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Bryan W. Bailey

Brian E. Haggard

Leslie B. Massey

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Bryan W. Bailey, Brian E. Haggard and Leslie B. Massey
Arkansas Water Resources Center

EXECUTIVE SUMMARY

Northwest Arkansas contains two 319 priority watersheds that the Arkansas Natural Resources Commission has identified as being impacted by point source and nonpoint source pollution (i.e., phosphorus, nitrogen, and sediment). This project specifically focused on determining water quality trends at select sites within the Illinois River (HUC# 11110103) and Beaver Reservoir (HUC# 11010001) priority watersheds, including Ballard Creek, Osage Creek, Illinois River, White River, West Fork White River and the Kings River where sufficient constituent data were available. Water quality trends were analyzed using flow-adjusted constituent concentrations of phosphorus, nitrogen, sediment, sulfate and chloride, and parametric and non-parametric statistical techniques to determine if constituent concentrations were increasing, decreasing or not significantly changing over time. Overall, flow-adjusted concentrations of phosphorus and sediment have been decreasing across these watersheds 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 transboundary watersheds. 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.

KEY WORDS: Water Quality, Trends, Phosphorus, Nitrogen, Sediment, Illinois River Watershed, Beaver Reservoir Watershed

INTRODUCTION

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 decisions 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 infor-

mation 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 led 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 with its 319 priority watersheds. The AWRC has been awarded grants for the last decade to monitor the water quality within two 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.

Northwest Arkansas contains two 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 319 Program has funded the AWRC for the last decade (or less) to monitor the water quality at six sites in these watersheds. Several studies that have evaluated the ANRC 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). However, a comprehensive evaluation of the available water-quality data from the ANRC 319 Program has not yet been completed using acceptable statistical methods to determine long-term water-quality trends.

STUDY SITE DESCRIPTION

The Illinois River Watershed (IRW; HUC# 11110103) and the Upper White River Basin (UWRB; HUC# 11010001; see Appendix A) have been identified by the Arkansas Natural Resources Commission (ANRC) as nutrient surplus watersheds and classified as priority watersheds by the 319 Program. In addition, Arkansas is the upstream state in both watersheds and can be required to meet water quality standards set by downstream states, Oklahoma and Missouri, respectively. The purpose of this project was to conduct a comprehensive evaluation of the available data in these priority watersheds using acceptable statistical methods to determine long-term trends in water quality.

The IRW has a drainage area of approximately 195,285 ha in northwest Arkansas; the Illinois River originates near Hogeye, southwest of Fayetteville, Arkansas flowing through the Ozark Highlands into Oklahoma. From 1990 to 2000, the watershed saw a 48 percent increase in population, from 131,240 to 193,914 (CAST, 2006). According to the 2010 Census, the population further increased by over 30 percent from 2000 to 2010. 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).

The UWRB is composed of four counties in northwest Arkansas with a drainage area of approximately 574,718 ha and contains Beaver Lake which is northwest Arkansas's primary drinking water supply. 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 percent 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 over the past 10 years, respectively.

METHODS

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 319 Program (Table 1) and water samples were analyzed by the AWRC Water Quality Lab following approved quality assurance project plans (QAPP). During the previous monitoring projects, 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. Concentrations of 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 measured. The event mean constituent concentration data was paired with mean daily discharge obtained from the USGS or AWRC that represented the time frame during which samples were collected. When TN was not directly measured, it was calculated as the sum of total Kjeldahl nitrogen (TKN) plus NO_3-N.

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 sensored values reported.   Due to the small

Table 1. Selected study sites with global positioning coordinates in the Illinois River Watershed (HUC: 11110103) and the Upper White River Basin (Beaver Reservoir HUC: 11010001) – 319 Priority Watersheds, 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[c]	USGS Station	Latitude	Longitude	Area[a] (ha)	Land Use ( )[b]					Water Quality Period of Record
					U	W	H	F	P	
1-BC	AWRC	35°59'49"	94°31'38"	5,956	3.9	0.2	4.1	32	59	2000-2010
2-OC	7195000	36°13'19"	94°17'18"	33,669	30	0.2	4.6	14	47	2007-2010
3-IR	7195430	36°06'31"	94°32'00"	148,924	13	0.4	4.2	37	45	1997-2010
4-KR	7050500	36°25'38"	93°37'15"	136,492	1.7	0.1	6.3	71	20	2001-2010
5-WFWR	7048550	36°03'14"	94°04'59"	31,856	14	0.4	5.6	66	14	2002-2010
6-WR	7048700	36°06'21"	94°00'42"	106,707	5.8	0.5	4.7	76	13	2003-2010

[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] 1-BC: Ballard Creek on County Road 76 near Summers, AR, 2-OC: Osage Creek on Snavely Road near Elm Springs, AR, 3-IR: Illinois River on Highway 59 near Siloam Springs, AR, 4-KR: Kings River on Highway 143 near Berryville, AR, 5-WFWR: West Fork of the White River on County Road 195 near Fayetteville, AR, 6-WR: White River on Highway 45 near Goshen, AR.

number of censored values in these databases, the censored data were excluded from the trend analyses.

Databases were organized by date sampled, stage level, instantaneous discharge, lab sample ID 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 were explored with descriptive statistics (see Appendix B). Next, the original (n_o) water quality data were collapsed to a single daily value when multiple samples were collected in a day 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) for each constituent was calculated by dividing the sum of discharge (Q) times concentration (C) by the sum of discharges in that day. This produced water quality databases that were more consistent across the study sites and minimized autocorrelation between the data. Descriptive

statistics were evaluated and summarized (see Appendix B).

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), and 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. Constituent concentrations are often a function of discharge (Q); therefore, discharge 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
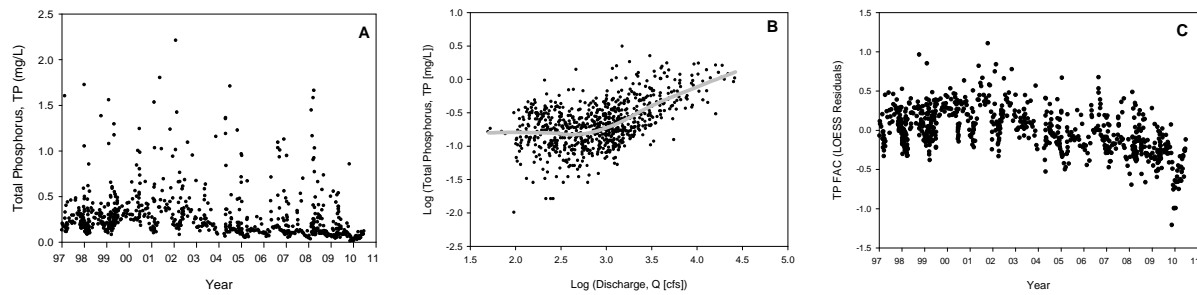
Figure 1. Example calculation, 774 daily samples (n_d): (a) Total phosphorus concentration from daily water quality samples at Illinois River from 1997-2010, (b) log-transformed total phosphorus concentration and log-transformed discharge with LOESS smoothing, and (c) LOESS residuals (i.e., flow-adjusted concentrations, FACs) as a function of time.

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) (e.g., see Figure 1). First, a scatter plot of the constituent concentration as a function of time was created for visual inspection (Figure 1a). Next, the log-transformed concentration data were plotted against log-transformed discharge (Figure 1b), 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 1c shows FACs of total phosphorus as a function of time at the Illinois River in Arkansas.

Removal of Outliers. Errors in measuring or recording of data may result in data outliers. 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, an upper and lower prediction interval was determined for each individual constituent's dataset. The 99 percent prediction interval was calculated for the FACs using the standard score equation,

$$z=(x-\mu)/\sigma \qquad (1)$$

and was solved for the x variable (i.e., FAC value), which represented the upper and lower 99 percent 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 potential influence from 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 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.

WQStat Plus v9 (Sanitas Technologies, Shawnee, KS) was used to estimate the Sen Slope which is, the magnitude of change in FACs over time. Since the water quality data was log-transformed prior to trend analysis, the slope represented a trend that was expressed in log units and was converted back to the original units. The slope was expressed in percent change per year using the equation,

$$S = (10^{b1} - 1) \times 100 \qquad (2)$$

RESULTS

Data Considerations

Outliers. The percentage of the removed outliers for the six sites ranged from zero to 3.5 percent for sulfate, 4.2 percent for chloride, 3.2 percent for nitrate-nitrogen, 3.5 percent for total nitrogen, 1.6 percent for ammonium-nitrogen, 2.6 percent for soluble reactive phosphorus, 2.8 percent for total phosphorus, and 2.2 percent for total suspended solids.

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). The correlation between these two variables demonstrates different kinds of physical phenomena, which include dilution effect (i.e., decreasing), wash-off 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

Graphs of the LOESS smoothing technique applied to the log transformed constituent conencetrations as a function of daily discharge and graphs of the LOESS residual (FAC) over time are presented in Appendices D and E, respectively. The results of trend analyses on FACs, representing the daily (n) and monthly (n_m) data are presented in Tables 2 and 3. Trends were considered statistically significant if the p-value was less than 0.05 ($p < 0.05$).

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 2 and 3, Figure 2). 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).

Chloride. Flow-adjusted Cl^- concentrations did not show any significant monotonic trends at Osage Creek and the West Fork of the White River during the study period (Tables 2 and 3, Figure 3). 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% per year) at the Illinois River during the study period.

Nitrate-Nitrogen. Overall, FACs of NO_3-N were not significantly changing over time across these sites, except at Ballard Creek (Tables 2 and 3, Figure 4). 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.

Total Nitrogen. Flow-adjusted TN concentrations showed no monotonic changes over time at Ballard Creek and Osage Creek during the study period (Tables 2 and 3, Figure 5). 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 significant 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, whereas the nonparametric test did not suggest FACs were changing at any other sites.

Ammonium-Nitrogen. Flow-adjusted NH_4-N concentrations showed 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 2 and 3, Figure 6). 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 to -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 2

Table 2. Regression statistics from trend analyses of the flow-adjusted concentrations (FACs) at 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. Nonparametric statistics from trend analyses on the seasonal flow-adjusted concentrations (FACs) at 319 water quality monitoring sites, northwest Arkansas.

