FINAL REPORT

Characterization and Quantification of Nonpoint Source Pollution in a Conduit-Flow Dominated Karst Aquifer Underlying an Extensive Use Agricultural Region - Phase III

SPONSOR ID: MOA# 016080

UKRF # 4-29444

Funded through 319(h) Non-point Source Implementation Program

Cooperative Agreement #C9994506-94

Covers grant period from May 1, 1995 through December 31, 1999

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December 1, 1999

Funding for this project was provided, in part, by a grant from the U.S. Environmental Protection Agency through the Kentucky Division of Water, Nonpoint Source Section, as authorized by the Clean Water Act Amendments of 1987, Section 319(h) Nonpoint Source Implementation Grant #C9994506-94. The contents of this document do not necessarily reflect the views and policies of the EPA, nor does the mention of trade names or commercial products constitute endorsement.

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ABSTRACT

Water quality in the Pleasant Grove Spring karst ground-water basin was monitored to determine the effectiveness of Best Management Practices (BMP's) implemented through the U. S. Department of Agriculture 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 began in October 1993, the major objective of which was to monitored the water quality for one 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 were previously reported. This report covers the specific findings of the interim extension and Phase III [October 1994 through October 1998]. It also summarizes the overall findings of the project and evaluates the outcome of the WQIP implemented BMP's, which began in 1995.

Pleasant Grove Spring discharges runoff from a 4,069 hectares (10,054 ac) karst ground-water basin in southern Logan County, southwestern Kentucky. The basin is mature karst topography developed on Mississippian age carbonates mantled with residuum. Sinkholes and sinking streams dominate the landscape and perennial surface flowing streams only occur in the headwaters of the basin. Most of the area of the basin (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 grown are dairy and beef cattle and swine. Over 70 percent of the area of the watershed was enrolled in the WQIP.

Analyses of samples collected since October 1994 at 7 locations in the basin indicated the principal contaminants found of probable agricultural origin remained herbicides, nitrate-nitrogen, suspended sediment, orthophosphate, and high bacteria counts. The maximum nitrate-nitrogen concentration measured in the basin between 1994 through 1998 was 13.1 mg/L observed at Leslie Page karst window and the average concentration was 5.05 mg/L. The maximum orthophosphate concentration was 1.397 mg/L at Pleasant Grove Spring and the median was 0.17 mg/L. The total suspended solids maximum was 3,267 mg/L with a median concentration of 53 mg/L. The maximum ELISA triazines concentration was 393.0 µg/L observed at Leslie Page karst window, with a median concentration of 1.15 µg/L. Maximum bacteria counts were 200,000 col/100mL fecal coliform and 810,000 col/100mL fecal streptococci with medians of 400 col/100mL and 640 col/100mL, respectively.

Water quality at Pleasant Grove Spring was monitored continuously 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 never exceeded the Maximum Contaminant Level (MCL). The average concentration was 4.8 mg/L nitrate-nitrogen. The maximum orthophosphate concentration was 1.397 mg/L and the median was 0.53 mg/L. The total suspended solids maximum was 3,073 mg/L with a median concentration of 55 mg/L. The maximum ELISA triazines concentration was 62.2 µg/L. Triazine concentrations briefly exceed MCL's during the spring season of 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 are the highest

measured in the basin. Median concentrations of these pesticides, 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/100mL). Maximum bacteria counts were 60,000 col/100mL fecal coliform and 200,000 col/100mL fecal streptococci.

The pre-BMP and post-BMP quality of ground water discharging at Pleasant Grove Spring 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 the other contaminants. The flux and annual statistics of nitrate-nitrogen were unchanged over the course of the BMP program. Atrazine-equivalent flux and triazines geometric averages indicated an increase. Total suspended solids concentrations decreased slightly while orthophosphate exhibited a slight increase. Fecal streptococci counts showed an improvement.

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 ground water in karst aquifers should largely limit BMP's to the installation of buffer strips around sinkholes, the exclusion of livestock from streams, and the removal of land from agricultural production.

INTRODUCTION

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

Karst terrain 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 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, ground water can be easily contaminated. When a karst terrain is subjected to intensive land use, the potential for ground-water contamination from any of mans activities which produce waterborne pollution, including agriculture, is significant.

Reducing the potential for non-point source pollution from agriculture of karst aquifers is important because some of the most productive agricultural lands in Kentucky occur in the karst regions of the state. The farms located within 35 counties which are predominantly karst terrain produce over 50 percent of the annual agricultural receipts in Kentucky (Kentucky Agricultural Statistics Service, 1998). Logan County, where this study was conducted, 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 and has developed, along with other farming related institutions, best management practices (BMP's) intended to minimize of soil loss and protect water quality. The purpose of this project was to test whether an economic incentive program intended to encourage farmers to use BMP's designed to protect ground-water would reduce non-point source pollution of ground water in a karst aquifer. The financial incentive for the adoption of BMP's was administered through the Water Quality Incentive Program (WQIP) which was in effect during the mid-1990s'. The WQIP paid farmers to adopt farming practices (BMP's), which had been shown at field and farm scales to protect water quality.

This project was divided into three phases. During Phase I (August 1990 through October 1993) reconnaissance and mapping of the karst ground-water basin was conducted. Phase II (October 1993 through October 1994) continued reconnaissance field work and began the first full year of pre-BMP water quality monitoring. An interim phase followed (October 1994 through October 1995) due to the early initialization of

Phase II and a delay in funding of Phase III. This report covers specific results from the interim phase and it also covers field work and water quality monitoring results during the post-BMP period of Phase III from October 1995 through October 1998. Further, it summarizes the overall findings of the project from its' initial inception in August of 1990 through its conclusion in October 1998.

ACKNOWLEDGMENTS

Support for project development and initial fieldwork was through the Kentucky Geological Survey, University of Kentucky. The author wishes to thank the University of Kentucky College of Agriculture and the U.S. Environmental Protection Agency, through the Kentucky Division of Water Nonpoint-Source Program, for financial support. Field reconnaissance and sampling, and the purchase of major equipment, was begun in February, 1991 when funding was received through the University of Kentucky College of Agriculture from Kentucky Senate Bill 271 (1990). Funding for Phase I was received from the U. S. Environmental Protection Agency's Nonpoint-Source Program (of the Clean Water Act) through the Kentucky Division of Water (Memorandum of Agreement 11399) in April, 1992. Additional Section 319 funding was received September 1993 for Phase II (Memorandum of Agreement 12875) and an interim continuance of Phase II in September of 1994 (Memorandum of Agreement 15424). Three years of funding for Phase III was received in May 1995 (Memorandum of Agreement 16080) and a no-cost extension was granted to continue the monitoring through October 1998, the end of the 1997-1998 water year.

No individual can undertake a project of this magnitude alone. The support of a large number of people was needed for its successful completion. Ms. Ruthi Steff and Ms. Kay Joy of the Bowling Green regional office of the U.S. Department of Agriculture, Natural Resources Conservation Service (NRCS) prepared the Water Quality Incentive Program proposal to obtain the funding for the implementation of BMP's. The help of the entire staff of the Logan County office of the NRCS is acknowledged. Mr. Bill Johnson, Mr. Craig Givens and Mr. Jimmy Christian provided invaluable help in contacting farmers, acquiring crop data and chemical-use data, general field support, but most notably managing the WQIP grant. Mr. Stan Asbridge of the U.S. Department of Agriculture, Consolidated Farm Services Agency, graciously loaned annual aerial photographs of crops, and his staff provided training in their interpretation. Mr. Steve Crabtree of the Boone County office of the Natural Resources Conservation Service digitized land-use maps into a GIS system and calculated the basin and crop areas. KGS field technician Steve Webb made significant contributions to the success of the project since September 1995. His help and that of many current, and past, KGS staff was essential. Over 40 study-area farmers have graciously allowed access to their property and have helped locate springs and other karst features. The farmers' interest and cooperation was vital for the successful completion of this project and their help is gratefully acknowledged. Finally, the help and advice of others to numerous to name individually is also appreciated. This project would not have succeeded without the help of all of these people.

Study Area Description

Geographic Location

The Pleasant Grove Spring karst ground-water 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 portions of the Russellville, Dennis, Dot, and Adairville 7 1/2 minute quadrangles. As determined by ground-water dye tracing, the total surface catchment area of the ground-water basin is 4,069 hectares (10,054 ac). The ground-water basin is roughly bounded on the east by US highway 431. Kentucky 96 traverses the basin from north to south along the western third of the basin. Mortimer Road connects from Kentucky 96 east to US 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) upstream 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 Upper Mississippian age. The geology of the area was mapped by Rainey (1965), Shawe (1966a, 1966b), and Miller (1968). Only two mappable units, the St. Louis Limestone, and the overlying Ste. Genevieve Limestone, occur at the surface in the basin. A prominent horizon of bedded chert at the top of the St. Louis Limestone has a significant influence of 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 commun., 1994). The strata dip gently to the northwest at 11 meters per kilometer (60 ft./mi.) into the Illinois structural basin. Previous hydrogeologic investigations in the area are by Brown and Lambert, (1962), Van Couvering, (1962), and Currens, (1999).

The ground-water basin is a shallow, unconfined, carbonate aquifer (Currens, 1999) and can be divided into two areas with differing flow regimes based on ground-water flow velocities. The northern, headwaters half of the basin is characterized by a slow-flow (diffuse) regime whereas the southern, downstream half is predominantly fast-flow (conduit-flow) (Plate 1). Although two flow regimes are recognized, the preponderance of ground-water flow in both regimes is turbulent and occurs through a dendritic system of tributary conduits and caves. The gradient of the potentiometric surface in the headwaters area is uniformly gentle and flow velocities are relatively slow (0.002 m/sec, 0.005 ft./sec.) probably due to local restriction of conduit development by a bedded chert unit (Currens, 1999). The depth to ground-water is shallow in the headwaters area of the basin and indicates significant ground water is temporarily stored in joints and bedding planes in the headwaters area. Throughout the basin an unquantified, but probably significant, volume of water storage occurs in the epikarst consisting of the near surface weathered bedrock and overlying soil. In the downstream area of the basin quantitative ground-water dye traces (discussed below) show that flow

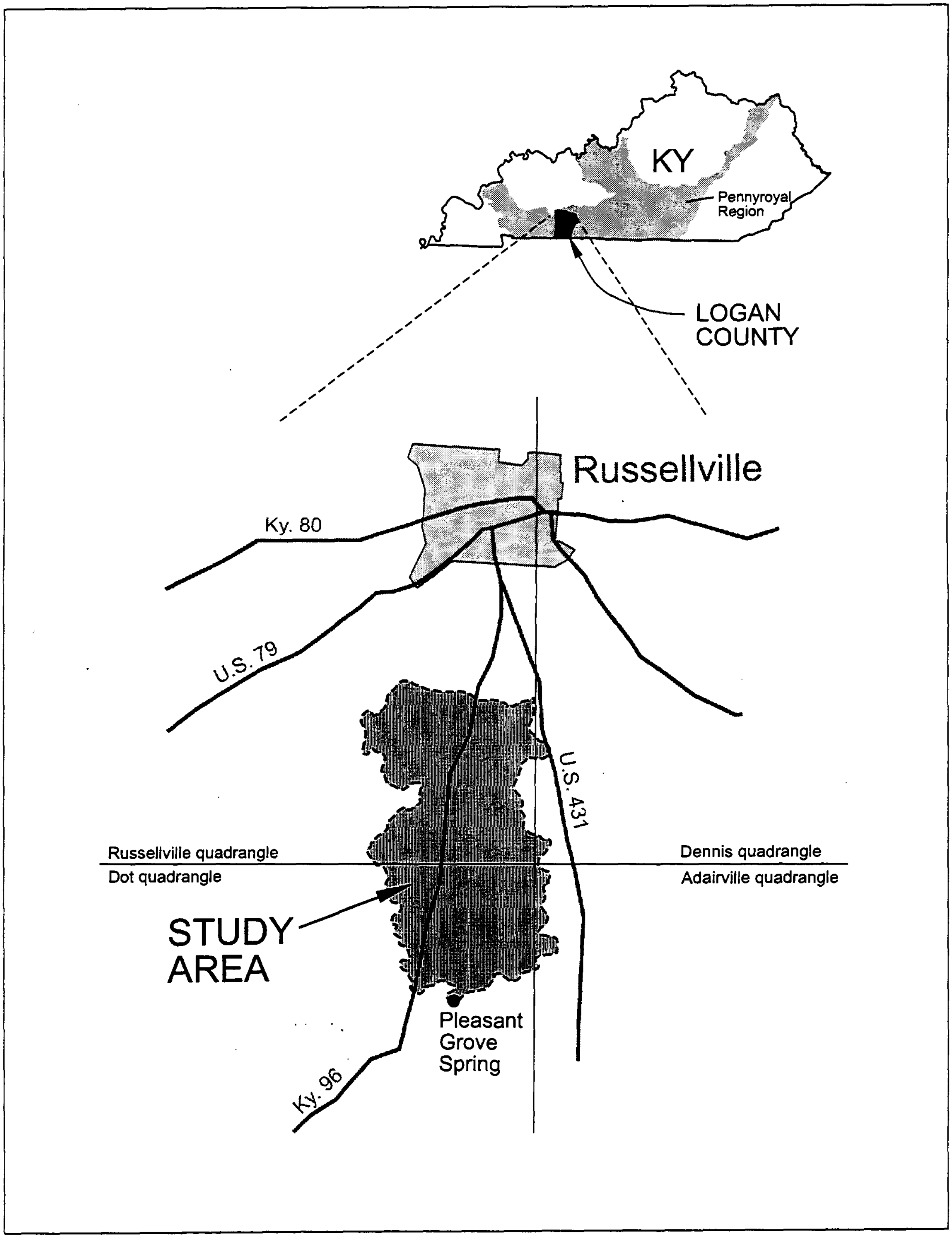

Figure 1. Location of the Pleasant Grove Spring Karst ground-water basin.

in the conduits is fast and may exceed 0.10 m/sec (0.39 ft./sec.) during high-flow events. 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 ground-water basin. Thus, Pleasant Grove Spring is an alluviated, underflow spring (Worthington, 1991) discharging from a totally submerged cave.

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 ridge tops 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 sub-soils. The soils are deep to very deep and have a thickness as great as 2 meters (76 in.) of thickness to the base of the sub-soil. Six holes drilled with a soil auger 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 meters (5 to 19 ft.) but none hit bedrock.

Land Use

The Pleasant Grove Spring watershed was chosen as the study area after field reconnaissance of the southwestern Kentucky karst area in May of 1989. The area was selected because of the presence of several karst features that would facilitate access to ground-water and the general absence of non-agricultural land use. The only non-agricultural business in the watershed is a privately owned 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, crosses the basin. There is no significant history of 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 are hay fields and pasture. The predominant agriculture production system is no-till corn on a two-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 ground-water in general, as well as karst specific studies through the early 1990's, was reviewed at length by Currens (1999). A brief recapitulation of that discussion follows along with a review of more recent karst related literature.

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

The presence of pesticides and other agriculturally derived non-point source pollutants in the ground water of karst aquifers also began to be studied in the 1980's. The most widely cited study was conducted in Iowa, which investigated the water quality of the Big Spring karst ground-water 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 out-wash and till (Hallberg and others, 1983) and, therefore, has a significant diffuse flow component characterized by fewer 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 exceed 0.85 µg/l but peaked at 5.1 µg/l during one spring season storm event. 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. Further, they report 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 spring season pesticide pulse, and little difference in atrazine or nitrate between springs overlain by agricultural and residential land uses. Their sampling schedule included only single grab samples during a few storm events. More recent work has been completed in southeastern West Virginia by Boyer and Pasquarell (1994, 1996, Pasquarell and Boyer, 1995, 1996). They found a strong positive linear relationship between nitrate concentrations and percentage of the ground-water basin area used for agriculture. Further, the occurrence of atrazine coincided with spring application season, and the counts of fecal bacteria found in springs increased with percent of land in agricultural production. Boyer and Pasquarell (1994) found average fecal coliform counts of less than 1 col/100 mL in a spring draining a pristine karst basin. Panno and others (1998) monitored the principally agricultural land-use Fogelpole Cave ground-water basin in southwestern Illinois. They found that triazines and sediment increased in response to spring season storm events during the application period and nitrate-nitrogen becomes elevated in the winter and peaks during the spring season. High bacteria counts occur during high flow events but are attributed to human waste.

Two other significant studies have been conducted in Kentucky by monitoring karst springs for agricultural non-point source pollution. Felton (1991) monitored Garretts Spring, in north western Jessamine County, which drains the Sinking Creek basin in the inner Bluegrass region of Kentucky. Felton found that nitrate concentrations varied seasonally and were highest during wet, winter months, but pesticide concentrations only occurred in low concentrations throughout the year. Agriculture conducted in the basin is primarily livestock (thoroughbred horses), with relatively few acres in row crops, and suburban development the next major land-use. Ryan and Meiman (1996) identified discrete time periods of high flow events when waters containing higher suspended sediment and bacteria counts arrived from agricultural lands bordering Mammoth Cave National Park. Ground-water dye traces from the suspected source areas were conducted simultaneously with the storm event 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, oral commun., 1994).

In an earlier report on the Pleasant Grove Spring project, for the period from August 1990 through October 1994, Currens (1999) reported that significant contaminants in the basin are herbicides (specifically atrazine), bacteria, and sediment. Nitrate was the most widespread, persistent contaminant in the basin, but concentrations averaged 5.2 mg/L basin wide and generally did not exceed U. S. E.P.A maximum contaminant levels (MCL's), but were above concentrations expected in an unpopulated setting. Atrazine had been consistently detected in low concentrations, and other pesticides were occasionally detected. Concentrations of triazines (including atrazine) and alachlor had exceeded drinking water MCL's during spring season 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. Basin wide, samples averaged 465 fecal coliform colony-forming units per 100 mL (col/100 mL) and 1,891 fecal streptococci col/100 mL; maximum counts were 14,000 and 24,000 col/100 mL respectively. A biological assessment showed an adverse impact on aquatic biota downstream, probably due to sedimentation. Several sites upstream of Pleasant Grove Spring were also sampled with similar results.

The mass flux of an atrazine-equivalent triazine (atrazine and other related chemicals) and nitrate were estimated 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 due to 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, 111 lbs. to 68 lbs.). The sediment flux was not estimated in the 1999 report due to 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.

A program charged to asses the impact of agricultural practices in Kentucky on water-quality was conducted by staff of the University of Kentucky College of

Agriculture under funding provided in 1990 by 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, G. R., undated). The sample site location is not named in the report but identified as Spring-711. The author, however, has first hand knowledge that the site is the Canyon Karst Window in the Pleasant Grove Spring ground-water basin study area. Physical parameters were determined by College of Agriculture staff and samples analyzed for nitrate-nitrogen, triazines and alachlor by ELISA, fecal coliform, fecal streptococci, and salmonella. These data are not used in the evaluation of the effectiveness of the Best Management Practices because of differences in sampling protocol, analytical methods, and quality assurance/quality control practices and because Pleasant Grove Spring was the primary focus of this project.

A summary of the statewide findings of the College of Agriculture are reported by Taraba and others (1995) and concludes that overall there was little correlation between agricultural activity and the occurrence of nitrate, herbicides, and bacteria in ground-water. The exception was the "shallow, rapid circulation ground-water zone" or karst. 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. It was also noted that only a small percentage of samples contain concentrations of triazines that exceed the maximum contaminate level (MCL) for atrazine. High bacteria populations were associated with the presence of domestic animals.

METHODOLOGY

Project Design

The strategy used to accomplish the goal of testing the effectiveness of Best Management Practices (BMP's) in a karst setting is to characterize the quality of water discharge from Pleasant Grove spring before and after BMP implementation. Specifically, the mass flux of water borne constituents discharged is to be estimated and the totals compared for each water year. The implementation of BMP's was initially planned to be through established USDA programs and by USDA staff but with emphasis on the area of the basin. It transpired, however, that a major grant was awarded by the USDA to the Logan County office of the Natural Resources Conservation Service (NRCS) to implement a Water Quality Incentive Program (WQIP) in the drainage basin of Pleasant Grove Spring. Activities not included in the monitoring program were a detailed inventory of chemical applications, a livestock census, one-on-one attempts to influence farmers to participate in any BMP program, or routine domestic water-well monitoring. These activities were not included principally due to budgetary, logistical, and man-power limitations but also because if was thought they would both have a poor response and create an atmosphere of distrust. However, 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 for monitoring was to focus intensive monitoring on the principal discharge point and most important contaminants while conducting less intensive monitoring at up-gradient sites. Four principal contaminants of likely agricultural origin were identified during reconnaissance of the basin; atrazine, nitrate, suspended sediment, and bacteria from animal waste. Additionally, orthophosphate was later identified as a pollutant and data are available from samples collected at Pleasant Grove Spring quarterly to monthly. 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 (PGSP) several upstream sites were monitored to identify the general source-area of any pollutants found at PGSP. Water level gauging stations were placed at four locations. The first two are on upper Pleasant Grove Creek at George Delaney Swallow Hole (GDSW) and at the box culvert where Johnson-Young Road crosses the creek (UPGC). Two more water level recorders were placed at Spring Valley karst window (SVKW) and Leslie Page karst window (LPKW). The LPKW and UPGC water level recorders were installed in April and June of 1993. During the reconnaissance period samples were also collected at Shackelford Spring (SKSP), Thad Flowers' Blue Hole (TFBH), The Canyon Karst Window (TCKW), and Joe Harper water well (JHWW), an estavelle lined with masonry and formerly used as a hand-dug water well. Monitoring at three sites SVKW, SKSP, and TFBH was discontinued for logistical, budgetary, and hydrologic reasons in October 1994. The water level recorder at Spring Valley Karst Window (SVKW) was decommissioned in October 1997. For a complete description of the SVKW, SKSP, and TFBH sites and for analytical data from these sites see Currens, 1999. An additional site, Miller School House Well (MSHW) 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 is being used as a control since the well is up-gradient of most agricultural activity.

Constituents Analyzed

The constituents determined for a sample were contingent upon the water-quality characterization needed 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 GC, four pesticides by enzyme-linked immunosorbent assay (ELISA); triazines, metolachlor, alachlor, and carbofuran, 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 ground water in the basin is generally well oxygenated (Pleasant Grove Spring is typically over 70 percent oxygen saturated) reduced ionic species are typically in very low concentrations. 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 PGSP by ISCO® 3700[1] automatic samplers. Samples were also collected at LPKW by automatic sampler but total dissolved solids were omitted from the constituent 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 methods and field methods used in this study are described in detail in Currens (1999) and the reader is referred to this earlier report. 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 in the field monthly 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 (ELISA). The Ogden Environmental Laboratory at Western Kentucky University in Bowling Green conducted bacterial determinations. Bacteria counts were determined 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). Analysis of nitrogen isotopes ($^{15}N/^{14}N$) was performed by Global Geochemistry Corporation, Canoga Park, California on a gas chromatograph, mass-spectrometer.

Quantification of ELISA

Analysis of pesticides by enzyme-linked immunosorbent assay (ELISA or immunoassay) was chosen because the number of analyses needed for mass-flux estimation was cost prohibitive and logistically impractical by gas chromatograph. 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 a r^2 of 0.95 and ELISA versus GC metolachlor had a r^2 of 0.80, both at the 95% 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).

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[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.

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 pre-washed 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 enumeration of bacteria 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 isotopes ($^{15}N/^{14}N$) analysis were collected by dipping the cubitainers. The samples were preserved with metallic silver, and shipped in ice chests within 24 hours via over-night express. Conductivity, pH, and temperature were measured in the field for samples collected at the beginning of the month and bi-weekly. See Currens (1999), Appendix B 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 upon the installation of each automatic sampler then the intake hose was purged with water from the sample site and the hose left empty. A water-presence sensor activated the sampling machines. When activated, the sampler was programmed to fill and purge the intake lines three times before filling the sample container.

Duplicate samples for suspended sediment analyses 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 correlated 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-inch-diameter glass funnel emptied into a 4-inch-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 under method 507.

Sampling Schedule

Samples were not collected on a strict time interval due to logistical and budgetary constraints. Previous studies of karst springs, however, have shown that rapid changes in the concentration of water borne constituents occur during high-flow events (Ashton, 1966, Meiman, 1985, Quinlan and Alexander, 1987, White, 1988, Ford and Williams, 1989). Therefore, sampling was planned to be frequent at Pleasant Grove Spring (PGSP) during storm events, so as to precisely represent the rapidly changing chemical concentrations during high-flow, and less frequent during base flow. Apart from high-flow events, the sampling frequency at PGSP was monthly through the reconnaissance phase (spring of 1992) and approximately bi-weekly (every two weeks) thereafter. The base-flow analysis suite was determined on the bi-weekly samples through spring 1995. Comprehensive samples were collected quarterly at PGSP. For high-flow events an attempt was made to collect a suite of samples by automatic sampler for every storm causing a 3 cm (0.1 ft.) or greater rise in stage at PGSP from mid-March to July. Beginning in the spring of 1995, a second automatic sampler was deployed during the spring season to collect samples daily as a supplement to the high-flow samples. If no storm event had occurred a bi-daily (every two days) sample was submitted for analysis. If an event had occurred and the high-flow sampler had failed to collect one or more samples the missed samples were replaced as possible from the daily set. Also beginning in 1995, all samples analyzed for total suspended solids were collected through the automatic samplers. During a no-cost extension period between funded phases (September 1994-March 1995), sampling frequency was reduced to minimize cost. For a discussion of the validity of the sampling schedule see Currens, 1997.

Leslie Page karst window (LPKW) was sampled monthly in the summer, fall, and winter using the base-flow analysis suite and bi-weekly during the spring season through the spring of 1995 and at least bi-weekly year-round there after. During the spring season an ISCO® model 2900 automatic sampler was deployed. Stage response at Leslie Page karst window was frequently minor so that water failed to reach the water level actuator and event samples were therefore not collected. This sampler was reprogrammed to collect samples every 12 hours. Unless a storm had occurred, samples were submitted for bi-daily intervals 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 (TCKW) and George Delaney swallow hole (GDSW) were sampled manually monthly to bi-weekly using the base-flow suite. Flow in Upper Pleasant Grove Creek would commonly cease at GDSW in mid-summer or early fall and when this occurred samples were collected at the Upper Pleasant Grove Creek (UPGC) station. When TCKW was flooded, and flowing water was inaccessible, a sample was collected at JHWW. Sampling at TCKW was begun early in 1992, then suspended until the spring of 1995 but was resumed and continued without interruption through October 1998. The UPGC station is upstream of GDSW and dye tracing has demonstrated that JHWW is 300 m (1000 ft.) upstream of TCKW. Also, some special case samples were collected at GDSW by automatic sampler in the spring seasons of 1997 and 1998.

Samples for bacteria enumeration were collected monthly to bi-weekly at PGSP and LPKW and monthly at TCKW (replaced by JHWW when TCKW was flooded), and GDSW (replaced by UPGC when GDSW was dry). Sampling for bacteria was discontinued in June 1992, resumed in early 1994, and continued through the 1997-98 water year. In addition, two sets of bacteria samples were collected manually 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 Schoolhouse well (MSHW) and a few other domestic water wells, and from rainwater. Most of the samples were analyzed for the base-flow constituent list, but one comprehensive sample was collected. Samples for nitrogen isotopes (N^{15}/N^{14}) analysis were collected at PGSP and LPKW 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 and 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 season.

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 ten-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 includes 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 by line power and the YSI® and the Marsh-McBirney® had battery backup. After samples for a high-flow event were missed due to a power failure caused by a thunderstorm, the automatic samplers were converted to exclusively batter power during the spring and summer. Other battery powered ISCO® samplers were temporarily installed at GDSW and LPKW as needed.

A simple weather station was also 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 non-recording 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. Interruptions in the data logger records occurred at various times during the project. The outages were mostly due to pressure sensor failure, but also included battery failure, electrical damage from lightning, water damage from a leaking cabinet, and programming errors.

A second non-recording rain gage was installed at the Leslie Page residence at the corner of Kentucky 96 (Orndorff Mill Road) and Joe Harper Road. This location was near the center of the ground-water basin and approximately 3.7km (12,000 feet) 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 PGSP rain gage.

Validity of Fecal Coliform/Fecal Streptococci Ratios

Geldreich and Kenner (1969) recommended using the count of fecal coliform bacteria colony-forming units divided by the count of fecal streptococci bacteria 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, while 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 fecal coliform-fecal streptococci ratios as an indicator of contamination origin is no longer recommended by the American Water Works Association (1992) for identifying sources of fecal contamination because of the rapid die off of fecal streptococci in treated water. Because fecal streptococci die off 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 ground-water flow rates in the basin are relatively fast, particularly during high flow, minimizing die off of streptococci after they enter the water. Further, all samples were of untreated water, which reduced the possibility of skewed ratios, and Ogden lab used m-enterococcus agar (Rose Huellett, oral commun., 1995), not the KF agar suspected of causing false positives.

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 bi-weekly, beginning in May 1995.

