VARIATION IN STREAM WATER QUALITY IN AN URBAN HEADWATER STREAM IN THE SOUTHERN APPALACHIANS

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Abstract. We examined the influence of a forested landscape on the quality of water in a stream originating on an urban landscape and flowing through National Forest lands. Sample sites included an urban stream (URB), a site on the same stream but within a National Forest (FOR) and 2 km downstream from the URB site, and a small, undisturbed, forested reference tributary of the main stream (REF). We monitored stream water quality from March 2002 through June 2003. Average base flows for the three stream sites were URB = 184 L s^{-1}, FOR = 420 L s^{-1}, and REF = 17 L s^{-1}. We analyzed weekly stream water samples for NO_3^-, NH_4^+, PO_4^+, Cl^-, K, Ca, Mg, SO_4, SiO_2, pH, conductivity, total suspended solids (TSS), and bacteria on a monthly basis. Most solutes were higher in concentration at the URB site, as were conductivity, TSS, and bacteria counts. Reductions in NO_3^-, NH_4^+, and PO_4^+ concentrations between the URB and FOR sites were inferred from changes in nutrient:chloride ratios. Bacteria populations were greater and more responsive to stream temperature at the URB site. Water quality responses to changes in stream discharge varied among sites but were greater at the URB site. By all measures, water quality was consistently higher at the FOR site than at the URB site.

Keywords: water quality, surface water, urbanization, forest, sediment, bacteria

1. Introduction

Land use is one of the most important factors determining water quality (Allan and Flecker, 1993). As human populations increase and land use patterns change, resource managers, planners, and regulators need to understand the impacts of urbanization along the wildland-urban interface on water quality and aquatic resources. Paul and Meyer (2001) found that the most consistent effect of urbanization on stream ecosystems was an increase in impervious surface areas within urbanized catchments. Runoff from these urbanized surfaces and municipal discharges result in increased loading of nutrients (Tufford *et al.*, 2003) and other contaminants to streams (Davis *et al.*, 2003). Lenat and Crawford (1994) found that suspended sediment yield was greater for an urban catchment than for a forested catchment in the North Carolina piedmont. Swank and Bolstad (1994) found that the percentages of land use in non-forest cover and the surface area of paved roads per unit of land area were among the most important influences on baseline water quality in a southern Appalachian watershed. Similarly, Hunsaker and Levine (1995) found that the percentage of land in forest and other uses were the best predictors of overall water quality in river basins of Illinois and Texas. Assessing the potential impacts of urbanization on resource conditions is increasingly important in determining the management of forested lands because such lands are often juxtaposed with urban areas, especially in the eastern U.S.

Regulation of stream water nutrient concentrations by external and internal processes has received much attention. Studies of in-stream processes have focused primarily on nitrate and phosphorus depletion or retention in headwater streams. Swank and Caskey (1982) determined nitrate depletion in a typical southern Appalachian headwater stream following clear-cutting. In their study, denitrifying enzymes in sediments caused the loss of an estimated 1.7 kg N yr^{-1} from the watershed by converting nitrate to nitrite. Similarly, Mulholland (1992) found that in an eastern Tennessee stream, in-stream immobilization of inorganic N as a result of microbial and algal uptake resulted in declines in concentration of that element with distance downstream. However, Mulholland *et al.* (1995) demonstrated experimentally that increased in-stream nutrient cycling may offset some longitudinal changes in nutrient concentrations downstream. Peterson *et al.* (2001) demonstrated that despite low ammonium concentrations in stream water, nitrification rates were high and ammonium removal took place along shorter stream distances than did nitrate removal across a variety of biomes. They report that some of the ammonium and nitrate becomes temporarily sorbed onto biofilms and other submerged surfaces, but that release of inorganic nitrogen from the stream bottom can offset effects of N removal to some degree. Terrestrial controls on stream water nutrient concentrations have also been examined. For example, nitrogen uptake and denitrification in riparian zones of forests can reduce NO_3^- concentrations in drainage water entering streams (Groffman *et al.*, 1996; Hill, 1996). In addition, research that has often focused on upland sources of nutrients in agricultural landscapes has shown that soils and riparian vegetation serve as nutrient sinks, thereby buffering streams from upland perturbation (Lowrance *et al.*, 1984; Peterjohn and Correll, 1984).

In the southern Appalachians, the headwaters of major streams and rivers are often occupied by National Forest lands. Indeed, the protection of headwaters of navigable waterways was a basic premise for the establishment of the National Forest system. In this setting, streams drain minimally disturbed watersheds and enter more developed landscapes where water quality can be reduced as a cumulative result of both point and non-point inputs from sedimentation, agricultural runoff, and urban development. In many cases the opposite occurs; streams originate in urban or suburban settings and flow into undisturbed forested landscapes. The objective of this study was to examine (1) variation in water quality among land use types, and (2) the influence of a forested landscape on the quality of water in a stream originating on an urban landscape.

2. Methods

2.1. Site description

The study was conducted in the Blue Ridge Physiographic Province of western North Carolina (35°6′ N, 83°6′ W). The region receives approximately 2000 mm of precipitation annually, with less than 10% of this falling as snow or ice. Mean annual temperature is 13 °C. Elevation ranges from approximately 880 m at the lower sampling site to 1050 m at the upper site.

The study area is located approximately 40 km south of the city of Sylva, North Carolina along HWY 107 in Jackson County and lies within the upper Chattooga River watershed. This portion of the upper Chattooga River watershed (East Fork of the Chattooga River) is made up of a mixture of urban, rural, and forested landscapes and is approximately 1500 ha. The largest population center within the watershed is the town of Cashiers, North Carolina, which occupies its extreme northern portion. A municipal sewage treatment facility, which utilizes an aerobic biological treatment method, chlorination (trichloro-s-triazinetrione), and de-chlorination (sodium sulfite), treats sewage from the town. Treated effluent is discharged into Cashiers Creek, a major headwater tributary of the East Fork of the Chattooga River. Within 1 km of the treatment facility Cashiers Creek enters the Nantahala National Forest, from which it exits as the East Fork of the Chattooga River. Several small tributaries flow into the river. Our approach was to assess the condition of (1) Cashiers Creek (Urban:URB) near where it enters National Forest, (2) the Chattooga River near where it exits the National Forest (Forest:FOR), and (3) a small tributary, which lies entirely within National Forests and drains an area of the watershed below Devil's Courthouse and Whiteside Mountain. This tributary is regarded as an undisturbed stream (Reference:REF). Baseflow was taken to be 25% or less of maximum discharge and storm flow 75% or greater than maximum discharge. Streams draining the two sub-watersheds were not sampled for chemistry, bacteria, or TSS; however, because they were undisturbed, we assumed that water quality parameters were comparable to the reference stream. The URB stream reflected the cumulative influences of housing developments, water impoundments, stormwater runoff, roads, and the waste-water treatment facility. The FOR stream travels approximately 1.6 km within the Nantahala National Forest before reaching the downstream sampling site.

