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Urban Influences on Stream Chemistry and Biology in the Big Brushy Creek Watershed, South Carolina

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Abstract Naturally high total dissolved solids and upstream agricultural runoff often mask the influence of urban land cover on stream chemistry and biology. We examined the influence of headwater urbanization on the water chemistry, microbiology, and fish communities of the Big Brushy Creek watershed, a 96 km^2 drainage basin in the piedmont of South Carolina, USA. Concentrations of most major anions and cations (especially nitrate, sulfate, chloride, sodium, potassium, and calcium) were highest in the urban headwaters and decreased downstream. Generally, the highest concentrations of suspended coliform bacteria occurred in the urban headwaters. In contrast, stream habitat quality and the abundance, species richness, and species diversity of fishes did not differ significantly between urban and rural sites. Discharge of wastewater treatment plant effluent at one rural location caused an increase in concentrations of many solutes and possibly the abundance of benthic algae. We hypothesize that atmospheric dry deposition and domestic animal wastes are important sources of stream solutes and of coliform bacteria, respectively, in the urban headwaters. The lack of significant differences in fish abundance and diversity between urban and rural sites may indicate that urban development in the Big Brushy Creek watershed has not yet degraded habitat conditions greatly for stream fishes. Alternatively, agriculture or other land uses may have degraded stream habitat quality throughout the watershed prior to urbanization.

Keywords bacteria · coliform · dissolved carbon · *Escherichia coli* · fish · nutrients · streams · urban land cover · wastewater treatment plant

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1 Introduction

The expansion of urban land areas affects the chemistry and biology of streams in important ways (Paul & Meyer, 2001; Walsh et al., 2005). Many of the deleterious effects of urban growth on streams stem from the alteration of land cover and runoff patterns caused by urbanization within the stream's drainage basin. For example, streams are sensitive to increased impervious surface cover (ISC) in their drainage basins (e.g., parking lots, roads, and buildings). As ISC increases in urban areas, the infiltration of precipitation into soils

decreases, resulting in peak stream discharges that are higher, occur earlier, and have shorter durations than in areas with lower ISC (Paul & Meyer, 2001; Walsh et al., 2005). Marked changes in stream solute concentrations and bacterial abundance may also be associated with urban storm runoff (e.g., McConnell, 1980). Effects of urban land cover on stream chemistry and biology are evident under baseflow conditions, as well.

Compared to streams in rural areas, urban streams often have elevated concentrations of solutes, such as nitrate, sulfate, phosphate, chloride, and base cations, even under baseflow conditions (Hoare, 1984; Smart, Jones, & Sebaugh, 1985; Wahl, McKellar, & Williams, 1997; Wernick, Cook, & Schreier, 1998; Williams, Hopkinson, Rastetter, Vallino, & Claessens, 2005). There are many causes of these elevated concentrations. For example, industrial and wastewater treatment plant (WWTP) point sources add significant amounts of solutes, especially nitrate, sulfate, phosphate, chloride, and sodium, to streams (e.g., Andersen, Lewis, & Sargent, 2004; Cameron, Hall, Veizer, & Krouse, 1995; Ceasar et al., 1976; Flintrop et al., 1996; House & Denison, 1997; Jarvie, Whitton, & Neal, 1998; Roy, Gaillardet, & Allegre, 1999). In some urban residential areas, septic tanks and lawn fertilizers may increase phosphate or nitrate concentrations in streams (e.g., La Valle, 1975; Hoare, 1984; Wernick et al., 1998). Road salt runoff may contribute sodium and chloride to urban streams in colder climates (e.g., Ceasar et al., 1976; Douglas, Chamberlain, & Blum, 2002; Williams et al., 2005). Elevated dry deposition (including dust, nitrogen oxides, and sulfur oxides) in urban areas may enhance elemental fluxes to soils both directly and indirectly (Chiwa, Kim, & Sakugawa, 2003; Lovett et al., 2000). Finally, the lower biomass of vegetation in urban areas may reduce nutrient retention in urban watersheds and reduce the supply of dissolved organic carbon to urban streams (Wahl et al., 1997).

The physical and chemical changes associated with urban areas in turn can have important effects on stream organisms and communities. Negative effects of urbanization include increased sedimentation and habitat instability, reduced habitat complexity, inputs of various toxins (e.g., oils, heavy metals, pesticides), and increased fluctuations in water temperature associated with removal of riparian vegetation (Paul & Meyer, 2001). As a result of these changes, diversity of sensitive stream organisms, such as many invertebrates and fish, declines in urban streams (Paul & Meyer, 2001). Increased nutrient loading to streams could stimulate algal (and therefore secondary) productivity, although this response depends in part on other factors such as shading by riparian vegetation, turbidity, stability of streambed sediments, and pollutant levels (Paul & Meyer, 2001). Finally, bacterial abundances, especially of coliform bacteria, can be high in urban streams, possibly due to leaking or overflowing sanitary sewers (Duda, Lenat, & Penrose, 1982), runoff from impervious surfaces and lawns (Young & Thackston, 1999), or discharges from storm sewer drains (Frenzel & Couvillion, 2002). Although often peaking during storm events, bacterial abundances also may be high under baseflow conditions (Duda et al., 1982; Young & Thackston, 1999).

Clearly identifying the effects of urban land cover on streams can be difficult in the presence of other anthropogenic and certain natural influences. In particular, agricultural land use around the headwaters of a river can significantly modify stream chemistry upstream of an urban area, as is the case in the Connecticut (Douglas et al., 2002), Great Ouse (Neal et al., 2000), Seine (Roy et al., 1999), upper Rhine (Flintrop et al., 1996), and Pearl (Zhu et al., 2002) Rivers. As a result, the urban signature, sometimes referred to as communal input (Roy et al., 1999), cannot be detected directly in these cases. In addition, streams in watersheds with carbonate rocks naturally have high concentrations of many solutes, especially calcium, magnesium, and bicarbonate (Elwood & Turner, 1989; Smart et al., 1985). As a result, high "background" solute concentrations may mask the contributions of urban sources. Additionally, watersheds near the ocean have increased sea salt deposition, and streams in those regions have high concentrations of sodium, chloride, and other solutes (Ceasar et al., 1976; Douglas et al., 2002; Flintrop et al., 1996). This complexity requires the use of methods such as inverse modeling to identify the urban signature (e.g., Roy et al., 1999).

In contrast to other regions, the piedmont of the southeastern United States is an excellent region in which to test for the influences of urbanization on stream chemistry and biology. Piedmont streams naturally have very low solute concentrations because of the low solubility of minerals in the bedrock and soils (e.g., Andersen, Sargent, J. Wheeler, & S. Wheeler, 2001). Atmospheric input of sea salts likely is low because

the upper piedmont is more than 250 km from the coast, and sea salt inputs decline exponentially with distance from the ocean (Stallard & Edmond, 1981). In addition, because of the mild winter season of the southeastern United States, road de-icing salts are used infrequently and are unlikely to affect stream chemistry. In addition, urban areas commonly are located in the headwaters of piedmont watersheds, as opposed to downstream of rural areas. As a result, determination of an urban signature in piedmont streams should be considerably easier than in regions with streams of higher natural salinity and agricultural headwaters.

Our objective was to determine if the urbanization of headwater streams lacking point source inputs leads to a distinct chemical and biological signature associated with urban land cover. We examined spatial variations in solute chemistry, the abundance of suspended bacteria, and fish abundance and diversity in the Big Brushy Creek watershed, a predominantly rural watershed in northwestern South Carolina with headwaters in a small but rapidly growing urban area. Additionally, we compared the impact of urbanization to the impact of a WWTP point source input, including an examination of how nutrient input affected benthic algal productivity.

2 Materials and Methods

2.1 Study Area and Sampling Sites

We studied Big Brushy Creek, a fourth order stream that drains a 96 km^2 watershed within the larger Saluda River basin (Fig. 1). Big Brushy Creek has two major branches with headwaters in the southeastern portion of Easley (Fig. 1), a city with a population of approximately 18,500 (United States Bureau of Census, 2002). Recent population growth in the city has been rapid, with a 17% increase in population during 1990–2000 (United States Bureau of Census, 2002). According to the South Carolina Department of Health and Environmental Control (2003), major land cover types in the watershed are forest (49%), agriculture/pasture (30%), and urban (20%). Approximately 16% of the watershed lies within the city limits of Easley (S. Muthukrishnan, personal communication) with most of the urbanization occurring in the headwater region. The area within the city limits, which includes both residential and commercial land cover, lacks significant point source inputs and is served by sewer. One WWTP is located downstream of the urbanized region. The urban land cover grades into rural land cover in the downstream direction. Our observations suggest that most of the agriculture/pasture land cover is pasture rather than row crop agriculture.

The Easley area has a warm temperate climate with average monthly maximum air temperatures of 11–32° C and average annual precipitation of about 140 cm (data from Pickens, South Carolina, 1951–2005; Southeast Regional Climate Center, 2006). Seasonal variation in precipitation is relatively low. For example, precipitation during autumn (September–November), the driest season, is on average about 18% lower than during winter (December–February), the rainiest season (National Climatic Data Center, 2002). During June–July 2003, the main period of our study, monthly precipitation totals for the nearby city of Pickens, South Carolina, (~11.5 km from Easley) were 13 cm for June and 27 cm for July (National Climatic Data Center, 2004). These totals were above the average of 12 cm for each of those months (Southeast Regional Climate Center, 2006).

Granites and gneisses are the predominant rocks in the watershed (Overstreet & Bell, 1965). The dominant soils are ultisols (Byrd, 1972; Herren, 1979), which are underlain by sandy loam or sandy clay loam saprolites (Byrd, 1972). The stream substrate varied from bedrock to sand, and canopy cover varied from dense forest cover to completely open (e.g., along pastures, near roads, and in residential areas).

