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Water Quality Trends for Section 319 Priority Watersheds in Northwest Arkansas, 1997-2010

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ABSTRACT

Northwest Arkansas contains two Section 319 Priority Watersheds that the Arkansas Natural Resources Commission (ANRC) has identified as being impacted by point and nonpoint sources of pollution (i.e., phosphorus, nitrogen, and sediment), and the Arkansas Water Resources Center (AWRC) has monitored the water quality at several sites within these watersheds. Water-quality data has been collected over the last decade within the Illinois River Watershed (HUC #11110103) and the Upper White River Basin (Beaver Reservoir HUC# 11010001), each watershed containing three sampling sites. The Illinois River Watershed sites are located on the Illinois River, Osage Creek, and Ballard Creek, and the Upper White River Basin sites are located on the West Fork of the White River, White River, and Kings River. The objective of this study was to determine monotonic water quality trends at these six sites from water-quality data accumulated between 1997 and 2010. Specifically, the study used flow-adjusted constituent concentrations (i.e., SO_4, Cl^-, NO_3-N, TN, NH_4-N, SRP, TP, and TSS) to examine long term trends in the water-quality data with parametric (i.e., linear regression) and non-parametric (i.e., Seasonal Kendall test and Sen’s slope estimator) statistical techniques. The goal was to understand if constituent concentrations have increased, decreased, or not changed over time. These changes in water quality were then compared with changes in watershed management as to suggest how certain actions have influenced these streams and rivers. Overall, TN, SRP, TP, and TSS have shown significant decreases in flow-adjusted concentrations (FACs) across these two watersheds over the defined study period, based upon both statistical approaches. The decrease in phosphorus was likely the most important observation, because most water quality concerns in this region have focused on elevated phosphorus concentrations in these trans-boundary watersheds.

This thesis is approved for recommendation
to the Graduate Council

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CHAPTER 1: INTRODUCTION

BACKGROUND

Water quality is most commonly represented as the chemical, physical, and biological characteristics of water relative to the water body's designated uses. Under the Clean Water Act (CWA), 1972, the State of Arkansas is able to protect, regulate, and enhance the quality of water within its jurisdiction. Presently, the CWA establishes the basic framework for regulating both water-quality standards for surface waters and discharging of pollutants into the waters of the United States. The Clean Water Act requires each State to develop and maintain water-quality standards, which in the State of Arkansas are prepared and revised every three years by the Arkansas Department of Environmental Quality (ADEQ). Water-quality standards, in Arkansas, consist of narrative and numerical limits on individual constituents and are set based on each water body's designated uses, such as for drinking, recreation, fisheries, agriculture and industry. Water bodies are then routinely monitored by agencies and organizations such as ADEQ, the United States Geological Survey (USGS), and the Arkansas Water Resources Center (AWRC), to provide long-term databases of water quality. Water resources management and planning rely heavily on information harvested from water-quality databases to assist in decision making and help develop water-quality assessments for streams, rivers, and watersheds.

Water-quality databases can be assessed using trend analyses, which examine the changes in the water quality (e.g., constituent concentrations) over time. Water-quality trends can provide valuable information that allows a better understanding of the conditions and characteristics of the water quality within watersheds. Also, trend analyses give insight on if human interactions with the environment have positively or negatively influenced the water quality. Finally, water-quality trends can be used along with other watershed information to improve the knowledge of how past, current and future watershed management decisions have or might have influenced changes in the water quality.

In 1987, under Section 319 of the CWA, the Nonpoint Source (NPS) Management program was established by Congress, providing funds to individual State management programs. In recent years Section 319 Programs have focused primarily on watersheds, where nonpoint source pollution has lead to water quality issues. The Arkansas Natural Resources Commission (ANRC) was appointed the task to allocate funds to various studies and projects within impaired watersheds, such as monitoring water quality within its Section 319 priority watersheds. The AWRC has been awarded grants for the last decade to monitor the water quality within two Section 319 priority watersheds, the Illinois River Watershed and the Upper White River Basin within Arkansas. Water-quality data from individual sites within these watersheds has been collected over the last decade and compiled into long-term databases.

PROBLEM STATEMENT

Northwest Arkansas contains two Section 319 priority watersheds that the ANRC has identified as being impacted by point source and nonpoint source pollution (i.e., phosphorus, nitrogen, and sediment). The ANRC Section 319 Program has funded the AWRC for the last decade (or less) to monitor the water quality at six sites in these watersheds. While there have been several studies that have evaluated the ANRC Section 319 and other water-quality data to estimate annual constituent loads at each of the six selected sites and compare differences qualitatively between years (e.g., see Green and Haggard, 2001; Haggard et al., 2003; Nelson and Soerens, 2001; Massey et al., 2009a,b; 2010a,b,c). To date, a comprehensive evaluation of the available water-quality data from the ANRC Section 319 Program has not been completed using acceptable statistical methods to determine long-term water-quality trends.

STUDY SITE DESCRIPTION

Northwest Arkansas has two of the ten Section 319 Priority Watersheds across the state, and ANRC has been funding water-quality monitoring in these basins (ANRC, 2011). Also, ANRC has identified nutrient surplus areas across Arkansas, which includes these two watersheds. This study has six sampling sites, three within the Illinois River Watershed (HUC# 11110103) and three in the Upper White River Basin (Beaver Reservoir HUC# 11010001). The study sites are located at the Ballard Creek, Osage Creek, Illinois River, Kings River, West Fork of the White River, and White River.

ILLINOIS RIVER WATERSHED

The Illinois River (fig. 1-1) originates near Hogeye, southwest of Fayetteville, Arkansas, and it flows through the Ozarks Highlands into Oklahoma. The watershed has a catchment area of approximately 195,300 ha in northwest Arkansas (CAST, 2006). In recent years, the watershed has seen considerable population growth (i.e., 48% increase from 1990-2000) due to local economic growth and stability, resulting in significant increases in residential, commercial and industrial developments. Land coverage is primarily pasture (45%) and forest (36%); however, there is also a fraction of urban development (13%) and other minor land covers (CAST, 2006).

Ballard Creek: This site is located on County Road 76 near Summers, Arkansas. The drainage area is 6,000 ha and land coverage is predominately pasture (59%) and forest (32%) (CAST, 2006). The stage level and discharge (Q, cfs) for this site was monitored by the AWRC. Latitude 35°59’49”, Longitude 94°31’38”.

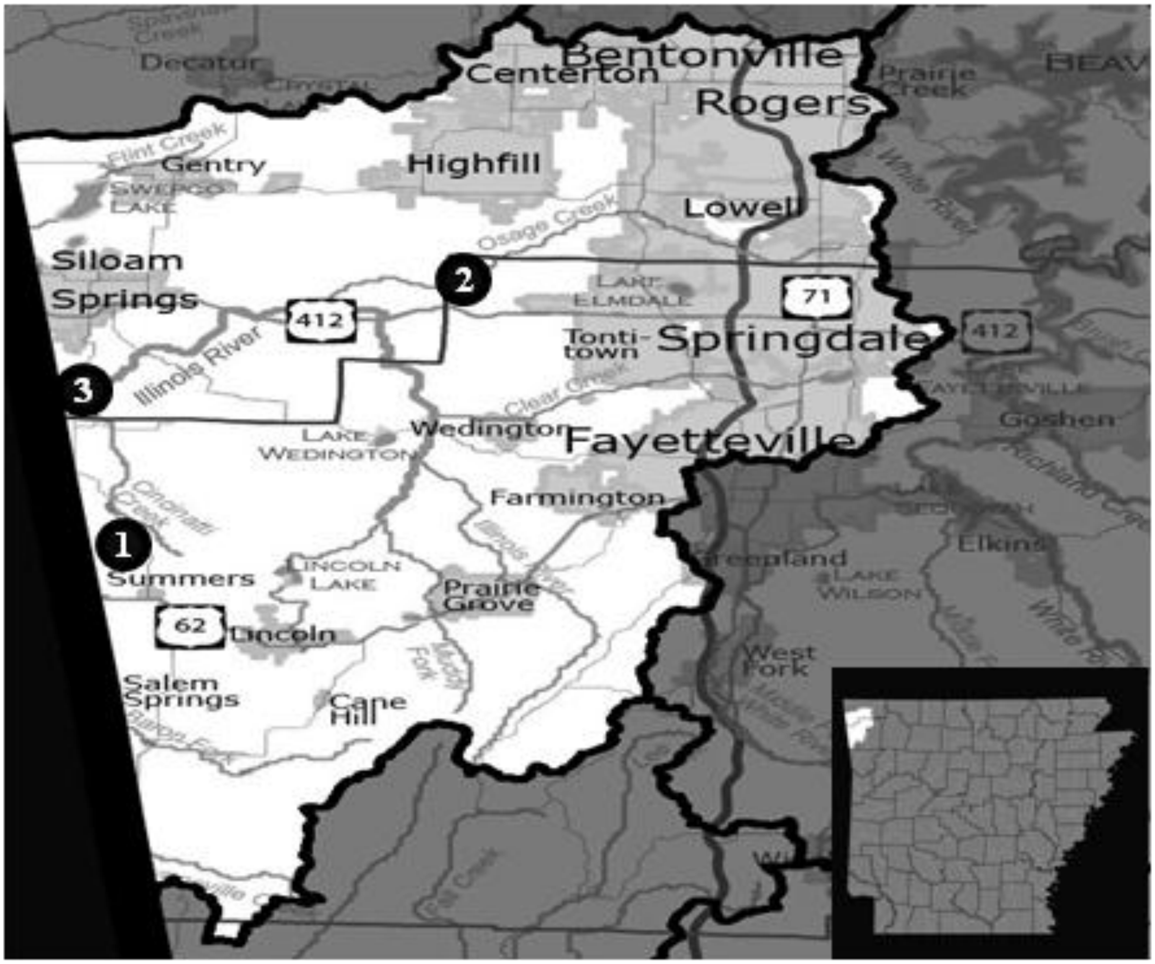

Figure 1-1. The location of the three sampling sites within the Illinois River Watershed in northwest Arkansas (ArkWater, 2011); (1) Ballard Creek, (2) Osage Creek, and the (3) Illinois River.

Osage Creek: This site (USGS site 07195000) is located on Snavely Road near Elm Springs, Arkansas. The drainage area is 33,700 ha and land uses consist primarily of pasture (47%) and urban (30%) with some forest (14%) coverage (CAST, 2006). This stream also receives treated effluent from WWTPs in Rogers and Springdale. Latitude 36°13’19”, Longitude 94°17’18”.

Illinois River: This site (USGS site 07195430) is located on Highway 59 near Siloam Springs, Arkansas. The drainage area is 149,000 ha and the main tributaries include Osage Creek, Clear Creek, and Muddy Fork. Also, several tributaries of the Illinois River receive treated effluent from WWTPs in Fayetteville, Rogers, and Springdale. Land coverage is primarily pasture (45%) and forest (37%) with some urban areas (13%) (CAST, 2006). Latitude 36°06’31”, Longitude 94°32’00”.

UPPER WHITE RIVER BASIN

The Upper White River Basin (UWRB) (fig. 1-2) is composed of four counties in northwest Arkansas, approximately 575,000 ha, and crosses into southwest Missouri (CAST, 2006). In recent decades, the region has seen rapid growth and development, specifically in Benton and Washington Counties. According to the 2010 Census data, from 2000 to 2010 the populations have increased in Benton County from 153,406 to 221,339 and Washington County from 157,715 to 203,065. Land coverage for the Arkansas portion of the UWRB is dominated by forest (64%) and pasture (23%) with a fraction of urban development (4%), water (2%) and herbaceous (7%) (CAST, 2006). Also, Beaver Lake is located within the UWRB, which is northwest Arkansas’s primary drinking water supply.

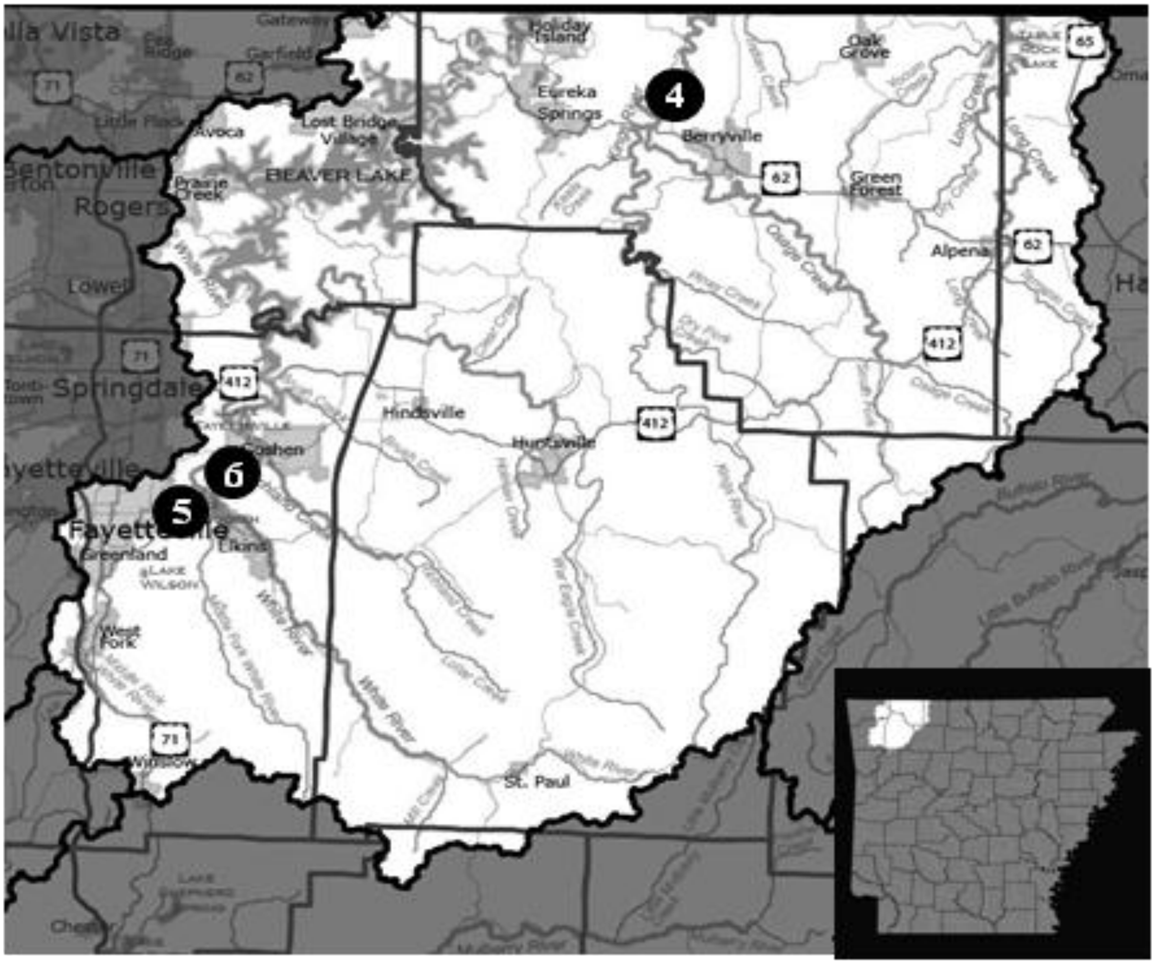

Figure 1-2. The location of the three sampling sites within the Upper White River Basin (UWRB) in northwest Arkansas (ArkWater, 2011); the (4) Kings River, (5) West Fork of the White River, and the (6) White River.

Kings River: This site (USGS site 07050500) is located on Highway 143 near Berryville, Arkansas. The drainage area is 136,500 ha and the land use consists mostly of forest (71%) with some pasture (20%) and urban (2%) uses. The Kings River receives treated effluent from Berryville Wastewater Treatment Plant (WWTP), which receives wastewater from a small population plus poultry processing facilities. Latitude 36°25'38", Longitude 93°37'15".

West Fork of the White River: This site (USGS site 07048550) is located on Country Road 195 just east of Fayetteville, Arkansas. The drainage area is 31,900 ha and land cover is primarily forest (66%) but also includes some grassland and pasture (14%) as well as urban development (14%). Also, the West Fork of the White River is listed on ADEQ's 2008 303(d) list (ADEQ, 2008) as being impaired from sediment. Latitude 36°03'14", Longitude 94°04'59".

White River: This site (USGS site 07048700) is located on Highway 45 near Goshen, Arkansas. The drainage area is 106,700 ha and the dominate land coverage is forest (76%) with some pasture (13%) and urban development (6%). However, there has been an increased amount of residential growth that has spread east from Fayetteville, Arkansas, which according to the 2010 Census Fayetteville has seen the population increase from 58,047 to 73,580 in the past 10 years. Also, the Paul Noland WWTP treats wastewater from the City of Fayetteville, AR and discharges into a small tributary of the White River. Latitude 36°06'21", Longitude 94°00'42".

OBJECTIVES

This study will evaluate long-term trends in the water-quality data collected through the ANRC Section 319 Program over the last decade, or where sufficient constituent concentration data is available to analyze (i.e., preferably a minimum of approximately five years of data). This study will determine water-quality trends at six selected sampling sites within the Illinois River Watershed and the Upper White River Basin, located on the Ballard Creek, Osage Creek, Illinois River, Kings River, West Fork of the White River, and White River. Specifically, this study will use flow-adjusted constituent concentrations to examine trends in the water-quality data with (1) parametric (i.e., linear regression) and (2) nonparametric (i.e., Seasonal Kendall test and Sen's slope estimator) statistical techniques.

RESEARCH HYPOTHESES

Null Hypothesis: The constituent concentrations are not changing over time.

Alternative Hypothesis: The constituent concentrations are increasing or decreasing over time.

CHAPTER 2: LITERATURE REVIEW

The evaluation of long-term water-quality data for trends has become an important tool used in assessing the quality of water in streams and rivers within watersheds. Trends provide information to watershed managers and stakeholders, so that they can develop and apply more effective solutions to water-quality issues. This literature review will introduce the basic concepts and various statistical methods used to evaluate trends in water-quality data. A trend is defined as a change in water quality (i.e., constituent concentration in this study) over time. The purpose for trend testing is to determine if the measured concentrations for a specified constituent have increased or decreased over time and whether those changes are statistically significant (Helsel and Hirsch, 1991).

Trend detection incorporates statistical testing of the null hypothesis and the alternative hypothesis. The null hypothesis is that the constituent concentrations are not changing over time (i.e., no trend) and the alternative hypothesis being that the constituent concentrations are increasing or decreasing over time at a specified significance level, α-value. The α-value is defined as the probability of incorrectly rejecting the null hypothesis, when it is actually true (Helsel and Hirsch, 1991). Helsel and Hirsch (1991) state that an α-value of 5% (0.05) is normally used in statistics but there are not any reasons why other values may not be used. A trend is deemed to be statistically significant when a p-value smaller than the α-value (0.05) is computed. Therefore, the smaller the p-value, the less likely the null hypothesis is true and a stronger case is made for the null hypothesis to be rejected.

SELECTION OF A TREND DETECTION METHOD

When selecting a statistical method for evaluating the changes in water quality (i.e., constituent concentrations) over time, several important decisions are required. These decisions include: (1) taking into account the characteristics of the water-quality data; (2) the type of trend (monotonic or step trend); (3) the selection of appropriate general method to use (parametric or nonparametric); (4) the different data manipulation considerations, such as transformations and removal of natural factors (e.g., stream flow, seasonality) that influence constituent concentrations; and (5) the objectives of the study (Hirsch et al., 1982; Hirsch et al., 1991; Ngwenya, 2006).

CHARACTERISTICS OF WATER QUALITY DATA

Water-quality data have several characteristics that are generally problematic for trend analysis methods (Lettenmaier et al., 1991; Helsel and Hirsch, 1991). Helsel and Hirsch (1991) discuss characteristics that are commonly found in water-quality data that include:

- a lower bound of zero (i.e., no negative values are possible);
- distribution (i.e., non-normal, log-normal, skewness);
- outliers (i.e., extreme values, not related to measurement error);
- cycles (i.e., seasonal, monthly, weekly, daily);
- missing values (i.e., a few isolated values or large gaps);
- censored data (i.e., less-than or greater-than a threshold value);
- and serial correlation (i.e., autocorrelation).

The ability to recognize and account for various characteristics of water-quality data is important in the selection and application of appropriate statistical methods to evaluate water-quality trends. The use of inappropriate methods due to invalid assumptions about the characteristics of the water-quality data may lead to incorrect or inconclusive results from the interpretations of the analysis (Helsel and Hirsch, 1991).

TYPES OF TRENDS

There are two primary types of trends that should be considered for hypothesis testing and estimations of trends in water-quality data, known as monotonic and step trends (Hirsch et al., 1991).

Monotonic Trend: This type of trend occurs when the water quality is changing monotonically over time. A monotonic trend is described as being a unidirectional, gradual (or sudden) change during some time period (Hirsch et al., 1982). Many of the trend detection methods whether parametric (e.g., simple linear regression) or nonparametric (e.g., Mann-Kendall test, Seasonal Kendall test, Sen Slope estimator) tests are based on the assumption of a monotonic change and are most often selected.

Step Trend: This type of trend occurs when there is a change in water quality from one specific, constant level to another completely different level, and the evaluation of step trends is useful in two cases. The first situation is when the data records represent two distinct periods of time with a relatively long gap between them (Helsel and Hirsch, 1991; Hirsch et al., 1991). The second case is when there is a change in water quality that can be traced to a known event that occurred at a specific time in the data records, which divides the record into “before” and “after” periods (Helsel and Hirsch, 1991; Hirsch et al., 1991). Both Helsel and Hirsch (1991) and Hirsch et al. (1991) recommend that step trends should be preselected before any of the data is examined, or based on some prior knowledge of an event that occurred at a specific time that could have influenced a change in water quality. Trend detection methods that are applied to step trends include parametric (e.g., two sample t test) or nonparametric (e.g., Wilcoxon-Mann-

Whitney test) methods. These tests are based on the assumption that the data is collected before and after a specific period of time, which represent distinctly different locations (mean or median) of the data. More recently, change point analysis has been applied to trends to identify changes in data deviations that occur at a specific time over the study period (Scott et al., 2011).

STATISTICAL TREND ANALYSES METHODS

Many statistical methods are available to determine trends in water-quality data, but as Griffith et al. (2001) discovered none are published as the 'standard' data analysis method. However, a few of these methods have gained popularity and are more commonly applied in water-quality trend testing. All the statistical methods used to detect trends are incorporated into two broad categories, parametric and nonparametric techniques.

Parametric Methods

Parametric statistical techniques are based on the assumptions that the data is normally distributed and independent. When these assumptions are valid, then parametric methods are the most powerful tests for any given significance level (Hirsch et al., 1991). However, water-quality data are most commonly skewed causing the data to exhibit non-normal distributions; therefore, reducing the overall power of parametric tests to detect trends (Helsel and Hirsch, 1991; Hirsch et al., 1991). However, data transformation might be useful to allow the transformed data to fit required assumptions.

Linear Regression: The most commonly used parametric method is simple linear regression, which detect a monotonic trend over time (Hirsch et al., 1991). Linear regression describes the relationship between the response variable (i.e., constituent concentrations) and the explanatory variable (i.e., discharge, seasonality). In addition, the regression line provides a calculation for the slope coefficient, which is an estimate of the magnitude of the trend.

Nonparametric Methods

Nonparametric statistical methods are tests that are distribution free; requiring no assumption about the data distribution. These tests are based on the use of rank order statistics and require the data be independent. Nonparametric methods, such as the Seasonal Kendall test, Mann-Kendall test, and Rank-Sum test, provide information about the existence of a trend in the data; however, the magnitude of a trend is not given. The magnitude of the trend is calculated using other nonparametric tests such as the Sen's slope estimator or Seasonal Kendall slope estimator.

Hirsch et al. (1991) stated that nonparametric tests are just as powerful as parametric tests when data are normally distributed and require fewer assumptions. The farther the data departs from normality; nonparametric tests have shown to be more powerful and efficient than their parametric counterparts (Helsel and Hirsch, 1991; Hirsch et al., 1991; Esterby, 1996). Nonparametric methods have become commonly used in trend studies that involve multiple stations and multiple constituents due to the overwhelming work load that is caused from checking assumptions for each individual data set (Helsel and Hirsch, 1991; Hirsch et al., 1991).

Seasonal Kendall Test: Hirsch et al. (1982) developed a modified version of the Mann-Kendall test for monotonic trends, known as the Seasonal Kendall test. This test is the most frequently used trend analysis method because it is not sensitive to seasonality, which normally exists within time series data. Since it is a nonparametric trend analysis method, the Seasonal Kendall test doesn't use the actual data values but uses only the ranks and signs of the data (Smith et al., 1996). Also, it brings all the robust statistical properties offered by the Mann-Kendall test and is applicable to either raw data or residuals from a previous analysis (Helsel and Hirsch, 1991; Zipper et al., 1992). The Seasonal Kendall test is based on the assumptions that water quality is cyclical (i.e., water quality varies with the seasons in the year) and has a period of one year (Esterby, 1996). The test accounts for the effects of seasonality by applying the Mann-Kendall test to each season separately and then combines the results (Helsel and Hirsch, 1991).

For example, when seasons are set as monthly, then January values are compared with only January values, February values against only February values and so on for all twelve months of the year. Also, comparisons cannot be made across the seasonal boundaries (Helsel and Hirsch, 1991). The Kendall S statistic, S_i are computed and summed to provide an overall Seasonal Kendall statistic, S'. The Kendall S statistic is defined as the measurement of the monotonic dependence of constituent concentration on the time (Helsel and Hirsch, 1991). Where a positive or negative value of S' indicates either an upward (i.e., increasing values with time) or downward trend (i.e., decreasing values with time), respectively (Hirsch et al., 1982).

The Seasonal Kendall test also provides a Kendall tau (τ) (i.e., Kendall's correlation coefficient) value, which is a measurement of the strength of the monotonic relationship between time and constituent concentrations (Kendall, 1938; Kendall, 1975; Helsel and Hirsch, 1991). Where a tau value equal to -1 or +1 indicates either a perfect negative or positive relationship, or a tau value equal to zero shows no relationship (i.e., no trend) (Cavanaugh and Mitsch, 1989).

Sen Slope Estimator: The Sen slope estimator is a method that provides an estimation of the trend magnitude (Sen, 1968). This nonparametric method is closely related to the Mann-Kendall test. The Sen slope estimator is most effective when used to determine monotonic trends and is not greatly affected by outliers, missing data, and censored data. It is computed as the median of all pair wise slopes between data observations for a particular season (Sen, 1968;

Hirsch et al., 1991; Sprague and Lorenz, 2009; Gilbert, 1987). This slope can be used to estimate percent change in constituent concentrations over time.

MANIPULATION OF WATER-QUALITY DATA

Transformations

Helsel and Hirsch (1991) state that transformations should be applied for three reasons, which are to make data more symmetric, linear, and constant in variance. The more commonly used monotonic transformations for water-quality data are logarithm, cube root, and square root. Also, when working with multiple data sets that are similar; avoid determining the 'best' transformation for each specific data set; and instead, select one transformation that works reasonably well for all of the data sets (Helsel and Hirsch, 1991).

Water-quality data (i.e., constituent concentrations and stream discharge) are typically characterized as having a log-normal distribution, so it has become common practice to log-transform the data prior to trend analysis (Richards and Baker, 2002; White et al., 2004). Log-transforming the data is particularly beneficial for parametric methods because the assumptions of regression analysis are more often met after data is transformed. On the other hand, nonparametric methods do not rely on normal distribution, and these statistical tests are applicable to either raw data or transformed data (Helsel and Hirsch, 1991; Hirsch et al., 1991; Lettenmaier et al., 1991). Helsel and Hirsch (1991) recommended that water-quality data be log-transformed when variables have a range of more than one order of magnitude, so that the results are more robust.

Flow Adjustment of Water Quality Data

Water-quality data (e.g., chemical concentrations) are often influenced by a combination of natural, random variables (e.g., discharge, rainfall, and temperature) and anthropogenic factors, which make obtaining the true trends in the data very difficult. These exogenous variables cause variations in the water-quality data and need to be accounted for and removed from the data (Helsel and Hirsch, 1991). The two most common methods of flow adjustment are the parametric linear regression and the nonparametric locally weighted regression and smoothing scatterplots (LOESS) (Bekele and McFarland, 2004).

It is well known that stream flow concentrations are typically a function of the stream discharge. Helsel and Hirsch (1991) describe that this can be attributed to two different types of physical phenomena, dilution and runoff. Dilution is when a solute is released at a near constant rate into a stream as the discharge varies over time, which results in the concentration decreasing as the flow increases. This effect is usually due to a point source (e.g., WWTP) or ground-water discharge to the stream. The other effect is diffuse runoff, which is when a solute, sediment, or a constituent attached to sediment is transported into the stream by overland flow (i.e., surface runoff) (Hirsch and Slack, 1984). This results in the concentration increasing as the flow increases and is attributed to nonpoint source. There are some cases where constituents (e.g., phosphorus) can show evidence of a combination of both these effects (Helsel and Hirsch, 1991).

Locally Weighted Scatterplot Smoothing (LOESS): The most commonly applied method of flow adjustment that accounts for variations in chemical concentration due to discharge is the locally weighted scatterplot smoothing (i.e., LOESS or LOWESS) technique (Cleveland, 1979; Helsel and Hirsch, 1991). This regression method is preferred over parametric methods, because it avoids the problems that often occur when formulating and selecting a best fit model (Lettenmaier et al., 1991). In addition, LOESS is more resistant to outliers and applicable to both raw and transformed data.

LOESS uses nonlinear smoothing (i.e., locally weighted regression) algorithms to provide a nonlinear fit to the data based on the fraction of data (i.e., sampling proportion) that influences the local regression (Lettenmaier et al., 1991; Bekele and McFarland, 2004; Helsel and Hirsch, 1991). The sampling proportion is also referred to as the smoothing parameter (*f*), where values range between 0 and 1. Traditionally, an effective *f* is determined through a trial and error approach in which the fit of various estimated relations are visually inspected until an accurate LOESS model is developed (Marron and Tsybakov, 1995). However, Bekele and McFarland (2004) determined that a sampling proportion (*f*) of 0.5, which is normally the default value in statistical packages, for LOESS regression is adequate for reducing variability in water-quality data (i.e., constituent concentrations) due to stream discharge.

Flow adjustment using the LOESS technique generates residuals, where each residual value represents the difference between the measured value and the LOESS smooth line (i.e., predicted value). The LOESS residuals (i.e., flow-adjusted concentrations, FACs) are then evaluated using appropriate trend analyses methods to detect significant trends over time.

Seasonality Adjustments of Water-Quality Data

Another major source of variation in water-quality data (i.e., constituent concentrations) results from the changes between the different seasons of the year. Seasonal patterns are often strongly exhibited in concentrations of surface waters (Helsel and Hirsch, 1991). These seasonal variations are credited to the influence of several factors such as stream discharge and sources of water (e.g., groundwater, snowmelt, or surface runoff), and biological activity (i.e., natural and anthropogenic). Generally, when accounting for the variation caused by discharge, it also explains some of the seasonal variation in water quality. However, seasonality frequently remains in the data even after discharge effects have been removed (Hirsch et al. 1982).

The parametric procedures used to account for seasonal variation are trigonometric functions (e.g., Fourier series) and stratification (i.e., separating data into particular pre-defined seasons). The nonparametric procedure applied to remove seasonality is the Seasonal Kendall test (Hirsch et al., 1982). The selection of an effective method that adjusts for seasonal variability in water-quality data is critical to increasing the overall ability to detect trends.

STUDIES OF WATER-QUALITY TRENDS

Table 2-1. Water-quality studies evaluating trends using various statistical methods that are available and used flow-adjusted concentrations (FACs).