2.2. Water quality parameters and methods

Stream water samples were collected from March 2002 through June 2003. Automated stream water pumping samplers ([1]American Sigma, Norwalk, CN) were

[1]The use of trade or firm names in this publication is for reader information and does not imply endorsement by the U.S. Department of Agriculture of any product or service.

installed at each site to provide periodic stream water samples. Stream depth was measured weekly and was combined with data obtained from periodic surveys of channel cross-sections and steam velocity to calculate discharge. The stream water samplers were visited weekly for collection of water samples and to download stream depth data. The sampler can collect a maximum of 24 1-L samples over a 1-wk period. Samples taken during baseflow were composited, and those taken during storms remained discrete. Stream water samples were analyzed for NH_4^+, PO_4^+, and SiO_2 on a Perstorp Model 3590 Autoanalyzer (Wilsonville, OR), K, Na, Ca, and Mg on a Perkin Elmer Model 300 Atomic Absorption Spectrophotometer (Shelton, CN), and SO_4, NO_3^-, and Cl^- on a Dionex Model 4500i Ion Chromatograph (Sunnydale, CA). We also calculated nutrient to Cl^- ratios to characterize biological uptake and retention potentials between the URB and FOR sites for NO_3^-, NH_4^+, and PO_4^+. Because Cl^- is a conservative tracer, these ratios may correct for the effects of dilution from surface and subsurface water sources between the URB and FOR sampling sites. Conductivity and pH were measured using digital conductivity and pH meters (Orion Models 122 and 611, respectively). Total suspended solids (TSS) was determined using a vacuum filtration system with 1.5 micron glass microfiber filters (Whatman, Clifton, NJ). All analyses were conducted at the Coweeta Hydrologic Laboratory.

Monthly grab samples were taken at each site for determination of fecal and total coliform, and fecal Streptococcus population densities. A few grab samples were taken during high stream flows, as well; however, because the sites were remote from our headquarters only two storms were sampled. Standard filtration methods (Millipore 1986) were used in the analysis of stream bacteria. Pre-sterilized HA-type (0.45 um pore size) membrane filters to collect Streptococcus and total coliform, and HC-type filters (0.7 um pore size) were used to collect fecal coliform. Pre-prepared commercial media were used for growth media. Dilutions were conducted using 99 ml commercially pre-loaded dilution bottles.

Fecal coliform:fecal Streptococcus ratios (FC:FS) have been used to differentiate among contamination from human (>4.0), domestic animal (0.1–0.6), and wild animal (<0.1) sources (Geldreich, 1976; Howell *et al.*, 1995). Several criteria need to be met for accurate source identification using this ratio: stream travel time of <24 h, >100 FS counts per 100 ml, and sample pH between 4 and 9 (Geldreich, 1976). During the course of the study, FS fluctuated around 100 for the FOR site and was consistently <100 at the REF site. In contrast, FS was consistently >100 at the URB site. Stream travel time between the URB and FOR sites was estimated to be less than 24 h, and pH was consistently within the range specified.

2.3. Data analysis

Data were expressed on a monthly basis for purposes of comparing base and storm flow, and on a weekly basis for examining seasonal differences in water chemistry and TSS among the URB, FOR, and REF stream sites. PROC GLM (SAS Inst.,

1994) was used in multiple comparisons of season and site, and Duncan's multiple range test (SAS Inst., 1994) was used to separate means. Values measured near peak stream flow were used for analysis of stormflows. Simple linear regression (PROC REG, SAS Inst., 1987) was used to examine the relationship between solute concentration and stream discharge for each site. Differences among the slopes of the regression lines were determined using PROC GLM (SAS Inst., 1987) with the appropriate interaction terms. Differences among slopes were interpreted as differences among rates of solute concentration response to changes in discharge. Statistical significance was evaluated at the $\alpha = 0.05$ level.

3. Results and Discussion

3.1. Silicates, conductivity, and pH

Over the study period, average concentrations of solutes other than SiO_2 were consistently higher at the URB stream site than at the FOR and REF sites (Figure 1), and patterns of site-to-site variation in solute concentrations were consistent from season to season (Figure 2). SiO_2 concentration is influenced by a combination of factors. These include use of SiO_2 by diatoms in the construction of frustules; groundwater residence time, which when long can permit SiO_2 to accumulate before entering the stream; and substrate mineral content within the catchment. Conductivity was 3 to 4 times greater at the URB site as at the REF site during all seasons and was near double that at the FOR site (Figure 2). Conductivity was intermediate at the FOR site because of reductions in ionic concentrations in the stream water due to dilution and in-stream processing between the URB and FOR sites. Chloride concentrations ranged from <1.0 ppm at the REF site to near 7 ppm at the URB site at baseflow (Table I). The higher concentration in the URB and FOR streams may be due to the use of chlorine in the treatment of municipal sewage and its subsequent release into the stream above the URB sample site; however, a sulfur compound (Na_2SO_3) is used as a de-chlorinator and oxidizes chlorine to form chloride in the treated effluent before release. The pH level was consistently higher at the URB site than at the other two sites, both seasonally and for the study period (Table I; Figure 3).

3.2. Total suspended solids

TSS at the REF site during stormflow was roughly equivalent to baseflow TSS at the URB site (Table I). There was an approximately 3-fold increase in TSS from base- to stormflow at the REF site, a 4-fold increase at the FOR site, and a 5-fold increase at the URB site. The magnitude of the increase in stormflow sediment at the URB site helps explain the differences among the slopes of the rising limbs of the hydrographs for the three sites (Figure 4). At the URB site, sediment transport and

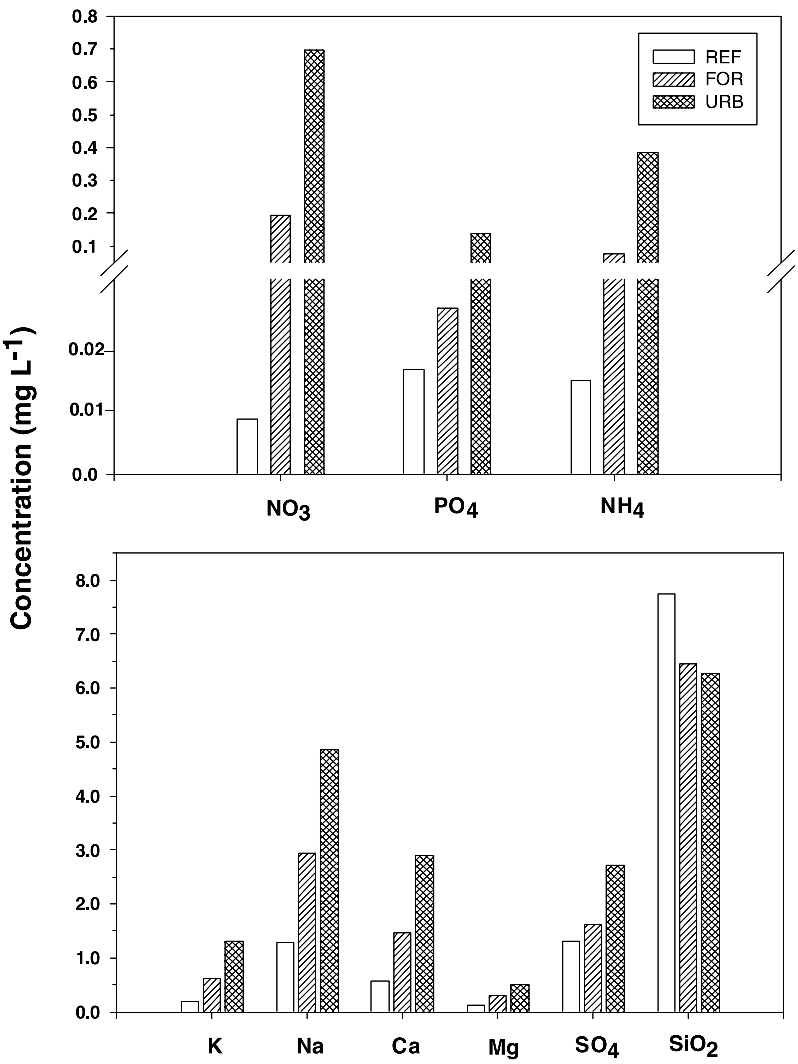

Figure 1. Means of solute concentrations over the study period by site.

delivery were more sensitive to increases in the magnitude of the storm. This was most likely related to the presence of a higher percentage of impervious surfaces that increase stormflow, and to land disturbances that increase sediment loading.