Of a total of 23 sampling sites, seven occurred within the city limits of Easley and were considered "urban" (Fig. 1). The two uppermost sites on each branch of the river (18, 19, 20, 21) were located in residential areas. In those areas, the stream channels were bordered by grass lawns. One sampling site on the eastern branch of the stream (16) was immediately downstream of a golf course (Fig. 1). Further downstream of the golf course, the Middle Branch WWTP discharged effluent directly into the stream (Fig. 1). We considered the remaining sample sites "rural." Land cover near those sites was a mixture of forest, pasture, residences, and small commercial areas. Riparian zones in the rural areas generally were forested.

To assess the influence of the WWTP on river discharge, we measured river discharge at site 14 (upstream of the WWTP) on 16 July 2003, using velocity

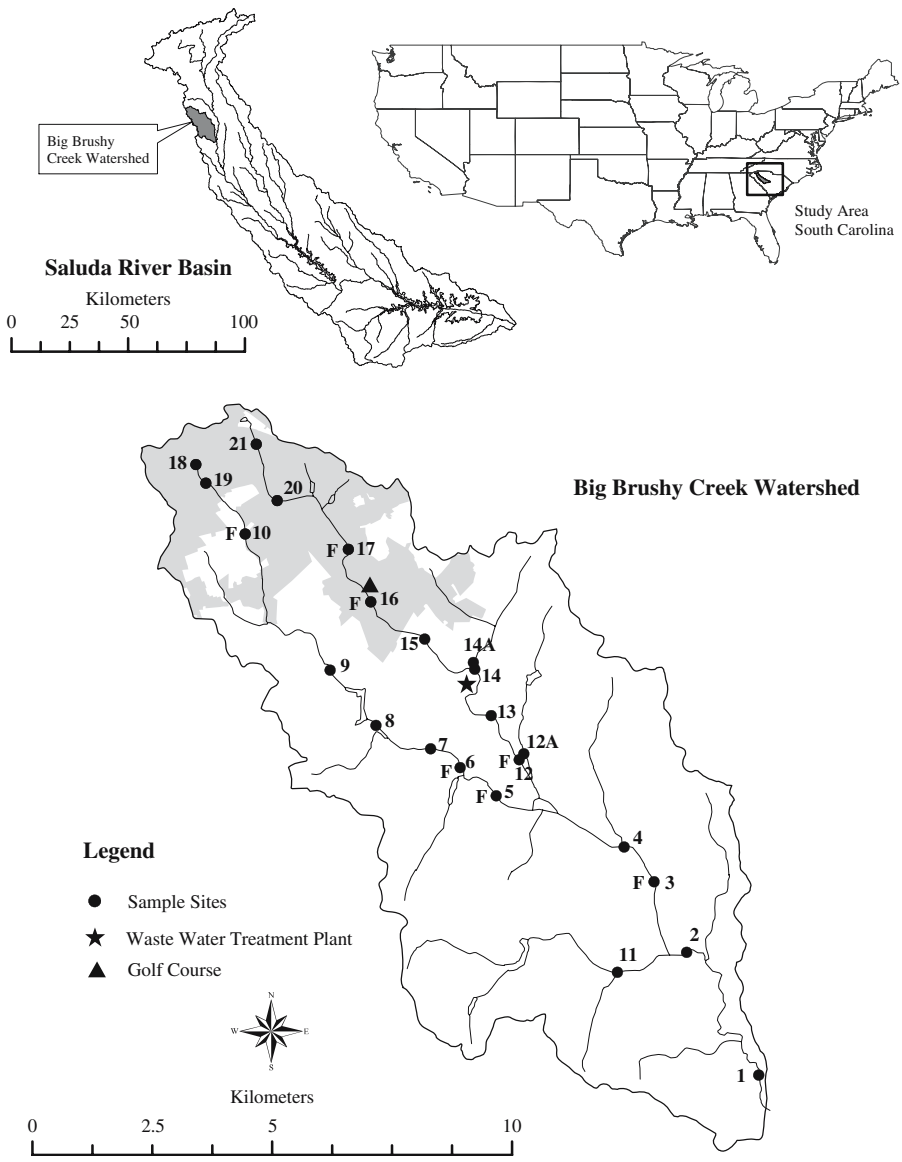

Fig. 1 Location of the Big Brushy Creek watershed in the Saluda River basin, South Carolina, and sampling locations within the watershed. The *gray shaded area within the watershed* represents land within the city limits of Easley. Water samples were collected at locations indicated by *black circles*. Fish collection sites are indicated by *F*

measurements obtained with a bucket wheel Mini Current Meter and channel cross-sectional area. The effluent discharge rate was obtained from the WWTP operators.

2.2 Water Sample Collection and Processing

We collected grab samples primarily from June 6 to July 31, 2003. Of the 23 sites, 21 were sampled from three to six times each during the summer sampling period. The two remaining sites (12A and 14A), which were on tributaries of the eastern branch, were sampled only once each. In addition, a sample of the WWTP effluent was collected on July 16, 2003. On October 5, 2003, we re-sampled the two sites immediately upstream (14 and 15) and one site closest downstream (13) of the WWTP. Samples were collected during baseflow conditions, with the exception of the June 6 sampling, which occurred one day after a rain event.

Water temperature, pH, conductivity, and dissolved oxygen were measured in the field at all sites with Fisher Scientific AP62 Accumet pH meters, YSI 30 salinity/conductivity meters, and YSI 55 dissolved oxygen meters. Samples for chemical analysis were collected in pre-cleaned, high-density polyethylene bottles that were rinsed three times with river water before sample collection. An additional sample was

collected for turbidity analysis. A sample for bacterial analysis was collected using a sterile polystyrene bottle. Samples were stored in the dark and on ice during transport to the laboratory. Samples for chemical analysis were filtered in the laboratory through 0.45 μm membrane filters using positive pressure. An aliquot from each sample was preserved with trace metal-grade nitric acid for cation analysis, a second aliquot was preserved with trace metal-grade sulfuric acid for total dissolved nitrogen (TDN) analysis, and a third aliquot was left unpreserved for dissolved organic carbon (DOC), alkalinity, ammonium (NH_4^+), and anion analyses. These aliquots were refrigerated until analysis. Turbidity was measured the same day of collection using a LaMotte 2020 turbidity meter.

2.3 Chemical Analyses

We measured cation (Na^+, K^+, Mg^{2+}, Ca^{2+}) and dissolved silicon (as Si^{4+}) concentrations using a Varian 2000 ICP-AES spectrophotometer and anion (F^-, Cl^-, Br^-, $H_2PO_4^-$, NO_2^-, NO_3^-, SO_4^{2-}) concentrations using a Dionex 120 ion chromatograph. The detection limits for anions were approximately 50 μg/l, with the exception of $H_2PO_4^-$ (100 μg/l) and F^- (20 μg/l). Alkalinity was measured using the Gran titration method, and all alkalinity was assumed to be in the form of bicarbonate (HCO_3^-) for charge balance purposes. This assumption holds well for piedmont stream waters (Andersen, 2002). Analytical accuracy was checked using the charge balance method of Freeze and Cherry (1979). Charge balance errors including nitrate were <5% for 90% of samples, and no sample had an error >10%.

Total dissolved nitrogen concentrations were measured with an O. I. Analytical Flow Solution IV autoanalyser using a cadmium reduction colorimetric method following UV-persulfate digestion. The detection limit for TDN was 0.10 mg N/l. We estimated dissolved organic nitrogen (DON) concentrations by subtracting dissolved inorganic N (DIN, the sum of NO_2–N, NO_3–N, and NH_4–N) concentrations from TDN concentrations. Ammonium concentrations, determined using Protocol B of Holmes, Aminot, Kérouel, Hooker, and Peterson (1999) on a Turner Designs 10-AU fluorometer, were only available for samples from sites 2, 4, 6, 7, and 10 on July 7, 2003. The range of concentrations from those samples was 0.06 to 0.09 mg/l (mean=0.07 mg/l), which is comparable to concentrations from streams in similar watersheds in the region (G. P. Lewis and C. B. Andersen, unpublished data). Therefore, we used the mean NH_4^+ concentration of 0.07 mg/l to determine DON concentrations for samples lacking measured NH_4^+ concentrations.

We calculated total dissolved carbon (TDC) concentrations as the sum of carbon from dissolved organic carbon (DOC) and dissolved inorganic carbon (DIC). We measured DOC concentrations with a Tekmar–Dohrman Phoenix 8000 total organic carbon analyser using a UV-persulfate digestion method. Dissolved inorganic carbon consisted of HCO_3^- and dissolved carbon dioxide ($CO_{2(aq)}$). To estimate $CO_{2(aq)}$, we calculated the carbonate species distribution ($CO_{2(aq)}$, HCO_3^-, CO_3^{2-}) for each sample using a thermodynamic method (Andersen, 2002). The equation for the calculation of the partial pressure of carbon dioxide (PCO_2), which uses measurements of water temperature, pH, and HCO_3^-, did not need to be modified to account for the dissolution of calcite (Neal, House, & Down, 1998) because the Big Brushy Creek watershed lacks carbonate rocks. Equilibrium constants were calculated using the equations of Plummer and Busenburg (1982), and activity coefficients were calculated using the extended Debye–Huckel equation. The ratio of $PCO_{2(aq)}$ in river water to PCO_2 in the atmosphere indicates the degree of CO_2 supersaturation in the river relative to the atmosphere (Huh, Tsoi, Zaitsev, & Edmond, 1998; Pinol & Avila, 1992). We refer hereafter to this ratio as PCO_2 saturation.