Author(s)	Test Used
White et al., 2004	Censored linear regression on FACs (i.e., LOESS) comparing all data, base flow, and storm runoff.
Bekele & McFarland, 2004	Kendall tau test on FACs; flow-adjusted with LOWESS & ordinary least squares, OLS.
Cavanaugh & Mitsch, 1989	Seasonal Kendall test on censored data, FACs (i.e., regression); Seasonal Kendall slope estimator.
Richards & Baker, 2002	ANCOVA and linear regression on FACs (i.e., LOWESS).
Sprague & Lorenz, 2009	Regional Seasonal Kendall test and Seasonal Kendall test on censored raw data and FACs (i.e., LOWESS).
Johnson et al., 2009	QWTREND and Seasonal Kendall test on FACs
Walker, 1991	Seasonal Kendall test on raw data and FACs (i.e., regression); Seasonal Kendall slope estimator
Lettenmaier et al., 1991	Kendall test on FACs (LOESS) and raw data.

CHAPTER 3: WATER QUALITY TRENDS FOR SECTION 319 PRIORITY WATERSHEDS IN NORTHWEST ARKANSAS, 1997-2010.

INTRODUCTION

Water resources management and planning rely heavily on information harvested from water-quality databases to assist in decision making and develop management strategies for streams, rivers, and watersheds. Water-quality databases can be assessed using various methods of trend analysis, which examine the changes in water quality (i.e., constituent concentrations) over time. Water-quality trends provide valuable information evaluating if human interaction or management have positively or negatively influenced water quality. These trends can be used along with other watershed information to improve the knowledge of how past, current, and future management decisions have influenced the watershed.

The typical steps used to evaluate water-quality trends are as follows: First, the water-quality data (i.e., stream flow and constituent concentrations) would be transformed to account for the log-normal distribution of the data and reduce the effects of extreme values (Richards and Baker, 2002; Helsel and Hirsch, 1991; Hirsch et al., 1982; Lettenmaier et al., 1991; Haggard, 2010). The log-transformed constituent concentrations would then be adjusted for the effects of stream flow, typically using a two-dimensional smoothing technique like locally weighted regression (LOESS), which produces flow-adjusted constituent concentrations (FACs) (e.g., Bekele and McFarland, 2004; Cavanaugh and Mitsch, 1989; Richards and Baker, 2002; Helsel and Hirsch, 1991; Hirsch et al., 1982; Lettenmaier et al., 1991). Flow-adjusted constituent concentrations (i.e., LOESS residuals) would then be used to evaluate changes over time. Several studies (e.g., see White et al., 2004; Haggard, 2010) have evaluated trends using simple linear regression on FACs over time. However, many studies (e.g., see Cavanaugh and Mitsch, 1989; Lettenmaier et al., 1991; Johnson et al., 2009; Walker, 1991; Sprague and Lorenz, 2009) have used the nonparametric Seasonal Kendall test on FACs to detect monotonic trends, removing seasonality in the data. Monotonic trends assume FACs increase or decrease over time, whereas FACs might display step changes or multiple trends overtime. Recently, Scott et al. (2011) used change-point analysis to show changes in FAC deviation and correlate these thresholds to watershed management or monitoring changes.

In 1987, under Section 319 of the CWA, the Nonpoint Source (NPS) Management program was established by Congress, providing funds to individual State management programs. In recent years, Section 319 Programs have focused primarily on watersheds, where nonpoint source pollution has lead to water quality issues. Since 1990, the Arkansas Natural Resources Commission (ANRC) was appointed the task to allocate funds to various studies and projects within impaired watersheds, such as water-quality monitoring. The Arkansas Water Resources Center (AWRC) has been awarded grants for the last decade to monitor the quality of water within two Section 319 Priority Watersheds, the Illinois River Watershed and the Upper White River Basin within northwest Arkansas. Water-quality data from individual sites within these watersheds has been collected over the last decade and compiled into long-term databases.

The purpose of this study was to evaluate long-term trends in the water-quality data collected through the ANRC Section 319 Program over the last decade or where sufficient constituent concentration data was available. Six sampling sites were selected within the Illinois River drainage area and the Upper White River Basin in northwest Arkansas to investigate trends in constituent concentrations. Specifically, this study used flow-adjusted constituent concentrations to examine long-term trends in the water-quality data with parametric and nonparametric statistical techniques.

MATERIALS AND METHODS

STUDY SITE DESCRIPTION

The focus of this study was on two watersheds located in northwest Arkansas, the Illinois River Watershed and the Upper White River Basin. These watersheds have been identified by ANRC as being nutrient surplus watersheds and classified as priority watersheds by the Section 319 Program (ANRC, 2011). Also, Arkansas is the upstream State in both watersheds and can be required to meet water-quality standards set by downstream States, Missouri and Oklahoma. The study used six sampling sites, three within each watershed that includes the Ballard Creek (1), Osage Creek (2), Illinois River (3), Kings River (4), West Fork of the White River (5), and White River (6) (fig. 3-1).

The Illinois River Watershed has a drainage area of approximately 195,300 ha in northwest Arkansas and the Illinois River originates near Hogeye, southwest of Fayetteville, Arkansas flowing through the Ozark Highlands into Oklahoma. In recent years, the watershed has seen an increase in population, 131,240 to 193,914 from 1990 to 2000, which is a 48% increase in population (CAST, 2006). According to the 2010 Census, the population of residents has increased for the cities of Bentonville, Springdale, and Rogers by over 30 % in the past 10 years. The population growth is credited to local economic growth and stability, resulting in considerable increases in residential, commercial and industrial developments. In 2006, land coverage was primarily pasture (45%), forest (36%) and urban (13%) (CAST, 2006). Table 3-1 provides the land use land cover (LULC) percentages for the three sites within this watershed.

The Upper White River Basin (UWRB) is composed of four counties in northwest Arkansas with a drainage area of approximately 575,000 ha and crosses into southwest Missouri.

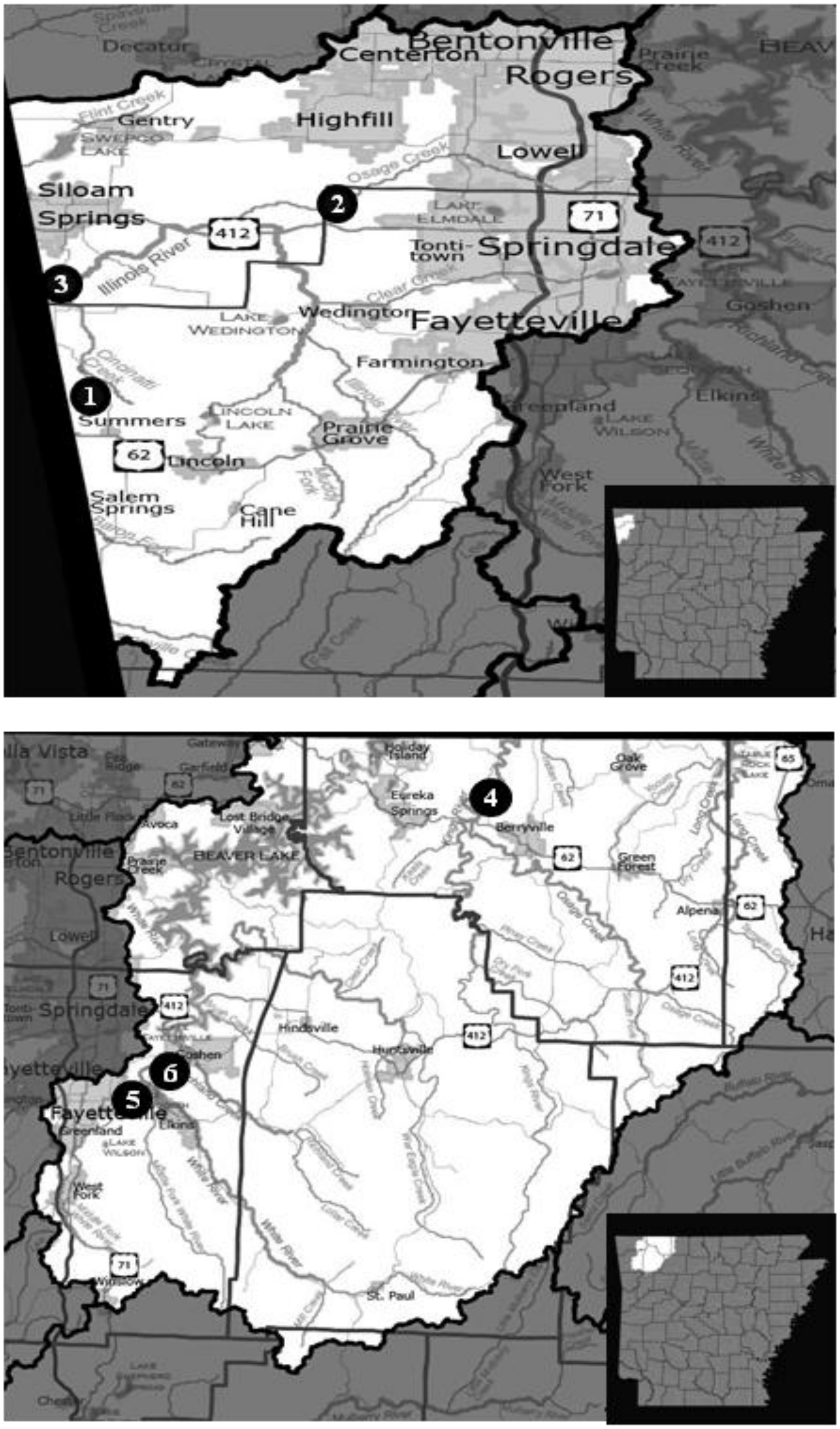

Figure 3-1. The Illinois River Watershed (top) and the Upper White River Basin (bottom) with the location of the six selected sampling sites in northwest Arkansas.

In 2006, land coverage in Arkansas was dominated by forest (64%) and pasture (23%) with a fraction of urban (4%), water (2%) and herbaceous (7%) (CAST, 2006). The population of residents in the watershed increased from 77,661 to 101,859 from 1990 to 2000, which is approximately 31% increase within the watershed (CAST, 2006). According to the 2010 Census, the populations of residents in Benton and Washington Counties have increased from 153,406 to 221,339 and 157,715 to 203,065 in the past 10 years, respectively. Also, located within the UWRB is northwest Arkansas's primary drinking water supply, Beaver Lake. Table 3-2 shows the land use land cover (LULC) percentages for the three sites within this watershed.

WATER-QUALITY DATA

Water-quality data were obtained from the AWRC in an electronic format (i.e., Excel files). The sampling sites had been monitored long-term through the ANRC Section 319 Program and water samples were analyzed by the AWRC Water Quality Lab following approved quality assurance project plans (QAPP). Constituent concentrations, including sulfate (SO_4), chloride (Cl^-), nitrate-nitrogen (NO_3-N), total nitrogen (TN), ammonium-nitrogen (NH_4-N), soluble reactive phosphorus (SRP), total phosphorus (TP), and total suspended solids (TSS) were available. When total nitrogen (TN) was not directly measured, it was calculated as the sum of total Kjeldahl nitrogen (TKN) plus nitrate-nitrogen (NO_3-N). Concentration data were then paired with respective discharge data that was obtained from the US Geological Survey (USGS) or stations maintained by the AWRC.

Water samples were collected every other week to monthly during base flow as grab samples or during storm events as discrete storm grab samples and/or composite samples from automated sampling equipment. The storm composite samples were flow-weighted; the event

Table 3-1. Selected study sites with global positioning coordinates in the Illinois River Watershed (HUC: 11110103) – Section 319 Priority Watershed, U.S. Geological Survey (USGS) site identification, land use for the specified drainage area (CAST, 2006), and available water quality data collected by Arkansas Water Resources Center (AWRC).

Site	USGS Station	Latitude	Longitude	Area[a] (ha)	Land Use (%) [b] U	W	H	F	P	Period of Record
1-BC[c]	AWRC	35°59’49”	94°31’38”	5,956	3.9	0.2	4.1	32	59	2000-2010
2-OC[d]	7195000	36°13’19”	94°17’18”	33,669	30	0.2	4.6	14	47	2007-2010
3-IR[e]	7195430	36°06’31”	94°32’00"	148,924	13	0.4	4.2	37	45	1997-2010

[a] Drainage area (ha) of study site.
[b] Land use categories: urban (U), water (W), herbaceous (H), forest (F), pasture (P), with crop and barren less than 1% in all the watersheds.
[c] Site 1: Ballard Creek on County Road 76 near Summers, Arkansas.
[d] Site 2: Osage Creek on Snavely Road near Elm Springs, Arkansas.
[e] Site 3: Illinois River on Highway 59 near Siloam Springs, Arkansas.

Table 3-2. Selected study sites with global positioning coordinates in the Upper White River Basin (Beaver Reservoir HUC: 11010001) – Section 319 Priority Watershed, U.S. Geological Survey (USGS) site identification, land use for the specified drainage area (CAST, 2006), and available water quality data collected by Arkansas Water Resources Center (AWRC).

Site	USGS Station	Latitude	Longitude	Area[a] (ha)	Land Use (%) [b]					Period of Record
					U	W	H	F	P	
4-KR[c]	7050500	36°25’38”	93°37’15”	136,492	1.7	0.1	6.3	71	20	2001-2010
5-WFWR[d]	7048550	36°03’14”	94°04’59”	31,856	14	0.4	5.6	66	14	2002-2010
6-WR[e]	7048700	36°06’21”	94°00’42”	106,707	5.8	0.5	4.7	76	13	2001-2010

[a] Drainage area (ha) of study site.
[b] Land use categories: urban (U), water (W), herbaceous (H), forest (F), pasture (P), with crop and barren less than 1% in all the watersheds.
[c] Site 4: Kings River on Highway 143 near Berryville, Arkansas.
[d] Site 5: West Fork of the White River on County Road 195 near Fayetteville, Arkansas.
[e] Site 6: White River on Highway 45 near Goshen, Arkansas.

mean constituent concentration data was paired with mean discharge that represented the time frame during which samples were collected. Next, databases were organized by date sampled, stage level, instantaneous discharge, water sample lab number, and constituent concentrations and then compiled for each of the six study sites. Finally, the original (i.e., raw (n_o)) water-quality data for each of the six sampled sites within the two watersheds were explored with descriptive statistics (see appendix A).

Next, the original (n_o) water-quality data were collapsed to a single daily value when multiple samples were collected in a day. This produced water-quality databases that were more consistent across the study sites and minimized autocorrelation between the data. The daily values were calculated using two simple procedures. First, the event mean discharge (EMQ, cfs) was determined by taking the average of all individual discharges representative of the samples collected. Then, the event mean concentration (EMC, mg L^{-1}) for each constituent was calculated by dividing the sum of discharge (Q, cfs) times concentration (C, mg L^{-1}) by the sum of discharges in that day. Descriptive statistics were evaluated and summarized (see appendix A).

Transformation of Water-Quality Data

The daily (n_d) water-quality data (i.e., constituent concentration and discharge) were log-transformed prior to trend analysis. This has become a common practice because stream discharge and concentrations are typically log-normally distributed (Richards and Baker, 2002). Log-transformation is suggested when values range across orders of magnitude (Helsel and Hirsch, 1991; Hirsch et al., 1991).

Flow-Adjustment of Water-Quality Data

Stream discharge is an exogenous variable that must be accounted for and removed when analyzing trends in water quality data, because constituent concentrations are often a function of discharge; it causes variation in the data that make trend detection more difficult (Helsel and Hirsch, 1991; Hirsch et al., 1991). Constituent concentration data were flow-adjusted using locally weighted scatterplot smoothing (LOESS) regression (Cleveland, 1979). The LOESS regression was accomplished by using a combination of an add-on program to Excel, called XLSTAT (Addinsoft, Inc., New York, NY) and SigmaPlot (Systat software Inc., San Jose, CA).

Flow-adjusting the daily (n_d) water-quality data was completed following the three step process outlined by White et al. (2004) (see fig. 3-2, as an example). First, a scatter plot of the constituent concentration as a function of time was created for visual inspection (fig. 3-2a; see Appendix B). Next, the log-transformed concentration data were plotted against log-transformed discharge (fig. 3-2b; see Appendix C), and then the LOESS two-dimensional smoothing technique was applied (Richards and Baker, 2002; Hirsh et al., 1991; White et al., 2004). The LOESS regression used a sample proportion of 0.5, which Bekele and McFarland (2004) showed to be effective at flow-adjusting constituent concentrations. Finally, the LOESS residuals (i.e., flow-adjusted concentrations, FACs) were used in both parametric and nonparametric trend analyses methods. Figure 3-2(c) shows FACs of total phosphorus as a function of time at the Illinois River in northwest Arkansas.

Removal of Outliers

An outlier is an observation that has a value that is quite different from others in the data set, and should not be removed just because it appears unusual (Helsel and Hirsch, 1991). Outliers should be checked for errors that might have occurred during measurement or recording and then removed accordingly. In this study, outliers were detected by assuming the FACs (i.e., LOESS residuals) were normalized after the daily (n_d) water-quality data were log-transformed and flow-adjusted. Since the FACs were assumed to be normally distributed, then an upper and

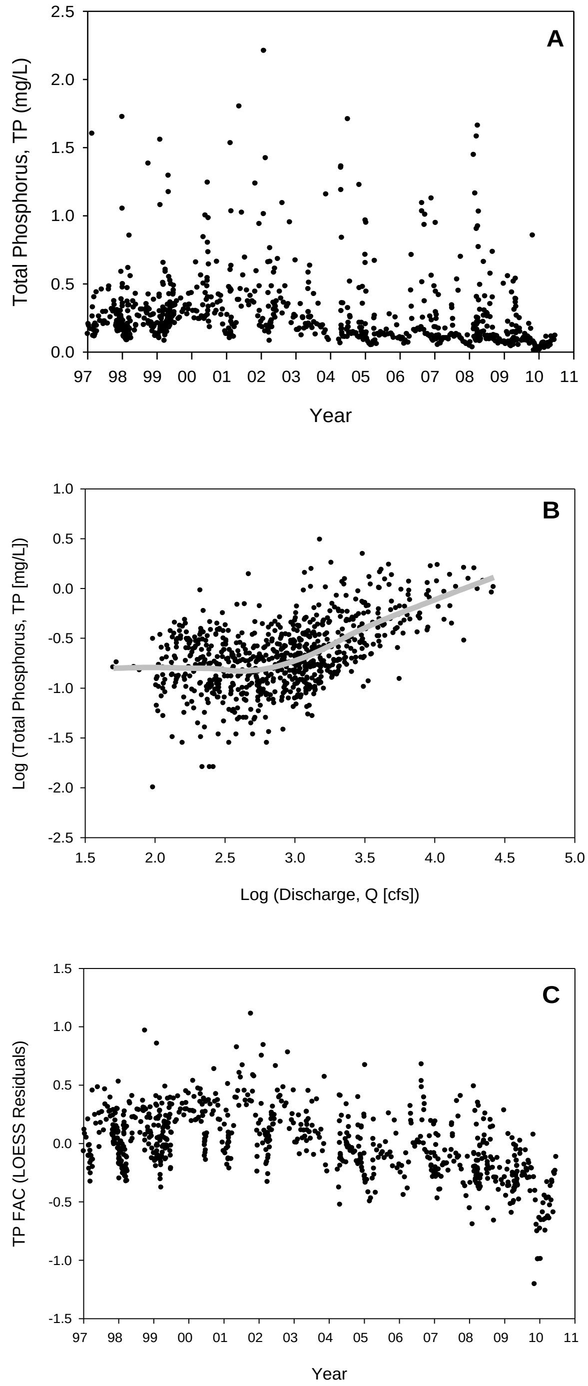

Figure 3-2. Example calculation, 774 daily samples (n_d): (a) Total phosphorus concentration from daily water quality samples at Illinois River from 1997-2010, (b) log-transformed total phosphorus concentration and log-transformed discharge with LOESS smoothing, and (c) LOESS residuals (i.e., flow-adjusted concentrations, FACs) as a function of time.

lower prediction interval was determined for each individual constituent's dataset. The 99% prediction interval was calculated for the FACs using the standard score equation, $z = (x - \mu)/\sigma$ and was solved for the x variable (i.e., FAC value), which represented the upper and lower 99% prediction value. Then the FAC observations outside of this prediction were removed. After the outliers were removed from the daily (n_d) water-quality data, the remaining water-quality data (n) were run through the three step process again to attain FACs independent of the outliers.

TREND ANALYSES

Simple linear regression between the FACs (i.e., LOESS residuals) and time was the parametric method used to examine the long-term trends in water quality. The Seasonal Kendall test and Sen's slope estimator were the nonparametric methods used in determining trends. The major advantage of the Seasonal Kendall test was accounting for seasonality. However, prior to being analyzed by the Seasonal Kendall test, the water-quality data had to be collapsed down to one sample per season, where a season was set as each individual month. The one sample per season (i.e., month) was determined by using the median FAC (i.e., LOESS residual) from the available data in that particular season, when three or more samples existed. If only two samples were in a season, then an average of the values was used. These FACs that represent monthly (n_m) water-quality data were examined for trends by the Seasonal Kendall test in XLSTAT. The program provided the Kendall tau (τ) value, which showed if a trend existed and whether it increased (positive) or decreased (negative) over time.

Also, WQStat Plus v9 (Sanitas Technologies, Shawnee, KS) was used to estimate the Sen's slope, the magnitude of change in FACs over time. However, the water-quality data was log-transformed prior to trend analysis; therefore, the slope represented a trend that was expressed in log units and can be converted back to the original units. Commonly to make the interpretation of a trend easier, the slope (b_1) is expressed in percent change per year using the equation: $S = (10^{b_1} - 1) \times 100$.

RESULTS

DATA CONSIDERATIONS

Outliers

Outliers were identified and reviewed before being removed from the flow-adjusted daily (n_d) water-quality data. The percentage of the removed outliers for the six sites ranged from zero to 3.5 % for SO_4, 4.2 % for Cl^-, 3.2 % for NO_3-N, 3.5 % for TN, 1.6 % for NH_4-N, 2.6 % for SRP, 2.8 % for TP, and 2.2 % for TSS. After the outliers were removed, the remaining water-quality data (n) were flow-adjusted again and used in trend analyses.

Censored

The Arkansas Water Resources Center (AWRC) Water Quality Lab generally reports constituent concentrations as measured, which allows the user to evaluate data below the method detection limit (MDL). The lab provides MDL as well as practical quantitation limits (PQL) for every constituent. Only select parameters, including NH_4-N and SRP, had a small number of censored values reported. Due to the very small number of censored values in these databases, the decision was made to exclude those data from the trend analyses instead of using censored data.

FLOW-ADJUSTING

The results from flow-adjusting the water-quality data produced graphs that illustrate the complex relationship between stream discharge and constituent concentrations (see Appendix C;

LOESS log (Q)·log (C) plots). The correlation between these two variables demonstrates different kinds of physical phenomena, which include the dilution effect (i.e., decreasing), runoff effect (i.e., increasing), or combinations of both across the range of discharge (Hirsch et al., 1991). These relationships were examined on a constituent by site basis, focusing on two flow regimes, base flow conditions and surface runoff events.

Base Flow Conditions

During base flow conditions, the relationship between concentration and discharge was variable across constituents and study sites. A total of 48 flow-concentrations were evaluated and approximately 65% showed decreasing concentrations as base flow discharge increased. Overall, SO_4 and Cl^- concentrations decreased with increasing discharge during base flow conditions; except SO_4 at Ballard Creek, where it increased. Both, NO_3-N and TN concentrations showed decreasing relationships at Ballard Creek and the White River, and increasing relationships at Osage Creek, Illinois River, Kings River, and West Fork of the White River. Ammonium-N concentrations decreased with increasing base flow discharge across all sites, except Osage Creek. Soluble reactive P and TP concentrations showed decreasing relationships across all sites, except the relatively constant concentration seen at the West Fork of the White River during base flow conditions. Total SS concentrations decreased with increasing base flow discharge at the Kings River; however, all other sites displayed a slight increase in concentration with flow.

Surface Runoff Events

The relationship between constituent concentrations and discharge varied during surface runoff events across the study sites, where about half the relationships showed concentrations that were decreasing with increasing flow and the others increased. Overall, SO_4, Cl^- and NO_3-N concentrations decreased with increasing discharge during surface runoff events across all sites. Total N concentrations exhibited decreasing relationships at Ballard Creek, Osage Creek, Illinois River, and the Kings River, while the other two sites displayed increasing relationships during surface runoff events. Ammonium-N, SRP, TP, and TSS concentrations increased with increasing discharge during surface runoff events across all sites.

FLOW-ADJUSTED CONCENTRATION TRENDS

The results of trend analyses on FACs, representing the daily (n) and monthly (n_m) data are presented in Tables 3-3 and 3-4. Trends were considered statistically significant if the p-value was less than 0.05 ($p < 0.05$); therefore, the null hypothesis, H_o (i.e., no trend) was rejected. Otherwise, the null hypothesis failed to be rejected, suggesting that FACs were not changing over time. For the plots of FACs and monthly FACs over time, refer to Appendices D and E.

Sulfate

Flow-adjusted SO_4 concentrations did not significantly change over time at Ballard Creek, Osage Creek, and the White River during the study period (tables 3-3 and 3-4, fig. 3-3). The regression analysis suggested that FACs significantly decreased at rates between -2.2 to -6.4 percent per year at the Illinois River, Kings River, and the West Fork of the White River over the period of the study (based on simple linear regression). The Seasonal Kendall analysis indicated a decreasing trend of -6.2 percent per year in the FACs at the Illinois River, but FACs did not significantly change at the other sites (based on Seasonal Kendall).

Table 3-3. Regression statistics from trend analyses of the flow-adjusted concentrations (FACs) at Section 319 water-quality monitoring sites, northwest Arkansas.

Constituent	Sampling Site	*n*	Outliers	R^2	p-value	% Change[a]
SO_4	Ballard Creek	210	3	0.002	0.522	
	Osage Creek	138	5	0.011	0.223	
	Illinois River	225	3	0.125	<0.001	-5.3
	Kings River	285	5	0.063	<0.001	-2.2
	West Fork White River	197	2	0.057	0.001	-6.4
	White River	320	8	0.003	0.341	
Cl^-	Ballard Creek	210	3	0.028	0.014	-3.3
	Osage Creek	137	6	<0.001	0.868	
	Illinois River	221	6	0.068	<0.001	-4.4
	Kings River	286	4	0.107	<0.001	-3.0
	West Fork White River	194	5	0.016	0.075	
	White River	315	13	0.012	0.052	2.1
NO_3-N	Ballard Creek	387	3	0.039	<0.001	4.1
	Osage Creek	140	3	0.001	0.703	
	Illinois River	765	7	0.003	0.155	
	Kings River	277	9	0.000	0.984	
	West Fork White River	366	12	0.001	0.667	
	White River	323	4	0.002	0.402	
TN	Ballard Creek	384	6	<0.001	0.909	
	Osage Creek	138	5	0.001	0.782	
	Illinois River	764	8	0.021	<0.001	-0.8
	Kings River	286	4	0.028	0.005	-2.6
	West Fork White River	377	6	0.083	<0.001	-5.2
	White River	322	6	0.080	<0.001	-5.5
NH_4-N	Ballard Creek	359	6	0.011	0.040	-4.1
	Osage Creek	131	0	0.014	0.155	
	Illinois River	642	10	0.020	<0.001	2.9
	Kings River	248	4	0.006	0.208	
	West Fork White River	337	5	0.001	0.594	
	White River	307	1	0.001	0.534	
SRP	Ballard Creek	380	10	0.038	<0.001	-5.3
	Osage Creek	142	1	0.173	<0.001	-17.5
	Illinois River	690	15	0.323	<0.001	-7.9
	Kings River	284	6	0.013	0.052	-4.0
	West Fork White River	373	6	0.050	<0.001	-7.0
	White River	319	5	0.068	<0.001	-10.5
TP	Ballard Creek	383	7	0.097	<0.001	-8.7
	Osage Creek	139	4	0.133	<0.001	-19.9
	Illinois River	760	14	0.230	<0.001	-6.7
	Kings River	286	4	0.068	<0.001	-8.1
	West Fork White River	375	7	0.102	<0.001	-10.9
	White River	321	7	0.112	<0.001	-11.7
TSS	Ballard Creek	387	2	0.185	<0.001	-20.2
	Osage Creek	141	2	0.122	<0.001	-40.2
	Illinois River	757	17	0.013	0.001	-2.5
	Kings River	277	5	0.050	<0.001	-8.4
	West Fork White River	378	4	0.085	<0.001	-13.7
	White River	321	7	0.140	<0.001	-18.1

[a] The percent change per year, negative and positive values correspond to decreasing and increasing flow-adjusted constituent concentrations over time, respectively.

Table 3-4. Nonparametric statistics from trend analyses on the seasonal flow-adjusted concentrations (FACs) at Section 319 water-quality monitoring sites, northwest Arkansas.

Constituent	Sampling Site	*n*	τ[a]	p-Value	S'[b]	Sen Slope[c]
SO_4	Ballard Creek	46	-0.167	0.451	-6	
	Osage Creek	30	-0.500	0.149	-6	
	Illinois River	46	-0.500	0.010	-18	-6.2
	Kings River	82	-0.056	0.625	-10	
	West Fork White River	40	0.056	0.880	2	
	White River	80	-0.100	0.357	-18	
Cl^-	Ballard Creek	46	0.278	0.175	10	
	Osage Creek	30	-0.333	0.386	-4	
	Illinois River	46	-0.389	0.050	-14	-5.5
	Kings River	83	-0.122	0.255	-22	
	West Fork White River	40	-0.278	0.175	-10	
	White River	80	0.100	0.357	18	
NO_3-N	Ballard Creek	90	0.175	0.164	44	
	Osage Creek	30	0.333	0.386	4	
	Illinois River	159	0.081	0.187	76	
	Kings River	83	-0.056	0.625	-10	
	West Fork White River	80	0.033	0.786	6	
	White River	81	-0.078	0.481	-14	
TN	Ballard Creek	89	0.063	0.515	16	
	Osage Creek	30	0.333	0.386	4	
	Illinois River	159	-0.061	0.324	-57	
	Kings River	83	-0.067	0.551	-12	
	West Fork White River	84	-0.278	0.003	-70	-6.6
	White River	81	-0.111	0.303	-20	
NH_4-N	Ballard Creek	88	-0.183	0.051	-46	-7.0
	Osage Creek	28	-0.167	0.773	-2	
	Illinois River	135	-0.050	0.724	-6	
	Kings River	82	-0.111	0.303	-20	
	West Fork White River	83	0.078	0.481	14	
	White River	80	0.144	0.175	26	
SRP	Ballard Creek	89	-0.103	0.278	-26	
	Osage Creek	30	0.167	0.773	2	
	Illinois River	142	-0.378	< 0.001	-68	-10.8
	Kings River	83	-0.400	< 0.001	-72	-8.5
	West Fork White River	84	-0.214	0.022	-54	-5.6
	White River	80	-0.078	0.481	-14	
TP	Ballard Creek	90	-0.238	0.011	-60	-8.2
	Osage Creek	30	0.333	0.386	4	
	Illinois River	159	-0.427	< 0.001	-400	-9.2
	Kings River	84	-0.365	< 0.001	-92	-11.5
	West Fork White River	84	-0.452	< 0.001	-114	-15.9
	White River	81	-0.311	0.003	-56	-13.4
TSS	Ballard Creek	90	-0.500	< 0.001	-126	-20.6
	Osage Creek	30	-0.333	0.386	-4	
	Illinois River	159	-0.135	0.028	-126	-4.4
	Kings River	84	-0.119	0.209	-30	
	West Fork White River	83	-0.250	0.040	-30	-16.7
	White River	81	-0.356	0.001	-64	-19.4

[a] Seasonal Kendall tau (τ);
[b] Seasonal Kendall statistic (S');
[c] Sen's Slope Estimator; the percent change per year.

Chloride

Flow-adjusted Cl^- concentrations did not significantly show monotonic trends at Osage Creek and the West Fork of the White River during the study period (tables 3-3 and 3-4, fig. 3-4). The change in FACs ranged from -3.0 to -4.4 percent per year across Ballard Creek, Illinois River, and the Kings River (based on simple linear regression). In addition, regression analysis indicated an increasing trend in FACs of 2.1 percent per year at the White River. The Seasonal Kendall analysis suggested that FACs decreased (-6.2 percent per year) at the Illinois River during the study period, whereas no other trends were observed across these sites based on this nonparametric approach.