3.3. Stream discharge and water quality

Average base flows for the three stream sites, calculated as twenty-five percent or less of maximum flow, were URB $= 184\,\mathrm{L\,s^{-1}}$, FOR $= 420\,\mathrm{L\,s^{-1}}$, and

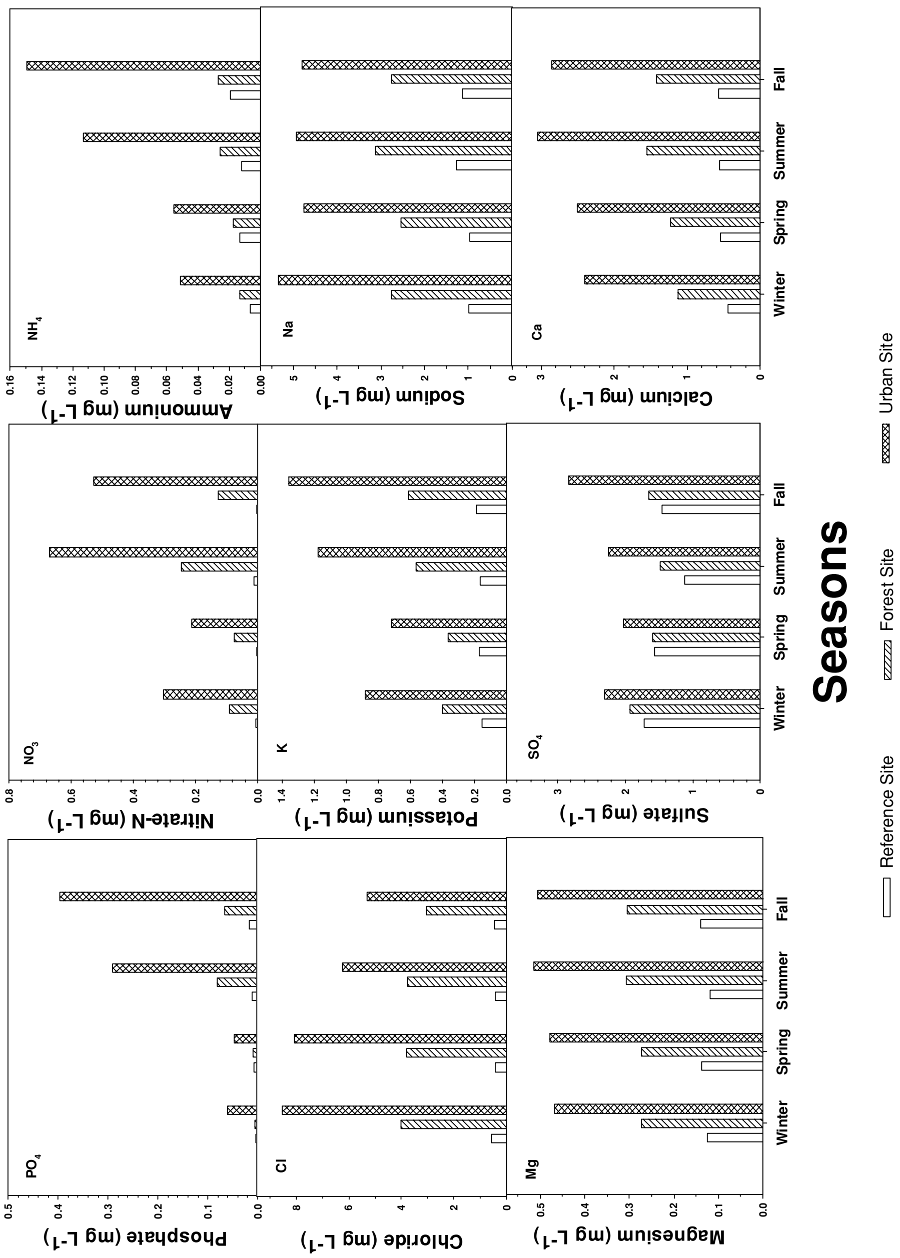

Figure 2. Mean concentration by season and site for major cations and anions in stream water.

TABLE I

Means for stream discharge, pH, solute concentrations, and TSS for base and storm flow by site

Parameter		REF	URB	FOR
Discharge $L\,s^{-1}$	Base	17 (<1–48)	182 (<1–523)	418 (52–622)
	Storm	121 (27–161)	1088 (658–1885)	1721 (1383–2352)
pH	Base	6.3 (5.8–6.8)	6.8 (6.5–7.2)	6.6 (6.3–6.9)
	Storm	5.69 (5.2–5.9)	6.68 (6.5–6.8)	6.35 (6.1–6.6)
No_3^- mg L^{-1}	Base	0.007 (0–0.03)	0.60 (0.12–2.18)	0.20 (0.02–0.74)
	Storm	0.001 (0–0.004)	0.10 (0–0.17)	0.059 (0.03–0.12)
NH_4^+ mg L^{-1}	Base	0.01 (0–0.03)	0.109 (0.02–0.62)	0.018 (0–0.04)
	Storm	0.06 (0–0.03)	0.046 (0.03–0.08)	0.024 (0–0.04)
PO_4^+ mg L^{-1}	Base	0.008 (0–0.03)	0.284 (0.01–1.39)	0.054 (0–0.30)
	Storm	0.003 (0–0.01)	0.022 (0–0.05)	0.010 (0–0.06)
Cl^- mg L^{-1}	Base	0.558 (0.4–2.5)	7.01 (3.5–16.3)	3.98 (2.4–7.5)
	Storm	0.415 (0.3–0.5)	4.91 (2.6–9.1)	3.48 (1.8–7.5)
K mg L^{-1}	Base	0.17 (0.07–0.45)	1.12 (0.33–2.88)	0.67 (0.16–1.06)
	Storm	0.16 (0.07–0.25)	0.92 (0.37–1.31)	0.45 (0.30–0.76)
Na mg L^{-1}	Base	1.21 (0.53–2.65)	5.21 (2.10–10.77)	3.36 (1.71–5.00)
	Storm	0.78 (0.54–1.16)	3.38 (1.85–4.65)	2.57 (1.65–4.98)
Ca mg L^{-1}	Base	0.54 (0.31–1.26)	2.79 (1.82–4.70)	1.57 (1.03–2.24)
	Storm	0.51 (0.38–1.45)	2.49 (1.21–2.83)	1.29 (0.88–2.51)
Mg mg L^{-1}	Base	0.12 (0.08–0.29)	0.50 (0.34–0.83)	0.31 (0.23–0.38)
	Storm	0.14 (0.10–0.23)	0.46 (0.27–0.50)	0.29 (0.23–0.46)
TSS ppm	Base	2.84 (<0.1–31.4)	11.85 (1.5–52.7)	6.42 (1.6–21.6)
	Storm	11.66 (3.2–30.2)	47.8 (12.0–82.9)	41.73 (8.3–205.5)

Values in parentheses represent the observed range.