Quality-control samples included equipment blanks, trip blanks, and field blanks. The KGS laboratory made analyses of pesticides in replicate as part of its internal quality assurance protocol. Duplicate samples for nitrate and pesticide analysis by ELISA 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 plotted in figures 2, 3, and 4. The correlation coefficients of these relationships is high ($r^2 = 0.90$ or higher) and is statistical 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 respective minimum detection limits (4 of 84 samples) was insufficient to allow calculation of meaningful correlation's. In addition, nine duplicate samples were left in the sample tub of the automatic samplers for 14 to 16 days while the

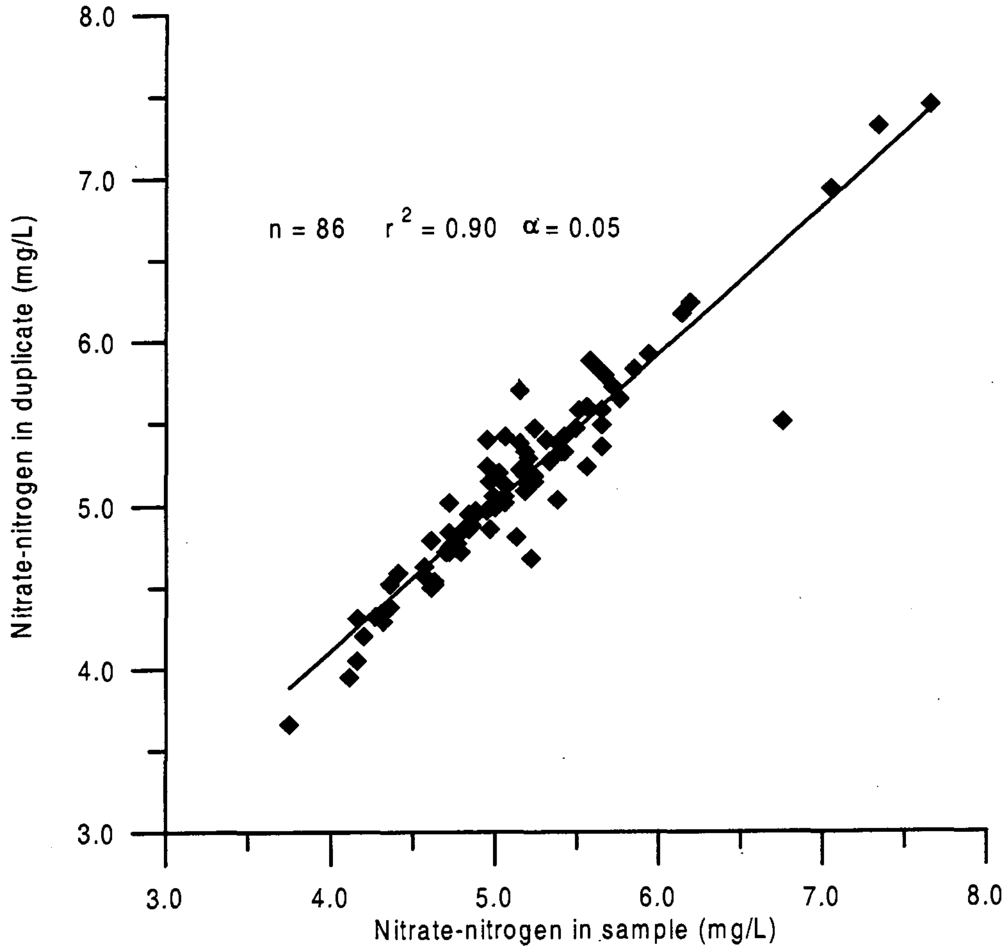

Figure 2. Cross-plot of nitrate-nitrogen determined for samples and duplicates collected at Pleasant Grove Spring between December 1993 and September 1998

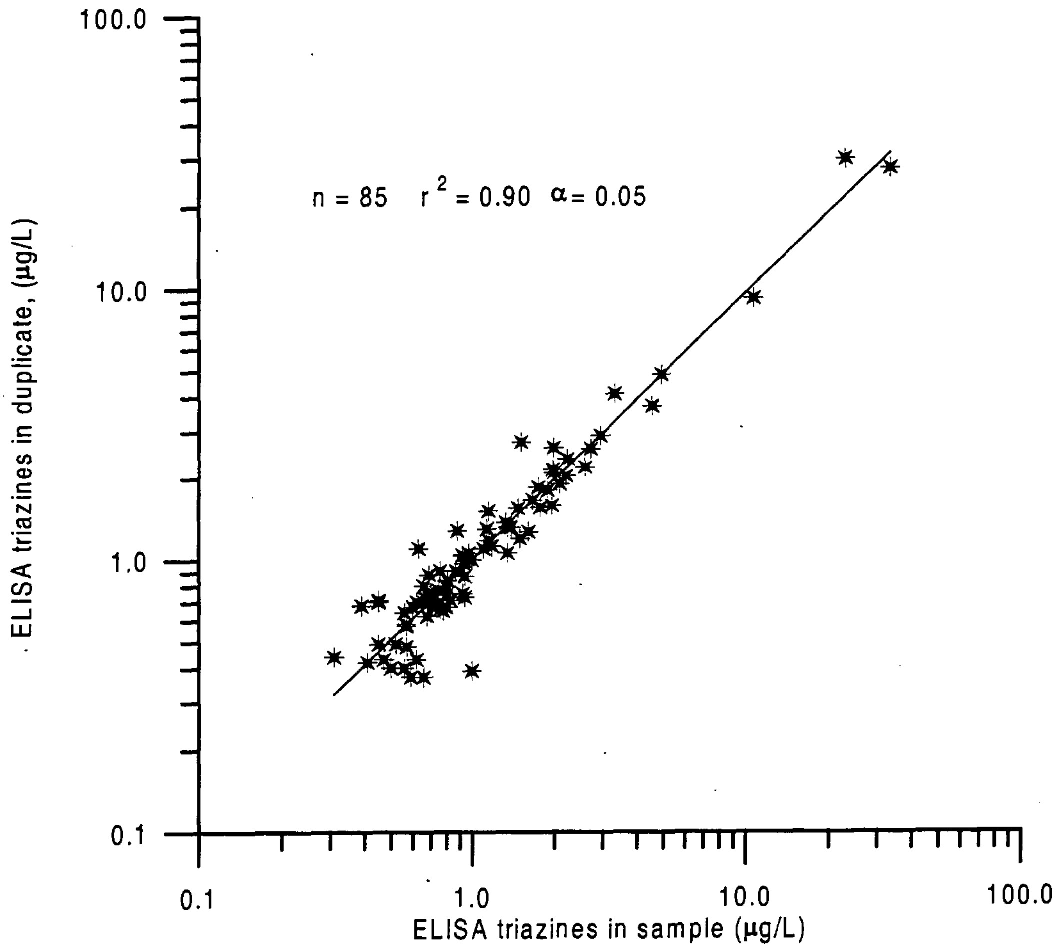

Figure 3. Cross-plot of ELISA triazines determined for samples and duplicates collected at Pleasant Grove Spring between December 1993 and September 1998

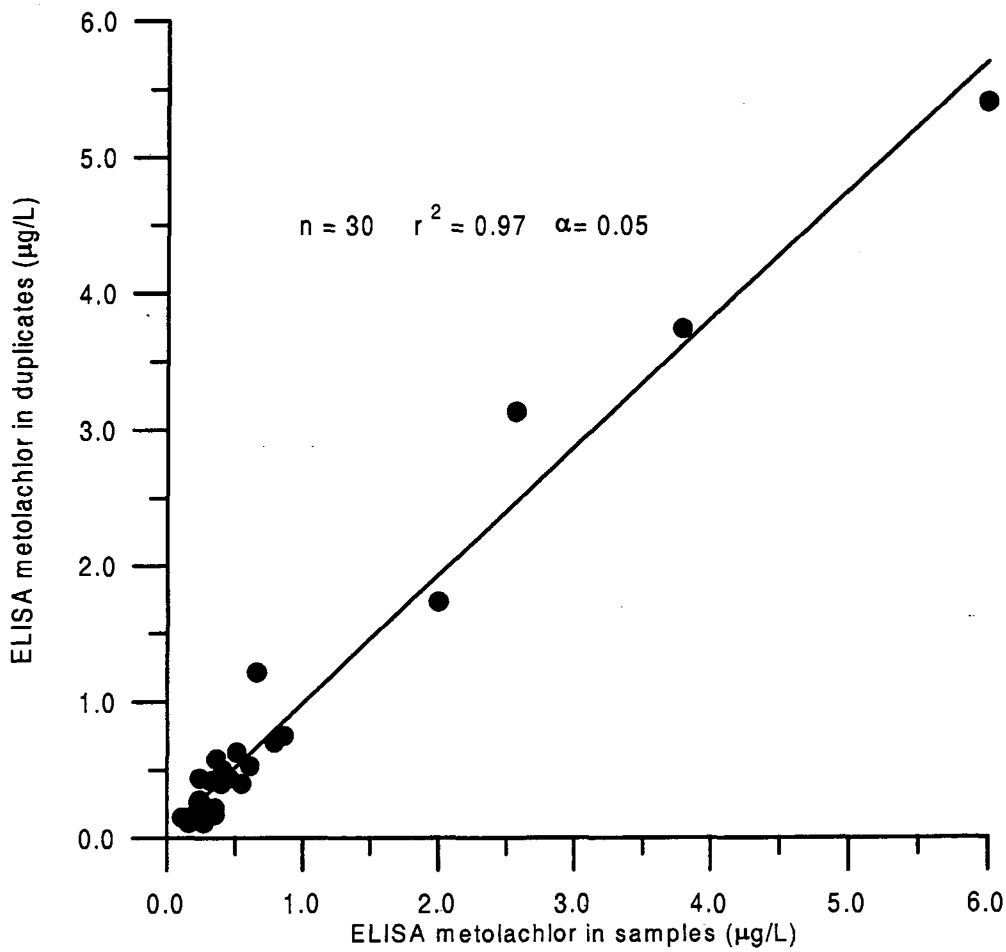

Figure 4. ELISA metolachlor determined for samples cross-plotted against duplicates collected at Pleasant Grove Spring between December 1993 and September 1998

actual sample was submitted for analysis as soon as possible. The purpose of the delayed analysis of the duplicates was to determine if there was any adverse effect on nitrate-nitrogen and triazines 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 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 season when 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 ELISA triazines detection limit is 0.06 µm/L. 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 triazines concentrations were less than the detection limit and the maximum concentration determined was 0.60 µm/L. The next highest triazines concentration was 0.12 µm/L.

Ground-water Tracing

Extensive qualitative ground-water 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 trace was conducted from the vicinity of Oakville, which verified the previously established ground-water basin boundary. Further, an attempt was made to conduct qualitative traces to delineate the boundary of the sub-basin drained by the spring in Leslie Page karst window (LPKW). There were no natural features into which dye could be injected near LPKW so excavated dye injection points (EDIPS) (Aley, 1997) were drilled. In this case the EDIPS were holes drilled by a hand-held, 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 hole was 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 drilled had an adequate rate of inflow.

Ground-water 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 expected dye arrival time period. 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 µm/L but fluorescein was determined semi-quantitatively. The first arrival of dye and time of travel of the plume were determined from the dye concentration curves.

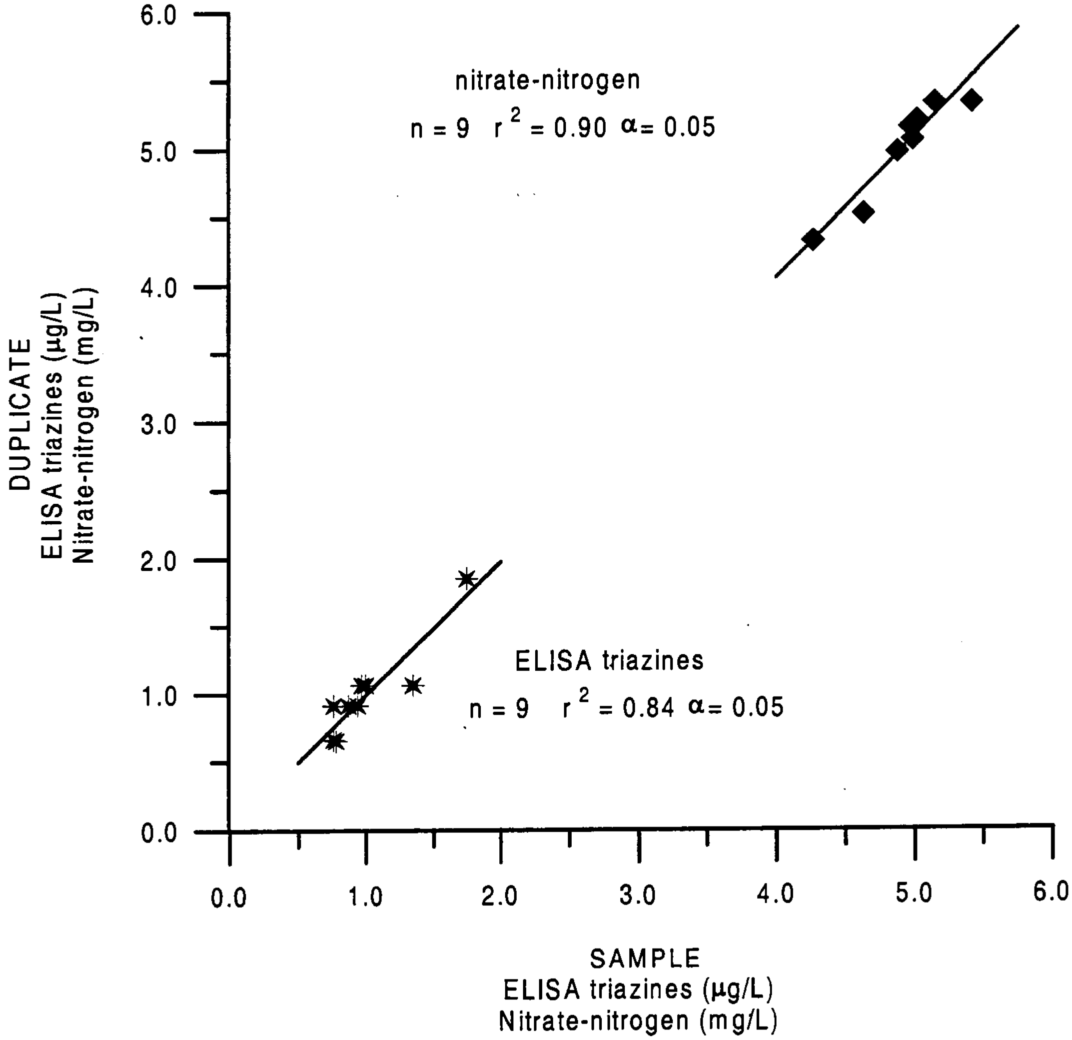

Figure 5. Cross-plot of ELISA triazines and nitrate-nitrogen determined for samples and duplicates collected at Pleasant Grove Spring, June 1996 through April 1997. Duplicate held under field conditions 14 to 16 days.

Discharge Rating Curve Development

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 a broad-crested weir was installed at LPKW. All discharge measurements were made by the partial-sections method and from a boat or by wading (Buchanan and Somers, 1976) with a Marsh-McBirney 2000 magnetic water flow meter. Stage-discharge graphs are plotted and stage-discharge relationships 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 because of changing channel conditions at UPGC and LPKW and due the difficulty of positioning field crews in advance of storms and simultaneously making measurements at multiple sites. However, all discharge results presented in this report were calculated using the latest stage-discharge rating, as applicable.

Of critical importance was accounting for flow bypassing Pleasant Grove Spring. During extreme high-flow, water overflows Johnson swallow hole, flows through a box culvert under Kentucky Highway 96, then 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 were 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 PGSP rating curve and the new high-flow segment.

The LPKW gauging 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 below zero stage. The erosion was probably due to the channel reestablishing its pre-agriculture 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 back flooding occurs at the swallow hole. A second rating curve was developed for back flooded conditions. Because of the limited number of flow measurements at LPKW the stage at which back water occurred was assumed the same for both the rising and falling limbs of the hydrograph.

Also, the water level data logger 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 also changed during the project. A dam was constructed by beavers across Upper Pleasant Grove Creek two hundred meters (660 ft.) downstream of the UPGC gauging station in August 1994. The beaver-dam was removed by the property owner and the stream was channelized in October 1997. Thus, three stage-discharge relationships are used to estimate discharge at UPGC.

The inflow from Upper Pleasant Grove Creek into George Delaney swallow hole (GDSW) was also problematical. The George Delaney swallow hole station was chosen because it is closest to the point where flow goes underground during median and high flow. However, because the site is occasionally dry between July and November, an algorithm was developed to shift discharge calculation and flux estimation to the Upper Pleasant Grove Creek station when flow into the GDSW stopped. Flow stopped at GDSW approximately 4 percent of the time during the 5 years it was monitored.

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 of time. Mass flux was calculated for Pleasant Grove Spring, upper Pleasant Grove Creek (GDSW and UPGC stations), and for Leslie Page karst window. For this project, 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 results of flux calculations presented in this report are based on the revised stage-discharge ratings curves. The annual flux was estimated for nitrate-nitrogen, atrazine-equivalent triazines, metolachlor, carbofuran, and total suspended solids. The concentrations of triazine 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 flux of alachlor was not estimated because of the poor correlation between GC and ELISA. The nitrate-nitrogen concentration was used without adjustment. The calculations were performed using algorithms programmed in Digital DataTrieve® by the author. For additional discussion see Currens, 1999.

Samples were not collected during some high flow events due to various mechanical failures, human errors, and budget limitations. It is known, for example, that samples were missed during the peak concentration of triazines at PGSP in May 1998. This circumstance 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 PGSP 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. However, an automatic sampler had been deployed at GDSW and collected nine samples distributed over the event. The triazine and nitrate-nitrogen analyses for the GDSW samples were extrapolated to PGSP in accordance with travel times determined from dye traces and concentrations proportioned in accordance to observed discharge. The mass flux at PGSP was recalculated using the daily analyses from PGSP and the extrapolated analyses from GDSW. The PGSP atrazine-equivalent flux using the extrapolated data was 86 percent of the flux based on the daily analyses alone. Using the daily analyses from PGSP the flux at PGSP was 6.85 kg versus 6.12 kg at GDSW (using 9 analyses) for the same 7-day time interval. Another high-flow event for which sampling frequency was analyzed is May 7 through May 10, 1996 (Currens, 1997). Twenty seven samples covered the entire high-flow hydrograph of this event with most samples concentrated during the early part of the event as planned. The analytical data set was reconfigured into bi-hourly (11 samples) and daily (4 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 atrazine-equivalent for the bi-hourly analysis set was 124 percent of the of the flux for the complete analysis set. The nitrate-nitrogen flux was 92 percent and 100 percent for the daily and bi-hourly data sets respectively. No attempt was made to estimate the accuracy of the suspended sediment flux, however the availability of turbidity data minimizes the consequences of missed samples for that constituent.

Based on these findings, it is thought that the annual mass flux of atrazine-equivalent is accurate within plus or minus 15 percent and that of nitrate-nitrogen is accurate within plus or minus 8 percent for partially sampled, individual high-flow events during the spring season. On an annual basis, however, the accuracy of the mass flux for atrazine-equivalent and nitrate-nitrogen is thought to be better than these ranges because of the relatively constant concentrations of both nitrate-nitrogen and triazines during base-flow.

Total Suspended Solids. Flux for total suspended solids was not estimated in the reconnaissance report because the data logger record was interrupted and because of occasional fouling of the turbidity probe. There were two causes of the fouling of the turbidity probe. 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. The sediment filling resulted in a constant turbidity reading at the maximum end of the range of the instrument (approximately 1,100 NTU's). At the manufacture's recommendation the reflection cone was removed during deployment. A dilution series of turbidity standards 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

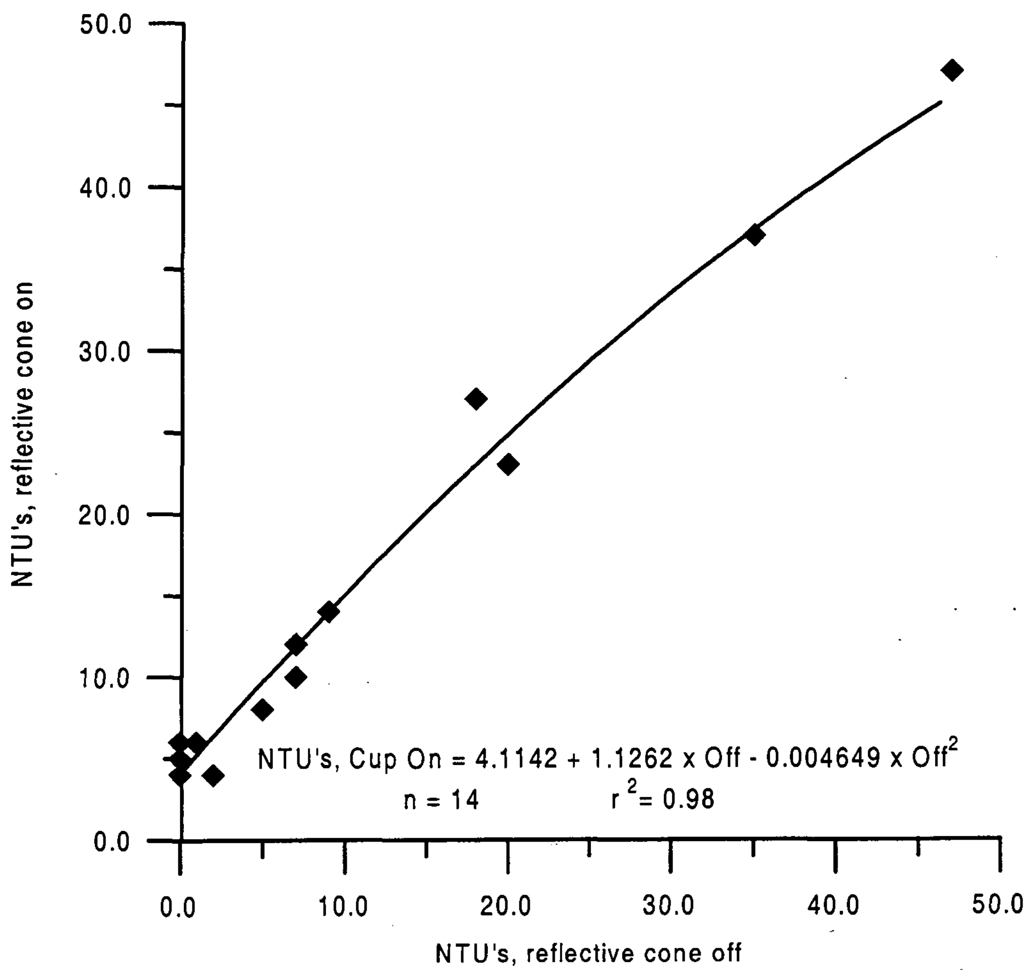

Figure 6. Turbidity probe observations plotted with the instruments reflective cone off versus with the reflective cone installed and to which a polynomial regression is fitted. The two observation methods produce equivalent readings above 46.26 NTU's.

fouling of the probe was the growth of a biological film (bacteria slime?) over the probes' optics. Biofilm growth also caused an increasing apparent turbidity. After cleaning the optics the increase was initially slow but continued at an exponentially increasing rate which accelerated following high-flow events. The problem was further complicated by the random partial removal of the growth by grazing aquatic snails. Beginning late in 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, and other indicators of high flow had occurred. When no storm-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 reduced the 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 exponential decay interpolation. Conversely, turbidities determined during high-flow events were commonly more accurate (biofilm growth generally began after the high-flow period ended) and were accompanied by suspended sediment samples. Further, the interpolated data have a relative low contribution to flux because the preponderance of sediment flux occurs during storms and the portions of the record which required interpolation were generally for base-flow periods with simultaneously lower discharge. This circumstance 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 time increment being evaluated, the turbidity derived concentration was used. Turbidity data that were missing because the data logger was halted during calibration or were otherwise lost were not estimated, but rather the most recent total suspended solids analysis was substituted. Time increments where no suspended sediment concentration could be estimated were rare, but when they occurred the suspended sediment concentration was

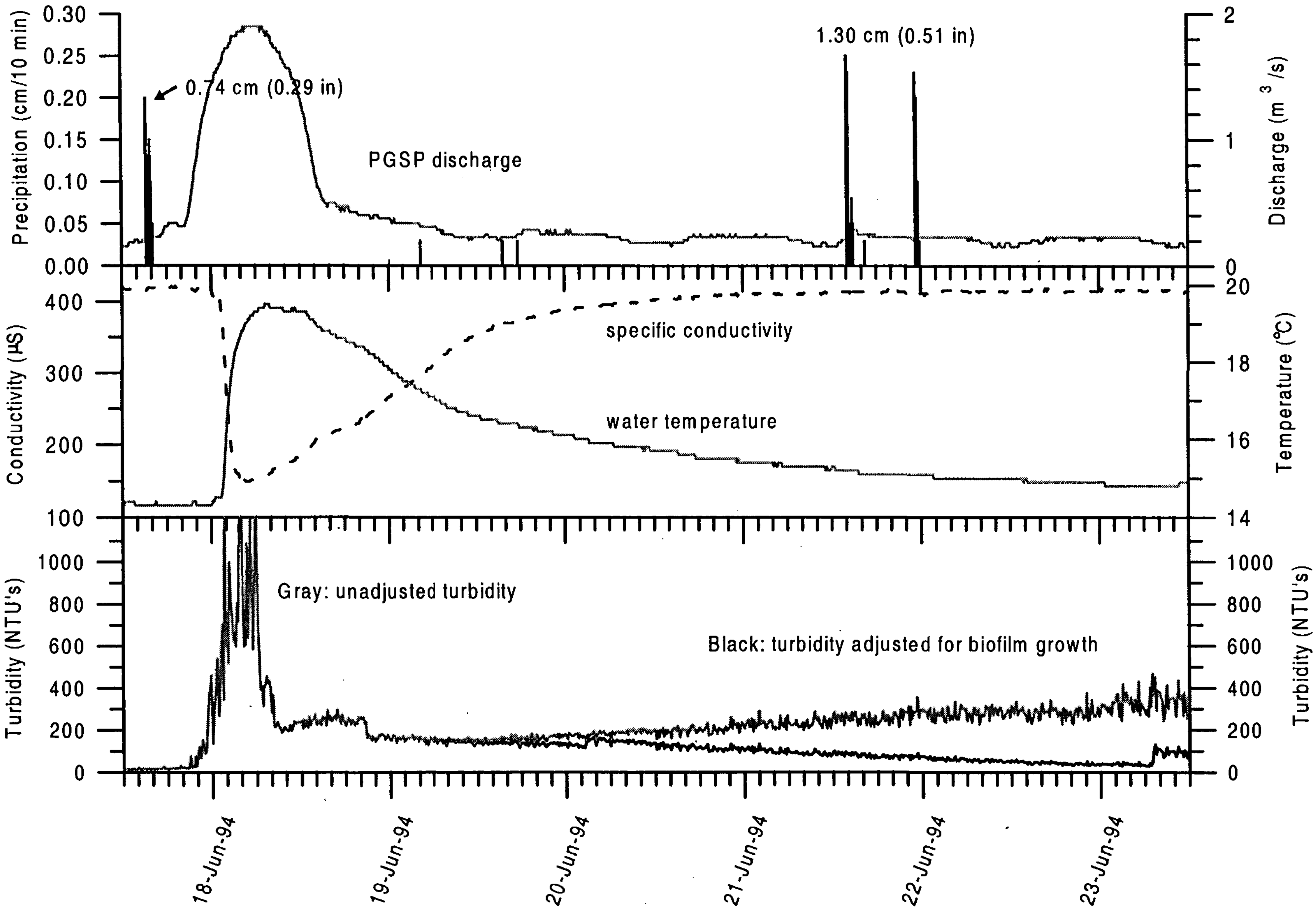

Figure 7. An example of the rise in turbidity readings caused by growth of a biological film on submerged equipment following high-flow events. Graphs are for the June 1994 event at Pleasant Grove Spring.

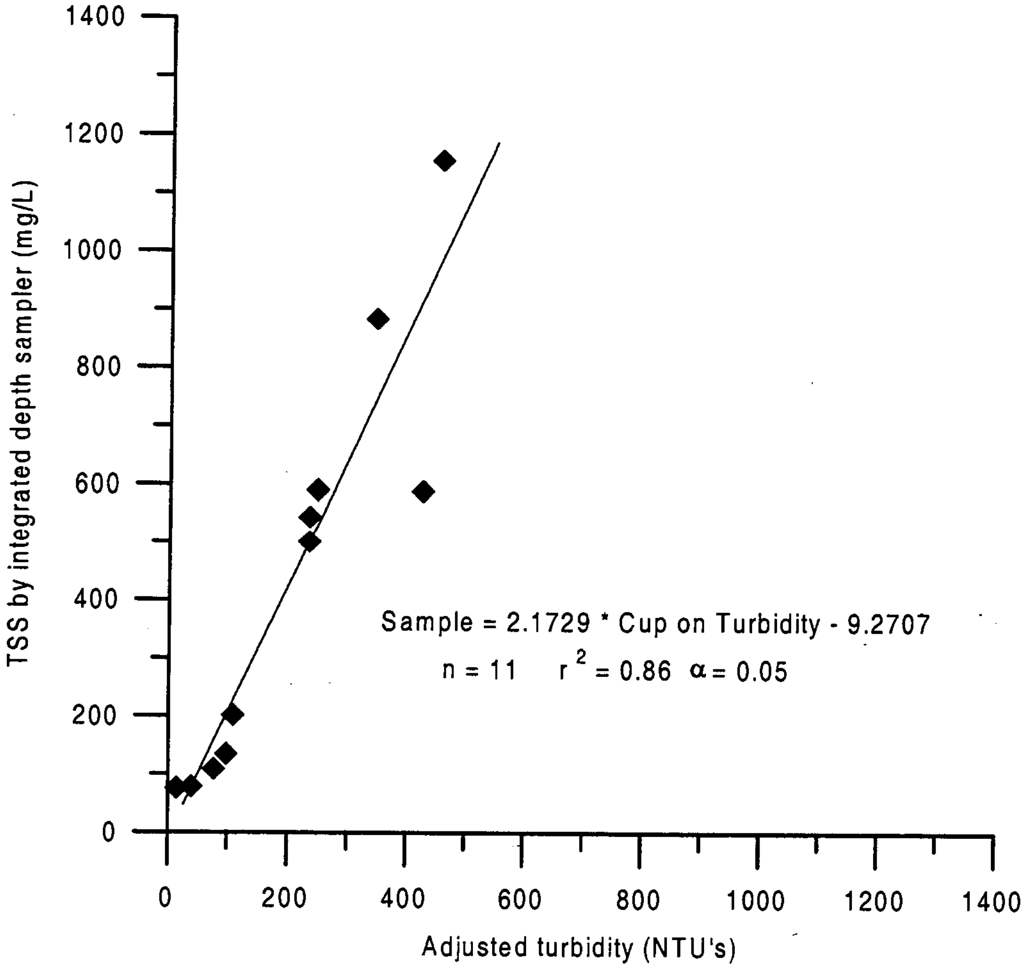

Figure 8. Plot of total suspended solids as determined in samples collected with an integrated depth sampler versus adjusted turbidity.

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 though 1997–98 water years.

Biological Inventory of Pleasant Grove Creek

Biological inventories of Pleasant Grove Creek were conducted in the reaches of the spring run immediately down stream of Pleasant Grove Spring for a bio-assay confirmation of the water-quality monitoring. The surveys were conducted by Kentucky Division of Water staff in April of 1994 and 1998 (Sampson, 1995, McMurray, 1999). The surveys used the same methodology, however water flow was significantly higher during the 1994 survey. Fish were collected by seining for one hour. Macroinverterbrates were collected with three one-minute, ten-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 (WQIP) 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 five years but were typically one to three years. By the fall of 1995 most BMP's were implemented in the field and the post BMP period is defined to begin October 1, 1995. Approximately 90 percent of the agricultural producers operating in the basin participated, which resulted in over 70% of the watershed being under one BMP or another.

The list of WQIP permitted BMP's relevant to the karst setting of Logan County eligible for cost share support was short (Table 1). Producers were allowed to chose the 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. While WQIP money was not available for animal manure management, exclusion of animals from streams was provided for. Additionally, 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 non-participating farmers and although the relative impact these farms had on the water-quality is unknown the area involved was comparatively small. One dairy farm is know 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 is unknown.

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 non-crop plants with 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 (90,262 lbs.) of atrazine alone are sold in Logan County annually (Ernest Collins, Kentucky Division of Pesticides, pers. commun., 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 for corn and wheat in the Pleasant Grove Spring basin recommended by the U. S. Department of Agriculture (Bill Johnson, NRCS Logan County Office, pers. commun., 1992) is 154kg/ha (137lbs/ac.) nitrate-nitrogen. The application rate for atrazine on corn recommended rate by the University of Kentucky College of Agriculture (Martin and Green, 1992) is 2.8 kg/ha (2.5 lbs./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, pers. commun., 1997).

Table 1. Total areas within the Pleasant Grove Spring ground water basin enrolled in each BMP as of September 29, 1998. Of 4,069 hectares (10,054 ac) in the watershed, 68 percent were enrolled in one or more BMP's of the of the USDA Water Quality Incentive Program (WQIP) for its three year duration.

