WATER QUALITY AT THE BUFFALO NATIONAL RIVER, ARKANSAS, 1991−2001

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ABSTRACT. *The Buffalo National River (BNR) is a relatively unpolluted, free−flowing river with riffle−pool geomorphology, located in north−central Arkansas. The specific objectives of this study were to: (1) evaluate differences between physicochemical properties and concentrations in water quality samples representing base flow and surface runoff conditions, (2) determine trends in physicochemical properties and concentrations using three datasets (all data, data representing base flow conditions, and data representing surface runoff conditions), and (3) compare flow−weighted constituent concentrations and yields at the BNR to relatively undisturbed catchments and a relatively developed catchment. Water quality trends were evaluated (α = 0.1) using constituent data from 1991 through 2001 and using subsets of these data representing water quality samples collected during either base flow or surface runoff conditions. Trends were assessed by (1) appropriately transforming water quality data and daily discharge, (2) flow−weighting water quality data using a smoothing technique, and (3) evaluating residuals from smoothing versus time for trends. Trend analyses suggested that only nitrogen, sediment, and E. coli concentrations increased from 1991 through 2001 in the BNR, particularly during surface runoff conditions. Most temporal changes in constituents occurred during surface runoff conditions, and these changes were not necessarily reflected during base flow conditions. Flow−weighted nutrient concentrations and yields were greater at the BNR compared to median values for relatively undeveloped basins across the U.S. Nutrient concentrations and yields at the BNR were only slightly greater than or equal to the values representing the 75th percentile of reference streams. However, nutrient concentrations and yields at the BNR were less than at relatively developed basins within the same ecoregion. By evaluating base flow and surface runoff water quality samples separately for trends, we gained additional insight into the particular flow conditions exhibiting significant trends. Identification of flow conditions associated with trends aids in determining constituent sources and hence appropriate constituent abatement.*

Keywords. *Nutrient concentrations, Nutrient yields, Stream flow, Water quality.*

The first National River in the U.S. was the Buffalo River in the Ozark Plateaus of north−central Arkansas. The Buffalo National River (BNR) is a relatively unpolluted, free−flowing river with swift−running and placid stretches. These characteristics have made the BNR unique among rivers in the U.S. today, and therefore, the BNR is often the focus of scientific investigations (National Park Service, 2002). Several studies at the BNR have assessed: geology; sediment and nutrient transport; stream morphology; land use, cover, and changes; and ecosystem processes (e.g., Petersen et al., 2002; Jaster, 1997; Hofer, 1995; Scott and Smith, 1994; Petersen, 1992; Springer, 1977).

In particular, water quality trends at the BNR have been assessed by evaluating temporal changes in nutrient, oxygen, or sediment concentrations. Petersen (1992) indicated that from 1975 to 1986 dissolved oxygen, biological oxygen demand, and dissolved sulfate concentrations increased at the BNR, whereas fecal coliforms, dissolved chloride, and total suspended solids concentrations decreased. Other physicochemical properties and concentrations showed no significant changes at the BNR during this period (Petersen, 1992).

A growing concern at the BNR is increasing agricultural land use and its potential impact on nutrient and sediment concentrations (Scott and Smith, 1994). As reported in Scott and Smith (1994), only 44% of the Buffalo River drainage area is managed by the National Park Service, the U.S. Forest Service, or the State of Arkansas; the remaining portion is characterized by increased development of agricultural farms. Scott and Smith (1994) analyzed land use data from 1965 to 1979 and described agricultural land use increasing from 14% to 20% of all land use. Land use and management practice changes potentially impact water quality, primarily by increasing the potential for nonpoint−source pollution during episodic runoff events. For example, other Ozark streams have shown an increase in nutrient concentrations with increasing proportions of pasture and agricultural land use in their catchment (Haggard et al., 2003a). Understanding the connection between land use, land management, and water quality changes will allow appropriate management strategies to be developed to protect the unique condition of the BNR.

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Historically, studies (Peterson, 1992; Lettenmaier et al., 1991; Walker, 1991; Cavanaugh and Mitsch, 1989) have examined water quality trends as a function of stream flow using flow−weighted or normalized constituent concentrations. Evaluating water quality trends using water samples representing specific flow regimes, i.e., base flow and surface runoff conditions, may provide an insight into constituent sources, transport, and potential impact at the BNR. In this study, we expected to find significant differences between physicochemical properties and concentrations between specific flow regimes as well as differences between temporal changes in these flow regimes. The specific objectives of this study were to: (1) present summary statistics and evaluate differences between physicochemical properties and concentrations in water quality samples representing base flow or surface runoff conditions, (2) determine trends in physicochemical properties and concentrations using three datasets (all data, data representing base flow conditions, and data representing surface runoff conditions), and (3) compare flow−weighted constituent concentrations and yields at the BNR to relatively undisturbed catchments across the U.S. and a developed catchment in the Ozarks.

SITE DESCRIPTION

The BNR headwaters begin in Newton County, Arkansas, and continue west approximately 246 km through Newton, Searcy, Marion, and Baxter Counties. The two dominant soil associations in the watershed are the Enders−Nella−Mountainburg−Steprock (42.3%) and the Clarksville−Nixa−Noark (34%). Enders−Nella−Mountainburg−Steprock is primarily in the Boston Mountain physiographic area, and Clarksville−Nixa−Noark is in the Springfield Plateau physiographic area (Scott and Smith, 1994). Along with the Boston Mountain and Springfield Plateau physiographic provinces, the Salem Plateau physiographic province is also found in portions of the BNR (Scott and Smith, 1994). BNR surface geology is characterized by the Boone formation, resulting in limestone bluffs.

