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Effects of instream processes, discharge, and land cover on nitrogen export from southern Appalachian Mountain catchments

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Abstract

Catchments with minimal disturbance usually have low dissolved inorganic nitrogen (DIN) export, but disturbances and anthropogenic inputs result in elevated DIN concentration and export and eutrophication of downstream ecosystems. We studied streams in the southern Appalachian Mountains, USA, an area dominated by hardwood deciduous forest but with areas of valley agriculture and increasing residential development. We collected weekly grab samples and storm samples from nine small catchments and three river sites. Most discharge occurred at baseflow, with baseflow indices ranging from 69% to 95%. We identified three seasonal patterns of baseflow DIN concentration. Streams in mostly forested catchments had low DIN with bimodal peaks, and summer peaks were greater than winter peaks. Streams with more agriculture and development also had bimodal peaks; however, winter peaks were the highest. In streams draining catchments with more residential development, DIN concentration had a single peak, greatest in winter and lowest in summer. Three methods for estimating DIN export produced consistent results. Annual DIN export ranged from less than 200 g ha^{-1} year^{-1} for the less disturbed catchments to over 2,000 g ha^{-1} year^{-1} in the catchments with the least forest area. Land cover was a strong predictor of DIN concentration but less significant for predicting DIN export. The two forested reference catchments appeared supply limited, the most residential catchment appeared transport limited, and export for the other catchments was significantly related to discharge. In all streams, baseflow DIN export exceeded stormflow export. Morphological and climatological variation among watersheds created complexities unexplainable by land cover. Nevertheless, regression models developed using land cover data from the small catchments reasonably predicted concentration and export for receiving rivers. Our results illustrate the complexity of mechanisms involved in DIN export in a region with a mosaic of climate, geology, topography, soils, vegetation, and past and present land use.

KEYWORDS

baseflow, catchment, discharge, land cover, nitrogen, nonpoint sources, storms, stream export

1 | INTRODUCTION

Catchments with minimal disturbance usually have low export of dissolved inorganic nitrogen (DIN = nitrate + ammonium), but disturbances and anthropogenic inputs associated with agriculture and development result in elevated stream DIN concentration and export (e.g., Allan, 2004; Boyer, Goodale, Jaworski, & Howarth, 2002; Galloway et al., 2004; Howarth et al., 2012). Nitrogen often limits plant growth in both terrestrial and aquatic ecosystems, and the use of nitrogen fertilizers in agriculture and horticulture has increased soil available nitrogen and nitrogen export to many freshwater and coastal marine ecosystems, leading to unwanted eutrophication (e.g., Baron et al., 2013; Caraco & Cole, 1999; Glibert, Maranger, Sobota, & Bouwman, 2014; Howarth et al., 1996).

Estimating catchment DIN export is difficult because DIN concentration varies both seasonally and with stream discharge. Many methods have been developed for estimating solute export (e.g., Aulenbach et al., 2016) with some incorporating seasonality (e.g., Runkel, Crawford, & Cohn, 2004; Swistock, Edwards, Wood, & Dewalle, 1997). Seasonal patterns of baseflow DIN concentration differ regionally across the United States. In forested catchments of northeastern United States, DIN concentration typically peaks in winter and spring and is lowest in summer and fall, a pattern attributed to the seasonality of snow melt and DIN uptake (Vitousek & Reiners, 1975). However, in other streams, especially in southeastern United States, a contrasting pattern often occurs with greatest DIN concentrations in summer and least in fall (Duncan, Band, Groffman, & Bernhardt, 2015; Swank & Vose, 1997; Webster, Knoepp, Swank, & Miniat, 2016; Webster, Newbold, & Lin, 2016; Worrall, Swank, & Burt, 2003). This pattern has been attributed to increased soil nitrate production (nitrification) in summer (Brookshire, Gerber, Webster, Vose, & Swank, 2011; Duncan et al., 2015; Goodale et al., 2009; Goodale et al., 2015; Knoepp & Swank, 1998) and instream immobilization of DIN following autumn leaffall (e.g., Sebestyen, Shanley, Boyer, Kendall, & Doctor, 2014). In streams where adequate light reaches the streambed for autochthonous production, a bimodal pattern of DIN concentration with both fall and spring minima has been observed (Bernhardt et al., 2005; Lutz, Mulholland, & Bernhardt, 2012; Mulholland & Hill, 1997).

These typical seasonal patterns in baseflow DIN concentration can be overridden when available DIN exceeds terrestrial and instream uptake and regeneration (Lin, Webster, Hwang, & Band, 2015; Webster, Newbold, & Lin, 2016). In catchments with extensive agriculture or development, seasonal patterns of baseflow DIN concentration often resemble the terrestrially produced signal of peak winter concentration and low summer concentration. Fall fertilization may produce a winter peak (Royer, David, & Gentry, 2006) followed by low summer concentration attributed to crop plant uptake. However, in regions where most fertilization occurs in early spring, peak nitrate and DIN concentrations occur in spring and early summer (Sobota, Harrison, & Dahlgren, 2009; Tian et al., 2016), suggesting that DIN in many agricultural areas may come from rapid, near-surface transport processes. Some sites in the Mississippi River exhibit dual peaks due to both fall and spring fertilization (Sprague, Hirsch, & Aulenbach, 2011).

Stream concentrations of DIN can also change during periods of high flow caused by flushing of accumulated DIN during snowmelt (Creed et al., 1996; Creed & Band, 1998; Sickman et al., 2003) or flushing of accumulated DIN present in shallow soil flowpaths during storms (e.g., Ocampo, Oldham, Sivapalan, & Turner, 2006; Poor & McDonnell, 2007) especially when storms follow periods of extended drought (Carey, Wollheim, Mulukutla, & Mineau, 2014; Goodridge & Melack, 2012). Stream nitrogen dynamics during storms are highly variable. DIN to discharge relationships can be positive (DIN concentration increasing with discharge), negative (i.e., dilution), or chemostatic (no change in DIN concentration with discharge). In streams draining undisturbed forest, storms often have little effect on DIN concentration, and where there is an observable effect, it is usually dilution rather than elevated DIN (e.g., Webster, Knoepp, et al., 2016). The relationship between DIN and discharge can be affected by season (e.g., Barco, Hogue, Curto, & Rademacher, 2008; Poor & McDonnell, 2007), current land use (e.g., Correll, Jordan, & Weller, 1999; Poor & McDonnell, 2007; Shields et al., 2008; Wagner, Vidon, Tedesco, & Gray, 2008), and previous land use that left a legacy of accumulated nitrogen in the catchment (Basu et al., 2010; Thompson, Basu, Lascurain, Aubeneau, & Rao, 2011).

Differences in the relationship between DIN and discharge affect the annual export of nitrogen with some studies reporting higher DIN export during storms (Buffam, Galloway, Blum, & McGlathery, 2001; Owens, Edwards, & Keuren, 1991; Royer et al., 2006; Zhu, Schmidt, Buda, Bryant, & Folmar, 2011), whereas others have higher export during baseflow (e.g., Inamdar, O'Leary, Mitchell, & Riley, 2006). Estimating the importance of storms is usually based on comparing nitrogen export during storms and during times between storms (baseflow). However, baseflow continues during storms and usually increases (e.g., Gordon, McMahon, Finlayson, Gippel, & Nathan, 2004). Only a few studies have attempted to partition transport into stormflow and baseflow or into run-off and groundwater (Miller et al., 2016; Schilling & Zhang, 2004; Vanni, Renwick, Headworth, Auch, & Schaus, 2001; Zhu et al., 2011).

Estimates of nitrogen transported as baseflow or stormflow are useful because they can identify dominant flowpaths of nitrogen export and provide guidance for managing nitrogen export (e.g., Jordan, Correll, & Weller, 1997; Schilling & Zhang, 2004). The primary objective of this study was to quantify DIN export, taking into account land cover (a proxy for land use), seasonal changes in baseflow concentration, and changes in concentration during storms. Our focus was on DIN because nitrate and ammonium are the forms of nitrogen most available for uptake by plants and microbes and are generally responsible for downstream eutrophication. Although labile forms of organic nitrogen such as urea, which is commonly applied as fertilizer (Glibert et al., 2014), are biologically available, they are rapidly transformed or taken up in soils and headwater streams (Brookshire, Valett, Thomas, & Webster, 2005; Glibert et al., 2014; Lutz, Bernhardt, Roberts, & Mulholland, 2011), and forms of dissolved organic nitrogen (DON) in most stream water are highly refractory (Qualls & Haines, 1992) except where there are sources such as sewage effluent.

This study was done in the upper Little Tennessee River basin (ULTRB) of Western North Carolina and north Georgia, USA, in the southern Appalachian Mountains, a region dominated by hardwood deciduous forest. 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 (Kirk, Bolstad, & Manson, 2012). Much of this new development has occurred on the midslopes and upper slopes of the mountains where the new, incoming inhabitants value isolation and distant views (Chamblee, Colwell, Dehring, & Depkin, 2011). Synoptic sampling of streams in this area has shown that many streams have high DIN concentrations associated with either agriculture or development (Webster et al., 2012).

2 | METHODS

2.1 | Site description

The ULTRB (Figure 1) lies within the Blue Ridge physiographic province. This region of the southern Appalachian Mountains features rugged topography, usually forested slopes, and relatively flat colluvial and alluvial valleys. Annual precipitation averages approximately 1,500 mm, but within-basin climate variability is significant, ranging from 2,050 mm in the south-west to 1,350 mm in the north-east portion of ULTRB (data from PRISM Climate Group, Oregon State University, http://prism.oregonstate.edu). Lower elevations have a marine humid subtropical climate, whereas higher elevations have a marine humid temperate climate. Winters are mild with little snowfall, and summer highs rarely reach above 30°C (Laseter, Ford, Vose, & Swift, 2012; Swift, Cunningham, & Douglass, 1988).

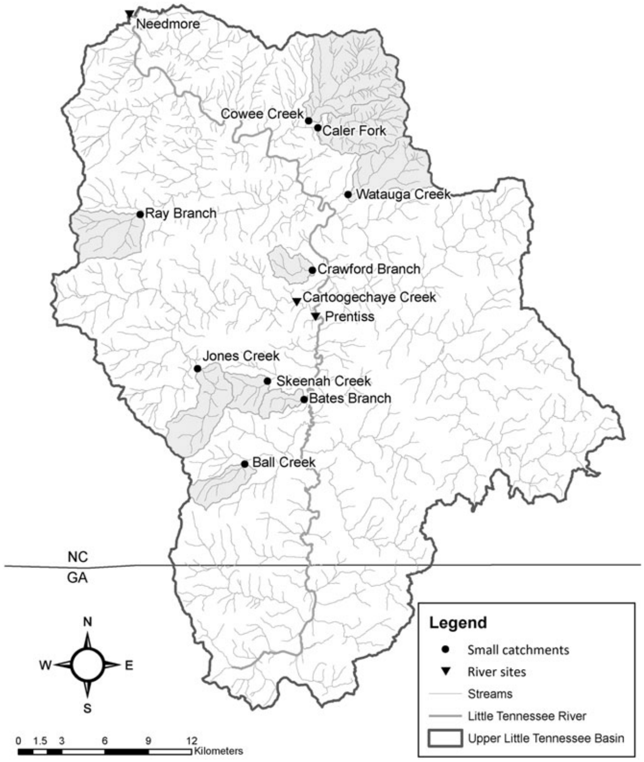

FIGURE 1 Study catchments within the upper Little Tennessee River basin, North Carolina and Georgia, USA. The Little Tennessee River starts in Georgia and flows northward to the Needmore site

The ULTRB is mostly rural with a relatively low population density. A majority of the basin is forested (78%) with only 7.6% of the land area categorized as developed (Hepinstall-Cymerman & Allen, 2011). More than 50% of the land in the basin is publicly owned, primarily within the Nantahala National Forest. Suburban development in the area has increased in recent years primarily due to second homes and retiree homes (Jackson, Leigh, Scarbrough, & Chamblee, 2015; Kirk et al., 2012). Most of these homes rely on individual septic systems. The two towns in the study area, Franklin and Highlands, NC, 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, whereas Franklin has a population of about 4,000 permanent and 8,000 seasonal residents (data from 2010 US census).

