

## AUTHORS

C. BRANNON ANDERSEN ~ *Department of Earth and Environmental Sciences, Furman University, Greenville, South Carolina 29613; Brannon.andersen@furman.edu*

C. Brannon Andersen is an associate professor of earth and environmental sciences and associate director of the River Basins Research Initiative at Furman University. His main research interests focus on biogeochemical processes controlling the aqueous chemistry of rivers and the impact of urbanization on the water quality of rivers in the piedmont of the eastern United States.

GREGORY P. LEWIS ~ *Department of Biology, Furman University, Greenville, South Carolina 29613; Greg.lewis@furman.edu*

Gregory P. Lewis is an assistant professor of biology at Furman University. He has broad interests in watershed biogeochemistry and linkages between terrestrial and aquatic ecosystems. He has conducted research on influences of forest insect defoliations, forest species composition, wetlands, and man-made impoundments on the nutrient chemistry of streams and rivers in the eastern United States.

KENNETH A. SARGENT ~ *Department of Earth and Environmental Sciences, Furman University, Greenville, South Carolina 29613; Ken.sargent@furman.edu*

Kenneth A. Sargent is a professor of earth and environmental sciences and director of the River Basins Research Initiative at Furman University. His main research interests focus on the hydrology and geochemistry of watersheds, particular those undergoing rapid urbanization, and the transport of sediment in urbanized systems.

# *Influence of wastewater-treatment effluent on concentrations and fluxes of solutes in the Bush River, South Carolina, during extreme drought conditions*

**C. Brannon Andersen, Gregory P. Lewis, and Kenneth A. Sargent**

## ABSTRACT

As the human population in the piedmont of South Carolina grows, the release of treated effluents from wastewater-treatment plants (WWTPs) will increasingly affect the chemical composition and biogeochemical processes of the region's rivers. We examined the impact of WWTP effluent on the solute chemistry of one such river, the Bush River, South Carolina, which experienced extremely low flow during the drought of 1998–2002. Two WWTPs discharge into the river and accounted for at least 70% of the river flow during the summer of 2002. The response of river solute concentrations to discharge from the downstream WWTP followed the expected dilution pattern. In contrast, the response to discharge from the upstream WWTP only followed the expected pattern for nonnutrient solutes (e.g., chloride and sodium). Concentrations of total dissolved nitrogen, nitrate, phosphate, and sulfate were all far below those expected from simple mixing calculations. At downstream sampling localities, however, conservative ions such as chloride and sodium had concentrations well below those predicted by mixing calculations. Instream biological processes associated with very low flow conditions, such as denitrification and sulfate reduction, may have caused the observed decrease in some nutrients. The cause of the discrepancy between the observed and predicted concentrations of conservative solutes remains unclear. Fluxes of solutes were much higher below the downstream WWTP. Our results indicate that the treated effluents of WWTPs have a significant impact on the biogeochemistry of piedmont rivers during drought periods. The impact is particularly large in rivers with small discharges. Extreme low flow conditions, however, may actually increase the

opportunity for biological activity to remove dissolved nutrients from river water.

## INTRODUCTION

Riverine fluxes of nutrients to the oceans have increased greatly in the last century (Meybeck and Helmer, 1989; Berner and Berner, 1996). The discharge of effluent from domestic wastewater-treatment plants (WWTPs), also called communal input, is one important component of this increased flux (e.g., Roy et al., 1999). Improvements in domestic wastewater treatment and reduction of phosphorus in domestic products have reduced, but not eliminated, the discharge of nutrients from WWTPs into rivers. Despite modern treatments, WWTP effluents typically contain high concentrations of nitrate, phosphate, sulfate, sodium, and chloride (Verbanck et al., 1989; Thibert, 1994, cited in Roy et al., 1999; Meybeck, 1998). Exact concentrations of solutes in effluents vary among WWTPs, but the solute ratios in effluents are consistent among WWTPs, at least in Europe, and commonly differ markedly from ratios in natural stream waters (Verbanck et al., 1989; Roy et al., 1999).

Past studies have focused on the impact of WWTP effluents on large rivers, such as the Seine River (Roy et al., 1999), the Loire River (Grosbois et al., 2001), the Rhine River (Flintrop et al., 1996), the Piracicaba River (Williams et al., 2001), and the Pearl River (Zhu et al., 2002). In such cases, the impact of effluent discharge is integrated with agricultural and industrial discharge, and separating the sources is difficult. Two examples of the impact of agricultural runoff are the Thames River and Seine River. Nitrate concentrations in the upper Thames Basin are not greatly increased by the discharge of WWTP effluent because of the high background concentrations associated with agricultural runoff (Jarvie et al., 2002). Communal input, mainly from WWTP effluent, consists of less than 8% of the nitrates in the Seine River (Roy et al., 1999). Additionally, these large river systems drain watersheds with rocks that contain soluble minerals such as calcite. As a result, the rivers have relatively high background salinity, making it difficult to isolate the contribution of effluent to river salinity (e.g., Roy et al., 1999).

In contrast to the large rivers previously studied, rivers in the piedmont of the southeastern United States drain high-grade metamorphic rocks and highly weathered soils that contain minerals with low solubility. As a result, the river waters naturally have mixed cation-bicarbonate compositions with low salinity (e.g., Andersen et al., 2001), making the detection of human impact on solute chemistry easier than in regions with high natural river salinity. In this region, WWTP effluent constitutes the major human influence on the chemical composition of rivers because industrial discharge and agricultural runoff are minor. The purpose of this study is to examine the response of the Bush River to WWTP effluent discharge during extreme drought, when the effect of effluent discharge is likely to be greatest. During the period of the study, river water

## ACKNOWLEDGEMENTS

This research was supported by grant EQ-2-411 from the South Carolina Department of Health and Environmental Control, grants EAR-0139135 and EAR-0116487 from the National Science Foundation, and funds from Furman University. We would like to thank all the students that participated in our 2002 National Science Foundation Research Experience for Undergraduates program that contributed to this study by collecting samples in the field and performing chemical analyses of the water samples, with special thanks to J. Brown, A. Irizzary, M. Peterson, and S. Plowman. Thanks to S. Muthukrishnan for developing Figures 1 and 7, to J. and S. Wheeler for help with Inductively coupled plasma-atomic emission spectrometer (ICP-AES) analyses, and to L. Elango for excellent suggestions.

downstream of two WWTPs consisted of at least 70% WWTP effluent by volume. We demonstrate that the discharge of WWTP effluent controls the chemical composition of the river downstream of the WWTPs, and that concentrations of specific solutes are diluted by tributary influx. We suggest that the extremely low flow conditions of the upper Bush River actually served to diminish instead of increase nutrient concentrations as would be expected during conditions where the bulk of the river water is WWTP effluent.

## STUDY AREA

The 298-km<sup>2</sup> (115-mi<sup>2</sup>) Bush River watershed is a tributary watershed of the Saluda River and is located in the lower piedmont region of South Carolina (Figure 1). The Bush River watershed is 52 km (32 mi) long and relatively flat, with an overall gradient of 1.7 m/km (9.0 ft/mi). The watershed drains southeast into the northern estuary of Lake Murray. The land cover in the Bush River watershed is 56% forest, 36% agricultural (cropland and pasture), and 8% urban. Two WWTPs discharge effluent into the Bush River (Figure 1). The