Riverside bluffs along the stream contribute to its steep slopes and hence flashy nature during runoff events (Panfil and Jacobson, 2001). Stream flow data have been collected by the U.S. Geological Survey (USGS) at the Buffalo River near St. Joe, Arkansas (station number 07056000) since 1939 (fig. 1). The Buffalo River watershed (HUC 1101005) encompasses 348,000 ha; however, only 62% of this area is within the catchment boundary of the St. Joe water quality station. Average daily discharge between 1940 and 2001 was approximately 29.4 m^3/s, with mean monthly flows greatest between February and May (45.6 to 60.6 m^3/s) and lowest between July and October (4.5 to 8.8 m^3/s). Less than 8 km from the USGS station, daily precipitation records have been recorded at Gilbert, Arkansas, by the National Oceanic and Atmospheric Administration (NOAA) (Southern Regional Climate Center, 2002). The average annual precipitation for Gilbert is 112 cm for the years 1940−2001. The time span considered in this study, 1991−2001, exhibited similar hydrologic characteristics, with an average annual stream flow of 30.7 m^3/s and an average annual precipitation of 117 cm. One− to four−year recurrence interval flood events (as determined by an annual peaks series) occurred during the ten−year study period; thus, extreme hydrologic events did not occur during this study period.

Analysis of land use from 1992 (National GAP data) and 1999 (Center for Advanced Spatial Technologies land use and land cover data) indicates that land use for the 348,000 ha catchment has not changed substantially over this period. However, between 1965 and 1992, forest land use decreased by 12% and agricultural and urban land use increased 11% and 1%, respectively (Scott and Hofer, 1995). The greater part of land use change has occurred on the 66% of the catchment owned by private individuals. The remaining portion of the catchment is controlled by state and federal government entities. Because private individuals own a majority of the catchment, preservation of the BNR remains a constant challenge (Panfil and Jacobson, 2001).

Animal production numbers in the watershed are maintained by Arkansas Agricultural Statistic Service (AASS) (www.nass.usda.gov/ar/). Annual production of cattle and hogs is available on a county basis and was obtained for Newton and Searcy Counties, which represent 97% of the catchment area of the BNR St. Joe water quality station. (Additional counties in the drainage area include Pope, Boone, and Madison Counties with 1.3%, 1.2%, and 0.24% of the drainage area, respectively.) Searcy County experienced minimal changes in annual cattle production over the study period; cattle decreased from 38,000 head in 1991 to 37,000 head in 2001. However, cattle in Newton County increased 2% annually on average, with 17,000 cattle in 1991

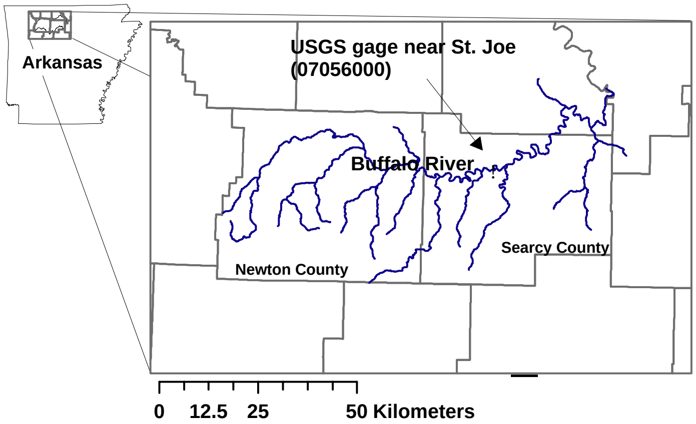

Figure 1. Location of the Buffalo National River water quality monitoring site and stream flow gauge.

and 20,000 in 2001. Conversely, annual hog production substantially decreased (>50%) from 1991 through 2001, with Newton County decreasing from 10,500 to 5,000 swine and Searcy County decreasing from 6,400 to 3,000 swine. The number of poultry produced was not available on a county-wide basis at AASS.

METHODS

Trend analysis was performed on physicochemical properties [specific conductance, dissolved oxygen (DO), and pH]; nutrients [ammonia (NH_3−N), nitrite (NO_2−N), ammonia plus organic nitrogen (NH_3−N plus organic N), nitrite plus nitrate (NO_2−N plus NO_3−N), total nitrogen (TN), total phosphorus (TP), dissolved phosphorus (DP), and orthophosphate (PO_4−P)]; sediments (percent sediment suspended <0.062 mm and suspended sediment concentrations); and bacteria (fecal coliforms, *E. coli*, and fecal streptococci) between 1991 and 2001 to evaluate changes in water quality at the BNR (table 1). Constituent concentrations and corresponding daily mean flow values were collected, analyzed, and maintained by USGS (http://waterdata.usgs.gov/ar/nwis/). Water samples were collected using depth−integrated, equal−width increment sampling methods (Edwards and Glysson, 1999). Samples were collected about monthly from 1991 through 2001, with six additional high−flow storm events collected annually from 1999 through 2001 (Petersen et al., 2002). Other studies regarding trends in water quality data used monthly samples over a ten−year period (e.g., Lettenmaier et al., 1991; Cavanaugh and Mitsch, 1989). This same water quality sampling scheme (monthly plus supplemental storm samples) is also adequate for determining annual nutrient loads from large watersheds (e.g., see Haggard et al., 2003b).

Water quality samples were designated as those representing base flow or surface runoff conditions using hydrograph separation. The stream flow hydrograph was separated into base flow and surface runoff components using the computer software program Base Flow Index (BFI) (Petersen et al., 2002; Wahl and Tortorelli, 1997; Wahl and Wahl, 1988). BFI estimates the portion of stream flow generally considered base flow using an automated technique from the Institute of Hydrology (Institute of Hydrology, 1980a, 1980b). BFI uses the minimum daily mean flow in five consecutive days, and minimum flows less than 90% of adjacent minimum flows are defined as turning points. The turning points are used to interpolate the base flow hydrograph. Base flow water samples were defined as those water quality samples collected when base flow discharge was greater than or equal to 70% of mean daily discharge (total stream flow), and surface runoff water samples were defined as those collected when base flow discharge was less than 70% of mean daily discharge (total stream flow).