Nitrate-Nitrogen

Overall, FACs of NO_3-N were not significantly changing over time across these sites, except at Ballard Creek (tables 3-3 and 3-4, fig. 3-5). Nitrate-N increased at a rate of 4.1 percent per year over the study period (based on simple linear regression). This NO_3-N trend was not statistically significant based on the Seasonal Kendall analysis, nor were any other trends suggested at the other sites.

Total Nitrogen

Flow-adjusted TN concentrations showed no monotonic changes over time at Ballard Creek and Osage Creek during the study period (tables 3-3 and 3-4, fig. 3-6). Several decreasing trends were observed (based on simple linear regression), ranging from -0.8 to -5.5 percent per year across the Illinois River, Kings River, West Fork of the White River, and the White River. A decreasing trend of -6.6 percent per year was also observed at the West Fork of the White River based on the Seasonal Kendall analysis; however, the Seasonal Kendall tau (τ) did not show any other significant trends in FACs of TN.

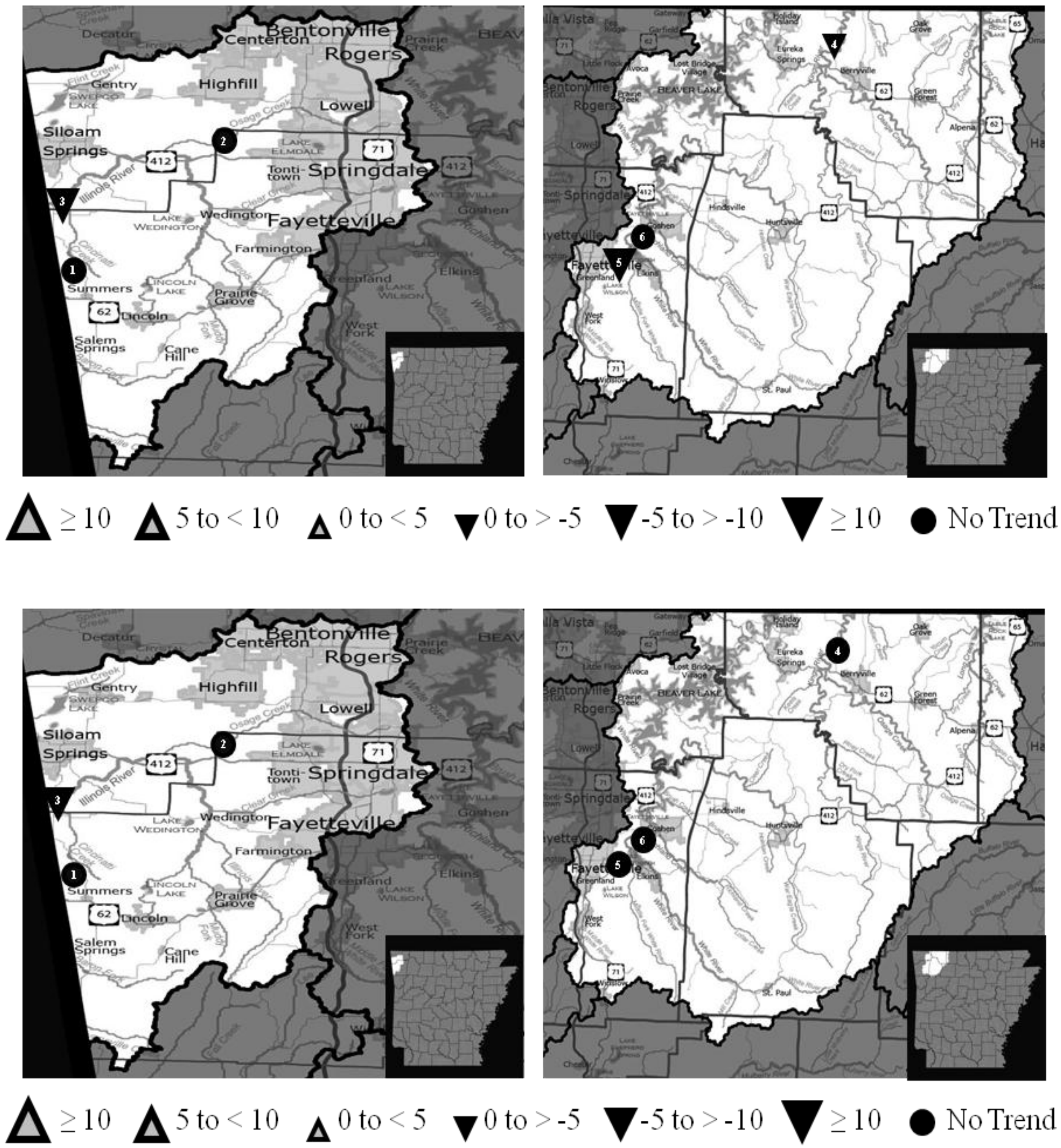

Figure 3-3. Flow-adjusted trends (percent change per year) in sulfate concentrations applying simple linear regression (top) and the Seasonal Kendall test (bottom).

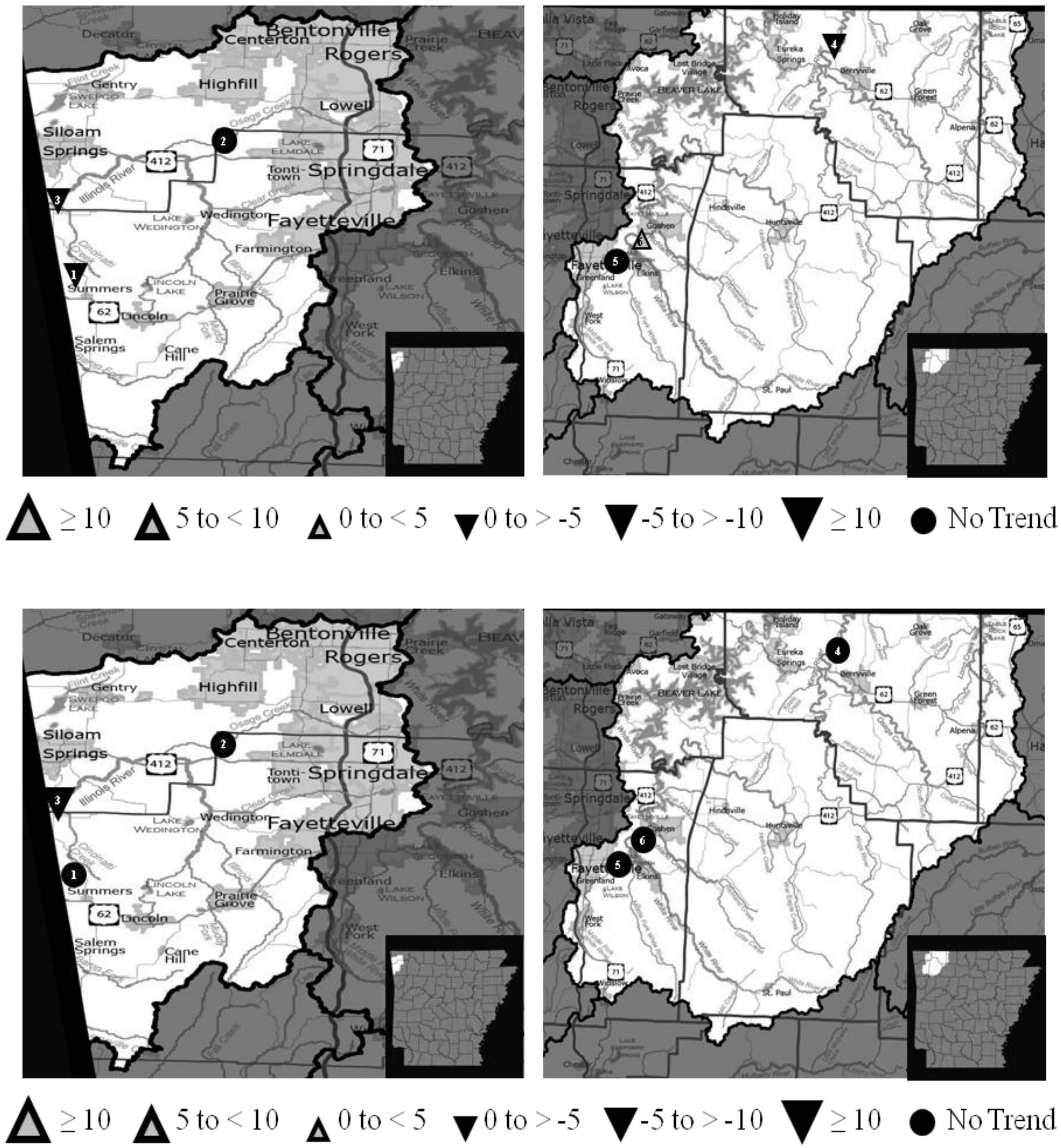

Figure 3-4. Flow-adjusted trends (percent change per year) in chloride concentrations applying simple linear regression (top) and the Seasonal Kendall test (bottom).

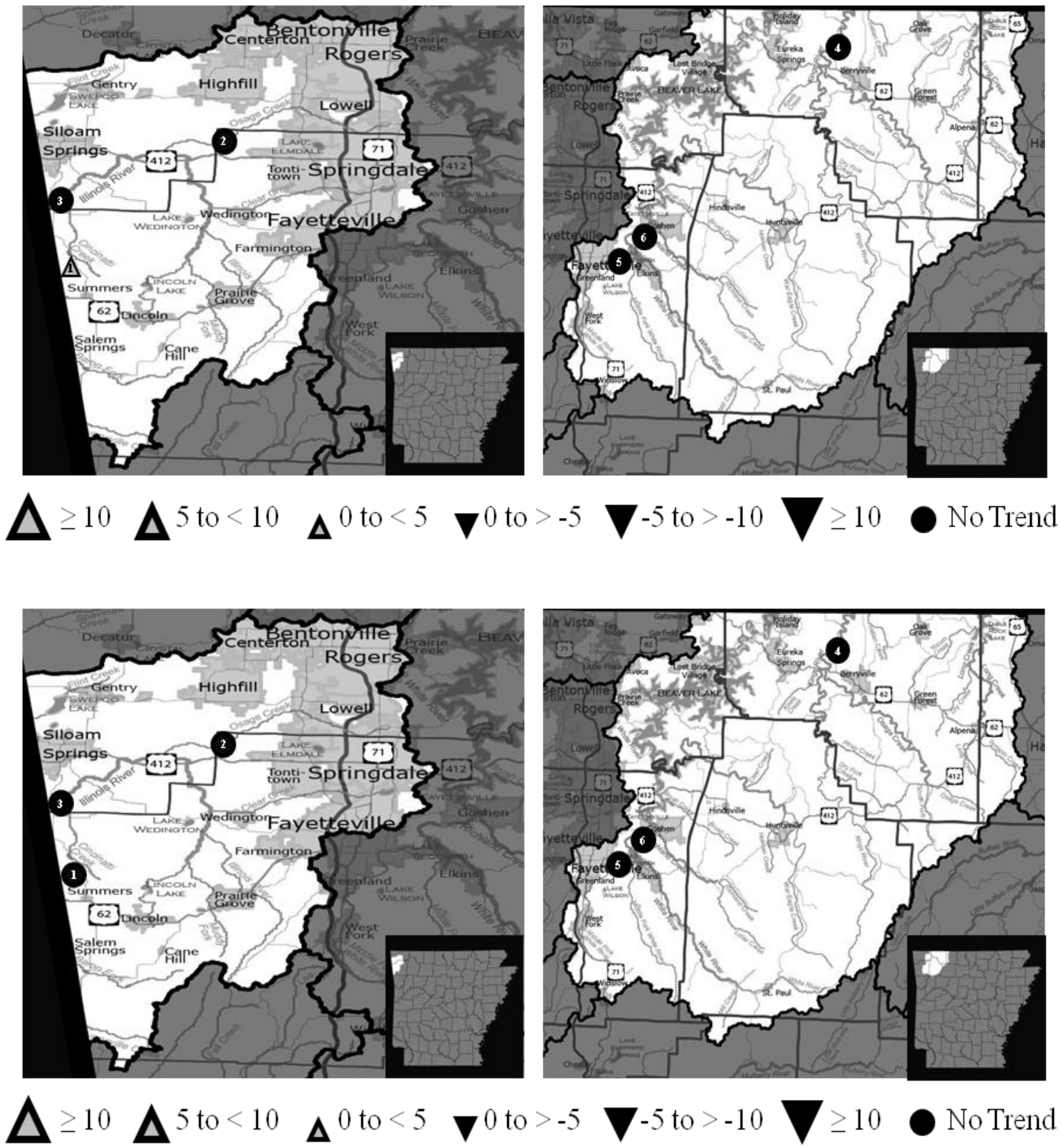

Figure 3-5. Flow-adjusted trends (percent change per year) in nitrate-nitrogen concentrations applying simple linear regression (top) and the Seasonal Kendall test (bottom).

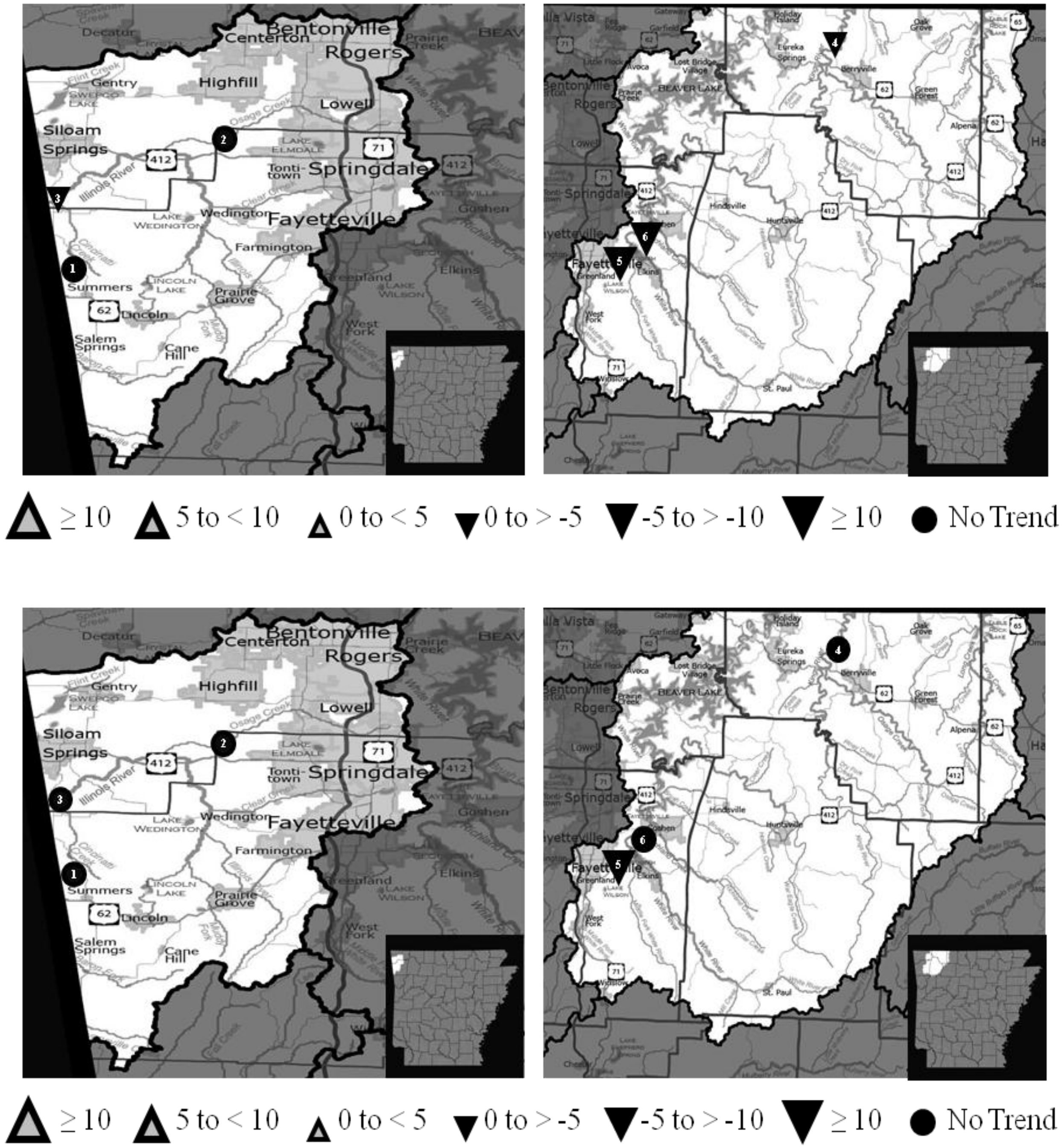

Figure 3-6. Flow-adjusted trends (percent change per year) in total nitrogen concentrations applying simple linear regression (top) and the Seasonal Kendall test (bottom).

Ammonium-Nitrogen

Flow-adjusted NH_4-N concentrations indicated no significant changes over time at Osage Creek, Kings River, West Fork of the White River, and the White River during the study period (tables 3-3 and 3-4, fig. 3-7). However, FACs of NH_4-N showed decreasing trends at Ballard Creek, where the rate of change varied from -4.1 percent per year based on regression and -7.0 percent per year based on the Seasonal Kendall analysis. Based on simple linear regression analysis, FACs of NH_4-N increased at a rate of 2.9 percent per year at the Illinois River over the study period.

Soluble Reactive Phosphorus

Flow-adjusted SRP concentrations showed decreasing trends across all sites during the study period (tables 3-3 and 3-4, fig. 3-8). Highly significant decreasing trends in FACs were observed across these sites, except at the Kings River (based on simple linear regression), ranging from -4.0 to -17.5 percent per year during the study period. The Seasonal Kendall analysis suggested that FACs of SRP decreased at rates between -5.6 to -10.8 percent per year at the Illinois River, Kings River, and the West Fork of the White River, whereas no significant change over time was observed at the other sites based on this nonparametric approach.

Total Phosphorus

Flow-adjusted TP concentrations exhibited decreasing trends across all sites during the study period (tables 3-3 and 3-4, fig. 3-9). The regression analysis suggested that FACs significantly decreased at rates between -6.7 to -19.9 percent per year across all sites. Based on the Seasonal Kendall analysis, FACs of TP significantly decreased at rates ranging between -8.2 to -15.9 percent per year across all sites; except at Osage Creek where FACs showed no significant change over time (based on Seasonal Kendall).

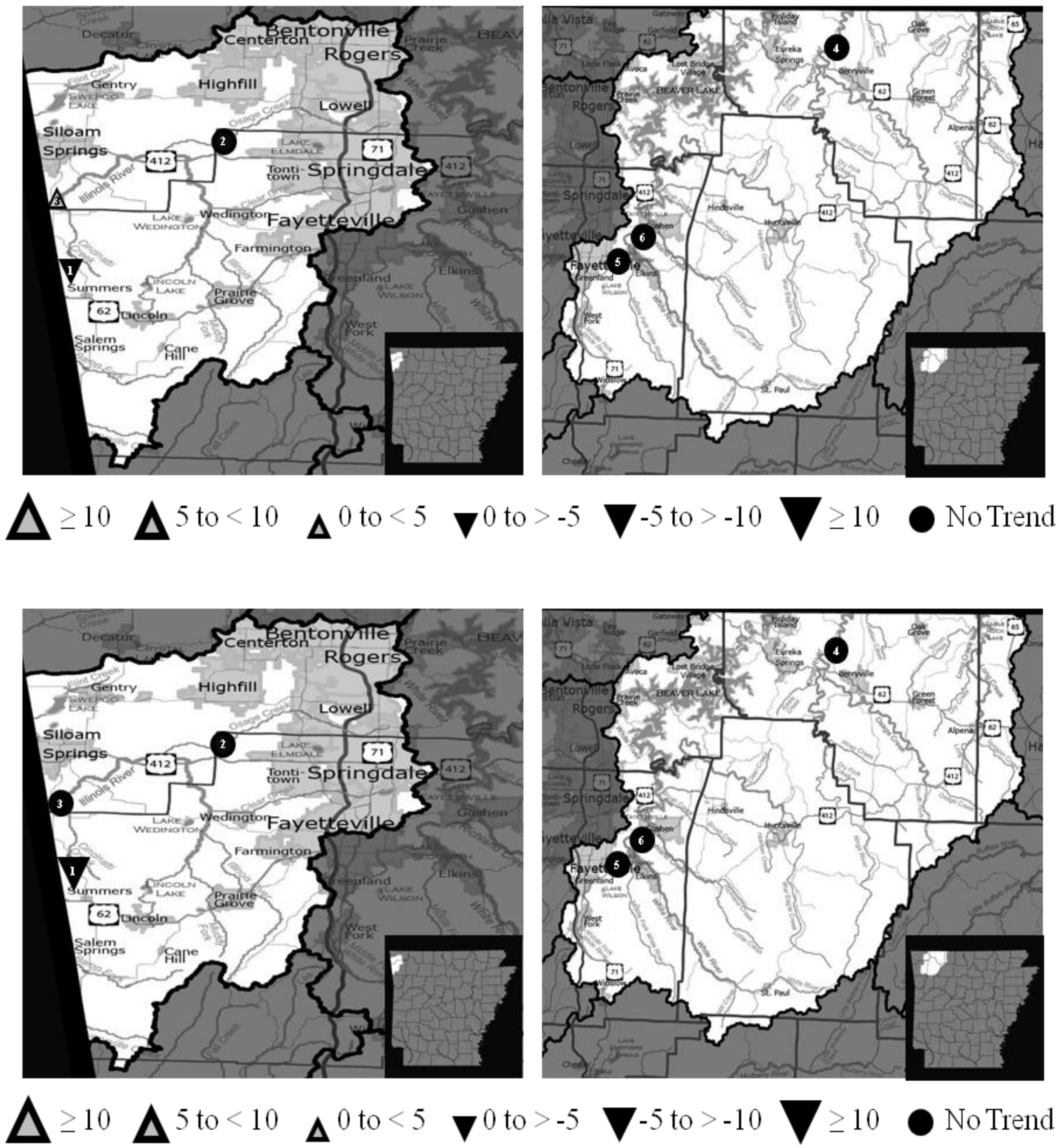

Figure 3-7. Flow-adjusted trends (percent change per year) in ammonium-nitrogen concentrations applying simple linear regression (top) and the Seasonal Kendall test (bottom).

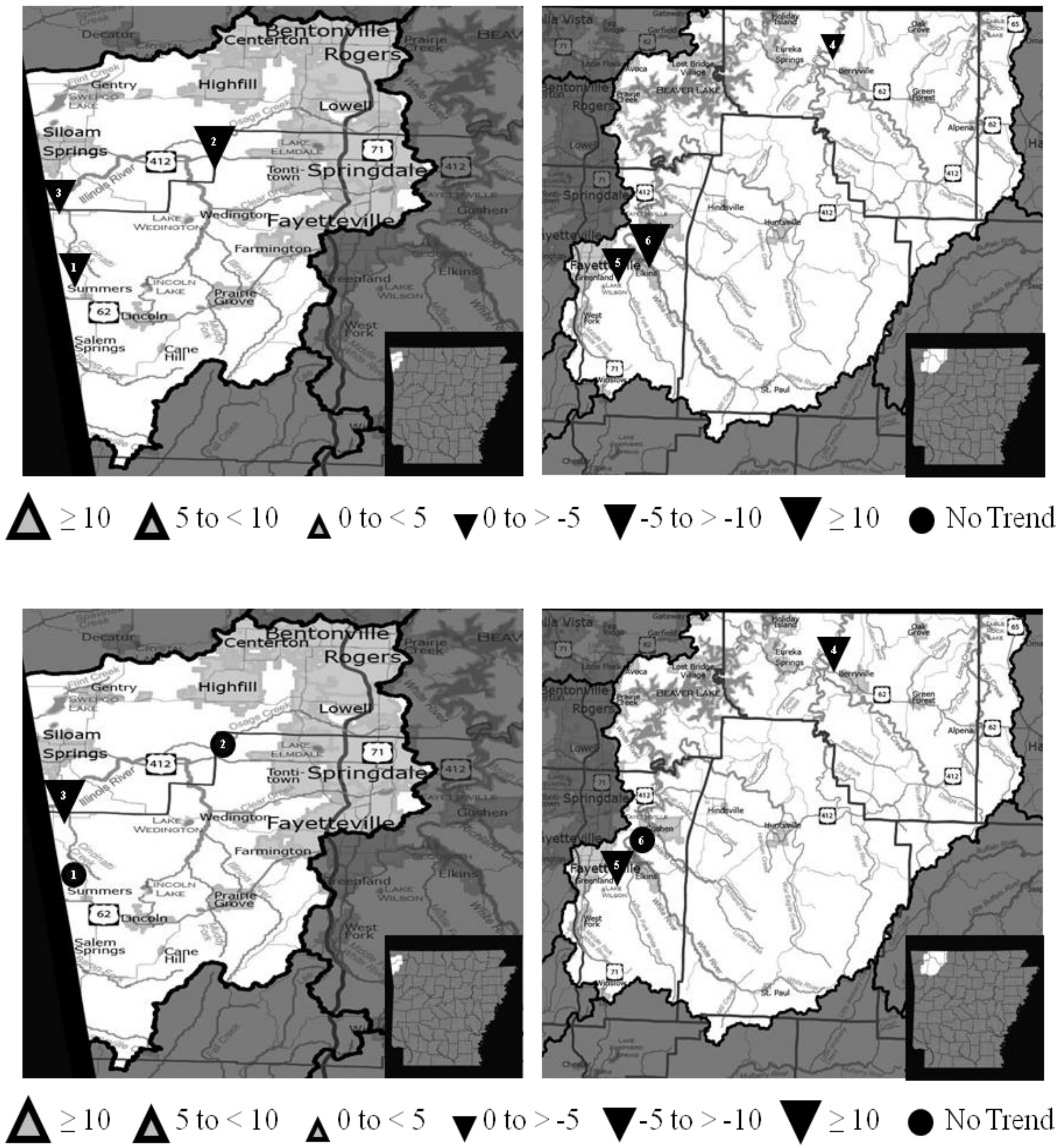

Figure 3-8. Flow-adjusted trends (percent change per year) in soluble reactive phosphorus (SRP) concentrations applying simple linear regression (top) and the Seasonal Kendall test (bottom).

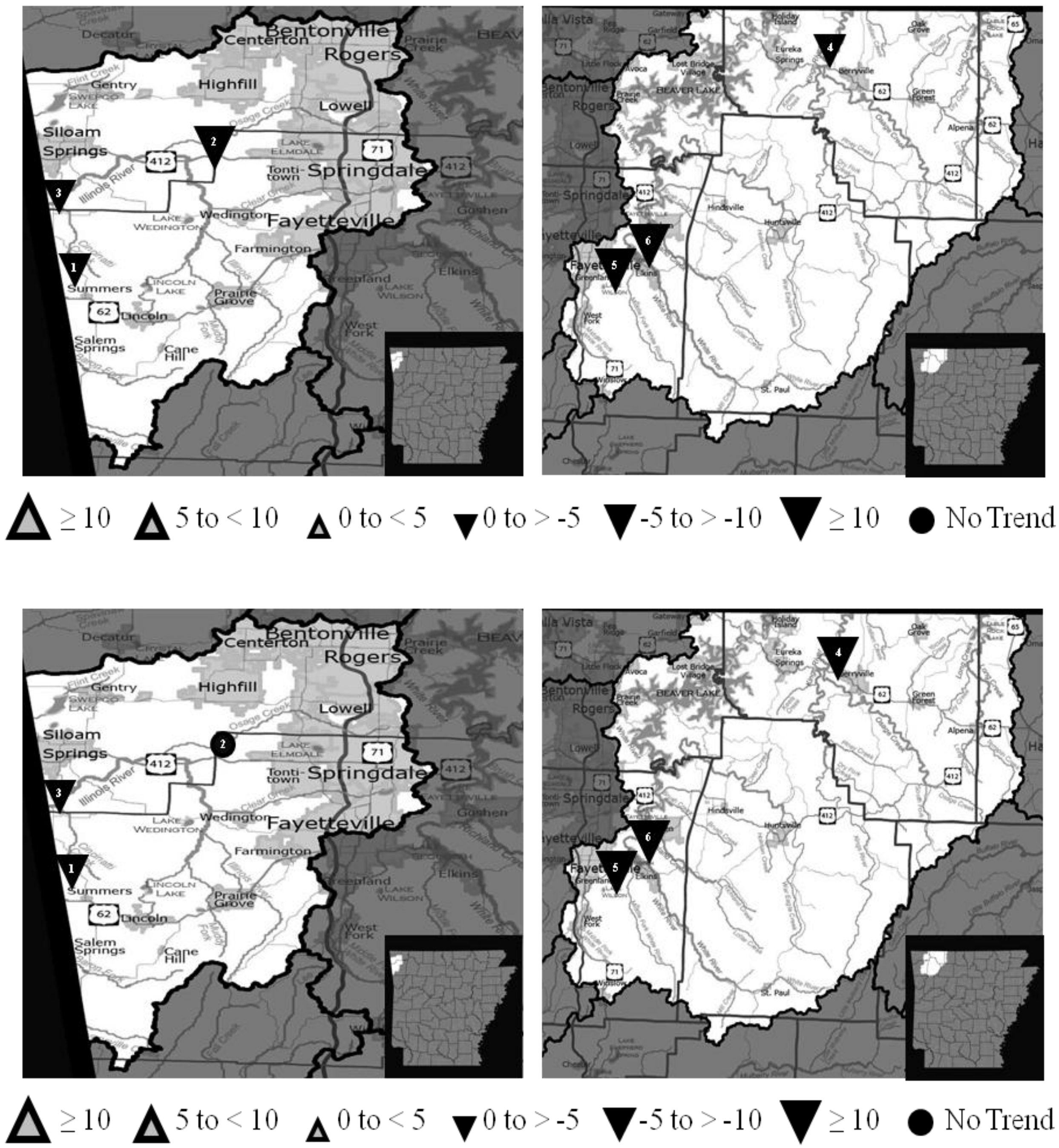

Figure 3-9. Flow-adjusted trends (percent change per year) in total phosphorus concentrations applying simple linear regression (top) and the Seasonal Kendall test (bottom).

