# Land Cover Influences on Stream Nitrogen Dynamics During Storms

Rebecca Marie Stewart

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J.R.Webster
E. F. Benfield
W. C. Hession
K. J. McGuire

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ABSTRACT

Previous studies on the effects of land cover influence on stream nitrogen have focused on base flow conditions or were conducted specifically within urbanized or primarily agricultural watersheds. While these studies have shown relationships between land cover and nitrogen, this relationship and the scale of influence could change during storms. The purpose of my study was to understand how land cover influences nitrogen in streams during storms. This was address using nine watersheds within the Little Tennessee Basin in North Carolina. While this basin is primarily forested, the nine watersheds have mixed agricultural, built, and forest land cover. Land cover influences were addressed through nitrogen concentration/discharge patterns, nitrogen concentration relationship to land cover, and comparison of storm and base flow nitrogen concentrations over time. Weekly base flow samples and samples from six storm were collected in 2010-2011. Total dissolved nitrogen (TDN), nitrate ($NO_3^-$), dissolved organic nitrogen (DON), and ammonium ($NH_4^+$) concentrations were compared among sites. During most storms, DON peaked before the peak of the discharge while $NO_3^-$ peaked after the peak of the storm. This suggest that DON could be coming from a near stream source or surface runoff while $NO_3^-$ could be from longer pathways such as subsurface flow or from sources further away on the watershed. $NO_3^-$ concentration varied among sites, while DON concentration varied more between base flow and storm samples. Examining the different landscape scales from 200-m local corridor, 200-m stream corridor, and entire watershed, watershed land cover was the best predictor for all the nitrogen concentrations. Agricultural and built combined best predicted TDN and $NO_3^-$, while agricultural land cover was a better predictor of DON. For storms, nitrogen concentrations did not show seasonal patterns but was more related to discharge. Nitrogen concentration increased with discharge during storms and the more intense and longer storms had higher TDN and $NO_3^-$ concentrations. However, conflicting seasonal trends were seen in monthly base flow. The more forested watersheds had high $NO_3^-$ during the summer and low $NO_3^-$ in the winter. For sites with higher $NO_3^-$, the

seasonality was reversed, with higher winter $NO_3^-$ concentration.  The least forested site had relatively constant nitrogen through the year at base flow and concentration decreased for most storms.  Further studies on storms and nitrogen transport are needed to understand better the seasonal patterns of nitrogen input during storms.

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## Introduction

*Landscape influences on nitrogen in streams*

Streams are strongly connected to their surrounding landscape. Considering a stream in the context of its watershed was conceptualized by Frissel et al. (1986) through a hierarchical organization ranging from microhabitat to watershed. Today, understanding streams and their watershed land cover is becoming increasingly important because of human impacts to the landscape. Changes of land cover have been shown to affect stream ecosystem including habitat, sediment through erosion, and nutrients (Allan, 2004).

Nitrogen in streams is closely tied to the terrestrial landscape through nitrogen fixation by bacteria in the soils, uptake by terrestrial plants and microbes, mineralization and nitrification in soils, and nitrogen cycling back into the atmosphere through denitrification. Changes in the landscape such as removal of vegetation through logging and soil disturbance has been associated with increased nitrogen in streams (Bormann et al., 1968; Vitousek et al., 1979; Swank et al., 2001) while seasonal growth of vegetation has been associated with the decrease of nitrogen in streams in the northeast (Vitousek and Reiners, 1975).

Nitrogen inputs to streams have been shown to vary with land cover and land use. A three-year study of nitrate export in a multi sub basin forested, suburban, and agricultural watersheds showed varying nitrate concentrations in streams for those land cover watersheds (Groffman et al., 2004). The agricultural land cover watershed had the highest stream nitrate concentrations while the forest watershed had consistently lower stream nitrate concentrations. The suburban watershed nitrate concentrations were intermediate between the agriculture and forest watershed nitrate concentrations and varied more over the three years. The largest contributors to the increase of nitrogen in streams have been human inputs through fertilizer, manure, sewage, industrial sources, and atmospheric deposition (Puckett, 1994; Howarth et al., 2002; Dubrovsky and

Hamilton, 2010). For examples, cropland and seasonal application of fertilizers have been related to high nitrogen concentration in streams (Jordan et al., 1997; Howarth et al. 2002). Nitrogen concentration has also been shown generally to be greater in large rivers that drain more density-populated watersheds (Jordan and Weller, 1996). Osborne and Wiley (1988) reported that urban land cover and its distance from the stream were the most important factors in predicting stream nitrogen concentrations.

Depending on the stream parameter measured, local corridor or stream corridor land cover can have greater influence on a stream than the entire watershed. For nutrient retention, the watershed scale was predicted to have the most influence over stream concentrations (Allen et al., 1997). However, some studies have shown different relationships between local and watershed land cover influences over stream nitrogen. Some studies found little difference between local land cover and watershed land cover relationships with nitrogen concentration. This was attributed to the similarity of local and watershed land cover (Johnson et al., 1997). Others have shown entire watershed land cover as being the best predictor for nitrogen concentrations in streams (Webster et al., 2012).

