major sales volumes are glyphosate, metolachlor, acetochlor, 2,4-D, paraquat, bentazon, and disulfoton. The rate of application for nitrogen fertilizer

Table 2. Total areas within the Pleasant Grove Spring groundwater basin enrolled in each BMP as of September 29, 1998. Of 4,069 hectares (10,054 acres) in the watershed, 68 percent were enrolled in one or more BMP's of the USDA Water Quality Incentive Program for its 3-year duration. From U.S. EPA (1993).

Practice Code	Practice	Area Enrolled, Hectares (acres)
327	Conservation cover	284 (701)
328	Conservation cropping sequence	2,046 (5,055)
329	Conservation tillage	165 (407)
344	Crop residue use	1,839 (4,543)
393	Filter strips	0.8 (2)
411	Grasses and legumes in rotation	77 (191)
472	Livestock exclusion	8 (20)*
510	Pasture and hayland management	301 (743)
512	Pasture and hayland planting	37 (92)
590	Nutrient management	299 (739)
595	Pest management	302 (746)
633	Waste utilization	54 (133)
991	Record keeping	2,365 (5,843)

*Participated in 1995, 1996, and 1997

Figure 9. Runoff from a holding pasture for a dairy owned by a producer not participating in the WQIP.

Figure 10. Application of agricultural chemicals in the Pleasant Grove Spring karst groundwater basin.

for corn and wheat in the Pleasant Grove Spring Basin recommended by the U.S. Department of Agriculture is 137 lb/acre (Bill Johnson, NRCS Logan County office, written communication, 1992). The application rate for atrazine on corn recommended by the University of Kentucky College of Agriculture (Martin and Green, 1992) is 2.5 lb/acre of 80 percent active ingredient.

Producers enrolled in the WQIP received incentive payments to keep records of both the pesticides and nutrients applied to their fields. Approximately 60 percent of row crop area of the basin was included in the record-keeping BMP. Staff of the Logan County office of the Natural Resources and Conservation Service compiled the data submitted by individual farmers into a summary report, which was available for use in this project (Craig Givens and Jimmy Christian, NRCS Logan County office, written communication, 1997).

Informational and educational meetings with producers who were operating farms in the Pleasant

Grove Spring Basin were held each February beginning in 1993. Typically, 25 to 50 percent of the study-area farmers attended each meeting. Topics discussed included goals of the project, addressing concerns of the farmers, and the current findings. More significantly, the importance of managing field runoff, the impact of runoff on groundwater, and the relevance of groundwater quality to human health were discussed. Guest speakers discussed regulatory issues and government programs available to farmers to assist in reducing nonpoint-source pollution.

Land-Use Mapping

Steve Crabtree of the Burlington office of the Natural Resources and Conservation Service of the U.S. Department of Agriculture digitized crop and soil area maps for the Pleasant Grove Spring Basin and calculated annual crop areas using GRASS geographic information system software. A stable-base field-boundary base map was prepared from aerial photographs. The fields were assigned a serial number and their areas calculated. Crops were identified by the Kentucky Geological Survey by field inspection and from aerial photographs taken annually for the Farm Service Administration, USDA. The crop or other land use determined for the fields was entered into a database, and the files transferred to the NRCS. The total acreage for each crop was then calculated. Crop maps were completed for the 1991 through 1998 growing seasons.

Statistical Analysis

Because the project design was to judge the success or failure of the BMP program by the changes in water quality at Pleasant Grove Spring, only the analytical data for the spring were subjected to statistical evaluation. Furthermore, the sample set at Pleasant Grove Spring is the most complete among the sites in the basin and the most likely to be representative. The statistical tools that could be used were restricted because the frequency and timing of sampling during the monitoring was neither statistically random nor on a strict schedule. This was caused by logistical constraints and further complicated by the need to intensively collect samples during high-flow events in the spring for calculating annual flux and detecting peak concentrations of herbicides. To partially overcome this limitation, the analytical data for water samples from 1992 through 1998 were divided into various subsets based on frequency of sampling. The quarterly sample set is composed of all the analyses of the first sample of each calendar quarter during the project period. Similarly, the analyses of the first water

sample collected at the beginning of each month comprised the monthly analysis set. The analyses of water samples collected at the beginning of each biweekly period comprised the biweekly analysis set. An additional sample set was assembled by augmenting the biweekly sample set with analyses of water samples collected every other hour during high flow; this comprised the bihourly/biweekly analysis set. The biweekly set made up of all water samples collected during high flow comprised the biweekly/high-flow analysis set. Finally, the set of analyses from every water sample, which included some opportunistically collected samples and some samples collected every other day during the spring, is the complete analysis set.

The data were then evaluated using Statgraphics 3.0 software (by Manugistics Inc.). The sample subsets were tested against normal, log normal, gamma, and Laplace distributions for the triazines, nitrate-nitrogen, total suspended solids, and orthophosphate analyses using the chi-square statistic. Further statistical tests were conducted on the complete analysis set using a Mann-Whitney test of the equivalence of the medians. This test is valid for data that do not follow a normal distribution, which none of the constituents did for the complete set of analyses.

A second strategy was also used for statistical analysis of the water-quality data. Means, geometric means, total annual mass flux, flow-weighted means, and medians were calculated for total suspended solids, triazines (atrazine-equivalent for flux), and nitrate-nitrogen for each water year. The annual mean, geometric mean, and medians were calculated for bacteria counts and orthophosphate. These statistics were grouped pre- and post-BMP and compared using Dunnet's t-test and Mann-Whitney nonparametric tests. The statistics were computed using Microsoft Excel.

Data Archiving

Location data, water analyses, stage data, and field parameters collected by continuous monitoring and portable instruments are permanently archived at the Kentucky Geological Survey. All data have been entered into digital databases, and paper copies of the analytical data are also permanently on file. The water-quality data are available through the Kentucky Groundwater Data Repository.

Naming Conventions for Samples and Data Files. Many of the names for geographic locations in the Pleasant Grove Spring study area, including George Delaney swallow hole and Leslie Page karst window, are long. Four-character abbreviations were used for each of the sites where samples or other data were collected (e.g., PGSP for Pleasant Grove Spring). An attempt was made

for the abbreviation to sound like or be logically derived from the place name. Appendix A lists the abbreviations used for locations and the type of data the abbreviations were used for. During field work, the abbreviations were routinely used as a substitute for the place name. The four-character abbreviations were used in most of the field records, data files, chain-of-custody reports, and analytical results. The linkage between the place names discussed in this report and the abbreviations used in the data files must be preserved because the data for this report are archived digitally and are not printed in this publication. The data logger allowed a maximum of eight characters for file names. This restriction resulted in a finite limit for the names of at least data files. For example, Pleasant Grove Spring was equipped with four data loggers, so the file names included PGSP (for stage data), PGRG (for precipitation data), and PGTP (for air temperature data). The single character "P" was used for the YSI 3800 water-quality logger, because of machine-specific restrictions. The abbreviation was followed by the month and day of the month.

A short, unambiguous identification system for samples was also needed. The place name abbreviation was therefore combined with a four-digit serial number, allowing identification numbers for up to 9,999 samples. The serial number sequence was preserved with preprinted labels that were applied to the sample tag or destroyed when used. For example, LPKW plus sample 99 yielded LPKW0099. More than one sample type may be associated with a given site, in addition to routine water samples. Examples of other sample designations include PGDP (duplicate sample), PGEB (equipment blank), and PGFB (field blank).

Results of Supportive Investigations
Flow at Monitoring Stations

Revised stage-discharge rating curves were developed for all of the water-level monitoring stations as new measurements were obtained. The new data resulted in little change on the low-flow discharges determined from the curves published in the reconnaissance report (Currens, 1999). Accounting for overflow from Johnson swallow hole, however, resulted in major changes to the high-flow segment of the Pleasant Grove Spring rating curve. The revised discharge stage-rating curve for Pleasant Grove Spring is illustrated in Figure 11. Because the stage at Pleasant Grove Spring remained mostly within the low-flow segment of the rating curve during the 1992–93 and 1993–94 water years, the annual discharge for Pleasant Grove Spring is nearly the same for those years, as was previously reported. The discharge determined with the new rating
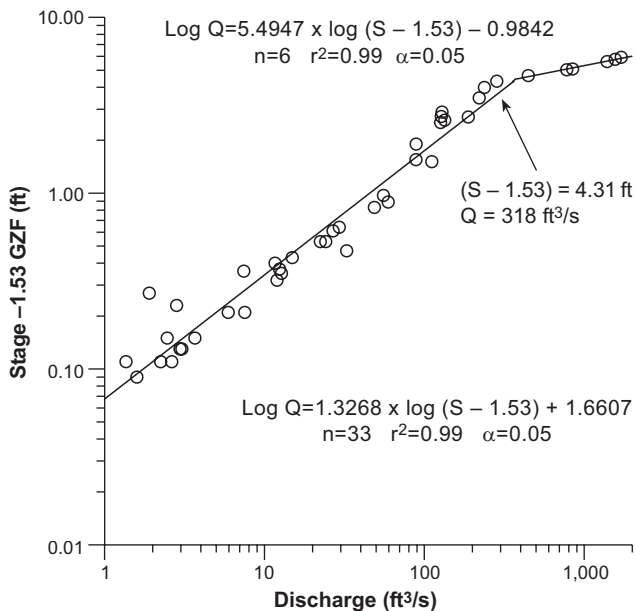
Figure 11. Stage-discharge rating curve for Pleasant Grove Spring. When the flow rate in upper Pleasant Grove Creek exceeds the intake capacity of all swallow holes in the upper reaches of the creek, the stage at Pleasant Grove Spring is 5.84 ft (gage zero flow [GZF] 4.31 ft) or higher. Under these conditions, water flows overland to Pleasant Grove Creek. The overland flow is accounted for in the upper segment of the rating curve.

Figure 12. Rating curve of stage versus inflow at the Leslie Page karst window swallow hole. Lower segment of rating curve represents free-air surface-flow conditions. Segment in upper left represents inflow when the conduit is filled and the karst window is flooded. Dashed line indicates instant when pipe-full conditions begin and the flow/stage relationship is undefined. Data collected after October 1, 1995.

curve for Pleasant Grove Spring was unchanged for the 1992–93 water year at 10.2×10^7 m^3/yr (3.6×10^8 ft^3/yr). The discharge for the 1993–94 water year decreased slightly from 3.18×10^7 m^3/yr (11.3×10^8 ft^3/yr) to 3.15×10^7 m^3/yr (11.2×10^8 ft^3/yr) when recalculated using the revised rating curve. The highest annual discharge recorded was for the 1996–97 water year (4.25×10^7 m^3/yr [15.0×10^8 ft^3/yr]), whereas the average annual discharge for the 1992–98 monitoring period for Pleasant Grove Spring is 2.54×10^7 m^3/yr (8.96×10^8 ft^3/yr). The maximum instantaneous discharge recorded was 38.05 m^3/s (1,343.5 ft^3/s) on April 11, 1994, at 12:50 hours. The average instantaneous discharge is 0.96 m^3/s (34 ft^3/s), whereas base flow is a more modest 0.11 m^3/s (4.0 ft^3/s). Revised stage-discharge rating curves used for mass-flux calculations at Leslie Page karst window, George Delaney swallow hole, and upper Pleasant Grove Creek station are presented in Figures 12 through 15.

The discharge rating curve at Leslie Page karst window is complex, because the swallow hole draining the karst window backfloods. An instantaneous shift in the stage-discharge relationship occurs when the conduit becomes completely filled (between observations 35 and 31 on Figure 12). The first suspected cause of the backflooding is limited cross section of the conduit. During intense, short-lived downpours, inflow rates

Figure 13. Stage versus inflow rating curve for George Delaney swallow hole. Gage zero flow chosen by maximizing correlation coefficients for nontransformed data. The minimum stage observed in the field at which flow occurred is 0.14 ft.

$$Q = S \times 26.9911 - 19.6815$$
$$n=7 \quad r^2=0.98 \quad \alpha=0.05$$
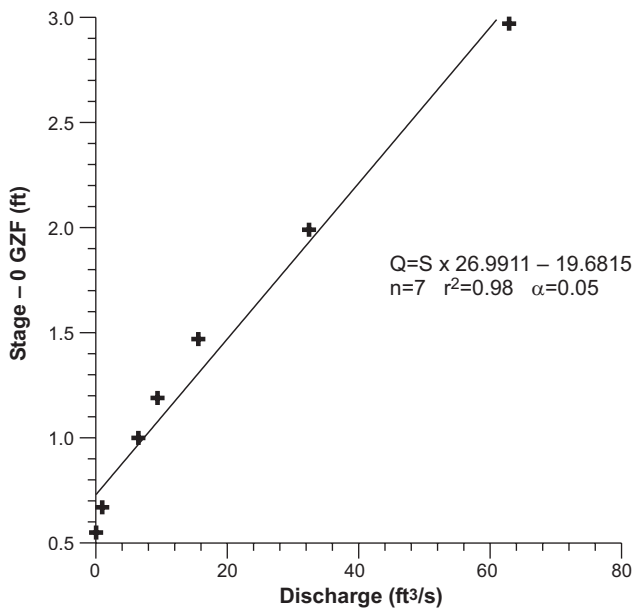
Figure 14. Stage versus discharge rating curve for upper Pleasant Grove Creek gaging station for the period a beaver dam existed downstream of the station (August 28, 1994–October 31, 1997).

$$\log(Q) = \log(S) \times 2.9031 + 1.2290$$
$$n=7 \quad r^2=0.98 \quad \alpha=0.05$$
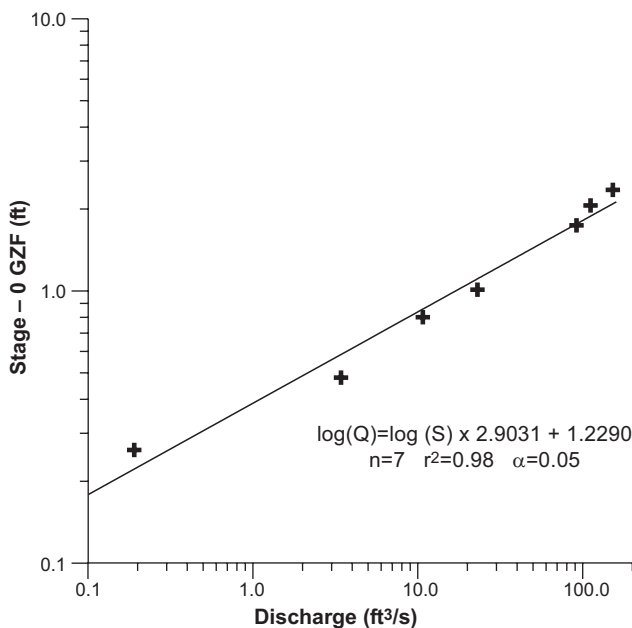
Figure 15. Stage versus discharge rating curve for upper Pleasant Grove Creek gaging station after channelization (after October 31, 1997).

frequently, but briefly, exceed the intake capacity of the swallow hole. The duration of backflooding due to brief downpours is typically less than 3 hours. Although the cross-sectional area of the swallow hole entrance and the visible section of conduit is large (0.4 m high by 1.5 m wide), the cross section of the conduit is thought to

be reduced somewhere along a downstream reach. A reduced cross section would limit the hydraulic capacity of the conduit. The recent deepening of the stream channel approach to the swallow hole was mentioned previously as evidence of higher sedimentation rates prior to this study, and suggests the likely cause of the blockage is sediment.

The second cause of backflooding is thought to be a reversal of the slope of the potentiometric surface in the conduit draining Leslie Page karst window, caused by higher hydraulic head in the main-stem conduit. No flow reversal (discharge) from the swallow hole at Leslie Page karst window has been directly observed. The stage hydrograph for Leslie Page karst window has been observed to continue rising, however, when stage at the other monitoring stations in the basin have begun to fall. Figure 16 illustrates the rising limb of the backflooding segment of the hydrograph corresponding to a declining stage at George Delaney swallow hole, upper Pleasant Grove Creek station, and Spring Valley karst window, despite these stations having significantly larger contributing areas. The recession hydrograph at the other stations, and rain gage records, indicate precipitation has ended and runoff is slowing at the stations. The stage at Leslie Page karst window, however, continues to rise. Furthermore, two types of high-flow hydrographs have been recorded at Leslie Page karst window, which suggests that there are two hydrologic conditions. The response to short, intense storms is a steeply sloping hydrograph, which quickly returns to low-flow conditions. The type of hydrograph suspected to be caused by backflooding via the downstream conduit is characterized by a broad, gradually rising and gradually falling slope that persists much longer than the peak expected from short, intense storms.

The backflooding hydrograph at Leslie Page karst window only occurs when the stage at Spring Valley karst window exceeds approximately 4 m (13 ft) or an elevation of approximately 159 m (523 ft). The backflooding hydrograph at Leslie Page karst window has not been recorded when stage at Spring Valley karst window remains below 4 m. Also, the swallow hole at Spring Valley karst window is partially blocked with logs and other debris, which further promotes flooding of the main-stem conduit draining from George Delaney swallow hole. During the high-flow periods when overland flow from Johnson swallow hole flows through the box culvert under Ky. 96, head on the main-stem conduit system is near a maximum. The elevation of Leslie Page karst window is 166.7 m (547 ft), and the elevation of Spring Valley karst window is near 155.4 m (510 ft). George Delaney swallow hole is some 15 m higher than Leslie Page karst window at 181.3 m (595 ft); thus, there
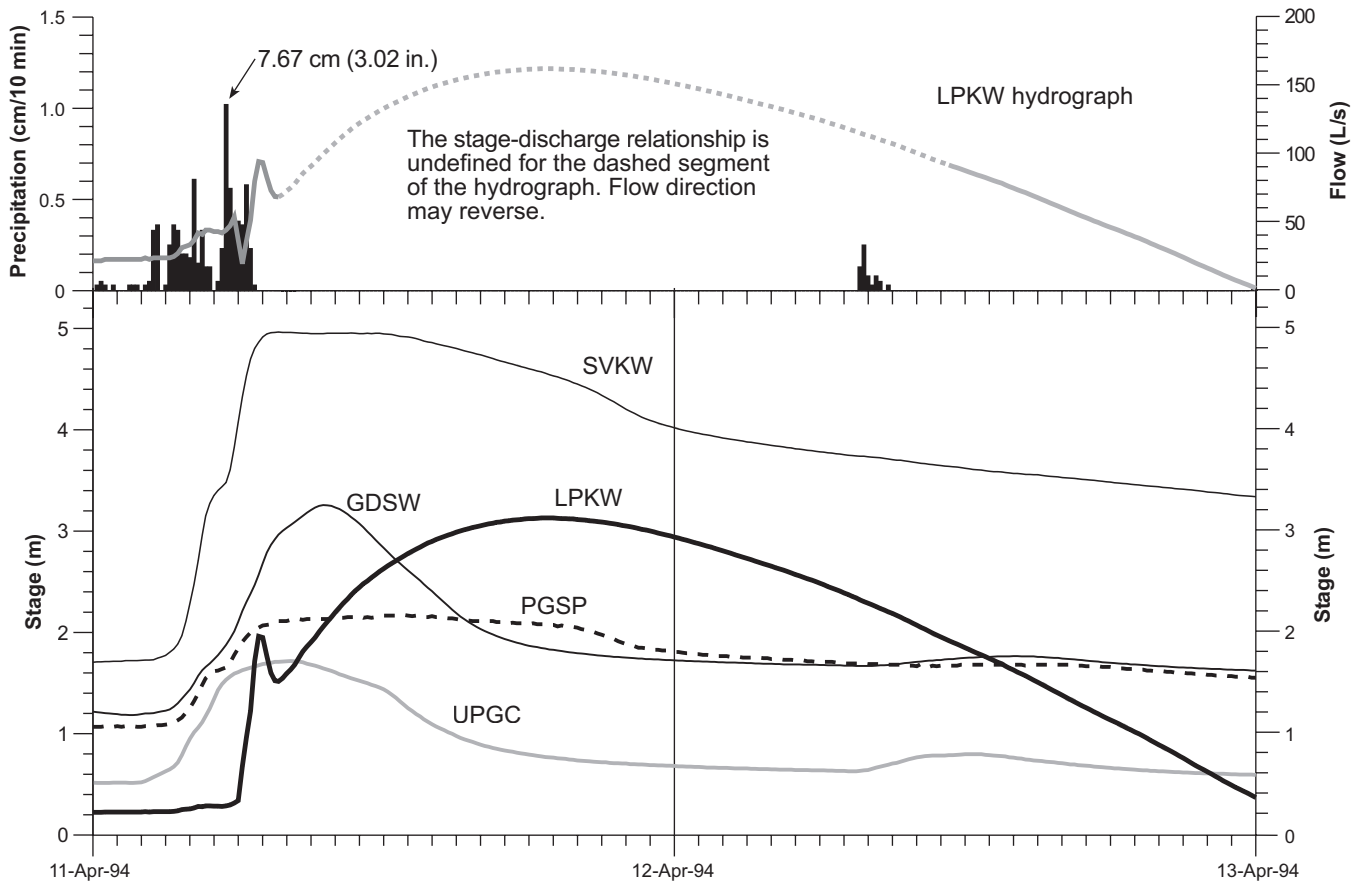
Figure 16. Inflow hydrograph at Leslie Page karst window and stage hydrographs for the April 1994 high-flow event in the Pleasant Grove Spring groundwater basin. See Appendix A for explanation of abbreviations.

is ample head to backflood Leslie Page karst window when the main conduit is flooded (pipe full).

Further evidence for sedimentation as a cause of the reduction of conduit cross-sectional area at Leslie Page karst window, and in the basin in general, is found in Oakville Cave, which lies only 600 m (2,000 ft) south-southwest of Leslie Page karst window. When explored in 1989, the intermittently flooded passages of Oakville Cave exhibited significant and apparently recent sediment deposition. Sediment deposition occurs readily when the velocity of sediment-laden water is slowed, as during backflooding. The transport of sediment through conduits in the study area is further discussed in Currens (1999).

Quantitative Dye Traces

Seven quantitative traces were attempted from George Delaney swallow hole to Pleasant Grove Spring and four from Leslie Page karst window to Pleasant Grove Spring. Only one complete dye breakthrough curve was obtained from Leslie Page karst window and two from George Delaney swallow hole. The low success rate was caused by the difficulty of synchronizing highly

variable tracer travel times, because of differing flow conditions, with the finite sampling period of the automatic sampler, while simultaneously trying to minimize the interval between samples. Only one attempt was made to synchronize quantitative dye traces with high-flow events, although this was highly desirable because of the above limitations coupled with the simultaneous need to obtain essential discharge measurements at other locations during high flow.

Usable time-of-travel data were obtained, however, from the first arrival of the dye. Figure 17 shows the delay time to first detection of dye from George Delaney swallow hole to Pleasant Grove Spring versus the stage at Pleasant Grove Spring at the time of dye injection. The dye first-arrival times at Pleasant Grove Spring are known to be accurate for all traces except for number 4, which was detected visually an unknown period after the dye started arriving. A polynomial regression curve was fitted to the data. The first-arrival time decreases dramatically with stage (discharge), and the graph illustrates the effect of flow conditions on the travel time of entrained constituents. The minimum travel time was 9 hours, observed following a light rain when Pleasant
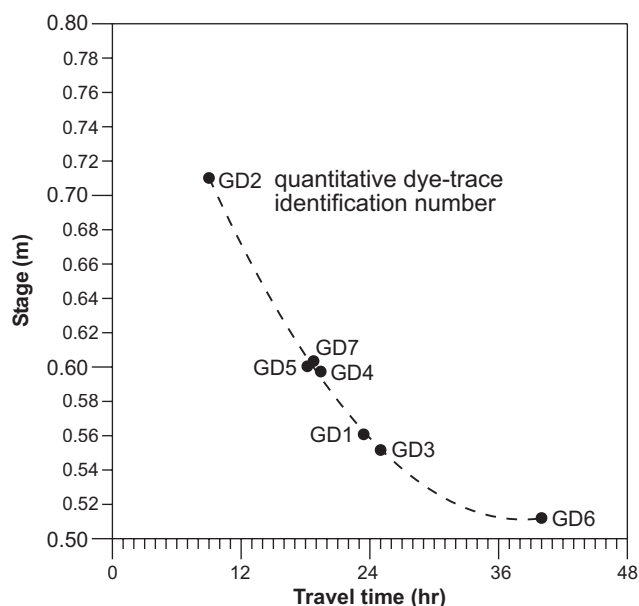
Figure 17. Elapsed time from introduction of tracing dye into George Delaney swallow hole to first detection at Pleasant Grove Spring plotted against stage at Pleasant Grove Spring.

Grove Spring was at a modest stage of 0.71 m (2.33 ft); stage rose only an additional 0.5 cm (0.19 ft) during the trace. The trace was done in anticipation of a significant storm, which produced less rainfall than forecast. The fastest travel time approximates the delay between peak stage at George Delaney swallow hole and changes in turbidity, conductivity, and temperature at Pleasant Grove Spring (Figure 22 of Currens, 1999) during high-flow events.

Dye-trace travel times during low flow from Leslie Page karst window to Pleasant Grove Spring are roughly twice that from George Delaney swallow hole to Pleasant Grove Spring (36.7 hours versus 18.2 hours), although the length of the straight vector path from Leslie Page karst window to Pleasant Grove Spring is only 60 percent of the distance from George Delaney swallow hole to Pleasant Grove Spring. The travel time from George Delaney swallow hole to Pleasant Grove Spring is significantly shorter during high-flow conditions (9 hours). Although dye travel times from Leslie Page karst window and George Delaney swallow hole to Pleasant Grove Spring were not obtained under identical high-flow conditions, the travel time from Leslie Page karst window is expected to always remain longer, provided precipitation was uniformly distributed. The longer dye-trace travel time from Leslie Page karst window is thought to be at least partly due to the conduit from Leslie Page karst window trending southwest, parallel to the local strike, before joining with the conduit draining from George Delaney swallow hole to Pleasant Grove Spring. If true, the actual flow path is slightly longer than the dye-trace vector, but remains shorter than the distance from George Delaney swallow hole to Pleasant Grove Spring. This hypothesis is supported by the tendency for conduits to form at the junction of the bedding plane and the water table (Palmer, 1991). In addition, backflooding, which may occur in the tributary conduit draining Leslie Page karst window, would further lengthen travel times for traces from Leslie Page karst window during high flow.