In this study, small streams, approximately second and third order, draining nine different catchments (382–3,012 ha) of ULTRB were sampled from September 2010 through September 2011. These catchments cover 10% of the ULTRB and reflect a gradient of land cover characteristics (Figure 2). The land cover classification (Hepinstall-Cymerman & Allen 2011) was derived from 2006 NASA Landsat Thematic Mapper imagery (30 × 30 m pixels), and the stream corridor-derived analysis (Joelle Freeman, Warnell School of Forestry and Natural Resources, University of Georgia, Athens, GA 30602) was based on the National Hydrography Dataset (http://nhd.usgs.gov/). Catchment land cover data were provided by the Coweeta Long Term Ecological Research, a National Science Foundation collaborative programme located at the United States Department of Agriculture Forest Service Coweeta Hydrologic Laboratory.

Among the nine catchments, forested land cover varied from 29% to 97% (Table 1). Crawford Branch, the most urban site (29% forested and 48% developed), included the town of Franklin. Agriculture within these nine catchments was primarily pastureland and hay fields. There were no livestock feedlots or row-crop agriculture within the catchments, and residential areas included lawns as well as noncommercial flower and vegetable gardens. 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. We found that the 200-m total riparian corridor (100 m on each side for the entire stream length) and the 200-m local riparian corridor (100 m on each side of the 1,000-m reach upstream of the sampling site) were similar to the entire catchment land cover for the most forested catchments, but in more developed catchments, there were greater differences between catchment and riparian land cover because most development and agriculture occur near streams (Figure 2). Along with a gradient in land cover, these nine catchments provided a gradient in baseflow stream nitrogen concentration ranging from 70 μg L^{-1} total dissolved nitrogen (TDN = DIN + DON) in the forested catchments to over 500 μg L^{-1} TDN in the least forested catchment (Crawford Branch, Table 1).

We also collected water samples from three fourth- to sixth-order “river” sites, Cartoogechaye Creek (14,789 ha) and the Little Tennessee River at Prentiss (36,260 ha) and Needmore (112,923 ha) United

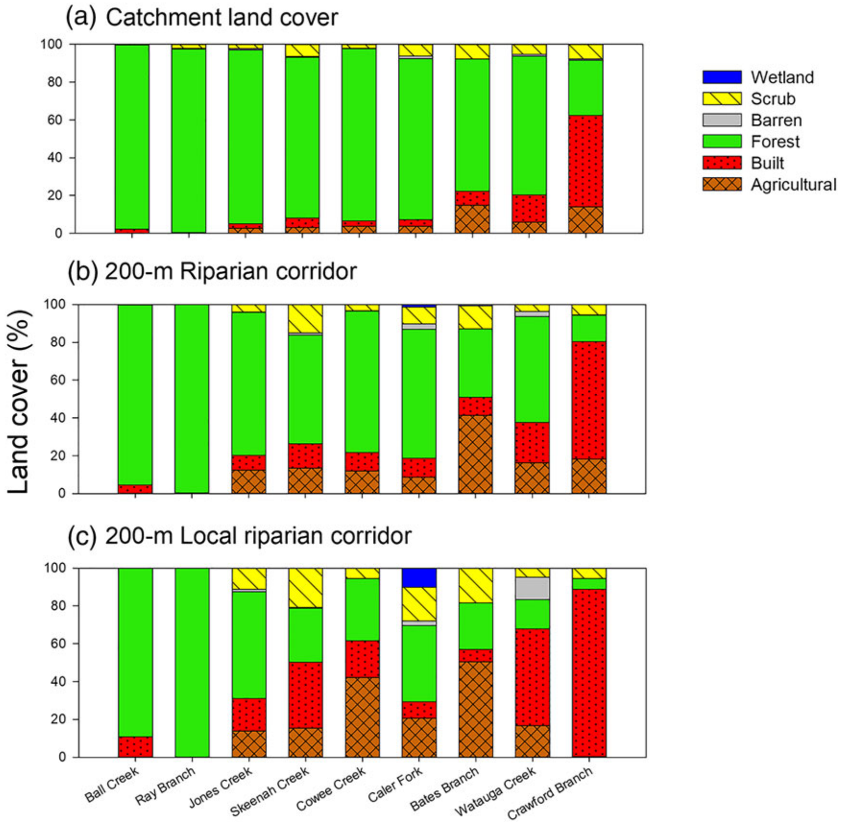

FIGURE 2 Per cent land cover for the nine smaller catchments ranging from the most to the least per cent forested with three different scales: (a) catchment land cover, (b) 200-m corridor for the entire length of the stream, and (c) 200-m corridor for 1,000-m reach upstream from the sampling site

States Geological Survey (USGS) gage sites (Figure 1). Several stream sampling sites are nested within the Cartoogechaye and Prentiss sites; the Needmore site defines the entire ULTRB and includes all other sites. Land use within these larger catchments includes intensive agriculture in some areas adjacent to the rivers. The primary crops are vegetables, including tomatoes, cabbage, peppers, and strawberries (Joe Deal, personal communication, North Carolina Cooperative Extension, Macon County, NC). There are also small areas of no-till corn. The rivers receive effluents from three sewage treatment plants in the basin.

2.2 | Field methods and water chemistry analysis

During the year of the study, we collected grab samples weekly by sample bottle immersion at the same sample location each week. Streamside autosamplers (ISCO™, Lincoln, NE) were installed to collect storm water samples. We collected samples from six of about 15 storms, including the two largest storms, three small storms, and one intermediate storm (Figure 3). During storms, autosamplers were programmed to collect one 1-L sample every 30 min for the first 6 hr of the storm and then every hour for the remainder of the storm, but times were adjusted for the predicted storm's length and intensity. All sample bottles were washed and rinsed five times with tap water and five times with deionized water before use. The total number of samples collected from each stream ranged from 164 to 211.

Stream stage was automatically recorded every 15 min through the year using a pressure transducer and a data logger attached to the autosampler at each of the nine stream sites. Point discharge was measured approximately monthly using the salt dilution technique (Gordon et al., 2004). Additionally, we estimated high flow using stream cross-section measurements and Manning's equation with the roughness factor calibrated from measured flows. These measurements were used to develop a discharge-stage height rating curve for each of the nine stream sites (Jackson, Bahn, & Webster, 2017). The three river sampling sites were co-located with USGS stream gages. Annual precipitation to each of the nine smaller catchments was determined using PRISM (PRISM Climate Group, Oregon State University, http://prism.oregonstate.edu).

Water samples were processed by the staff at the United States Department of Agriculture Forest Service Coweeta Hydrologic Laboratory and Long Term Ecological Research Analytical Laboratory (Miniat, Brown, Harper, Gregory, & Welch, 2016). Samples were filtered (0.7-μm pore size glass fiber filters, Millipore APFF04700) within 24 hr of collection and frozen until analysis. Nitrate (NO_3^-) was measured by an ion chromatograph (Dionex 25A Ion) using an AS18 column, and ammonium (NH_4^+) was measured using an Astroia 2 autoanalyzer. TDN was determined with a Shimadzu DOC-VCPH TNM-1 analyzer, and DON was calculated as TDN minus DIN.

2.3 | Data analysis

Stormflow and baseflow were separated using the Lyne and Hollick recursive digital filter (Ladson, Brown, Neal, & Nathan, 2013; Nathan & McMahon, 1990). We used mean daily flows for 1 year, padded each end of the data with 30-day reflection, and used three passes (forward, backward, and forward). For each stream, we ran a series of calculations with α values ranging from 0.8 to 0.98. For all streams, the baseflow index (BFI = annual baseflow as a fraction of total annul

TABLE 1 Characteristics of the 12 study sites

Site (figure symbol)	Catchment land cover (%)				Catchment area (ha)	Mean discharge September 26, 2010–September 25, 2011 ($m^3 s^{-1}$)	Area specific discharge September 26, 2010–September 25, 2011 (cm $year^{-1}$)	Precipitation September 26, 2010–September 25, 2011 (cm $year^{-1}$), from PRISM	Yield (Q/ppt, %)	Baseflow index (% Q as baseflow)	Mean and range of grab samples (μgN L^{-1})		
	Forest	Agriculture	Developed	Scrub							[NH_4–N]	[NO_3–N]	[DON]
Ball Creek (BC)	97.4	0.0	2.2	0.1	720	0.177	77	196	39.6	82.5	6 1–15	31 1–184	35 0–106
Ray Branch (RB)	96.9	0.0	0.6	2.1	1,470	0.390	84	153	54.7	69.0	6 1–58	34 2–95	30 0–140
Jones Creek (JC)	92.1	2.7	2.3	2.2	1,560	0.326	66	182	36.2	81.2	9 1–117	36 5–99	43 0–427
Cowee Creek (CC)	91.1	3.7	2.8	2.2	3,012	0.334	35	125	27.9	89.0	8 2–40	47 4–99	42 7–192
Caler Fork (CF)	85.1	3.8	3.5	6.0	1,738	0.166	30	125	24.2	91.3	12 2–107	40 4–83	38 0–112
Skeenah Creek (SC)	84.9	3.2	4.8	6.5	601	0.144	76	152	50.0	91.6	7 2–19	84 25–198	32 0–96
Watauga Creek (WC)	73.2	6.0	14.4	5.5	1,669	0.222	42	133	31.7	85.7	12 4–62	166 93–247	41 0–144
Bates Branch (BB)	70.0	15.0	7.2	7.7	382	0.111	92	162	56.6	81.9	10 4–21	170 72–346	45 0–193
Crawford Branch (CB)	29.3	13.9	48.4	7.9	528	0.076	46	133	34.4	94.8	42 15–148	447 214–695	78 0–252
Cartoogechaye Creek (CG)	76.1	9.1	7.2	6.2	14,789	3.14	67			73.5	12 4–79	122 46–286	49 0–151
Little Tennessee at Prentiss (TP)	78.7	7.8	8.0	4.5	36,260	9.09	79			74.0	10 2–107	153 53–268	57 0–187
Little Tennessee at Needmore (TN)	78.5	8.8	7.6	4.1	112,923	23.4	65			74.3	9 2–26	114 1–287	72 10–165

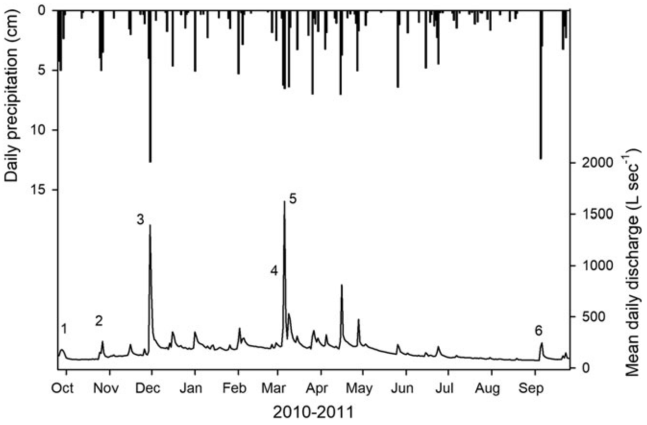

FIGURE 3 Daily precipitation and Ball Creek discharge for September 26, 2010, through September 26, 2011. The six storms sampled are numbered. Precipitation data are from Coweeta Rain Gage 96 located within the Ball Creek catchment

flow) tended to asymptote at values of α below 0.9, so we used an α value of 0.85 for all streams.