After dividing water quality samples into those representing base flow or surface runoff conditions, summary statistics were used to describe the two data sets for each constituent including maximum, minimum, median, and mean values. The Wilcoxon−Mann−Whitney test was used to identify significant differences ($\alpha = 0.1$) between base flow samples and surface runoff samples for each constituent. The Wilcoxon−Mann−Whitney statistic tests whether two independent samples represent two populations with different medians (Sheskin, 2000).

We used constituent concentrations (instead of flux measurements) to evaluate water quality trends because of our interest in the ambient stream water quality rather than stream storage characteristics (Hirsch et al., 1991). To evaluate water quality trends, we followed three steps (figs. 2−4): (1) water quality data and daily discharge was appropriately transformed, (2) water quality data was flow−weighted using a smoothing technique, and (3) residuals from the flow−weighted smoothing were analyzed for temporal changes, i.e., increasing or decreasing trends.

Step 1: Stream flow and constituent concentrations were log−transformed to account for the log normal distribution of water quality data and to minimize the effect of outliers within the data (Hirsch et al., 1991; Lettenmaier et al., 1991); the proportion or percent of fine sediments was arcsine−square root transformed (Freund and Wilson, 1993).

Step 2: These appropriately transformed physicochemical properties or concentrations were flow−weighted against

Table 1. Constituents, U.S. Geological Survey parameter codes, sampling period, and number of samples, including the proportion of base flow and censored samples, at the Buffalo National River.

Constituent	USGS Parameter Code	Number of Base Flow Samples	Number of Censored Samples	Number of Total Samples	Period of Record
Specific conductance	00095	41	0	99	May 1993 − Sept. 2001
DO	00300	56	0	125	Oct. 1991 − Sept. 2001
pH	00400	61	0	132	Oct. 1991 − Sept. 2001
NH_3−N	00608	41	56	89	May 1993 − Sept. 2001
NO_2−N	00613	41	78	89	May 1993 − Sept. 2001
NH_3−N plus organic N	00625	41	46	90	May 1993 − Oct. 2000
NO_2−N plus NO_3−N	00631	42	28	89	May 1993 − Sept. 2001
TN	[a]	41	17	89	May 1993 − Sept. 2001
TP	00665	61	53	122	Oct. 1991 − Sept. 2001
DP	00666	41	48	89	May 1993 − Sept. 2001
PO_4−P	00671	40	70	88	May 1993 − Aug. 2001
Fecal coliforms	31625	41	1	88	May 1993 − Sept. 2001
E. coli	31633	38	6	82	Nov. 1992 − Sept. 2001
Fecal streptococci	31673	41	0	89	May 1993 − Sept. 2001
Percent sediment suspended <0.062 mm	70331	41	0	89	May 1993 − Sept. 2001
Suspended sediment concentration	80154	41	0	89	May 1993 − Sept. 2001

[a] TN was defined as the sum of NO_2−N plus NO_3−N (00631) and NH_3−N plus organic N (00625).

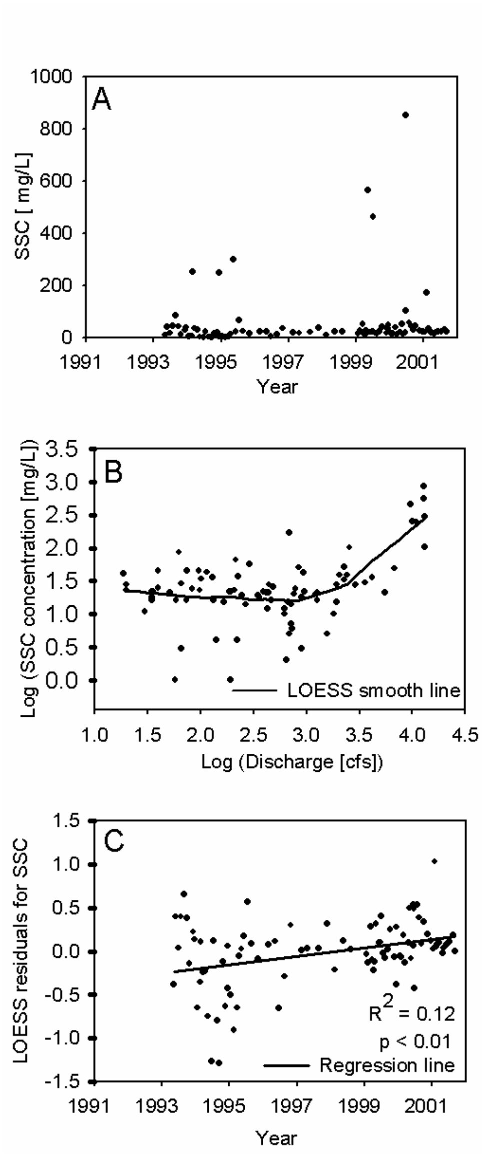

Figure 2. (A) Suspended sediment concentration from all water quality samples at the Buffalo National River from 1991 through 2001, (B) log−transformed suspended sediment concentration and log−transformed daily discharge with LOESS smoothing, and (C) residuals from LOESS smoothing of log−transformed suspended sediment concentrations and log−transformed daily discharge as a function of time from 1991 through 2001 where linear regression represents trend analysis. We used cfs (ft^3/s) because all USGS data is reported and available on the internet in these units (1 m^3/s = 35.3 cfs).