*Storm influence on nitrogen in streams*

Most studies of nitrogen and landscape influences have focused on base flow or a few sampling events (Bolstad and Swank, 1997; Webster et al., 2012). While these studies have shown relationships between landscape and nitrogen, this relationship and the scale of influence could change during storms. Storms may contribute only a fraction of annual stream flow, yet storms potentially increase nitrogen input to streams. A study in the southern Appalachia Mountains compared nitrogen concentrations during base and storm flow at multiple sites along an 8.7-km reach of a stream (Bolstad and Swank, 1997). At base flow, nitrogen concentration increased by 7% at the downstream site compared to the upstream site while storm flow nitrogen was 34% higher. Over a year, the contribution of nitrogen during storms to total annual nitrogen export has been shown to vary depending on landscape and type of watershed. On two mixed agricultural watersheds, Owen et al. (1991) reported that for a 10-year average, 75-50% of nitrogen was lost during storm flow. However other studies of agricultural and urban watersheds have shown the majority of nitrogen loss occurred during base flow (Groffman et al., 2004; Schilling and Zhang, 2004; Zhu et al., 2011).

Nitrogen loss during storms could increase in the future due to climate change. Several studies have found that there has been an increase in intense rainfall rather than more days of rainfall (Karl and Knight, 1998; Easterling et al., 2000; Stone et al., 2000). This trend was first cited by Sun and Groisman (2004) for northeastern US. They described an increase or no change in precipitation totals but a decrease in the number of days with precipitation. If this continues, the East Coast is projected to have prolonged drought periods coupled with short periods of intense rainfall (USGCRP, 2000). Especially for the Southeast, the average autumn precipitation has increased by 30 percent since 1901 (Bates et al., 2008). Projected climate models have predicted the number of freezing days to decline and days with peak temperature over 32˚C to increase significantly. That will cause more and longer periods of droughts in the Southeast. Sea-level rise and the increase of hurricanes from the Atlantic have been predicted to increase the frequency and intensity of storms (Bates et al., 2008). Because of the potential increase in storms, there could be a change to the way that nitrogen is transported to streams.

*Timing of nitrogen during storms*

Studying nitrogen export during storms can help predict where nitrogen has originated on the landscape. By sampling the rising and falling limbs of discharge of storms, the timing of nitrogen concentration can be related to discharge. Poor and McDonnell (2007) found nitrate increasing with increasing discharge during a spring storm on an agricultural watershed. This indicated a concentration effect, which is the increase of concentration with increase of discharge. However, a dilution effect for nitrate occurred during fall and winter storms on the same watershed. This difference was attributed to fertilizer application during spring (Poor and McDonnell, 2007).

Nitrogen sources can be understood through the timing of delivery of nitrogen during storms. One pattern seen during storms is the first flushing effect. First flush is used to describe the peak of solute concentration that comes before the discharge peak during a storm or snowmelt (Burns, 2005). Intense but short first flush can imply overland runoff or a near-stream source, while a longer flush after the peak of discharge implies sub-surface flows or a large nitrogen source in the watershed. These two different pathways can be quantified as clockwise or counter-clockwise concentration/discharge loops. A study from an intensively grazed watershed in Tasmania compared concentration/discharge loops for 3 years and demonstrated that total phosphorus that generally peaked before the discharge peak came from surface runoff processes (Holz, 2010). Because of the initial dilution, nitrate runoff was explained by sub-surface pathways. Another study attributed the flush of nitrate before peak discharge to the displacement of groundwater during storms (Inamdar et al., 2004).

*Purpose and goals of study*

Studies of nitrogen during storms have generally only included two or three watersheds for a few storms. Poor and McDonnell (2007) examined three storms over a year on three watersheds that had separate land cover types (agricultural, forested, and residential). Other studies have looked at agriculturally dominated watersheds for two to four storms (Rodriguez-Blanco et al., 2009; Jiang et al., 2010). To expand these studies, I sampled storms for a year on nine watersheds with mixed land cover. The purpose of my study was to understand how landscape influences nitrogen in streams during storms. This was addressed using nine watersheds with a mix of agricultural, built, and forest land cover. Land cover influences were addressed through concentration/discharge patterns for every site and storm, relationships between mean nitrogen concentration and land cover, and seasonal patterns of storm and base flow nitrogen concentrations. I also evaluated landscapes at three spatial scales to determine which was the best predictor of nitrogen concentrations.

## Methods

*Site description - Little Tennessee Watershed*

This study took place in western North Carolina in the upper Little Tennessee River Basin (Fig. 1). This region of the southern Appalachian Mountains has an average annual precipitation of approximately 1400 mm. Fall is characterized by isolated hurricane-influenced storms, and summer and spring are characterized by having frequent shorter storms. Lower elevations have a humid subtropical climate, while higher elevations have a humid temperate climate. Winters are mild with little snowfall and summer highs rarely reach above 30°C (Swift et al., 1998; Webster et al., 2012).

The Little Tennessee River basin is rural with a relatively low population density. A majority of the basin is forested (75%) with less than 5% of the land area categorized as developed. More than half of the land in the basin is publicly owned, primarily within the Nantahala National Forest. Urban development in the area has increased in recent years primarily due to second homes and retiree homes (NCDENR, 2002; Webster et al., 2012).