Practice Code	Practice	Area Enrolled ha/ac
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. Photograph of runoff from a holding pasture for a dairy owned by a producer not participating in the WQIP.

Informational and educational meetings were held each February beginning in 1993 with producers who were operating farms within the Pleasant Grove Spring basin. Typically, 25 to 50 percent of the study area farmers attended. Topics discussed included goals of the project, addressing concerns of the farmers, and the findings to date. More significantly the importance of managing field runoff, the impact of runoff on ground water, and the relevance or protecting ground-water quality to human health were discussed. Guest speakers discussed regulatory issues and government programs available to farmers to assist in reducing non-point source pollution.

Land Use Mapping

Mr. Steve Crabtree of the Burlington Ky., office of the Natural Resources and Conservation Service (NRCS) 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 GIS 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 1991 through the 1998 growing seasons.

Statistical Analysis

Only the analytical data for Pleasant Grove Spring were considered for statistical evaluation because the success or the failure of the BMP's for the whole basin would be judged by the water-quality at the spring. Further, the sample set at PGSP is the most voluminous among the sites in the basin and the most likely to be representative. A restriction on the statistics used is that the frequency and timing of sampling during the monitoring of Pleasant Grove Spring was not statistically random or on a strict chronological schedule. This was caused by logistical constraints and further complicated by the need to intensively collect samples during high-flow events in the spring season for calculating annual flux and detecting peak concentrations of herbicides. To partially overcome this limitation the analytical data of water samples from 1992 through 1998 were divided into various subsets of the complete set of analytical data based on frequency. The analyses of the first water sample collected at the beginning of the calendar quarter comprised the quarterly analysis set. Analyses of the first water sample collected after the first of the month comprised the monthly analysis set. The analyses of water samples collected at the beginning each bi-weekly period (every other week) comprise the bi-weekly analysis set. The bi-weekly sample set augmented with analyses of water samples collected bi-hourly (every other hour) during high-flow comprised the bi-hourly/biweekly analysis set. The bi-weekly set composited with all water samples

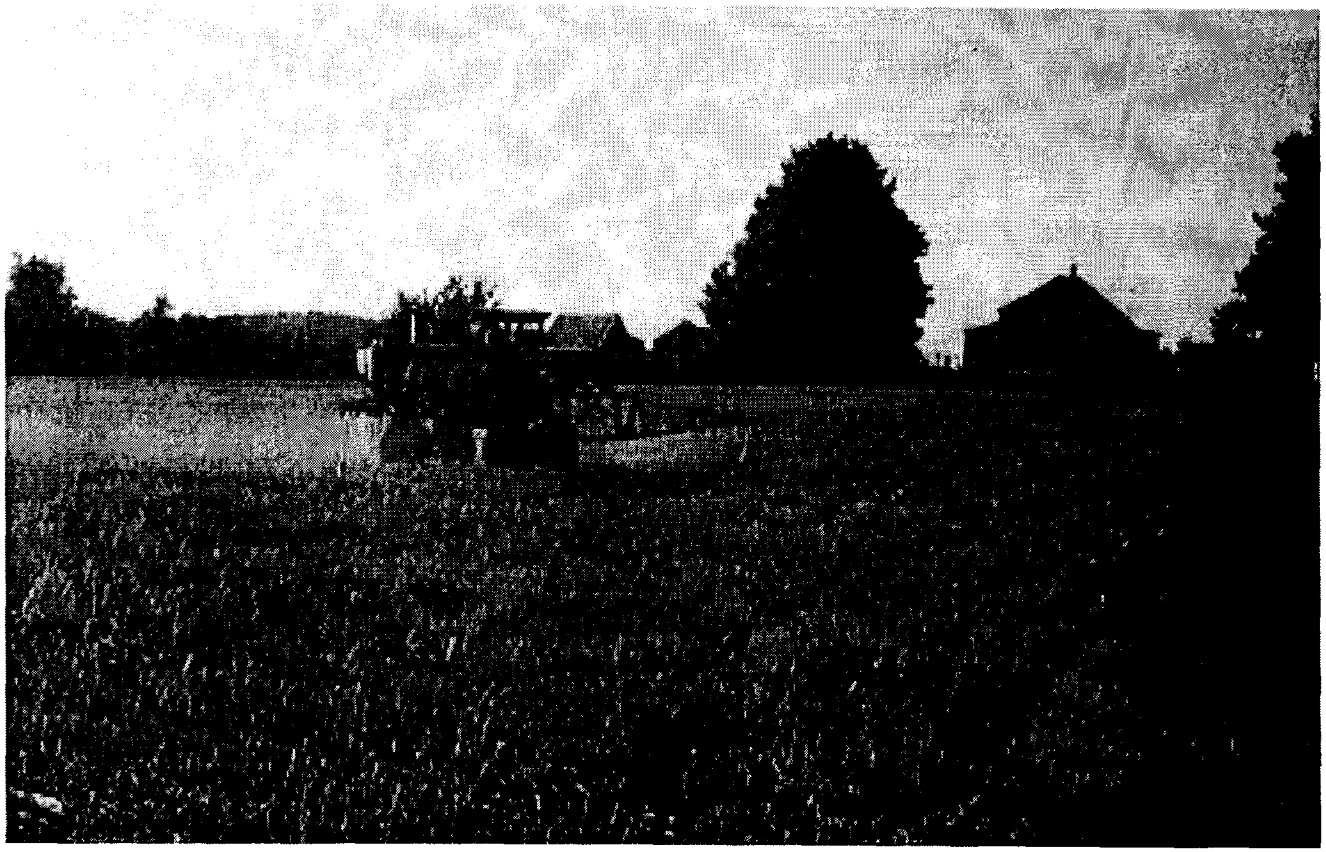

Figure 10. Example of the application of agricultural chemicals in the Pleasant Grove Spring karst ground-water basin.

collected during high-flow comprise the bi-weekly/hi-flow analysis set. Finally the set of analyses from every water sample, which included some opportunistically collected samples and some bi-daily samples during the spring season, is the complete analysis set.

The data were then evaluated using Statgraphics® 3.0 software (Manugistics, Inc., 1997). The sample sub-sets were tested against normal, log normal, Gamma, and Laplace distributions for the triazines, nitrate-nitrogen, total suspended solids, and orthophosphate analyses using the χ^2 (Chi squared) 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 for statistical analysis of the water quality data was also used. 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 non-parametric tests. The statistics were computed using MS Excel® spreadsheet.

Data Archival

Site location data, water analyses, stage data, and field parameters 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.

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 had little effect on the low flow discharges determined from the curves published in the reconnaissance report (Currens, 1999). The 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 PGSP is illustrated in figure 11. Because the stage at PGSP remained mostly within the low flow segment of the rating curve during the 1992–93 and 1993-94 water years the annual discharge for PGSP was nearly the same for those years as previously reported. The discharge determined with the new rating curve for PGSP was unchanged for 1992–93 water year at 1.02 X 10^7 m^3/yr. (3.6 X 10^8 $ft.^3$/yr.). The discharge for the 1993-94 water year decreased slightly from 3.18 X 10^7 m^3/yr. (11.3 X 10^8 $ft.^3$/yr.) to 3.15 X 10^7 m^3/yr. (11.2 X 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 X 10^7 m^3/yr. (15.0 X 10^8 $ft.^3$/yr.), whereas the average annual discharge for the 1992–98 monitoring period for PGSP is 2.37 X 10^7 m^3 (8.40 X 10^8 $ft.^3$). The maximum instantaneous discharge recorded was 38.05 m^3/sec. (1,343.5 $ft.^3$/sec.) on April 11, 1994 at 12:50 hrs. The average instantaneous discharge is 0.96 $m^{3/}$sec. (34 $ft.^3$/sec.), whereas base flow is a more modest 0.11 $m^{3/}$sec. (4.0 $ft.^3$/sec.).

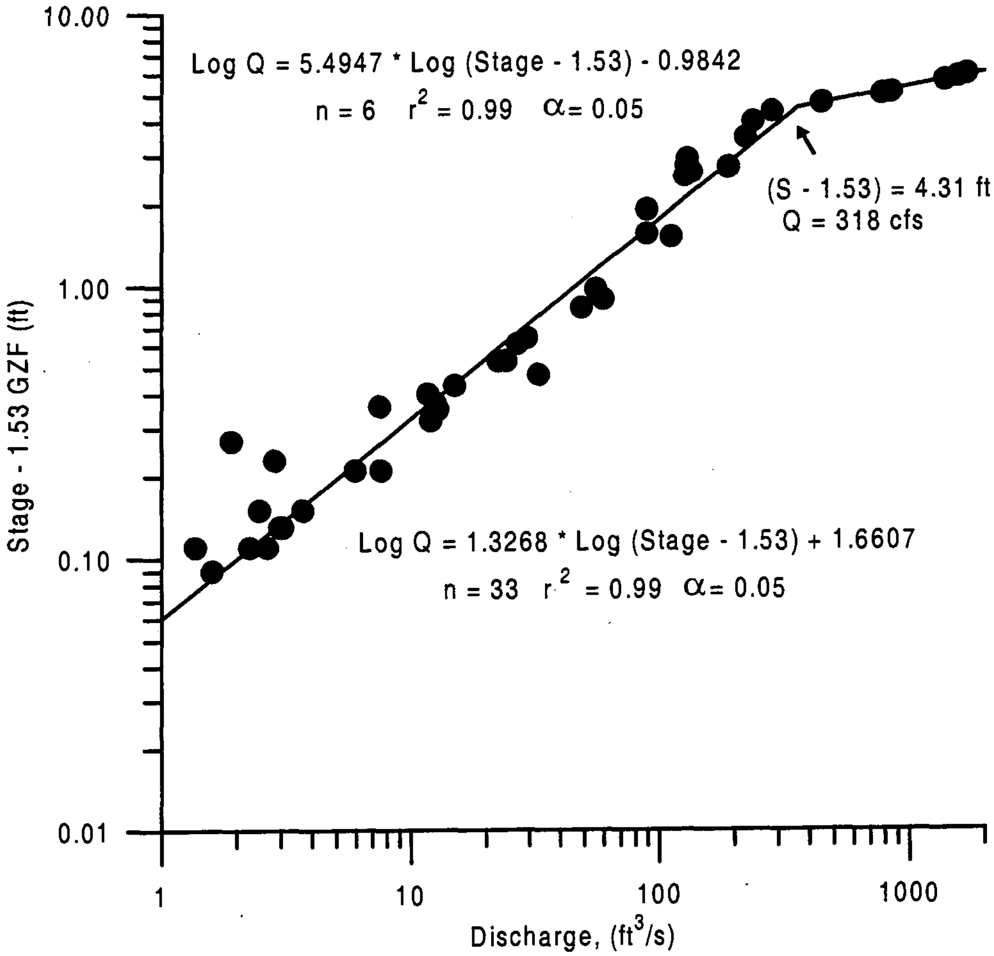

Figure 11. Stage-discharge rating curve for Pleasant Grove Spring (PGSP). When the stage at PGSP exceeds 5.84 feet flow in the upbasin streams has exceeded the intake capacity of all swallow holes. Water then flows overland to Pleasant Grove Creek, which is accounted for in the upper segment of the rating curve.

Revised stage-discharge rating curves used for mass flux calculations at LPKW, GDSW, and UPGC are presented in figures 12, 13, 14, and 15.

The discharge rating-curve at Leslie Page karst window is complex because the conduit draining the karst window back floods. The back flooding is thought to have two causes. First, during intense, short lived downpours inflow rates frequently, but briefly, exceed the intake capacity of the swallow hole. The duration of back flooding due to excessive inflow is typically less than three hours, the time of concentration after intensive rainfall. Although the cross-sectional area of the swallow hole entrance and the visible section of conduit is large, it is thought there is a reduction of the conduit cross-section by sedimentation somewhere along a downstream reach of the conduit. 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 above as evidence of higher sedimentation rates prior to this study.

The second cause of back flooding is thought to be a reversal of the slope of the potentiometric surface in the conduit draining Leslie Page karst window caused by high stage in downstream conduit reaches, which are monitored at Spring Valley karst window (SVKW). No direct observation of flow reversal (discharge) from the swallow hole at Leslie Page karst window has been made, but rising stage at LPKW in the absence of rainfall at PGSP has been recorded, which suggests that flow reversal is possible. The timing of other hydrogeologic events in the basin to the back flooding at LPKW is illustrated in figure 16. Unlike the steeply sloping hydrograph response to short, intense storms, the back flooding hydrograph is characterized by a broad, gradually rising and gradually falling slope which persists much longer than the peak expected from short storms. Further, the rising limb of the back flooding segment of the hydrograph is accompanied by a declining stage at George Delaney swallow hole and at the UPGC station. The back flooding hydrograph at LPKW only occurs when the stage at Spring Valley karst window exceeds approximately 4 meters (13 ft.) or an elevation of approximately 159.4 m. (523 ft.). The rising limb and crest of the LPKW back flooding curve also coincides with overland flow from Johnson Swallow Hole through the box culvert underlying Kentucky highway 96. During the period when overland flow through the box culvert occurs, head on the conduit system is at maximum. The swallow hole at SVKW is partially blocked with logs and other debris, which promotes flooding of the conduit draining from GDSW. The elevation of LPKW is 166.7 m. (547 ft.) and the elevation of Spring Valley Karst window is near 155.4 m. (510 ft.). GDSW is some 15 meters higher than LPKW at 181.3 m. (595 ft.), thus there is ample elevation head to back flood LPKW when the main conduit is flooded.

Further evidence for sedimentation as a cause of the reduction of conduit cross-sectional area is found in Oakville Cave, which lies only 600 m (2,000 ft.) south-southwest of LPKW. 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 back flooding. The transport of sediment through study-area conduits is further discussed in Currens, 1999.

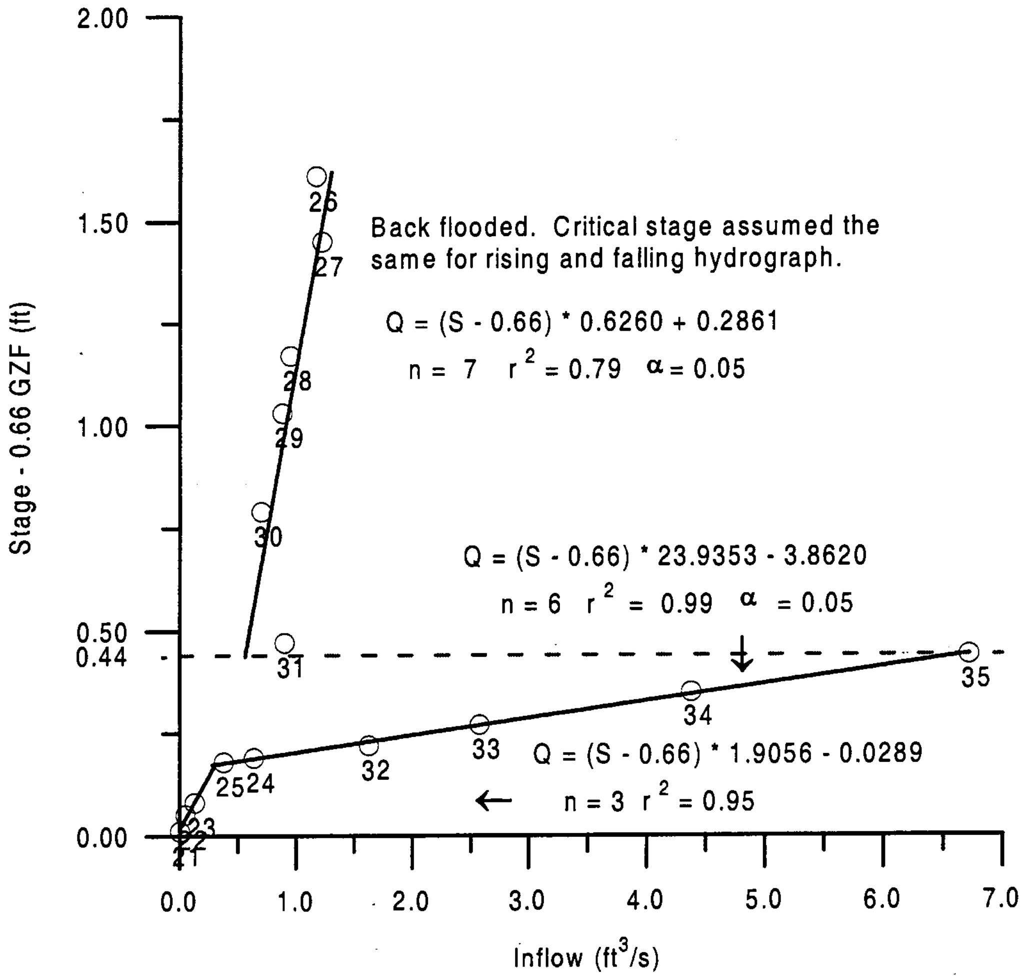

Figure 12. Rating curve of stage versus inflow at the Leslie Page karst window swallow hole. Data collected after October 1, 1995. Segment in upper left of figure represents inflow when the karst window is flooded.

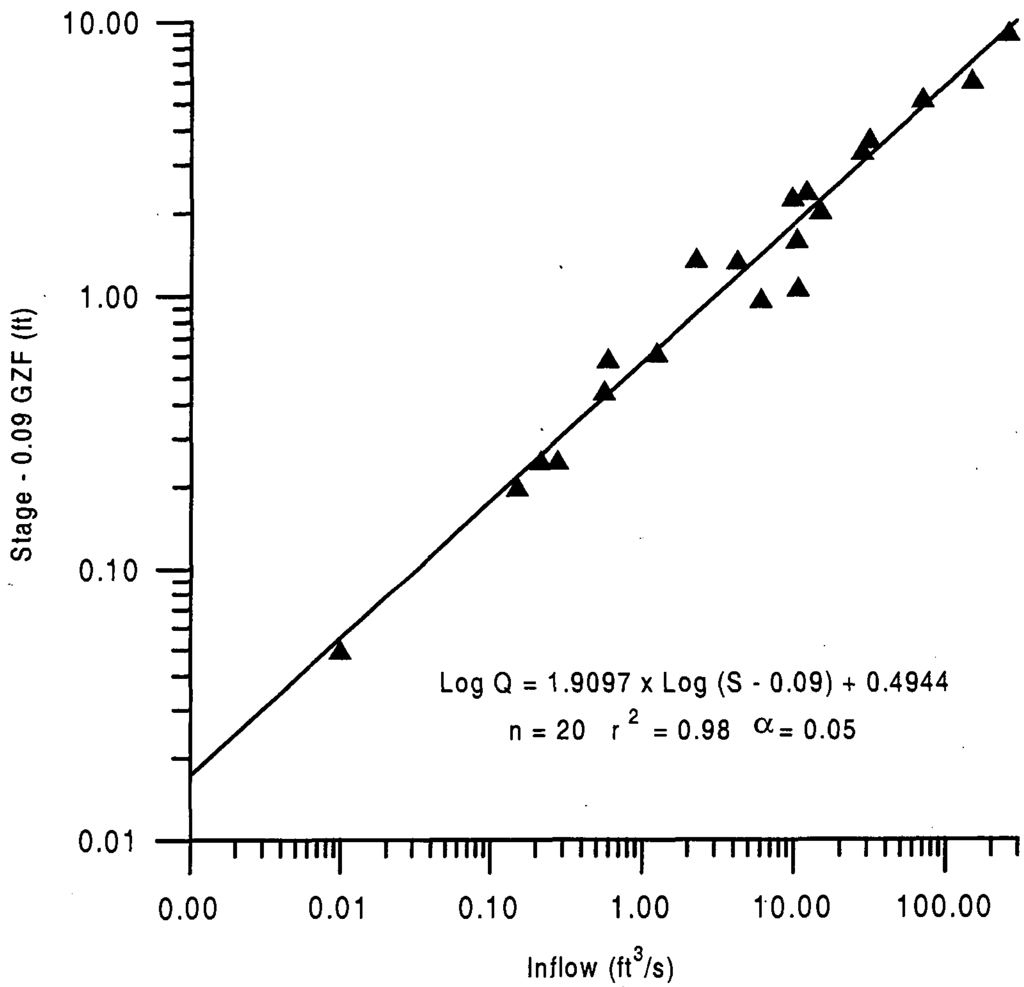

Figure 13. Stage versus inflow rating curve for George Delaney swallow hole. Gage zero flow (GZF) chosen by maximizing correlation coefficients for non-transformed data. The minimum stage observed in the field at which flow occurred is 0.14 ft.

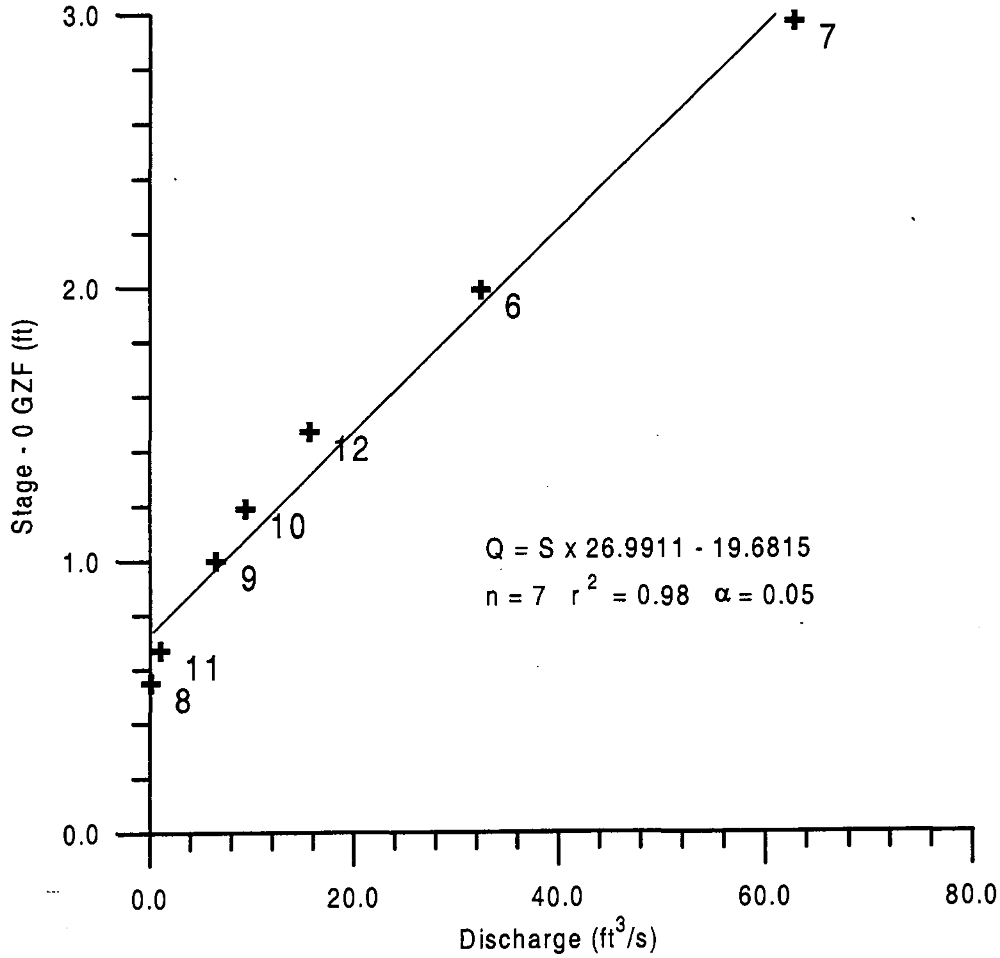

Figure 14. Stage versus discharge rating curve for Upper Pleasant Grove Creek (UPGC) gaging station for the period a beaver dam existed down stream of the station (August 28, 1994 through October 31, 1997).

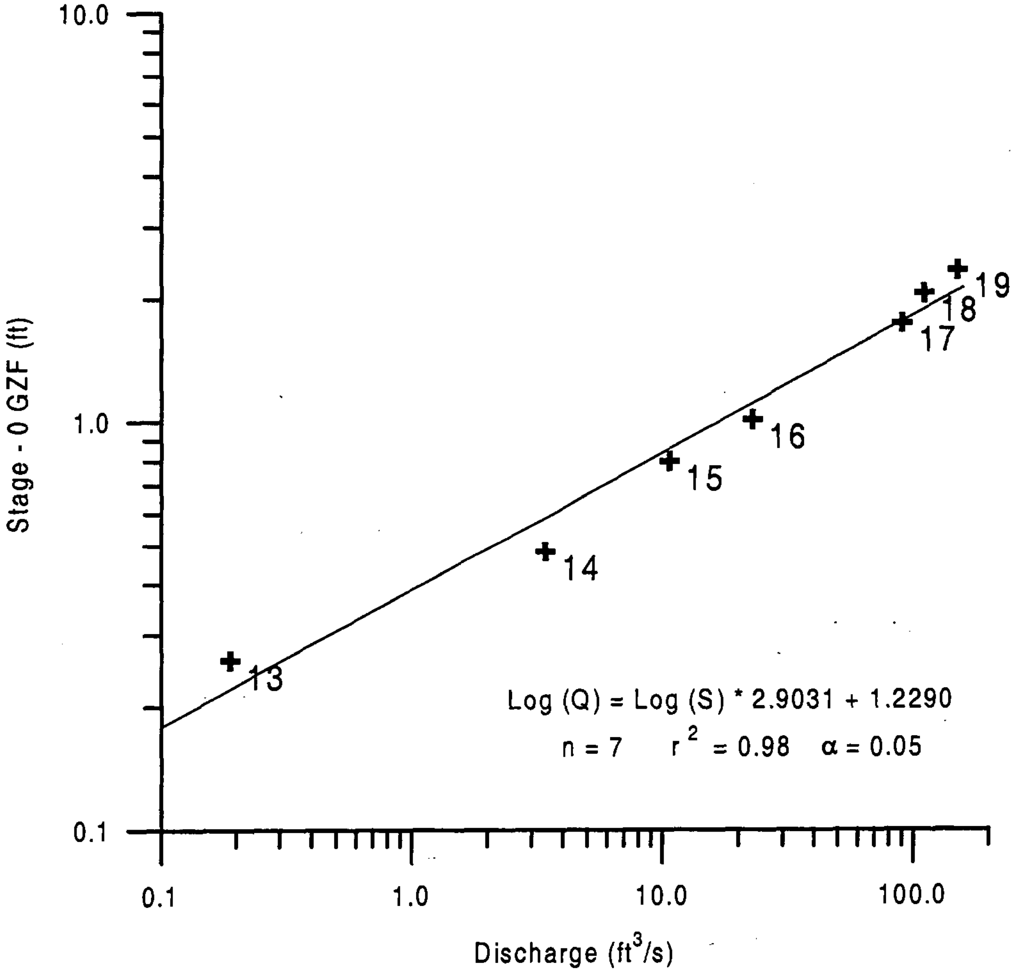

Figure 15. Stage versus discharge rating curve for Upper Pleasant Grove Creek (UPGC) gaging station for after channelization (after October 31, 1997).

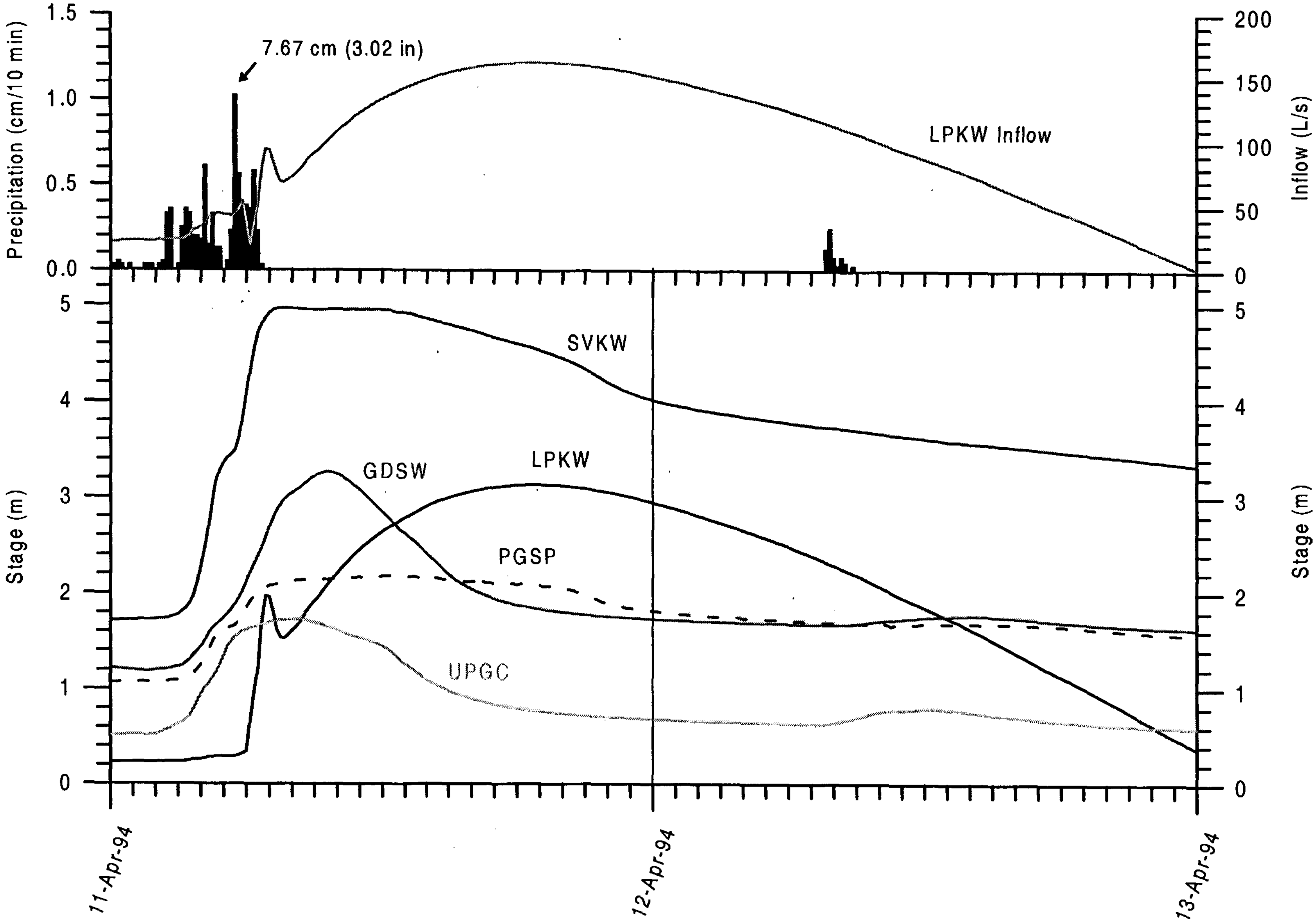

Figure 16. Inflow hydrograph at Leslie Page Karst Window and stage hydrographs for the April 1994 high-flow event in the Pleasant Grove Spring ground-water basin.

Quantitative Dye Traces

Seven quantitative traces were attempted from George Delaney swallow hole to PGSP and four from Leslie Page karst window to PGSP. Only one complete dye break through curve was obtained from LPKW and two from GDSW. This was primarily due to the difficulty of synchronizing highly variable tracer travel times, under 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 for personnel to obtain essential discharge measurements during storms.