2.4 Bacterial Analyses

Concentrations of total coliform bacteria, *Escherichia coli*, and total heterotrophic bacteria suspended in stream water were estimated using IDEXX™ test kits (IDEXX Laboratories, Inc., Westbrook, Maine), which are approved by US Environmental Protection Agency. Colilert® and Colilert®-18 were used to test for total coliforms and *E. coli* (Eckner, 1998). The Colilert® dehydrated medium contains the nutrient substrate o-nitrophenyl β-D-galactopyranoside, which is metabolized by β-galactosidase, a characteristic enzyme of coliforms, and 4-methyl-unbelliferyl β-D-glucuronide, which is metabolized by β-glucuronidase, a characteristic enzyme of *E. coli*. A 1:50 dilution was made for each water sample using sterile double-distilled water, and the Colilert® dehydrated medium was added

to 100 ml of the diluted water sample. After the medium was completely dissolved, the mixture was poured into a sterile Quanti-Tray®/2000 tray and heat sealed. All the trays were incubated at 35°C for 24 h (Colilert® test kit) or 18 hr (Colilert®-18 test kit). The number of yellow wells in the tray was converted into the most probable number (MPN) of coliforms using the MPN table provided by the manufacturer. The number of the fluorescing wells (366 nm) in the tray was converted into the MPN of *E. coli* using the same MPN table.

SimPlate for HPC (IDEXX Laboratories, Inc.) was used to test for total heterotrophic bacteria (Jackson et al., 2000). The dehydrated medium contains several unique enzyme substrates that target the common enzymes of waterborne bacteria. A 1:50 dilution was made for each water sample using sterile double-distilled water. The dehydrated medium was added to 1 ml of the diluted water sample plus 9 ml of sterile double-distilled water. After the medium was completely dissolved, the mixture was poured onto the center of the SimPlate, followed by gentle swirling to distribute the sample into all the wells. The plate was tipped at 90° to drain excess liquid into the absorbent pad then incubated upside down to prevent condensation at 35°C for 48 h. The number of the fluorescing wells (366 nm) in the plate was converted into the MPN of heterotrophic bacteria using the MPN table provided by the manufacturer.

2.5 Fish Sampling

Between June 6 and June 11, 2003, fish were collected at seven of the water sampling sites (three urban, four rural) where stream depth permitted use of a backpack electrofisher (Fig. 1). Each of these sites was sampled once by using a Smith-Root© backpack electrofisher, a 4′×10′×1/8″ seine, and long-handled dip nets. Fishing time was standardized by collecting for 480 s of shocking time at each site. All available in-stream habitats were sampled at each site. We preserved the fishes collected in 10% formalin, transferred them to 70% ethanol, and then sorted and identified them to species in the laboratory. We calculated species richness, Simpson's diversity (using the inverse Simpson's index; Gurevitch, Scheiner, & Fox, 2002), and Shannon–Weiner diversity for each sample site. In-stream habitat quality was assessed at each site using a standardized metric, the Qualitative Habitat Evaluation Index (QHEI; Burton & Pitt, 2001). The habitat was scored for substrate, in-stream cover, channel morphology, riparian zone and bank erosion, and pool/glide and riffle/run quality. These individual metrics were summed to generate an overall habitat score.

2.6 Estimation of Algal Abundance

For sample sites near the WWTP, algal abundance was estimated by measuring chlorophyll *a* on glazed ceramic tiles (each 23 cm^2) incubated in the stream. Tiles were glued with non-toxic aquarium sealer to nylon window screen and anchored in the stream on rock-filled plastic baskets (eight tiles per basket). Baskets were placed onto the streambed so that the surfaces of the tiles were parallel to the water flow. On September 6, 2003, five baskets were placed at one site downstream of the WWTP (site 13) and two sites immediately upstream of the WWTP (sites 14 and 15) for a total of 15 baskets. By the collection date (October 5, 2003) eight of the baskets had been washed away by storm flow, leaving two baskets each at sites 13 and 14 and three baskets at site 15. In the field, the biofilms on the tiles from each remaining basket were scraped with a razor blade onto Whatman GF/F glass fiber filters, and a hand pump was used to draw water through each filter. Samples were transported to the laboratory in the dark on ice and then stored frozen (<0°C) until analysis two days later. Standard methods for the extraction and spectrophotometric analysis of chlorophyll *a* were used (APHA, 1995). Chlorophyll *a* concentrations were corrected for pheophytin *a* concentrations by acidification (APHA, 1995). For statistical comparisons of algal chlorophyll among sites, the chlorophyll from all tiles in a basket was used as the statistical unit.

2.7 Statistical Analyses

Solute and bacteria concentrations that were below the detection limit were treated as one-half the detection limit for statistical purposes. Because DON concentrations were calculated by difference of TDN and DIN, some concentrations had slightly negative values. We made no adjustments to these negative values for conducting statistical tests. Independent samples *t*-tests were used to compare solute concentrations, physical parameters, and bacteria concentrations at urban and rural sites. Sites downstream of the WWTP (13, 12, 4, 3, 2, 1) were excluded from these analyses because of possible influences of the WWTP effluent. However,

sites on tributaries unaffected by the WWTP (11, 12A, 14A) were included. Degrees of freedom for *t*-tests were adjusted as necessary if variances were not homogeneous according to Levene's tests. For comparisons of physical, chemical, and bacterial parameters from sites immediately upstream and downstream of the WWTP, we used paired *t*-tests or, in the case of $H_2PO_4^-$, a Wilcoxon Signed Ranks test. Concentrations of F^-, Br^-, and NO_2^- often were near or below detection. Therefore, we did not conduct any statistical tests on those data. Fish species richness, Simpson's diversity, Shannon–Weiner diversity, and abundance at urban (sites 10, 16, and 17) and rural (3, 5, 6, 12) sites were compared using independent samples *t*-tests. We considered the results of statistical tests to be statistically significant if $p \leq 0.05$. We used SPSS 12.0 for Windows to conduct all statistical tests.

3 Results

3.1 Water Chemistry and Related Variables

Stream water in the Big Brushy Creek watershed was chemically dilute, generally with a total cationic charge of 350–1,050 μeq/l and conductivity <100 μS/cm (Fig. 2). The stream water showed a mixed cation-bicarbonate composition (Fig. 3). The dilute nature of the stream water and the proportional chemical composition are consistent with piedmont streams elsewhere

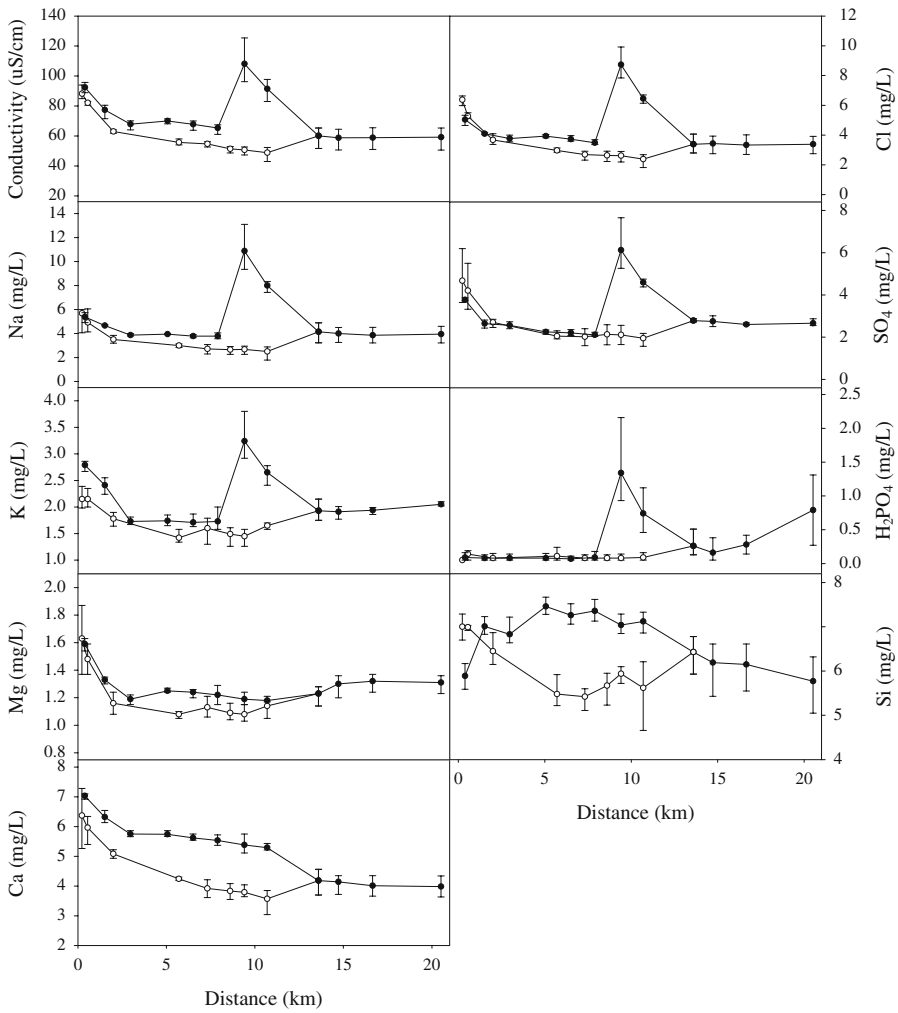

Fig. 2 Variations in conductivity and solute concentrations with distance from headwaters in Big Brushy Creek. *Circles* represent mean values from three sampling dates between June 16 and July 9, 2003. *Filled circles* represent sites from the eastern branch of the river and from the main channel. *Open circles* represent sites from the western branch of the river. *Error bars* represent ranges. The Middle Branch Wastewater Treatment Plant was located at a distance of ~8.5 km along the eastern branch of the river

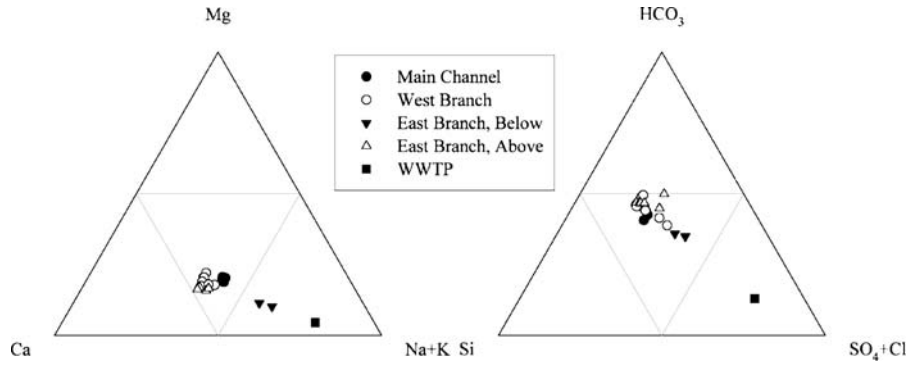

Fig. 3 Ternary plots of solute proportions in stream water from Big Brushy Creek and in effluent from the Middle Branch Wastewater Treatment Plant (WWTP). *Symbols for stream water* represent mean values of samples from multiple dates in June–July 2003. The *symbol for WWTP effluent* represents data from a single sample collected in July 2003

in the southeastern United States (e.g., Andersen et al., 2001; Lenat & Crawford, 1994). Solute proportions were similar among stream sites with the exception of the two sites immediately downstream from the WWTP (Fig. 3).