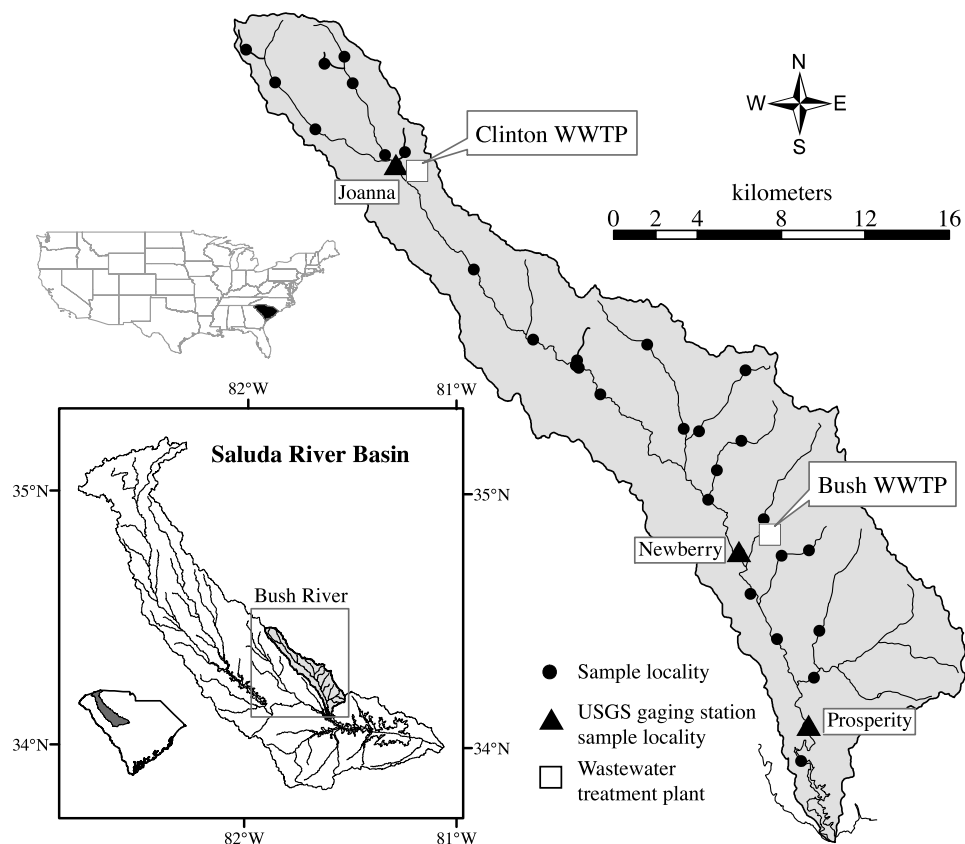
Clinton WWTP discharges directly into the main channel of the Bush River near the town of Clinton. The Bush River WWTP discharges into a small tributary stream near the town of Joanna approximately 2 km (1 mi) from the confluence with the Bush River.

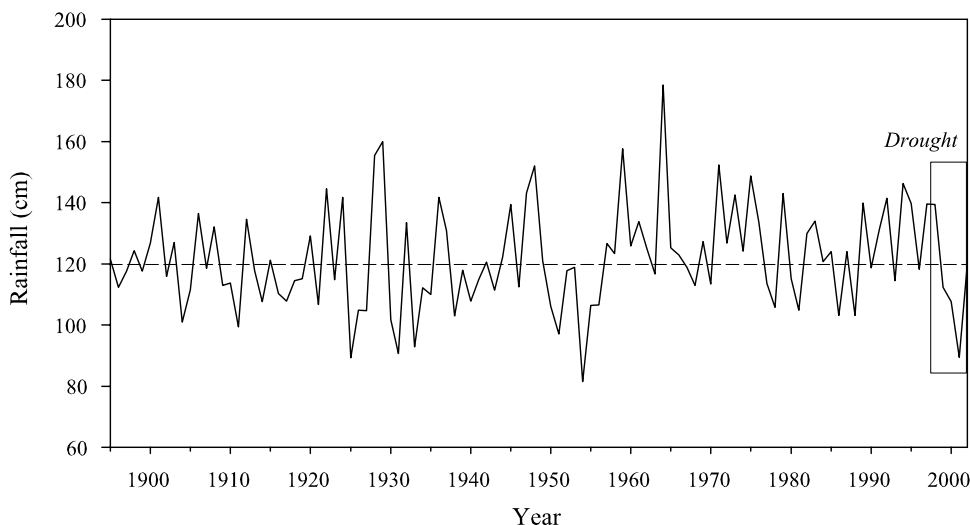
Three U.S. Geological Survey gaging stations are located on the main channel of the Bush River (Figure 1). All discharge data used in mixing and flux calculations were gathered from provisional U.S. Geological Survey real-time records (U.S. Geological Survey, 2003).

## Climate and Hydrology

The lower piedmont region of South Carolina has a warm temperate climate, with an average daily maximum temperature of 22°C and an average of more than 50 days/yr in which the temperature exceeds 32°C. Based on archived data from the National Climatic Data Center of the National Oceanographic and Atmospheric Administration, the annual rainfall averages 112 cm (44 in.) in Newberry, South Carolina, which is similar to the South Carolina average annual rainfall of nearly 120 cm (47 in.) (National Climatic Data Center, 2003). Drought conditions occurred in

**Figure 1.** The Bush River watershed in the Saluda River Basin, South Carolina. Thirty-two localities were sampled in the watershed, including three associated with the Joanna (02167557), Newberry (02167563), and Prosperity (02167582) U.S. Geological Survey gaging stations (filled triangles). Two WWTPs (white squares) discharge effluent in the watershed.





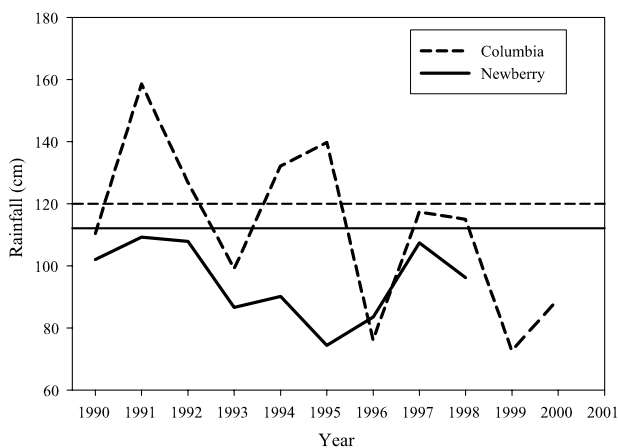
**Figure 2.** Record of precipitation for South Carolina from 1895 through 2002. The boxed area indicates the recent drought. This drought is similar in magnitude to the drought period in the mid-1950s.

South Carolina during 1998–2002; in 2001, the state received less than 90 cm (35 in.) of rainfall. The result was the most severe drought since the 1950s (Figure 2). Based on rainfall at Newberry, South Carolina, the Bush River watershed received below-normal rainfall for more than a decade (Figure 3), which resulted in extremely low summer discharge during 2002.

Records from the Prosperity gaging station (U.S. Geological Survey station 02167582) near the mouth of the Bush River show a median discharge of  $1.0 \text{ m}^3/\text{s}$  ( $35 \text{ ft}^3/\text{s}$ ) for June and July during the period from 1990 to 2000. The mean discharge of  $1.5 \text{ m}^3/\text{s}$  ( $53 \text{ ft}^3/\text{s}$ ) is skewed by very high discharges during June of both 1994 and 1995. The recent deficit of rainfall had a sig-

nificant impact on discharge (Figure 4). During 1998–2002, the frequency and intensity of winter stormflow events were exceptionally low, and both winter and summer base flow decreased.

Low flow conditions were reached in the summer of 2002 when base flow averaged  $0.24 \text{ m}^3/\text{s}$  ( $8 \text{ ft}^3/\text{s}$ ) at the Prosperity gaging station (Figure 5), approximately one-fourth of median flow and one-sixth of mean flow. Although the flow conditions were very low, discharge was variable during the sampling period (Figure 6). Part of the variability is the result of declining base flow, and part is the result of 16 rain events recorded at the Joanna gaging station during the sampling period. The rain events produced a total of 6.5 cm (2.5 in.), and only 2 days had rainfall greater than 1 cm (0.4 in.).

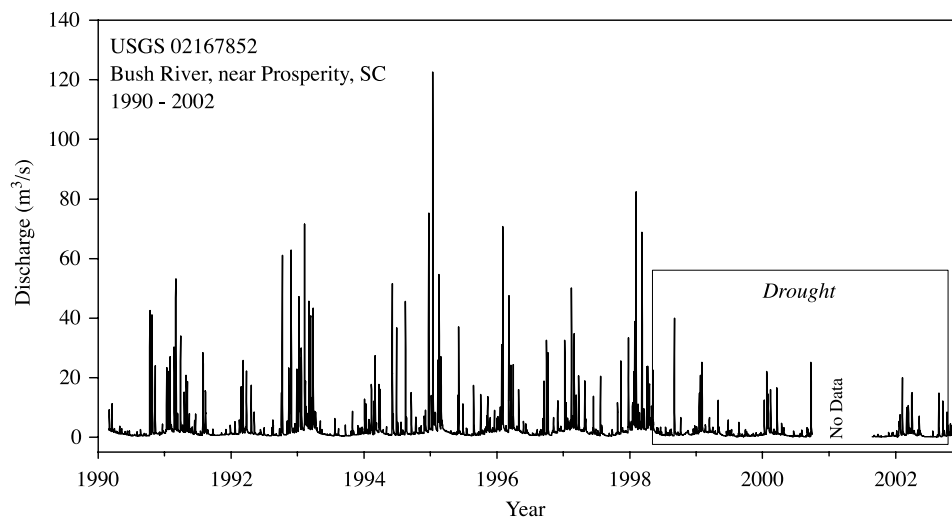


**Figure 3.** Record of precipitation for Newberry and Columbia, South Carolina. Rainfall in the Bush River watershed has been below normal for at least a decade.

