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Can small stream solute–land cover relationships predict river solute concentrations?

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Abstract
Most studies of land use effects on solute concentrations in streams have focused on smaller streams with watersheds dominated by a single land-use type. Using land cover as a proxy for land use, the objective of this study was to determine whether the hydrologically-driven response of solutes to land use in small streams could be scaled up to predict concentrations in larger receiving streams and rivers in the rural area of the Little Tennessee River basin. We measured concentrations of typically limiting nutrients (nitrogen, phosphorus), abundant anions (chloride, sulfate), and base cations in 17 small streams and four larger river sites. In the small streams, total solute concentration was strongly related to land cover -- highest in streams with developed watersheds, lowest in streams with forested watersheds, and streams with agricultural watersheds were in between. In general, the best predictor of solute concentrations in the small streams was forest land cover. We then predicted solute concentrations for the river sites based on the solute--land cover relationships of the small streams using multiple linear regressions. Results were mixed -- some of the predicted river concentrations were close to measured values, others were greater or less than measured concentrations. In general, river concentrations did not scale with land cover-solute relationships found in small tributaries. Measured values of nitrogen solutes in the river sites were greater than predicted, perhaps due to the presence of waste water treatment plants. We attributed other differences between measured and predicted river concentrations to the heterogeneous geochemistry of this mountainous region. The combined complexity of hydrology, geochemistry, and human land-use of this mountainous region make it difficult to scale up from small streams to larger river basins.

KEYWORDS
geochemistry, land use, rural, solutes, stream, watershed

1 | INTRODUCTION

Stream solutes have characteristic behaviours based on their sources, transport processes, and biogeochemical activity within a watershed and thus respond differently to landscape change and disturbance. Solute behaviours also depend on watershed-specific factors such as topography, geology, soils, climate, and presence of lakes (e.g., Hynes, 1975; Shogren et al., 2019). Many studies have shown that anthropogenic changes to land use alter solute concentrations in streams (e.g., Bolstad & Swank, 1997; Hunsaker & Levine, 1995; Moerke & Lamberti, 2006; Osborne & Wiley, 1988; Stets et al., 2020; Webster et al., 2019). Some of the earliest studies looked at how clear-cutting increased solute concentrations, particularly nitrate (Likens et al., 1970) and how various forest management practices modify stream solute response to tree removal (e.g., Swank, 1988). Other early studies focused on how agriculture could elevate solute concentrations, particularly nitrogen and phosphorus (e.g., Dillon & Kirchner, 1975; Osborne & Wiley, 1988). More recently, research has shown that urbanization can also elevate stream solutes (e.g., Groffman et al., 2004; Kaushal et al., 2014; Kaye et al., 2006; Osborne & Wiley, 1988; Paul & Meyer, 2001). Most of the many studies of solute–land use relationships have looked at nutrients, nitrogen (N) and phosphorus (P), but a few have looked at a wider variety of solutes (e.g., Herlihy et al., 1998; Kaushal et al., 2018; Ledesma et al., 2013; Likens et al., 1970; Swank, 1988; Wilcke et al., 2017). For timber harvest, the effect on stream solutes is mostly related to soil and vegetation processes, such as the lack of tree uptake and rapid decomposition of logging residue. With agriculture and urban development, inputs from subsidies, such as fertilization, waste water, and concrete weathering, are the primary causes of elevated stream solutes (e.g., Frei et al., 2021; Howarth et al., 1996, 2002; Trentman et al., 2021).

A number of studies have compared land cover in whole watersheds to riparian corridors for predicting solute concentration in streams (Buck et al., 2004; Chang, 2008; Hunsaker & Levine, 1995; Moerke & Lamberti, 2006; Pan et al., 2004; Townsend et al., 1997; Wilkin & Jackson, 1983). The results have been variable, but most have shown that the riparian corridor land cover was a better predictor for small streams and that whole watershed land cover a better predictor for larger streams. Other studies have looked at the importance of riparian buffer strips in protecting streams from nutrient inputs from agriculture and logging, generally showing that 10 to 30 m buffer strips were effective (e.g., Castelle et al., 1994; Clinton, 2011; Knoepp & Clinton, 2009).

Most studies of solute–land use relationships have focused on smaller streams with watersheds dominated by a single land-use type. Scaling up from these small watershed relationships to larger rivers involves several problems (e.g., Allan, 2004; Burt & Pinay, 2005; Lowe et al., 2006). As streams become larger, they develop disproportionately larger floodplains where more intensive land use, particularly agriculture and riparian forest conversion, might have strong effects on solute concentrations. Furthermore, rivers meandering through larger floodplains can create conditions more favourable to hyporheic exchange, denitrification, and sediment deposition, and thus alter biogeochemical processes in these larger river systems. In some watersheds, the effects of past accelerated erosion have larger effects on streambank sediment in larger channels (Leigh, 2010, 2016). Point sources of solutes such as waste water treatment plants (WWTPs), feed lots, and industrial wastes usually discharge directly to larger rivers and not to small streams, and these critical sources become important at larger scales (Frei et al., 2021). Finally, large watersheds are often not geologically homogeneous, and scaling up may necessitate a consideration of geologic differences within the river's watershed (e.g., McGuire et al., 2014; Trentman et al., 2021). At even larger scales, there may be variation in precipitation inputs. This heterogeneity of larger watersheds makes it difficult to predict how river solutes respond to land-use changes (Basu et al., 2010).

The objective of this study was to determine whether the response to land use of a suite of solutes in small streams could be scaled up to predict concentrations of larger rivers in a rural area of the southern Blue Ridge Mountains. As with most previous studies, we used land cover (including roads and buildings) as a surrogate for land use. We then used the land cover–solute concentration relationships of the small streams to predict solute concentrations in larger river sites and compared the predictions to measured values. Our study area was the upper Little Tennessee River basin (URTLB) in the southern Blue Ridge physiographic province of the southeastern USA, a region with a complex topographic, geologic, and climatic template overlain by an equally complex mosaic of past and current human land use. The solutes were three forms of nitrogen, nitrate (NO_3—N), ammonium (NH_4—N), and dissolved organic N (DON); soluble reactive phosphorus (SRP); two abundant anions, chloride (Cl) and sulfate (SO_4); and four base cations, potassium (K), sodium (Na), calcium (Ca), and magnesium (Mg).

2 | SITE DESCRIPTION

The ULTRB is located in western North Carolina and north Georgia, USA, in the southern Appalachian Mountains (Figure 1). The basin

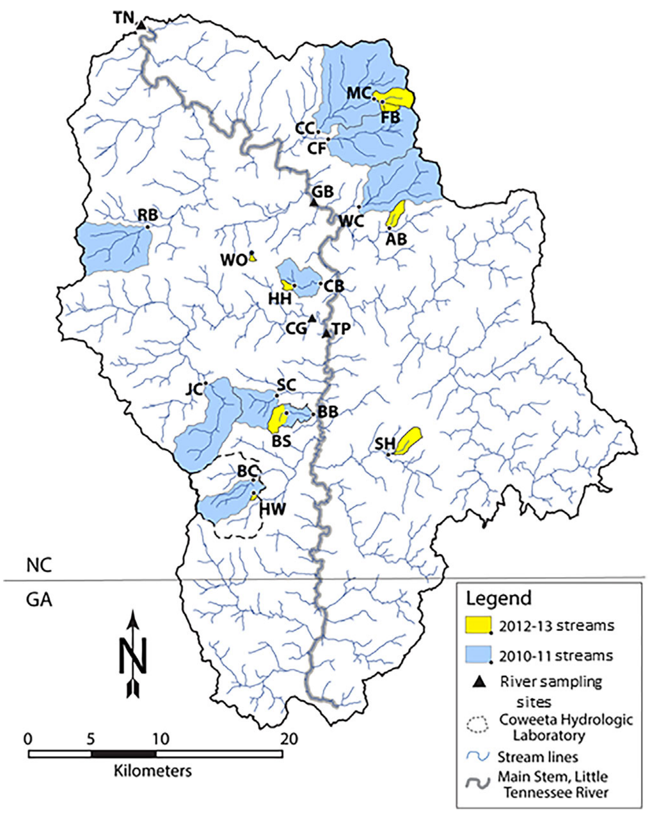

FIGURE 1 Study streams and watersheds within the upper Little Tennessee River basin, North Carolina and Georgia, USA. The Little Tennessee River starts in Georgia and flows northward to the Needmore site. Stream symbols are listed in Table 1.

includes Coweeta Hydrologic Laboratory (Coweeta), a US Forest Service Experiment Station and Long-Term Ecological Research site, and features rugged topography with relatively flat colluvial and alluvial valleys. The geology of the area is weathered granite consisting of high-grade metamorphosed gneiss and schist as well as metasedimentary material such as phyllite, metagraywacke, and amphibolite (Clark, 2008; Soil Survey Staff, 2014). The soils are predominately in the Inceptisols and Ultisols orders (Soil Survey Staff, 2014) with profiles generally characterized by a well-developed mor-type O-horizon (Oa-horizon 2–4 cm), A horizon (10–22 cm), transitional horizon (AB or BA; 10–30 cm), and total soil pedon depth ranging from 60–100 cm. Soils are underlain by a highly weathered saprolite layer just above the bedrock.