Conductivity and concentrations of Na^+, Cl^-, TDN, NO_3^-, K^+, SO_4^{2-}, Ca^{2+}, and Mg^{2+} were highest in the urban headwaters and decreased downstream (Figs. 2 and 4). With the exception of Mg^{2+}, mean values were significantly higher at urban than rural sites on at least three sample dates (Figs. 2 and 4; Table 1). Nitrate concentrations differed the most between urban and rural sites. The mean NO_3^- concentration for urban sites was as high as 2.6 times the mean concentration for rural sites (Table 1). Mean concentrations of dissolved O_2, Si^{4+}, Mg^{2+}, and HCO_3^- tended to be higher at urban than rural sites, but the differences were significant on only one or two dates (Figs. 2, 5; Table 1). Mean DOC concentrations and turbidity tended to be lower at urban than rural sites, but the differences were significant on only one or two dates (Fig. 5; Table 1). For $H_2PO_4^-$, pH, DON, PCO_2 saturation, and TDC, there were no significant differences between means for urban and rural sites on any date (Figs. 2, 4, and 5).

The eastern and western branches of Big Brushy Creek exhibited differences in concentrations of some solutes (Figs. 2, 4, and 5), although solute proportions were similar in most cases (Fig. 3). The eastern branch generally had higher pH, conductivity, and concentrations of HCO_3^-, Cl^-, Ca^{2+}, Si^{4+}, K^+, Na^+, and Mg^{2+} (Figs. 2 and 5). The western branch generally had higher PCO_2 saturation than the eastern branch (Fig. 5). The western branch and the main channel typically had higher proportions of dissolved CO_2 than the eastern branch, regardless of WWTP input (Fig. 6). The two branches had similar DOC concentrations (Fig. 5).

The chemical and physical properties of the WWTP effluent differed from the composition of stream water upstream of the WWTP. Compared to stream water immediately upstream (site 14), the effluent had higher concentrations of solutes except Si^{4+}, HCO_3^-, and DOC (Table 2). Magnesium and NO_2^- concentrations in the effluent were only marginally greater than concentrations in stream water. Proportionately, the effluent had higher proportions of $Na^+ + K^+$ and $SO_4^{2-} + Cl^-$ (Fig. 3). In addition, the effluent was less turbid than stream water (Table 2).

Stream chemistry changed significantly downstream of the WWTP on the eastern branch of the river. Among all sampling sites in the watershed, the highest conductivity and mean concentrations of Na^+, K^+, Cl^-, $H_2PO_4^-$, NO_3^-, SO_4^-, TDN, and DON occurred at the two sites downstream of the WWTP (Figs. 2 and 4). Conductivity, pH, and concentrations of Na^+, K^+, Cl^-, $H_2PO_4^-$, NO_3^-, SO_4^-, TDN, DON, and DOC were significantly higher downstream than upstream of the WWTP, though in the case of pH and DOC these differences were small (Figs. 2, 4, and 5). In addition, temporal variations in conductivity and concentrations of Na^+, Cl^-, TDN, NO_3^-, $H_2PO_4^-$, K^+, and SO_4^- were greater at the site (13) immediately downstream of the WWTP than at most other sites in the watershed (Figs. 2 and 4). This was especially evident in $H_2PO_4^-$ concentrations. Carbon dioxide saturation was significantly lower downstream than upstream of the WWTP (Fig. 5). However, the differences in concentrations of Ca^{2+}, Mg^{2+}, Si^{4+}, HCO_3^-, and TDC (Figs. 2 and 5), as well as differences in water temperature, dissolved O_2, and turbidity (data not shown), were not significant. The mixing of

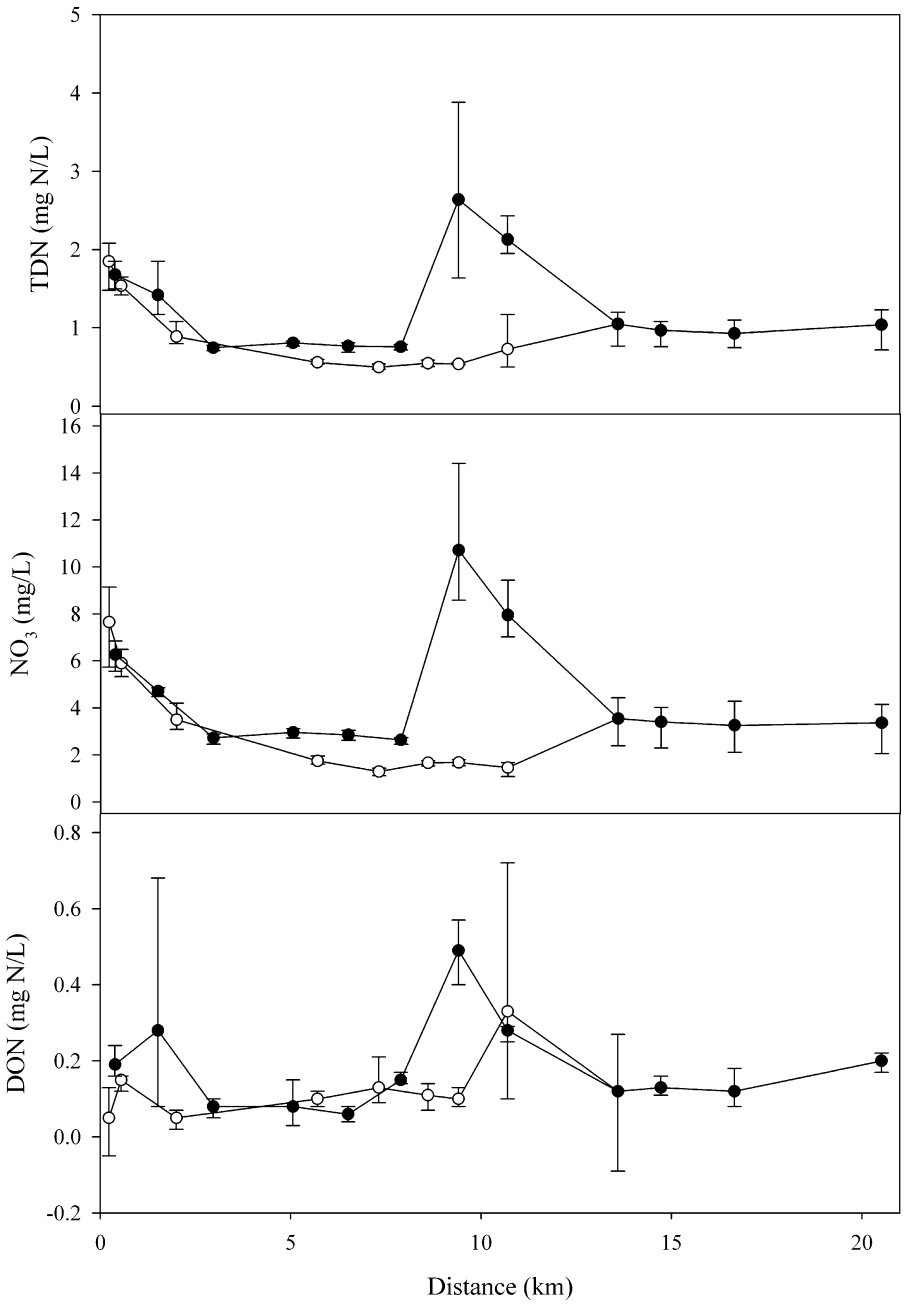

Fig. 4 Variations in nitrogen concentrations with distance from headwaters to mouth in Big Brushy Creek. *Circles* represent mean values from three sampling dates between June 16 and July 9, 2003. *Filled circles* represent sites from the eastern branch of the river and from the main channel. *Open circles* represent sites from the western branch of the river. *Error bars* represent ranges. Negative values for dissolved organic nitrogen (DON) resulted when dissolved inorganic nitrogen concentrations slightly exceeded total dissolved nitrogen (TDN) concentrations. The Middle Branch Wastewater Treatment Plant was located at a distance of ~8.5 km along the eastern branch of the river

the eastern and western branches of the river essentially erased the signature of the WWTP in terms of the proportions of major cations and anions (Fig. 3). Concentrations of Na^+, K^+, Cl^-, SO_4^-, NO_3^-, TDN, and $H_2PO_4^-$ in the main channel (sites 1–4) were intermediate between concentrations in the two branches (Figs. 2 and 4), reflecting the mixing of the branches.

