Prepared in cooperation with the

Arkansas Soil and Water Conservation Commission

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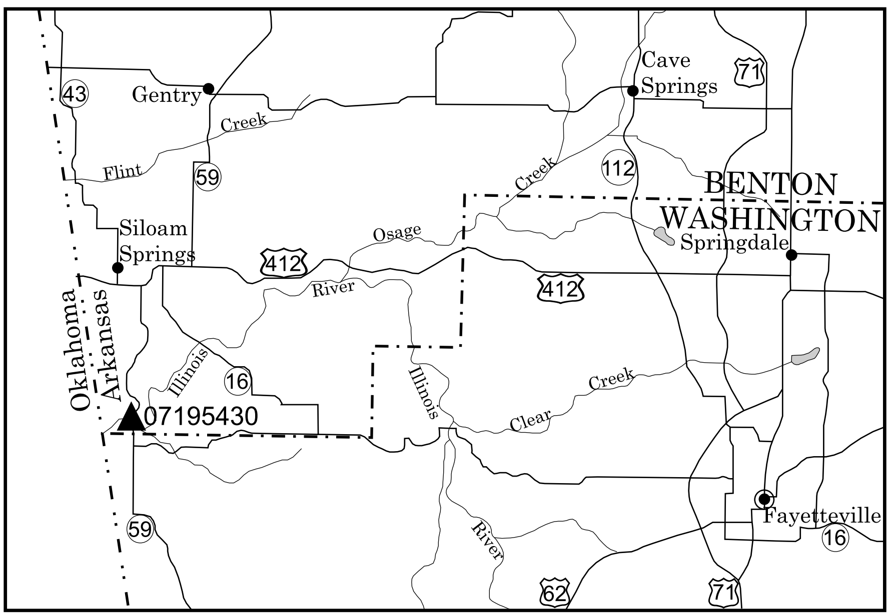
Water-Resources Investigations Report 01-4217



U.S. Department of the Interior
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by W. Reed Green and Brian E. Haggard

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CONTENTS

ILLUSTRATIONS

TABLES

Phosphorus and Nitrogen Concentrations and Loads at Illinois River South of Siloam Springs, Arkansas, 1997-1999

by W. Reed Green and Brian E. Haggard

ABSTRACT

Water-quality sampling consisting of every other month (bimonthly) routine sampling and storm event sampling (six storms annually) is used to estimate annual phosphorus and nitrogen loads at Illinois River south of Siloam Springs, Arkansas. Hydrograph separation allowed assessment of base-flow and surface-runoff nutrient relations and yield. Discharge and nutrient relations indicate that water quality at Illinois River south of Siloam Springs, Arkansas, is affected by both point and nonpoint sources of contamination. Base-flow phosphorus concentrations decreased with increasing base-flow discharge indicating the dilution of phosphorus in water from point sources. Nitrogen concentrations increased with increasing base-flow discharge, indicating a predominant ground-water source. Nitrogen concentrations at higher base-flow discharges often were greater than median concentrations reported for ground water (from wells and springs) in the Springfield Plateau aquifer. Total estimated phosphorus and nitrogen annual loads for calendar year 1997-1999 using the regression techniques presented in this paper (35 samples) were similar to estimated loads derived from integration techniques (1,033 samples). Flow-weighted nutrient concentrations and nutrient yields at the Illinois River site were about 10 to 100 times greater than national averages for undeveloped basins and at North Sylamore Creek and Cossatot River (considered to be undeveloped basins in Arkansas). Total phosphorus and soluble reactive phosphorus were greater than 10 times and total nitrogen and dissolved nitrite plus nitrate were greater than 10 to 100 times the national and regional averages for undeveloped basins. These results demonstrate the utility of a strategy whereby samples are collected every other month and during selected storm events annually, with use of regression models to estimate nutrient loads. Annual loads of phosphorus and nitrogen estimated using regression techniques could provide similar results to estimates using integration techniques, with much less investment.

INTRODUCTION

Several tools are available to estimate the transport or load (flux) of specific water-quality constituents past a fixed point on a stream. The most accurate approach includes continuous recording of streamflow and frequent collection of water-quality samples, particularly during storm events. Loads are estimated by multiplying the concentration values by the stream discharge (volumetric rate) for the given time period between samples. Concentrations for time periods not accounted for can be estimated using integration techniques (mass accumulation) or regression models. Using integration techniques (U.S. Geological Survey, 2001), constituent concentrations are plotted through time, and missing concentrations are estimated by interpolating between measured concentrations (Porterfield, 1972). Integration generally is considered the most accurate method to estimate loading if "sufficient" data are collected to describe the changes in water quality. “Sufficient” data typically means that many samples must be collected to reflect variability in water quality. Large numbers of samples collected to validate the integration method increase the cost of a monitoring program. Loads estimated using integration methods commonly are used as references to evaluate results from other methods.