Constituent	Sampling Site	n	τ[a]	p-Value	S'[b]	Sen Slope[c]
SO₄	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	
NO₃-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	
NH₄-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');
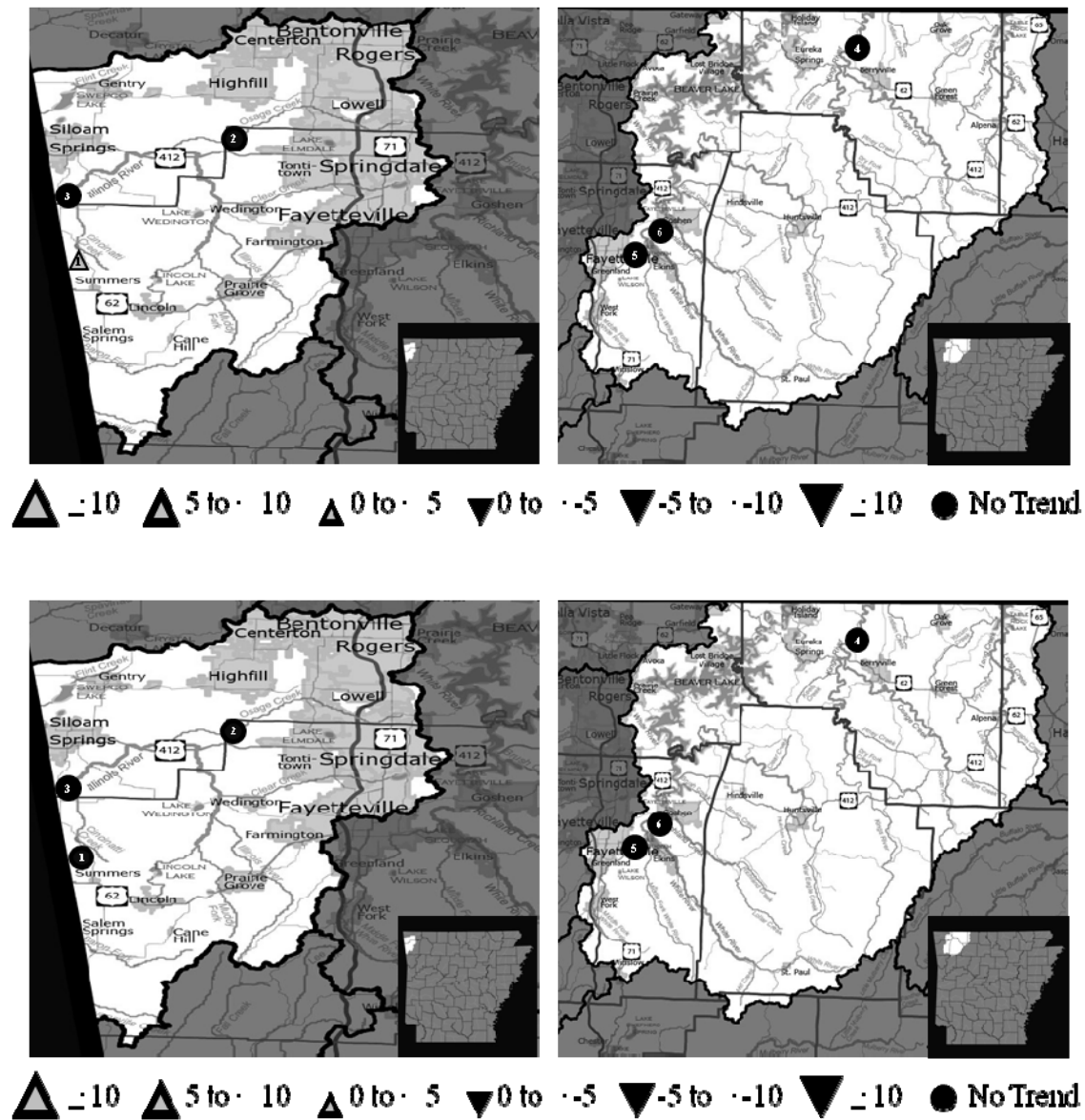[c] Sen's Slope Estimator; the percent change per year.
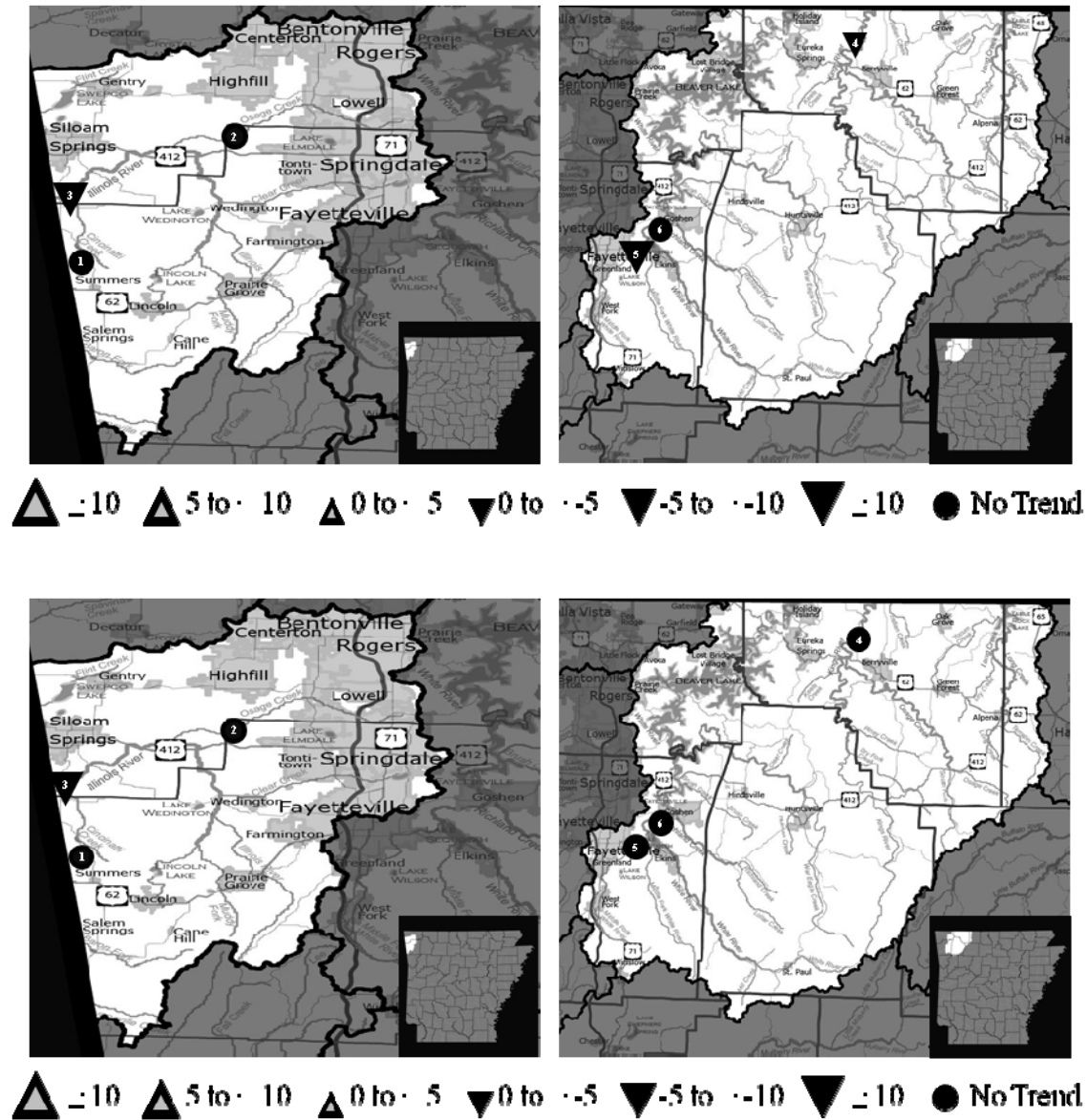
Figure 2. Flow-adjusted trends (percent change per year) in sulfate concentrations applying simple linear regression (top) and the Seasonal Kendall Test (bottom).
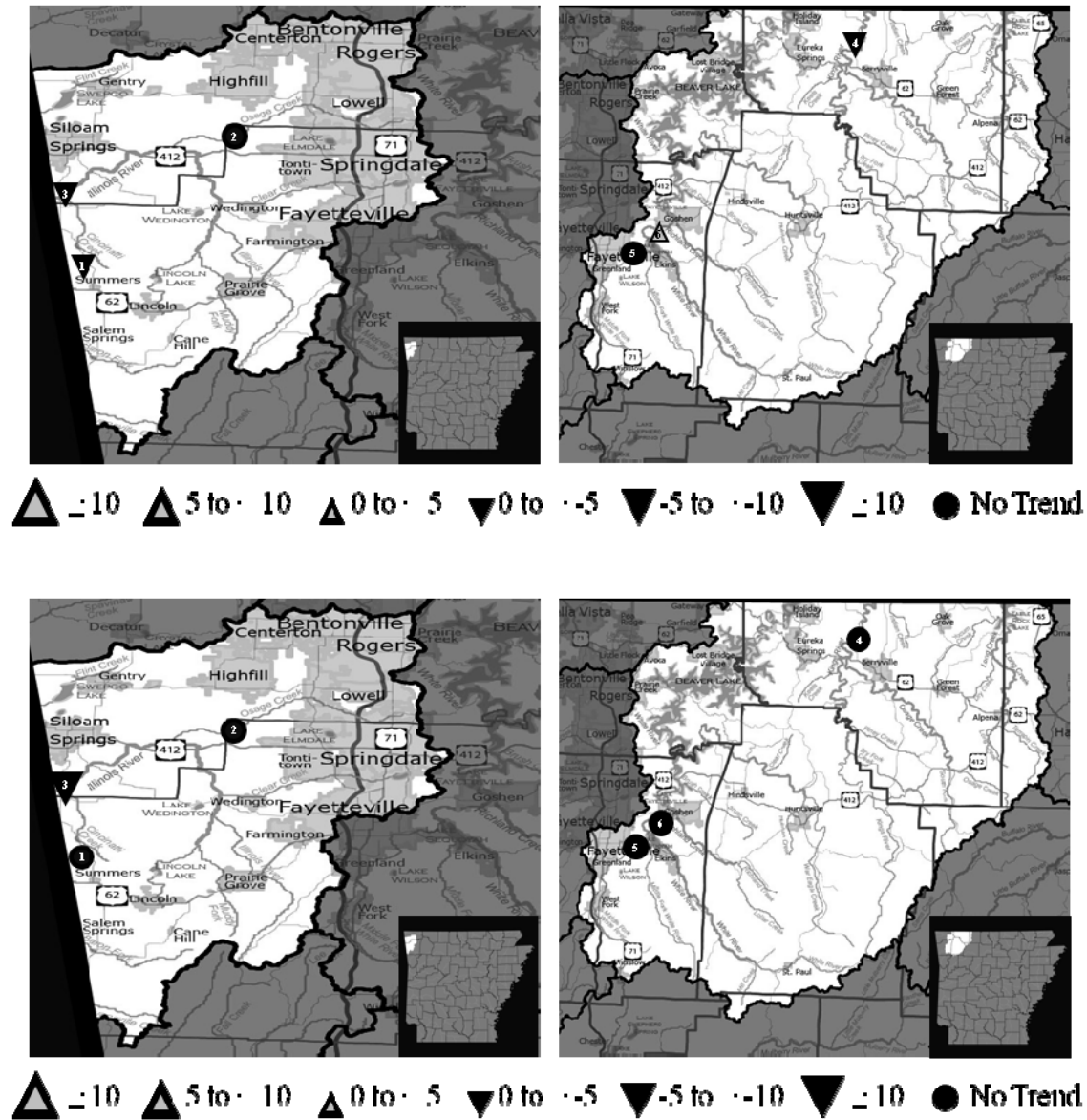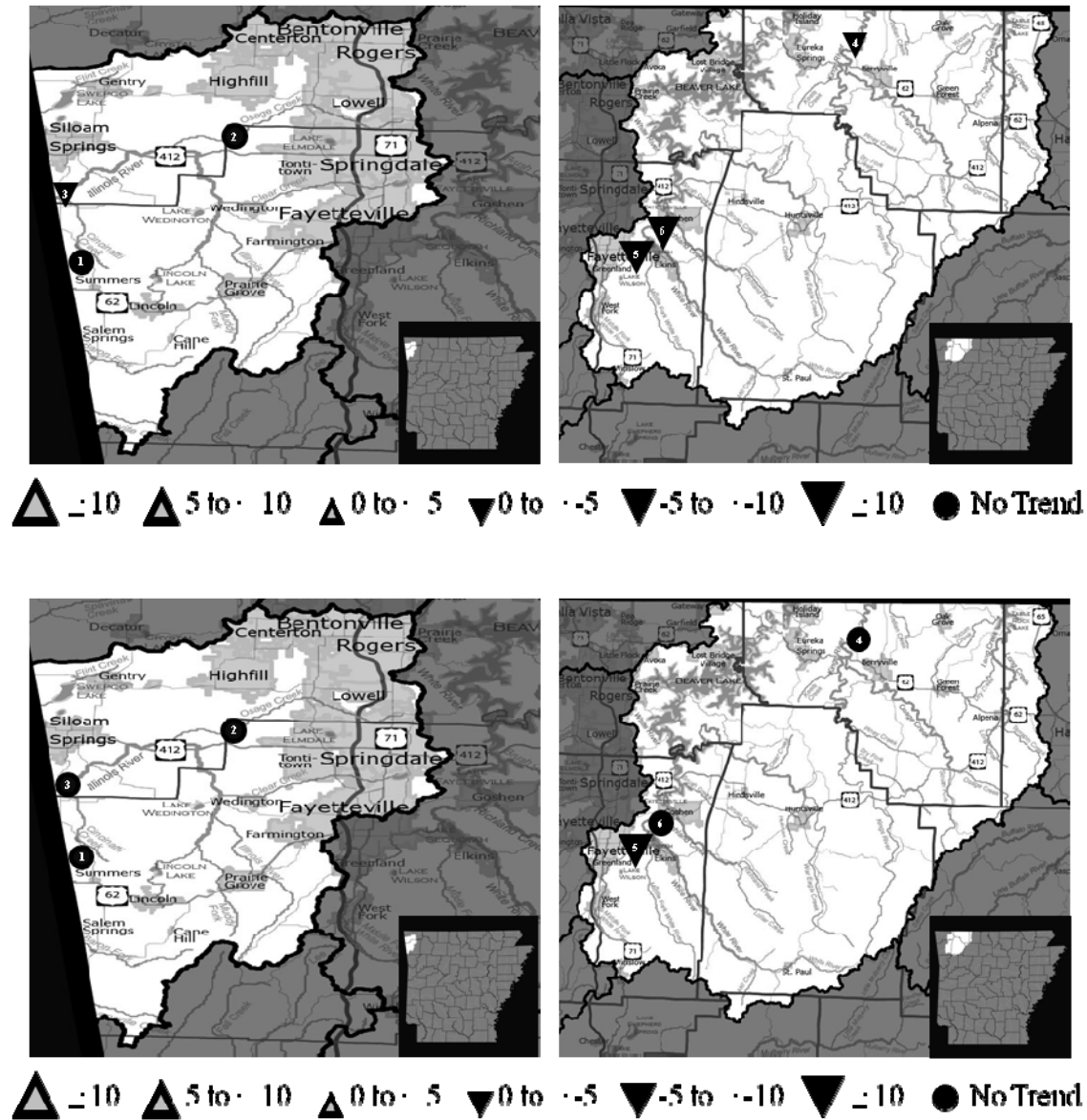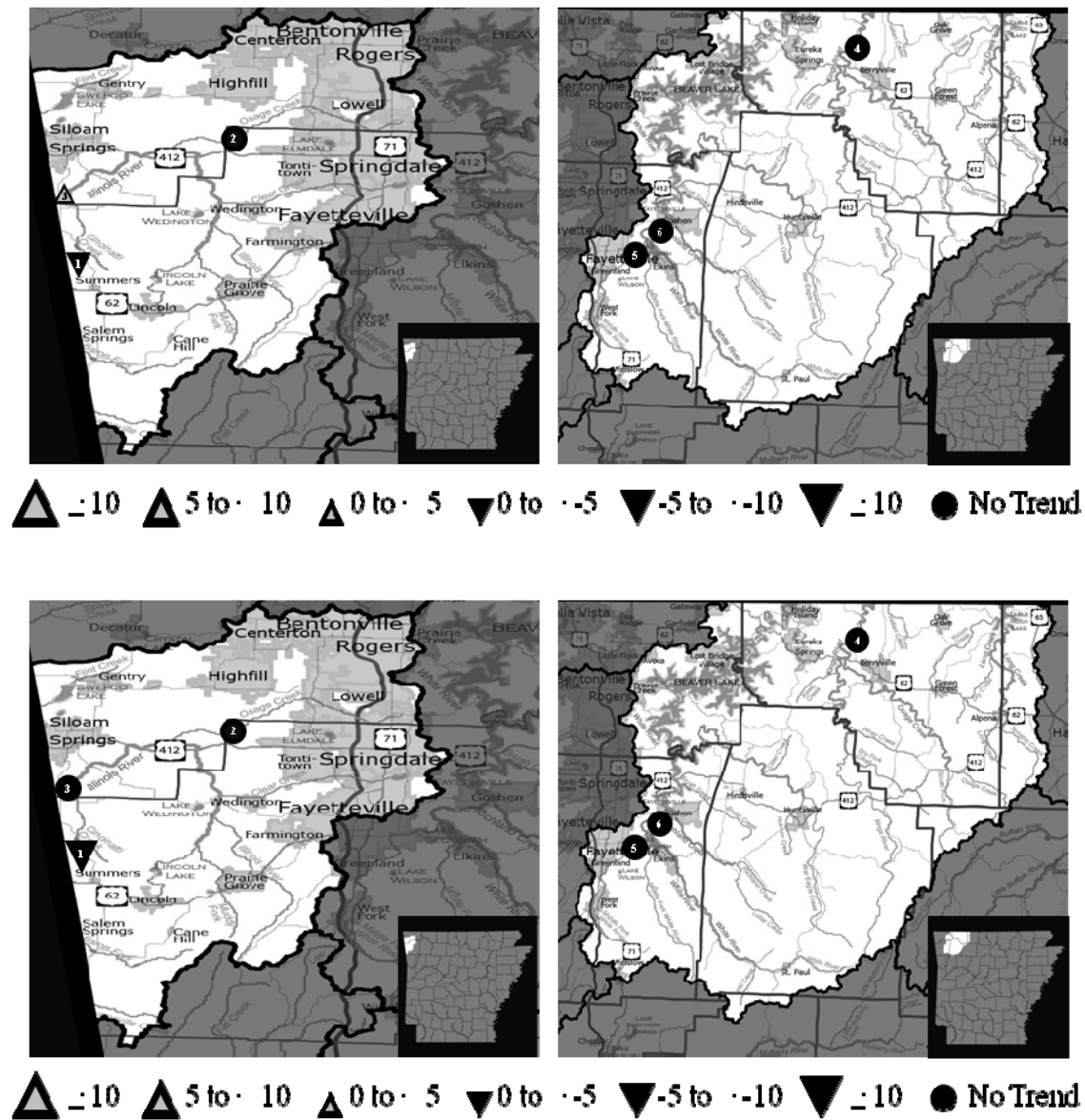
Figure 3. Flow-adjusted trends (percent change per year) in chloride concentrations applying simple linear regression (top) and the Seasonal Kendall Test (bottom).

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

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

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

and 3, Figure 7). Significant decreasing trends in FACs were observed across these sites (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.

Total Phosphorus. Flow-adjusted TP concentrations exhibited decreasing trends across all sites during the study period (Tables 2 and 3, Figure 8). 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 did not change over time (based on Seasonal Kendall).

Total Suspended Solids. Flow-adjusted TSS concentrations indicated decreasing trends across all sites during the study period (Tables 2 and 3, Figure 9). Based on regression analysis, 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).

SUMMARY AND CONCLUSIONS

This project has successfully evaluated trends in water quality at six sites in the priority watersheds of the IRW and UWRB in northwest Arkansas. Overall, the nonparametric (i.e., Seasonal Kendall Test and Sen Slope Estimator) method agreed well with the parametric (i.e., linear regression) method for identifying trends in water quality data except for in the case of small datasets. All of the selected sites in both

priority watersheds exhibited significant decreasing trends in SRP and TP, and decreasing trends in TSS were also evident across these watersheds. 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 transboundary watersheds. 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.

Over the past decade, the ANRC 319 Program has invested nearly $4,149,900 in demonstration and implementation projects including low impact development, poultry litter feasibility, stream restoration, erosion and nutrient management plan development, and streambank stabilization. The decreasing trends in phosphorus and sediment suggest that there have been watershed management changes or restoration activities which have influenced water quality (especially FACs of phosphorus and sediment). The regional WWTPs have worked hard and invested $180,000,000 into municipal facility upgrades and legislation within the State of Arkansas has been enacted (i.e., Titles 19, 20, 21 and 22) which were intended at improving environmental quality in nutrient surplus watersheds. All of these efforts combined with the investment and activities of the 319 Program have no doubt influenced water quality. While one cannot differentiate the proportion of improvement between these efforts, it is more important that phosphorus and sediment have been decreasing in these priority, transboundary watersheds.