The release of effluent from the WWTP markedly increased discharge of the eastern branch, at least in mid-July. On 16 July 2003, discharge at site 14 was 0.19 m^3/s. Effluent discharge on the same day was 0.08 m^3/s. Therefore, effluent would have increased river flow by ~40%, accounting for the change in chemical composition.

Table 1 Selected physical and chemical properties of stream water from urban and rural sites in the Big Brushy Creek watershed, South Carolina, June–July 2003

Variable	Land cover	June 9–11	June 16–18	June 23–25	July 7–9
Dissolved O_2	Urban	8.2±0.1	7.9±0.3	8.2±0.1	7.9±0.16
	Rural	7.2±0.2*	6.8±0.4	8.1±0.2	7.4±0.16
Conductivity (μS/cm)	Urban	65.0±1.1	77.3±4.0	75.0±3.9	79.7±4.6
	Rural	55.4±1.6*	58.9±2.5*	52.7±2.5*	59.9±2.8*
Turbidity (NTU)	Urban	5.7±0.8	6.1±1.3	7.7±0.8	9.4±2.3
	Rural	9.7±1.2	12.6±2.7	19.1±2.8*	22.2±3.4*
Na^+	Urban	3.82±0.05	4.21±0.23	5.01±0.46	4.48±0.29
	Rural	3.11±0.14*	3.08±0.13*	2.72±0.26*	3.29±0.16*
K^+	Urban	1.71±0.03	2.04±0.16	2.05±0.16	2.23±0.15
	Rural	1.35±0.08*	1.39±0.07*	1.62±0.06*	1.71±0.05*
Ca^{2+}	Urban	5.67±0.12	6.12±0.26	5.81±0.25	6.18±0.29
	Rural	4.43±0.25*	4.33±0.31*	4.12±0.32*	4.41±0.28*
Mg^{2+}	Urban	1.21±0.03	1.36±0.08	1.34±0.05	1.43±0.10
	Rural	1.20±0.05	1.17±0.07	1.13±0.03*	1.24±0.13
Si^{4+}	Urban	6.94±0.18	6.70±0.22	6.98±0.18	6.73±0.20
	Rural	6.34±0.23	6.28±0.25	5.85±0.40*	6.18±0.25
HCO_3^-	Urban	21.4±1.2	21.6±0.8	21.9±0.9	22.7±1.2
	Rural	19.0±1.0	19.6±0.6	17.6±1.0*	18.8±0.8*
Cl^-	Urban	3.97±0.05	4.46±0.41	4.66±0.34	4.65±0.41
	Rural	2.99±0.15*	3.00±0.11*	2.61±0.23*	3.05±0.17*
NO_3^-	Urban	3.12±0.27	4.61±0.77	4.70±0.54	5.14±0.88
	Rural	2.18±0.25*	2.02±0.21*	1.81±0.24*	2.14±0.25*
SO_4^{2-}	Urban	2.35±0.11	2.99±0.23	3.60±0.62	3.18±0.26
	Rural	1.80±0.08*	1.75±0.10*	2.20±0.10	2.14±0.07*
TDN	Urban	0.79±0.08	1.22±0.18	1.32±0.17	1.28±0.20
	Rural	0.68±0.05	0.71±0.08*	0.64±0.05*	0.64±0.06
DOC	Urban	1.3±0.2	5.3±0.2	5.1±0.1	5.6±0.2
	Rural	2.0±0.2	5.5±0.3	6.4±0.4*	5.9±0.2

Values are means ± SE

Sample sizes were 3 urban and 10 rural sites during June 9–11 and 7 urban and 8 rural sites during all other intervals.

Units of measurement are mg/l except as noted.

*indicates significant difference between mean urban and rural values for that variable on that date (independent samples *t*-test, $p < 0.05$).

3.2 Bacterial Abundance

Mean concentrations of total coliforms were up to five times higher and mean concentrations of *E. coli* were up to six times higher at urban than rural sites (Table 3). Although this trend was consistent over time, there was considerable temporal variation in concentrations at some sites (Fig. 7), and concentrations at urban and rural sites did not differ significantly in three of the eight comparisons (Table 3). Mean concentrations of total heterotrophic bacteria did not differ significantly between urban and rural sites on any date ($p>0.20$). There also were no significant differences in bacterial concentrations upstream and downstream of the WWTP ($p>0.19$).

3.3 Fish Abundance and Diversity

A total of 344 fish belonging to 16 species were collected in our samples. Nearly all fish (94%) belonged to species in either the Cyprinidae ($n=200$) or Centrarchidae ($n=124$). The three most abundant species were the centrarchid *Lepomis macrochirus* Rafinesque ($n=83$) and the cyprinids *Nocomis leptocephalus* Girard ($n=81$) and *Notropis lutipinnis* Jordan and Brayton ($n=70$).

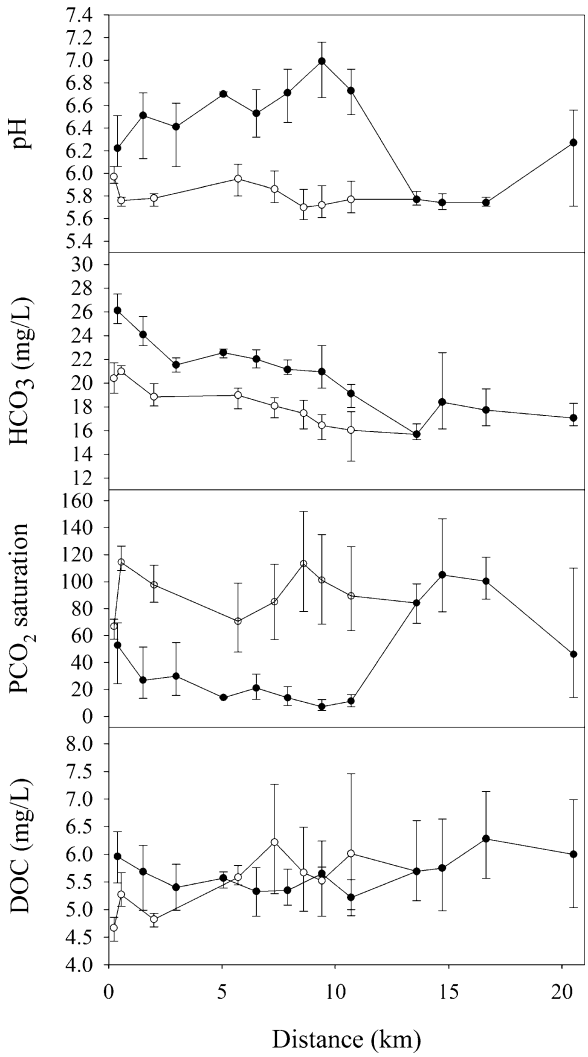

Fig. 5 Variations in pH and dissolved carbon concentrations with distance from headwaters in Big Brushy Creek. *Circles* represent mean values from three sampling dates between June 16 and July 9, 2003. *Filled circles* represent sites from the eastern branch of the river and from the main channel. *Open circles* represent sites from the western branch of the river. *Error bars* represent ranges. The Middle Branch Wastewater Treatment Plant was located at a distance of ~8.5 km along the eastern branch of the river

Fish abundance did not differ significantly (p=0.98) between rural and urban sites (rural mean=48.7, SE=16.5; urban mean=49.7, SE=21.2). Compared to urban sites, rural sites had slightly higher species richness (rural mean=7.5, SE=2.1; urban mean=5.7, SE=1.3), Simpson's diversity (rural mean=4.0, SE=1.1; urban mean=2.8, SE=0.5), and Shannon–Weiner diversity (rural mean=0.65, SE=0.14; urban mean=0.52, SE=0.09), although these differences were not statistically significant (p>0.34). A total of 14 species were found among all rural sites, whereas nine species were found among the urban sites. Seven species were found only in rural sites: *Ameiurus platycephalus* Girard, *Cyprinella chloristia* Jordan and Brayton, *C. nivea* Mayden, *Etheostoma thalassinum* Jordan and Brayton, *Gambusia holbrooki* Girard, *Hybopsis zanema* Gilbert, and *Notropis scepticus* Jordan and Brayton. Two species were found only at urban sites: *Clinostomus funduloides* Girard and *Semotilus atromaculatus* Mitchill. Mean QHEI scores for urban (56.3, SE=3.7) and rural (53.3, SE=5.7) sites did not differ significantly (p=0.70).

3.4 Algal Abundance

Mean algal chlorophyll *a* at site 13 downstream of the WWTP (0.25 μg/cm^2; SE=0.0009) was approximately 12 times higher than the mean chlorophyll upstream at site 14 (0.02 μg/cm^2; SE=0.006). However, algal chlorophyll was highly variable at site 15 further upstream from the WWTP (mean=0.10 μg/cm^2; SE=0.09). As a result, chlorophyll *a* did not differ significantly among the three sites (Kruskal-Wallis test, p=0.51).