Nitrogen Isotopes Ratio

Nitrogen isotopes have been used for over 30 years as indicators of nitrate source (Freyer and Aly, 1974; Aravena and others, 1993). The higher the $^{15}N/^{14}N$ ratio, the more likely that the nitrogen has been biologically fractionated, compared to being derived from manufactured commercial fertilizer. The $\delta^{15}N$ values of commercial N-fertilizers range from –3 to +6 parts per thousand (Herbel and Spalding, 1993), whereas human- and animal-waste-derived nitrate is +10 parts per thousand and higher. Intermediate values are interpreted as soil-process derived and naturally occurring, or as mixtures of biological and manufactured fertilizer (Fogg and others, 1998).

The nitrogen isotope data from both Pleasant Grove Spring and the spring at Leslie Page karst window suggest the application of commercial fertilizers has a strong influence on the nitrate concentration (Table 3). This interpretation is further supported by the absence of humans or livestock within the estimated drainage basin of Leslie Page karst window. The relatively constant $^{15}N/^{14}N$ ratio at Leslie Page karst window through the year suggests that weather conditions have little influence on the source of nitrate. The more variable $^{15}N/^{14}N$

Table 3. Nitrogen-15 and nitrogen-14 isotope ratios for samples collected at Pleasant Grove Spring and Leslie Page karst window.

Sample Number	Date	Total Nitrate-Nitrogen (mg/L)	$^{15}N/^{14}N$ δ‰
PGSP0841	May 7, 1996	5.2	0.4
PGSP0978	Oct. 8, 1996	1.2	4.0
PGSP1002	Jan. 7, 1997	5.5	3.3
LPKW0256	May 8, 1996	6.5	2.3
LPKW0289	Oct. 8, 1996	5.7	2.3
LPKW0301	Jan. 8, 1997	5.9	2.1

ratio at Pleasant Grove Spring is likely influenced by direct run-in carrying animal waste. Human waste may also influence the ratio very slightly. The October 8, 1996, samples were collected on the recession limb of a significant, early fall, high-flow event. These samples may over-represent manufactured nitrate fertilizer because of the leaching of residual nitrate temporarily stored in the soil during the dryer summer months.

Land-Use Mapping

Land-use mapping of the Pleasant Grove Spring karst groundwater basin by the NRCS revealed significant trends in land use from 1991 through 1998. The total percentage of land in agricultural production increased from 82.7 to 88.8 percent of the basin over the course of the project. Land area in pasture declined from 14.2 to 10.9 percent, and wooded areas declined from 15.8 to 9.7 percent; areas in row crop production correspondingly increased from 68.5 percent to 77.9 percent. Developed areas (farmsteads, suburban areas, roadways) increased less than a tenth of a percent, and the area covered by water remained unchanged. Large areas were cleared of trees and converted to crop fields from 1991 through 1993, as indicated by field observations, and resulted in a 2.5 percent (246 hectare [608 acre]) decline in woodland from 1991 to 1992. A slower loss of woodland from 1995 through 1998, however, was compensated for by the conversion of pasture to row crop during those years. Therefore, the WQIP did not stop the trend of converting more land to crop production.

Livestock are concentrated in several areas of the basin. A livestock census made in 1995 counted 40 horses, 275 dairy cattle, 1,357 beef cattle, and 1,100 hogs (Jimmy Christian, NRCS Logan County office, written communication, June 21, 1995). There are two dairies, one small and two large swine operations, and a feeder dairy-calf operation. The two dairies and the small swine operations are the most visible contributors to potential bacterial contamination of water. One of the two large swine operations was visited by KGS personnel, and it has a state-of-the-art waste-holding facility with no history of lagoon leakage since its construction in about 1992. KGS personnel did not visit the other swine operations. A dairy southeast of the junction of Johnson-Young Road and Ky. 96 does not have a waste-holding facility, and overland runoff from the dairy leaves the property (Fig. 9). The runoff ultimately reaches a sinkhole southwest of the road junction. The other dairy, north of Johnson-Young Road, installed a stack pad and holding pond during the July 1992 to July 1993 period.

Cattle and hogs were fed and grazed in fields surrounding George Delaney swallow hole through July 1, 1995. After that date, only a few head of horses were pastured there. The feeder calves grazed in the fields surrounding Spring Valley karst window, but were provided with alternative water supply and excluded from the karst window as a result of the WQIP. Most of the beef cattle are grazed in the southern end of the basin, including pastures surrounding Pleasant Grove Spring.

Acceptance of the Water Quality Incentive Program

The selection of BMP's by the producers was disappointing, although the percentage of the basin enrolled under the WQIP was large. Almost every producer in the watershed adopted conservation cover as a BMP. At the time the WQIP began, however, most of the farmers were already using no-till or minimum-tillage techniques, and the additional cover crop residue was a minor change. Although these practices greatly reduce soil loss, they require the use of significant quantities of herbicides. Thus, the WQIP may have perpetuated the use of triazine herbicides in the basin.

The experience of the staff of the Logan County NRCS with WQIP suggests there were four concomitant circumstances for the lack of interest in the other BMP's, which might have been more effective (Craig Givens, NRCS Logan County office, personal communication, April 9, 1999). First, most of the producers in the basin are over 50 years old and some may not have been receptive to changing their farming practices. Second, the financial incentives for the filter strip practice was only 10 percent of the fair-market annual income a landowner could obtain by leasing the same land for crop production. Third, the integrated crop management system (ICM) was poorly received. The ICM practice follows guidelines of the University of Kentucky College of Agriculture and uses intensive pest scouting coupled with precise timing of chemical applications to minimize pesticide and nutrient use. Most producers used commercial crop consultants and soil test labs that do not follow the University guidelines, however. Thus, most producers did not adopt the ICM practice. Fourth, all WQIP BMP's were management practices, rather than structural. For example, no money beyond the existing cost-share program was available for animal waste-handling facilities.

A survey of Iowa farmers asking them about their attitudes toward government incentive programs to address runoff from agricultural areas flowing into sinkholes indicated that they were generally unwilling to enroll sinkhole areas in the Conservation Reserve Program as then administered (Huber, 1990). If the program were modified, however, to provide for a permanent forage-use easement, most would enroll if they received at least 70 percent of the full land value.

They would agree to a permanent reforestation only if they received 107 percent of the land value, because of the long delay between planting and harvesting of trees. Unlike in the study area in Iowa, in which sinkholes occupied a small percentage of the study area (average of one sinkhole per 14 hectares [35 acres]), sinkholes occupy an estimated 80 percent of the Pleasant Grove basin, so acceptance of such a program in this study area may require greater incentives.

Record-Keeping BMP and Actual Chemical Usage

Although the KGS monitoring project was unable to inventory actual chemical use in the Pleasant Grove Spring area, the WQIP included a record-keeping BMP provision. In addition to the amount of agricultural chemicals applied each growing season, the producers reported an inventory of the area planted for each crop from 1996 through 1998. The pesticides used in the basin were very diverse. Table 4 lists the reported pesticides with 45 kg (100 lb) or more of active ingredient used for any reporting year. Recent trends in the development of

new pesticides are reflected in the presence of chemicals not listed in the reconnaissance report (Currens, 1999). Because the accuracy of the producers' personal records of chemical use and their reporting compliance cannot be tested, the accuracy of the WQIP chemical totals is unknown. Furthermore, the variability of the atrazine application rate over the 3 years of the WQIP inventory was greater than previously assumed (Currens, 1999). The relative quantities of chemicals reported are proportional to the total area of crops, however, and are near the recommended application rates, which indicates the data are within an expected range.

The average application rate of atrazine was estimated for this report from the atrazine use and area of corn cultivated, as reported through the WQIP for each growing season from 1996 through 1998. The annual average application rate was computed by totaling the reported atrazine use and dividing by the area in corn. The inventory also reported nitrate-nitrogen applied on all crops grown. Total nitrogen usage was summed for three categories of crop: corn, pasture, and other row crops. The category sums were then used to calculate

Table 4. Pesticides used in the Pleasant Grove Spring Basin as reported by producers in response to the record-keeping BMP*. Some pesticides were not reported every year because of changing product prices, the availability of new products, and other causes. Only compounds for which more than 45 kg (100 lb) was reported for at least 1 year are listed.

Active Ingredient	1996 Total Usage, kg (lb)	1997 Total Usage, kg (lb)	1998 Total Usage, kg (lb)
acephate	92.1 (203)	108.9 (240)	127.6 (281)
acetochlor	752.1 (1,658)	1,632.5 (3,599)	815.1 (1,797)
atrazine	1,085.4 (2,393)	832.8 (1,836)	1,727.1 (3,808)
bentazon	574.2 (1,266)	97.1 (214)	83.6 (184)
butylate	94.3 (208)	0 (0)	0 (0)
carbofuran	78.0 (172)	145.1 (320)	68.9 (152)
clomazone	15.4 (34)	176.4 (389)	6.4 (14)
cyanazine	59.0 (130)	30.1 (67)	81.1 (179)
glyphosate	1,046.9 (2,308)	836.4 (1,844)	1,126.7 (2,484)
metalaxyl	21.8 (48.0)	13.6 (30.0)	50.8 (112)
metribuzin	47.2 (104)	31.3 (69)	2.6 (6)
metolachlor	625.1 (1,378)	689.5 (1,520)	527.3 (1,163)
paraquat	34.0 (75)	117.9 (260)	98.7 (218)
pendimethalin	117.9 (260)	7.3 (16)	5.4 (12)
phosphorodithioate	145.1 (320)	130.6 (288)	101.6 (224)
sodium acifluoren	285.8 (630)	63.5 (140)	48.9 (108)
sulfosate	0 (0)	0 (0)	183.7 (405)
thifensulfuron	48.5 (107)	28.1 (62)	99.0 (218)
2,4-D	89.8 (198)	50.3 (111)	478.7 (1,055)

*Craig Givens and Jimmy Christian, NRCS Logan County office, personal communication, 1997, 1998, 1999.

the average application rate for each crop category for the WQIP inventory years. The average application rate for the three WQIP years was used to estimate again the atrazine and total nitrate-nitrogen application rates for the uninventoried years. The chemical application rates developed from the WQIP data were then multiplied by the areas of crop, as determined from aerial photographs, to calculate tons of chemicals applied in the entire basin.

The average application rate for atrazine determined for the 3 years of record was 1.24 kg/hectare (1.1 lb/acre), significantly less than that recommended, whereas the nitrate-nitrogen estimated application rate of 157 kg/hectare (141.07 lb/acre) is nearly identical to the median recommended rate for corn and wheat. The application rate for atrazine varied significantly, however, from 0.77 kg/hectare (0.69 lb/acre) of corn in 1997 to 1.79 kg/hectare (1.59 lb/acre) in 1998. The application rate for nitrate-nitrogen varied more narrowly, from 149.77 kg/hectare (136.77 lb/acre) of row crop to 167.13 kg/hectare (149.12 lb/acre).

Biological Inventory

McMurray (1999) reported on the condition of the fauna in Pleasant Grove Creek and compared the April 1994 survey by Sampson (1995) with conditions after BMP implementation in April 1998. McMurray (1999) compared several metrics calculated for both collections. The index of biotic integrity (IBI) for fishes was 28 for the post-BMP sampling, a slight improvement over 26 for the pre-BMP sampling, but still in the poor category. There were no species in common between the two samplings. The total number of taxa for macroinvertebrates increased dramatically from 21 to 41 and the total number of individuals also improved from 241 to 522. The percent community similarity and Jaccard coefficient of community similarity metrics showed that the two collections of macroinvertebrates were not very similar. The Ephemeroptera-Plecoptera-Trichoptera metric, which measures pollution-intolerant taxa, did not vary between the pre-BMP and post-BMP collections, whereas the modified Hilsenhoff biotic index improved slightly (6.92 to 5.42).

McMurray (1999) concluded the lack of similarity of the fish and macroinvertebrate collections indicated a temporal shift in water quality. He further hypothesized that slightly different flow conditions (stage and turbidity) at the time of sampling may have affected the collections. Because of the poor IBI for fishes, however, the shift could not be described as an improvement in aquatic diversity. Thus, the biological inventory does not indicate a significant improvement in water quality.

Education Meetings

The Pleasant Grove Spring education program consisted of meetings each February for study area producers. The meeting agenda included a review of the monitoring results for the previous growing season, discussion of nonpoint-source-related programs available to assist farmers, and encouragement of pollution control beyond the WQIP. Each meeting was typically attended by roughly half of the producers operating farms in the basin. Most attended at least one of the four meetings, but some did not come to any. Progress on the WQIP and the monitoring project were also reported in the NRCS Logan County newsletter. Logan County elementary school students were exposed to the concept of protecting groundwater from pollution, with an emphasis on karst aquifers, at the annual NRCS environmental workshops in 1997 and 1998.

Miscellaneous Findings and Observations

On June 16, 1997, a dump that included over 200 pesticide containers was discovered in a gully that drains to Leslie Page karst window. The dump site is obscured from casual view and is completely out of sight of the monitoring station. When found, the containers were in a condition that suggested the dump was relatively recent. The dump was not there when the site was scouted for such materials in 1993, and no pesticide containers were found at the monitoring station until the spring of 1997. The containers were probably dumped sometime during the summer of 1996, because vehicle tracks approaching the gully were seen during that time. The farm owner and operator were unaware of the dump's existence, and therefore the guilty persons were quite probably from outside the study area and did not attend the educational meetings.

After the dump was found, abandoning Leslie Page karst window as a monitoring station was considered. Because continuing the station would incur minimal additional costs, however, and because the original purpose of the site remained valid (monitoring the quality of water flowing into the aquifer), the Leslie Page station continued operation. In cooperation with the operator of the farm, KGS personnel attempted to clean up the dump. Approximately 85 intact plastic containers were rinsed, and the rinse water was collected for proper disposal. The clean containers were taken to a recycling center. Approximately another 75 containers were rusted-through steel or degraded, broken, or dirty plastic, so they could not be recycled and were stockpiled for later removal to a landfill. Of the recovered containers, most retained their labels and none were of products containing atrazine, although some contained

alachlor and several contained pesticides not being analyzed for this study. Fewer than 50 containers were not recovered and remained in the gully, but none of the labels indicated atrazine. The container found near the swallow hole, which led to the discovery of the dump, was rinsed with distilled water and analyzed by ELISA for triazines, alachlor, carbofuran, and metolachlor. All four pesticides were detected, but triazines had the lowest relative concentration.

Because only one container containing atrazine was identified from over 200 containers examined, atrazine contamination of groundwater from the dump is thought to be unlikely. Also on the positive side, the spring is partly isolated from the dump because it discharges downgradient of the dump and is bypassed by the runoff from the gully except when, rarely, the entire karst window backfloods. Furthermore, the sampling record does not indicate year-round pesticide occurrence, as would be expected from a dump. Concentrations greater than 10 µg/L of triazines, metolachlor, and carbofuran are absent from the sampling record between November and February of each year, which suggests contamination by these pesticides from the dump is infrequent at worst.

Although the potential for pesticides to leach from the dump into the conduit draining to the spring is thought to be minimal, both sampling points in Leslie Page karst window are downstream of the confluence with the gully. Storms intense enough to produce runoff from the adjacent fields and into the karst window are known to cause water to flow through the dump and past the sampling points. Continuing discharge from the spring would dilute and wash away high concentrations of pesticides from the gully after a storm, however.

Buffer strips were planted or maintained around some sinkholes in crop fields (including at Leslie Page karst window), but other fields were tilled to the sinkhole rim (Fig. 18). The spacing of sinkholes in a large part of the study area is so dense that establishing buffer strips around each would preclude planting row crops. Relatively few of the sinkholes have open throats, however, which are the most direct run-in points. A relatively small total area of new buffer strip was established in the basin under the WQIP (Fig. 19). Vegetated buffer strips are also difficult to maintain in karst settings, because equipment must be maneuvered around them during tillage and planting. The grassed areas are then isolated and cannot be accessed for mowing while crops are growing.

Figure 18. Open-throated sinkhole in newly planted cornfield. Runoff from the field directly enters the groundwater via the sinkhole.

Figure 19. Buffer strip around The Canyon karst window created as a result of the WQIP.

Monitoring Results Since October 1994

Water-quality analyses conducted since October 1994 have focused on constituents identified as significant contaminants in the reconnaissance report: nitrate, triazine herbicides, suspended sediment, and bacteria (Currens, 1999). Since then, water samples have been collected at seven locations in the basin: Pleasant Grove Spring, Leslie Page karst window, upper Pleasant Grove Creek station, George Delaney swallow hole, The Canyon karst window, Joe Harper water well, and Miller School House well. Samples for analysis of major and minor ions continued to be collected quarterly at Pleasant Grove Spring, but were not routinely collected at the other sites. Overall, the water-quality analysis results were similar to those of the reconnaissance report. Basinwide, the principal contaminants remain nitrate, triazine herbicides, suspended sediment, and bacteria. Orthophosphate is also an important groundwater contaminant in the basin.

Nutrients

Nitrate-nitrogen and orthophosphate concentrations, although not a human health concern in the Pleasant Grove Spring groundwater basin, are an environmental issue. Nitrate-nitrogen averaged 5.05 mg/L (median: 5.1 mg/L) for samples collected from all sites between October 1, 1994, and October 1, 1998. The maximum concentration measured was 13.10 mg/L at Leslie Page karst window (sample LPKW0139) on April 20, 1995. The maximum concentration prior to 1994 was 10.8 mg/L, measured at the upper Pleasant Grove Creek station in December 1993. The minimum concentration measured was 0.40 mg/L at Joe Harper water well (sample JHWW0011) on April 2, 1997, following a major high-flow event in late March. The low concentration was probably the result of the time of year, dilution during high flow, and the relatively lower average nitrate concentrations (4.47 mg/L) of the northeastern sub-basin draining from the vicinity of Oakville through Joe Harper water well and The Canyon karst window. Upper Pleasant Grove Creek averaged 5.77 mg/L and reached a maximum of 11.0 mg/L at the George Delaney swallow hole gaging station in late June 1995, during the summer recession of the spring storm season. Accordingly, Pleasant Grove Spring averaged 4.75 mg/L (median: 4.93 mg/L) and reached a maximum concentration of 8.11 mg/L (PGSP0994) on December 1, 1996.

All samples analyzed for orthophosphate were collected at Pleasant Grove Spring, except one. The median orthophosphate concentration was 0.17 mg/L, whereas the minimum was 0.020 mg/L. The maximum ortho-phosphate concentration was 1.4 mg/L (PGSP0957) on August 7, 1996, during the recession of a summer storm at the end of July.

Pesticides

The detection of one or more pesticides in the Pleasant Grove Spring Basin, in both groundwater and surface water, was commonplace during the last 4 years. The EPA has determined maximum contaminant levels for drinking water for approximately 14 pesticides; the sale of some of these is now banned in the United States. Of those pesticides used in the Pleasant Grove Spring groundwater basin, MCL's have been set for atrazine (3 µg/L), simazine (4 µg/L), alachlor (2 µg/L), and carbofuran (40 µg/L). Of those, triazines (atrazine, cyanazine, and simazine combined) exceeded the MCL for atrazine nearly every spring season somewhere in the basin, whereas alachlor rarely exceeded its MCL. Most of the triazine concentration is attributed to atrazine (Currens, 1999). Other pesticides analyzed either did not exceed the MCL, or no MCL had been determined.

The maximum concentrations determined by ELISA for two of the four pesticides in the groundwater basin for the 1994–95 through the 1997–98 water years were from Leslie Page karst window. The maximum triazine concentration determined by ELISA before October 1994 was 44.0 µg/L, measured May 4, 1993 (PGSP0216), although higher concentrations have been detected at Pleasant Grove Spring since then. For the 1994–95 through 1997–98 water years, the average triazine concentration for the basin was 6.08 µg/L, but the median was only 1.15 µg/L. The maximum concentration of any pesticide detected for the basin, over the entire 7-year project period, was 393 µg/L of triazines from runoff of a modest storm (2.31 cm [0.91 in.]) on April 16, 1998, at Leslie Page karst window (LPKW0402). This storm followed the planting of corn for the first time since 1994 in a field that drains overland directly into the karst window. There is some uncertainty whether the herbicides detected at Leslie Page karst window from mid-1996 are from field runoff or the pesticide container dump discussed above; however, the pesticide detections, except for alachlor, are consistent with the crops surrounding the karst window at the time the sample was collected. The maximum alachlor concentration determined by ELISA for the basin, 2.51 µg/L, was also from sample LPKW0402. The maximum alachlor concentration prior to October 1994 was 12.0 µg/L, which was measured at Pleasant Grove Spring on May 4, 1993 (PGSP0216). The average for the basin was 0.15 µg/L, whereas the median was 0.07 µg/L, reflecting the predominance of below-detection analyses. The maximum carbofuran concentration determined by ELISA for the basin, also from Leslie Page karst window, was 3.99

µg/L for a sample collected May 8, 1995. Carbofuran for the April 16, 1998, event at Leslie Page karst window was below detection in all samples. The maximum carbofuran concentration before October 1994 was 7.4 µg/L on April 30, 1994 (PGSP0430). The average carbofuran concentration was 0.11 µg/L, whereas the median was 0.085 µg/L.

The maximum metolachlor concentration determined by ELISA was 29.60 µg/L from a sample collected March 18, 1997, at Pleasant Grove Spring (PGSP1043); it exceeded the maximum from before October 1994 of 9.6 µg/L (PGSP0216; May 4, 1993). The average basin-wide metolachlor concentration since October 1994 was 0.94 µg/L, and the median was 0.18 µg/L. The significantly lower medians for pesticides determined by ELISA, compared to the averages, reflect the skewed distribution of the data as a result of the large number of samples with concentrations at or below detection limits.

At Pleasant Grove Spring, the principal monitoring site in the basin, the maximum concentration of triazines observed was 62.20 µg/L, for a sample collected May 7, 1996 (PGSP0844), whereas the minimum concentration was 0.28 µg/L for a sample collected December 17, 1996, only 7 months later. The average triazine concentration was 5.39 µg/L, and the median was 1.24 µg/L. The maximum alachlor concentration was 0.94 µg/L, and the maximum carbofuran concentration was 1.18 µg/L. The maximum concentration of metolachlor was 29.6 µg/L, but the average concentration was 0.77 µg/L and the median only 0.22 µg/L. An ad hoc suite of samples was collected at Pleasant Grove Spring during a high-flow event in June 1996 and was analyzed by ELISA for chlorpyrifos; concentrations were below 0.2 µg/L.

Samples for gas chromatograph analysis of pesticides were collected manually at Leslie Page karst window and Pleasant Grove Spring. The maximum concentration of atrazine in the basin determined by GC since October 1994 was 20.51 µg/L on May 7, 1996 (PGSP0842). The maximum metolachlor concentration was 3.75 µg/L on April 2, 1997 (LPKW0319). Metribuzin, trifluralin, and simazine were also detected by GC in concentrations less than 0.1 µg/L.

The analysis of duplicate samples for pesticides by gas chromatography and ELISA continued on a quarterly basis through the end of the project. These analyses were continued to verify and expand upon the linear relationship between the two analytical methods established prior to October 1994 (Currens, 1999). The strong linear positive correlation for triazines and metolachlor established in the earlier report was confirmed.

Suspended Sediment

Samples for suspended sediment were collected by automatic sampler at two locations: Leslie Page karst window and Pleasant Grove Spring. The relationship between the sediment concentration as collected by the sampling machines and the concentration collected by standard methods is unknown for Leslie Page karst window, but the relationship is nearly one to one at Pleasant Grove Spring. The maximum suspended sediment concentration for the groundwater basin was 3,267 mg/L, from storm runoff entering the swallow hole at Leslie Page karst window on April 27, 1997 (LPKW0331). The maximum at Pleasant Grove Spring was 3,073 mg/L on May 9, 1995 (PGSP0625). The previous maximum total suspended sediment was 2,278 mg/L on April 29, 1994 (PGSP0429). The average suspended sediment concentration for Pleasant Grove Spring for the 1994–95 through 1997–98 water years was 217.8 mg/L, and the median was 59 mg/L.

Bacteria

Since 1994, bacteria counts in the Pleasant Grove Spring groundwater basin have continued to exceed drinking-water standards and frequently exceed the standard for water-supply sources (2,000 col/100 mL). The slime growth on instrumentation discussed earlier is further evidence of organic waste pollution. The maximum bacteria count determined for the basin during the entire study was 810,000 col/100 mL of fecal streptococci at George Delaney swallow hole on June 20, 1995 (GDSW0033) during a modest storm occurring during the recession of two consecutive high-flow events earlier in June. Prior to October 1994, the maximum was 24,000 col/100 mL of fecal streptococci on February 26, 1992 (GDSW0006). For the basin as a whole (Pleasant Grove Spring, Leslie Page karst window, George Delaney swallow hole, upper Pleasant Grove Creek, The Canyon karst window, Joe Harper water well sampling sites), fecal coliform averaged 3,839 col/100 mL and fecal streptococci averaged 13,437 col/100 mL.

Topical samples were also collected at Pleasant Grove Spring during high-flow events, when bacteria counts are expected to be elevated. The median values were 1,200 col/100 mL of fecal coliform and 914 col/100 mL of fecal streptococci. When only monthly values are considered, the medians were 400 and 640 col/100 mL, respectively. For all samples, the average fecal coliform count for Pleasant Grove Spring was 6,837 col/100 mL, and the average fecal streptococci count was 20,097 col/100 mL.