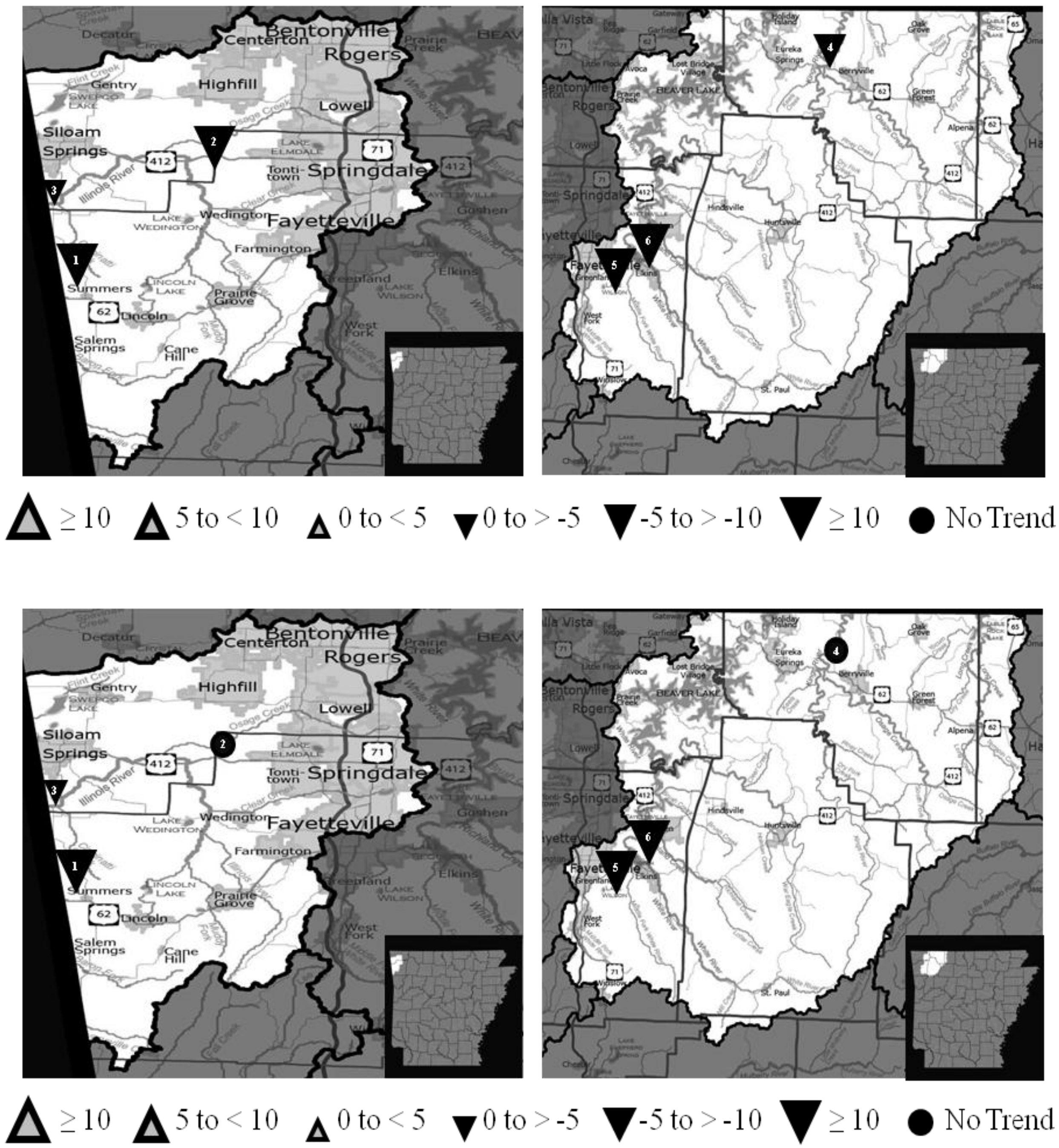

Figure 3-10. Flow-adjusted trends (percent change per year) in total suspended solids concentrations applying simple linear regression (top) and the Seasonal Kendall test (bottom).

Total Suspended Solids

Flow-adjusted TSS concentrations indicated decreasing trends across all sites during the study period (tables 3-3 and 3-4, fig. 3-10). Based on regression analysis, highly significant decreasing trends were observed across these sites and ranged between -2.5 to -40.2 percent per year over the period of the study. The change in FACs of TSS ranged from -4.4 to -20.6 percent per year across Ballard Creek, Illinois River, West Fork of the White River, and the White River (based on Seasonal Kendall).

DISCUSSION

General Approach Comparison

Overall, the nonparametric (i.e., Seasonal Kendall test and Sen's slope estimator) method agreed fairly well with the results from the parametric (i.e., simple linear regression) method. Basically, the datasets that were too small (e.g., less than 3 years) were problematic for the Seasonal Kendall test, which was the case with Osage Creek. In general, the two methods showed similar changes ($R^2 = 0.8945$, slope = 0.9551, $p < 0.0001$) in FACs when both methods detected significant trends; however, the magnitudes of these changes were slightly different. The discrepancies that were observed within statistical results could be attributed to the data's lack of adherence to each statistical test's required assumptions. When data fails to conform to these assumptions, it tends to decrease the power (i.e., probability to reject the null hypothesis when it is truly false) of the test and lead to incorrect or inconclusive results (Helsel and Hirsch, 1991).

In this study, the two statistical methods provided certain advantages and disadvantages when they were used to evaluate the water-quality data for trends. The advantage of the nonparametric Seasonal Kendall test was that it required fewer assumptions about the data, which was beneficial for this study since it evaluated multiple constituents at multiple stations. However, the Seasonal Kendall test doesn't quantify the magnitude of change, once a trend was detected; therefore, it required the use of the Sen's slope estimator. Another disadvantage was prior to the application of the Seasonal Kendall test; the data had to be collapsed into a monthly, median value, while simple linear regression was applied to multiple values per month. As a result, sample sizes varied between methods, and the number of observations used decreased for the Seasonal Kendall test. The advantage of the simple linear regression method was that it provided a measure of significance based on the calculated slope coefficient, which was an estimate of the magnitude of change. Additionally, the three step process that applied simple linear regression was much easier to use, replicate, interpret, and communicate with the funding agency and stakeholders than the nonparametric Seasonal Kendall test. However, a disadvantage of simple linear regression was that it required the data to be normally distributed and independent to be deemed appropriate and reliable; therefore, water-quality data were log-transformed and the slope had to be re-transformed to provide the percent change per year.

Also, this study assumed that all trends within the water-quality data were changing monotonically over time, so both statistical techniques would be appropriately used. However, different human activities can change the quality of water from a particular level to another; therefore, separating the water-quality data into diverse groups and step trend analysis would be more appropriate. For instance, several FACs at the Illinois River showed this type of change over the study period, sometime around 2002, which could be related to several watershed management changes. Even though the water-quality data were examined for monotonic trends, the statistical methods can still suggest that there was a significant change in the water quality over time; however, the magnitude of trend would be incorrect, since the slope of the change is inaccurate.

TRENDS

Overall, P concentrations have decreased across northwest Arkansas at these select Section 319 monitoring sites. Specifically, flow-adjusted TP and SRP concentrations have shown decreasing trends across all sites in the Illinois River drainage area (IRDA) and the Upper White River Basin (UWRB), which could be related to a number of changes in P management. For instance, several point sources (i.e., WWTPs) within the IRDA voluntarily adopted P management strategies and began operating with regard to these strategies. The WWTPs at Rogers and Springdale changed to meet voluntary effluent limits of 1 mg TP L^{-1} in 1997 and 2002, respectively; the City of Fayetteville had a regulatory effluent of 1 mg TP^{-1} since the early 1990s. However, prior to the Springdale facility significantly reducing its effluent P concentration in 2002; elevated P concentrations at Osage Creek and the Illinois River were traced upstream to the facility's effluent discharge (Haggard, 2010). Once the Springdale WWTP started operating near this limit, P concentrations in the Spring Creek (i.e., tributary of the Illinois River) decreased over time and was shown to be significantly correlated to the facility's effluent P concentrations (Ekka et al., 2006).

Decreasing P concentrations at the Kings River in the UWRB could be attributed to new management strategies implemented at the City of Berryville WWTP, which discharges approximately 9 km upstream of the Kings River site into the Osage Creek (not the site included in trend analyses). In 2005, the effluent showed a drastic reduction in P concentration, which was attributed to a significant decrease in P that was being received as influent from a poultry processing plant (Nelson et al., 2005). Typically, 19 to 38 liters of wastewater with an average

TP concentration of 16.1 mg L^{-1} is produced per bird processed at a poultry processing plant (Rusten et al., 1998). Also, the facility upgraded its biological nutrient removal processes (BNR) in 2008, attempting to meet a new permit effluent limit of 1 mg TP L^{-1} by 2012.

Effluent P reductions from WWTP management have definitely decreased P concentrations in select streams and rivers, but several sites are not influenced by major WWTPs or WWTPs that have altered management strategies to reduce P in the effluent. During this time, the transition from nitrogen (N)-based management strategies to P-based nutrient management strategies could have contributed to reductions in P from nonpoint sources within the two watersheds. For instance, northwest Arkansas has been a national leader in poultry production the last few decades and one major environmental concern and focus of watershed managers was the application of poultry litter as a fertilizer on pastures. Prior to this transition, poultry litter was applied based on the N demand of crops; however, this resulted in P accumulation in surface soils (Sharpley et al., 2007) that could be lost in surface runoff. In 2003, Arkansas enacted three new laws to regulate and manage poultry litter, and one of these laws required the proper application of nutrients and utilization of poultry litter in nutrient surplus areas. One tool that was developed was the P index, which guides application rates of poultry litter on pastures (see DeLaune et al., 2004; Sharpley et al., 2010).

Another, important watershed management decision during this time was to transport poultry litter outside of nutrient surplus areas. The litter is purchased from poultry farms located in nutrient surplus areas; usually through broker services and then a portion of the hauling expenses were offset by federal grants offered through ANRC's poultry litter cost sharing program. In the adjacent Eucha-Spavinaw Basin, these types of agricultural practices have resulted in a reduction of litter application rates from 3 to 1.5 ton $acre^{-1}$ yr^{-1} between 2003 and

2008 (DeLaune et al., 2006; Sharpley et al., 2009). Several recent studies in Ozark basins have shown a positive relationship between increasing stream P concentrations and the percentage of pasture or agricultural land use within the basin (Peterson et al., 1992; Haggard et al., 2003a, 2007). Thus, it is conceivable that reducing P applied to the landscape would translate into decreased P concentrations within the steam.

Overall, flow-adjusted TSS concentrations have decreased across all selected Section 319 monitoring sites within the Illinois River drainage area (IRDA) and the Upper White River Basin (UWRB), which could be attributed to a combination of effective best management practices (BMPs) and other factors (i.e., number of animals, cropping patterns, and land uses) that have changed during the study period. Generally, TSS concentrations increased with increasing stream discharge at all sites, suggesting the primary contributors of sediment were nonpoint sources. The most likely source of sediment was from stream bank erosion; in fact, excessive stream bank erosion has been connected to human activities in northwest Arkansas, which has accelerated the naturally occurring process (ADEQ, 2004; Haggard et al., 2010). Therefore, water resource management has focused on improving management strategies that effectively reduce erosion caused by increases in runoff, alterations in stream channels (e.g., gravel mining), and removal of riparian zones and other potentially negative activities in the watersheds. In addition, various agencies and organizations have initiated numerous restorations projects within the IRWB and UWRB. For example, the Illinois River Watershed Partnership (IRWP) completed a project in 2010 that restored riparian buffers at six creeks in the IRWB.

CONCLUSIONS

The last decade, the major environmental concern in northwest Arkansas has been the impact of point and nonpoint sources of pollution (i.e., phosphorus, nitrogen, and sediment).

Therefore, watershed management has focused on identifying and quantifying the changes in water quality by monitoring and collecting water-quality data at select sites. In order to better understand the changes in water quality (i.e., constituent concentrations) over time within the Illinois River Watershed and the Upper White River Basin, the objective of the study was to use flow-adjusted constituent concentrations to examine trends in water-quality data with parametric (i.e., linear regression) and nonparametric (i.e., Seasonal Kendall test and Sen's slope estimator) statistical techniques. Overall, there was substantial congruence in the results of the two trend analyses methods. And based on the results, this study concludes that the quality of water in the watersheds in northwest Arkansas has generally improved over the period of the study, which suggests watershed management strategies have been effectively implemented. Overall, TN, SRP, TP and TSS have shown significant decreases in FACs across these two watersheds over the defined study period.

CHAPTER 4: CONCLUSIONS AND RECOMMENDATIONS

CONCLUSIONS

The purpose of this study was to evaluate long-term trends in the water-quality data collected through the ANRC Section 319 Program over the last decade at six selected sites in northwest Arkansas. In order to detect changes in constituent concentrations (i.e., sulfate, chloride, nitrate-nitrogen, total nitrogen, ammonium-nitrogen, soluble reactive phosphorus, total phosphorus, and total suspended solids) over time within the Illinois River Watershed and the Upper White River Basin the following study objectives were completed:

Objective 1: Apply a parametric (i.e., linear regression) statistical technique to flow-adjusted concentrations, FACs to identify trends in the water-quality data. The null hypothesis to be tested was that constituent concentrations were not changing over time. There were six study sites, which included eight constituents per site; therefore, a total of 48 flow-adjusted concentrations were evaluated for trends. Trend analyses detected 32 (66.6 %) significant trends in flow-adjusted concentrations, where 29 (90.6 %) FACs were decreasing trends and 3 (9.4 %) were increasing trends, respectively. These results could lead to the conclusion that the water quality in the watersheds has generally improved (i.e., decreasing concentrations) over the time of the study; therefore, the null hypothesis was rejected at least 66.6 % of the time.

Objective 2: Apply nonparametric (i.e., Seasonal Kendall test and Sen's slope estimator) statistical techniques to flow-adjusted concentrations, FACs to identify trends in the water-quality data. The null hypothesis to be tested was that constituent concentrations were not changing over time. The 48 flow-adjusted concentrations were examined for trends; in all, 16

(33.3 %) FACs trends were detected, which were all significantly decreasing over time. These results suggest that the quality of water has somewhat improved over time; so, the null hypothesis was reject at least 33.3 % of the time.

RECOMMENDATIONS

This study focused on a comprehensive evaluation of all the water-quality data that was collected through the Section 319 program; however, conducting separate trend analyses studies on water-quality data from base flow conditions and surface runoff conditions would be beneficial. This type of study could provide further knowledge about the changes in water quality that occurred during the different flow regimes at each site. Another possible study would be to investigate the relationships between changes in land use and water quality at each site, which could provide more information on possible sources of pollution within that specific basin.

This study is limited due to possible changes in sampling protocols (e.g. collection frequency and analytical methods) over the duration of the study, which compromises the reliability of the data. Because of these types of changes, it is difficult, if not impossible, to obtain long-term water-quality databases without having some uncertainty and/or variability in the data. Therefore, it is suggested that the results from trend analyses be interpreted cautiously because of the data limitations and influences of other external factors.

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APPENDIX A: DESCRIPTIVE STATISTICS OF WATER-QUALITY DATA

Table A-1: Descriptive statistics of stream discharge and constituent concentrations in water-quality samples collected at Ballard Creek, 2000-2010.

BC	Variable	n	Mean	Median	Range	Min	Max	STD
***n*₀** [a]	Q (cfs)	508	133	49	4258	7	4265	376
	SO_4 (mg/L)	237	14.33	14.16	23.54	3.95	27.49	4.50
	Cl (mg/L)	237	9.82	10.18	16.15	1.92	18.07	3.22
	NO_3-N (mg/L)	508	1.99	1.76	5.80	0.01	5.81	1.14
	TN (mg/L)	508	2.86	2.67	8.43	0.72	9.15	1.06
	NH_4-N (mg/L)	483	0.12	0.07	1.62	0.001	1.62	0.16
	SRP (mg/L)	508	0.21	0.15	1.68	0.005	1.69	0.20
	TP (mg/L)	508	0.42	0.27	3.18	0.008	3.19	0.45
	TSS (mg/L)	508	71	18	1612	< 1	1612	157
n_d [b]	Q	390	116	45	4258	7	4265	356
	SO_4	213	14.59	14.33	23.54	3.95	27.49	4.44
	Cl	213	10.05	10.36	16.15	1.92	18.07	3.13
	NO_3-N	390	2.25	2.14	5.80	0.009	5.81	1.14
	TN	390	2.91	2.79	5.28	0.72	6.00	1.01
	NH_4-N	365	0.11	0.06	1.62	0.001	1.62	0.16
	SRP	390	0.19	0.11	1.10	0.005	1.10	0.19
	TP	390	0.36	0.18	3.18	0.008	3.19	0.44
	TSS	389	55	10	834	< 1	835	121
n [c]	Q	390	116	45	4258	7	4265	356
	SO_4	210	14.56	14.31	23.54	3.95	27.49	4.36
	Cl	210	10.03	10.34	16.15	1.92	18.07	3.09
	NO_3-N	387	2.27	2.17	5.45	0.36	5.81	1.12
	TN	384	2.93	2.80	4.94	1.06	6.00	0.98
	NH_4-N	359	0.10	0.06	0.81	0.004	0.81	0.12
	SRP	380	0.18	0.11	0.98	0.009	0.98	0.18
	TP	383	0.36	0.18	3.17	0.02	3.19	0.43
	TSS	387	55	10	834	< 1	835	121
n_m [d]	Q	90	47	41	146	7	153	25
	SO_4	46	15.38	14.72	15.74	8.95	24.69	3.51
	Cl	46	11.16	11.26	11.08	5.24	16.32	2.37
	NO_3-N	90	2.23	2.31	4.46	0.55	5.01	0.88
	TN	89	2.81	2.86	3.32	1.14	4.46	0.73
	NH_4-N	88	0.09	0.06	0.38	0.01	0.39	0.07
	SRP	89	0.13	0.10	0.55	0.01	0.56	0.11
	TP	90	0.23	0.17	0.79	0.03	0.82	0.18
	TSS	90	22	9	200	< 1	201	34

[a] n_o, original (i.e., raw) data;
[b] n_d, daily (i.e., flow-weighted) data;
[c] n, data (i.e., after extreme outliers were removed from a 99 % P.I. of FACs n_d data);
[d] n_m, monthly (i.e., seasonally) data.

Table A-2: Descriptive statistics of stream discharge and constituent concentrations in water-quality samples collected at Osage Creek, 2007-2010.

OC	Variable	n	Mean	Median	Range	Min	Max	STD
n_o [a]	Q (cfs)	170	693	289	14865	57	14922	1599
	SO_4 (mg/L)	170	17.98	16.44	39.02	5.06	44.09	8.09
	Cl (mg/L)	170	16.91	15.75	39.15	3.39	42.53	8.36
	NO_3-N (mg/L)	170	3.40	3.71	4.90	0.82	5.72	1.19
	TN (mg/L)	170	3.81	3.93	4.59	1.57	6.16	1.01
	NH_4-N (mg/L)	152	0.06	0.03	0.48	0.01	0.49	0.08
	SRP (mg/L)	170	0.10	0.10	0.20	0.03	0.23	0.04
	TP (mg/L)	170	0.26	0.14	2.48	0.04	2.52	0.33
	TSS (mg/L)	170	118	13	1970	< 1	1970	256
n_d [b]	Q	143	490	230	9828	57	9886	1056
	SO_4	143	18.59	17.18	35.16	5.34	40.50	7.53
	Cl	143	17.74	17.12	34.16	4.34	38.50	7.83
	NO_3-N	143	3.50	3.78	4.90	0.82	5.72	1.12
	TN	143	3.90	4.00	4.23	1.65	5.88	0.92
	NH_4-N	131	0.05	0.03	0.42	0.01	0.43	0.07
	SRP	143	0.09	0.09	0.18	0.03	0.20	0.04
	TP	143	0.24	0.14	1.69	0.04	1.74	0.28
	TSS	143	108	11	1970	< 1	1970	251
n [c]	Q	143	490	230	9828	57	9886	1056
	SO_4	138	18.81	17.77	34.12	6.38	40.50	7.29
	Cl	137	17.95	17.14	34.03	4.47	38.50	7.62
	NO_3-N	140	3.55	3.80	4.77	0.95	5.72	1.07
	TN	138	3.95	4.04	4.23	1.65	5.88	0.88
	NH_4-N	131	0.05	0.03	0.42	0.01	0.43	0.07
	SRP	142	0.09	0.09	0.18	0.03	0.20	0.04
	TP	139	0.22	0.13	1.69	0.04	1.74	0.27
	TSS	141	91	11	1065	< 1	1065	192
n_m [d]	Q	30	236	161	573	80	652	161
	SO_4	30	20.89	19.98	28.90	8.62	37.52	6.95
	Cl	30	20.18	19.98	29.06	6.71	35.77	6.83
	NO_3-N	30	3.61	3.84	3.17	1.65	4.83	0.79
	TN	30	3.98	4.01	2.96	2.19	5.15	0.64
	NH_4-N	28	0.04	0.03	0.11	0.01	0.12	0.03
	SRP	30	0.09	0.10	0.12	0.03	0.15	0.03
	TP	30	0.16	0.12	0.44	0.05	0.48	0.10
	TSS	30	45	6	503	< 1	503	98

[a] n_o, original (i.e., raw) data;
[b] n_d, daily (i.e., flow-weighted) data;
[c] n, data (i.e., after extreme outliers were removed from a 99 % P.I. of FACs n_d data) ;
[d] n_m, monthly (i.e., seasonally) data.

Table A-3: Descriptive statistics of stream discharge and constituent concentrations in water-quality samples collected at Illinois River, 1997-2010.

IR	Variable	n	Mean	Median	Range	Min	Max	STD
***n*o** [a]	Q (cfs)	1751	2644	1326	32238	50	32288	3841
	SO_4 (mg/L)	281	12.73	12.27	25.60	4.91	30.51	3.70
	Cl (mg/L)	280	10.59	9.83	23.27	2.32	25.60	4.65
	NO_3-N (mg/L)	1749	2.33	2.26	5.73	0.18	5.91	0.75
	TN (mg/L)	1751	3.05	2.96	10.10	0.37	10.48	0.86
	NH_4-N (mg/L)	1611	0.07	0.04	0.57	0.0002	0.57	0.08
	SRP (mg/L)	1672	0.17	0.16	0.96	0.005	0.96	0.10
	TP (mg/L)	1751	0.41	0.27	4.62	0.01	4.63	0.42
	TSS (mg/L)	1751	129	45	3550	< 1	3550	229
***n*d** [b]	Q	774	1660	865	26391	50	26441	2811
	SO_4	228	13.23	12.90	25.28	5.23	30.51	3.67
	Cl	227	11.37	10.46	22.93	2.67	25.60	4.66
	NO_3-N	772	2.46	2.40	5.34	0.57	5.91	0.79
	TN	774	2.95	2.92	5.84	0.37	6.21	0.81
	NH_4-N	652	0.06	0.04	0.49	0.001	0.49	0.07
	SRP	705	0.15	0.13	0.62	0.005	0.62	0.09
	TP	774	0.30	0.20	3.06	0.01	3.07	0.30
	TSS	774	73	18	2277	< 1	2277	153
n [c]	Q	774	1660	865	26391	50	26441	2811
	SO_4	225	13.12	12.90	18.73	5.23	23.96	3.46
	Cl	221	11.31	10.42	22.93	2.67	25.60	4.66
	NO_3-N	765	2.47	2.41	4.09	0.75	4.84	0.77
	TN	766	2.95	2.93	5.35	0.37	5.72	0.79
	NH_4-N	642	0.06	0.04	0.49	0.004	0.49	0.07
	SRP	690	0.15	0.13	0.60	0.02	0.62	0.09
	TP	760	0.29	0.20	1.69	0.03	1.72	0.26
	TSS	757	67	17	958	< 1	959	124
***n*m** [d]	Q	159	729	477	3410	75	3485	649
	SO_4	46	14.43	14.27	13.53	9.24	22.77	3.09
	Cl	46	13.18	12.86	19.10	6.31	25.40	4.47
	NO_3-N	159	2.34	2.34	3.15	1.07	4.22	0.64
	TN	159	2.73	2.70	3.23	1.45	4.68	0.65
	NH_4-N	135	0.05	0.04	0.43	0.01	0.44	0.05
	SRP	142	0.15	0.12	0.45	0.03	0.48	0.09
	TP	159	0.22	0.20	0.66	0.03	0.69	0.12
	TSS	159	27	12	213	< 1	214	36

[a] n_o, original (i.e., raw) data;
[b] n_d, daily (i.e., flow-weighted) data;
[c] n, data (i.e., after extreme outliers were removed from a 99 % P.I. of FACs n_d data);
[d] n_m, monthly (i.e., seasonally) data.

Table A-4: Descriptive statistics of stream discharge and constituent concentrations in water-quality samples collected at Kings River, 2001-2010.

KR	Variable	n	Mean	Median	Range	Min	Max	STD
n_o [a]	Q (cfs)	337	2344	687	28690	9	28698	4031
	SO_4 (mg/L)	337	7.15	5.91	33.17	0.05	33.22	4.02
	Cl (mg/L)	337	5.78	3.94	30.53	0.50	31.03	4.76
	NO_3-N (mg/L)	332	0.68	0.64	4.10	0.003	4.10	0.51
	TN (mg/L)	337	1.04	1.00	4.00	0.06	4.06	0.62
	NH_4-N (mg/L)	294	0.06	0.03	0.42	0.001	0.42	0.07
	SRP (mg/L)	337	0.06	0.03	0.49	0.001	0.49	0.06
	TP (mg/L)	337	0.20	0.10	2.04	0.006	2.05	0.28
	TSS (mg/L)	336	101	9	1589	< 1	1589	228
n_d [b]	Q	291	1739	509	24491	9	24500	3175
	SO_4	291	7.52	6.17	33.17	0.05	33.22	4.18
	Cl	291	6.21	4.27	30.53	0.50	31.03	4.94
	NO_3-N	287	0.65	0.63	4.10	0.004	4.10	0.50
	TN	291	0.97	0.92	2.97	0.06	3.03	0.58
	NH_4-N	253	0.05	0.03	0.42	0.001	0.42	0.06
	SRP	291	0.06	0.04	0.49	0.001	0.49	0.06
	TP	291	0.16	0.09	1.37	0.006	1.38	0.20
	TSS	290	66	7	1140	< 1	1140	149
n [c]	Q	290	1742	502	24491	9	24500	3180
	SO_4	285	7.29	6.13	19.72	2.41	22.13	3.57
	Cl	286	6.11	4.25	22.55	1.37	23.93	4.73
	NO_3-N	277	0.66	0.63	2.22	0.006	2.22	0.45
	TN	286	0.98	0.94	2.91	0.12	3.03	0.58
	NH_4-N	248	0.05	0.03	0.38	0.003	0.38	0.05
	SRP	284	0.06	0.04	0.49	0.004	0.49	0.06
	TP	286	0.15	0.08	1.37	0.01	1.38	0.19
	TSS	284	64	6	1140	< 1	1140	147
n_m [d]	Q	84	700	328	4503	12	4515	977
	SO_4	82	8.48	6.61	16.32	3.74	20.06	4.01
	Cl	83	7.51	5.09	19.13	2.20	21.33	5.14
	NO_3-N	83	0.53	0.53	2.15	0.007	2.15	0.42
	TN	83	0.79	0.72	2.02	0.14	2.16	0.46
	NH_4-N	82	0.04	0.03	0.13	0.004	0.14	0.03
	SRP	83	0.06	0.04	0.26	0.006	0.27	0.05
	TP	84	0.10	0.09	0.32	0.02	0.34	0.07
	TSS	84	17	5	165	< 1	166	33

[a] n_o, original (i.e., raw) data;
[b] n_d, daily (i.e., flow-weighted) data;
[c] n, data (i.e., after extreme outliers were removed from a 99 % P.I. of FACs n_d data);
[d] n_m, monthly (i.e., seasonally) data.

Table A-5: Descriptive statistics of stream discharge and constituent concentrations in water-quality samples collected at West Fork White River, 2002-2010.

WFWR	Variable	n	Mean	Median	Range	Min	Max	STD
$\boldsymbol{n_o}$ [a]	Q (cfs)	468	592	325	11782	< 1	11782	1129
	SO_4 (mg/L)	219	21.82	20.18	51.69	4.49	56.18	10.16
	Cl (mg/L)	219	4.38	3.89	12.21	1.17	13.38	2.08
	NO_3-N (mg/L)	464	0.43	0.42	2.66	0.01	2.67	0.22
	TN (mg/L)	468	0.87	0.79	2.94	0.13	3.06	0.46
	NH_4-N (mg/L)	425	0.09	0.05	0.76	0.002	0.76	0.11
	SRP (mg/L)	463	0.02	0.01	1.97	0.001	1.97	0.09
	TP (mg/L)	468	0.20	0.10	1.24	0.001	1.24	0.23
	TSS (mg/L)	468	98	33	1098	1	1099	145
$\boldsymbol{n_d}$ [b]	Q	382	536	254	11782	< 1	11782	1131
	SO_4	199	22.22	20.34	50.75	5.43	56.18	10.24
	Cl	199	4.44	3.92	12.14	1.24	13.38	2.10
	NO_3-N	378	0.41	0.39	2.66	0.01	2.67	0.22
	TN	382	0.80	0.73	2.84	0.13	2.96	0.43
	NH_4-N	343	0.09	0.05	0.76	0.002	0.76	0.11
	SRP	379	0.02	0.01	1.97	0.001	1.97	0.10
	TP	382	0.18	0.08	1.24	0.001	1.24	0.23
	TSS	382	90	23	720	1	721	138
$\boldsymbol{n}$ [c]	Q	382	536	254	11782	< 1	11782	1131
	SO_4	197	22.12	20.34	48.71	5.43	54.14	9.95
	Cl	194	4.26	3.86	11.52	1.24	12.76	1.79
	NO_3-N	366	0.41	0.39	1.11	0.02	1.13	0.18
	TN	377	0.79	0.73	2.84	0.13	2.96	0.41
	NH_4-N	337	0.09	0.05	0.68	0.004	0.68	0.11
	SRP	373	0.01	0.01	0.09	0.001	0.09	0.01
	TP	375	0.18	0.08	1.23	0.01	1.24	0.23
	TSS	378	87	23	720	1	721	134
$\boldsymbol{n_m}$ [d]	Q	84	212	153	792	< 1	792	210
	SO_4	40	24.99	22.46	38.47	10.61	49.08	9.40
	Cl	40	4.71	4.22	5.08	2.71	7.79	1.49
	NO_3-N	80	0.35	0.36	0.78	0.03	0.81	0.16
	TN	84	0.71	0.66	1.49	0.21	1.70	0.30
	NH_4-N	83	0.06	0.04	0.26	0.008	0.27	0.05
	SRP	84	0.02	0.01	0.08	0.001	0.08	0.01
	TP	84	0.11	0.07	0.46	0.01	0.47	0.10
	TSS	83	44	22	266	2	268	57

[a] n_o, original (i.e., raw) data;
[b] n_d, daily (i.e., flow-weighted) data;
[c] n, data (i.e., after extreme outliers were removed from a 99 % P.I. of FACs n_d data);
[d] n_m, monthly (i.e., seasonally) data.

Table A-6: Descriptive statistics of stream discharge and constituent concentrations in water-quality samples collected at White River, 2001-2010.

WR	Variable	n	Mean	Median	Range	Min	Max	STD
***n*$_o$ [a]**	Q (cfs)	683	3797	799	50197	3	50200	8033
	SO_4 (mg/L)	683	15.08	11.03	87.73	1.52	89.25	12.67
	Cl (mg/L)	683	6.44	3.43	74.40	0.84	75.24	8.97
	NO_3-N (mg/L)	678	0.58	0.48	5.05	0.001	5.05	0.53
	TN (mg/L)	683	1.25	0.99	6.89	0.13	7.01	0.80
	NH_4-N (mg/L)	578	0.12	0.07	0.67	0.001	0.67	0.13
	SRP (mg/L)	679	0.04	0.02	1.04	0.001	1.04	0.09
	TP (mg/L)	683	0.35	0.17	5.33	0.001	5.33	0.48
	TSS (mg/L)	683	214	69	3405	2	3407	320
***n*$_d$ [b]**	Q	328	1886	512	44360	3	44363	4299
	SO_4	328	15.99	11.59	85.62	3.63	89.25	13.46
	Cl	328	7.84	4.05	74.15	1.09	75.24	11.37
	NO_3-N	327	0.68	0.53	5.05	0.001	5.05	0.61
	TN	328	1.15	0.93	5.08	0.13	5.20	0.75
	NH_4-N	308	0.10	0.06	0.59	0.001	0.59	0.10
	SRP	324	0.02	0.01	0.17	0.001	0.17	0.02
	TP	328	0.23	0.11	2.30	0.008	2.31	0.30
	TSS	328	128	34	1434	2	1436	223
***n* [c]**	Q	328	1886	512	44360	3	44363	4299
	SO_4	320	15.26	11.58	85.62	3.63	89.25	11.94
	Cl	315	7.00	3.99	69.00	1.09	70.08	9.22
	NO_3-N	323	0.69	0.53	4.96	0.10	5.05	0.61
	TN	322	1.15	0.94	4.82	0.38	5.20	0.72
	NH_4-N	307	0.10	0.06	0.59	0.003	0.59	0.10
	SRP	319	0.02	0.01	0.11	0.001	0.11	0.01
	TP	321	0.21	0.11	2.29	0.02	2.31	0.27
	TSS	321	114	33	1434	2	1436	203
***n*$_m$ [d]**	Q	81	753	359	8567	4	8571	1216
	SO_4	80	18.68	13.65	74.10	5.62	79.72	14.26
	Cl	80	9.80	5.09	52.50	1.97	54.47	11.37
	NO_3-N	81	0.81	0.57	4.77	0.28	5.05	0.75
	TN	81	1.27	1.02	4.68	0.52	5.20	0.81
	NH_4-N	80	0.07	0.05	0.25	0.01	0.25	0.05
	SRP	80	0.01	0.01	0.11	0.001	0.11	0.01
	TP	81	0.14	0.09	0.60	0.02	0.62	0.12
	TSS	81	52	28	384	2	387	68

[a] n_o, original (i.e., raw) data;
[b] n_d, daily (i.e., flow-weighted) data;
[c] n, data (i.e., after extreme outliers were removed from a 99 % P.I. of FACs n_d data);
[d] n_m, monthly (i.e., seasonally) data.