We calculated annual export (load) of dissolved nitrogen components for each stream by period-weighted trapezoidal integration: Using the weekly grab samples, the flow-weighted average DIN concentration at the beginning and end of the week was multiplied by the total volume of flow during the week, and these weekly loads were summed for the year. Because weekly grab samples do not usually include storms, this method can underestimate or overestimate annual load if concentration increases or decreases during storms (e.g., Aulenbach et al., 2016), so for DIN, we used two additional methods to estimate annual export, LOADEST and load separation. For the USGS LOADEST program (Runkel et al., 2004), we used storm and grab sample concentrations and instantaneous streamflow data to calibrate load–discharge relationships for each stream and determine the adjusted maximum likelihood estimate of daily load. We used the best-fitting model using Akaike information criterion (AIC). For seven of the nine streams, the best model was a linear function between ln load and ln discharge (ln load = $a_1 + a_2$ ln$Q$, Q = discharge) with two separate functions, one for October–November and one for the rest of the year. For Bates Branch, the best model included a quadratic term (ln load = $a_1 + a_2$ ln$Q$ + a_3 lnQ^2), and the best model for Ball Creek included sine and cosine functions and a linear increase with time. For the rivers, the Prentiss site required the two linear functions, but Cartoogechaye Creek required only a single linear model. For the Needmore river site, the best model included the quadratic term. Data for all six storms for all 12 sites are provided in Figure S2.

As an alternative to simply relating concentration or load to discharge, we developed a model using load separation, similar to that used by Vanni et al. (2001), Schilling and Zhang (2004), and Zhu et al. (2011). We modelled baseflow concentrations using all weekly grab samples collected on days when baseflow accounted for more than 90% of the total flow. Efforts to fit a function to these data using non-linear regression analysis were mostly unsuccessful due to high variability, that is, the optimization programme would not converge on a best fit function. We were able to fit a statistically significant sinusoidal function with 1-year wavelength to the data collected from Bates Branch and Crawford Branch. For the other streams, we visually fit a damped sine wave with a one-half year wavelength and a linear increase or decrease (Table 2 and Figure 4). For the most forested catchments, Ball Creek and Ray Branch, the damping was negative (i.e., summer peak > winter peak). For the other streams, the damping was positive (winter peak > summer peak). For most streams, the linear function had a positive slope, because the concentration was higher at the end than at the beginning of our year of study; Jones Creek had no slope; and Skeenah Creek, Watauga Creek, and the Little Tennessee River at Prentiss had negative slopes.

We used the baseflow DIN concentration model to calculate baseflow DIN load for each day of the year (baseflow load = baseflow concentration * baseflow discharge). For each sample, the baseflow load for that day was subtracted from the total load for that sample (sample DIN concentration * discharge at time of sampling) to get the stormflow load at each sample time. This value was divided by stormflow discharge (discharge at time of sampling minus daily baseflow) to get stormflow concentration. These estimated stormflow concentrations varied considerably when stormflow discharge was low, but variability decreased as discharge increased until stormflow DIN concentration converged on a single value characteristic of each stream (Figure S3). We used these values to calculate annual stormflow DIN concentration for each stream, defined as the average of all stormflow concentrations in samples when stormflow was

TABLE 2 Parameters of the damped sine wave equations used to model baseflow in each study stream

Stream	Number of samples	Amplitude (μg L^{-1})	Wavelength (days)	Phase shift (radians)	Damping	Initial value (μg L^{-1})	Linear increase (μg L^{-1} per day)	r^2
Ball Creek	38	5	182.5	2.5	−500	5	0.15	0.53
Ray Branch	27	10	182.5	3.5	−400	5	0.15	0.57
Jones Creek	39	26.3	182.5	2.56	440	38.3	0.0	0.17
Cowee Creek	41	30	182.5	2.56	400	30	0.11	0.41
Caler Fork	41	30	182.5	3.0	200	45	0.02	0.59
Skeenah Creek	42	70	182.5	3.0	200	125	−0.15	0.45
Watauga Creek	36	120	182.5	3.0	200	200	−0.15	0.47
Bates Branch	44	71	365	5.4	—	180	—	0.80
Crawford Branch	46	64.2	365	5.9	—	498	—	0.62
Cartoogechaye Creek	33	60	182.5	3.0	1,000	100	0.08	0.60
Little Tennessee River at Prentiss	34	175	182.5	3.25	150	200	−0.20	0.49
Little Tennessee River at Needmore	31	175	182.5	3.25	125	150	−0.20	0.37

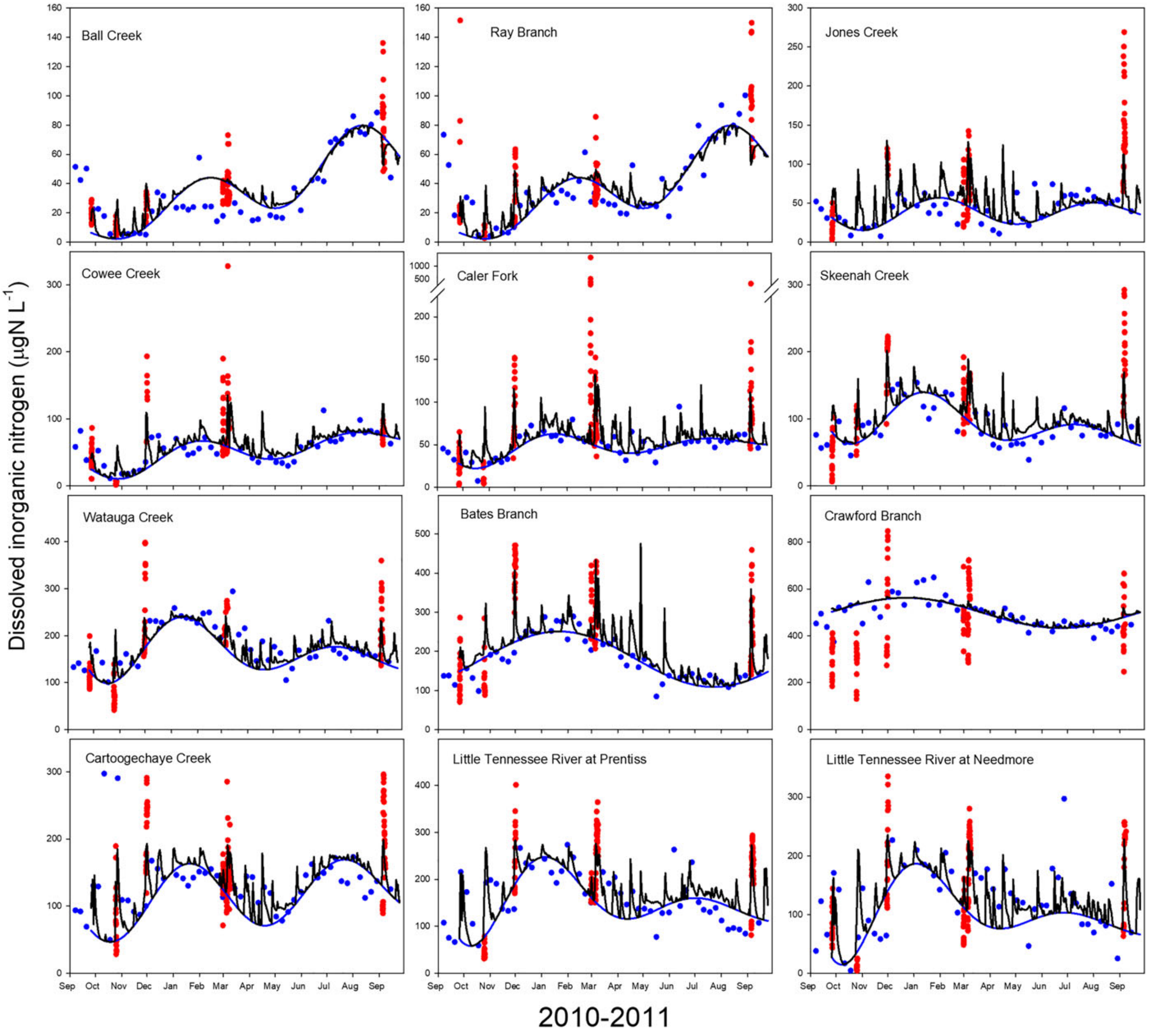

FIGURE 4 Dissolved inorganic nitrogen concentration versus date for each site showing sampled data (blue symbols are grab samples, and red symbols are samples collected during storms), modelled baseflow concentration (blue line), and modelled total (baseflow plus stormflow) concentration (black line). Sampled data are point measurements, and modelled points are daily averages. Note that the scale of the *y* axis is not the same for each site

greater than 50% of the flow. Daily total DIN load was calculated as baseflow load plus stormflow load (average stormflow concentration * daily stormflow discharge) and summed to get annual export. Average annual concentrations (total and baseflow) were calculated as annual export (total or baseflow) divided by annual discharge (total or baseflow). Because of an unusually high NH_4 concentration during Storm 4 in Caler Fork (1 mgN L^{-1} at peak flow, Figure S2e), perhaps due to a septic overflow or inundation of an area with a high density of cattle, this storm was not included in the calculation for Caler Fork.

2.4 | Statistical analyses

Statistical analyses were run using SigmaPlot (Systat Software, Inc.) except for the comparisons of multiple regression equations relating export or concentration to land cover variables, which were run using R software (R Core Team, 2016).

3 | RESULTS

3.1 | Hydrology

Average discharge from the 12 catchments ranged from 0.11 m^3 s^{-1} for Bates Branch to 23.4 m^3 s^{-1} for the Little Tennessee River at Needmore (Table 1). During our study, average discharge at the Prentiss gage site was 8.97 m^3 s^{-1}, similar to the long-term average of 10.7 m^3 s^{-1}. Annual averages at this site have ranged from 4.90 to 16.6 m^3 s^{-1} (1945–2015). Area specific discharge ranged from 30 to 42 cm year^{-1} in the catchments in the northern part of the study area (Cowee Creek, Caler Fork, and Watauga Creek) and 66 to 92 cm year^{-1} in the streams in the south-western part of the basin (Table 1). This difference reflects the gradient in annual precipitation (125 to 196 cm year^{-1}), with lower precipitation to the north (Table 1). Water yield (discharge/precipitation) was less than 30% from the catchments with the lowest precipitation and over 50% from some catchments with higher precipitation. These differences reflect variation in soils and forest vegetation as well as vagaries of precipitation during the study. For example, one storm in April 2011 accounted for nearly 10% of the annual discharge in Bates Branch but less than 1% from nearby Skeenah Creek. Area-specific discharge was not significantly related to forest land cover (Figure 5, linear regression, $p > 0.05$) or to any catchment land cover parameter (multiple regression, $p > 0.05$).

Flow separation showed large differences in baseflow fraction among the catchments (Table 1). Discharge in all streams was dominated by baseflow, with the baseflow index ranging from 69.0% (Ray Branch) to 94.8% (Crawford Branch; Figure 6). As with discharge, the baseflow index was not significantly related to forest land cover (Figure 5, linear regression, $p > 0.05$) or to any catchment land cover parameter (multiple regression, $p > 0.05$).

