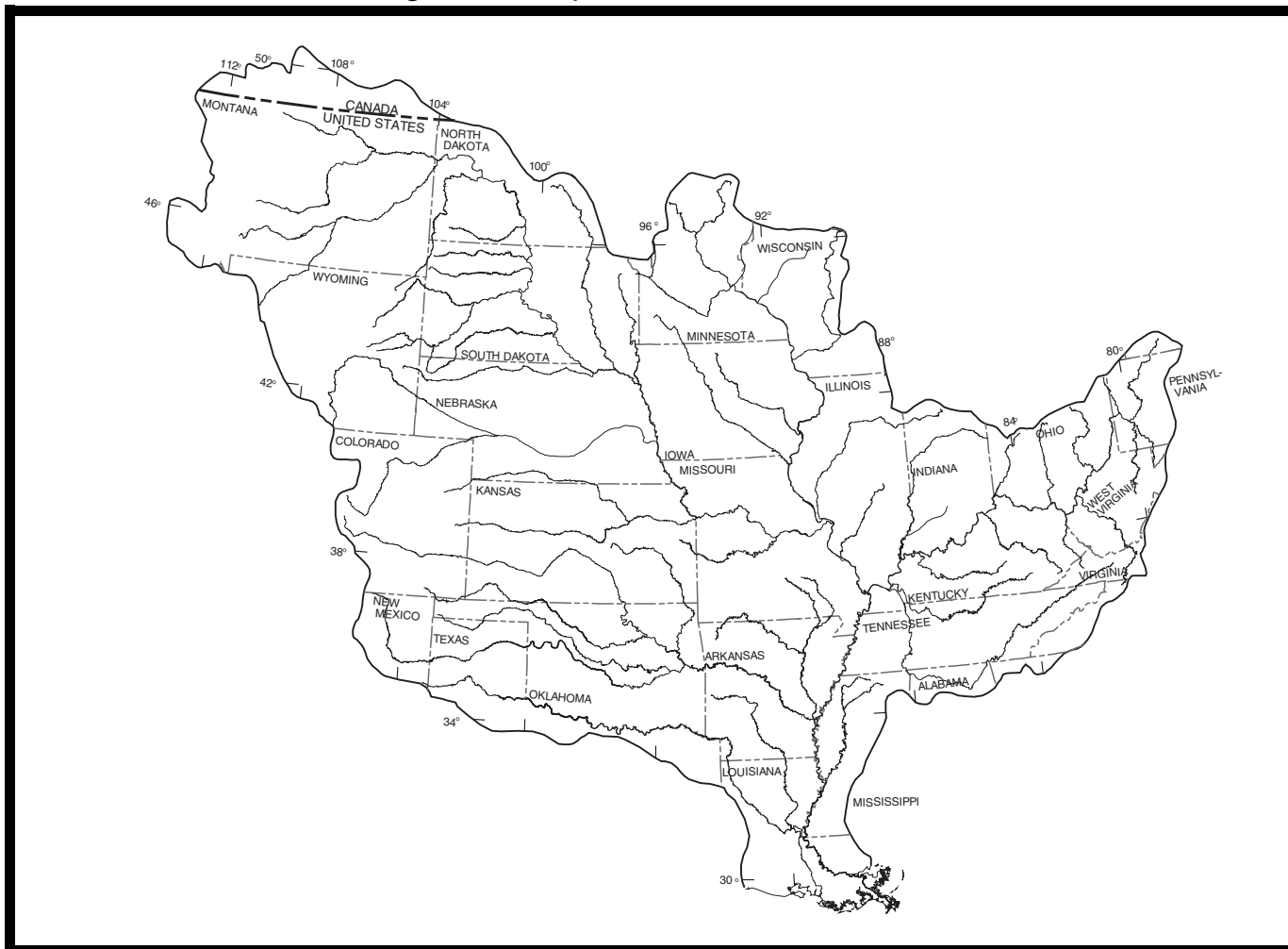


# TRENDS IN NUTRIENT CONCENTRATION AND LOAD FOR STREAMS IN THE MISSISSIPPI RIVER BASIN, 1974–94

U.S. GEOLOGICAL SURVEY  
Water-Resources Investigations Report 97–4223



*Prepared in cooperation with the*  
U.S. ENVIRONMENTAL PROTECTION AGENCY  
GULF OF MEXICO PROGRAM,  
NUTRIENT ENRICHMENT ISSUE COMMITTEE



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By D.L. Lurry and D.D. Dunn

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For additional information write to:

District Chief  
U.S. Geological Survey  
8011 Cameron Rd.  
Austin, TX 78754-3898

Copies of this report can be purchased from:

U.S. Geological Survey  
Branch of Information Services  
Box 25286  
Denver, CO 80225-0286

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## CONVERSION FACTORS

Multiply	By	To obtain
acre-foot (acre-ft)	1,233	cubic meter
gallon per day (gal/d)	0.003785	cubic meter per day
square mile (mi <sup>2</sup> )	2.590	square kilometer
ton, short	0.9072	megagram
ton per square mile (ton/mi <sup>2</sup> )	0.35026	megagram per square kilometer

# Trends in Nutrient Concentration and Load for Streams in the Mississippi River Basin, 1974–94

By D.L. Lurry *and* D.D. Dunn

## Abstract

Trends in nutrient concentration and load are computed for 40 stations on 24 streams in the Mississippi River Basin. The drainage area of the Mississippi Basin covers about 42 percent of the conterminous United States, and the Mississippi River discharges about 420 billion gallons per day of freshwater to the Gulf of Mexico. The period for which trends are analyzed varies for each station but generally comprises water years 1974–94. Stations included in this analysis are part of the National Stream Quality Accounting Network operated by the U.S. Geological Survey.

LOWESS (LOcally WEighted Scatterplot Smoothing) smooth lines superimposed on graphs of flow-adjusted residuals of concentration versus time and load versus time indicate short-term trends for each station. Kendall-Theil robust lines superimposed on the same graphs indicate long-term trends. Long-term trends were evaluated using the slope of the Kendall-Theil robust line and Kendall's tau. Annual loads are estimated with regression analysis and corrected for log-transformation bias with the MVUE (Minimum Variance Unbiased Estimator). Trends in annual streamflow are presented to aid in the interpretation of nutrient trends.

Statistically significant long-term increases in flow-adjusted residual concentrations of total nitrogen were detected at 14 stations, decreases were detected at 6 stations, and no significant trends were detected at 20 stations. Statistically significant long-term increases in total nitrogen load were detected at 5 stations, decreases were detected at 4 stations, and no significant trends were detected at 31 stations.

Statistically significant long-term increases in flow-adjusted residual concentrations of total phosphorus were detected at 2 stations, decreases were detected at 25 stations, and no significant trends were detected at 13 stations. Statistically significant long-term increases in total phosphorus load were detected at 1 station, decreases were detected at 13 stations, and no significant trends were detected at 26 stations.

The mean annual yields were computed from the estimated mean annual loads. Mean annual nitrogen yields are largest for three watersheds in the upper Mississippi Basin; estimated yield of each is greater than 5.0 tons per square mile. Nine stations in the Ohio River Basin have estimated mean annual nitrogen yields greater than 2.0 tons per square mile. Estimated mean annual phosphorus yield is greater than 0.250 ton per square mile at 7 stations, 5 in the Ohio Basin and 2 in the upper Mississippi Basin. Statistically significant trends in annual streamflow were detected at seven stations. Annual streamflow influences trends in load, even when the streamflow trends are not statistically significant.

## INTRODUCTION

The drainage area of the Mississippi River Basin covers about 42 percent of the conterminous United States, and the Mississippi River discharges about 420 billion gal/d of freshwater to the Gulf of Mexico (Meade, 1995). Trends in nutrient concentration and load are computed for 40 streamflow stations on 24 rivers in the Mississippi Basin in a study done by the U.S. Geological Survey (USGS) in cooperation with the U.S. Environmental Protection Agency's Gulf of Mexico Program (GMP). The GMP was initiated to develop and implement a comprehensive strategy to protect and conserve the resources of the Gulf. The GMP coordinates

its work through many committees. The Nutrient Enrichment Issue Committee was instrumental in coordinating this study.

A nutrient is defined as a substance necessary for growth or reproduction of an organism. Two principal nutrients are nitrogen and phosphorus. Under pristine conditions, nitrogen and phosphorus are not abundant in streams and usually limit aquatic plant growth. Excessive aquatic plant growth can occur in waters with an abundance of nutrients. As plants die and sink to the bottom, bacteria that decompose them consume oxygen at a much faster rate than can be replenished (U.S. Water Resources Council, 1978). As a result, oxygen-depleted waters cannot support marine life vital to a commercial fisheries economy (Rabalais, 1995).

Increased nutrient loads carried by the Mississippi River to the Gulf of Mexico have been identified as a contributing factor to seasonal hypoxic water conditions (oxygen concentrations less than about 2 milligrams per liter [mg/L]) along the Gulf Coast of Louisiana (Turner and Rabalais, 1991). A general overview of nutrient enrichment issues is given in Rabalais and others (1996). The current study is one of many the Nutrient Enrichment Issue Committee has initiated to gain an understanding of issues integral to the management of the Gulf's resources.

## Purpose and Scope

This report presents trends in flow-adjusted concentration and estimated annual load of total nitrogen and total phosphorus for 40 stations on 24 rivers in the Mississippi Basin. Annual streamflow trends are included to assist in the interpretation of the nutrient trends. The period analyzed varies with the availability of data for each station but is generally from water year<sup>1</sup> (WY) 1974 through WY 1994.

Trends illustrated in this report are short term and long term. Short-term trends depict year-to-year fluctuations in flow-adjusted nutrient concentrations or loads. They are indicated with best-fit curvilinear lines computed using the LOcally WEighted Scatterplot Smoothing (LOWESS) technique (Cleveland, 1979; Helsel and Hirsch, 1992). Long-term trends are computed using the Kendall-Theil robust line and their statistical significance evaluated on the basis of the p-value

<sup>1</sup>A water year is the 12-month period October 1–September 30. The water year is designated by the year in which it ends; thus, the water year ending September 30, 1994, is water year 1994.

associated with Kendall's tau (Helsel and Hirsch, 1992). P-values indicate whether the slope of the trend line is significantly different from zero. Statistical significance is reported at three levels: strongly significant,  $p \leq 0.05$ ; significant,  $0.05 < p \leq 0.10$ ; and nonsignificant,  $p > 0.10$ . Annual loads are estimated using linear regression and are corrected for log-transformation bias with a Minimum Variance Unbiased Estimator (MVUE) (Cohn and others, 1989). Streamflow, unless otherwise noted, refers to the water discharge that occurs in a natural channel. Annual values of streamflow and load presented in this report consist of daily values aggregated on an annual, water year basis.

## Previous Studies

Several previous investigations have documented nutrient concentrations, loads, and water-quality trends in rivers in the Mississippi Basin. The USGS, in cooperation with the Nutrient Enrichment Issue Committee of the GMP, summarized and analyzed trends in nutrient concentrations and loads in 37 freshwater inflows to the Gulf of Mexico (Dunn, 1996). The USGS, in cooperation with the Freshwater Inflows Committee of the GMP, summarized and analyzed trends and sources of trends in freshwater streamflow to the Gulf (Judd, 1995). The USGS, in cooperation with the Nutrient Enrichment Issue Committee of the GMP, quantified nutrient fluxes (nutrient volume per unit time per unit cross-sectional area) at 21 National Stream Quality Accounting Network (NASQAN) stations in the Mississippi Basin for WYs 1988 and 1991 (C.R. Demas, U.S. Geological Survey, written commun., 1995).

Smith and others (1993) summarized streamwater-quality trends in the 1980s. They present trends and yields in nitrate loads for 1980–89 and total phosphorus loads for 1982–89 in the major rivers of the conterminous United States. Rivers within the Mississippi Basin show decreases in both constituents that range from -0.4 to -1.6 percent change per year for nitrates and from -1.0 to -3.8 percent change per year for total phosphorus. Goolsby, Battaglin, and Thurman (1993) determined that heavy rainfall and severe flooding in mid-1993 flushed extraordinarily large amounts (compared with those reported in a 1991–92 study) of agricultural chemicals into the Mississippi River, many of its tributaries, and ultimately, the Gulf of Mexico. Turner and Rabalais (1991), using mainly USGS data, evaluated nitrogen trends since 1905 in the Mississippi River at St. Francisville, La. They report substantial

increases in nitrogen loadings and attribute these to nitrogen-bearing runoff from fertilized soils. Smith and others (1982) analyzed trends in flow-adjusted concentrations of total phosphorus for 5- to 8-year periods in the late 1970s at 300 NASQAN stations. They report 4 significantly ( $p \leq 0.1$ ) decreasing trends and 4 significantly increasing trends for 8 of the 40 stations included in their study.

USGS studies as part of the National Water-Quality Assessment (NAWQA) Program are ongoing (WYs 1994–99) in the Allegheny and Monongahela Basins, Eastern Iowa Basins, Kanawha-New River Basin, Lower Illinois River Basin, Mississippi Embayment, Upper Mississippi River Basin, and Upper Tennessee River Basin study units. Intensive studies under the NAWQA program are concluding (WYs 1991–96) in Central Nebraska Basins, Ozark Plateaus, South Platte River Basin, and White River Basin study units; low-level studies are being continued in these study units. NAWQA programs are scheduled to begin during WY 1997 (WYs 1997–2002) in the Great and Little Miami River Basins, Lower Tennessee River Basin, Middle Arkansas River Basin, Upper Illinois River Basin, and Yellowstone River Basin study units. These programs could provide additional detailed information on nutrients in the rivers of the Mississippi Basin.

### **Sources and Description of Data**

Data used in this study were collected generally during WY 1974–94 at 40 streamflow-gaging stations that monitor rivers throughout the Mississippi Basin. These stations were operated by the USGS as part of NASQAN. The total drainage area of the Mississippi Basin as shown in figure 1 is about 1,268,000 mi<sup>2</sup>. Stations were selected for inclusion in this study on the basis of availability of sufficient data. A station was considered to have sufficient data if (1) analyses for total nitrogen and total phosphorus were available for at least 80 percent of the desired period (WYs 1974–94), (2) at least 50 analyses for both total nitrogen and total phosphorus were available over the period analyzed, and (3) no substantial gaps in data exist (generally, less than 6 consecutive years with no available data). Nutrient data were obtained from the water-quality data bases of local USGS offices responsible for operating the stations.

Daily mean streamflow data were available for the entire period analyzed at 34 of the 40 stations. For the remaining six stations, streamflow data were

substituted with data from adjacent stations on the same stream for the period of record. These substitutions were recommended by USGS personnel most familiar with specific stations and their respective streamflow values. Streamflow data were obtained from the National WATER data STORAGE and RETRIEVAL (WATSTORE) system, local USGS offices, and the U.S. Army Corps of Engineers.

Station locations are shown in figure 1. Abbreviated names, station names, USGS station numbers, latitude and longitude, and drainage areas are listed in table 1. The USGS station numbers are unique eight-digit numbers assigned by the USGS. Footnotes in table 1 indicate that streamflow data at a station were supplemented with data from a nearby station. The periods of record and total number of analyses for total nitrogen and total phosphorus for each station are listed in table 2. The period of record used at a station corresponds to the longer of the two constituent periods. Stations names are assigned 3- or 4-letter abbreviations for identification in figures and tables.

## **METHODS OF ANALYSIS**

### **Computation of Flow-Adjusted Nutrient Concentrations**

Natural variables, such as streamflow and rainfall, fluctuate over time and can make detection of trends in constituents, such as nitrogen and phosphorus, difficult. Streamflow conditions, sources and sinks of nutrients, and the processes of dilution and erosion affect the relation between nutrient concentrations and stream discharge. For example, consider the relation between flow conditions and nutrient concentrations where a point-source discharge, such as a municipal wastewater-treatment-plant outfall, occurs. During base-flow conditions large nutrient concentrations could be evident because the streamflow is dominated by the effluent. However, nutrient concentrations could decrease during high-streamflow conditions because of the dilution effect of surface runoff.

During base-flow conditions for streams where nutrient sources are dominated by fertilized cropland or urban runoff, nutrient concentrations can vary depending on the ground-water quality. This is true because low streamflow comprises mostly ground water. During high streamflow conditions, these streams could contain larger nutrient concentrations than during base-flow





Figure 1. Locations of streamflow-gaging stations on rivers in the Mississippi Basin.

**Table 1.** Locations and drainage areas for selected streamflow-gaging stations in the Mississippi Basin[mi<sup>2</sup>, square miles; L&D, lock and dam]

Abbreviated name	Station name	Station number	Latitude	Longitude	Drainage area (mi <sup>2</sup> )
MS1	Mississippi River near St. Francisville, La. <sup>1</sup>	07373420	30°45'30"	91°23'45"	1,125,300
MS2	Mississippi River at Vicksburg, Miss.	07289000	32°18'45"	90°54'25"	1,144,500
MS3	Mississippi River near Arkansas City, Ark.	07265450	33°33'27"	91°14'15"	1,130,600
ARK	Arkansas River at James W. Trimble L&D near Van Buren, Ark.	07250550	35°20'56"	94°17'54"	150,547
CAN	Canadian River near Whitefield, Okla.	07245000	35°15'45"	95°14'19"	47,576
CIM	Cimarron River near Buffalo, Okla.	07157950	36°51'07"	99°18'54"	12,004
MS4	Mississippi River at Memphis, Tenn.	07032000	35°07'37"	90°04'25"	932,800
MS5	Mississippi River at Thebes, Ill.	07022000	37°13'00"	89°27'50"	713,200
MO1	Missouri River at Hermann, Mo.	06934500	38°42'36"	91°26'21"	524,200
KAN	Kansas River at DeSoto, Kans.	06892350	38°59'00"	94°57'52"	59,756
PLT	Platte River at Louisville, Nebr.	06805500	41°00'55"	96°09'28"	85,800
MO2	Missouri River at Sioux City, Iowa	06486000	42°29'10"	96°24'47"	314,600
WH1	White River near Oacoma, S. Dak.	06452000	43°44'54"	99°33'22"	10,200
CHY	Cheyenne River at Cherry Creek, S. Dak.	06439300	44°36'10"	101°29'24"	23,900
CNB	Cannonball River at Breien, N. Dak.	06354000	46°22'33"	100°56'03"	4,100
MO3	Missouri River at Garrison Dam, N. Dak.	06338490	47°30'08"	101°25'50"	181,400
YLS	Yellowstone River near Sidney, Mont.	06329500	47°40'42"	104°09'22"	69,103
KAS	Kaskaskia River near Venedy Station, Ill.	05594100	38°27'02"	89°37'39"	4,393
MS6	Mississippi River below Alton, Ill. <sup>2</sup>	05587550	38°51'41"	90°08'15"	171,500
IL1	Illinois River at Valley City, Ill.	05586100	39°42'10"	90°38'40"	26,564
IL2	Illinois River at Marseilles, Ill.	05543500	41°19'40"	88°43'10"	8,259
MS7	Mississippi River at Keokuk, Iowa	05474500	40°23'37"	91°22'27"	119,000
IOW	Iowa River at Wapello, Iowa	05465500	41°10'48"	91°10'57"	12,499
MS8	Mississippi River at Clinton, Iowa	05420500	41°46'50"	90°15'07"	85,600
WIS	Wisconsin River at Muscoda, Wis.	05407000	43°11'54"	90°26'26"	10,400
MS9	Mississippi River at Winona, Minn.	05378500	44°03'20"	91°38'15"	59,200
CHI	Chippewa River at Durand, Wis.	05369500	44°37'40"	91°58'10"	9,004
STC	St. Croix River at St. Croix Falls, Wis.	05340500	45°24'25"	92°38'49"	5,930
MIN	Minnesota River near Jordan, Minn.	05330000	44°41'35"	93°38'30"	16,200
MS10	Mississippi River near Royalton, Minn.	05267000	45°51'40"	94°21'30"	11,600
OH1	Ohio River at Dam 53 near Grand Chain, Ill. <sup>3</sup>	03612500	37°12'13"	89°02'27"	203,100
TEN	Tennessee River at Hwy. 60 near Paducah, Ky. <sup>4</sup>	03609750	37°02'16"	88°31'46"	40,330
CUM	Cumberland River near Grand Rivers, Ky.	03438220	37°01'18"	88°13'16"	17,598
WH2	White River at Hazelton, Ind. <sup>5</sup>	03374100	38°29'23"	87°33'00"	11,305
OH2	Ohio River at Cannelton Dam, Ky.	03303280	37°53'58"	86°42'20"	97,000
OH3	Ohio River at Markland Dam near Warsaw, Ky.	03277200	38°46'29"	84°57'52"	83,170
SCI	Scioto River at Higby, Ohio	03234500	39°12'44"	82°51'50"	5,131
OH4	Ohio River at Greenup Dam near Greenup, Ky.	03216600	38°38'48"	82°51'38"	62,000
MON	Monongahela River at Braddock, Pa.	03085000	40°24'19"	79°52'53"	7,337
ALL	Allegheny River at New Kensington, Pa. <sup>6</sup>	03049625	40°33'52"	79°46'22"	11,500

<sup>1</sup> Mississippi River at Tarbert Landing, Miss., 07295100, used for daily values of streamflow for period of record.<sup>2</sup> Mississippi River at Grafton, Ill., 05587450, used for daily values of streamflow for period of record.<sup>3</sup> Ohio River at Metropolis, Ill., 03611500, used for daily values of streamflow for period of record.<sup>4</sup> Tennessee River at Paducah, Ky., 03609500, used for daily values of streamflow for period of record.<sup>5</sup> White River at Petersburg, Ind., 03374000, used for daily values of streamflow for period of record.<sup>6</sup> Allegheny River at Natrona, Pa., 03049500, used for daily values of streamflow for period of record.

**Table 2.** Period of record and number of nutrient analyses available for selected streamflow-gaging stations in the Mississippi Basin

Abbreviated name (table 1)	Total nitrogen			Total phosphorus		
	Period of record		Number of analyses	Period of record		Number of analyses
	Begin	End		Begin	End	
MS1	1974	1994	160	1974	1994	221
MS2	1973	1994	140	1973	1994	144
MS3	1974	1993	129	1974	1993	134
ARK	1973	1992	159	1969	1992	190
CAN	1975	1986	90	1973	1986	130
CIM	1974	1994	96	1975	1994	108
MS4	1973	1994	137	1973	1994	143
MS5	1973	1994	132	1973	1994	137
MO1	1973	1994	224	1969	1994	256
KAN	1974	1991	120	1973	1991	144
PLT	1974	1994	215	1974	1994	220
MO2	1974	1985	94	1974	1986	120
WH1	1974	1994	133	1974	1994	142
CHY	1972	1994	146	1972	1994	153
CNB	1974	1992	117	1974	1992	123
MO3	1974	1994	133	1974	1994	137
YLS	1970	1994	229	1969	1994	276
KAS	1974	1994	122	1974	1994	125
MS6	1975	1989	67	1975	1989	69
IL1	1974	1994	195	1974	1994	200
IL2	1974	1994	121	1974	1994	125
MS7	1974	1992	99	1974	1992	120
IOW	1978	1994	82	1977	1994	103
MS8	1974	1992	145	1974	1992	169
WIS	1974	1994	139	1974	1994	142
MS9	1974	1986	80	1970	1986	111
CHI	1974	1994	144	1974	1994	147
STC	1974	1986	98	1974	1986	103
MIN	1973	1994	146	1971	1994	152
MS10	1975	1994	131	1975	1994	134
OH1	1972	1994	112	1972	1994	113
TEN	1973	1984	107	1973	1984	106
CUM	1973	1986	120	1972	1986	123
WH2	1973	1994	206	1973	1994	210
OH2	1976	1986	82	1976	1986	87
OH3	1974	1986	98	1974	1986	102
SCI	1974	1993	125	1974	1993	131
OH4	1974	1986	103	1974	1986	105
MON	1973	1993	140	1973	1993	157
ALL	1973	1994	127	1973	1994	142

conditions because the streamflow contains surface runoff from the fertilized cropland or urban landscape.

The variations in concentration attributable to streamflow must be removed to clearly detect any temporal trends in constituent concentration. The effects of streamflow were removed before the evaluation of nutrient concentration trends by using the adjustment procedure described in Helsel and Hirsch (1992, p. 329–335). This procedure uses LOWESS to produce a curvilinear smooth line through a scatterplot of the relation between concentration and streamflow. The smoothed line is a moving average computed by fitting multiple-weighted least-squares to the data. LOWESS is considered robust in statistical terms because the smoothed line is affected less by outliers than by data more toward the center of the pattern. The differences between LOWESS-fitted concentrations and actual concentration were calculated and are referred to as flow-adjusted residuals of nutrient concentrations. These residuals more accurately reflect trends in concentration over time without the dominant influence of streamflow. It is the residual-time data pairs that are tested to indicate trends in the flow-adjusted concentrations shown in tables 3 and 4.

### Computation of Nutrient Loads

The ESTIMATOR program (Cohn and others, 1992) was used to compute the annual loads of total nitrogen and total phosphorus from daily streamflow and periodic nutrient analyses. The ESTIMATOR program uses multivariate linear regression and the MVUE procedure to correct for log-transformation bias (Cohn and others, 1989). The ESTIMATOR regression technique is a multivariate expansion of typical univariate rating-curve methods for estimating constituent loads from daily streamflow and periodic constituent analyses. The univariate rating curve fits an exponential function to the observed data (daily loads computed from measured concentrations as a function of streamflow) graphically or through regression (Dunn, 1996). The function takes the form

$$\log(\hat{L}_{RC}) = B_0 + B_1 \log(Q), \quad (1)$$

where

$L_{RC}$  = estimated load (kilograms per day);

$B_0, B_1$  = regression coefficients; and

$Q$  = streamflow (cubic feet per second).

However, bias is introduced in the retransformation from log units to linear units. The ESTIMATOR program corrects for this bias by adjusting the regression function using the MVUE procedure. The load estimate, using this correction, becomes:

$$\hat{L}_{MVUE} = \hat{L}_{RC} g_m \left( \frac{m+1}{2m} [1-V] s^2 \right), \quad (2)$$

where

$L_{MVUE}$  = unbiased load estimate (kilograms per day);

$g_m$  = a Bessel function (Cohn and others, 1989);

$V$  = estimated variance of  $L_{RC}$ ;

$s^2$  = estimated variance of the residuals following regression; and

$m$  = number of observations used in model calibration minus number of model parameters.

The ESTIMATOR program does the linear regression for daily load using streamflow, time, and seasonal indicators (sine and cosine transformations of time) as explanatory variables. Then it computes daily loads, applies the MVUE bias correction to those daily estimates, and finally sums them to monthly and annual values. Because the MVUE is unbiased, the percentage error in load estimates declines approximately in proportion to the square root of the number of observations (T.A. Cohn, U.S. Geological Survey, written commun., 1996).