## Geology

The primary rock types of the Bush River watershed (Figure 7) are late Precambrian–Cambrian high-grade granitoid gneisses, later Paleozoic granites, and an Ordovician–Mississippian mafic dike swarm (Overstreet and Bell, 1965). The mafic dike swarm may be manifested as a gabbro in the Bush River watershed (Peper et al., 2001). The rocks have weathered to form a red regolith consisting of ultisols, and occasional alfisols, overlying a thick saprolite. The soils have poorly developed A and B horizons that overlie the saprolite, suggesting the soil developed on the saprolite instead of on bedrock (Gardner, 1992). The typical clay minerals in the soils are kaolinite and gibbsite, although smectites may be present in the minor alfisols found in some forested upland areas, particularly around the gabbro (Camp

**Figure 4.** Record of discharge for the Prosperity gaging station near the mouth of the Bush River. Boxed area shows the discharge pattern associated with the drought. Storm events have lower discharge and are less frequent during the drought. The period of “no data” is the gap between provisional and historical discharge data.



et al., 1960; Camp et al., 1975). The rocks and regolith consist of silicate minerals that have relatively low solubility, resulting in river water with low conductivity and ionic strengths less than  $10^{-3}$  m, typical of the piedmont of South Carolina (e.g., Andersen et al., 2001).

## METHODS

### Chemical Analyses

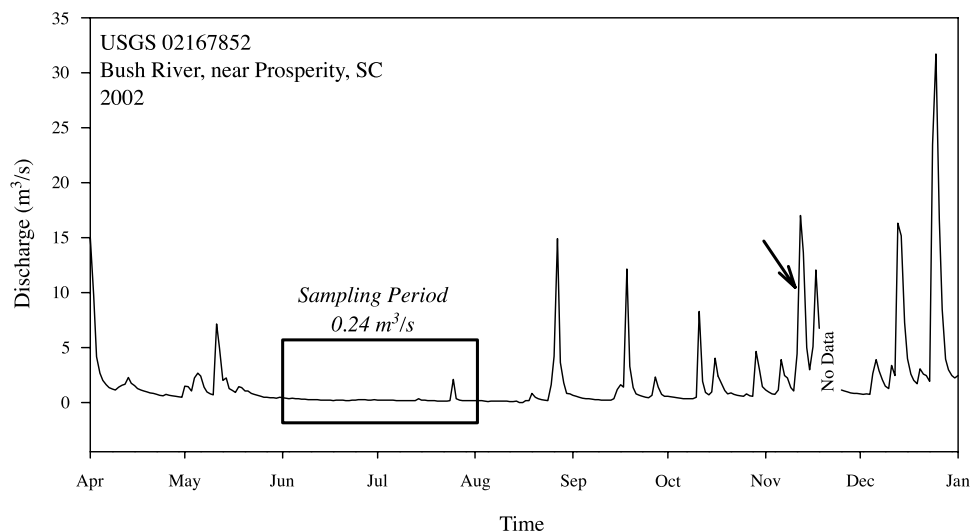
Grab samples were collected between June 1 and August 1, 2002, at 30 locations in the watershed (Figure 1). Each location was sampled between three and five times during a period of extremely low base-flow conditions (Figure 6). One sample of the wastewater effluent from each WWTP was collected during the

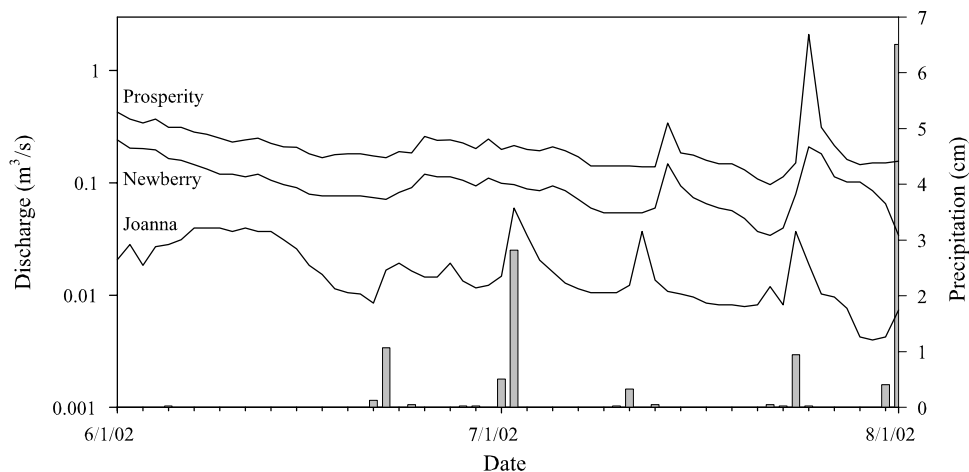
summer. In addition, samples were collected directly upstream and downstream of both WWTPs during the rising limb of a small stormflow event in November 2002.

At each location, a sample for chemical analysis was collected in a precleaned high-density polyethylene (HDPE) bottle after the bottle was rinsed three times with river water. Additionally, a separate sample was collected for turbidity analysis. At the time of collection, pH, conductivity, dissolved oxygen, and temperature were measured in situ. Sample bottles were placed on ice and returned to the laboratory.

In the laboratory, samples for chemical analysis were filtered through a 0.45- $\mu$ m membrane filter using positive pressure. An aliquot of the sample for total dissolved nitrogen (TDN) analysis was preserved with trace-metal-grade sulfuric acid, and an aliquot for cation analysis was preserved with trace-metal-grade nitric

**Figure 5.** Record of discharge for the Prosperity gaging station during summer and fall 2002. Boxed area indicates the period of sampling. Arrow indicates date of samples collected during a rain event. “No data” is a gap in the provisional data set associated with a storm event.