Furthermore, ANRC has funded a comprehensive monitoring program in the IRW and UWRB, for the next four years (July 2011 through June 2015). Annual loads will continue to be estimated at the selected sites and others and will contribute to the historical water quality databases for these watersheds which
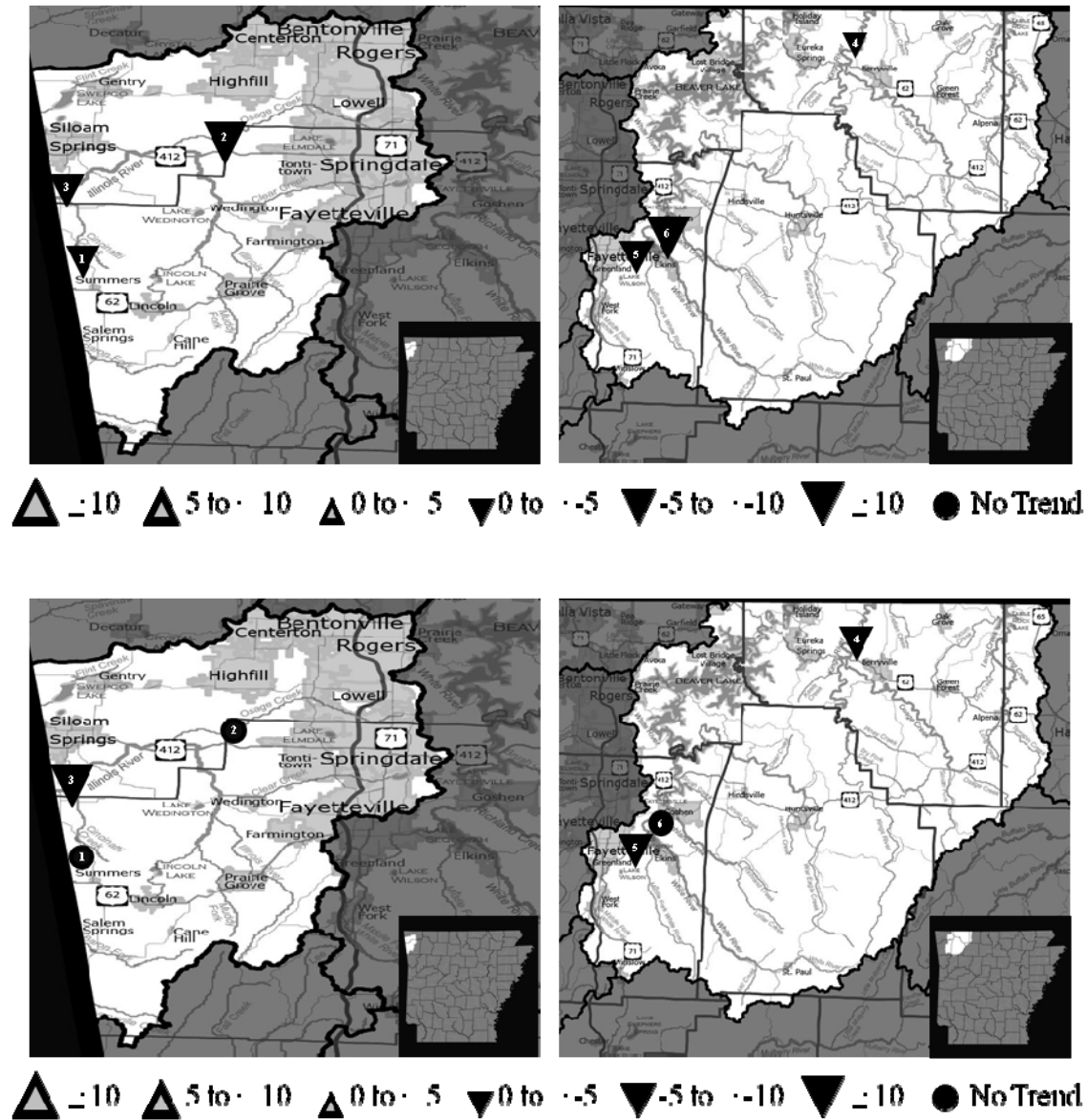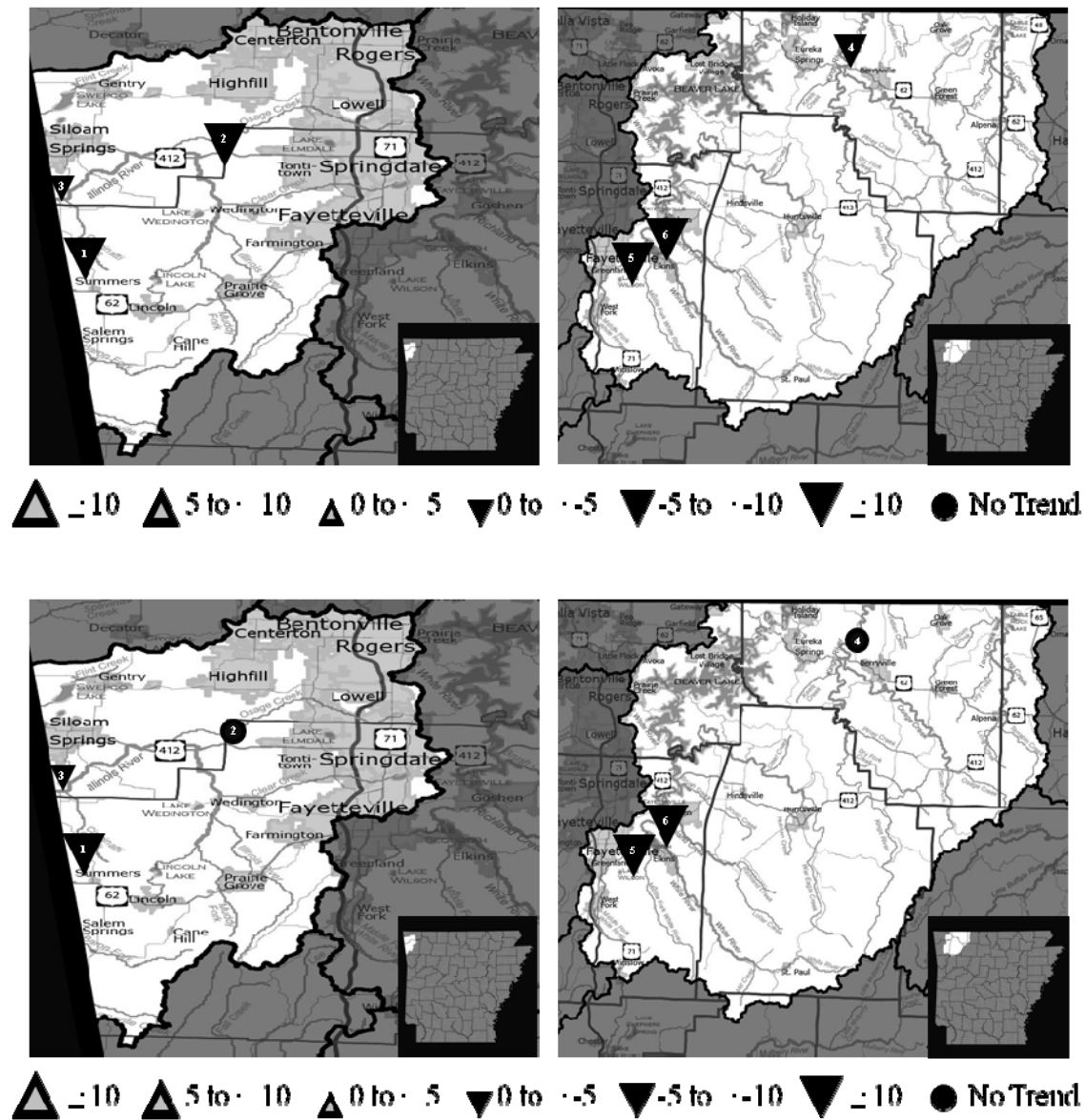
Figure 7. Flow-adjusted trends (percent change per year) in soluble reactive phosphorus (SRP) concentrations applying simple linear regression (top) and the Seasonal Kendall Test (bottom).
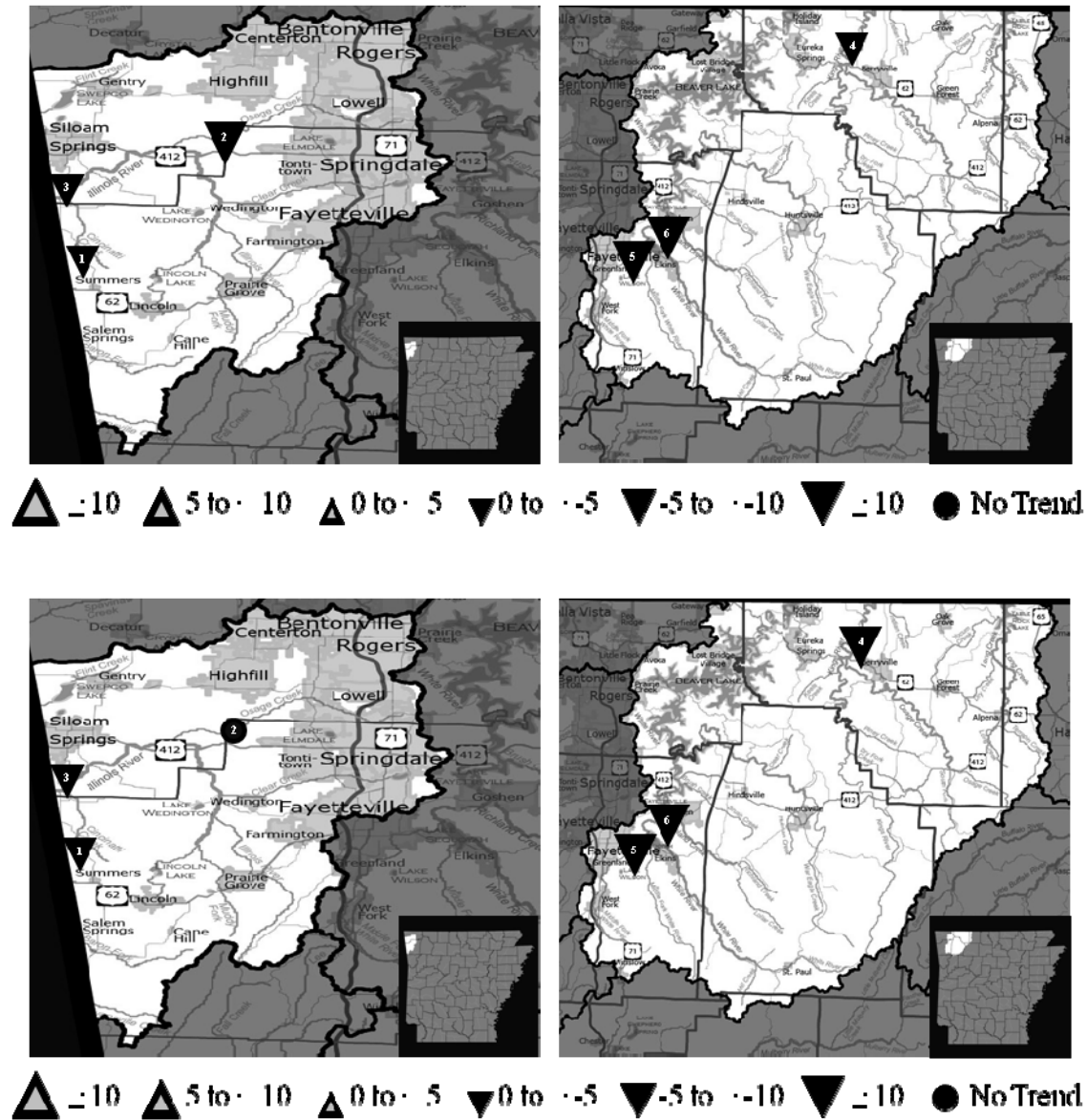
Figure 8. Flow-adjusted trends (percent change per year) in total phosphorus concentrations applying simple linear regression (top) and the Seasonal Kendall Test (bottom).

**Figure 9.** Flow-adjusted trends (percent change per year) in total suspended solids concentrations applying simple linear regression (top) and the Seasonal Kendall Test (bottom).

can be used to re-evaluate trends in water quality over time. This project will complete a five year database at 19 sites in northwest Arkansas, which will allow trends to be estimated showing possible, continued improvement in water quality from the various 319 projects, or other watershed management changes that result from state and federal programs.

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APPENDIX A: The Illinois River Watershed (top) and the Upper White River Basin (bottom) with the location of the six selected sampling sites in northwest Arkansas. Refer to Table 1 for complete site descriptions.
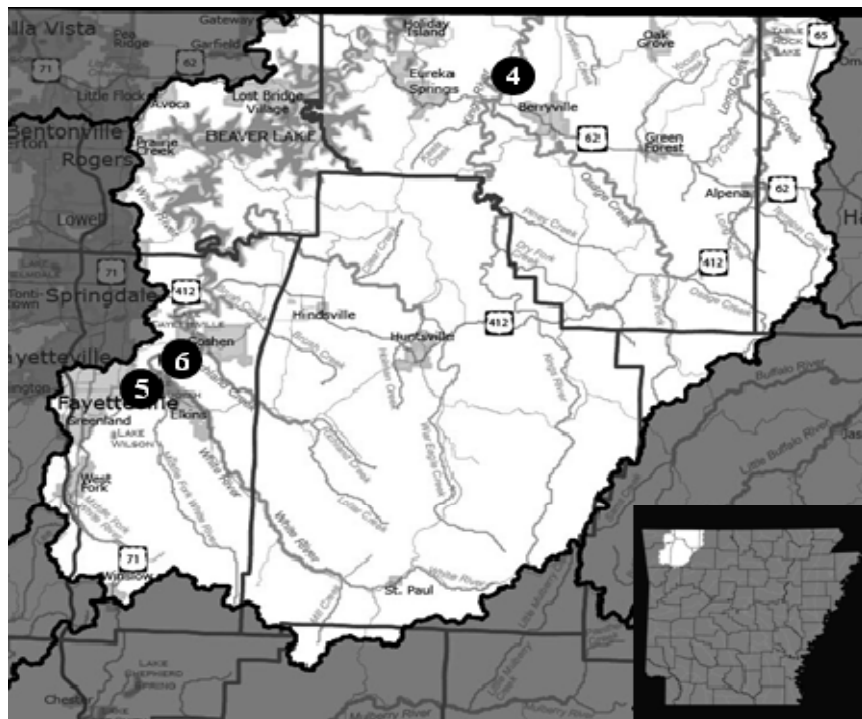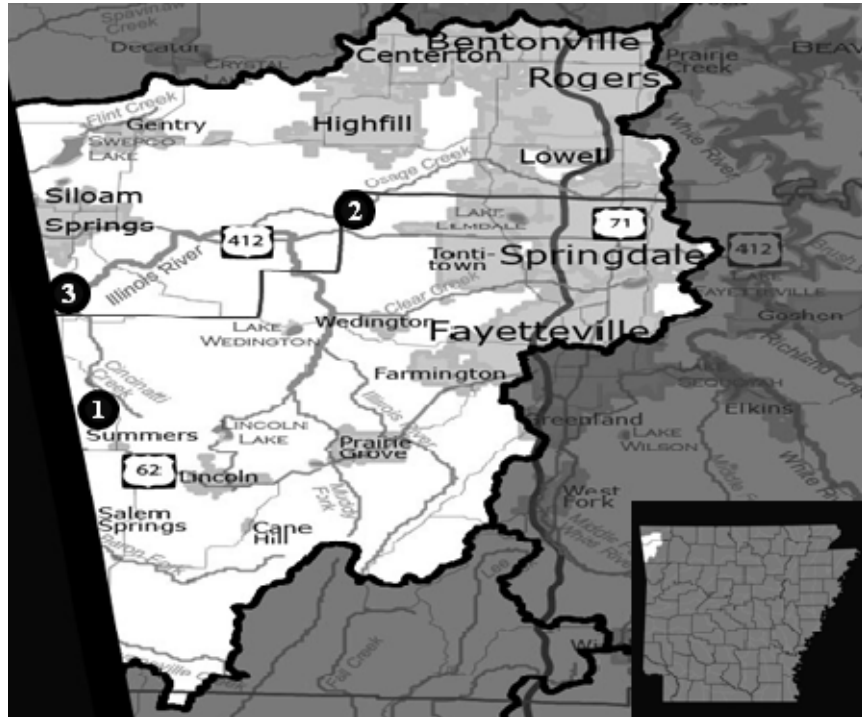
APPENDIX B: Descriptive Statistics of Water Quality Data

Table B-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_o [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 B-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 B-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 B-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 B-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
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
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
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
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 B-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.