This study took place in Macon County, which has a population of approx 21,500 (US Census Bureau, 2010). The two towns in Macon County, Franklin and Highlands, experience seasonal population fluctuations due to recreation and tourism. The population in Highlands ranges from 924 permanent residents to 18,000 in summer, while Franklin has a residential population of 3,845 (US Census Bureau, 2010; Webster et al., 2012).

In this study, second and third order streams were sampled within nine different sub-watersheds of the Little Tennessee Basin from September 2010 through August 2011. These nine watersheds reflect a gradient of land cover characteristics within the larger Little Tennessee Basin. Watershed land cover data were provided by the Coweeta Long Term Ecological Research (LTER) site at the Coweeta Hydrological Laboratory. The land cover classification was derived from 2010 NASA Landsat Thematic Mapper. Imagery was classified by Jeffrey Hepinstall-Cymerman and Hunter Allen, and the corridor-derived analysis was provided by Joelle Freeman (Warnell School of Forestry and Natural Resources, University of Georgia, Athens, GA 30602). The stream definition for the stream corridor and local corridor land cover was based on the National Hydrography Dataset (http://nhd.usgs.gov/).

Among the nine watersheds, forested land cover varies from 29% to 94% with the most urban site (29% forested and 48% built) within the town of Franklin (Table 1). Agriculture within these nine watersheds is predominantly pastureland and hay fields (Webster et al., 2012). Built land cover was considered to be impervious surfaces of any type such as roads, building roofs, and parking lots covering more than 400 $m^2$. The 200-m stream corridor (100 m on each side for the entire stream length) and the 200-m local corridor (100-m on each side of the 1000-m reach upstream of the sampling site) were similar to the watershed land cover for the most forested watersheds, but in more built watersheds, there were greater differences (Fig. 2). Along with the different land covers, these nine watersheds also had a gradient in background stream nitrogen concentration ranging from 70 ug/L total dissolved nitrogen in the most forested watershed to over 500 ug/L in the least forested watershed (Table 2).

*Field methods and water chemistry analysis*

Streamside autosamplers (ISCO™, Lincoln, NE) were installed to collect storm and base flow water samples in each study stream. Sample bottles were acid washed before use in the field. Base flow samples were collected weekly. During storms, autosamplers were preprogrammed to sample 1 L every 30 minutes from the start of storm for 6 hours and then every hour for the rest of the storm based on what could be predicted from the weather forecast. These times were adjusted for the predicted storm's length and intensity. Stage was automatically recorded through the year using a pressure transducer in the stream and data logger attached to the ISCO at each site. Discharge measurements were determined using the salt-dilution technique (Gordon et al., 2004) and then related to the stage at that time. These data were used to generate rating curves for each stream (Table 3).

Water samples were processed by the staff at the US Forest Service Coweeta Hydrological Laboratory and Long Term Ecological Research (LTER) site. Samples were filtered (0.7-µm pore size glass fiber filters, Millipore APFF04700) within 24 hours of collection and frozen until analysis. Total dissolved nitrogen (TDN), nitrate ($NO_3^-$), dissolved organic nitrogen (DON), and ammonium ($NH_4^+$) concentrations were analyzed for all samples using standard methods (APHA, 1995). TDN was determined using a Shimadzu TOC-VCPH TN analyzer. $NO_3^-$ was measured by an ion chromatograph (Dionex 25A Ion) using an AS18 column, and $NH_4^+$ was measured using an Astroia 2 autoanalyzer. DON was calculated by subtracting $NO_3^-$ -N and $NH_4^+$ -N concentrations from TDN.

*Data analysis*

Flow-weighted mean concentrations were calculated for each storm at each site by dividing the total mass of nitrogen transported during a storm by the total storm runoff volume. Flow-weighted means were compared to landscape variables by linear regression as well as compared to the mean base flow nitrogen concentration. Flow-weighted mean concentrations were not calculated for the base flow nitrogen concentrations because those water samples were taken weekly instead of hourly.

Statistical analysis included linear regression comparing mean nitrogen concentrations with land cover variables. Also, linear regression was used to determined slope for concentrations/discharge relationships. The concentration/discharge graphs were categorized as positive or negative slope and clockwise or counter clockwise directional hysteresis (Evan and Davies, 1998).

## Results

*Storm characteristics*

Six storms were sampled from September 2010 through the beginning of September 2011 (Fig. 3). Each storm varied in length, amount of precipitation, and antecedent precipitation index (Table 4). The antecedent precipitation index ($API_7$) indicated the rain history seven days before the sampled storm to reflect the soil moisture. $API_7$ was calculated as the summation of precipitation where the day before the storm has the largest weight (daily precipitation divided by one) while the week ago rain has the least weight (precipitation divided by seven) (Kohler and Linsley, 1951). The fall storms (Sep. 2010, Oct. 2010, Sep. 2011) were isolated from each other and had low $API_7$. One winter and two spring storms (Nov. 2010, Feb. 2011, and Mar. 2011) occurred closely with other rain events. Feb. 2010 and Mar. 2011 storms were sampled within four days of each other. In general storms generating the largest hydraulic responses occurred in Mar. 2011 and Sep. 2011, while the smallest were Sep. 2010, Oct. 2010, and Feb. 2011 (Appendix 1, 2, 3). The large precipitation for the Sep. 2010 and the Oct. 2010 storms occurred in two periods. The first rain period was not sampled for the Sep. 2010 storm and the last rain period was not sampled for the Oct. 2010 storm resulting in a small hydraulic response despite the large precipitation (Table 4).