The southern Appalachian Mountains receive the highest rainfall in eastern US, with an annual average of 1500 mm. Within the ULTRB, precipitation variability is significant, ranging from 2050 mm in the southwest to 1350 mm in the northeast portion of the basin (data from PRISM Climate Group, Oregon State University, http://prism.oregonstate.edu). Lower elevations have a marine humid subtropical climate, while higher elevations have a marine humid temperate climate. Winters are mild with little snowfall and summer high temperatures rarely reach above 30°C (Laseter et al., 2012; Swift et al., 1988).

Beginning about 1200 years before present, Native American expansion began to modify this region with settlements, especially along the rivers. Subsequent activities by European immigrants further changed the land. The forest was extensively logged in the late 19th and early 20th centuries. Throughout the early half of the 20th century, agriculture became important in the broader valleys, but many agricultural areas have been abandoned and have reverted to second-growth forest (Gragson & Bolstad, 2006). In the last 50 years, the area has experienced considerable transformation from traditional valley agriculture to exurban vacation and second home developments (Jackson et al., 2015; Kirk et al., 2012). Much of this new development has occurred on the mid- and upper-slopes of the mountains where the new inhabitants value isolation and distant views (Chamblee et al., 2011). The ULTRB is still mostly rural with a relatively low population density. A majority of the basin is forested (81%) with only 8.4% of the land area categorized as developed. More than 50% of the land in the basin is publicly owned, primarily within the Nantahala National Forest. Most of the rural homes rely on individual wells and septic systems. The two towns in the study area, Franklin and Highlands, North Carolina, experience seasonal population fluctuations due to recreation and tourism. The population in Highlands is about 900 permanent residents, but the population increases to over 10 000 in summer, while Franklin has a population of about 4000 permanent and 8000 seasonal residents (data from US Census Bureau 2010).

We sampled 17 small tributaries of the upper Little Tennessee River, ranging from first- to third-order, for at least one full year between January 2010 and September 2013. Nine streams were sampled between January 2010 and September 2011 (hereafter referred to as 2010–2011 streams), and eight were sampled between November 2011 and September 2013 (2012–2013 streams). Forested land cover varies from 29% to 100% among the watersheds that drain to these 17 streams (Table 1). The watershed of Crawford Branch includes the town of Franklin. Agricultural areas within the watersheds are primarily pasture and hay fields, with no livestock feedlots and little row-crop agriculture. Residential areas include lawns as well as non-commercial flower and vegetable gardens.

We also collected water samples from four larger river sites: Cartoogechaye Creek and three sites on the Little Tennessee River representing the upper (Prentiss), middle (Gibson Bottoms), and lower (Needmore) part of the ULTRB (Figure 1). Gibson Bottoms was sampled for 1 year (2012–2013), and the other three sites were sampled for 3 years (2010–2013). The Needmore site defines the entire ULTRB. Drainage areas for the river sites are generally an order of magnitude greater than the small watersheds. Land use within the river watersheds includes some intensive agriculture in areas adjacent to the rivers. The Little Tennessee River receives effluents from four WWTPs within the ULTRB: Franklin, Highlands, and two smaller WWTPs in north Georgia (the headwaters of the Little Tennessee River).

For discussion purposes, we grouped the sites into four categories: forested, seven watersheds with land cover >97% forest; agricultural, seven watersheds with 3–16% agricultural land cover and less than 10% developed land cover; developed, three watersheds with >15% developed land cover; and the four river sites (Table 1). The agricultural and developed watersheds all have a mix of agricultural and developed land cover. Note that we identify watersheds with the names of the streams that drain from them.

3 | METHODS

3.1 | Data collection

We collected stream grab samples weekly (2010–2011) or biweekly (2012–2013) by sample bottle immersion. All sample bottles were washed and rinsed five times with tap water and five times with deionized water before use. Because the conductivity of the streams is so low, QC data showed it was better to omit the acid wash (USDA Forest Service, 2017).

At 15 of the small stream sites, stage was recorded every 15 min using a pressure transducer and a data logger attached to an ISCO sampler (Teledyne ISCO, Lincoln, Nebraska, Model 6712). Point discharge was measured approximately monthly using the salt-dilution technique (Gordon et al., 2004). Between 8 and 15 discharge measurements were taken from low to above-average flows. We estimated higher flows beyond the discharge measurements using stream cross-section measurements and Manning's equation with the roughness factor calibrated from measured flows. These measurements and high-discharge estimates were used to develop a discharge–stage height rating curve for each stream (Jackson et al., 2017). Goodness of fit measures (r^2) were above 0.6 for all rating curves. Hugh White Creek discharge was estimated using discharge from the Coweeta WS

TABLE 1 Characteristics of the study watersheds.

Watershed (figure symbol)	Watershed area (ha)	Roads (m/ha)	Buildings (number/ha)	Land cover (%) Forested	Agricultural	Developed	Shrub
Forested watersheds							
Hugh White Creek (HW)	14.5	0.0	0.00	100.0	0.0	0.0	0.0
		0.0	0.00	100.0	0.0	0.0	0.0
Falls Branch (FB)	50.3	0.0	0.00	100.0	0.0	0.0	0.0
		0.0	0.00	100.0	0.0	0.0	0.0
Willis Cove (WO)	15.5	0.0	0.00	100.0	0.0	0.0	0.0
		0.0	0.00	100.0	0.0	0.0	0.0
Ball Creek (BC)	720.1	10.5	0.00	97.4	0.0	2.1	0.6
		13.7	0.00	97.0	0.0	3.0	0.0
Ray Branch (RB)	1470	2.0	0.02	98.4	0.4	0.8	0.4
		4.0	0.03	97.9	0.8	1.3	0.3
Mica City Creek (MC)	335.2	1.6	0.02	98.7	0.8	0.4	0.0
		3.3	0.03	96.6	2.5	0.8	0.0
Stillhouse Branch (SH)	179.5	7.0	0.06	97.2	0.0	2.4	0.5
		15.3	0.12	96.3	0.0	3.7	0.0
Agricultural watersheds							
Skeenah Creek (SC)	601.4	19.1	0.21	88.1	5.1	5.5	1.3
		35.5	0.36	78.4	9.6	9.6	2.4
Jones Creek (JC)	1560	1.3	0.08	93.0	4.3	2.2	0.4
		19.2	0.12	88.0	7.5	4.1	0.5
Cowee Creek (CC)	3012	10.3	0.06	92.8	3.6	2.6	0.9
		16.0	0.09	88.9	5.7	4.1	1.2
Caler Fork (CF)	1738	19.9	0.10	91.3	4.4	3.8	0.5
		23.9	0.14	86.9	7.6	4.7	0.7
Bates Branch at Sunny Ln (BS)	170.9	20.5	0.15	89.6	5.8	3.2	1.3
		43.5	0.27	79.7	11.9	6.8	1.5
Ammons Branch (AB)	121.3	23.8	0.06	79.1	14.4	4.1	1.6
		55.5	0.00	60.2	30.00	9.9	0.8
Bates Branch (BB)	364.4	38.6	0.36	75.9	16.6	6.3	1.3
		66.7	0.48	63.1	26.2	9.2	1.3
Developed watersheds							
Hemlock Hills (HH)	38.7	55.1	0.62	78.8	0.3	19.6	1.3
		51.2	0.70	70.8	0.6	27.5	0.0
Watauga Creek (WC)	1669	44.4	0.32	77.2	5.5	15.9	1.3
		52.0	0.36	66.4	8.1	24.0	1.5
Crawford Branch (CB)	517.6	77.5	1.28	38.2	5.1	55.3	1.4
		76.7	1.21	31.4	7.1	60.4	1.1
River sites							
Cartoogechaye Creek (CG)	14 551	20.4	0.18	82.3	8.6	7.7	1.4
		24.6	0.20	75.7	12.7	10.2	1.3
Little Tennessee at Prentiss (TP)	36 134	15.5	0.13	79.9	10.6	7.8	1.8
		18.6	0.15	73.9	14.6	10.0	1.6
Little Tennessee at Gibson Bottoms (GB)	83 536	22.2	0.21	79.8	8.9	9.8	1.5
		26.6	0.23	73.1	12.6	12.7	1.4
Little Tennessee at Needmore (TN)	113 048	19.8	0.18	81.5	8.5	8.4	1.5
		24.4	0.20	75.2	12.0	11.0	1.4

Note: The first row for each site refers to the total watershed, and the second row is the riparian area. Shrub land cover includes barren areas.