Three high-flow events were sampled at Pleasant Grove Spring to determine the fecal coliform/fecal streptococci ratio as an indicator of a suspected shift from animal toward human sources following high
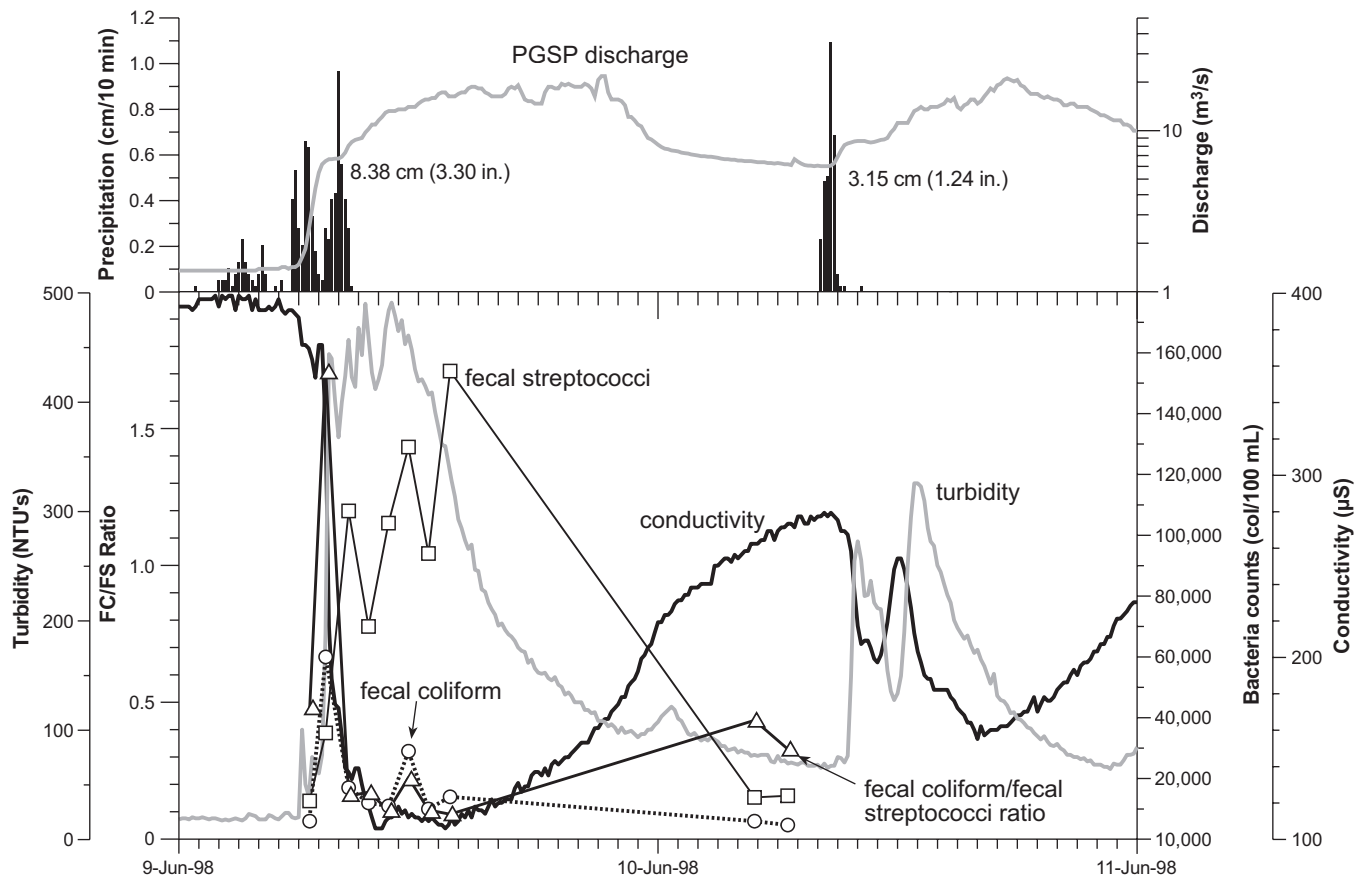
Figure 20. The occurrence of high bacteria counts compared to discharge, turbidity, and conductivity at Pleasant Grove Spring during the June 1998 event. Note the increase in fecal coliform during the initial rise in stage and the increase in fecal streptococci later in the event.

flow. Unfortunately, on each attempt the sampling was either begun late in the event or was stopped before the event was over in order to accommodate the laboratory operating schedule or maximum holding time for the earliest sample. The best-represented event was June 9, 1998 (Fig. 20). The fecal coliform/fecal streptococci ratio briefly shifted toward human influence early in the event, then returned to animal-dominated. The results for the March 5, 1996, event also indicated a shift toward the higher ratio early in the event, followed by a drop toward the animal-dominated range. The ratio, however, reached the fourth highest value recorded in the basin, 9.80, during this event (PGSP0761). During the May 7, 1996, event the ratio did not reach the human-dominated range, although it did shift in that direction late on the recession of the hydrograph. The highest ratio recorded for Pleasant Grove Spring was 13.67 on April 11, 1995 (PGSP0595). This sample was collected during a low-flow period, and the bacteria counts were also atypically low. Because of the low counts, the ratio may have been skewed by a minor error in the analysis. If accurate, however, the ratio suggests the dominance of human waste during the prevailing low-flow conditions.

The fecal coliform/fecal streptococci ratio was expected to make a pronounced shift toward the human-influenced end of the ratio scale on the recession of storm hydrographs, as suggested by earlier results. The shift in ratio during the rising limb of discharge hydrographs, however, was unexpected. It is clear that the ratio shifts toward animal-dominated values during the interval when overland runoff is arriving at Pleasant Grove Spring. Therefore, animal waste is probably the principal cause of the high bacteria counts during the arrival of overland runoff, but there is also a human source. The most probable source of human waste is from straight pipes discharging into sinkholes, or from improperly functioning septic tanks. Sewage has a relatively constant inflow rate, because rainfall is not always needed for its induction into the epikarst or aquifer. Furthermore, it can linger in the epikarst and smaller conduits during low flow. During a storm the recharge into the epikarst mobilizes the accumulated human waste, and transports it to the spring.

Most housing in the groundwater basin is in Oakville, distant from Pleasant Grove Spring; however, other housing is scattered throughout the basin, and some is closer to Pleasant Grove Spring. Therefore, human waste dominates at Pleasant Grove Spring during the very early part of a high-flow event, because stores in the conduits have human-influenced ratios, while overland runoff from pastures in the groundwater basin has not had time to sink and reach the spring. The ratio shifts to animal-dominated while the runoff arriving from pastures is discharged, and shifts again to human-influenced when runoff has ceased. During drought, although the total bacteria counts are among the lowest, the fecal coliform/fecal streptococci ratio tends toward the human-dominated range.

Miscellaneous Analyses

Although the systematic sampling of wells in the basin was beyond the budget of the project, some wells were sampled opportunistically. Data for three wells are reported in Currens (1999) or are on file at KGS. One well, Miller School House, was routinely sampled one or two times each spring beginning in April 1994. The well is near the east-central groundwater basin boundary of Pleasant Grove Spring and upgradient of most agricultural activity. It is a drilled well, with steel casing from the surface to the top of bedrock and an open hole to a total depth of 25.6 m (84.2 ft). The casing is cut off at ground level and is capped with a rock. Nevertheless, the well has some of the lowest concentrations of agricultural chemicals among sites sampled in the basin. Nitrate-nitrogen concentrations of seven samples collected from April 1994 through May 1998 averaged 1.84 mg/L. Triazines determined by ELISA averaged 0.30 µg/L; three samples were below detection limits and maximum concentration was 0.91 µg/L. Carbofuran and alachlor were below detection limits for all samples, whereas metolachlor had one sample above detection at 0.57 µg/L. The well was sampled for bacteria in April 1996 (MSHW0005). Fecal coliform was 364 col/100 mL and fecal streptococci was 1,636 col/100 mL. The high bacteria count may be due to the construction of the well, including the lack of a secure cap, but there is also a dog kennel within 30 m (100 ft) of the well. During the few occasions the site was visited while it was raining, overland runoff from the kennel was not observed flowing into the well bore, however.

Rainfall was collected for analysis at Pleasant Grove Spring intermittently throughout the project. Five samples were collected since October 1994, and most were analyzed for pesticides (by ELISA) and nitrate-nitrogen. Two samples collected in June 1995 were below detection for triazines and less than 0.50 mg/L for nitrate-nitrogen. A sample collected in May 1996

measured less than 1 µg/L for all pesticides determined by ELISA and only 0.14 mg/L of nitrate-nitrogen. Two samples collected in April and May 1997 (RAIN0011 and RAIN0012) had significant concentrations of triazines and metolachlor, however. The sample collector was deployed for 7 days in both cases. Sample RAIN0011 represented 0.94 cm (0.37 in.) of precipitation and RAIN0012 represented 1.04 cm (0.41 in.). Alachlor and carbofuran were near or below detection limits in both samples. Sample RAIN0011 had 4.18 µg/L of triazines, 2.76 µg/L of metolachlor, and 0.66 mg/L of nitrate-nitrogen; sample RAIN0012 had 1.69 µg/L of triazines, 0.88 µg/L of metolachlor, and 0.66 mg/L of nitrate-nitrogen. A field adjacent to and northeast of Pleasant Grove Spring was planted in corn for the first time in several years and was sprayed with Bicep in the spring of 1997. Spray from the field probably drifted into the funnel of the rain collector. Samples collected as early as 6 weeks following the spring application period showed essentially no triazines. Furthermore, other samples also collected in May, but when chemicals were being applied farther away, also had very low concentrations of triazines. The rainfall analyses indicate there is little airborne pesticide transport except locally and immediately after application. The effect on groundwater samples collected at Pleasant Grove Spring is thought to be negligible, because the samples from May 1997 were all collected with an automatic sampling machine and the intake was 6 ft underwater and directly in the outflow from the cave. The sample bottles are protected from airborne contamination by the cabinet of the sampling machine.

Comparative Evaluation of Pre-BMP Versus Post-BMP Water Quality

Descriptive statistics and annual mass flux (i.e., pollutant loading) of several constituents of probable agricultural origin were calculated for Pleasant Grove Spring for the pre- and post-BMP periods. The mass flux was also estimated for upper Pleasant Grove Creek (George Delaney swallow hole supplemented with upper Pleasant Grove Creek station) and Leslie Page karst window. The flux was calculated for the 3 water years prior to implementation of best management practices and for the 3 years the BMP's were adopted. For this report, the flux for Pleasant Grove Spring was calculated for the 1992–93 through 1997–98 water years, using the revised discharge rating curve. The upper Pleasant Grove Creek flux, representing the contaminant load sinking underground at George Delaney swallow hole, was calculated using the revised discharge rating

curve for George Delaney swallow hole and the three rating curves for upper Pleasant Grove Creek station, which are dependent on channel conditions (as discussed earlier). Similarly, the mass flux for Leslie Page karst window was estimated for the 1995–96 through 1997–98 water years, using rating curves for pre- and post-weir installation.

Flow-weighted averages derived from flux calculations were used prominently in the reconnaissance report (Currens, 1999) to characterize the concentration of various constituents discharged from Pleasant Grove Spring. The flow-weighted average is calculated by dividing the annual mass flux by the total annual discharge, and represents the average annual exposure of aquatic plants and animals to contaminants. The flow-weighted averages for dissolved constituents generally paralleled arithmetic averages for dissolved constituents, whereas the constituents associated with high flow (triazines and sediment) varied more widely from these statistics. The differences are partly caused by the difficulty of monitoring mass flux by using discrete samples, but are more likely caused by the additional variability introduced by large changes in annual discharge compared to a relatively constant source of chemicals. The flow-weighted average for atrazine-equivalent proved difficult to relate to crop patterns, and a 2-year cycle of alternating higher and lower atrazine-equivalent flow-weighted averages, apparent from 1991 to 1994 at Pleasant Grove Spring, did not continue in 1995 and subsequent years. Therefore, the flow-weighted average

Figure 21. High flow at Pleasant Grove Spring during the February 4, 1997, event.

is not emphasized in this report, and although presented in Table 5, is not discussed further.

High-Flow Event Monitoring and Mass Flux

Pleasant Grove Spring. Water-quality indicators and pollutants change magnitude rapidly during high-flow events at karst springs (Fig. 21). Continuous monitoring of water temperature, pH, conductivity, and turbidity helps characterize the source and travel time of pollutants to Pleasant Grove Spring. Runoff from spring and summer storms elevates water temperature and turbidity, and decreases pH and specific conductivity. Winter storms decrease water temperature. Irregular

Table 5. Annual statistics for contaminants discharged in significant concentrations from Pleasant Grove Spring calculated from the complete sample set.

| Water Year | Triazines | | | | Nitrate-Nitrogen | | Total Suspended Solids | Ortho-phosphate |
	Average (µg/L)	Median (µg/L)	Geometric Average (µg/L)	Flow-Weighted Average (µg/L)	Average (mg/L)	Flow-Weighted Average (mg/L)	Median (mg/L)	Median (mg/L)
1991–92	1.64	1.40	1.42	NA	4.2	NA	NA	0.036
1992–93	4.84	0.83	1.38	4.50	4.98	5.0	45	0.045
1993–94	1.85	1.30	1.52	0.99	4.86	5.7	65	0.053
1994–95	6.61	1.62	2.72	4.11	4.57	4.9	189	0.051
1995–96	4.67	1.05	1.44	1.84	4.88	5.0	46.5	NA
1996–97	3.37	1.17	1.54	1.68	4.56	4.7	33	0.254
1997–98	7.27	2.21	2.74	4.33	4.77	4.79	64	0.153

NA=not available

rises and falls in the water-quality measurements are attributed to variations in rainfall distribution and intensity across the surface of the groundwater basin. For example, the first change recorded by the YSI 3800 water-quality logger is frequently caused by surface run-off in the local surface catchment of the spring rise pool. This deflection is absent when a summer thunderstorm rains only in the headwaters area. Also, when a sudden, intense, widely distributed rainfall occurs, water-quality parameters are deflected smoothly and without any temporary reversals. The delay during high-flow events between hydrograph peaks at George Delaney swallow hole and changes in turbidity, conductivity, and temperature at Pleasant Grove Spring closely approximate the travel times determined by quantitative groundwater dye tracing (Fig. 17).

The December 16–17, 1996, event is an excellent example of the effect the distribution of precipitation has on the hydrograph and chemograph response at Pleasant Grove Spring (Fig. 22). A slow-moving cold front ended a warming trend, which peaked with a high air temperature of 19.3°C on December 15; a steady light rain began on the 16th, continuing through noon on the 17th, with only one minor period of more intense rain late in the storm. Air temperatures rapidly fell below freezing on the evening of the 17th, effectively stopping overland runoff. The light steady rain resulted in a modest high-flow event, with discharge at Pleasant Grove Spring peaking at 26 m³/s (923 ft³/s). The stage hydrograph for George Delaney swallow hole and the turbidity chemograph rise smoothly to modest peak values when compared to hydrographs and chemographs of other storms. The water temperature declines smoothly in response to the cold rain, and the conductivity also decreases. The smooth curves do not exhibit any structure evident of contrasting water quality caused by confluent flow from major tributaries. The uniform chemographs suggest that flow in the conduit from George Delaney swallow hole dominated the chemograph responses at Pleasant Grove Spring.

The calculation of mass flux during high flow is critical to quantifying the water quality of karst springs, because the concentrations of most constituents change significantly over the course of an event. Significant
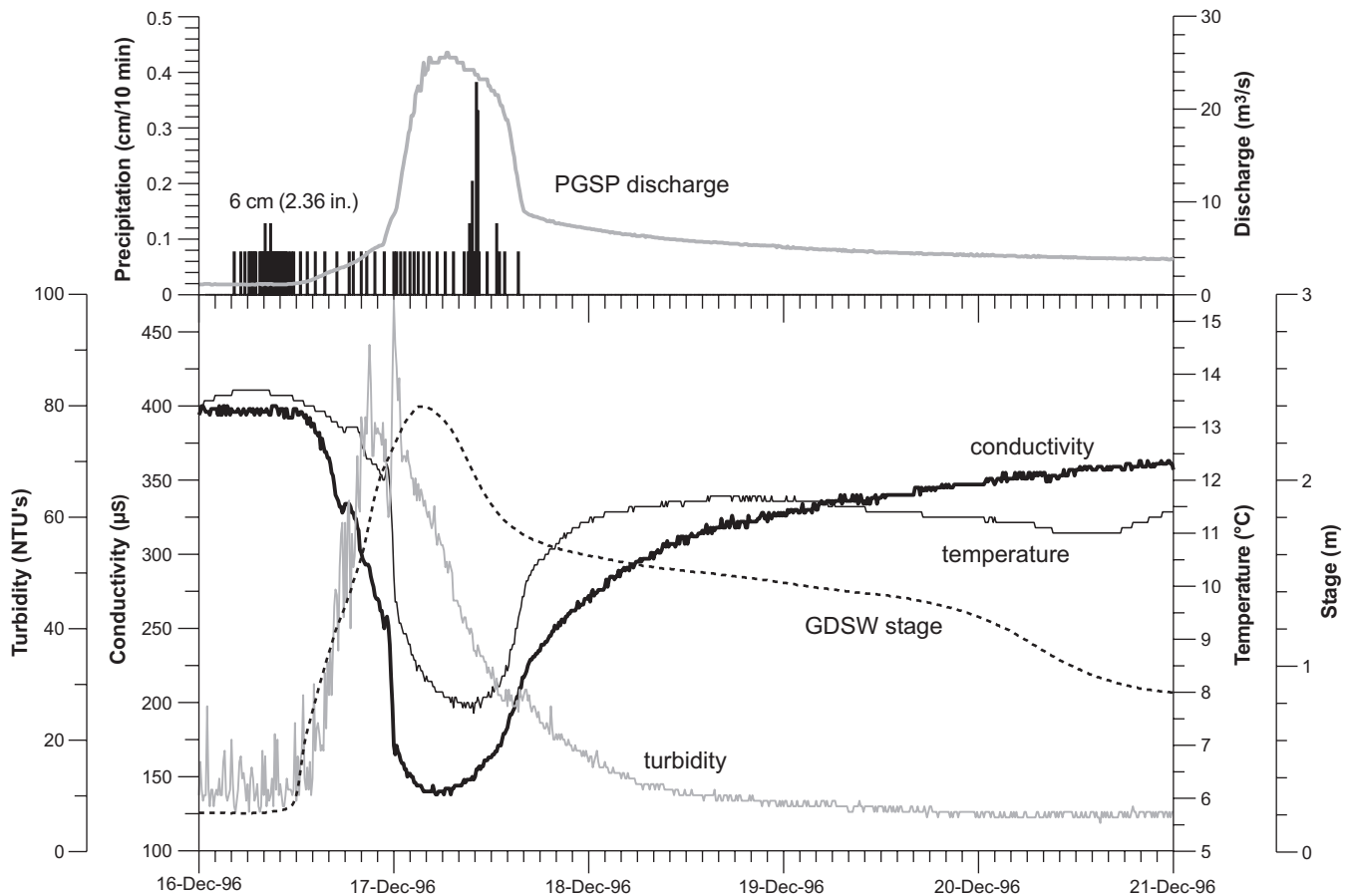

Figure 22. Hydrograph and chemographs for Pleasant Grove Spring for the December 1996 event. The smooth graph curves do not exhibit any structure evident of contrasting water quality caused by confluent flow from major tributaries.
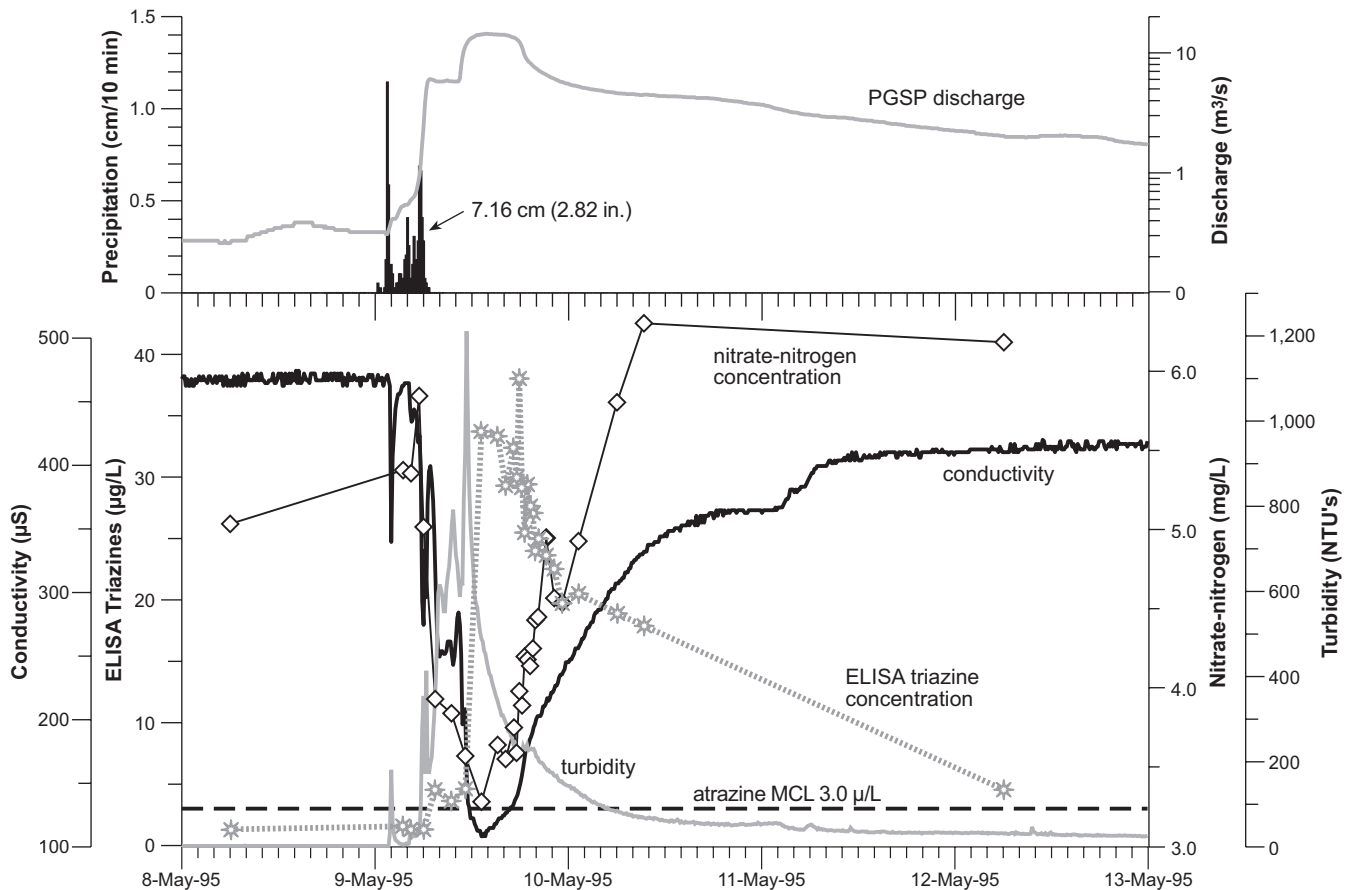
Figure 23. Concentrations of triazines measured by ELISA change rapidly during springtime high-flow events at Pleasant Grove Spring. Shown are hydrographs and chemographs for the May 1995 high-flow event. Note the peak in triazines occurs after the peak in turbidity.

quantities of contaminants associated with runoff, particularly pesticides, may be discharged during a single storm following ill-timed application to fields. For example, the May 1995 high-flow event at Pleasant Grove Spring discharged 24.5 kg of atrazine-equivalent during the 72-hour period from 00:00 hours on May 9 through 00:00 hours on May 12 (Fig. 23). The atrazine-equivalent discharged during this storm represented 39 percent of the annual atrazine-equivalent for the 1994–95 water year.

The importance of the connection between major springtime storms and triazine peak concentrations is obvious, but deserves restatement because of its implications for managing nonpoint-source runoff in karst areas. A high-flow event in 1996 is one of the best-documented and thoroughly sampled examples of the relationship between mass flux of triazines and high flow. From 00:00 hours on May 7, 1996, to 00:00 hours on May 10, 26.94 kg of atrazine-equivalent was discharged from Pleasant Grove Spring. In contrast, during all of the 1995–96 water year, 36.42 kg of atrazine-equivalent was discharged from the spring. The May 1996 event

accounted for 73 percent of the total annual mass flux of atrazine-equivalent for the 1995–96 water year. Typically, nitrate-nitrogen concentrations are reduced during high-flow events, whereas other constituents also associated with field runoff are increased.

Several patterns in the shifting of constituent concentrations repeat themselves in the graphs of high-flow events (Fig. 23). The increase in triazine concentration is delayed until near the peak of the discharge hydrograph, whereas the nitrate-nitrogen concentration generally decreases with increasing discharge. For most springtime storms, the peak in triazine concentration follows the peak in turbidity or suspended sediment by 4 to 6 hours. This lack of correlation between suspended sediment and triazine concentrations is discussed in Currens (1999), and is indirect evidence that most triazine transport is in a dissolved or colloidal phase, as opposed to being sorbed on filterable suspended sediment. Once the runoff volume arriving at Pleasant Grove Spring begins decreasing, as indicated by the records for turbidity, conductivity (Fig. 23), and water temperature (not

shown), the triazine concentration gradually returns to pre-storm levels.