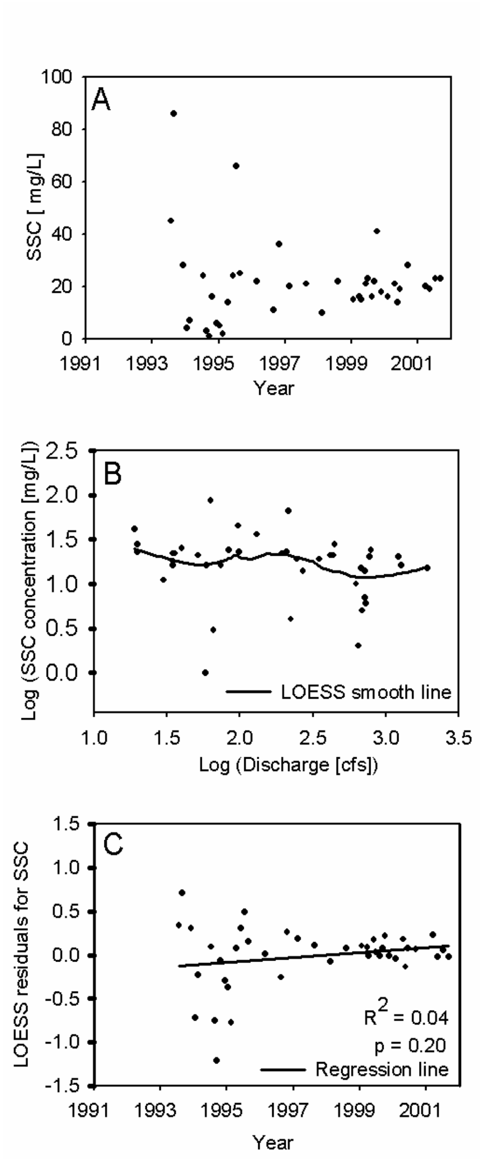

Figure 3. (A) Suspended sediment concentration from water quality samples representing base flow conditions at the Buffalo National River from 1991 through 2001, (B) log−transformed suspended sediment concentration and log−transformed daily discharge with LOESS smoothing, and (C) residuals from LOESS smoothing of log−transformed suspended sediment concentrations and log−transformed daily discharge as a function of time from 1991 through 2001 where linear regression represents trend analysis. We used cfs (ft^3/s) because all USGS data is reported and available on the internet in these units (1 m^3/s = 35.3 cfs).

log−transformed daily mean discharge using the LOESS two−dimensional smoothing technique (Richards and Baker, 2002; Petersen, 1992; Hirsch et al., 1991; Cleveland, 1979). The LOESS technique was chosen because it employs locally weighted regression algorithms, which avoids the difficulties and limitations of using a parametric model that is more sensitive to outliers in flow and concentration (Lettenmaier et al., 1991).

Step 3: Residuals from this LOESS smoothing of appropriately transformed data against log−transformed data were regressed against their respective time to evaluate changes in constituents. These residuals from LOESS smoothing represent the difference between the measured water quality value and the LOESS smooth line or predicted value. Because the time step between each sampling date was variable due to changes in water quality monitoring over this decade, we used simple linear regression between these residuals and time to determine if any temporal changes were present.

We used these three steps to determine changes in water quality using three datasets representing: (1) all water quality samples collected at the BNR from 1991 through 2001, (2) water quality samples representing base flow conditions, and (3) water quality samples representing surface runoff conditions. We used a significance level of α = 0.1 to determine if physicochemical parameters or concentrations significantly changed with time.

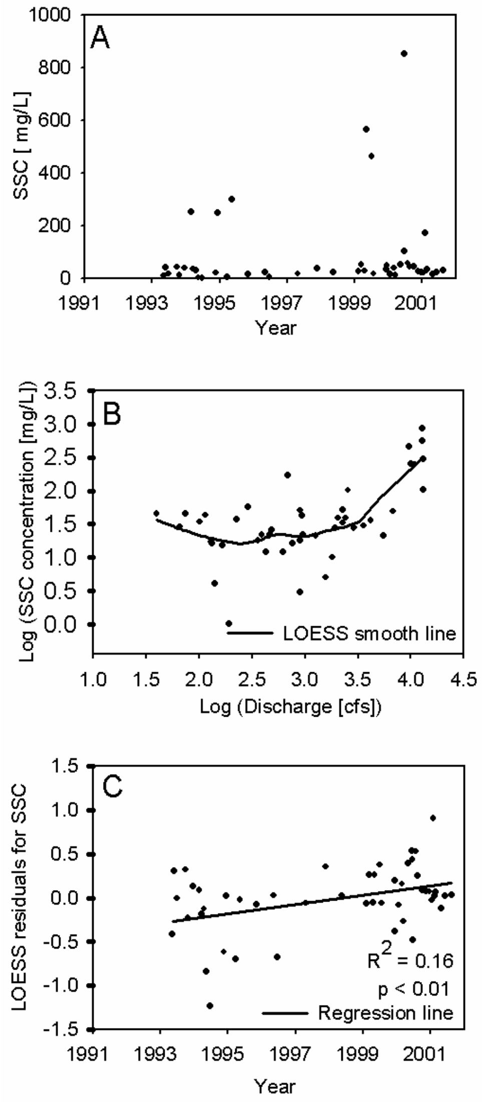

Figure 4. (A) Suspended sediment concentration from water quality samples representing surface runoff conditions at the Buffalo National River from 1991 through 2001, (B) log−transformed suspended sediment concentration and log−transformed daily discharge with LOESS smoothing, and (C) residuals from LOESS smoothing of log−transformed suspended sediment concentrations and log−transformed daily discharge as a function of time from 1991 through 2001 where linear regression represents trend analysis. We used cfs (ft^3/s) because all USGS data is reported and available on the internet in these units (1 m^3/s = 35.3 cfs).

Analytical techniques for evaluating nutrient concentrations in the water quality samples varied over the study period; thus, the minimum reporting level (MRL, i.e., the smallest measurable concentration of a constituent that may be reliably reported using a given analytical method) also varied. Trend analyses on constituents with censored values were evaluated using data with censored values replaced with the greatest MRL for each constituent and with only data that was not censored (without any censored values) for each constituent. However, trends in constituents were only reported for those datasets with censored values replaced with the greatest MRL because similar significant trends generally were observed when censored values were omitted as well.