A common set of explanatory variables was chosen for each station included in the analysis. Not all explanatory variables were statistically significant for each station. However, statistically nonsignificant explanatory variables do not impair the accuracy of the model; regression coefficients for nonsignificant explanatory variables will be small and have little effect on predicted values (Dunn, 1996). The explanatory variables used for each station in this analysis produced regression equations of the form

$$\log_e(\hat{L}_{RC}) = B_0 + B_1 \log_e \left( \frac{Q_d}{\bar{Q}} \right) + B_2 (T - \bar{T}) + B_3 \sin(2\pi T) + B_4 \cos(2\pi T), \quad (3)$$

where

$B_0, B_1, B_2, B_3, B_4$  = regression coefficients;

$Q_d$  = daily mean streamflow (cubic feet per second);

**Table 3.** Trends in annual streamflow and total nitrogen concentration and load for selected streamflow-gaging stations in the Mississippi Basin

[**bold print**, strongly significant (attained significance level [p-value] less than 0.05); --, nonsignificant trend (attained significance level [p-value] greater than 0.10); acre-ft, acre-feet; acre-ft/yr, acre-feet per year; (mg/L)/yr, milligrams per liter per year; ton/yr, tons per year; ton/mi<sup>2</sup>, tons per square mile]

Abbreviated name (table 1)	Mean annual streamflow (acre-ft)	Trend in annual streamflow (acre-ft/yr)	Trend in total nitrogen concentration [(mg/L)/yr]	Trend in estimated annual total nitrogen load (ton/yr)	Estimated mean annual total nitrogen load (tons)	Standard deviation of estimated annual total nitrogen load (tons)	Estimated mean annual total nitrogen yield (ton/mi <sup>2</sup> )
MS1	389,000,000	--	<b>0.016</b>	21,100	1,280,000	344,000	1.14
MS2	493,000,000	--	<b>.031</b>	--	1,540,000	404,000	1.34
MS3	464,000,000	--	<b>.024</b>	--	1,530,000	409,000	1.35
ARK	28,600,000	--	--	--	47,400	25,100	.315
CAN	4,110,000	--	<b>.037</b>	--	5,430	3,540	.114
CIM	79,900	<b>-3,780</b>	<b>-.028</b>	<b>-17.1</b>	192	139	.016
MS4	409,000,000	--	--	--	1,520,000	452,000	1.62
MS5	174,000,000	--	--	--	944,000	424,000	1.32
MO1	67,700,000	--	--	--	250,000	120,000	.478
KAN	6,200,000	--	<b>-.058</b>	-1,460	28,400	22,900	.475
PLT	5,660,000	--	--	--	28,400	19,500	.331
MO2	23,900,000	--	<b>.051</b>	<b>4,840</b>	35,800	23,300	.114
WH1	374,000	--	<b>-.046</b>	--	3,280	2,330	.321
CHY	548,000	--	<b>-.043</b>	--	3,510	3,260	.147
CNB	163,000	--	--	--	616	742	.150
MO3	15,400,000	<b>-430,000</b>	--	<b>-311</b>	11,300	2,960	.062
YLS	8,950,000	<b>-167,000</b>	.010	<b>-326</b>	15,400	4,920	.223
KAS	2,790,000	--	--	--	10,600	5,610	2.42
MS6	83,400,000	--	--	--	532,000	227,000	3.10
IL1	18,900,000	--	--	--	161,000	58,500	6.07
IL2	7,990,000	--	<b>-.073</b>	--	71,800	15,600	8.69
MS7	57,500,000	--	<b>.057</b>	--	360,000	208,000	3.03
IOW	7,280,000	--	-.071	--	81,800	61,400	6.55
MS8	38,100,000	--	<b>.028</b>	<b>4,890</b>	141,000	64,300	1.65
WIS	6,590,000	--	<b>.011</b>	--	12,800	3,480	1.23
MS9	24,900,000	<b>725,000</b>	.055	<b>5,570</b>	88,800	44,500	1.50
CHI	5,830,000	--	--	--	10,000	2,090	1.11
STC	3,890,000	160,000	--	<b>251</b>	5,230	1,840	.881
MIN	3,900,000	--	--	--	53,600	49,200	3.31
MS10	3,820,000	--	--	--	5,310	2,160	.458
OH1	226,000,000	--	<b>.017</b>	--	591,000	173,000	2.91
TEN	51,400,000	-1,710,000	<b>.022</b>	--	56,400	15,900	1.40
CUM	29,000,000	<b>-1,140,000</b>	<b>.028</b>	--	37,800	9,930	2.15
WH2	9,940,000	--	--	--	45,600	13,900	4.03
OH2	93,100,000	--	--	--	290,000	64,600	2.99
OH3	85,400,000	--	<b>.028</b>	--	247,000	45,200	2.97
SCI	3,680,000	--	--	--	24,000	9,150	4.68
OH4	66,400,000	--	--	--	152,000	24,500	2.46
MON	9,540,000	--	--	--	19,400	3,480	2.64
ALL	15,100,000	--	--	--	23,200	2,870	2.01

**Table 4.** Trends in annual streamflow and total phosphorus concentration and load for selected streamflow-gaging stations in the Mississippi Basin

[**bold print**, strongly significant (attained significance level [p-value] less than 0.05); --, nonsignificant trend (attained significance level [p-value] greater than 0.10); acre-ft, acre-feet; acre-ft/yr, acre-feet per year; (mg/L)/yr, milligrams per liter per year; ton/yr, tons per year; ton/mi<sup>2</sup>, tons per square mile]

Abbreviated name (table 1)	Mean annual streamflow (acre-ft)	Trend in annual streamflow (acre-ft/yr)	Trend in total phosphorus concentration [(mg/L)/yr]	Trend in estimated annual total phosphorus load (ton/yr)	Estimated mean annual total phosphorus load (tons)	Standard deviation of estimated annual total phosphorus load (tons)	Estimated mean annual total phosphorus yield (ton/mi <sup>2</sup> )
MS1	389,000,000	--	--	--	110,000	23,500	0.098
MS2	493,000,000	--	<b>-0.004</b>	<b>-3,600</b>	140,000	50,500	.123
MS3	464,000,000	--	<b>-0.004</b>	--	127,000	34,200	.112
ARK	28,600,000	--	<b>-0.002</b>	--	4,900	2,790	.033
CAN	4,110,000	--	--	--	531	370	.011
CIM	79,900	<b>-3,780</b>	<b>-0.005</b>	<b>-2.26</b>	23.2	21.8	.002
MS4	409,000,000	--	<b>-0.003</b>	-3,150	125,000	40,900	.134
MS5	174,000,000	--	--	--	81,200	36,800	.114
MO1	67,700,000	--	<b>-0.003</b>	--	30,700	12,600	.059
KAN	6,200,000	--	--	--	2,680	1,490	.045
PLT	5,660,000	--	-0.003	--	4,790	2,970	.056
MO2	23,900,000	--	<b>.004</b>	<b>365</b>	3,380	1,690	.011
WH1	374,000	--	<b>-0.049</b>	--	4,650	4,150	.456
CHY	548,000	--	<b>-0.008</b>	--	1,490	1,600	.062
CNB	163,000	--	--	--	66.1	81.3	.016
MO3	15,400,000	<b>-430,000</b>	--	<b>-14.0</b>	480	105	.003
YLS	8,950,000	<b>-167,000</b>	--	<b>-204</b>	3,730	2,260	.054
KAS	2,790,000	--	<b>.005</b>	--	1,070	566	.244
MS6	83,400,000	--	<b>-0.007</b>	--	30,200	12,000	.176
IL1	18,900,000	--	<b>-0.007</b>	-177	8,780	2,690	.331
IL2	7,990,000	--	<b>-0.005</b>	<b>-89.5</b>	4,650	828	.564
MS7	57,500,000	--	<b>-0.002</b>	--	21,000	9,310	.176
IOW	7,280,000	--	-0.004	--	3,080	1,820	.246
MS8	38,100,000	--	--	--	9,360	3,330	.109
WIS	6,590,000	--	--	--	742	197	.071
MS9	24,900,000	<b>725,000</b>	<b>-0.004</b>	--	5,180	1,370	.088
CHI	5,830,000	--	-0.001	--	852	221	.095
STC	3,890,000	160,000	--	--	288	93	.048
MIN	3,900,000	--	<b>-0.005</b>	--	1,350	827	.083
MS10	3,820,000	--	<b>-0.001</b>	--	253	111	.022
OH1	226,000,000	--	-0.001	--	56,800	19,400	.280
TEN	51,400,000	-1,710,000	<b>-0.001</b>	<b>-432</b>	6,310	2,390	.157
CUM	29,000,000	<b>-1,140,000</b>	<b>-0.003</b>	<b>-397</b>	4,520	1,990	.257
WH2	9,940,000	--	<b>-0.003</b>	<b>-47.8</b>	3,180	1,040	.281
OH2	93,100,000	--	--	--	27,100	8,990	.279
OH3	85,400,000	--	-0.003	<b>-881</b>	18,000	5,630	.216
SCI	3,680,000	--	<b>-0.015</b>	<b>-84.7</b>	1,450	662	.282
OH4	66,400,000	--	--	--	11,600	2,700	.187
MON	9,540,000	--	<b>-0.002</b>	<b>-60.7</b>	1,090	440	.149
ALL	15,100,000	--	--	--	1,170	201	.102

T = time (decimal years);

$\bar{Q}$  = the centering value for streamflow calculated by the model; and

T = the centering value for time calculated by the model.

This method of estimating constituent loads does not allow for event-oriented variations. Although this method can account for seasonal variations in constituent concentrations and loads, no mechanism is included to allow for the timing of a sample with respect to runoff conditions.

### Detection of Trends

A short-term trend is defined as the change (increase or decrease) with respect to time of the central tendency of subsets (moving windows) of the data. Short-term trends as defined in this study depict year-to-year fluctuations in the central tendency of flow-adjusted nutrient concentrations or loads. Because of the small number of data points and the arbitrary method of determining the width of the data subsets, these short-term trends were not assigned any statistical significance and should be evaluated visually. They are illustrated by LOWESS smooth lines superimposed on graphs of the relations between flow-adjusted residuals and time and between load and time.

Long-term trends in this study were detected using Kendall's tau and Kendall-Theil robust line. These non-parametric statistics are computed from relative ranking and the median of data points. Kendall's tau measures the strength of a monotonic relation between variables, making it suitable for skewed data and data having outliers. Skewed data and outliers are common characteristics of water-quality data. Kendall's tau ranges from 1.0 to -1.0, and the sign indicates an increasing (+) or decreasing (-) trend. The statistical significance (p-value) of the trend is a function of the magnitude of tau and the sample size. The Kendall-Theil line represents the straight-line slope of the trend.

An additional (parametric) trend test was applied to residuals of flow-adjusted concentration and load to support and verify the nonparametric test results. In this test, the regression coefficient for time ( $B_2$  in equation 3) is tested for statistical significance.  $B_2$  will be identical in regression equations for either concentration or load at a station. The test compensates for the effects of streamflow because streamflow is included in the

regression equation (Helsel and Hirsch, 1992, p. 335). The sign and p-value of  $B_2$  can be compared to the sign and p-value of Kendall's tau computed for residuals of flow-adjusted concentration and load.

Trends presented in this study represent data only from the period analyzed and the reader should not extrapolate results beyond the period of analyses (generally WYs 1974–94).

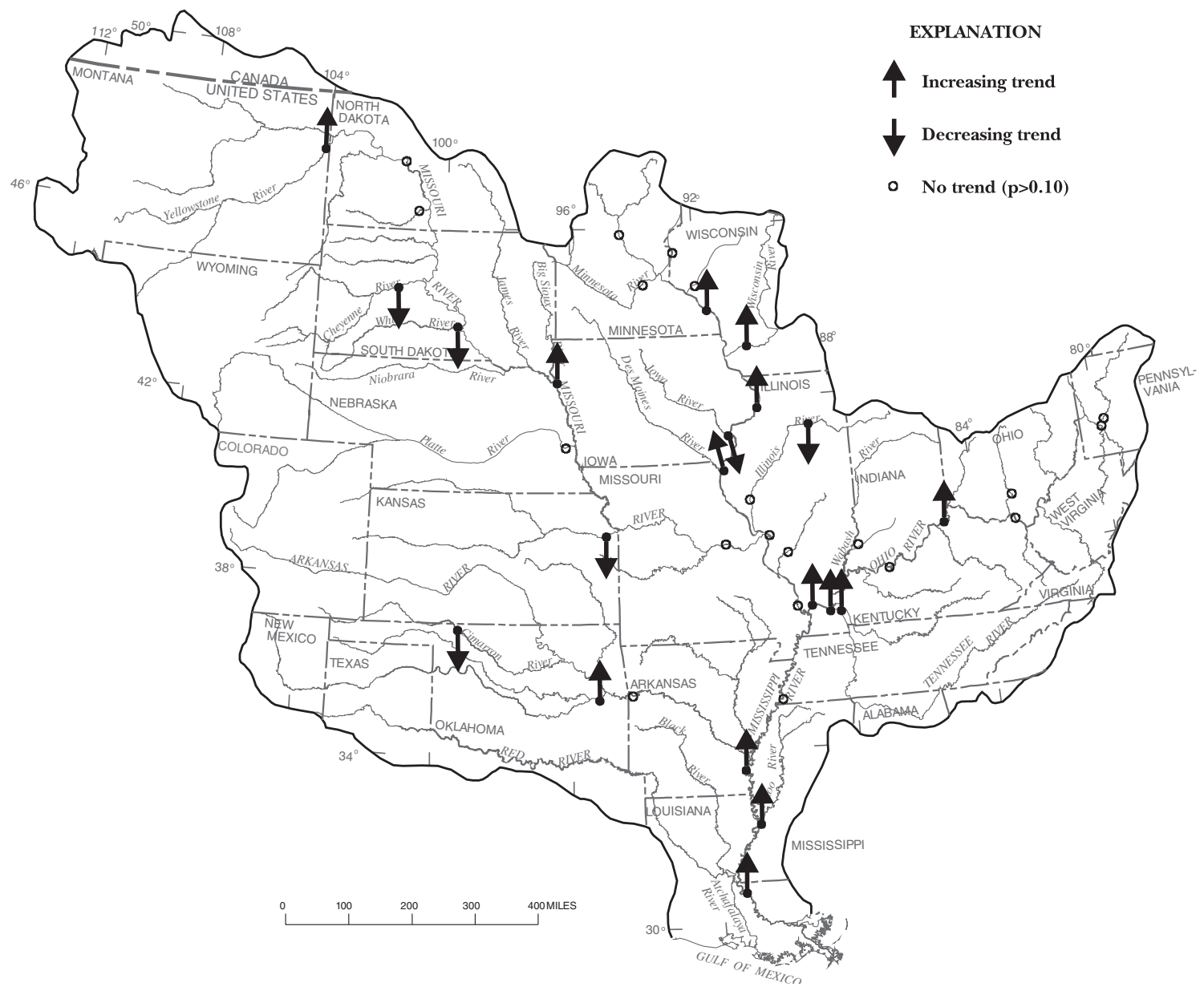
### NUTRIENT TRENDS

Annual streamflows are depicted by LOWESS smooth lines, and a Kendall-Theil robust line is superimposed on the streamflow-time graph for each station in figures 6–45 (at end of report). Short-term variations in annual streamflow are reflected in the LOWESS smooth lines. Long-term trend is shown by the Kendall-Theil line. Results of analyses of trends in annual streamflow are listed in tables 3 and 4.

Statistically significant trends in annual streamflow were detected for seven streams in the Mississippi Basin. Increasing trends were detected for 2 streams, and decreasing trends were detected for 5 streams. The increasing trends were for the Mississippi River at Winona, Minn. (MS9), and the St. Croix River at St. Croix Falls, Wis. (STC). Two of the streams with decreasing streamflow trends in Kentucky—the Cumberland River near Grand Rivers (CUM) and the Tennessee River near Paducah (TEN)—are regulated with large reservoirs immediately upstream from the stations (Moody and others, 1986, p. 246). The remaining three streams with decreasing streamflow trends are the Yellowstone, Missouri (N. Dak.), and Cimarron. The Yellowstone River in Montana (YLS) is a major source of irrigation withdrawals, and the station on the Missouri River in North Dakota (MO3) is just below Garrison Dam (Moody and others, 1986, p. 310, 366). The decreasing streamflow trends for the Cimarron (CIM) in Oklahoma might be related to large declines in the Ogallala Formation underlying the basin (R.L. Tortorelli, U.S. Geological Survey, written commun., 1996).

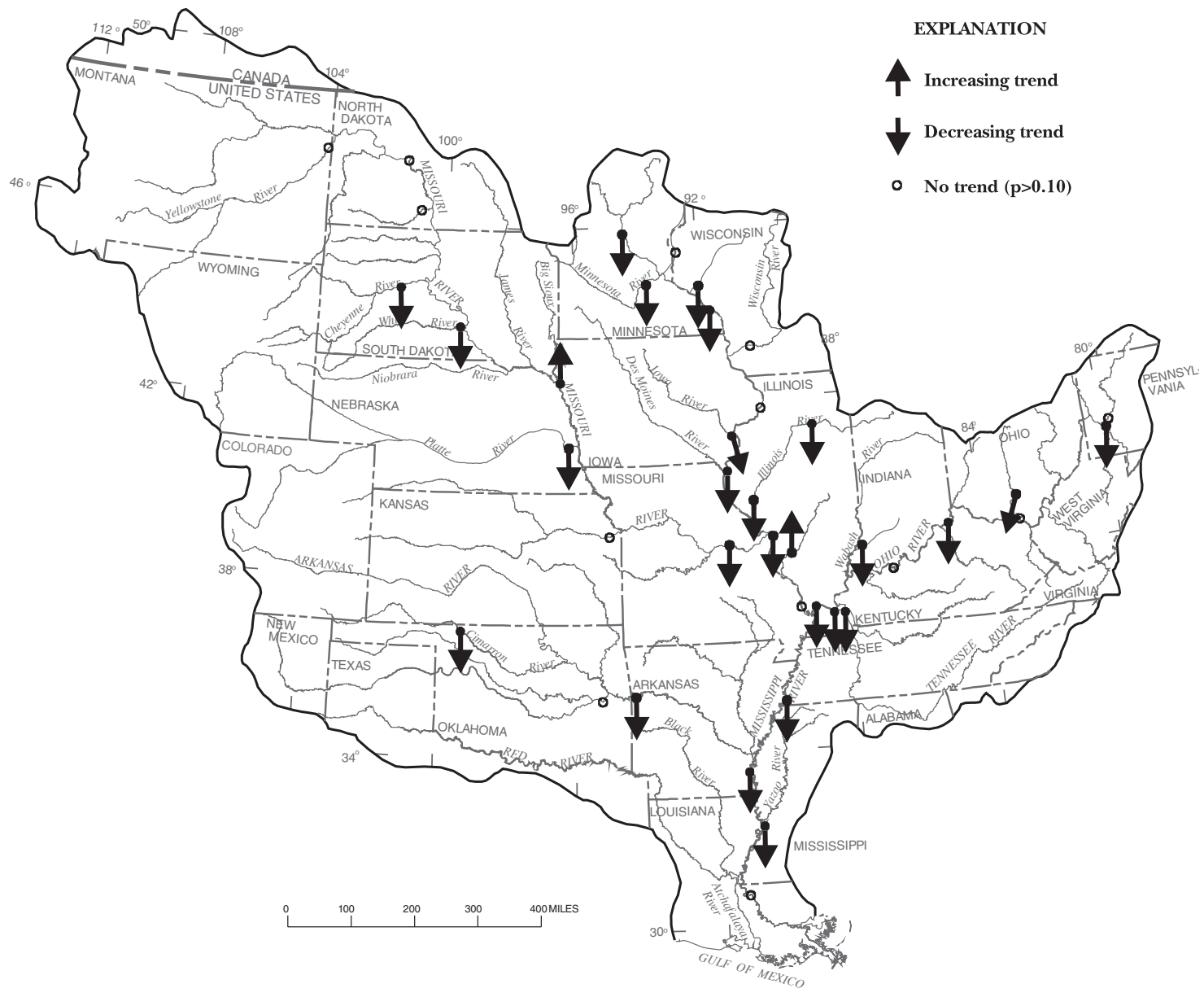
### Trends in Nutrient Concentration

Results of analyses of trends in nutrient concentration for all 40 stations are shown in figures 2 and 3 and listed in tables 3 and 4. Graphs of the relation between nutrient concentration and daily mean streamflow for each station (figs. 6–45) show the streamflow range in which nutrient samples were taken. Graphs of



11 **Figure 2.** Trends in flow-adjusted residuals of total nitrogen concentration for rivers in the Mississippi Basin, 1974–94.





**Figure 3.** Trends in flow-adjusted residuals of total phosphorus concentration for rivers in the Mississippi Basin, 1974-94.

time series of flow-adjusted residuals of nutrient concentrations with LOWESS smooth lines and Kendall-Theil robust lines superimposed show the presence or absence of short- and long-term trends (figs. 6–45).

### Total Nitrogen

Strongly significant ( $p \leq 0.05$ ) or significant ( $p \leq 0.10$ ) long-term increases in flow-adjusted residuals of total nitrogen concentration were detected at 14 stations, strongly significant or significant decreases were detected at 6 stations, and 20 stations show no detectable long-term trend (fig. 2; table 3). The upper Mississippi Basin (above confluence with the Ohio River), the Ohio-Tennessee-Cumberland River Basin, and the lower Mississippi River Basin (below Memphis, Tenn.) each have four stations where increasing trends in total nitrogen concentration were detected. The Missouri River Basin had two stations where increasing trends in total nitrogen concentration were detected.

Increased nitrogen concentration has been associated with increases in nitrogen fertilizer use and population that affect agricultural and urban runoff (Hem, 1989). Significant increases in nitrogen concentration at Mississippi River near Keokuk, Iowa (MS7), could be attributed to increased inflows of nitrogen from the Des Moines River at the confluence of the Des Moines and Mississippi Rivers. Urban runoff and municipal wastewater-treatment-plant discharges affect segments of the Des Moines River primarily downstream from Des Moines. Also the principal land use in the Des Moines River Basin is agriculture (Paulson and others, 1993, p. 272).

One station, Missouri River at Sioux City, Iowa (MO2), shows strongly significant increasing trends in concentrations and loads for total nitrogen (and total phosphorus). Several factors could be contributing to these trends. The station is downstream from the confluence of the Niobrara, James, and Big Sioux Rivers, respectively, and the Missouri River. Runoff from feedlots in the Niobrara River Basin could have contributed to increased nitrogen in the Niobrara because of increased livestock on grain feed (Paulson and others, 1993, p. 377). The James and Big Sioux Rivers could contribute increased nutrients from both agricultural and urban runoff to the Missouri River (Paulson and others, 1993, p. 494).

### Total Phosphorus

Strongly significant or significant long-term increases in flow-adjusted residuals of total phosphorus concentration were detected at 2 stations, strongly significant or significant decreases were detected at 25 stations, and 13 stations show no detectable long-term trend (fig. 3; table 4).

The decreases in total phosphorus concentration in the 25 stations throughout the study area could be attributed to several factors, which include combined effects of improved municipal- and industrial-wastewater treatment, reduced phosphate content of detergents, reduced fertilizer use, and reduced quantities of livestock wastes (Smith and others, 1993).

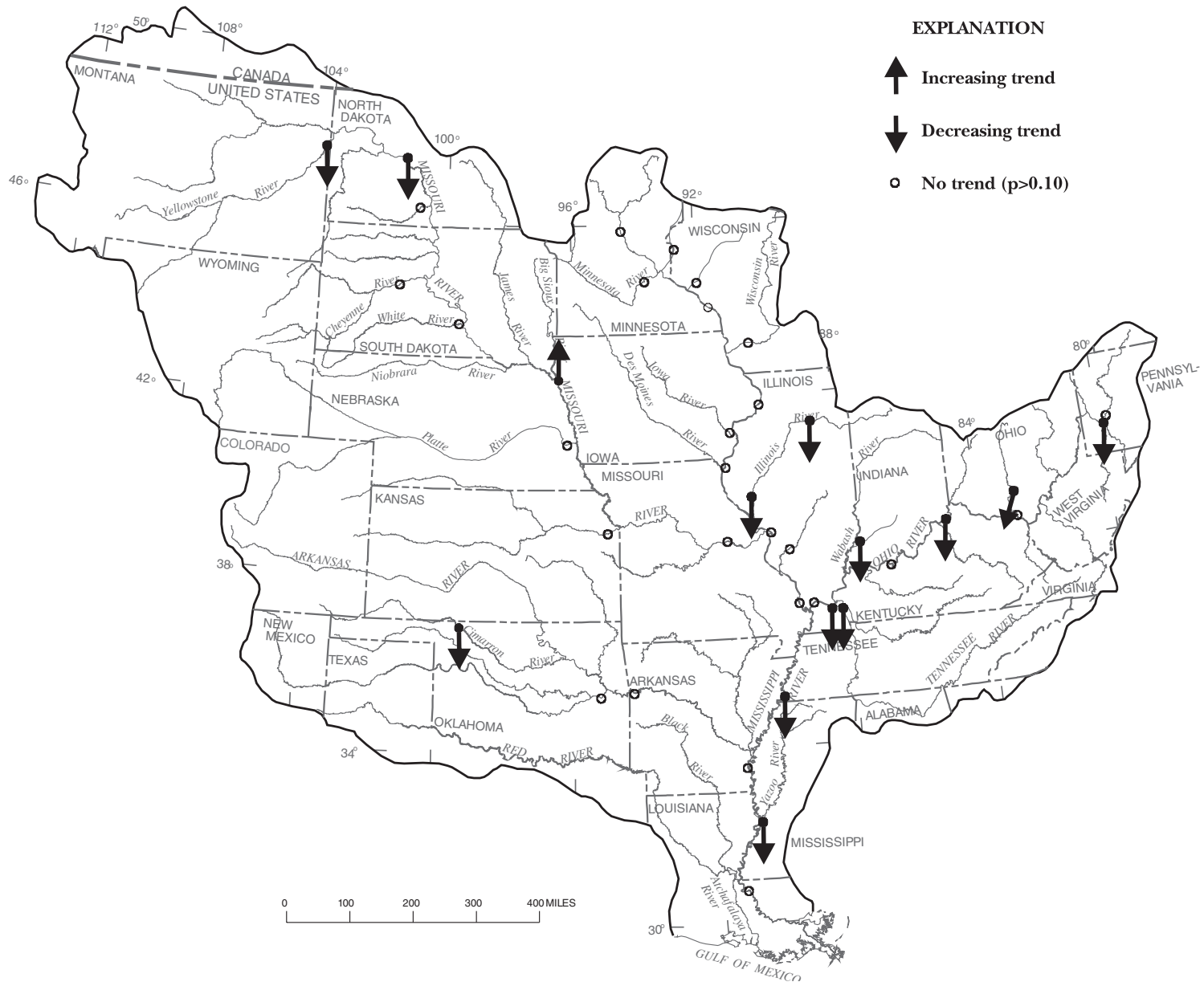
Trends were detected for flow-adjusted residuals of both total nitrogen concentration and total phosphorus concentration at 14 stations throughout the study area. At 8 of the 14 stations, trends show nitrogen concentration increasing and phosphorus concentration decreasing. These findings could be attributed to increased application of nitrogen-based fertilizers, increased improvements in wastewater-treatment facilities and decreased use of phosphate detergents (Smith and others, 1993). Decreases in both total nitrogen concentration and total phosphorus concentration were detected at 5 stations, and an increase in both total nitrogen concentration and total phosphorus concentration was detected at 1 station.

### Trends in Nutrient Load

Table 3 shows the computed means and standard deviations of the estimated annual nitrogen loads. Yield, also shown in table 3, is calculated by dividing mean annual load by watershed area. Table 4 shows the same information for total phosphorus. The presence or absence of trends in estimated annual nutrient loads is shown in figures 4 and 5. Diagnostic statistics and coefficients from the regression analyses for nutrient loads are listed in tables 5 and 6. The standard deviations of the annual load estimates range from 12 to 120 percent of the mean annual loads of total nitrogen and from 17 to 123 percent of the mean annual loads of total phosphorus. Because load is related to streamflow, the variations in these annual loads are influenced by runoff conditions that can fluctuate greatly between years because of rainfall variability. Annual load estimates are shown in figures 6–45 at end of report. The uncertainty associated with each individual estimate of annual load



**Figure 4.** Trends in estimated annual loads of total nitrogen for rivers in the Mississippi Basin, 1974–94.



**Figure 5.** Trends in estimated annual loads of total phosphorus for rivers in the Mississippi Basin, 1974–94.

**Table 5.** Parameter estimates for total nitrogen load model

[model:  $\log_e(\text{LOAD}) = B_0 + B_1 \log_e(\text{FLOW}/\text{CENTERED FLOW}) + B_2(\text{TIME} - \text{CENTERED TIME}) + B_3 \sin(2\pi[\text{TIME}]) + B_4 \cos(2\pi[\text{TIME}])$  where LOAD is estimated daily total load in kilograms per day; FLOW is daily mean streamflow in cubic feet per second; CENTERED FLOW is a centering variable as calculated by the model; TIME is time in decimal years; CENTERED TIME is a centering variable as calculated by the model; p-value, attained significance level;  $R^2$ , coefficient of determination (variability explained by the model); s, standard deviation of the residuals from ordinary least squares fit, in log units]

Abbreviated name (table 1)	$B_0$ (p-value)	$B_1$ (p-value)	$B_2$ (p-value)	$B_3$ (p-value)	$B_4$ (p-value)	$R^2$	s
MS1	14.6103 (0.0000)	1.2108 (0.0000)	0.0052 (0.1983)	0.0444 (0.2770)	-0.1059 (0.0018)	84.1	0.3001
MS2	14.8607 ( .0000)	1.1423 ( .0000)	.0128 ( .0019)	.1052 ( .0149)	-.1003 ( .0017)	86.0	.2785
MS3	14.6917 ( .0000)	1.2808 ( .0000)	.0002 ( .9718)	.0320 ( .5138)	-.0734 ( .0595)	85.4	.3128
ARK	9.4719 ( .0000)	1.0286 ( .0000)	-.0126 ( .0328)	.1884 ( .0001)	.0487 ( .2731)	93.8	.4062
CAN	8.0651 ( .0000)	1.0300 ( .0000)	.0385 ( .0021)	-.0931 ( .1191)	-.0207 ( .7348)	92.3	.4612
CIM	-6.9585 ( .0000)	1.0787 ( .0000)	-.0599 ( .0000)	-.0261 ( .8251)	-.0394 ( .6868)	95.3	.8359
MS4	14.6803 ( .0000)	1.3104 ( .0000)	-.0017 ( .6769)	.1053 ( .0123)	-.1067 ( .0024)	88.3	.2873
MS5	14.1867 ( .0000)	1.3397 ( .0000)	.0071 ( .0899)	.1986 ( .0000)	.0092 ( .7928)	84.7	.3519
MO1	12.9074 ( .0000)	1.3931 ( .0000)	.0014 ( .7405)	.3159 ( .0000)	-.0913 ( .0161)	81.9	.4146
KAN	10.0577 ( .0000)	1.1984 ( .0000)	-.0329 ( .0000)	.0516 ( .2439)	.1823 ( .0003)	90.3	.4002
PLT	10.6695 ( .0000)	1.4242 ( .0000)	-.0113 ( .0160)	-.0901 ( .0300)	-.0442 ( .2446)	84.2	.4520
MO2	10.7476 ( .0000)	1.4719 ( .0000)	.1514 ( .0000)	.2477 ( .0011)	.0864 ( .2798)	62.7	.4636
WH1	6.0162 ( .0000)	1.2396 ( .0000)	-.0195 ( .0822)	-.1643 ( .1045)	-.3379 ( .0015)	86.4	.8021
CHY	7.6369 ( .0000)	1.3233 ( .0000)	-.0248 ( .0104)	.2455 ( .0025)	.5248 ( .0000)	80.3	.7355
CNB	4.7273 ( .0000)	1.1691 ( .0000)	-.0097 ( .3399)	.0036 ( .9603)	.0099 ( .8989)	95.4	.5550
MO3	10.2052 ( .0000)	1.2568 ( .0000)	.0084 ( .3776)	-.1292 ( .0390)	-.1043 ( .0857)	43.4	.5090
YLS	10.3553 ( .0000)	1.3308 ( .0000)	.0035 ( .5808)	.2679 ( .0000)	.0720 ( .2102)	76.7	.5200
KAS	8.5047 ( .0000)	1.1456 ( .0000)	-.0012 ( .8210)	.3031 ( .0000)	-.0887 ( .0374)	95.8	.4066
MS6	13.5027 ( .0000)	1.3411 ( .0000)	-.0076 ( .2926)	.2020 ( .0000)	.1274 ( .0049)	88.9	.3504
IL1	12.4908 ( .0000)	1.1393 ( .0000)	-.0005 ( .8698)	.2565 ( .0000)	.1625 ( .0000)	91.5	.3018
IL2	11.9316 ( .0000)	1.0451 ( .0000)	-.0052 ( .0368)	.1951 ( .0000)	.1387 ( .0000)	90.0	.2351
MS7	12.9077 ( .0000)	1.4770 ( .0000)	.0172 ( .0253)	.2068 ( .0005)	.1515 ( .0115)	84.0	.4234
IOW	11.4913 ( .0000)	1.2916 ( .0000)	-.0156 ( .0298)	.0682 ( .2055)	.2055 ( .0004)	92.6	.3609
MS8	12.4323 ( .0000)	1.3817 ( .0000)	.0159 ( .0000)	.1049 ( .0015)	.2008 ( .0000)	90.2	.2873
WIS	10.3379 ( .0000)	1.0671 ( .0000)	.0091 ( .0024)	.1390 ( .0000)	.1298 ( .0000)	91.8	.2143
MS9	11.9277 ( .0000)	1.3987 ( .0000)	.0238 ( .1260)	.0956 ( .1734)	.2156 ( .0027)	85.8	.4220
CHI	10.1670 ( .0000)	.9465 ( .0000)	.0067 ( .0734)	.1519 ( .0000)	.1119 ( .0005)	86.0	.2657
STC	9.3553 ( .0000)	1.1732 ( .0000)	.0033 ( .7771)	.1569 ( .0020)	-.0210 ( .6862)	88.1	.3484
MIN	10.0953 ( .0000)	1.4791 ( .0000)	-.0078 ( .2796)	-.0206 ( .6950)	.3127 ( .0000)	94.1	.4801
MS10	9.0070 ( .0000)	1.0612 ( .0000)	.0009 ( .8783)	.1380 ( .0085)	-.0261 ( .6071)	82.1	.4071
OH1	13.5985 ( .0000)	1.1556 ( .0000)	.0203 ( .0015)	.1357 ( .0445)	-.0068 ( .9116)	79.6	.5191
TEN	11.6577 ( .0000)	1.1863 ( .0000)	.0443 ( .0000)	.1711 ( .0002)	.1078 ( .0161)	88.1	.3046
CUM	10.8243 ( .0000)	1.1756 ( .0000)	.0428 ( .0000)	.1584 ( .0001)	.0958 ( .0294)	89.8	.3173
WH2	10.8099 ( .0000)	1.1266 ( .0000)	-.0017 ( .6255)	.2421 ( .0000)	.0673 ( .0700)	91.2	.3790
OH2	13.0983 ( .0000)	1.1322 ( .0000)	.0104 ( .1991)	-.0186 ( .6301)	.0151 ( .6993)	96.0	.2260
OH3	12.9045 ( .0000)	1.0641 ( .0000)	.0081 ( .3708)	.0104 ( .8192)	.0603 ( .1803)	93.0	.2834
SCI	10.5616 ( .0000)	1.0757 ( .0000)	.0049 ( .4081)	.1274 ( .0138)	-.0349 ( .4517)	89.9	.3633
OH4	12.4774 ( .0000)	1.0604 ( .0000)	.0062 ( .4125)	-.0873 ( .0249)	.0551 ( .1492)	93.8	.2398
MON	10.4570 ( .0000)	.9442 ( .0000)	.0106 ( .0786)	-.0365 ( .5141)	-.0080 ( .8751)	80.6	.4016
ALL	10.5509 ( .0000)	1.0298 ( .0000)	.0062 ( .1704)	.0819 ( .0527)	.1115 ( .0058)	90.2	.2995