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APPENDIX C: Constituent Concentration as a Function of Time
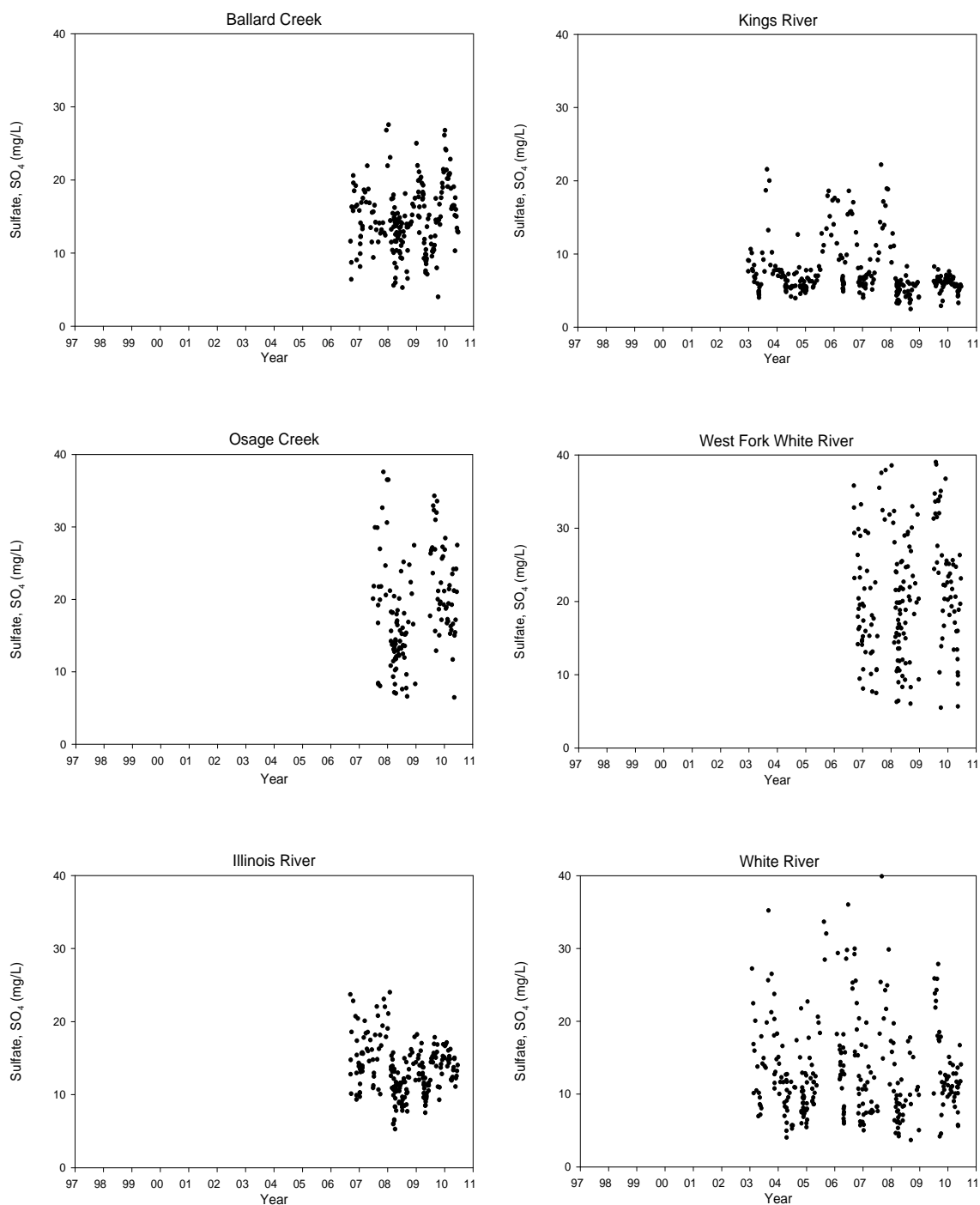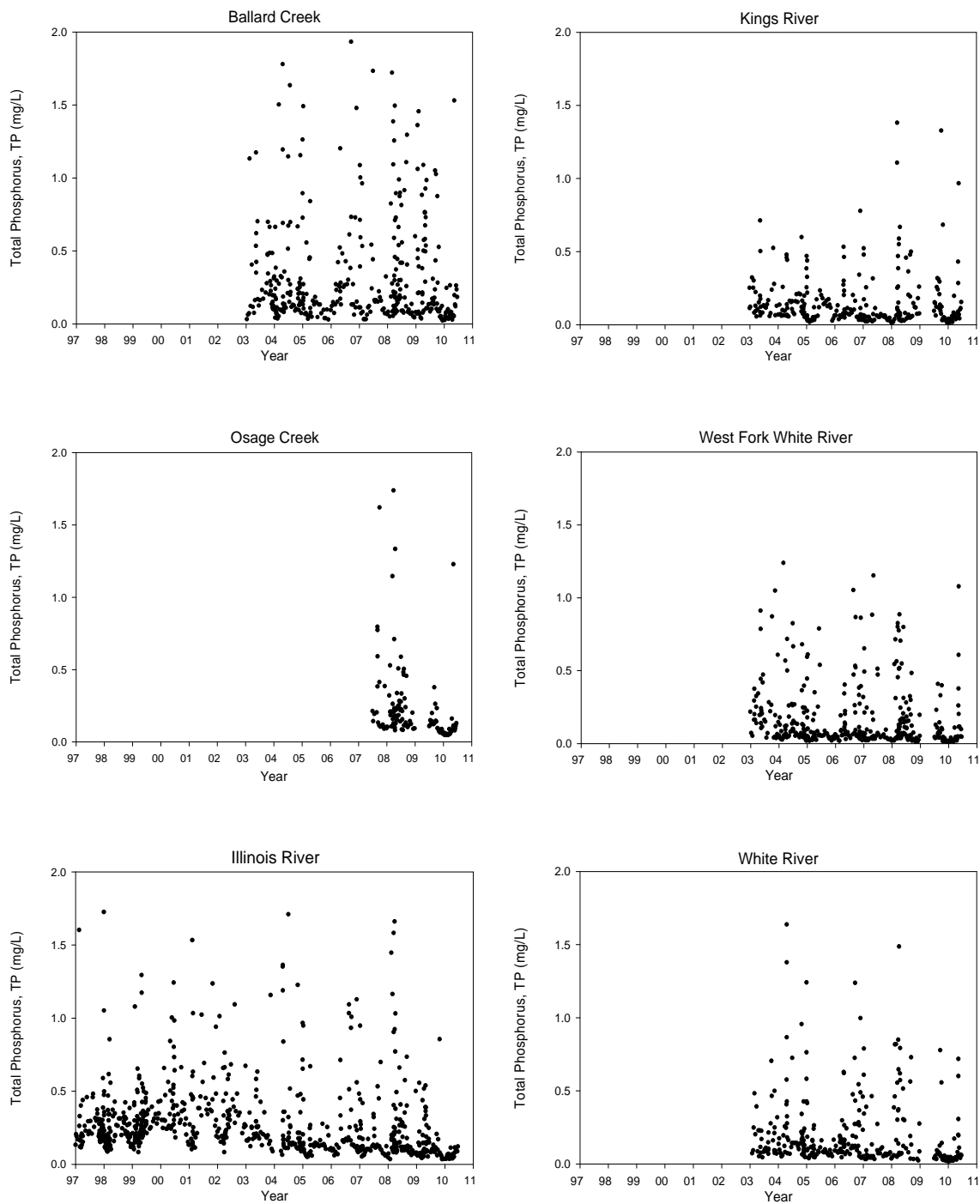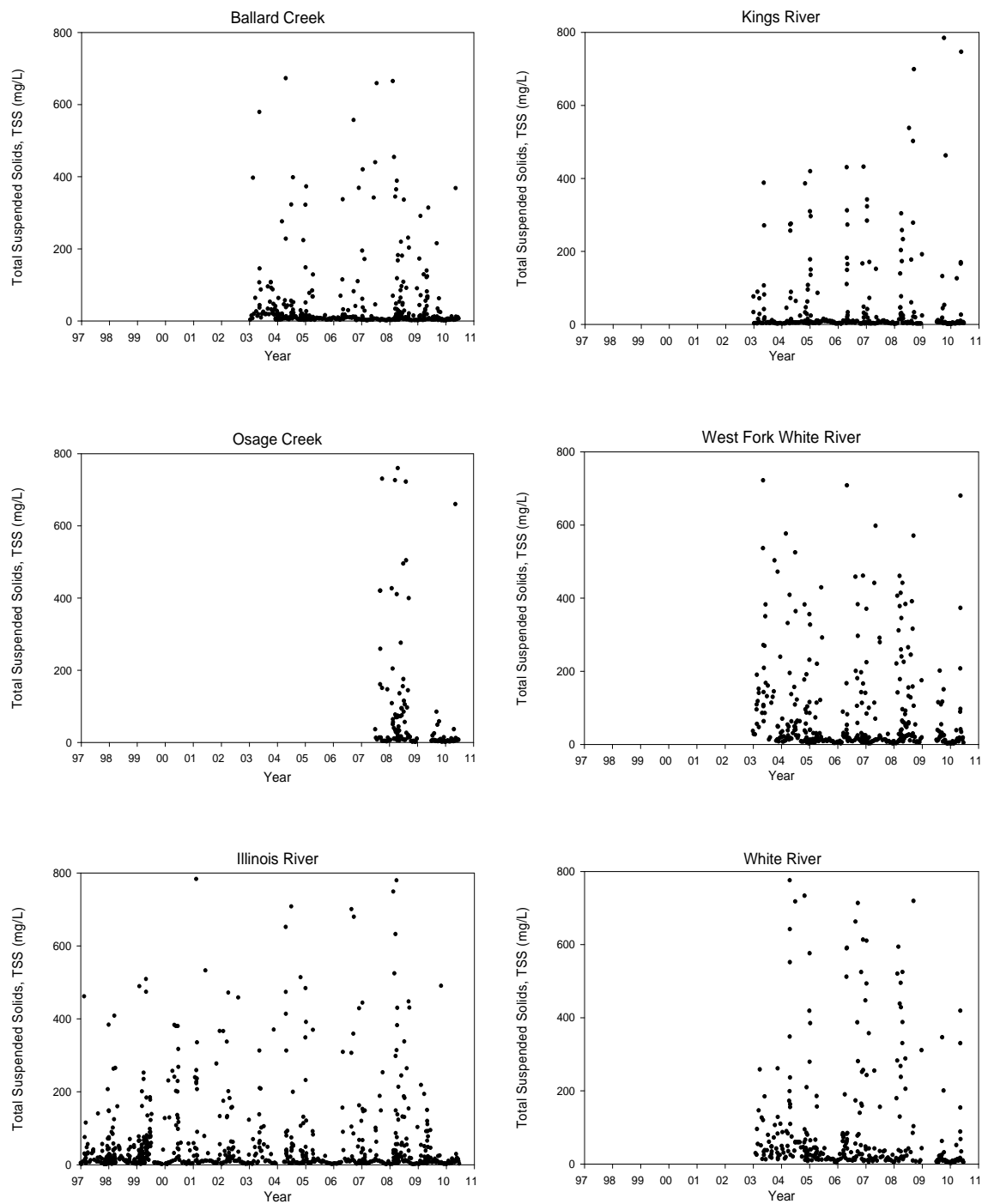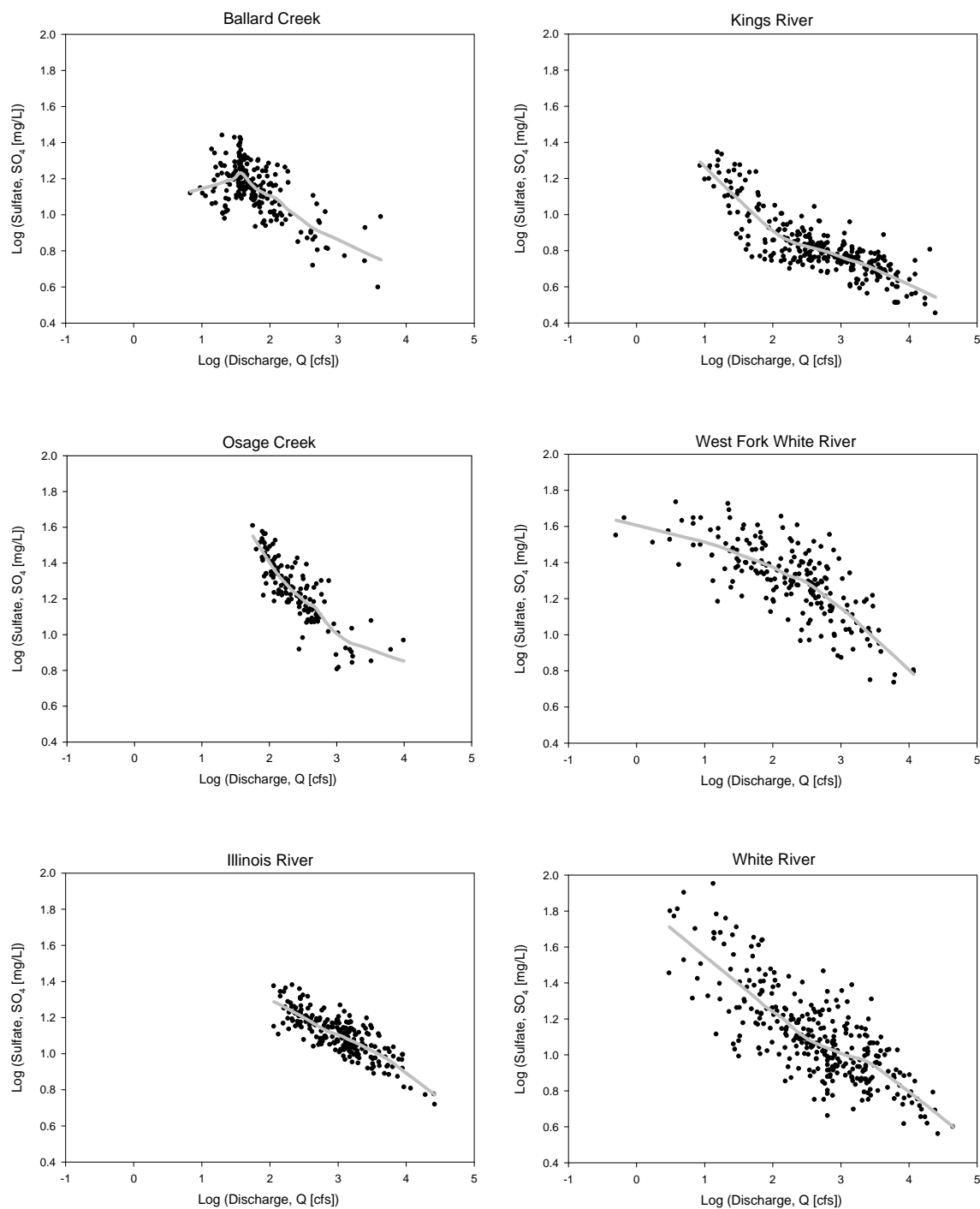

Figure C-1. Sulfate (SO_4) concentrations from water quality samples taken at the six sampled sites from 1997 through 2010. Some outliers were not included on certain graphs to eliminate clumping the lower, more representative data towards the bottom of the graph.
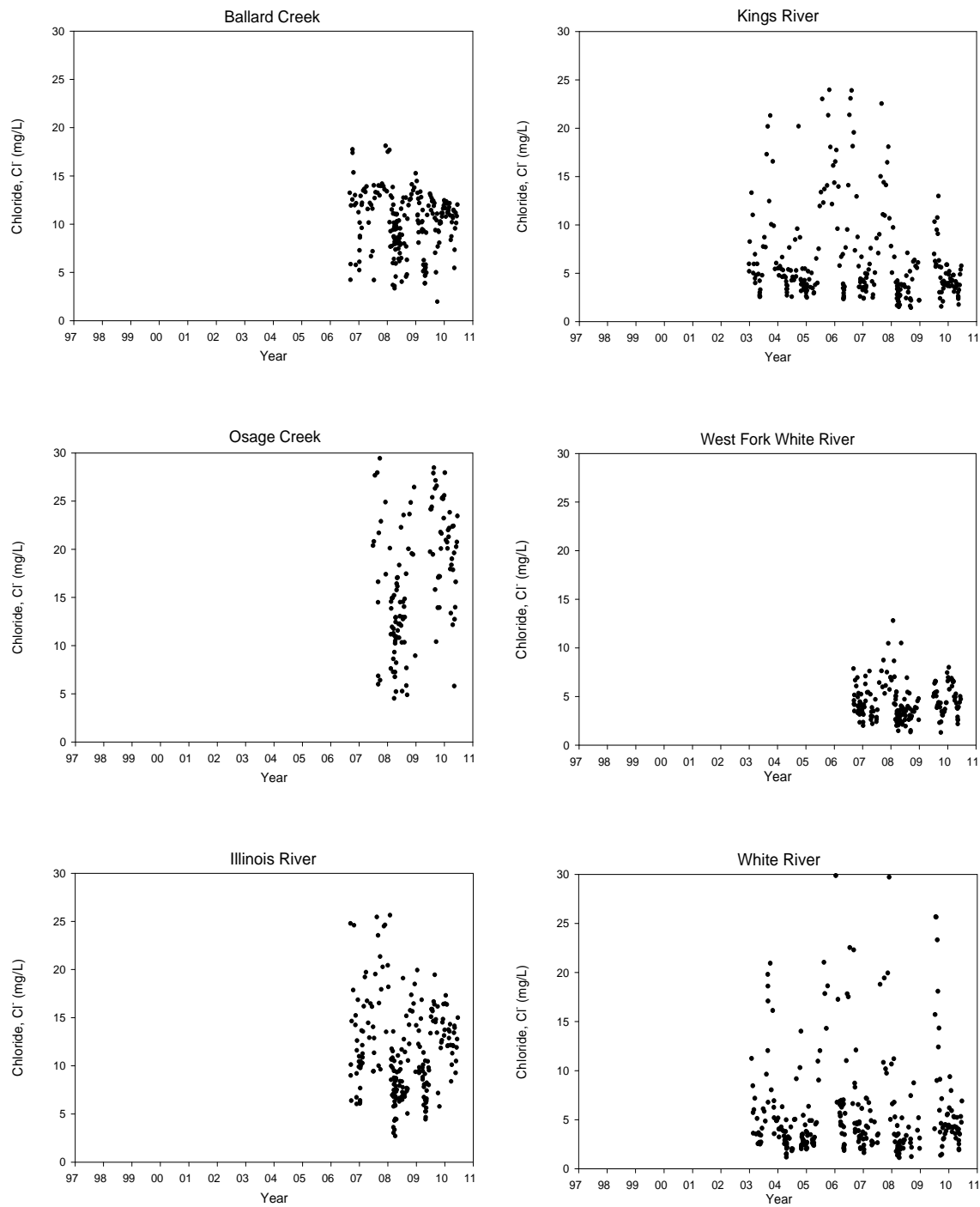
Figure C-2. Chloride (Cl⁻) concentrations from water quality samples taken at the six sampled sites from 1997 through 2010. Some outliers were not included on certain graphs to eliminate clumping the lower, more representative data towards the bottom of the graph.
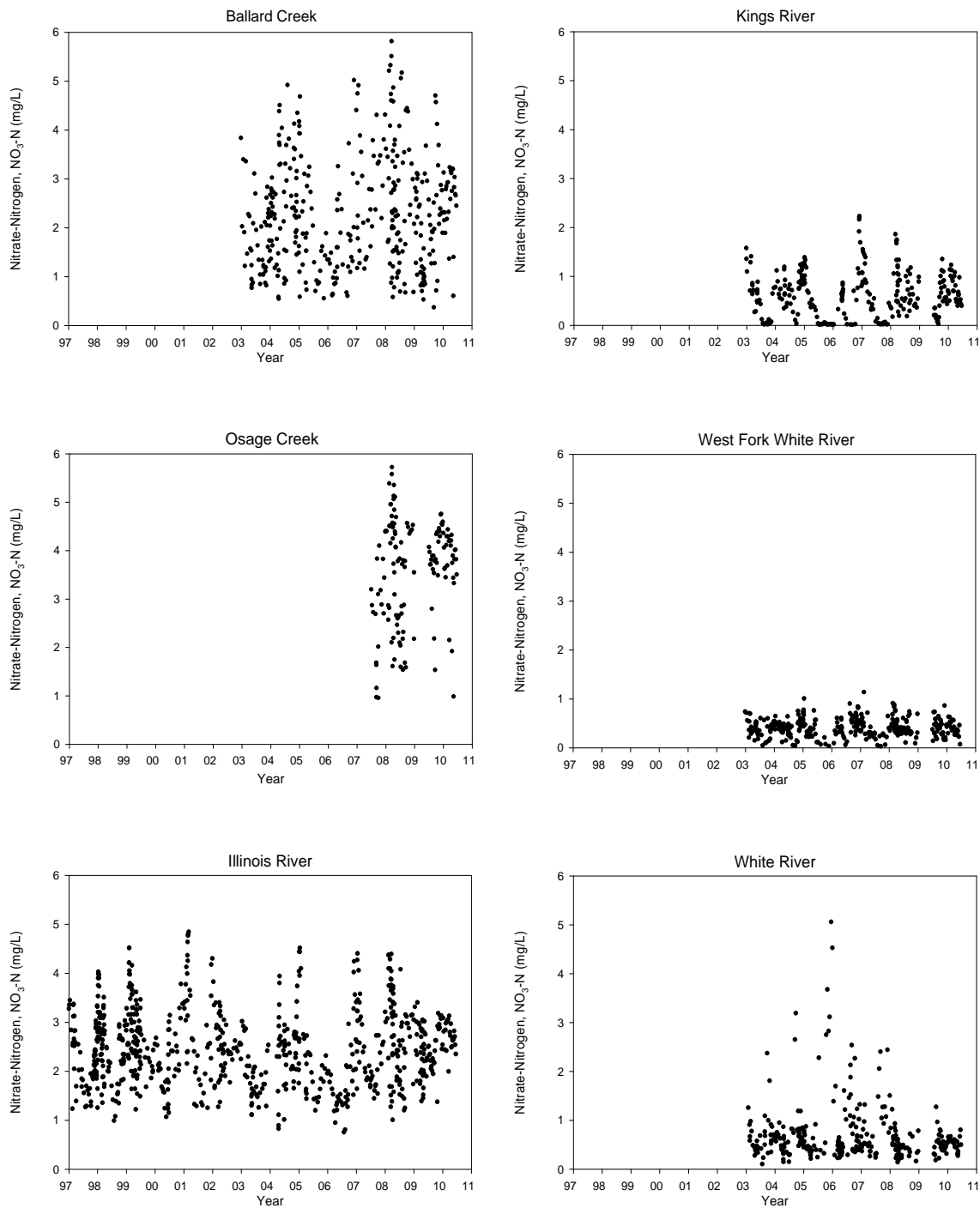
Figure C-3. Nitrate-nitrogen (NO$_3$-N) concentrations from water quality samples taken at the six sampled sites from 1997 through 2010. Some outliers were not included on certain graphs to eliminate clumping the lower, more representative data towards the bottom of the graph.
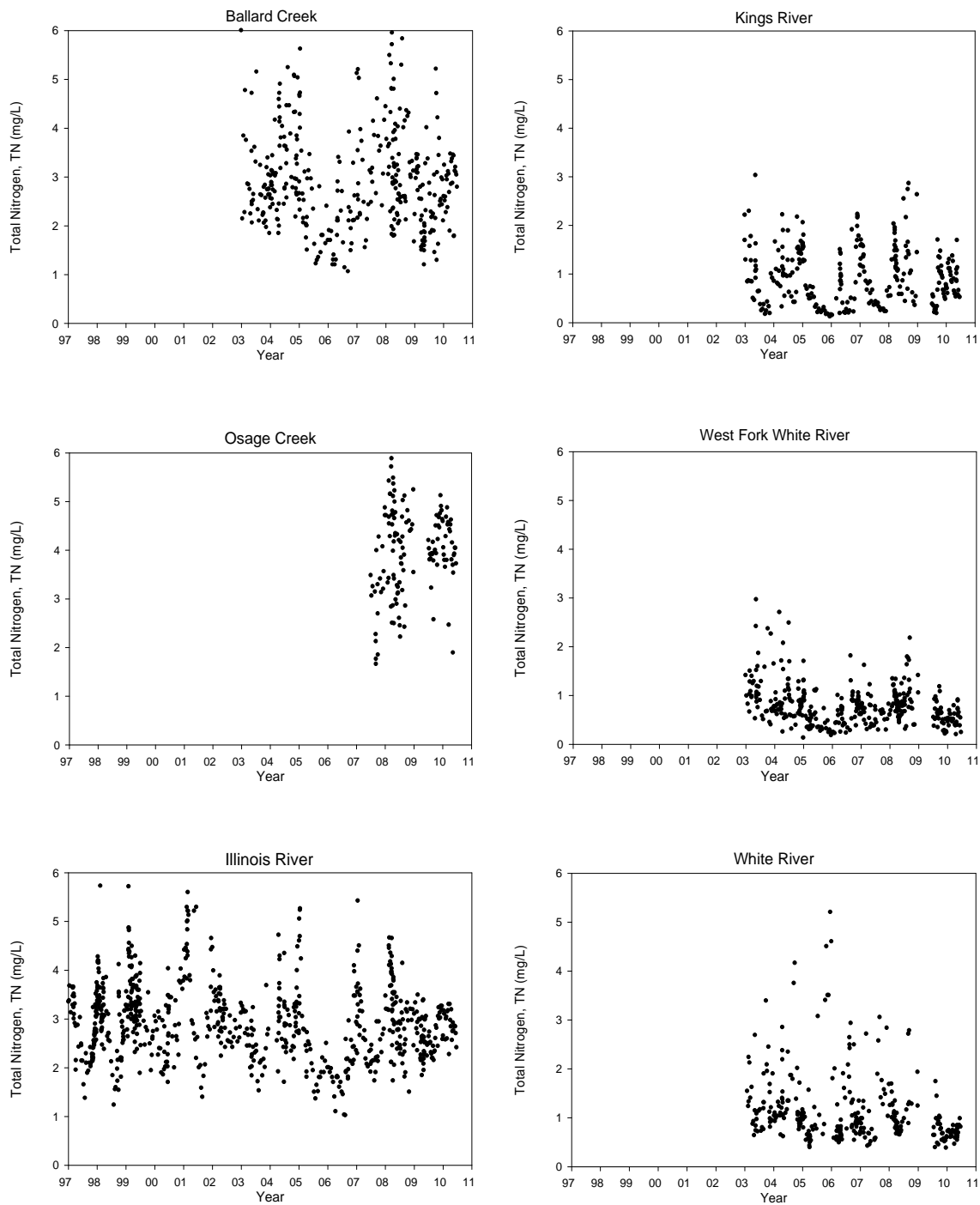
Figure C-4. Total nitrogen (TN) concentrations from water quality samples taken at the six sampled sites from 1997 through 2010. Some outliers were not included on certain graphs to eliminate clumping the lower, more representative data towards the bottom of the graph.
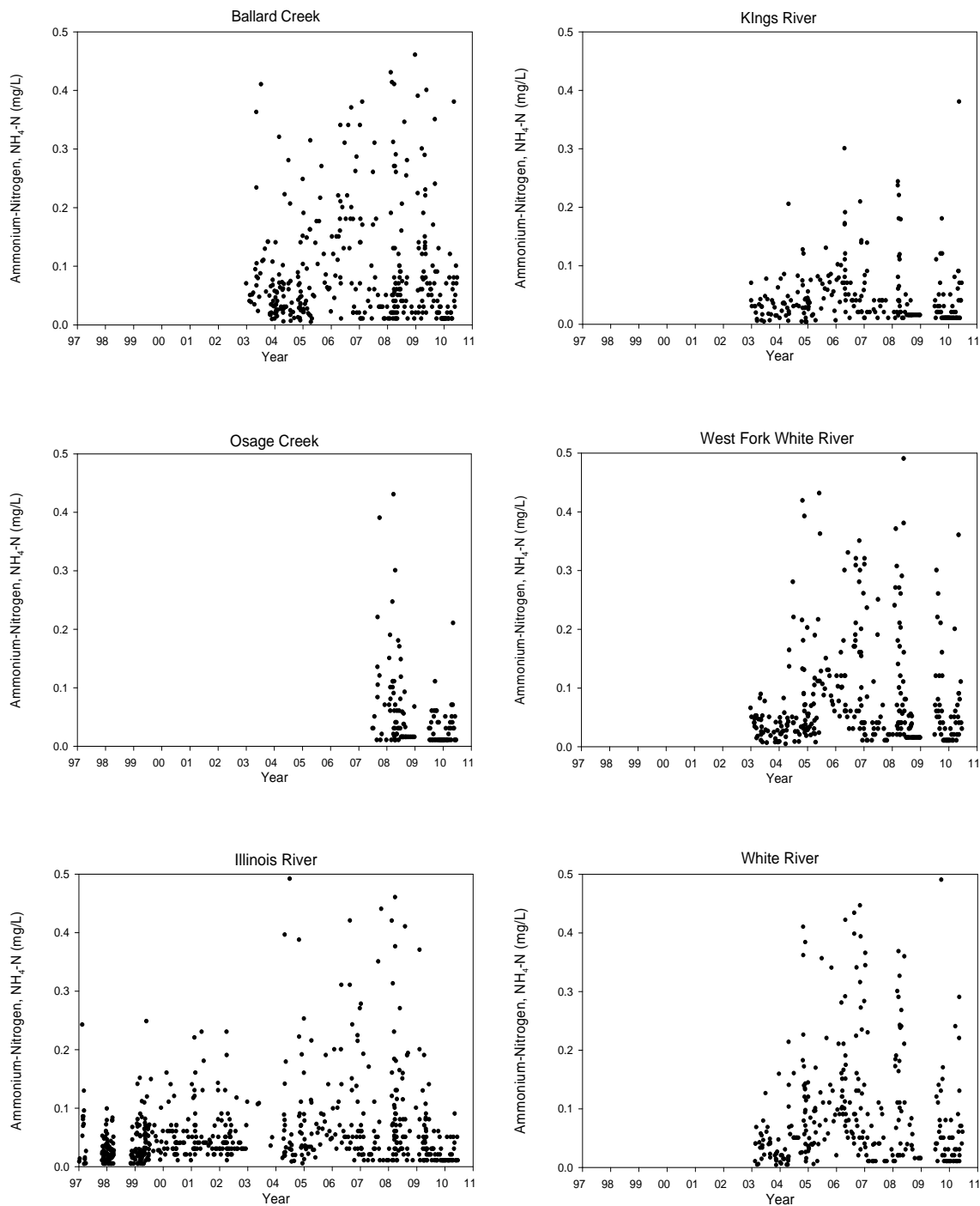
Figure C-5. Ammonium-nitrogen (NH$_4$-N) concentrations from water quality samples taken at the six sampled sites from 1997 through 2010. Some outliers were not included on certain graphs to eliminate clumping the lower, more representative data towards the bottom of the graph.