The regression method uses the relation between concentration (or load) and daily average flow to estimate daily concentrations (or loads) of a constituent (Cohn and others, 1989; Cohn and others, 1992; Cohn, 1995). Daily load estimates are accumulated to provide monthly, seasonal, and annual estimates. The regression method began as simple linear relations between concentration (or load) and flow and has been modified to account for nonlinearities, seasonal and long-term variability, censored data, biases associated with using logarithmic transformations, and serial correlations in residuals of the analyses (Cohn, 1995). The regression approach has come into widespread use because it requires less data (lower costs) than the integration method, can be used to produce estimates for periods beyond when concentration data were collected, and enables confidence limits to be placed on the estimates as a measure of the regression-model error. The regression method commonly is used with relatively small datasets that have been assembled over several years.

Historically, the Illinois River in northwestern Arkansas has been affected by point-source wastewater-treatment plant discharges (seven permitted discharges), and more recently by nonpoint-source runoff from pastures (61 percent of land use) fertilized with poultry litter (Arkansas Department of Environmental Quality, 2000). Information is needed to better understand the fate and transport of the materials affecting the quality of water in the Illinois River.

Both the U.S. Geological Survey (USGS) and the Arkansas Water Resources Center (AWRC) at the University of Arkansas monitor water quality on the Illinois River south of Siloam Springs, Arkansas, at the State Highway 59 Bridge, but monitoring strategies and objectives differ between the two programs. However, monitoring objectives overlap to a certain extent —both provide data for the estimation of annual constituent loads (for example, total phosphorus). Information is needed to optimize sampling strategies for load estimation at this site and others. Similar investigations have been conducted to evaluate different monitoring strategies and load estimation techniques working with small streams in southern Wisconsin (Robertson and Roerish, 1999). Stream size and, therefore, discharge at the Illinois River study site is considerably larger than those monitored by Robertson and Roerish (1999).

The purpose of this report is to present phosphorus (P) and nitrogen (N) load estimation using a regression technique approach at Illinois River south of Siloam Springs, Arkansas. Phosphorus and nitrogen load and yield determinations from the regression method are compared with other determinations made at the same site, at other sites within the region, and national averages. This report was prepared in cooperation with the Arkansas Soil and Water Conservation Commission.

METHODS

The USGS operates and maintains a water-quality and streamflow-discharge gaging station (07195430) at Illinois River south of Siloam Springs, Arkansas (fig. 1). River stage is recorded every 0.25 hours and converted to discharge using a stage-discharge relation maintained by the USGS. Prior to water year 1999 (October 1, 1998 through September 30, 1999), water-quality samples were collected by the USGS at this site bimonthly (every other month) using cross-sectional integrated composite methods (equal-width increment) described by Edwards and Glysson (1999). Starting in water year 1999, samples were collected bimonthly and during selected high-flow storm events (fig. 2). Samples were analyzed by USGS for total phosphorus, soluble reactive phosphorus (dissolved orthophosphorus), dissolved nitrite plus nitrate nitrogen, total ammonia nitrogen, and total ammonia plus organic nitrogen (total Kjeldahl nitrogen). Total nitrogen was defined as the sum of total ammonia plus organic nitrogen plus dissolved nitrite plus nitrate nitrogen.

Daily discharge was separated into base flow and surface runoff using a hydrograph separation program (HYSEP; Sloto and Crouse, 1996). Samples collected on days when base flow was greater than or equal to 70 percent of total flow were considered to be base-flow samples. Surface-runoff samples were defined as samples collected on days that base flow was less than 70 percent of total flow (surface runoff was greater than 30 percent of total flow). Of the 35 water-quality samples collected between November 11, 1996 and June 18, 2000, 19 samples were considered to be base flow and 16 were considered to be surface-runoff samples (fig. 2). Stream-flow discharge and water-quality data are available at http://water.usgs.gov/ar/nwis.

Constituent load (L) is a function of volumetric rate of water passing a point in the stream (Q) and the constituent concentration in the water (C). A typical log-linear regression model for load (L, kilogram/day) can be expressed as:

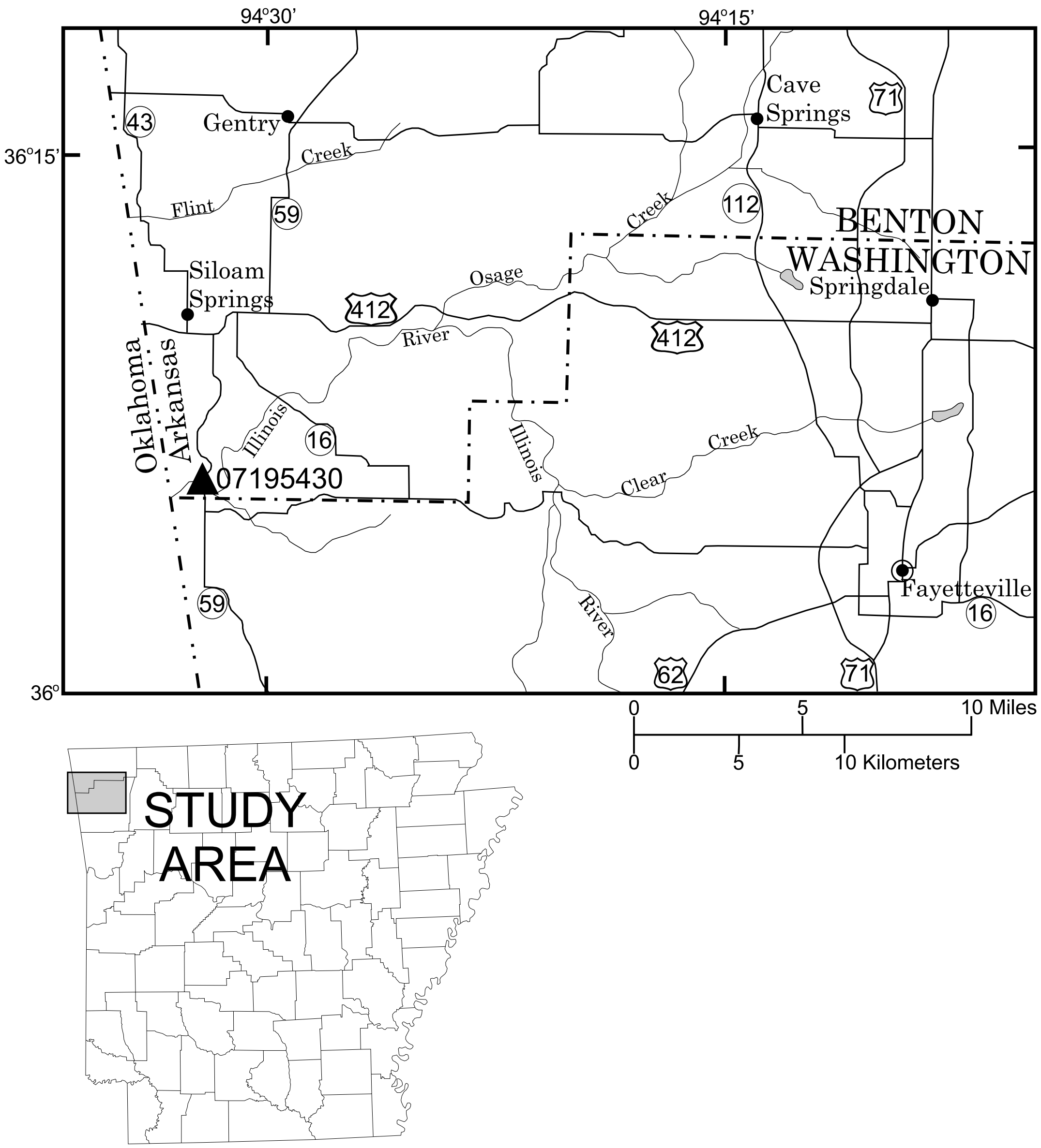

Figure 1. Illinois River study area and study site.

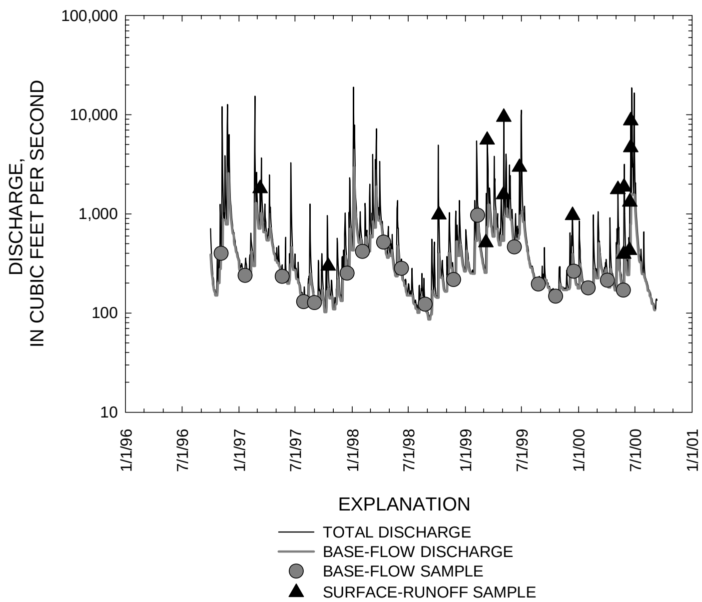

Figure 2. Streamflow at Illinois River south of Siloam Springs, Arkansas, for water years 1997-2000 and points on the hydrograph when base-flow or surface-runoff samples were collected.

$$\ln(L) = \beta_o + \beta_1 \ln(Q_d) + \beta_2 T + \beta_3 \sin(2\pi T) + \beta_4 \cos(2\pi T) \quad (1)$$

where ln ( ) represents the natural logarithm function;

β_o, β_1 , β_2, β_3, and β_4 are the coefficients of the model;

Q_d is the daily mean discharge (m^3/s); and

T is decimal time.