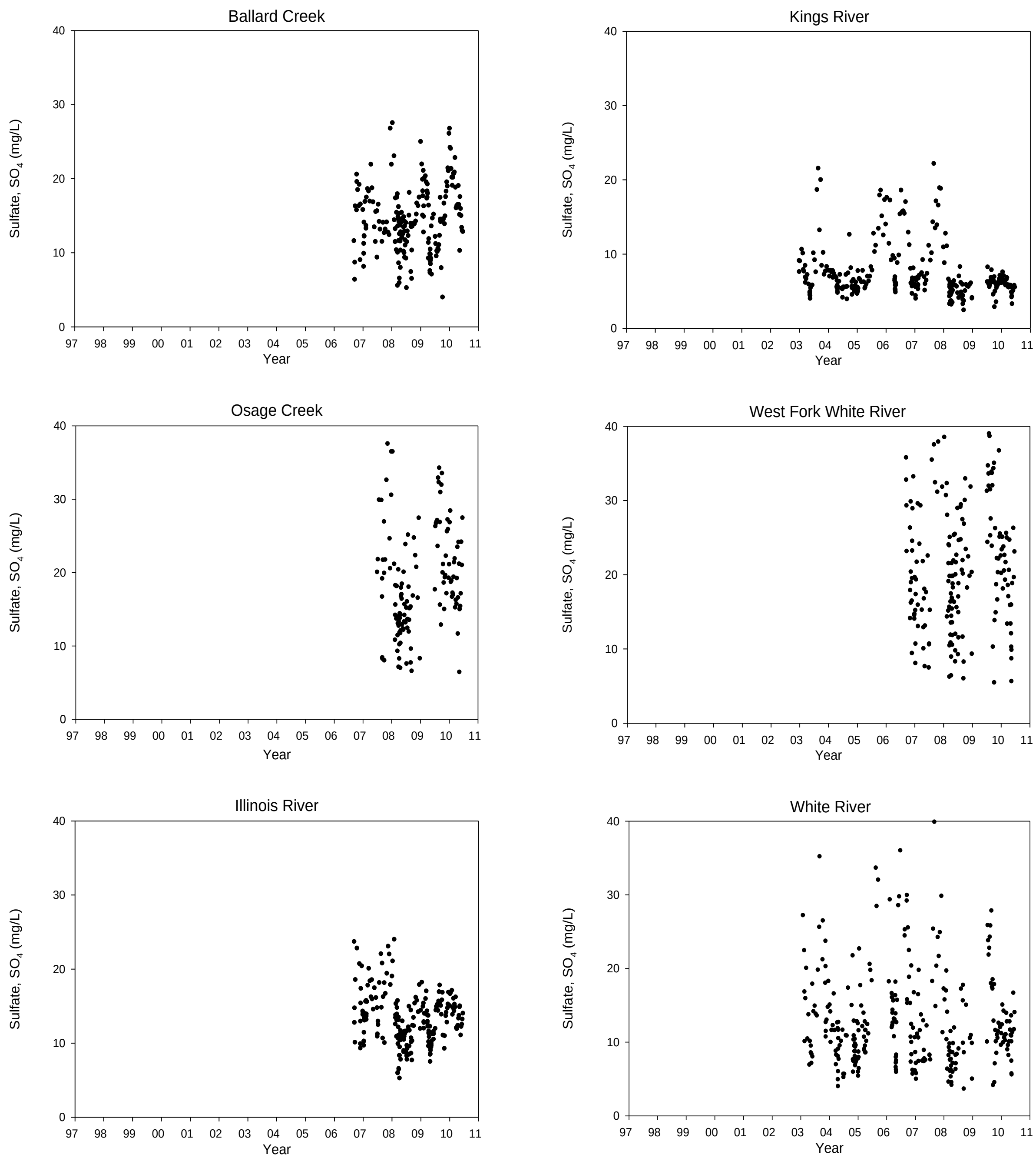

Figure B-1. Sulfate (SO_4) concentrations from water-quality samples taken at the six sampled sites from 1997 through 2010. Some extreme values were not included on certain graphs to eliminate clumping the lower, more representative data towards the bottom of the graph.

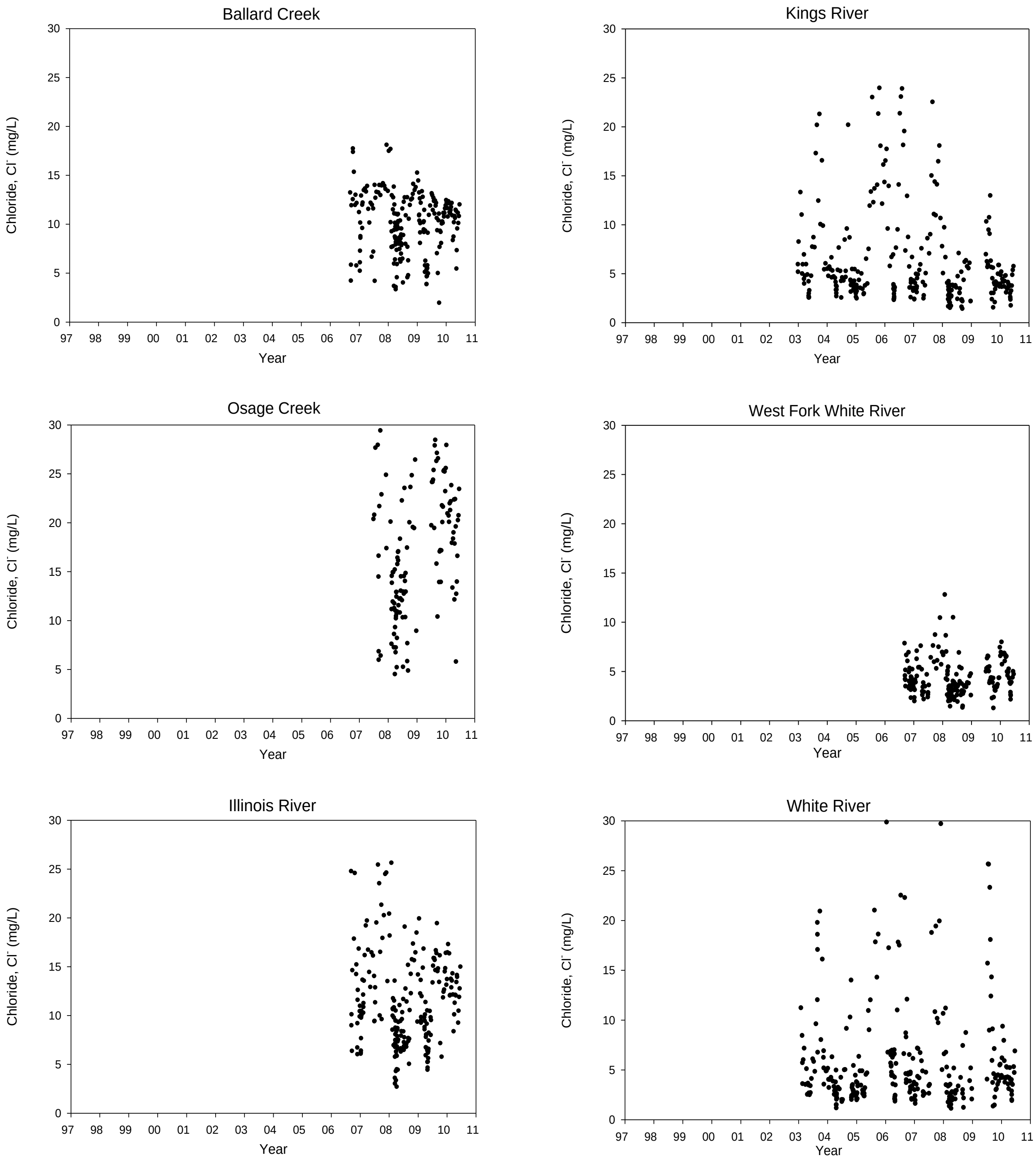

Figure B-2. Chloride (Cl^-) concentrations from water-quality samples taken at the six sampled sites from 1997 through 2010. Some extreme values were not included on certain graphs to eliminate clumping the lower, more representative data towards the bottom of the graph.

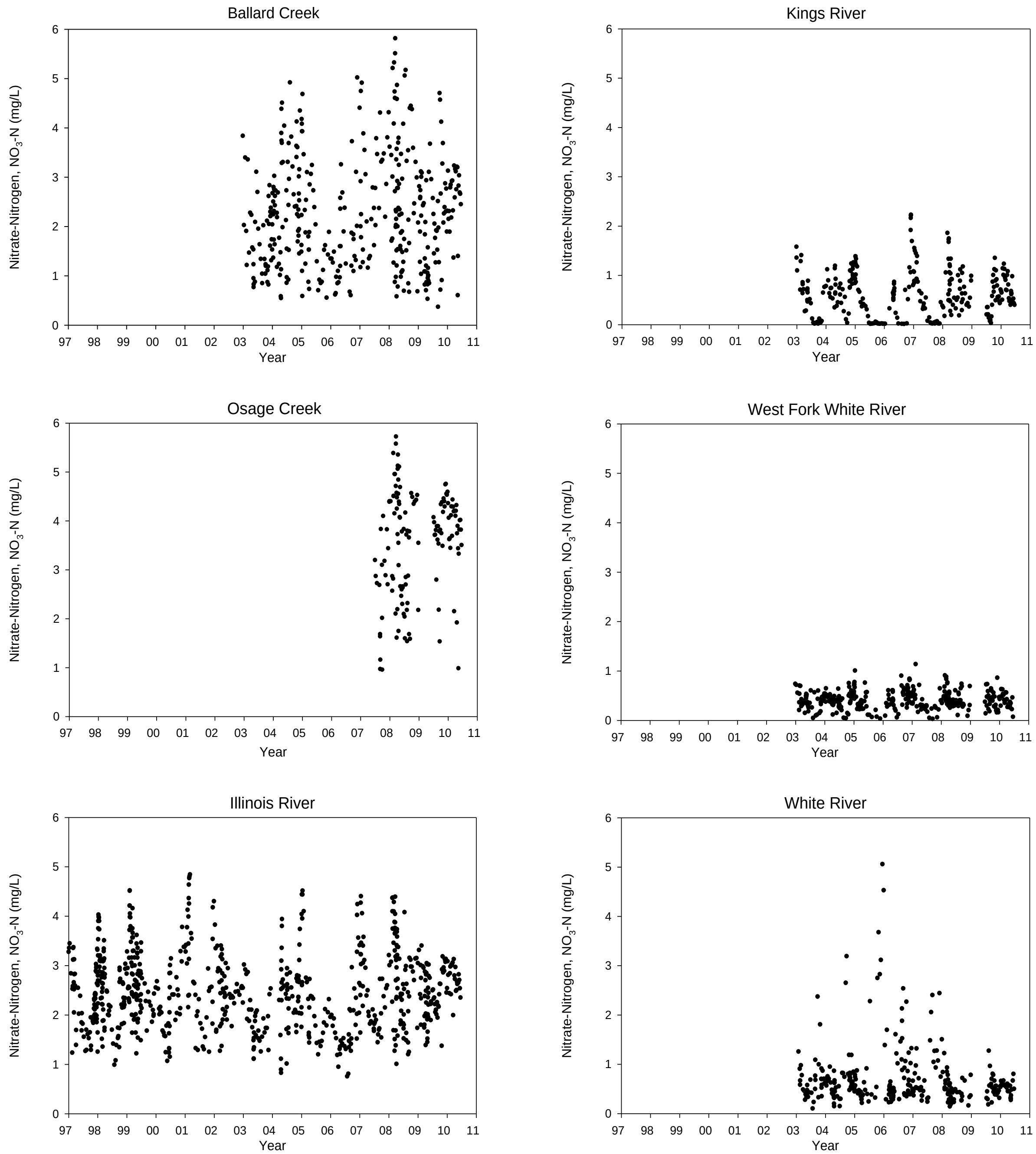

Figure B-3. Nitrate-nitrogen (NO_3-N) concentrations from water-quality samples taken at the six sampled sites from 1997 through 2010. Some extreme values were not included on certain graphs to eliminate clumping the lower, more representative data towards the bottom of the graph.

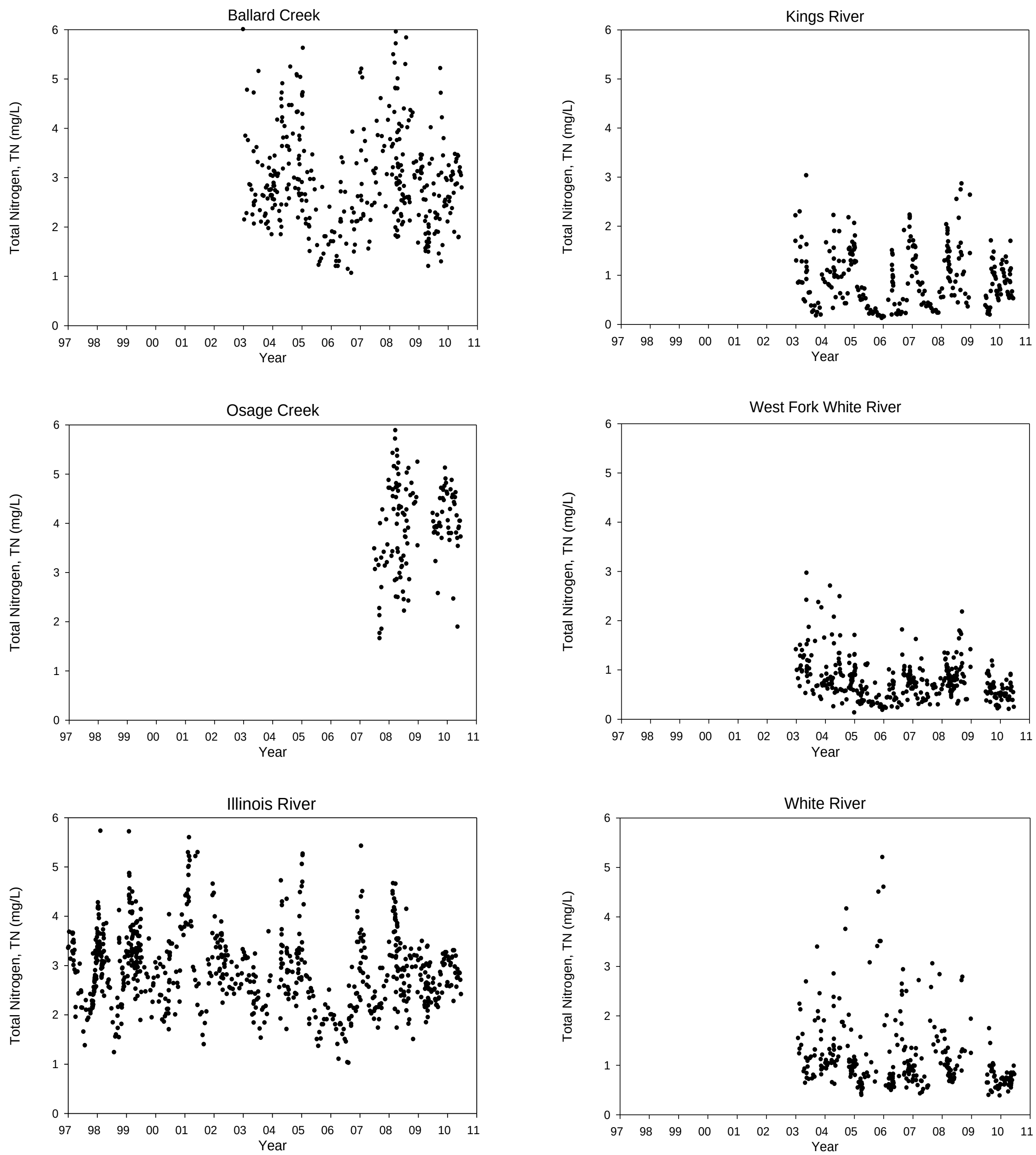

Figure B-4. Total nitrogen (TN) concentrations from water-quality samples taken at the six sampled sites from 1997 through 2010. Some extreme values were not included on certain graphs to eliminate clumping the lower, more representative data towards the bottom of the graph.

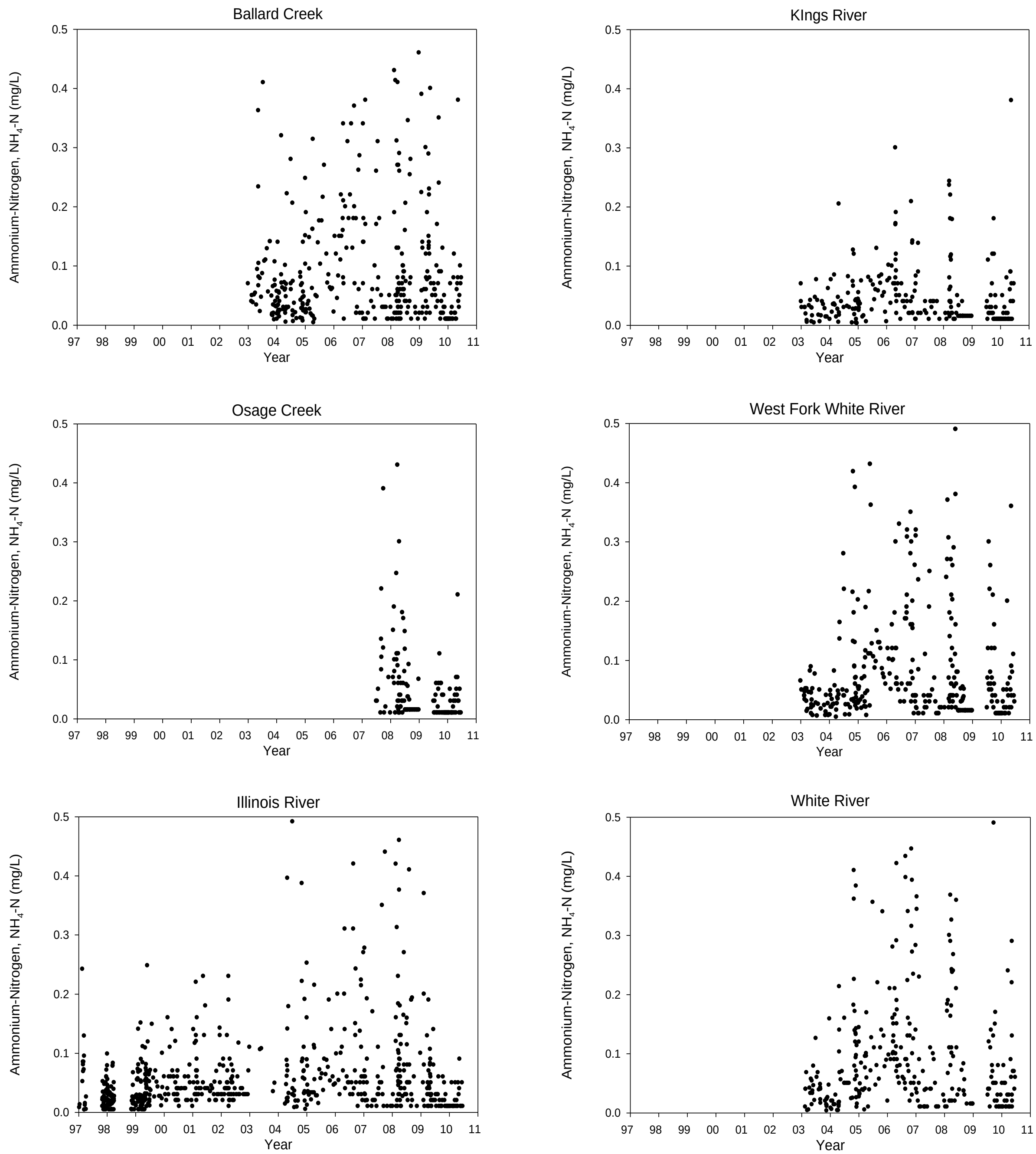

Figure B-5. Ammonium-nitrogen (NH_4-N) concentrations from water-quality samples taken at the six sampled sites from 1997 through 2010. Some extreme values were not included on certain graphs to eliminate clumping the lower, more representative data towards the bottom of the graph.

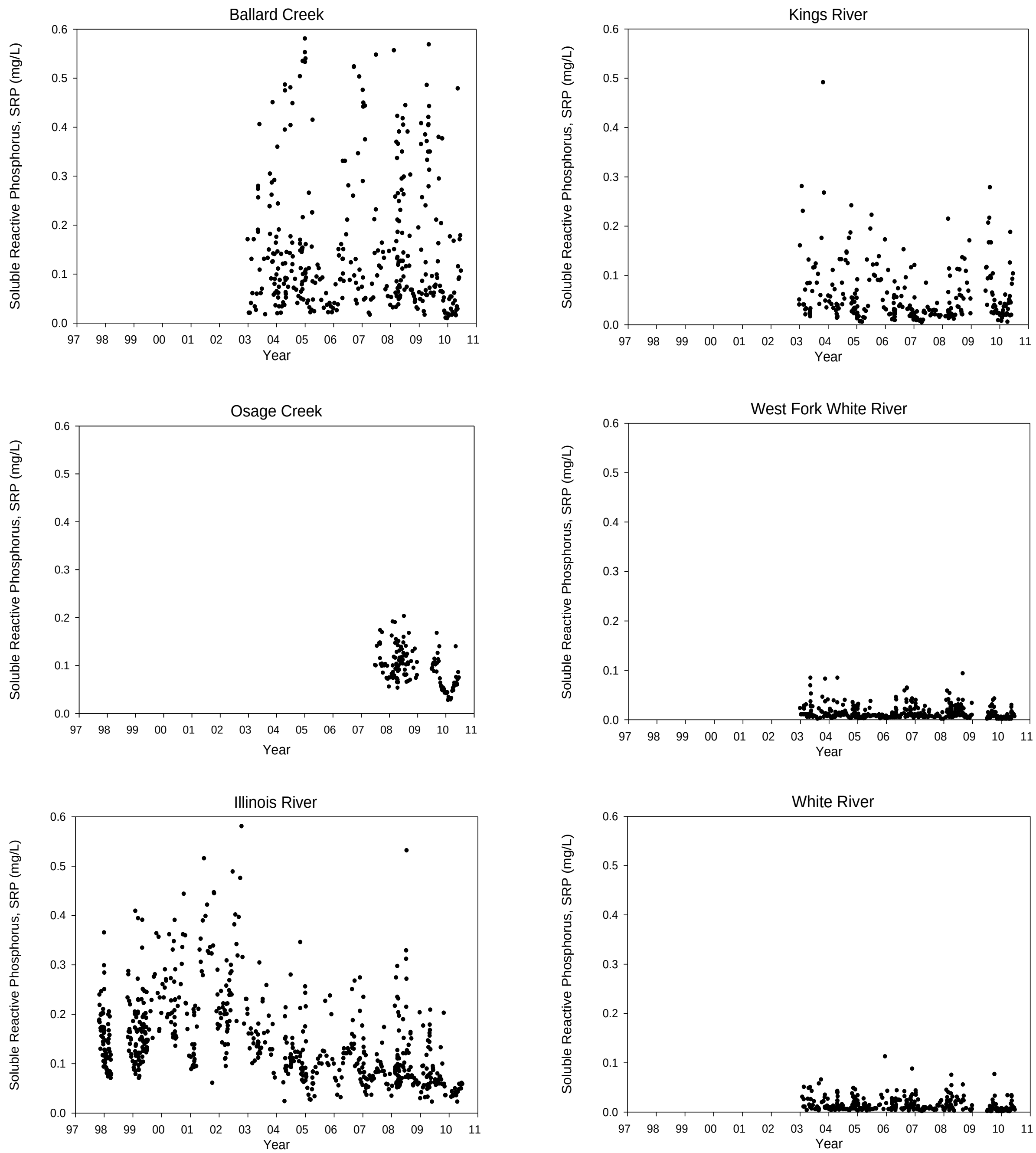

Figure B-6. Soluble reactive phosphorus (SRP) concentrations from water-quality samples taken at the six sampled sites from 1997 through 2010. Some extreme values were not included on certain graphs to eliminate clumping the lower, more representative data towards the bottom of the graph.

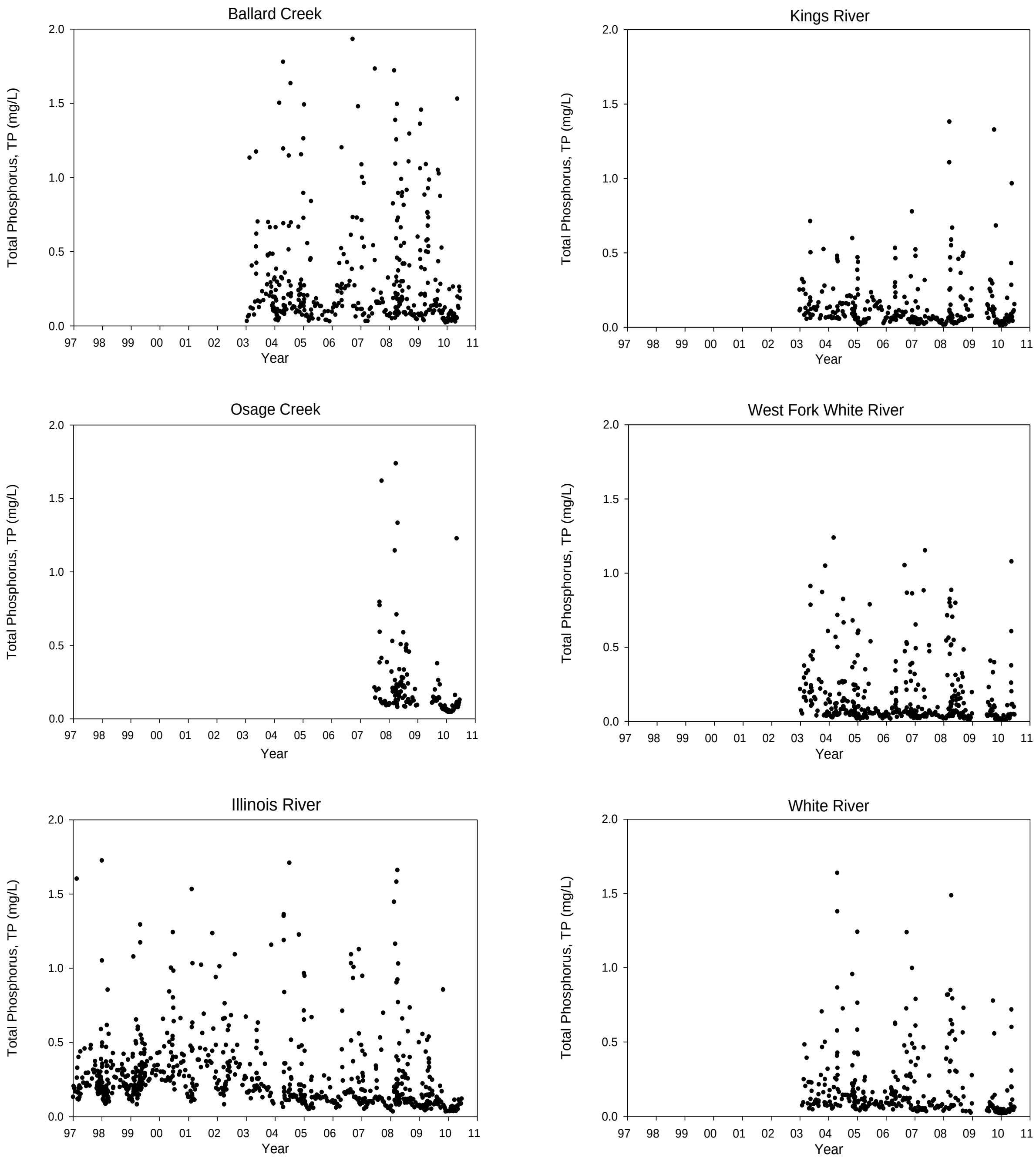

Figure B-7. Total phosphorus (TP) concentrations from water-quality samples taken at the six sampled sites from 1997 through 2010. Some extreme values were not included on certain graphs to eliminate clumping the lower, more representative data towards the bottom of the graph.

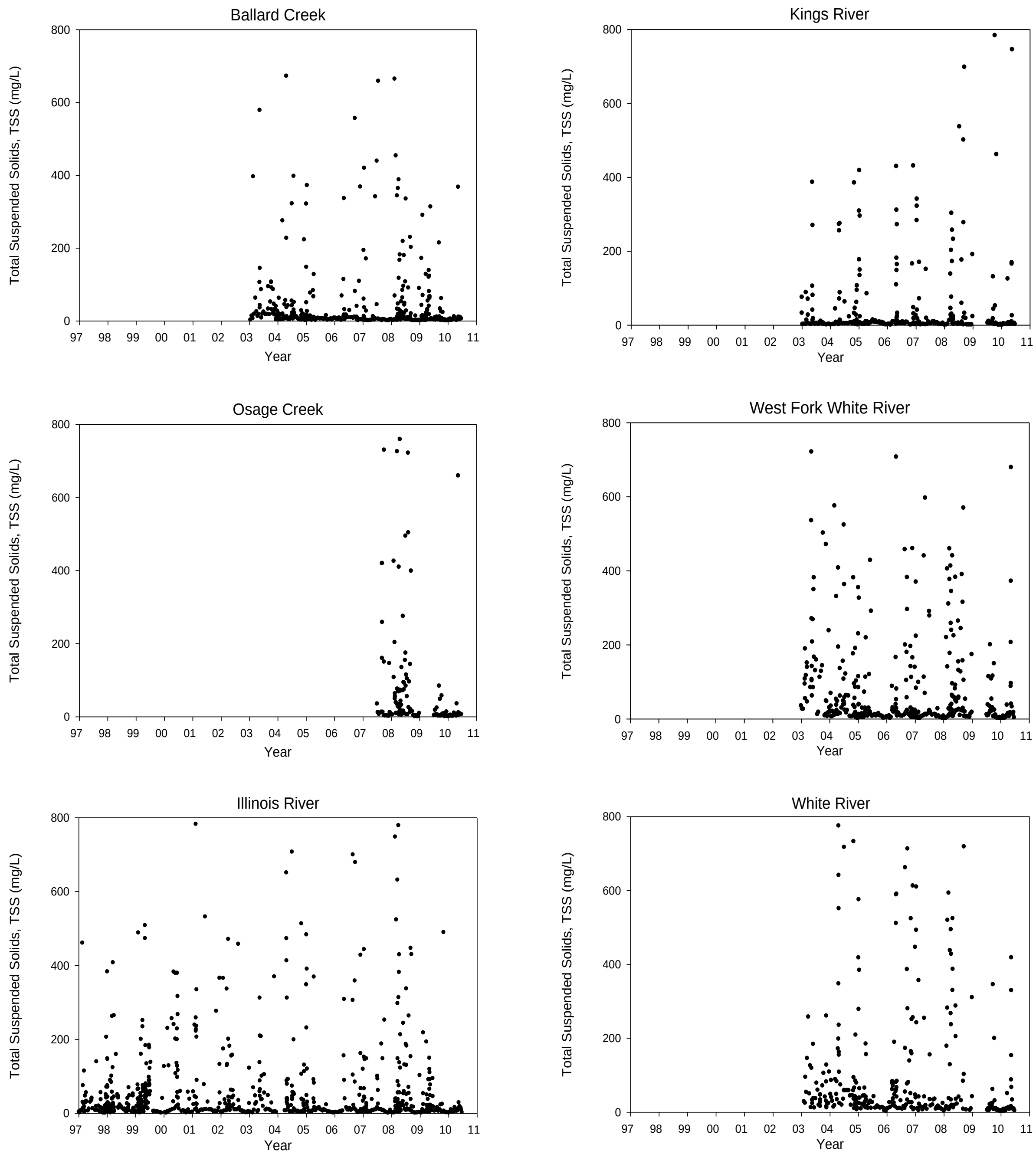

Figure B-8. Total suspended solids (TSS) concentrations from water-quality samples taken at the six sampled sites from 1997 through 2010. Some extreme values were not included on certain graphs to eliminate clumping the lower, more representative data towards the bottom of the graph.