Following the dilution of the nitrate-nitrogen concentration during peak discharge to the 2 to 3 mg/L range, the concentration returns to pre-event concentrations (5 mg/L), then often increases slightly to 6 or 7 mg/L for 1 or 2 days. The increase is thought to be caused by the late arrival of water with higher nitrate-nitrogen concentration resulting from enhanced leaching of nitrate-nitrogen from soil and water displaced from storage in the soil and epikarst (subsoil and regolith zone). Water stored in soil below the root zone underlying crop fields may have nitrate-nitrogen concentrations as high as 50 mg/L (Canter, 1997; Steinheimer and others, 1998). As the high flow and dilution by runoff ends, the nitrate-nitrogen that was stored in the epikarst and smaller conduits has had time to be partially displaced by water infiltrating through the soil and more rapidly through macropores. Displacement of the soil and epikarstic stores results in the concentration of nitrate-nitrogen rising again as the displaced water arrives at Pleasant Grove Spring. When the displacement of nitrate-nitrogen from the soil and epikarst slows, the concentration at the spring returns to the typical 5 mg/L range.

For some high-flow events there is an initial increase in the nitrate-nitrogen concentration at Pleasant Grove Spring from a baseline concentration of 5 to near 6 mg/L before dilution by later-arriving runoff (Fig. 23). There are two possible causes of the nitrate-nitrogen spike. The first is water displaced from stores in the larger conduits and major tributaries. Inspection of many of the storm graphs indicates the spikes of greatest magnitude are preceded by an earlier, less significant precipitation event, which would have leached water from soil and epikarst to the conduits. The second potential cause is the slow-flowing channel of upper Pleasant Grove Creek. As noted by Currens (1999), some of the highest concentrations of nitrate-nitrogen in the basin have been measured at the upper Pleasant Grove Creek station. Because flow in upper Pleasant Grove Creek is slow, and was partly impounded when there was a beaver dam, dissolved constituents in the water may have been concentrated by evaporation when weather conditions permitted. Upstream runoff from storms will displace the higher-nitrate water stored in the channel near upper Pleasant Grove Creek, resulting in its early arrival at the spring. As the high-flow event proceeds, dilution overwhelms the relatively small volume of high nitrate-nitrogen water stored in the channel.

Leslie Page Karst Window. Changes in water quality during high-flow events at Leslie Page karst window are not as well characterized as those at Pleas-ant Grove Spring because of the less frequent sampling schedule, the absence of continuous water-quality monitoring equipment, and the gaps and uncertainties for the inflow record. Some high-flow events were well documented, however, and they illustrate the importance of basin hydrology and land use on the characteristics of inflow into the aquifer.

The maximum concentration of any pesticide detected in the basin for the entire 7-year project period was 393 µg/L of triazines from runoff of a moderate storm (2.31 cm [0.91 in.]) on April 16, 1998 (LPKW0402). This relatively minor flow event was quickly followed by a second minor event and then a more significant event (4.65 cm [1.83 in.]), which resulted in short-lived flooding of the karst window. The concentrations measured in the three following samples, while lower, were also significant. Figure 24 illustrates the stage hydrograph at Leslie Page karst window and the occurrence of samples analyzed for triazines and nitrate-nitrogen. The clefts in the inflow hydrograph are caused by the undefined relationship of stage to inflow during backflooding from the swallow hole. The flux graph reflects the hydrograph, because the rate of water flow has a significant effect on the calculation of mass flux, except where the lower triazine concentration reduces the flux in any case. Nitrate-nitrogen concentration was also higher for the first high-flow event, much lower during the later high-flow event, then returned to higher concentrations as overland runoff diminished and the dominant effect of groundwater discharge from the spring was reestablished. The stage hydrograph indicates that the high stage at the time the sample was collected was not from a flow reversal. Therefore, the reduction in concentration of triazines and nitrate-nitrogen is likely caused by depletion of chemicals easily mobilized from the field. As a result, subsequent storms transported lesser quantities of chemical. Corn was planted immediately adjacent to the karst window, and gullies had formed in the cornfield and through the grass buffer surrounding the karst window as a result of late winter–early spring storms. This suggests that when buffer strips are used they must be maintained to prevent channels being eroded through them, which render the strips relatively ineffective.

The high concentration of triazines in LPKW0402 could be a consequence of the previously discussed dump; however, the evidence indicates otherwise. The concentration of triazines in LPKW0402 is easily explained by the presence of corn adjacent to the karst window. Furthermore, atrazine application in the basin, as inventoried by the WQIP, was high in the spring of 1998. Significant concentrations of triazines were not detected at Leslie Page karst window through the winter of 1997–98, as might be expected if the dump were the
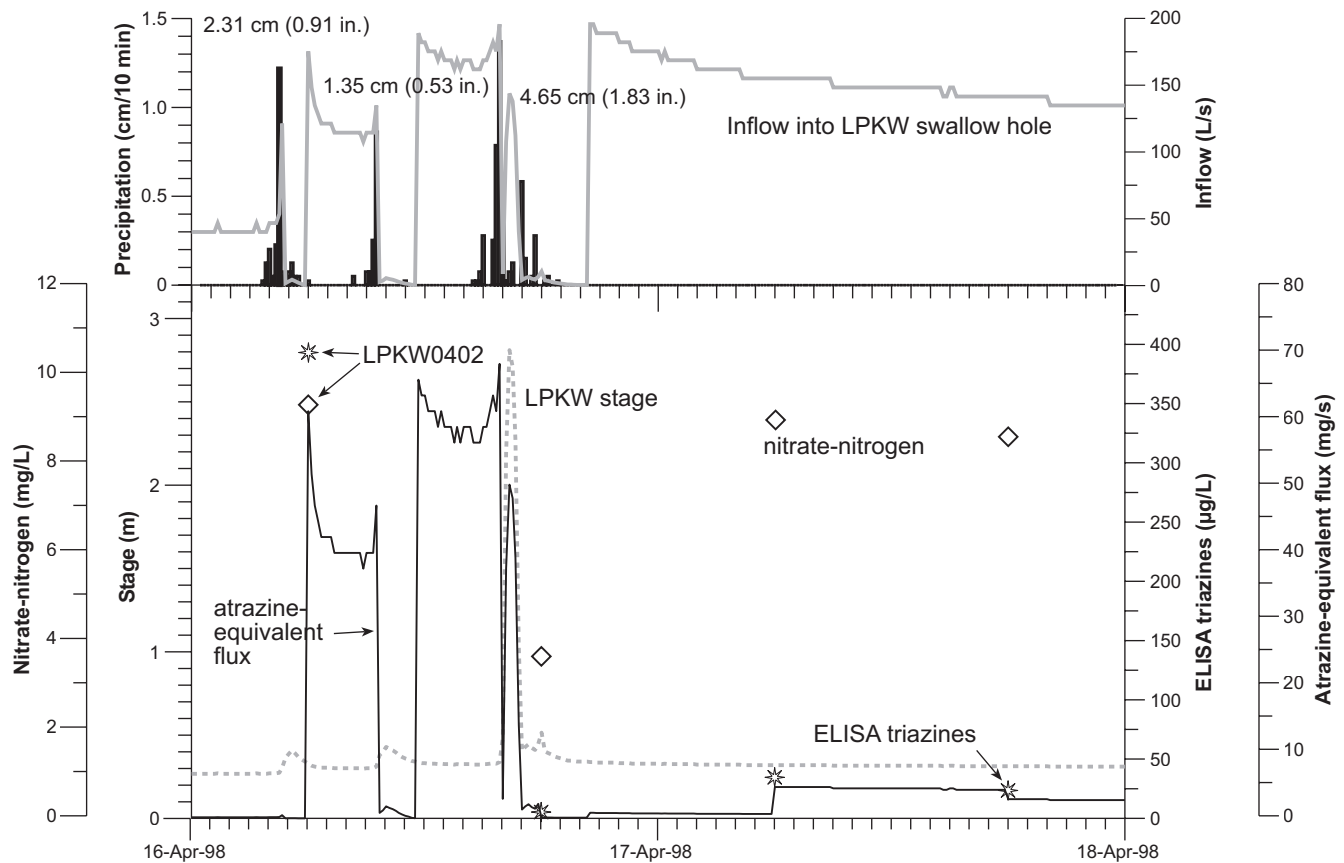
Figure 24. The highest concentration of triazines detected during the study was measured in runoff entering the swallow hole at Leslie Page karst window during the April 1998 high-flow event.

source. High concentrations of triazines were measured at Pleasant Grove Spring throughout the spring of 1998. Also, high concentrations of triazines were measured at The Canyon karst window (TCKW0072) on April 15, 1998, and more notably at George Delaney swallow hole on April 15 (GDSW0012), April 16 (GDSW0113), and particularly on April 17 (GDSW0114) at 40.4 µg/L. Joe Harper water well was sampled May 12, 1998: 41.6 µg/L of triazines was measured. None of these sites receive flow from Leslie Page karst window. This shows that the triazines measured at Pleasant Grove Spring originated from areas of the groundwater basin in addition to Leslie Page karst window.

Annual Mass Flux

Pleasant Grove Spring. The annual mass flux of atrazine-equivalent triazines, nitrate-nitrogen, and suspended solids discharged from Pleasant Grove Spring was significant each year (Table 6). Atrazine-equivalent recovery at Pleasant Grove Spring averaged 4.2 percent of the estimated quantity of atrazine applied between 1993–94 and 1997–98. The mass flux of carbofuran was negligible, but the annual mass flux of metolachlor was

important. Mass flux of alachlor, orthophosphate, and bacteria was not calculated, as discussed previously. Graphs of atrazine-equivalent and nitrate-nitrogen flux and triazine and nitrate-nitrogen concentrations for each water year are presented in Figures 25 through 30. Graphs of total suspended solids flux are not presented; unlike the case for triazines, the peaks in suspended sediment occur year round, whenever loosened soil is susceptible to erosion. The annual statistics for nitrate-nitrogen and triazines (atrazine-equivalent) are plotted for each year of the project on Figure 31. There is no discernible trend on the graph for geometric average of triazines, average nitrate-nitrogen, or nitrate-nitrogen annual flux. The atrazine-equivalent flux increased distinctly over the period of the WQIP.

One of the assumptions used in planning this project was that atrazine was applied only to corn and that almost all corn received atrazine applications. More important, it was also assumed that atrazine was applied at an average rate near the rate recommended by the University of Kentucky College of Agriculture and varied little from year to year. Therefore, the total recovery of atrazine should correlate strongly with the

Table 6. Total annual precipitation, discharge, and mass flux of contaminants detected in significant quantities at Pleasant Grove Spring.

Water Year	Precipitation (cm)	Discharge (m³)	Atrazine-equivalent (kg)	Metolachlor (kg)	Nitrate-nitrogen (metric tons)	Suspended sediment (metric tons)
1992–93	87.8	10,228,000	46.01	5.97	51.13	2,124
1993–94	132.6	31,552,000	31.13	0.89	180.62	3,802
1994–95	110.0	15,292,000	62.82	3.92	75.03	2,255
1995–96	136.8	19,775,000	36.42	2.25	98.69	1,591
1996–97	140.2	42,544,000	70.52	6.61	197.63	4,553
1997–98	135.8	32,914,000	142.52	7.79	157.65	3,625

percentage of the basin planted in corn, all other factors being equal. Although the WQIP record-keeping has shown the first two assumptions to be largely true, it also showed the average rate of atrazine application to corn varied significantly over the 3 years of WQIP record-keeping. Accordingly, the relationship of various measures of atrazine (triazine) occurrence at Pleasant Grove Spring to the percentage of the basin planted in corn is weak. The flow-weighted average of atrazine-equivalent, the total annual flux of atrazine-equivalent, the average triazines, the median triazines, and the geometric average of triazines all have low correlation coefficients relative to the percentage of the basin growing corn when data for all 6 years are used.

The topography and hydrogeology of the groundwater basin, and the subsequent effect on the distribu-
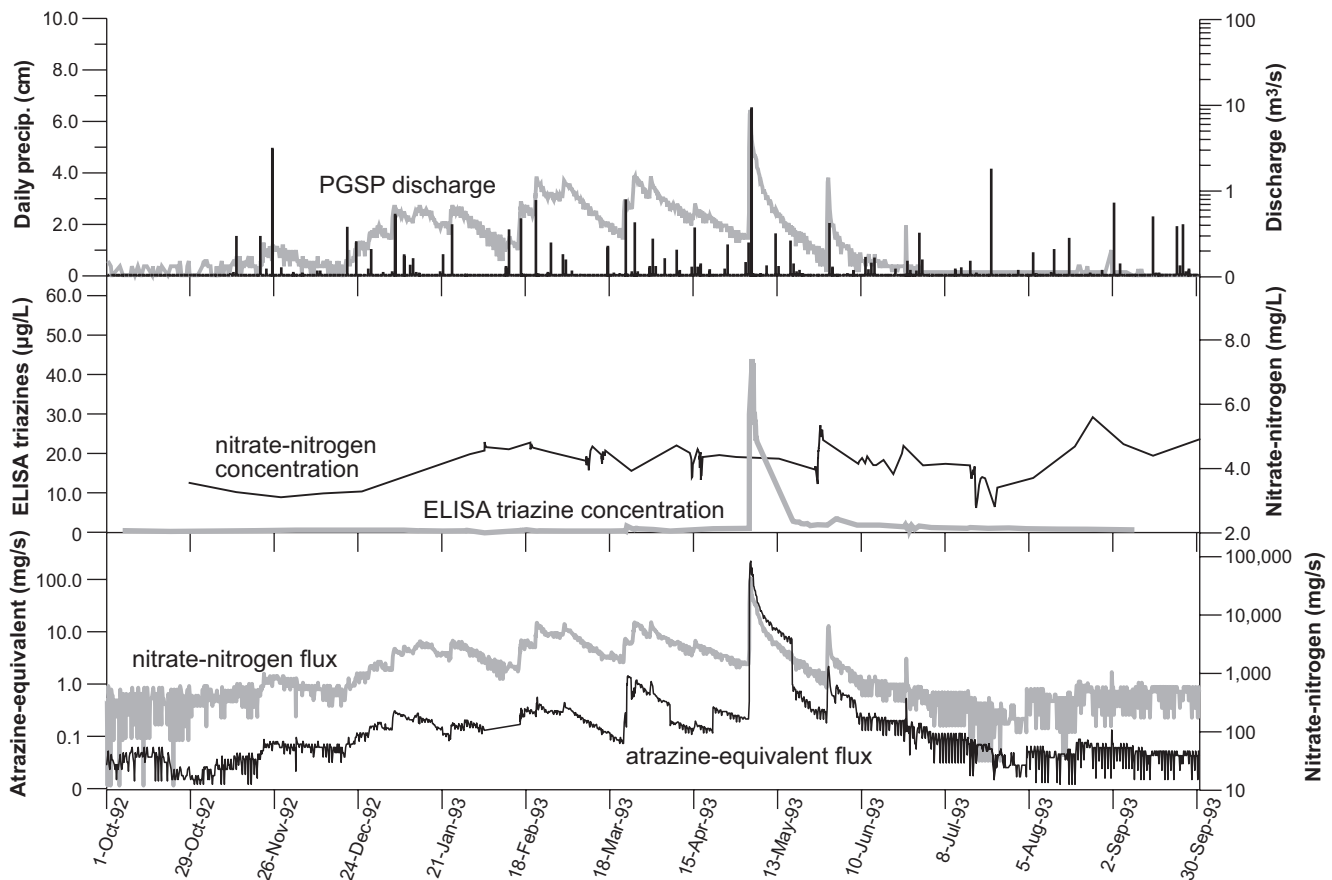

Figure 25. Plot of daily precipitation, discharge, nitrate-nitrogen concentration and flux, and ELISA triazine concentration and atrazine-equivalent flux for Pleasant Grove Spring for the 1992–93 water year.
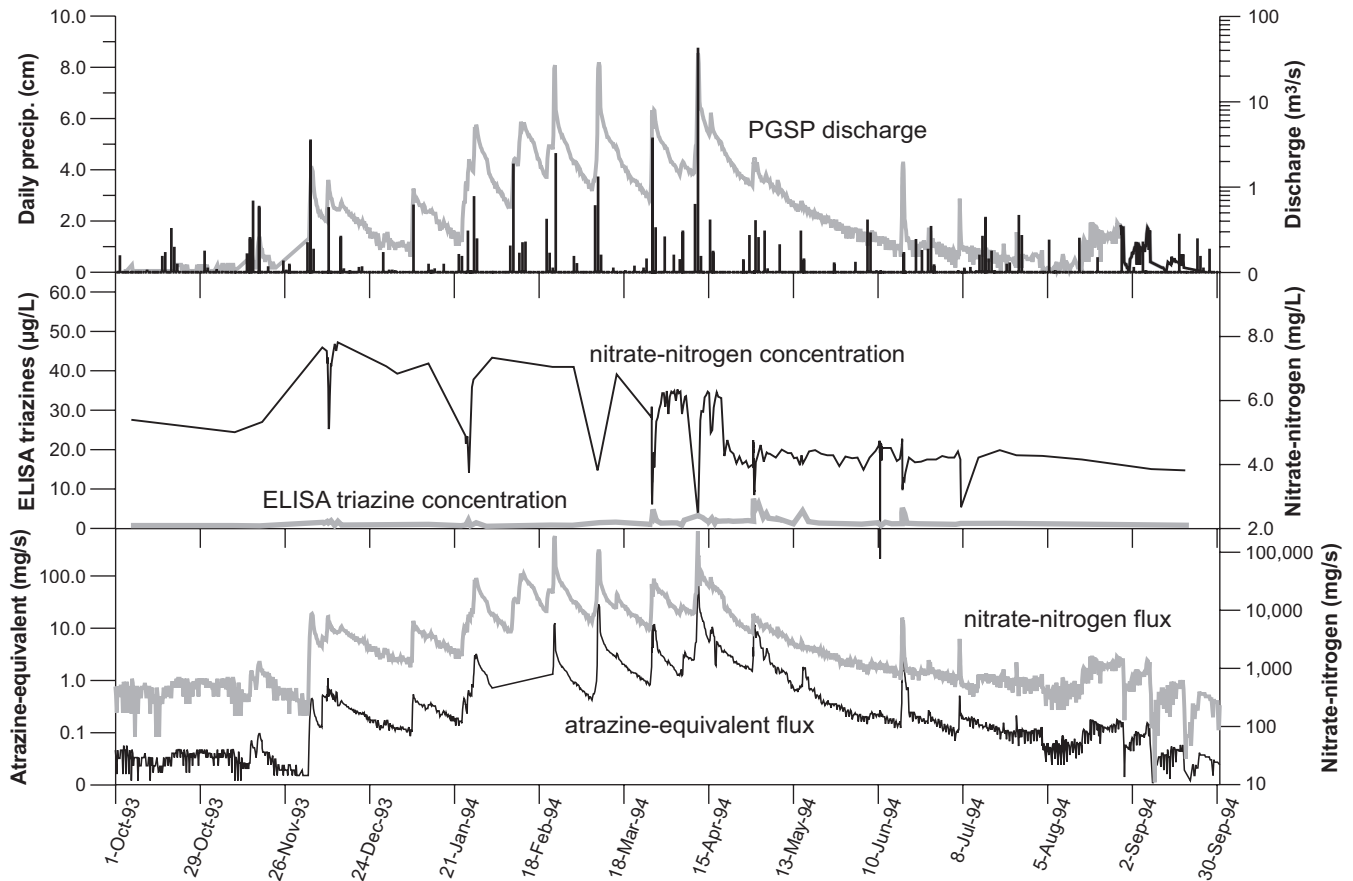
Figure 26. Plot of daily precipitation, discharge, nitrate-nitrogen concentration and flux, and ELISA triazine concentration and atrazine-equivalent flux for Pleasant Grove Spring for the 1993–94 water year.

tion of crops, is also thought to affect the relationship between chemical applied and chemical reaching groundwater. In the slow-flow, headwaters part of the basin there are relatively few open-throated sinkholes, a more integrated surface drainage system, and relatively little unsaturated void space for storage in the epikarst or carbonate aquifer because of the shallow depth to groundwater. A larger percentage of the land surface in the headwaters area is planted in row crop than in the downstream area (average of 78 percent versus 68 percent) because the fields are relatively uninterrupted by sinkholes and are easier to cultivate. During prolonged storms, infiltration saturates the epikarst, forcing precipitation to take overland routes, and the normal surface drainage system concentrates flow into upper Pleasant Grove Creek. The stream directs runoff into the groundwater at George Delaney swallow hole, which rapidly transports the pulse of triazine-laden water to Pleasant Grove Spring. In the downstream, conduit-flow-dominated regime, the open-throated sinkholes with small surface catchments provide multiple run-in points. Observations of corn being planted adjacent to open-throated sinkholes and significant concentrations

of atrazine being used on these fields suggest that a few open-throated sinkholes surrounded by a small percentage of the cornfields may measurably influence the concentration of pesticides measured at Pleasant Grove Spring.

The seasonal pattern of occurrence of triazine at Pleasant Grove Spring is nearly identical from year to year. Concentrations of triazine near or above 1 µg/L appear beginning in March and continue through June, with the highest concentrations between April 15 and May 15. Peak concentrations typically occur during high-flow events that follow periods of dry weather when chemical-application equipment can be driven on the fields. Triazine concentrations decrease at the sampling sites as the growing season progresses because of assimilation by plants, depletion, and degradation. Other pesticides applied in quantity in the basin that have leaching or runoff potential and a sufficiently long half-life show a similar pattern in their detection. Significantly, the graph for the 1993–94 water year (Fig. 26) shows lower-than-typical triazine concentrations, resulting in the lowest total mass flux of atrazine-equivalent of any year (31.13 kg). This water year was the second most
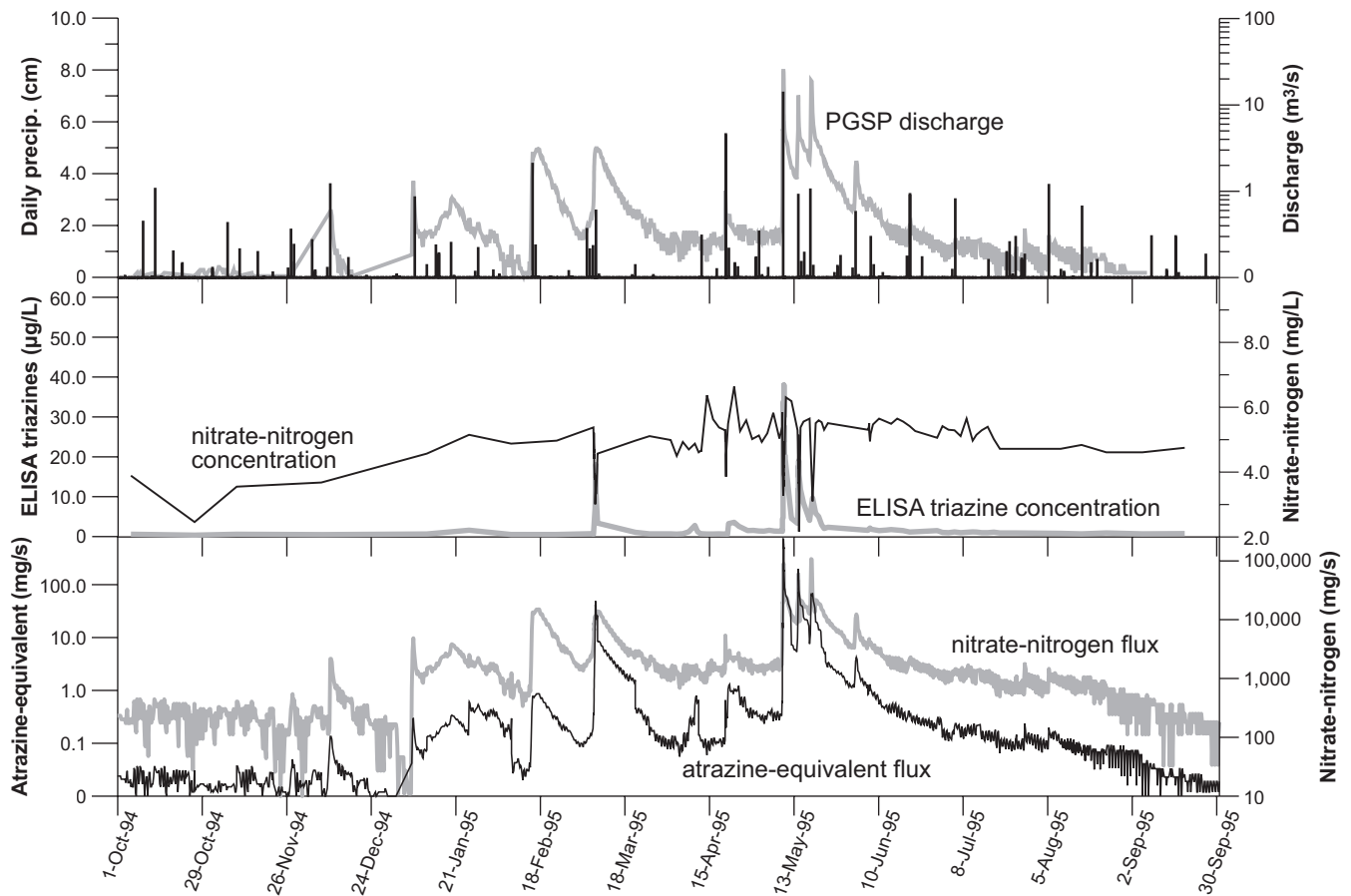
Figure 27. Plot of daily precipitation, discharge, nitrate-nitrogen concentration and flux, and ELISA triazine concentration and atrazine-equivalent flux for Pleasant Grove Spring for the 1994–95 water year.

frequently sampled during the project. All springtime runoff events for the 1993–94 water year were sampled, and therefore it is unlikely that peak concentrations were missed. Although 1993–94 had the second highest total precipitation during the calendar spring season (March 20 through June 22), there were no major storms from mid-April to mid-May, the principal application period for atrazine. The lower triazine concentrations during the 1993–94 water year are thought to be the result of the absence of major storms during the critical chemical application period. Major storms did occur from mid-April to mid-May during each of the other years monitored. Thus, the 1993–94 data are excluded from several correlations because of the unusually dry spring.