In this model, if a relation between discharge and load exists, then the β_1 coefficient will be significantly different from zero. Temporal trends are identified by β_2, and seasonal influences are identified by β_3 and β_4.

Because of the limited sample size and relatively short duration of data collection, the regression models used to estimate loads at the Illinois River study site were simple linear equations that included only the constant (β_o) and the coefficient for discharge (β_1), of the form:

$$\ln(L) = \beta_o + \beta_1 \ln(Q_d) \quad (2)$$

A minimum variance unbiased estimator (Bradu and Mundlak, 1970; Cohn and others, 1989; Cohn and others, 1992) was used to transform the logarithmic results back to linear space.

Daily load estimates were summed into monthly loads and annual loads. Loads were expressed both for calendar years and water years (October through September) in kilograms per year. Annual load was divided by accumulated annual discharge to provide the annual flow-weighted mean concentration (converted to milligrams per liter). Also, annual load was divided by drainage area to provide annual yield (kilograms per square kilometer). Flow-weighted mean concentration and yield from the regression estimates were compared to estimates based on integration methods at the same site (Nelson and Soerens, 2000) and at sites considered to be undeveloped basins (Clark and others, 2000).

PHOSPHORUS AND NITROGEN CONCENTRATIONS AND LOADS

The Illinois River south of Siloam Springs, Arkansas, is affected by both point and nonpoint sources of contamination. Total phosphorus and soluble reactive phosphorus concentrations in base flow decreased with increasing discharge (fig. 3) demonstrating the dilution of stream water contaminated by point sources by less contaminated ground water. Greater ground-water discharges occur on the receding limb of a storm hydrograph than in base flow and these increased ground-water discharges dilute contaminant concentrations discharged to a stream by point sources.

Unlike phosphorus concentrations, dissolved nitrite plus nitrate nitrogen and total nitrogen concentrations increased in base flow with increasing discharge, indicating that ground water is the predominant source (fig. 3). This relation is probably due to greater movement of nitrogen in water through the soil horizon, into the saturated zone, and eventual discharge into the stream channel during the receding limb of a storm hydrograph. All nitrite plus nitrate nitrogen concentrations in base-flow samples were greater than the median concentration (1.0 mg/L as N) in ground water sampled from wells in the Springfield Plateau aquifer (Adamski, 1997), which underlies this region. Many of the base-flow samples collected during higher discharges also were greater than the median concentration (2.6 mg/L as N) in ground water sampled from springs discharging from that aquifer (Adamski, 1997).

Constituent loads were estimated using regression models for all data and for base-flow and surface-runoff data independently (table 1). The coefficient of determination (R^2) for each regression, times 100, provides an estimate (percent) of the amount of weight that discharge (Q) along with its coefficient β_2 has on predicting load (L). Figure 4 and table 2 show load estimates for total phosphorus, soluble reactive phosphorus, nitrite plus nitrate nitrogen, and total nitrogen for water years 1997-1999. Estimations for water year 2000 are not included because stream discharge for all of water year 2000 was not available at the time this analysis was conducted. Thus, the regression models were based on data from 35 samples collected during water years 1997-1999 and most of water year 2000, but load estimates were made only for water years 1997-1999. The sum of the independently determined base-flow plus surface-runoff loads provided the total load estimate. Estimations for water year 2000 are not included because stream discharge for all of water year 2000 was not available at the time this analysis was done. Thus, the regression models were based on data from 35 samples collected during water years 1997-1999 and most of water year 2000, but load estimates were made only for water years 1997-1999.

Most of the phosphorus load was contributed during surface runoff. On average, base flow contributed 15 percent of the annual total phosphorus load; surface runoff contributed 85 percent of the annual total phosphorus load. On average, 72 percent of the soluble reactive phosphorus annual load was contributed during surface runoff.

Unlike phosphorus, a large portion of the annual load of nitrogen was contributed during base flow. On average, base flow contributed 46 percent of the annual total nitrogen; surface runoff contributed 54 percent of the annual total nitrogen load. On average, 42 percent of the dissolved nitrite plus nitrate nitrogen annual load was contributed during surface runoff.