Flow−weighted constituent concentrations and yields at the BNR were compared to relatively undisturbed catchments across the U.S. and to a relatively developed catchment in the Ozarks (Petersen et al., 2002; USGS, 2002; Green and Haggard, 2001; Clark et al., 2000). For undisturbed catchments, Clark et al. (2000) determined the frequency distribution of annual flow−weighted nutrient concentrations and mean annual yields using water quality and stream flow data from 1990 to 1995, which has been used as a reference to develop water quality standards in some states (OWRB, 2002). We compared the BNR (17% pasture and agriculture and less than 1% urban) to the Illinois River basin, which has 56% pasture and agriculture and 6% urban (relatively developed catchment in the Ozarks). The Illinois River also receives substantial point sources of nutrients (White et al., 2002).

Annual constituent loads for the BNR using data from 1991 through 2001 were determined using measured values and the LOADEST2 computer software program (Crawford, 1991, 1996). The relation between the natural logarithms of load and discharge were used to estimate daily loads, which were summed to estimate annual loads:

$$\ln(L) = \beta_0 + \beta_1 \ln(Q) \tag{1}$$

where L represents daily constituent load (kg/day), β_0 represents regression constant, β_1 represents regression coefficient, and Q represents daily mean discharge (ft^3/s). The values for β_0 and β_1 were determined by the LOADEST2 software using the water quality data and respective flows over the study time period. For constituents with significant trends, an additional term (*dectime*, which is time in fractional years) was added to the equation to account for changes in constituent concentrations (or load) occurring with time:

$$\ln(L) = \beta_0 + \beta_1 \ln(Q) + \beta_2 \, dectime \tag{2}$$

The *dectime* term provides for a component that changes over time. Equation 1 is used when load was only a function of flow, and equation 2 was used when load was a function of both flow and time.

Annual flow−weighted concentrations (C) were determined by dividing the average annual load (from LOADEST2 output) by the average annual flow (Q) (from BFI output):

$$C = \frac{L}{Q} \tag{3}$$

and average annual constituent yields (Y) were estimated by dividing average annual total loads by the watershed area (WA):

$$Y = \frac{L}{WA} \tag{4}$$

RESULTS AND DISCUSSION

CONSTITUENT CONCENTRATIONS

Hydrograph separation allowed separation of water quality data at the BNR into that collected during base flow and surface runoff conditions. The reason for analyzing and comparing these different flow regimes is that different external factors may influence water quality. For example, stream water quality during base flow conditions would be more affected by discrete pollution sources such as municipal wastewater treatment plants, nonpoint pollution sources from groundwater recharge, and various abiotic and biotic processes within the stream system. Alternatively, water quality during surface runoff conditions would be more influenced by resuspension of temporarily retained instream constituents and nonpoint−source pollutants entrained by surface runoff during episodic precipitation events. Thus, it would be expected to observe differences between constituents and water quality of these flow regimes, and we observed several significant differences (table 2). Dissolved oxygen, NO_2−N, DP, and percent sediment suspended <0.062 mm did not exhibit significant differences between median values during base flow and surface runoff conditions; however, the remaining constituents did, supporting the suggestion of differences in water quality and constituent transport characteristics during these flow regimes.

Overall, water quality and constituent concentrations were influenced by flow regime, demonstrating the need for water quality monitoring programs to specifically target the collection of water quality samples during surface runoff conditions (i.e., storm events) and to characterize the distribution of constituent values in each flow regime at the BNR (including base flow conditions). Several constituents, particularly suspended sediment and sediment−bound constituents, often display hysteresis, i.e., concentrations may increase rapidly on the rising limb of the storm hydrograph and have a slower decrease on the falling limb (e.g., see Richards et al., 2001; Richards and Holloway, 1987; Thomas, 1988). Thus, constituent concentrations and their relation to mean daily discharge during surface runoff conditions may be variable depending on the portion of the hydrograph where the water sample was collected. These significant differences further suggest that changes in water quality should be evaluated independently during base flow and surface runoff conditions, and our observations supported the need to investigate water quality trends at the BNR during these different flow regimes.

WATER QUALITY TRENDS

Physicochemical Properties

Physicochemical properties clearly showed some differences when evaluating temporal changes at the BNR using the three different groups of water quality samples (table 3), although specific conductivity showed the same trend when using all three datasets. Dissolved oxygen and pH exhibited negative trends at the BNR when using all data collected from 1991 through 2001. However, if we looked at temporal changes during the different flow regimes, pH did not show any changes with time during either base flow or surface runoff conditions. On the other hand, DO significantly decreased with time during base flow conditions and when using all data collected from 1991 through 2001, contrary to the results of the previous decades when DO significantly increased with time (Petersen, 1992). Because physicochemical properties are affected by a myriad of factors within a stream system, it would be difficult to identify causative factors of these changes.

Nutrients

We discovered that changing detection limits of nutrient concentrations in water quality samples at the BNR may substantially influence the potential results of trend analyses. Interestingly, we observed both (potential) false positive and false negative trends resulting from changes in the MRL when we did not censor nutrient concentrations at the greatest MRL observed within the respective data. In many circumstances, we were not able to conduct our trend analyses because the majority of water quality samples had nutrient concentrations less than the greatest MRL observed in the datasets, especially those samples representing base flow conditions (table 1). However, the observation that nutrient concentrations were often less than the MRL may suggest that elevated nutrient concentrations might not be a current water quality concern in the BNR. Nutrient concentrations were censored in a majority of the analyzed water samples, with an average of 56%, ranging from 16% to 88% (table 1).

Table 2. Descriptive statistics of constituents in water quality samples collected for base flow and surface runoff conditions at the Buffalo National River, 1991−2001.