Useable time-of-travel data were obtained from the first arrival of the dye. Figure 17 shows the delay time to first detection of dye from GDSW to PGSP versus the stage at PGSP at the time of dye injection. The dye first-arrival times at PGSP 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 velocity increases dramatically with stage (discharge) and the graph illustrates the importance of flow conditions on the travel time of entrained constituents. The minimum travel time was 9 hours observed following a light rain and PGSP at a modest stage of 0.71m (2.33 ft.), which rose only an additional 0.5cm (0.17 ft.) during the trace. The trace was done in anticipation of a significant storm, which produced less rainfall than forecast. Notably, the fastest travel time corresponds to the delay between peak stage at GDSW and changes in turbidity, conductivity, and temperature at PGSP (Currens, 1999, figure 22) during high-flow events.

Dye-trace travel times from LPKW to PGSP are roughly twice (36.7 hours versus 18.2 hours) that from GDSW during low flow. The travel time from GDSW to PGSP is significantly shorter during high-flow conditions (9 hours). Although dye travel times to PGSP were not obtained from LPKW and GDSW under identical high-flow conditions the travel time from GDSW is expected to always remain less than from LPKW. In contrast to the travel time, the length of the straight vector path from LPKW to PGSP is only sixty percent of the distance from GDSW to PGSP. The long dye-trace travel time from LPKW is thought to be due to back flooding conditions which occur in the tributary conduit draining LPKW near the tributaries' confluence with the main conduit.

Nitrogen Isotopes N^{15}/N^{14} 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 N^{15}/N^{14} ratio, the more likely that the nitrogen has been biologically fractionated as compared to commercial fertilizer. The δN^{15} values of commercial N-fertilizers range from -3 to +6 $^0/_{00}$ (Herbel and Spalding, 1993) while human and animal waste derived nitrate is +10 $^0/_{00}$ and higher. Intermediate values are interpreted as soil process derived and naturally occurring (Fogg, 1998).

The nitrogen isotope data from both Pleasant Grove Spring and the spring at Leslie Page karst window suggest strong influence on the nitrate concentration by the application of commercial fertilizers (Table 2). This interpretation is further supported by

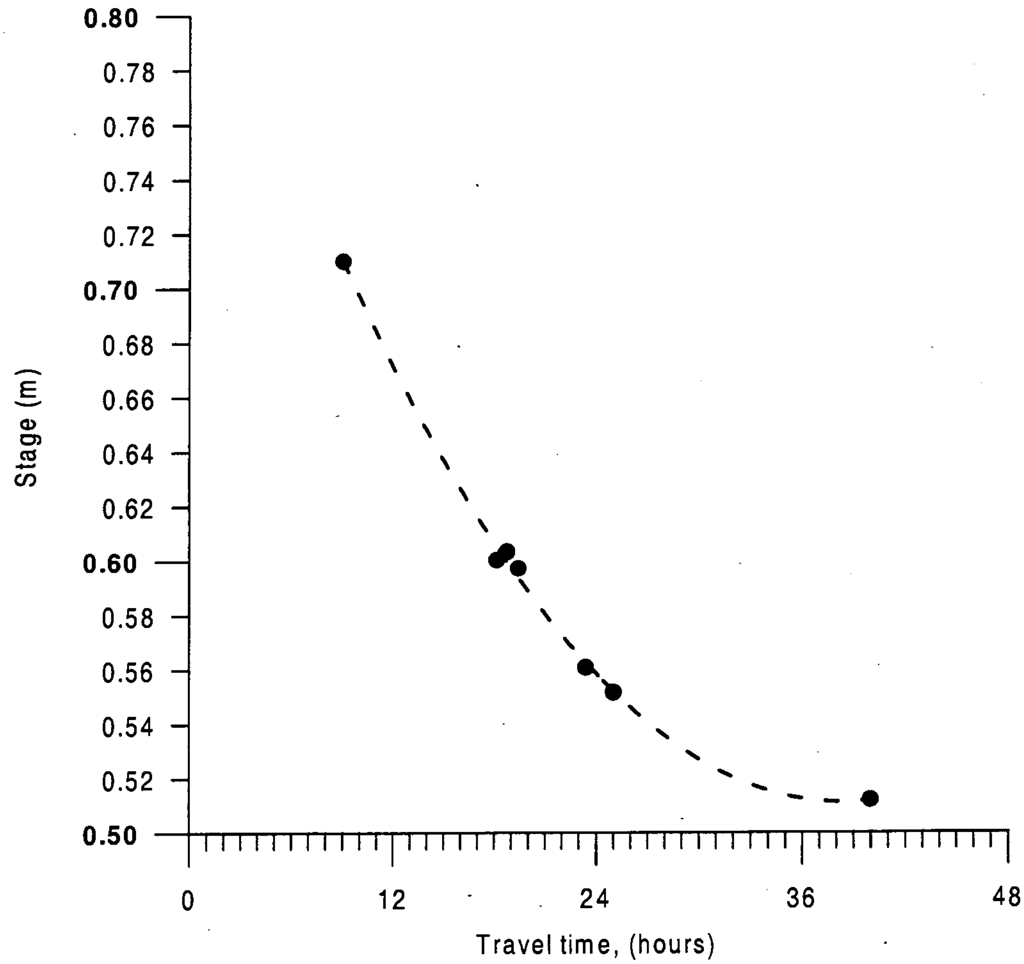

Figure 17. Elapsed time from introduction of tracing dye into George Delaney swallow hole to first detection at Pleasant Grove Spring plotted against stage at Plesant Grove Spring.

the absence of humans or livestock within the apparent drainage basin of LPKW. The relatively constant N^{15}/N^{14} ratio at LPKW through the year further suggests weather conditions have little influence on the nitrate source. The more variable N^{15}/N^{14} ratio at PGSP 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.

Table 2. Nitrogen-15 and nitrogen-14 isotope ratios for samples collected at Pleasant Grove Spring (PGSP) and Leslie Page Karst Window (LPKW).

Sample Number	Date	Total Nitrate-nitrogen, mg/L	N^{15}/N^{14} δ $^0/_{00}$
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

Land Use Mapping

The land use mapping of the Pleasant Grove Spring karst ground-water basin by the NRCS revealed significant trends in land use from 1991 through 1998. The total surface catchment of the ground-water basin is 4,069 hectares (10,054 ac) and was measured by the NRCS from a map of the watershed boundary as determined with ground-water dye tracing. 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 while areas in row crop production correspondingly increased from 68.5 percent to 77.9 percent. Developed areas (farmsteads, suburban, roadways) increased less than a tenth of a percent and the area covered by water remained unchanged. Large areas were cleared of trees from 1991 through 1993 as indicated by field observations and a 2.5 percent (246hc/ 608 ac.) decline in woodland from 1991 to 1992. A slower loss of woodland in 1995 through 1998, however, was made up by the conversion of pasture to row crop during those years. Thus, 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, pers. commun., 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 operation are the most visible contributors to bacteria contamination. One of the two large swine operations was visited by KGS 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 have not visited the other hog farms. A dairy southeast of the junction of Johnson-Young Road and Kentucky Highway 96 (see

Currens, 1999) does not have a waste-holding facility and overland runoff reaches a sinkhole southwest of the junction of those roads. The other dairy, north of Johnson-Young Road, installed a stack pad and holding pond during the July 1992 and 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 BMP's selected 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. However, at the time of the WQIP initiation most of the farmers were already using no-till or minimum-tillage techniques and the addition of additional cover was a minor change. While 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 Logan County NRCS with WQIP (Craig Givens, NRCS Logan County Office, pers. commun., April 9, 1999) suggests there were four concomitant circumstances for the lack of interest in the other BMP's, which might have been more effective. First, most of the producers in the basin are over 50 years old and some may not have been personally 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 land owner 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 utilizes intensive pest scouting coupled with precise timing of chemical applications practice to minimize pesticide and nutrient use. However, most producers utilized commercial crop consultants and soil test labs that do not follow the University guidelines. 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.

Huber (1990) reported on the results of a survey of Iowa farmers. The survey asked farmers about their attitudes toward government incentive programs to address runoff from agricultural areas flowing into sinkholes. The Iowa farmers were generally unwilling to enroll sinkhole areas in the Conservation Reserve Program (CRP) as then administered. If the CRP 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 the study area in Iowa, which averaged one sinkhole per 14 ha (35 ac), sinkholes occupy an estimated 80 percent of the Pleasant Grove basin.

Record Keeping BMP and Actual Chemical Usage

Although the monitoring project did not have the resources needed 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, an inventory of the area planted for each crop was reported by the producers from 1996 through 1998. The pesticides reported used in the basin were very diverse. Table 3 lists the reported pesticides with 45kg (100 lbs.) or greater of active ingredient used for any reporting year. Recent trends in the development of new pesticides is 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 are not testable, the accuracy of the WQIP chemical totals is unknown. Furthermore, the variability of the atrazine application rate over the three years of the WQIP inventory was greater than previously assumed (Currens, 1999). However, the relative quantities of chemicals reported are proportional to the total area of crops and are near the recommended application rates, which indicates the data are within a logically expected range.

Table 3. 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 due to changing product prices, the availability of new products, and other causes. Only compounds for which more than 45kg (100 lbs.) was reported for at least one year are listed.

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

*Craig Givens and Jimmy Christian, NRCS Logan County Office, pers. commun., 1997, 1998, and 1999.

The average application rate of atrazine used for this report was estimated 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 usage and dividing the by the area in corn. The inventory reported nitrate-nitrogen applied on all crops grown. Total usage was summed for three categories of crop; corn, pasture, and all other row crops, and was used to calculate the average applications rate for each crop category for the WQIP inventory years. Further, the average application rate of the three WQIP years was used to re-estimate atrazine and total nitrate-nitrogen applications rates for the earlier, uninventoried years. The estimated application rates from the WQIP 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 keeping is 1.24 kg/ha. (1.11 lbs./ac.), significantly less than that recommended, whereas the nitrate-nitrogen estimated application rate 157 kg/ha (141.07 lbs./acre) crop is nearly identical to the median recommended rate for corn and wheat. However the application rate for atrazine varied significantly from 0.77kg/ha corn (0.69lbs/ac corn) in 1997 to 1.79kg/ha corn (1.59lbs/ac corn) in 1998. The application rate for nitrate-nitrogen varied more narrowly from 149.77kg/ha row crop (136.77lbs/ac row crop) to 167.13kg/ha row crop (149.12lbs/ac row crop).

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 post BMP implementation conditions in April 1998. McMurray 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 (TNT) for macroinvertebrates showed dramatic increase from 21 to 41 post-BMP and the Total Number of Individuals (TNI) also improved from 241 to 522. The Percent Community Similarity and Jaccard Coefficient of community similarity metrics showed the two collections of macroinvertebrates were not very similar. However, the Ephemeroptera-Plecoptera-Trichoptera (EPT) metric, which measures pollution intolerant taxa, did not vary between the pre-BMP and post-BMP collections, whereas the modified Hilsenhoff Biotic Index (mHBI) showed a slight improvement (6.92 to 5.42).

McMurray concluded the lack of similarity of fish and macroinvertebrates 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. However, due to the poor IBI for fishes, 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 annual meetings each February for study area producers. The meeting consisted of a review of the monitoring results for the previous growing season, discussion of non-point source related programs available to assist farmers, and encouragement of pollution control beyond the WQIP. The meetings typically were 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 ground water from pollution, with an emphasis on karst aquifers, at the annual NRCS Environmental Workshop in 1997 and 1998.

Miscellaneous Findings and Observations

On June 16, 1997 a dump which included over two hundred pesticide containers was discovered in a gully which drains to Leslie Page karst window (LPKW). The dump-site is obscured from casual view and is completely out of site of the monitoring station. When found, the condition of most of the containers suggested the dump was relatively recent. The dump did not exist 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. It is conjectured that the containers were 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 dumps existence and therefore it is quite probable that the guilty persons were from outside of the study area.

After the dump was found consideration was given to abandoning Leslie Page karst window as a monitoring station. However, because continuing the station would incur minimal additional costs and because the original purpose of the site remained valid, which was monitoring the quality of water flowing into the aquifer, it was decided that operation would continue. In cooperation with the operator of the farm, the KGS decided to attempt to clean up the dump. Over 86 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, and dirty plastic so that 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. Fewer than 50 containers were not recovered and remained in the gully, but none were for products containing atrazine.

On the positive side, the spring is partly isolated from the dump because it discharges down gradient of the dump and is bypassed by the runoff from the gully except when, rarely, the entire karst window back floods. The sampling record does not indicate persistent, 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 potential for pesticides to leach into the conduit draining to the spring is though to be minimal, both sampling points in LPKW are down stream of the confluence with the gully. It is known that storms intense enough to produce runoff from the adjacent fields and into the karst window will also cause water to flow through the dump and past the sampling points. However, if the conduit were effectively isolated from the dump, then discharge from the spring would dilute and wash away high concentrations of pesticides from the gully after a storm. The container found near the swallow hole, which lead to the discovery of the dump, was rinsed with distilled water and analyzed for triazines, alachlor, carbofuran, and metolachlor by ELISA. All four pesticides were detected but triazine had the lowest relative concentration. Because only one container containing atrazine was identified from over two hundred containers examined, atrazine contamination from the dump is unlikely

While buffer strips were planted or maintained around some sinkholes in crop fields (including LPKW), other fields were tilled to the sinkhole rim (Fig. 18). The aerial spacing of sinkholes in a large part of the study area is so dense that establishment of buffer strips around each would preclude planting row crops. However, relatively few of the sinkholes have open throats, 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 program (Fig. 19). A disincentive to using buffer strips, additional to the comparatively low WQIP incentive rate, is they are difficult to maintain in karst settings because equipment must be maneuvered around them during tillage and planting, and the grassed area are isolated and cannot be accessed for mowing while crops are growing.

MONITORING RESULTS SINCE OCTOBER 1994

Water-quality analyses conducted since October 1994 have focused on those constituents identified as significant contaminants in the reconnaissance report (Currens, 1999). Water samples were collected at 7 locations in the basin; PGSP, LPKW, UPGC, GDSW, TCKW, JHWW, and MSHW. 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 analyses were similar to those of the reconnaissance report. Basin wide, for those constituents being determined, the principal contaminants are nitrate, triazine herbicides, suspended sediment, and bacteria. Orthophosphate is also an important ground-water contaminant in the basin. The maximum nitrate-nitrogen concentration measured in the basin between 1994 through 1998 was 13.1 mg/L observed at Leslie Page karst window and the average concentration was 5.05 mg/L. The maximum orthophosphate concentration was 1.397 mg/L at Pleasant Grove Spring and the median was 0.17 mg/L. The total suspended solids maximum was 3,267 mg/L with a median concentration of 53 mg/L. The maximum ELISA triazines concentration was 393.0 μg/L observed at Leslie Page karst window, with a median concentration of 1.15 μg/L. Maximum bacteria counts were 200,000 col/100mL fecal coliform and 810,000 col/100mL fecal streptococci with medians of 400 col/100mL and 640 col/100mL, respectively.

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

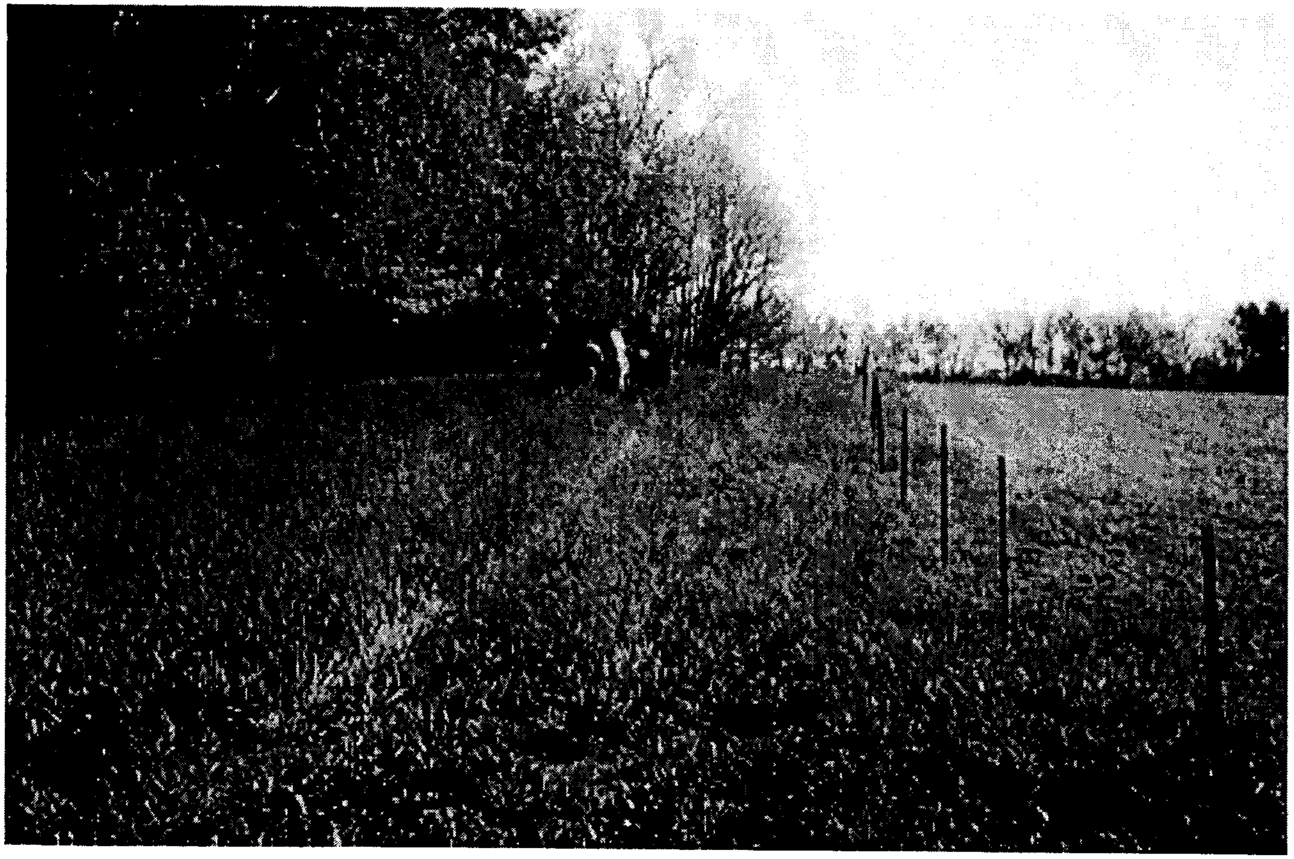

Figure 19. Buffer strip around The Canyon karst window created as a result of the WQIP.

Nutrients

Nitrate-nitrogen and orthophosphate concentrations, while not a human health concern in the Pleasant Grove Spring ground-water 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 number LPKW0139) on April 20, 1995. The maximum concentration prior to 1994 was 10.8 mg/L nitrate-nitrogen 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 number JHWW0011) collected April 2, 1997 following a major high-flow event in late March. The low concentration probably reflects both dilution during high-flow and the relatively lower average nitrate concentrations (4.47 mg/L) of the north-eastern sub-basin draining from the vicinity of Oakville through JHWW and The Canyon karst window (TCKW). Upper Pleasant Grove Creek averaged 5.77 mg/L and reached a maximum of 11.0 mg/L at the GDSW gauging station in late June, 1995 on 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 collected 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 while the minimum was 0.020 mg/L. The maximum orthophosphate concentration was 1.397 mg/L (PGSP0957, August 7, 1996) collected on the recession of a major summer storm at the end of July.

Pesticides

The detection of one or more pesticides in the Pleasant Grove Spring basin, in both ground water and surface water, was commonplace during the last 4 years. The EPA has determined maximum contaminant levels (MCL's) for drinking water for approximately 14 pesticides, of which the sale of some is now banned in the United States. Of those pesticides used in the Pleasant Grove Spring ground-water 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, while 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, for two of the four pesticides determined by ELISA, in the ground-water basin for the 1994–95 through the 1997–98 water-years were from Leslie Page karst window. The maximum ELISA triazines before October 1994 was 44.0 μg/L measured May 4, 1993 (PGSP0216) although higher concentrations have been detected at PGSP since then. For the 1994–95 through the 1997–98 water years the average triazines 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, and the entire 7-year project period, was 393 μg/L of triazines from runoff of a modest storm event (2.31 cm/0.91 in.), April 16 1998 (LPKW0402) at Leslie Page karst window. This event followed the planting of corn for the first time since 1994 in a field that drains overland directly into the karst window. As discussed above, there is some uncertainty whether the herbicides detected at LPKW from mid-1996 are from field runoff or the pesticide container dump, 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 ELISA alachlor concentration 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 (PGSP0216, May 4, 1993). The average for the basin was 0.15 μg/L while the median was 0.065 μg/L, reflecting the predominance of below detection analyses. The maximum ELISA carbofuran concentration for the basin, also from LPKW, 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 pre-October, 1994 maximum carbofuran was 7.4 μg/L (PGSP0430, April 30, 1994). The average carbofuran concentration was 0.11 μg/L, while the median was 0.085 μg/L.

The maximum ELISA metolachlor concentration was 29.60 μg/L from a sample collected March 18, 1997 at Pleasant Grove spring (PGSP1043) which exceeded the pre-October, 1994 maximum 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 the ELISA pesticides, when compared to the averages, reflects the skewed distribution of the data as a result of the large number of samples with low concentrations at or below detection limit concentrations.

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) while the minimum concentration was 0.28 μg/L for a sample collected December 17, 1996, only 7 months later. The average triazines concentration was 5.39 μg/L while 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 metolachlor concentration was 0.77 μg/L and the median only 0.22 μg/L. Concentrations of chlorpyrifos below 0.2 μg/L were measured by ELISA in an ad-hoc suite of samples collected at PGSP during a high-flow event in June 1996.

Samples for gas chromatograph analysis of pesticides were collected manually at LPKW and PGSP. The maximum concentration of atrazine in the basin determined by GC since October, 1994 was 20.51 μg/L (PGSP0842, May 7, 1996). The maximum metolachlor concentration was 3.75 μg/L (LPKW0319, April 2, 1997). Metribuzin, trifluralin, and simazine, were also detected in concentrations less than 0.1 μg/L by GC. Also, the analysis of duplicate samples for pesticides by gas chromatography (GC) and ELISA continued on a quarterly basis through the end of the project. These analyses were continued to expand upon the relationship between the two analytical methods established prior to October 1994 (Currens, 1999). The strong, linear, positive correlation for triazines and for metolachlor established in the earlier report were confirmed.

Suspended Sediment

Samples for suspended sediment were collected by automatic sampler at two locations, Leslie Page karst window (LPKW) and Pleasant Grove Spring (PGSP). The relationship between the sediment concentration as collected by the sampling machines and samples collected by standard methods is unknown for LPKW, but the relationship is nearly one to one at PGSP. The maximum suspended sediment concentration for the ground-water basin was 3,267 mg/L, from storm runoff entering the swallow hole at Leslie Page Karst Window (LPKW0331, April 27, 1997). The maximum at PGSP was 3,073 mg/L (PGSP0625, May 9, 1995). The previous maximum total suspended sediment was 2,278 mg/L (PGSP0429, April 29, 1994). The average suspended-sediment concentration for PGSP 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 ground-water basin have continued to exceed drinking water standards and frequently exceed the standard for water supply sources (2,000 col/100 mL). For the basin as a whole (PGSP, LPKW, GDSW, UPGC, TCKW, JHWW sampling sites) fecal coliform averaged 3,839 col/100 mL and fecal streptococci averaged 13,437 col/100 mL. Topical samples were collected at Pleasant Grove Spring during high-flow events, when bacteria counts are expected to be elevated, and therefore median values of 400 and 640 col/100 mL respectively, are more representative of typical counts. 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 on the recession of two consecutive high-flow events earlier in June. Prior to October 1994 the maximum was 24,000 col/100 mL fecal streptococci (GDSW0006, February 26, 1992). The average fecal coliform count for PGSP was 6,837 col/100 mL and fecal streptococci was 20,097 col/100 mL, while the medians were 1200 col/100 mL fecal coliform and 914 col/100 mL fecal streptococci. The slime growth on instrumentation mentioned in Methodology is further evidence of organic waste pollution.

Three high-flow events were sampled at Pleasant Grove Spring to investigate the suspected shift of the fecal coliform/fecal streptococci ratio from animal influenced toward human influenced following high-flow. Unfortunately, on each attempt the sampling was begun late in the event or was stopped before the event was over 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 lower end of the range. The ratio, however reached the fourth highest value recorded in the basin, 9.80 (PGSP0761) during this event. 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 (PGSP0595, April 11, 1995). This sample was collected during a low

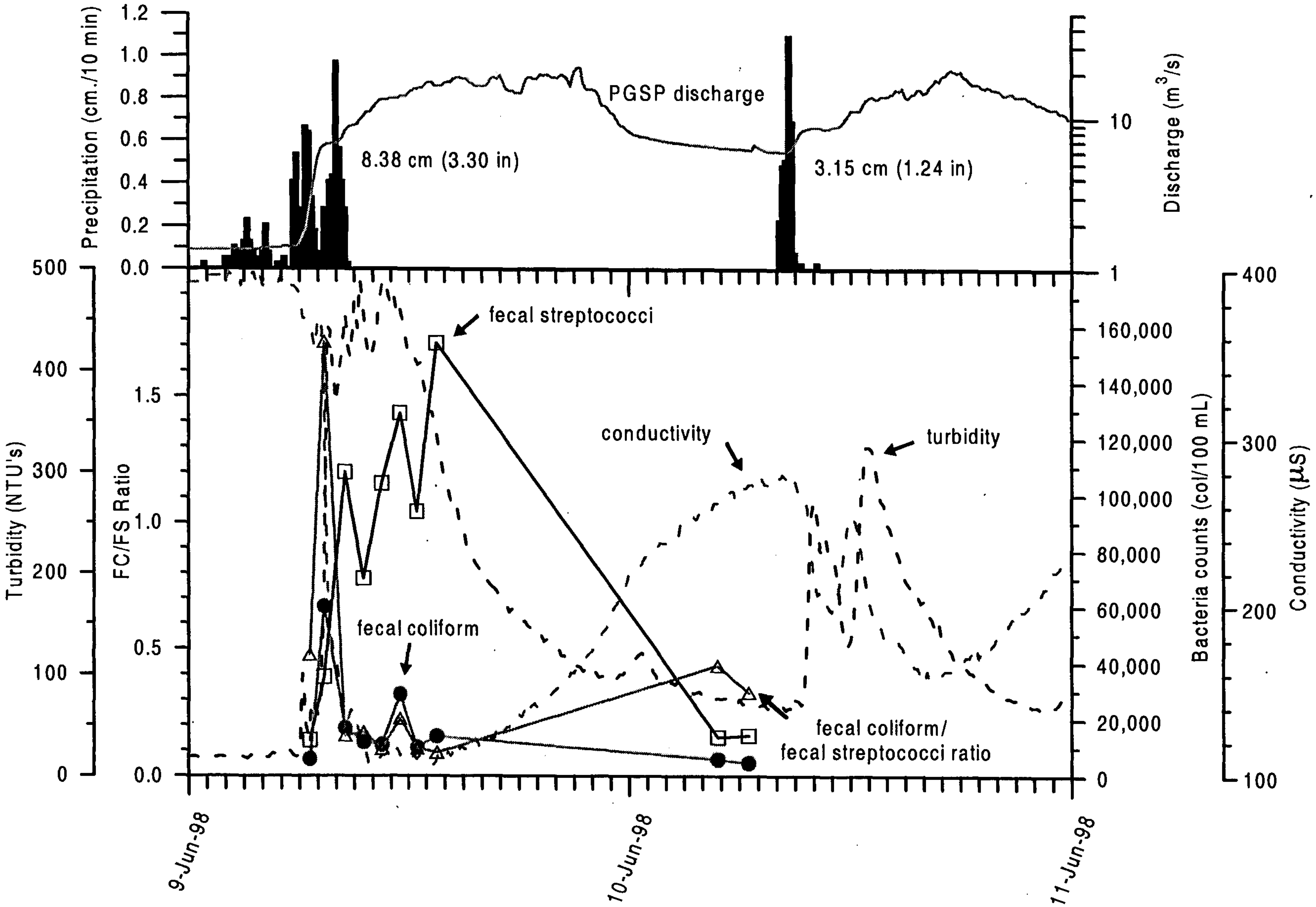

Figure 20. The occurrence of high bacteria counts compared to discharge, turbidity, and conductivity at Pleasant Grove spring during the June 1998 event. Note the increase in fecal coliform during the initial rise in stage and the increase in fecal streptococci later in the event.

flow period and the bacteria counts were also atypically low. Because of the low counts the ratio may be more easily effected by a minor error in the analysis, but more likely the ratio reflected the prevalence of human waste during the prevailing flow conditions.

It was expected that the fecal coliform-fecal streptococci ratio would make a pronounced shift toward the human influenced end of the ratio scale on the recession of storm hydrographs, as suggested by earlier results. Therefore, the occurrence of the shift in ratio during the rising limb of discharge hydrographs was unexpected. It is clear, however, that the ratio shifts toward animal dominated values during the time interval when overland runoff is arriving at Pleasant Grove Spring. Therefore, it is probable that animal waste is 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 as rainfall is not needed for its transportation and furthermore, it possibly lingers in the epikarst and smaller conduits during low flow. During a storm event, the recharge into the epikarst mobilizes the accumulated human waste, which is transported to the spring. Most housing in the ground-water basin is in Oakville, distant from Pleasant Grove Spring, however other housing is scattered throughout the basin and some is closer to PGSP. Therefore, the human waste dominates at PGSP during the very early part of the high-flow event because stores in the conduits have human influenced ratios, while runoff from pastures in the ground-water basin has not had time to reach the spring. The ratio shifts to animal dominated while the runoff is discharged and shifts again to human influence when the arrival of overland runoff at Pleasant Grove Spring has ceased. During drought, while 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). One well was routinely sampled each spring beginning in April, 1994, Miller Schoolhouse Well (MSHW). The well is near the east-central ground-water basin boundary of Pleasant Grove Spring and up-gradient of most agricultural activity. The MSHW is a drilled well, cased from the surface to bedrock with open hole to 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. ELISA triazines averaged 0.30 μg/L with three samples below detection limits and a maximum concentration of 0.91 μg/L. Carbofuran and alachlor were below detection limits for all samples while 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 were 1,636 col/100 mL. The high bacteria count may be due to the construction of the well, but there is also a dog kennel within 30 m (100 ft.) of the well. Overland runoff from the kennel has not been observed flowing into the well bore.

One other domestic water well (Assembled Kentucky Groundwater database number 0001-7181; see Currens, 1999 for location) was sampled in May, 1998 (sample number EGWW0001) at the request of the owner. It too is near the ground-water basin boundary but at the northern end of the watershed. The four pesticides determined by ELISA were all below detection limit and nitrate-nitrogen was only 1.65 mg/L. Bacteria counts were below 5 col./100 mL for both fecal coliform and fecal streptococci.