Nelson and Soerens (2000) estimated total phosphorus and total nitrogen annual (calendar year) loads using discrete and flow-weighted composite samples collected from an autosampler positioned at a single point within the cross-section at the Illinois River south of Siloam Springs, Arkansas, site. The autosampler was activated by the USGS streamflow gaging station (07195430) and programmed to collect samples based on prescribed changes in stage and time (Nelson and Soerens, 2000). Loads for 1997 (215 samples), 1998 (449 samples), and 1999 (369 samples) were estimated using integration techniques. In all, Nelson and Soerens (2000) used 1,033 samples to estimate total phosphorus and nitrogen loads over the 3-year period.

Regression-based annual (calendar year) load estimates (35 samples) for total phosphorus, total nitrogen, and nitrite plus nitrate nitrogen were similar to annual loads estimated using integration techniques (Nelson and Soerens, 2000; 1,033 samples) for the same (calendar year) time period (fig. 5). The only common parameter used in both load estimation models was stream discharge. Over the 3-year period, total phosphorus loads estimated using regression techniques averaged 1 percent greater than loads estimated using integration techniques, and total nitrogen loads averaged 10 percent greater. Considering that data were collected using different sampling methods, samples were analyzed by different laboratories using different techniques, and load estimation models differed, the similarity of results is notable. These results demonstrate the utility of a strategy whereby samples are

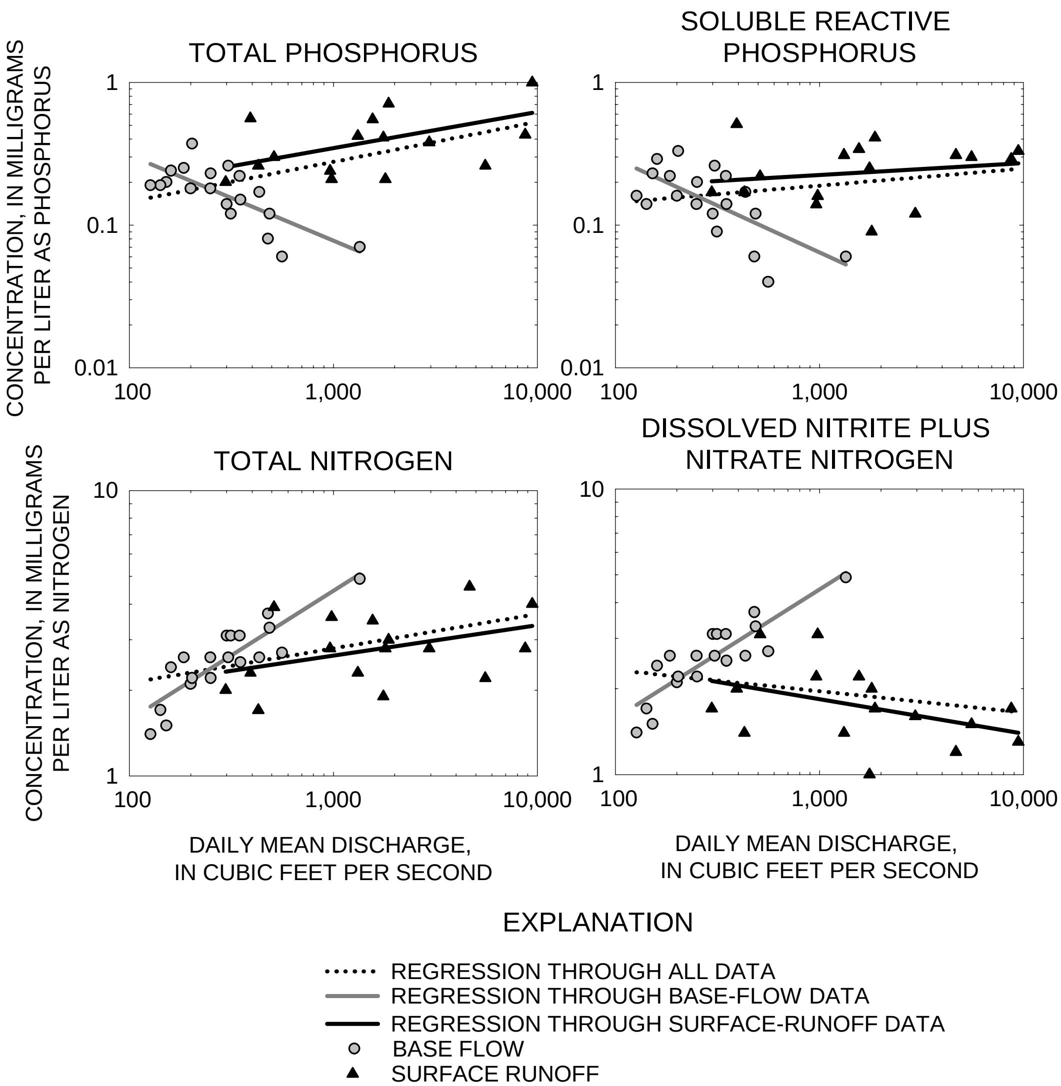

Figure 3. Flow and concentration relations for all samples, and samples collected during base flow and surface runoff at Illinois River south of Siloam Springs, Arkansas, water years 1997-2000.