Appendix C: Log-Transformed Water-Quality Data with LOESS Smoothing

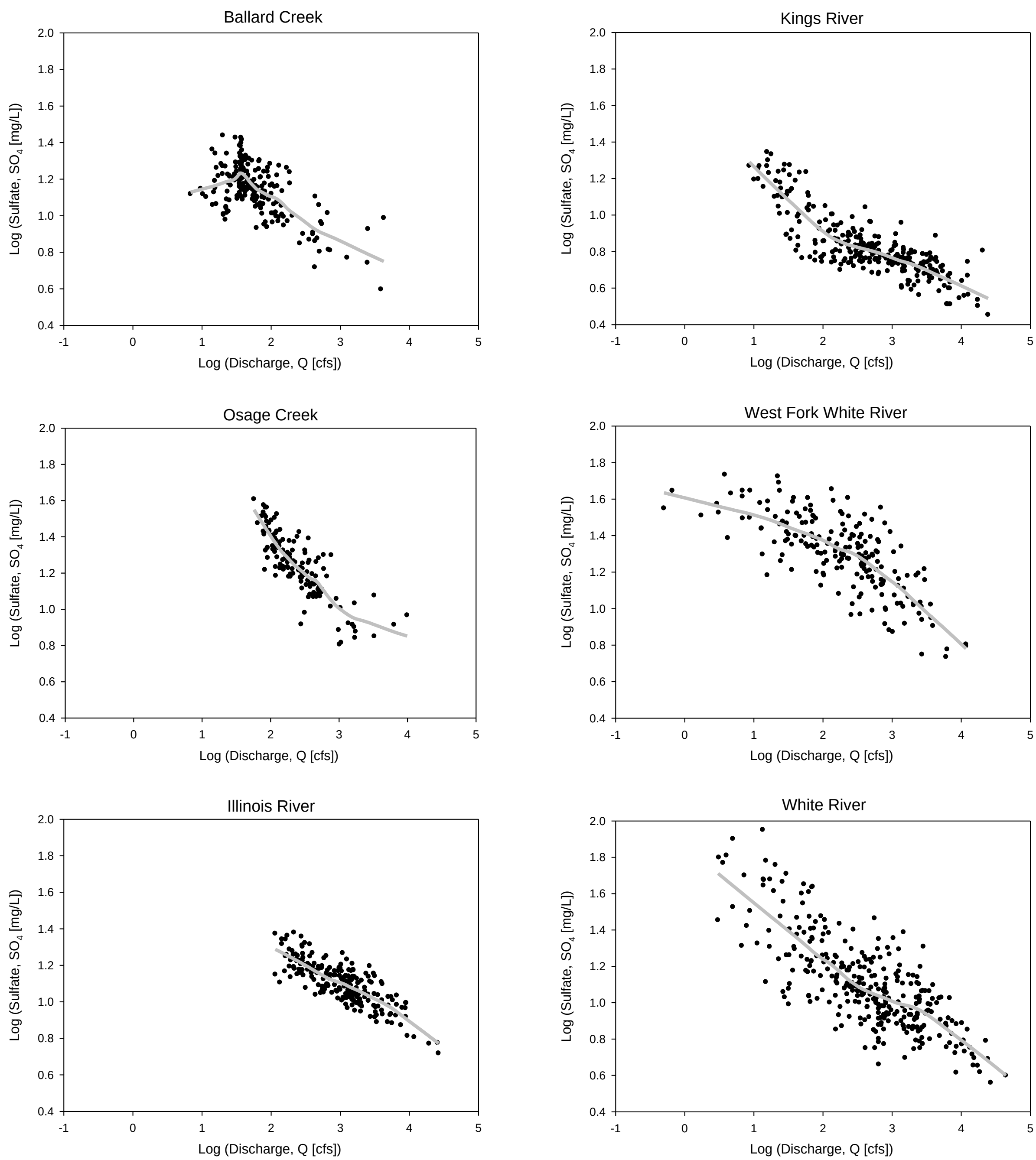

Figure C-1. Log-transformed sulfate (SO_4) concentrations and log-transformed daily discharge with locally weighted regression (LOESS) line; the LOESS smoothing technique shows the relation between concentration and stream flow at each specific sampling site.

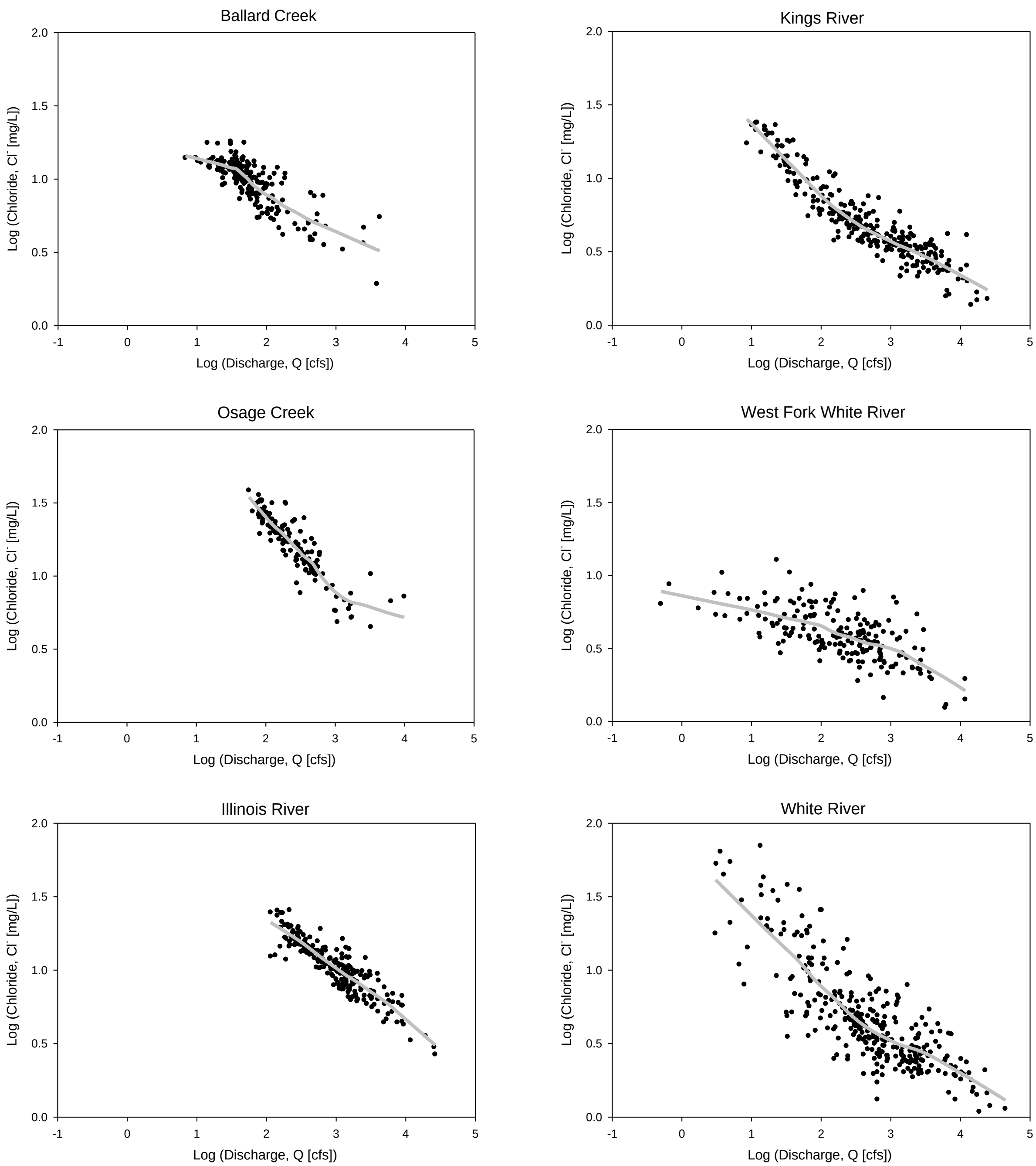

Figure C-2. Log-transformed chloride (Cl^-) concentrations and log-transformed daily discharge with locally weighted regression (LOESS) line; the LOESS smoothing technique shows the relation between concentration and stream flow at each specific sampling site.

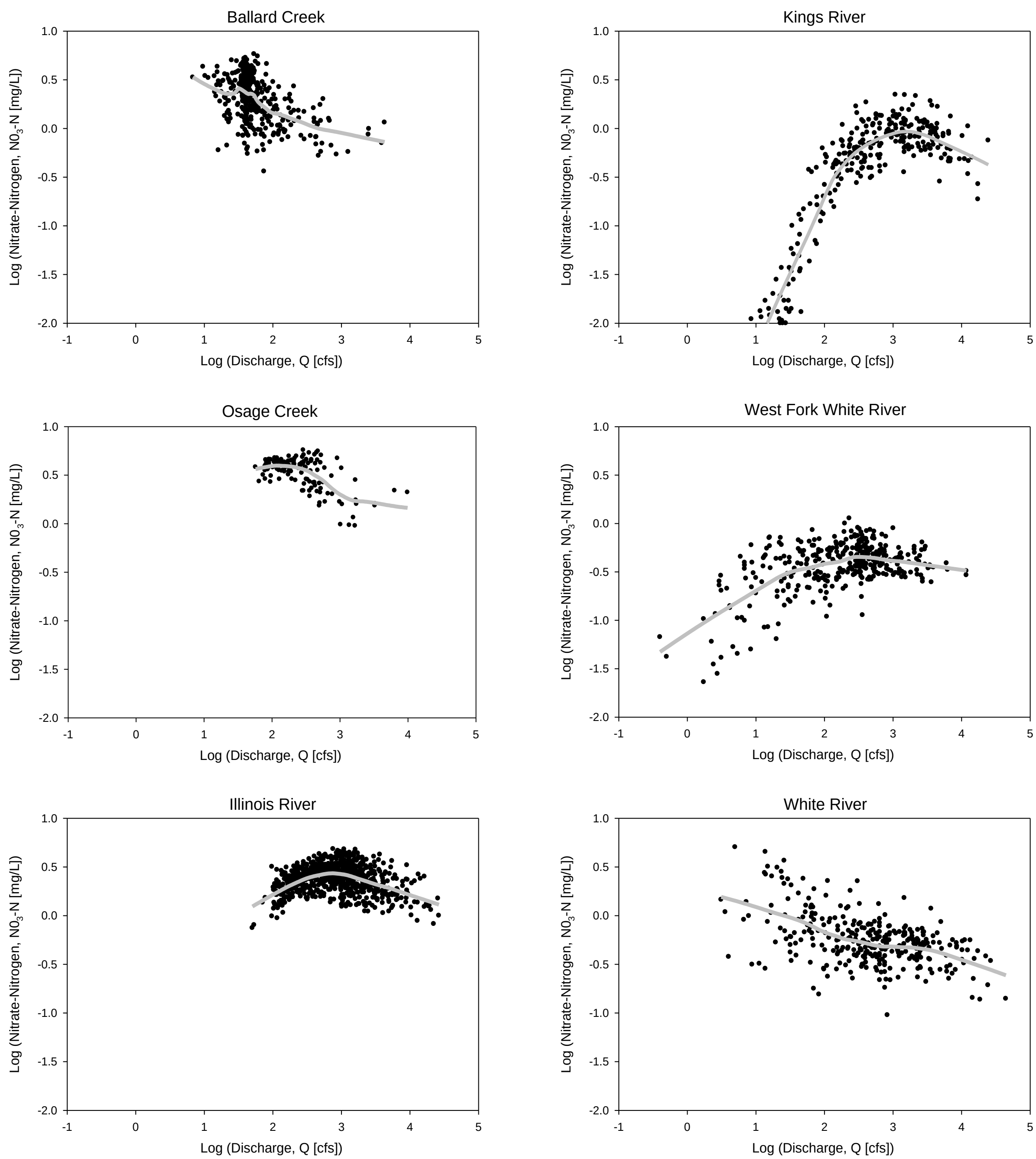

Figure C-3. Log-transformed nitrate-nitrogen (NO_3-N) concentrations and log-transformed daily discharge with locally weighted regression (LOESS) line; the LOESS smoothing technique shows the relation between concentration and stream flow at each specific sampling site.

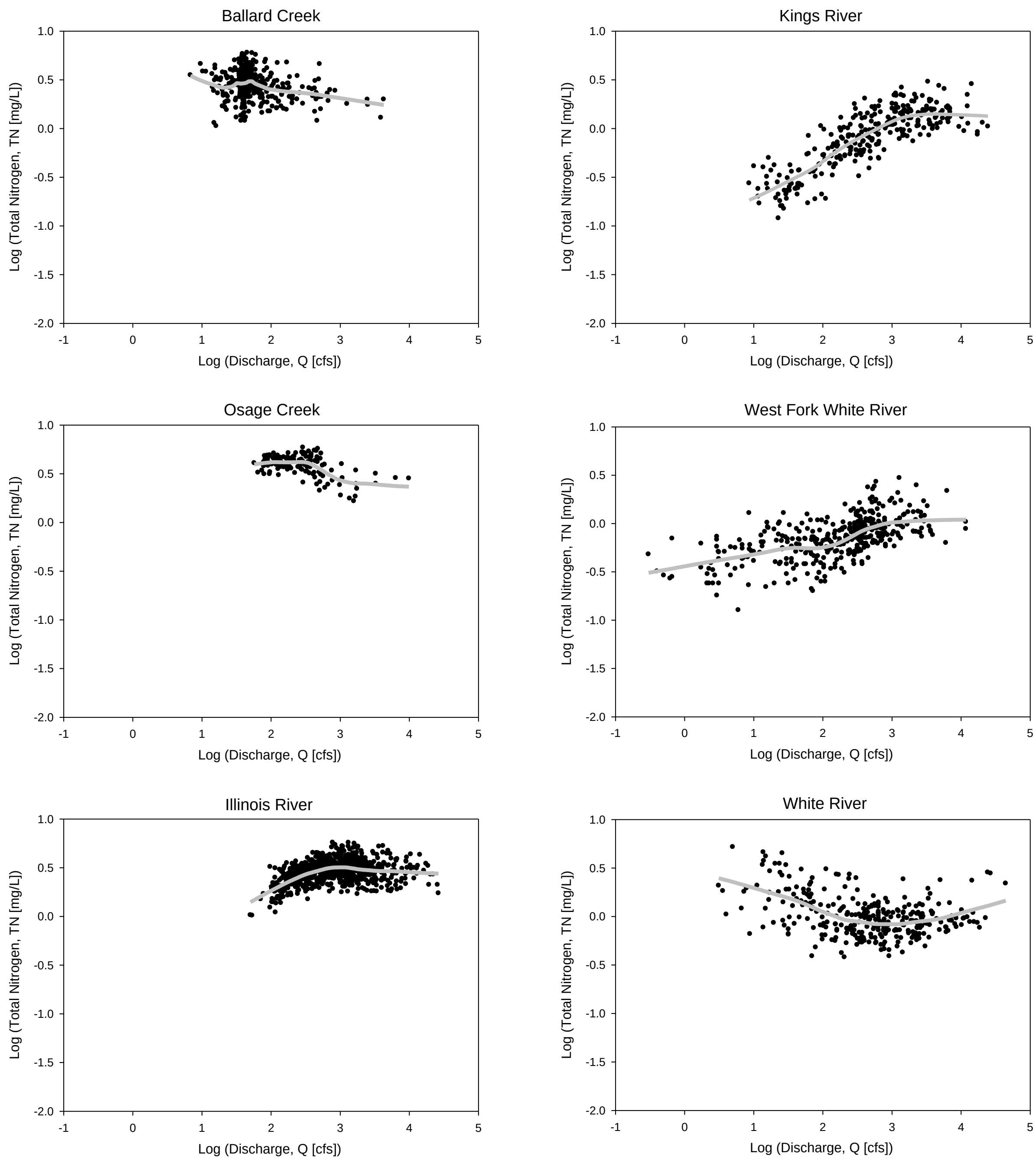

Figure C-4. Log-transformed total nitrogen (TN) concentrations and log-transformed daily discharge with locally weighted regression (LOESS) line; the LOESS smoothing technique shows the relation between concentration and stream flow at each specific sampling site.

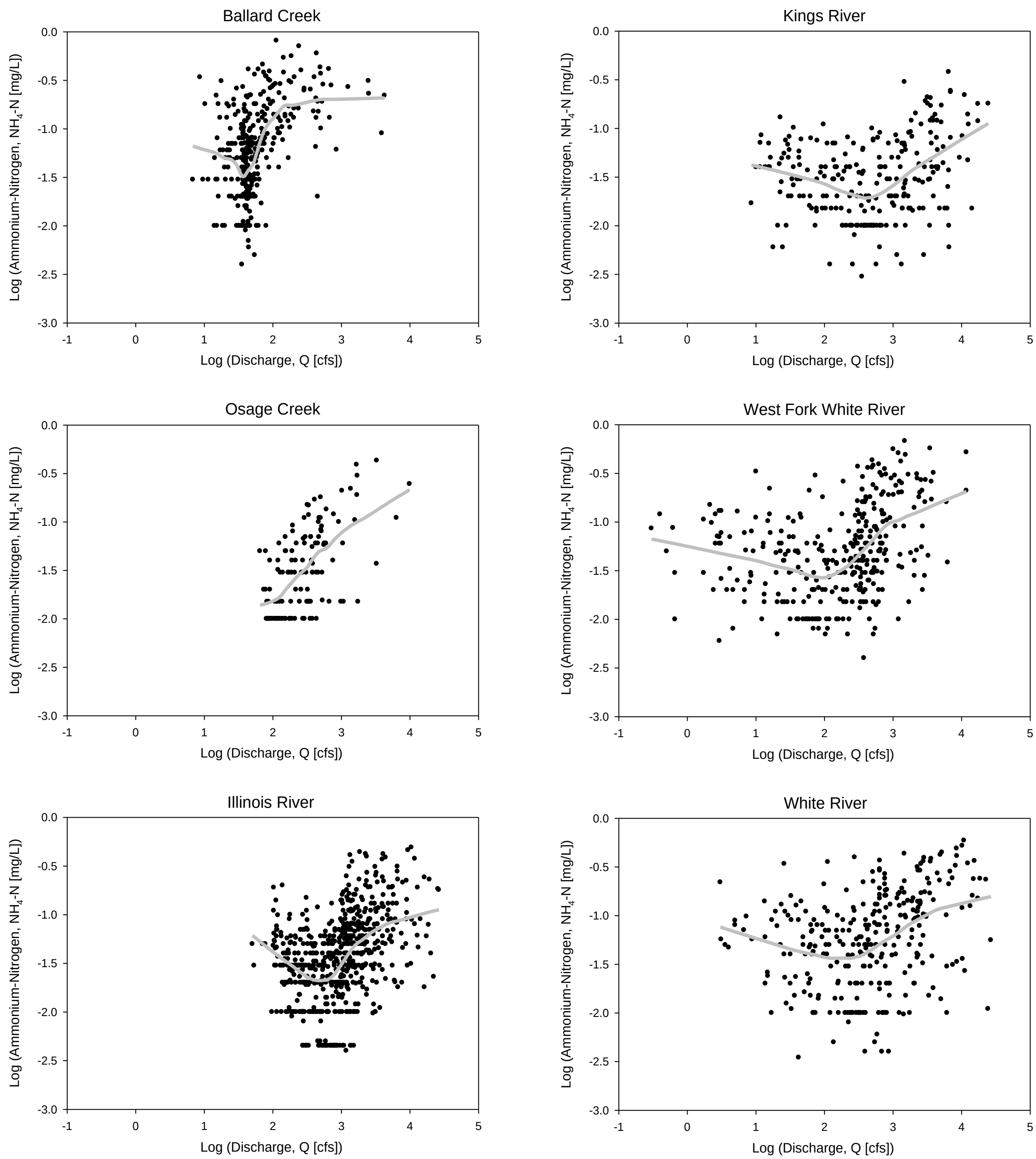

Figure C-5. Log-transformed ammonium-nitrogen (NH_4-N) concentrations and log-transformed daily discharge with locally weighted regression (LOESS) line; the LOESS smoothing technique shows the relation between concentration and stream flow at each specific sampling site.

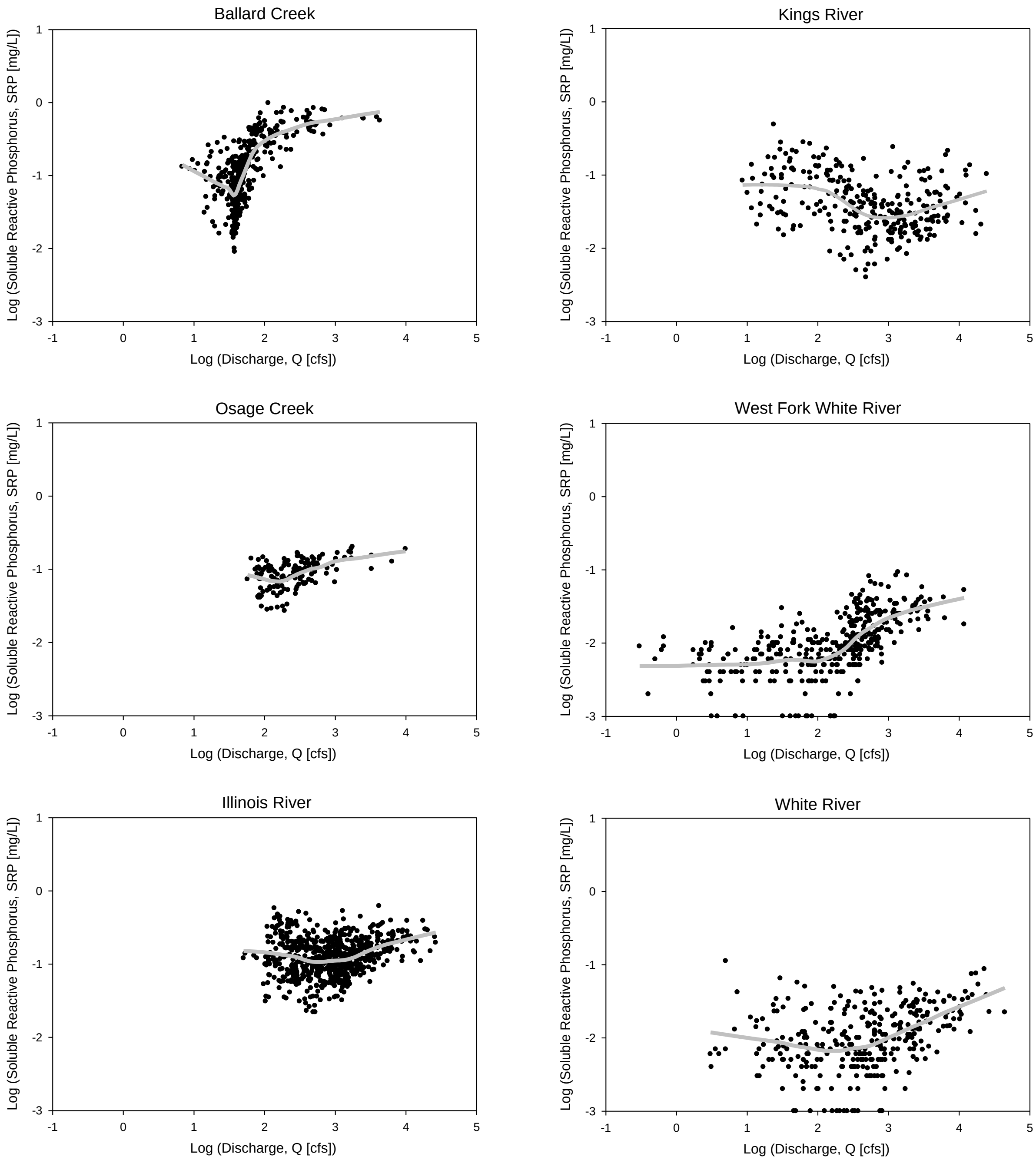

Figure C-6. Log-transformed soluble reactive phosphorus (SRP) concentrations and log-transformed daily discharge with locally weighted regression (LOESS) line; the LOESS smoothing technique shows the relation concentration and stream flow at each specific sampling site.

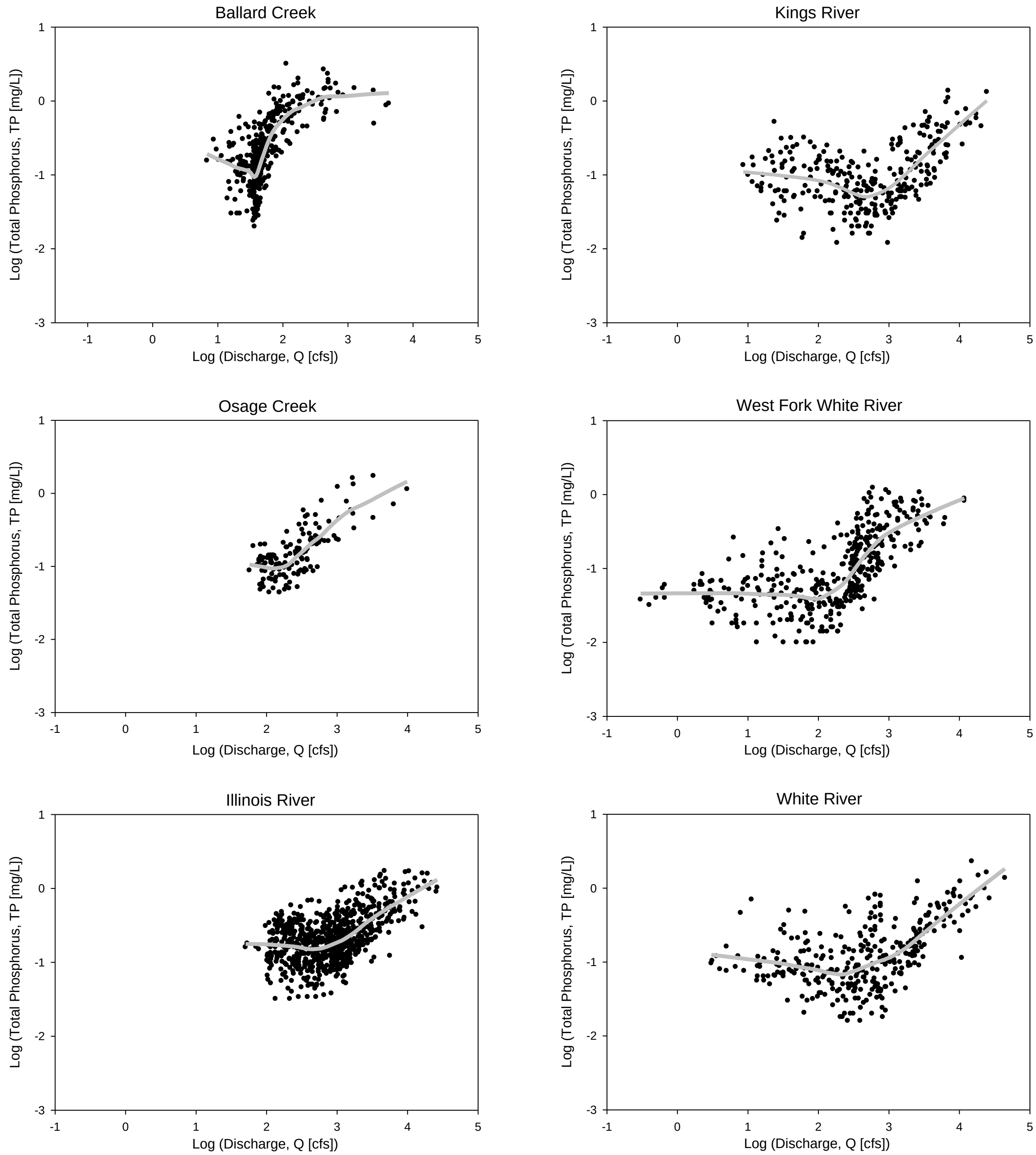

Figure C-7. Log-transformed total phosphorus (TP) concentrations and log-transformed daily discharge with locally weighted regression (LOESS) line; the LOESS smoothing technique shows the relation between concentration and stream flow at each specific sampling site.

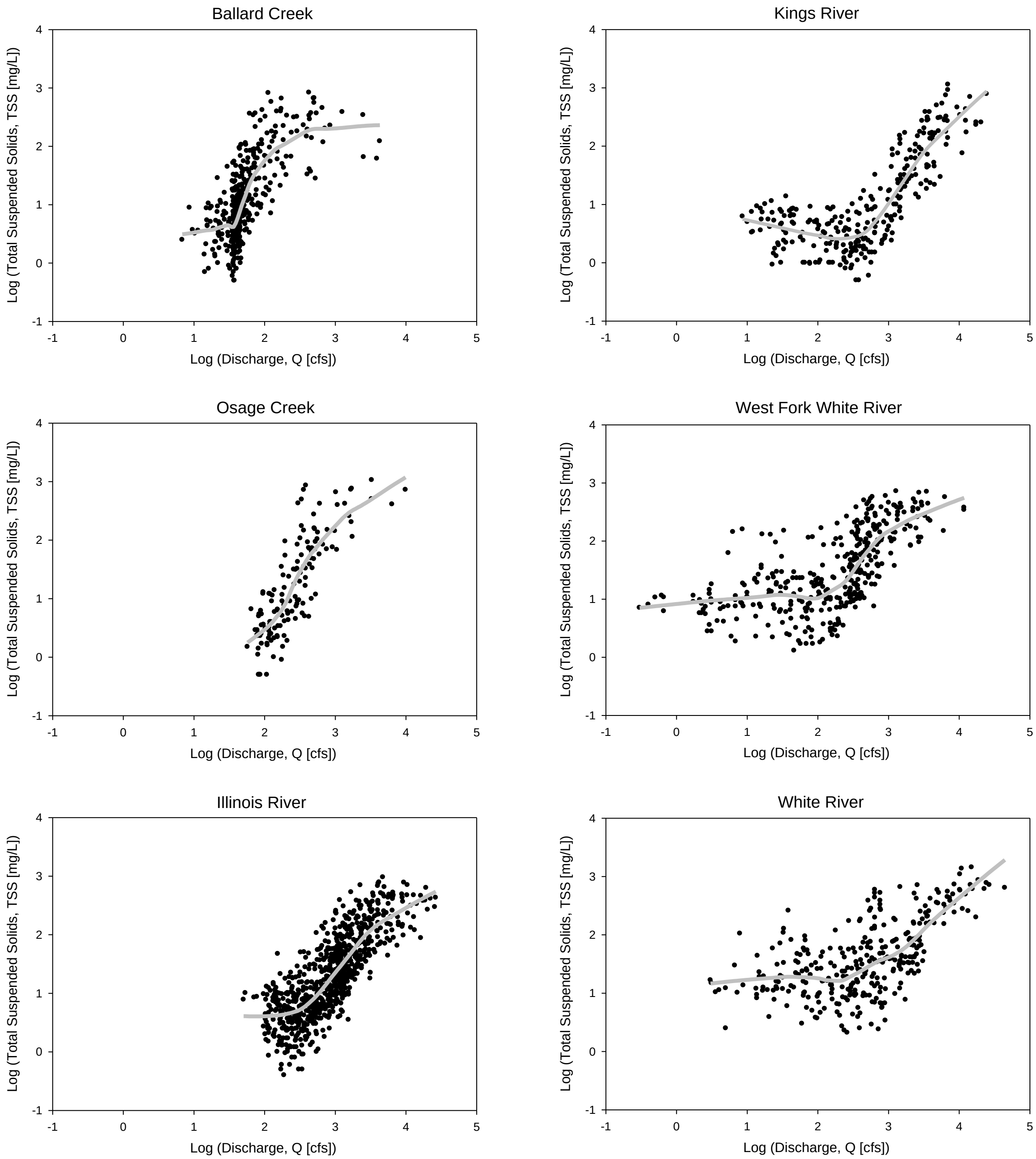

Figure C-8. Log-transformed total suspended solids (TSS) concentrations and log-transformed daily discharge with locally weighted regression (LOESS) line; the LOESS smoothing technique shows the relation between concentration and stream flow at each specific sampling site.