Rainfall was collected for analysis intermittently through out the project at Pleasant Grove Spring. Five samples were collected since October 1994 and most were analyzed for pesticides by ELISA and nitrate-nitrogen. Two samples collected in June 1995 had below detection for triazines and less than 0.50 mg/L nitrate-nitrogen. A sample collected in May, 1996 measured less than 1 μg/L for all ELISA pesticides and only 0.14 mg/L nitrate-nitrogen. However two samples collected in April and May 1997 (RAIN0011 and RAIN0012) had significant concentrations of triazines and metolachlor. The sample collector was deployed for 7 days in both cases. Sample RAIN0011 represented 0.94 cm (0.37 in.). and RAIN0012 represented 1.04 cm (0.41 in.) of precipitation. Alachlor and carbofuran were near or below detection limits in both samples. Sample RAIN0011 had 4.18 μg/L triazines, 2.76 μg/L metolachlor, and 0.66 mg/L nitrate-nitrogen and sample RAIN0012 had 1.69 μg/L triazines, 0.88 μg/L metolachlor, and also 0.66 mg/L 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. Further, other samples 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 air borne pesticide transport except locally and immediately after application. The effect on ground-water samples collected at PGSP is thought to be negligible because the samples collected in May 1997 were all collected with an automatic sampling machine and the intake is some 6 feet underwater and directly in the outflow from the cave. The sample bottles are protected from air borne contamination by the cabinet of the sampling machine.

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

Descriptive statistics and annual mass flux, or pollutant loading, of several constituents of probable agricultural origin was calculated for Pleasant Grove Spring for the pre- and post-BMP periods. The mass flux was also estimated for upper Pleasant Grove Creek (GDSW supplemented with UPGC) and Leslie Page karst window. The flux was calculated for the three water-years prior to implementation of best management practices and for the three years the BMP's were adopted. For this report the flux for PGSP was recalculated for the 1992–93 through 1997–98 water-years using the revised discharge rating curve. The upper Pleasant Grove Creek flux, representing the contaminate load sinking underground at GDSW was calculated using the revised discharge rating curve for GDSW and the three rating curves for UPGC, which are dependent on channel conditions as discussed in methodology. Similarly the mass flux for LPKW was estimated for the 1995–96 through 1997–98 water-years using rating curves for pre-weir and post-weir installation.

Flow-weighted averages derived from flux calculations were used prominently in the reconnaissance report 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. While the flow-weighted averages for dissolved constituents generally paralleled arithmetic averages for dissolved constituents the constituents associated with high flow (triazines and sediment) varied more widely from these statistics. The differences are partly due to the difficulty of monitoring mass flux by using discrete samples, but more likely are due to the additional variability introduced by large changes in annual discharge when 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 at PGSP apparent from 1991 to 1994 did not continue in 1995 and subsequent years. Therefore, the flow-weighted average is not emphasized in this report and although presented in Table 4, flow-weighted averages are not discussed further.

Table 4. Annual statistics for those contaminants discharged in significant concentrations from Pleasant Grove Spring (PGSP) for the complete sample set.

Water-year	Triazines, average µg/L	Triazines, median µg/L	Triazines, geometric average µg/L	Triazines, flow-weighted average µg/L	Nitrate-nitrogen, average mg/L	Nitrate-nitrogen, flow-weighted average mg/L	Total Suspended Solids, median mg/L	Ortho-phosphate, 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

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. Continuously monitored water temperature, pH, conductivity, and turbidity data help characterize the source and travel time of pollutants to Pleasant Grove Spring. Runoff from spring- and summertime storms elevates water temperature and turbidity and decreases pH and specific conductivity. Winter storms decrease water temperature. Irregular rises and falls in the water quality measures are attributed to variations in rainfall distribution and intensity across the surface of the ground-water basin. For example, the first deflection is caused by runoff in the local surface catchment of the springs' rise pool. This deflection is absent when a summer thunderstorm rains only in the headwater area. Also, when a sudden, intense, and widely distributed rainfall occurs, water quality parameters are deflected smoothly and without any temporary reversals.

The December 16 and 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. 21). A slow moving cold front ended a warming trend, which peaked with a high air temperature on December 15th of 19.3 °C (66.7 °F), and began a steady light rain 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 on the 17th, effectively stopping overland runoff. The light steady rain resulted in a modest high-flow event, discharge at PGSP peaking at 26 m^3/sec (923 $ft.^3$/sec). The stage hydrograph for GDSW and the turbidity chemograph rise smoothly, when compared to other storms, to modest peak values (Fig. 22). 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 dominates the physical 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 the event. Significant quantities of contaminants associated with runoff, particularly pesticides, may be discharged during a single, ill-timed storm. The May 1995 high-flow event at PSGP 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 May 1996 high-flow event is one of the best-documented examples. From 00:00 hours on May 7 to 00:00 hours on May 10, 26.54 kg of atrazine-equivalent was discharged. During all of the 1995–96 water-year 36.42 kg of atrazine-equivalent was discharged from Pleasant Grove Spring, therefore the May event accounted for 73 percent of the total annual mass flux of atrazine-equivalent. The importance of the connection between major storms and triazine peak concentrations is intuitively obvious but deserves restatement because of its implications for managing nonpoint-source runoff in karst areas. Nitrate-nitrogen concentrations are reduced during high-flow events, while other constituents also associated with field runoff are increased. For an example of changes in bacteria counts at PGSP during high-flow see figure 20.

Several patterns in the shifting of constituent concentrations repeat themselves in the graphs of high-flow events (Fig. 23). The triazines concentration increases near the peak of the discharge hydrograph, whereas the nitrate-nitrogen concentration decreases. For most storms occurring in the spring-season, the peak in turbidity or suspended sediment is followed four to six hours later by the peak in triazines concentration. This lack of correlation between suspended sediment and triazines concentrations was discussed by 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

Figure 21. High-flow at Pleasant Grove Spring during the December 1996 event.

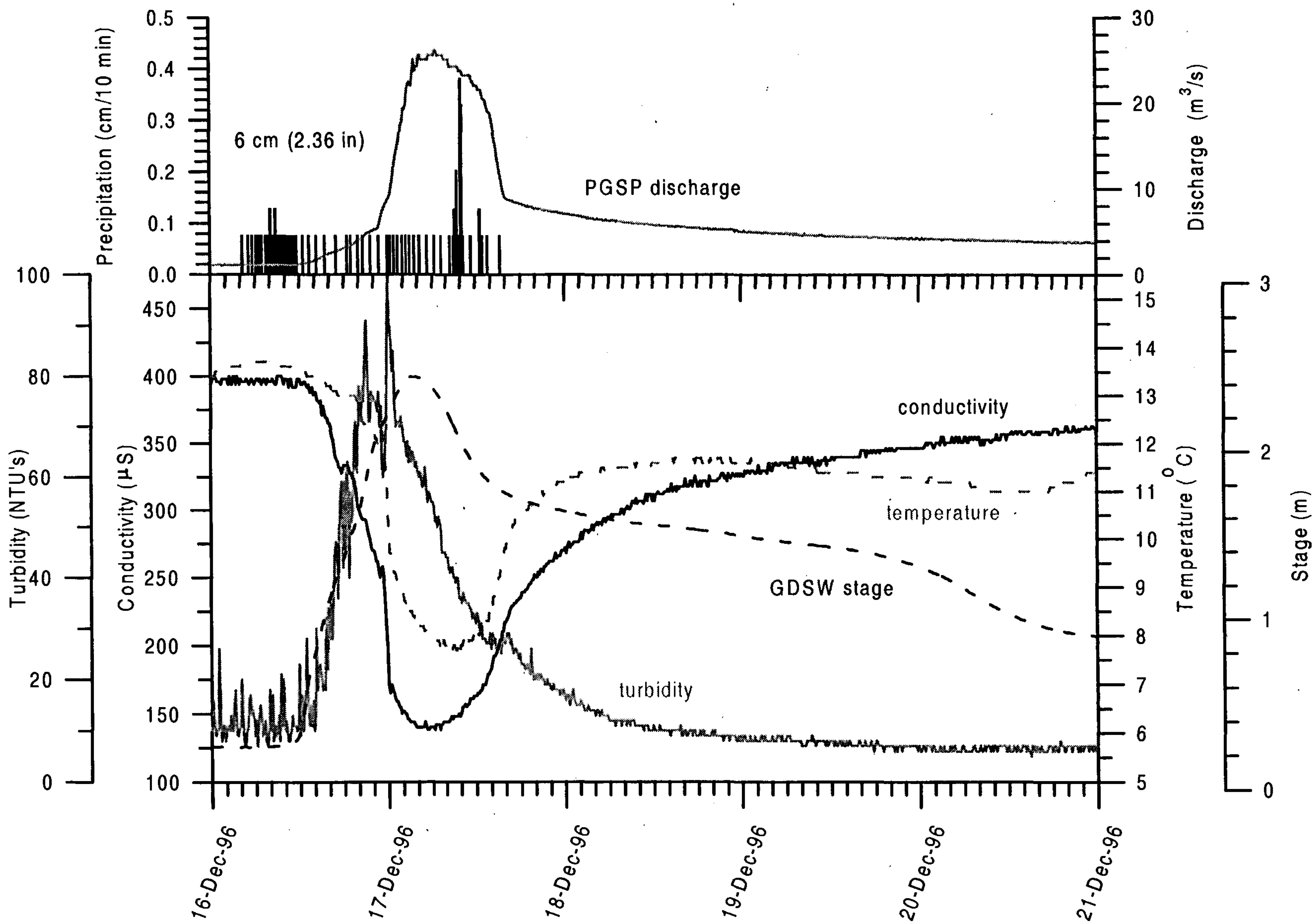

Figure 22. Hydrograph and chemographs for Pleasant Grove Spring for the December 1996 event. The smooth graph curves do not exhibit any structure evident of contrasting water quality caused by confluent flow from major tributaries.

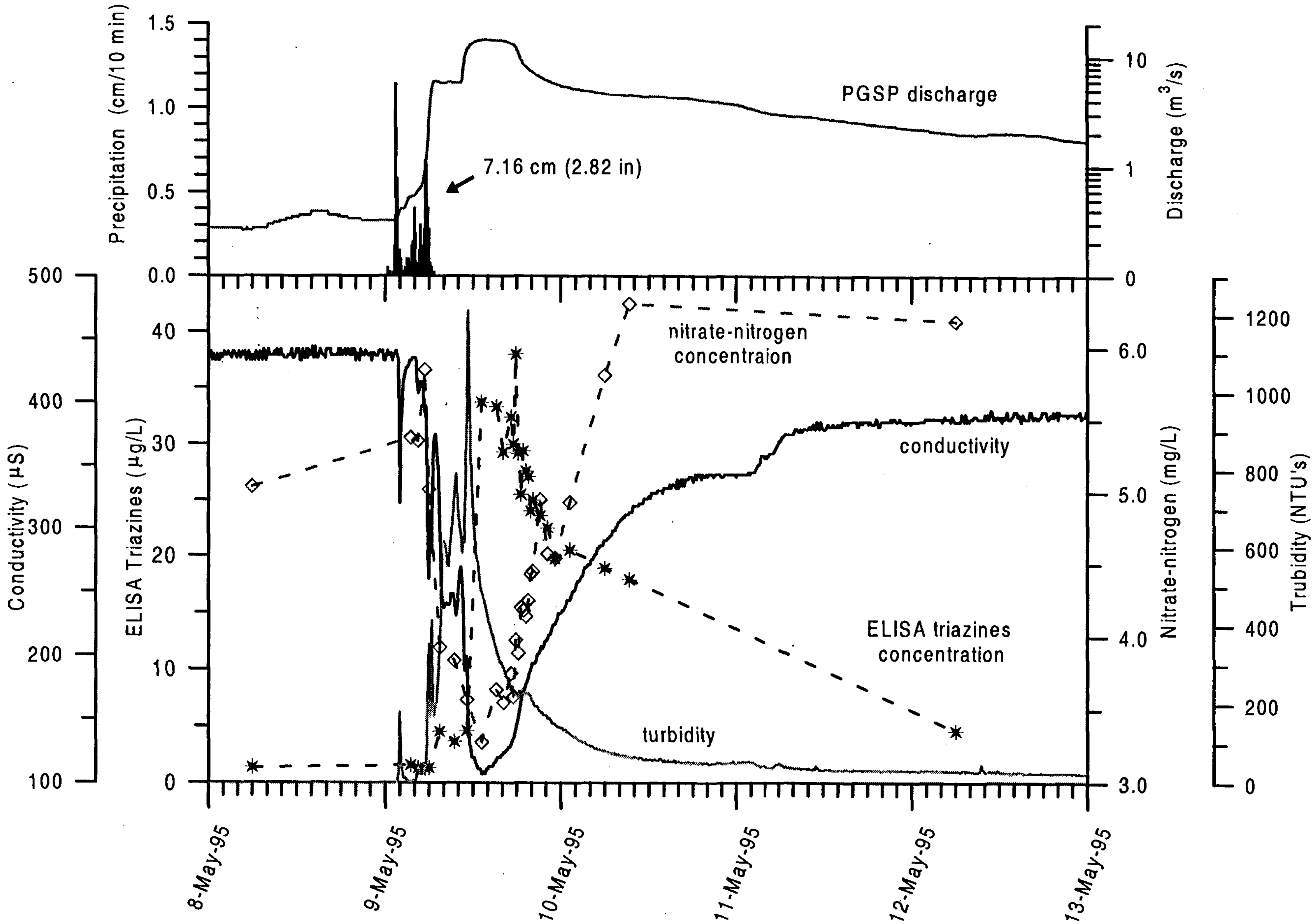

Figure 23. Concentrations of ELISA triazines in water change rapidly during springtime high-flow events at Pleasant Grove Spring. Shown are hydrographs and chemographs for the May 1995 high-flow event. Note the peak in triazines occurs after the peak in turbidity.

sediment. Once the arrival of runoff at PGSP has slowed, as indicated by the records for turbidity, conductivity (Fig. 23), and water-temperature (not shown), the triazine concentration gradually returns to pre-storm levels. After the dilution of the of 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 one or two 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 macro pores. This results in the concentration of nitrate-nitrogen rising again as the displaced stores from the soil and epikarst arrive at PGSP. 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 PGSP from a baseline concentration of 5 mg/L before the dilution by runoff occurs (Fig. 23). It is thought the source of the higher nitrate-nitrogen concentration is water displaced from 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 UPGC station. Because flow in upper Pleasant Grove Creek is slow, and was partly impounded during the period when a beaver dam existed, 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 UPGC 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 Pleasant 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. However, some high-flow events were well documented which illustrate the importance of basin hydrology and land use on the characteristics of inflow into the aquifer.

As mentioned in the discussion of monitoring results, 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 event (2.31 cm/0.91 in.) 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, are also significant. Figure 24 illustrates the stage hydrograph at LPKW and the occurrence of samples analyzed for triazines and nitrate-nitrogen. The clefs in the inflow hydrograph are caused by the undefined relationship of stage to inflow during back flooding 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,

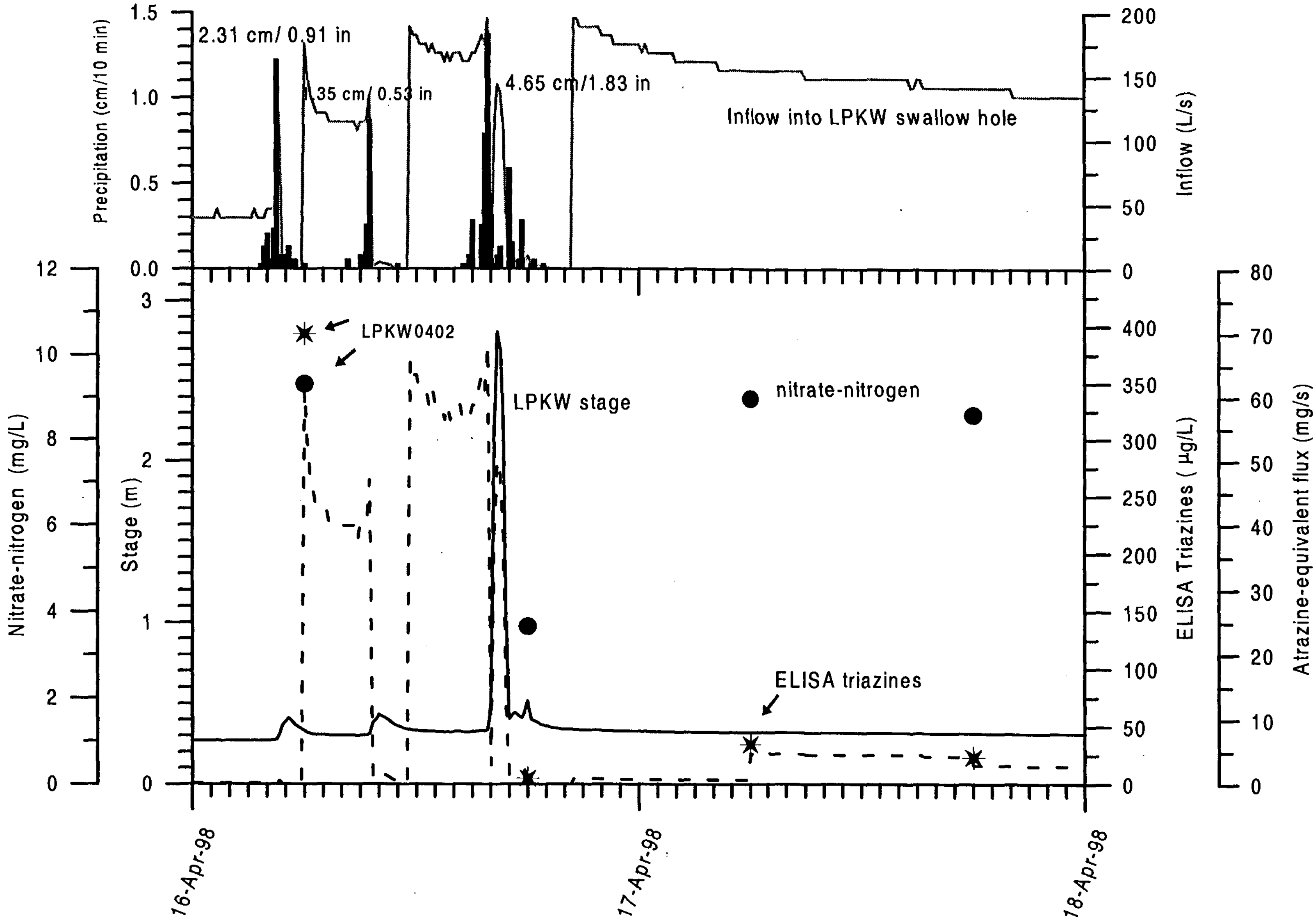

Figure 24. The highest concentration of triazines detected during the study was measured in runoff entering the swallow hole at Leslie page karst window during the April 1998 high-flow event.

except where the lower triazines 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 ground-water 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 and gullies had formed in the corn field and through the grass buffer surrounding the karst window as a result of late winter, early spring storms. This circumstance suggests that when buffer strips are used, unless the runoff can be prevented from eroding channels through them, the buffers may be of relatively little use.

The high concentration of triazines in LPKW0402 is potentially a consequence of the presence of the 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. Futher, 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 LPKW through the winter of 1997–1998 as might be expected if the dump were the source. High concentrations of triazines were measured at PGSP throughout the spring of 1998. Also, high concentrations of triazines were measured at The Canyon karst window on April 15, 1998 (TCKW 0072) and more notably at George Delaney swallow hole on April 15 (GDSW0112) and April 16 (GDSW0113) and particularly on April 17 (GDSW0114) at 40.4 μg/L. Joe Harper water well was sampled May 12, 1998 and 41.6 μg/L triazines was measured. None of these sites receive flow from LPKW. These facts show the triazines originated from areas of the ground-water 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 5). Atrazine-equivalent recovery at PGSP 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 also important. Mass flux of alachlor was not calculated as discussed in Methodology. The mass flux of orthophosphate and bacteria were not calculated because samples were not collected frequently. Graphs for each water-year of atrazine-equivalent and nitrate-nitrogen flux, and triazine and nitrate-nitrogen concentrations, are presented below (figures 25, 26, 27, 28, 29, and 30). Graphs of total suspended solids flux are not presented and unlike the triazines the peaks in suspended sediment occur year round, whenever field conditions exist where 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 (Fig. 31). There is no visually discernible trend on the graph for triazines geometric average, average nitrate-nitrogen, or nitrate-nitrogen annual flux. The atrazine-equivalent flux exhibits a distinct increase over the period of the WQIP.

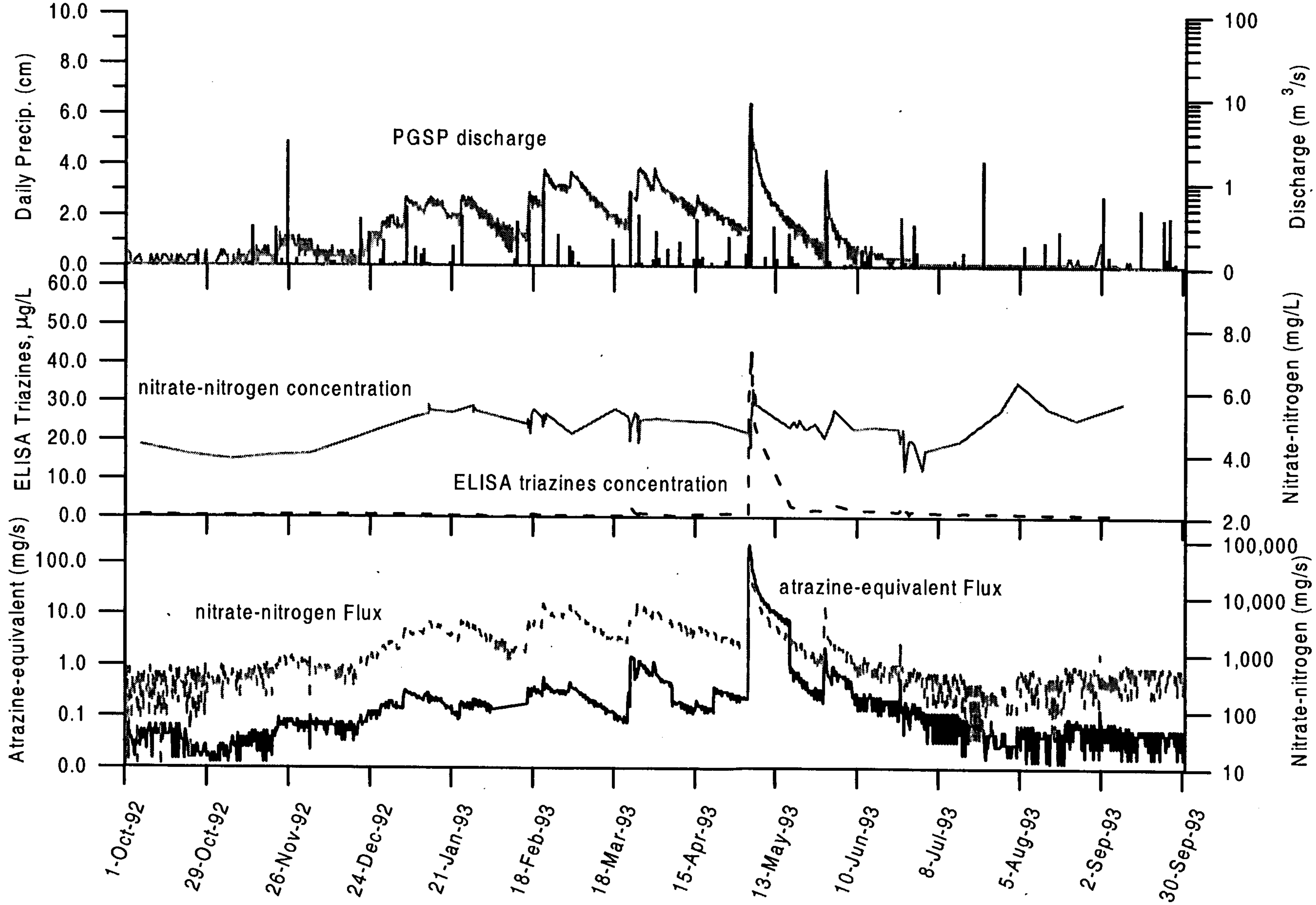

Figure 25. Plot of daily precipitation, discharge, nitrate-nitrogen concentration, nitrate nitrogen flux and ELISA triazines concentration, and atrazine-equivalent flux for Pleasant Grove Spring for the 1992-93 water year.

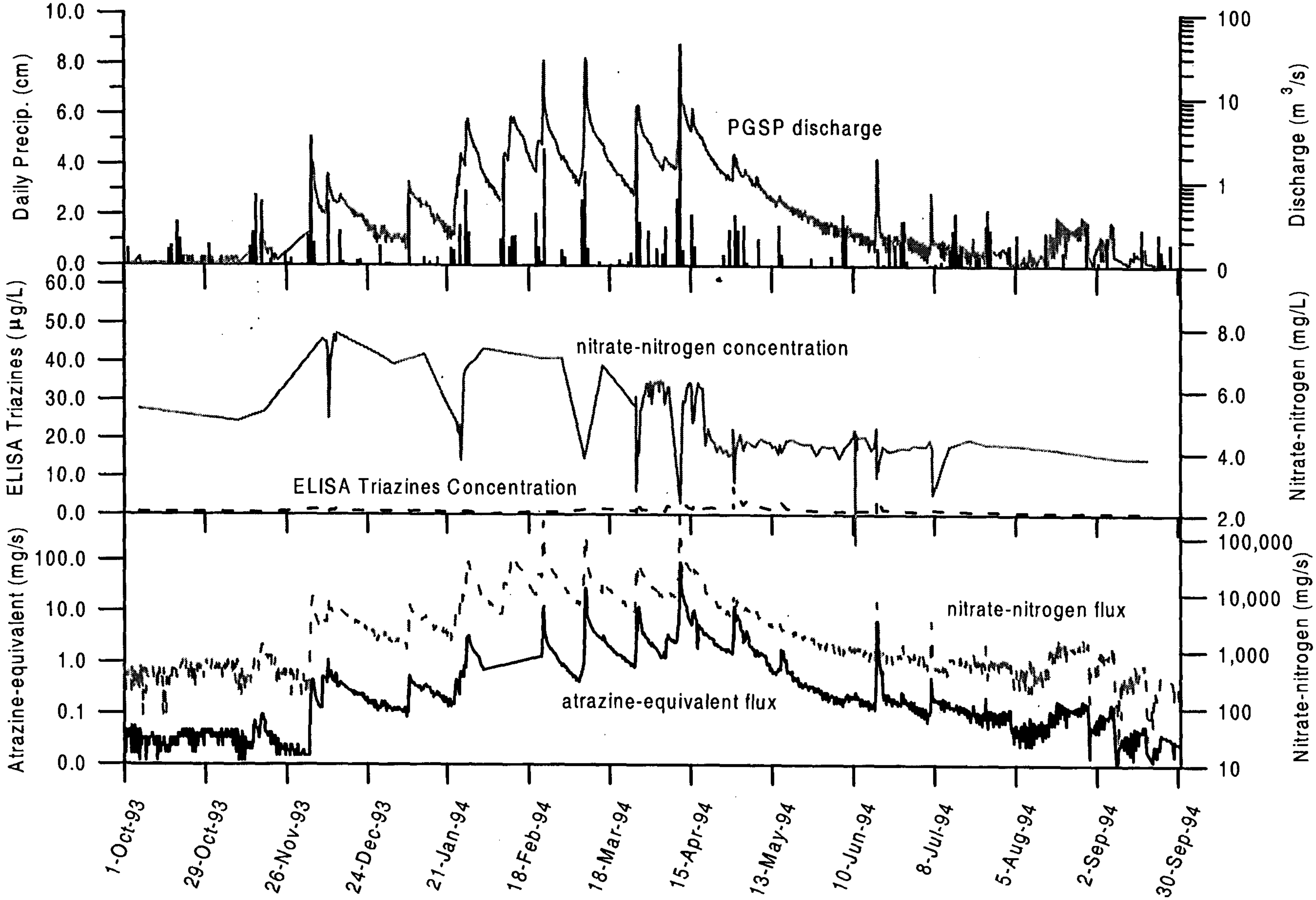

Figure 26. Plot of daily precipitation, discharge, nitrate-nitrogen concentration and flux, ELISA triazines concentration, and atrazine-equivalent flux for Pleasant Grove Spring for the 1993-1994 water year.

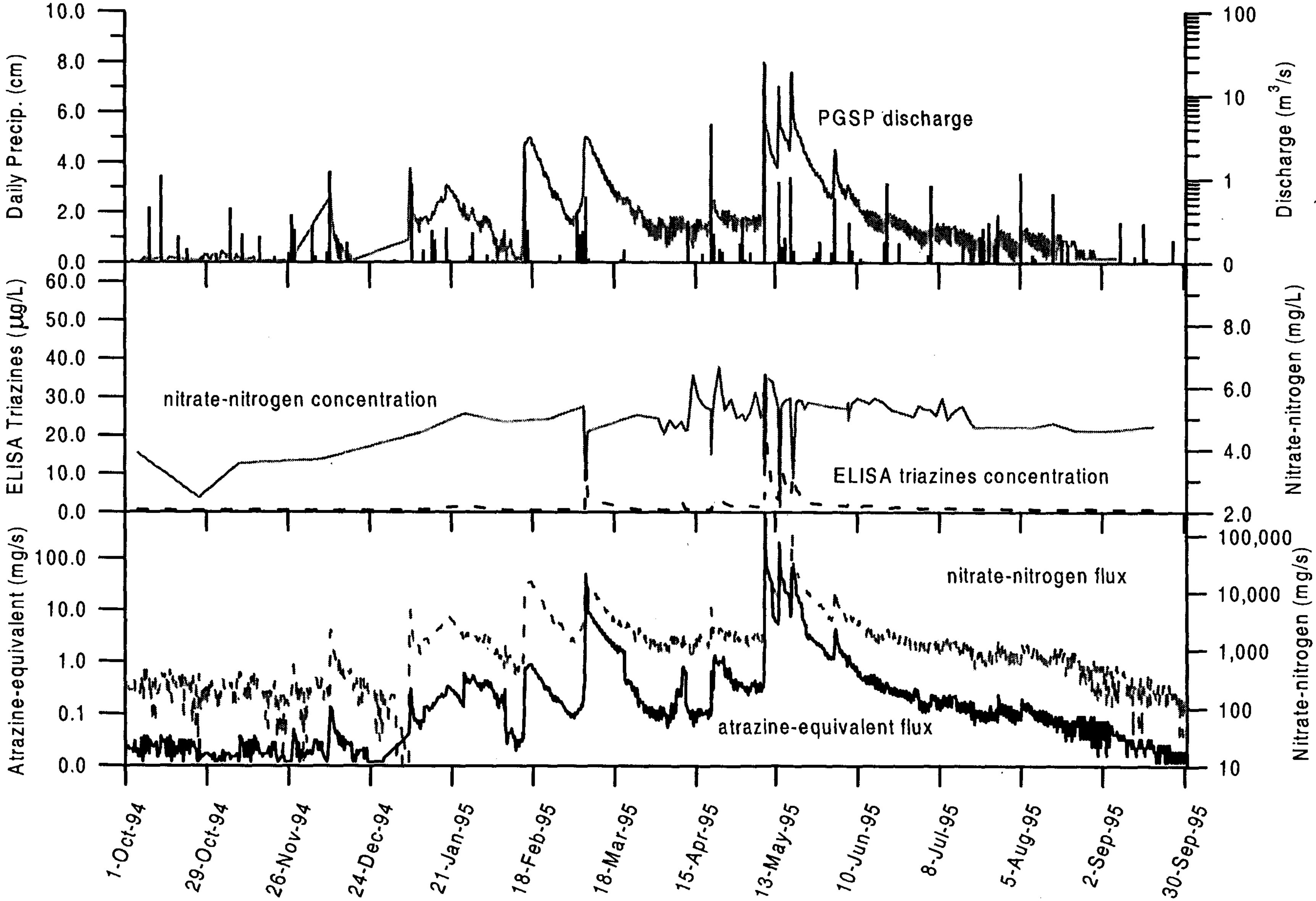

Figure 27. Plot of daily precipitation, discharge, nitrate-nitrogen concentration, nitrate-nitrogen flux, ELISA triazines concentration, and atrazine-equivalent flux for Pleasant Grove Spring for the 1994-95 water year.