Because atrazine is principally used for corn, there should be a correlation between the area of corn planted and triazines measured in runoff within a drainage basin. Essentially no correlation was found, however, between total annual flux of atrazine-equivalent and the percentage of the basin planted in corn when all 6 years of flux data were graphed. The correlation improves when the 1993–94 and 1997–98 data are excluded

($r^2=0.65$). The conditions during the 1993–94 water year were discussed earlier. The 1997–98 values were excluded because the WQIP inventory indicated the average application rate of atrazine in 1998 was double that of previous years. Consequently, the 1997–98 water year had the highest mass flux of atrazine-equivalent ever recorded at Pleasant Grove Spring. The atrazine-equivalent flux does correlate well with the percentage of the basin in row crop ($r^2=0.80$), in contrast to the area in corn (Fig. 32). The improved correlation, when compared to the area in corn, may be caused by a higher certainty of distinguishing row crops from other land uses when using aerial photographs, as opposed to distinguishing corn from all other crops, and to the occasional use of atrazine on other crops. An alternative explanation is that increasing the total area in cultivation somehow promotes the loss of all agricultural chemicals in a drainage basin by enhancing runoff.

The mass flux should correlate more strongly with the amount of atrazine actually applied in the basin than simply with the area in corn because of variable application rates from field to field. When the mass of atrazine
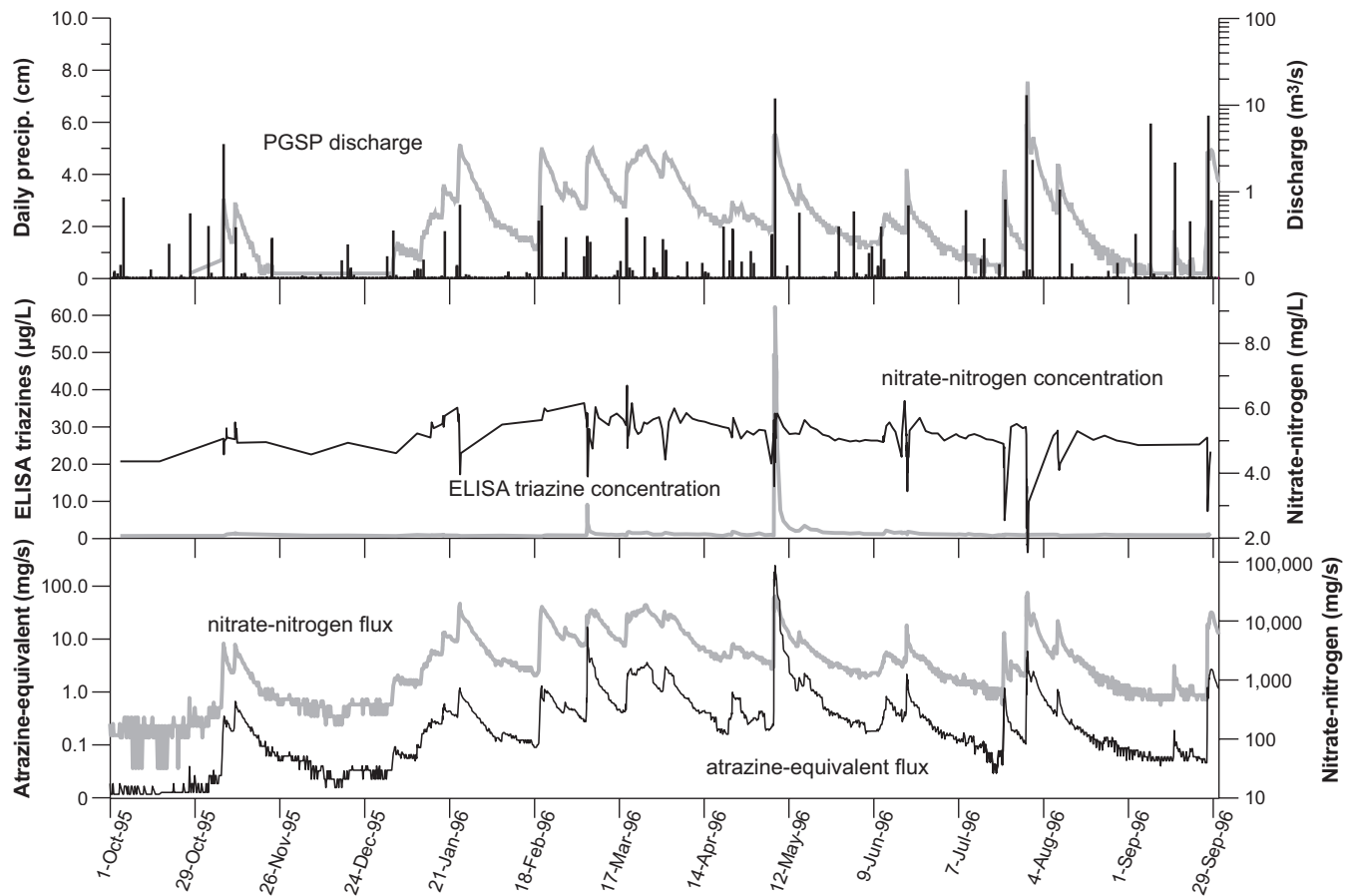
Figure 28. Plot of daily precipitation, discharge, nitrate-nitrogen concentration and flux, and ELISA triazine concentration and atrazine-equivalent flux for Pleasant Grove Spring for the 1995–96 water year.

applied in the basin is estimated and then compared to the annual mass flux of atrazine-equivalent measured at Pleasant Grove Spring, there is a strong correlation (r^2=0.97), but only if the data for the 1993–94 and 1996–97 water years are excluded (Fig. 33). The lowest application rate reported for atrazine occurred during the spring of 1997. If the annual arithmetic average triazine concentrations are correlated with the estimated mass of atrazine applied in the basin, the relationship is strong (r^2=0.93) when only the 1993–94 water year is excluded. The misalignment of the 1996–97 water year is probably also because of the minimal use of atrazine during the spring of 1997.

To test the importance of the coincidence of rainfall after pesticide application, the relationships of rainfall and percentage of runoff to various atrazine measurements was considered for the April 15–May 15 period of each year. An average of 54 percent of the total annual mass flux of atrazine-equivalent occurs during this 1-month period. An arithmetic average was used for one correlation because it was strongly influenced by outlying high values, such as peak chemical concentrations,

which occur only during high-flow events (Fig. 34). The correlation of average triazines to total precipitation during the application period is strong (r^2=0.88), and all years align along the trend. Because rainfall during the April–May period commonly is the result of intense spring storms, the correlation is thought to be caused by intensive runoff events transporting recently applied herbicide. The annual mass flux of atrazine-equivalent was also compared to the percentage of precipitation (runoff) discharging at Pleasant Grove Spring during the atrazine application season (Fig. 35). The percentage of runoff quantifies the volume of water available to carry chemicals into the karst aquifer. The correlation is strong (r^2=0.86) when the 1993–94 water year is excluded. The 1993–94 water year does not fall on the trend because discharge continued at a high rate through the application period (the recession of a major storm in early April), although little rain fell during the actual application period. The effect of the April 1994 storm on the percentage of runoff is removed when the depth of precipitation for the April 15–May 15 period is plotted against the triazine arithmetic average.
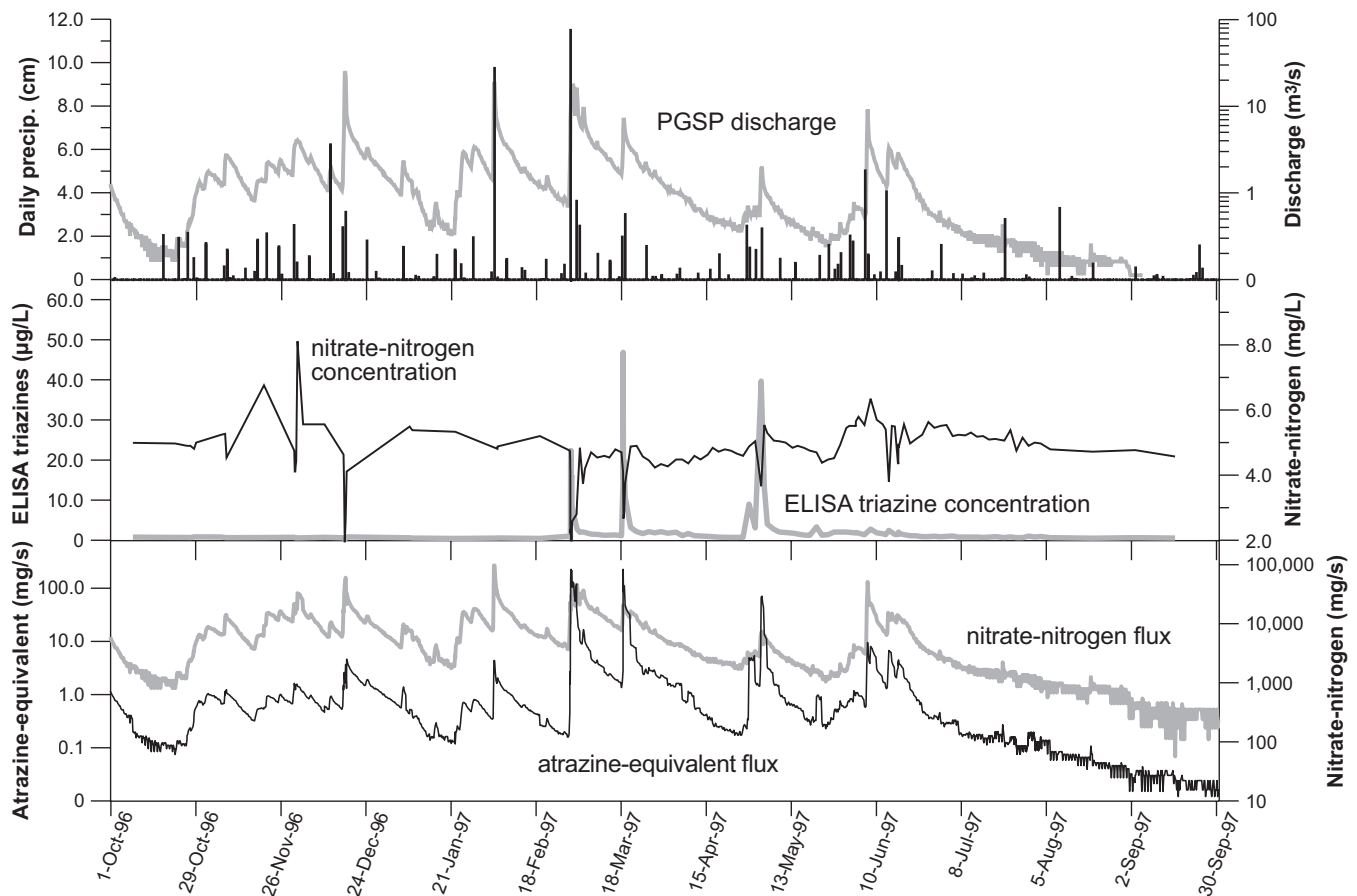
Figure 29. Plot of daily precipitation, discharge, nitrate-nitrogen concentration and flux, and ELISA triazine concentration and atrazine-equivalent flux for Pleasant Grove Spring for the 1996–97 water year.

Nitrate-nitrogen concentrations and flux at Pleasant Grove Spring have a more narrow range of values through the year than atrazine-equivalent values, but rise slightly in late winter and during the planting season, and decrease for short periods during high flow, but flux increases (Figs. 25–30). Thus, the nitrate-nitrogen concentrations are crudely reciprocal of the triazine concentrations. As in the case of atrazine-equivalent, there is no discernible trend on the graphs in nitrate-nitrogen flux or concentration over the period of the WQIP (October 1995–October 1998).

Although nitrate-nitrogen fertilizer is applied to most crops in the basin, the annual mass flux of nitrate-nitrogen discharged from Pleasant Grove Spring does not correlate well with the area of the basin in row crop (r^2=0.25) (Fig. 36). Once again, the 1993–94 and 1997–98 water years are poorly aligned with data for the other 4 years. These two years had the highest and second highest total precipitation during the calendar spring season (March 20–June 22) when most cultivation occurs. When the BMP data from the WQIP inventory are used to estimate tons of nitrate-nitrogen applied (Fig.

37), the correlation between amount applied and the annual flux improves (r^2=0.62). When the annual flux of nitrate-nitrogen is compared with the percentage of the precipitation discharged from Pleasant Grove Spring, a strong correlation (r^2=0.95) is readily apparent (Fig. 38); data for all years align along the trend. Because of the high solubility of nitrate, its annual flux should be greater with increased availability of water moving through the soil and a large nitrate source. The strength of this correlation suggests again that weather plays a significant role in the loss of agricultural chemicals from fields. To be effective, any future BMP program will have to improve the availability of accurate weather forecasts, and further educate farmers on how to avoid chemical application too close to a forecast storm.

Suspended sediment shows trends partly analogous to both atrazine-equivalent and nitrate-nitrogen. When the suspended sediment flux is correlated with percentage of precipitation in the basin discharging from Pleasant Grove Spring (Fig. 39), the relationship is strong (r^2=0.92). Although, as in the case of nitrate, the mathematical commonality of discharge in the calcula-
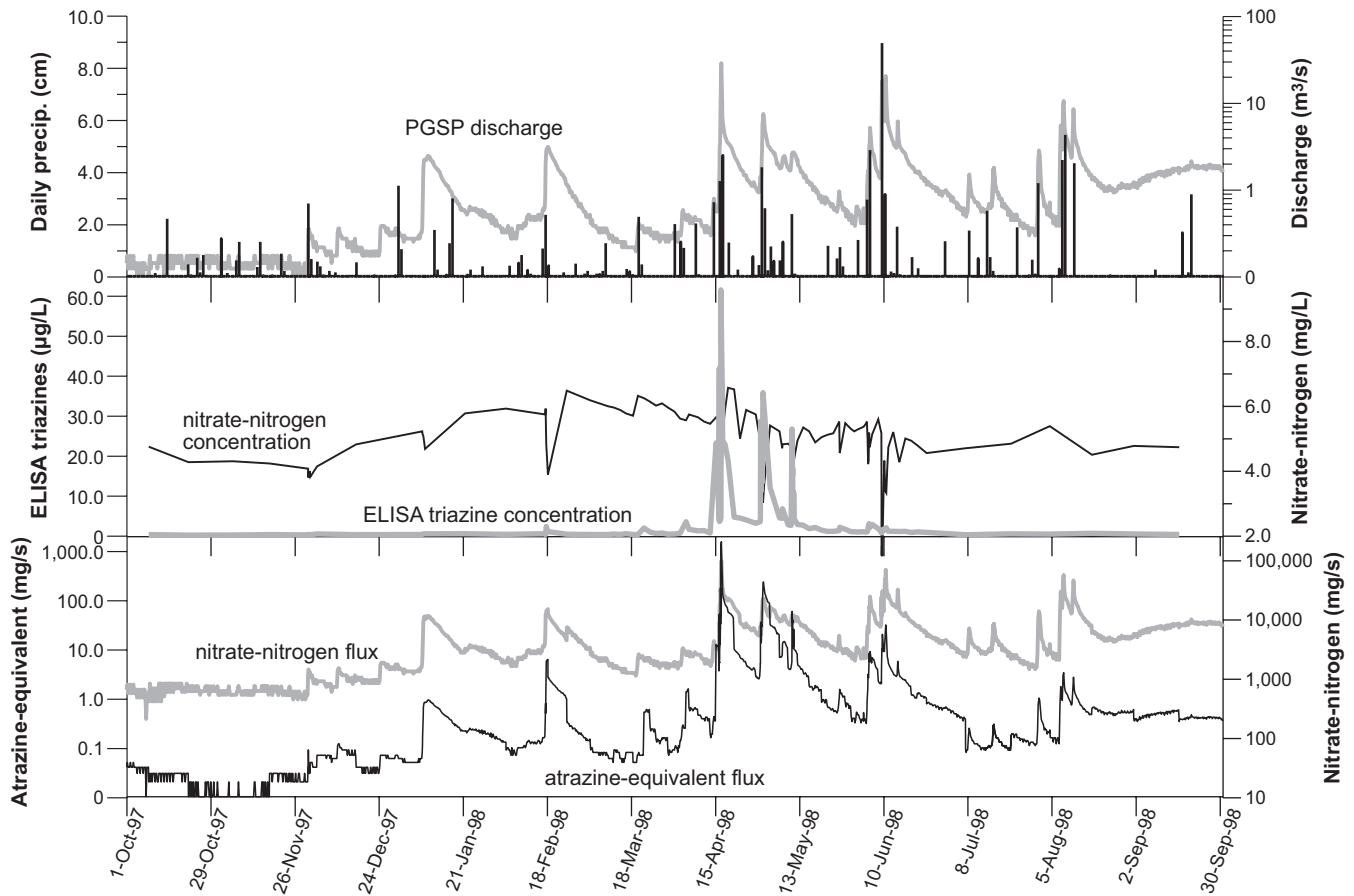
Figure 30. Plot of daily precipitation, discharge, nitrate-nitrogen concentration and flux, and ELISA triazine concentration and atrazine-equivalent flux for Pleasant Grove Spring for the 1997–98 water year.

tion of both flux and percentage of runoff may contribute to the correlation, the transport of suspended sediment requires the increased availability of runoff. The relationship with runoff again indicates the importance of weather to the transport of agricultural pollutants. In contrast, the relationship of percentage of the basin planted in row crop to the total annual flux of suspended sediment is poor. The 1993–94 and 1997–98 water years do not align with data for the other 4 years. As in the case for nitrate-nitrogen, the flux of sediment is higher than expected for the 1993–94 water year and lower than expected for the 1997–98 water year. The higher suspended solids during the 1993–94 water year is easily explained by a period during which woodlands were cleared in the basin, from 1991 through the summer of 1993. The lower-than-expected suspended sediment flux during the 1997–98 water year may indicate that the slowing of the clearing of land, coupled with the slightly increased use of conservation tillage as a result of WQIP, was beginning to have a positive effect when monitoring ended.

Leslie Page Karst Window. The annual mass flux calculations for Leslie Page karst window are not as accurate as those for Pleasant Grove Spring because the high-flow events were not sampled as frequently and because of the gaps and uncertainties for the hydrograph record. Also, during the 1993–94 and 1994–95 water years, a period of drought followed by erosion of the channel bottom sequentially lowered the stage below the rating's zero flow height much of the time. Therefore, mass flux for the first 2 years was not calculated. The hydrograph record for the 3 years following installation of the broad-crested weir are accurate, except for the brief time when backflooding occurred, as discussed earlier. The flux results for these years are summarized in Table 7.

The increase in atrazine-equivalent flux for the 1997–98 water year is noticeable. As mentioned in the discussion of monitoring results and high-flow events, the spring of 1998 was the first in several years in which corn was planted in the fields immediately adjacent to the karst window. The sudden increase in triazines at this site indicates that the BMP's relevant to herbicide
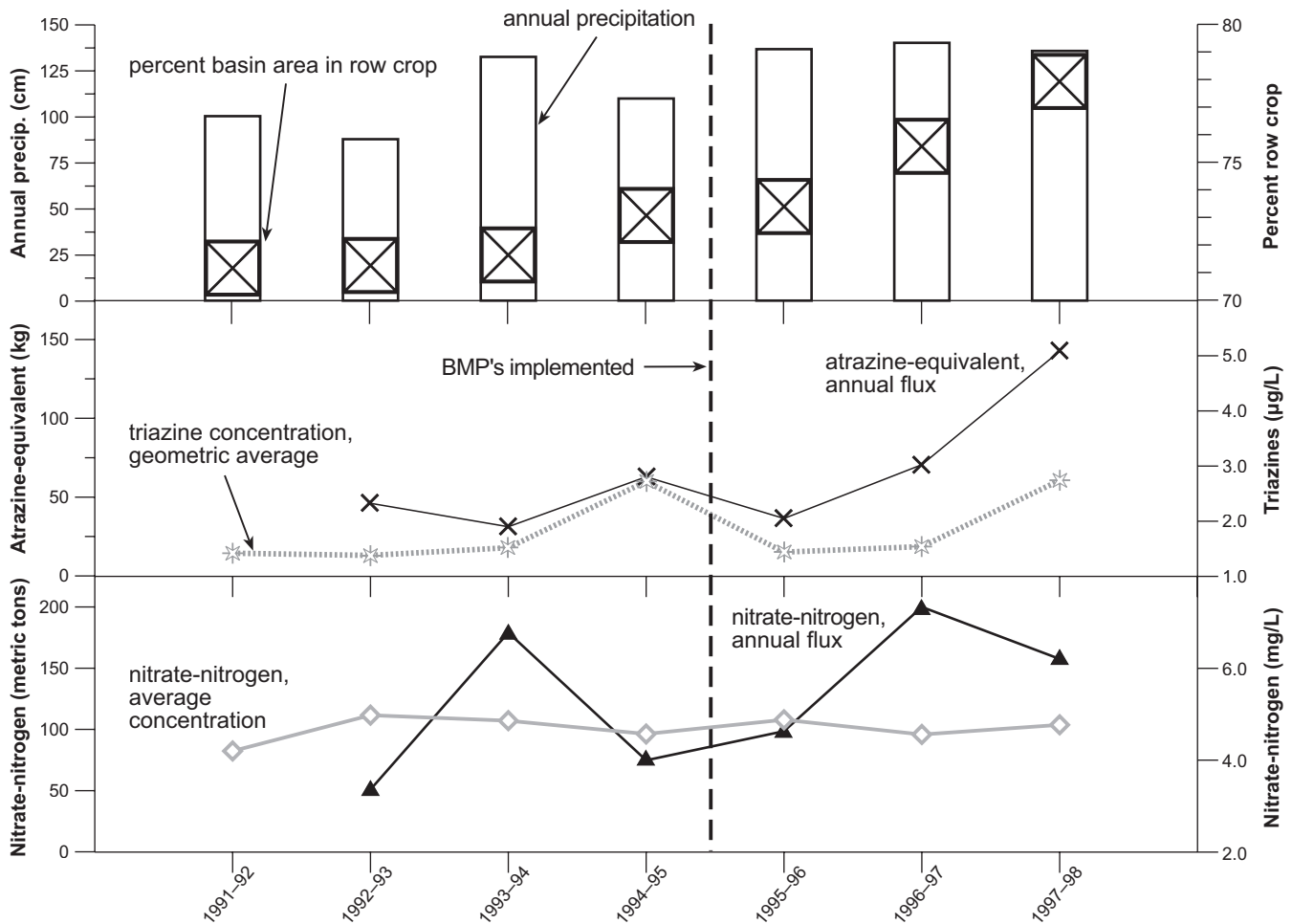
Figure 31. Trends in total annual mass flux of atrazine-equivalent and nitrate-nitrogen concentrations during the Pleasant Grove Spring project.

runoff did not have a measurable positive effect at this location. An alternative explanation is that pesticides could have been released from a container in the dump. The release of pesticides from the dump is thought to be unlikely, however, as discussed earlier.

Although the annual flux data for Leslie Page karst window are incomplete, the concentration data can be considered directly. The detection and peak concentrations of pesticides at Leslie Page karst window are highly seasonal, as illustrated in Figure 40, and detection at times other than during planting season is minimal. For each year of monitoring during the springtime planting season, pesticides were measured in the run-in to the swallow hole in concentrations that were consistent with the crops being grown within the surface catchment area of the karst window. Figure 40 reveals essentially no change in the occurrence of pesticides other than the sudden reappearance of triazines during the spring of 1998. Hence, changes in cropping patterns and associ-

ated herbicide use overwhelmed the benefits of the grass buffer strip surrounding the karst window.

The mass flux of nitrate-nitrogen increases slightly over the course of the last 3 years of monitoring, but it is probably strictly caused by the increase in measured inflow. The concentration data for nitrate-nitrogen (Fig. 40) clearly show the cyclic annual increase in nitrate-nitrogen (6 to 8 mg/L) during the winter and the spring planting season (wet months), however. Lower concentrations persist during the growing season and the dry fall months. Inspection of the analytical data does not reveal any long-term trend in nitrate-nitrogen concentrations, either increasing or decreasing, that might be linked to the BMP installation.