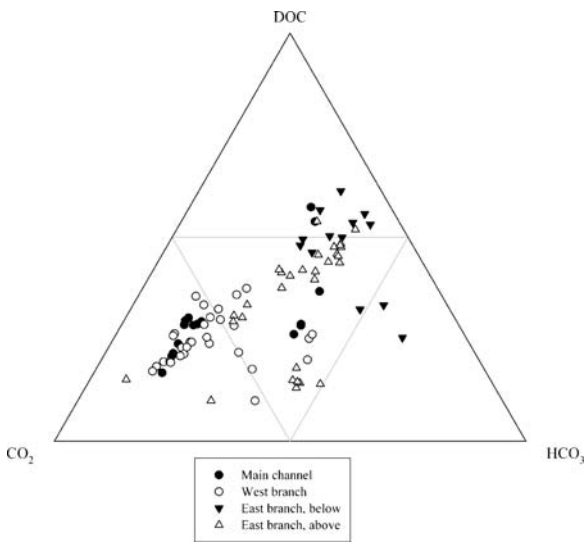

Fig. 6 Ternary plot of the proportions of dissolved carbon species in water samples from sites in Big Brushy Creek, June–July 2003. *Symbols* represent values from individual samples. *Separate symbols* are used to represent sites upstream and downstream of the Middle Branch Wastewater Treatment Plant

Table 2 Solute concentrations and turbidity of treated effluent from the Middle Branch Wastewater Treatment Plant and sites 14 and 13 on Big Brushy Creek, South Carolina, July 16, 2003

	Site 14	WWTP effluent	Site 13
Na^+	3.74	35.87	12.47
K^+	1.63	7.44	3.36
Ca^{2+}	5.24	8.12	5.57
Mg^{2+}	1.15	1.25	1.16
Si^{4+}	7.14	6.16	6.84
HCO_3^-	21.5	11.5	18.3
Cl^-	3.41	23.80	9.84
$H_2PO_4^-$	<0.10	4.79	1.15
NO_3^-	2.62	46.0	13.76
SO_4^{2-}	1.90	17.8	6.37
TDN	0.74	11.31	2.96
DON	0.10	0.89	NA
DOC	6.2	5.5	6.1
Turbidity (NTU)	6.9	1.71	6.3

Units of measurement are mg/l except as noted.

NA = datum not available.

4 Discussion

4.1 Urban Land Cover and Stream Chemistry

In previous studies of urban influences on stream chemistry, the effects of urban land cover often have been confounded by influences of upstream agricultural land use and/or effluent discharges from point sources such as WWTP's or industry (Cameron et al. 1995; Ceasar et al., 1976; Douglas et al., 2002; Flintrop et al., 1996; Jarvie et al., 1998; Roy et al., 1999; Wernick et al., 1998; Zhu et al., 2002). Additionally, streams in many of those previous studies drain carbonate bedrock and therefore naturally have high conductivities and pH. Because urban development occurred in the headwaters of the Big Brushy Creek watershed, we were able to demonstrate the influence of urban land cover without the confounding influences of upstream agriculture. Also, the influence of urban land cover was not confounded by large inputs of solutes from bedrock. Finally, we could separate the effects of urban land cover and discharges from point sources because the only licensed point source in the watershed (the WWTP) was located downstream of the city limits in rural land (South Carolina Department of Health and Environmental Control, 2003).

Previous studies have proposed explanations other than agriculture or effluents from point sources for the elevated solutes in urban streams. However, we suggest that those explanations do not fully account for the patterns we have documented in the Big Brushy Creek watershed. For example, in some urban areas, septic systems may contribute to elevated stream phosphate (La Valle, 1975) or nitrate (Hoare, 1984; Wernick et al., 1998) concentrations. However, residences and businesses in the city of Easley were served by sewer, rather than septic, systems (J. Gilliam, Pickens County Public Health Department, Pickens, South Carolina, personal communication). Other studies have proposed that leaking sewer lines affect stream chemistry (Duda et al., 1982; Paul & Meyer, 2001). Presumably, sewage contamination would have a chemical signa-

Table 3 Concentrations of suspended coliform bacteria at urban and rural sites in the Big Brushy Creek watershed, South Carolina, June–July 2003

	Date			
	June 9–11	June 16–18	June 23–25	July 7–9
Total coliforms (cells/100 ml)				
Urban	22,332±7,934	54,179±14,080	20,984±4,214	41,270±4,580
Rural	11,958±2,351	10,589±3,166*	7,908±1,563*	17,660±4,997*
Escherichia coli (cells/100 ml)				
Urban	577±142	3,383±1,313	1,639±486	1,971±563
Rural	320±99.9	646±238	272±63*	496±174*

Values are means ± SE

Sample sizes were 3 urban and 10 rural sites during June 9–11, 7 urban and 7 rural sites during June 16–18, and 7 urban and 8 rural during the other two intervals.

* indicates significant difference between mean urban and rural values for that variable on that date (independent samples *t*-test, $p<0.05$).

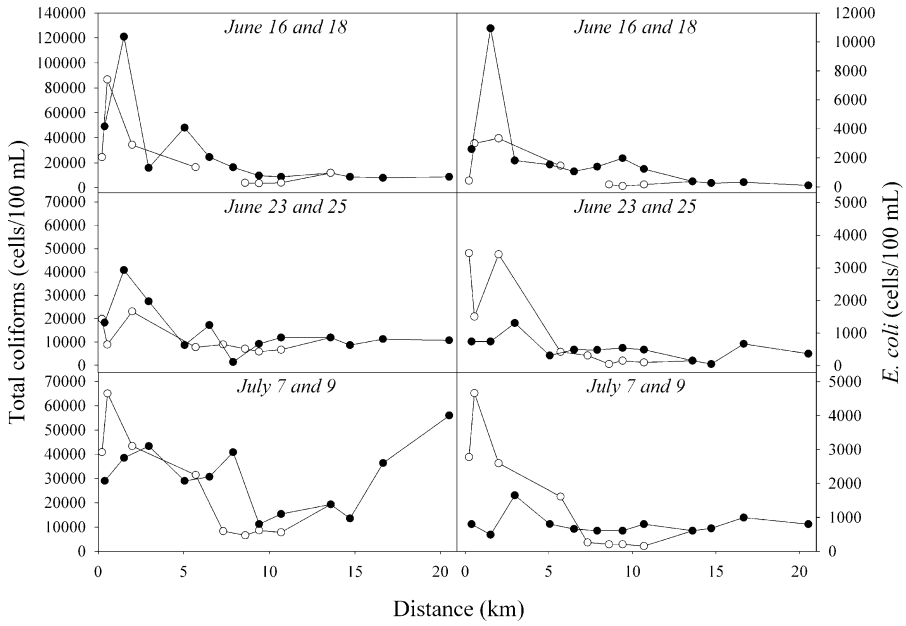

Fig. 7 Variations in concentrations of total coliform bacteria and of *Escherichia coli* with distance from headwaters in Big Brushy Creek. *Circles* represent values from individual samples. *Filled circles* represent sites from the eastern branch of the river and from the main channel. *Open circles* represent sites from the western branch of the river

ture similar to that of WWTP effluent (i.e., a predominance of $Na^+ + K^+$ and $Cl^- + SO_4^{2-}$; Fig. 3). This was not the case in the urban headwaters, which had ion ratios similar to downstream rural areas that were unaffected by the WWTP (Fig. 3). Lawn fertilizers are another possible urban source of stream solutes (La Valle, 1975; Paul & Meyer, 2001). However, the golf course at site 16, which presumably used fertilizers, did not alter stream chemistry appreciably (Figs. 2, 4, and 5). In addition, road deicing salts, although potentially important sources in colder regions (Ceasar et al., 1976; Douglas et al., 2002; Williams et al., 2005), are not routinely used in the Big Brushy Creek watershed.

The major sources of solutes to the urban headwaters in our study are unclear. The bedrock and saprolite in this region are unlikely to supply appreciable quantities of Cl^-, SO_4^{2-}, or NO_3^-. One important source of solutes could be atmospheric dry deposition. Recent studies have demonstrated that dry deposition of NO_3^-, NH_4^+, SO_4^{2-}, Cl^-, Ca^{2+}, Mg^{2+}, and Na^+ is higher in and near cities than in rural areas (Chiwa et al., 2003; Lovett et al., 2000). This suite of solutes closely matches the suite that is elevated in the urban headwaters of Big Brushy Creek. In addition, NH_4^+ from dry deposition could be nitrified in soils and thus contribute to the elevated NO_3^- in urban streams. Many of the same solutes (NO_3^-, SO_4^{2-}, Cl^-, K^+, Na^+, Ca^{2+}, and Mg^{2+}) were elevated in urban streams unaffected by agriculture or point sources of wastewater on the Missouri Ozark Plateau (Smart et al., 1985).

Although stream solute concentrations differed significantly between urban and rural sites, most of the decline in solute concentrations that occurred downstream of the uppermost sampling sites in Big Brushy Creek (Figs. 2, 4, and 5) occurred within areas of urban land cover. Therefore, the declines were not caused by inputs of more dilute groundwater from rural land. Nonetheless, declines in Cl^- concentrations suggest dilution by groundwater, as opposed to biological uptake or sorption onto streambed minerals. Why urban groundwater downstream of the uppermost sampling sites would be more dilute is unknown. Groundwater chemistry may vary among different types of urban land cover. Both residential areas with some tree cover and commercial areas with mostly impervious surfaces occur within the drainage areas of the urban headwaters. However, we have not quantified the proportions of residential and commercial areas, nor have we examined their spatial distributions in relation to the stream channels.

Nitrate concentrations declined more than did concentrations of other solutes in the urban headwaters. For example, the molar ratio of NO_3^- to Cl^- declined from 0.68 to 0.54 between sites 18 and 10 on the western branch and from 0.71 to 0.41 between sites 21 and 17 on the eastern branch. Thus, some of the

decline in NO_3^- concentrations in the urban headwaters appears to have been due to in-stream biological activity (e.g., assimilation or denitrification) as well as dilution.

In both our study and in the study by Smart et al. (1985), NO_3^- concentrations differed more than did other solutes between urban and rural land cover. In our study, mean NO_3^- concentrations at urban sites were up to 2.6 times higher than mean concentrations at rural sites. Furthermore, mean NO_3^- concentrations at the upper urban headwater sites were five to six times higher than mean concentrations for some rural sites downstream (excluding those downstream of the WWTP). This pattern may reflect larger supplies of nitrogen than other elements in dry deposition. For example, Lovett et al. (2000) note that urban dry deposition was more enriched in NO_3^- than in Ca^{2+}, suggesting that both dust and nitrous oxide gases were sources of NO_3^-. In addition, incision of urban stream channels may reduce the capacity for NO_3^- removal or retention in riparian zones (Groffman et al., 2002).