Table 1. Regression models applied to all data, base flow, and surface runoff to estimate constituent loads

[Water-quality data collected between November 11, 1996 and June 18, 2000. Regression model described previously in equation 2]

	Sample size	Constant (β_0)	Slope coefficient (β_1)	Coefficient of determination (R^2)
Total phosphorus				
All data	35	6.498	1.280	87.8
Base flow	19	4.843	0.4021	34.9
Surface runoff	16	7.413	1.253	89.2
Soluble reactive phosphorus				
All data	35	6.114	1.092	84.6
Base flow	19	4.711	0.3450	18.6
Surface runoff	16	6.886	1.084	86.2
Total nitrogen				
All data	35	8.809	1.119	96.5
Base flow	19	7.820	1.448	96.9
Surface runoff	16	9.364	1.103	95.2
Nitrite plus nitrate nitrogen				
All data	35	8.458	0.9255	91.8
Base flow	19	7.725	1.447	95.1
Surface runoff	16	8.881	0.8787	91.8

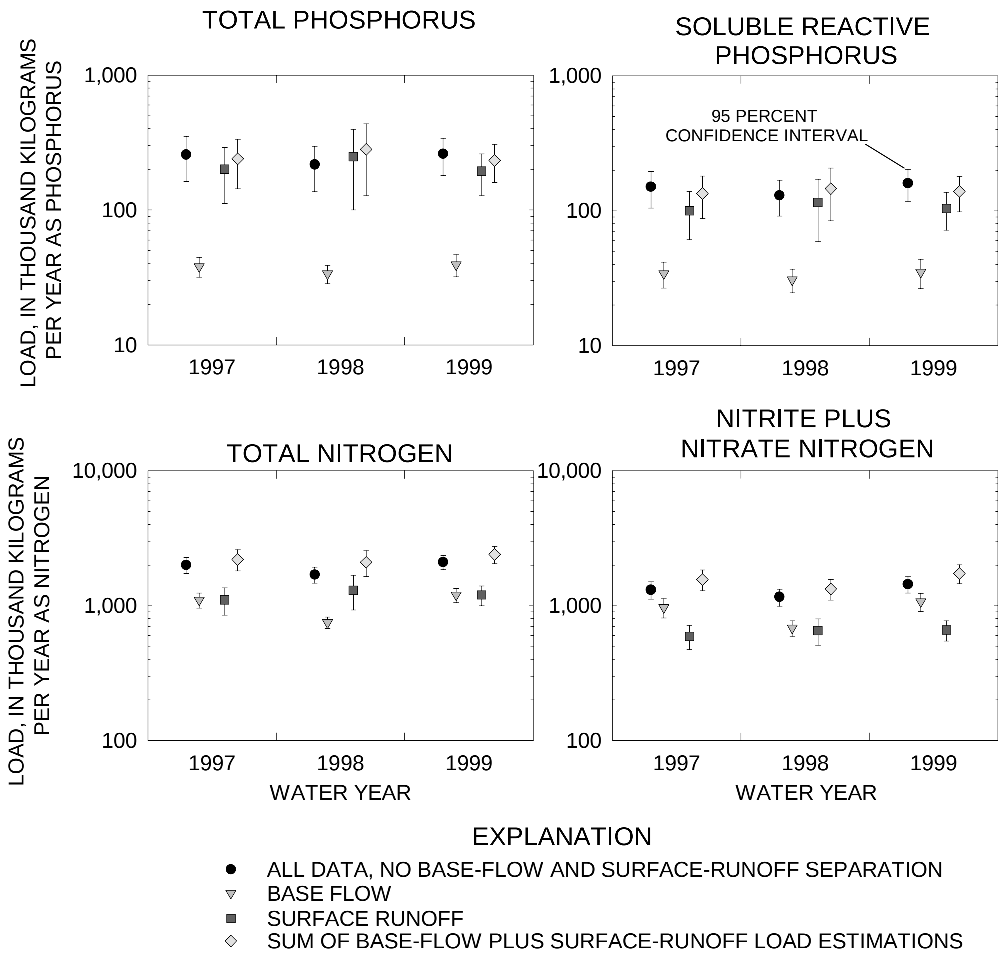

Figure 4. Nutrient loads for Illinois River south of Siloam Springs, Arkansas, for total flow, base flow, surface runoff, and the sum of base flow and surface runoff, based on regression models using data from water years 1997-2000.