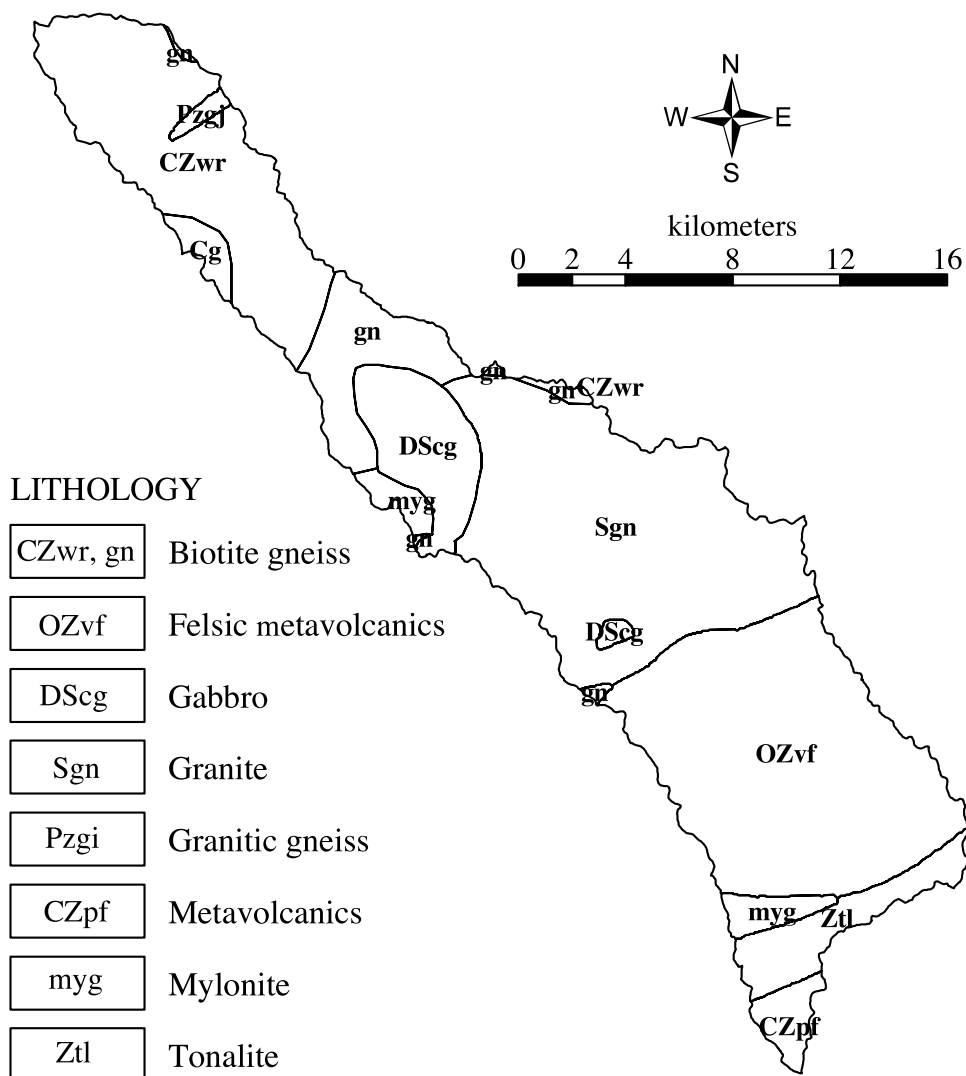




**Figure 6.** Detailed record of discharge for the Joanna, Newberry, and Prosperity U.S. Geological Survey gaging stations. Precipitation is that recorded at the Joanna gaging station. The largest rain event was apparently a local storm that only affected discharge at the Joanna gaging station.

acid. A third aliquot was left unpreserved for dissolved organic carbon (DOC), alkalinity, and anion analysis. Samples were refrigerated until analysis.

Concentrations of base cations ( $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Mg}^{2+}$ , and  $\text{Ca}^{2+}$ ) and dissolved silicon ( $\text{Si}^{4+}$ ) were measured using a Varian 2000 ICP-AES. Anion ( $\text{F}^-$ ,  $\text{Cl}^-$ ,  $\text{Br}^-$ ,



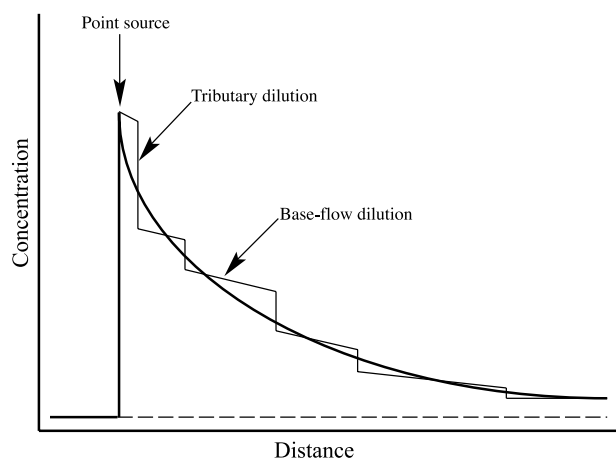
**Figure 7.** Geologic map of the Bush River watershed. Rocks consist of high-grade metamorphic lithologies, granitic intrusions, and a small gabbro intrusion. Rocks consist primarily of silicate minerals with relatively low solubility. Rocks range in age from Proterozoic to Permian. The map was generated from data in Peper et al. (2001).

$\text{NO}_2^-$ ,  $\text{NO}_3^-$ ,  $\text{H}_2\text{PO}_4^-$ , and  $\text{SO}_4^{2-}$ ) concentrations were measured using a Dionex 120 ion chromatograph. The detection limits for anions is approximately 50  $\mu\text{g/L}$ , except for phosphate (100  $\mu\text{g/L}$ ) and fluoride (20  $\mu\text{g/L}$ ). Alkalinity was determined by Gran titration, and all alkalinity was assumed to be in the form of bicarbonate for charge-balance purposes. This assumption holds well for piedmont stream waters (Andersen, 2002). Analytical quality was checked using the charge-balance method of Freeze and Cherry (1979). Charge-balance errors were less than 10% and commonly less than 5%.

Dissolved organic carbon concentrations were measured with a Tekmar-Dohrman Phoenix 8000 total organic carbon analyzer using a UV-persulfate digestion method. Total dissolved nitrogen concentrations were measured with an O.I. Analytical Flow Solutions IV autoanalyzer using a cadmium reduction colorimetric method following UV-persulfate digestion. Dissolved organic nitrogen was calculated by subtracting the total dissolved inorganic nitrogen (dissolved inorganic nitrogen = nitrate-N + nitrite-N, assuming ammonium-N was negligible) from TDN.

### Mixing Model

As a hypothesis, we use a conceptual model for point-source dilution to predict the fate of solutes downstream from the WWTPs (Figure 8). The model assumes a well-mixed, hydrologically unimpeded system where conservative solutes are diluted by groundwater input



**Figure 8.** Conceptual model of downstream dilution of point-source discharge. The thinner, stair-step line shows gradual ground-water dilution in stream reaches and abrupt dilution at confluences with tributaries. The thicker curve shows the hypothetical change in concentration for samples collected at bridge crossings.

and tributary input. Studies of larger river systems suggest that groundwater input is a small percentage of the water contribution to the stream system (Lesack, 1993). As a result, dilution rates should be low along stream reaches between tributary confluences and rapid at a tributary confluence. The result should be a “stair-step”-type dilution. Sampling reaches between tributary confluences would then give the appearance of a continuous dilution. Nonconservative solutes, such as nutrients, that are affected by other processes may decrease in concentration faster than conservative solutes. Another important assumption of the model is that the point-source input has much higher concentrations than the background chemical composition of the streams. The Bush River appeared to meet these assumptions because no dams are used to control discharge, the river is small enough to be well mixed, and samples are collected far enough downstream for the sample localities to be runoff dominated.

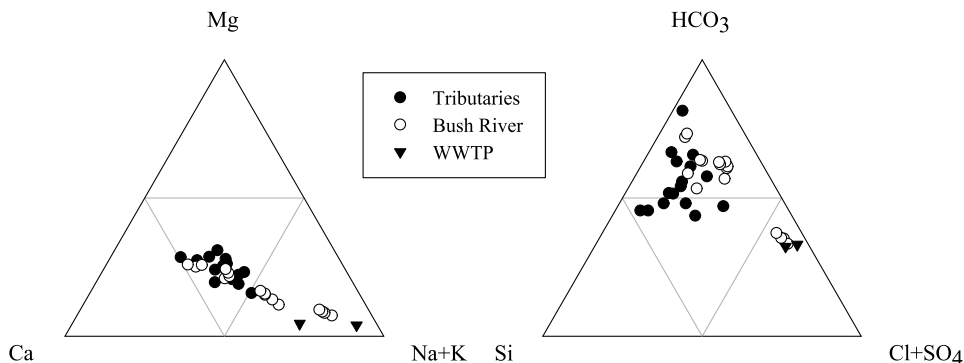
## RESULTS

### Natural Stream Water Composition

The tributaries and headwaters of the Bush River had a mixed cation-bicarbonate composition (Figure 9). The average concentrations of the headwater and tributary samples are reported in Table 1. The major cation and anion composition of the streams was a function primarily of the weathering of silicate minerals along with additions from rainwater (e.g., Andersen et al., 2001). The background concentration of nitrate was typical for the region, averaging about 1.5 mg/L (Andersen, unpublished data), although this concentration is much higher than the maximum of 0.60 mg/L found in undeveloped watersheds elsewhere in the United States (Clark et al., 2000). Many of the tributaries had phosphate concentrations above the detection limit of 0.1 mg/L, although in all cases, concentrations were less than 1.0 mg/L. Chloride concentrations ranged from 2.5 to 20 mg/L, with an average of about 8 mg/L. The most likely source of chloride is cyclic salts in rainwater because there are no evaporites in the area (e.g., Berner and Berner, 1996). Dissolved organic carbon concentrations averaged about 9 mg/L.