14 weir scaled by watershed area, and Falls Branch was similarly estimated from Mica City discharge. The four river sampling sites were co-located with USGS stream gages, and we used the discharge from USGS (Cartoogechaye Creek – 0350011450; Prentiss – 03501975; Gibson Bottoms – 03503000; Needmore – 03503000).

Annual precipitation for the 2010–2011 streams was determined using PRISM except for Ball Creek precipitation, which was measured at Coweeta Climate Station 1. For the 2012–2013 streams, precipitation was directly measured at five sites (Mica City and Falls Branch measured together), Hugh White Creek precipitation was measured at Coweeta, and Willis Cove precipitation was estimated using PRISM. Precipitation chemistry was determined using the USDA Forest Service Coweeta Lab chemical data for bulk precipitation (wet plus dry) in Rain Gage 6 (RG6) located at Coweeta Climate Station 1.

3.2 | Laboratory analyses

Water samples were processed at the USDA Forest Service Coweeta Hydrologic Laboratory and Long-Term Ecological Research Analytical Laboratory (USDA Forest Service, 2017). Stream samples were filtered (0.7-μm pore size glass fibre filters, Millipore APFF04700) within 24 h of collection. All samples were frozen for storage until analysis.

NO_3—N, Cl, and SO_4 were measured using an ion chromatograph (Dionex ICS4000) with an AS18 column (minimum detection limit MDL: NO_3—N = 0.003 mg N/L, Cl = 0.007 mg/L, SO_4 = 0.04 mg/L), and NH_4—N was measured colorimetrically using an Astroia 2 autoanalyser (MDL = 0.002 mg N/L). Total dissolved nitrogen (TDN) was determined with a Shimadzu DOC-VCPH TNM-1 analyser (MDL = 0.011 mg N/L), and DON was calculated as TDN minus dissolved inorganic nitrogen (DIN = NO_3—N + NH_4—N).

SRP was measured with an Astroia 2 autoanalyser using the colorimetric molybdate technique (MDL = 0.002 mg/L).

The base cations were measured with a Perkin Elmer model Analyst 300 atomic absorption spectrophotometer (MDL: K = 0.02, Na = 0.02, Ca = 0.02, Mg = 0.006 mg/L).

Any solute concentration less than the MDL was recorded as one half the MDL. All stream solute concentrations are expressed as flow-weighted averages.

3.3 | Land cover

We used the National Land Cover Data (NLCD) that were released in 2011, but the satellite images were collected mostly from 2008 to 2010. Because the NLCD data under-represented small or narrow features, we augmented the landcover classes with higher resolution data. Buildings and roads were identified and manually digitized from ortho-corrected image sources, primarily 1-m resolution National Agricultural Statistical Service summer aerial photographs, but also from 46-cm to 4.3-meter resolution satellite images from Geoeye, Worldview, and Planet platforms. Roads were visually identified on leaf-off images, supplemented by existing road vector line-work maintained by the North Carolina Department of Transportation. We classified developed land cover as land areas with any type of impervious surface, such as roads, building roofs, and parking lots, covering more than 400 m^2. These data were then rasterized at a 30 m resolution and merged with the NLCD landcover class. Near-stream land-use was defined as 100 m on each side (i.e., a 200-m corridor) of all streams within a watershed. We refer to this area as riparian, recognizing that it is considerable larger than the actual riparian area of small streams and probably smaller than some of the riparian area along the larger rivers (Baker et al., 2006; Verry et al., 2004). Watershed areas were determined through standard delineation methods (Bolstad, 2019) using the North Carolina statewide 6-m LiDAR derived digital elevation model (data retrieved from website https://sdd.nc.gov/).

3.4 | Data analysis

Simple linear regressions, correlations, multiple regressions, t-tests, and analysis of variance were run using SigmaPlot (Systat Software, Inc.). Principal components analyses were run using R software (R Core Team, 2016), IBM SPSS, or Minitab. Models relating solute concentrations to land-use were developed using best subsets multiple linear regressions with average annual concentrations as the dependent variables. Independent variables were road density (m/ha), number of buildings (number per ha), and land cover percentage as forest, developed, agriculture, and shrub + barren for both the whole watersheds and the riparian zones. The analyses for whole watershed and riparian zone were run separately because of co-linearity between variables at the two scales. Best subsets multiple linear regression finds all possible models and then ranks them based on adjusted R^2. The best two 1, 2, and 3 variable models were selected, and then models with significant co-linearity (any variance inflation factors >5) or models in which one or more coefficients had $p > 0.05$ (based on t-test) were discarded. To scale-up from the small sites to the larger river sites, we predicted solute concentrations for the river sites based on solute–land cover relationships of the small streams using the best multiple linear regression models.

4 | RESULTS

4.1 | Land cover

The ULTRB is over 80% forested (Little Tennessee at Needmore, Table 1) with 8.5% agricultural and 8.4% developed land cover with a few shrub and barren areas. Forested watersheds include first-order streams that are 100% forested as well as larger third-order streams in watersheds that are >97% forested with mixed forest management history, small areas of agriculture and houses in the downstream region, and a network of gravel roads. The agricultural watersheds have less than 6% agricultural land cover, except for Bates Branch and

TABLE 2 Precipitation (P), areal discharge (Q, discharge/watershed area), P-Q, and water yield (Q/P). Unless otherwise noted, discharge and precipitation were directly measured at the sites. Discharge, P-Q, and water yield estimates for Ammons Branch are probably erroneous (see text for explanation).

Site	Precipitation (cm)	Discharge (cm)	P-Q (cm)	Water yield (%)
2010–2011 streams				
Ball Creek	178[a]	78	100	43.6
Ray Branch	153[b]	84	69	54.7
Jones Creek	182[b]	66	116	36.1
Cowee Creek	125[b]	35	90	28.0
Caler Fork	125[b]	30	95	24.2
Skeenah Creek	152[b]	76	96	50.0
Watauga Creek	133[b]	42	91	31.6
Bates Branch	162[b]	96	66	59.4
Crawford Branch	133[b]	47	86	35.0
2012–2013 streams				
Mica City Creek and Falls Branch	175	28	147	16.1
Stillhouse Branch	174	55	119	31.6
Bates Branch at Sunny Lane	178	90	88	50.7
Hemlock Hills	107	33	74	30.7
Willis Cove	178[b]	97	81	54.3
Ammons Branch	139	15	124	10.8
Hugh White Creek	269[c]	153[d]	116	56.9

[a]Coweeta raingage 6.
[b]Estimated from PRISM.
[c]Coweeta raingage 96.
[d]Based on Coweeta WS 14 stream gage.

Ammons Branch, which have 14.4% and 16.6% agricultural land cover. Developed watersheds are Watauga Creek (15.9% developed land cover), Hemlock Hills (19.6%), and Crawford Branch (55.3%). Riparian land cover generally reflected watershed land cover, though there was slightly more agriculture and development in the riparian area (Table 1).

Building density and road density in each watershed were strongly correlated (Pearson correlation, $r = 0.931$, $p < 0.001$), and both were negatively related to forest land cover (linear regression, $r^2 = 0.830$, $p < 0.001$ and $r^2 = 0.837$, $p < 0.001$) and positively related to developed land cover (linear regression, $r^2 = 0.945$, $p < 0.001$ and $r^2 = 0.851$, $p < 0.001$). Neither building density nor road density was related to agricultural land cover (linear regression, $r^2 = 0.04$, $p = 0.18$ and $r^2 = 0.15$, $p = 0.08$). Developed land cover and agricultural land cover were not related, either in the whole watersheds or in the riparian areas (Pearson correlation, $r = 0.13$, $p = 0.63$, and $r = 0.13$, $p = 0.63$).