Table 2. Annual loads for total phosphorus, soluble reactive phosphorus, total nitrogen, and dissolved nitrite plus nitrate nitrogen at Illinois River south of Siloam Springs, Arkansas, water years 1997-1999

[All values in kilograms per year]

	1997	1998	1999
Total phosphorus			
All data	257,000	217,000	260,000
Base flow (BF)	38,000	33,700	39,200
Surface runoff (SRO)	201,000	248,000	194,000
Sum of BF plus SRO data	239,000	282,000	233,000
Soluble reactive phosphorus			
All data	150,000	130,000	160,000
Base flow (BF)	34,300	30,700	35,000
Surface runoff (SRO)	100,000	115,000	104,000
Sum of BF plus SRO data	134,000	146,000	139,000
Total nitrogen			
All data	2,000,000	1,700,000	2,100,000
Base flow (BF)	1,100,000	750,000	1,200,000
Surface runoff (SRO)	1,100,000	1,300,000	1,200,000
Sum of BF plus SRO data	2,200,000	2,100,000	2,400,000
Dissolved nitrite plus nitrate nitrogen			
All data	1,310,000	1,160,000	1,440,000
Base flow (BF)	967,000	682,000	1,070,000
Surface runoff (SRO)	593,000	652,000	659,000
Sum of BF plus SRO data	1,560,000	1,330,000	1,730,000

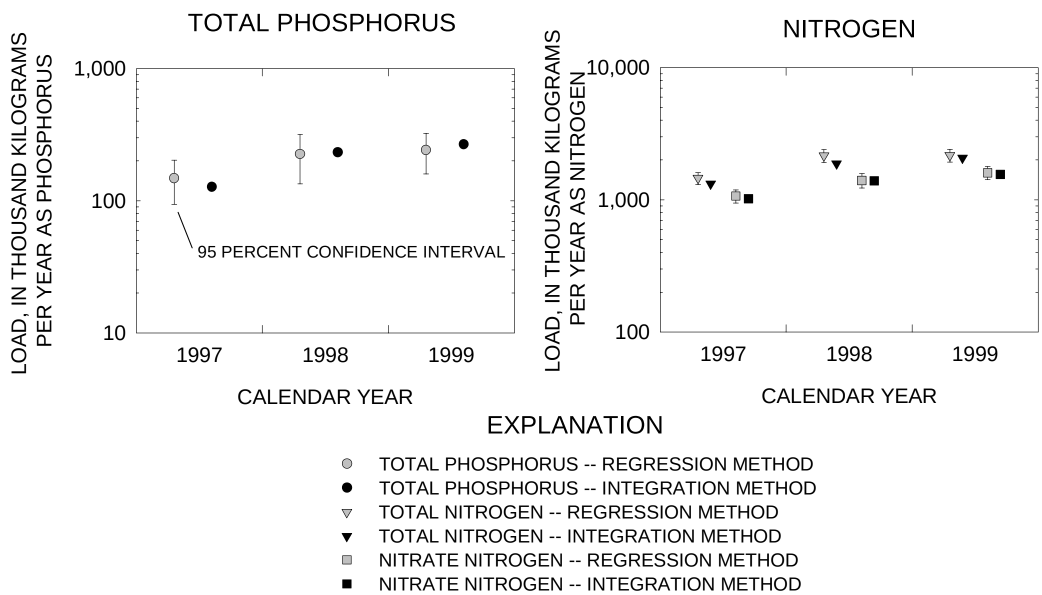

Figure 5. Load comparisons between regression and integration (Nelson and Soerens, 2000) methods at Illinois River south of Siloam Springs, Arkansas, calendar years 1997-1999.

collected every other month and during selected storm events annually, with use of regression models for estimating nutrient loads.

From the regression load estimates using all data over the 3-year period (water years 1997-1999), annual flow-weighted concentration and yield can be determined and used to compare the Illinois River south of Siloam Springs, Arkansas, site with other sites. Clark and others (2000) presented flow-weighted nutrient concentrations and yields in undeveloped stream basins of the United States during the period (calendar years) 1990-1995. Two stream basins considered to be undeveloped are North Sylamore Creek located in the Ozark Plateaus in north-central Arkansas and Cossatot River located in the Ouachita Mountains in west-central Arkansas. Total phosphorus and soluble reactive phosphorus flow-weighted concentrations at the Illinois River site were an order of magnitude (about 10x) greater than national averages for sites in undeveloped basins and at North Sylamore Creek and Cossatot River (fig. 6). Total nitrogen and dissolved nitrite plus nitrate nitrogen flow-weighted concentrations at the Illinois River site were one to two orders of magnitude (about 10 to 100x) greater than national averages and at North Sylamore Creek and Cossatot River. Comparison of yields showed similar results (fig. 6). The results probably reflect the effects of point and nonpoint sources of phosphorus and nitrogen in the area drained by the Illinois River in northwestern Arkansas.