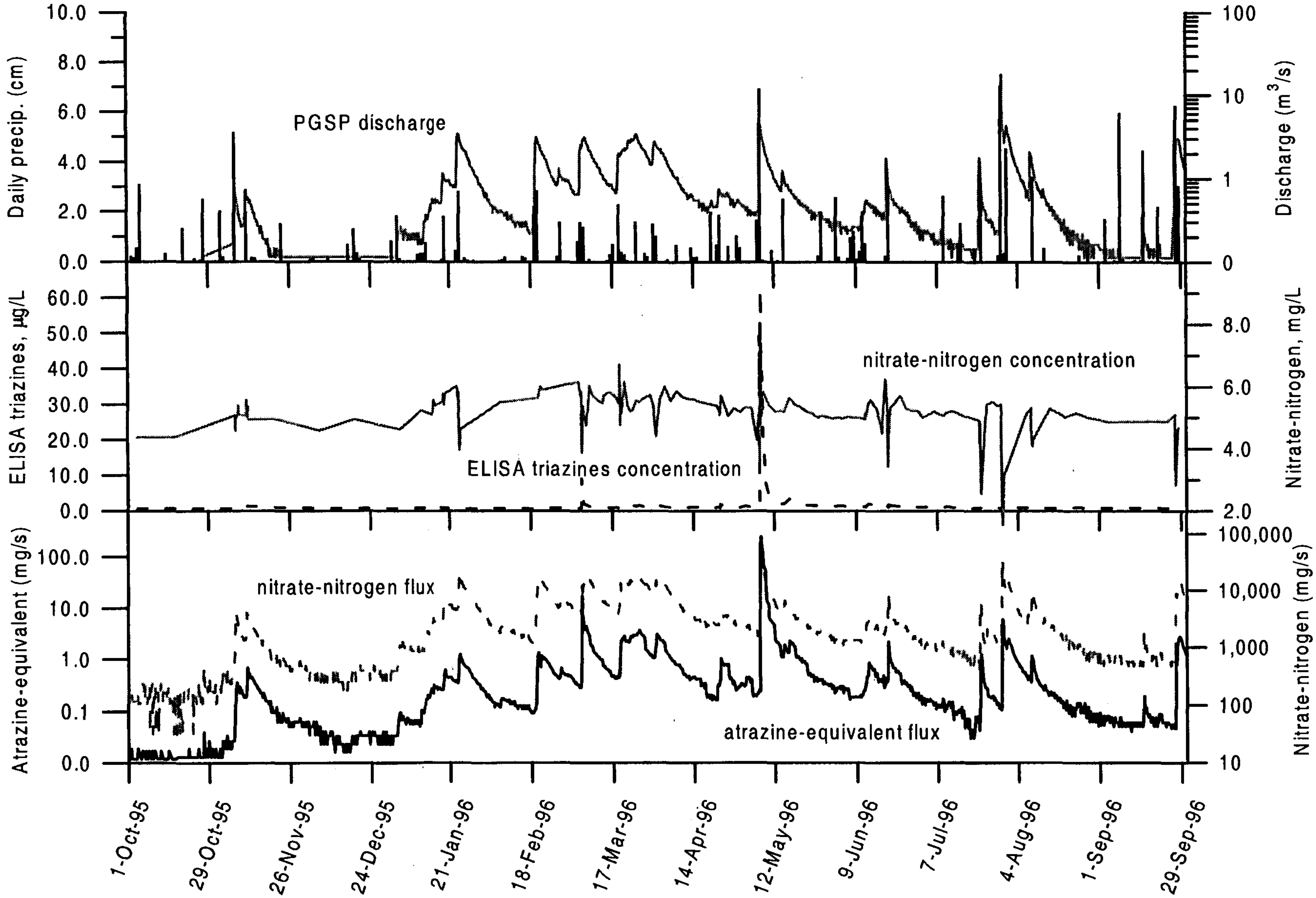

Figure 28. Plot of daily precipitation, discharge, nitrate-nitrogen concentration and flux, ELISA triazines concentration, and atrazine-equivalent flux for Pleasant Grove Spring for the 1995-96 water year.

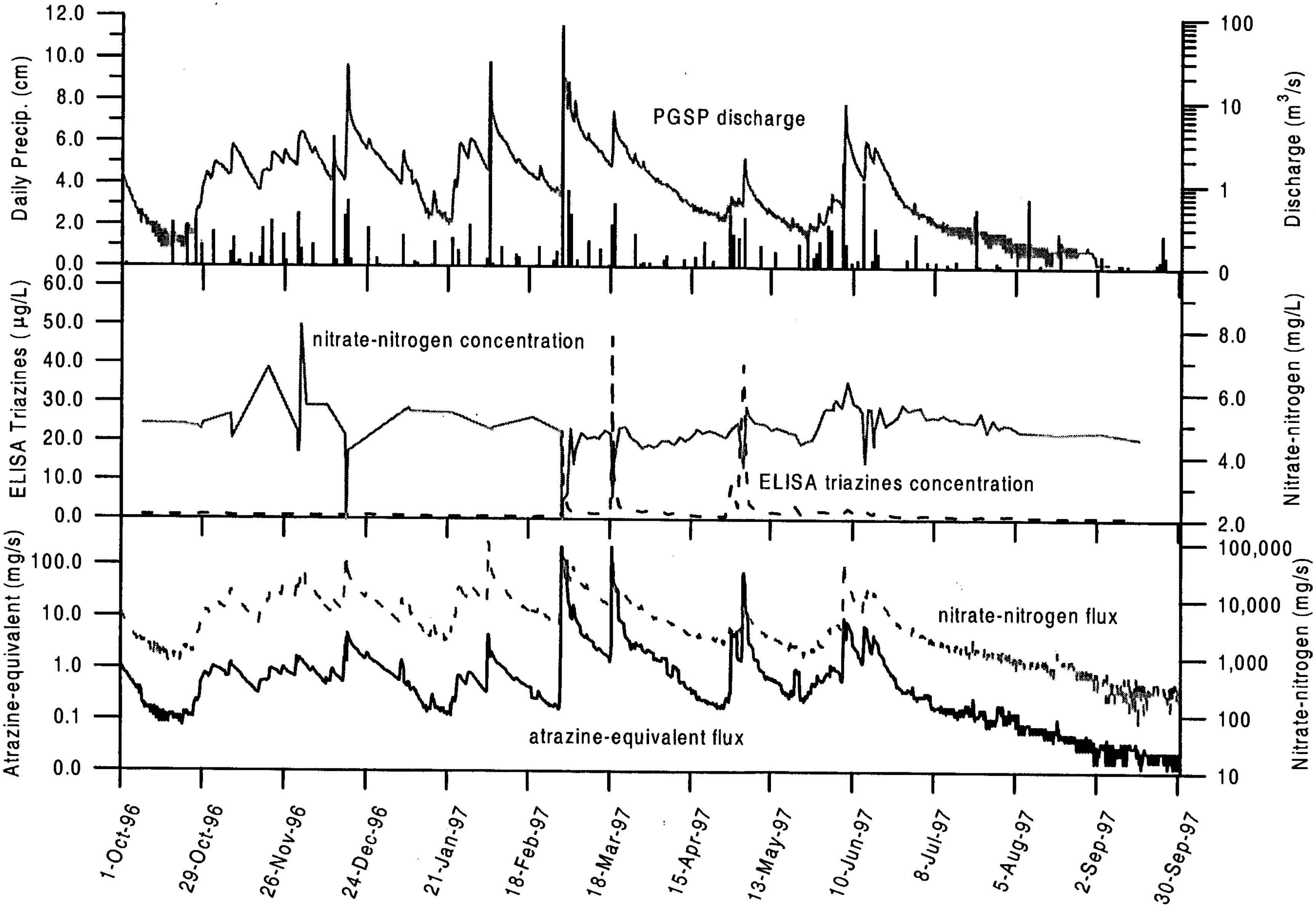

Figure 29. Plot of daily precipitation, discharge, nitrate-nitrogen concentration and flux, ELISA triazines concentration, and atrazine-equivalent flux for Pleasant Grove Spring for the 1996-97 water year.

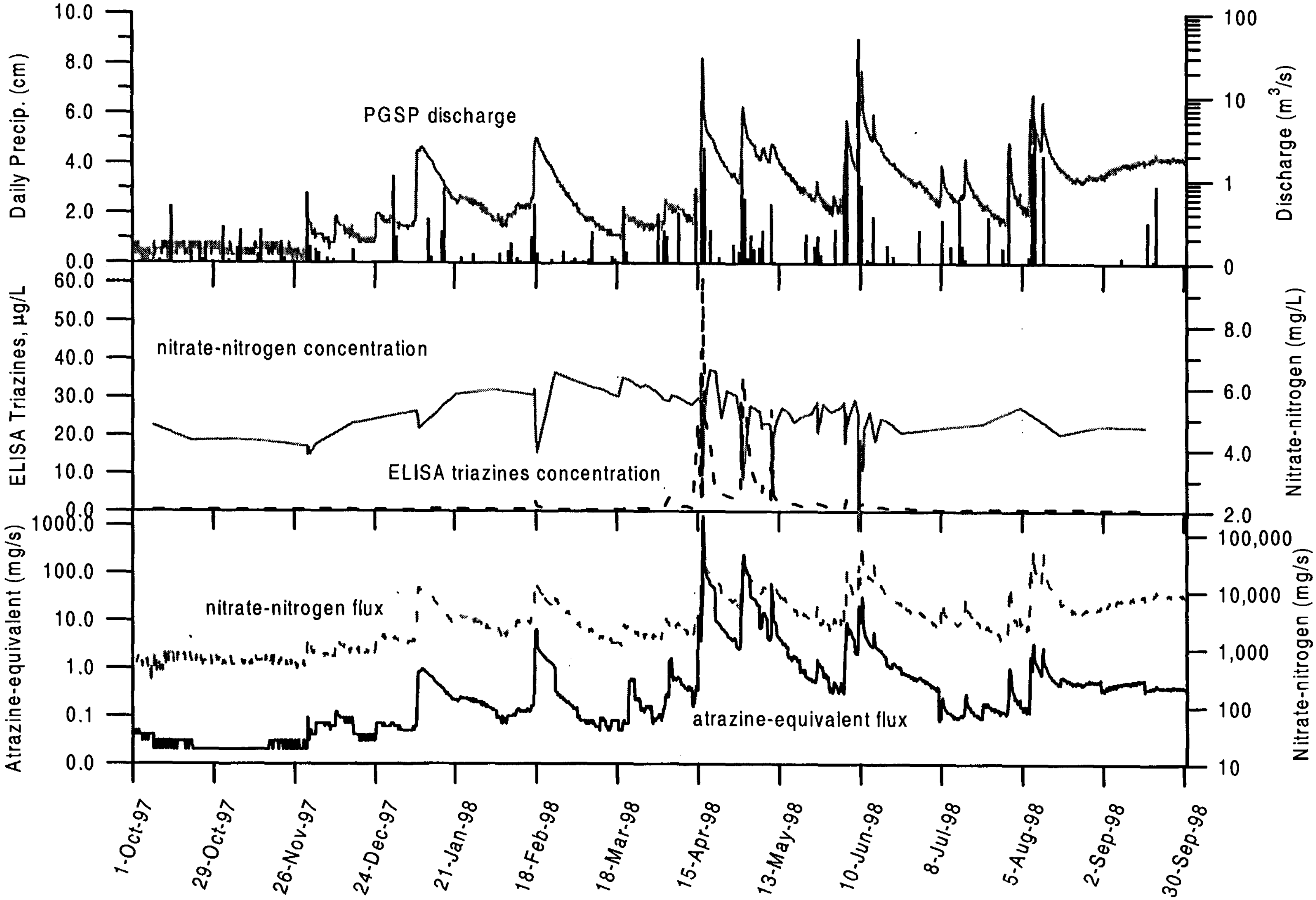

Figure 30. Plot of daily precipitation, discharge, nítrate-nitrogen concentration and flux, ELISA triazines concentration, and atrazine-equivalent flux for Pleasant Grove Spring for the 1997-98 water year.

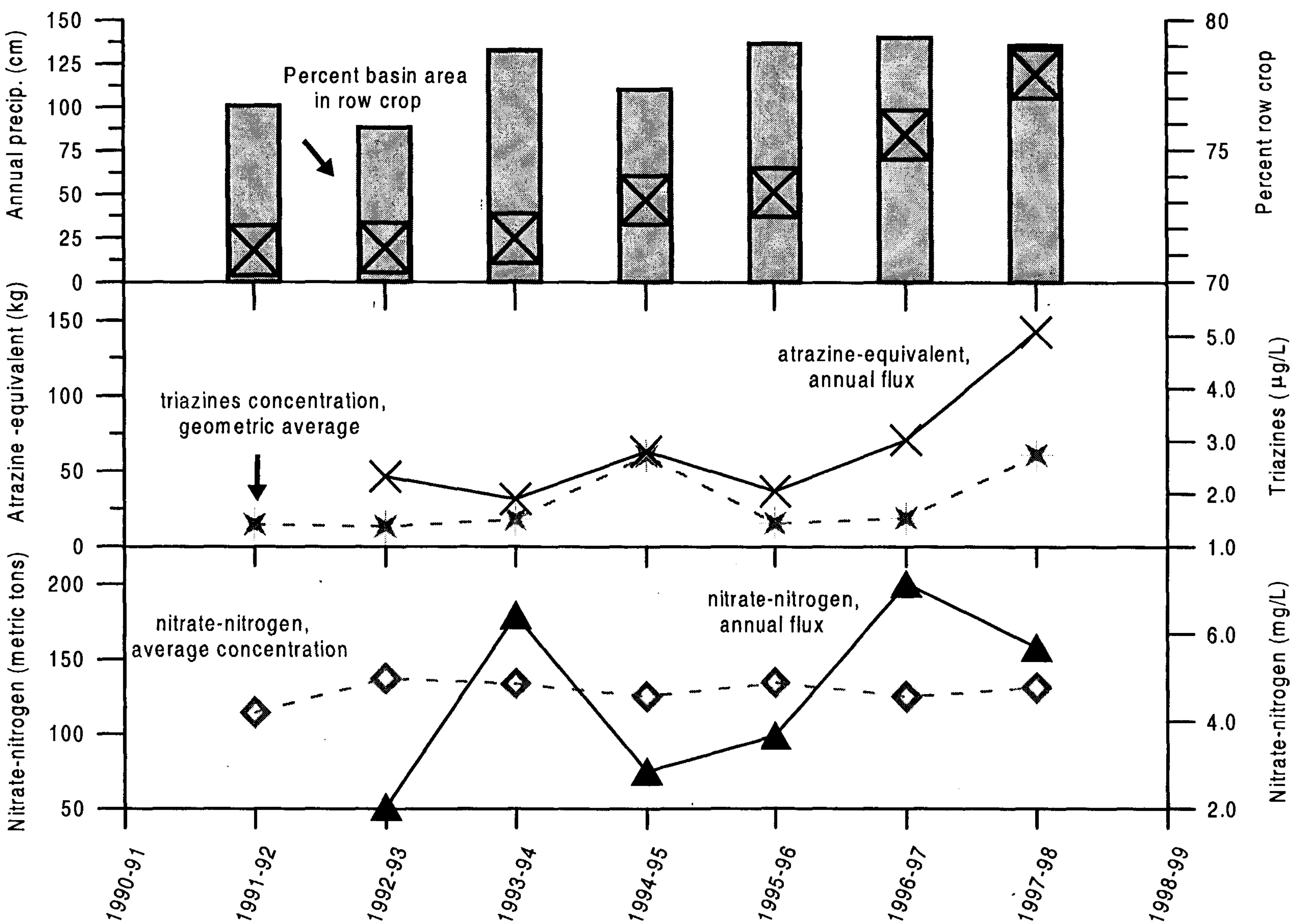

Figure 31. Trends in total annual mass flux of atrazine-equivalent and nitrate-nitrogen concentrations during the Pleasant Grove Spring project.

Table 5. Total annual precipitation, discharge, and mass flux of those contaminants detected in significant quantities at Pleasant Grove Spring (PGSP).

Water-year	Precipitation, cm	Discharge, m^3	Atrazine-equivalent, kg	Metolachlor, kg	Nitrate-nitrogen, metric tons	Suspended sediment, metric tons
1992–93	87.8	10,227,907	46.01	5.97	51.13	2124
1993–94	132.6	31,556,357	31.13	0.89	180.62	3802
1994–95	110.0	15,294,231	62.82	3.92	75.03	2255
1995–96	136.8	19,777,227	36.42	2.25	98.69	1591
1996–97	140.2	42,550,052	70.52	6.61	197.63	4553
1997–98	135.8	32,918,453	142.52	7.79	157.65	3625

One of the assumptions used in this project was that atrazine herbicide was applied only to corn and that almost all corn received atrazine applications. More importantly 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 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 generally true it also showed the average rate of atrazine application to corn varied significantly over the three 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 ground-water basin, and the subsequent effect on the distribution of crops, is also thought to affect the relationship between chemical applied and chemical reaching ground water. 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 volume for storage in the epikarst or carbonate aquifer because of the shallow depth to ground water. A larger percentage of the land surface in the headwaters area is planted in row crop (average of 78% versus 68%) than the downstream area 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 run off in to the ground water 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. Field observations of the planting of corn adjacent to open throated sinkholes coincident with significant atrazine concentrations suggest that a few open throated sinkholes surrounded by a small percentage of the corn fields may measurably influence the concentration of pesticides measured at Pleasant Grove Spring.

The seasonal pattern of occurrence of triazine at PGSP is nearly identical from year to year. Concentrations of triazine near or above 1 μg/L occur 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 followed periods of dry weather when chemical application equipment could 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, which 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 frequently sampled during the project. All spring-time runoff events were sampled and therefore it is unlikely that peak concentrations were missed. Although the 1993–94 water year 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 due to 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 datum is excluded from several correlations because of the unusually diminished runoff of agriculture chemicals.

Because atrazine is principally used for corn there logically should be a correlation between the area of corn planted and triazines measured in runoff within a drainage basin. However, essentially no correlation was found between total annual flux of atrazine-equivalent and the percentage of the basin planted in corn when the flux data for all 6 years were graphed. The correlation improves, however, when the 1993–94 and 1997–98 data are excluded ($r^2 = 0.65$). The conditions during the 1993–94 water-year were discussed above. The justification for excluding the 1997–98 value is that the WQIP inventory indicated the average application rate of atrazine in 1998 was double previous years. Consequently, the 1997–98 water-year had the highest mass flux of atrazine-equivalent ever recorded at PGSP. In contrast to the area in corn, the atrazine-equivalent flux does correlate well with the percentage of the basin in row crop ($r^2 = 0.80$) (Fig. 32). The improve correlation over the area in corn only 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 possible explanation is 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 applied in the basin is estimated and then compared to the annual mass flux of atrazine-equivalent measured at Pleasant Grove

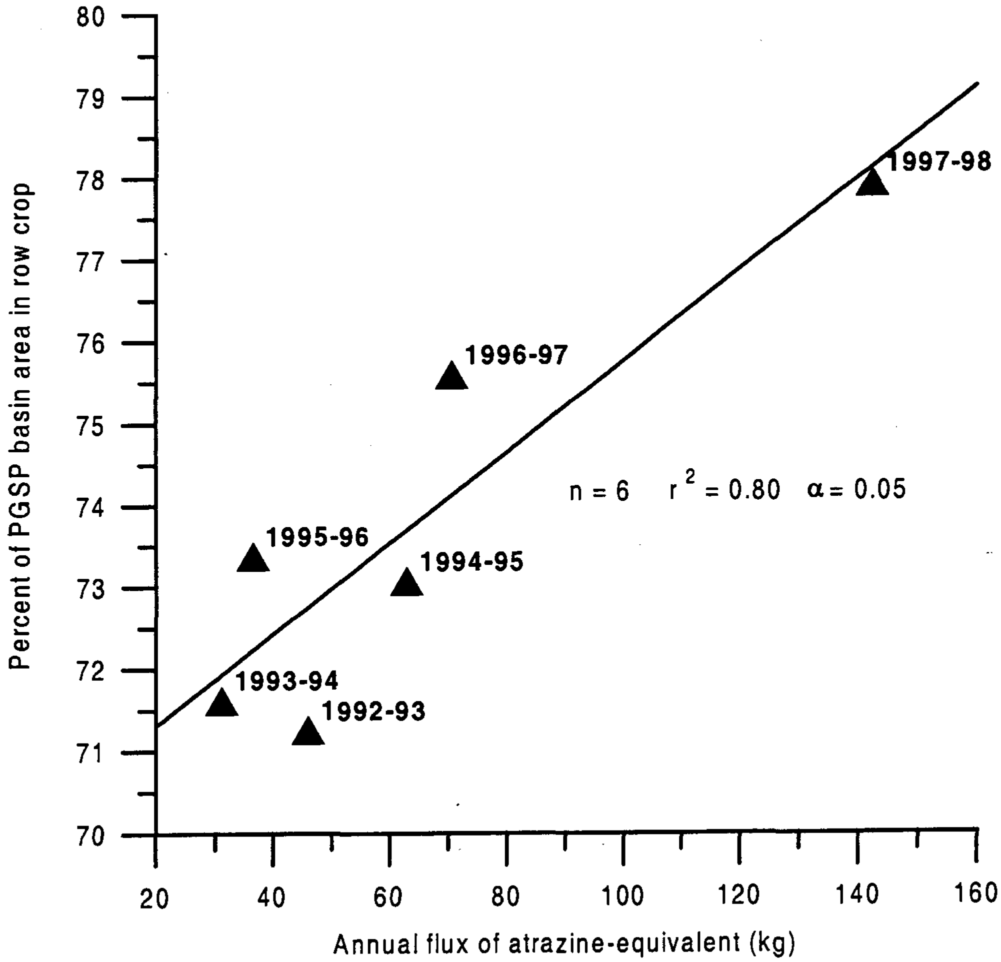

Figure 32. Comparison of the percentage of the ground-water basin area planted in row crop each spring season to the total annual mass flux of atrazine-equivalent discharged from Pleasant Grove Spring.

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 due to the minimal use of atrazine during the spring of 1997.

To test the importance of the coincidence of rainfall after pesticide application, the relationship of rainfall and percent runoff to various atrazine measures was considered for the April 15 through May 15 period of each year. An average of 54 percent of the total annual mass flux of atrazine-equivalent occurs during this one-month period. An arithmetic average was used for one correlation because it is 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 data for all years align along the trend. Because rainfall during the April-May period commonly occurs as a result of intense spring storms the relationship is thought to represent the result of intensive runoff events transporting recently applied herbicide. To further investigate the importance of the timing of rainfall, the annual mass flux of atrazine-equivalent was compared to the percent of precipitation (runoff) discharging at PGSP during the atrazine application season (Fig. 35). The percent 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 due to 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 percent runoff is removed when the depth of precipitation for the April 15 through May 15 period is plotted against the arithmetic average.

Nitrate-nitrate concentrations and flux at Pleasant Grove Spring have a narrower range of values through the year than atrazine-equivalent values, but exhibit slight rises in late winter and during the planting season and short-lived concentration decreases (but flux increases) during high-flow (figures 25, 26, 27, 28, 29, and 30). Thus the nitrate-nitrogen concentrations are crudely reciprocal of the triazine concentrations. As in the case of atrazine-equivalent, there is no visually discernible trend on the graphs in nitrate-nitrogen flux or concentration over the period of the WQIP.

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 the 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 through June 22) when most cultivation occurs. When the WQIP inventory BMP data 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 percent of the precipitation

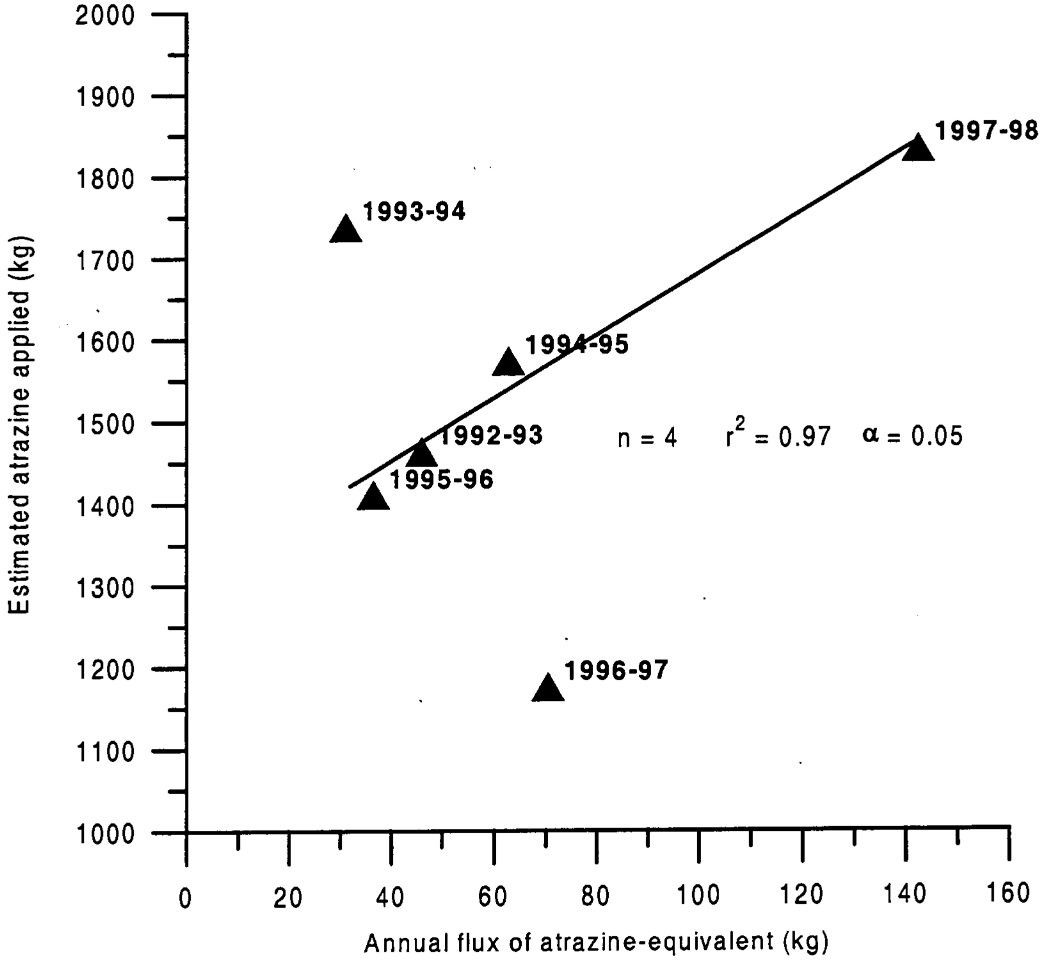

Figure 33. Annual mass flux of atrazine-equivalent discharged from Pleasant Grove Spring plotted against the estimated atrazine applied to crops in the ground-water basin. Water-years 1992-1993 through 1994-1995 assume an average application rate of 1.24 kg/ha corn whereas later years use the average annual application rate reported via the WQIP.