**Table 6.** Parameter estimates for total phosphorus load model

[model:  $\log_e(\text{LOAD}) = B_0 + B_1 \log_e(\text{FLOW}/\text{CENTERED FLOW}) + B_2(\text{TIME} - \text{CENTERED TIME}) + B_3 \sin(2\pi[\text{TIME}]) + B_4 \cos(2\pi[\text{TIME}])$  where LOAD is estimated daily total load in kilograms per day; FLOW is daily mean streamflow in cubic feet per second; CENTERED FLOW is a centering variable as calculated by the model; TIME is time in decimal years; CENTERED TIME is a centering variable as calculated by the model; p-value, attained significance level;  $R^2$ , coefficient of determination (variability explained by the model); s, standard deviation of the residuals from ordinary least squares fit, in log units]

Abbreviated name (table 1)	$B_0$ (p-value)	$B_1$ (p-value)	$B_2$ (p-value)	$B_3$ (p-value)	$B_4$ (p-value)	$R^2$	s
MS1	12.2191 (0.0000)	1.0377 (0.0000)	-0.0037 (.5328)	-0.0555 (0.3569)	-0.0027 (0.9542)	54.3	0.4939
MS2	12.4325 (.0000)	1.2563 (.0000)	-.0240 (.0001)	-.0977 (.1071)	-.0033 (.9419)	72.6	.4011
MS3	12.2658 (.0000)	1.1758 (.0000)	-.0199 (.0050)	-.1375 (.0386)	-.0940 (.0747)	67.9	.4328
ARK	7.2434 (.0000)	1.1007 (.0000)	-.0234 (.0000)	.0114 (.7944)	.0507 (.2317)	92.2	.4432
CAN	5.5583 (.0000)	1.1755 (.0000)	-.0088 (.5662)	-.1551 (.0523)	.1707 (.0294)	84.6	.7464
CIM	-10.5347 (.0000)	1.1334 (.0000)	-.0994 (.0000)	-.2533 (.1356)	-.1260 (.3867)	92.1	1.1801
MS4	12.2299 (.0000)	1.2524 (.0000)	-.0203 (.0010)	-.1558 (.0094)	-.0906 (.0680)	70.7	.4199
MS5	11.8007 (.0000)	1.3664 (.0000)	-.0044 (.2902)	-.0924 (.0154)	-.0949 (.0087)	81.9	.3696
MO1	10.7946 (.0000)	1.2638 (.0000)	-.0116 (.0208)	-.0085 (.8691)	-.2337 (.0000)	64.5	.6071
KAN	8.1720 (.0000)	.9370 (.0000)	-.0099 (.1653)	.0275 (.6101)	-.0703 (.2296)	79.2	.5360
PLT	8.9022 (.0000)	1.3041 (.0000)	-.0289 (.0000)	-.2211 (.0000)	-.2576 (.0000)	74.2	.5450
MO2	8.4773 (.0000)	1.8157 (.0000)	.1076 (.0000)	.2424 (.0036)	.0625 (.5114)	57.0	.6094
WH1	4.8781 (.0000)	1.4503 (.0000)	-.0606 (.0015)	-.4414 (.0108)	-.8897 (.0000)	76.1	1.4029
CHY	5.3070 (.0000)	1.5340 (.0000)	-.0385 (.0311)	.2625 (.0799)	-.0836 (.6500)	68.7	1.3887
CNB	1.8409 (.0000)	1.2401 (.0000)	.0040 (.8083)	.1425 (.2267)	-.3474 (.0074)	90.4	.9232
MO3	6.8823 (.0000)	.6900 (.0027)	-.0102 (.4916)	-.0881 (.3503)	-.1451 (.1236)	16.3	.7146
YLS	8.0541 (.0000)	1.6215 (.0000)	-.0274 (.0021)	.3471 (.0000)	-.6361 (.0000)	72.5	.9244
KAS	6.4230 (.0000)	1.0516 (.0000)	.0246 (.0014)	.0182 (.7826)	-.1107 (.0755)	88.6	.5996
MS6	10.7171 (.0000)	1.2570 (.0000)	-.0361 (.0001)	-.0750 (.1824)	.0433 (.4352)	78.8	.4472
IL1	9.7354 (.0000)	.9147 (.0000)	-.0216 (.0000)	-.0488 (.2038)	.0317 (.3532)	77.5	.3775
IL2	9.2900 (.0000)	.8438 (.0000)	-.0210 (.0000)	-.0435 (.1173)	.0399 (.1263)	69.9	.3206
MS7	10.3313 (.0000)	1.3386 (.0000)	-.0178 (.0068)	-.0280 (.5515)	-.0211 (.6557)	83.7	.3730
IOW	8.4139 (.0000)	.9664 (.0000)	-.0114 (.2268)	.0417 (.5378)	-.1434 (.0393)	78.6	.4980
MS8	9.7213 (.0000)	1.1873 (.0000)	-.0082 (.1304)	-.1798 (.0002)	-.1989 (.0000)	73.0	.4442
WIS	7.4159 (.0000)	1.1155 (.0000)	-.0136 (.0235)	-.0120 (.8113)	-.2286 (.0000)	71.1	.4389
MS9	9.2385 (.0000)	1.0136 (.0000)	-.0182 (.0414)	-.0408 (.4239)	-.1550 (.0027)	79.6	.3684
CHI	7.6186 (.0000)	1.1522 (.0000)	-.0165 (.0108)	-.0602 (.2668)	-.1307 (.0160)	71.7	.4629
STC	6.3363 (.0000)	1.2542 (.0000)	-.0214 (.2116)	.0974 (.1694)	-.2011 (.0076)	79.0	.5148
MIN	6.9558 (.0000)	1.0776 (.0000)	-.0352 (.0000)	.1097 (.0183)	-.1602 (.0018)	92.6	.4271
MS10	5.8960 (.0000)	.9834 (.0000)	-.0166 (.0191)	.0938 (.1147)	-.4135 (.0000)	79.2	.4622
OH1	11.1252 (.0000)	1.4215 (.0000)	-.0111 (.0732)	-.0606 (.3517)	.0783 (.1997)	84.4	.5141
TEN	9.4136 (.0000)	1.3030 (.0000)	-.0180 (.2006)	-.0669 (.2954)	.0376 (.5522)	77.9	.4350
CUM	8.5753 (.0000)	1.2195 (.0000)	-.0394 (.0003)	-.0769 (.1479)	.0062 (.9120)	84.1	.4192
WH2	8.1943 (.0000)	1.1126 (.0000)	-.0126 (.0107)	-.0663 (.2435)	.0617 (.2372)	80.8	.5393
OH2	10.3567 (.0000)	1.5271 (.0000)	-.0072 (.6446)	-.2264 (.0024)	.2098 (.0051)	91.8	.4381
OH3	10.0061 (.0000)	1.2829 (.0000)	-.0336 (.0606)	-.2345 (.0109)	.1932 (.0291)	83.0	.5607
SCI	7.9678 (.0000)	.7922 (.0000)	-.0456 (.0000)	-.1579 (.0154)	.0318 (.5804)	72.3	.4652
OH4	9.4826 (.0000)	1.5105 (.0000)	.0437 (.0440)	-.2946 (.0065)	.0383 (.7142)	77.6	.6680
MON	7.2283 (.0000)	1.0620 (.0000)	-.0496 (.0001)	-.0189 (.8658)	-.0203 (.8438)	57.2	.8420
ALL	7.0956 (.0000)	1.5442 (.0000)	-.0036 (.7215)	-.1398 (.1527)	-.0348 (.7102)	74.3	.7124

is depicted by an error bar. The length of the error bar represents the 90-percent confidence interval for the load estimate.

The parameter estimates for the total nitrogen load and total phosphorus load models are listed in tables 5 and 6. The nitrogen model performed better than the phosphorus model as indicated by the generally larger  $R^2$  values and smaller residual standard deviations. The performance of the total phosphorus model could be attributed partly to the tendency of phosphorus to adsorb onto sediment particles. Therefore, sediment transport would influence phosphorus transport.

### Total Nitrogen

Strongly significant or significant long-term increases in estimated annual total nitrogen loads were detected at 5 stations, strongly significant or significant decreases were detected at 4 stations, and 31 stations exhibit no detectable long-term trend (fig. 4; table 3). Statistical significance is influenced by sample size so that the likelihood of detecting a significant trend increases as the number of samples increases. The sample size for load is 20 for most stations (1 per year), and the sample size for concentration ranges from 67 to 276. Therefore, trend tests for concentration are more likely to detect statistically significant trends than are trend tests for streamflow or load. Long-term trends in total nitrogen (concentration or load) detected using the regression coefficient for time,  $B_2$  (table 5), from the load model agree with the results of Kendall's tau for all but 10 stations. The sign of  $B_2$ , however, agrees with the direction of the trend detected by Kendall's tau for 8 of the 10 stations.

Estimated mean annual load of total nitrogen ranges from 192 tons for the Cimarron River near Buffalo, Okla. (CIM), to 1.53 million tons for the Mississippi River near Arkansas City, Ark. (MS3). Estimated mean annual yield ranges from 0.016 ton/mi<sup>2</sup> for the same Cimarron River station to 8.69 ton/mi<sup>2</sup> for Illinois River at Marseilles, Ill. (IL2). The large yield at this Illinois River station probably is a result of the population stress of the highly urbanized Chicago metropolitan area upstream from Marseilles. Population stress is the ratio of human population upstream from a gaging station to the mean discharge, in cubic meters per second. The Illinois River Basin has the largest population stress of the Mississippi River tributary basins (14,600 people per cubic meter per second) (Meade, 1995, p. 39). The second largest mean annual yield for

total nitrogen in the Mississippi Basin was estimated for Iowa River at Wapello, Iowa (IOW). Large segments of the Iowa River are affected by discharge from municipal wastewater-treatment facilities, and urban and agricultural runoff (Paulson and others, 1993, p. 271). Mean annual total nitrogen yields are largest for three watersheds in the upper Mississippi Basin; estimated yield of each is greater than 5.0 ton/mi<sup>2</sup>. Nine stations in the Ohio Basin have estimated mean annual total nitrogen yields greater than 2.0 ton/mi<sup>2</sup>.

Generally, along the mainstem of the Mississippi River, mean annual nitrogen yield increases downstream from Royalton, Minn., to Alton, Ill. The estimated yield tripled between Royalton and Winona (upstream and downstream of the Minneapolis-St. Paul area, respectively). The estimated yield doubled between Clinton and Keokuk, Iowa, the reach of the Mississippi River where the Iowa and Des Moines Rivers join it. Dilution by the Missouri River decreased the estimated mean annual yield by more than 50 percent between Alton and Thebes, Ill. Alternately, the contributions of the Ohio River between Thebes and Memphis, Tenn., increased the yield by 23 percent. The estimated nitrogen yield then decreased steadily from Memphis to St. Francisville, La.

### Total Phosphorus

Strongly significant or significant long-term increases in estimated annual total phosphorus load were detected at 1 station, strongly significant or significant decreases were detected at 13 stations, and 26 stations show no detectable long-term trend (fig. 5; table 4). Long-term trends in total phosphorus (concentration or load) detected using the regression coefficient,  $B_2$  (table 6), from the load model agree with the results of Kendall's tau tests for all but five stations. The sign of  $B_2$ , however, agrees with the direction of the trend detected by Kendall's tau for the five stations.

Estimated mean annual load of total phosphorus ranges from 23.2 tons for the Cimarron River near Buffalo, Okla. (CIM), to 140,000 tons for the Mississippi River at Vicksburg, Miss. (MS2). Estimated mean annual yield ranges from 0.002 ton/mi<sup>2</sup> at the same Cimarron River station to 0.564 ton/mi<sup>2</sup> for the Illinois River at Marseilles, Ill. (IL2). Estimated mean annual phosphorus yield is greater than 0.250 ton/mi<sup>2</sup> at 7 stations, 5 in the Ohio Basin and 2 in the upper Mississippi Basin. Decreasing trends in phosphorus loads were detected throughout the Mississippi Basin,

specifically in the Ohio, upper Missouri, and lower Mississippi Basins.

## Factors Affecting Nutrient Trends

### Data Limitations

These analyses and associated trend tests are subject to the availability and quality of data for each station. Sample collection, preservation, and laboratory analysis within the USGS are standardized, but biased data do exist primarily because of changes in methods reflecting technological advancements and policy and budgetary decisions. Studies of quality-assurance data (R.B. Alexander, U.S. Geological Survey, written commun., 1992) indicate that a positive bias is likely in total phosphorus and total ammonia plus organic nitrogen analyses that were done during the early 1980s by the USGS National Water-Quality Laboratory, Arvada, Colo. Because this laboratory generally did water-quality analyses for states west of the Mississippi River, the bias generally is greater in those states (Paulson and others, 1993, p. 151).

Another limiting factor with the analyses and trends indicated in this study is the accuracy of the reported analytical results compared to the actual concentration in the sample at the time of analysis. Hem (1989, p. 163) states that, "the analytical results for major constituents of water have an accuracy of  $\pm 2$  to  $\pm 10$  percent under optimum conditions. The accuracy for solutes present in concentrations below 1 mg/L is generally not better than  $\pm 10$  percent and can be poorer." Additionally, errors in field sampling, sample preservation, and laboratory analysis should be considered when interpreting the significance of trends indicated in this report.

### Influence of Streamflow on Loads

Because load is the product of concentration and streamflow, the direction of annual streamflow trends influences the direction of annual load trends. Even if streamflow trends are nonsignificant they must be considered when interpreting trends in computed loads. A couple of examples for the Ohio River illustrate the influence that annual streamflow trends can have on annual load trends: The Ohio River at Markland Dam near Warsaw, Ky. (OH3), shows strongly significant increasing trends in nitrogen concentration and a nonsignificant decreasing trend in annual streamflow (fig. 41). Annual total nitrogen load for this station shows a

nonsignificant decreasing trend. The decreasing trend in streamflow affects both the direction and statistical significance of the trend in load. Similarly, the Ohio River at Dam 53 near Grand Chain, Ill. (OH1), shows a strongly significant increasing trend in total nitrogen concentration and a nonsignificant decreasing trend in annual streamflow (fig. 36). However, the annual load for total nitrogen shows a nonsignificant increasing trend. At this station, the trend in streamflow does not change the direction of the trend in load but might affect the ability to detect a significant trend in load.

### Mississippi River Diversion to Atchafalaya River

A portion (about one-fourth, on average) of the Mississippi River streamflow past Vicksburg, Miss. (MS2), is diverted to the Atchafalaya River (fig. 1) before it reaches St. Francisville, La. (MS1). This diversion influences the loads and trends in loads estimated for the Mississippi River. The Old River Outflow Channel diverts flow from the Mississippi River to the Atchafalaya River to prevent abandonment of the main river channel through New Orleans. The Old River Outflow Channel is operated such that 30 percent of the combined flow of the Atchafalaya and Mississippi Rivers is in the Atchafalaya. This outflow channel discharges to the Atchafalaya River below the confluence of the Red and Black Rivers; the confluence of the outflow channel with the Red River represents the head of the Atchafalaya River. Mississippi River streamflow and nutrients measured below the diversion are reduced and Atchafalaya River streamflow and nutrients measured below the outflow channel are increased by this diversion. The relative contribution of nutrients from the outflow channel to the Atchafalaya River was estimated using the daily load computed for the Mississippi River. The daily nutrient load estimated for the Mississippi River was divided by the corresponding daily mean streamflow to obtain daily nutrient concentration for the Mississippi River. Daily load in the outflow channel was computed by multiplying these concentrations by the daily mean discharge in the outflow channel and then summing the daily values to annual totals. The differences between the loads estimated for the Atchafalaya River and for the outflow channel represent the nutrient contributions from the Red River.

The Mississippi River station MS1 is near the outflow channel diversion, so concentrations in the Mississippi River at that station can be considered representative of the concentrations in the outflow chan-



**Table 7.** Mean annual streamflow and nutrient inflows for the Mississippi River, Atchafalaya River, Old River Outflow Channel, and Red River, 1978–93 (Dunn, 1996, table 7)

[acre-ft, acre-feet; ton/mi<sup>2</sup>, tons per square mile; --, not computed]

	Mean annual streamflow (acre-ft)	Annual total nitrogen inflows		Annual total phosphorus inflows	
		Load (tons)	Yield (ton/mi <sup>2</sup> )	Load (tons)	Yield (ton/mi <sup>2</sup> )
Mississippi River	396,000,000	1,340,000	<sup>1</sup> 1.51	112,000	<sup>1</sup> 0.127
Atchafalaya River	170,000,000	474,000	--	47,800	--
Old River Outflow Channel	108,500,000	364,000	--	30,700	--
Red River	61,500,000	110,000	<sup>2</sup> 1.18	17,100	<sup>2</sup> .183

<sup>1</sup> The yields for the Mississippi River are computed as the sum of the loads computed for the Mississippi River and the Old River Outflow Channel, divided by the drainage area above the Mississippi River station. The resulting figures represent the yields from the Mississippi River Basin without a diversion to the Atchafalaya River.

<sup>2</sup> The yields for the Red River are computed as the difference between the loads computed for the Atchafalaya River and the Old River Outflow Channel, divided by the drainage area above the Atchafalaya River station. The resulting figures represent the yields from the Red River Basin without the diversion from the Mississippi River.

nel. This assumption could be tenuous due to the adsorption of nutrients, particularly phosphorus, onto sediment particles. The rates of sediment transport in the Mississippi River and the outflow channel are not proportional to the discharges in the respective channels, and the effects of this phenomenon on nutrient inflows is difficult to determine with the available data. The mean of the annual loads estimated for the outflow channel and the Red River, however, are assumed to represent the long-term mean annual nutrient inflows to the Atchafalaya River from those two channels for the period analyzed. The mean annual loads of total nitrogen and total phosphorus in the Atchafalaya River contributed from the Old River Outflow Channel represent about 70 percent of the total load of each constituent in that river. Estimates of mean annual streamflow and annual loads and yields of total nitrogen and total phosphorus (for 1978–93) for the Mississippi River, Atchafalaya River, Old River Outflow Channel, and Red River as reported by Dunn (1996) are shown in table 7.

## SUMMARY AND CONCLUSIONS

Trends in nutrient concentration and load (total nitrogen and total phosphorus) from 40 stations throughout the Mississippi Basin are presented. The period analyzed varies for each streamflow station, but generally includes WYs 1974–94. Short-term trends for each station are indicated by LOWESS smooth lines superimposed on graphs of the relations between flow-

adjusted residuals of concentrations and time and between load and time. Long-term trends were evaluated using Kendall's tau and the slope of the Kendall-Theil robust line. Long-term trends for each station are indicated by Kendall-Theil robust lines superimposed on the aforementioned graphs.

The relation between nutrient concentrations and streamflow, and trends in annual streamflow, are presented to aid in the interpretation of trends in nutrient loads at each station. Statistically significant long-term trends in streamflow were detected at seven stations. However, the trends in streamflow, even where not statistically significant, have a substantial effect on the trends in annual nutrient load.

Nutrient concentrations were flow-adjusted to remove the effects of streamflow, and the flow-adjusted residuals of concentrations were tested for long-term trend. Significant long-term increases in flow-adjusted residuals of total nitrogen concentration were detected at 14 stations, significant decreases were detected at 6 stations, and no long-term trends were detected at 20 stations. Significant long-term increases in flow-adjusted residuals of total phosphorus concentration were detected at 2 stations, significant decreases were detected at 25 stations, and no long-term trends were detected at 13 stations.

Annual loads of total nitrogen and total phosphorus were estimated using a regression technique. Load estimates were corrected for log-transform bias

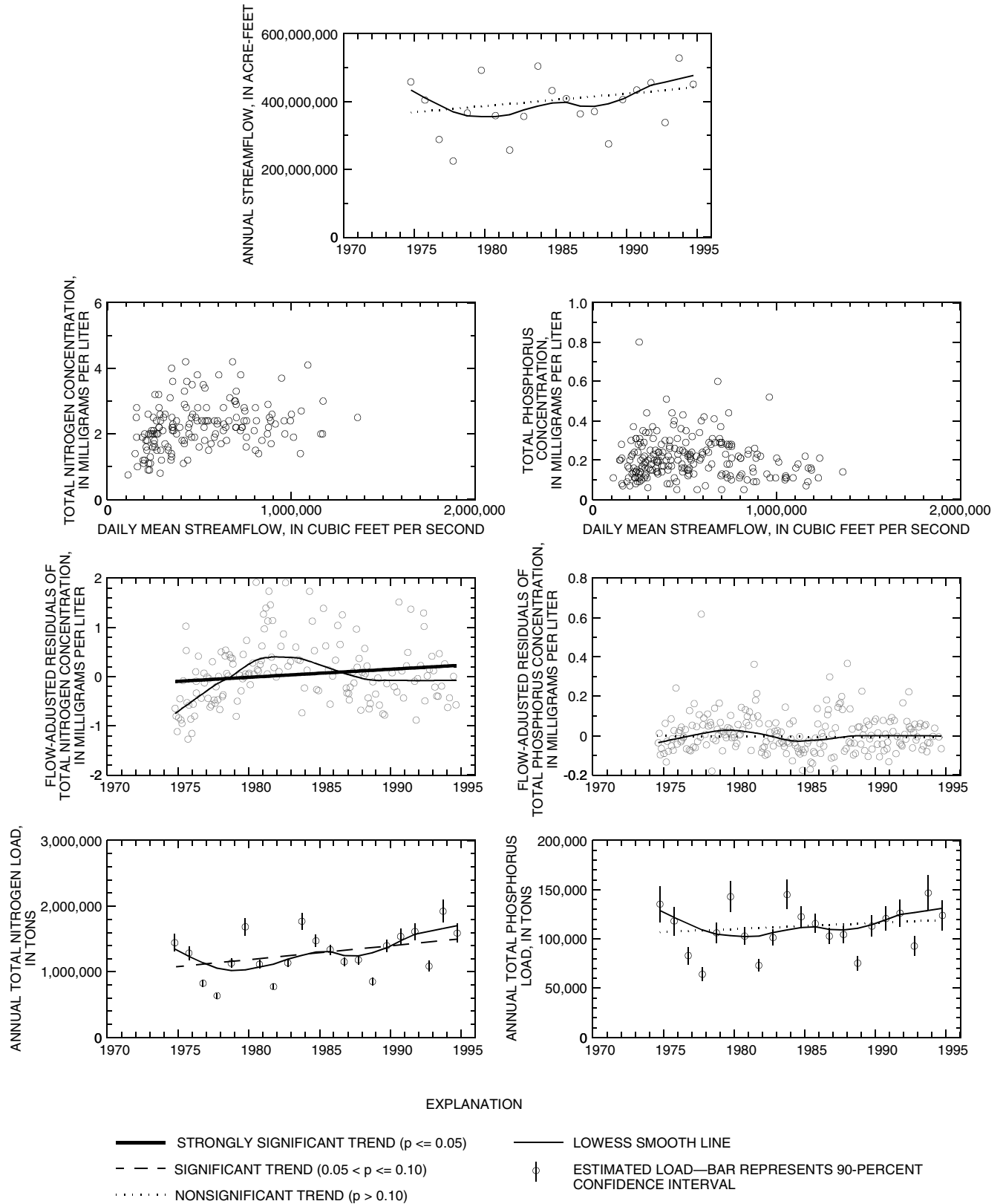
using the Minimum Variance Unbiased Estimator (MVUE). Explanatory variables used in the regression are logarithm of daily mean streamflow; time, in decimal years; and sine and cosine of time, in decimal years. Trends estimated using Kendall's tau generally agree with trends estimated using the sign and attained significance level (p-value) of the regression coefficient for time.

Significant long-term increases in estimated annual total nitrogen loads were detected at 5 stations, significant decreases were detected at 4 stations, and no long-term trends were detected at 31 stations. Significant long-term increases in estimated annual total phosphorus loads were detected at 1 station, significant decreases were detected at 13 stations, and no long-term trends were detected at 26 stations. The mean annual yields were computed from the estimated mean annual loads. Mean annual total nitrogen yields are largest for three watersheds in the upper Mississippi Basin; estimated yield of each is greater than 5.0 ton/mi<sup>2</sup>. Nine stations in the Ohio Basin have estimated mean annual total nitrogen yields greater than 2.0 ton/mi<sup>2</sup>. Estimated mean annual phosphorus yield is greater than 0.250 ton/mi<sup>2</sup> at 7 sites, 5 in the Ohio Basin and 2 in the upper Mississippi Basin.