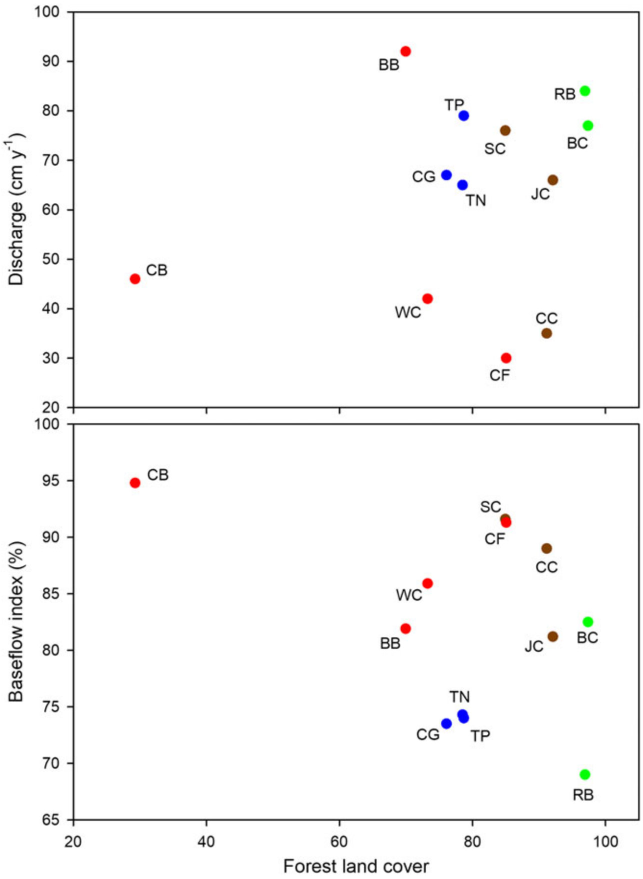

FIGURE 5 Discharge and baseflow index versus catchment forest land cover for each of the 12 study sites. Colours indicate catchment land cover: Green are predominantly forested catchments, brown have more agriculture, and red have more developed areas. Blue symbols are the river sites. BB: Bates Branch; BC: Ball Creek; CB: Crawford Branch; CC: Cowee Creek; CF: Caler Fork; CG: Cartoogechaye Creek; RB: Ray Branch; JC: Jones Creek; SC: Skeenah Creek; TN: Little Tennessee at Needmore; TP: Little Tennessee at Prentiss; WC: Watauga Creek

3.2 | Concentrations, general patterns, and changes during storms

Across all streams, TDN ranged from 70 to over 500 μgN L^{-1}. On average, TDN was made up of 60% nitrate, 7% ammonium, and 33% DON (Table 1). The average concentration of DIN in grab samples ranged from 37 μgN L^{-1} in Ball Creek to 489 μgN L^{-1} in Crawford Branch. DIN concentrations did not differ significantly among the five streams with lowest average concentrations (Ball Creek, Ray Branch, Jones Creek, Cowee Creek, and Caler Fork; $p > 0.05$, analysis of variance followed by Tukey multiple comparisons). These catchments also had the most forest land cover (Table 1). DIN in Skeenah Creek, with a catchment of mixed development and agriculture, differed from all other streams. Watauga Creek (significant developed land cover) and Bates Branch (greatest agricultural land cover) were not different from each other but differed significantly for all other streams, and DIN in Crawford Branch, with the greatest developed land cover, was significantly greater than all other streams.

We identified three basic seasonal patterns of baseflow DIN concentration in the streams (Figure 4). The first pattern was evident in the two streams with mostly forest cover, Ball Creek and Ray Branch, and was characterized by low DIN concentration and bimodal peaks, summer and winter. Spring minima were weak, and summer peaks were greater than winter peaks. Other small streams with less forested land cover (Jones, Cowee, Caler, Skeenah, and Watauga) also had bimodal summer and winter peaks; however, DIN concentration was highest in winter. The third pattern was evident in Bates Branch and Crawford Branch (small streams with the least forest cover) where we observed a single winter peak of DIN concentration and lowest concentration in summer. The three river sites showed strong seasonal bimodality with greatest DIN concentration in winter (Figure 4).

The changes in DIN concentration during storms were highly variable (Figure S2). The most common pattern was increasing DIN concentration with counterclockwise hysteresis. However, we also saw examples of dilution with clockwise, counterclockwise, or no hysteresis; flushing, that is, increasing concentration during the rising limb of the storm with clockwise hysteresis; essentially flat concentration responses; and hysteresis with increasing concentration versus discharge on one limb and decreasing concentration versus discharge on the other limb. When the data for all storms and grab samples were combined for each stream, the relationship between DIN concentration and discharge was generally positive but highly variable (Figure S1). In all streams, DIN concentration rapidly returned to near prestorm levels after peak discharge (Figure S2).

3.3 | Annual export

We estimated annual DIN export with period-weighted integration, LOADEST, and our load separation model and obtained similar values from the three methods (Table 3). In general, period-weighted

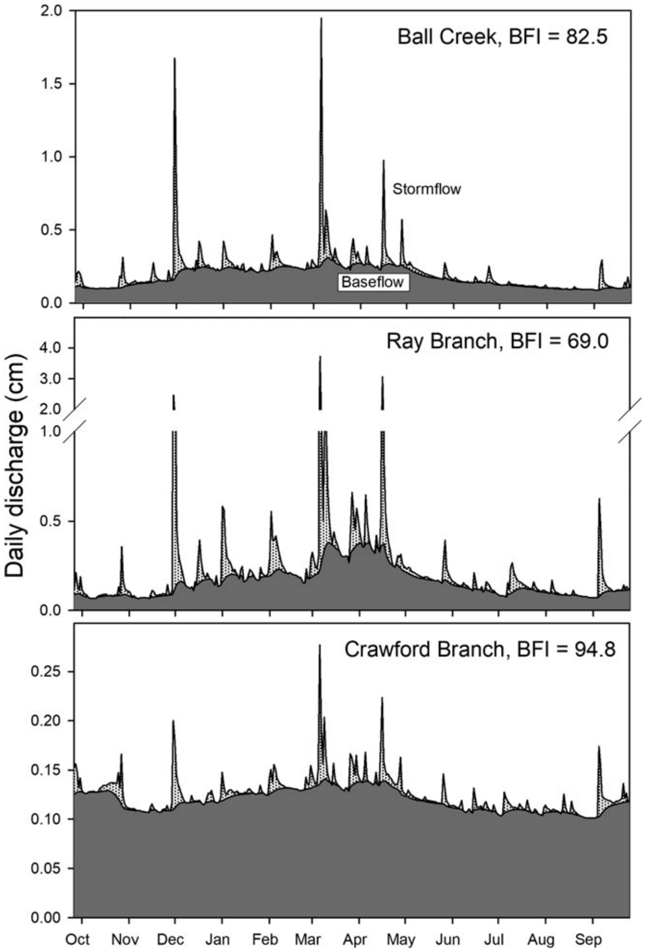

FIGURE 6 Discharge in three study streams with flow separated into baseflow and stormflow. BFI: baseflow index

integration gave the lowest values (9% lower than load separation on average), LOADEST was the highest (7% higher than load separation), and load separation was intermediate, though for several sites, the load separation estimate was the highest. The ranking of all 12 streams from greatest to least DIN export was almost the same for all three methods except that period weighted integration reversed the ranking of the sixth and the seventh highest loads (Table 3). Because the load separation model allowed us to compare baseflow and stormflow concentrations and export among catchments, the following results are based on this method.

Stormflow DIN concentrations were greater than average baseflow concentrations in all streams (Table 3). Differences between baseflow and stormflow were least in the forested streams (Ball Creek and Ray Branch) and in the stream with the greatest developed land cover and the highest DIN concentration (Crawford Branch; Figure 7). The greatest difference between baseflow and stormflow DIN concentration was in the catchment with the highest agricultural land cover, Bates Branch.

Annual total DIN export varied more than an order of magnitude, from 179 gN ha^{-1} year^{-1} (Caler Fork) to 2,303 gN ha^{-1} year^{-1} in Crawford Branch (Table 3). In all streams, annual baseflow export exceeded stormflow export, ranging from 53% of total export in Jones Creek to 94% in Crawford Branch (Figure 7 and Table 3).

3.4 | Export and concentration versus land cover

The relationships between land cover, average annual DIN concentration, and annual DIN export were evaluated using the estimates from the load separation model for the nine smaller catchments. Total, baseflow, and stormflow DIN concentrations were all closely related to forest land cover in the catchments (all $p < 0.001$, Figure 8). These relationships were partially driven by Crawford Branch (CB in the figures), but the regressions were still statistically significant when Crawford Branch was not included (all $p < 0.001$). Total and baseflow DIN export (Figure 9) were also significantly related to forest land cover, and the regressions were still significant with Crawford Branch removed ($p = 0.024$ and 0.015, respectively). However, stormflow DIN export was not significantly related to forest land cover (Figure 9) with or without Crawford Branch. In general, the relationships between concentration and land cover were much stronger than between export and land cover.

All DIN concentration and export variables (total average annual concentration, baseflow concentration, stormflow concentration, total DIN export, baseflow export, and stormflow export) for the nine smaller catchments were further evaluated against three land cover variables, agricultural, developed, and scrub, using multiple regression. Because forest land cover is 100% minus the sum of all other land cover variables, it was not included in this analysis. Also, because of collinearity among land cover at the three spatial scales, entire catchment, total riparian, and local riparian, multiple regression models at each spatial scale were evaluated separately. Within these separate multiple regressions, there was no significant collinearity among the land cover categories (the variance inflation factors ranged from 1.08 to 3.58). We selected the best spatial scale for each dependent variable based on AIC values (Table 4). Entire catchment land cover was the best predictor for most variables (total average annual concentration, baseflow concentration, stormflow concentration, total DIN export, and baseflow export), and the AIC values for land cover prediction of stormflow export were very similar for entire catchment and total riparian (Table 4). Local riparian land cover was not the best spatial scale for any dependent variable. On the basis of these results, we used the total catchment land cover equations for the nine smaller catchments (Table 5) to estimate DIN concentration and export for all 12 catchments (Figures 10 and 11). In all cases, DIN concentration and export for the larger catchments were well predicted from the smaller catchment equations.

4 | DISCUSSION

Our results suggest that including storm data in calculating DIN export does not greatly change estimates (Table 3). In part, this is because stormflow represented a surprisingly small fraction of total annual flow (Table 1), but our estimates of BFI are very similar to previous estimates for streams in this area (Price, Jackson, & Parker, 2010; Swift et al., 1988). The period-weighted integration method generally gave the lowest estimates of annual DIN export, but LOADEST, which included storm effects, resulted in export estimates that averaged only 16% greater than period-weighted integration, and, for the most

TABLE 3 Annual DIN export from the 12 study catchments

Site	Annual nitrogen export by period-weighted integration (gN ha^{-1} year^{-1})			Annual DIN export (gDIN ha^{-1} year^{-1})			Average DIN concentration (μgN L^{-1})		DIN export (gDIN ha^{-1} year^{-1})		Baseflow DIN export (%)	Total DIN concentration (μgN L^{-1})	F_{75}	
	NH_4–N	NO_3–N	DON	Period-weighted integration	LOADEST	Load separation	Baseflow	Stormflow	Baseflow	Stormflow			(mm day^{-1})	%
Ball Creek	47	205	242	252	294	281	37.3	43.3	222	59	79.0	43.9	3.10	75.9
Ray Branch	51	248	222	299	400	338	37.3	50.3	207	130	61.4	40.4	5.73	78.6
Jones Creek	53	245	244	299	431	374	37.2	140.9	199	175	53.2	56.7	3.60	87.8
Cowee Creek	27	170	141	197	281	219	51.5	157.2	159	60	72.5	62.7	1.55	79.9
Caler Fork	37	124	107	161	222	179	47.6	179.3	132	47	73.7	59.4	1.06	81.6
Skeenah Creek	56	683	222	739	881	807	90.5	254.4	641	167	79.3	106.4	2.71	78.6
Watauga Creek	60	739	174	799	807	747	163.0	263.6	588	159	78.2	177.4	1.70	77.1
Bates Branch	98	1,618	392	1,716	1,777	2,200	180.0	485.7	1,395	805	63.4	239.9	4.44	87.2
Crawford Branch	194	2,072	350	2,266	2,115	2,303	497.5	576.7	2,166	137	94.1	502.9	1.36	75.7
Cartoogechaye Creek	70	786	281	856	882	860	115.4	204.7	514	345	59.8	134.8		
Little Tennessee at Prentiss	78	1,348	424	1,426	1,460	1,483	150.9	291.8	884	599	59.6	187.7		
Little Tennessee at Needmore	69	880	435	949	914	919	100.7	244.0	507	411	55.2	140.1		

Note: The first three columns are export of the three components of dissolved nitrogen based on period-weighted integration. The next three columns compare three methods of export estimation. The other columns are based on results of the load separation model. Average baseflow DIN concentration is from the modelled seasonal patterns for each site (Figure 4), and the average stormflow DIN concentration is the convergent value from the DIN concentration versus stormflow graphs (Figure S4). Total DIN concentration was calculated as total annual export/total annual discharge. F_{75} is the cumulative discharge to carry 75% of the annual DIN export, expressed as area-normalized discharge and per cent of annual discharge. F_{75} was not calculated for the three larger sites. DIN: dissolved inorganic nitrogen. DON: dissolved organic nitrogen.