*Storms and sites: nitrogen concentration/discharge patterns*

For most storms and sites there was one peak with rise and fall in discharge over the sampling period. Generally there was a positive relationship between TDN, $NO_3^-$, and DON concentrations and storm discharge (Table 5). The changes in DON and $NO_3^-$ concentrations with discharge varied from storm to storm among the nine sites (Appendix 4-15). For most storms, DON concentration peaked before peak flow whereas $NO_3^-$ concentration peaked after the peak flow, resulting in clockwise and counter-clockwise hysteresis respectively (Table 5). $NH_4^+$ concentrations remained low and changed little during most storms.

The general trend of DON and $NO_3^-$ dynamics and the differences among sites can be seen in the Sept 2010 storm for Ball Creek and Crawford Branch, the most forested site and the least forested site. In Ball Creek, DON increased during the storm with little hysteresis, whereas $NO_3^-$ had almost no change during the storm other than some dilution in the early part of the storm (Fig. 4). During the same storm, DON for Crawford Branch initially diluted but generally did not change during the storm, whereas $NO_3^-$ concentration was initially diluted but then peaked after the peak of the discharge resulting in a strong counter-clockwise hysteresis (Fig 5). Crawford Branch was the only site where TDN and $NO_3^-$ had a negative relationship with storm discharge for the majority of storms (Table 5).

*Land cover: nitrogen concentration among sites*

The total flow-weighted mean nitrogen concentrations for all storms were compared for all sites. TDN varied from 100 µg/L to over 500 µg/L: the site with most percent forest had the lowest nitrogen concentration (Ball Creek) and the least percent forest site had the highest nitrogen concentration (Crawford Branch) (Fig. 6). $NO_3^-$ was the dominant form of nitrogen across all sites compared to DON and $NH_4^+$and contributed the most to TDN pattern. DON was the second dominate form of nitrogen and did not show a pattern with forest land cover. $NH_4^+$ was low for all sites with no pattern with forest land cover except for Caler Fork in which the relatively high mean $NH_4^+$ concentration was the result of one sample during the peak of the Feb. 2011 storm.

Flow-weighted mean nitrogen concentrations were compared with watershed, stream corridor, and local corridor land cover. All show similar trends of forest cover (Fig. 2). The most forested site, Ball Creek, had 97% forest cover and the least forested site, Crawford Branch, varied in forest cover depending on watershed, stream corridor, or local corridor land cover (30% - 43%). For the analysis, agricultural and built land covers combined were used instead of percent forest because decreasing forest was generally replaced with agricultural and built land cover.

Watershed land cover had the strongest regression relationship to all forms of nitrogen (Fig. 7). The stream corridor had the second strongest relationship (Fig. 8). The local corridor land cover had the weakest relationship with nitrogen concentrations (Fig. 9). These relationships did not change when analyzed by storm. DON was best predicted by percent agriculture ($p = 0.0008$, $r^2 = 0.82$), and $NO_3^-$ was best predicted by combined percent agriculture and built land cover ($p < 0.0001$, $r^2 = 0.95$). TDN was best related to agriculture ($p < 0.0001$ $r^2 = 0.90$) while still related to combined percent agriculture and built land cover ($p = 0.0003$ $r^2 = 0.87$). Including wetland, scrub, and barren land cover did not provide better relationships at any spatial extent. The land cover and nitrogen concentrations relationship results were not because of Crawford Branch, the most built and least forested site. When this site was removed, the regressions for nitrogen concentrations and percent land cover remained the same or improved.

*Storm and base flow samples: nitrogen concentration change over time*

Among all nine sites, the mean TDN storm nitrogen concentrations were generally higher than the mean base flow concentrations (Fig. 10). Crawford Branch, the least forested site, was the only site that had lower TDN concentrations during storms than during base flow. Both storm and base flow TDN concentrations were higher in the most forested than in least forested streams.

Different forms of nitrogen contributed to base flow and storm concentrations (Fig. 10). Overall, $NH_4^+$ was low for both storm and base flow concentrations except for Crawford Branch and Caler Fork. High $NH_4^+$ concentration for Caler Fork storm samples was the result of one sample in the Feb 2010 storm. DON concentration was generally higher during storms than at base flow for all sites. There was little variability in $NO_3^-$ concentrations within a single site, but $NO_3^-$ varied greatly among sites for both base flow and storm samples. On average, storm $NO_3^-$ concentrations were similar to base flow concentrations for Ball Creek, Ray Branch, and Cowee Creek. Crawford Branch had lower $NO_3^-$ concentrations for storm samples than base flow samples, while all other sites had higher mean storm $NO_3^-$ concentrations (Fig. 10).