4.2 | Precipitation and discharge

Precipitation, annual discharge, and water yield varied both among watersheds and between the 2 years of our study. Precipitation was greater during the 2012–2013 measurements than during the 2010–2011 measurements. Precipitation was generally higher in the southern part of the ULTRB than in the northern part. Discharge at the Needmore gage averaged 23.6 m^3/s during the 2010–2011 measurements and 39.3 m^3/s during the 2012–2013 measurements. The long-term average (1944–2017) is 19.4 m^3/s. Across all streams, discharge generally followed precipitation inputs, however, there were differences in water yield (discharge/precipitation, Table 2). Due to the differences in precipitation, watersheds in the southern, higher precipitation part of the ULTRB had higher water yield, while watersheds in the northwest, lower precipitation area had lower water yield. Ammons Branch had unusually low discharge and water yield, suggesting erroneous discharge estimates due to either an inaccurate rating curve or subsurface flow, and therefore we excluded it from discharge calculations. Neither areal discharge or water yield (Table 2) was related to forest land cover (linear regression, $r^2 = 0.04$, $p = 0.44$; $r^2 < 0.01$, $p = 0.97$).

4.3 | Precipitation chemistry

The most abundant solute in precipitation was SO_4 (Table 3), however, measured SO_4 was much lower than peak historical SO_4 concentrations, which were reached in 1988–1990 according to the National Atmospheric Deposition Program (NADP, 2017). NO_3—N was the

TABLE 3 Bulk precipitation chemistry at Coweeta Hydrologic Laboratory.

	Concentration (mg/L)			
	1955[a]	1974–1983[b]	2010–2011[c]	2012–2013[c]
NO_3—N	—	0.144	0.127	0.104
NH_4—N	—	0.097	0.176	0.128
SRP	—	0.013	0.040	0.035
Cl	0.13	0.269	0.238	0.198
SO_4	1.15	3.176	0.725	0.549
K	0.07	0.095	0.100	0.053
Na	0.18	0.167	0.142	0.089
Ca	0.31	0.194	0.190	0.112
Mg	—	0.040	0.034	0.025

[a]Estimated from Junge and Werby (1958).
[b]Swank and Waide (1988), volume-weighted averages of all Coweeta rain gages.
[c]Volume-weighted averages from RG6 (Coweeta Climate Station).

second most abundant solute but has also declined over time since regionally peaking in 1990. However, NH_4—N concentration has increased, resulting in little change in total DIN concentration. Other solutes (Cl, K, Na, Ca, Mg) vary from year to year but have shown no trends over time (NADP, 2017).

4.4 | Stream chemistry

In general, all solute concentrations were low (Table 4) compared to streams throughout North America (e.g., Wetzel, 2001). Anions were dominated by Cl and SO_4, and base cations (Na, K, Ca, Mg) were relatively abundant. Among the important nutrients, SRP was very low in all streams, often below detection (69% of samples ≤ MDL of 0.002 mg/L). NH_4—N was also often near or below detection levels at all streams (12% ≤ MDL of 0.002 mg N/L). NO_3—N was very low in the most forested streams (<0.05 mg N/L) but higher in the streams draining agricultural and developed watersheds and in the river sites. DON showed little variability among streams, ranging between 0.018 and 0.092 mg N/L.

Median solute concentrations were lowest in streams with forested watersheds, intermediate in agricultural watersheds, and highest in developed watersheds (analysis of variance on ranks using all grab, non-storm samples followed by pairwise comparison using Dunn's method). One exception was SRP where the median concentrations for forested and agricultural streams were both 0.001 mg/L (one half the MDL). River sites were not included in this analysis.

The differences in discharge between the streams sampled in 2010–2011 and those sampled in 2012–2013 did not affect the differences in solute concentrations relationships with land cover. Comparing the seven forested sites, the only significant difference between streams sampled in 2010–2011 and 2012–2013 was for NH_4—N (0.006 mg N/L in 2010–2011 and 0.004 mg N/L in 2012–2013, t-test, $p = 0.03$, all other solutes $p > 0.05$). There were no significant differences between sampling years for the seven agricultural streams for any solutes (t-test, $p > 0.05$).

Principal components analysis of standardized mean annual concentrations identified the three groups of streams on the first PC axis reflecting total solute concentrations (river sites not included in this analysis, Figure 2, Appendix A1). Streams with forested watersheds were at one end of this axis and the developed watersheds were at the other end with agricultural watersheds in between. The one outlier was Hemlock Hills (HH in Figure 2), which has a high percentage of developed land cover but fell near the agricultural streams.

The second PC axis was positively related to N solutes and negatively related to SO_4 and Cl. The third PC axis was positively related to cation concentrations and negatively to SRP. In the plot of PC2 versus PC3 (Figure 2), most of the streams were fairly similar, but there were four distinct outliers. Crawford Branch fell at the positive end of the PC2 axis because of high N solutes, and Watauga Creek fell at the other extreme of the PC2 axis because of high SO_4 and Cl. Ammons Branch, one of the streams with the most agricultural land cover, plotted at the high end of the PC3 axis because of high base cation concentrations. Mica City was an outlier because of several unusually high concentration samples of SRP (> 50 mg/L), probably the result of cattle access to the stream just upstream of our sampling site.

4.4.1 | Relationships between solute concentrations and land cover

In general, the best and very strong predictor of solute concentrations in ULTRB streams was forest land cover (Table 5). Using riparian land cover, roads, and buildings improved regressions for most solutes, but the improvement was not large (Table 5). For example, $R^2 = 0.973$ for NO_3—N concentration with watershed forest land cover, and $R^2 = 0.979$ for NO_3—N concentration with riparian agricultural and developed land cover (Table 5).

The strongest land cover (we include buildings and roads in this terminology) predictions were for NO_3—N and NH_4—N (Figure 3). Crawford Branch, which includes the town of Franklin, was an outlier with very high NO_3—N concentration. For NO_3—N, removing Crawford Branch only slightly reduced the strength of the regression, but for NH_4—N and DON the regressions with forest land cover were much weaker when Crawford Branch was not included (Figure 3). It is curious and perhaps spurious why the coefficient for riparian agriculture was negative in the best NO_3—N versus riparian land cover equation (line 3 in Table 5).

Average Cl concentration was weakly related to forest land cover and roads (Table 5), but removing one outlier with high Cl concentrations (Watauga Creek) greatly improved the relationship between chloride and land cover (Table 5, Figure 4). The weak relationship between Cl concentration and road length suggests that road salt may contribute to Cl in streams. However, most of the roads in the watersheds are gravel, which are not salted. We estimated the length of gravel and paved roads based on Google Earth images, and when we

TABLE 4 Flow-weighted average solute concentrations in each of the streams.

	Year	NO_3—N	NH_4—N	DON	Cl	SRP	SO_4	K	Na	Ca	Mg
Forested watersheds											
Hugh White Creek	2012–2013	0.013	0.003	0.019	0.52	0.002	0.31	0.35	0.98	0.41	0.24
Willis Cove	2012–2013	0.026	0.004	0.018	0.60	0.002	0.91	0.67	1.75	1.55	0.93
Falls Branch	2012–2013	0.018	0.004	0.024	0.50	0.002	1.49	0.57	1.02	0.49	0.44
Ball Creek	2010–2011	0.024	0.006	0.032	0.48	0.002	0.57	0.41	0.98	0.61	0.31
Ray Branch	2010–2011	0.030	0.006	0.026	0.49	0.002	0.86	0.45	1.12	0.70	0.43
Mica City Creek	2012–2013	0.046	0.005	0.026	0.59	0.008	1.31	0.62	1.09	0.56	0.42
Stillhouse Branch	2012–2013	0.016	0.005	0.024	0.86	0.002	0.89	0.46	1.62	0.67	0.33
Agricultural watersheds											
Skeenah Creek	2010–2011	0.090	0.007	0.029	0.89	0.003	1.09	0.66	1.73	2.76	1.30
Jones Creek	2010–2011	0.037	0.008	0.037	0.71	0.004	1.13	0.60	1.51	2.34	0.84
Cowee Creek	2010–2011	0.049	0.008	0.040	0.76	0.003	1.03	0.72	1.49	1.08	0.51
Caler Fork	2010–2011	0.041	0.012	0.036	0.91	0.002	1.24	0.80	2.11	1.63	1.03
Bates Branch at Sunny Lane	2012–2013	0.095	0.006	0.034	1.00	0.003	0.73	0.67	1.65	1.85	0.94
Ammons Branch	2012–2013	0.181	0.006	0.030	2.29	0.003	1.72	1.19	2.74	2.38	1.44
Bates Branch	2010–2011	0.176	0.011	0.043	1.45	0.002	0.79	0.81	1.89	2.24	1.00
Developed watersheds											
Hemlock Hills	2012–2013	0.200	0.007	0.022	1.25	0.002	0.68	0.78	1.62	0.91	0.63
Watauga Creek	2010–2011	0.176	0.014	0.041	4.67	0.007	2.43	1.30	3.83	2.75	1.51
Crawford Branch	2010–2011	0.453	0.042	0.076	2.75	0.005	1.71	1.15	2.88	3.19	1.80
River sites											
Cartoogechaye Creek	2010–2011	0.123	0.011	0.044	1.76	0.003	2.73	0.77	2.03	2.56	1.21
	2011–2012	0.107	0.011	0.055	1.69	0.019	2.68	0.78	1.99	2.33	1.11
	2012–2013	0.115	0.008	0.031	1.51	0.001	2.34	0.65	1.86	2.14	1.04
Little Tennessee River at Prentiss	2010–2011	0.170	0.010	0.053	1.37	0.004	1.22	0.74	1.78	1.65	0.60
	2011–2012	0.160	0.015	0.092	1.32	0.013	1.27	0.86	1.80	1.66	0.58
	2012–2013	0.186	0.006	0.027	1.25	0.004	1.19	0.65	1.68	1.33	0.51
Little Tennessee River at Gibson Bottoms	2012–2013	0.156	0.011	0.047	1.81	0.006	1.68	0.75	1.97	1.60	0.65
Little Tennessee River at Needmore	2010–2011	0.134	0.010	0.066	1.99	0.009	1.58	0.81	2.12	1.83	0.73
	2011–2012	0.127	0.010	0.088	1.78	0.004	1.63	0.84	2.03	1.72	0.70
	2012–2013	0.136	0.008	0.062	1.69	0.005	1.53	0.75	1.90	1.55	0.64