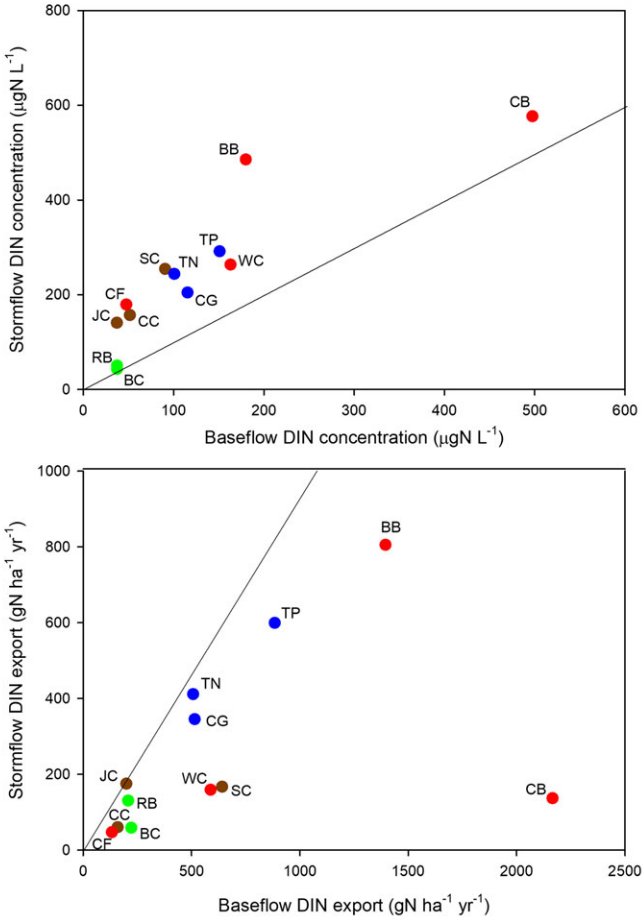

FIGURE 7 Average annual stormflow versus baseflow dissolved inorganic nitrogen (DIN) concentration in each study site (upper panel) and annual stormflow versus baseflow DIN export in each study site (lower panel). The lines in each panel are 1:1 lines. Colours are as in Figure 5. BB: Bates Branch; BC: Ball Creek; CB: Crawford Branch; CC: Cowee Creek; CF: Caler Fork; CG: Cartoogechaye Creek; RB: Ray Branch; JC: Jones Creek; SC: Skeenah Creek; TN: Little Tennessee at Needmore; TP: Little Tennessee at Prentiss; WC: Watauga Creek

developed site (Crawford Branch) and the largest river site (Needmore), LOADEST estimates were lower than period-weighted integration.

DIN concentration changes during storms were highly variable (Figure S2), which is consistent with other studies showing that the relationship between nitrate or DIN and discharge varies both temporarily and spatially (e.g., Carey et al., 2014; Jiang et al., 2010; Lloyd, Freer, Johnes, & Collins, 2016; Shields et al., 2008). The stream with the highest DIN concentration, Crawford Branch, frequently exhibited dilution, which is typical of solutes in many urban and suburban streams (e.g., Barco et al., 2008; Koenig, Shattuck, Snyder, Potter, & McDowell, 2017; Rose, 2003; Shields et al., 2008). The streams with the lowest DIN concentration (Ball Creek and Ray Branch) had the most complex patterns, probably because there was little difference between baseflow and stormflow DIN concentrations in these streams. During storms, streams draining more agricultural and developed catchments generally exhibited increasing concentration with counterclockwise hysteresis.

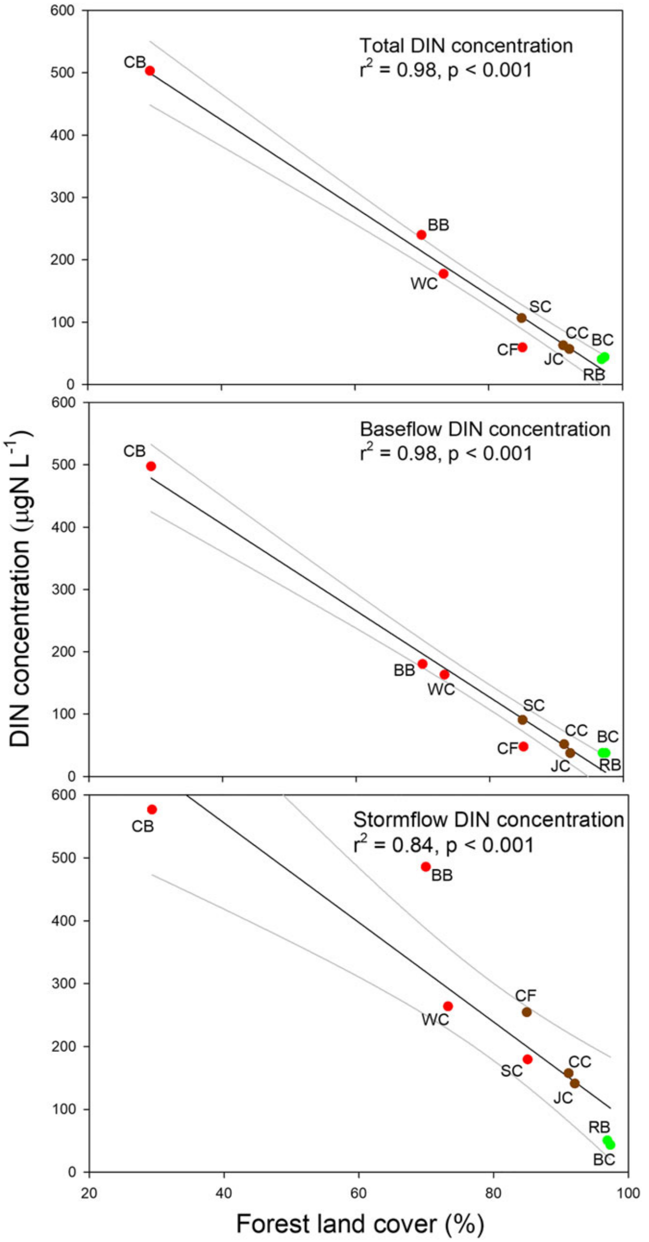

FIGURE 8 Total, baseflow, and stormflow dissolved inorganic nitrogen (DIN) concentration calculated with the load separation model versus per cent forest land cover in each of the nine smaller catchments. Linear regression lines with 95% confidence bounds are shown in each panel. Symbol colours are as in Figure 5. BB: Bates Branch; BC: Ball Creek; CB: Crawford Branch; CC: Cowee Creek; CF: Caler Fork; RB: Ray Branch; JC: Jones Creek; SC: Skeenah Creek; WC: Watauga Creek

Our observation that most streams exhibited increasing DIN concentration during storms with counterclockwise hysteresis is consistent with the understanding that DIN reaches streams primarily via long, groundwater flow paths (e.g., Lutz et al., 2012; Strayer et al., 2003; Wagner et al., 2008). Though concentration–discharge (*C*–*Q*) relationships were highly variable (Figures S1 and S2), we identified three general relationships based on the data from all samples (Figure S1). In most streams, both DIN concentration and discharge were low in fall. This was also observed in several forested streams

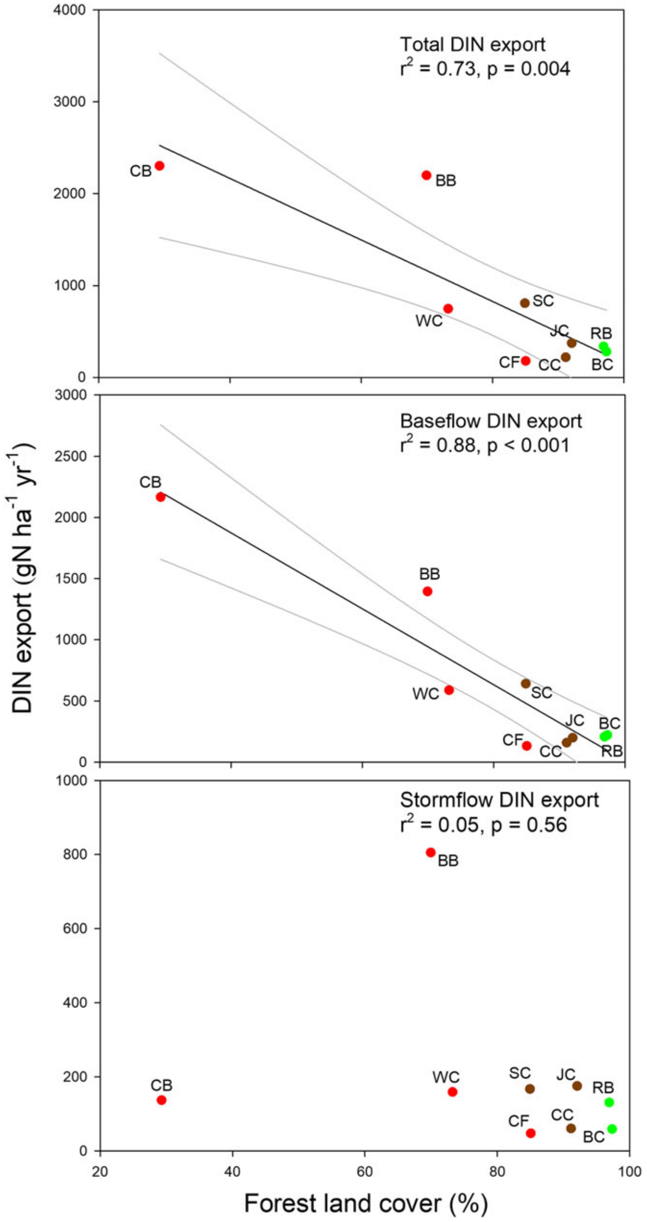

FIGURE 9 Total, baseflow, and stormflow dissolved inorganic nitrogen (DIN) export calculated with the load separation model versus per cent forest land cover in each of the nine smaller catchments. Linear regression lines with 95% confidence bounds are shown in each panel where the relationship was statistically significant. Symbol colours are as in Figure 5. BB: Bates Branch; BC: Ball Creek; CB: Crawford Branch; CC: Cowee Creek; CF: Caler Fork; RB: Ray Branch; JC: Jones Creek; SC: Skeenah Creek; WC: Watauga Creek

TABLE 4 Land cover relationships with annual DIN export and average annual DIN concentration

Parameter	Entire catchment	Total riparian	Local riparian
Total DIN export	134.7 (0.90, 0.006)	138.5 (0.85, 0.017)	150.2 (0.45, 0.35)
Baseflow export	128.8 (0.93, 0.003)	133.5 (0.88, 0.010)	144.7 (0.58, 0.20)
Stormflow export	114.2 (0.87, 0.01)	113.7 (0.88, 0.010)	128.1 (0.40, 0.42)
Total concentration	83.3 (0.99, >0.001)	95.9 (0.96, >0.001)	113.4 (0.72, 0.08)
Baseflow concentration	81.1 (0.99, 0.001)	95.0 (0.96, >0.001)	111.7 (0.76, 0.05)
Stormflow concentration	89.4 (0.99, >0.001)	92.3 (0.98, >0.001)	116.8 (0.72, 0.075)

Note: At all three scales, land cover includes per cent agricultural, developed, and scrub cover. Total riparian is a 200-m-wide strip (100 m either side of the stream) for the entire stream length, and local riparian is a 200-m strip for a 1,000-m reach upstream of the sampling site. The numbers are the Akaike information criteria for the multiple linear regressions relating export or concentration to the three land cover variables at that scale. The numbers in parentheses are the R^2 and *p* value for the multiple regression. These regressions are based only on the nine smaller catchments. DIN: dissolved inorganic nitrogen.