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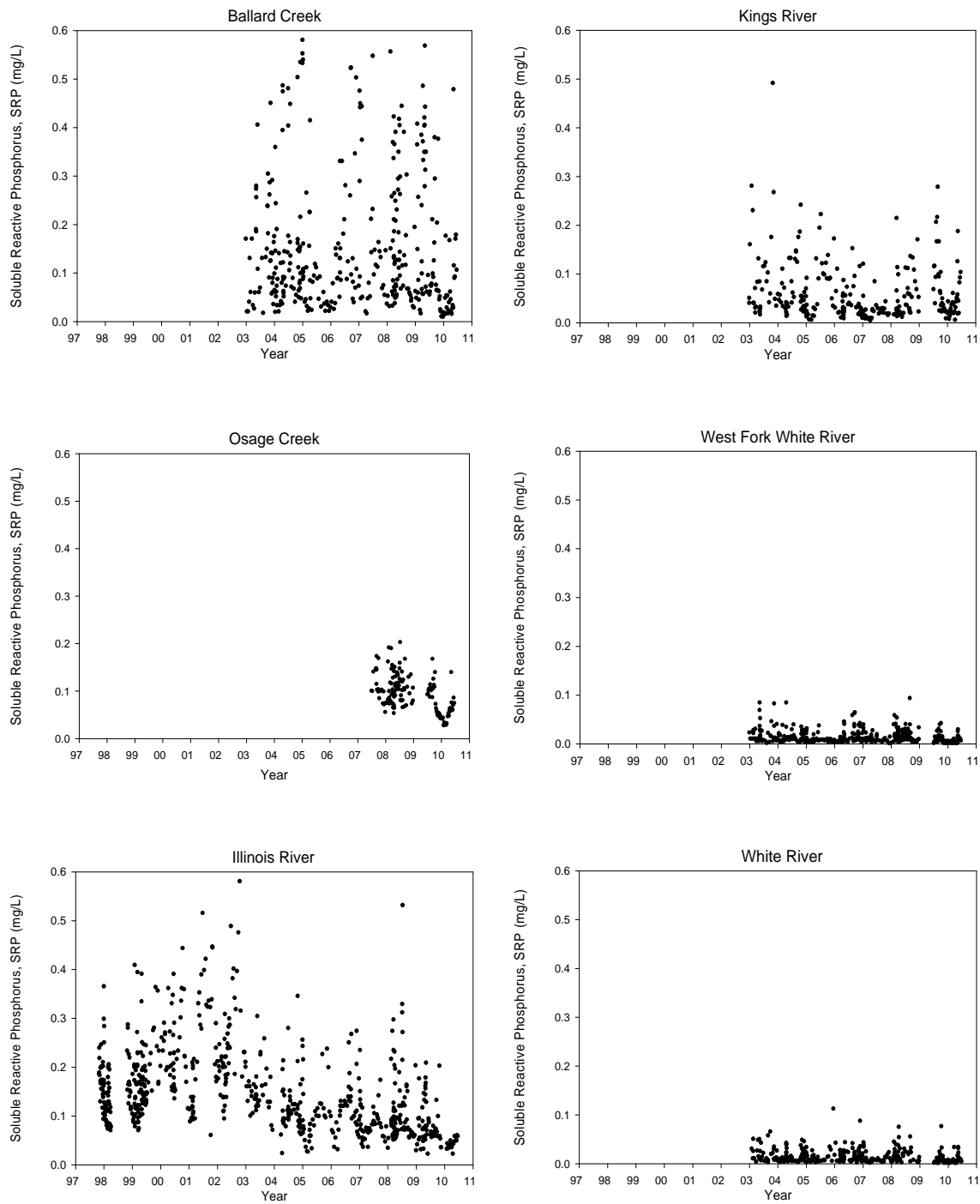
Figure C-6. Soluble reactive phosphorus (SRP) concentrations from water quality samples taken at the six sampled sites from 1997 through 2010. Some outliers were not included on certain graphs to eliminate clumping the lower, more representative data towards the bottom of the graph.

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

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

**APPENDIX D:** Log-Transformed Water Quality Data with LOESS Smoothing

Figure D-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.