	Base Flow Samples				Surface Runoff Samples			
Constituent	Min.	Max.	Median	Mean	Min.	Max.	Median	Mean
Specific conductance (µS/cm)	163	273	216	217	88	277	191[a]	188
DO (mg/L)	5.0	13.1	9.4	9.3	5.2	15.5	9.1	8.9
pH	6.8	8.4	7.9	7.9	6.5	8.6	7.6[a]	7.7
NH_3−N (mg/L)	<0.01	0.041	<0.02	<0.02	<0.01	0.19	<0.02[a]	<0.03
NO_2−N (mg/L)	<0.001	0.020	0.010	0.010	0.003	0.020	0.010	0.009
NH_3−N plus organic N (mg/L)	0.06	0.2	0.2	0.16	0.07	2.5	0.2[a]	0.32
NO_2−N plus NO_3−N (mg/L)	0.03	0.27	0.05	0.09	0.04	0.75	0.14[a]	0.18
TN (mg/L)	0.09	0.37	0.23	0.21	0.12	2.63	0.30[a]	0.48
TP (mg/L)	0.004	0.040	0.010	0.017	0.003	0.791	0.021[a]	0.071
DP (mg/L)	0.003	0.020	0.010	0.008	0.003	0.047	0.010	0.012
PO_4−P (mg/L)	0.010	0.020	0.010	0.010	0.010	0.036	0.010[a]	0.015
Fecal coliforms (col./100 mL)	1	230	10	22	4	22000	47[a]	964
E. coli (col./100 mL)	1	210	8	23	2	5800	14[a]	595
Fecal streptococci (col./100 mL)	1	170	21	38	2	26000	41[a]	2018
Percent sediment suspended <0.062 mm diameter	4	100	92	81	25	100	85	80
Suspended sediment concentration (mg/L)	1	86	16	21	1	852	30[a]	86

[a] Median values during base flow and surface runoff conditions significantly different ($p < 0.1$) for the Wilcoxon−Mann−Whitney test (also referred to as the Mann−Whitney U test). The Wilcoxon−Mann−Whitney statistic tests whether two independent samples represent two populations with different medians (Sheskin, 2000).

Table 3. Regression statistics from trend analyses (residuals from the LOESS smoothing versus time) for physicochemical properties, microbial numbers, and suspended sediments at the Buffalo National River, 1991−2001.

Constituent		R^2	p−Value[a]	Trend
Specific conductance				
	BF[b]	0.09	0.05	Negative
	SRO[c]	0.12	<0.01	Negative
	AD[d]	0.09	<0.01	Negative
DO				
	BF	0.07	0.05	Negative
	SRO	<0.01	0.76	
	AD	0.06	<0.01	Negative
pH				
	BF	<0.01	0.52	
	SRO	0.03	0.13	
	AD	0.05	<0.01	Negative
Fecal coliforms				
	BF	<.01	0.90	
	SRO	0.01	0.59	
	AD	0.03	0.13	
E. coli				
	BF	0.01	0.69	
	SRO	0.17	<0.01	Positive
	AD	0.06	0.03	Positive
Fecal streptococci				
	BF	0.02	0.34	
	SRO	0.01	0.56	
	AD	<0.01	0.98	
Percent sediment suspended <0.062 mm				
	BF	0.50	<0.01	Positive
	SRO	0.31	<0.01	Positive
	AD	0.38	<0.01	Positive
Suspended sediment concentration				
	BF	0.04	0.20	
	SRO	0.16	<0.01	Positive
	AD	0.12	<0.01	Positive

[a] p−value testing the null hypothesis that the slope of the regression line is equal to 0.

[b] Trend analyses of data representing water quality samples collected during base flow conditions.

[c] Trend analyses of data representing water quality samples collected during surface runoff conditions.

[d] Trend analyses of all water quality samples collected.

Table 4. Regression statistics from trend analyses (residuals from the LOESS smoothing versus time) at the Buffalo National River, 1991−2001, with nutrient concentrations censored at their respective greatest MRL.

Constituent		Greatest MRL (mg/L)[a]	R^2	p−Value[b]	Trend
NH_3−N					
	BF[c]	0.04	N/A	N/A	[d]
	SRO[e]		<0.01	0.66	
	AD[f]		<0.01	0.95	
NO_2−N					
	BF	0.01	N/A	N/A	[d]
	SRO		N/A	N/A	[d]
	AD		N/A	N/A	[d]
NH_3−N plus organic N					
	BF	0.20	N/A	N/A	[d]
	SRO		0.14	<0.01	Positive
	AD		0.08	<0.01	Positive
NO_2−N plus NO_3−N					
	BF	0.05	<0.01	0.71	Positive
	SRO		0.07	0.06	Positive
	AD		0.05	0.04	
Total N					
	BF	0.25	0.02	<0.36	Positive
	SRO		0.22	0.01	Positive
	AD		0.09	<0.01	
TP					
	BF	0.03	<0.01	0.59	
	SRO		0.04	0.14	
	AD		0.02	0.13	
DP					
	BF	0.02	N/A	N/A	[d]
	SRO		0.02	0.40	
	AD		0.01	0.35	
PO_4−P					
	BF	0.02	N/A	N/A	[d]
	SRO		N/A	N/A	[d]
	AD		N/A	N/A	[d]

[a] MRL = the smallest measurable concentration of a constituent that may be reliably reported using a given analytical method. Method reporting limits changed with time for some constituents; all concentrations less than the greatest MRL were set equal to this censored value for each individual constituent.

[b] p−value testing the null hypothesis that the slope of the regression line is equal to 0.

[c] Trend analyses of data representing water quality samples collected during base flow conditions.

[d] N/A indicates that there was insufficient number of samples greater than the greatest MRL to perform statistical tests.

[e] Trend analyses of data representing water quality samples collected during surface runoff conditions.

[f] Trend analyses of all water quality samples collected.

Although censored data limited trend analyses with nutrient concentrations, we observed significant increases in NO_2−N plus NO_3−N, NH_3−N plus organic N, and TN concentrations with time when evaluating concentrations from all water quality samples collected from 1991 through 2001 (table 4). With respect to temporal changes in nutrient concentrations during a particular flow regime, we did not observe any increases or decreases with time during base flow conditions, but significant increases with time were observed during surface runoff conditions. Overall, when significant trends in nitrogen concentrations were observed, time only explained a small portion ($\leq$9% when evaluating all data and $\leq$22% when using only samples collected during surface runoff conditions) of the variability in the residuals from the LOESS smoothing or flow weighting. Low R^2 values have been observed in assessing temporal changes in stream constituents (e.g., see Walker, 1991) because many abiotic and biotic factors may influence constituent (particularly nitrogen) concentrations and transformations within streams (Fenn and Poth, 1999; Meyer at al., 1988). Our observations were contrary to those observed from 1975 to 1986, when Petersen (1992) found no temporal changes in nitrogen at the BNR.