APPENDIX D: FLOW-ADJUSTED CONCENTRATIONS (FACs) AS A FUNCTION OF TIME

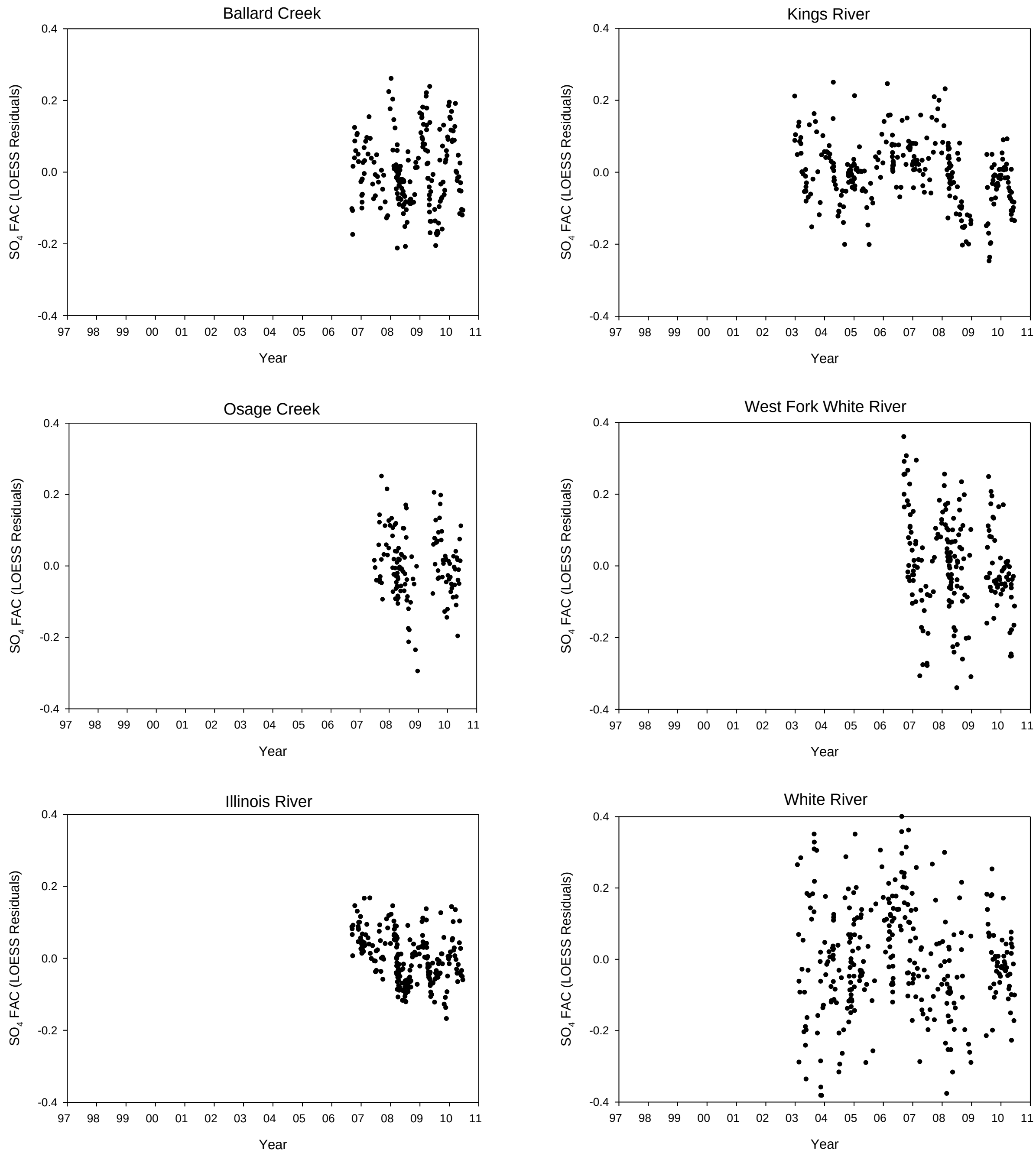

Figure D-1. Sulfate (SO_4): The flow-adjusted concentrations (FACs) as a function of time from 1997 through 2010; FACs are the residuals from LOESS smoothing of log-transformed concentrations and daily discharge as a function of time.

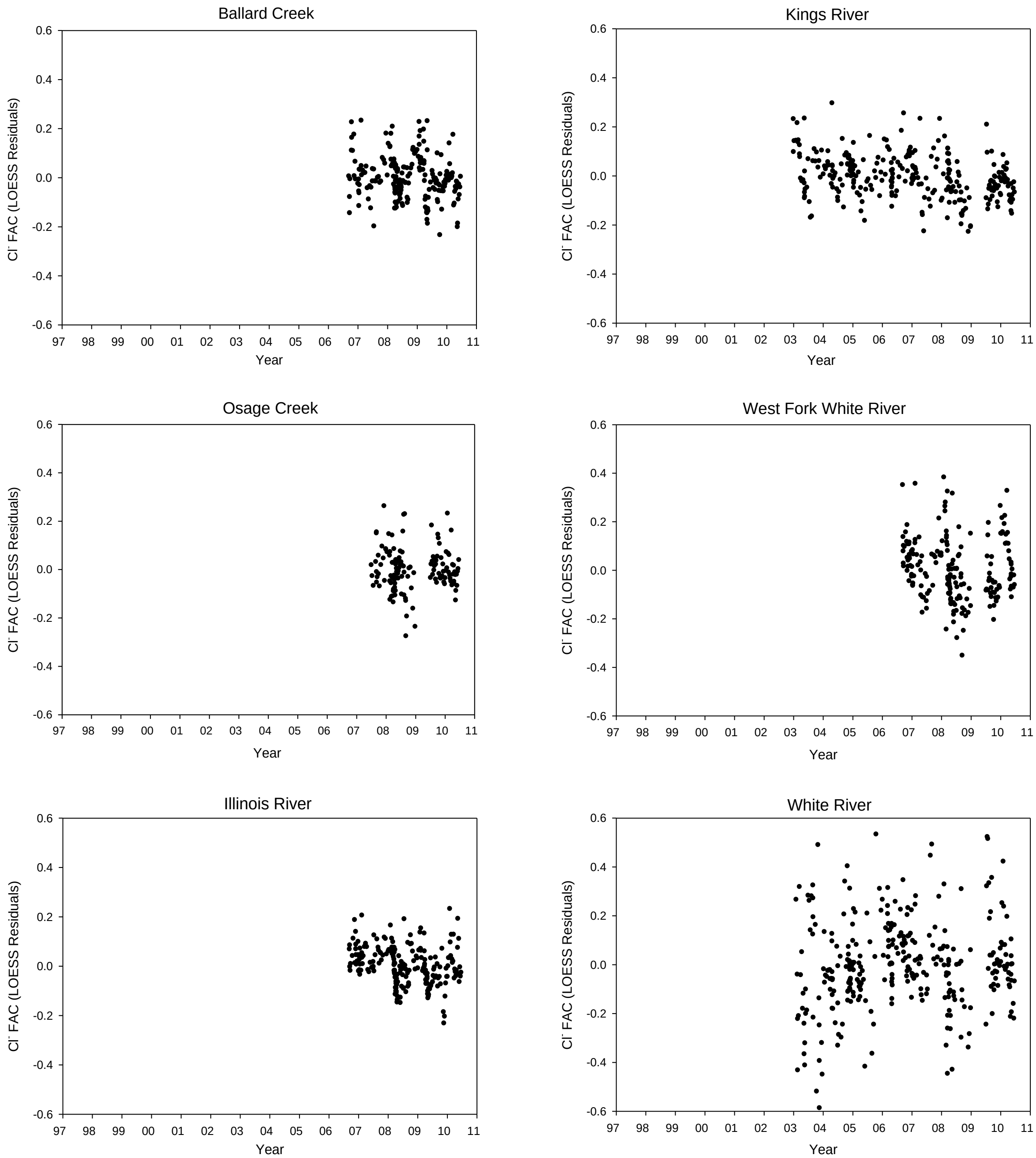

Figure D-2. Chloride (Cl^-): The flow-adjusted concentrations (FACs) as a function of time from 1997 through 2010; FACs are the residuals from LOESS smoothing of log-transformed concentrations and daily discharge as a function of time.

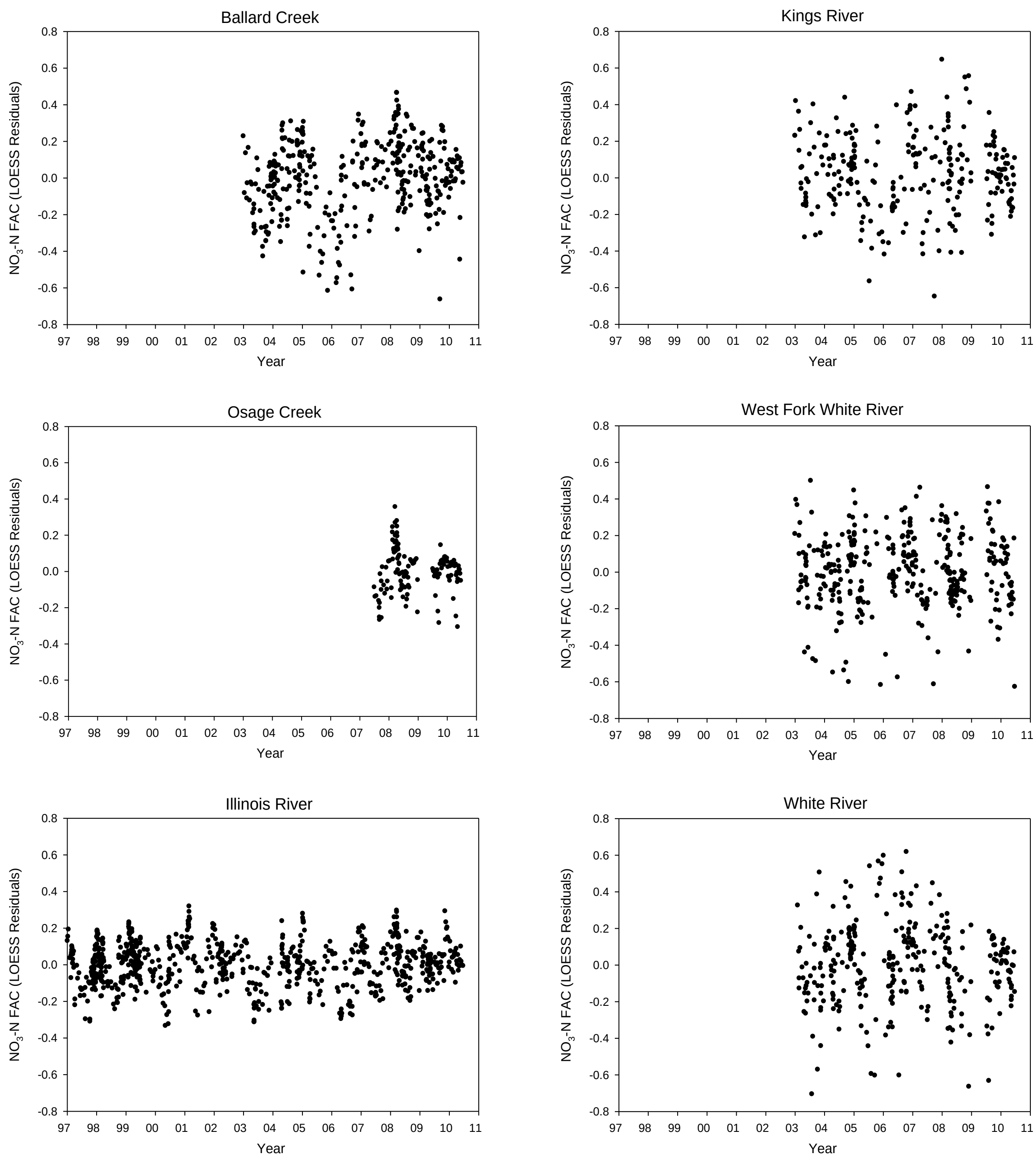

Figure D-3. Nitrate-nitrogen (NO_3-N): The flow-adjusted concentrations (FACs) as a function of time from 1997 through 2010; FACs are the residuals from LOESS smoothing of log-transformed concentrations and daily discharge as a function of time.

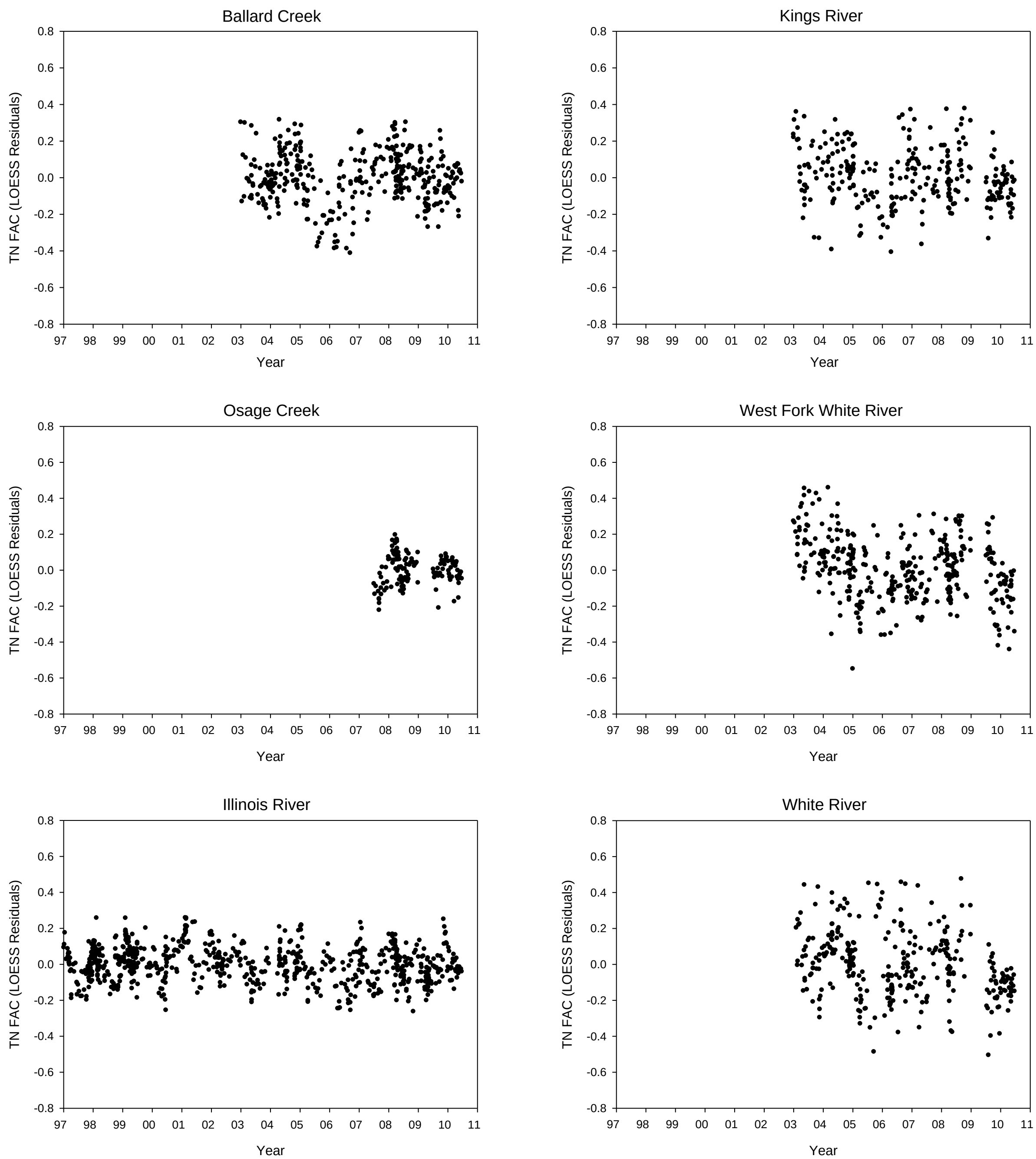

Figure D-4. Total nitrogen (TN): The flow-adjusted concentrations (FACs) as a function of time from 1997 through 2010; FACs are the residuals from LOESS smoothing of log-transformed concentrations and daily discharge as a function of time.

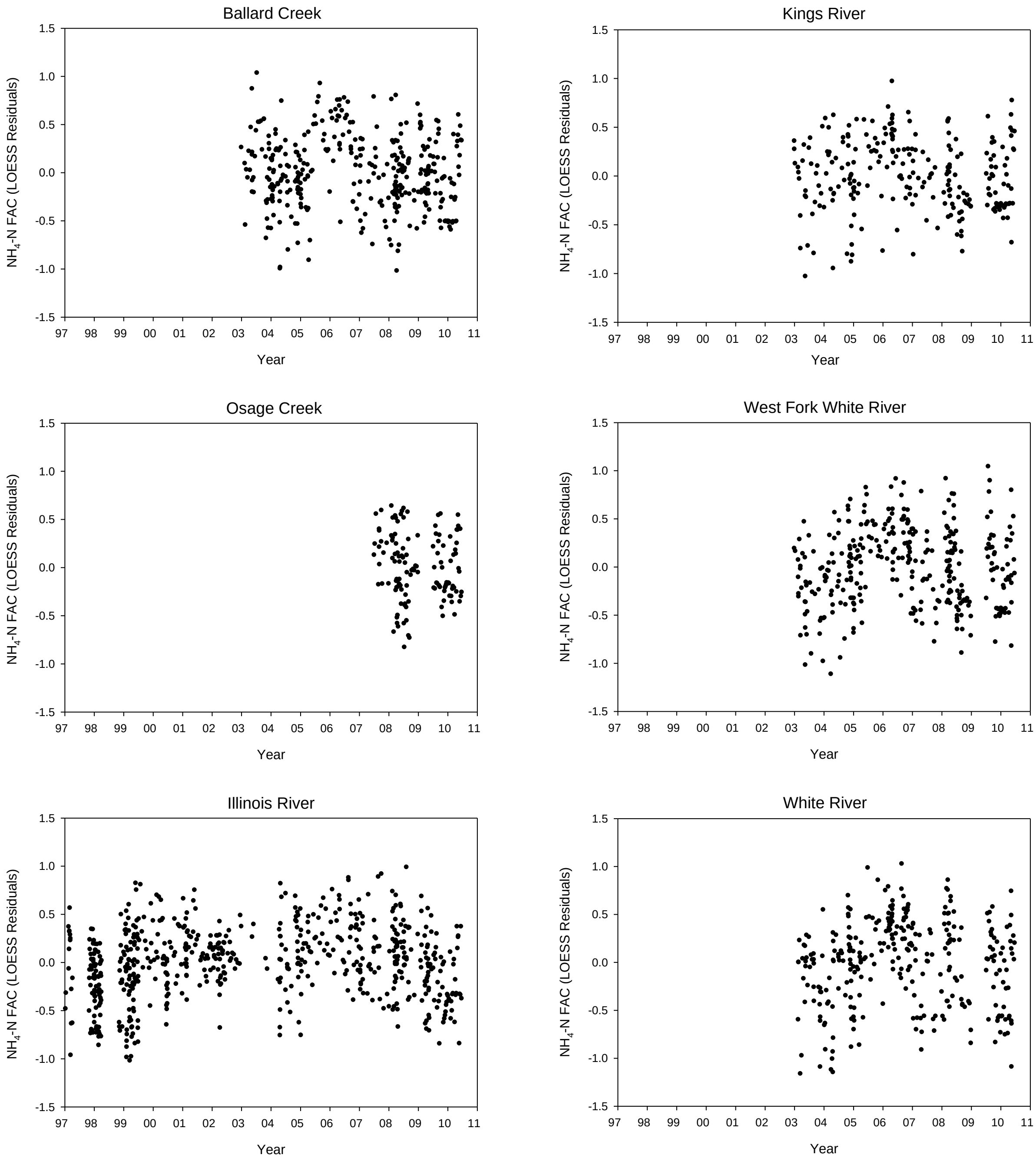

Figure D-5. Ammonium-nitrogen (NH_4-N): The flow-adjusted concentrations (FACs) as a function of time from 1997 through 2010; FACs are the residuals from LOESS smoothing of log-transformed concentrations and daily discharge as a function of time.

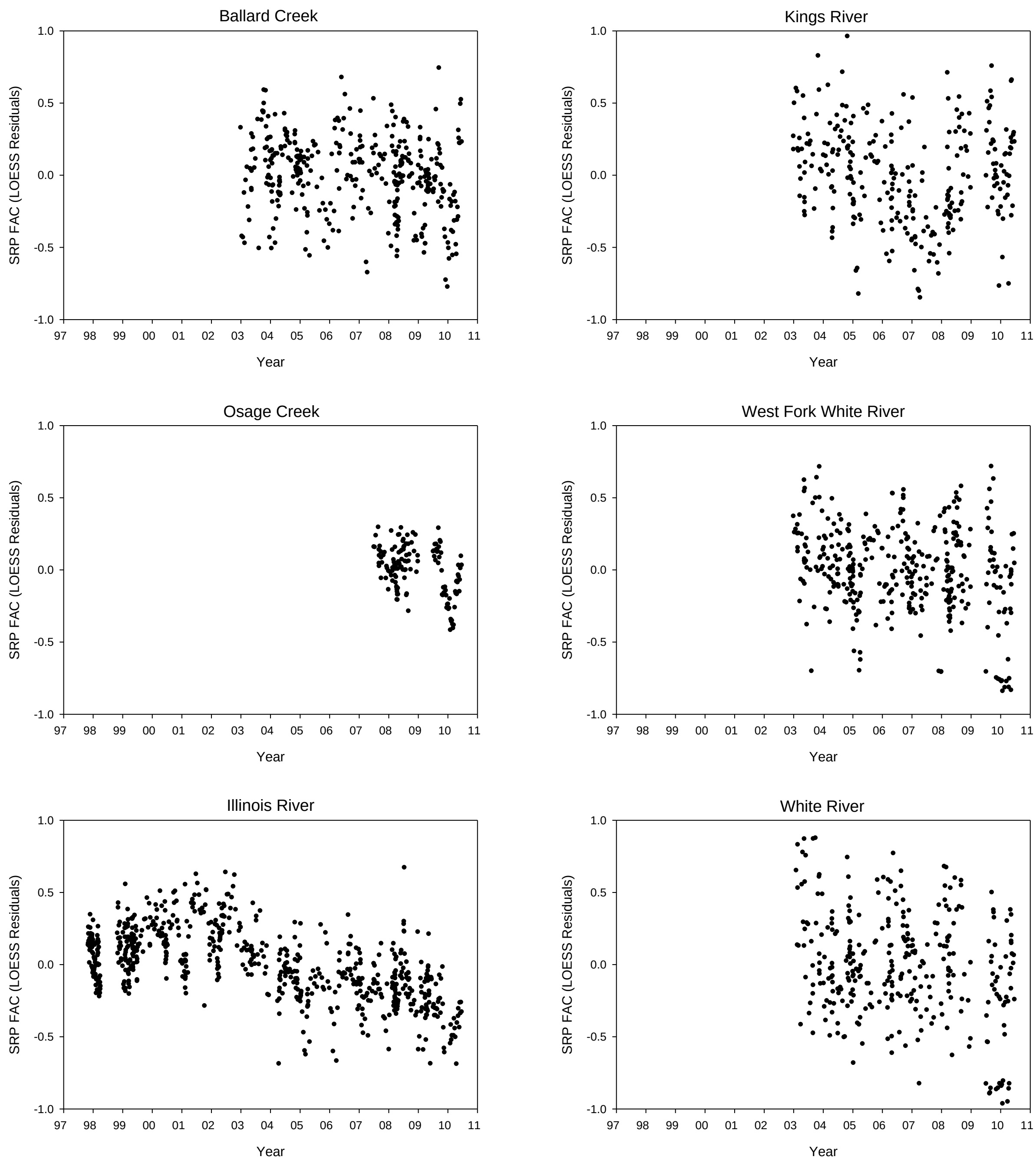

Figure D-6. Soluble reactive phosphorus (SRP): The flow-adjusted concentrations (FACs) as a function of time from 1997 through 2010; FACs are the residuals from LOESS smoothing of log-transformed concentrations and daily discharge as a function of time.

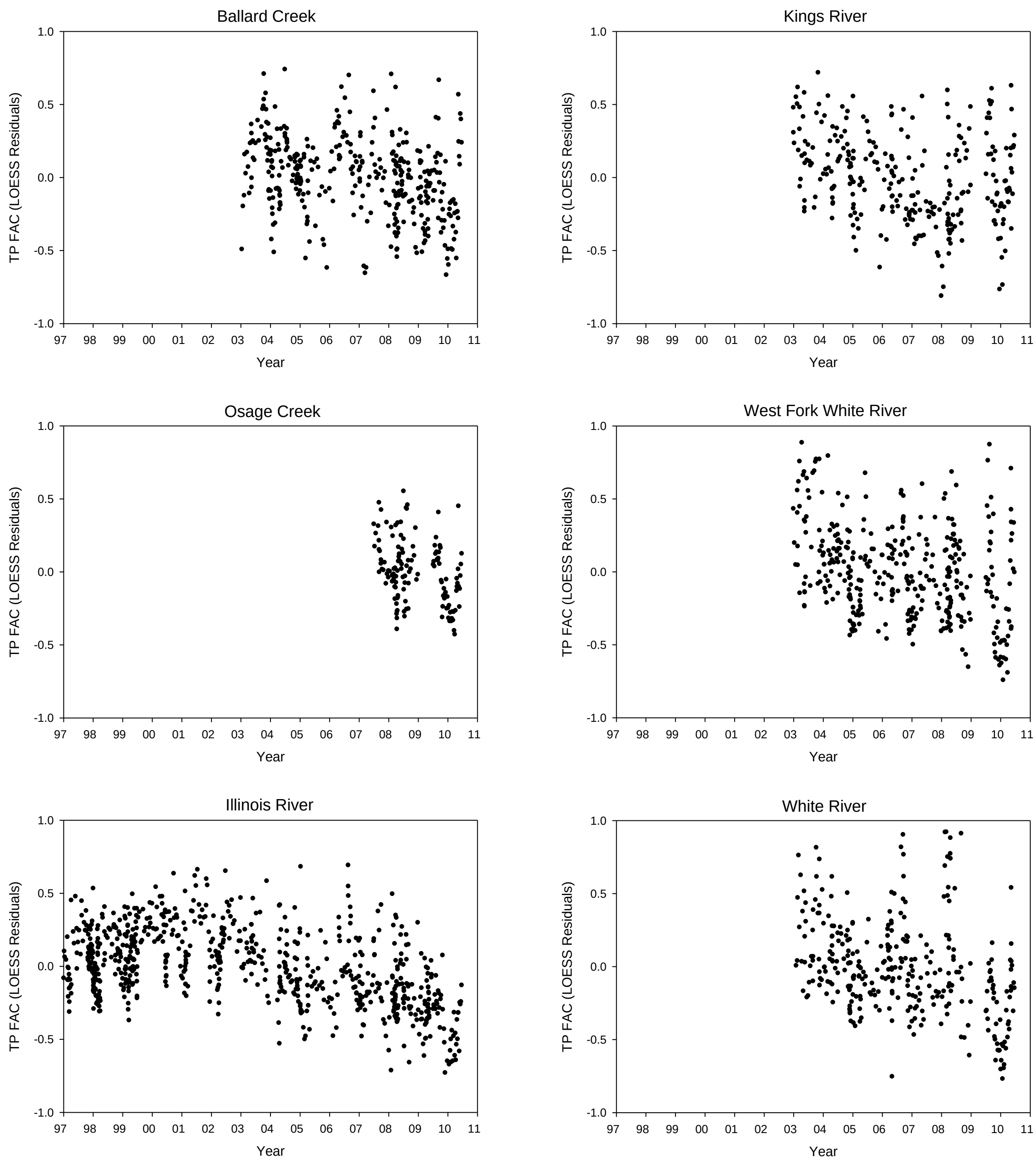

Figure D-7. Total phosphorus (TP): The flow-adjusted concentrations (FACs) as a function of time from 1997 through 2010; FACs are the residuals from LOESS smoothing of log-transformed concentrations and daily discharge as a function of time.

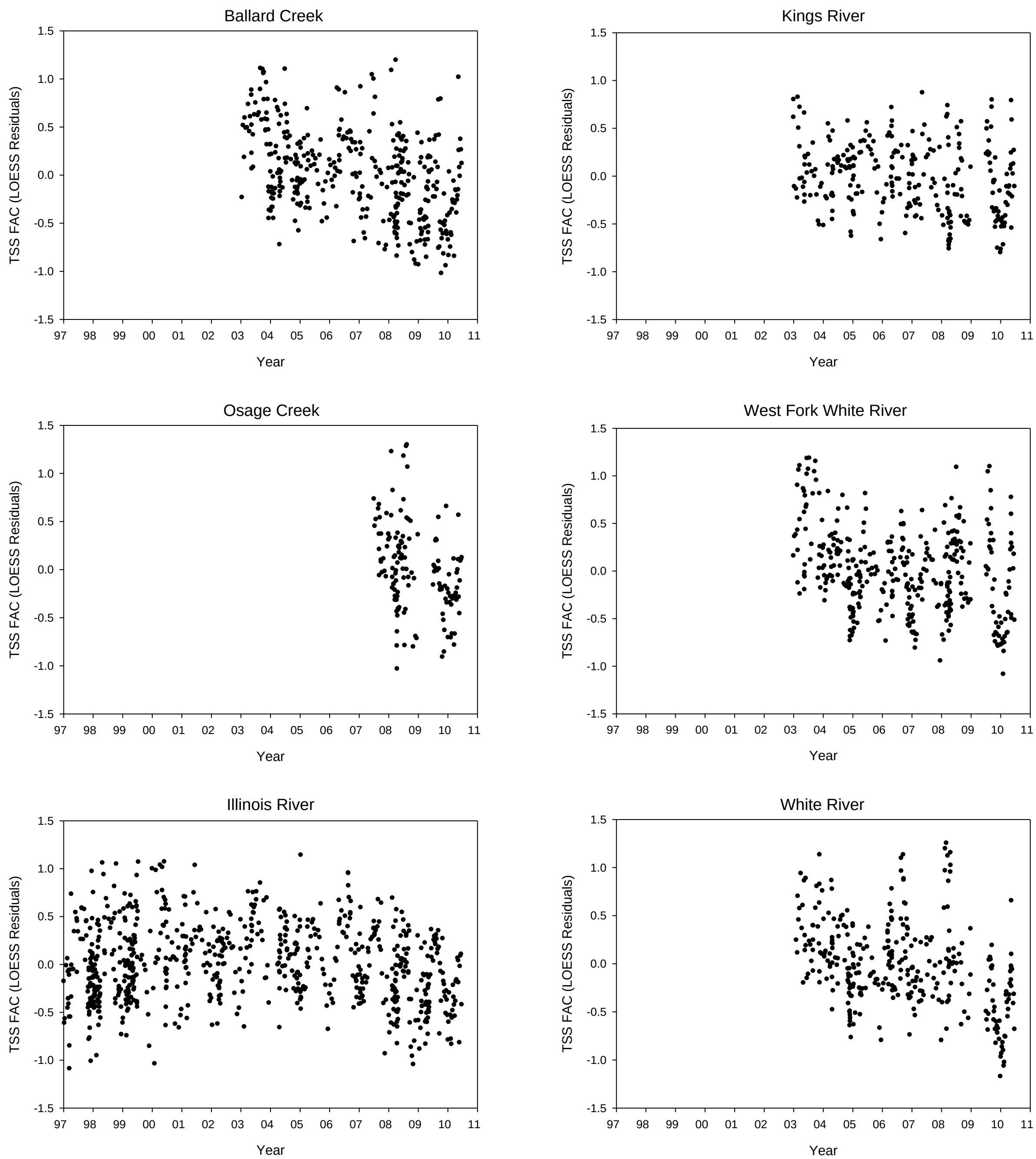

Figure D-8. Total suspended solids (TSS): The flow-adjusted concentrations (FACs) as a function of time from 1997 through 2010; FACs are the residuals from LOESS smoothing of log-transformed concentrations and daily discharge as a function of time.