TABLE 5 Land cover predictors of annual DIN export and average annual DIN concentration based on the load separation model

Parameter	Intercept	Agricultural land cover	Developed land cover	Scrub land cover
Total DIN export	71.25 (0.76)	129.89 (0.02)	8.87 (0.44)	−6.20 (0.93)
Baseflow export	18.34 (0.91)	71.26 (0.06)	22.32 (0.03)	4.19 (0.94)
Stormflow export	52.79 (0.49)	58.60 (0.006)	−13.45 (0.01)	−10.31 (0.66)
Total concentration	19.13 (0.19)	10.71 (0.006)	6.87	
(<0.0001)	0.16 (0.97)			
Baseflow concentration	12.79 (0.31)	6.48 (0.02)	8.04	
(<0.0001)	0.48 (0.90)			
Stormflow concentration	31.25 (0.14)	20.96 (0.001)	2.64 (0.03)	15.62 (0.04)

Note: The predictions are linear equations of the form *Y* = intercept + (*a* * agricultural land cover) + (*b* * developed land cover) + (*c* * scrub land cover), where *a*, *b*, and *c* are the estimated coefficient values. Land cover is the per cent land cover for the entire catchment. The table entries are the estimated coefficient values with probabilities of significance (*p* values) based on *t* tests in parentheses. These predictive equations are based only on the nine smaller catchments. DIN: dissolved inorganic nitrogen.

studied by Koenig et al. (2017) and probably results from high instream uptake just after leaf fall and typically low fall discharge. If we do not consider the data from this time of year, then the relationship between DIN concentration and discharge for the most forested catchments (Ball Creek and Ray Branch) is essentially chemostatic for both baseflow and storms. We suggest that this is because instream biological processes modify any affects that might be due to source differences in these streams that have very low DIN concentrations.

In other streams, those with moderate levels of agriculture and development, again ignoring the fall values, baseflow DIN concentrations were not related to discharge, but DIN generally increased during storms. The most likely explanation of this response is that inputs of relatively high DIN concentration water from shallow soils and near stream areas elevated stream concentrations during storms. This mixing of water from shallow and deep flowpaths has been used

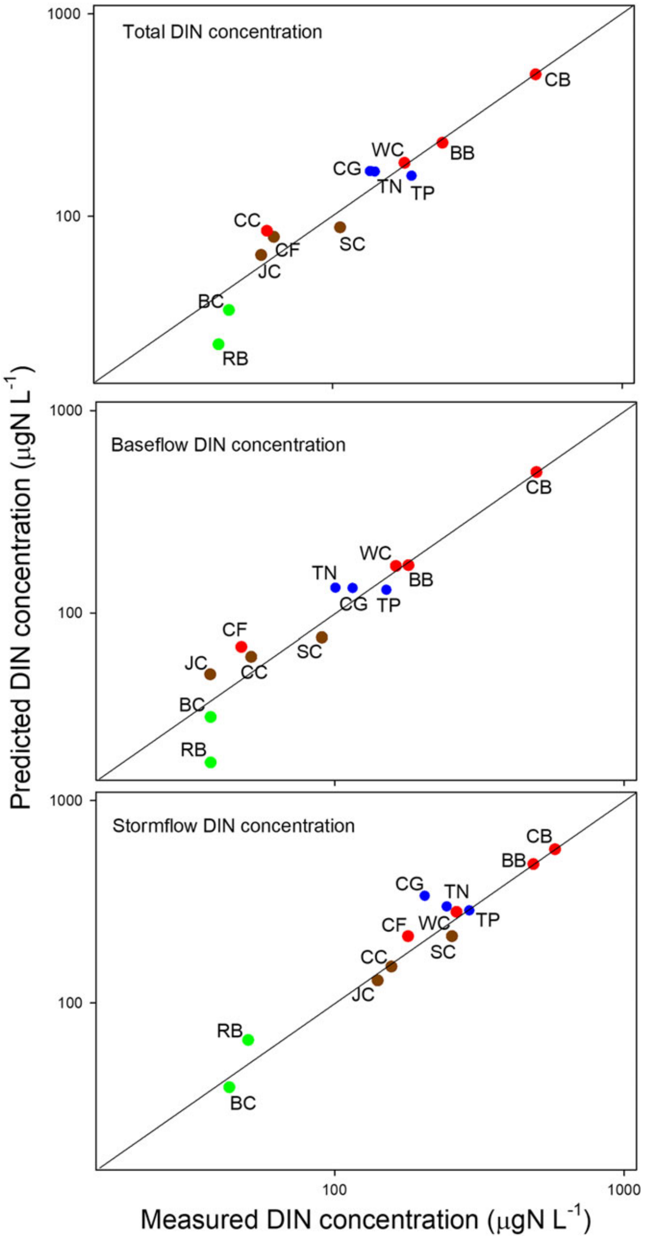

FIGURE 10 Measured versus predicted average annual dissolved inorganic nitrogen (DIN) concentration in each study site. For each concentration, predicted concentration was based on multiple linear regression of annual export (based on the load separation model) versus land cover for the nine smaller catchments (Table 5). The river sites, shown in blue, were not included in these regressions. The lines in each panel are 1:1 lines. Symbol colours are as in Figure 5. BB: Bates Branch; BC: Ball Creek; CB: Crawford Branch; CC: Cowee Creek; CF: Caler Fork; CG: Cartoogechaye Creek; RB: Ray Branch; JC: Jones Creek; SC: Skeenah Creek; TN: Little Tennessee at Needmore; TP: Little Tennessee at Prentiss; WC: Watauga Creek

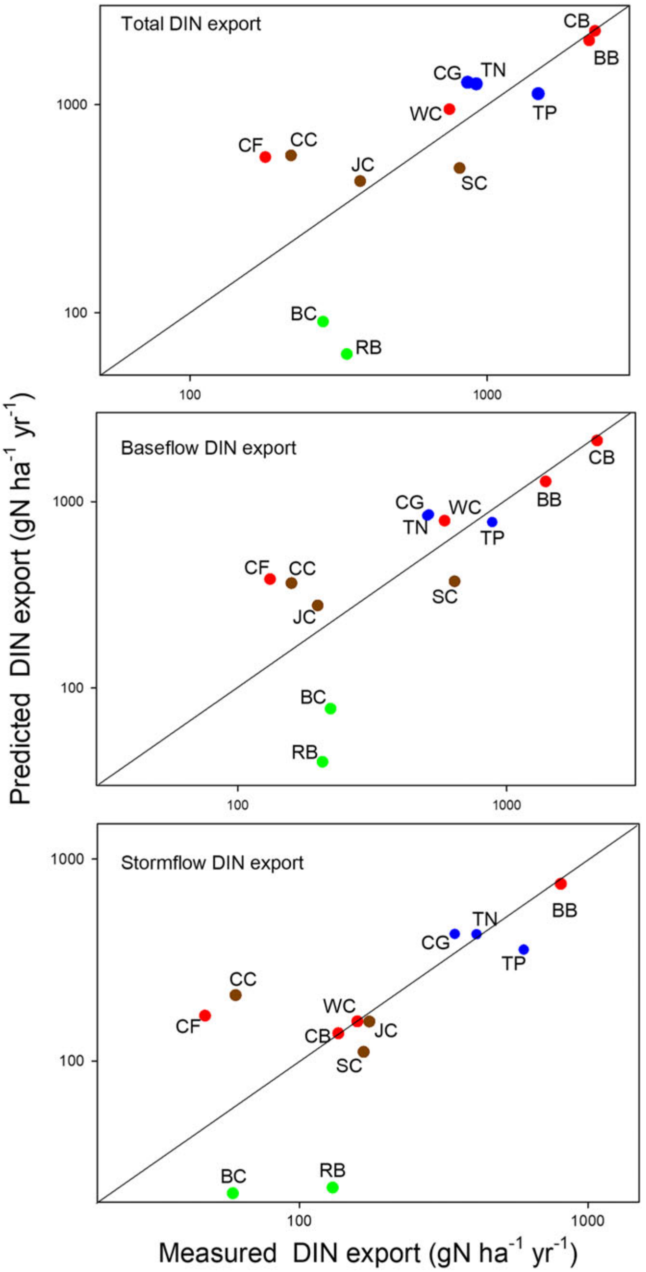

FIGURE 11 Measured versus predicted annual dissolved inorganic nitrogen (DIN) export in each study site. For each type of export, predicted export was based on multiple linear regression of annual export (based on the load separation model) versus land cover for the nine smaller catchments (Table 5). The river sites, shown in blue, were not included in these regressions. The lines in each panel are 1:1 lines. Symbol colours are as in Figure 5. BB: Bates Branch; BC: Ball Creek; CB: Crawford Branch; CC: Cowee Creek; CF: Caler Fork; CG: Cartoogechaye Creek; RB: Ray Branch; JC: Jones Creek; SC: Skeenah Creek; TN: Little Tennessee at Needmore; TP: Little Tennessee at Prentiss; WC: Watauga Creek

to explain *C*–*Q* relationships in many streams (e.g., Inamdar & Mitchell, 2006; Ocampo, Sivapalan, & Oldham, 2006; Walling & Webb, 1986) and depending on the relative concentration of DIN in deep versus shallow water can result in different *C*–*Q* relationships (Evans & Davies, 1998). Bates Branch, which has a mosaic (*sensu* Valiela & Bowen, 2002) of agricultural, development, and forest land cover, was somewhat different. DIN concentration decreased during the peak of two of the largest storms (Figure S3h), and during both storms, there was counterclockwise hysteresis with higher DIN concentration as discharge decreased. This complex relationship between concentration and discharge can result from differences in transit times from different areas of the catchment (e.g., Carey et al., 2014; Walling & Webb, 1986), especially in a catchment like Bates Branch.

Finally, in the two streams with the greatest area of development (Watauga Branch and Crawford Branch), there was little relationship between DIN concentration and discharge at the annual scale (Figure S1), though there were often distinct but variable *C*–*Q* curves during storms. Inputs from septic systems, sewage leaks, and lawn fertilizer likely contribute to the variable relationships between DIN concentration and discharge in these two streams. Other studies (e.g., Barco et al., 2008; Carey et al., 2014) have also reported variable *C*–*Q* relationships for suburban streams.

In general, storms did not have a large effect on DIN concentration. In many streams, the seasonal variation in baseflow concentration was about as large as the response to storms (Figure S1). The range of DIN concentrations was largely caused by very low autumn concentrations in all streams. In their comparison of methods to determine solute export, Aulenbach et al. (2016) found that nitrate export was best estimated by a period-weighted integration because of weak concentration–discharge relationships.

4.1 | DIN export

Our estimates of DIN export ranged from less than 200 g ha^{-1} year^{-1} for the less disturbed catchments to over 2,000 g ha^{-1} year^{-1} in the most disturbed catchments (Table 3). Exports for the forested catchments were similar to what has been reported for other headwater streams in the region (Adams, Knoepp, & Webster, 2014; Swank & Vose, 1997; Webster, Knoepp, et al., 2016), but our highest values were well below export estimates for catchments with intense agriculture in the Midwest (e.g., Royer et al., 2006; Schilling & Zhang, 2004; Tian et al., 2016), the central valley of California (Sobota et al., 2009), and urbanized catchments (e.g., Shields et al., 2008; Tian et al., 2016; Wollheim, Pellerin, Vorosmarty, & Hopkinson, 2005). Most DIN export occurred at baseflow for all of our streams, ranging from 53% for Jones Creek to 94% for Crawford Branch. Schilling and Zhang (2004) and Miller et al. (2016) also found that most nitrate export occurred at baseflow. In contrast, Vanni et al. (2001) found greater stormflow nitrate export, and Royer et al. (2006) found that most nitrate export from tile-drained agricultural catchments occurred at flows above the 75th flow percentile. These differences reflect differences in the predominance of baseflow and difference in DIN concentrations in shallow versus deep soil. For example, Vanni et al. (2001) suggested that nitrate leached from loess-dominated surficial soils resulted in the predominance of stormflow export of nitrate, whereas Shilling and Zang (2004) attributed high groundwater nitrate concentration and baseflow-dominated DIN export to leaching of nitrate to baseflow in a primarily row crop catchment.

The relationship between the percentage of DIN exported at baseflow and the baseflow index was weak but statistically significant (linear regression, r^2 = 0.50, p = 0.03, Figure 12). For all our streams, the percentage of DIN exported at baseflow was less than the baseflow index. This was also found in the three streams dominated by agriculture studied by Vanni et al. (2001) and the Potomac River streams studied by Miller et al. (2016), whereas Schilling and Zhang (2004) found the opposite relationship in the Raccoon River (Figure 12). The differences among the streams in our study are also apparent in the F_{75}, the cumulative annual discharge needed to carry 75% of the annual export (Table 3). When the average baseflow and stormflow DIN concentrations were similar, F_{75} was close to 75% (e.g., Ball Creek and Crawford Branch). However, in streams where the stormflow DIN concentration was much greater than the average baseflow concentration, a larger percentage of the annual flow was needed to carry 75% of the export (e.g., Jones Creek and Bates Branch). Thus, the relative contributions of baseflow and stormflow to annual DIN export depend on both the hydrological characteristics, that is, the baseflow index, and chemical differences of soils contributing to baseflow and stormflow.