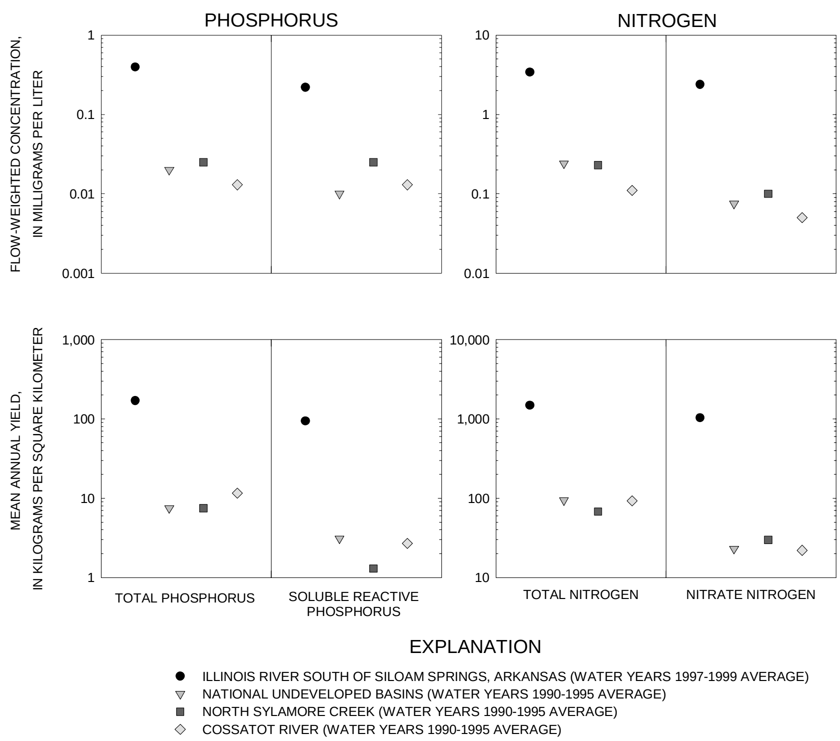

Figure 6. Phosphorus and nitrogen annual flow-weighted concentrations and mean annual yields at Illinois River south of Siloam Springs, Arkansas, compared to the national average at sites in undeveloped basins and at North Sylamore Creek and Cossatot River for 1990-1995 (Clark and others, 2000).

SUMMARY

A monitoring strategy consisting of sample collection every other month and during selected storm events (six storms annually) over multiple years provided sufficient data to assess nutrient relations and estimate annual nutrient loads at Illinois River south of Siloam Springs, Arkansas, using regression techniques. Hydrograph separation allowed assessment of base-flow and surface-runoff nutrient relations and yield. Discharge and nutrient relations indicate that water quality at Illinois River south of Siloam Springs, Arkansas, is affected by both point and nonpoint sources of contamination. Base-flow phosphorus concentrations decreased with increasing base-flow discharge, indicating the dilution of phosphorus discharged by point sources. Base-flow nitrogen concentrations increased with increasing base-flow discharge, indicating a predominant ground-water source. Nitrogen-compound concentrations at higher discharges often were greater than median values reported for ground water (from wells and springs) in the Springfield Plateau aquifer.

Total phosphorus and nitrogen annual loads estimated for calendar years 1997-1999 using regression techniques presented in this paper (35 samples) were similar to those using integration techniques (1,033 samples) (Nelson and Soerens, 2000). Over the 3-year period, total phosphorus loads estimated using regression techniques averaged 1 percent greater than the loads using integration techniques, and total nitrogen loads using regression techniques averaged 10 percent greater than loads using integration techniques. These results demonstrate the utility of a strategy whereby samples are collected every other month and during selected storm events annually with use of regression models for estimating nutrient loads.

Flow-weighted nutrient concentrations and nutrient yields at the Illinois River south of Siloam Springs, Arkansas, site were about 10 to 100 times greater than national averages for undeveloped basins and at North Sylamore Creek and Cossatot River (considered to be undeveloped basins in Arkansas). Total phosphorus and soluble reactive phosphorus concentrations were about 10 times greater and total nitrogen and dissolved nitrite plus nitrate concentrations were about 10 to 100 times greater. These results probably reflect the effects of point and nonpoint sources of phosphorus and nitrogen in the area drained by the Illinois River in northwestern Arkansas.

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