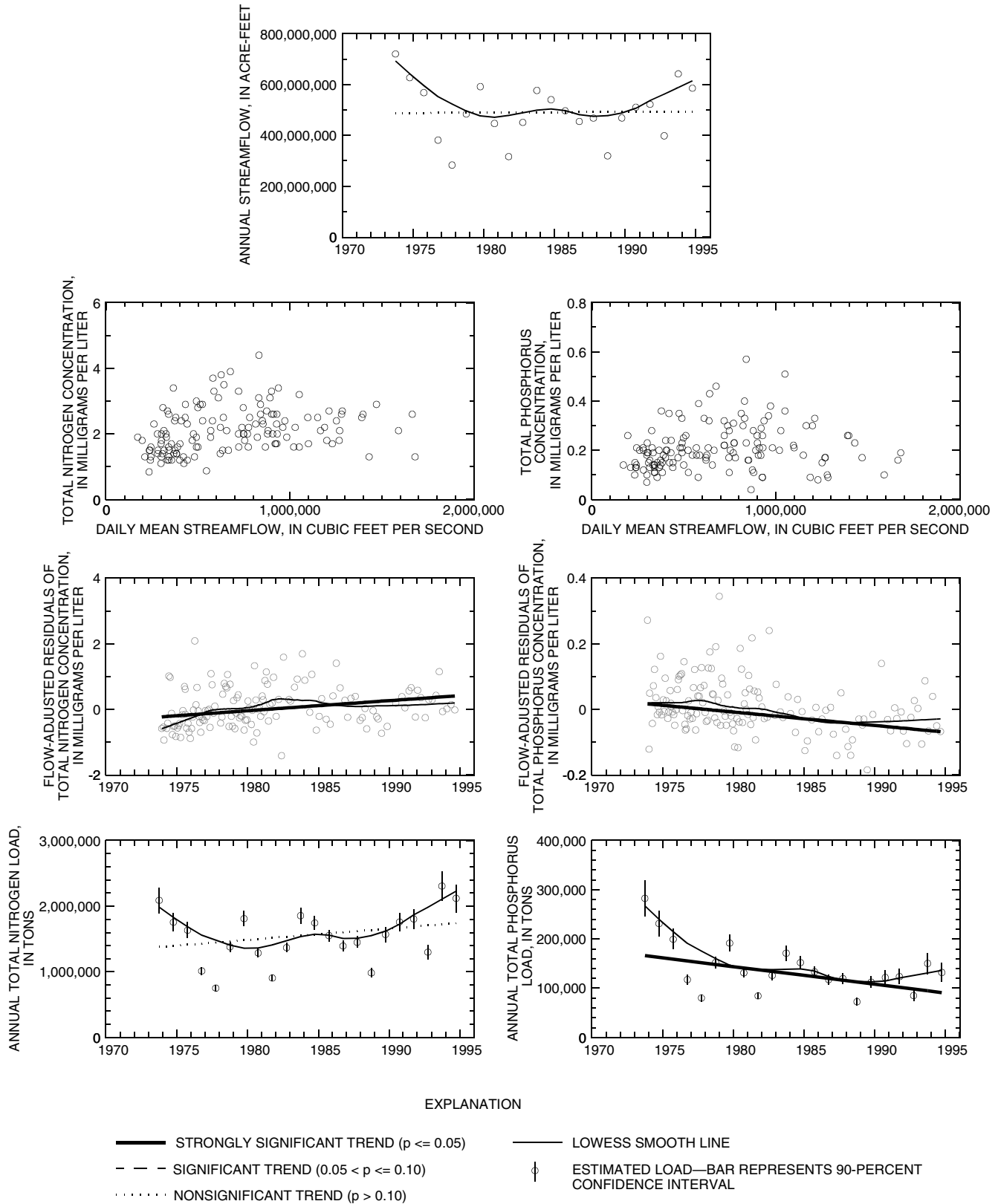
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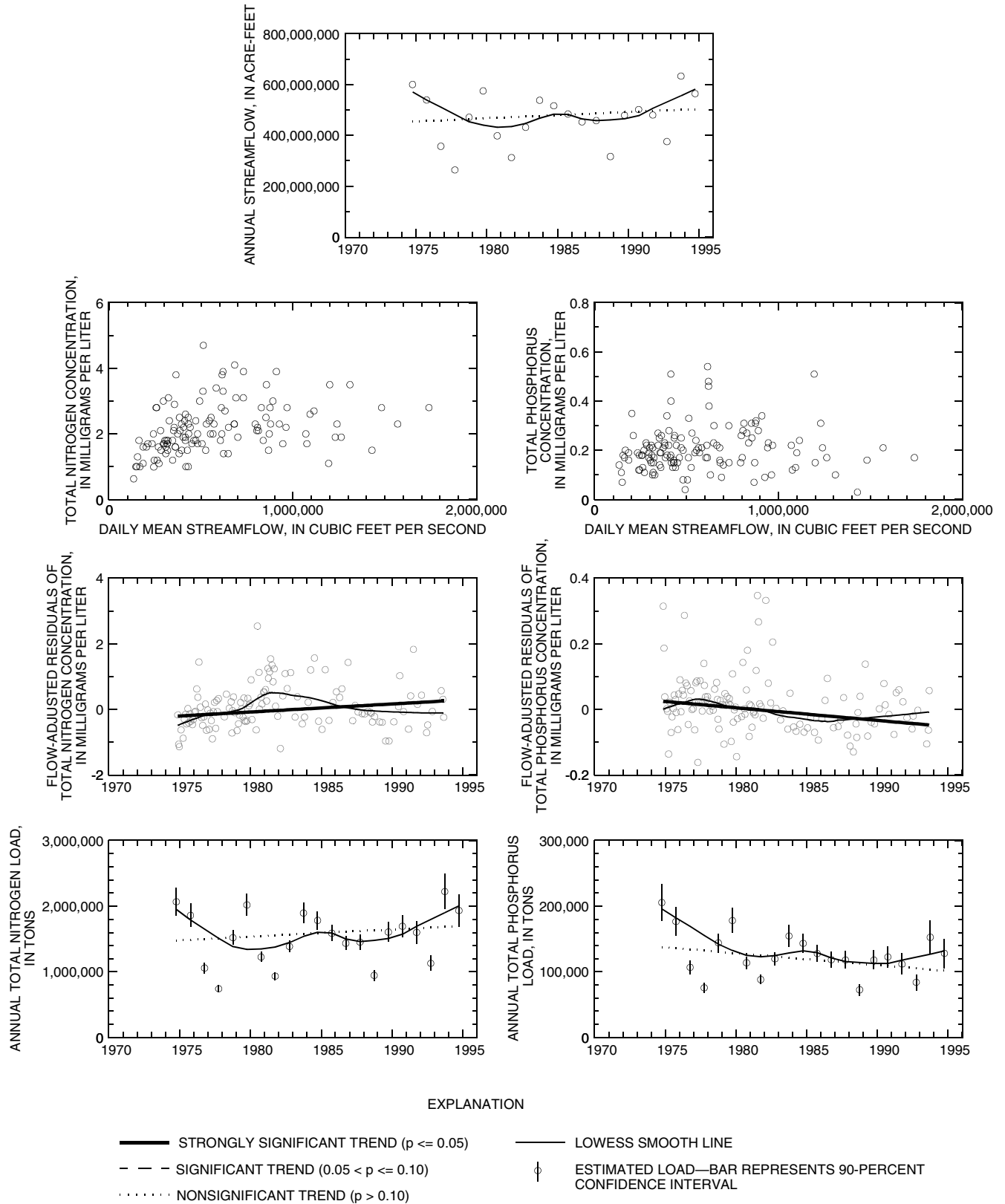
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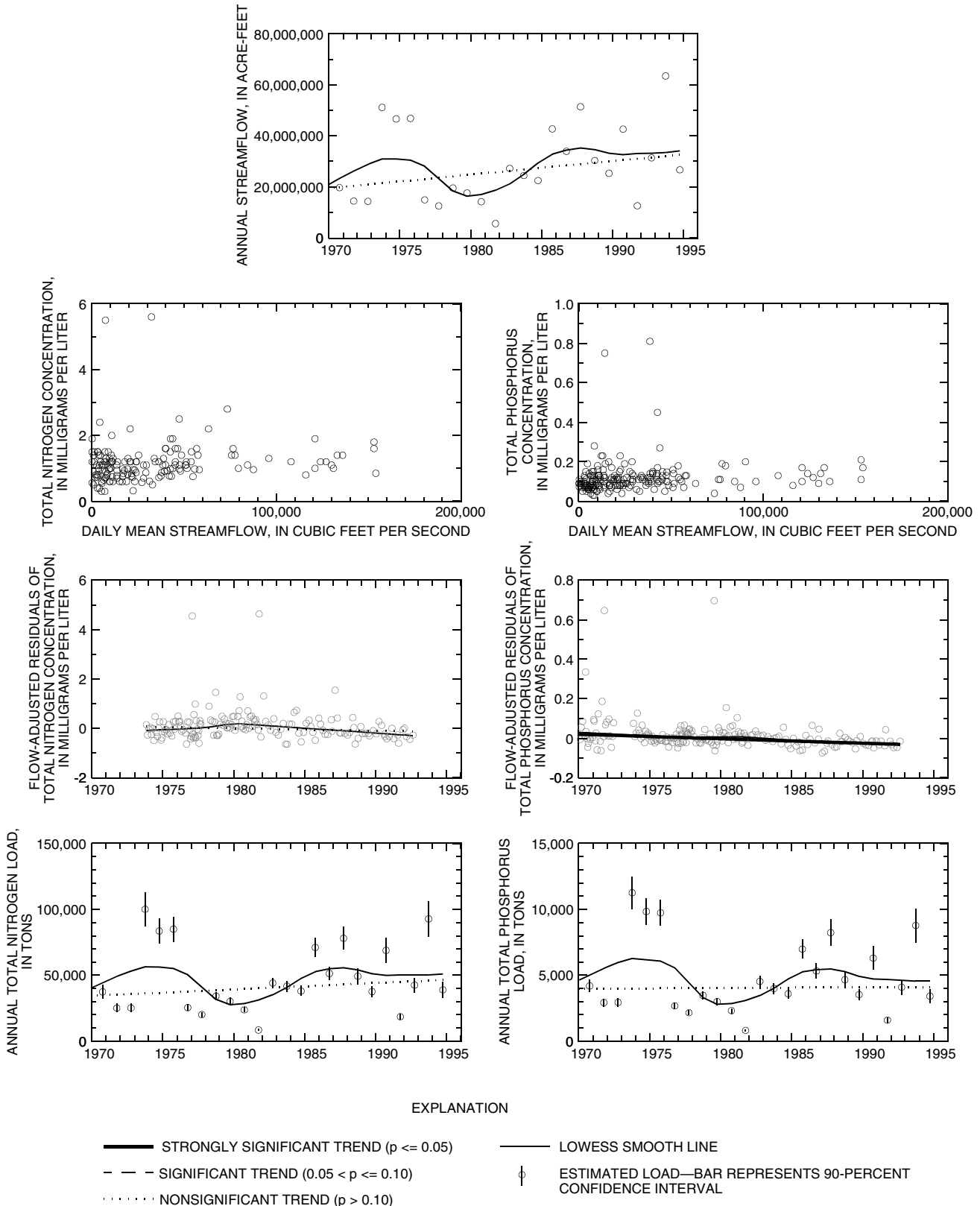
**Figure 6.** Relation of total nitrogen and total phosphorus concentration to daily mean streamflow and temporal trends in annual streamflow, in flow-adjusted residuals of total nitrogen and total phosphorus concentration, and in estimated annual total nitrogen and total phosphorus loads for Mississippi River, La. (MS1) (07373420).



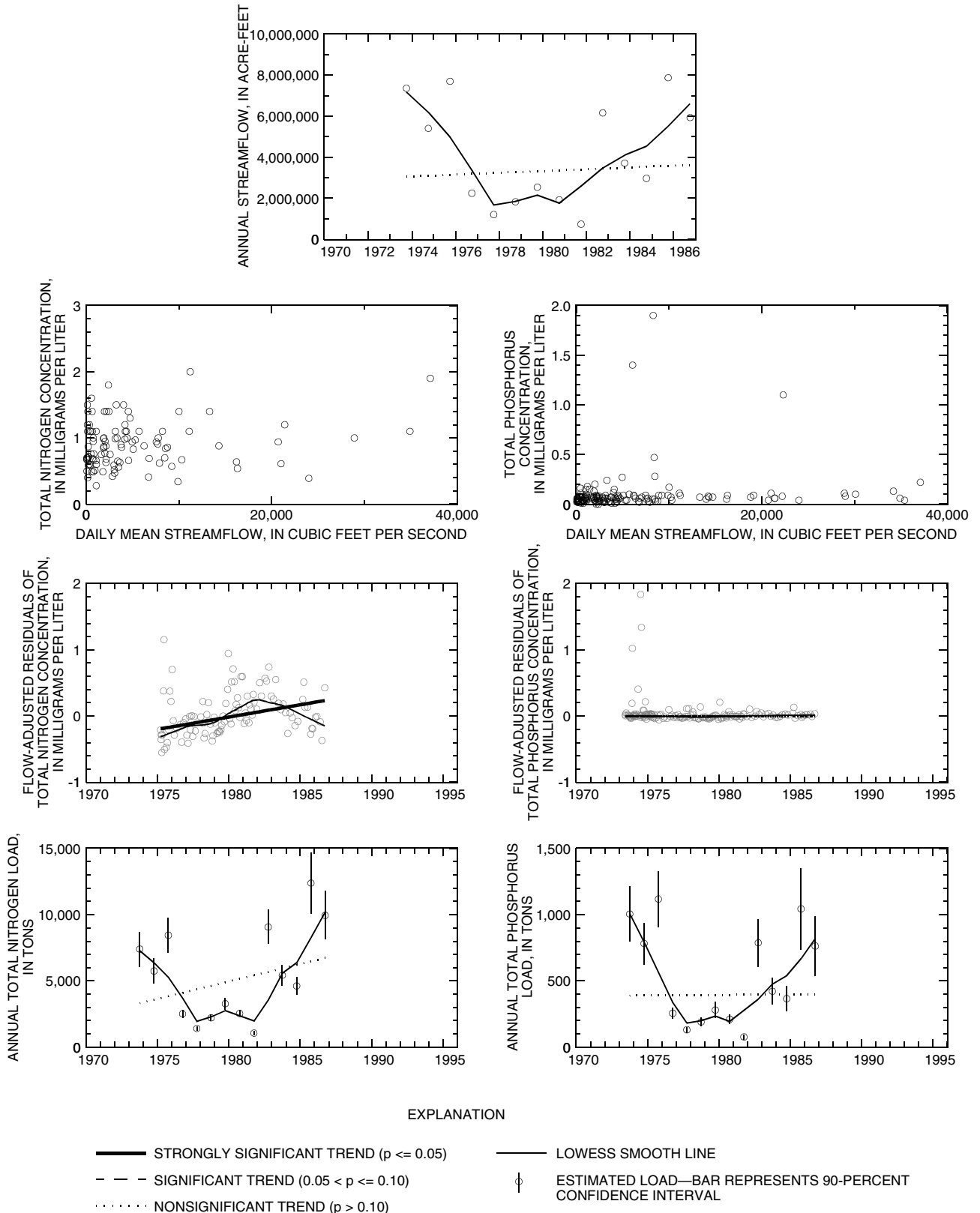
**Figure 7.** Relation of total nitrogen and total phosphorus concentration to daily mean streamflow and temporal trends in annual streamflow, in flow-adjusted residuals of total nitrogen and total phosphorus concentration, and in estimated annual total nitrogen and total phosphorus loads for Mississippi River, Miss. (MS2) (07289000).



**Figure 8.** Relation of total nitrogen and total phosphorus concentration to daily mean streamflow and temporal trends in annual streamflow, in flow-adjusted residuals of total nitrogen and total phosphorus concentration, and in estimated annual total nitrogen and total phosphorus loads for Mississippi River, Ark. (MS3) (07265450).

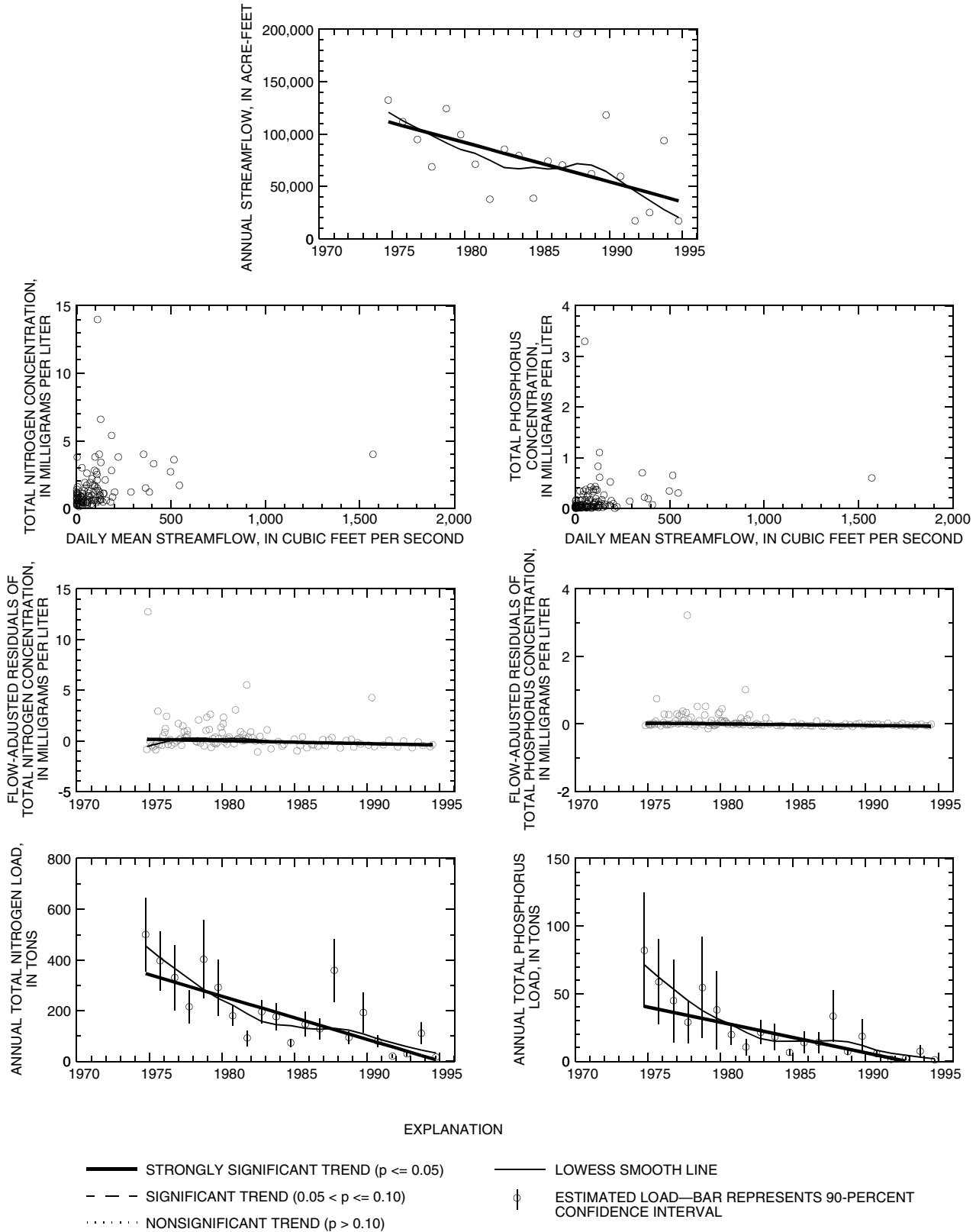


**Figure 9.** Relation of total nitrogen and total phosphorus concentration to daily mean streamflow and temporal trends in annual streamflow, in flow-adjusted residuals of total nitrogen and total phosphorus concentration, and in estimated annual total nitrogen and total phosphorus loads for Arkansas River, Ark. (ARK) (07250550).

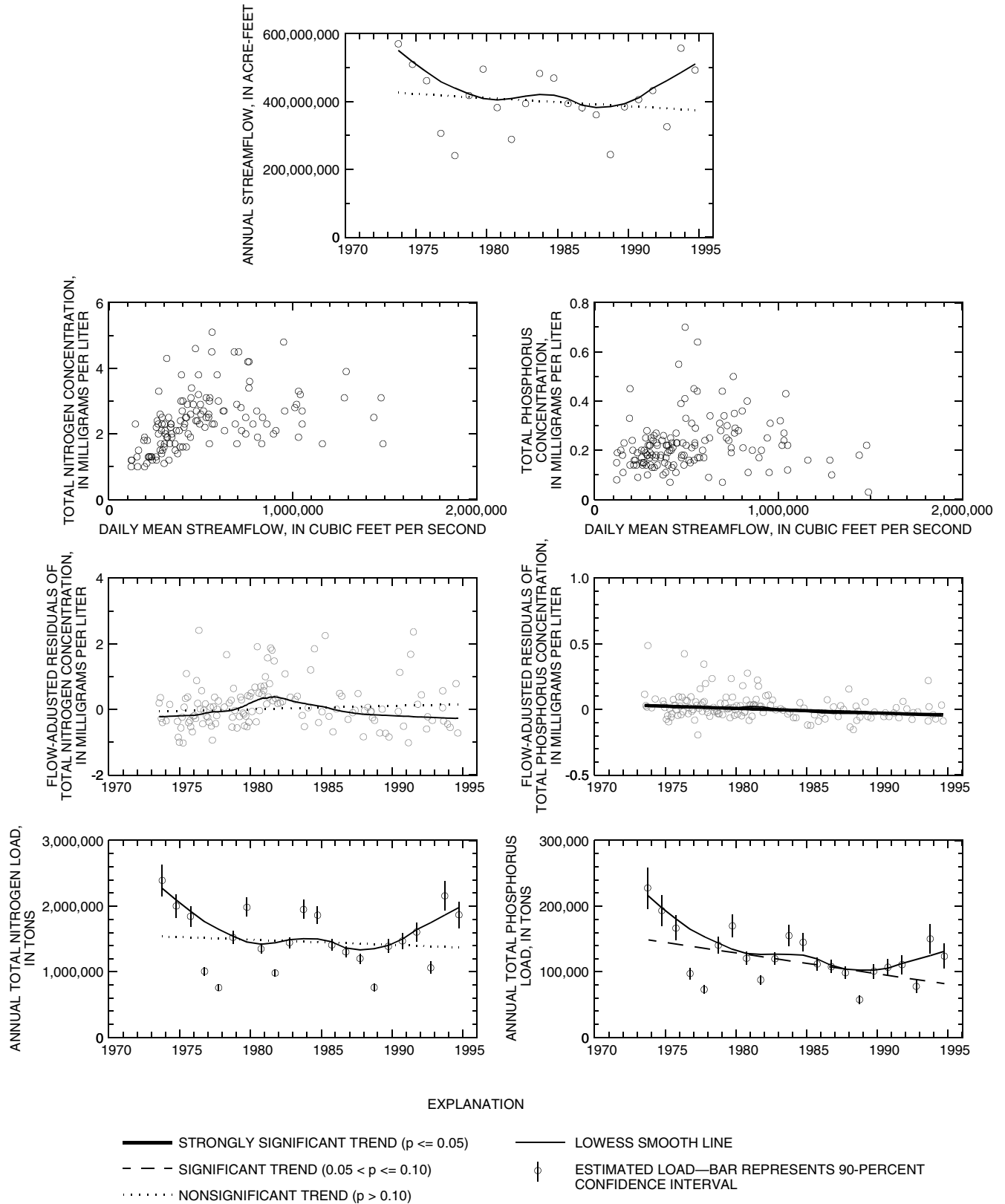


**Figure 10.** Relation of total nitrogen and total phosphorus concentration to daily mean streamflow and temporal trends in annual streamflow, in flow-adjusted residuals of total nitrogen and total phosphorus concentration, and in estimated annual total nitrogen and total phosphorus loads for Canadian River, Okla. (CAN) (07245000).

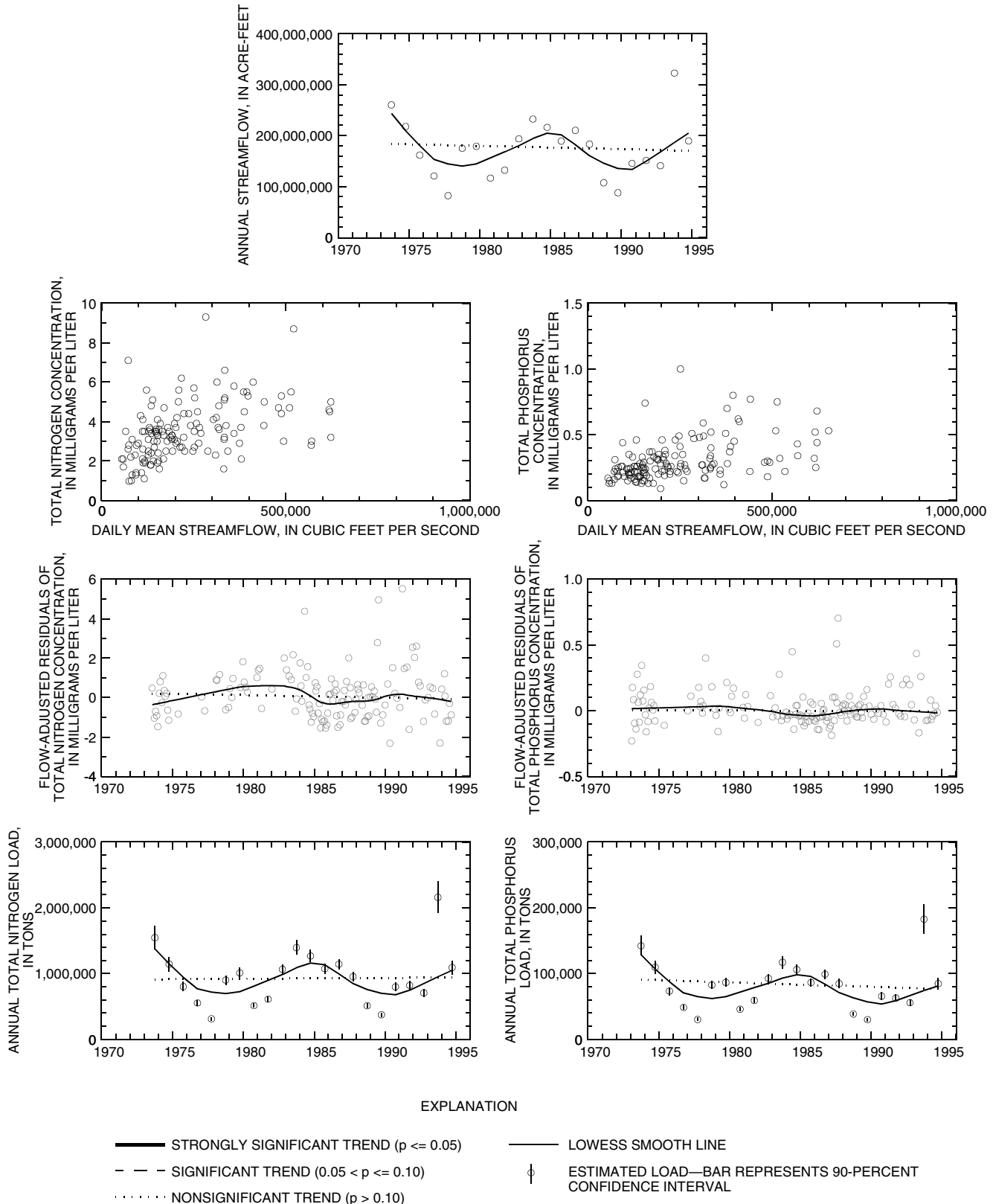




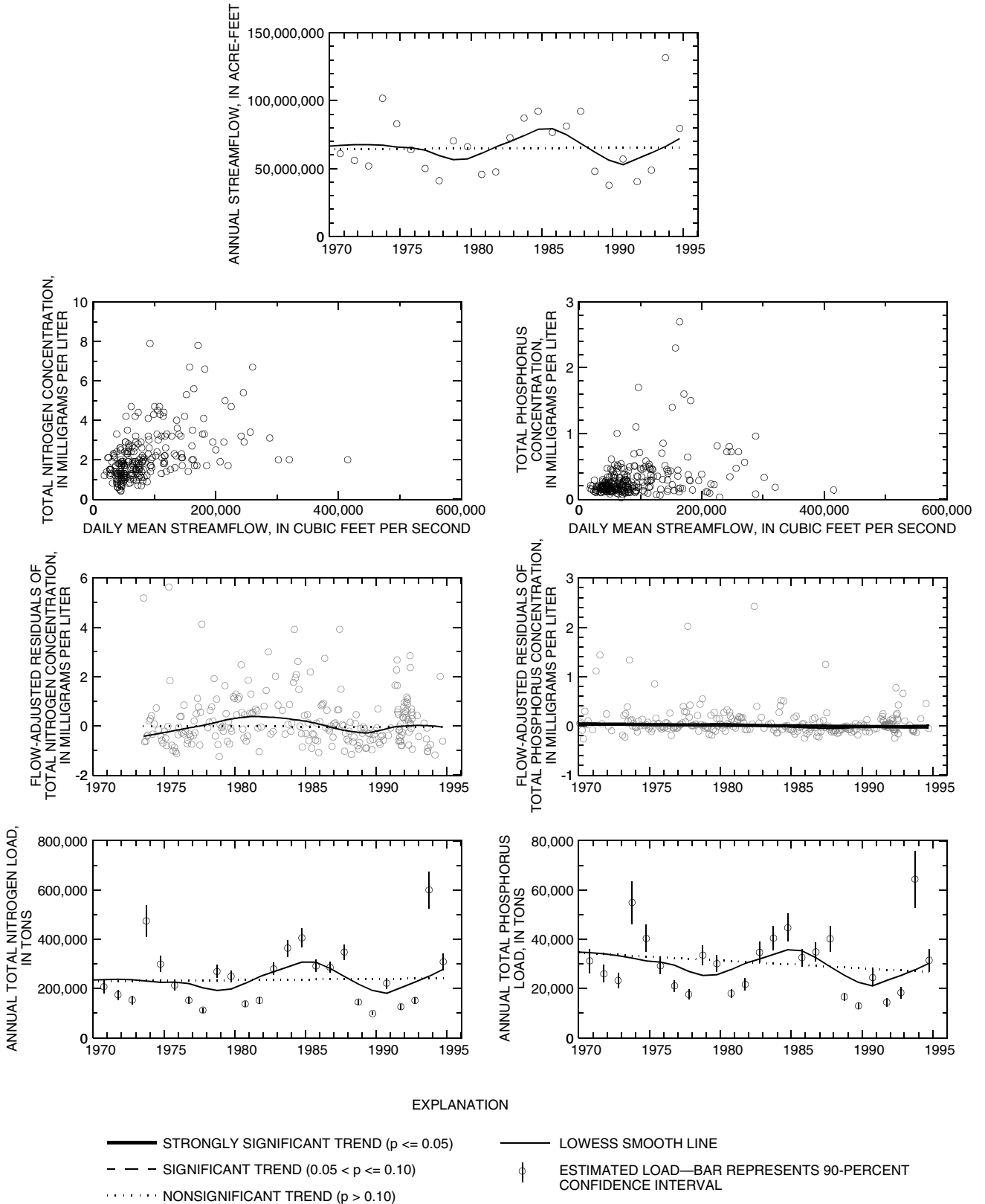
**Figure 11.** Relation of total nitrogen and total phosphorus concentration to daily mean streamflow and temporal trends in annual streamflow, in flow-adjusted residuals of total nitrogen and total phosphorus concentration, and in estimated annual total nitrogen and total phosphorus loads for Cimarron River, Okla. (CIM) (07157950).



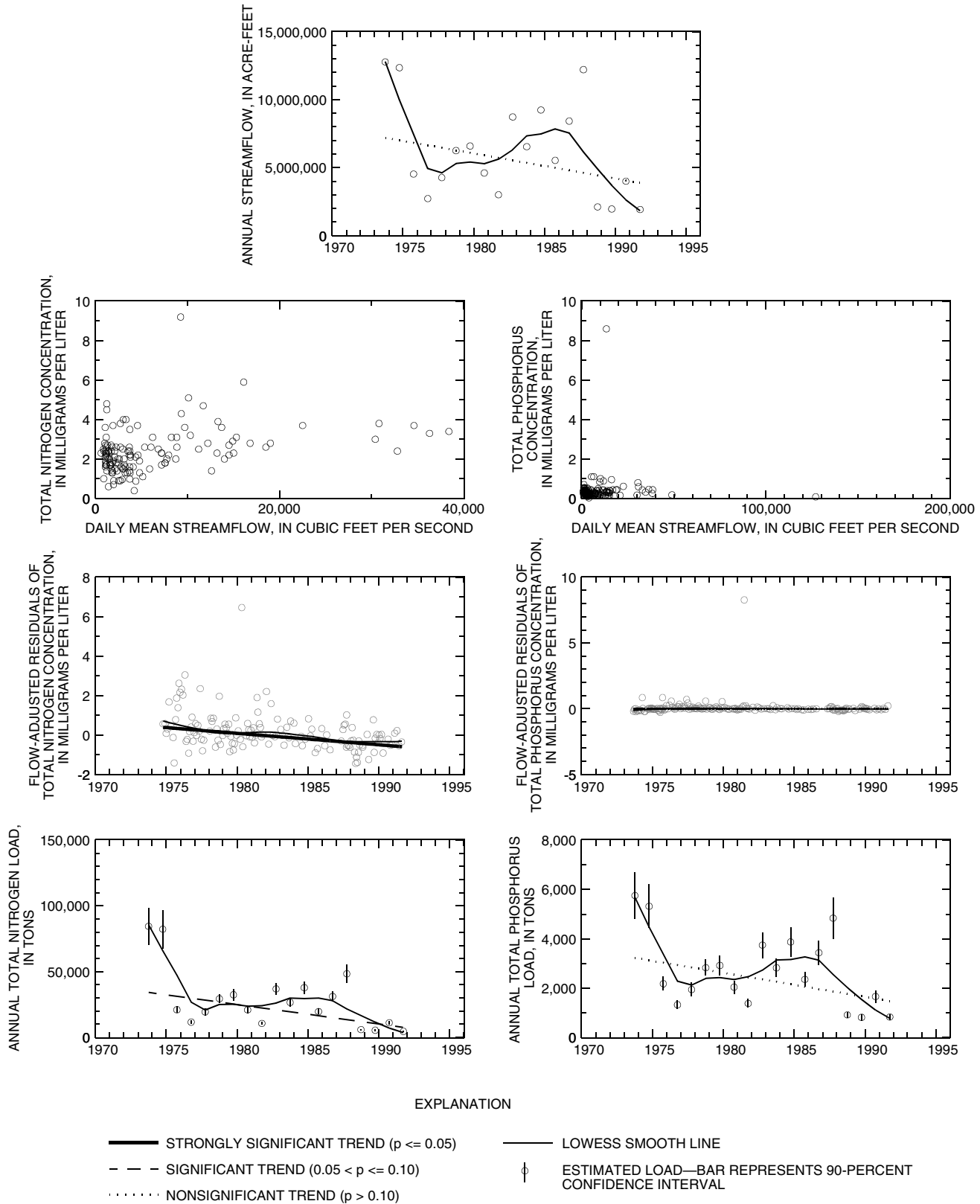
**Figure 12.** Relation of total nitrogen and total phosphorus concentration to daily mean streamflow and temporal trends in annual streamflow, in flow-adjusted residuals of total nitrogen and total phosphorus concentration, and in estimated annual total nitrogen and total phosphorus loads for Mississippi River, Tenn. (MS4) (07032000).