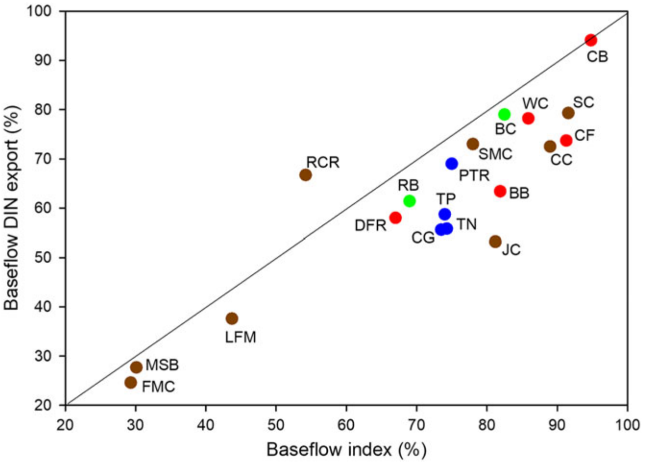

FIGURE 12 Baseflow dissolved inorganic nitrogen (DIN) export (% of total DIN export) compared with baseflow index (% of discharge as baseflow). For the sites not part of this study, the values are for nitrate rather than DIN. Colours are as in Figure 5. RCR: Raccoon River (Schilling & Zhang, 2004); FMC: Four Mile Creek; LFM: Little Four Mile Creek; MSB: Marshall's Branch (Vanni et al., 2001); PTR: Potomac River; SMC: Smith Creek; DFR: Difficult Run (Miller et al., 2016); BB: Bates Branch; BC: Ball Creek; CB: Crawford Branch; CC: Cowee Creek; CF: Caler Fork; CG: Cartoogechaye Creek; RB: Ray Branch; JC: Jones Creek; SC: Skeenah Creek; TN: Little Tennessee at Needmore; TP: Little Tennessee at Prentiss; WC: Watauga Creek. The line is the 1:1 line

4.2 | Sources of DIN

Our study corroborated what is well known—forested catchments have low DIN export and disturbances associated with agriculture and residential development result in elevated DIN concentration and export (e.g., Allan, 2004; Boyer et al., 2002; Galloway et al., 2004). Stream export of DIN has been related to several different sources of DIN (e.g., Boyer et al., 2002). One DIN source common to all catchments is nitrogen deposition (e.g., Pardo et al., 2015). In the upper Little Tennessee River basin, current bulk nitrogen deposition is about 6 kg ha^{-1} year^{-1} (Webster, Knoepp, et al., 2016) and is fairly uniform over the basin (2015 map, National Atmospheric Deposition Program/National Trends Network, http://nadp.isws.illinois.edu). Deposition is considerably higher than DIN export from any of the catchments we studied, suggesting that this nitrogen is strongly retained or transformed within the catchments. However, during large storms, depositional nitrogen may contribute to high DIN concentration at high discharge when saturated shallow soils become significant source areas.

Another potential nitrogen input is nitrogen fixation. Throughout the southern Appalachian Mountains, black locust (*Robinia pseudoacacia*) is a rapidly growing tree that shows a strong response following clear-cut logging (Boring & Swank, 1984; Elliott, Boring, Swank, & Haines, 1997). Nitrogen fixation by *Rhyzobium* bacteria associated with the roots of black locust is a major contributor of terrestrial nitrogen and ultimately to stream DIN export from logged catchments (Webster, Knoepp, et al., 2016). Both Ball Creek and Ray Branch are approximately third-order catchments and include areas that were clear-cut within the past 40 years, perhaps explaining why DIN export from these catchments is higher than DIN export from smaller reference catchments that have not been logged for over 90 years (e.g., Webster, Knoepp, et al., 2016). Similar clear-cut areas once dominated by black locust are likely present in all of our study catchments, and nitrogen fixation by other leguminous plants may contribute to DIN export from some agricultural areas. In western North America, red alder (*Alnus rubra*) is a similar host to nitrogen fixing symbionts and can contribute significantly to catchment nitrogen export (e.g., Compton, Church, Larned, & Hogsett, 2003).

In disturbed and logged catchments, increased decomposition of soil organic matter and mineralization of organic nitrogen is another source of DIN, at least in the first few years following disturbance (e.g., Vitousek & Melillo, 1979). In both agricultural and developed areas, fertilizer additions are a major source of stream DIN (e.g., Glibert et al., 2014; Howarth et al., 2012; Sobota et al., 2009; Valiela & Bowen, 2002). Springtime fertilizer application, which is typical in the ULTRB, may contribute to the summer peak of DIN concentration observed in the catchments with significant agriculture. Additionally, there are three sewage treatment plants within the ULTRB, for the towns of Franklin and Highlands and a facility in Rabun County, GA, near the headwaters of the Little Tennessee River. The surge of summer residents and visitors may contribute to the summer peak DIN concentration at the river sites. In most of the study area, homes in residential developments have individual septic systems for sewage treatment. Leakage from these systems may be a significant contributor to stream DIN especially in areas with older developments. In the low population density catchments of the Little Tennessee River basin, the particulars of wastewater management and landowner behaviour (e.g., ponds, livestock, and water diversion for home gardens) also contribute to substantial water quality differences among catchments, so we would not expect land cover alone to explain the variability in DIN concentrations and exports.

Though not considered in most catchment nitrogen budgets, rock weathering may be a significant source of DIN (Holloway & Dahlgren, 1999; Houlton & Morford, 2015). Morford, Houlton, and Dahlgren (2016) reported that nitrogen weathering from mica schist bedrock in a Northern California catchment was a significant source of DIN. This is similar to the geology of our study area (Hatcher, 1988), although the southern Appalachian Mountains are a much older, more weathered landscape. Where bedrock weathering is accelerated by developmental activities that expose parent material, weathering may become a source of DIN that contributes to high DIN in streams draining areas with developed land cover, especially where development is actively occurring.

4.3 | DIN seasonality

Our results and previous studies (e.g., Lutz et al., 2011; Mulholland & Hill, 1997) suggest that instream processes play a major role in seasonal patterns of baseflow DIN concentrations (Figure 4). We did not see the unimodal, strong summer peak pattern that typically occurs in small forested, headwater streams in this area (Webster, Knoepp, et al., 2016; Webster, Newbold, & Lin, 2016). Apparently, there is sufficient springtime light in the third-order, forested streams included in this study (Ball Creek and Ray Branch) to stimulate algal production and minimize DIN concentration in spring. Roberts, Mulholland, and Hill (2007) and Roberts and Mulholland (2007) found that primary production in Walker Branch, a small forested stream in Tennessee, had a large effect on nitrate concentration, creating a strong decline in nitrate concentration in spring. Lupon, Martí, Sabater, and Bernal (2016) found a similar decline in spring nitrate concentration in a forested stream in Spain, which they attributed to instream primary production.

Catchments with a greater proportion of agricultural land use (Jones Creek, Cowee Creek, and Caler Fork), and therefore canopy openings, had greater instream primary production (McTammany, Benfield, & Webster, 2007) and lower DIN concentration throughout the summer. Spring and summer primary production may also be stimulated by agricultural fertilizer application. In an analysis of stream metabolism in 70 streams in North America, including eight streams in the ULTRB, Bernot et al. (2010) found that DIN concentration was a significant factor in explaining both primary production and stream ecosystem respiration. Using nutrient releasing substrates in the same streams, Johnson, Tank, and Dodds (2009) found frequent nitrogen stimulation of ecosystem respiration. Primary production was less frequently nitrogen limited, but nitrogen limitation increased with light availability. In all streams in our study except Bates Branch and Crawford Branch, DIN concentrations were relatively low, and we observed a bimodal seasonal pattern of DIN concentration. The high DIN concentrations of Crawford Branch and perhaps Bates Branch apparently saturated instream uptake, resulting in a single winter peak. This is similar to the results reported by Webster, Knoepp, et al. (2016). Using a 42-year data set, they showed that a reference stream and prelogging data from another stream both exhibited a strong summer peak in DIN concentration. Following logging, DIN concentration in the experimental stream greatly increased and shifted to a late winter peak. They attributed this shift to high nitrogen inputs by nitrogen fixation that then saturated instream processes.

The three river sites reflected inputs from the larger area and tributary streams, with little apparent influence from near-stream agriculture. However, in these larger streams, uptake by algae and aquatic vascular plants may contribute to relatively low summer DIN. McTammany, Webster, Benfield, and Neatrour (2003) found highest primary production in the Little Tennessee River in summer at a site just upstream of our Needmore site. Instream uptake may reduce a potential summer DIN concentration peak caused by seasonal residents and tourists.

4.4 | Concentration versus export

We found that land cover was a better predictor of DIN concentration than of DIN export (Figures 8 and 9 and Table 4), due to the regulation of annual discharge by catchment hydrological properties and basin morphology. For example, Ray Branch, the stream with the lowest baseflow index is a forested catchment in a steep, narrow valley, whereas Crawford Branch, with the highest baseflow index, is in a broad valley that contains the town of Franklin. Baseflow in Crawford Branch is supplemented by irrigation with town-provided water to lawns and gardens and perhaps with leakage from water supply and sewage systems. Stormflow is rapidly transported or diverted into retention and detention ponds. In urban areas, discharge characteristics and DIN export are often related to the extent of impervious surface area (e.g., Shields et al., 2008), but, within the largely vegetated catchments of our study, the relatively small areas of pavement and compacted soils seem to have little effect on hydrological characteristics of the basins. Romeis (2008) found that the percentage of storm flow was lower from forested than from agricultural catchments, but his conclusion was complicated by the fact that the forested catchments were larger and steeper than the agricultural catchments. This interaction between land cover and basin morphology occurs frequently. For example, the broad valley of Crawford Branch was occupied and farmed by Native Americans long before it became a European settlement (Bartram, 1791; Harper, 1958; Rodning, 2002). In an extensive study of catchments within and near the Little Tennessee River basin, including several catchments used in this study, Price et al. (2010) found higher baseflow from forested catchments compared with morphologically similar, less-forested catchments, but factors associated with basin morphology were also important in controlling baseflow. Conversely, Woodruff and Hewlett (1970) found no significant relationships between hydrological response (stormflow/total flow) and any measure of basin morphology or land cover for streams throughout Eastern United States. Although most of their study streams were much larger than our nine smaller streams, they make the point that much of the variability in hydrological response must be due to subsurface characteristics that cannot be estimated from surface topographical characteristics.

4.5 | Scaling up

We found that the relationships between land cover and DIN export for the nine smaller streams could be extrapolated to the three larger river sites (Figures 10 and 11), suggesting that the nine smaller catchments were representative of the larger area. This could be simply because the nine smaller catchments are nested within the river sites, but there are significant valley-bottom areas of intense row-crop agriculture especially in the upper reaches of the Little Tennessee River, along the river just upstream of the Prentiss site, and in the lower reaches of Cartoogacheye Creek. Further, the sewage treatment plants for the towns of Franklin and Highlands are located upstream of the Needmore site. These localized inputs must be small compared with the diffuse inputs from throughout the catchments and are adequately represented by the inputs from agricultural and developed areas of the smaller catchments. These data support prior research indicating that the relative effect of basin-wide land cover versus near-stream land cover depends on the water quality variable of interest. In this case, catchment land cover was a better predictor of DIN concentration and export than was local or riparian land cover—as was also found by Strayer et al. (2003). Similarly, Scott, Helfman, McTammany, Benfield, and Bolstad (2002), working with streams in the ULTRB, found that including riparian land cover did not improve their model predictability of nitrate or ammonium concentrations. Other studies in the region have suggested that land use or land cover effects on other stream characteristics can be scaled up from local to regional scales (Price & Leigh, 2006; Scott et al., 2002). Conversely, regional studies of phosphorus and sediment export suggest that near-stream vegetation is an important control on stream concentrations and export (Jackson et al., 2017; Scott et al., 2002). The difference can probably be attributed to differences in transport mechanisms and travel distances. Whereas nitrogen transport occurs primarily in dissolved forms, sediment moves as particles, and dissolved phosphorus is highly reactive, biologically, chemically, and physically, with organic and inorganic particles, and has very short travel distance in streams in this area (e.g., Mulholland, Marzoff, Webster, Hart, & Hendricks, 1997). In either case, export of solutes and sediments in the southern Appalachians are complicated by the low predictive power of land cover on stream hydrology in this landscape with high climatic and geomorphic variability (Jackson et al., 2017).