Not only was there a presence of temporal changes in nitrogen concentrations during surface runoff conditions and not during base flow conditions, but the distribution of concentrations was significantly different as well. However, our trend analyses only explained a small portion of the variability in nitrogen with time, and it is possible that the additional directed storm sampling present in the later years

(1999−2001) may have influenced our analyses. Nonetheless, it seems that BNR managers should focus on sources of nitrogen, which may occur during episodic rainfall events and surface runoff conditions in the river, and the high mobility of NO_3 may serve as indicator of future changes in water quality at the BNR.

Sediment

As expected, suspended sediment concentrations were significantly greater during surface runoff conditions than during base flow conditions (table 2). A significant increase in suspended sediment concentration was observed with time when evaluating temporal changes in all water quality samples collected from 1991 through 2001, but (similar to nitrogen concentrations) this trend persisted only during surface runoff conditions and not during base flow conditions (table 3, figs. 2−4). Approximately 12% and 16% of the variability in flow−weighted residuals of suspended sediment concentrations were explained with time when evaluating temporal changes using all data and that collected during surface runoff conditions, respectively (table 3). Sediment sources at the BNR during surface runoff conditions include internal sources within the stream that may be eroded (i.e., stream banks) or resuspended from within the stream system itself (e.g., legacy sediments). Alternatively, nonpoint sources of sediment such as county roads and agriculture may also be contributing sediment during surface runoff conditions. However, Trimble (1999) suggested sediment sources, sinks, and storage in a stream catchment is highly variable in space and time, and that sediment transport (or yield) in a stream channel has limited diagnostic utility.

Interestingly, the proportion of finer sediments (<0.062 mm in diameter) showed an increasing trend when we evaluated temporal changes using all data, and this positive trend persisted with finer sediments when evaluating water quality samples during base flow and surface runoff conditions (table 3). The relation between flow−weighted residuals (of the proportion of fine sediments) with time explained the largest fraction (up to 50%) of the variability observed in our study. Increasing trends in fine sediment for base flow and surface runoff conditions could be attributed to multiple factors, such as decrease in erosion of larger soil particles due to management practices, change in precipitation and flow intensities, or potentially new sources of erosion. Again, it is difficult to ascertain sediment sources when considering only what is transported in the stream channel. Our observations of increasing suspended sediment concentrations (and proportion of fine sediments) are similar to that of nitrogen but may also be the result of directed storm sampling during the later years of our study period.

Bacteria

Although Petersen (1992) found that the number of fecal coliforms in water samples decreased from 1975 to 1986 at the BNR, we did not observe any temporal changes in the number of fecal coliforms or fecal streptococci (table 3). However, the number of *E. coli* increased when evaluating all water quality samples collected from 1991 through 2001. However, using hydrograph separation to separate samples into those collected during different flow regimes showed that *E. coli* did not change over time during base flow conditions but increased with time during surface runoff conditions (table 3). As with the other constituents, only a small portion of the variability of the residuals from LOESS smoothing (flow weighting) was explained by time. Accordingly, the distribution of *E. coli* numbers was significantly different in water quality samples collected during base flow and surface runoff conditions. While many sources may contribute to increased *E. coli* numbers, our analysis suggested that we should concentrate on factors affecting *E. coli* transport following surface runoff events, such as resuspension of these microbes from within the stream system or transport of these microbes during surface runoff from the landscape, e.g., from land−applied manure (Sauer et al., 2000) or from natural wildlife (Hagedorn et al., 1999). The increase in the number of *E. coli* was consistent with increased sediment and NO_3−N movement during surface runoff conditions following precipitation events at the BNR catchment.

FLOW-WEIGHTED NUTRIENT CONCENTRATIONS AND YIELDS

Stream water quality across the U.S. may be compared to some set of reference conditions within a catchment, sub−ecoregion, ecoregion, or defined boundary where the data developed in the target watershed should be comparable to how the reference condition is determined. For example, the U.S. Environmental Protection Agency (USEPA, 2000) released guidelines suggesting that the 75th percentile of nutrient concentrations from a set of reference streams (relatively undisturbed catchments) was indicative of unimpaired conditions. Clark et al. (2000) reported flow−weighted nutrient concentrations and mean annual yields at a set of “reference” streams (including the BNR), and these values have been used to develop water quality standards in some states, such as Oklahoma (OWRB, 2002). Overall, our data suggested that the BNR has relatively low nutrient concentrations and yields when compared to the distribution of values from the reference streams (Clark et al., 2000).

While average annual flow−weighted nutrient concentrations and yields at the BNR were slightly greater than or equal to the 75th percentile value from the reference streams, the values at the BNR are much less than a relatively developed catchment in the Ozark Plateaus of Arkansas (tables 5 and 6). Average annual flow−weighted TP concentrations and yields at the BNR were almost 6 and 4 times less than that observed at the Illinois River basin (Green and Haggard, 2001). Average annual flow−weighted NO_2−N plus NO_3−N concentrations and yields were 18 and 13 times greater at the Illinois River basin compared to the concentrations and yields at the BNR, whereas TN values were 10 and 8 times greater. Thus, the BNR has relatively low nutrient concentrations and yields compared to a developed catchment, but the increasing trends in nitrogen concentrations in water quality samples during surface runoff conditions suggest a potential for increases in nutrient loading at the BNR. Overall, it appears that water quality at the BNR over the last decade may be considered as a reference condition for the southern portion of the Ozark Plateaus in Arkansas based on the USEPA recommendations (USEPA, 2000).