In our study, most of the rural sampling sites occurred downstream of urban areas. As a result, the solute concentrations of at least some rural sites could have been higher because of inputs from upstream urban areas. However, differences in concentrations between urban and rural sites are similar if we restrict our comparison to sites that are independent of one another (i.e., in separate sub-basins within the watershed). For example, the two urban headwaters sampled at sites 19 (western branch) and 20 (eastern branch) had mean NO_3^- concentrations of 5.9 and 4.7 mg/l, respectively. By comparison, the NO_3^- concentration in the rural tributary sampled once at site 12A was 1.4 mg/l. The larger rural tributary sampled at site 11 had a mean NO_3^- concentration of 2.7 mg/l (range 1.6–3.2 mg/l). In this case, urban stream NO_3^- concentrations were about two to four times higher than rural NO_3^- concentrations. Similarly, concentrations of Na^+, K^+, Ca^{2+}, Cl^-, and SO_4^{2-} in the urban headwaters (sites 18, 19, 20, 21) were up to three to four times higher than concentrations in the two rural tributaries. Although there were no completely forested subbasins in the Big Brushy Creek watershed, NO_3^- and SO_4^{2-} concentrations (<0.45 and 1–2 mg/l, respectively) in mostly forested watersheds further upstream in the Saluda River basin and in the nearby Enoree River basin (Lewis, Garrett, Andersen, & Sargent, 2003) were well below concentrations in the urban headwaters of Big Brushy Creek (Figs. 2 and 4).

Human influence on nitrogen biogeochemistry is evident in other ways in the Big Brushy Creek watershed. In particular, NO_3–N was the dominant form of dissolved nitrogen at most sample sites. In all but six samples, NO_3–N accounted for >50% of TDN. Also, during all four sampling intervals in June and July, NO_3–N accounted for a significantly greater percentage of TDN at urban than rural sites (Table 4). This observation supports the hypothesis that NO_3^- becomes an increasingly important form of dissolved N in streams and rivers as human activity increases in watersheds (e.g., Hedin, Armesto, & Johnson, 1995).

In our study, the influence of urban land cover on carbon biogeochemistry did not appear to be as strong as its influence on nitrogen biogeochemistry. For example, we found DOC concentrations to be similar in urban and rural sites. In contrast, Wahl et al. (1997) report that stream DOC concentrations were half as high in an urban watershed compared to a forested watershed on the coast of South Carolina. In the coastal plain, where sandy soils have little capacity to retain DOC released from decaying vegetation (Schlesinger, 1997), differences in DOC concentrations between urban and forest streams may be more evident. In the Big Brushy Creek watershed there may have been sufficient vegetation (trees, shrubs, or lawn grasses) in the urban areas to supply DOC to the streams. Bicarbonate concentrations generally were higher in the urban headwaters than in downstream areas, but neither PCO_2 nor TDC differed significantly between urban and rural sites (Table 1; Fig. 5).

Table 4 Percentage of total dissolved nitrogen in nitrate at urban and rural sites in the Big Brushy Creek watershed, South Carolina, June–July 2003

	Date			
	June 9–11	June 16–18	June 23–25	July 7–9
Urban	89.6±2.8	84.0±2.2	81.4±3.8	89.7±1.7
Rural	71.4±3.1	67.0±5.6	62.8±5.0	74.3±2.2

Values are means ± SE.

Sample sizes were 3 urban and 10 rural sites during June 9–11 and 7 urban and 8 rural sites during all other intervals.

Means from urban and rural sites differed significantly ($p<0.05$) in all comparisons (independent samples *t*-tests).

Carbon dioxide saturation of stream waters in our study exceeded the levels of saturation reported from larger rivers, such as the Amazon (Stallard & Edmond, 1987), Lena (Huh et al., 1998), Thames (Neal, Harrow, & Williams, 1998), Hudson (Raymond, Caraco, & Cole, 1997), St. Lawrence (Hélie, Hillaire-Marcel, & Rondeau, 2002), and Niger Rivers (Martins & Probst, 1991) and from smaller rivers in the United Kingdom (Neal, House et al., 1998) and Spain (Pinol & Avila, 1992). In those studies, river water usually was no more than 5–20 times supersaturated, although some of the small rivers in Spain were as much as 55 times supersaturated (Pinol & Avila, 1992). In contrast, stream waters in our study often were more than 20 times supersaturated, even exceeding 100 times supersaturated along the western branch of Big Brushy Creek (Fig. 5). Because pH largely determines PCO_2 saturation, the differences in PCO_2 saturation between our study and previous studies reflect to a large degree differences in river pH. The rivers in the studies cited either drain carbonate rocks or have calcite dust input and therefore have pH >7 (and thus lower PCO_2 saturation) and often are saturated with respect to calcite. In contrast, the streams in the Big Brushy Creek watershed have pH <7 and are greatly undersaturated with respect to calcite. In particular, the western branch of Big Brushy Creek had pH <6.1, in which case CO_2 was the dominant form of DIC. We propose three explanations for the high CO_2 saturation of these streams. First, it is likely that the low pH is due to both the relative insolubility of the bedrock and acidic atmospheric deposition. Spatial variation in bedrock and saprolite mineralogy and land cover may account for the observed variations in pH throughout the watershed. Second, the stream CO_2 saturation may reflect high soil CO_2 partial pressures in shallow groundwater discharging into the headwaters (e.g., Jones & Mulholland, 1998). Third, biological activity within the stream may have influenced the pH (e.g., Neal, Harrow et al., 1998). Respiration, particularly in the more sluggish and organic-rich western branch of the stream, may have added CO_2 to the water thus lowering pH.

Finally, we recognize that our samples were collected almost exclusively during summer and that we did not determine if the spatial patterns in chemistry associated with urban land cover occurred during other seasons. At sites 14 and 15, concentrations of most solutes in early October fell within the range of summer concentrations. However, DOC concentrations at these sites in October were about one-fifth the summer median concentrations, and NO_3^- concentrations in October were approximately twice the summer median concentrations.

4.2 Influence of WWTP Effluent

Effluent from the WWTP strongly affected river conductivity and the concentrations of nine solutes (Figs. 2 and 4). These effects are consistent with effects of WWTP effluent on river chemistry in the lower piedmont of South Carolina (Andersen et al., 2004). Differences in solute concentrations immediately upstream and downstream of the WWTP in early October generally were consistent with the differences observed during the summer. However, HCO_3^- and DOC concentrations were higher, rather than lower, downstream of the WWTP during October (data not shown). Low temporal variability in concentrations of many solutes under baseflow conditions at sites upstream of the WWTP is consistent with results of a study of the Bush River, South Carolina (Andersen et al., 2004). The large temporal variation in river chemistry downstream of the WWTP (Figs. 2 and 4) probably reflects variation in river discharge (and thus the mixing of river water and WWTP effluent) rather than WWTP discharge, which is regulated carefully.

Although we did not find statistically significant differences in algal abundance on ceramic tiles upstream and downstream of the WWTP, our sample sizes were small due to loss of tiles from storm flow. Even if we combined the data from the upstream sites (14 and 15), we found no significant difference in chlorophyll *a* concentrations between upstream and downstream locations. Nonetheless, during both summer and autumn, we observed that the abundance of benthic algae on streambed rocks was markedly greater at site 13 downstream of the WWTP than at any other site in the watershed. At site 13, mats of algae several millimeters thick covered much of the bedrock streambed, and gas bubbles formed on the mats on sunny days, indicating high rates of photosynthesis. Therefore, we believe that nutrients from the WWTP effluent stimulated primary productivity in the eastern branch of the river. Although NO_3^- and $H_2PO_4^-$ concentrations also were elevated at site 12, we did not observe an abundance of algae there, probably because the streambed was sand, an unstable substrate for algae.

Concentrations of $H_2PO_4^-$ declined more rapidly downstream of the WWTP than did concentrations of other solutes. For example, during June–July, the mean decline in $H_2PO_4^-$ concentrations between sites 13 and 12 was ~40% (Fig. 2). By contrast, mean declines in concentrations of Na^+ and Cl^- were only ~16 and 15%, respectively (Fig. 2), probably due to inputs of more dilute groundwater. Abiotic processes within the river channel could have contributed to the decline in concentrations. Sorption onto iron or aluminum oxides common in the fine fraction of stream sediments can reduce dissolved phosphorus concentrations in the water of streams and rivers (Meyer, 1979). Biotic processes could explain this decline in $H_2PO_4^-$ concentration, as well. In particular, phosphate uptake by benthic algae, such as those observed at site 13, could have contributed to the decreasing $H_2PO_4^-$ concentrations. The mean decline in NO_3^- concentrations (13%) was similar to the decline in Na^+ and Cl^- concentrations and thus could have been caused by dilution alone. Thus, the much stronger decline in $H_2PO_4^-$ than NO_3^- concentrations (Figs. 2 and 4) suggests that algal growth was more phosphorus than nitrogen limited in Big Brushy Creek.

4.3 Urban Land Cover and Bacterial Abundance

Concentrations of coliform bacteria (including *E. coli*) tended to be higher in urban than rural portions of the Big Brushy Creek watershed. Similar results have been found by studies in other regions. For example, Frenzel and Couvillion (2002) found that concentrations of *E. coli*, fecal coliforms, and enterococci were higher in stream sub-basins with higher human population densities in and near Anchorage, Alaska. Similarly, Mallin, Williams, Esham, and Lowe (2000) found that fecal coliform abundance correlated positively with human population density, percentage of developed land, and percentage of impervious surface in five tidal creek basins in North Carolina.