REF = 17 $L\,s^{-1}$. Perennial streams from two undisturbed subwatersheds located between the URB and REF sites contributed an additional 206 $L\,s^{-1}$ of baseflow to the FOR stream. Summing baseflow quantities from all sources (e.g., URB + REF + the two other streams) accounted for nearly all the flow at the FOR site. Stream discharge response to rainfall varied among sample sites. The hydrograph in Figure 4 illustrates differences in stream discharge response time among sites for a typical storm in June 2002. Peak discharge occurred very near the same time at all sites; however, the slopes of the rising limbs of the hydrographs show that flow increased at a different rate at each site. The falling limbs of the REF and FOR stream hydrographs indicate a typical pattern of a post-storm decrease in stream discharge. In contrast, the response pattern observed on the URB stream appears to be the result of an altered hydrologic regime caused in part by the influence of a large reservoir within 2 km upstream of the sample site. Following storms, the steady release of storm water from the reservoir resulted in a slow decrease

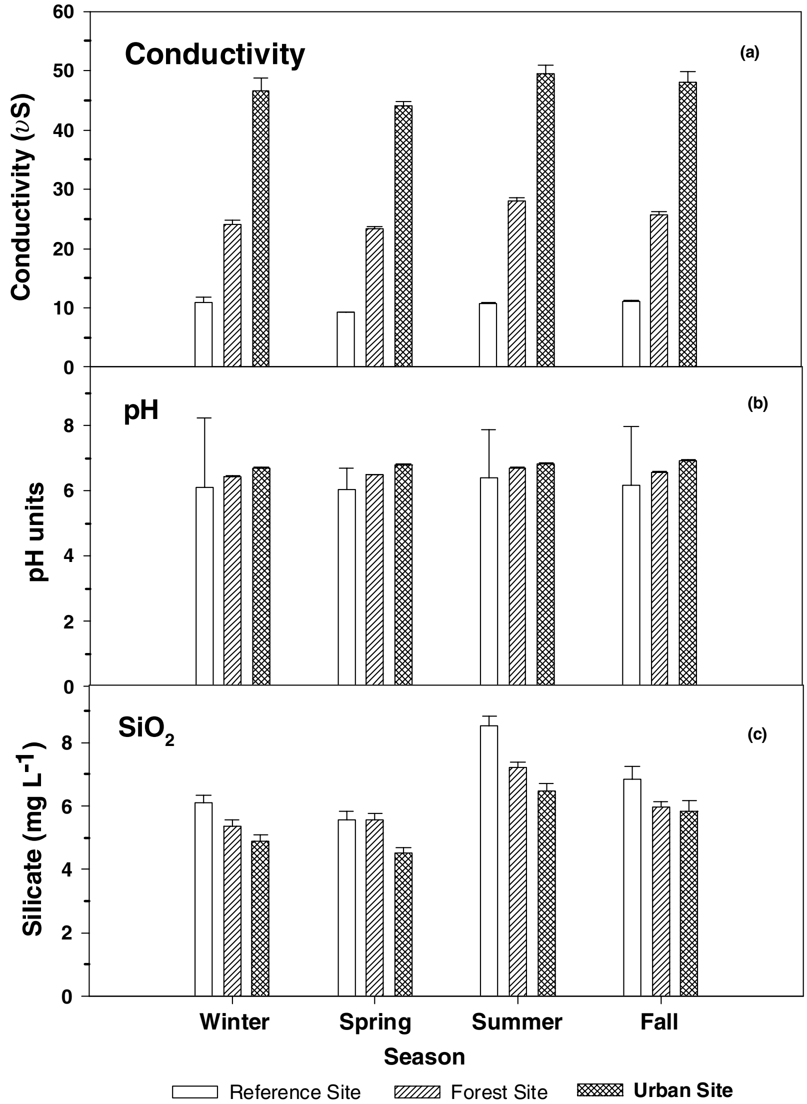

Figure 3. Means for conductivity (a), pH (b), and silicates (c) by season and site. Season was defined as: winter (n = 18), Nov. 15–Mar. 15; spring (n = 18), Mar. 16–May. 31; summer (n = 11), June 1–Aug. 31; fall (n = 11), Sept. 1–Nov. 14.

in discharge and may have masked effects of direct storm runoff on water volume and TSS. Similarly, TSS remained higher than pre-storm values for a longer period at the URB site than at the other sites. In contrast, fluvial processes (in-channel translocation of sediments) may be the primary drivers of TSS at the FOR site, rather than near-stream sediment inputs from land disturbance. It is also likely that

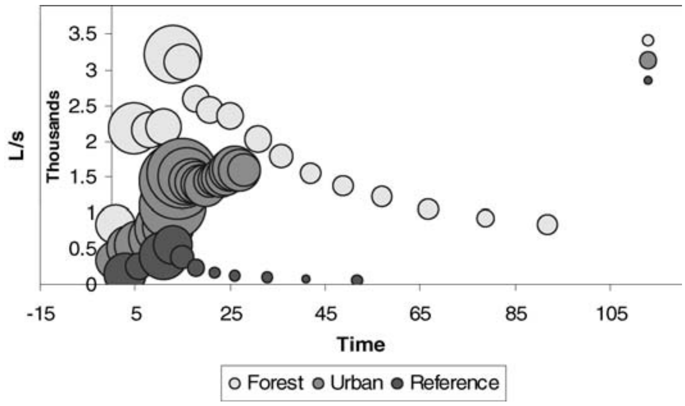

Figure 4. Hydrograph representing changes in stream discharge (Liters sec^{-1}) over time for a selected June 2002 storm for the three study sites. Also known as a sedigraph where the circles represent relative amounts of total suspended sediment (TSS). The three circles in the top right-hand corner represent relative TSS at baseflow for each site.

inputs of finer sediments originating farther up in the watershed contributed some TSS to the FOR site.

In many unimpaired streams, TSS typically begins to decrease before peak discharge and continues to decrease as the storm recedes (Glysson, 1987; Webster *et al.*, 1990; Burke and MacDonald, 1999; Riedel *et al.*, 2004). The REF stream responded in this manner but the URB and FOR streams did not. At these two sites, TSS reached a maximum at peak discharge, but TSS in the FOR stream decreased along the falling limb of the hydrograph. TSS in the URB stream decreased soon after peak discharge but remained high as discharge leveled off.

Single-variable regression models for NO_3^-, NH_4^+, PO_4^+, and Cl^- vs. stream discharge indicate that stream chemistry responses to variation in stream discharge were greatest at the URB site (Table II). For NO_3^-, NH_4^+, PO_4^+, and Cl^-, slopes of the regressions were significantly different from the FOR site (Table II). This suggests that although baseflow and stormflow concentrations of most solutes were greatest at the URB site, the dilution effects of increased discharge on chemical constituents were greater at the URB site than at the FOR site, where there was a steeper rate of decrease in solute concentrations per unit increase in discharge. TSS increased with increasing stream flow at all sites and showed the sharpest increase at the REF site.