Note: Each average is based on a single year. All concentrations are in mg/L.

re-ran the multiple regression with just paved roads, there were no acceptable models for Cl concentration that included paved roads as a predictor variable.

SRP was not related to any land cover parameter although this may be because most SRP measurements were below the level of detection. The only relationship between SO_4 and land cover was a weak relationship with riparian forest cover (Table 5).

All base cation concentrations were strongly and negatively related to forest land cover, especially to riparian forest land cover (Table 5). K was also negatively related to riparian building density in multiple regression analyses, that is, the more buildings the lower the K concentration. However, in a simple linear regression between K concentration and riparian buildings, the relationship was positive ($r^2 = 0.224$, $p = 0.031$), so we think the negative relationship with buildings is spurious. The regression relationships between Na and land cover were improved when Watauga Creek (an outlier with high Na concentration) was removed from the analysis (Table 5, Figure 4). Na concentration was not related to total roads or paved roads. Relationships between Ca and Mg and land cover were similar, though slightly better for Ca. Neither Ca nor Mg concentrations were related to total road length, but when we re-ran the analysis using gravel road length, the best model for Ca was a two-variable model including gravel road length and forest ($R^2 = 0.617$). However, adding gravel road length did not change the analysis for Mg.

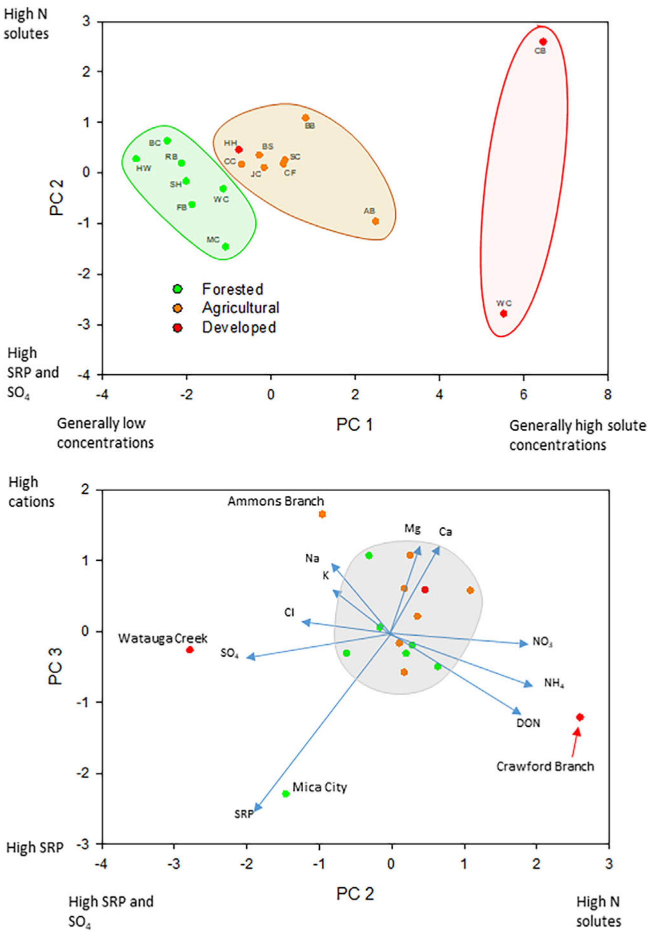

FIGURE 2 Results of principal components analysis on standardized mean annual solute concentrations in all small streams. Component scores are in Appendix A1. Stream symbols are listed in Table 1.

4.5 | Scaling up

We predicted solute concentrations for the river sites based on best (highest R^2) solute–land cover relationships of the small streams (Table 6). We did not attempt to predict SRP concentrations because there was no significant model for SRP. We used models for N solutes both with and without Crawford Branch, and we used models for Cl and Na with and without Watauga Creek. These predicted values were compared with the 1-year average for Gibson Bottoms and 3-year averages for the other three river sites (Figures 5 and 6). Because Gibson Bottoms and the Needmore site are downstream of other sites, the four river sites do not represent independent observations.

For the river sites, NO_3—N was higher than predicted except in Cartoogechaye Creek where the predicted value was very close to the measured value (Figure 5). Predicted NH_4—N and DIN concentrations were higher than measured values at all of the river sites. Whether using all small streams or excluding Watauga Creek, predicted chloride concentrations in the river sites were lower than measured except at the Prentiss site on the Little Tennessee River (Figure 6). Using the predictive equation without Watauga Creek, Na was similar to Cl – predicted concentrations were lower than measured except at the Prentiss site. Similarly, predicted SO_4 concentrations were lower than measured except at the Prentiss site. Predicted SO_4 concentration in Cartoogechaye Creek was about half the measured value. Unlike Cl, Na, and SO_4, predicted concentrations for K, Ca, and Mg were mostly higher than measured. This was the case for K at all four river sites and for Ca and Mg at all three Little Tennessee River sites but not at Cartoogechaye Creek where the predicted concentration was less than measured.

5 | DISCUSSION

Solute concentrations in the smaller streams were strongly related to land cover – highest in streams with developed watersheds, lowest in streams with forested watersheds, and streams with agricultural watersheds were in between (Figure 2). The differences among the solutes we studied relate largely to their biological importance with N solutes showing the strongest relationships to land cover. While all of the solutes are essential components of living organisms, their abundance in living organisms versus their environmental abundances vary widely (Vallentyne, 1974). Despite the biological importance of P, the very low stream concentrations of SRP in all streams resulted in no significant relationship with land cover. The lack of a significant relationship between SRP and land cover is probably because it is such an important limiting element in this area (Mulholland et al., 1997; Tank & Dodds, 2003; Webster et al., 1991), and stream concentrations are often reduced to levels below detection by instream and soil processes. Also, the lack of spatial information on the distribution of abandoned farmlands may mask the effects of leaching of legacy P stored in old farmland soils (e.g., Bennett et al., 2001; Fraterrigo et al., 2005; Kreiling et al., 2020). Human activities affect the environmental abundance of all of the solutes we studied, for example, fertilizer application increases N, P, K, Ca, and Cl and land development accelerates mineral weathering and adds many solutes to streams through septic and sewer systems. These inputs lead to strong relationships between solute concentrations and land cover.

The reason the predicted concentrations of N solutes in the Little Tennessee River sites were lower than measured is probably due to WWTPs for the towns of Franklin and Highlands and the two small WWTPs upstream in Georgia. Clinton and Vose (2006) also found that a WWTP near the headwaters of the Chattooga River (adjacent to the ULTRB) elevated solute concentrations. The point source inputs that come directly to the river are not accounted for in our small stream—land cover models. However, the higher than predicted values of NH_4—N and DON in Cartoogechaye Creek are surprising as there are no WWTPs upstream of the sampling site. Perhaps there are some other sources of NH_4—N and DON such as septic systems and leaky sewer lines upstream of the sampling site.

Measured chloride was higher than predicted at three of the river sites, but not at the Prentiss site on the Little Tennessee River. The differences between measured and predicted concentrations may be

TABLE 5 Predictors of solute concentrations in ULTRB streams.