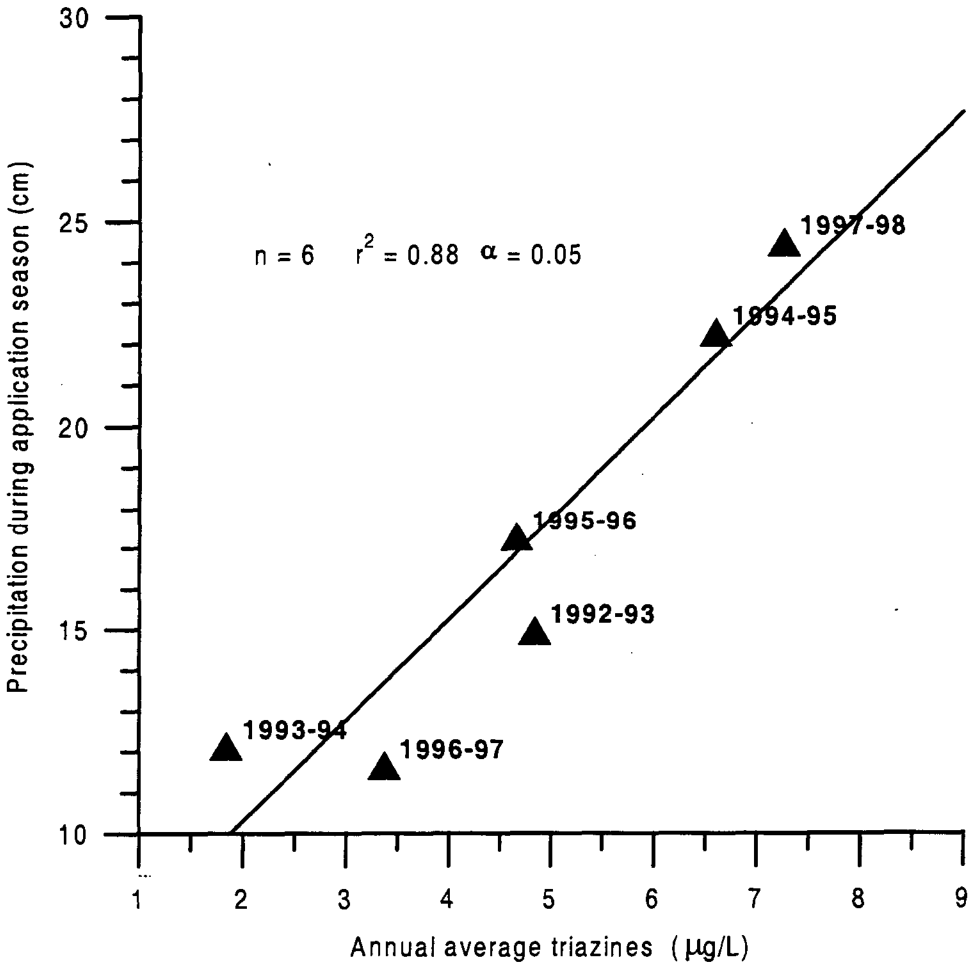

Figure 34. Cross plot of annual arithmatic average of triazines for water samples from Pleasant Grove Spring versus cumulative precipitation between April 15 and May 15. The relationship illustrates the significant effect on average concentrations of herbicides caused by storms occurring during the application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

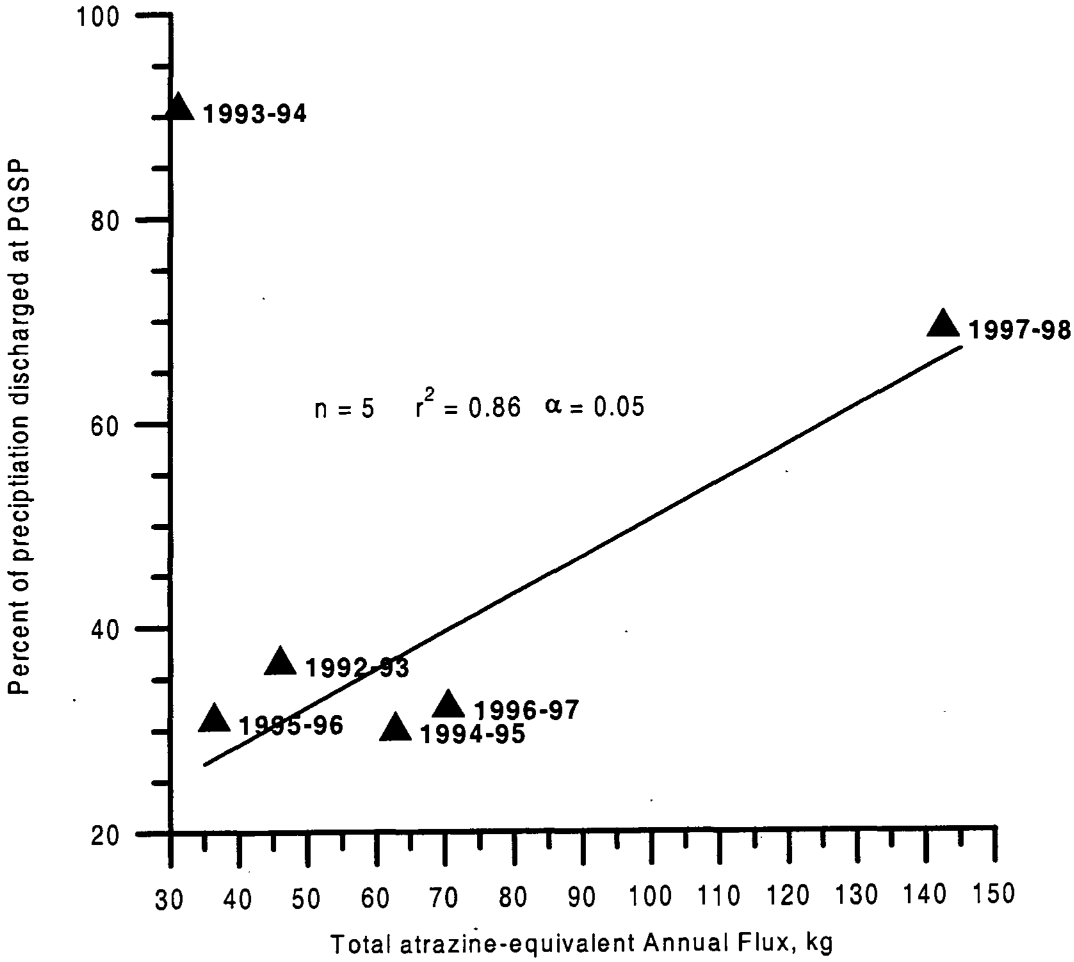

Figure 35. Annual mass flux of atrazine-equivalent discharged from Pleasant Grove Spring versus the percent of preciptitation, or runoff, discharged at PGSP during the herbicide application season (April 15 through May 15). There was little precipitation during this period of the 1993-1994 water-year, although discharge from the spring continued.

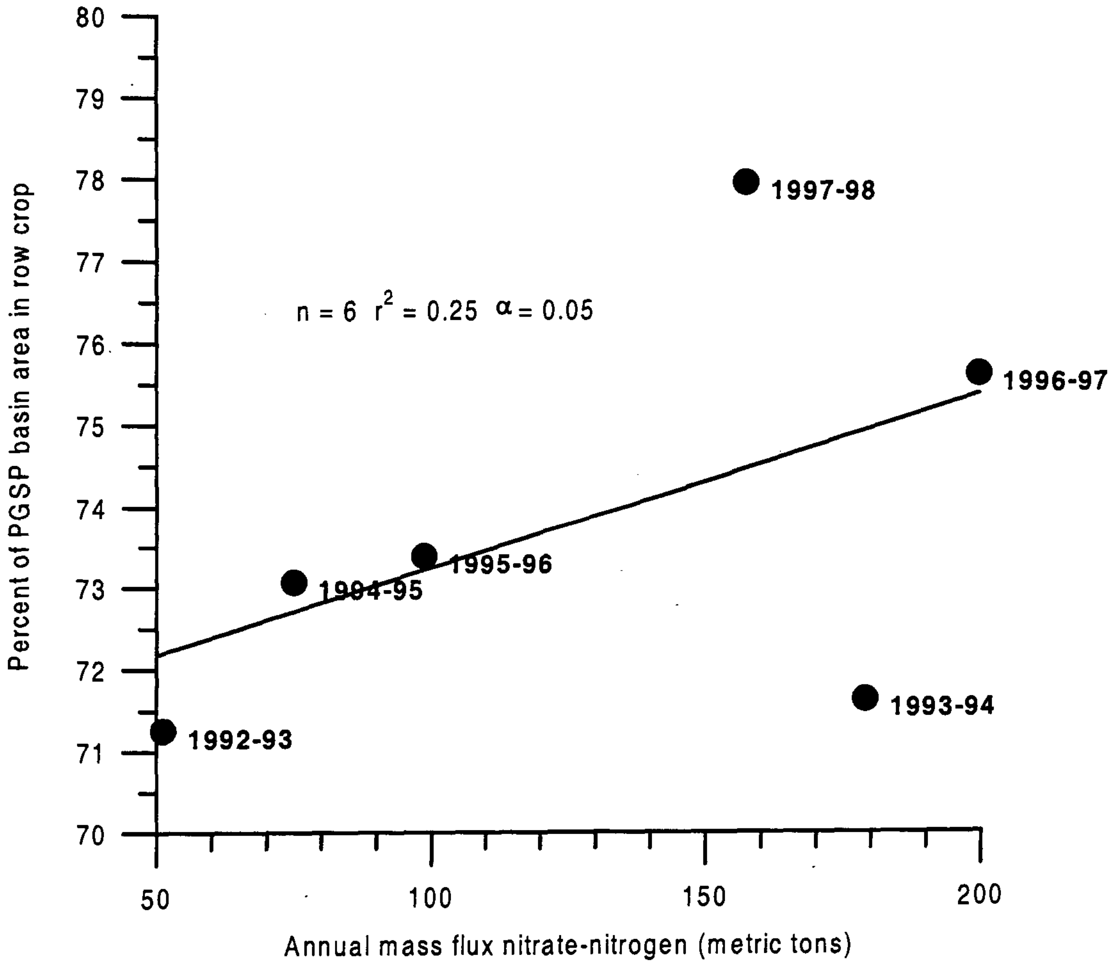

Figure 36. Cross-plot of annual flux of nitrate-nitrogen discharged from Pleasant Grove Spring versus the percentage of the ground-water basin planted in row crop.

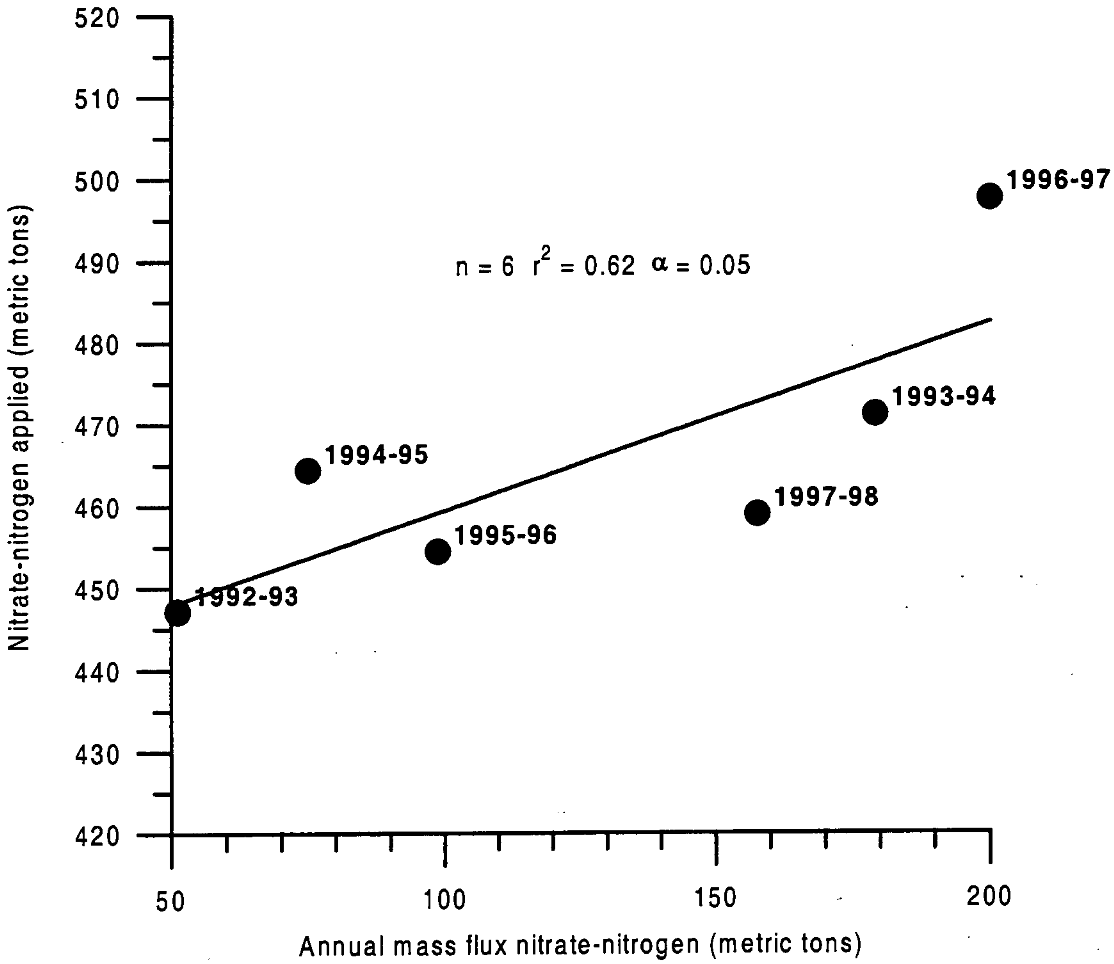

Figure 37. Annual mass flux of nitrate-nitrogen discharged from Pleasant Grove Spring versus the mass of nitrate-nitrogen applied in the ground-water basin. Water-years 1992-1993 through 1994-1995 assume an average application rate of 154 kg/ha row crop whereas later years use the average of the annual application rates reported via the WQIP.

discharged from Pleasant Grove Spring, a strong correlation ($r^2 = 0.95$) is readily apparent (Fig. 38) with data for all years aligning along the trend. The commonality of discharge in the calculation of flux and percent runoff may contribute to the correlation. However, because of the high solubility of nitrate, the annual flux should logically be greater with increased availability of water moving through the soil. The strength of this correlation suggests again that weather plays a significant role in the loss of agricultural chemicals from fields, and that any effective BMP program will have to overcome the effects of weather.

Suspended sediment shows trends partly analogous to both atrazine-equivalent and nitrate-nitrogen. When the suspended sediment flux is correlated with percent 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 calculation of both flux and percent runoff may contribute to the correlation, the transport of suspended sediment logically requires the increased availability of runoff. The relationship with runoff again indicates the importance of weather to the transport of agricultural runoff. In contrast, the relationship of percent of the basin planted in row crop to the total annual flux of suspended sediment is poor. The 1993–94 and the 1997-98 water years do not aligned 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 of woodland clearing in the basin from 1991 extending 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 at PGSP 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 and later erosion of the channel bottom lowered the stage below the rating's zero flow height much of the time. Therefore, mass flux for the first two years was not calculated. The hydrograph record for the three years following installation of the broad-crested weir are accurate, except for the brief effect of the back flooding discussed above. The flux results for these years are summarized below in Table 6.

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 year in which corn was planted in the fields immediately adjacent to the karst window in several years. The sudden increase in triazines at this site indicates that the BMP's relevant to herbicide runoff had inadequate positive effect at this location. An alternatively explanation is pesticides could have been released from a container in the dump. However the release of pesticides from the dump is thought unlikely, as discussed in Miscellaneous Findings and Observations.

Because the annual flux data for LPKW are incomplete, the concentration data must be considered directly. The detection and peak concentrations of pesticides at

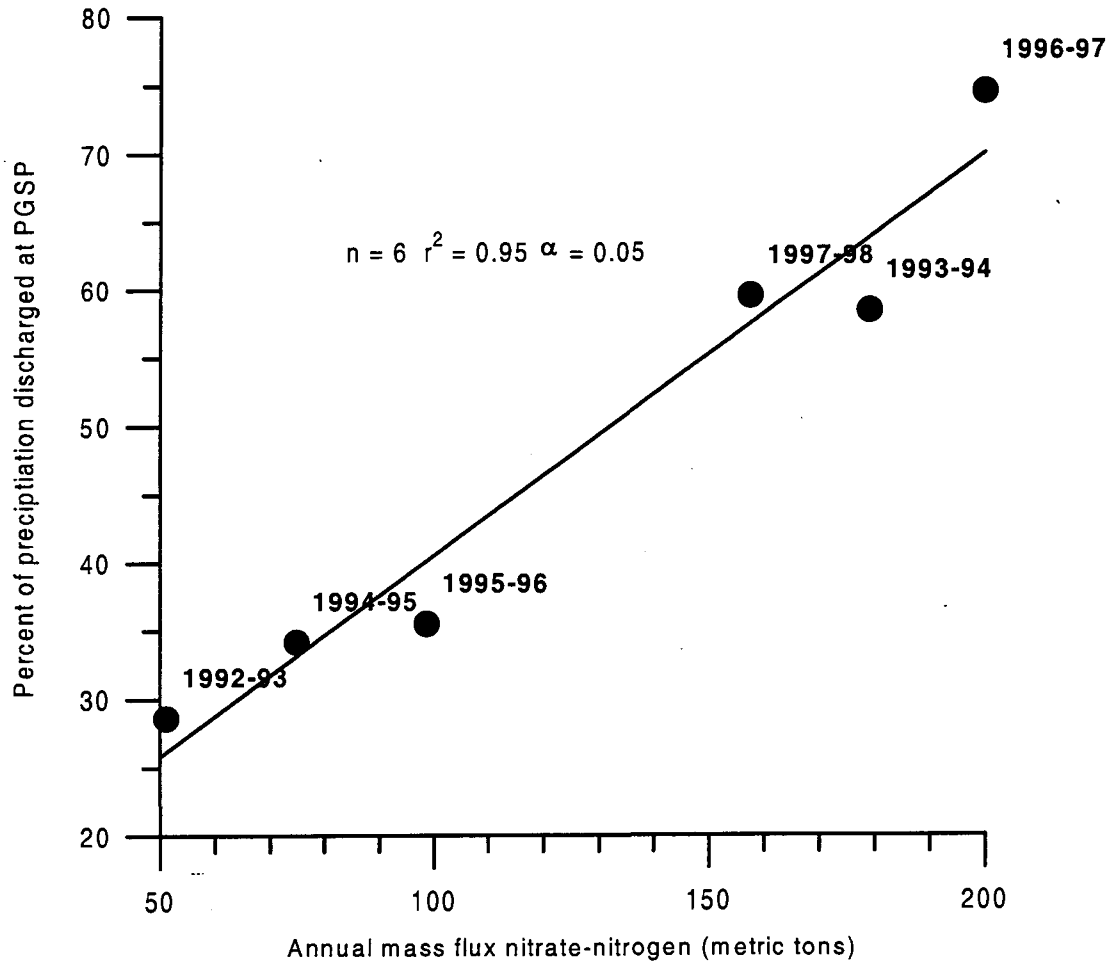

Figure 38. Percentage of total annual precipitation, or runoff, discharged from Pleasant Grove Spring plotted against the annual mass flux of nitrate-nitrogen.

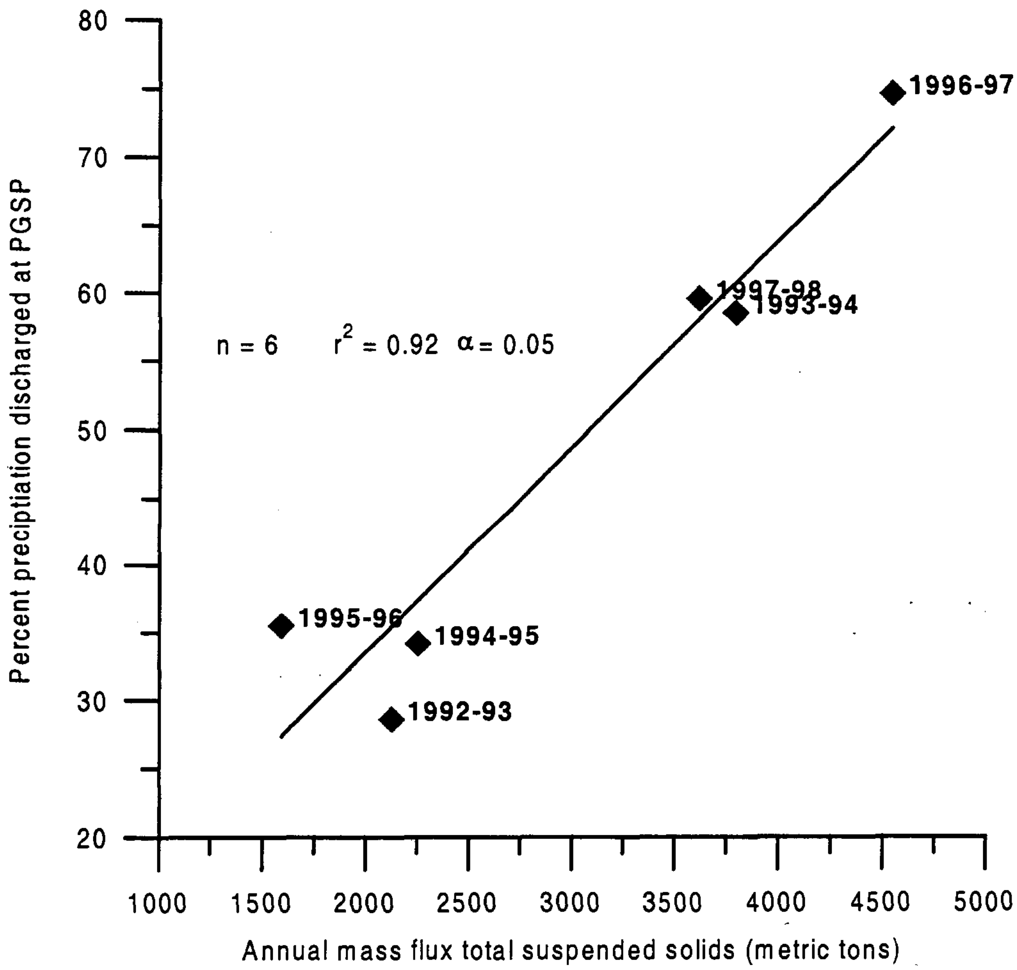

Figure 39. Annual mass flux of total suspended solids plotted against percentage of total annual precipitation, or runoff, discharged from Pleasant Grove Spring.

LPKW is highly seasonal as illustrated in figure 40 and detection at times other than during planting season are minimal. For each year of monitoring, pesticides were measured in the run-in to the swallow hole during the springtime planting season that were consistent with the crops being grown within the surface catchment area of the karst window. Inspection of 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 associated herbicide use overwhelmed the benefits of the grass buffer strip surrounding the karst window.

Table 6. Swallow hole inflow and mass flux of atrazine-equivalent and nitrate-nitrogen at Leslie Page karst window (LPKW monitoring station).

Water-year	Precipitation, cm	Inflow, m^3	Atrazine-equivalent, kg	Nitrate-nitrogen, metric tons
1995–96	136.8	440,205	0.39	2.47
1996–97	140.2	719,400	0.54	4.12
1997–98	135.8	789,925	5.39	4.87

The mass flux of nitrate-nitrogen shows a slightly increasing trend over the course of the last three years of monitoring but is probably due strictly to the increase in measured inflow. The concentration data for nitrate-nitrogen (Fig. 40) clearly show, however, the cyclic annual increase in nitrate-nitrogen (6 to 8 mg/L) during the winter and the spring planting season (wet months). 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 a decreasing trend that might be linked to the BMP installation.

Upper Pleasant Grove Creek. The monitoring stations at George Delaney Swallow Hole (GDSW) and at the box culvert where Johnson-Young Road crosses over upper Pleasant Grove Creek (UPGC) were used in concert to calculate mass flux of constituents in upper Pleasant Grove Creek. The majority of the samples, including a few for high-flow events, were collected at GDSW. Suspended sediment and orthophosphate were not monitored at either UPGC or GDSW, but bacteria samples were collected at both. Both stage and discharge data are not available for the 1992–93 water-year and 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 7). Conversely, when the atrazine-equivalent flux for the five years data available for upper Pleasant Grove Creed (GDSW and UPGC) 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 same magnitude. The implication is both sets of mass flux data are reasonable approximations of the actual flux.

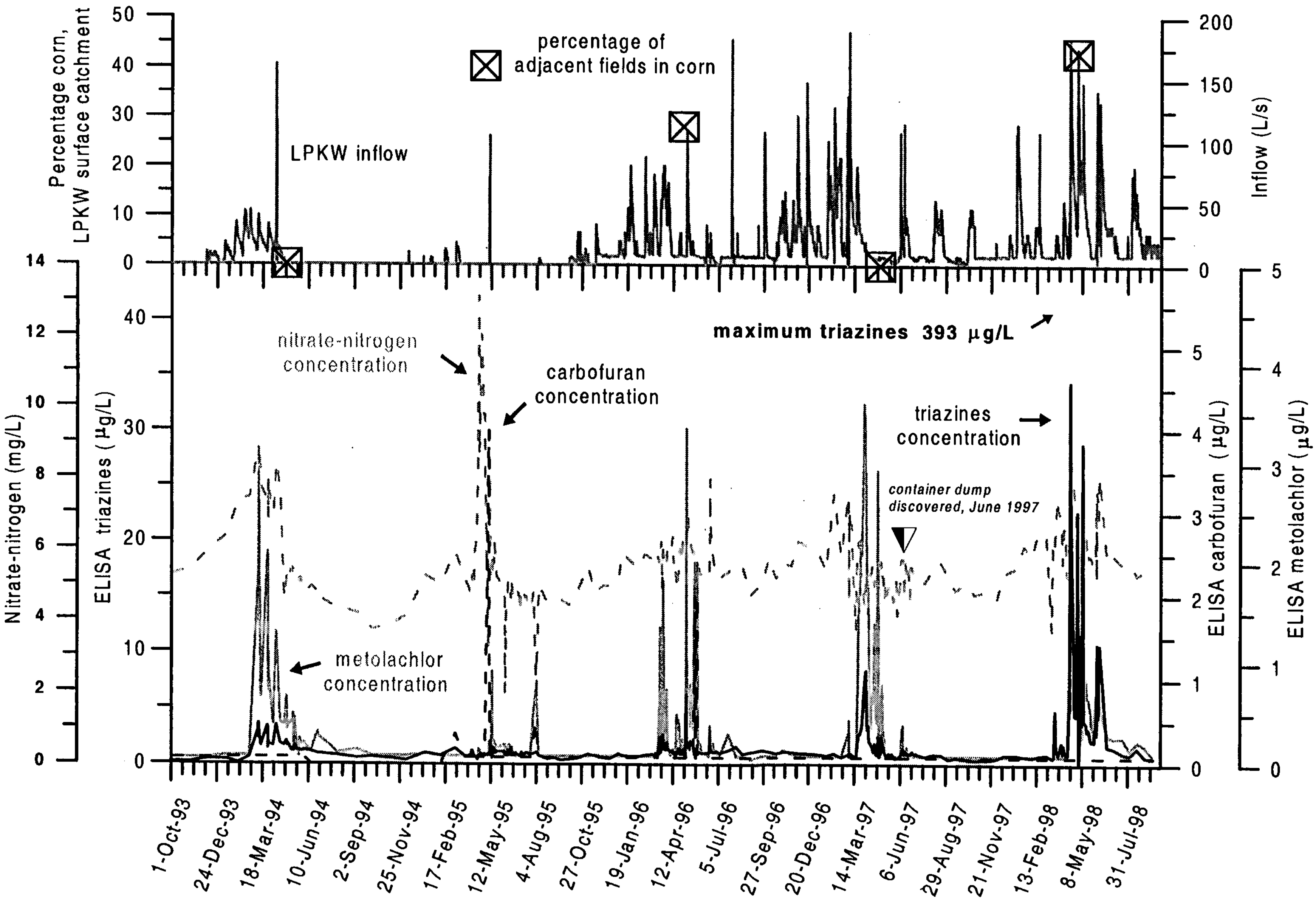

Figure 40. Water flow into the swallow hole at Leslie Page karst window and concentations of nitrate-nitrogen, and triazines, carbofuran, and metolachlor by ELISA for the 1993-1994 through 1997-1998 water years.

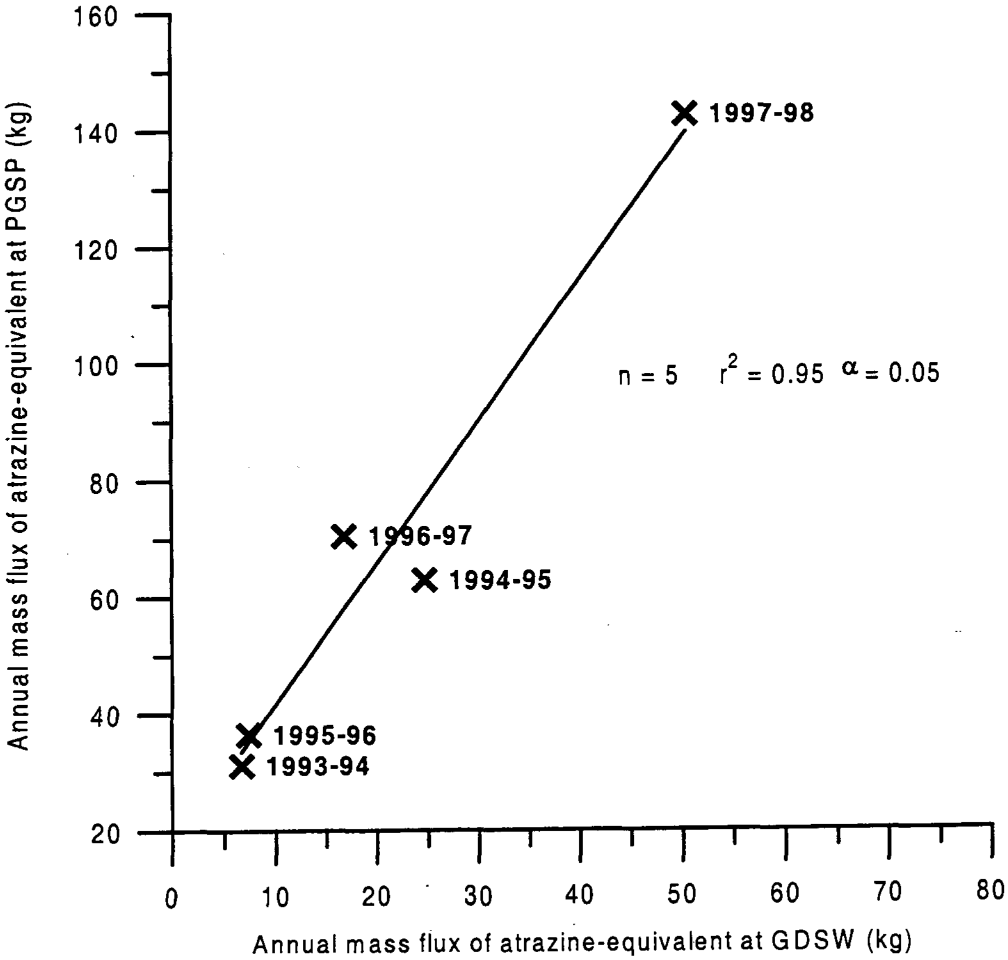

Figure 41. Cross-plot of annual mass flux of atrazine-equivalent inflow at George Delaney swallow holes versus flux of atrazine-equivalent at Pleasant Grove Spring.

Table 7. Discharge and mass flux of atrazine-equivalent and nitrate-nitrogen in upper Pleasant Grove Creek (GDSW and UPGC monitoring stations).

Water-year	Precipitation, cm	Discharge, m^3	Atrazine-equivalent, kg	Nitrate-nitrogen, metric tons
1993–94	132.6	9,494,368	6.68	75.53
1994–95	110.0	3,240,638	24.70	33.84
1995–96	136.8	3,195,310	7.41	20.36
1996–97	140.2	8,896,030	16.82	54.47
1997–98	135.8	5,877,549	50.40	30.16

Upper Pleasant Grove Creek carries an average 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 circumstance reflects the larger percentage of the headwaters area of the basin planted in row crops (78 percent versus 68 percent in the lower basin) each season. However, the cross plot of atrazine-equivalent flux versus the mass of atrazine applied in the headwater area shows a weak relationship. The water-years 1992–93 and 1993–94 do not plot on the trend of the other three 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 does not exhibit any temporal trend for upper Pleasant Grove Creek. However, there is an apparent increase of atrazine-equivalent during the post-BMP period.

Summary of Mass Flux Results

The mass flux for triazines and total suspended solids varied significantly from year to year, but nitrate-nitrogen varied less. The variability of triazines is a direct result of the amount (area and rate) of atrazine applied within the ground-water 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. Total suspended solids peak concentration is also related to the timing of rainfall to exposed soil. There is also a minor influence on triazines and nitrate-nitrogen storage in ground- and soil-water and transport from subtle differences in hydrogeology over the area of the basin. Most of the variability seen in the flux data can be readily explained by changes in chemical application rates and the timing of total rainfall. Therefore, the precision of the annual mass flux estimates are thought adequate for detecting overall changes in water-quality in response to changing farming practices in the basin.

Cross plots of pollutant flux or concentration showed no divergence 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, 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, when plotted against percentage of the basin in row crop, the annual flux of nitrate-nitrogen and suspended solids for the 1997-98 water-year was lower than expected, one year does not establish a trend. Conversely, the three years when the WQIP program was in effect showed a chronological increase in atrazine-equivalent flux in proportion to the percent of the basin in row crop. Of the other relationships examined (annual precipitation, percent cropped area, annual discharge, pesticide sales, etc.) none exhibited a temporal trend which 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. It was decided to delete orthophosphate 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 mid-summer 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, 1.397 mg/L. Routine sampling for orthophosphate was resumed as quickly as possible, and on a biweekly schedule 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 while 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 due to the high value measured at the beginning of the post-BMP monitoring period. When orthophosphate annual median concentrations are considered (Fig. 42) the 1996–97 and 1997–98 post-BMP are the highest and second highest respectively, suggesting a post-BMP increase. Although the concentrations of orthophosphate measured indicate higher than natural levels, the source has not been demonstrated. The coincidence of the high concentrations with high-flow events suggests an association with runoff from fields, whereas high concentrations coincident with the recession limb of the hydrograph would suggest human waste as the source.