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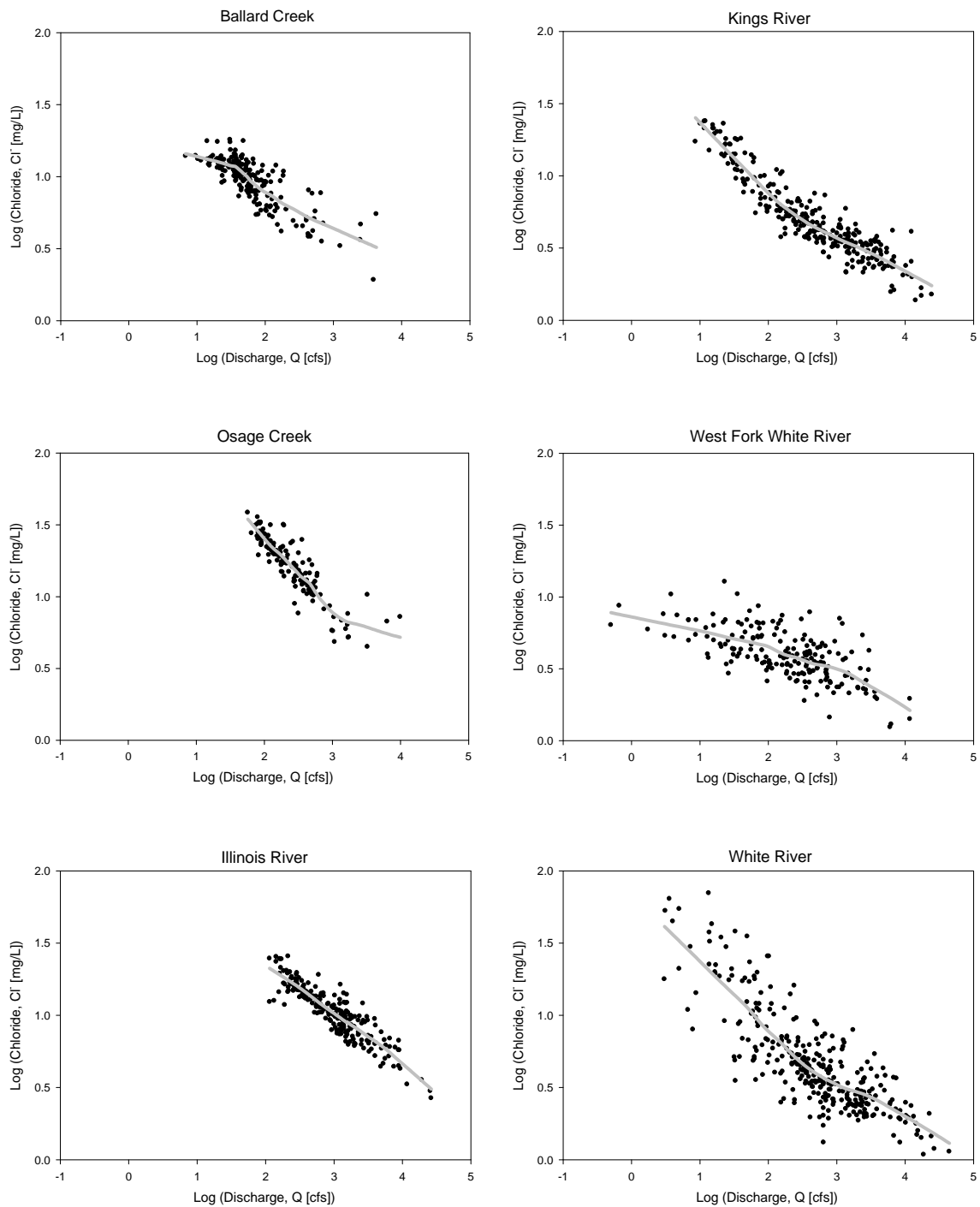
Figure D2. Log-transformed chloride (Cl⁻) concentrations and log-transformed daily discharge with locally weighted regression (LOESS) line; the LOESS smoothing technique shows the relation between concentration and stream flow at each specific sampling site.
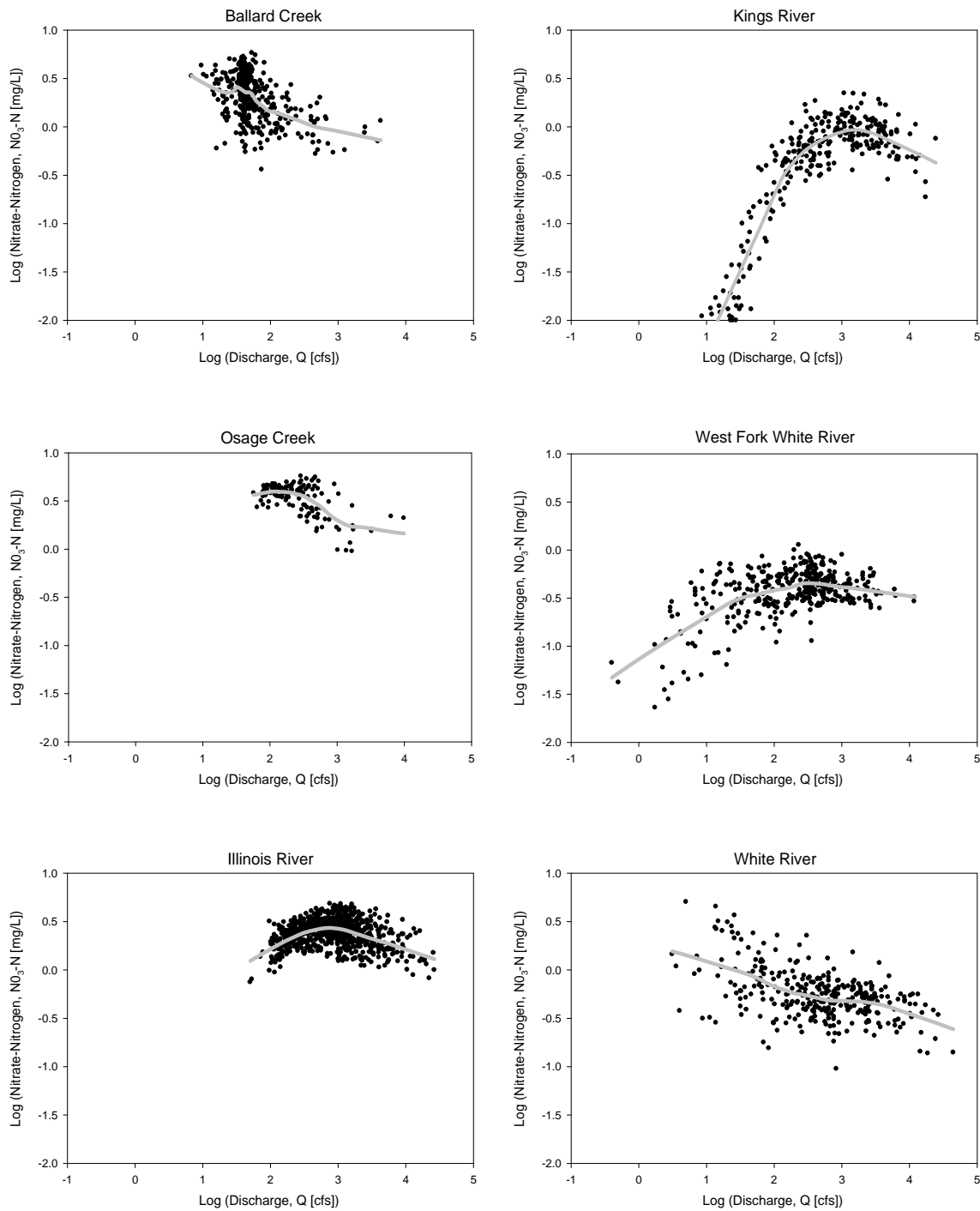
Figure D-3. Log-transformed nitrate-nitrogen (NO$_3$-N) concentrations and log-transformed daily discharge with locally weighted regression (LOESS) line; the LOESS smoothing technique shows the relation between concentration and stream flow at each specific sampling site.
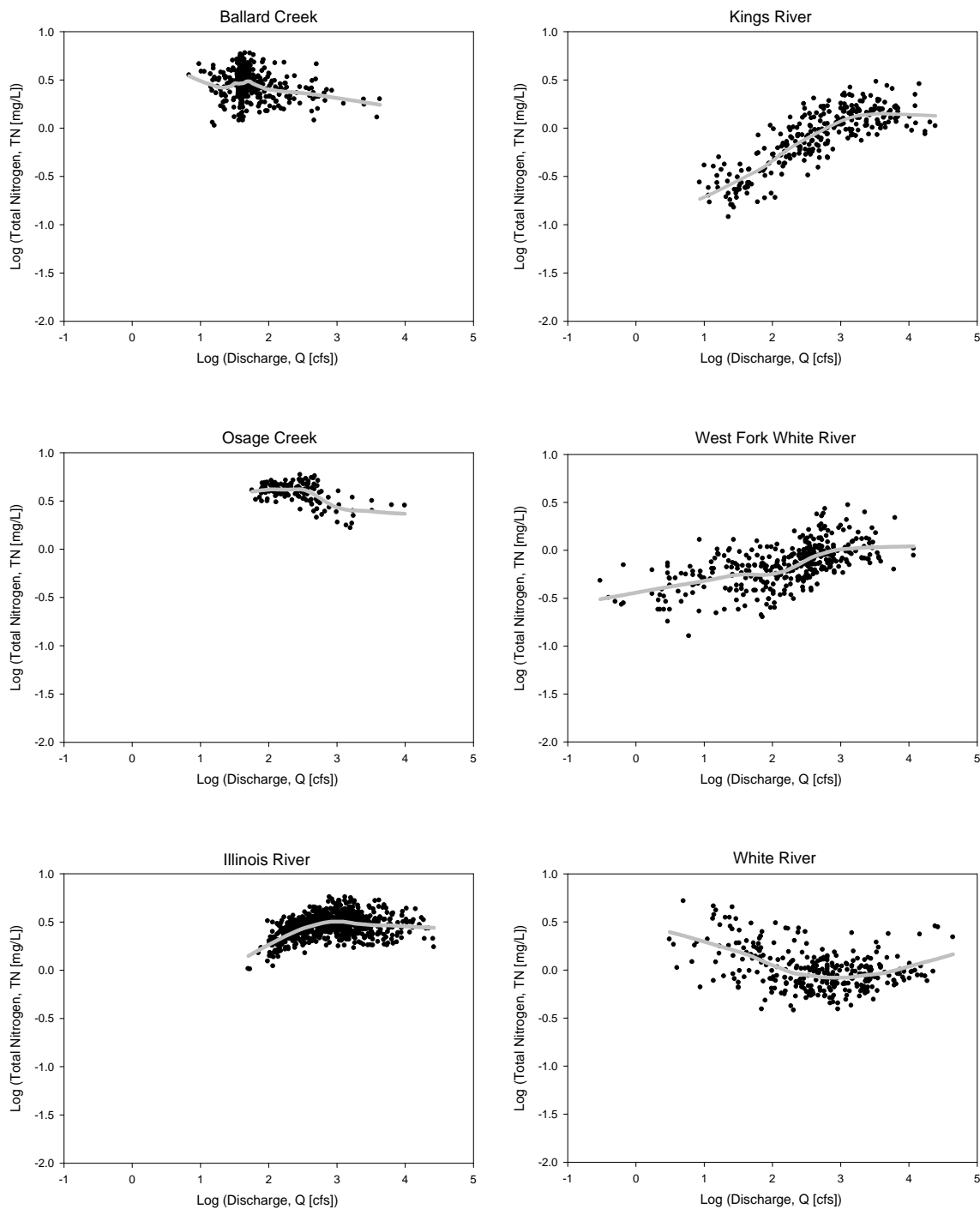
Figure D-4. Log-transformed total nitrogen (TN) concentrations and log-transformed daily discharge with locally weighted regression (LOESS) line; the LOESS smoothing technique shows the relation between concentration and stream flow at each specific sampling site.

Bailey et al., 2011
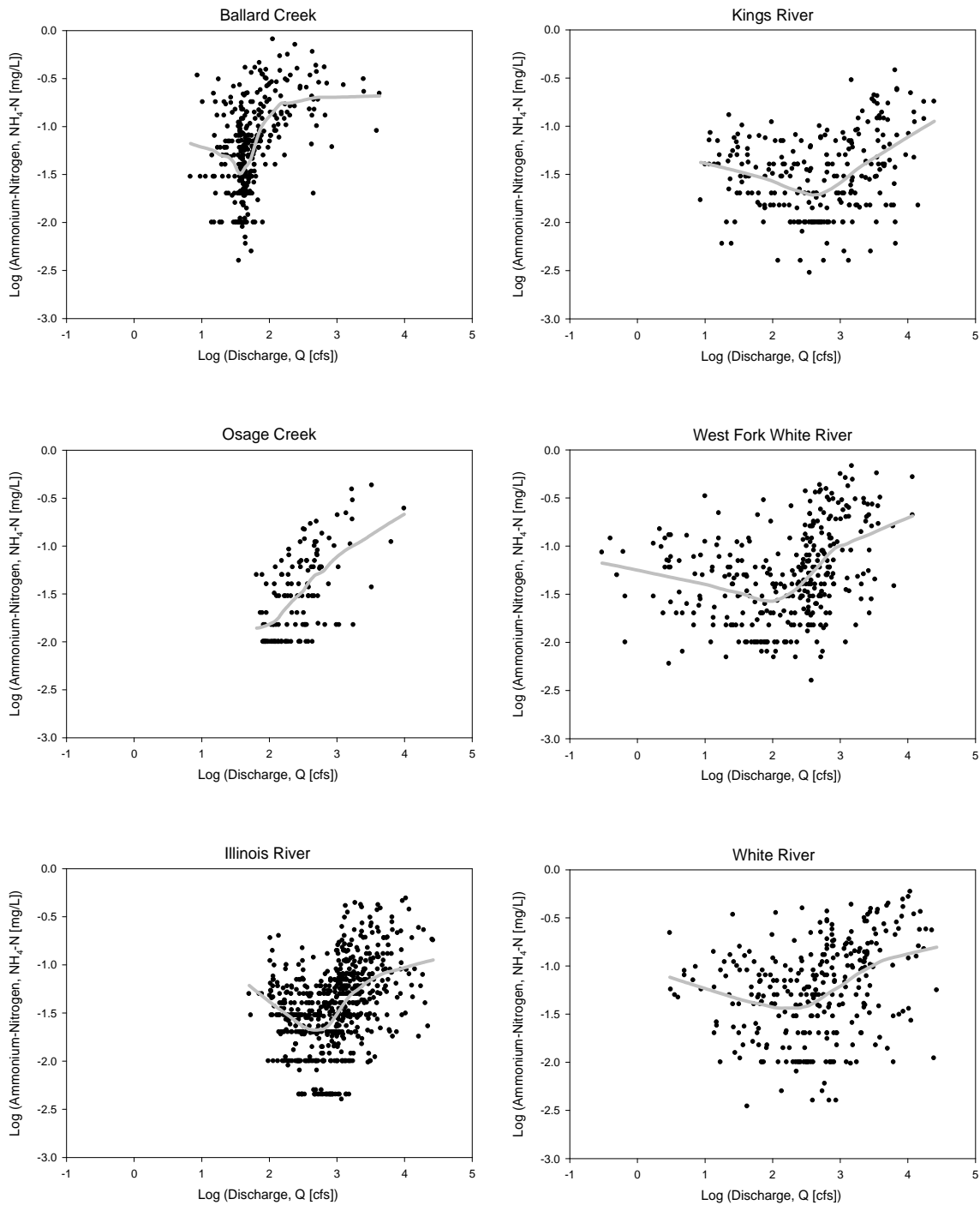
Figure D-5. Log-transformed ammonium-nitrogen (NH$_4$-N) concentrations and log-transformed daily discharge with locally weighted regression (LOESS) line; the LOESS smoothing technique shows the relation between concentration and stream flow at each specific sampling site.
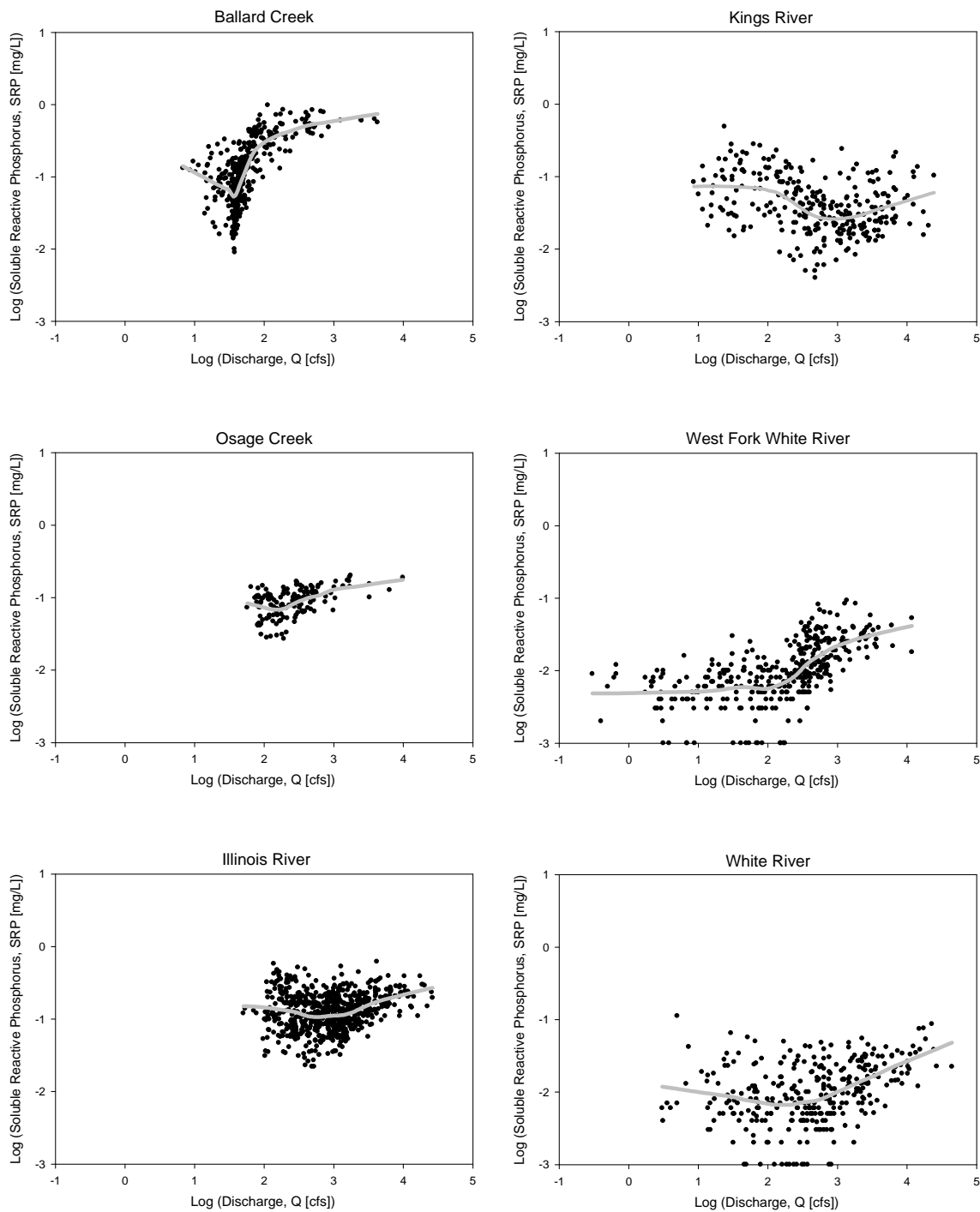
Figure D-6. Log-transformed soluble reactive phosphorus (SRP) concentrations and log-transformed daily discharge with locally weighted regression (LOESS) line; the LOESS smoothing technique shows the relation concentration and stream flow at each specific sampling site.
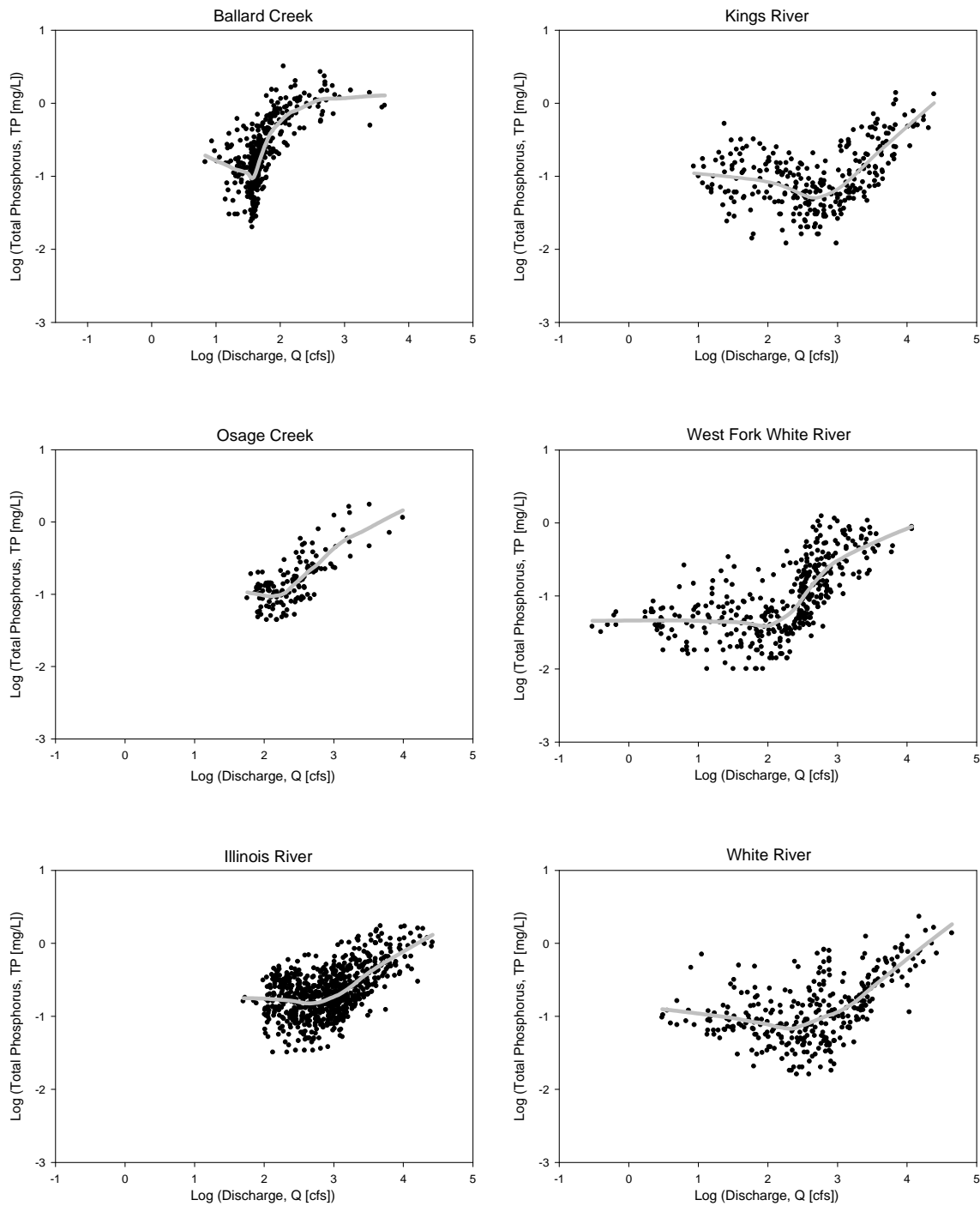
Figure D-7. Log-transformed total phosphorus (TP) concentrations and log-transformed daily discharge with locally weighted regression (LOESS) line; the LOESS smoothing technique shows the relation between concentration and stream flow at each specific sampling site.
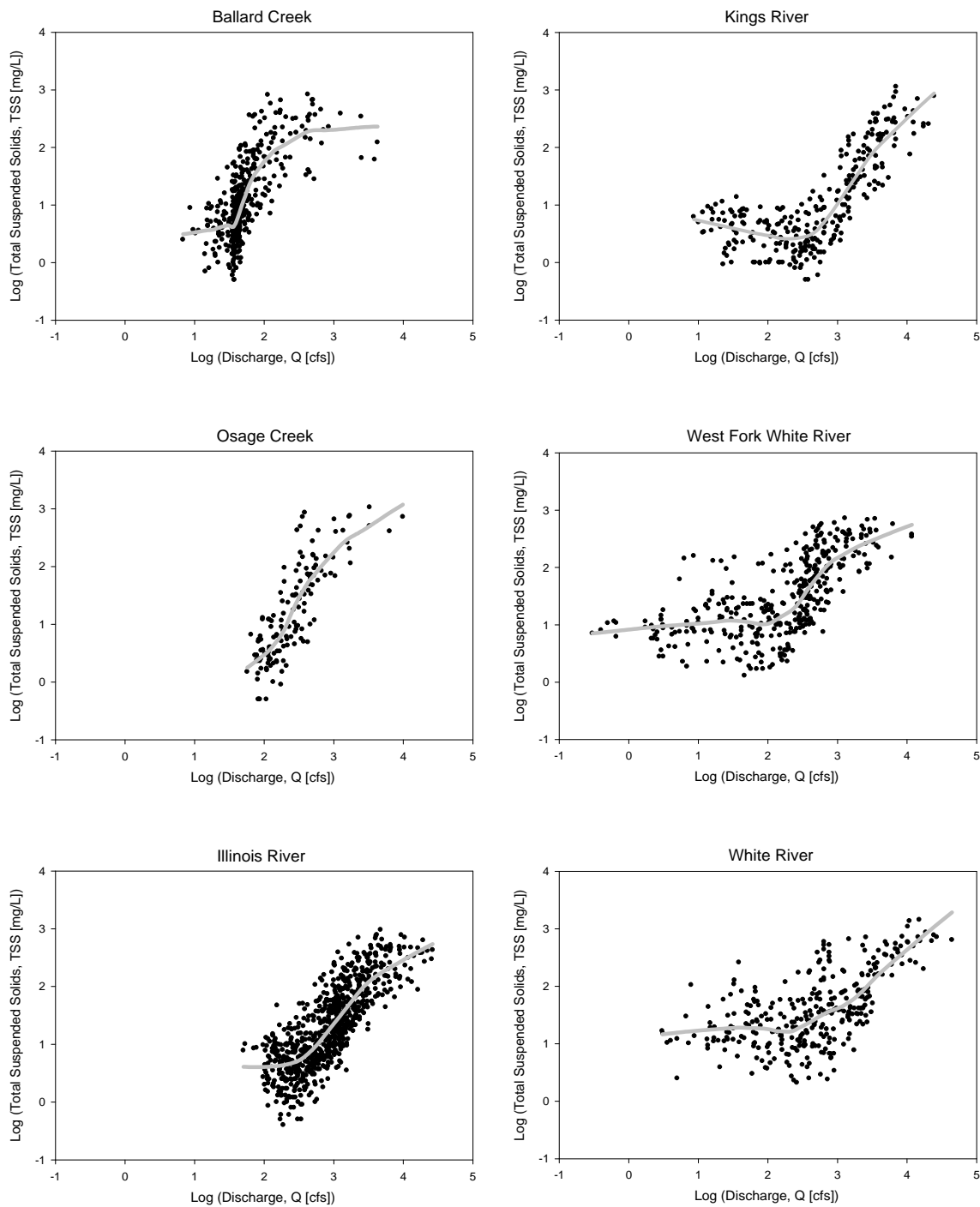
Figure D-8. Log-transformed total suspended solids (TSS) concentrations and log-transformed daily discharge with locally weighted regression (LOESS) line; the LOESS smoothing technique shows the relation between concentration and stream flow at each specific sampling site.