In general DON concentrations varied seasonally with low concentrations in winter and higher concentrations in spring and summer (Fig. 11). $NH_4^+$ showed little annual pattern because it varied only 10 μg/L over the study period. The seasonal pattern of $NO_3^-$ concentration varied among watersheds. Ball Creek showed high $NO_3^-$ concentration in summer and lower $NO_3^-$ concentration in the fall and winter, while Crawford Branch, the most built land cover watershed, showed no distinct seasonality in base flow concentrations (Fig. 12). Also Jones Creek, Caler Fork, and Cowee Creek had low $NO_3^-$ concentrations in the fall but did not have high $NO_3^-$ concentrations in the summer (Appendix 1, 2). Skeenah Creek, Bates Creek, and Watauga Creek had opposite $NO_3^-$ seasonality, high winter concentration and low summer concentration (Appendix 2, 3).

A seasonal trend was not seen in the storm samples. For all watersheds combined, DON and $NH_4^+$ storm concentrations did not show much variability (Fig. 13). For TDN and $NO_3^-$, the largest storms (Nov. 2010, Mar. 2010, and Sep. 2011) had the highest nitrogen concentrations, while the smallest storms (Sep. 2010 and Oct. 2010) had the lowest nitrogen concentrations (Fig. 13). All sites except for Crawford Branch generally had higher concentrations during high discharge (Appendix 1, 2, 3). However Crawford Branch showed a dilution effect for the majority of storms (Appendix 3). Seasonality was not observed for DON or $NO_3^-$ concentration/discharge relationship over the six storms (Appendix 4-15).

## Discussion

*Nitrogen and discharge flow pathway influences*

The data suggest that DON and $NO_3^-$ flow pathways and relationships with the landscape were distinctively different. This implies two different sources of nitrogen. DON increased with discharge showing a concentration effect and generally peaked before peak discharge (Table 5). This suggests a rapid flow pathway, which could come from surface runoff or a near stream source or mobilization. In Appalachian streams, this DON increase with discharge relationship was attributed to near stream or in-stream sources (Buffam et al., 2001).

In contrast to DON, $NO_3^-$ was delayed, i.e., it generally peaked after peak discharge (Table 5). This suggests a deeper, subsurface flow path compared to DON. Other studies have found the delay in $NO_3^-$ due to leaching of $NO_3^-$ from soils (Salvia- Castellvi, 2005; Rodriguez-Blanco, 2009). Buffman et al. (2001) attrbuted this delay to the buildup of $NO_3^-$ in unsaturated soils.

These contrasting patterns of DON and $NO_3^-$ have also been shown in base flow studies. Johnson et al. (1997) studied mixed land use watersheds and saw lower DON and higher of $NO_3^-$ concentrations with the increase in base flow over the year. They attributed this to surface runoff of DON and groundwater inputs of $NO_3^-$. For storms, DON in my study may also be attributed to surface runoff, while $NO_3^-$ seemed to follow a longer sub-surface pathway.

*Agricultural and built land cover influences*

Land cover influenced the different forms of in-stream nitrogen concentration. DON was best related to agriculture land cover (Fig. 7). This suggests that the source may be from animal waste on the surface. This is consistent with a surface or rapid flushing pathway during storms as observed in my study. Higher nitrogen from agriculture land cover was consistent with studies of cropland watersheds. Fertilizer application has been shown to be a major source of the increase of nitrogen export to streams (Allan, 2004). Johnson et al. (1997) related concentrations of different forms of nitrogen to percent cropland and percent forest. They examined 27 watersheds over a gradient of 0 to 67% cropland and found that concentrations of nitrogen were best related to percent of cropland. Even though the gradient of agriculture for this study was only 0 to 15% land cover, an effect of the agricultural land cover was still observed for DON. Agricultural land cover may not have been the best predictor for $NO_3^-$ because of the limited fertilizer use in pasture watersheds in this area.

Combined agricultural and built land cover was the best predictor for $NO_3^-$ concentration (Fig. 7). Previous studies have also shown that both agriculture and built land cover can affect nitrogen concentrations in streams. Groffman et al. (2004) showed that urban development raised storm water runoff and lowered nutrient retention . Also decreasing vegetation in a watershed and soil disturbance can increase nitrogen in streams (Bormann et al., 1968; Vitousek et al., 1979). This lack of vegetation, along with anthropogenic inputs associated with urbanization and agricultural landscapes, could have contributed to the high $NO_3^-$ in stream concentrations (Puckett, 1994; Howarth et al., 2002).

Landscape influences were also related to land cover of watershed, stream corridor, and local corridor scales. Whole watershed scale was the best predictor for all nitrogen species (Fig. 7). The second best predictor was entire stream corridor land cover (Fig. 8). This agrees with most nitrogen base flow studies (Allan et al., 1997; Johnson et al., 1997; Silva and William, 2001). A study in the same Little Tennessee Basin region reported that nitrogen and other chemicals associated with specific conductance were reflective of watershed land cover (Webster et al., 2012).

*Nitrogen concentration in streams: effects of seasonality*

On average, storm samples had higher TDN concentrations than base flow samples. I attributed this to the increase of DON during storms while $NO_3^-$ concentrations remained relatively the same if not lower for average storm samples (Fig. 10). This was similar to the results of a five-year study on mixed land-use watersheds in Pennsylvania (Zhu et al., 2001). Total nitrogen concentration increased with storm discharge while $NO_3^-$ concentration decreased. They attributed this to surface runoff of dissolved and particulate organic nitrogen and $NH_4^+$ during storms while $NO_3^-$ was being diluted. This could suggest that the DON source became more mobile during storms while the $NO_3^-$ source did not change between base flow and storms.