### Composition of WWTP Effluent

Effluent from the WWTPs was much more saline and had a different chemical composition than the tributaries



**Figure 9.** Ternary plots of river water and effluent compositions. Data show a mixing trend between stream water and WWTP effluent from both WWTPs for the cations, but for the anions, the mixing trend is only associated with the downstream Bush WWTP. See text for explanation.

entering the main Bush River channel. The concentrations of most of the solutes in the effluents were much greater than the concentrations in the Bush River upstream of the WWTPs and concentrations in tributaries (Table 1). The effluent composition is an estimate because it is based on a single sample from each WWTP. In general, both the chemistry of WWTP effluents (Verbanck et al., 1989) and the discharge of effluents are known to vary over time.

In particular, the effluent samples indicate that the Clinton WWTP, which is the farthest upstream, released effluent with nitrate concentrations twice that of the Bush River WWTP. For the Bush River WWTP,

dissolved inorganic nitrogen was 83% of TDN. Total dissolved nitrogen was not analyzed for the Clinton WWTP effluent. Nitrite was below detection for both samples. Phosphate concentrations were also much higher than concentrations in tributary streams, which averaged approximately 0.20 mg/L (range: below detection to 0.76 mg/L). The Cl/Na and K/Na molar ratios of 0.5 and 0.1 for the Clinton WWTP and 0.6 and 0.1 for the Bush River WWTP are similar to the Cl/Na and K/Na molar ratios of 0.7 and 0.1 reported in studies of effluent from France and Belgium (e.g., Thibert, 1994, cited in Roy et al., 1999; Meybeck, 1998). The SO<sub>4</sub>/Na molar ratios of 0.1 for the Clinton and Bush

**Table 1.** Average Solute Concentrations and Fluxes at Gaging Stations and WWTPs

	Tributary* (mg/L)	Joanna		Newberry		Prosperity		Clinton WWTP		Bush WWTP	
		(mg/L)	(kg/day)	(mg/L)	(kg/day)	(mg/L)	(kg/day)	(mg/L)	(kg/day)	(mg/L)	(kg/day)
Na	10.2	9.3	15.2	14.0	121.4	64.2	1332.3	77.7	489.9	112.5	932.9
K	3.4	2.7	4.4	5.1	44.3	12.0	249.1	12.4	78.3	15.8	131.3
Ca	11.1	13.8	22.7	14.5	125.3	12.0	249.0	25.0	157.5	7.7	64.2
Mg	4.3	4.9	8.0	5.7	49.2	4.3	89.8	2.9	18.0	2.8	23.5
Si	15.6	14.2	23.3	13.2	114.2	9.5	196.2	8.7	55.1	6.1	50.5
F	0.3	0.2	0.3	0.3	2.6	0.5	9.7	0.8	5.0	0.3	2.4
Cl	8.6	8.2	13.5	14.0	121.0	72.2	1498.1	58.2	367.3	109.7	909.6
HCO <sub>3</sub>	68.2	72.6	119.2	97.4	841.1	99.5	2062.4	80.6	508.0	122.9	1019.5
NO <sub>2</sub>	0.1	BDL**	–	0.1	0.5	0.1	2.7	BDL	–	0.1	0.7
Br	0.1	0.1	0.1	0.1	0.8	0.1	1.3	0.1	0.6	0.1	0.7
H <sub>2</sub> PO <sub>4</sub>	0.3	BDL	–	0.2	1.3	2.3	47.7	2.9	18.3	4.4	36.6
NO <sub>3</sub>	1.6	2.0	3.3	1.2	10.7	12.2	253.0	72.0	454.4	29.1	241.4
SO <sub>4</sub>	2.7	4.5	7.4	2.0	17.6	28.2	584.5	38.7	243.8	36.2	300.6
DOC	9.4	10.8	17.7	12.3	106.0	11.4	236.3	6.1	38.6	33.9	281.3
TDN	1.2	0.7	1.1	0.9	7.5	3.4	69.9	N.A. <sup>†</sup>	–	7.8	64.6

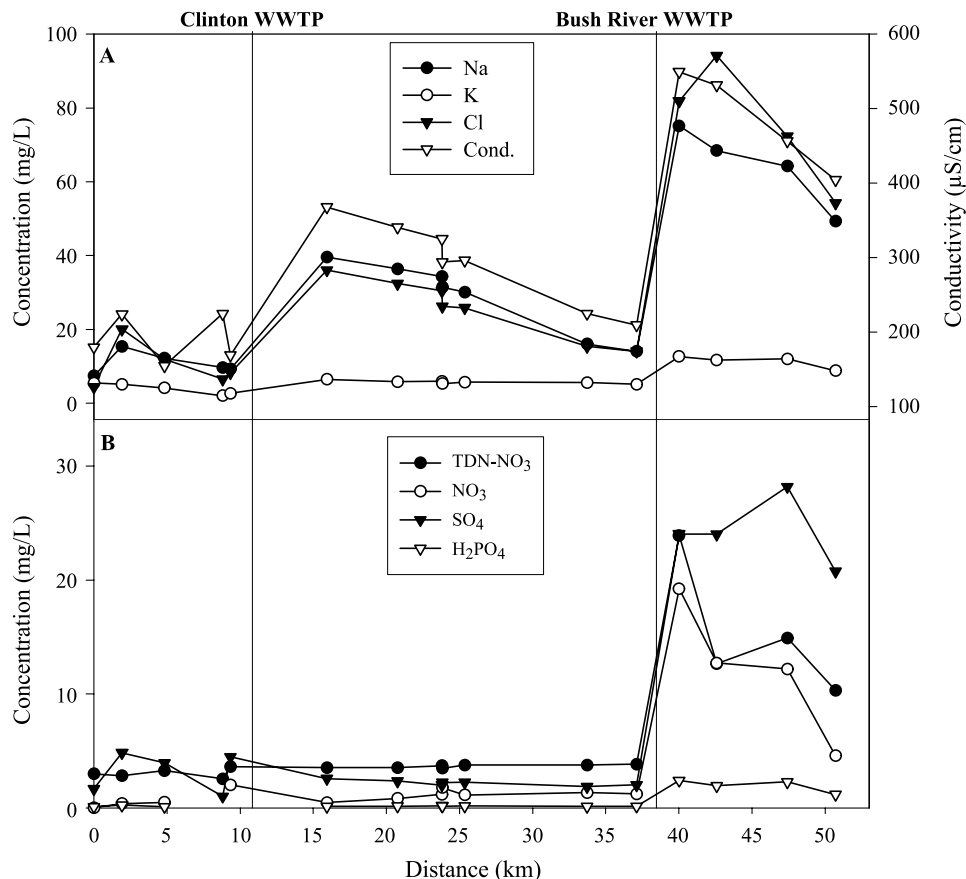
\*Average concentration of all tributary and headwater samples.

\*\*BDL = below detection limit.

<sup>†</sup>N.A. = not analyzed.



**Figure 10.** Downstream changes in the average composition of the Bush River. (A) Downstream changes in the average concentrations of sodium, potassium, chloride, and conductivity. (B) Downstream changes in the average concentrations of TDN, nitrate, sulfate, and phosphate. TDN is expressed as milligrams per liter of  $\text{NO}_3\text{-N}$  instead of milligrams per liter of N for scaling purposes. Nutrient concentrations are not affected by the discharge of WWTP effluent from the Clinton WWTP.



WWTPs are much lower than the 0.4 ratio reported in other studies (e.g., Thibert, 1994, cited in Roy et al., 1999; Meybeck, 1998). The  $\text{NO}_3/\text{Na}$  ratio of 0.0 reported by Thibert (1994) and Meybeck (1998) is much lower than the ratio of 0.1 for the Bush River WWTP effluent and 0.3 for the Clinton WWTP effluent. Ternary plots show the effluent had a sodium-chloride/sulfate composition that is similar to stream waters draining mixed carbonate-evaporite deposits (Figure 9). This composition differed from the mixed cation-bicarbonate composition of the headwater and tributary streams in the watershed.

The average daily discharges for the Clinton and Bush River WWTPs were 6435 and 8328  $\text{m}^3/\text{day}$  (227,250 and 294,100  $\text{ft}^3/\text{day}$ ), respectively. Using provisional data from the Joanna, Newberry, and Prosperity gaging stations, we estimated effluent to be 70–80% of the average Bush River discharge at the Newberry gaging station and 70–75% (Clinton WWTP and Bush WWTP combined) of the average Bush River discharge at the Prosperity gaging station. A total of nearly 700 kg/day of nitrate and sulfate, 55 kg/day of phosphate, and 320 kg/day of DOC are discharged in to the Bush River (Table 1).