Appendix E: Flow-Adjusted Concentrations (FACs) as a Function of Time
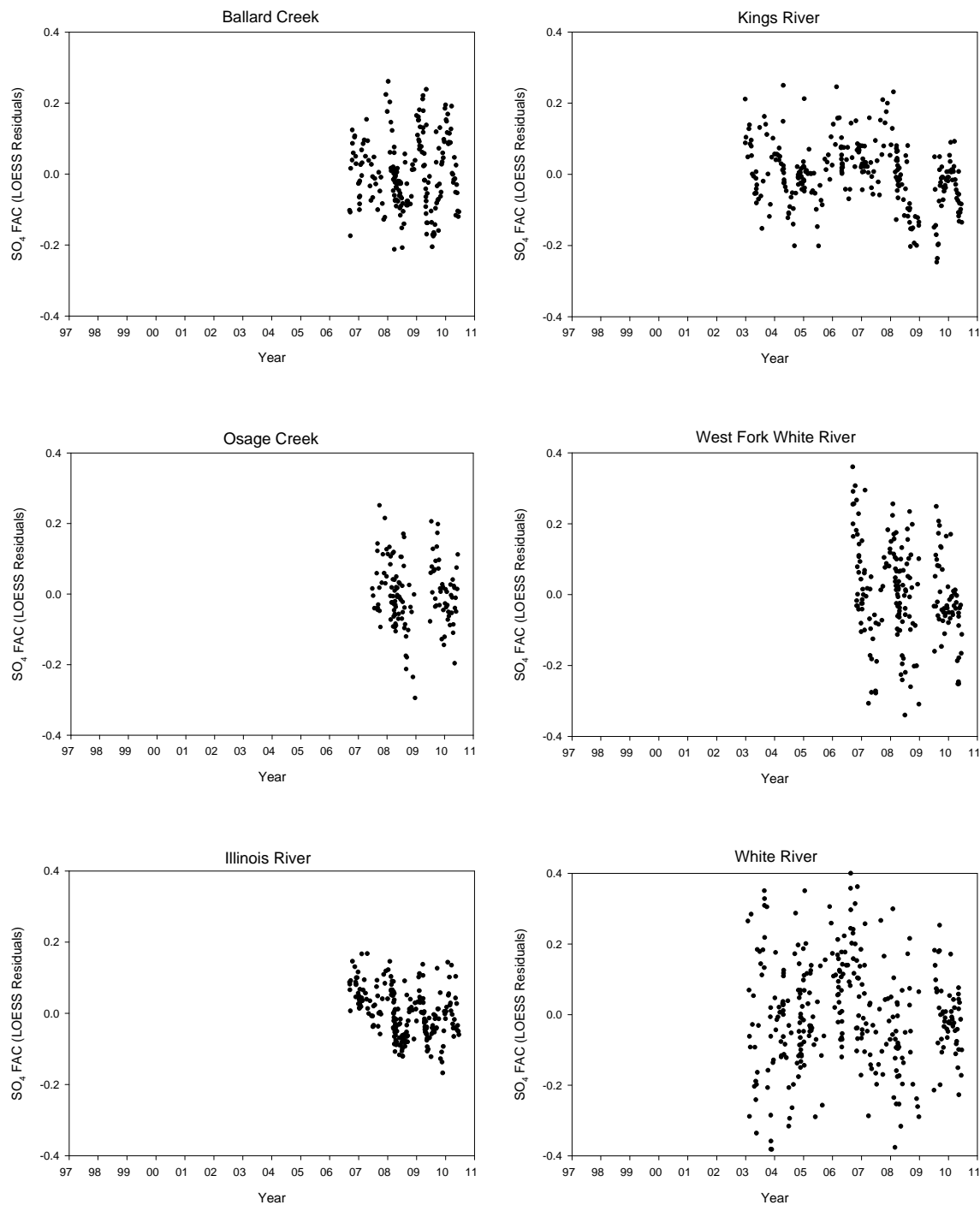
Figure E-1. Sulfate (SO$_4$): The flow-adjusted concentrations (FACs) as a function of time from 1997 through 2010; FACs are the residuals from LOESS smoothing of log-transformed concentrations and daily discharge as a function of time.
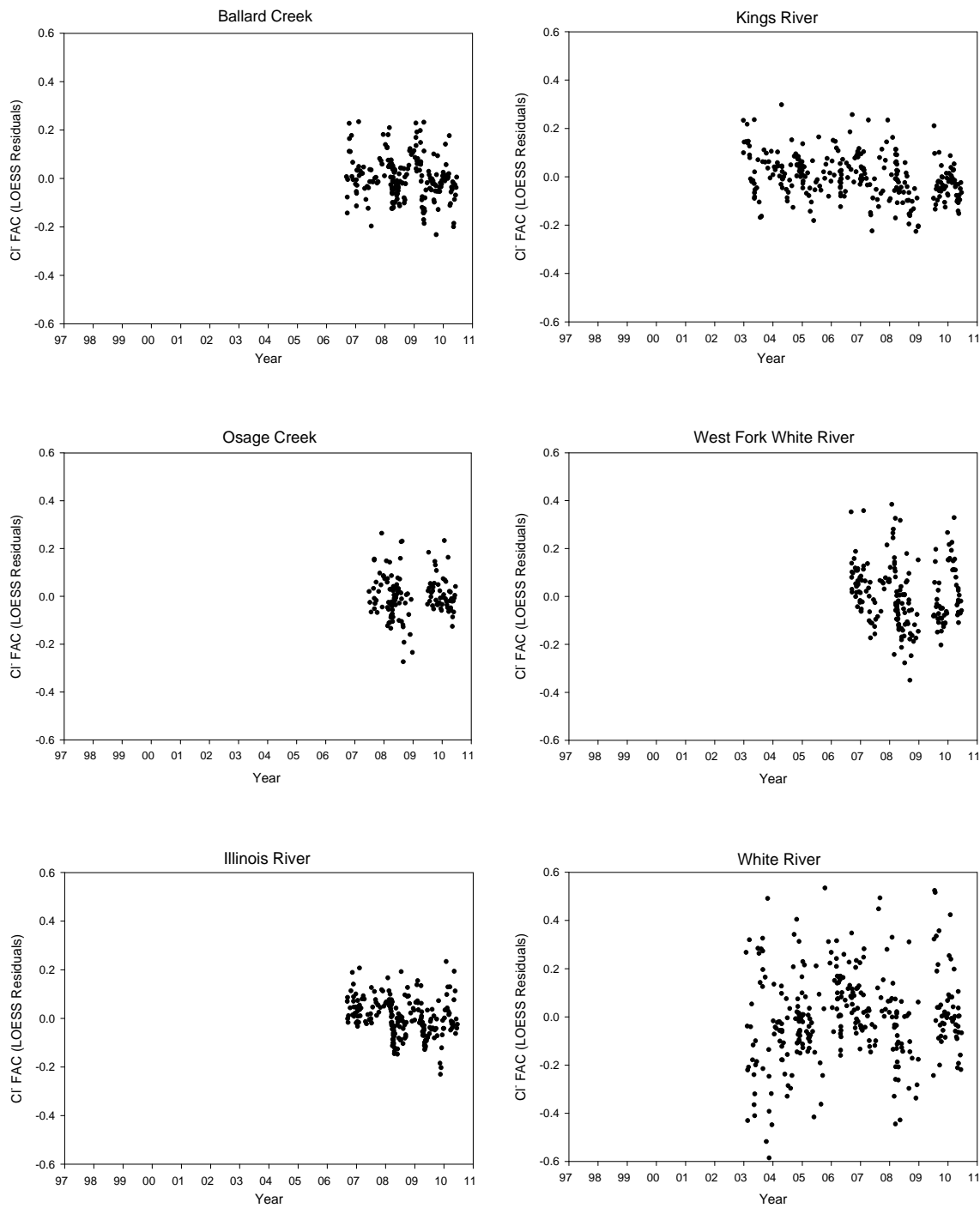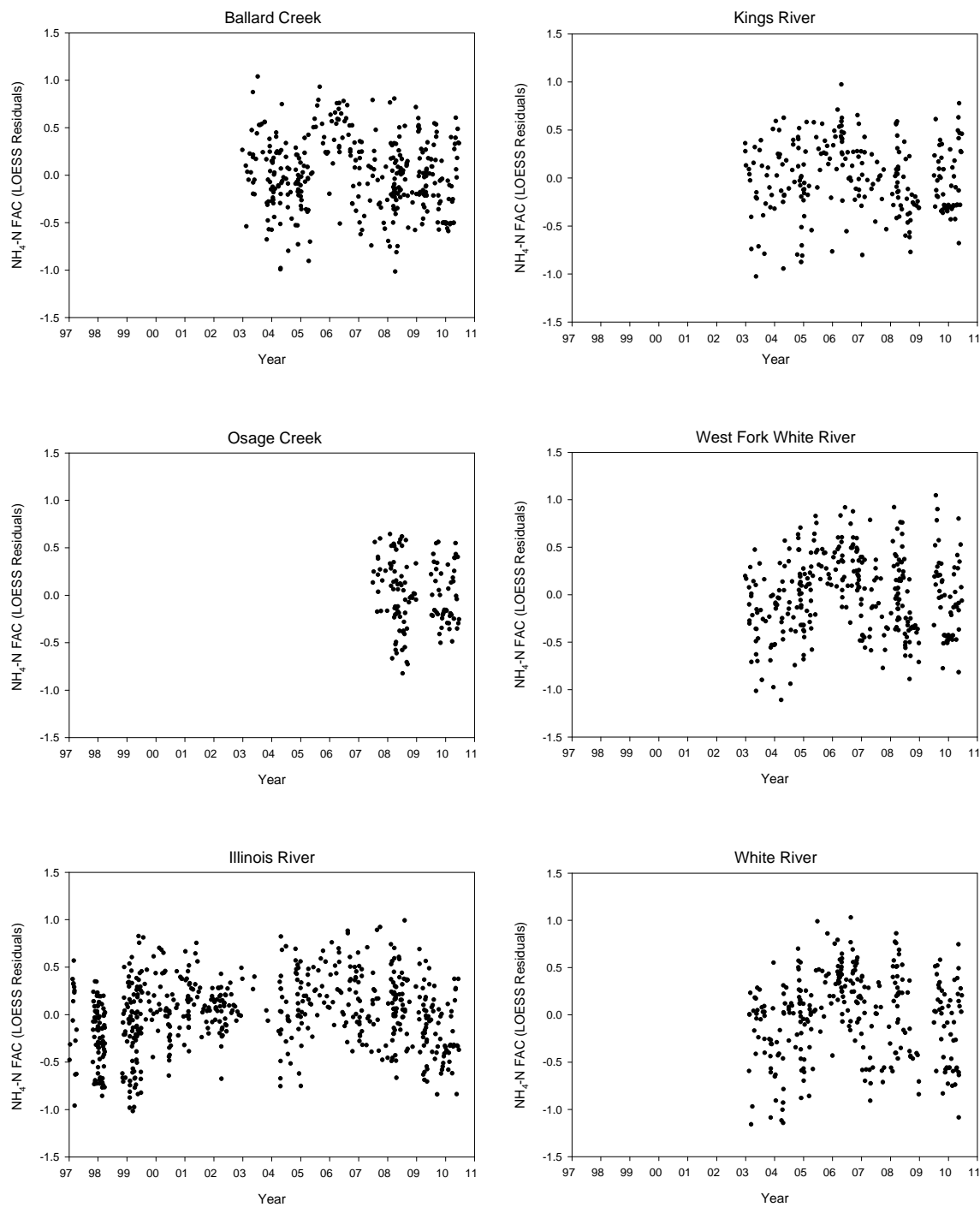
Figure E-2. Chloride (Cl⁻): The flow-adjusted concentrations (FACs) as a function of time from 1997 through 2010; FACs are the residuals from LOESS smoothing of log-transformed concentrations and daily discharge as a function of time.
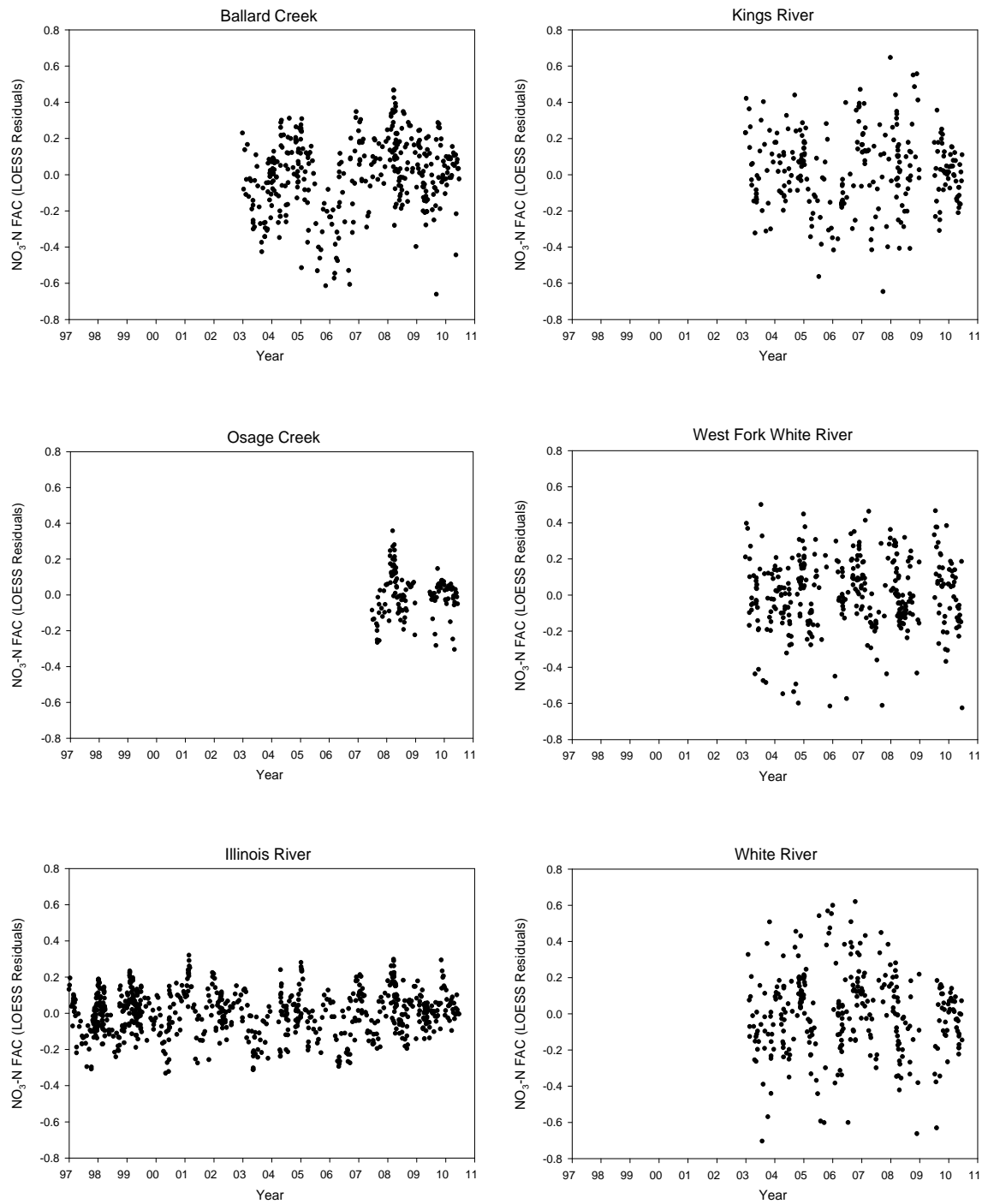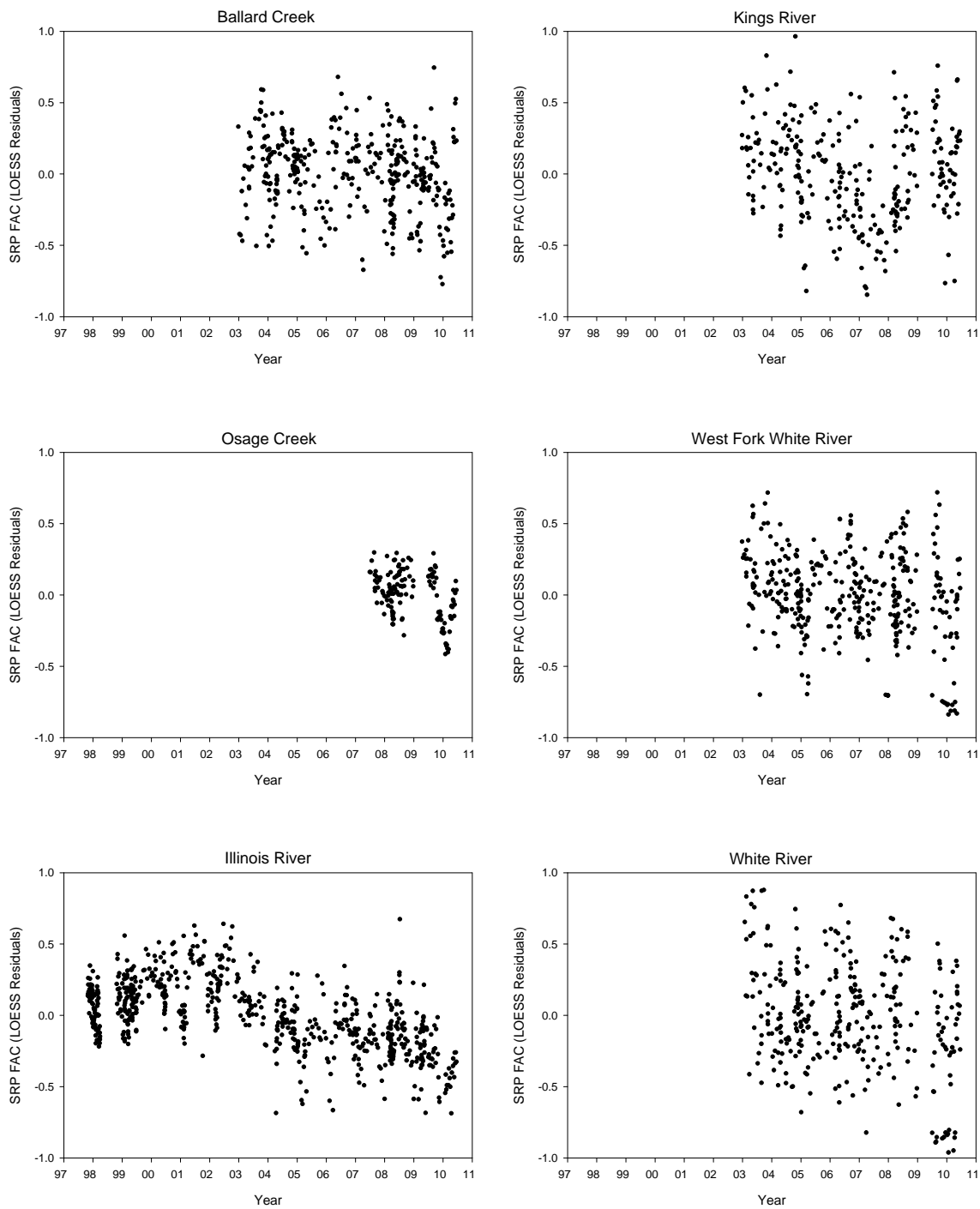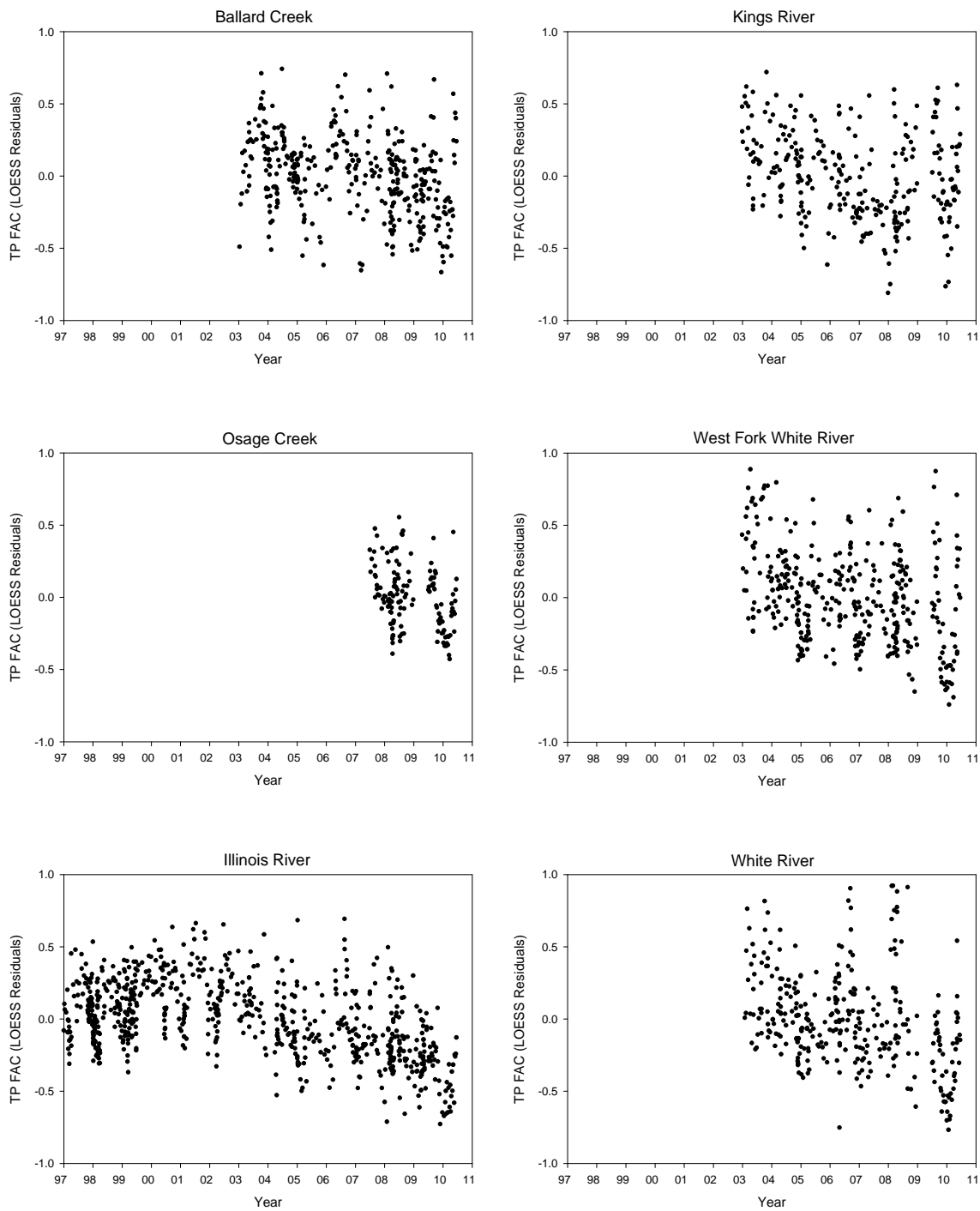
Figure E-3. Nitrate-nitrogen (NO$_3$-N): The flow-adjusted concentrations (FACs) as a function of time from 1997 through 2010; FACs are the residuals from LOESS smoothing of log-transformed concentrations and daily discharge as a function of time.
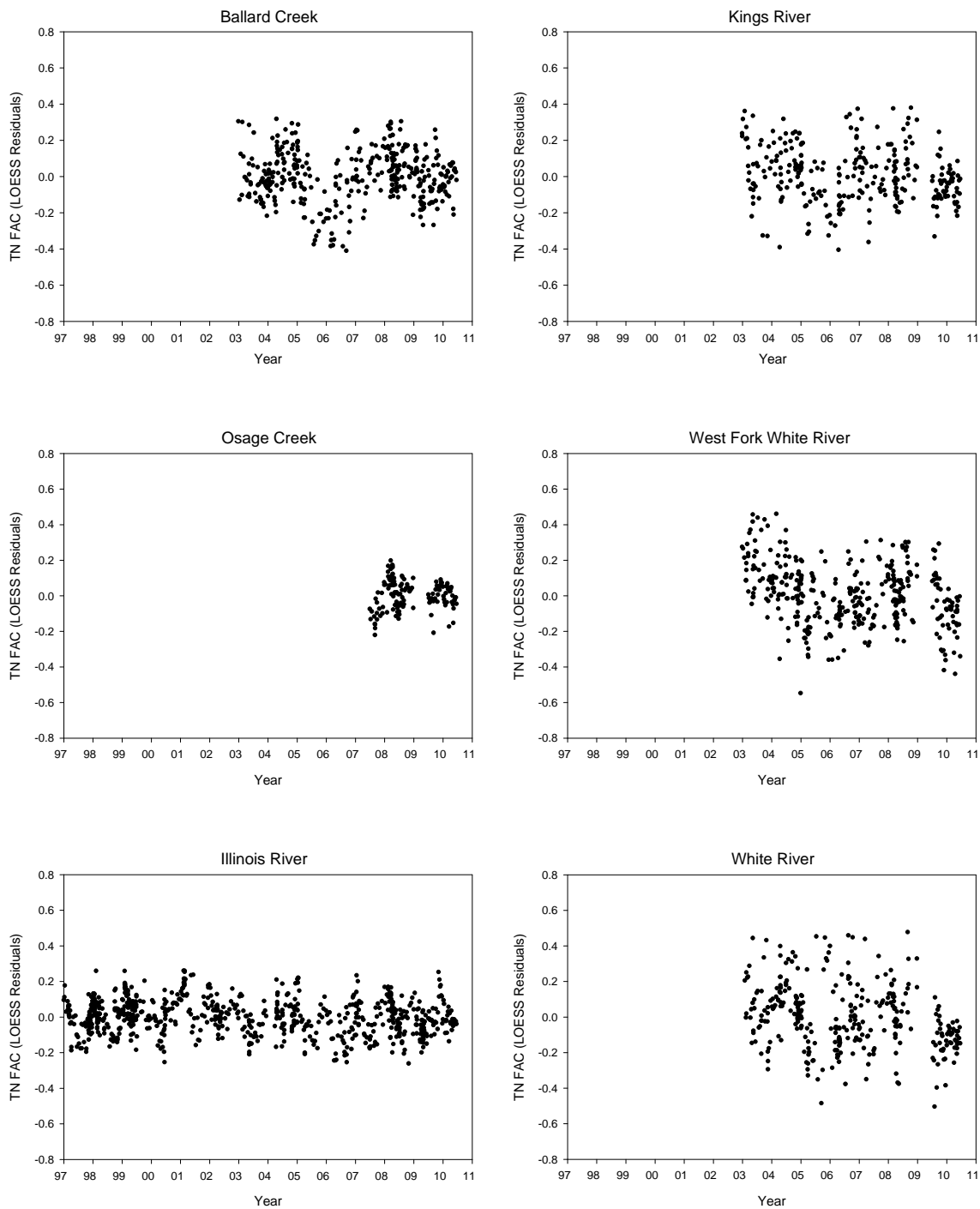
Figure E-4. Total nitrogen (TN): The flow-adjusted concentrations (FACs) as a function of time from 1997 through 2010; FACs are the residuals from LOESS smoothing of log-transformed concentrations and daily discharge as a function of time.