	Roads	Bldgs	Forest	Devel	ag	Shrub		r-roads	r-bldgs	r-forest	r-devel	r-ag	r-shrub
NO_3—N	— —	— —	0.973 (1) —	— —	— —	— —	— —	— —	— —	— 0.923 (1)	0.979 (2) —	0.979 (2) —	— —
NO_3—N w/o CB	— —	— —	0.920 (1) —	— —	— —	— —	— —	— —	— —	0.953 (3) —	— 0.944 (2)	0.953 (3) 0.944 (2)	0.953 (3) —
NH_4—N	— —	— —	0.911 (2) —	— 0.881 (1)	— —	0.911 (2) —	— —	— —	— —	— —	0.810 (1) —	— —	— —
NH_4—N w/o CB	0.426 (1) —	— —	— —	— —	— —	— —	— —	0.315 (1) —	— —	— —	— —	— —	— —
DON	— —	— —	0.727 (1) —	— —	— —	— —	— —	— —	— —	0.611 (1) —	— —	— —	— —
DON w/o CB	— —	— —	— —	— —	0.348 (1) —	— —	— —	— —	— —	— —	— —	— —	0.364 (1) —
Cl	0.444 (1) —	— —	— —	— —	— —	— —	— —	— —	— —	0.486 (1) —	— —	— —	— —
Cl w/o WC	— —	— —	0.829 (1) —	— —	— —	— —	— —	— —	— —	0.905 (1) —	— —	— —	— —
SRP	— —	— —	— —	— —	— —	— —	— —	— —	— —	— —	— —	— —	— —
SO_4	— —	— —	— —	— —	— —	— —	— —	— —	— —	0.188 (1) —	— —	— —	— —
SO_4 w/o WC	— —	— —	— —	— —	— —	— —	— —	— —	— —	— —	— —	— —	— —
K	— —	— —	0.517 (1) —	— —	— —	— —	— —	— —	0.729 (2) —	0.729 (2) 0.646 (1)	— —	— —	— —
Na	— —	— —	0.431 (1) —	— —	— —	— —	— —	— —	— —	0.525 (1) —	— —	— —	— —
Na w/o WC	— —	— —	0.592 (1) —	— —	— —	— —	— —	— —	— —	0.693 (1) —	— —	— —	— —
Ca	— —	— —	0.589 (2) 0.482 (1)	— —	0.589 (2) —	— —	— —	— —	— —	0.750 (2) 0.598 (1)	— —	— —	0.750 (2) —
Mg	— —	— —	0.575 (1) —	— —	— —	— —	— —	— —	— —	0.684 (1) —	— —	— —	— —

Note: These results are based on best subsets multiple linear regressions with average annual concentrations as the dependent variables. Independent variables were road density (roads, m/ha), number of buildings (bldgs, number per ha), and land cover percentage as forest, developed (devel), agriculture (ag), and shrub + barren (shrub) for both the whole watersheds and the riparian zones (indicated by R in the column headings). The best two (based on adjusted R^2) 1, 2, and 3 variable models are shown in the table. The numbers in the table are the adjusted R^2 for each predictor variable, and the numbers in parentheses are the number of variables in that model. Where a cell is blank, that predictor variable did not appear in the selected model. Where a line is blank, there was no acceptable model. Underlined values are models with negative values for the coefficients.
Abbreviations: CB, Crawford Branch; WC, Watauga Creek.

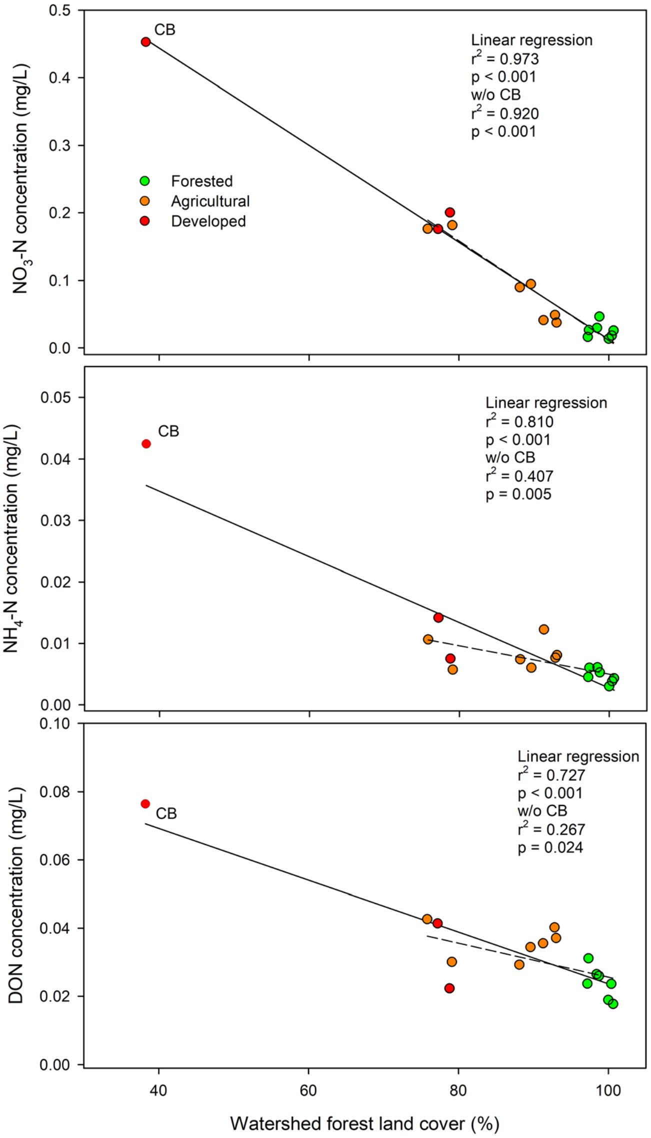

FIGURE 3 Relationships between dissolved N species and percent watershed forest land cover. CB is Crawford Branch. Concentrations are flow-weighted annual averages. The solid line is the regression line with CB, and the dashed line is the regression without CB. For NO_3—N, the lines are almost identical.

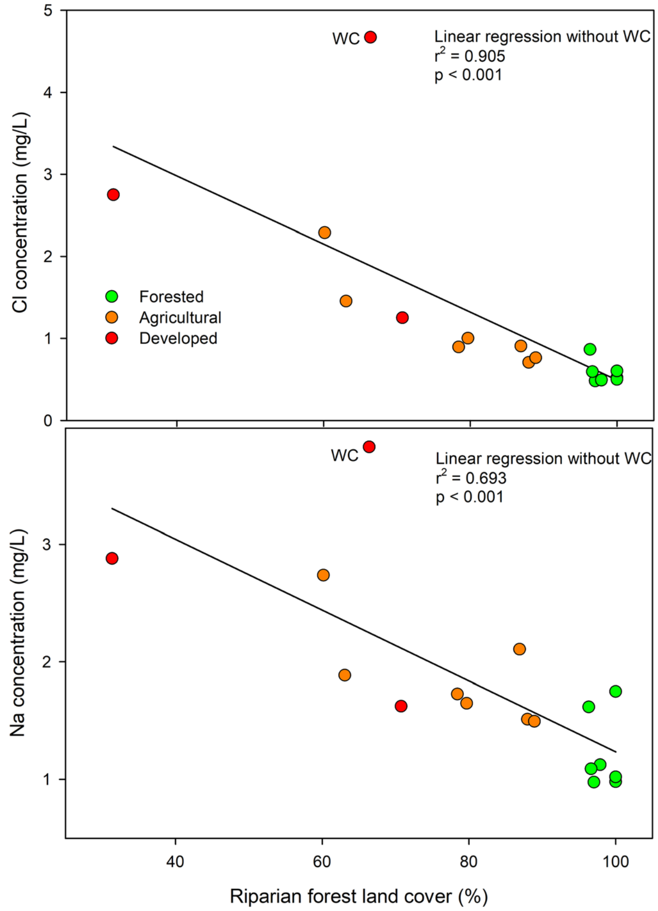

FIGURE 4 Relationships between Cl and Na and percent riparian forest land cover. WC is Watauga Creek and was not included in the regressions. Concentrations are flow-weighted annual averages.

due to geologic inputs. There is little Cl in the bedrock in most of our study area. However, some old and inactive mining sites in Macon County are described as having chlorite gangue (AboutTheDiggins, https://thediggings.com/). Our small stream sites may not adequately represent the variability of bedrock Cl – low in the Georgia headwaters and higher in in the downstream part of the ULTRB. Also, Cl concentration was especially high in Watauga Creek probably because of the use of water softeners in this watershed to reduce iron content and hardness.