Upper Pleasant Grove Creek. The monitoring stations at George Delaney swallow hole and at the box culvert where Johnson-Young Road crosses over upper Pleasant Grove Creek were used in concert to calculate mass flux of constituents in upper Pleasant Grove Creek.
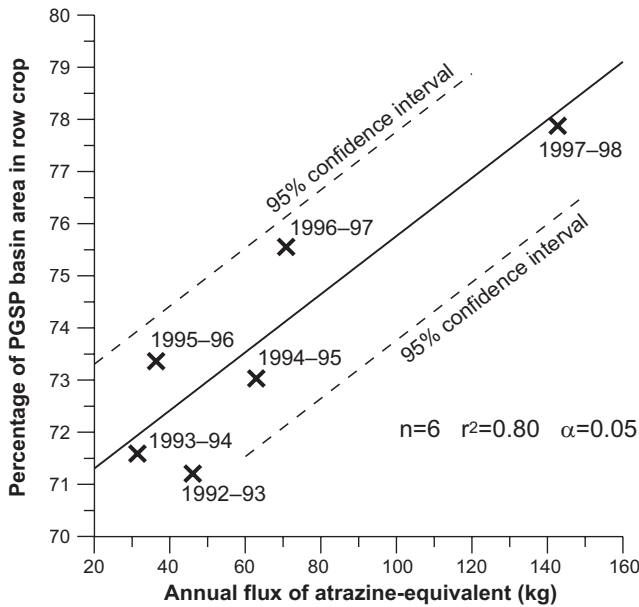
Figure 32. Comparison of the percentage of the groundwater basin area planted in row crop each spring to the total annual mass flux of atrazine-equivalent discharged from Pleasant Grove Spring.
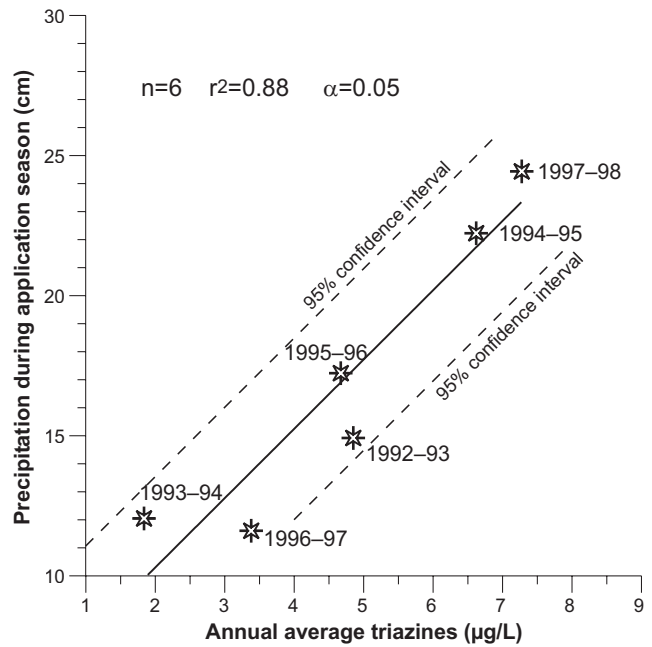

Figure 34. Cross plot of annual arithmetic average of triazines for water samples from Pleasant Grove Spring versus cumulative precipitation between April 15 and May 15. The relationship illustrates the significant effect of storms during the application season on average concentrations of herbicides.
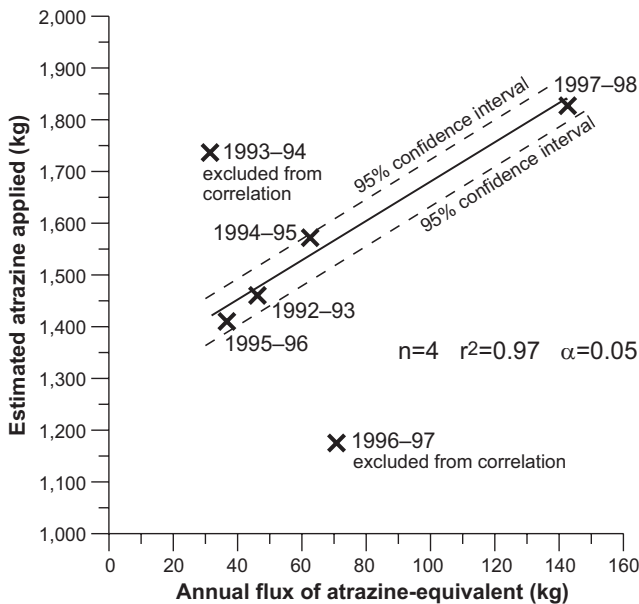

Figure 33. Annual mass flux of atrazine-equivalent discharged from Pleasant Grove Spring plotted against the estimated atrazine applied to crops in the groundwater basin. An average application rate of 1.24 kg/ha was assumed for water years 1992–93 through 1994–95, whereas the average annual application rate reported via the WQIP was used for later years.
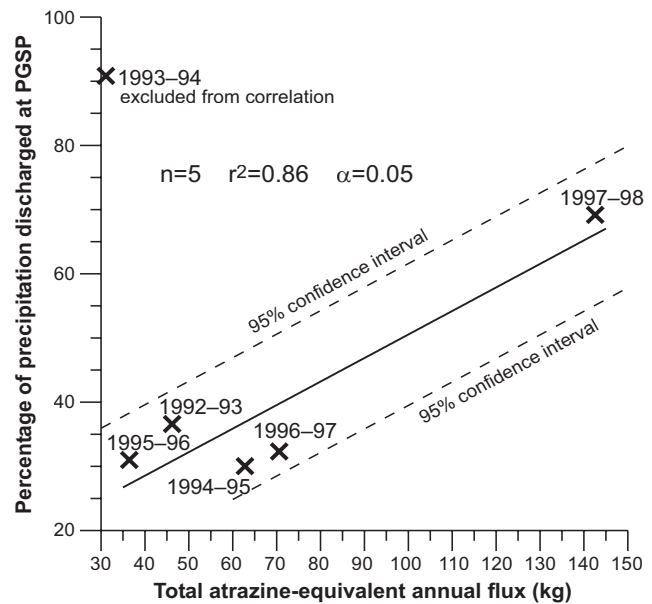

Figure 35. Annual mass flux of atrazine-equivalent discharged from Pleasant Grove Spring versus the percentage of precipitation, or runoff, discharged at Pleasant Grove Spring during the herbicide application season (April 15–May 15). There was little precipitation during this period in the 1993–94 water year, although discharge continued from the spring.
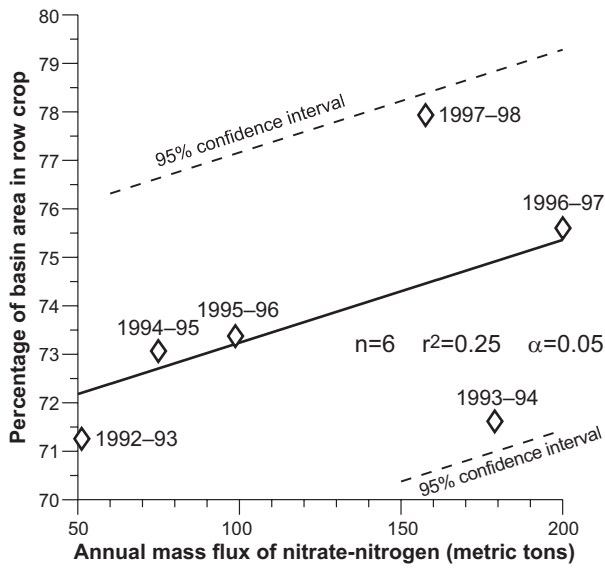
Figure 36. Cross-plot of annual flux of nitrate-nitrogen discharged from Pleasant Grove Spring versus the percentage of the groundwater basin planted in row crop.
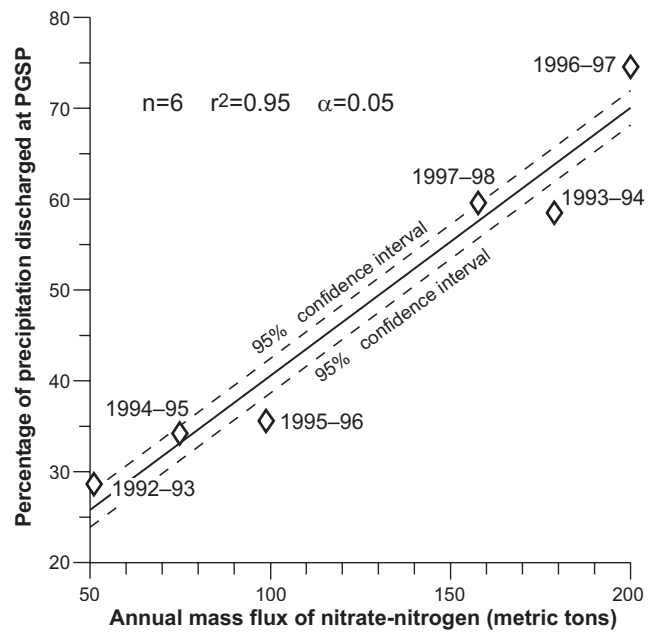

Figure 38. Percentage of total annual precipitation, or runoff, discharged from Pleasant Grove Spring plotted against the annual mass flux of nitrate-nitrogen.
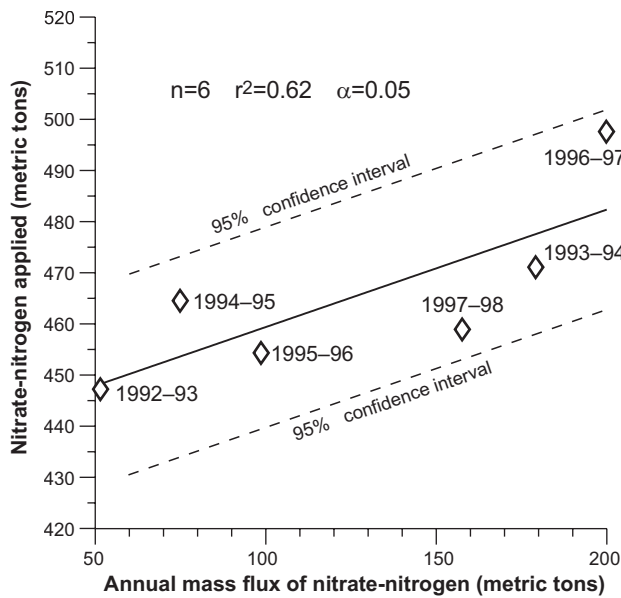
Figure 37. Annual mass flux of nitrate-nitrogen discharged from Pleasant Grove Spring versus the mass of nitrate-nitrogen applied in the groundwater basin. An average application rate of 1.24 kg/ha was assumed for water years 1992–93 through 1994–95, whereas the average annual application rate reported via the WQIP was used for later years.

Figure 39. Annual mass flux of total suspended solids plotted against percentage of total annual precipitation, or runoff, discharged from Pleasant Grove Spring.

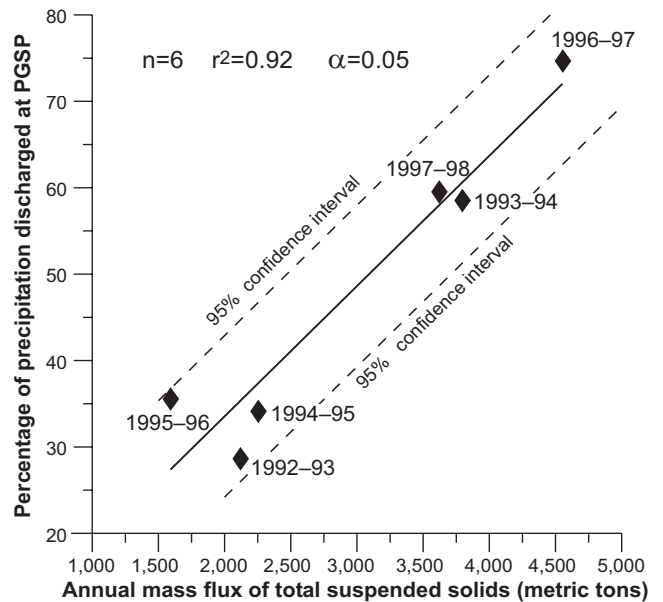**Table 7.** Swallow-hole inflow and mass flux of atrazine-equivalent and nitrate-nitrogen at Leslie Page karst window monitoring station.

Water Year	(cm)	Inflow (m³)	Atrazine-equivalent (kg)	Nitrate-nitrogen (metric tons)
1995–96	136.8	440,000	0.39	2.47
1996–97	140.2	719,000	0.54	4.12
1997–98	135.8	790,000	5.39	4.87

The majority of the samples, including a few for high-flow events, were collected at George Delaney swallow hole. Suspended sediment and orthophosphate were not monitored at either station, but bacteria samples were collected at both. Stage and discharge data are not available for the 1992–93 water year; furthermore, the sampling schedule was not as frequent as that at Pleasant Grove Spring. Therefore, the mass flux results for upper Pleasant Grove Creek are not as comprehensive or precise as those for Pleasant Grove Spring (Table 8). Conversely, when the atrazine-equivalent flux for

the 5 years of data available for upper Pleasant Grove Creek (both George Delaney swallow hole and upper Pleasant Grove Creek station) is compared to the flux for Pleasant Grove Spring, the relationship is very strong (Fig. 41). The strength of this relationship ($r^2=0.95$) suggests that if there is error in the flux values, the error coincidentally occurs at both sites during the same year and is of the same magnitude. The implication is that both sets of mass flux data are reasonable approximations of the actual flux.

Upper Pleasant Grove Creek carries an average of 21 percent of the flow discharged at Pleasant Grove Spring, but roughly 30 percent of the annual mass flux of atrazine-equivalent and nitrate-nitrogen. This reflects the larger percentage of the headwaters area of the basin being planted in row crops (78 percent versus 68 percent in the lower basin) each season. The cross plot
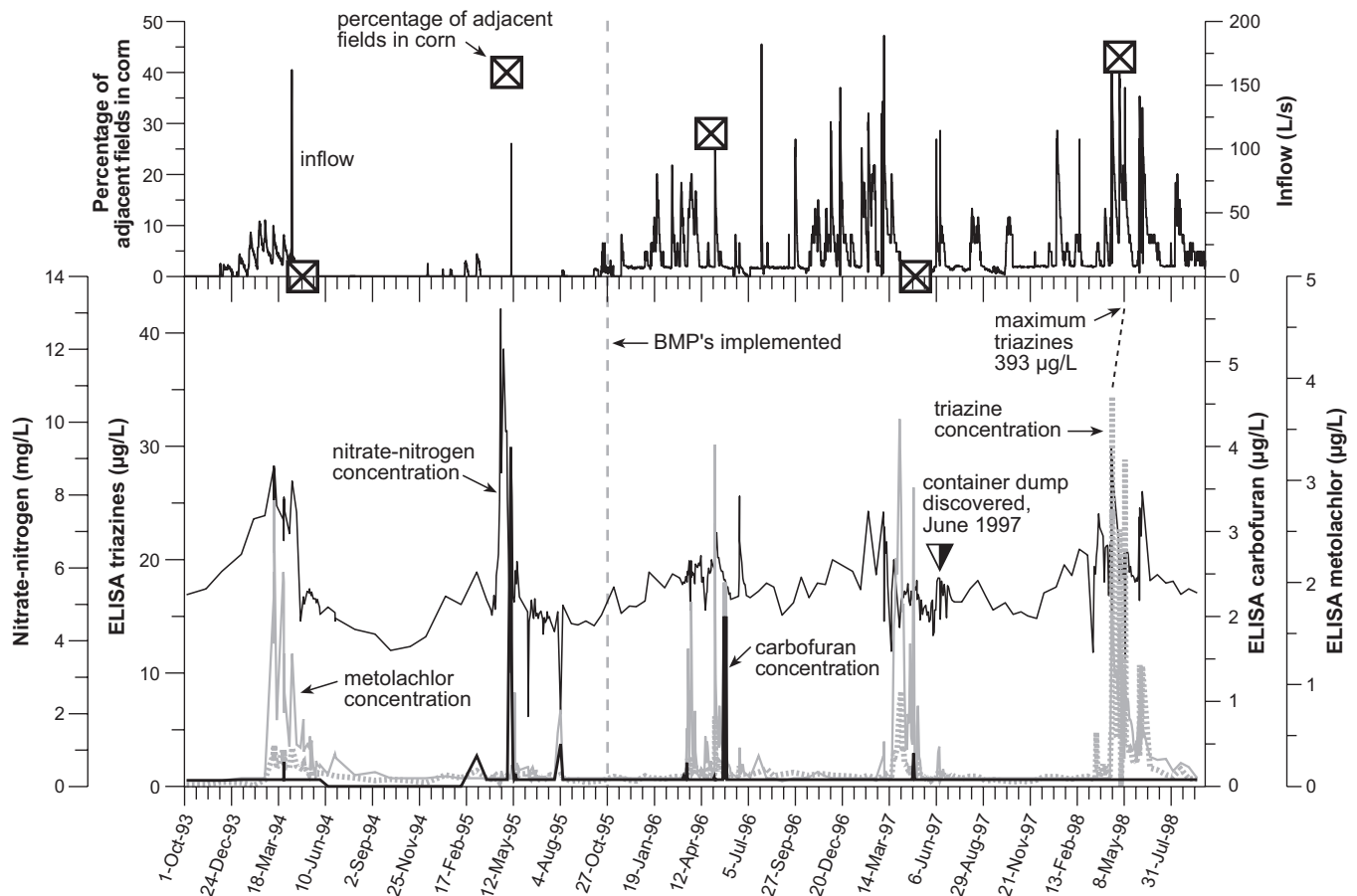

Figure 40. Water flow into the swallow hole at Leslie Page karst window and concentrations of nitrate-nitrogen, and triazines, carbofuran, and metolachlor by ELISA for the 1993–94 through 1997–98 water years.

Table 8. Discharge and mass flux of atrazine-equivalent and nitrate-nitrogen in upper Pleasant Grove Creek (George Delaney swallow hole and upper Pleasant Grove Creek monitoring stations).

Water Year	Precipitation (cm)	Discharge (m³)	Atrazine-equivalent (kg)	Nitrate-nitrogen (metric tons)
1993–94	132.6	9,494,000	6.68	75.53
1994–95	110.0	3,241,000	24.70	33.84
1995–96	136.8	3,195,000	7.41	20.36
1996–97	140.2	8,896,000	16.82	54.47
1997–98	135.8	5,878,000	50.40	30.16

of atrazine-equivalent flux versus the mass of atrazine applied in the headwaters area shows a weak relationship, however. The water years 1992–93 and 1993–94 do not plot on the trend of the other 3 years, probably because of the lack of precise application-rate data. Changes in the mass flux of nitrate-nitrogen from the pre-BMP period to the post-BMP period do not exhibit any temporal trend for upper Pleasant Grove Creek. There is an apparent increase of atrazine-equivalent during the post-BMP period, however.

Summary of Mass Flux Results

The mass flux for triazines and total suspended solids varied significantly from year to year, but flux for nitrate-nitrogen varied less. The variability of triazines

Figure 41. Cross-plot of annual mass flux of atrazine-equivalent inflow at upper Pleasant Grove Creek (George Delaney swallow hole supplemented with upper Pleasant Grove Creek station) versus flux of atrazine-equivalent at Pleasant Grove Spring.

is a direct result of the amount (area and rate) of atrazine applied within the groundwater basin and an indirect result of the timing of the application of atrazine relative to intense storms. Variability in the annual mass flux of nitrate-nitrogen and total suspended solids is more closely related to the total annual runoff. The peak concentration of total suspended solids is also related to the timing of rainfall to exposed soil. Subtle differences resulting from hydrogeology over the area of the basin also have a minor influence on occurrence in ground- and soil water of triazines and nitrate-nitrogen. Most of the variability seen in the flux data can be readily explained by changes in total amount of chemical applied and the timing of application to rainfall. Therefore, the precision of the annual mass flux estimates is thought to be adequate for detecting overall changes in water quality in response to basinwide changes in farming practices but not limited or incremental changes.

Cross plots of pollutant flux or concentration showed no change from pre-BMP trends when compared to precipitation or runoff. For example, when annual runoff is plotted against annual flux of nitrate-nitrogen, all years plot along the trend, but in no apparent chronological order. If nitrate-nitrogen leaching and transport was decreasing in response to WQIP, the flux should depart from the trend established by the pre-BMP years. Similarly, triazines and total suspended solids do not show a chronological trend suggesting departures from pre-BMP conditions. Although the annual flux of nitrate-nitrogen and suspended solids for the 1997–98 water year was lower than expected, when plotted against percentage of the basin in row crop, 1 year does not establish a trend. Conversely, during the 3 years when the WQIP program was in effect there was a chronological increase in atrazine-equivalent flux in proportion to the percentage of the basin in row crop. Of the other relationships examined (annual precipitation, percentage of cropped area, annual discharge, pesticide sales, etc.), none exhibited a temporal trend that could be attributed to a reduction in either concentration or mass flux of triazines (atrazine-equivalent) or nitrate-nitrogen in water discharging from Pleasant Grove Spring during the WQIP.
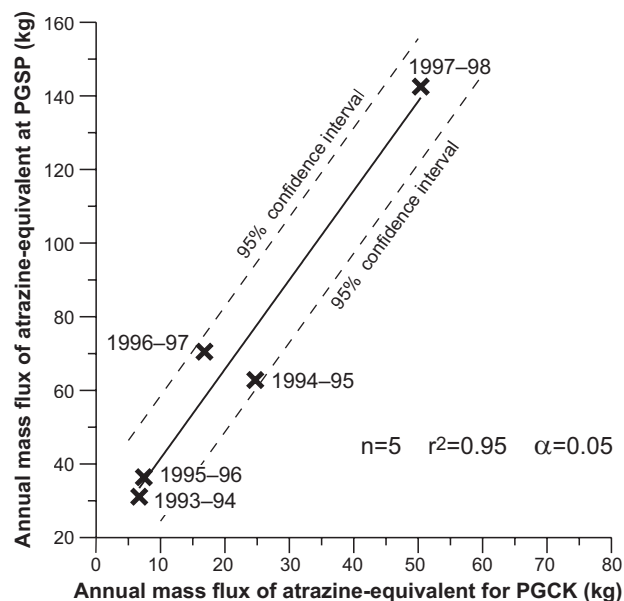
Evaluation of Other Constituents and Sites

Orthophosphate at Pleasant Grove Spring. Mass flux for phosphorous, reported as orthophosphate,

could not be calculated for Pleasant Grove Spring because of the limited number of samples as a consequence of short holding time and preservation requirements for orthophosphate. The maximum concentration detected in 38 samples collected prior to the implementation of BMP's was 0.51 mg/L, the average was 0.007 mg/L, and the median was 0.035 mg/L (Currens, 1999), which is borderline for environmental concern. Because of the low concentrations, orthophosphate was deleted from the constituent list to save analytical cost. An opportunity presented itself to verify that decision when a modest high-flow event occurred during a routine monthly sampling trip on August 7, 1996. This event was superimposed on the recession of an unusual and much larger midsummer event in late July. A sample was collected, and orthophosphate was analyzed (PGSP0957). The concentration of orthophosphate measured was the greatest ever determined at Pleasant Grove Spring, 1.4 mg/L. Routine sampling for orthophosphate was resumed as quickly as possible, and on a schedule of every other week instead of monthly. Although more samples were collected with concentrations over 0.5 mg/L, none were over 1.0 mg/L. The median orthophosphate concentration for the post-BMP period was 0.16 mg/L,

and the average was 0.323 mg/L, a possible increase in orthophosphate over the pre-BMP period. A graph of orthophosphate concentrations over time suggests a decreasing trend from August 1996, but the apparent trend may be partly the result of the high value measured at the beginning of the post-BMP monitoring period. When orthophosphate annual median concentrations are considered (Fig. 42), those for the 1996–97 and 1997–98 water years are the highest and second highest, respectively, suggesting a post-BMP increase. The common man-made sources of phosphorous in streams are fertilizer, livestock waste, and human waste. The coincidence of the high concentrations with the recession of a high-flow event suggests an association with runoff from fields. Other data, notably bacteria counts, suggest, however, that the water quality of the recession limb of high-flow events at Pleasant Grove Spring may be influenced by human waste. Although most of the orthophosphate concentrations measured in water samples from Pleasant Grove Spring have higher-than-natural background concentration, the source of these high levels at this location has not been unambiguously demonstrated.
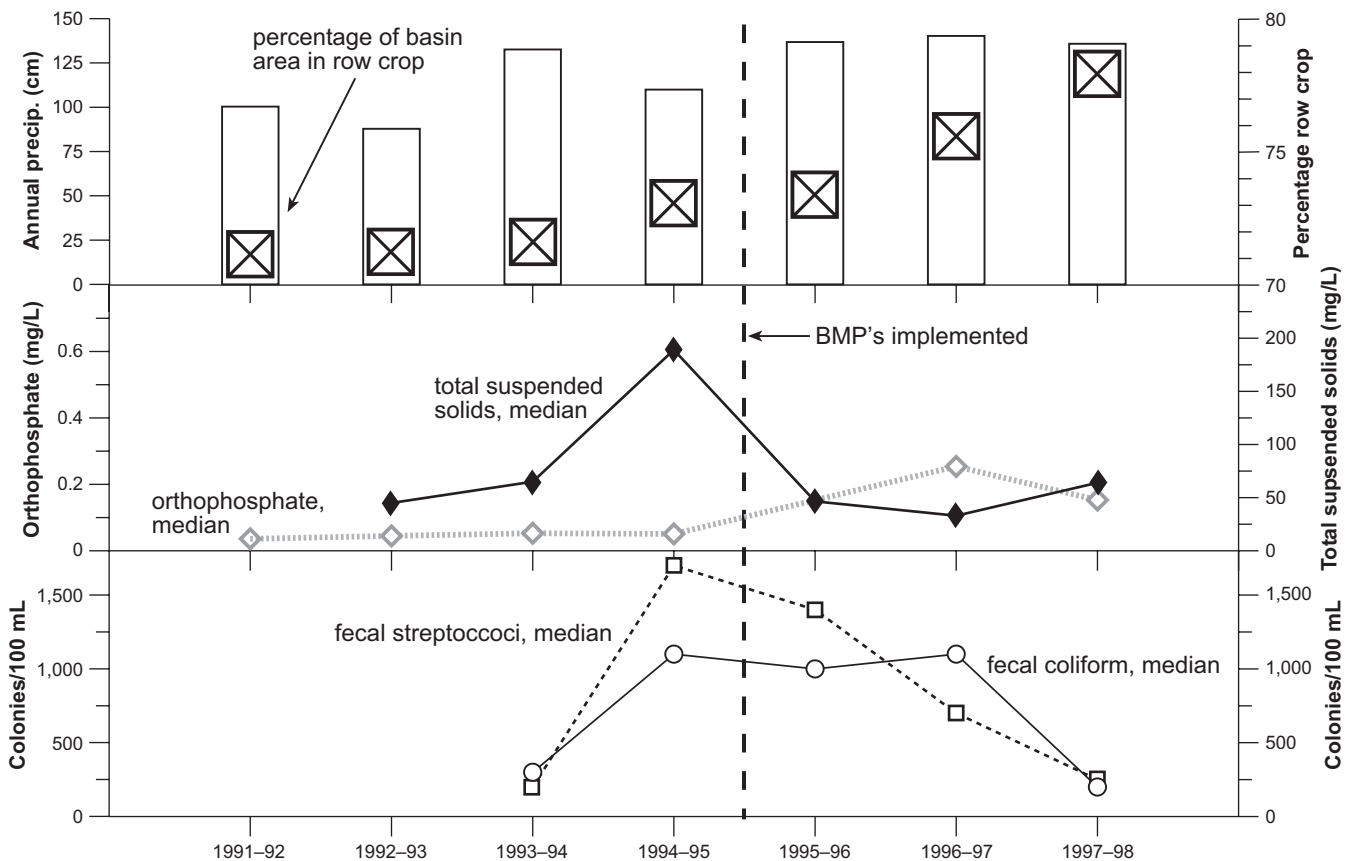

Figure 42. Trends in annual median concentrations of orthophosphate, total suspended solids, fecal streptococci, and fecal coliform during the Pleasant Grove Spring project.