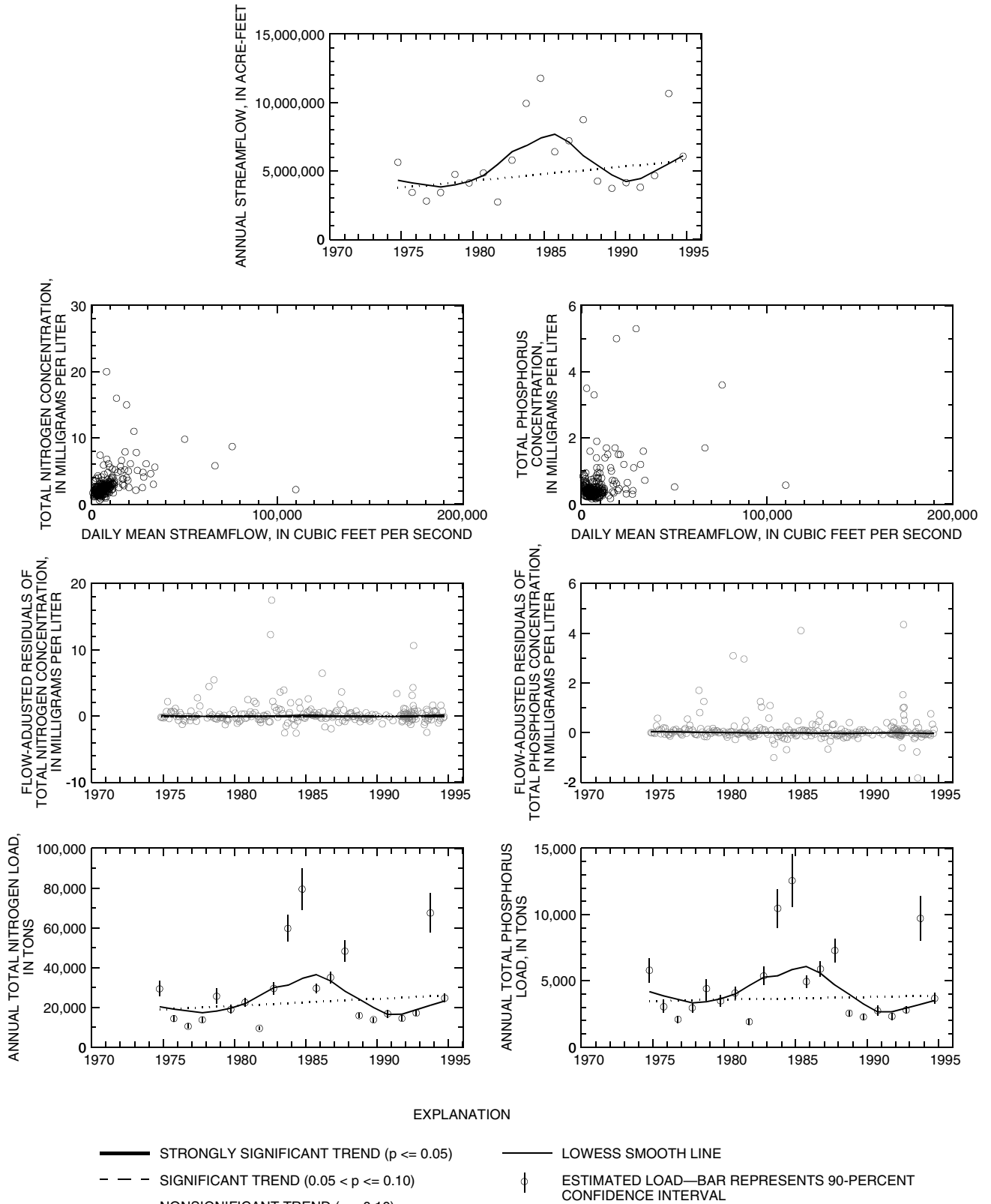
**Figure 13.** Relation of total nitrogen and total phosphorus concentration to daily mean streamflow and temporal trends in annual streamflow, in flow-adjusted residuals of total nitrogen and total phosphorus concentration, and in estimated annual total nitrogen and total phosphorus loads for Mississippi River, Ill. (MS5) (07022000).



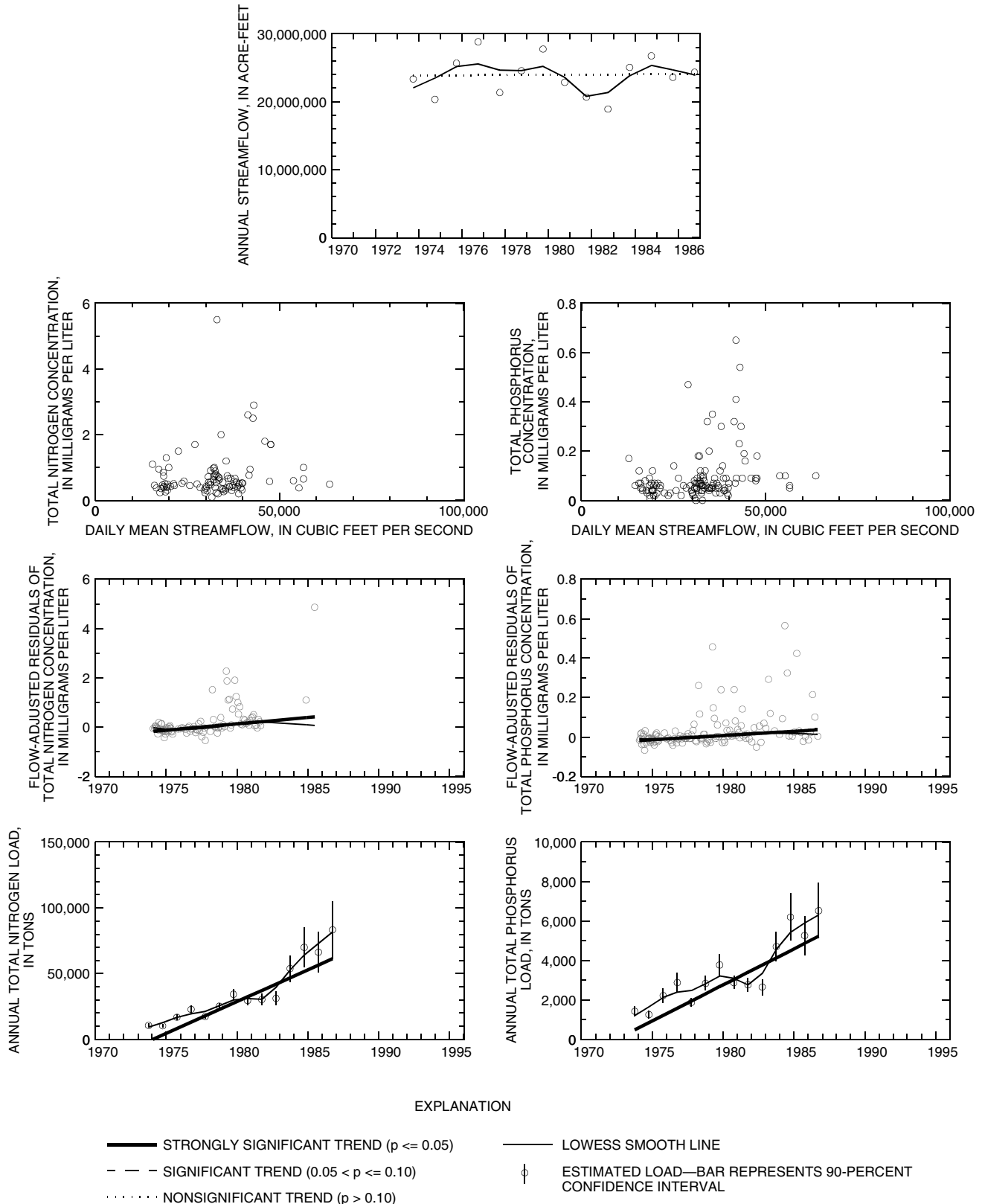
**Figure 14.** Relation of total nitrogen and total phosphorus concentration to daily mean streamflow and temporal trends in annual streamflow, in flow-adjusted residuals of total nitrogen and total phosphorus concentration, and in estimated annual total nitrogen and total phosphorus loads for Missouri River, Mo. (MO1) (06934500).



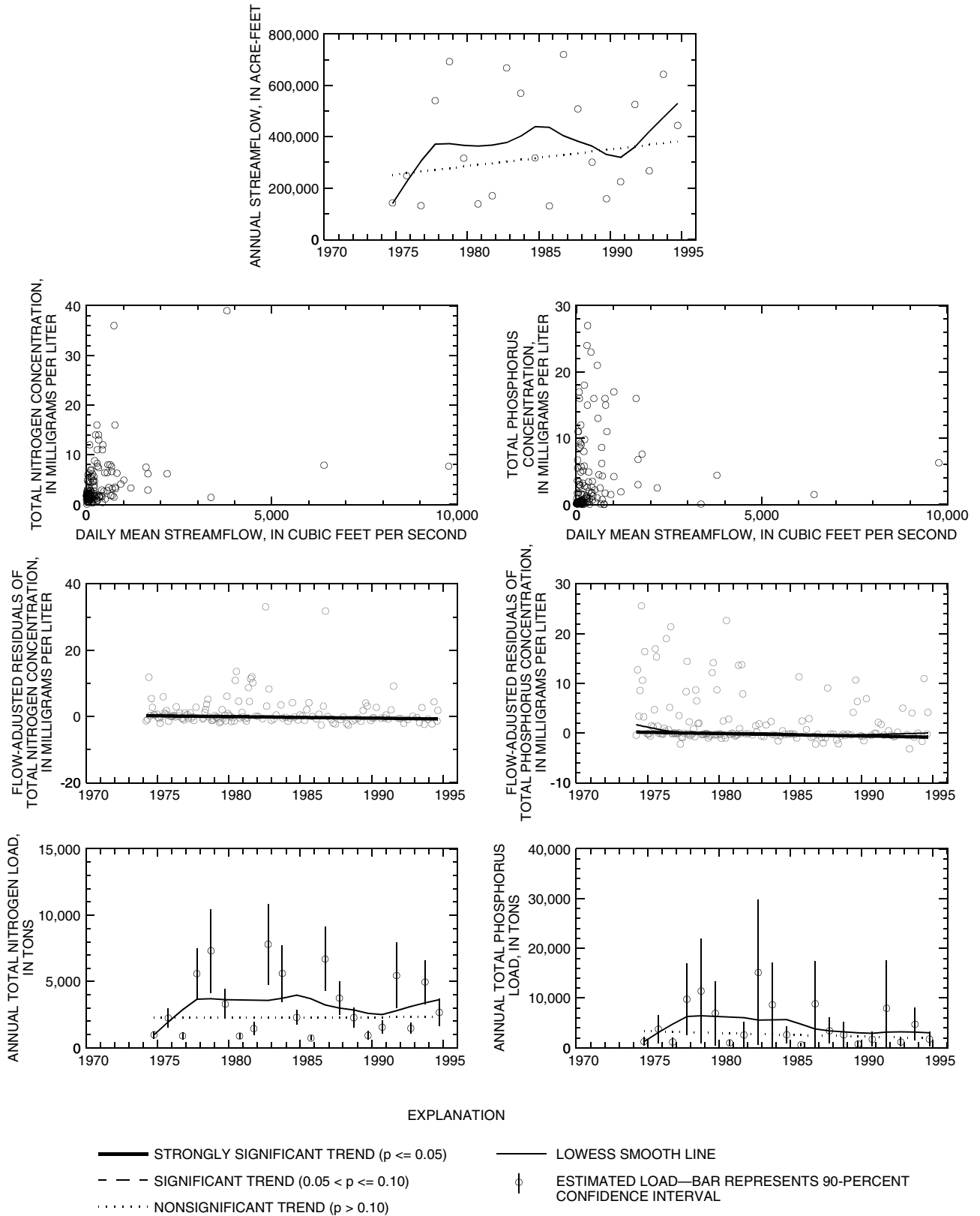
**Figure 15.** Relation of total nitrogen and total phosphorus concentration to daily mean streamflow and temporal trends in annual streamflow, in flow-adjusted residuals of total nitrogen and total phosphorus concentration, and in estimated annual total nitrogen and total phosphorus loads for Kansas River, Kans. (KAN) (06892350).



**Figure 16.** Relation of total nitrogen and total phosphorus concentration to daily mean streamflow and temporal trends in annual streamflow, in flow-adjusted residuals of total nitrogen and total phosphorus concentration, and in estimated annual total nitrogen and total phosphorus loads for Platte River, Nebr. (PLT) (06805500).

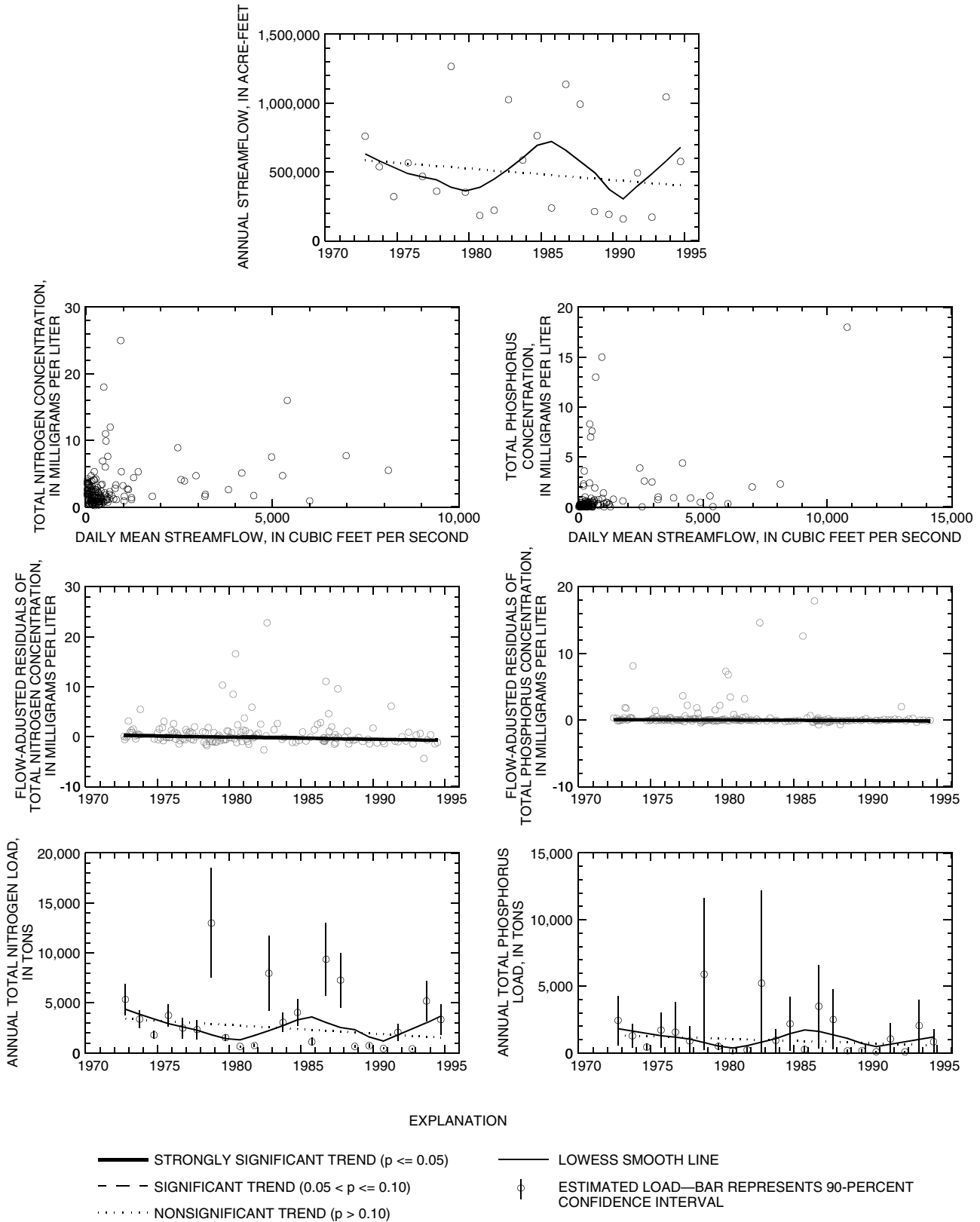


**Figure 17.** Relation of total nitrogen and total phosphorus concentration to daily mean streamflow and temporal trends in annual streamflow, in flow-adjusted residuals of total nitrogen and total phosphorus concentration, and in estimated annual total nitrogen and total phosphorus loads for Missouri River, Iowa (MO2) (06486000).

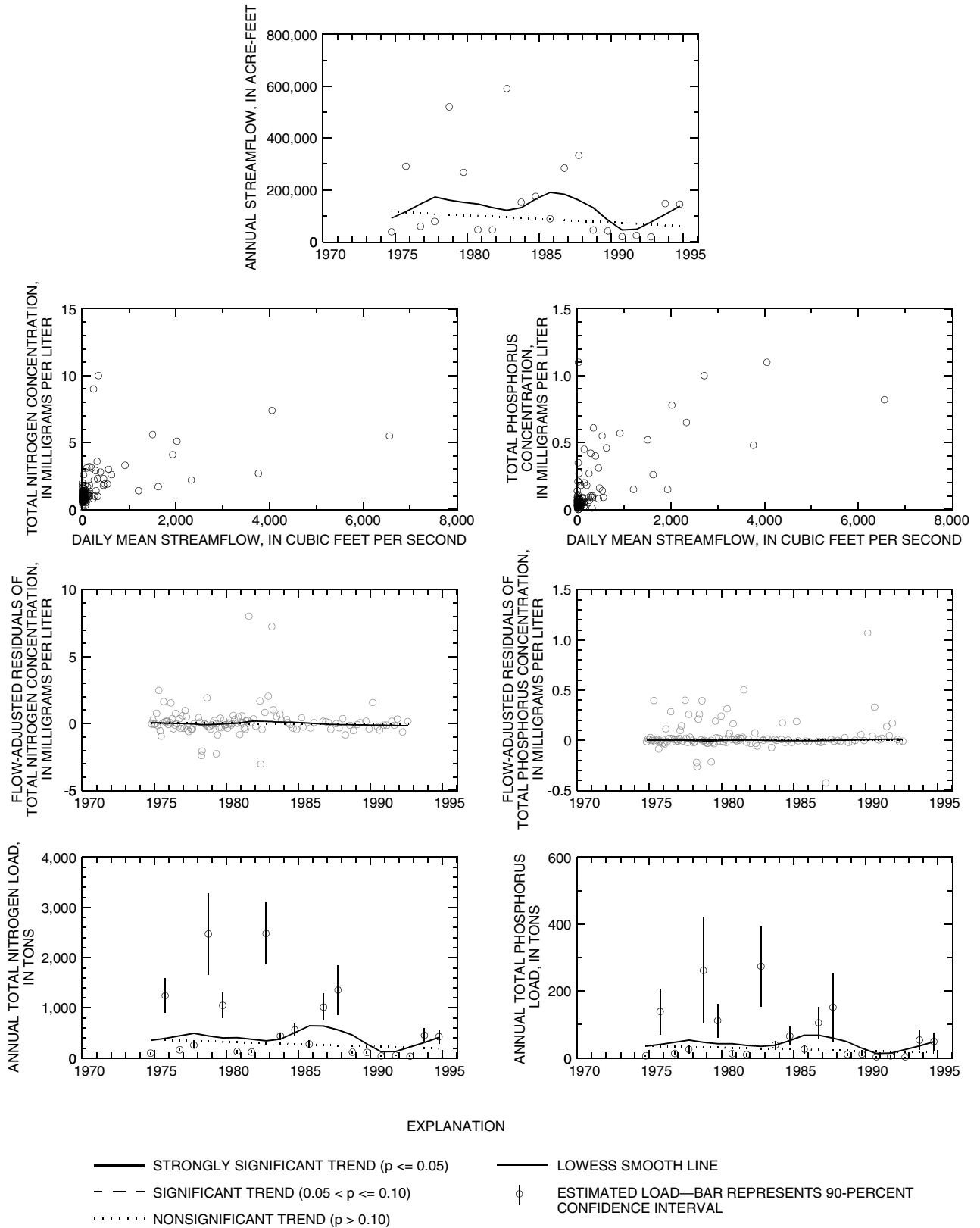


**Figure 18.** Relation of total nitrogen and total phosphorus concentration to daily mean streamflow and temporal trends in annual streamflow, in flow-adjusted residuals of total nitrogen and total phosphorus concentration, and in estimated annual total nitrogen and total phosphorus loads for White River, S. Dak. (WH1) (06452000).

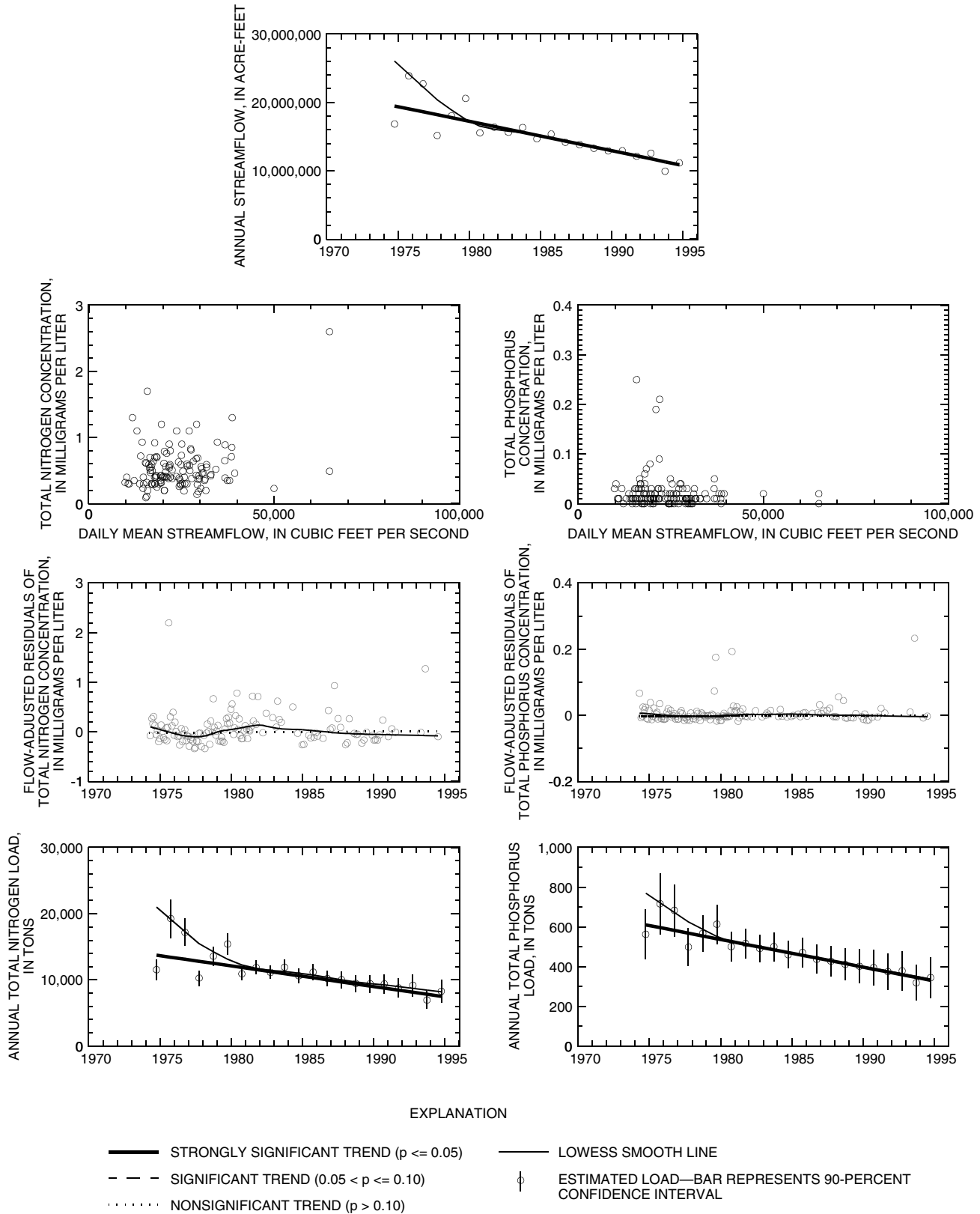




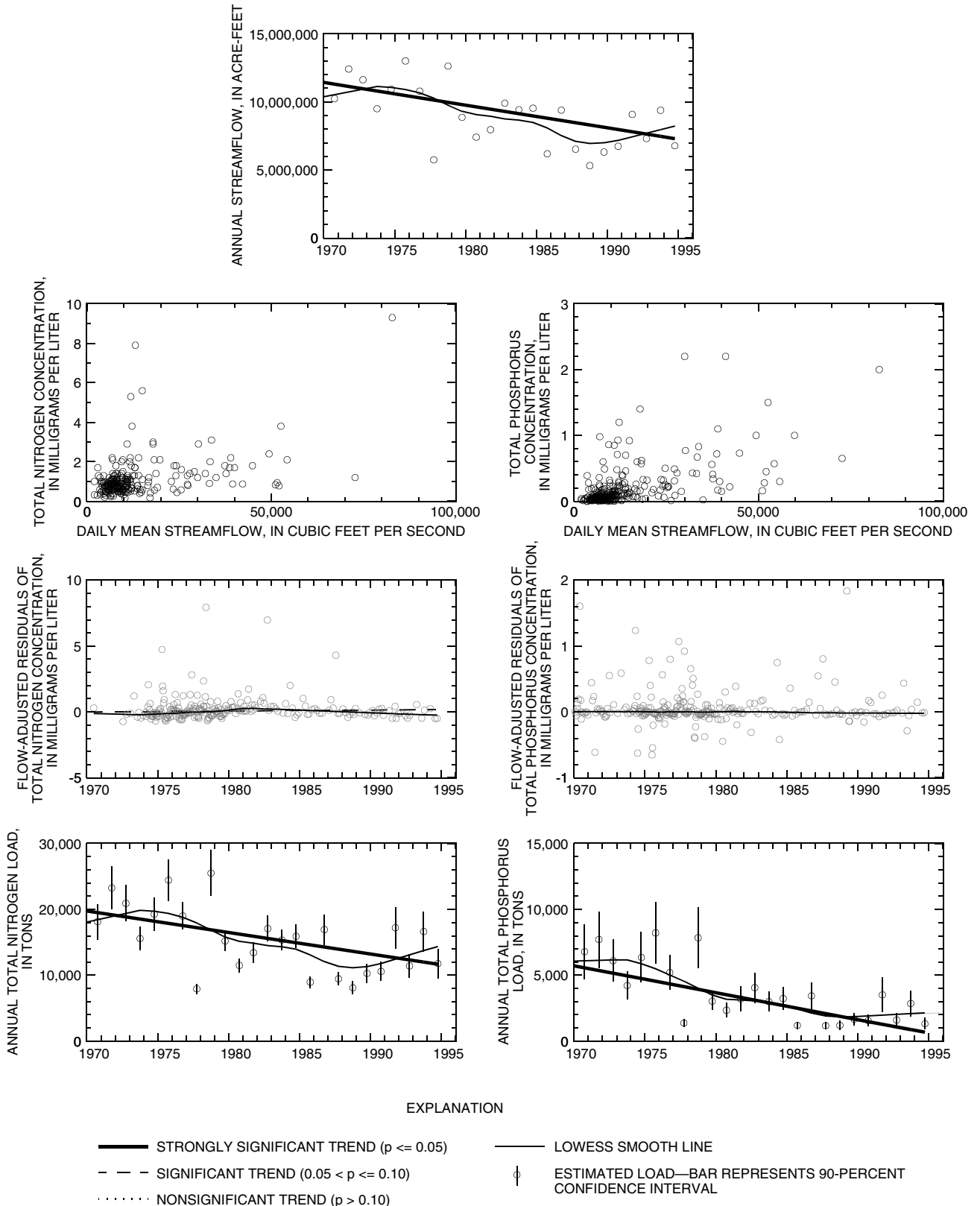
**Figure 19.** Relation of total nitrogen and total phosphorus concentration to daily mean streamflow and temporal trends in annual streamflow, in flow-adjusted residuals of total nitrogen and total phosphorus concentration, and in estimated annual total nitrogen and total phosphorus loads for Cheyenne River, S. Dak. (CHY) (06439300).