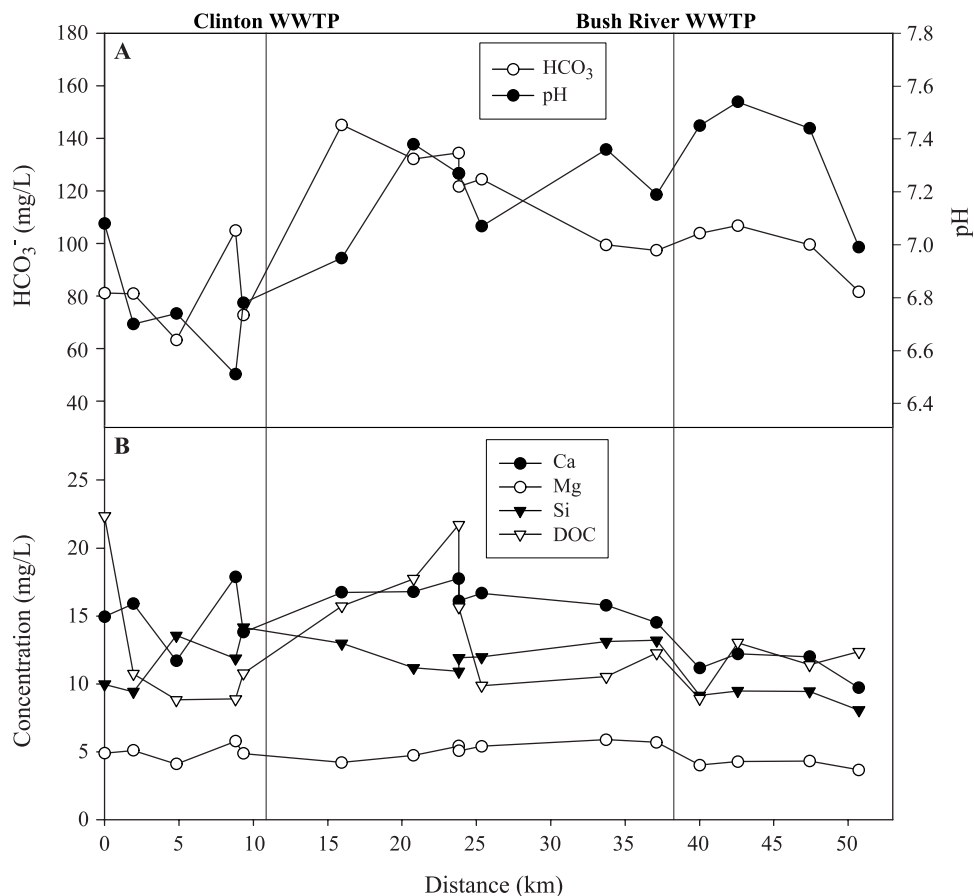
## Impact of WWTP Effluent

### Effluent-tributary Mixing

A mixing trend between the effluent and natural stream water is clearly shown on the ternary plots (Figure 9). For the cations, each WWTP has its own distinct composition, and therefore, two mixing trends are shown. For the anions and silicon, the composition only of the samples below the Bush WWTP shows a major influence along a mixing trend; samples downstream of the Clinton WWTP show a minimal influence. The data indicate that the addition of effluent at each location changes the chemical composition of the river.

### Downstream Change in Na, K, Cl, and Conductivity

The changes in average concentrations of sodium, potassium, and chloride and the conductivity of the stream water downstream from each of the WWTPs (Figure 10A) are similar to that predicted by the point-source dilution model (Figure 8). This result reflects the salinity and composition of the effluent and the expected downstream dilution by mixing with tributary stream water. The 6-km (4-mi) distance between the Clinton



**Figure 11.** Downstream changes in the average composition of the Bush River. (A) Downstream changes in the average pH and bicarbonate concentration. (B) Downstream changes in the average calcium, magnesium, dissolved silicon, and dissolved organic carbon concentrations. Note the effect of dilution by the discharge of effluent from the Bush River WWTP.

WWTP and the next downstream sampling site accounts for the greater downstream decrease in concentrations and conductivity compared to the Bush WWTP. At a downstream distance of about 24 km (15 mi), samples were collected immediately upstream and downstream of a tributary to the Bush River. The results show the stepwise dilution of the main channel by tributaries for sodium, potassium, chloride, and conductivity, as predicted by the model. A comparison of the stream response to effluent discharge 10 km (6 mi) downstream from each WWTP indicates that the concentrations downstream from the Clinton WWTP should be much higher. A simple mixing model between the water from Joanna gaging station and the Clinton WWTP effluent suggests that the concentrations of sodium and chloride should be two to three times higher for water at the Newberry gaging station. This is consistent with the observations of nutrient concentrations (below).

#### Downstream Change in Ca, Mg, Si, C, and pH

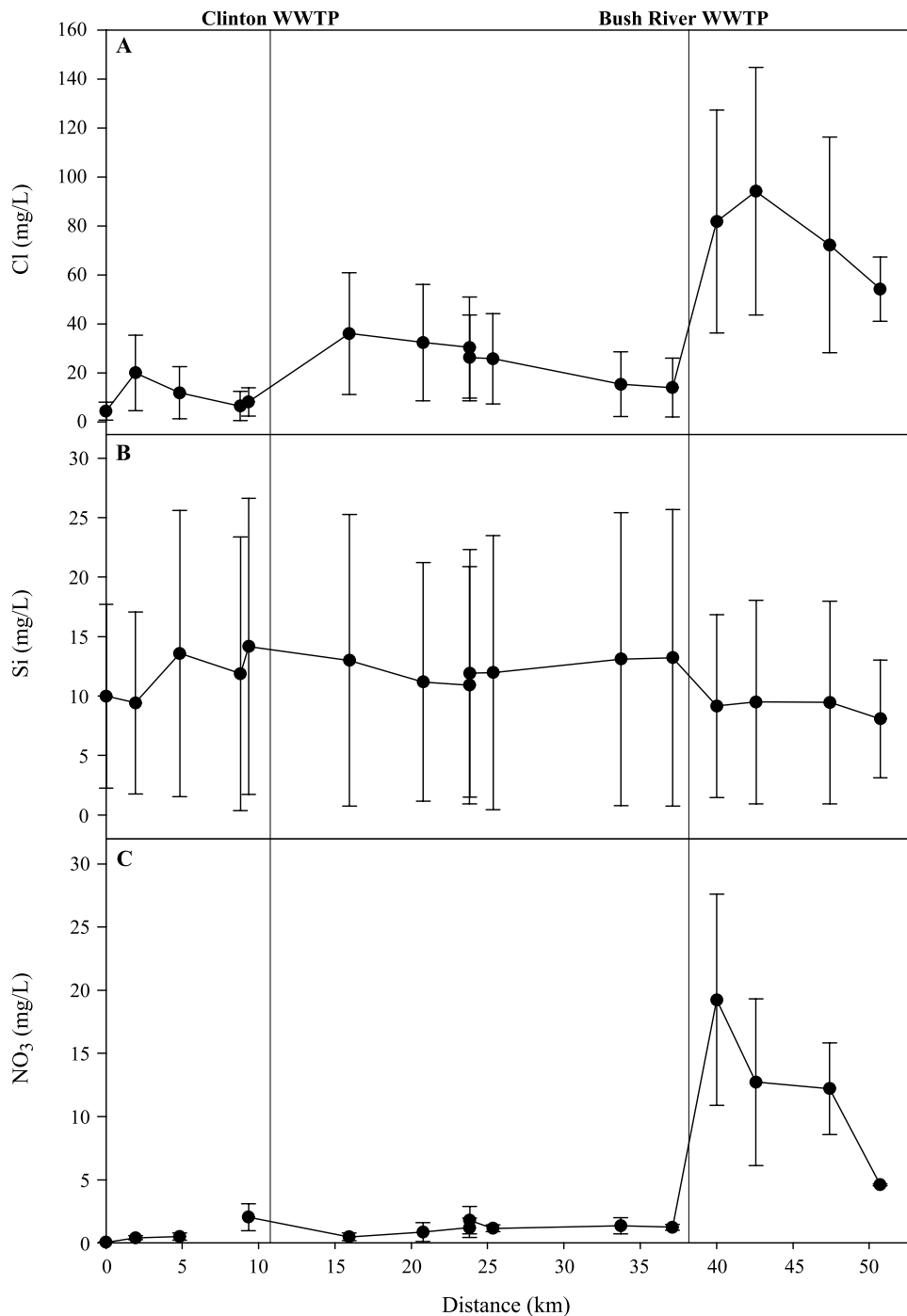
The discharge of effluent into the Bush River does not result in an increase in the concentrations of calcium, magnesium, bicarbonate, DOC, and dissolved silicon,

or a change in pH (Figure 11A). This reflects the similarity between the composition of the effluent and background streams for these solutes. The discharge of effluent from the Bush WWTP has a dilution effect, causing a decrease in the concentrations of calcium, magnesium, dissolved silicon, and DOC (Figure 11B). The decrease in DOC concentration below the Bush WWTP is unexpected given the high concentration in the effluent.