3.4. Base cations and other constituents

Concentrations of base cations (K, Na, Ca, Mg) were highest at the URB site both seasonally (Figure 2) and for the study period (Figure 1), and this contributed to higher conductivity at that site. At the URB site, Mg concentrations were on the

TABLE II

Parameter estimates for single-variable regressions of responses to stream discharge for the URB, FOR, and REF sites

Variable	Site	Intercept	Slope	Adj R-sq	*F*	*P*
TSS	FOR	−1.931	0.617[a]	0.16	12.23	0.0009
	REF	1.935	1.581[ab]	0.13	8.13	0.0061
	URB	5.879	1.012[b]	0.48	39.88	<0.0001
NO_3^-	FOR	0.248	−0.004[a]	0.22	18.72	<0.0001
	REF	0.0079	−0.002[ab]	0.16	10.97	0.0016
	URB	0.743	−0.019[b]	0.26	15.30	0.0003
NH_4^+	FOR			n.s.		
	REF			n.s.		
	URB	0.128	−0.003[b]	0.12	5.76	0.021
PO_4^+	FOR	0.0727	−0.00014[a]	0.18	14.82	0.0003
	REF	0.0096	−0.0022[ab]	0.07	6.33	0.0421
	URB	0.357	−0.010[b]	0.19	10.37	0.0024
Cl^-	FOR			n.s.		
	REF			n.s.		
	URB	7.353	−0.059[b]	0.11	5.5	0.0237

Values for the slope parameter with the same superscript are not statistically different within measured parameter. *F*- and *P*-statistics correspond to the individual site regressions. n.s. represents non-significance at $\alpha = 0.05$.

average more than double the North Carolina Department of Environment and Natural Resources (NCDENR) standard for freshwater. At the REF site, concentrations of cations other than Na were lower than those reported by Swank (1988) for small undisturbed headwater streams in the southern Appalachian region. Swank reported Mg, K, and Ca concentrations 2 to 3 times higher than those we observed. Sodium concentrations at the REF site were 10 percent higher than those reported by Swank. Base cation concentrations at the FOR site were higher than those at the REF site but lower than those at the URB site. Sodium was notably higher at both the URB and FOR sites than at the REF site, probably as a result of the addition of sodium sulfite (Na_2SO_3) to the treated effluent as a de-chlorinator before that effluent was released into Cashiers Creek.

3.5. Nitrogen and phosphorus

Stream water nitrate concentration is often used as an index of water quality because of its sensitivity to disturbance. It is highly mobile, and regulated by a variety of biological controls (Swank, 1988). In this study, NO_3^- concentrations were higher and more variable at the URB site during the growing season than at the FOR and REF sites (Figure 5). In addition, concentration increases toward the end of the

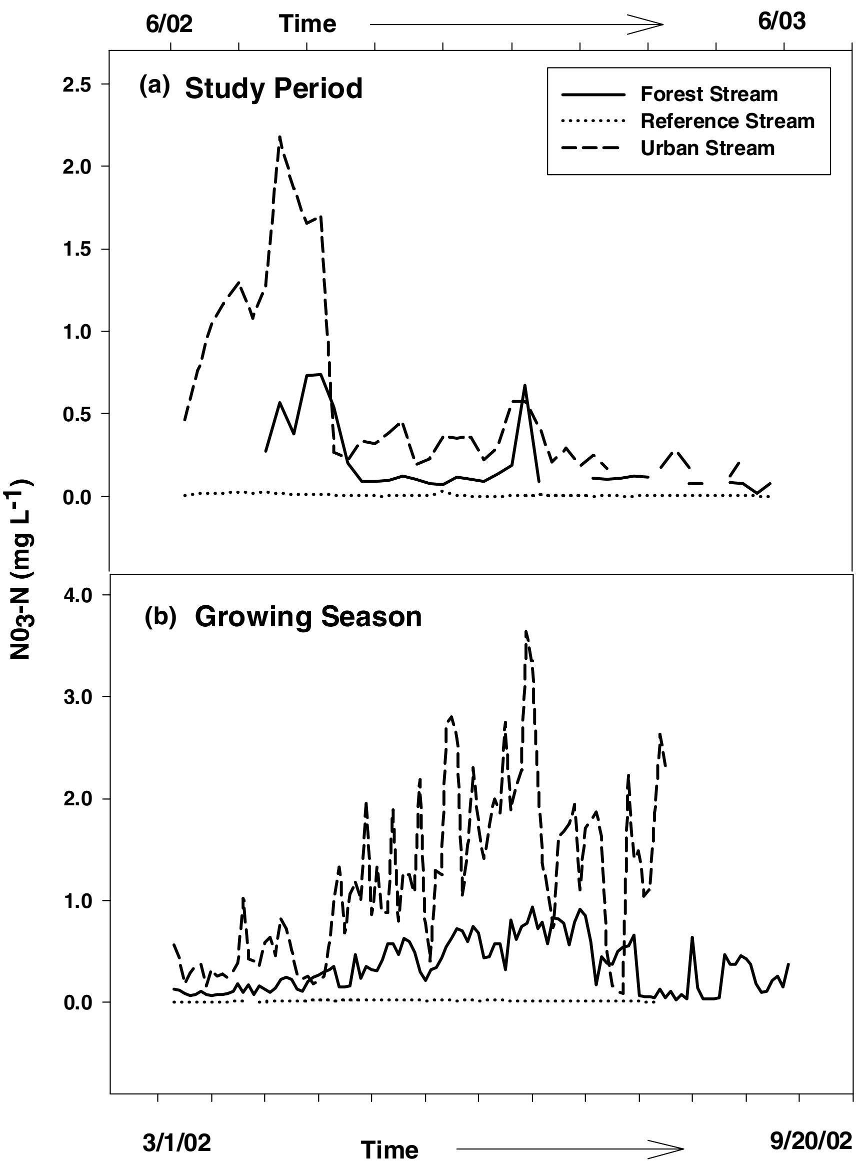

Figure 5. Annual (a) and seasonal (b) variation in stream water nitrate nitrogen concentration for each site. Points along graph in (a) are monthly means by site. Points along graph in (b) are means of weekly composited samples for both base and storm flow.

growing season at the URB, but not at the FOR site. The increase in concentration at the URB site may be a result of inputs from non-point sources such as septic drain-fields in the urban and non-urban portions of the watershed, and possibly fluctuating discharge from the local waste water treatment plant. The lack of an increase at the FOR site is likely due to retention or depletion along the stream reach. Ammonium was higher at the URB site, as well, and likely for the same reasons. Ammonium is produced during the decomposition of organic matter. Where dissolved oxygen is not limiting, ammonium is quickly nitrified to form nitrate, which undergoes denitrification to form nitrite and nitrous oxide gas. There is evidence in this study for substantial reductions in nitrate, ammonium, and phosphorus concentrations between the URB and FOR sites.