5 | CONCLUSIONS—WHAT CONTROLS DIN EXPORT?

The control of DIN export from catchments is complex, and understanding the mechanistic processes controlling nitrogen movement from terrestrial ecosystems to streams will require detailed study of small, headwater streams with close linkages to terrestrial systems. Temporal patterns of DIN concentration during storms may be highly influenced by transit time and catchment storage state, with transport pathways and source areas varying across and within storms (e.g., Davies & Beven, 2015; Lloyd et al., 2016). However, our results provide some insights on the controls of annual DIN export in this region.

In undisturbed or minimally disturbed catchments in the southern Appalachian Mountains, nitrogen is tightly retained (Adams et al., 2014; Swank, 1988; Swank & Vose, 1997; Swank & Waide, 1988; Webster, Knoepp, et al., 2016), and little DIN is lost from these forested catchments. However, forest logging can decrease nitrogen uptake by vegetation and increased nitrogen fixation (Webster, Knoepp, et al., 2016). Agricultural land use adds other nitrogen sources, fertilizer and animal wastes, resulting in increased nitrogen available for movement to streams. When land use is changed to residential or exurban development, septic systems and lawn and garden fertilizer also add additional nitrogen, and land excavation may expose mineral soils to weathering. The indirect effect of agriculture and development on DIN export through modification of hydrological processes seems to be less important in the catchments we studied because they are still predominantly forested.

Instream processes, including heterotrophic immobilization of DIN on decomposing leaves, autotrophic uptake by stream algae and plants, and mineralization of organic nitrogen, affect the timing and form of nitrogen exported from catchments but in the long term do not affect total nitrogen export (Brookshire, Valett, & Gerber, 2009). Instream denitrification may reduce nitrogen export by some streams, but in most streams, denitrification is a small fraction of total nitrogen output (Mulholland et al., 2008). These instream processes have little impact on DIN where DIN concentration is high.

Our separation of DIN export into baseflow and stormflow is based on our model assumptions of a defined seasonal pattern of baseflow concentration and a constant stormflow concentration specific to each stream and then a simple mixing of baseflow and stormflow during storms. This model could clearly benefit from long-term data to improve definition of the baseflow concentration pattern for each stream. Also, stormflow concentration is much more complicated than assumed in our model (e.g., Vaughan et al., 2017). This is especially evident in Crawford Branch where DIN concentration both decreased and increased during some storms (Figures 4 and S2i). These changes in DIN concentration may be largely determined by the flowpaths between rainfall and streamflow, which are largely dictated by catchment morphology. In broad, shallow valleys, most rainfall gets to streams by deep subsurface/groundwater flowpaths, whereas in steep, narrower valleys, water may reach streams through shallower and more rapid flowpaths. Our study area is characterized by deep soils with rapid infiltration rates and minimal snow cover. The highest soil solution DIN concentrations are typically found in surface soils (Knoepp, Vose, & Swank, 2008), but the majority of DIN export occurs during baseflow (Table 3). During some storms, there is increased connectivity between surface soils and streams resulting in increased stream DIN concentrations (Lupon, Sabater, Minarro, & Bernal, 2016; Lutz et al., 2012), but the increase is short lived as the available DIN is rapidly removed and diluted. Worrall et al. (2003) found that streams at Coweeta have a memory of nitrogen export, but it is on a 6-month or annual basis. The overall result is that a large proportion of DIN export occurs at baseflow. Groundwater (baseflow) DIN is generally well mixed and may have been in transit for years or even decades (Burt & Worrall, 2009; Nippgen, McGlynn, Emanuel, & Vose, 2016) and thus should have a fairly constant concentration (e.g., Miller et al., 2016). The seasonality of baseflow DIN concentrations in our study (Figure 4) suggests that groundwater DIN may be modified by near-stream and in-stream processes, especially in the streams with the greatest forest cover.

For all the catchments, the relationship between DIN export and discharge was positive (Figure 13), as expected, but because of the outliers, the relationship was not statistically significant (linear regression, r^2 = 0.08, p = 0.38; exponential growth non-linear regression, r^2 = 0.08, p = 0.37). The two most forested sites, Ball Creek and Ray Branch, had much less DIN export than predicted by their discharge because of their low DIN concentration, that is, DIN export was supply limited (e.g., Basu et al., 2010; Burns, 2005; Duncan, Band, & Groffman, 2017; Moatar, Abbott, Minaudo, Curie, & Pinay, 2017). In contrast, Crawford Branch, the least forested and most developed catchment, had much more export than predicted by discharge because of high DIN concentration, and export from this catchment could be described as transport limited. With these three sites removed, the regression between DIN export and discharge was statistically significant (linear regression, r^2 = 0.68, p = 0.006; exponential growth non-linear regression, r^2 = 0.83, p = 0.001).

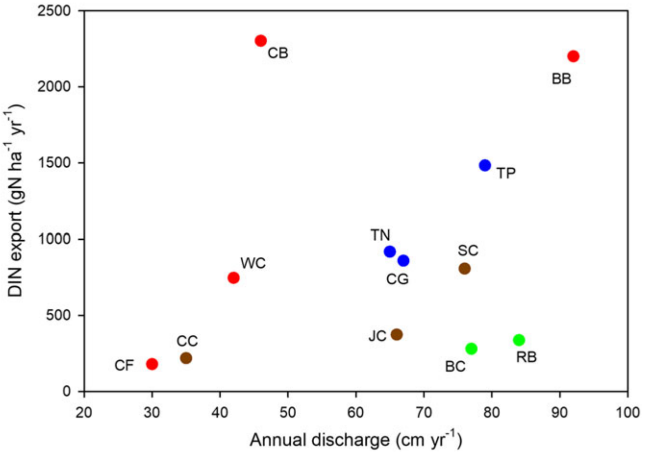

FIGURE 13 Dissolved inorganic nitrogen (DIN) export versus annual discharge in the 12 study sites. Symbols for the sites are given in Table 1. Symbol colours are as in Figure 5. BB: Bates Branch; BC: Ball Creek; CB: Crawford Branch; CC: Cowee Creek; CF: Caler Fork; CG: Cartoogechaye Creek; RB: Ray Branch; JC: Jones Creek; SC: Skeenah Creek; TN: Little Tennessee at Needmore; TP: Little Tennessee at Prentiss; WC: Watauga Creek

To understand and regulate nitrogen-caused eutrophication of downstream ecosystems, it is necessary to know export, that is, the actual nitrogen input to the downstream systems. However, estimating export requires estimating both nitrogen concentration and discharge. Catchment land cover was an excellent predictor of DIN concentration in the streams we studied but was less useful for predicting DIN export (Figures 8 and 9). As shown in Figure 13, discharge was a good predictor of export for most streams except in streams where DIN concentration was limited by instream uptake (Ball Creek and Ray Branch) or where transport processes have been modified by development (Crawford Branch). From our study, it is evident that the effect of land use on DIN concentration is very strong, but discharge is less related to land use and more related to precipitation patterns and geomorphic basin structure.

Because nitrogen is such an important element in biological processes, including human and human-related processes (agriculture, for example), any analysis of effects of various factors influencing nitrogen dynamics is complex. Figure 14 illustrates some of the more important factors and interactions. Catchment nitrogen dynamics occur on a backdrop of geology and topography. The topography affects hydrological processes such as the amount of run-off that occurs as baseflow versus stormflow. This geological/topographical backdrop also affects vegetation and soil structure and development and similarly influences patterns of human land use. In the ULTRB, human settlement was primarily in the broader valleys, such as Crawford Branch and along the river, because it was more amenable to agriculture. This pattern has changed as more people choose to live higher on the mountainsides. Human land use can either

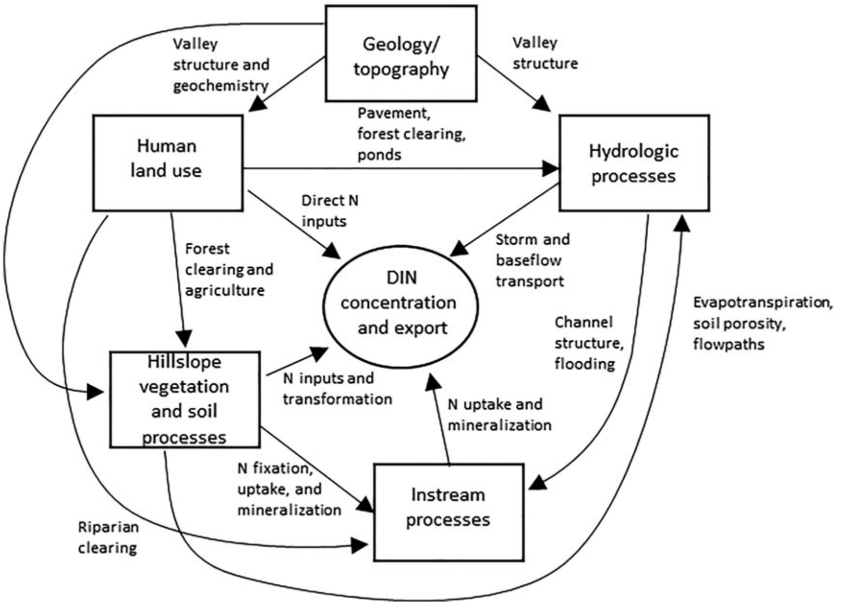

FIGURE 14 Factors and interactions affecting dissolved inorganic nitrogen (DIN) concentration and export in streams in the upper Little Tennessee River basin. The arrows represent effects, and the text on the arrows gives examples of the possible effects represented by the arrows

accelerate or slow water movement by forest clearing, creation of paved areas, or construction of ponds; affects vegetation and soil processes, especially when forests are converted to agriculture; and affects instream processes by changing or removing riparian vegetation. Riparian vegetation controls the input of light and energy that drive instream biogeochemical cycling. Human land use can also provide direct nitrogen inputs to streams through fertilizer, septic systems, and accelerated weathering. Hillslope vegetation and soil processes can directly influence the DIN getting to streams through nitrogen fixation, especially in early successional forests dominated by black locust, plant nitrogen uptake, and mineralization of soil organic nitrogen. The inputs and transformation of nitrogen also influence processes occurring in the streams draining these hillslopes. Vegetation and soil processes can also affect DIN concentrations across the hillslope, for example, the contributions of surface soils versus groundwater, thereby influencing DIN concentrations of baseflow and storm water flowpaths. DIN concentration and export is further modified by uptake and mineralization within the streams themselves.

Throughout the ULTRB, the importance of the factors illustrated in Figure 14 is highly variable. In the most forested catchments, Ball Creek and Ray Branch, human influences are minimal though not absent because of nitrogen deposition, historical land use, and vegetation changes (e.g., the loss of American chestnut). In these streams, instream processes have the most obvious effects on DIN dynamics. At the other extreme, the Crawford Branch catchment has been extensively modified by humans, including DIN inputs and modification of hydrological processes through paving, building ponds, and baseflow augmentation by the use of town water supply. Between these extremes, forest and riparian clearing, agricultural fertilization, and septic systems modify DIN concentration and export to greater or lesser extent. Thus, the explanation of DIN concentration and export in the streams of the ULTRB is not a simple story of, for example, point and nonpoint sources, but a complex story involving geology and topography, vegetation and soils, instream biological processes, and hydrological transport—all overlain by a mosaic of past and current human land use.

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SUPPORTING INFORMATION

Additional supporting information may be found online in the Supporting Information section at the end of the article.

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