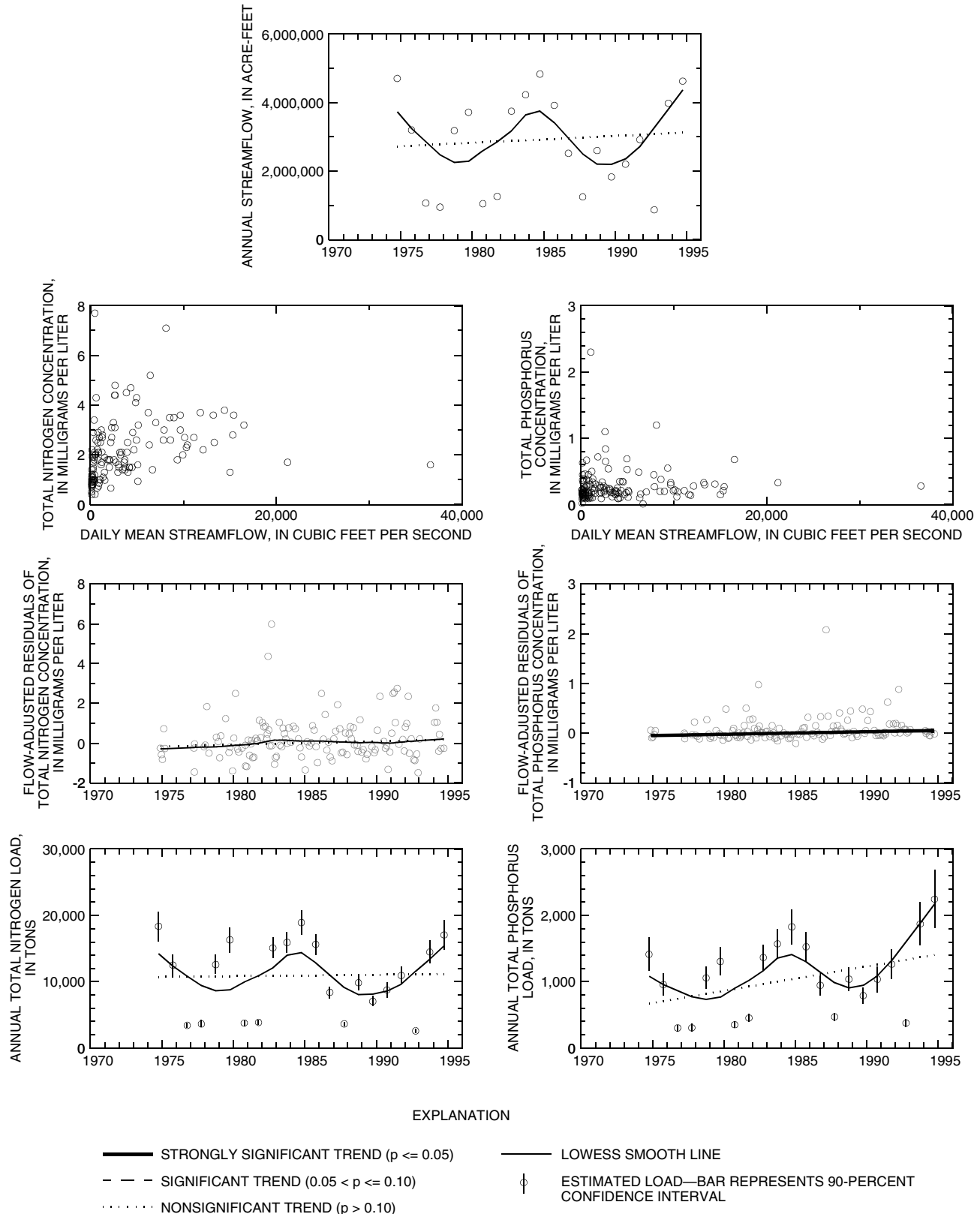
**Figure 20.** Relation of total nitrogen and total phosphorus concentration to daily mean streamflow and temporal trends in annual streamflow, in flow-adjusted residuals of total nitrogen and total phosphorus concentration, and in estimated annual total nitrogen and total phosphorus loads for Cannonball River, N. Dak. (CNB) (06354000).



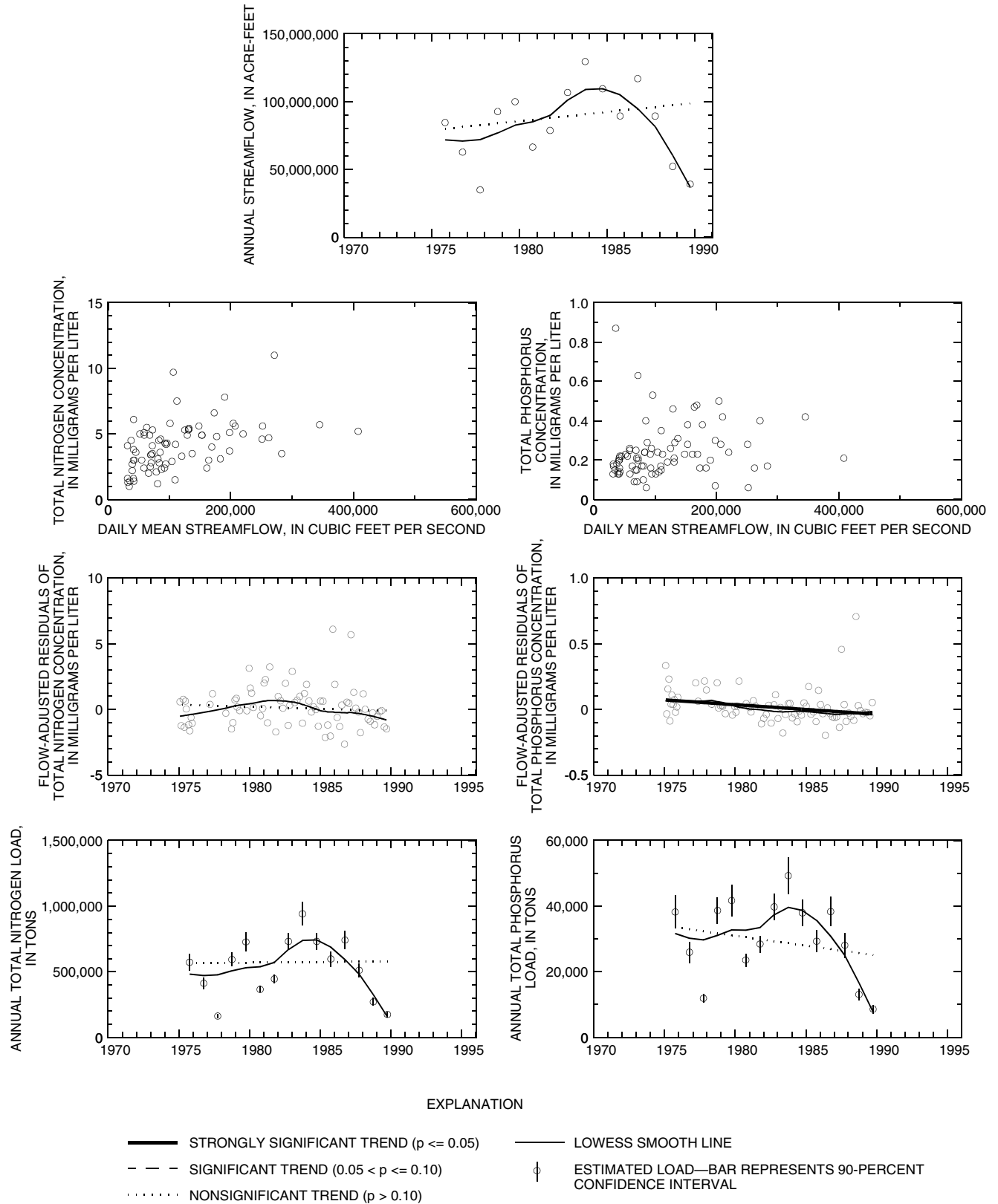
**Figure 21.** Relation of total nitrogen and total phosphorus concentration to daily mean streamflow and temporal trends in annual streamflow, in flow-adjusted residuals of total nitrogen and total phosphorus concentration, and in estimated annual total nitrogen and total phosphorus loads for Missouri River, N. Dak. (MO3) (06338490).



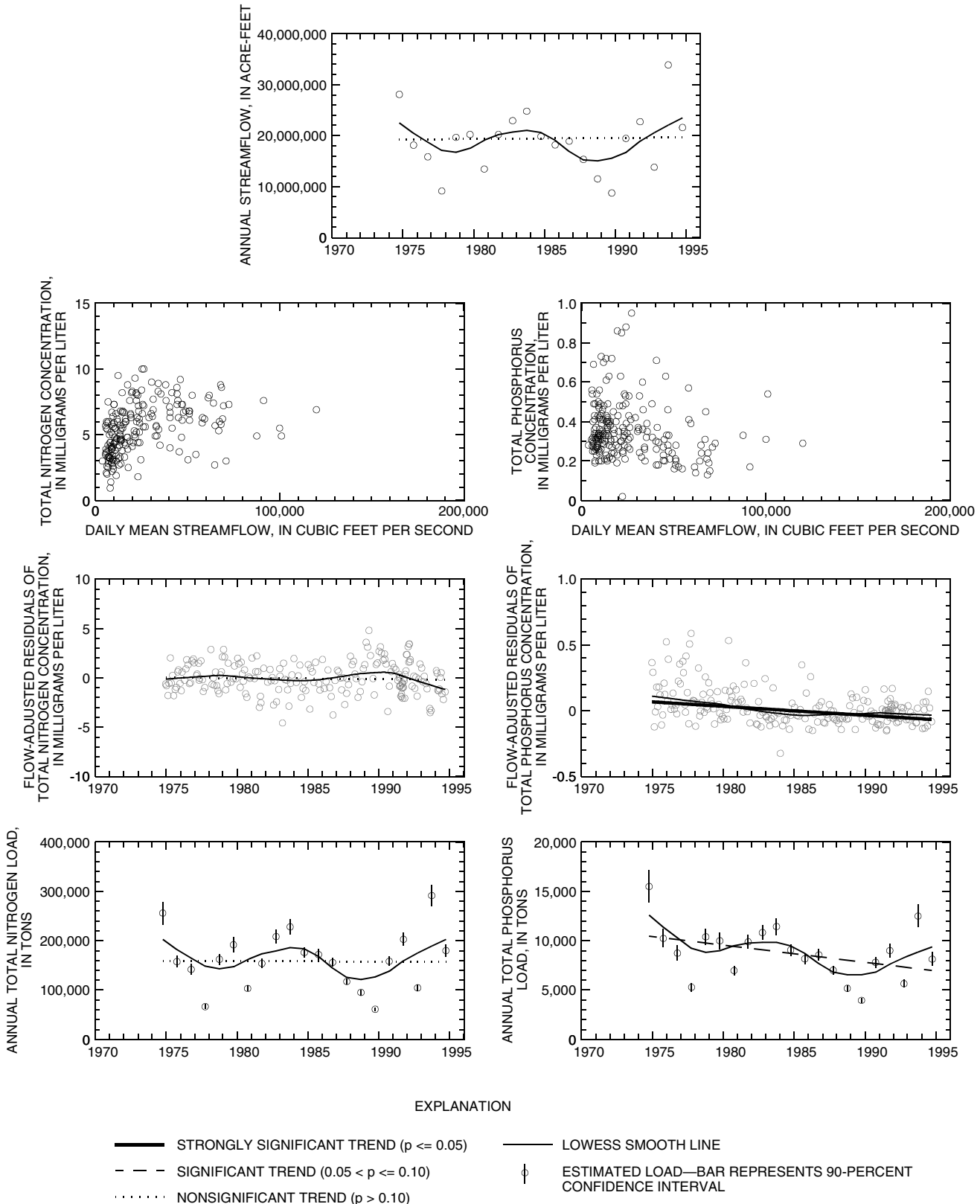
**Figure 22.** Relation of total nitrogen and total phosphorus concentration to daily mean streamflow and temporal trends in annual streamflow, in flow-adjusted residuals of total nitrogen and total phosphorus concentration, and in estimated annual total nitrogen and total phosphorus loads for Yellowstone River, Mont. (YLS) (06329500).



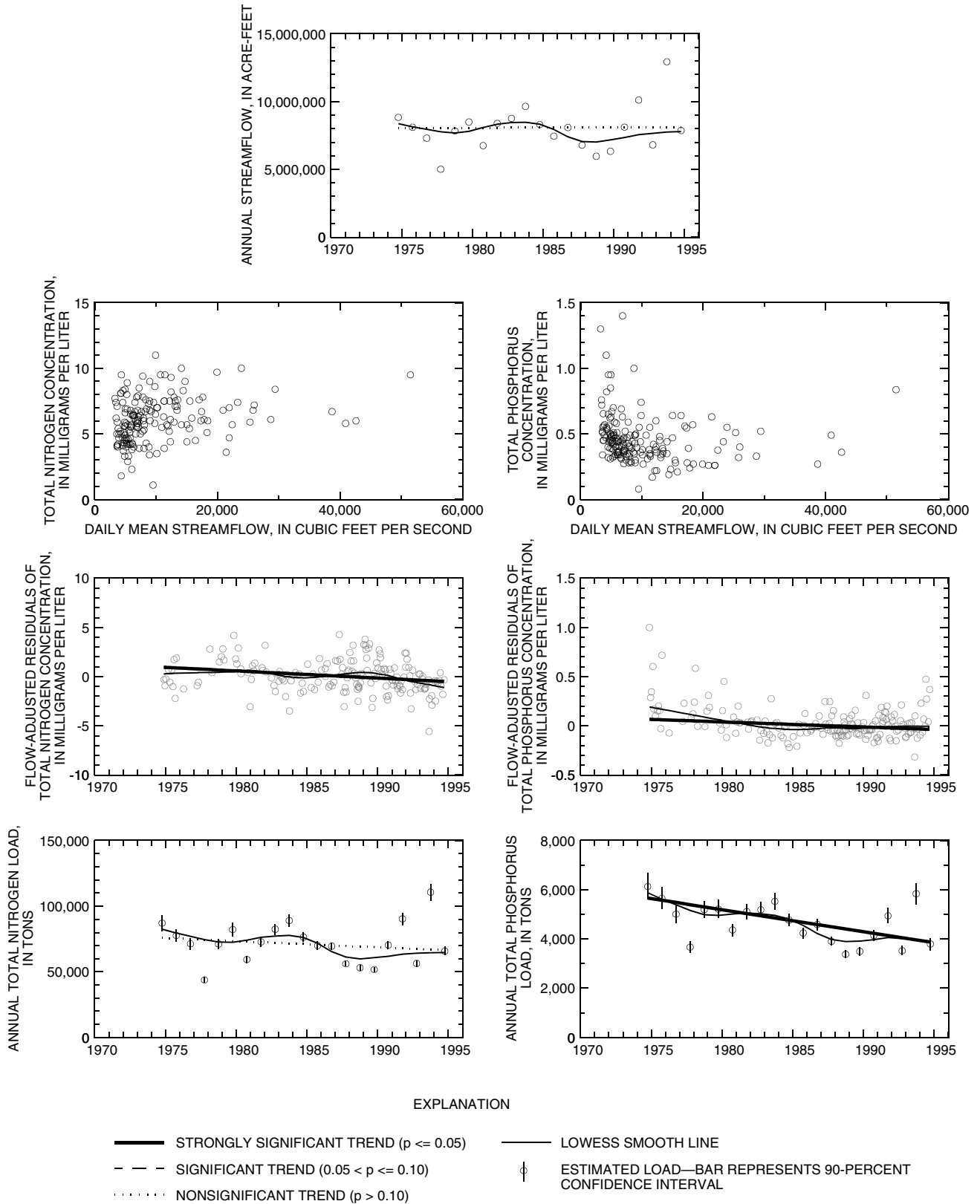
**Figure 23.** Relation of total nitrogen and total phosphorus concentration to daily mean streamflow and temporal trends in annual streamflow, in flow-adjusted residuals of total nitrogen and total phosphorus concentration, and in estimated annual total nitrogen and total phosphorus loads for Kaskaskia River, Ill. (KAS) (05594100).



**Figure 24.** Relation of total nitrogen and total phosphorus concentration to daily mean streamflow and temporal trends in annual streamflow, in flow-adjusted residuals of total nitrogen and total phosphorus concentration, and in estimated annual total nitrogen and total phosphorus loads for Mississippi River, Ill. (MS6) (05587550).

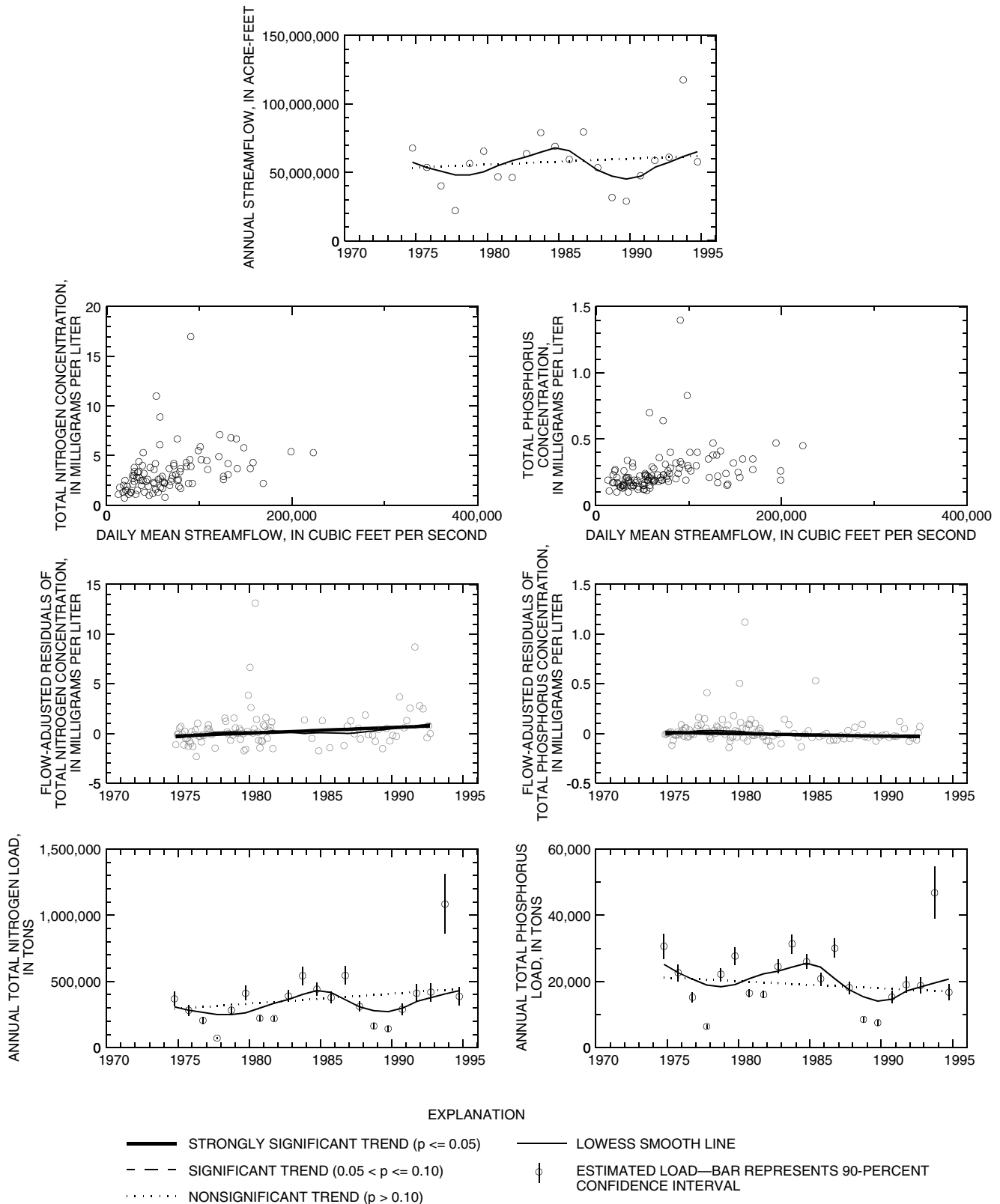


**Figure 25.** Relation of total nitrogen and total phosphorus concentration to daily mean streamflow and temporal trends in annual streamflow, in flow-adjusted residuals of total nitrogen and total phosphorus concentration, and in estimated annual total nitrogen and total phosphorus loads for Illinois River, Ill. (IL1) (05586100).

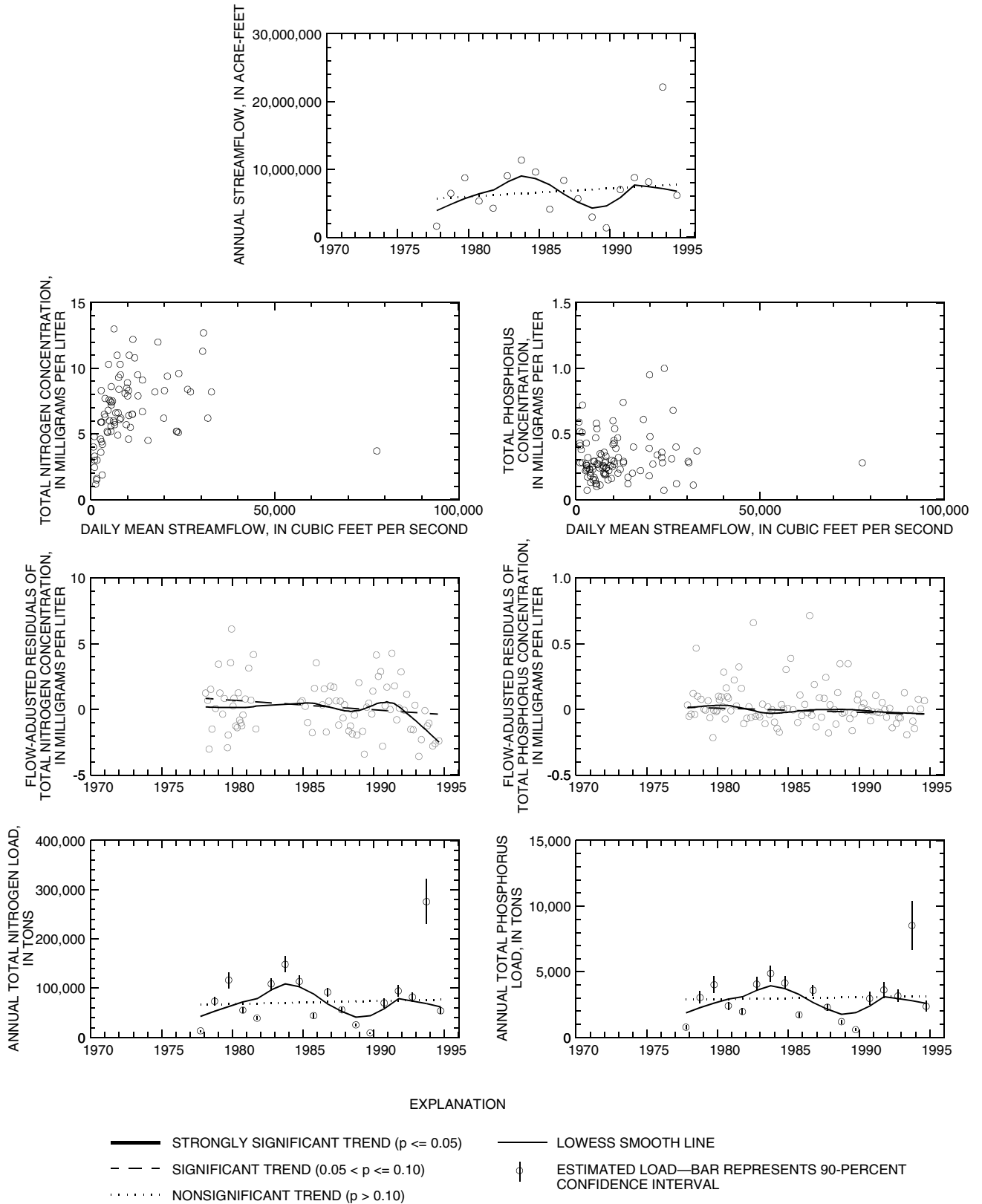


**Figure 26.** Relation of total nitrogen and total phosphorus concentration to daily mean streamflow and temporal trends in annual streamflow, in flow-adjusted residuals of total nitrogen and total phosphorus concentration, and in estimated annual total nitrogen and total phosphorus loads for Illinois River, Ill. (IL2) (05543500).

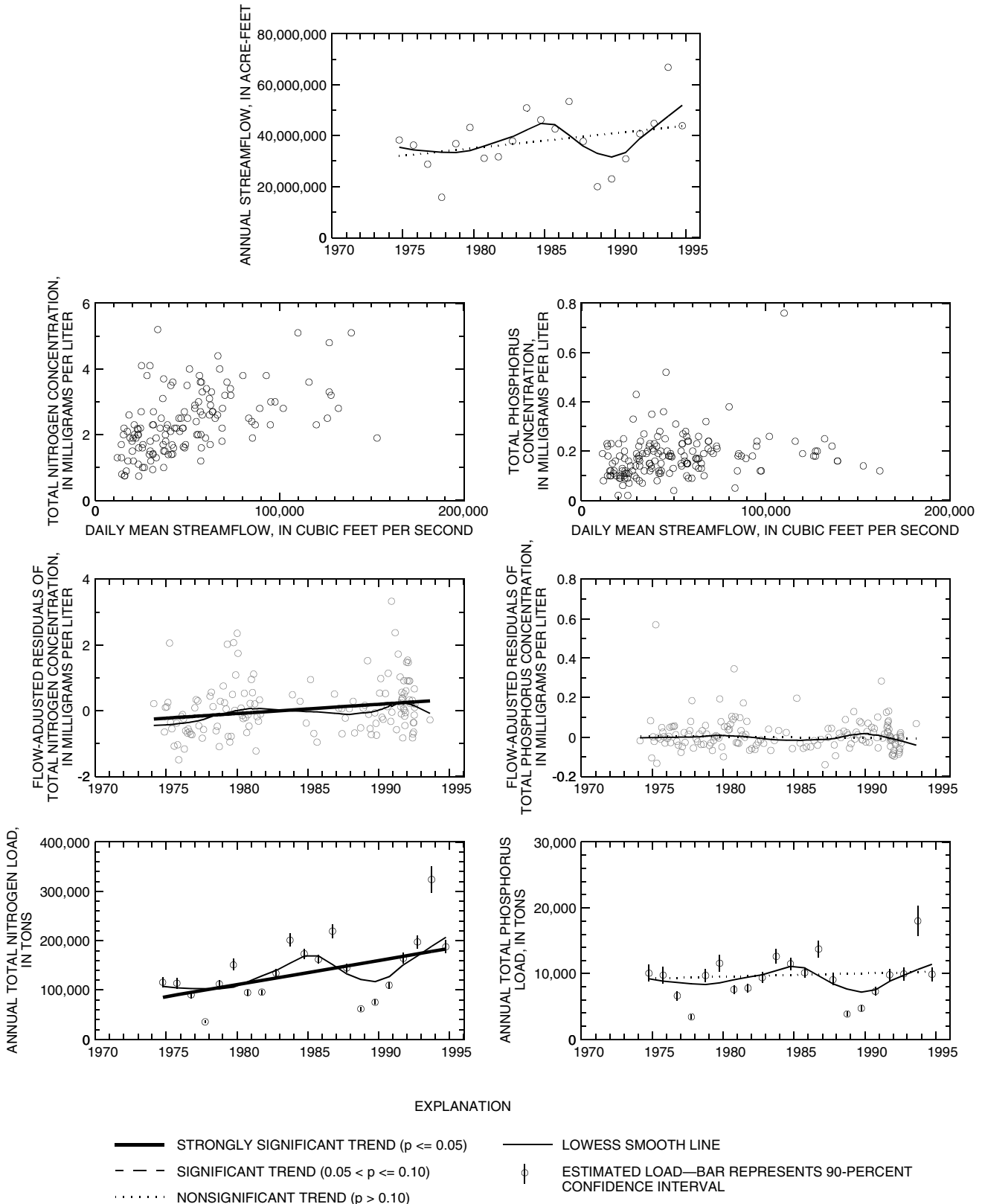




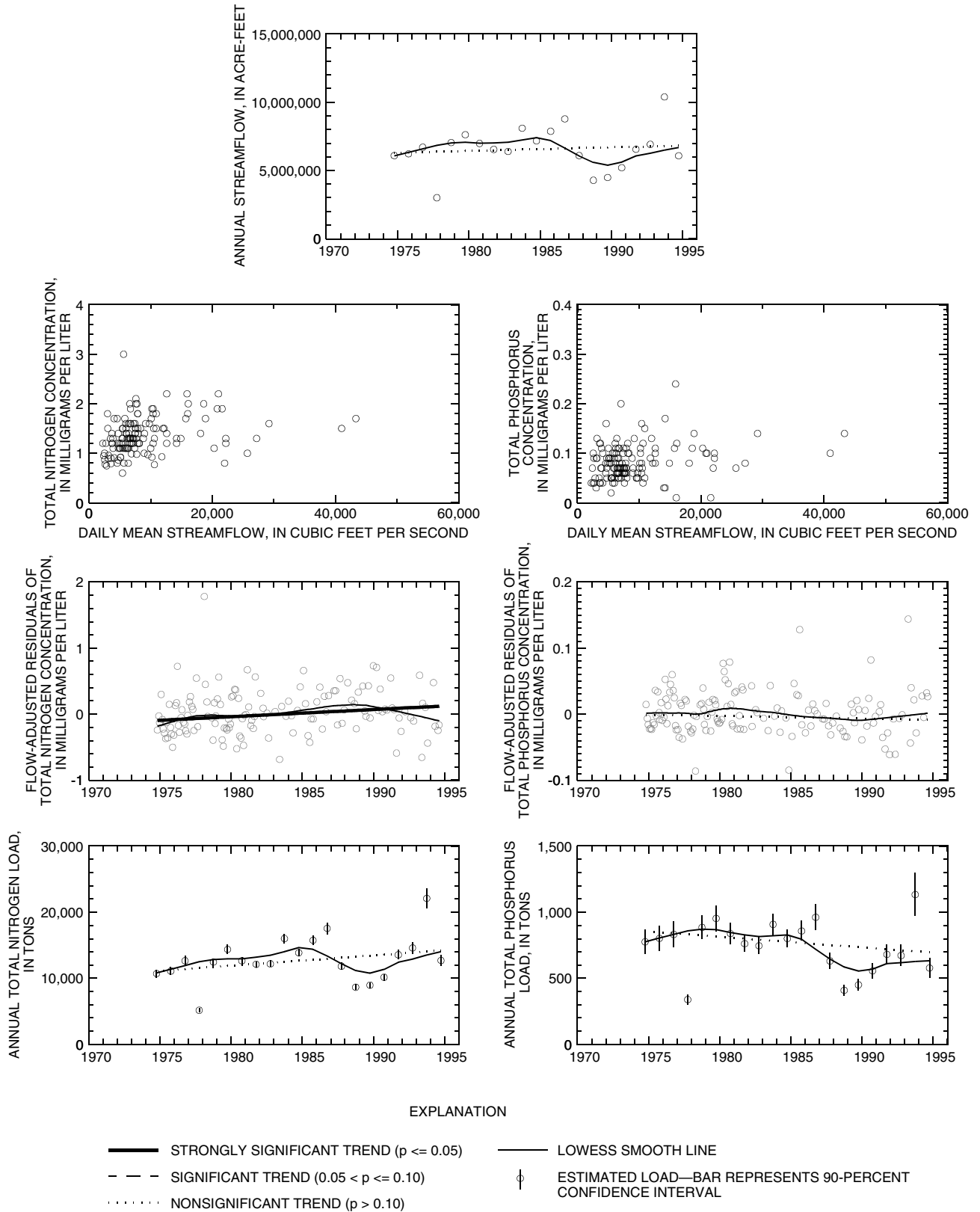
**Figure 27.** Relation of total nitrogen and total phosphorus concentration to daily mean streamflow and temporal trends in annual streamflow, in flow-adjusted residuals of total nitrogen and total phosphorus concentration, and in estimated annual total nitrogen and total phosphorus loads for Mississippi River, Iowa (MS7) (05474500).