Chloride is a biologically inert solute, and therefore useful for assessing in-stream nutrient cycling. When nitrogen or phosphorus is expressed as a ratio of chloride, dilution due to increased flows is taken into account; hence, the change in the ratio reflects real change in the solute concentration and suggests the presence of various mechanisms for nutrient retention. For the study period, ratios of nitrate, ammonium, and phosphorus to chloride decreased from the URB site to the FOR site during base flow by 43, 71, and 66%, respectively, suggesting that there was substantial retention or removal of these solutes between the two sites over the study period (Table III). However, seasonal values varied substantially. Reductions in nitrate occurred during the summer months (−52%) and in the fall (−51%) and in the winter (−25%) but no measurable change was found during the spring (Table III). Ammonium uptake remained similar throughout the year but began to decline in the fall. Although ammonium uptake has been shown to be high in the fall due to fresh organic inputs from litter fall (Tank *et al.*, 2000; Webster *et al.*, 2003), declining stream water temperatures as fall progressed may have reduced uptake (Tank *et al.*, 2000). Phosphorous retention was high during the winter and spring, and remained high relative to nitrate retention during the summer and fall (Table III). Webster *et al.* (2003) also reported greater retention or removal of phosphorous and ammonium than of nitrate in a wide variety of stream ecosystems; however, most streams in their study had greater surface:volume ratios than did our FOR site. The effect of low surface:volume ratios is to mask the apparent significance of detrital dynamics that serve as the source of much of the ammonium in stream water. Swank and Caskey (1982) measured denitrification in sediments of a stream

TABLE III

Percent change in the ratios of nitrate, ammonium, and phosphate to chloride from the URB site to the FOR site by season and study period

	Study period	Winter	Spring	Summer	Fall
		Change in ratios			
Nitrate	−43	−25	∼0	−52	−51
Ammonium	−71	−63	−63	−75	−72
Phosphate	−66	−88	−88	−65	−63

Season was defined as; winter (n = 18), Nov. 15–Mar. 15; spring (n = 18), Mar. 16–May 31; summer (n = 11), June 1–Aug. 31; fall (n = 11), Sept. 1–Nov. 14.

draining a 4-yr-old clearcut. They attributed nitrogen loss to denitrification, but suggested that N removal by algae and heterotrophic bacteria likely had occurred as well. Similarly, Mulholland and Hill (1997) found that in-stream processes were important determinants of stream water nitrate and ammonium concentrations and explained much of the strong seasonality they observed.

Nitrate, NH_4^+, and PO_4^+ concentrations were all at least twice as great at the URB site as they were at the FOR site during all seasons. NH_4^+ and PO_4^+ concentrations were highest during the fall, but these fall concentrations were significantly higher than those during other seasons only at the REF site. Tank *et al.* (2000) found that NH_4^+ uptake was greatest in the fall, but our data suggest that in this disturbed stream ecosystem uptake peaked in the spring and was lowest in the fall. Nevertheless, combined NO_3^- removal and retention was greatest in the fall (Table III). Nitrogen retention and depletion in streams are the result of heterotrophic and autotrophic activity, particularly in sediments and during the fall when organic matter inputs and biological activity and demand for nutrients are the greatest (Tank *et al.*, 2000).

3.6. Bacteria and Stream Temperature

Average stream temperature was generally lower at the REF site than at the URB or FOR sites, and during the summer was lower by more than 2 °C (Figure 6). There were no site-to-site differences in stream water temperature during the winter months. Bacteria population response to seasonal variation in stream water temperature varied considerably among sites (Figure 7). These responses were greatest at the URB site and lowest at the REF site, but populations generally began to increase substantially at approximately 15 °C. McSwain (1977) reported significant declines in total coliform (TC) in the fall when stream water temperature fell below 11 °C in a southern Appalachian headwater stream. At the REF site, fecal coliform (FC) and fecal Streptococcus (FS) showed very little response to increasing stream water temperature, and TC showed only a slight increase. All bacteria types were equally responsive to temperature at the FOR site, but they were considerably less responsive than the URB site in terms of both response to temperature and overall population densities (Figure 7). McSwain (1977) found increases in FC, FS, and TC during the late summer and early fall. These increases coincided with leaf fall and higher stream temperatures. In his study, seasonal variation in bacterial counts were slightly less than those observed at the REF site and considerably less than those at the FOR or URB sites. In our study populations densities varied considerably by season (Figure 6); moreover, FS was undetectable at the REF site during both winter and spring. Population densities of FC and FS at the URB site were significantly greater than those at the REF site but were not significantly different from those at the FOR site. TC had significantly higher population densities at the URB site than at either of the other two sites (Figure 8). These observed differences in stream water bacterial populations between the URB and FOR sites are partially explained by dilution effects; however, declines in populations can also be the result

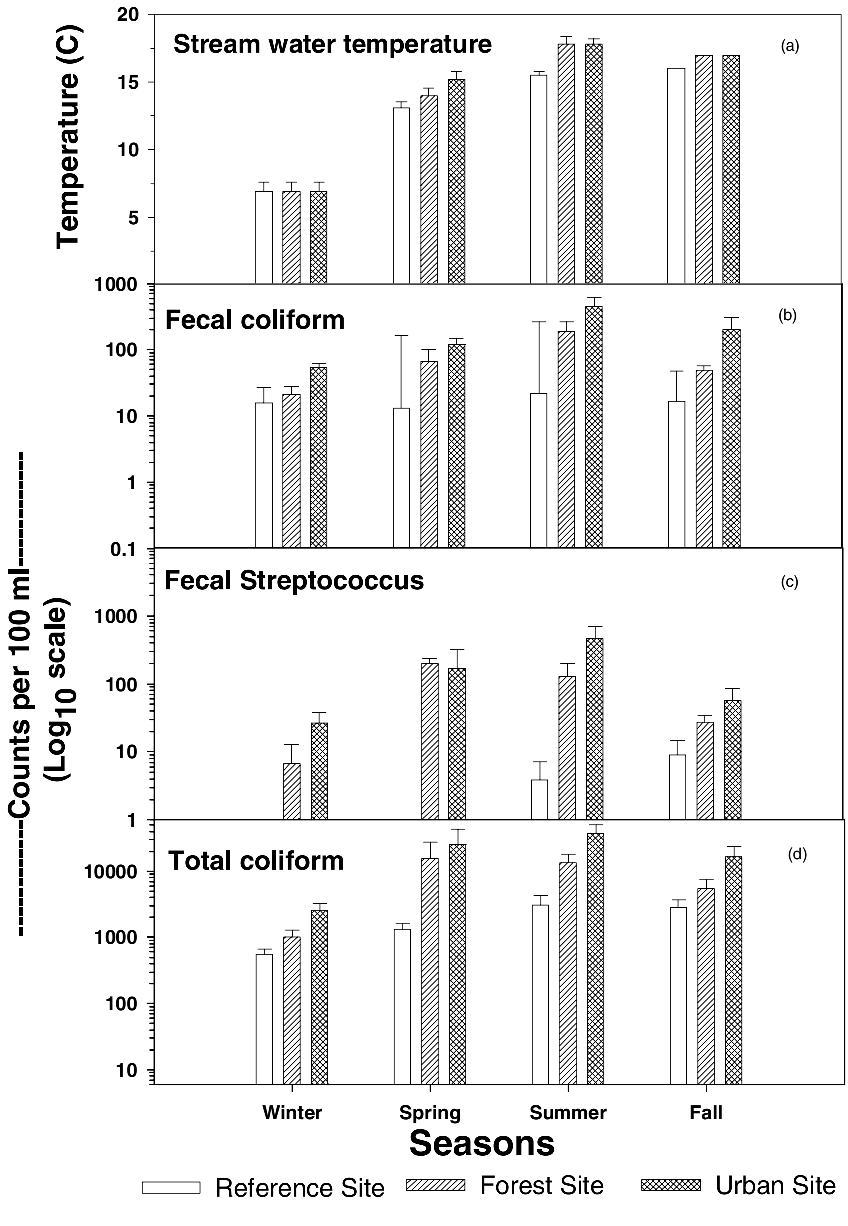

Figure 6. Log transformed fecal coliform, fecal Streptococcus, and total coliform, expressed as colony counts per 100 ml, and stream water temperature (°C) by season of year. Season was defined as: winter ($n = 18$), Nov. 15–Mar. 15; spring ($n = 18$), Mar. 16–May 31; summer ($n = 11$), June 1–Aug. 31; fall ($n = 11$), Sept. 1–Nov. 14. Stream temperature values are based on monthly measurements taken during bacteria sampling.