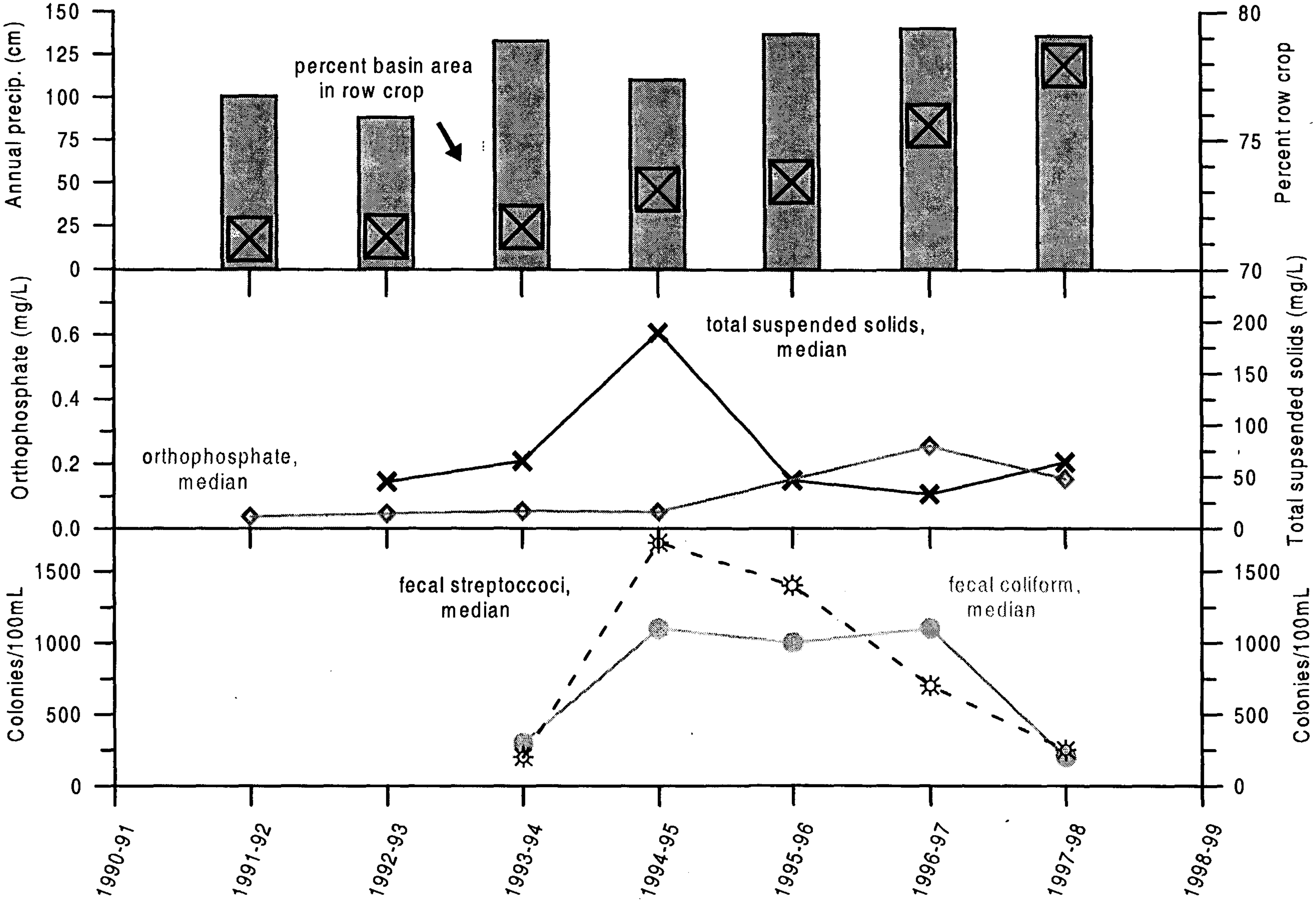

Figure 42. Trends in annual median concentrations of orthophosphate, total suspended solids, fecal streptococci, and fecal coliform during the Pleasant Grove Spring project.

Bacteria at Pleasant Grove Spring. A flux calculation was not practical for bacteria because of the limited number of samples. In lieu of a mass flux approach, analytical data for bacteria were grouped into pre- and post-BMP data sets and comparisons were made graphically and with descriptive statistics. Table 8 lists descriptive statistics for non-conditional monthly samples for each water year. Figure 43 and figure 44 show the occurrence of bacteria over time for the pre-BMP period the post-BMP period for the Pleasant Grove Creek stations (GDSW and UPGC combined) and Pleasant Grove Spring (PGSP). The visually apparent increase in the counts of bacteria on the graphs during the post-BMP period is an artifact of the inclusion of samples collected during storms in 1996 and 1998. The peak values were from samples collected during or after high-flow events. The maximum value for PGSP from all samples for fecal coliform 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 showed an increase from pre-BMP to post-BMP, but are significantly influenced by the maximum counts (Table 8). The median values are less influenced by extreme values. At PGSP, for monthly and storm samples combined, the median went up for fecal coliform from 418 col/100 mL pre-BMP to 1237 col/100 mL post-BMP and for fecal streptococci from 540 col/100 mL pre-BMP to 829 col/100 mL post-BMP. In contrast, when bacteria counts for only monthly samples are considered there is a very slight increase in fecal coliform medians from 418 col/100 mL pre-BMP to 432 col/100 mL post-BMP. Fecal streptococci monthly samples, however, show a 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, non-conditional samples (Fig. 42) for fecal streptococci but a less distinct trend for fecal coliform.

Table 8. Annual statistics for bacteria samples collected non-conditionally (monthly) at Pleasant Grove Spring.

Water-year	Number of Samples	Fecal Coliform, Average col/100mL	Fecal Coliform, Median col/100mL	Fecal Coliform, Geometric Average col/100mL	Fecal Streptococci, Average col/100mL	Fecal Streptococci, Median col/100mL	Fecal Streptococci, geometric average col/100mL
1991–92	6	529	100	127	2946	350	443
1992–93	NA	NA	NA	NA	NA	NA	NA
1993–94	4	180	300	95	174	200	172
1994–95	12	4141	1100	1160	3496	1700	719
1995–96	12	4904	1000	793	11852	1400	1261
1996–97	12	846	1100	440	1951	700	562
1997–98	12	563	200	204	1540	250	258

NA — Not available

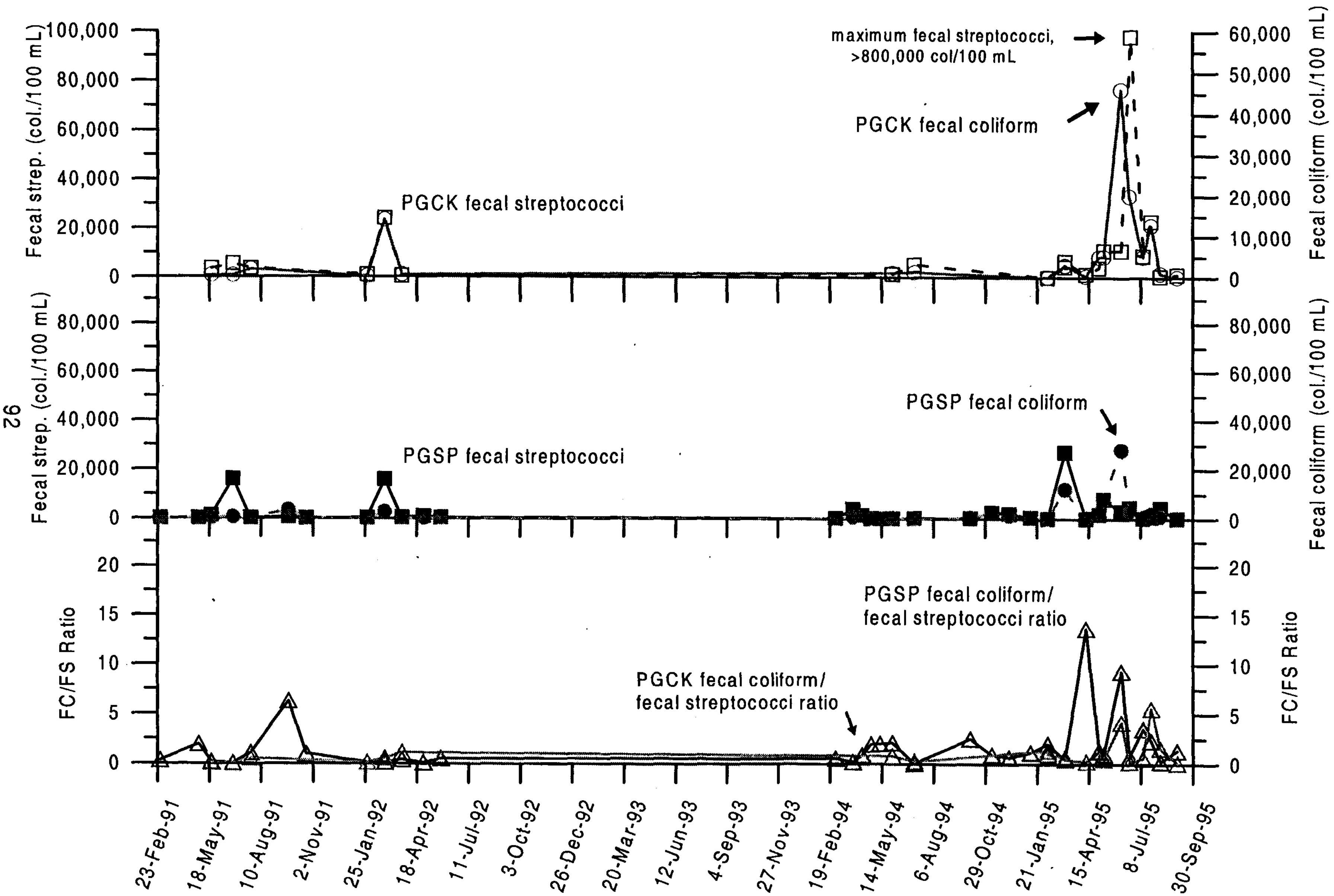

Figure 43. Line plot of bacteria counts and orthophosphate at Pleasant Grove Spring and upper Pleasant Grove Creek (GDSW and UPGC stations) for the pre-BMP period, begining in February 1991 through September 30, 1995.

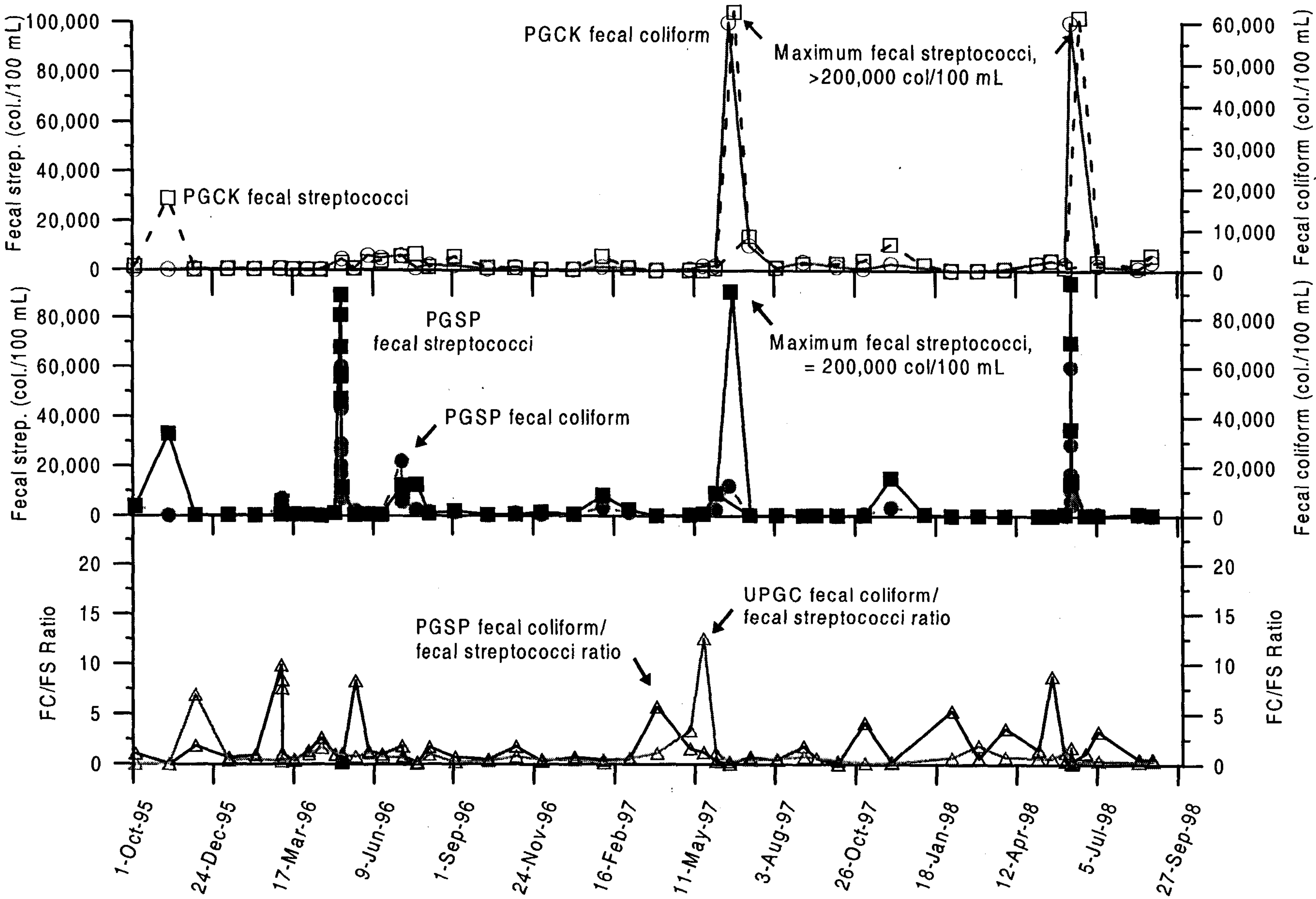

Figure 44. Plot of bacteria counts and orthophosphate at Pleasant Grove Spring and upper Pleasant Grove Creek (GDSW and UPGC stations) for the post-BMP period, October 1995 through October 1998.

Another method of comparing the data is to tabulate the number of samples falling into categories of 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 non-conditional samples only and one including both monthly samples and those collected during storm events. 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 of the post-BMP non-conditional sample set. It is interesting to note, however, the pre-BMP ratios are virtually identical to post-BMP storm sample set.

The observation that fecal streptococci exhibited a steady decrease in annual medians after BMP's were implemented, and a decrease from the pre-BMP overall median to the post-BMP median, and a change from animal to human influence suggests a real phenomena is observed and the changes are not due to chance. The argument the trend is genuine is strengthened when the lack of a parallel decrease in fecal coliform counts is also considered. A plausible explanation for the reduction in fecal streptococci with a corresponding shift in the ratio is that a reduction in runoff of animal waste occurred 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 fecal streptococci counts in monthly samples are encouraging, the maximum counts during high-flow events remain unsatisfactory.

Bacteria at Leslie Page Karst Window. Bacteria counts at Leslie Page karst window are among the lowest measured in the ground-water basin. One reason the site was chosen was because there are no livestock or human sources within the estimated ground-water sub-basin of LPKW. Bacteria sources are, therefore, mostly limited to the soil biota and wildlife. Another possible, but intermittent source of bacteria contamination is back flooding from flow reversals in the conduit draining the karst window. Several events have flooded the karst window to sufficient depth to induced contaminated water into the spring. The highest bacteria count (fecal streptococci 20,000 col/100 mL) followed a major flooding event in May 1995 (Fig. 23), but unfortunately the water level recorder at LPKW failed during this time. High bacteria counts also occurred following a high-flow event in the summer of 1998. However, samples collected following other episodes of flooding show more typical bacteria ranges. Although no BMP changes were made within the LPKW sub-basin that could effect bacteria counts, the pre- and post-BMP time frame is 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 little change and the higher averages probably reflect serendipitous collection of samples from back flooding events during the first years of the project.

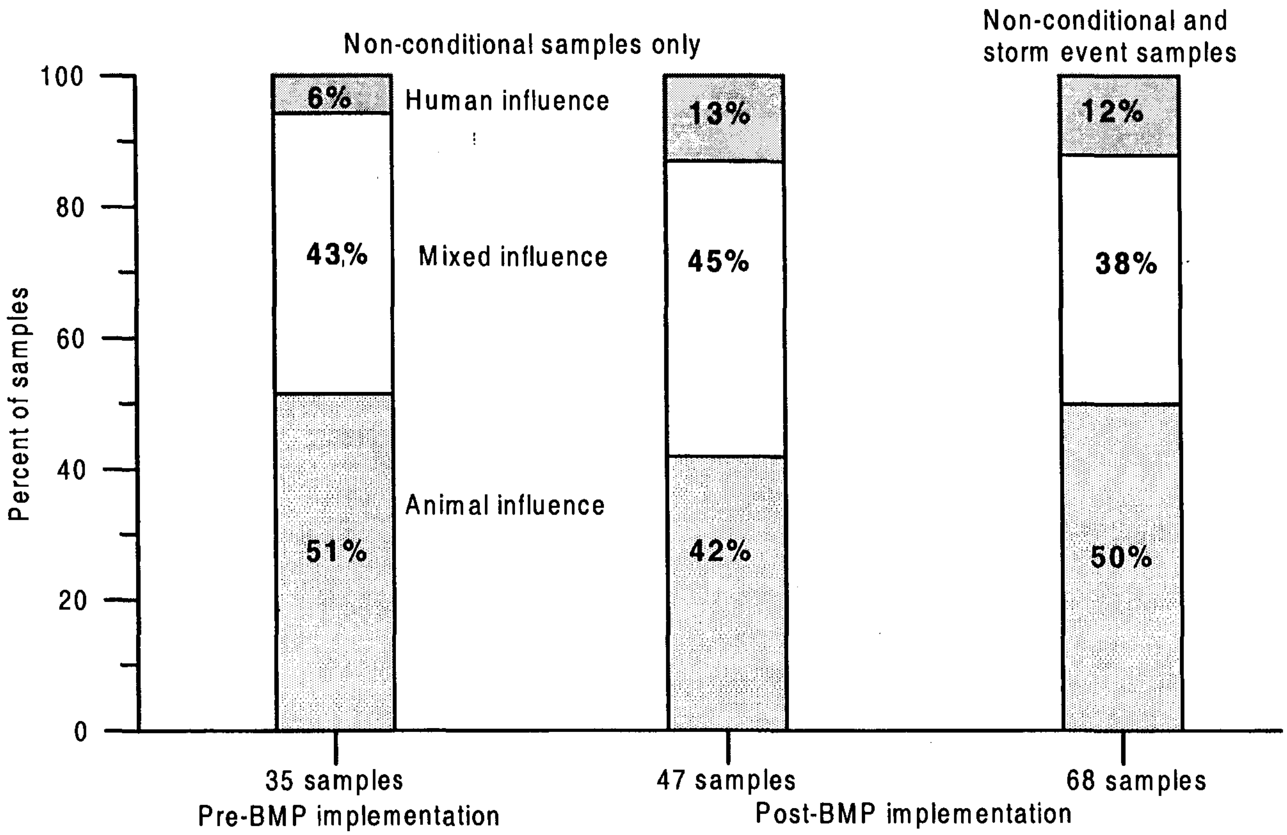

Figure 45. Percentage of fecal coliform/fecal streptococci ratios for water samples collected at Pleasant Grove Spring showing the relative influence of animals and humans before and after BMP implementation.

Graphs of bacteria counts over time for LPKW show no visually discernible trends through the project period. Because human induced sources of fecal contamination do not impact the spring the fecal bacteria counts at LPKW are thought to be natural. Therefore median "background" counts from unpolluted springs in the basin should be in the 10's to low 100's range and higher counts at other sites in the basin indicate the presence of fecal pollution .

Bacteria at upper Pleasant Grove Creek. The highest bacteria count recorded for the ground-water 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 June 20, 1995 (GDSW0033). Cattle and hogs were fed and grazed in fields surrounding George Delaney swallow hole through July 1, 1995, but after that date only a few head of horses were pastured there. This sample was collected before livestock were excluded from the area and on the recession of a modest storm event (3.9cm (1.53 in.) on June 19th. In addition to runoff of animal waste from the adjacent pasture into the creek at the time of sampling, livestock were loafing in the creek. Prior to BMP's, fecal coliform averaged 5,758 col/100 mL and fecal streptococci averaged 44,141 col/100 mL and the medians were 1,273 and 4,000 col/100 mL for fecal coliform and fecal streptococci, respectively.

After the livestock were excluded, the bacteria counts measured at GDSW 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 col/100 mL and the medians were 631 and 1,450 col/100 mL, respectively. Peaks in bacteria counts still occur, however, and correspond with peaks at Pleasant Grove Spring (Fig. 43 and 44). The correspondence of peaks reflects the synoptic sampling schedule and the large percentage of the discharge at Pleasant Grove Spring originating from inflow at GDSW, and its subsequent influence on the water quality at PGSP.

Ground-Water Quality at the Canyon Karst Window and Joe Harper Water Well. The Canyon karst window (TCKW) and Joe Harper water well (JHWW) were monitored to provide data on the quality of the water originating in the northeastern quadrant of the ground-water basin. However, physical limitations at the sites precluded flow monitoring and any calculation of the mass flux. The JHWW site was sampled when TCKW 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 TCKW was consistent with that observed at other sites in the basin. Triazines was the most commonly detected pesticide with a minimum concentration of 0.26 µg/L, above the ELISA detection limit. Metolachlor was also detected during planting season. During the pre-BMP 1992–95 period the maximum triazine concentration at TCKW was 3.9 µg/L and the median was 1.0, under the health limit for atrazine. However, samples collected by College of Agriculture staff had triazine concentrations as high as 15 µg/L in the spring of 1991 (Haszler, G. R., undated). From 1995 through the end of the post-BMP monitoring, peak triazines 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 TCKW corresponded to a significant peak at George Delaney swallow hole (46.2 μg/L). A peak in triazines detected during the same event at Pleasant Grove Spring corresponds to the peaks at GDSW and TCKW. Visual examination of a graph of triazine concentrations at TCKW indicates no change after BMP implementation.

Nitrate-nitrogen concentrations at TCKW varied narrowly during the entire monitoring period. Samples collected prior to October 1995 averaged 4.1 mg/L with a maximum concentration of 5.0 mg/L. Post-BMP nitrate-nitrogen concentrations averaged 4.5 mg/L with a maximum concentration of 7.3 gm/L. No trend can be discerned from graphs of the concentration data.

Bacteria samples from The Canyon 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 300 col/100 mL. The maximum fecal coliform and fecal streptococci counts observed for this portion of the study area were 33,000 and 200,000 col/100 mL respectively at Joe Harper water well (JHWW0012, June 17, 1997).

Results of the Comparative Evaluation of Pre-BMP versus 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 during high-flow events were examined. 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 othophosphate became worse but fecal streptococci counts decreased. Similar results were obtained from Leslie Page karst window, The Canyon karst window with Joe Harper well, and upper Pleasant Grove Creek (GDSW and UPGC). 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

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 pre- and post-BMP means, geometric means, medians, and annual mass flux as applicable. The original analytical data were also divided into various subsets as described in Methodology. These subsets were tested for equivalence of means using Student 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 Mann-Whitney non-parametric U-test. All tests were conducted at the 95% 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 traizines and total suspended solids concentrations and a normal distribution for nitrate-nitrogen concentration. However, when the χ^2 (Chi squared) squared statistic was calculated for the complete analysis set and various sub-sets of analyses, most of the sets were not normally, log-normally, gamma or Laplace distributed at the 95% confidence limit (Davis, 1986, Manugistics, Inc., 1997) for each of the constituents considered. Exceptions, which fit a tested distribution, are the monthly analysis sets for nitrate-nitrogen, which is 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, although it has only a slightly smaller number of members than the complete set, the number of values in the monthly analysis set was too small to establish a probability for the distribution. The bi-weekly/bi-hourly 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 Students 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 Students T-test was used to compare the means of the normally distributed or log-transformed analysis sets, which had equal variances. The means of the before-BMP monthly nitrate-nitrogen concentrations were not statistically different than those after BMP implementation. The means of the log-transformed before and after BMP total suspended solids concentrations for the bi-weekly/bi-hourly analysis set however were statistically different; the post-BMP mean was lower.

The Mann-Whitney W-test (Manugistics, Inc., 1997) was used to test for equivalence of the pre- versus post-BMP medians. The median is not as sensitive to population distribution and was tested for a number of sample sets for which testing means was inappropriate. The medians for the log-transformed complete analysis set and monthly orthophosphate concentrations were significantly different and the post-BMP medians were found to be larger. The post-BMP total suspended solids median (complete analysis set) was also found to be less than the pre-BMP median for both the log-transformed and non-transformed data. Triazines showed no difference between pre- and post-BMP medians for any analysis set. All other analysis sets for total suspended solids, nitrate-nitrogen, and orthophosphate had the same pre- and post-BMP medians.

A second strategy for comparison of any changes in the water quality was also used. The annual mean, annual geometric mean, total annual mass flux, and annual median was 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 median 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 Students T-test. The observed data were used for the tests except for triazines where both log-transformed and observed data were tested. It was found that the means of the bi-weekly/bi-hourly 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, is statistically indistinguishable from the means of the complete analysis set. The F statistic shows the variances are the same for the complete and bi-weekly/bi-hourly 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 herbicides and nitrate-nitrogen concentrations following the implementation of BMP's. The median concentration of total suspended solids did improve (decrease) while orthophosphate concentrations were worse (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 ground-water 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 N^{15}/N^{14} 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 storm events that generate overland runoff. Further, the fecal coliform/fecal streptococci ratio suggest 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 ground-water basin as demonstrated by the high percentage of study area agricultural producers who participated. Over 70 percent of the area of the ground-water basin was enrolled in at least one BMP. There were a few non-participants, but as importantly, 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 to protect the quality of ground water did not reach the right people.

Visual 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 and fecal streptococci counts. The improvement is the probable result of a reduced rate of land clearing, increased use of conservation tillage, construction of livestock waste handling facilities, and exclusion of livestock from streams and karst windows. However, there is no statistically significant change in triazines (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.

The monitoring results indicate the Water Quality Incentive Program was only partly successful in improving ground-water quality, although fully implemented and administered according to policy. To be successful, future BMP programs intended to protect ground water must be tailored to the crops being grown and to the hydrogeology of the ground-water basin. A "one size fits all" program will not work for karst terrain. It is critical that runoff carrying agricultural pollutants be prevented from entering swallow holes and open throated sinkholes. 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 the 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. Also, 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 (BMP's) which protect natural resources, including ground-water quality, from agriculturally derived contaminants. The purpose of this project was to test the effectiveness of a U.S.D.A. program to protect the ground water in a karst aquifer.

This project was located in the Pleasant Grove Spring ground-water basin with includes 4,069 hectares (10,054 ac) 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 two-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 ground-water 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 principal contaminants with an agricultural source were triazine herbicides, nitrate-nitrogen, total suspended sediment, orthophosphate, and bacteria.

The percentage of study area producer's participation in the WQIP was high. However, many of the BMP's offered were already being utilized by area farmers. Other BMP's offered unattractive cash incentive rates and were sparsely adopted. Although 68 percent of the basin was enrolled in at least one BMP, less than one 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 strategy 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. Also, 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 triazines 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 chemical applied. The occurrence of total suspended solids shows a slight decrease in mass flux and median values over the course of the program, while orthophosphate exhibits a slight increase in concentrations. 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 Students T-test, Dunnet's T-test, Mann-Whitney U-test and W-test as appropriate for the population distribution as determined by χ^2 (Chi squared) 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 shows an increase by all methods. 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 ground-water quality in the Pleasant Grove Spring basin. 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 ground-water basin. Programs in karst terrain should emphasize buffer strips, live stock exclusion, tree planting, and other practices that take land out of production. Conservation officers must have more power to influence the selection of the most effective BMP's and cash incentives to take land out of production must be adequate to offset lost revenue.

LESSONS LEARNED, SUCCESS, AND FAILURES

There were many successes during the Pleasant Grove Spring project. The most notable was the reduction in total suspended solids and bacteria at Pleasant Grove Spring. Critical to this success was the cooperative relationship developed between the staff of the Kentucky Geological Survey, the Natural Resources and Conservation Service staff, the Kentucky Division of Water, and the producers operating in the ground-water basin watershed. Accordingly, the water-quality monitoring was effective and the implementation of the BMP's through the Water Quality Incentive Program was thorough. Unfortunately, although cooperative participation by the U.K. College of Agriculture was sought, it did not materialize. Their help in implementing BMP's, mapping land use and crops grown, advising producers on the need for treatment of fields, and inventorying chemicals used would have made the project more beneficial to the agricultural producers, and the environment.

The sampling schedule for Pleasant Grove Spring was minimally acceptable during the first 3 years of the work. Routine field trips to collect samples should have been more closely spaced, every other week. The reallocation of money used to determine a wide variety of pesticides by gas chromatograph to an increased frequency of sampling for total suspended solids, orthophosphate, ELISA assays, and bacteria counts should have been done earlier in the project. Future projects should limit their GC "screening" for pesticides to an initial round of quarterly sampling and to high flow events during the chemical application season. After two such events have been sampled any pesticides not detected should be dropped from the analysis unless significant usage of the chemical is documented. The largest source of error in the mass flux calculations was missed samples during some critical events. Technologic advancements in sampling equipment are needed to improve the reliability of sampling high-flow events. Further, it was learned during the project that samples collected every other hour during high flow are minimally acceptable for characterizing a basin of this size. Never-the-less, more frequent sampling during storms is needed to provide detail on chemographs. The selection of discharge monitoring stations should be made as early in the project as possible, and staff gages installed immediately so rating curve development can begin quickly. Should a future study similar to Pleasant Grove Spring be funded the budget should allow more travel money for fieldwork; for personnel for inventorying chemical usage, land use, and educational activities; and money for periodically sampling domestic water wells. Funding for more frequent sampling and analyses for critical sites is also desirable.

As discussed above, the results of the monitoring indicate the Water Quality Incentive Program was only partly successful in improving ground-water quality in the Pleasant Grove Spring basin. The single most important lesson learned 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 ground-water basin. BMP programs in karst terrain should emphasize buffer strips, live stock exclusion, tree planting, and other practices that take land out of production. Conservation officers must have more power to indicate which BMP's are the most likely to succeed and cash incentives to take land out of production must be adequate to offset lost revenue.

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Significant Karst Features, Potentiometric Surface, and Hypothesized Flow Routes

Pleasant Grove Spring Karst Ground-Water Drainage Basin, Logan County, Kentucky