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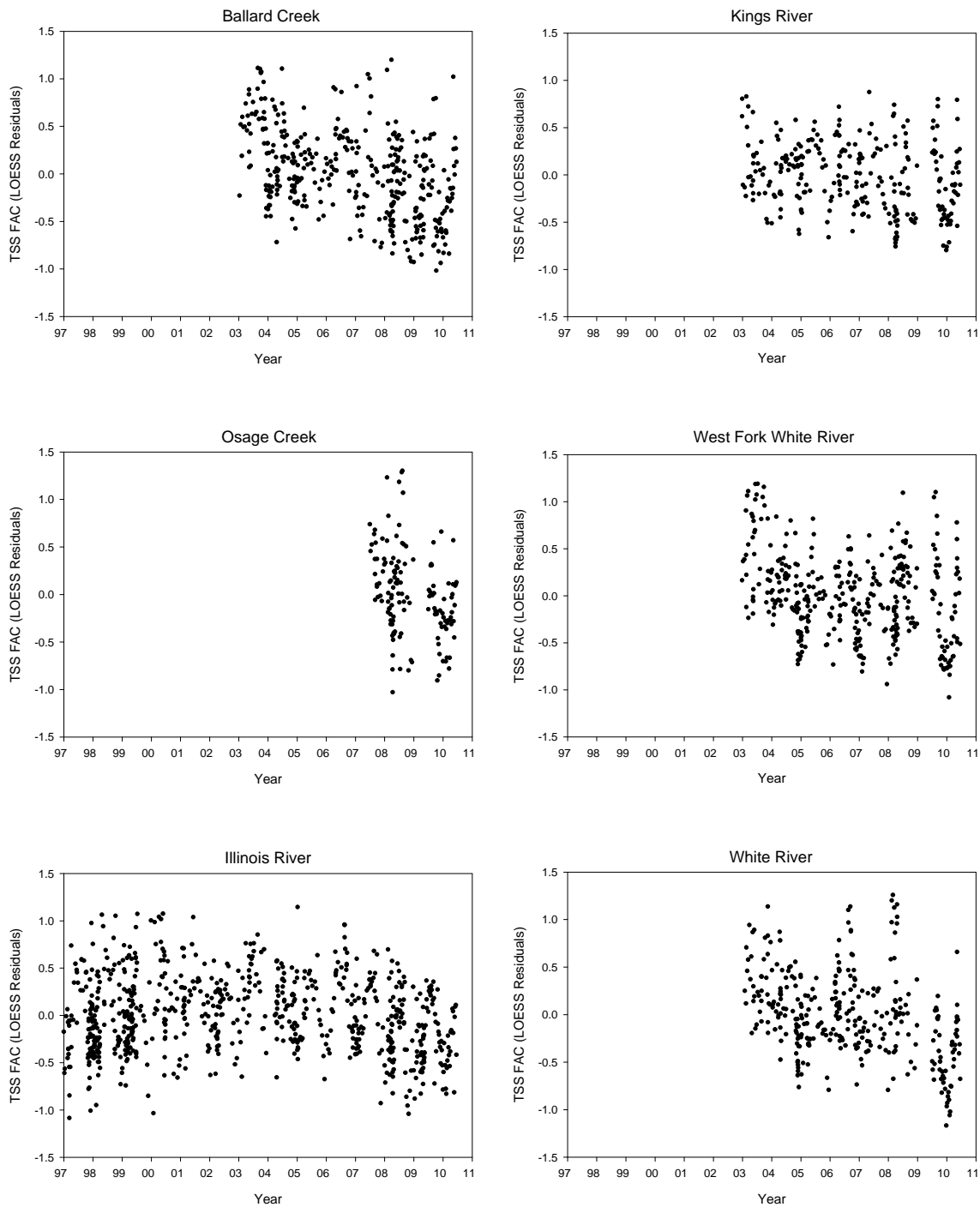
Figure E-6. Soluble reactive phosphorus (SRP): The flow-adjusted concentrations (FACs) as a function of time from 1997 through 2010; FACs are the residuals from LOESS smoothing of log-transformed concentrations and daily discharge as a function of time.

Figure E-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 E-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.