Comparing nitrogen concentration of base flow and storm flow over the entire year, storm samples did not show a seasonal effect while base flow samples did change over the year (Appendix 1, 2, 3). Nitrogen concentration of storm samples was most influenced by the intensity and length of the storm (Fig. 13), and there was no evidence of a seasonal effect of nitrogen during storms or a change in direction of concentration/discharge loops (Fig 13; Appendix 4-15). The relationship of nitrogen concentration with discharge was consistent for most sites and storms (Table 5). Other studies have shown $NO_3^-$ to have a dilution effect with discharge (Zhu et al., 2001; McHale et al., 2002; Kaushal et al., 2008). For my study, $NO_3^-$ concentration sometimes exhibited an initial dilution effect, but overall showed an increase in concentration with storm discharge (Table 5).

Previous studies have observed seasonality with storms. In the Arctic studying spring and summer storms, higher nitrogen concentrations were shown during spring snowmelt while nitrogen concentration was diluted in summer storms (Townsend-Small et al., 2011). In mountainous coastal California watersheds, high nitrogen concentrations occurred at the beginning of the wet season across multiple landuse watersheds while nitrogen concentrations remained lower during the dry summer months. (Goodridge and Melack, 2012). Also, studies on agricultural watersheds have shown storm seasonality with fertilizer application and the growing season (Poor and McDonnell, 2007). Within the Little Tennessee Basin, winters are mild so there is little snowmelt and weak difference between wet and dry seasons compared to the West Coast. For the land cover in my study, agricultural watersheds are mostly pasture land and not row crop farming where there would be seasonal fertilizer application.

However, for base flow samples, there was a clear seasonal trend for DON that could be attributed to agricultural practices (Fig. 11). DON concentration was higher in the summer but lower in the winter. This could be due to animal grazing in the agricultural land. This is a typical trend within agricultural watersheds because of the growing season and seasonal input of fertilizer or manure (Allan, 2004). For my study, animal waste may have contributed to the seasonal trends in base flow. However the DON seasonality was also observed for Ball Creek and Ray Branch, which have little to no agricultural in the watersheds, so for those sites DON maybe coming from near-stream decomposition of organic matter. This type of source would contribute to surface or shallow, rapid subsurface flow pathways.

Seasonal trends were observed for $NO_3^-$ base flow concentrations (Appendix 1-3). Ball Creek and Ray Branch had high nitrate in the summer, a decrease in the fall, and low nitrate in the winter (Appendix 1). This contrasts with forested watersheds in the Northeast where $NO_3^-$ concentrations in streams often peak during winter and spring and have low $NO_3^-$ during the summer (Vitousek and Reiners, 1975). This seasonal cycle has been attributed to snowmelt and decline in plant nitrogen uptake during the winter (Vitousek and Reiners, 1975). However, the cycle in Ball Creek and Ray Branch was typical for streams at Coweeta (Swank and Waide, 1988). Brookshire et al. (2011) attributed this $NO_3^-$ seasonality in Coweeta streams to microbial activity responding to warmer temperatures during the summer, which increases mineralization and nitrification and results in higher $NO_3^-$ concentrations. Also the decrease in $NO_3^-$ during the fall could be attributed to leaf fall and in-stream uptake of nitrogen by microbes (e.g., Goodale et al., 2009). The decrease of nitrogen concentration during the fall was also observed for Jones Creek, Caler Fork, and Cowee Creek (Appendix 1, 2).

I did not see the same high nitrogen concentration during the summer for the other seven watersheds. Crawford Branch had little variation of nitrogen over the year. Skeenah Creek, Bates Creek, and Watauga Creek all had high of $NO_3^-$ during the winter and decrease during the spring (Appendix 2, 3). This decrease of summer nitrogen concentration could be attributed to algae. The more agricultural streams like Skeenah Creek have little canopy. This would allow algae growth during the summer. Light can be a limiting factor for algae growth, and other studies have observed increase periphyton growth after decreasing forest cover that allowed more light to the streambed (Murphy and Hall, 1981; Lowe et al., 1986). For my study, the more light to agricultural streams with open canopies could have also contributed to lower nitrogen concentrations during the summer.

*Built land cover influences and dilution effects*

The highest nitrogen concentrations were in the sites with the least forest cover, Bates Creek, Watauga Creek, and Crawford Branch, which were also the most built land cover (7%, 14%, and 48% respectively). High nitrogen concentration with more development has been found in other land use studies and attributed to sewage, fertilizer, and loss of nitrogen from the soils (Owens et al., 1991; Jordan et al., 1997). For my study, the most built sites did not show any $NO_3^-$ seasonality in the base flow or storm flow samples. However this is not always the case with urbanization. Osborne and Wiley (1986) found increase of $NO_3^-$ during the summer and fall because of urban runoff. In another study in California Goodridge and Melack (2012) saw an increase of nitrogen during the start of the wet period in urban and less developed watershed. However, my study did not show a seasonal effect for the more built watersheds.