Table 9. Annual statistics for bacteria samples collected nonconditionally (monthly) at Pleasant Grove Spring.

Water Year	Number of Samples	Fecal Coliform			Fecal Streptococci		
		Average (col/100 mL)	Median (col/100 mL)	Geometric Average (col/100 mL)	Average (col/100 mL)	Median (col/100 mL)	Geometric Average (col/100 mL)
1991–92	6	529	100	127	2,946	350	443
1992–93	NA	NA	NA	NA	NA	NA	NA
1993–94	4	180	300	95	174	200	172
1994–95	12	4,141	1,100	1,160	3,496	1,700	719
1995–96	12	4,904	1,000	793	11,852	1,400	1,261
1996–97	12	846	1,100	440	1,951	700	562
1997–98	12	563	200	204	1,540	250	258

NA=not available

Bacteria at Pleasant Grove Spring. A flux calculation was not practical for bacteria because of the limited number of samples. Instead, analytical data for bacteria were grouped into pre- and post-BMP data sets and comparisons were made graphically and with descriptive statistics. Table 9 lists descriptive statistics for nonconditional (collected regardless of flow conditions) monthly samples for each water year. Figures 43 and 44 show the occurrence of bacteria over time for the pre-BMP and post-BMP periods for the upper Pleasant Grove Creek stations (data from George Delaney swallow hole and upper Pleasant Grove Creek station combined) and Pleasant Grove Spring. The apparent increase in the counts of bacteria indicated on the graphs during the post-BMP period is an artifact of including samples collected during storms in 1996 and 1998. All peak values are from samples collected during or on the recession of high-flow events. The maximum fecal coliform value for Pleasant Grove Spring from all samples went up from 28,000 col/100 mL pre-BMP to 60,000 col/100 mL post-BMP, and fecal streptococci went up from 27,000 col/100 mL to 200,000 col/100 mL. Arithmetic and geometric averages also increased from pre-BMP to post-BMP, but are significantly influenced by the maximum counts (Table 9). The median values are less influenced by extreme values. At Pleasant Grove Spring, for monthly and storm samples combined, the median went up for fecal coliform from 48 col/100 mL pre-BMP to 1,237 col/100 mL post-BMP, and for fecal streptococci from 540 col/100 mL to 829 col/100 mL. In contrast, when bacteria counts for only monthly samples are considered, there is only an insignificant increase in fecal coliform medians from 418 col/100 mL to 432 col/100 mL. Fecal streptococci monthly samples, however, decrease from 540 col/100 mL pre-BMP to 441 col/100 mL post-BMP. There is a definite trend of

decreasing counts for the yearly medians of monthly, nonconditional samples (Fig. 42) for fecal streptococci, but a less distinct trend for fecal coliform.

Another method of comparing the bacteria data is to tabulate the number of samples falling into the source categories for the fecal coliform/fecal streptococci ratio. A visual representation of these data is presented in Figure 45. The bar graph shows the percentage of samples falling into the animal-influenced, human-influenced, and mixed-influence categories. There are two bars for the post-BMP data, one of monthly nonconditional (uninfluenced by flow conditions) samples only and one including both monthly samples, and those collected following storms. There is a 9 percent decrease in the number of animal-influenced samples and a corresponding 7 percent increase in the number of human-influenced samples when the post-BMP nonconditional sample set is compared to the pre-BMP sample set. The pre-BMP ratios are virtually identical to the ratios in the post-BMP storm sample set, however.

That fecal streptococci annual medians steadily decreased after BMP's were implemented, the overall median decreased, and the influence changed from animal to human suggests the phenomenon is real and the changes are not due to chance. This is strengthened when the lack of a parallel decrease in fecal coliform counts is also considered. The probable explanation for the reduction in fecal streptococci with a corresponding shift in the ratio is that runoff of animal waste reduced while the input of human waste remained relatively constant. This suggests that the BMP's for animal waste (handling facilities and livestock exclusion) have had a measurable positive effect. Although the decline in the monthly fecal streptococci counts is encouraging, the maximum counts during high-flow events remain unsatisfactory.
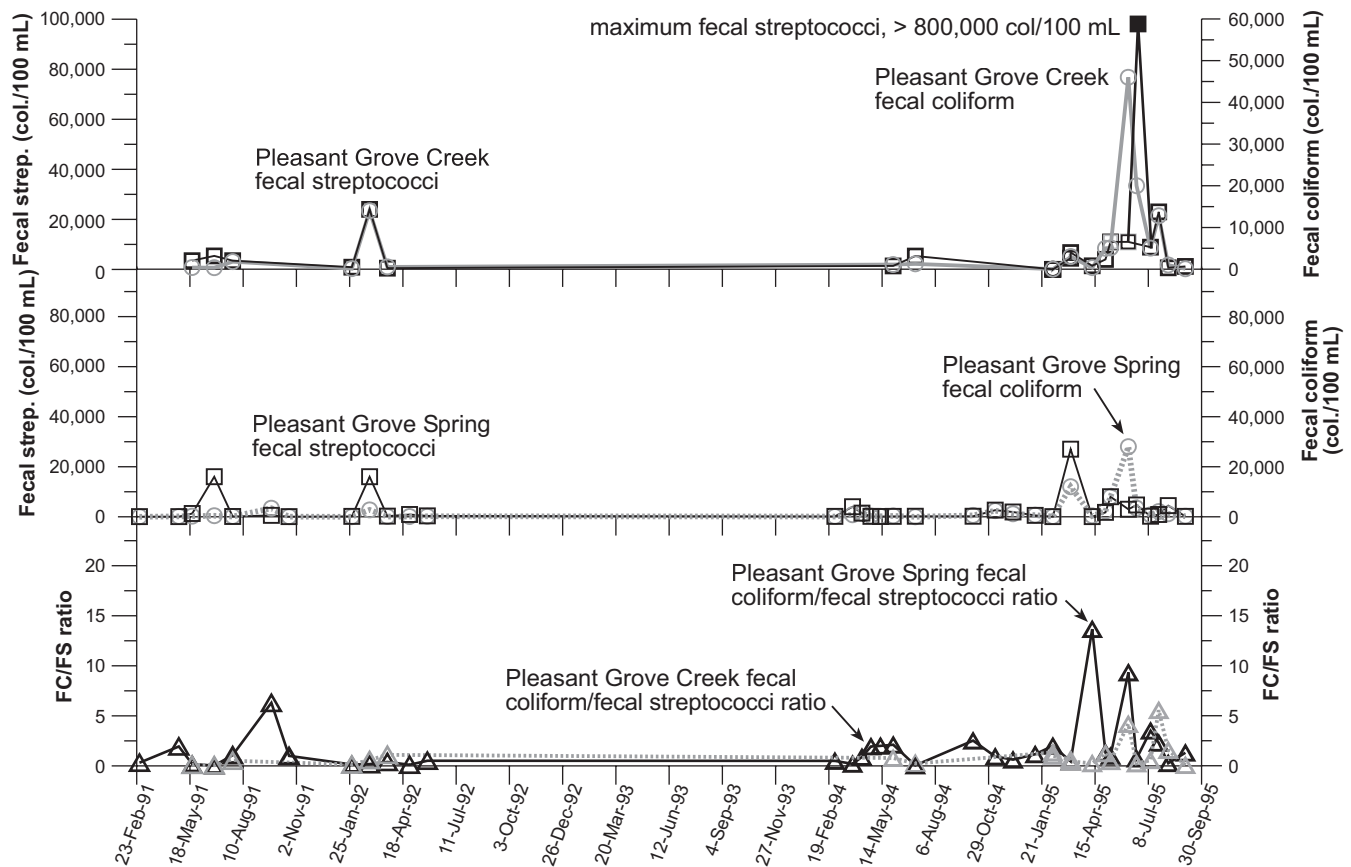
Figure 43. Line plot of bacteria counts and orthophosphate at Pleasant Grove Spring and upper Pleasant Grove Creek (George Delaney swallow hole and upper Pleasant Grove Creek stations combined) for the pre-BMP period, from February 1991 through September 30, 1995.

Bacteria at Leslie Page Karst Window. Bacteria counts at Leslie Page karst window are among the lowest measured in the groundwater basin. One reason the site was chosen was because there are no livestock or human sources within the estimated groundwater sub-basin of Leslie Page karst window. Bacteria sources are therefore mostly limited to the soil biota and wildlife. An intermittent source of bacterial contamination is backflooding from flow reversals in the conduit draining the karst window. Several events have flooded the karst window to sufficient depth to induce contaminated water into the spring. The highest bacteria count (fecal streptococci 20,000 col/100 mL) followed a major flood in May 1995 (Fig. 23), but unfortunately the water-level recorder at Leslie Page karst window failed during this time. High bacteria counts (fecal coliform 382 col/ 100 mL and fecal streptococci 12,200 col/100 mL) also occurred following a high-flow event in the summer of 1998. Samples collected following other episodes of flooding show more typical bacteria ranges, however. Although no BMP changes were made within the Leslie Page karst window sub-basin that could affect bacteria

counts, the pre- and post-BMP timeframe was used to partition the data so as to remain consistent with the other sites. Before October 1995 counts of fecal coliform typically remained below 3,000 col/100 mL and fecal streptococci below 5,000 col/100 mL, and averaged 1,162 and 2,069 col/100 mL, respectively. After October 1995, fecal coliform averaged 229 col/100 mL and fecal streptococci averaged 990 col/100 mL. The median fecal coliform dropped from 45 col/100 mL pre-BMP to 23 col/100 mL and the fecal streptococci from 909 col/ 100 mL to 439 col/100 mL after BMP implementation. These medians show minor changes. The high "pre-BMP" averages probably reflect serendipitous collection of samples following backflooding events during the first years of the project.

Graphs of bacteria counts over time for Leslie Page karst window show no discernible trends through the project period. Because human-induced or livestock sources of fecal contamination (aside from backflooding) do not affect the spring, the fecal bacteria counts at Leslie Page karst window are thought to be natural. Therefore, median "background" counts from unpol-
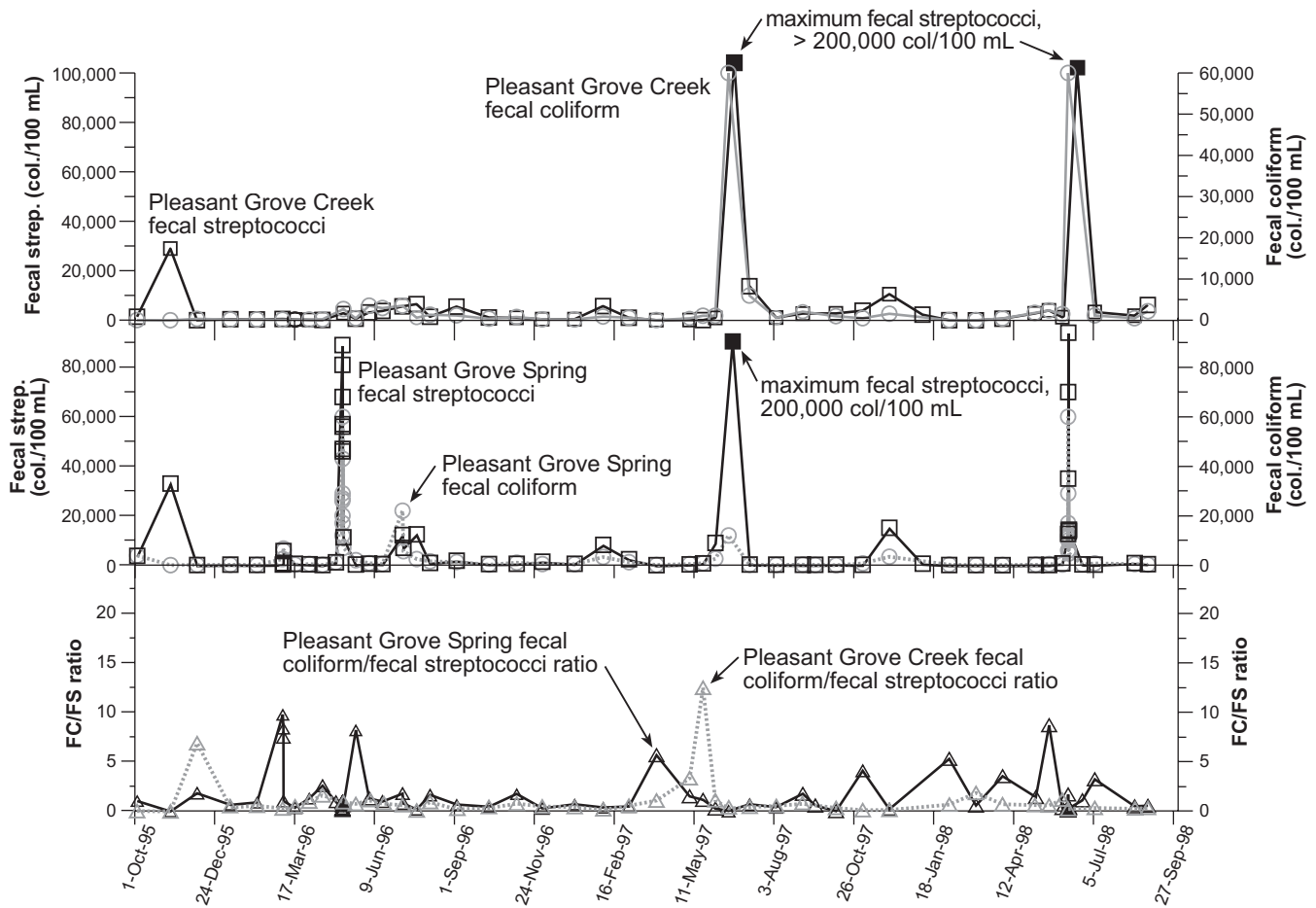
Figure 44. Plot of bacteria counts and orthophosphate at Pleasant Grove Spring and upper Pleasant Grove Creek (George Delaney swallow hole and upper Pleasant Grove Creek stations combined) for the post-BMP period, October 1995 through October 1998.

luted springs in the basin should be in the 10's to low 100's range, and higher counts at other sites in the basin may indicate the presence of fecal pollution.

Bacteria at Upper Pleasant Grove Creek. The highest bacteria count recorded for the groundwater basin (810,000 col/100 mL fecal streptococci and 200,000 col/100 mL fecal coliform) was measured in a sample collected at George Delaney swallow hole on June 20, 1995 (GDSW0033). Cattle and hogs were fed and grazed in fields surrounding the swallow hole through July 1, 1995, but after that date only a few head of horses were pastured there. The high-count sample was collected before livestock were excluded from the area and on the recession of a modest storm (3.9 cm [1.53 in.]) on June 19. Animal waste ran off from the adjacent pasture into the creek at the time of sampling, and livestock were loafing in the creek. Prior to BMP implementation, fecal coliform averaged 5,758 col/100 mL and fecal strepto-

cocci averaged 44,141 col/100 mL; the medians were 1,273 and 4,000 col/100 mL, respectively.

After the livestock were excluded, the bacteria counts measured at George Delaney swallow hole went down. The maximum count measured post-BMP was 253,000 col/100 mL fecal streptococci. Post-BMP averages were 3,769 fecal coliform col/100 mL and 12,975 fecal streptococci. Post-BMP averages were 3,769 fecal coliform col/100 mL and 12,975 fecal streptococci col/100 mL; the medians were 631 and 1,450 col/100 mL, respectively. Bacteria counts still peak, however, and correspond with peaks at Pleasant Grove Spring (Figs. 43–44). The correspondence of peaks reflects the synoptic sampling schedule and the large percentage of the discharge at Pleasant Grove Spring (21 percent) originating from inflow at George Delaney swallow hole, and subsequently influencing the water quality at Pleasant Grove Spring.

Nonconditional samples only   Nonconditional and
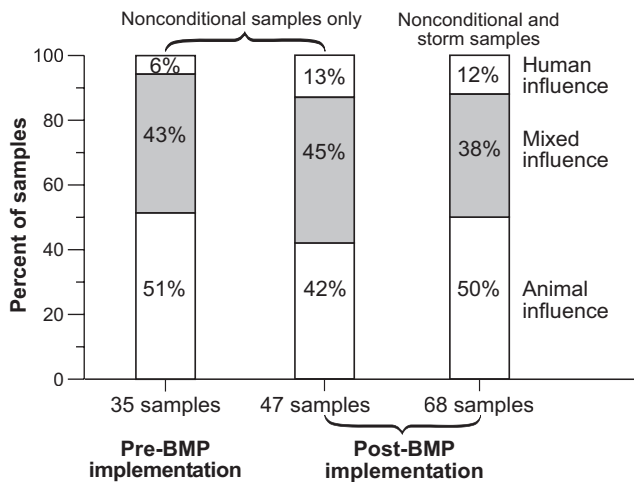storm samples

Figure 45. Percentage of fecal coliform/fecal streptococci ratios for water samples collected at Pleasant Grove Spring showing the relative influence of animals and humans before and after BMP implementation. Nonconditional samples were collected without regard to flow conditions.

Groundwater Quality at The Canyon Karst Window and Joe Harper Water Well. The Canyon karst window and Joe Harper water well were monitored to provide data on the quality of the water originating in the east-central quadrant of the groundwater basin. Physical limitations at the sites precluded flow monitoring and any calculation of the mass flux, however. Joe Harper water well was sampled when The Canyon karst window was flooded. Samples collected at either site were analyzed for triazines, metolachlor, carbofuran, alachlor, nitrate-nitrogen, and bacteria.

The timing of the occurrence of pesticides at The Canyon karst window was consistent with that observed at other sites in the basin. Triazines were the most commonly detected pesticide; minimum concentration was 0.26 µg/L. Metolachlor was also detected during planting season. During the pre-BMP (1992–95) period, the maximum triazine concentration at The Canyon karst window was 3.9 µg/L and the median was 1.0 µg/L, under the health limit for atrazine. College of Agriculture staff found concentrations as high as 15 µg/L in the spring of 1991, however (Haszler, 1994?). From 1995 through the end of the post-BMP monitoring, peak triazine concentrations were measured in the 11 to 12 µg/L range every spring until May 12, 1998, when a maximum concentration of 41.6 µg/L was measured. The median concentration, however, was 0.85 µg/L, essentially no change from the pre-BMP period. The maximum triazine concentration at The Canyon karst window (46.2 µg/L) corresponded to a significant peak at George Delaney swallow hole. A peak in triazines detected during the same event at Pleasant Grove Spring corresponds to the peaks at George Delaney swallow hole and The Canyon karst window. Comparison of triazine concentration data for The Canyon karst window before and after BMP implementation indicates no change after BMP implementation.

Nitrate-nitrogen concentrations at The Canyon karst window varied little during the entire monitoring period. Samples collected prior to October 1995 averaged 4.1 mg/L; maximum concentration was 5.0 mg/L. Post-BMP nitrate-nitrogen concentrations averaged 4.5 mg/L; maximum concentration was 7.3 mg/L. No trend can be discerned from graphs of the concentration data.

Bacteria samples from The Canyon karst window and Joe Harper water well also suggest essentially no change after BMP implementation. The median fecal coliform count was 30 col/100 mL and the median fecal streptococci count was 100 col/100 mL for the 1992–95 period for these two sites. After BMP implementation the median fecal coliform count was 200 col/100 mL and median fecal streptococci was 300 col/100 mL. The maximum fecal coliform and fecal streptococci counts observed for this part of the study area were 33,000 and 200,000 col/100 mL, respectively, at Joe Harper water well (JHWW0012; June 17, 1997).

Comparison of Pre-BMP Water Quality to Post-BMP Water Quality

Graphs of mass flux over time; cross-plots of water-quality parameters versus chemical usage, land use, or weather factors; and chemographs from high-flow events were examined (Figs. 20–45). High concentrations of triazines and high flux rates of both atrazine-equivalent and nitrate-nitrogen were observed during post-BMP high-flow events. The springtime occurrence of triazines and other pesticides continued and the seasonal patterns of nitrate-nitrogen and suspended sediment occurrence remained nearly unchanged. The annual mass flux of atrazine-equivalent increased, but the mass flux of nitrate-nitrogen remained nearly constant. The annual mass flux of suspended sediment decreased slightly. The occurrence of orthophosphate increased, but fecal streptococci counts decreased. Similar results were obtained from Leslie Page karst window, The Canyon karst window with Joe Harper water well, and upper Pleasant Grove Creek (George Delaney swallow hole and upper Pleasant Grove Creek station). Overall, contaminant transport to Pleasant Grove Spring has not significantly changed since the BMP program was initiated.

Statistical Evaluation of Pre-BMP Versus Post-BMP Water Quality at Pleasant Grove Spring

Pre- and post-BMP analytical data for triazines, nitrate-nitrogen, total suspended solids, orthophosphate, and bacteria counts from water samples collected at Pleasant Grove Spring were compared for differences between means, geometric means, medians, and annual mass flux, as applicable. The original analytical data were also divided into various subsets, as described previously. These subsets were tested for equivalence of means using the Student's t test, where valid. Statistical tests were also conducted on the complete analysis set using a Mann-Whitney w test of the equivalence of the medians. The annual statistics were compared using Dunnet's t test and the Mann-Whitney nonparametric u test. All tests were conducted at the 95 percent confidence level.

Population Distribution Testing

Inspection of frequency plots of the population distributions of analytical results for the complete analysis set from Pleasant Grove Spring indicates a log-normal distribution for triazines and total suspended solids concentrations and a normal distribution for nitrate-nitrogen concentration. When the chi-square statistic was calculated for the complete analysis set and various subsets of analyses, most of the sets were not normally, log-normally, gamma, or Laplace distributed at the 95 percent confidence limit (Davis, 1986) for each of the constituents considered. Exceptions, which fit a tested distribution, are the monthly analysis sets for nitrate-nitrogen, which are normally distributed, and the complete analysis set for orthophosphate, which is log-normally distributed. The monthly analysis set for orthophosphate is also log-normally distributed; however, the number of values in the monthly analysis set was too small to establish a probability for the distribution. The biweekly/bihourly analysis set for total suspended solids was log-normally distributed. The distribution of triazines was log-normal only for a quarterly analysis set for which the equivalence of the means could not be tested using the Student's t test, because the variances of the pre- and post-BMP analysis sets were different. None of the constituents for the complete analysis set were normally distributed.

Comparison of Pre-BMP to Post-BMP Water-Quality Statistics

The Student's t test was used to compare the means of the normally distributed or log-transformed analysis sets that had equal variances. The means of the pre-BMP monthly nitrate-nitrogen concentrations were not statistically different from the post-BMP means. The means of the log-transformed total suspended solids concentrations for the biweekly/bihourly analysis set were statistically different, however; the post-BMP mean was lower.

The Mann-Whitney w test was used to test for equivalence of the pre- versus post-BMP medians. The median is not as sensitive as the mean to population distribution, and was tested for a number of sample sets for which testing means was inappropriate. The statistic revealed that the medians for the log-transformed complete analysis set and monthly orthophosphate concentrations were significantly different. The post-BMP medians of the two populations were found to be larger. The median of the complete analysis set of post-BMP total suspended solids was found to be less than the pre-BMP median for both the log-transformed and nontransformed data. There was no difference between pre- and post-BMP triazine medians for any analysis set. All other sets of analyses for total suspended solids, nitrate-nitrogen, and orthophosphate had statistically the same pre- and post-BMP medians.

A second strategy for comparing any changes in the water quality was also used. The annual mean, annual geometric mean, total annual mass flux, and annual median were calculated for total suspended solids, triazines (atrazine-equivalent for flux), and nitrate-nitrogen for each water year. The annual mean, geometric mean, and medians were calculated for orthophosphate and also bacteria counts. The annual statistics were then grouped in pre-BMP and post-BMP years and treated as observations of statistical samples using Dunnett's t test (for small sample sizes) (Glantz, 1992) and the Mann-Whitney u test (Davis, 1986). There were no significant differences between the before- and after-BMP statistics for triazines, atrazine-equivalent flux, nitrate-nitrogen, or bacteria. The post-BMP medians and log-transformed means for orthophosphate were found to be larger than the pre-BMP values. The post-BMP medians of total suspended solids were found to be less, whereas flux and geometric average concentrations were unchanged.

An ancillary query was the comparison of the complete analysis set for triazines, nitrate-nitrogen, total suspended solids, and orthophosphate to each of the several analysis subsets using the Student's t test. The observed data were used for the tests, except for triazines, where both log-transformed and observed data were tested. The means of the biweekly/bihourly

subset (samples collected every other week combined with high-flow event samples collected every other hour) for all four principal constituents and log-transformed triazines were found to be statistically indistinguishable from the means of the complete analysis set. The F statistic shows the variances are the same for the complete and biweekly/bihourly analysis sets for all of the constituents.

Results of Statistical Analysis

The statistical analysis of the water-quality data for Pleasant Grove Spring shows there was little change in triazine herbicide and nitrate-nitrogen concentrations following the implementation of BMP's. The median concentration of total suspended solids improved (decreased), whereas orthophosphate concentrations worsened (increased). Bacteria counts were also statistically unchanged.

Conclusions

Agriculture and single-family residences are the only significant, long-term sources of pollutants within the mapped boundaries of the Pleasant Grove Spring groundwater basin. Field observations and analytical data indicate the major pollutants monitored at Pleasant Grove Spring were largely from agricultural sources. The pesticides measured, most notably atrazine, are generally used only by agriculture. The $^{15}N/^{14}N$ ratio strongly indicates commercial fertilizer is the source of the nitrate-nitrogen. The occurrence of total suspended solids is coincidental with land clearing and the bare-soil period of the planting cycle. The occurrence and magnitude of fecal streptococci counts is related to livestock accessibility to flowing water and to storms that generate overland runoff. Furthermore, the fecal coliform/fecal streptococci ratio suggests livestock sources. The determinations of orthophosphate indicate higher-than-natural concentrations associated with overland runoff.