#### Downstream Change in N, S, and P

In contrast, nutrient concentrations did not follow the trends that were expected for downstream of the Clinton WWTP (Figure 10B). The concentrations of TDN, nitrate, phosphate, and sulfate in the Clinton WWTP effluent were much higher than those in the river headwaters and tributary streams; however, concentrations of those solutes did not increase as expected downstream of the Clinton WWTP. Both nitrate and phosphate have concentrations near or below the detection limit upstream of the WWTP, and TDN, nitrate, and sulfate increase in concentration at the sample locality just upstream of the WWTP. The tributary

**Figure 12.** Range of downstream concentrations in the Bush River. Points represent mean concentrations, bars show the range between minimum and maximum values. (A) Solutes, such as chloride, strongly influenced by WWTP effluent discharge show the greatest range in concentration nearest the WWTPs, with the range decreasing downstream. (B) Solutes that have concentrations independent of WWTP effluent discharge, such as silicon, have ranges that show little variation downstream. (C) Nitrate (shown), TDN, sulfate, and phosphate, not only have low concentrations below the Clinton WWTP, but also show little variation in concentration. Gap in data represents samples that have nitrate concentrations below detection. Below the Bush River WWTP, the ranges of concentrations are similar to solutes such as chloride.



entering the river at about 24 km (15 mi) apparently caused an increase in nitrate and sulfate concentrations and a slight decrease in TDN concentrations. Concentrations of TDN, nitrate, sulfate, and phosphate did increase downstream of the Bush WWTP.

#### Temporal Variation

The combination of temporal variations in stream discharge and probable variations in effluent composition

and effluent discharge do have an impact on the temporal variation in stream composition. The solutes that had high concentrations in the WWTP effluent, such as chloride, show the greatest range in concentration just downstream of the WWTPs (Figure 12A). In contrast, solutes that have concentrations in river water comparable to effluent show a consistent range in concentration throughout the length of the river (Figure 12B). Nutrients, such as nitrate, show very little variation in

concentration downstream of the Clinton WWTP, but variation similar to that exhibited by chloride downstream of the Bush River WWTP (Figure 12C).

During the rising limb of a November 2002 storm event, samples were collected at the four localities on the Bush River immediately upstream and downstream of where each WWTP discharged into the river. At the time of sample collection, discharge was more than 40 times greater than the average summer flow. Chloride, sodium, potassium, calcium, and magnesium concentrations were lower than during the summer at all four localities. Sulfate concentration increased from about 3 to nearly 13 mg/L just below the Clinton WWTP and from about 2 to more than 6 mg/L at the Newberry gaging station. The concentration of nitrate, however, remained less than 1 mg/L just downstream of the Clinton WWTP, much lower than expected. Surprisingly, the concentration of nitrate rose to more than 2 mg/L further downstream at the Newberry gaging station. Immediately below the Bush River WWTP, the concentrations of all solutes were higher than at the Newberry gaging station, but were lower than during drought conditions. This pattern suggests that although the Bush River WWTP continued to influence river chemistry, increased runoff reduced that influence.

#### Solute Fluxes

The discharge of effluent increases the fluxes of solutes in the Bush River as measured at the Prosperity gaging station (Table 1). Fluxes predictably increased downstream as discharge increased. Consistent with the observed concentrations, however, fluxes at the Newberry gaging station downstream of the Clinton WWTP were lower than fluxes at the Joanna gaging station upstream of the Clinton WWTP. The nitrate flux was an order of magnitude larger at the Prosperity gaging station than at the Joanna gaging station. The total of 0.19 kg nitrate-N km<sup>-2</sup> day<sup>-1</sup> is in the same range as for the much larger Hudson and Potomac rivers in the northeastern United States (Mayer et al., 2002).

## DISCUSSION

Discharge of effluent into the Bush River from the two WWTPs has a large effect on solute concentrations in the river water. Because of the severe nature of the 1998–2002 drought, WWTP effluent dominated the discharge of the river in 2002, comprising more than 70% of the total flow downstream of the first WWTP (Clinton WWTP) on the river. The observed pattern of

chemical change was similar to that predicted by our point-source dilution model, particularly for the major cations and anions, such as sodium and chloride, for which there was a large difference between the chemical composition of the natural waters and the WWTP effluent. An increase in conductivity indicates that the effluent increased the salinity of the river as well. The observed downstream decrease in solute concentrations suggests that dilution occurs primarily by mixing with tributary streams. Along river reaches between tributary confluences, dilution by ground-water influx into the river probably is minimal. For example, subsurface outflow comprises less than 3% of the total discharge in the central Amazon Basin (Lesack, 1993).

Results from November 2002 supported our expectation that the very low flow conditions observed in the river in 2002 would result in elevated solute concentrations because of a lowered capacity for dilution by river water. Similar variations in solute concentrations with varying river discharge have been observed in the River Kennet in the United Kingdom (Neal et al., 2000).

Changes in concentrations of nitrates, phosphates, and sulfates downstream of the WWTPs differed in some cases from the changes in concentrations of biologically conservative solutes such as chloride and sodium. Similar to sodium and chloride, concentrations of nitrates, phosphates, and sulfates increased markedly downstream of the Bush WWTP (Figure 10A, B). However, nitrate concentrations declined more abruptly than did chloride and sodium concentrations, suggesting biological removal of nitrates occurred in addition to dilution by tributary waters. Downstream of the Clinton WWTP, sodium and chloride concentrations also increased (Figure 10A); however, nitrate and sulfate concentrations declined slightly, and there was no increase in phosphate concentrations (Figure 10B).

We hypothesize that stagnation of river water in the upper reaches of the Bush River during summer 2002 greatly increased the opportunity for plants and/or microbes to remove nitrates, phosphates, and sulfates from river water, thereby preventing an increase in concentrations of those solutes downstream of the Clinton WWTP.

In other river systems, there is evidence that biological uptake increases as river discharge decreases. For example, an increase in the rate of nitrate consumption was observed in the Seine River when river discharge fell below 400 m<sup>3</sup>/s (14,000 ft<sup>3</sup>/s) (Roy et al., 1999). Possible biological processes that would reduce the concentrations of nitrates, phosphates, and sulfates in

the river include assimilatory uptake, denitrification, and sulfate reduction. For example, in the upstream reaches of the Bush River, sand bars were exposed above water level during the drought. Terrestrial plants colonized these sand bars and may have removed some nitrates and phosphates from the river. Additionally, algae or aquatic plants in the river may have taken up nitrates and phosphates, as was observed in the River Thames (Jarvie et al., 2002). The stagnant river conditions also could have led to higher rates of denitrification and possibly sulfate reduction, particularly in the hyporheic zone. Substantial losses of nitrate from the South Platte River in Colorado caused by denitrification have been attributed to exchange of surface water with the hyporheic zone (Sjodin et al., 1997). Kellman and Hillaire (1998) used stable nitrogen isotope analyses to demonstrate that denitrification could account for summer reductions in nitrate concentrations along a small stream-draining agricultural land in Ontario, Canada. Gardner (1981) suggested that sulfate reduction in river flood plains accounted for sulfate retention in rivers of the South Carolina coastal plain. Sulfate reduction may have occurred in sediments in the Bush River because of the extremely low discharge.