Crawford Branch, the most built and least forested watershed, was the only site to show dilution effects and a large delay in $NO_3^-$ concentration increase for most storms. Crawford Branch is 30% forested compared to the other eight sites which range from 70 - 97% forested. The dilution and large delay of $NO_3^-$ suggest that the nitrogen input to

Crawford Branch could have come from a contributing area different than the other watersheds. $NO_3^-$ concentrations only increased above base flow concentration during the larger and longer storms (Mar 2011 and Sep 2011), which indicated that the input of $NO_3^-$ during storms was coming from further up the watershed, perhaps from overflow sewage that occurred in response to higher intensity storms. However, this does not always occur. For example, Poor and McDonnell (2007) observed little difference in $NO_3^-$ export from a forest and a residential development watershed. They attributed lower nitrogen concentration for the urban area to marshy retention ponds within the residential watershed. Crawford Branch also has a seasonal influence of population during the summer, but this change in population was not reflected in the annual trend of nitrogen.

*Conclusions*

This study highlighted the different forms of nitrogen that contributed to stream nitrogen concentration during storms from watersheds with varying land cover. Even where little fertilizer is applied, agricultural and built land cover influenced nitrogen concentrations in streams. DON had a clockwise concentration/discharge flow pattern that indicated an initial flushing. This suggests a near stream source of DON. $NO_3^-$ had a counter-clockwise pattern that indicated a delay in $NO_3^-$. This suggests $NO_3^-$ was coming from deeper, longer flow pathways. DON was higher in watersheds with more agricultural land cover while $NO_3^-$ was higher with more combined agricultural and built land cover. Studying storms and the possible flow pathways and land cover relationships can help with management practices to assess how change in land use in a watershed may affect nitrogen input to streams. Fencing out cows from a stream in pastureland as well as increasing vegetation near the stream may decrease DON input while $NO_3^-$ may need to be assessed by not just one land cover type but over the whole watershed.

Nitrogen was clearly related to whole watershed land cover. However, other chemicals, such as phosphorus, that would be more sediment related, might be better predicted by near stream conditions.  Examining those chemicals during storms would be useful in a larger understanding of landscape influences on stream nutrient concentrations.

This study also attributed high nitrogen to high discharge rather than seasonality.  Year-long storm studies and increased frequency of storm sampling including summer storms is needed to quantify seasonal variability in the mechanisms regulated nitrogen transport during storms.  Also, the mechanism behind the seasonal $NO_3^-$ concentration trends during base flow conditions and its relationship to land cover needs to be better understood.  For this study, the increase of DON from base to storm flow indicated the mobilization of TDN during storms and highlights the importance of studying storms rather than only collecting weekly grab samples.  With future changes in land cover and land use, understanding the effect of stream nutrient and potential sources of runoff during storms is important for watershed management.

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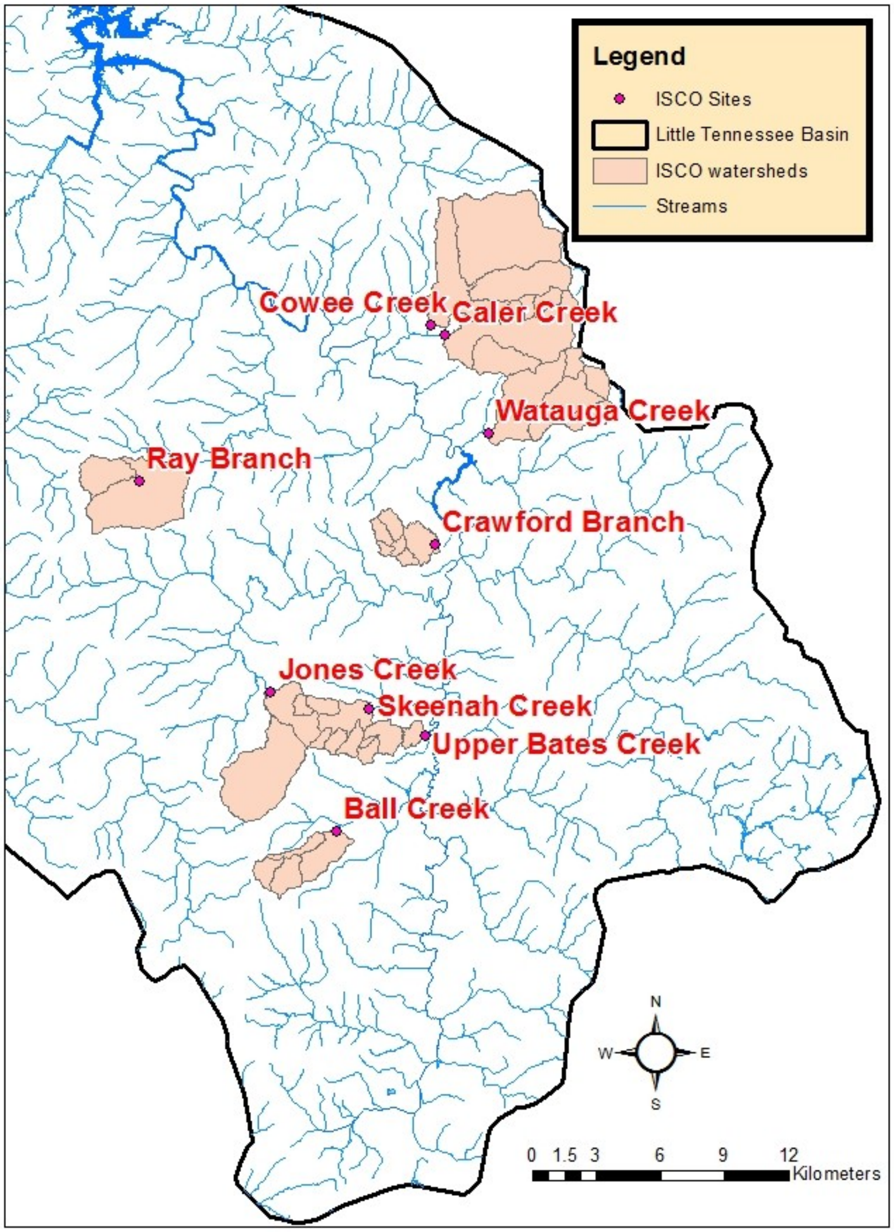