In our original statistical analyses, we excluded rural sites downstream of the WWTP because we were concerned that effluent from the plant, if incompletely treated, might introduce bacteria to the stream and therefore bias the results of our tests. However, we found no significant differences in bacteria concentrations upstream and downstream of the WWTP, suggesting that the plant effluent was treated sufficiently. The results of our urban–rural comparisons remained essentially the same if we included all rural sites. Specifically, mean concentrations of total coliforms were significantly greater at urban than rural sites for all sampling periods. For *E. coli*, mean concentrations were greater for urban than rural sites during all four sampling periods, although the differences were significant only during the third week and marginally (p=0.055) significant during the fourth week. As in the initial analyses, mean concentrations of total heterotrophs did not differ significantly between urban and rural sites during any sampling period.

As with stream chemistry, there is the possibility that bacteria concentrations at some rural sites were elevated because of inputs from upstream urban areas. However, even if we restrict our comparison of the urban headwaters to only the two rural tributaries (sites 11, 12A), differences between urban and rural areas still are evident: concentrations of *E. coli* and, with the exception of one sample from urban site 19, total coliforms were in all cases higher in the urban headwaters than in either rural tributary. In the case of total heterotrophs, however, there was broad overlap in the concentrations at urban and rural sites.

Cattle may be important sources of fecal bacteria to rural streams and rivers (Fernández-Alvarez, Carballo-Cuervo, de la Rosa-Jorge, & Rodríguez-de Lecea, 1991). In our study, cattle were observed wading into Big Brushy Creek at sites 2 and 3. However, only during the 7–9 July sampling period was there evidence of elevated coliform concentrations at those sites or at site 1 downstream (Fig. 7). Nonetheless, the highest concentrations of coliforms measured in our study (>60,000 cells/100 ml) occurred in the urban headwaters. A number of studies have provided evidence that pets (dogs and cats) are the primary sources of enteric bacteria in urban runoff and streams (Kelsey, Porter, Scott, Neet, & White, 2004; Mallin et al., 2000; Young & Thackston, 1999). The urban headwaters of Big Brushy Creek flow through residential areas where pet feces could be sources of coliform bacteria. In fact, dogs were observed near houses in those areas. In addition, there may have been less dilution of coliforms in the small urban headwaters compared to the much larger main channel of Big Brushy Creek.

Concentrations of coliforms and other enteric bacteria in streams often are higher during storm events than under baseflow conditions (e.g., Duda et al., 1982; Young & Thackston, 1999). In urban areas, the combination of extensive impervious surface cover and high

density of storm drains promote the rapid flushing of bacteria from lawns, roads, and other surfaces into streams (Frenzel & Couvillion, 2002; Mallin et al., 2000). However, we have documented high concentrations of *E. coli* and total coliforms under baseflow, rather than storm flow, conditions. Therefore, there appear to be sources of bacteria to Big Brushy Creek besides storm runoff. Some studies have suggested that coliforms can persist and even multiply in stream sediments (Muirhead, Davies-Colley, Donnison, & Nagels, 2004) and in riparian soils (Byappanahalli, Fowler, Shively, & Whitman, 2003; Solo-Gabriele, Wolfert, Desmarias, & Palmer, 2000), in spite of competition with or predation from other microbes. Although we lack data from seasons other than summer, we might expect coliform concentrations to be high in the urban headwaters during other seasons, as well. For example, given the mild climate, pets are active outdoors throughout the year. In addition, the slightly higher rainfall in winter may increase run-off of coliforms to streams.

Mallin et al. (2000) have noted that fecal coliform abundance correlates positively with nitrate and phosphate concentrations and turbidity in tidal creeks along the coast of North Carolina. This observation raises the possibility that increased nutrient loading and turbidity from urban areas might enhance the growth or survival of coliform bacteria in streams and rivers. In the Big Brushy Creek watershed, concentrations of coliforms (including *E. coli*) and some nutrients (e.g., NO_3^-, SO_4^{2-}, and base cations) were high in the urban headwaters. However, concentrations of NO_3^-, DON, $H_2PO_4^-$, K^+, and SO_4^{2-} were even higher downstream of the WWTP, yet bacterial abundance did not increase in response. Also, turbidity was higher in rural areas, probably due to erosion from pastures, construction areas, and other clearings, as well as from the greater erosive power of the river downstream. Thus, in our study, coliform abundance was inversely related to turbidity.

4.4 Fish Abundance and Diversity

We found no statistically significant differences in fish abundance, species richness, or diversity between urban and rural sites within the Big Brushy Creek watershed. This contrasts with other studies in which urbanization appears to negatively affect fish abundance, richness, and/or diversity in the southeastern United States (Lenat & Crawford, 1994; Long & Schorr, 2005; Weaver & Garman, 1994). Given our small sample sizes, it is possible that we failed to detect real effects of urban land cover on fish. However, mean species richness and diversity both were slightly higher at rural sites. Also, more species were found only at rural (seven species) than at urban sites (two species).

In addition to effects of urban land cover, smaller stream size also might account for lower abundance and diversity of fishes in the urban headwaters. Headwater streams naturally tend to have lower fish abundance and diversity than larger rivers, presumably because of factors such as lower habitat diversity and availability, as well as more variable flow and habitat conditions in the headwaters (Horwitz, 1978; Schleiger, 2000). As such, it is likely that *Gambusia holbrooki* was restricted to the downstream rural sites because of its preference for low gradient, slow water habitats (Meffe & Snelson, 1989). However, the differences in stream sizes (stream orders 1–3 only) among our sampling sites for fish on Big Brushy Creek were not large enough to exclude most species from either headwater or downstream reaches. The other six species found only at rural sites can inhabit smaller headwater streams of suitable habitat and water quality (e.g., Jenkins & Burkhead, 1994; Rohde, Arndt, Lindquist, & Parnell, 1994). The absence of those species from the urban sites is thus consistent with the generalization that a shift from sensitive to more tolerant species occurs during urbanization (Walsh et al. 2005). Further, one of the two species that was found only at an urban site, *S. atromaculatus*, is considered to be a pollution-tolerant species (Schleiger, 2000). In future studies, sampling a greater number of urban and rural streams of similar size might provide greater power to detect differences in fish communities between the two types of land cover.

Another potentially confounding influence in our comparison of fish communities at urban and rural sites was the input of WWTP effluent downstream of site 14 (Fig. 1). One of the rural sites (site 12) downstream of the WWTP had elevated nutrient concentrations as a result of the WWTP effluent (Figs. 2 and 4). If nutrients stimulate stream primary productivity, fish populations might increase as a result of increased food availability (either directly or indirectly). Alternatively, high nutrient levels might be deleterious to fishes intolerant of pollution. However, the ictalurid catfish *A. platycephalus*, which is considered to

be moderately intolerant of pollution (Schleiger, 2000) was captured at site 12 in spite of elevated nutrients from the WWTP. Also, one darter (*E. thalassinum*), was captured at that site. Darters also typically require high water quality (Jenkins & Burkhead, 1994). Exclusion of site 12 from our statistical analyses had no effect on the outcome of our urban–rural comparisons of QHEI scores, abundance, species richness, or diversity (i.e., no significant differences between urban and rural sites). The QHEI score for site 12 (53) fell well within the range of scores for other rural sites (42–69).

The lack of significant differences in fish abundance and diversity between urban and rural sites may indicate that the level of urban development in the Big Brushy Creek watershed has not degraded habitat conditions greatly for stream fishes. This interpretation is supported by the similar QHEI scores for urban and rural sites. However, agriculture or other land uses may have degraded stream habitat quality throughout the watershed prior to urbanization (Schleiger, 2000). Fish communities at both urban and rural sites in the Big Brushy Creek watershed were dominated by three species (*L. macrochirus*, *N. leptocephalus*, and *N. lutipinnis*) considered to be "pioneer" species that become established following habitat disturbance (Schleiger, 2000) or to be tolerant of degraded stream habitats (Weaver & Garman, 1994). The South Carolina piedmont has in fact undergone intensive agricultural land use which may have altered stream habitats in the past. In particular, intensive cotton farming was practiced in the region between the 1880s and the 1920s, resulting in widespread erosion and soil degradation (Edgar, 1998). In the southern Appalachian Mountains, agriculture measurably affects fish diversity and community structure for decades after reforestation (Harding, Benfield, Bolstad, Helfman, & Jones, 1998).

Urban land cover may affect fish in ways other than reducing abundance or diversity. For example, in watersheds of the lower piedmont in Georgia, fish species richness and diversity did not correlate significantly with percent urban land cover (Helms, Feminella, & Pan, 2005). However, with increasing percent urban land cover, herbivorous species became relatively more abundant and lithophilic spawners became relatively less abundant. Also, tolerant centrarchids tended to be more common in urban watersheds. In addition, fish health tended to be lower in more urbanized watersheds.

5 Conclusions

Our study of a stream drainage with urban headwaters receiving no agricultural inputs demonstrates that urban land cover influences stream chemistry and microbiology. Concentrations of major ions and suspended coliform bacteria generally were higher in the urban headwaters than in downstream rural areas. Because most if not all of the urban residences and businesses within the watershed were served by sewers, septic tank leachates probably were not important sources of solutes or coliforms to the streams. Further research will be needed to determine not only the major sources of solutes and coliforms but also the causes of downstream declines in solute and coliform concentrations in urban headwater streams. Also, it would be useful to determine if there are relationships between particular types of urban land cover (e.g., residential and commercial) and stream chemistry and microbiology.

In contrast to stream chemistry and microbiology, we found no statistically significant differences in the abundance, species richness, or species diversity of fish between urban and rural sites. However, rural sites had slightly higher species richness and diversity, and more species of fish were found exclusively at rural sites than at urban sites. An important unresolved question arising from our work is whether urban development in the Big Brushy Creek watershed has not yet degraded fish habitat or whether past land uses degraded habitat throughout the watershed prior to urbanization.

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