More problematic than the lack of increased nitrate, phosphate, and sulfate concentrations downstream of the Clinton WWTP is that the concentrations of sodium and chloride downstream of the Clinton WWTP are too low given the estimated volume of effluent in the river. It is possible for sodium and chloride to act in a nonconservative manner for reasons other than biological activity. For example, sodium is known to participate in cation-exchange reactions (Grasby et al., 1999), but the typical clay-sized mineralogy of kaolinite and gibbsite would preclude the magnitude of the decrease in concentration. Likewise, chloride could possibly participate in anion-exchange reactions on the surfaces of the iron oxyhydroxides found in the river sediments; chloride has been observed to act non-conservatively elsewhere (Viers et al., 2001). Again, however, the magnitude of the decrease in the Bush River cannot be explained by anion exchange. Another possibility is that the discharge of the Clinton WWTP varied much more or was lower than reported.

## CONCLUSIONS

The results of this study provide a model of the impact of wastewater-treatment effluent on the chem-

ical composition of rivers in the piedmont region of the southeastern United States. Piedmont rivers are particularly sensitive to the discharge of WWTP effluent because they are naturally dilute. If changing global climate results in an increased frequency and intensity of drought periods, however, the impact of the discharge of WWTP effluent on piedmont rivers will not be easy to predict, particularly for smaller rivers. The expected response during drought would be a greater impact on the chemical composition of rivers as dilution of effluent decreases. This type of response is seen in the lower Bush River below the Bush River WWTP. In areas that become very shallow and stagnant, however, drought may increase biological removal of nitrates, phosphates, and sulfates from river water. Additionally, sodium and chloride may act in a nonconservative manner during drought conditions, even in areas characterized by ultisols, although the cause of this behavior is not well understood.

## REFERENCES CITED

- Andersen, C. B., 2002, Understanding carbonate equilibria by measuring alkalinity in experimental and natural systems: *Journal of Geoscience Education*, v. 50, p. 389–403.
- Andersen, C. B., K. A. Sargent, J. Wheeler, and S. Wheeler, 2001, Fluvial geochemistry of selected tributary watersheds in the Enoree River Basin, SC: *South Carolina Geology*, v. 43, p. 57–71.
- Berner, E. K., and R. A. Berner, 1996, *Global environment: Water, air, and geochemical cycles*: New Jersey, Prentice Hall, 376 p.
- Camp, W., W. E. Jones, P. R. Miford, S. H. Hearn, and L. E. Aull, 1960, *Soil survey of Newberry County, South Carolina*: Washington, D.C., United States Government Printing Office, U.S. Department of Agriculture, 66 p. + maps.
- Camp, W., J. C. Meltzer, W. H. Fleming, and L. E. Andrew, 1975, *Soil survey of Laurens and Union Counties, South Carolina*: Washington, D.C., United States Government Printing Office, U.S. Department of Agriculture, 66 p. + maps.
- Clark, G. M., D. K. Mueller, and M. A. Mast, 2000, Nutrient concentrations and yields in undeveloped stream basins of the United States: *Journal of the American Water Resources Association*, v. 36, p. 849–867.
- Flintrop, C., B. Hohlmann, T. Jasper, C. Korte, O. G. Polaha, S. Scheele, and J. Veizer, 1996, *Anatomy of pollution: Rivers of North Rhine—Westphalia, Germany*: *American Journal of Science*, v. 296, p. 59–98.
- Freeze, R. A., and J. A. Cherry, 1979, *Groundwater*: New Jersey, Prentice Hall, 604 p.
- Gardner, L. R., 1981, Element mass balances for South Carolina coastal plain watersheds: *Water, Air, and Soil Pollution*, v. 15, p. 271–284.
- Gardner, L. R., 1992, Long-term isovolumetric leaching of aluminum from rocks during weathering: Implications for the genesis of saprolite: *Catena*, v. 19, p. 521–537.
- Grasby, S. E., I. Hutcheon, and L. McFarland, 1999, Surface-water-groundwater interaction and the influence of ion exchange reactions on river chemistry: *Geology*, v. 27, p. 223–226.
- Grosbois, C., P. Negrel, D. Grimaud, and C. Fouillac, 2001, An

- overview of dissolved and suspended matter fluxes in the Loire River Basin: Natural and anthropogenic inputs: *Aquatic Geochemistry*, v. 7, p. 81–105.
- Jarvie, H. P., E. Lycett, C. Neal, and A. Love, 2002, Patterns in nutrient concentrations and biological quality indices across the upper Thames River Basin: *The Science of the Total Environment*, v. 282–283, p. 263–294.
- Kellman, L., and M. C. Hillaire, 1998, Nitrate cycling in streams: Using natural abundances of  $\text{NO}_3\text{-}\delta^{15}\text{N}$  to measure in-situ denitrification: *Biogeochemistry*, v. 43, p. 273–292.
- Lesack, L. F. W., 1993, Export of nutrients and major solutes from a rain forest catchment in the central Amazon basin: *Water Resources Research*, v. 29, p. 743–758.
- Mayer, B. et al., 2002, Sources of nitrate in rivers draining sixteen watersheds in the northeastern U.S.: Isotopic constraints: *Biogeochemistry*, v. 57–58, p. 171–197.
- Meybeck, M., 1998, Man and river interface: Multiple impacts on water and particulates chemistry illustrated in the Seine River Basin: *Hydrobiologia*, v. 373–374, p. 1–20.
- Meybeck, M., and R. Helmer, 1989, The quality of rivers: From pristine stage to global pollution: *Palaeogeography, Palaeoclimatology, Palaeoecology*, v. 75, p. 283–309.
- National Climatic Data Center, 2003, South Carolina climate summary: (<http://lwf.ncdc.noaa.gov/oa/climate/research/cag3/SC.html>) (accessed February 2003).
- Neal, C., H. P. Jarvie, S. M. Howarth, P. G. Whitehead, R. J. Williams, M. Neal, M. Harrow, and H. Wickman, 2000, The water quality of the River Kennet: Initial observations on a lowland chalk stream impacted by sewage inputs and phosphorous remediation: *The Science of the Total Environment*, v. 251, p. 477–495.
- Overstreet, W. C., and H. Bell III, 1965, Geologic map of the crystalline rocks of South Carolina: U.S. Geological Survey Miscellaneous Geologic Investigations Map I-413, 1 sheet, scale 1:250,000.
- Peper, J. D., J. E. Gair, M. P. Foose, T. H. Kress, and C. L. Dicken, 2001, Lithologic units and mineral deposits of the Appalachian Orogen from Maine to Alabama: U.S. Geological Survey, Open-File Report 01-136, CD-ROM.
- Roy, S., J. Gaillardet, and C. J. Allegre, 1999, Geochemistry of dissolved and suspended loads of the Seine River, France: Anthropogenic impact, carbonate and silicate weathering: *Geochimica et Cosmochimica Acta*, v. 63, p. 1277–1292.
- Sjodin, A. L., W. M. Lewis Jr., and J. F. Saunders III, 1997, Denitrification as a component of the nitrogen budget for a large plains river: *Biogeochemistry*, v. 39, p. 327–342.
- Thibert, S., 1994, Exportations naturelles et anthropiques des ions majeurs et des elements nutritifs dans la basin de la Seine: Ph.D. thesis, University of Paris, France, 6 p.
- U.S. Geological Survey, 2003, Real time data for the nation: (<http://waterdata.usgs.gov/nwis/rt>) (accessed March 2003).
- Verbanck, M., J.-P. Vanderborght, and R. Wollast, 1989, Major ion content of urban wastewater: Assessment of per capita loading: *Research Journal of the Water Pollution Control Federation*, v. 61, p. 1722–1728.
- Viers, J., B. Dupre, J.-J. Braun, R. Freydier, S. Greenburg, J. N. Ngoupayou, and L. S. Nkamdjou, 2001, Evidence for non-conservative behaviour of chlorine in humid tropical environments: *Aquatic Geochemistry*, v. 7, p. 127–154.
- Williams, M. R., F. Solange, L. A. Martinelli, L. B. Lara, and P. B. Camargo, 2001, Precipitation and river water chemistry of the Piracicaba River Basin, southeast Brazil: *Journal of Environmental Quality*, v. 30, p. 967–981.
- Zhu, Z., Q. Deng, H. Zhou, T. Ouyang, Y. Kuang, N. Huang, and Y. Qiao, 2002, Water pollution and degradation in Pearl River delta, South China: *Ambio*, v. 31, p. 226–257.