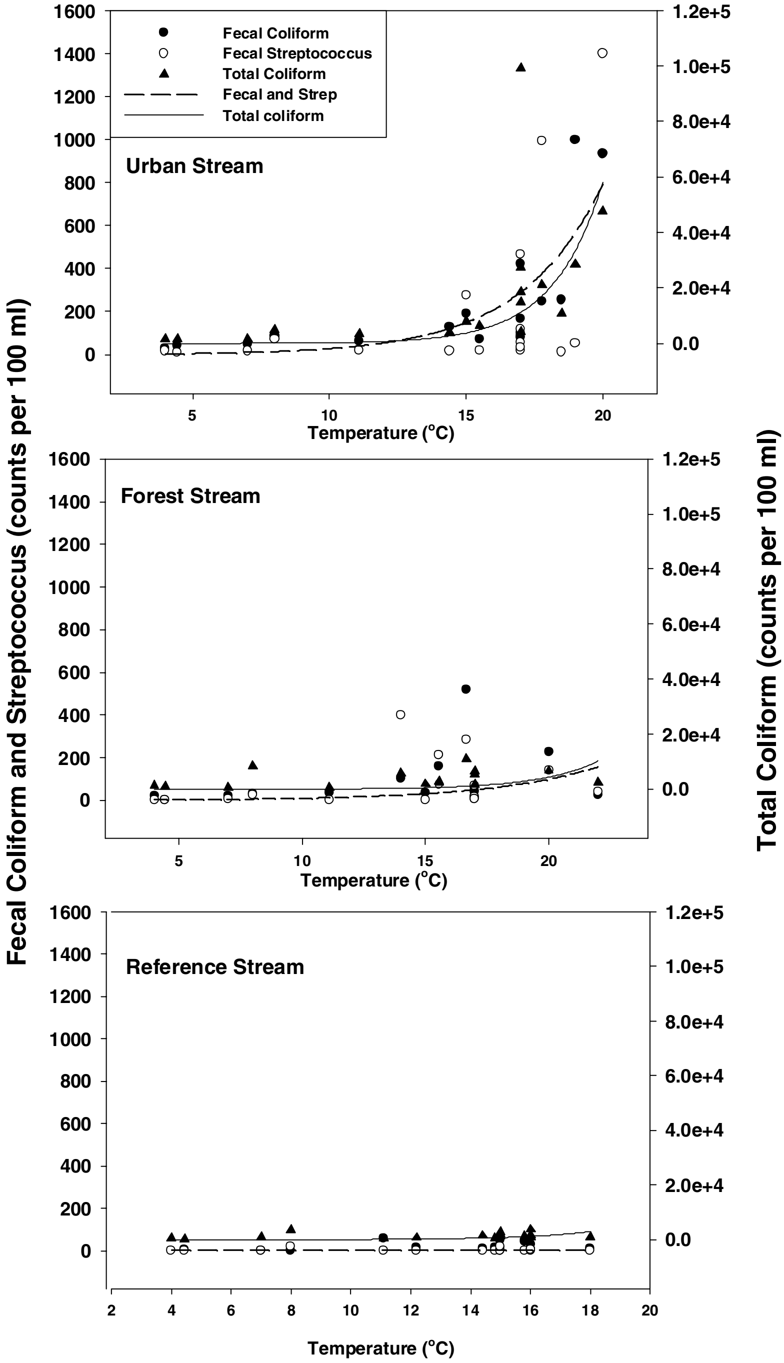

Figure 7. Bacteria responses to increasing stream water temperature by site. Solid line is the response curve ($y = e^{ax}$) for total coliform. The dashed line is the response curve ($y = e^{ax}$) for fecal coliform and fecal Streptococcus, combined.

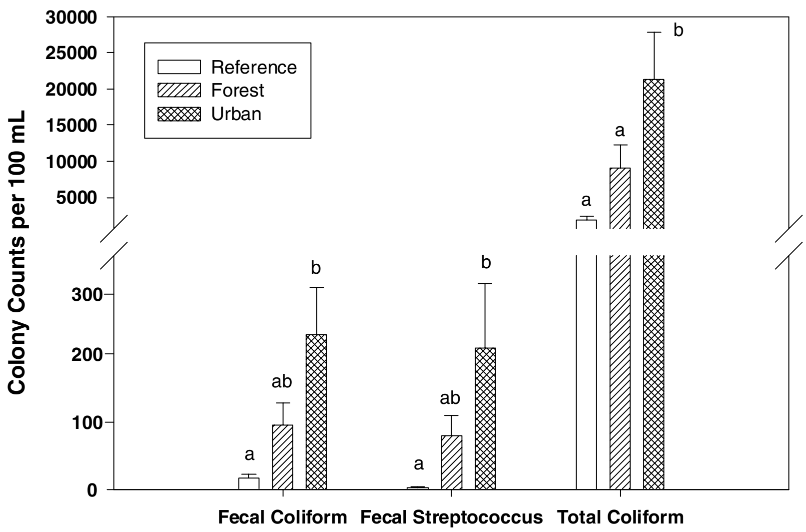

Figure 8. Means of bacteria colony counts (per 100 mL) by site. Bars with the same letter within bacteria type are not significantly different. Error bars represent one standard error of the mean. Means and standard errors are based on sample sizes ranging from 14–18 for each bacteria type.

of in-stream competition, predation, and resource limitation (Janakiraman and Leff, 1999).

The US Environmental Protection Agency National Watershed Database 305(b) report (US Environmental Protection Agency, 1999) ranks FC bacteria pollution as the most widespread pollution problem in the nation's rivers and streams. Non-point sources of fecal contamination that contribute to pollution are often difficult to identify, but human health risks are greater when FC is principally from human sources (Sinton *et al.*, 1993). Fecal coliform:fecal streptococcus ratios have been used to differentiate between contamination from human (>4.0), domestic animal (0.1–0.6), and wild animal (<0.1) sources (Geldreich, 1976; Howell *et al.*, 1995). Doran and Linn (1979) indicate that the FC:FS ratio is useful in distinguishing between domestic animal and wild animal sources, but the usefulness of FC:FS in differentiating between human and nonhuman sources is questionable. Nonetheless, a ratio of 5.28 at the URB site during baseflow suggests the presence of human sources of contamination. During stormflow, however, that ratio decreased to 0.47, which is well below the human contamination threshold value. Bolstad and Swank (1997), in a study of cumulative effects of land use with varying distance downstream, reported FC:FS values of 0.65 and 0.49 for baseflow and stormflow, respectively, at the sampling station furthest downstream in a southern Appalachian stream. The stormflow value for FC:FS at the URB site is similar to the value reported by Bolstad and Swank, but baseflow FC:FS values at the URB site were 8 times higher than those reported by Bolstad and Swank (1997). This could be explained by the proximity of the URB sampling site to the city of Cashiers and the influence of septic systems. Where stream water originating from storm runoff is relatively low in bacteria, point and non-point sources of bacteria, such as septic drain fields in the urban center, have a greater influence on the concentrations of bacterial populations during baseflow than during storms. The FOR site had an FC:FS value of 3.94 during baseflow, and that ratio was reduced to 0.68 during storms. The REF site had the lowest baseflow FC:FS value (3.0) but the highest value for storms (0.83). It is important to note that during the study period only 2 storms were sampled for bacteria due to the remoteness of the study sites. More samples would be required to accurately characterize bacteria populations. Therefore, we suggest caution in interpreting the data beyond a relative comparison among sites.