APPENDIX E: MONTHLY FLOW-ADJUSTED CONCENTRATIONS AS A FUNCTION OF TIME

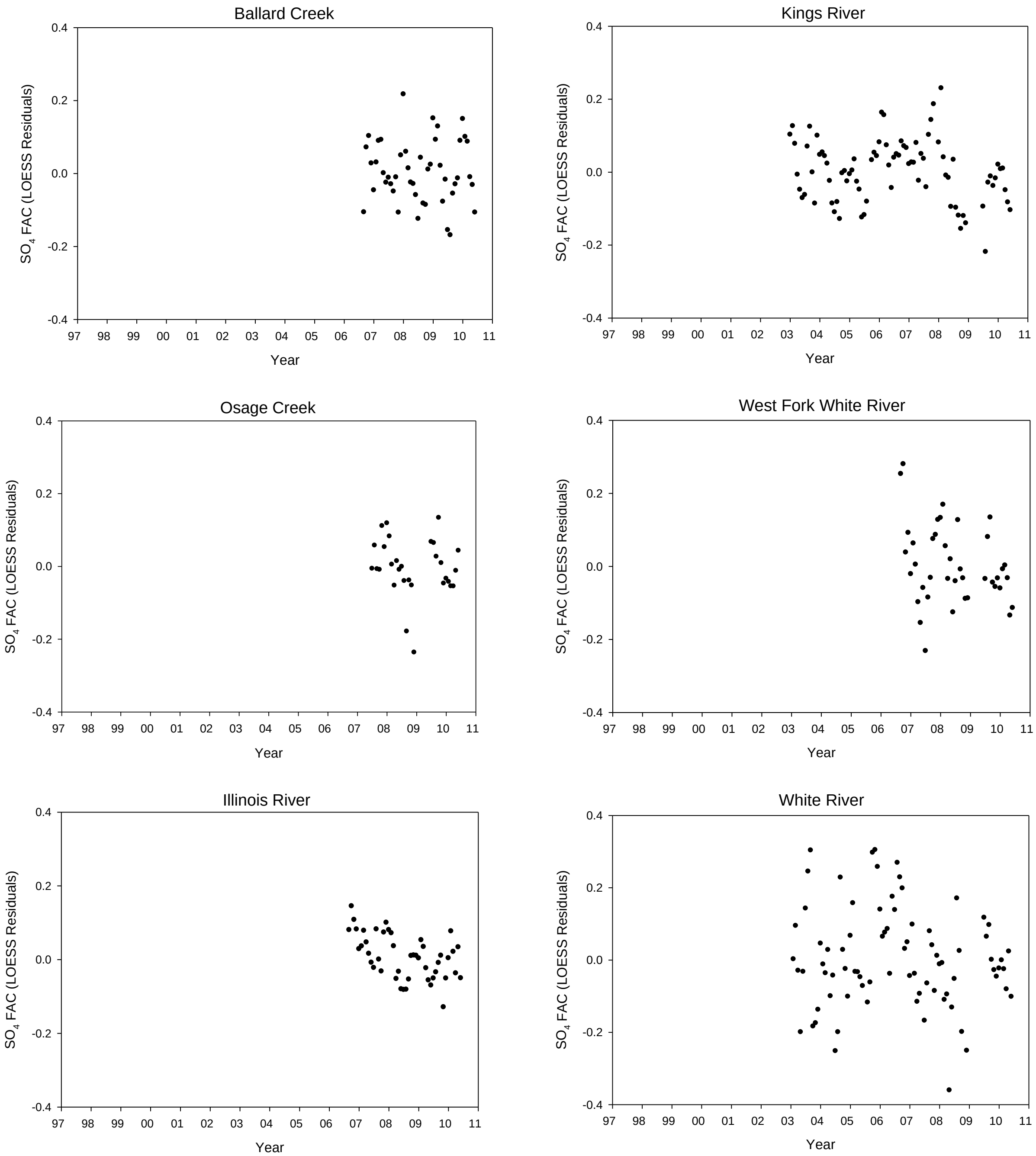

Figure E-1. Sulfate (SO_4): Seasonal flow-adjusted concentrations (FACs) as a function of time from 1997 through 2010.

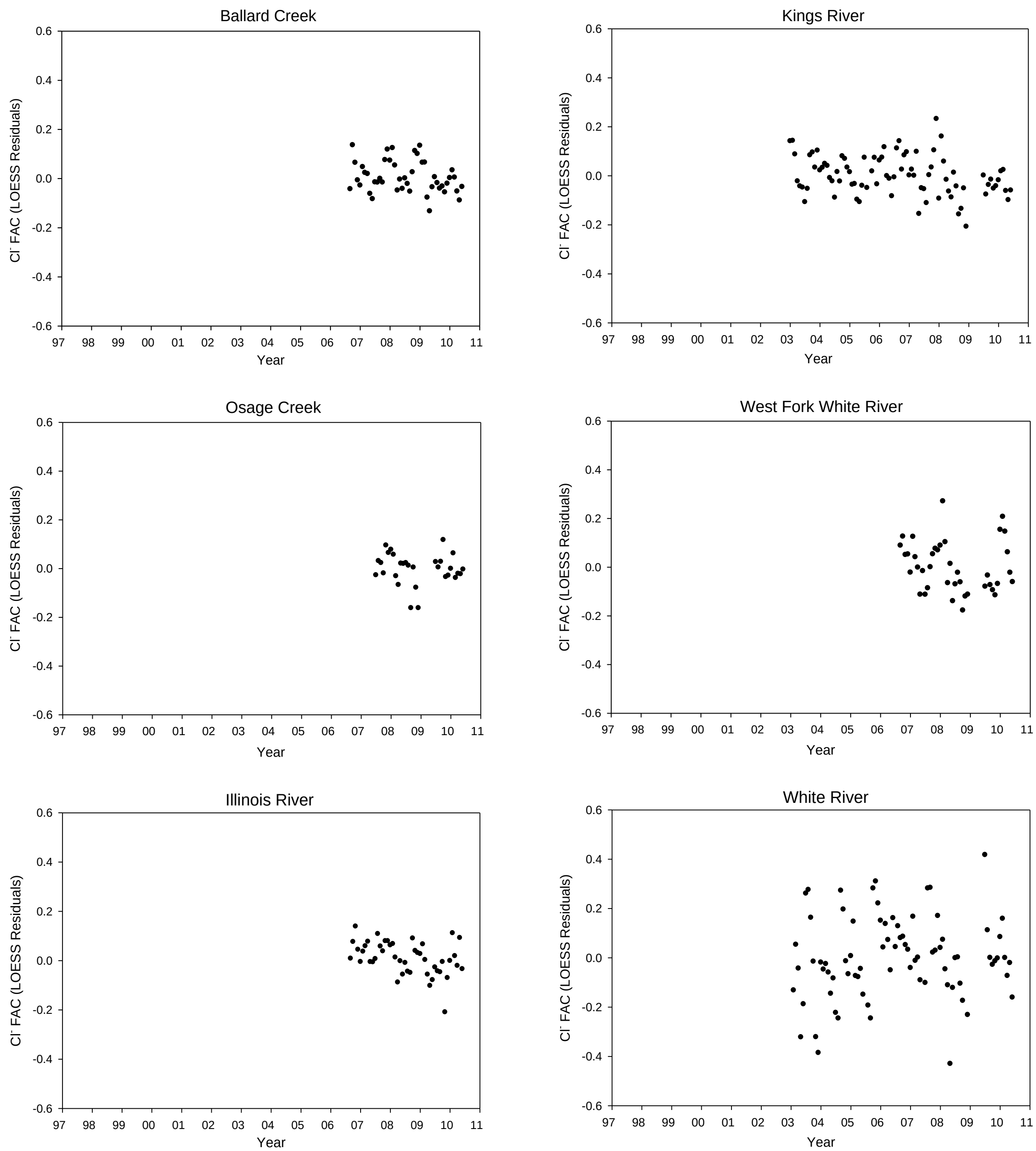

Figure E-2. Chloride (Cl^-): Seasonal flow-adjusted concentrations (FACs) as a function of time from 1997 through 2010.

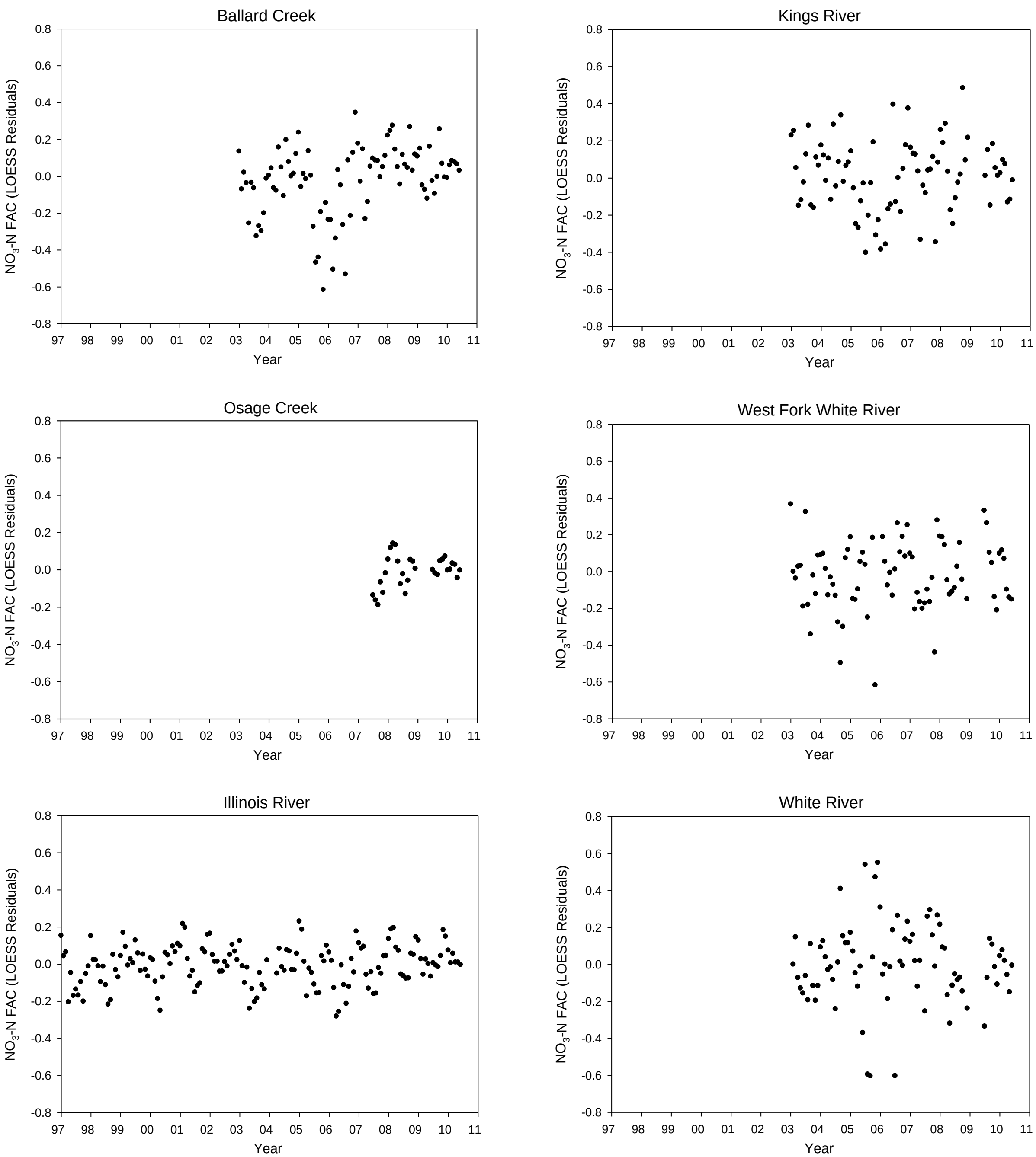

Figure E-3. Nitrate-nitrogen (NO_3-N): Seasonal flow-adjusted concentrations (FACs) as a function of time from 1997 through 2010.

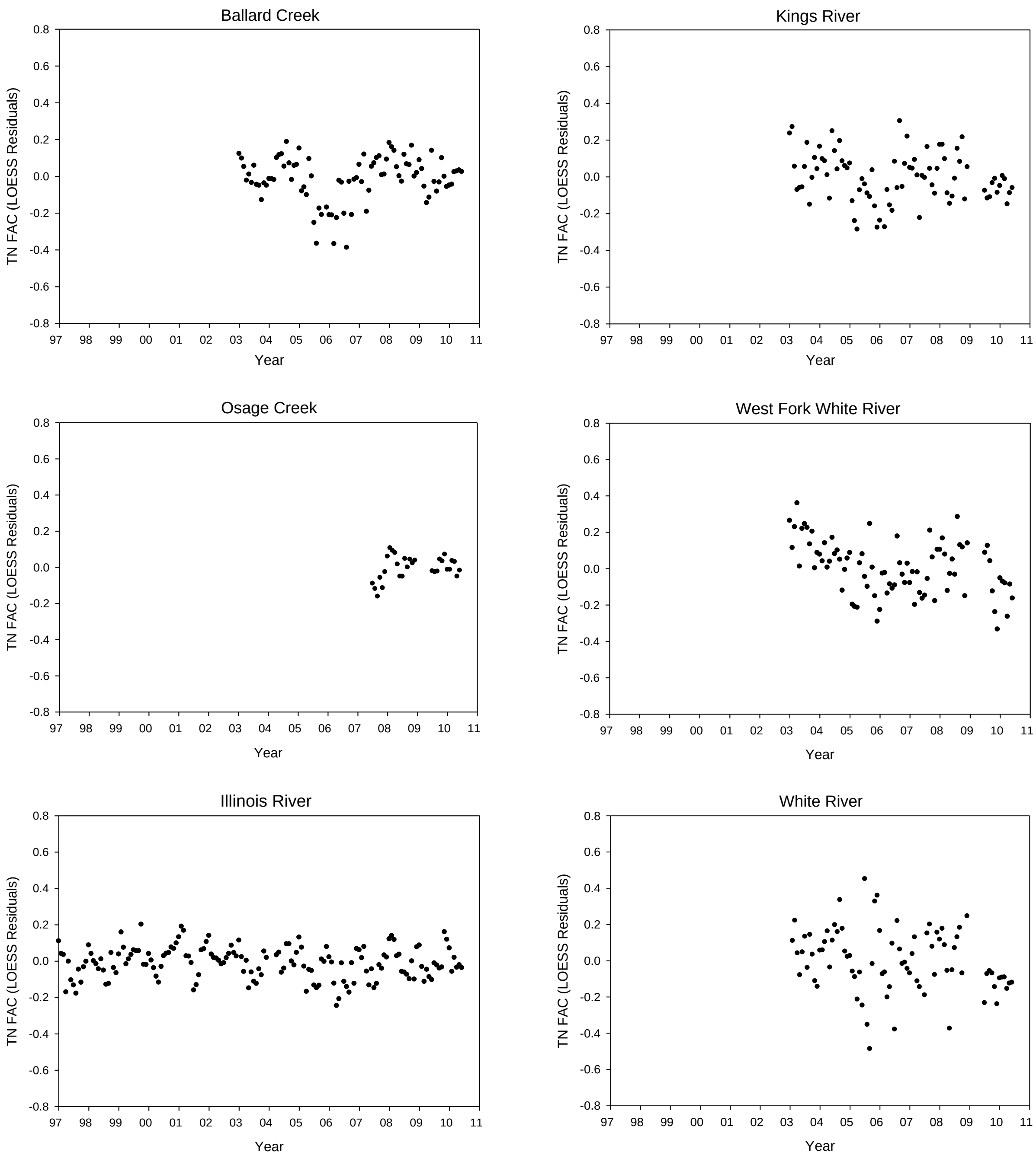

Figure E-4. Total nitrogen (TN): Seasonal flow-adjusted concentrations (FACs) as a function of time from 1997 through 2010.

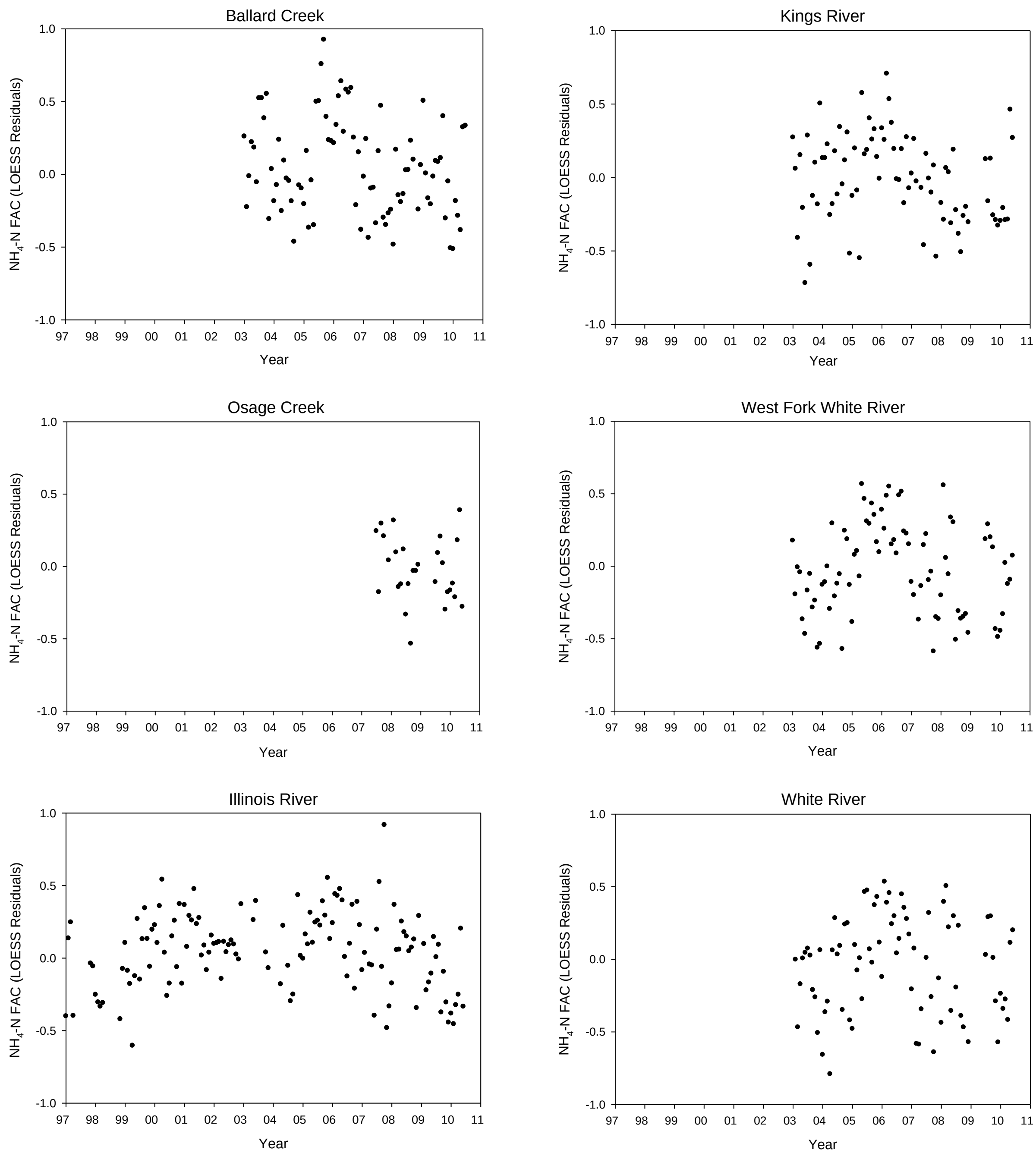

Figure E-5. Ammonium-nitrogen (NH_4-N): Seasonal flow-adjusted concentrations (FACs) as a function of time from 1997 through 2010.

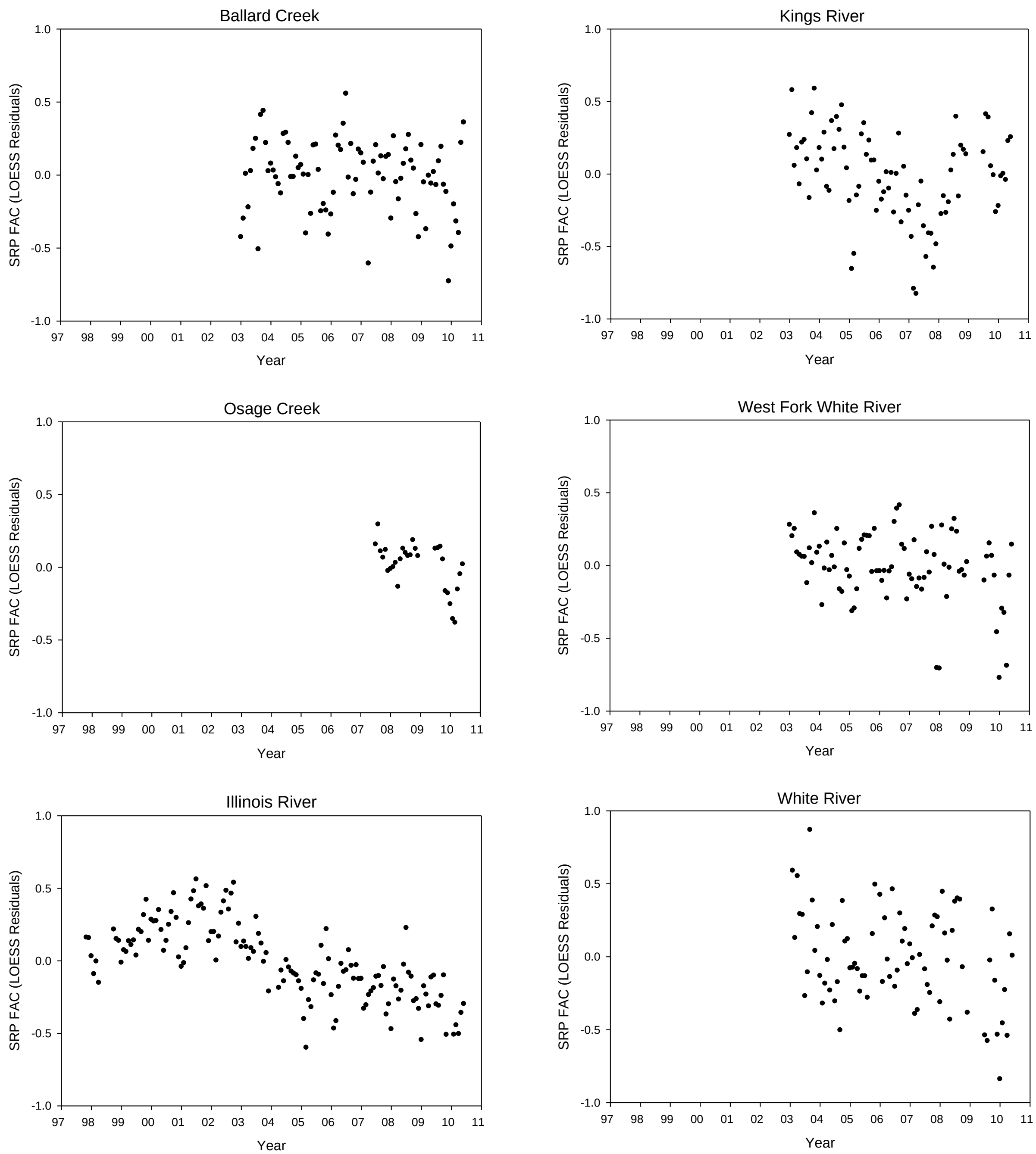

Figure E-6. Soluble reactive phosphorus (SRP): Seasonal flow-adjusted concentrations (FACs) as a function of time from 1997 through 2010.

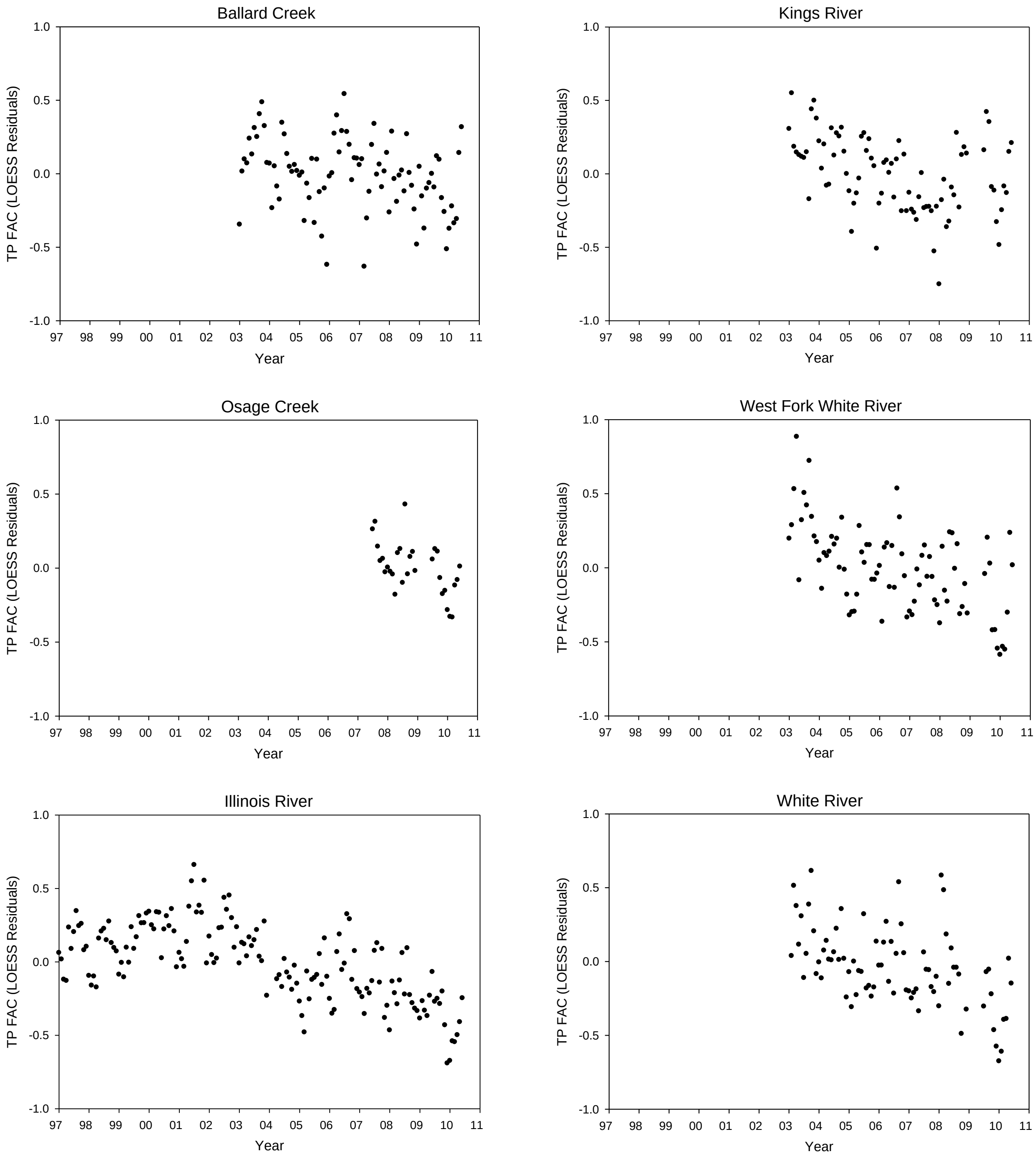

Figure E-7. Total phosphorus (TP): Seasonal flow-adjusted concentrations (FACs) as a function of time from 1997 through 2010.

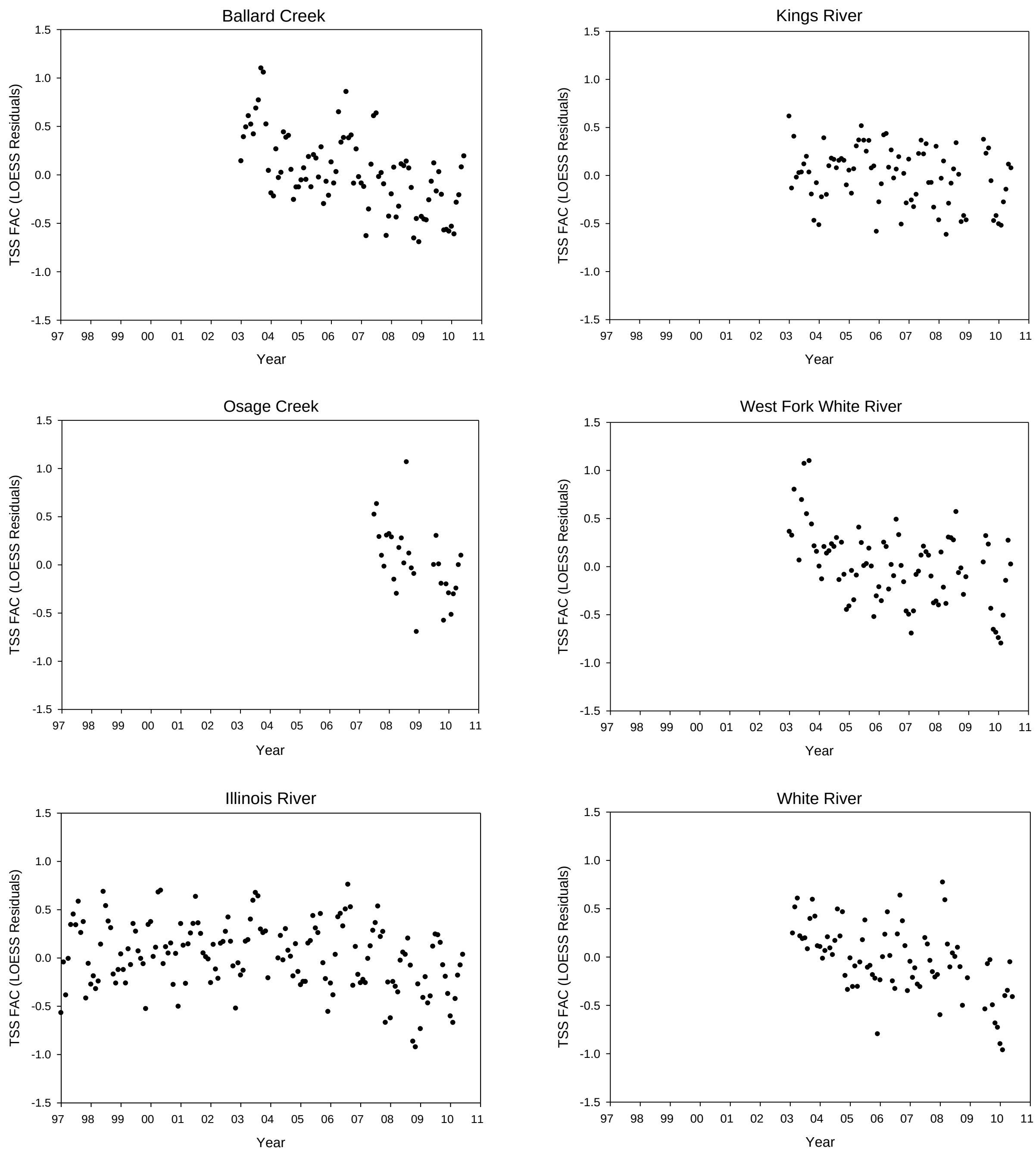

Figure E-8. Total suspended solids (TSS): Seasonal flow-adjusted concentrations (FACs) as a function of time from 1997 through 2010.