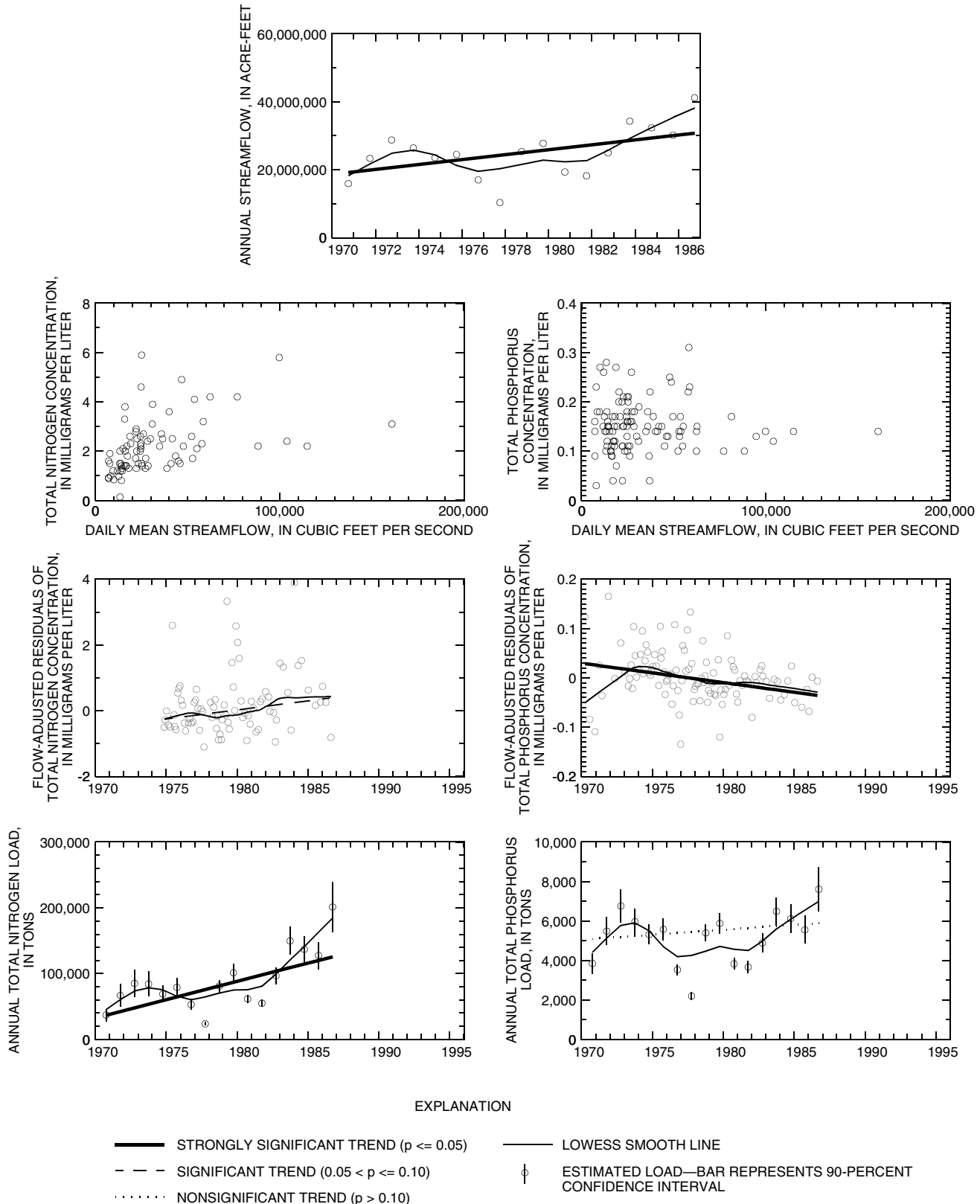
**Figure 28.** Relation of total nitrogen and total phosphorus concentration to daily mean streamflow and temporal trends in annual streamflow, in flow-adjusted residuals of total nitrogen and total phosphorus concentration, and in estimated annual total nitrogen and total phosphorus loads for Iowa River, Iowa (IOW) (05465500).



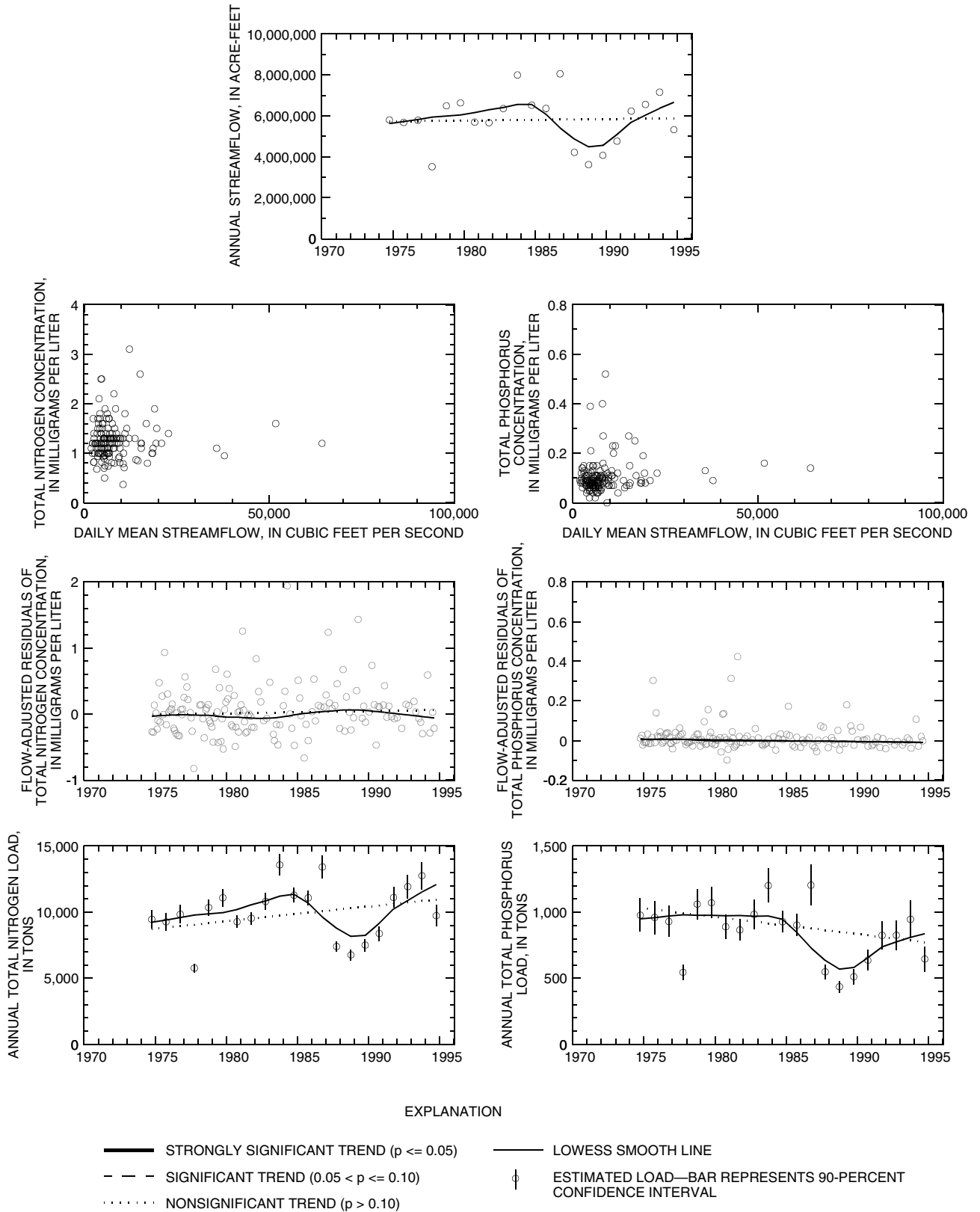
**Figure 29.** Relation of total nitrogen and total phosphorus concentration to daily mean streamflow and temporal trends in annual streamflow, in flow-adjusted residuals of total nitrogen and total phosphorus concentration, and in estimated annual total nitrogen and total phosphorus loads for Mississippi River, Iowa (MS8) (05420500).



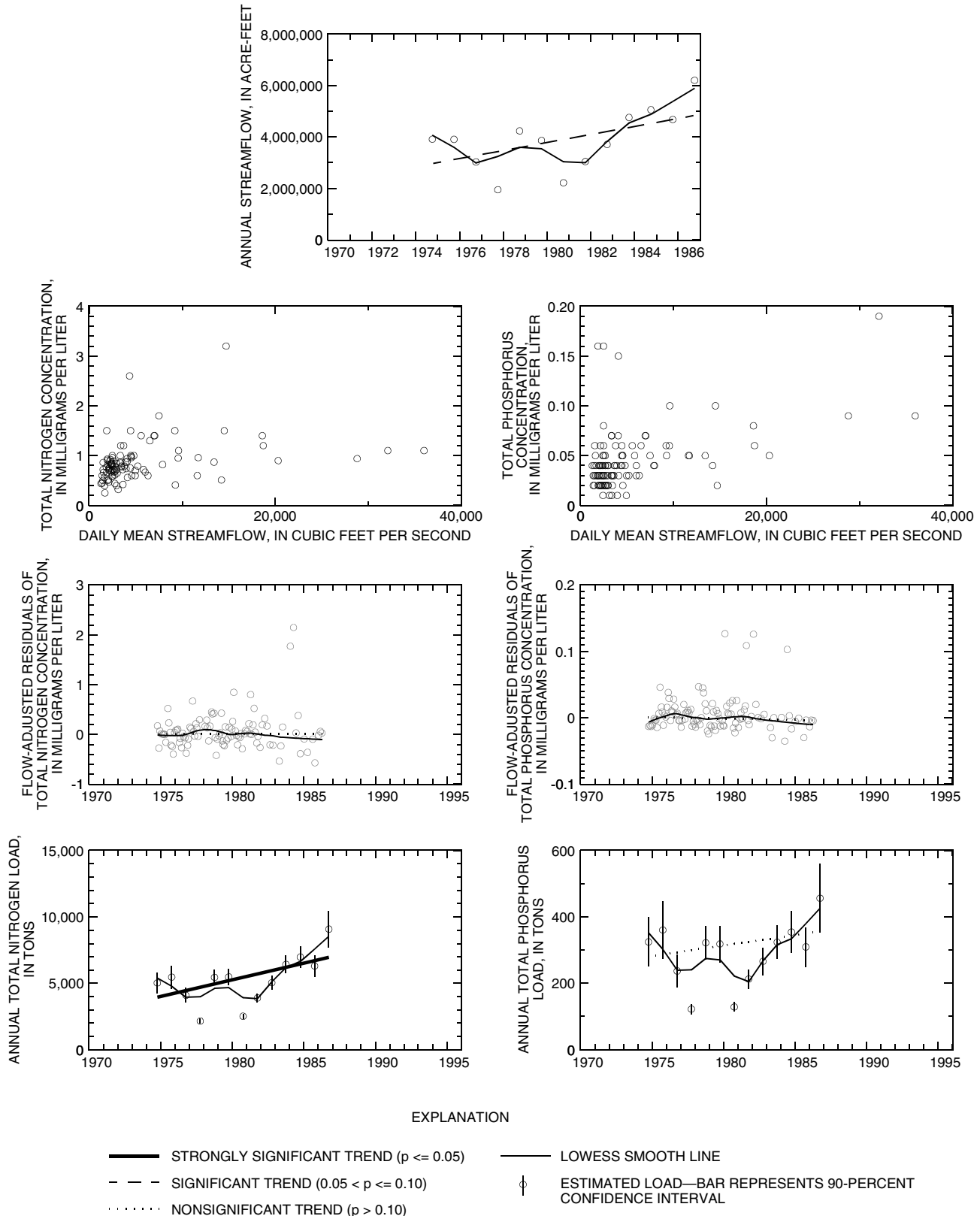
**Figure 30.** Relation of total nitrogen and total phosphorus concentration to daily mean streamflow and temporal trends in annual streamflow, in flow-adjusted residuals of total nitrogen and total phosphorus concentration, and in estimated annual total nitrogen and total phosphorus loads for Wisconsin River, Wis. (WIS) (05407000).



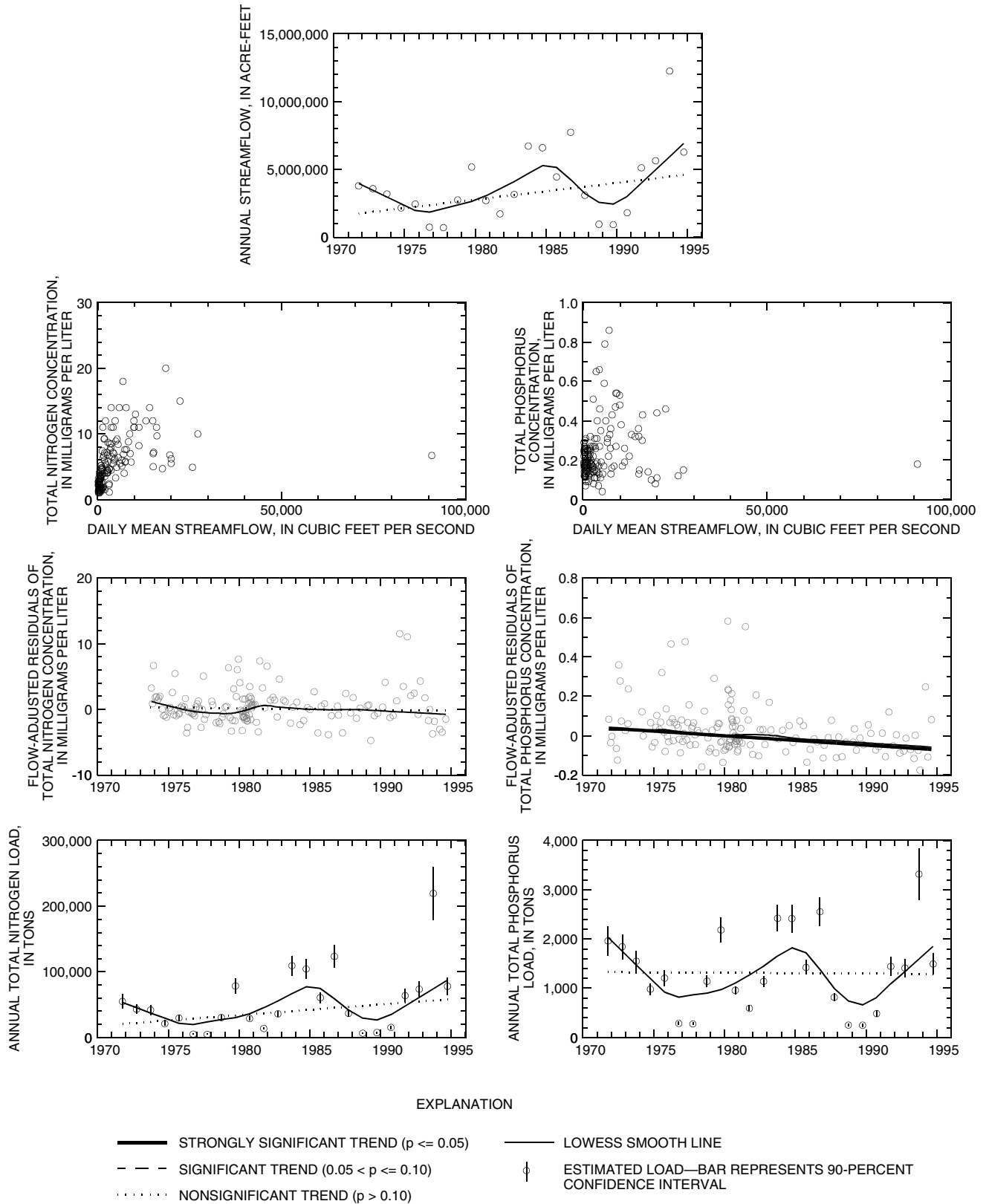
**Figure 31.** Relation of total nitrogen and total phosphorus concentration to daily mean streamflow and temporal trends in annual streamflow, in flow-adjusted residuals of total nitrogen and total phosphorus concentration, and in estimated annual total nitrogen and total phosphorus loads for Mississippi River, Minn. (MS9) (05378500).



**Figure 32.** Relation of total nitrogen and total phosphorus concentration to daily mean streamflow and temporal trends in annual streamflow, in flow-adjusted residuals of total nitrogen and total phosphorus concentration, and in estimated annual total nitrogen and total phosphorus loads for Chippewa River, Wis. (CHI) (05369500).

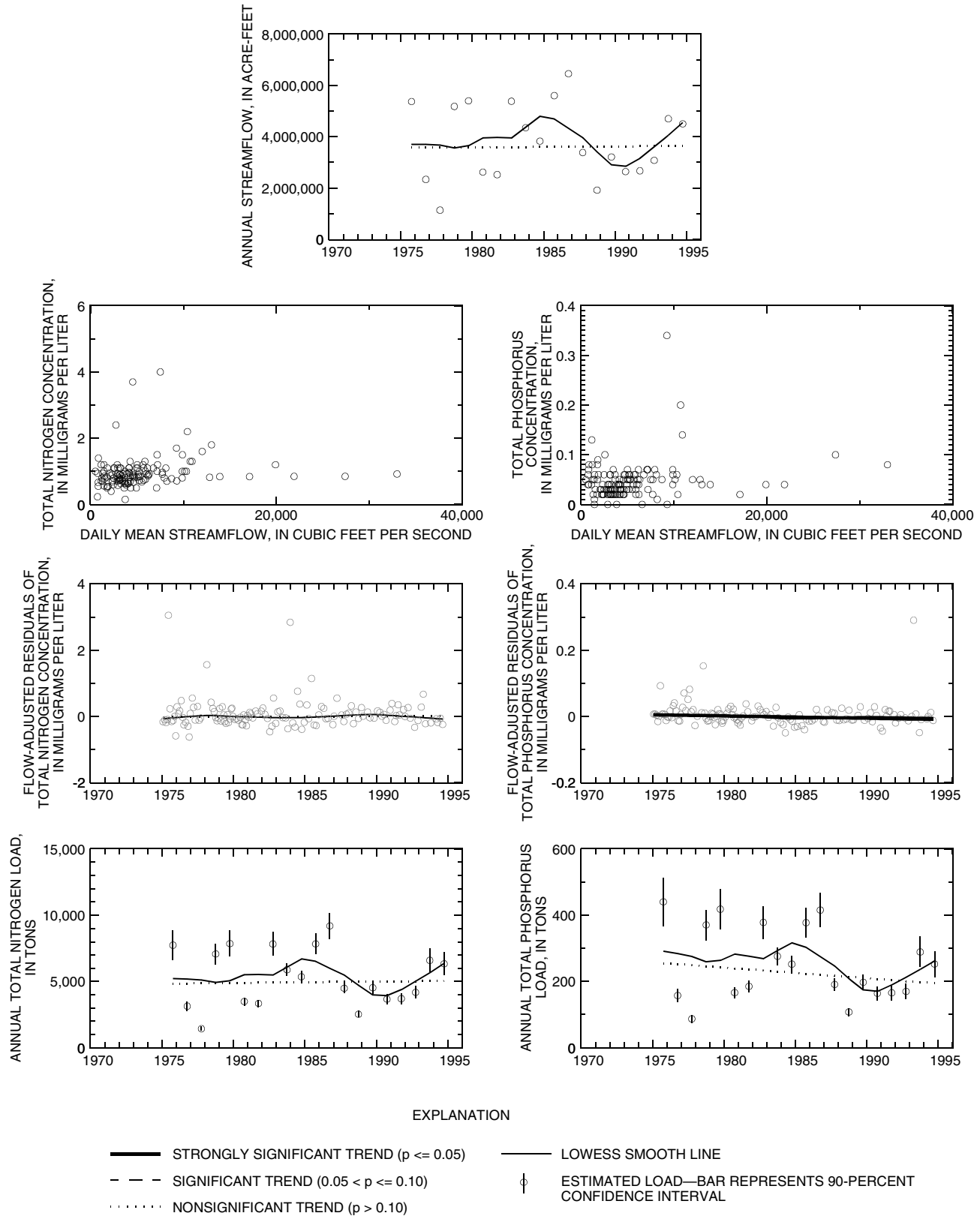


**Figure 33.** Relation of total nitrogen and total phosphorus concentration to daily mean streamflow and temporal trends in annual streamflow, in flow-adjusted residuals of total nitrogen and total phosphorus concentration, and in estimated annual total nitrogen and total phosphorus loads for St. Croix River, Wis. (STC) (05340500).

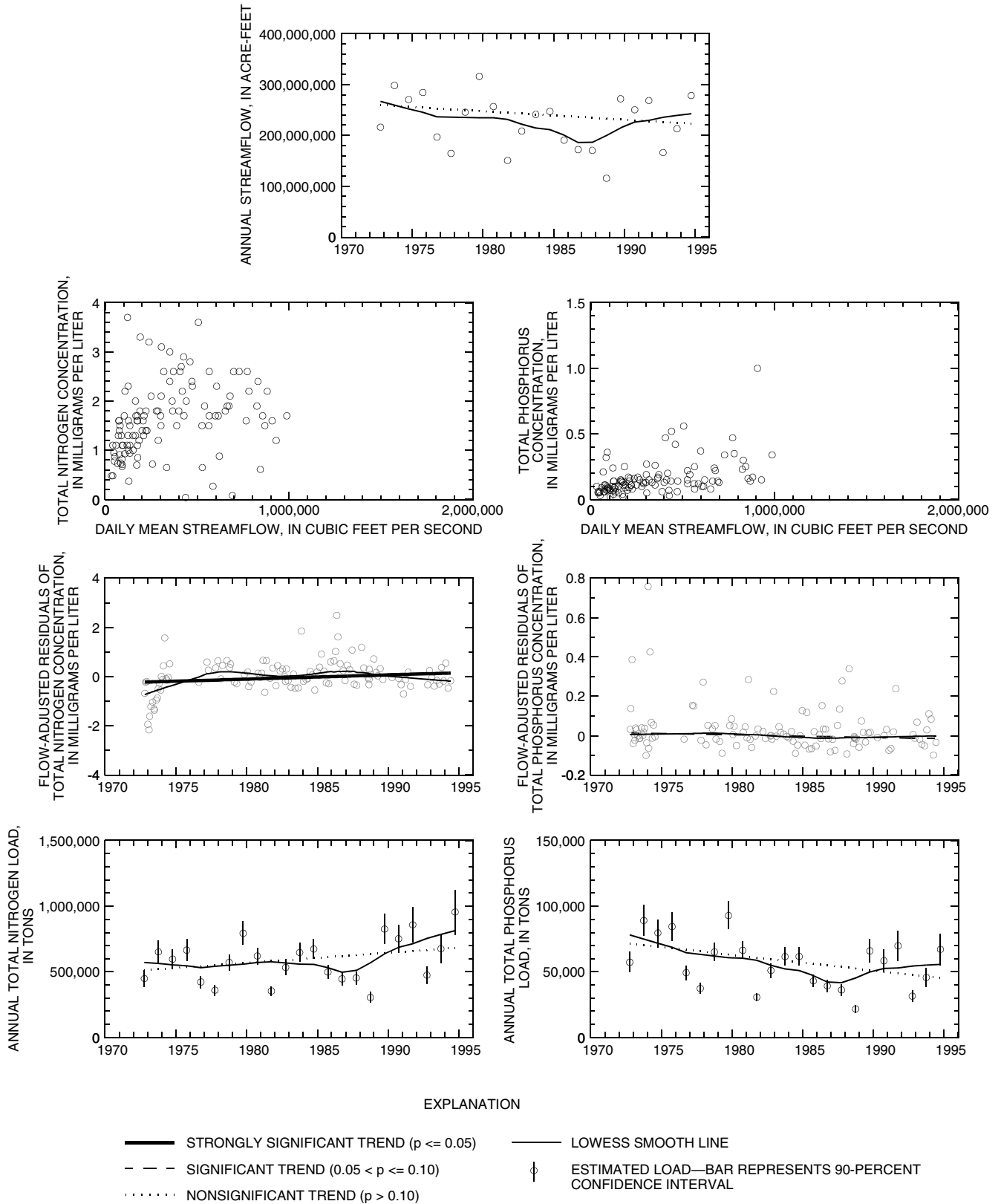


**Figure 34.** Relation of total nitrogen and total phosphorus concentration to daily mean streamflow and temporal trends in annual streamflow, in flow-adjusted residuals of total nitrogen and total phosphorus concentration, and in estimated annual total nitrogen and total phosphorus loads for Minnesota River, Minn. (MIN) (05330000).

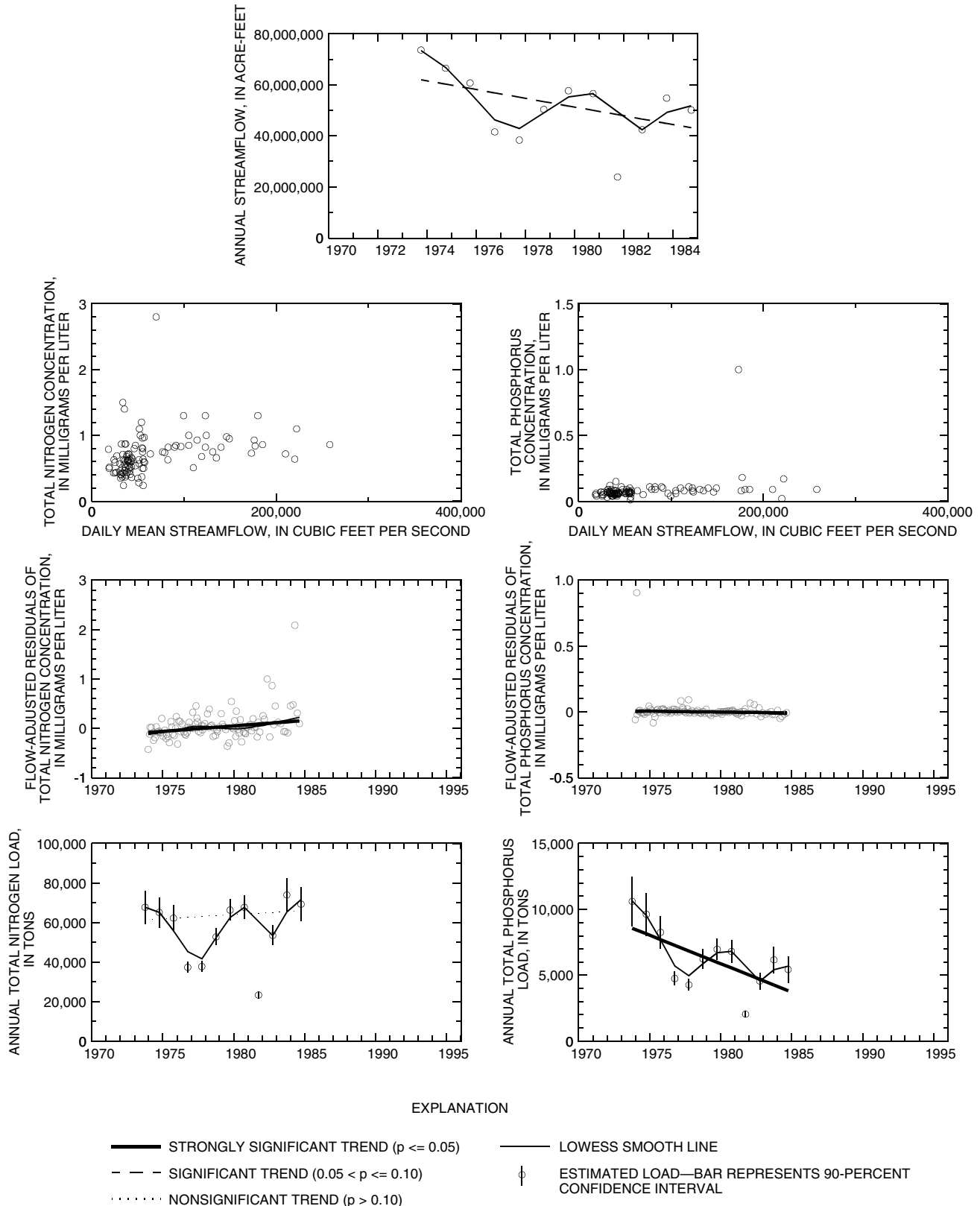




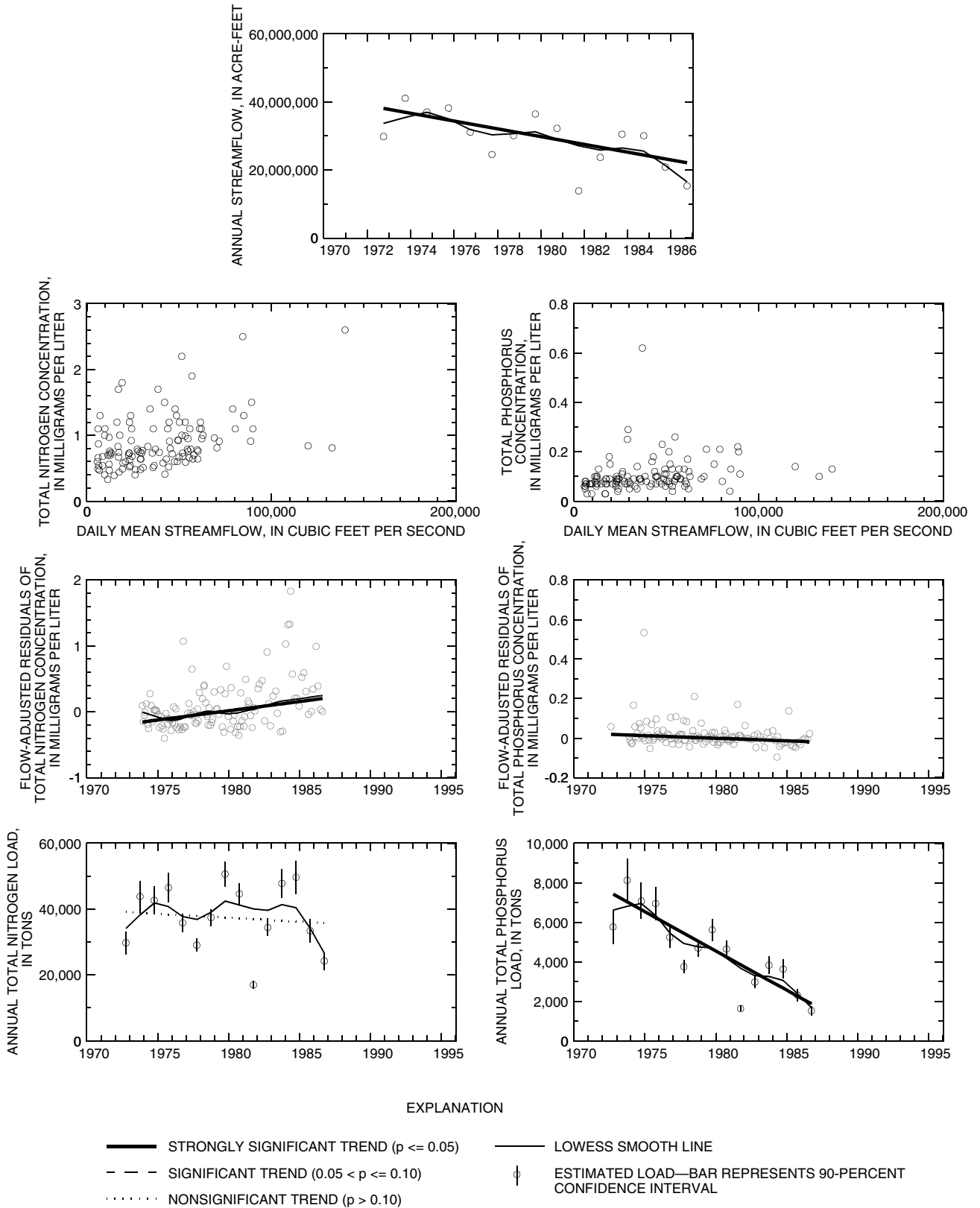
**Figure 35.** Relation of total nitrogen and total phosphorus concentration to daily mean streamflow and temporal trends in annual streamflow, in flow-adjusted residuals of total nitrogen and total phosphorus concentration, and in estimated annual total nitrogen and total phosphorus loads for Mississippi River, Minn. (MS10) (05267000).