4. Comparisons with Published Standards

To put our results in context, we compared our data to a compilation of published standards and guidelines (Table IV). Chloride concentrations at baseflow ranged from <1.0 ppm at the REF site to near 8 ppm at the URB site. The addition of sodium sulfite to the treated effluent as a de-chlorinator oxidizes chlorine to form chloride, resulting in higher concentrations of that element in the stream water both at the URB and FOR sites. Still, those concentrations were well below the 230 ppm NCDENR published allowable maximum for aquatic life (Table IV). Standards for cation concentrations do exist, but with the exception of Mg at the URB site, observed concentrations are well below published allowable maximums for freshwater. Maximum Mg concentrations were 4 times greater the NCDENR allowable maximum for freshwater. The source of Mg is uncertain, but is probably a combination of point and non-point sources. Mean values ranged from 0.46 mg L^{-1} during stormflow to 0.50 mg L^{-1} during baseflow (Table I), considerably lower than the NCDENR allowable maximum.

The United States Environmental Protection Agency (US EPA, 1995) standard for drinking water is frequently considered the threshold for desirable versus undesirable water quality. Nitrate concentrations are typically well below this threshold maximum (10 mg L^{-1}; Table IV) in southern Appalachian streams. However, this published EPA standard is useful as a standard reference when one is comparing water quality at different points along streams or in different watersheds for the purpose of assessing the effects of upland disturbance or urbanization. It is important to note that although NO_3^- concentrations were highest at the URB site, these values were well below the EPA allowable maximum for drinking water (10 mg L^{-1}) (Table IV). Moreover, neither of the stream sites in this study are direct sources of drinking water.

The USEPA standard for fecal coliform in stream water, including all surface water, is applicable to "primary contact waters." Primary contact waters are defined as all surface freshwater where human contact during recreation or other uses

TABLE IV

Published standards for parameters measured in the study for which published standards exist

Parameters	Current study maximum	Freshwater CCC†	Aquatic life	Human health****	Water supply***	High Quality Waters (HQW)[c]	Source of standard
Chloride mg L^{-1}	16.3		230		250		NC*
Nitrate mg L^{-1}	6.8				10 MCL‡		NC
pH	5.8–7.2		6.0–9.0				NC
TSS mg L^{-1}	Baseflow – 53					10 (Tr & PNA)[b]	NC
	Stormflow – 83						NC
Calcium mg L^{-1}	4.7	7.3					ECOTOX**
Magnesium mg L^{-1}	0.8	0.2					NC
Potassium mg L^{-1}	2.9	30					NC
Sodium mg L^{-1}	10.8	400					NC 0208
Sulfates mg L^{-1}	6.3				250		NC
Fecal coliform counts/100 ml	1400			200 (N)[a]			USEPA
Total coliform counts/100 ml	99200				50£ (N)		NC

Included are the observed maxima for the current study, all of which were observed at the URB site. The standards, criteria, or toxic concentrations are either from 15A NCAC 2B or are National Criteria as per USEPA. For a more complete listing, go to http://h2o.enr.state.nc.us/csu/.

*North Carolina 2B Standard.

**USEPA ECOTOXicology Database System.

***Water supply standards are applicable to all Water Supply Classifications. Standard is based on the consumption of fish and water.

****Standard for Primary Contact Waters.

†Chronic Criterion Concentration.

‡Maximum Contaminant Level used in drinking water and groundwater.

[a]Narrative description of limits or additional narrative language (See NC 2B).

£Applies only to unfiltered Water Supplies.

[b]Tr = Trout Waters as defined by 2B.0101 and.0301; PNA = Primary Nursery Areas.

[c]HQW = High Quality Waters – see 02B.0101 and 02B.0201.

could occur. The allowable maximum of 200 colony counts per 100 ml (Table III) is based on the mean of a minimum of 5 samples over a 30-day period. Fecal coliform counts often exceeded 200 at the URB site, but those counts were based on monthly samples. Although values for fecal coliform at the URB site were high throughout the study period, and the absolute maximum value observed well exceeds the standard (Table IV), it is unknown whether those values would have exceeded the standard had we applied the sampling criteria stated above.

5. Role of Undisturbed Stream Reaches

There have been numerous studies of the role of undisturbed headwater streams or stream reaches in improving stream water quality. Many have demonstrated the role of near-stream or riparian vegetation in mitigating upland sources of nutrients. For example, forested watersheds conserve nutrients through biological and geochemical processes that retain N and P in upper soil horizons (Wood *et al.*, 1984; Qualls *et al.*, 1991). Riparian vegetation also plays an important role in the regulation of nutrient fluxes through incorporation and storage and through the filtering of sediment and other material released during upslope disturbances, particularly from agricultural activities (Lowrance *et al.*, 1984; Peterjohn and Correll, 1984). However, in-stream processes have been shown to further reduce transport of nutrients, particularly inorganic forms of nitrogen. Net transformations of nutrients from inorganic to organic or particulate form are key mechanisms for nutrient retention in streams (Meyer and Likens, 1979). It has also been shown that prolonged periods of in-stream nutrient retention in undisturbed headwater streams or stream reaches are often punctuated by nutrient losses during storms (Meyer and Likens, 1979; Grimm, 1987). Transient storage, the routing of water along flow paths moving much more slowly than the average in-channel stream velocity (e.g., in pools and low-gradient stream sections), creates zones in which stream metabolism and storage within the channel bed (Grimm and Fisher, 1984; Fellows *et al.*, 2001) increase a variety of in-stream biogeochemical processes (Baker *et al.*, 2000). During high flows these pools of transformed and stored nutrients are flushed out to be taken up or stored in locations farther downstream.

In this study, concentrations of most stream solutes were higher at the URB site than at the FOR and REF sites during base and stormflow. Lower concentrations at the FOR and REF sites probably resulted from a combination of dilution from stream water draining less disturbed upland areas and in-stream processing. This study suggests that undisturbed stream reaches are effective at improving water quality in streams where headwater reaches are heavily affected by urbanization or other land uses. We recognize that our ability to extrapolate these results to other streams with mixed land uses is limited by a lack of replication. However, it is extremely difficult to truly replicate large-scale studies of this nature without introducing numerous confounding factors that make inferences equally limited. Understanding the cumulative effects of mixed land uses will require approaches that combine large-scale monitoring, replicated mid or large-scale studies where possible, and detailed small scale studies and experiments. Our approach is strengthened by the fact that the patterns we observed can be explained by processes determined from small-scale experimental approaches (e.g., Mulholland *et al.* (1995)); however, monitoring of other sites will be needed to increase confidence in the generality of the patterns we observed.

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