When Watauga Creek was excluded from the predictive model, the pattern for Na was similar to Cl – measured values higher than predicted except for the Prentiss site. This may also be the result of water softener salt used in areas of high iron hardness and to inputs from septic systems and WWTPs.

Measured SO_4 was about double the predicted value in Cartoogechaye Creek, clearly due to geologic input. There is a deposit of iron in the Cartoogechaye Creek watershed that was never mined (AboutTheDiggins), and this iron probably occurs as pyrite, FeS_2. There is also an inactive mine site in the Watauga Creek watershed, which was mined for copper and iron. The description of the mine site says "The sulphides present are chalcopyrite, pyrite, and pyrrhotite" (AboutTheDiggins). Geologic inputs are probably why SO_4 at Gibson Bottoms and Needmore are also above predicted vales, as they are downstream of both Cartoogechaye Creek and Watauga Creek. Atmospheric input is another major source of SO_4, and watersheds with higher precipitation have higher inputs of SO_4 than watersheds with lower precipitation. However, stream chemistry data do not support this input as a direct source to streams. For example, Hugh White Creek and Ball Creek, two of the forested watersheds with highest precipitation (Table 2), had lower stream SO_4 concentration than Mica City Creek and Falls Branch, streams with forested watersheds and relatively low precipitation.

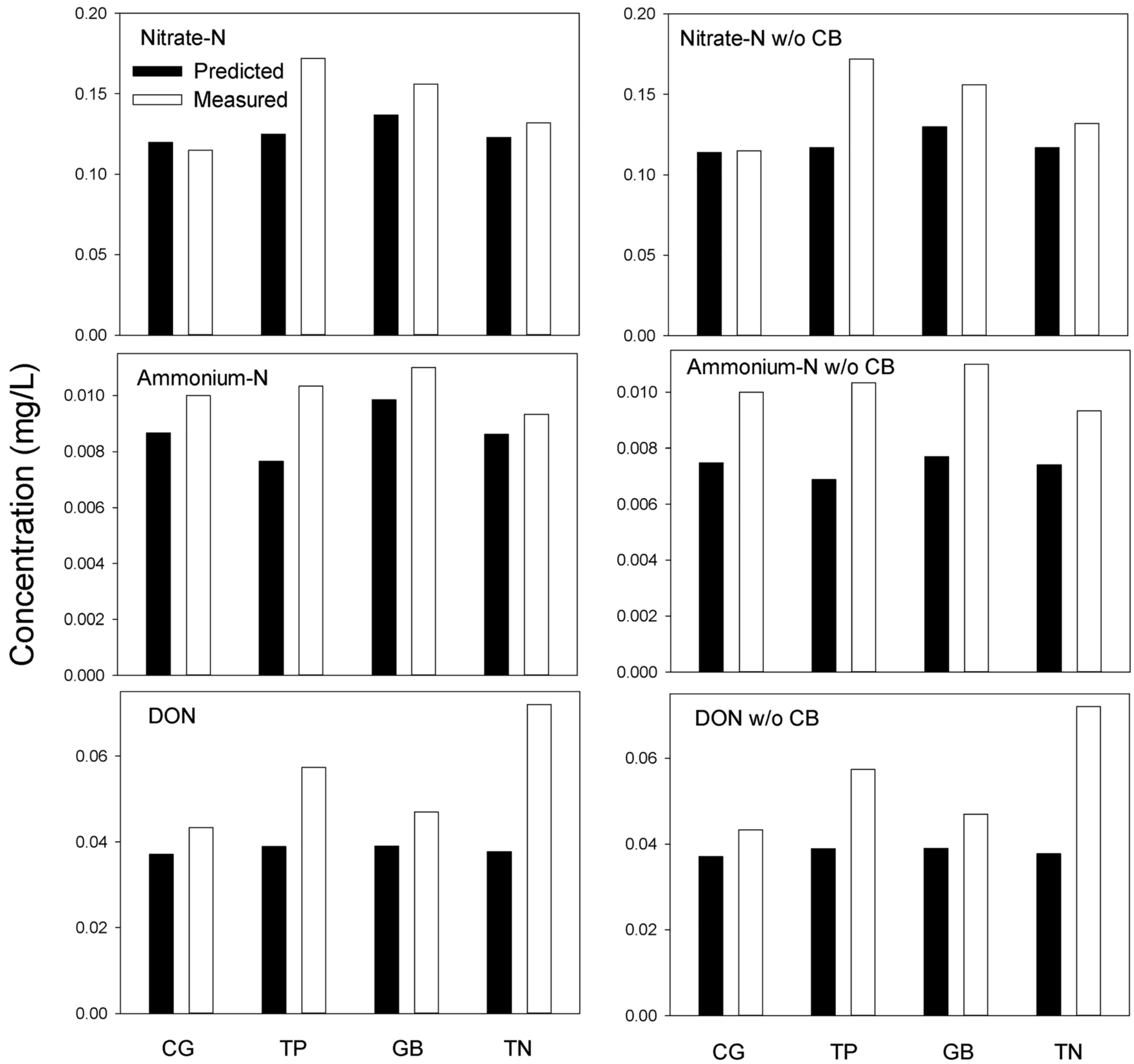

FIGURE 5 Predicted and measured N solute concentrations in the river sites. CG is Cartoogechaye Creek, TP is the Little Tennessee River at Prentiss, GB is the Little Tennessee River at Gibson Bottoms, and TN is the Little Tennessee River at Needmore.

Measured potassium was below predicted values at all four river sites. Calcium and magnesium values were higher than predicted in Cartoogechaye Creek but below predicted values at the other sites. These differences are probably due to differences in geology. For example, Willis Cove, a stream with a forested watershed, had substantially higher Ca and Mg than other forested streams (Table 4), suggesting a region of different geologic chemistry in that part of the ULTRB. There is also evidence of a forest fire in the Willis Cove watershed and surrounding areas more than a decade ago, which may have elevated Ca and Mg export.

In the ULTRB, biogeochemical processes are strongly influenced by three factors, two natural and one anthropogenic – precipitation, geology, and land cover/land use. The precipitation gradient across the basin has a large effect on water yield of the watersheds and consequently affects solute export. While precipitation chemistry is a major component of biogeochemical cycles, especially for N and S with high levels of anthropogenic deposition, we found no evidence that these inputs were impacting stream solute concentrations.

Over large watersheds with relatively homogenous climate and geology, solute variance typically collapses at some basin size threshold (e.g., Johnson et al., 2019; Shogren et al., 2019). At such scales, the effects of the variance in small watershed characteristics driving solute sourcing and transport becomes homogenized, and in the absence of internal biogeochemical processes that cause gains or losses of solutes within larger river valleys, the effects of landscape characteristics on solute concentrations should scale linearly with basin area (Abbott et al., 2018; Johnson et al., 2019; Shogren et al., 2019). However, water chemistry homogenization with increasing watershed scale may be absent for some solutes (e.g. McGuire et al., 2014).

While the entire ULTRB has a geology of highly weathered metamorphic rock, there are clear geologic differences among watersheds