When we compared flow−weighted nutrient concentrations and yields to other studies (i.e., USGS, 2002; Petersen et al., 2002) reporting concentrations and yields at the BNR, some differences were observed (tables 5 and 6). The average annual flow−weighted nutrient concentrations and yields from Clark et al. (2000) did not include directed storm sampling in 1990−1995, which our study included in the later years, as does Petersen et al. (2002). Furthermore, water quality monitoring at the BNR has been highly variable in nature from 1991 through 2001. The values reported by Clark et al. (2000) at the BNR may slightly underestimate the average annual flow−weighted nutrient concentrations and yields because fixed period sampling (monthly or bimonthly) may underestimate annual loads without directed storm sampling (Haggard et al., 2003b). Differences in load estimation technique and regression models used by Petersen et al. (2002) or Clark et al. (2000) may contribute to some of the inequalities observed in load estimates as well. Several different regression models are often used to estimate daily loads at water quality monitoring stations because the regression approach may be modified to account for seasonal or long−term changes, nonlinearities, censored data, logarithmic transformation biases, or residual serial correlations (Cohn, 1995). These regression models may also be developed and applied under different flow regimes (e.g., see Petersen et al., 2002; Green and Haggard, 2001).

Table 5. Annual flow−weighted nutrient concentrations at the Buffalo National River, relatively underdeveloped streams across the U.S., and a developed watershed in the southwestern Ozark Plateaus, Arkansas.

	TP (mg/L)	NO_3−N plus NO_2−N (mg/L)	TN (mg/L)
Relatively undeveloped streams in the U.S.[a]			
All data	0.04	0.21	0.50
HBN[b]	0.03	0.14	0.52
NAWQA[c]	0.05	0.17	0.49
Buffalo River, 1990−1995[d]	<0.03	<0.05	<0.20
Buffalo River, 1999−2000[e]	0.06	0.37	0.84
This study, 1991−2001	0.05	0.14	0.31
Illinois River, 1997−1999[f]	0.40	2.4	3.4

[a] 75th percentile from Clark et al. (2000).
[b] Hydrologic Benchmark Network (USGS program).
[c] National Water Quality Assessment (USGS program).
[d] USGS (2002).
[e] Petersen et al. (2002).
[f] Green and Haggard (2001).

Table 6. Annual nutrient yields at the Buffalo National River, relatively underdeveloped streams across the U.S., and a developed watershed in the southwestern Ozark Plateaus, Arkansas.

	TP (kg/km^2)	NO_3−N plus NO_2−N (kg/km^2)	TN (kg/km^2)
Relatively undeveloped streams in the U.S.[a]			
All data	12	871	220
HBN[b]	11	392	170
NAWQA[c]	25	793	280
Buffalo River, 1990−1995[d]	<17	<28	<110
Buffalo River, 1999−2000[e]	91	164	478
This study, 1991−2001	29	86	195
Beaver Lake basin, 1993−1995[f]	34	391	604
Illinois River, 1997−1999[g]	168	1,034	1,507

[a] 75th percentile from Clark et al. (2000).
[b] Hydrologic Benchmark Network − U.S. Geological Survey program.
[c] National Water Quality Assessment − U.S. Geological Survey program.
[d] Clark et al. (2000).
[e] Petersen et al. (2002).
[f] Haggard et al. (2003a).
[g] Green and Haggard (2001).

STUDY LIMITATIONS

In conducting analysis on water quality data, there is always the restriction regarding availability of data, especially for the period of record during which the data were collected. In this study, samples were collected about monthly from 1991 through 2001, with six additional high−flow storm events collected annually from 1999 through 2001 (Petersen et al., 2002). Although this is not ideal (the ideal case being that the extra high−flow samples would have been collected from 1991 through 2001), it reflects current limitations found in water quality data. Seldom will an investigator find water quality data over a ten−year period with the same sampling protocol (collection frequency and analytical methods). However, the potential influence that these additional high−flow storm events may have on trend analysis was minimized by performing log−transformations (Hirsch et al., 1991; Lettenmaier et al., 1991) and flow−weighting the data using a LOESS smoothing technique (Richards and Baker, 2002; Petersen, 1992; Hirsch et al., 1991; Cleveland, 1979). Additional uncertainty may also be introduced when samples are randomly collected on the rising limb, peak, or falling limb of the storm hydrograph because of hysteresis in constituent concentrations. This limitation is common in water quality datasets due to the expense of collecting more frequent water quality samples across the storm hydrograph, e.g., flow−weighted composite sampling using autosamplers (see King and Harmel, 2003). In addition, there is variability in constituent concentrations between collecting point samples (i.e., autosamplers) versus collecting representative samples across the stream cross−section, especially for constituents associated with sediments (e.g., see Ging, 1999; Martin et al., 1992). Because these are common limitations in water quality data, we simply suggest that trend analysis should be evaluated using water quality samples from specific flow regimes and that the results should be interpreted cautiously based on data limitations and influences of other external factors.

CONCLUSIONS

While many factors may influence temporal changes in constituents in streams, our study was limited in its ability to discern these factors such as timing, magnitude, and aerial extent of precipitation. At the BNR, we showed clear differences in physicochemical properties (conductivity and pH) and concentrations (nitrogen, phosphorus, sediment, and bacteria) of water quality samples collected during base flow and surface runoff conditions (objective 1). We also observed some differences when interpreting temporal changes in constituents from the three different datasets from 1991 through 2001 (objective 2). It appeared as though temporal changes in constituents (nitrogen, sediment, and *E. coli*) occurred during surface runoff conditions and were only reflected during base flow for the proportion of finer sediments.

Overall, nutrient concentrations reflected the relatively nutrient limited status of the BNR. Flow−weighted nutrient concentrations and yields at the BNR were similar to the 75th percentile values of a set of reference streams, suggesting that this catchment may serve as a reference stream for the southern Ozarks (objective 3). Furthermore, flow−weighted nutrient concentrations and yields were much less than those observed in a relatively developed Ozark catchment (objective 3).

However, the presence of increasing nitrogen concentrations, particularly during surface runoff conditions, suggests that BNR watershed managers should focus on potential diffuse sources of nutrients that occur during precipitation events and surface runoff conditions in streams.

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