The Water Quality Incentive Program was effectively implemented across the catchment area of the Pleasant Grove Spring groundwater basin, as demonstrated by the high percentage of agricultural producers in the study area who participated. Over 68 percent of the area of the groundwater basin was enrolled in at least one BMP. There were a few nonparticipants, but as important, many of the agricultural producers in the basin were already using some best management practices similar to those listed under the WQIP. Naturally, the producers chose the BMP's that were the easiest and most profitable for them to implement (namely, conservation cover and no-till options), as they were permitted to do under existing policy. Therefore, despite the large

percentage of the basin area enrolled under the WQIP, little change was made to actual farming practices. Also, the dumping of pesticide containers at Leslie Page karst window during the second year of the WQIP indicates that the message of the necessity of protecting the quality of groundwater did not reach some people.

Comparison of concentration and mass flux trends, results of the biological inventory, field observations, the list of best management practices adopted, and statistical analysis of the pre- and post-BMP water-quality data all indicate limited success of the WQIP in improving the quality of water discharged from Pleasant Grove Spring. There is both an apparent and a statistical decrease in total suspended sediment flux. The improvement is probably the result of a reduced rate of land clearing and increased use of conservation tillage. Although graphical trends indicate an improvement in fecal streptococci counts (possibly due to construction of livestock waste-handling facilities and exclusion of livestock from streams and karst windows) and the median count decreased, the changes are too small to be statistically significant. There are no statistically significant changes in triazine (or atrazine-equivalent) and nitrate-nitrogen occurrence. Indeed, 1997–98, the final year of monitoring, had the highest concentrations and greatest annual flux of triazines recorded during the study. The apparent increase in triazines may also be partially attributed to the increased use of no-till production methods.

Although the Water Quality Incentive Program was fully implemented and administered according to policy, the monitoring results indicate it was only partly successful in improving groundwater quality. To be successful, future BMP programs intended to protect groundwater must be tailored to the crops being grown and to the hydrogeology of the groundwater basin. A "one size fits all" program will not work for karst terrain. Preventing runoff carrying agricultural pollutants from entering swallow holes and open-throat sinkholes is critical. To minimize cost, BMP implementation could be reserved for critical areas within a given watershed and stringently applied to those areas. The incentive program policy should be changed to strongly encourage producers to install on their farm the BMP that will result in the greatest improvement in water quality. The conservation officer must be authorized to strongly suggest, if not direct, which of the BMP's must be used if cost-share money is to be obtained by the agricultural producer. Finally, for BMP's requiring reseeding to pasture, planting trees, or otherwise taking land out of production, the amount of cost-share money provided must completely offset the lost revenue so as to entice enrollment.

Summary

Karst aquifers are an important water-supply resource in Kentucky, but are also overlain by some of the most productive agricultural lands in the Commonwealth. Furthermore, karst aquifers are vulnerable to pollution from many sources, including agriculture. The U.S. Department of Agriculture supports incentive programs to encourage the use of best management practices that protect natural resources, including groundwater, from agriculturally derived contaminants. The purpose of this project was to test the effectiveness of a USDA program to protect the groundwater in a karst aquifer.

The project was located in the Pleasant Grove Spring groundwater basin, which includes 4,069 hectares (10,054 acres), in Logan County, south-central Kentucky. The study area is mature karst with abundant sinkholes, caves, and springs. About 70 percent of the basin is cultivated in row crop, mostly corn in a 2-year rotation with wheat and soybeans. Beef cattle, dairy cattle, and swine are also raised. Water quality at Pleasant Grove Spring and at other sites in the karst groundwater basin was monitored from 1991 until the implementation of BMP's under the Water Quality Incentive Program in 1995 and during the BMP implementation period through the 1997–98 water year. The quality of water discharged from Pleasant Grove Spring and at the surface in other locations was poor at the beginning of the monitoring project. The principal contaminants with an agricultural source were triazine herbicides, nitrate-nitrogen, total suspended sediment, orthophosphate, and bacteria.

The percentage of agricultural producers in the study area who participated in the WQIP was high. Many of the BMP's offered were already being used by area farmers, however. Other BMP's offered unattractive cash incentives and were sparsely adopted. Although 68 percent of the basin was enrolled in at least one BMP, less than 1 percent of land was taken out of production. Also, clearing trees from land to increase production continued after the WQIP began, but at a slower rate.

The project compared water quality before and after BMP implementation. The principal constituents monitored were four pesticides (triazines, alachlor, metolachlor, and carbofuran) determined by ELISA, nitrate-nitrogen, total suspended solids, orthophosphate, fecal coliform, and fecal streptococci. Samples for these constituents were collected monthly to every few minutes during high-flow events. Other constituents, including additional pesticides, were determined less frequently. The mass flux of triazines, metolachlor, nitrate-nitrogen, and total suspended solids was calculated for Pleasant Grove Spring from the analytical data and continuous discharge hydrograph. Kentucky Division of Water staff conducted biological inventories of Pleasant Grove Creek immediately downstream of the spring at the beginning and end of the project.

The graphical trends, annual mass flux values, original analytical data, and annual descriptive statistics were evaluated for changes in water quality over the monitoring period. There was no discernible trend in nitrate-nitrogen concentration on the temporal graphs, but there was a distinct increase in atrazine-equivalent flux and a weaker increase in triazine geometric average. There was no chronological trend in triazines or nitrate-nitrogen when comparing averages, medians, or annual mass flux to other activity in the basin, such as amount of chemical applied. The concentration of total suspended solids decreased slightly in mass flux and median values over the course of the program, whereas orthophosphate concentrations increased slightly. Graphs of the bacteria data suggest a slight improvement in fecal streptococci counts and a shift toward a human-dominated source.

Statistical comparisons were made of analyses, annual means and medians, and annual flux totals using the Student's t test, Dunnett's t test, and Mann-Whitney u test and w test, as appropriate, for the population distribution as determined by chi-square comparison to normal and log-normal distributions. The statistics largely confirmed the findings from inspection of the trends of graphs, data, and annual statistics. There were no statistically significant changes in the occurrence of triazines or nitrate-nitrogen. Total suspended sediment had a statistically significant decrease when comparing the sample analytical data, but no change when comparing the annual statistics. Orthophosphate increased by all methods. Annual statistics for bacteria did not show a statistically significant change.

The results of the monitoring indicate the Water Quality Incentive Program was only partly successful in improving groundwater quality in the Pleasant Grove Spring Basin. Water quality at Pleasant Grove Spring did not meet many water-quality standards before the project began, and continued to fail to meet those standards at the project's conclusion. The BMP's approved for use at the time this project started, and those used during the WQIP, were being applied by the farmers conscientiously throughout most of the basin. For both periods, the approved BMP's were not the most effective for karst. The single most important lesson from the Pleasant Grove Spring study is that "one size fits all" BMP programs will not work for karst terrain. BMP's must be tailored to the crops being grown and the hydrogeology of the groundwater basin. Programs in karst terrain should emphasize buffer strips, livestock exclusion, and tree planting. Conservation officers must have more power to influence the selection of the most

effective BMP's, and cash incentives for the farmers to voluntarily take land out of production must be adequate to offset lost revenue.

Acknowledgments

References Cited

Aley, T., 1997, Groundwater tracing in the epikarst, *in* The engineering geology and hydrogeology of karst terranes: Proceedings of the Sixth Multidisciplinary Conference on Sinkholes and the Engineering and Environmental Impacts of Karst, Springfield, Mo., April 6–9, p. 207–211.

American Water Works Association, 1992, Standard methods for the examination of water and wastewater: American Public Health Association, American Water Works Association, Water Environment Federation, p. 9–70.

Aravena, R., Evans, M.L., and Cherry, J.A., 1993, Stable isotopes of oxygen and nitrogen in source identification of nitrate from septic systems: Ground Water, v. 31, no. 2, p. 180–186.

Ashton, K., 1966, The analysis of flow data from karst drainage systems: Transactions of the Cave Research Group of Great Britain, v. 7, p. 161–203.

Bennett, H.H., and Chapline, W.R., 1928, Soil erosion a national menace: U.S. Department of Agriculture Circular 33.

Boyer, D.G., and Pasquarell, G.C., 1994, Agricultural land use impacts on karst groundwater quality, *in* Effects of human-induced changes on hydrologic systems: American Water Resources Association, p. 791–799.

Boyer, D.G., and Pasquarell, G.C., 1996, Agricultural land use effects on nitrate concentrations in a mature karst aquifer: American Water Resources Association, Water Resources Bulletin, v. 32, no. 3, p. 565–573.

Brown, R.F., and Lambert, T.W., 1962, Availability of ground water in Allen, Barren, Edmonson, Green, Hart, Logan, Metcalfe, Monroe, Simpson, and Warren Counties, Kentucky: U.S. Geological Survey Hydrologic Investigations Atlas HA-32, 3 plates, scale 1:125,000.

Buchanan, T.J., and Somers, W.P., 1976, Discharge measurements at gauging stations, *in* Techniques of water-resources investigations of the United States Geological Survey: U.S. Geological Survey, Applications of Hydraulics, book 3, chapter A8, 65 p.

Canter, L.W., 1997, Nitrates in groundwater: Boca Raton, Fla., CRC Press, 263 p.

Currens, J.C., 1997, A sampling plan for conduit-flow karst springs: Minimizing sampling cost and maximizing statistical utility, *in* The engineering geology and hydrogeology of karst terranes: Proceedings of the Sixth Multidisciplinary Conference on Sinkholes and the Engineering and Environmental Impacts of Karst, Springfield, Mo., April 6–9, p. 193–198.

Currens, J.C., 1999, Mass flux of agricultural nonpoint-source pollutants in a conduit-flow-dominated karst aquifer, Logan County, Kentucky: Kentucky Geological Survey, ser. 12, Report of Investigations 1, 151 p.

Dao, T.H., Lavy, T.L., and Sorensen, R.C., 1979, Atrazine degradation and residue distribution in soil: Soil Science Society of America Journal, v. 43, p. 1129–1133.

Davis, J.C., 1986, Statistics and data analysis in geology [2nd ed.]: New York, John Wiley, 646 p.

Dye, J.W., Barton, A.J., and Froedge, R.D., 1975, Soil survey of Logan County, Kentucky: U.S. Department of Agriculture, Soil Conservation Service, 78 p.

Felton, G.K., 1991, Agricultural chemicals at the outlet of a shallow carbonate aquifer: American Society of Agricultural Engineers, 1991 International Summer Meeting, Albuquerque, N.M., Paper 91-2109, 26 p.

Fogg, G.E., Rolston, D.E., Decker, D.L., Louie, D.T., and Grismer, M.E., 1998, Spatial variation in nitrogen isotope values beneath nitrate contamination sources: Ground Water, v. 36, no. 3, p. 418–426.

Ford, D.C., and Williams, P.W., 1989, Karst geomorphology and hydrology: London, Unwin Hyman, 601 p.

Freyer, H.D., and Aly, A.J.M., 1974, ^{15}N studies on identifying fertilizer excess in environmental systems, *in* Isotopic ratios as pollutant source and behavior indicators: International Atomic Energy Agency, p. 21–33.

Garner, W.Y., Honeycutt, R.C., and Nigg, H.N., eds., 1986, Evaluation of pesticides in groundwater: American Chemical Society Symposium Series 315, 573 p.

Geldreich, E.E., and Kenner, B.A., 1969, Concepts of fecal streptococci in stream pollution: Journal of Water Pollution Control Federation, Research Supplement, v. 41, p. R336–R351.

Gish, T.J., Isensee, A.R., Nash, R.G., and Helling, C.S., 1990, Impact of pesticides on shallow ground-

water quality: Transactions of the American Society of Agricultural Engineers, v. 34, no. 4, p. 1745–1753.

Glantz, S.A., 1992, Primer of biostatistics [3rd ed.]: New York, McGraw-Hill, 440 p.

Guy, H.P., and Norman, V.W., 1970, Field methods for measurement of fluvial sediment, *in* Techniques of water-resources investigations of the United States Geological Survey: U.S. Geological Survey, Applications of Hydraulics, book 3, chapter C2, 59 p.

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

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

Haszler, G.R., ed., 1994?, Water quality assessment in agricultural areas of Kentucky, second year report, October 1992–September 1993: University of Kentucky, Department of Agronomy, 188 p.

Herbel, M.J., and Spalding, R.F., 1993, Vadose zone fertilizer-derived nitrate and δ^{15}N extracts: Ground Water, v. 31, no. 3, p. 376–382.

Hippe, D.J., Witt, E.C., and Giovannitti, R.M., 1994, Hydrogeology, herbicides, and nutrients in groundwater and springs, and relation of water quality to land used and agricultural practices near Carlisle, Pennsylvania: U.S. Geological Survey Water-Resources Investigations Report 93-4172, 66 p.

Honeycutt, R.C., and Schabacker, D.J., eds., 1994, Mechanisms of pesticide movement into groundwater, a compilation of research papers presented at the 1991 American Chemical Society meeting in Atlanta, Georgia, April 18: Boca Raton, Fla., CRC Press Lewis Publishers, 189 p.

Huber, G., 1990, Landowner perceptions of sinkholes and groundwater contamination: Journal of Soil and Water Conservation, v. 45, March-April, p. 323–327.

Johnston, W.R., Ittihadieh, F.T., Craig, K.R., and Pillsbury, A.F., 1967, Insecticides in tile drainage effluent: Water Resources Research, v. 3, no. 2, p. 525–537.

Kentucky Agricultural Statistics Service, 1998, 1997–1998 Kentucky agricultural statistics: U.S. Department of Agriculture and Kentucky Agricultural Statistics Service, 144 p.

Libra, R.D., 1987, Impacts of agricultural chemicals on groundwater quality in Iowa, *in* Fairchild, D.M., ed., Groundwater quality and agricultural practices: Chelsea, Mich., Lewis Publishers, p. 185–215.

Libra, R.D., Hallberg, G.R., Hoyer, B.E., and Johnson, L.G., 1986, The Big Spring Basin study in Iowa, *in* Agricultural impacts on groundwater, a conference: National Water Well Association, p. 253–273.

Libra, R.D., Hallberg, G.R., Ressmeyer, G.G., and Hoyer, B.E., 1984, Groundwater quality and hydrogeology of Devonian-carbonate aquifers in Floyd and Mitchell Counties, Iowa: Iowa Geological Survey, Open-File Report 84-2, pt. 1, 106 p.

Lichtenstein, E.P., 1958, Movement of insecticides in soils under leaching and non-leaching conditions: Journal of Economic Entomology, v. 51, no. 3, p. 380–383.

Martin, J.R., and Green, J.D., 1992, Chemical control of weeds in Kentucky farm crops: University of Kentucky, College of Agriculture, Cooperative Extension Service, 87 p.

McMurray, S.E., 1999, Post-BMP biological survey of Pleasant Grove Spring, Logan County, Kentucky: Kentucky Division of Water, Water Quality Branch, Nonpoint Source Section, Technical Bulletin 2, 3 p.

Meiman, J., 1985, Investigation of flood pulse movement through a maturely karstified aquifer at Mammoth Cave National Park: Richmond, Eastern Kentucky University, master's thesis, 343 p.

Miller, R.C., 1968, Geologic map of the Russellville quadrangle, Logan County, Kentucky: U.S. Geological Survey Geologic Quadrangle Map GQ-714, scale 1:24,000.

Palmer, A.N., 1991, Origin and morphology of limestone caves: Geological Society of America Bulletin, v. 103, p. 1–25.

Panno, S.V., Kelly, W.R., Weibel, C.P., Krapac, I.G., and Sargent, S.L., 1998, The effects of land use on water quality and agrachemical loading in the Fogelpole Cave groundwater basin, southwestern Illinois, *in* Proceedings of the Eighth Annual Conference of the Illinois Groundwater Consortium's Research

on Agricultural Chemicals in Illinois Groundwater, Status and Future Directions, Makanda, Ill., April 1–2, 1998: Illinois Groundwater Consortium, 13 p.

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

Pasquarell, G.C., and Boyer, D.G., 1996, Herbicides in karst groundwater in southeast West Virginia: Journal of Environmental Quality, v. 25, p. 755–765.

Quinlan, J.F., and Alexander, E.C., 1987, How often should samples be taken at relevant locations for reliable monitoring of pollutants from an agricultural, waste disposal, or spill site in a karst terrane? A first approximation, *in* Proceedings of the 2nd Multidisciplinary Conference on Sinkholes and the Environmental Impacts of Karst, Orlando, Fla., February 9–11, 1987: Rotterdam, A.A. Balkema, p. 277–286.

Rainey, H.C., III, 1965, Geologic map of the Dennis quadrangle, Logan County, Kentucky: U.S. Geological Survey Geologic Quadrangle Map GQ-450, scale 1:24,000.

Ritter, W.F., 1986, Pesticide contamination of groundwater—A review: American Society of Agricultural Engineers, ASAE Paper 86-2028, 24 p.

Rowden, R.D., Libra, R.D., and Liu, H.P., 1999, Big Spring Basin demonstration project [abs.]: Iowa Department of Natural Resources, Geological Survey Bureau, www.igsb.uiowa.edu/inforsch/bigsprng/bigsprng.htm [accessed 1/22/99].

Ryan, M., and Meiman, J., 1996, An examination of short-term variations in water quality at a karst spring in Kentucky: Ground Water, v. 34, no. 1, p. 23–30.

Sampson, W.F., 1995, Biological survey of Pleasant Grove Spring, Logan County, Kentucky, for "Characterization and Quantification of Nonpoint-Source Pollutant Loads in a Karst Aquifer Underlying an Agricultural Region": Kentucky Division of Water, Water Quality Branch, 10 p.

Shawe, F.R., 1966a, Geologic map of the Adairville quadrangle, Kentucky-Tennessee: U.S. Geological Survey Geologic Quadrangle Map GQ-569, scale 1:24,000.

Shawe, F.R., 1966b, Geologic map of the Dot quadrangle, Kentucky-Tennessee: U.S. Geological Survey Geologic Quadrangle Map GQ-568, scale 1:24,000.

Shuster, E.T., and White, W.B., 1971, Seasonal fluctuations in the chemistry of limestone springs: A possible means for characterizing carbonate aquifers: Journal of Hydrology, v. 14, p. 93–128.

Smith, M.C., Bottcher, A.B., Campbell, K.L., and Thomas, D.L., 1988, Measurement of pesticide transport to shallow groundwater: American Society of Agricultural Engineers, ASAE Paper 88-2640, 44 p.

Steinheimer, T.R., Scoggin, K.D., and Kramer, L.A., 1998, Agricultural chemical movement through a field-size watershed in Iowa: Subsurface hydrology and distribution of nitrate in groundwater: Environmental Science and Technology, v. 32, no. 8, p. 1039–1047.

Taraba, J.L., Dinger, J.S., Sendlein, L.V.A., Felton, G.K., Conrad, P.G., Currens, J.C., and Keagy, D.M., 1995, Agricultural chemical use impacts on Kentucky groundwater resources—Assessment report 1990–1993: University of Kentucky, College of Agriculture; Kentucky Geological Survey; Kentucky Water Resources Research Institute, 76 p.

U.S. Environmental Protection Agency, 1983, Handbook for sampling and sample preservation of water and waste water: U.S. Environmental Protection Agency, EPA-600/4-82/029, 402 p.

U.S. Environmental Protection Agency, 1986, Working Group on Pesticides in Groundwater: U.S. Environmental Protection Agency, Office of Groundwater Protection, EPA 440/6-86-002, 72 p.

U.S. Environmental Protection Agency, 1989, Method 507. Determination of nitrogen- and phosphorus-containing pesticides in water by gas chromatography with a nitrogen-phosphorus detector (revision 2.0), *in* Methods for the determination of organic compounds in drinking water: U.S. Environmental Protection Agency, EPA/600/4-88/039, p. 143–146.

U.S. Environmental Protection Agency, 1993, Guidance specifying management measures for sources of nonpoint pollution in coastal waters, management measures for agricultural sources: U.S. Environmental Protection Agency, Office of Water, chapter 2, EPA 840-B-92-002, 724 p.

U.S. Geological Survey, 1982, U.S. Geological Survey national handbook of recommended methods

for water-data acquisition; chapter 5, chemical and physical quality of water and sediment: U.S. Geological Survey, p. 5-1–5-194.

Van Couvering, J.A., 1962, Characteristics of large springs in Kentucky: Kentucky Geological Survey, ser. 10, Information Circular 8, 37 p.

Wartenberg, D., 1988, Groundwater contamination by Temik aldicarb pesticide; the first eight months: Water Resources Research, v. 24, no. 2, p. 185–194.

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

Williams, W.M., Holden, P.W., Parsons, D.W., and Lorber, M.N., 1988, Pesticides in groundwater data base, 1988 interim report: U.S. Environmental Protection Agency, Office of Pesticide Programs, 33 p.

Worthington, S.R.H., 1991, Karst hydrogeology of the Canadian Rocky Mountains: Hamilton, Ontario, McMaster University, doctoral dissertation, 380 p.

Appendix A

Abbreviations used as a prefix to identification numbers for water samples and for digital files collected from data loggers during the study. The italicized abbreviations are used only occasionally in this report, but are included here to facilitate retrieval of archived data from the Kentucky Groundwater Data Repository.

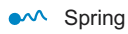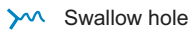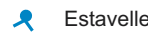| Site/Sample Abbreviation	Sample Site or Monitoring Station	Data Type	Latitude	Longitude	Elevation (ft)
PGSP		Water samples and data files for stage			
P		Data files for water-quality parameters			
PGRG		Data files for precipitation gage			
PGTP	Pleasant Grove Spring	Data files for air temperature	364244	865419	510
PGDP		Duplicate samples			
PGEB		Equipment blanks			
PGFB		Field blanks of water			
PGUC		Duplicates in uncapped bottles in ISCO sampler			
RAIN		Precipitation samples			
LPKW		Water samples and data files for stage			
LPDP		Duplicate water samples			
LPEB	Leslie Page karst window	Equipment blanks of water samples	364408	865347	555
LPFB		Field blanks of water samples			
GDSW		Water samples and data files for stage			
GDEB	George Delaney swallow hole	Equipment blanks for water samples	364425	865512	540
GDFB		Field blanks of water samples			
UPGC	upper Pleasant Grove Creek at Johnson-Young Road	Water samples and data files for stage	364535	865450	575

Appendix A—Continued.

Site/Sample Abbreviation	Sample Site or Monitoring Station	Data Type	Latitude	Longitude	Elevation (ft)
PGCK	Reach of Pleasant Grove Creek between GDSW and UPGC stations	Represents calculated values only	not applicable	not applicable	not applicable
TCKW	The Canyon karst window	Water samples	364451	865358	550
JHWW	Joe Harper water well (estavelle)	Water samples	364554	865333	580
SVKW	Spring Valley karst window	Water samples and data files for stage	364307	865353	510
SKSP	Shackelford Spring	Water samples	364619	865500	585
TFBH	Thad Flowers blue hole	Water samples	364635	865348	600
DDSP	David Dotson Spring	Water samples	364218	865438	505
HHKW	Hickory Hill karst window	Water samples	364528	865610	575
LDWW	Logan Dawson	Water samples collected from miscellaneous domestic wells	364628	865746	590
MMWW	Martha McGuire		364500	865238	620
MSHW	Miller School House		364440	865228	620
MHWW	Mark Hopkins		364530	865250	620
EGWW	Eugene Gooch		364740	865345	650
CAWW	City of Adairville	Water Works Treatment Plant	363942	865111	500
FIBK	Used early in the study for various sites	Field blanks of distilled water	not applicable	not applicable	not applicable

KENTUCKY GEOLOGICAL SURVEY
James C. Cobb, State Geologist and Director
UNIVERSITY OF KENTUCKY, Lexington

https://doi.org/10.13023/kgs.ri11.12

REPORT of INVESTIGATIONS 11
Series XII, 2005
PLATE 1

Significant Karst Features, Potentiometric Surface, and Hypothesized Flow Routes

Pleasant Grove Spring Karst Groundwater Drainage Basin, Logan County, Kentucky

EXPLANATION

- Spring
- Swallow hole
- Drilled well
- Estavelle
- Sinkhole
- Karst window

- Mapped cave
- Slow-flow sub-basin
- Permanent stream course
- Intermittent stream course

- Hypothesized groundwater flow (route and direction; dashed where intermittent)
- –510' Projected potentiometric surface contour line (feet above mean sea level)
- Groundwater basin boundary

SCALE 1:48,000

1   0   1 Mile
1000 0 1000 3000 5000 7000 Feet
1   .5   0   1 Kilometer

N

RUSSELLVILLE

Turkey Knob

Green Downs Road

Hindman sinkhole

Thad Flower blue hole (estavelle) (TFBH)

Shackelford Spring (SKSP)

Upper Pleasant Grove Creek monitoring station (UPGC)

Johnson-Young Road

Piper estavelle

Joe Harper karst windows
#2 #1

Gooch sinkhole

Mark Harper well

Base flow only

The Canyon karst window (TCKW)

Joe Harper well (estavelle) (JHWE)

Miller School House well (MSHW)

Delaney swallow hole (GDSW)

Wheatfield estavelle

Miller sinkhole

Dotson karst window

Leslie Page karst window (LPKW)

Poison Ivy karst window

Oakville Cave

Johnson swallow hole

Spring Valley karst window (SVKW)

Spring Valley Rd.

Campground Road

Whippoorwill

Little Whippoorwill Cr.

Beauchamp Road

Pleasant Grove Spring (PGSP)

Wash Gunn Road

Mortimer Road

RED RIVER

Creek