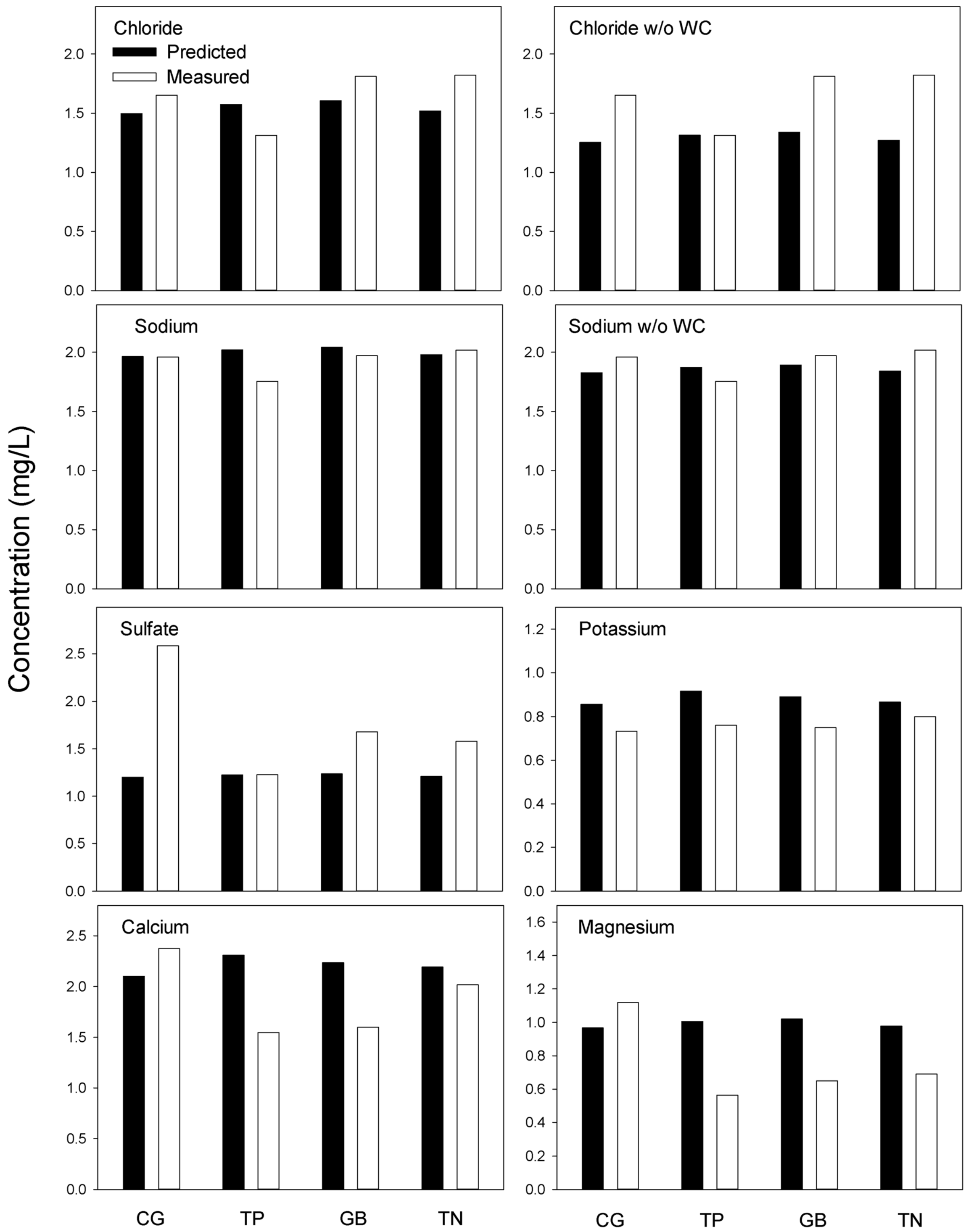

FIGURE 6 Predicted and measured Cl, SO_4, and base cation solute concentrations in the river sites. CG is Cartoogechaye Creek, TP is the Little Tennessee River at Prentiss, GB is the Little Tennessee River at Gibson Bottoms, and TN is the Little Tennessee River at Needmore.

that are not always evident in geologic maps (Knoepp et al., 2016). Evidence of this variability include records of old iron mines in two of the watersheds, Watauga Creek and Cartoogechaye Creek. The consequences of these iron deposits to stream solute concentrations is high SO_4, because iron deposits usually include S, and high Cl and Na because residents of these areas often use water softeners to reduce iron hardness in their well water. Other evidence of geochemical variability comes from differences in Ca and Mg concentrations in streams with forested watersheds (Table 4).

Land cover had the most significant effect on NO_3—N and NH_4—N, increasing with lower forest cover. Cl, Na, and base cations also increased with lower forest cover. Except for occasional high

TABLE 6 Equations for predicting solute concentrations from land-use.

Equation	Adjusted R^2
$[NO_3\text{—}N] = 0.00705 + 0.0068$ (R devel) $+ 0.00342$ (R ag)	0.979
w/o Crawford Branch	
$[NO_3\text{—}N] = 0.636–0.00624$ (R for) – 0.00214 (R ag) – 0.0166 (R shrub)	0.953
$[NH_4\text{—}N] = 0.0785–0.00073$ (WS for) – 0.00709 (WS shrub)	0.911
w/o Crawford Branch	
$[NH_4\text{—}N] = 0.00496 + 0.000124$ (WS roads)	0.426
[DON] = 0.0996–0.00076 (WS for)	0.727
w/o Crawford Branch	
[DON] = 0.0257 + 0.0067 (R shrub)	0.364
[Cl] = 4.642–0.0415 (R for)	0.486
w/o Watauga Creek	
[Cl] = 3.745–0.0329 (R for)	0.905
$[SO_4]$ = 2.201–0.0132 (R for)	0.188
[K] = 2.362–0.0186 (R for) – 0.48 (R bldg)	0.729
[Na] = 4.251–0.0302 (R for)	0.525
w/o Watauga Creek	
[Na] = 3.742–0.0253 (R for)	0.693
[Ca] = 3.35–0.0268 (R for) + 0.591 (R shrub)	0.750
[Mg] = 2.55–0.0209 (R for)	0.684

Note: Equations are the best multiple linear regressions based on the adjusted R^2 from Table 5. There were no acceptable models for SRP. Abbreviations: ag, percent agriculture; bldg, number of buildings/ha; devel, percent developed; for, percent forest; R, riparian; roads, road length (m/ha); shrub, percent shrub + barren; WS, watershed.

values, SRP was low in all streams and not related to land cover. However, for SRP it may be necessary to consider more detailed agricultural land cover (Trentman et al., 2021), including historical land use (Fraterrigo et al., 2005) and legacy inputs (e.g., Frei et al., 2021; Kreiling et al., 2020). SO_4 was only weakly related to land cover, but we believe this is because the relatively high concentrations of SO_4 due to atmospheric deposition are well above biological needs. The high SO_4 deposition of the 1980's is slowly being released from soil across the ULTRB. Agricultural land cover had most effect on solutes that are components of fertilizer (K, Ca, P, N, and Cl).

6 | CONCLUSIONS

By looking at different solutes and streams draining watersheds with different land use, we can gain insight into both natural processes and the human influences on stream chemistry. Environmental and anthropogenic complexity complicates water quality scaling relationships. Every solute tells a different story, and every watershed has unique and spatially-variable natural properties. Because the number of landowners in each of these rural watersheds is small, water quality is subject to the idiosyncratic behaviours of the local residents (Jackson et al., 2017). Furthermore, these stories are not static. Land use in the region continues to change (Chamblee et al., 2011; Kirk et al., 2012), legacy effects of past land use continue to affect water quality (e.g., Harding et al., 1998), precipitation variability and air temperatures are increasing as growing seasons lengthen (Burt et al., 2018; Hwang et al., 2018; Oishi et al., 2018), NO_3—N and SO_4 deposition continue to decrease while NH_4—N increases, and invasions of pests and diseases continue to alter forest composition and function (Ford et al., 2012; Knoepp et al., 2011).

The diversity of biogeochemical characteristics of the ULTRB is not unique to this basin. The geochemical variability and complex topography and soils of the southern Appalachian Mountains are major variables underlying stream and watershed biogeochemistry, and the mountains themselves produce variable patterns in vegetation, precipitation, and deposition. In many ways, these characteristics of the mountains also have dictated the historical and current mosaic of land use and human development. The combined physical/geochemical complex and human land-use mosaic make it difficult to scale up from small streams to larger river basins. The mismatches between predicted and measured river solute concentrations could occur because of differing biogeochemical processes in large rivers, inputs to the large rivers that do not occur in small streams, and differences in geologic controls on large river chemistry. We suggest that in order to accurately predict solute concentrations in larger rivers, it is necessary to include information beyond that included in a small set of small watersheds. The needed information varies with each solute. For nutrients such as nitrogen solutes, point sources like WWTPs need to be included. For other solutes such as SO_4, mines and geochemical inputs are critical. And for geologically derived chemicals such as Ca and Mg, it is necessary to incorporate the geologic chemistry and hydrologic variability of the basin.

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DATA AVAILABILITY STATEMENT

The data used in this study are available at the EDI data portal -- Data Portal - Home | Environmental Data Initiative (EDI) (edirepository.org).

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APPENDIX A

TABLE A1 Results of principal components analysis on standardized mean annual solute concentrations in all 2010–2011 and 2012–2013 streams. Data were normalized before running the PCA.

	Component 1 score	Component 2 score	Component 3 score
Nitrate-N	0.32	0.35	−0.05
Ammonium-N	0.30	0.45	−0.31
DON	0.30	0.42	−0.32
Cll	0.34	−0.27	0.04
SRP	0.21	−0.40	−0.70
Sulfate	0.30	−0.43	−0.11
K	0.35	−0.17	0.19
Na	0.35	−0.20	0.24
Ca	0.32	0.11	0.32
Mg	0.35	0.06	0.32
Variance explained (%)	**69.5**	**12.6**	**8.6**