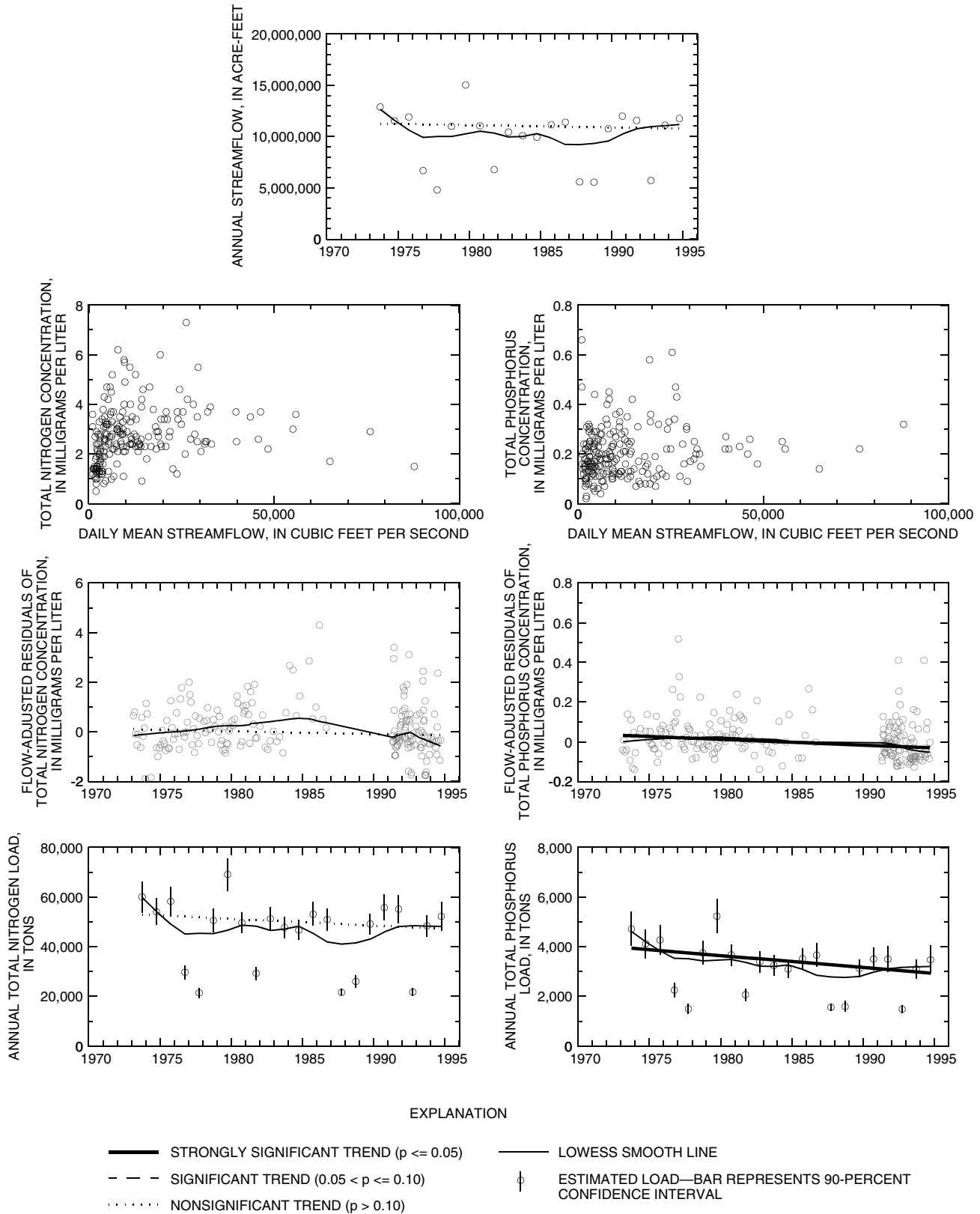
**Figure 36.** Relation of total nitrogen and total phosphorus concentration to daily mean streamflow and temporal trends in annual streamflow, in flow-adjusted residuals of total nitrogen and total phosphorus concentration, and in estimated annual total nitrogen and total phosphorus loads for Ohio River, III. (OH1) (03612500).



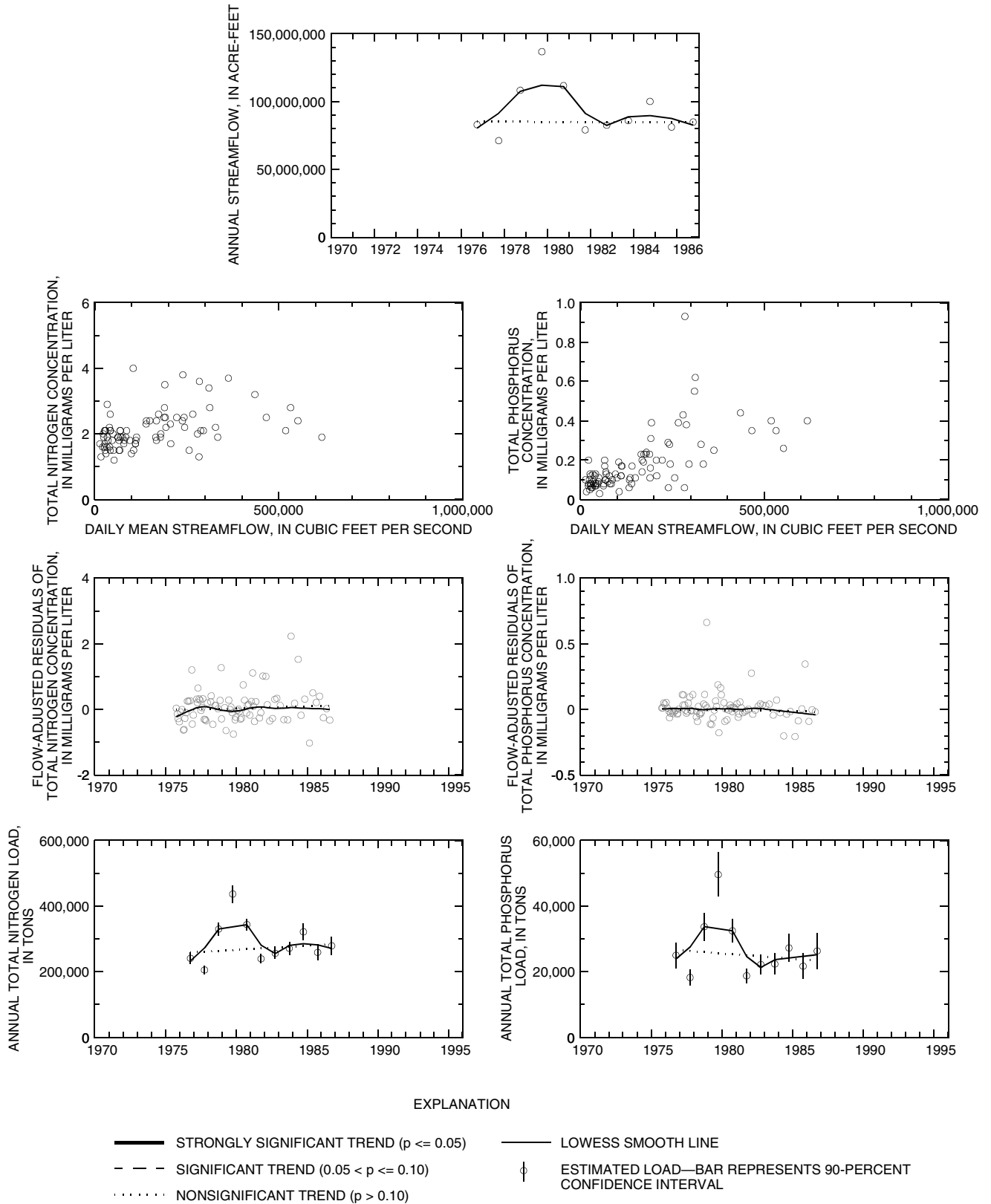
**Figure 37.** Relation of total nitrogen and total phosphorus concentration to daily mean streamflow and temporal trends in annual streamflow, in flow-adjusted residuals of total nitrogen and total phosphorus concentration, and in estimated annual total nitrogen and total phosphorus loads for Tennessee River, Ky. (TEN) (03609750).



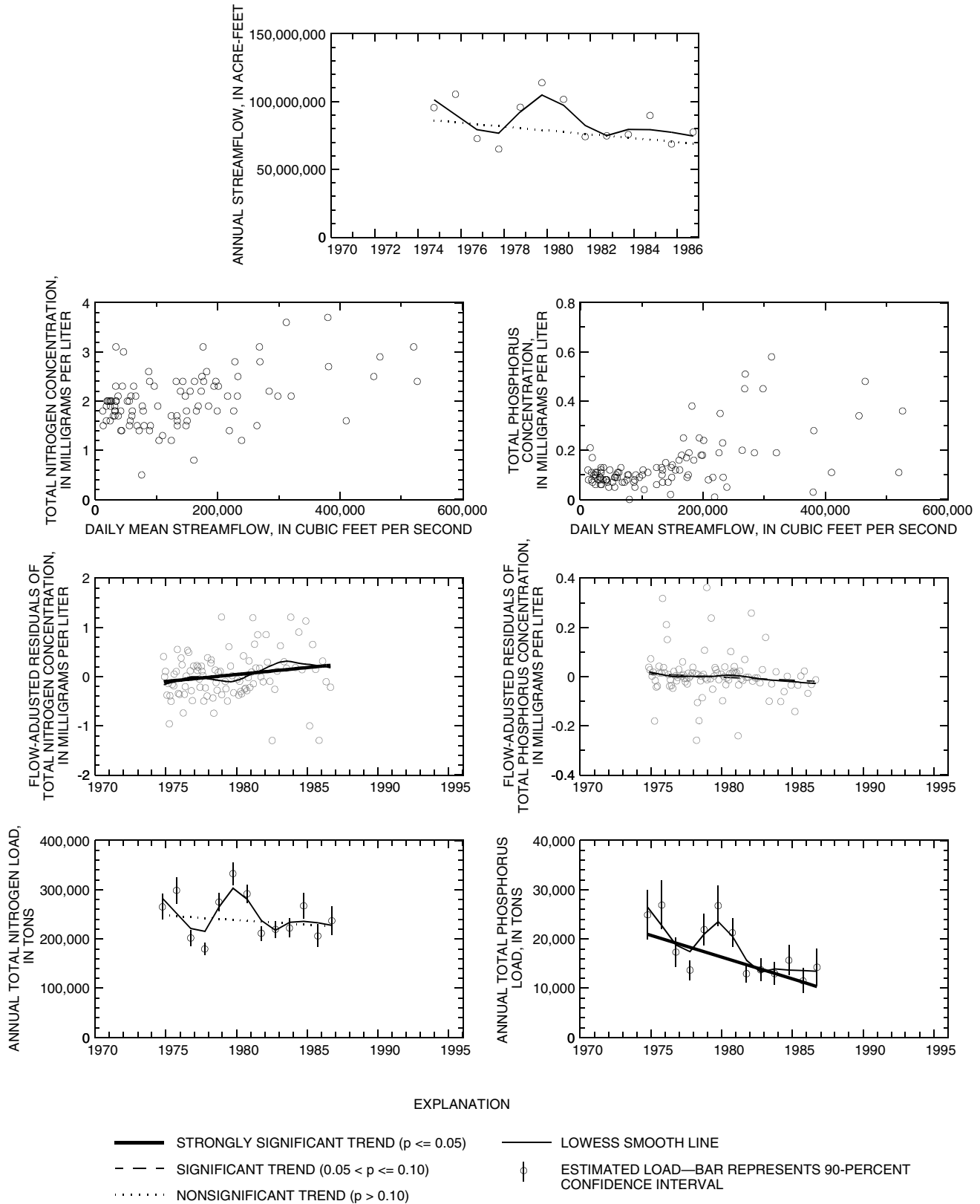
**Figure 38.** Relation of total nitrogen and total phosphorus concentration to daily mean streamflow and temporal trends in annual streamflow, in flow-adjusted residuals of total nitrogen and total phosphorus concentration, and in estimated annual total nitrogen and total phosphorus loads for Cumberland River, Ky. (CUM) (03438220).



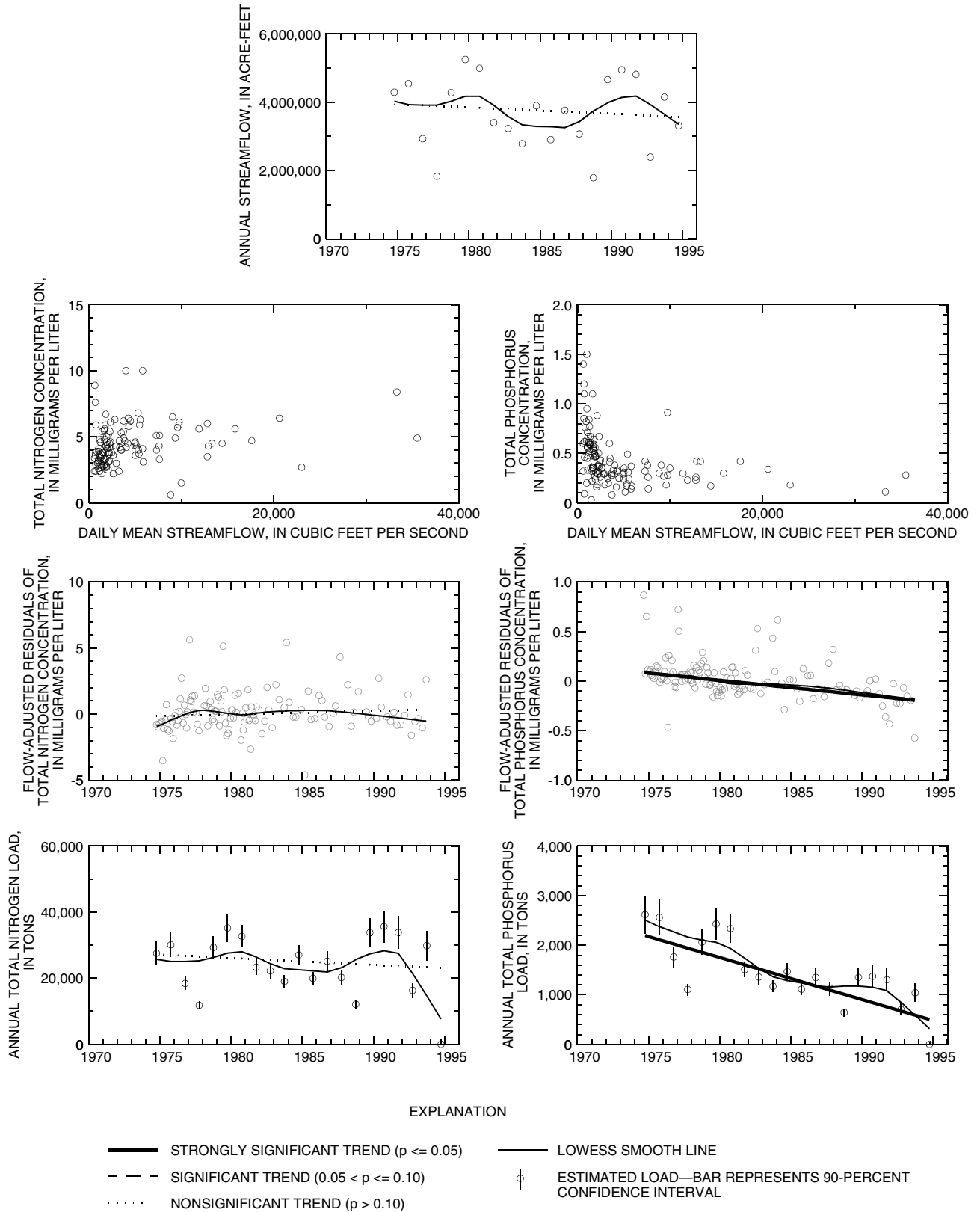
**Figure 39.** Relation of total nitrogen and total phosphorus concentration to daily mean streamflow and temporal trends in annual streamflow, in flow-adjusted residuals of total nitrogen and total phosphorus concentration, and in estimated annual total nitrogen and total phosphorus loads for White River, Ind. (WH2) (03374100).



**Figure 40.** Relation of total nitrogen and total phosphorus concentration to daily mean streamflow and temporal trends in annual streamflow, in flow-adjusted residuals of total nitrogen and total phosphorus concentration, and in estimated annual total nitrogen and total phosphorus loads for Ohio River, Ky. (OH2) (03303280).

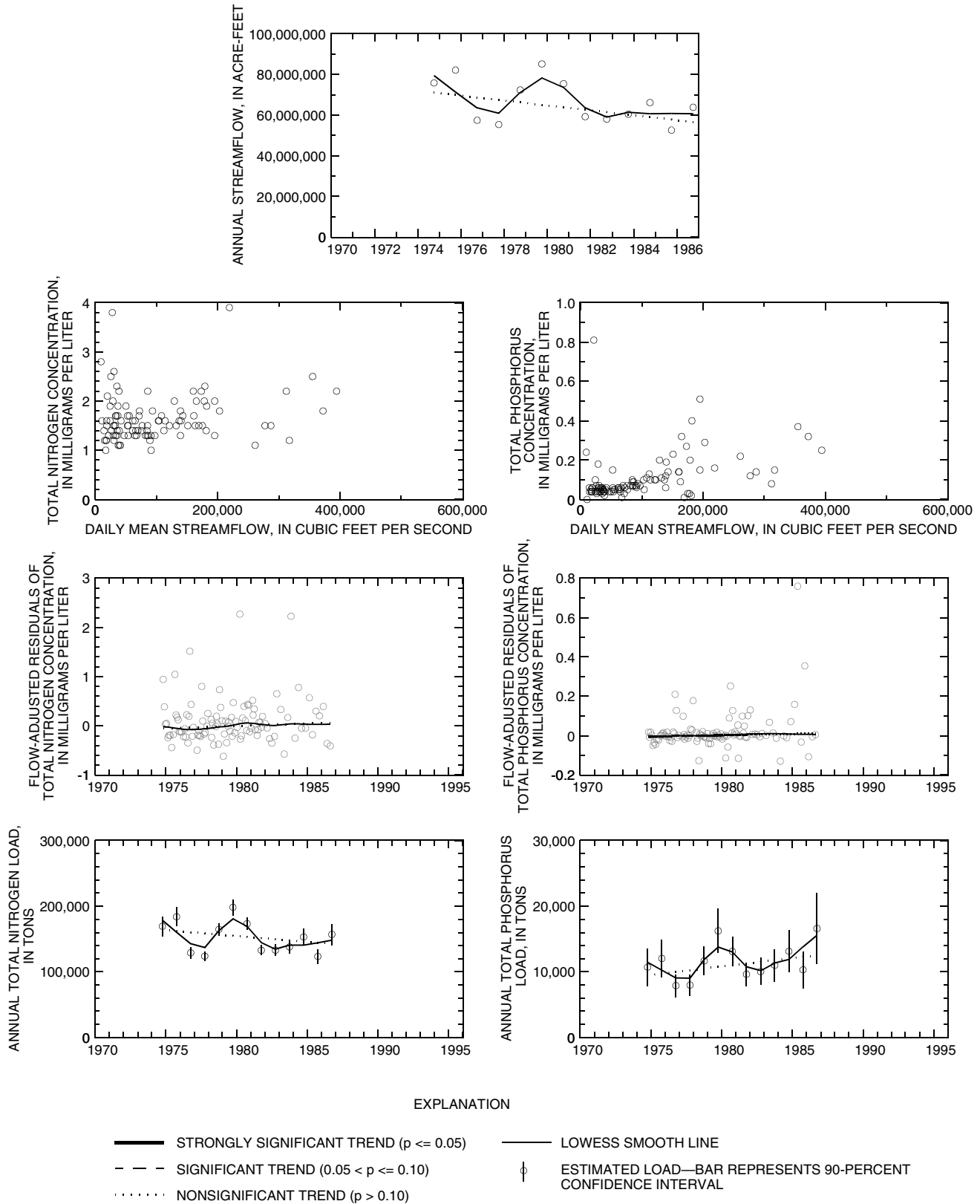


**Figure 41.** Relation of total nitrogen and total phosphorus concentration to daily mean streamflow and temporal trends in annual streamflow, in flow-adjusted residuals of total nitrogen and total phosphorus concentration, and in estimated annual total nitrogen and total phosphorus loads for Ohio River, Ky. (OH3) (03277200).

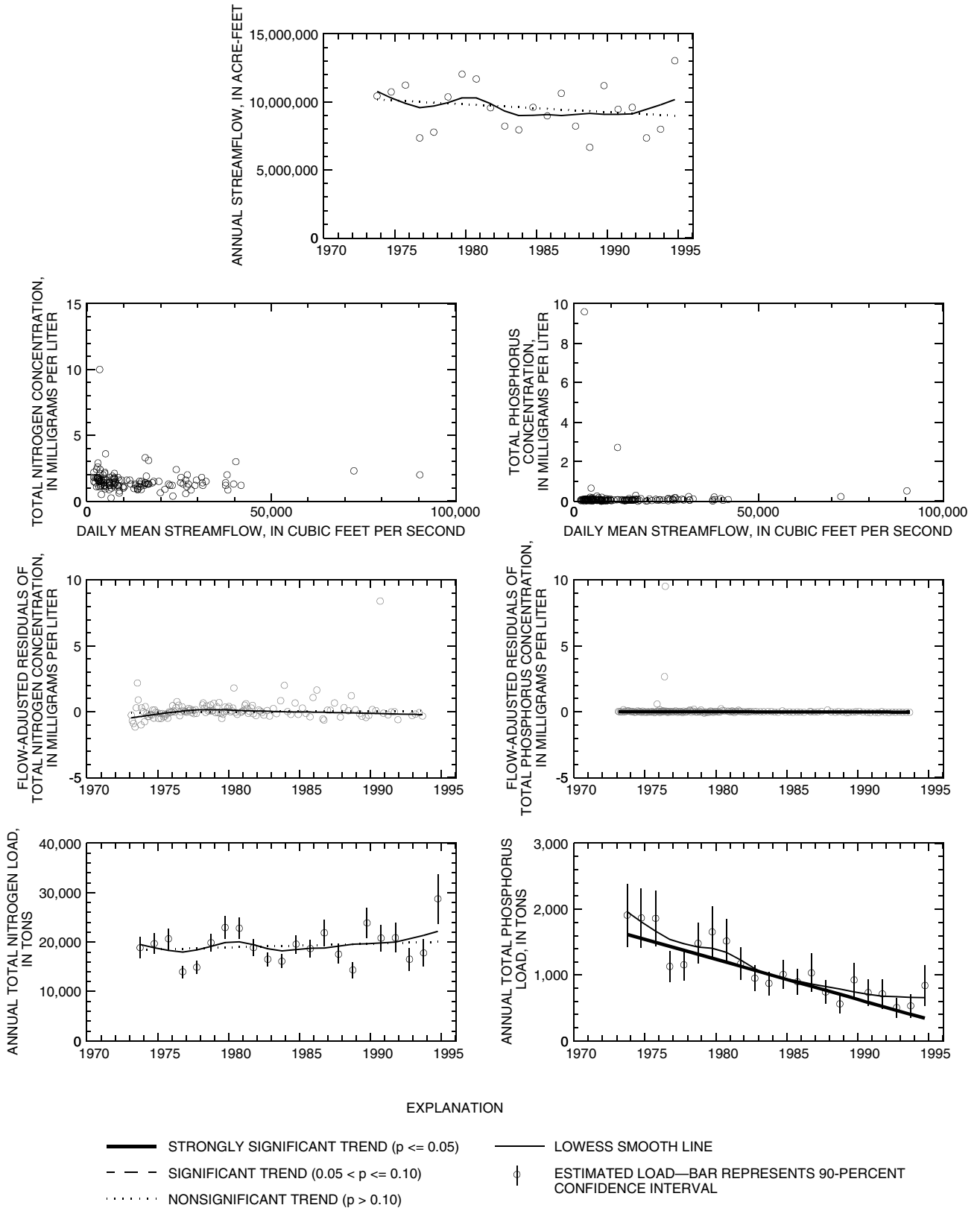


**Figure 42.** Relation of total nitrogen and total phosphorus concentration to daily mean streamflow and temporal trends in annual streamflow, in flow-adjusted residuals of total nitrogen and total phosphorus concentration, and in estimated annual total nitrogen and total phosphorus loads for Scioto River, Ohio (SCI) (03234500).

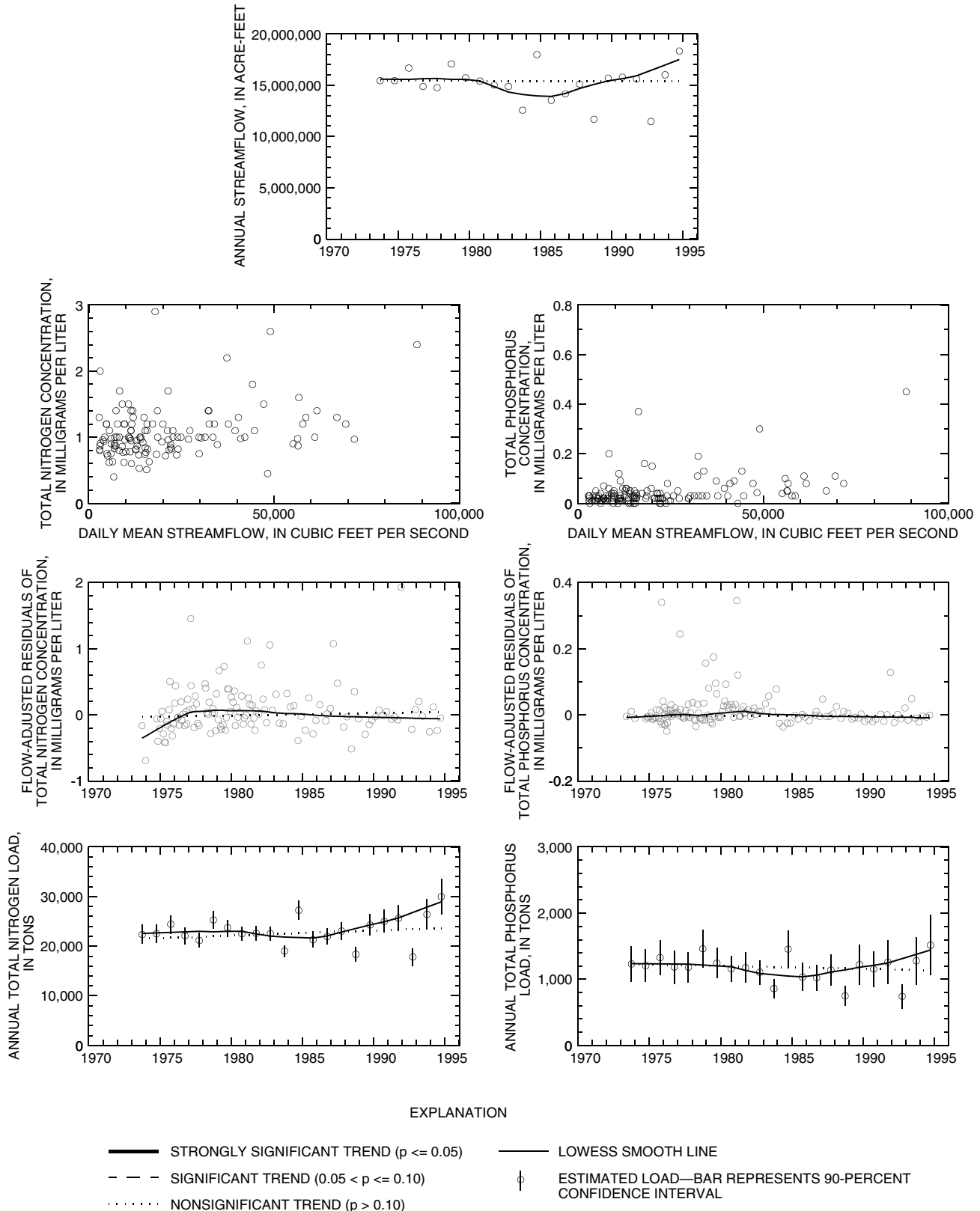




**Figure 43.** Relation of total nitrogen and total phosphorus concentration to daily mean streamflow and temporal trends in annual streamflow, in flow-adjusted residuals of total nitrogen and total phosphorus concentration, and in estimated annual total nitrogen and total phosphorus loads for Ohio River, Ky. (OH4) (03216600).



**Figure 44.** Relation of total nitrogen and total phosphorus concentration to daily mean streamflow and temporal trends in annual streamflow, in flow-adjusted residuals of total nitrogen and total phosphorus concentration, and in estimated annual total nitrogen and total phosphorus loads for Monongahela River, Pa. (MON) (03085000).



**Figure 45.** Relation of total nitrogen and total phosphorus concentration to daily mean streamflow and temporal trends in annual streamflow, in flow-adjusted residuals of total nitrogen and total phosphorus concentration, and in estimated annual total nitrogen and total phosphorus loads for Allegheny River, Pa. (ALL) (03049625).