Figure 1. Location of the nine study watersheds in the Little Tennessee Watershed. Map made using ArcGIS.

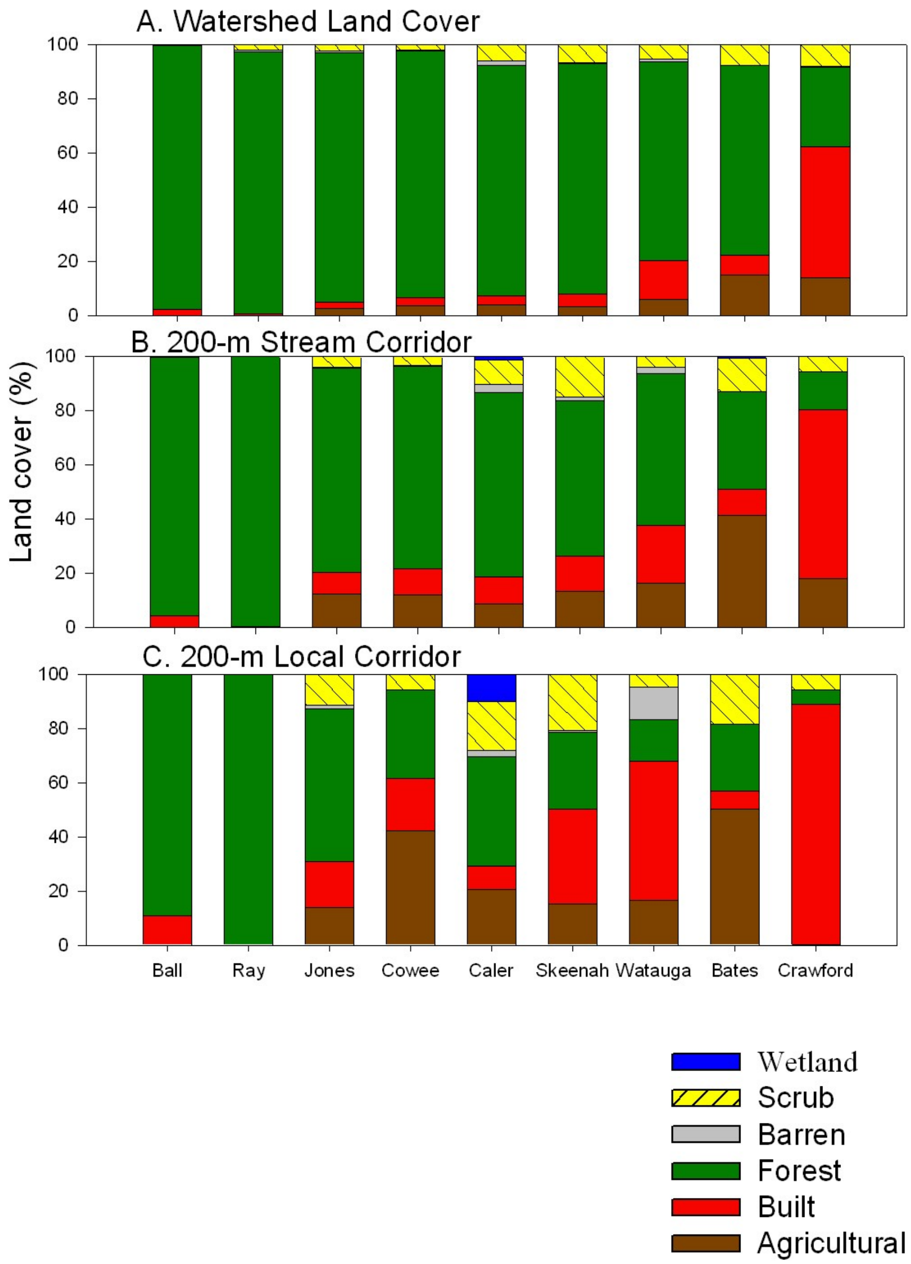



Figure 2. Percent land cover for all nine sites ranging from most to least percent forested with three different scales: watershed land cover (A), 200-m corridor for the entire length of the stream (B), and 200-m corridor for 1000 m reach upstream from site (C).

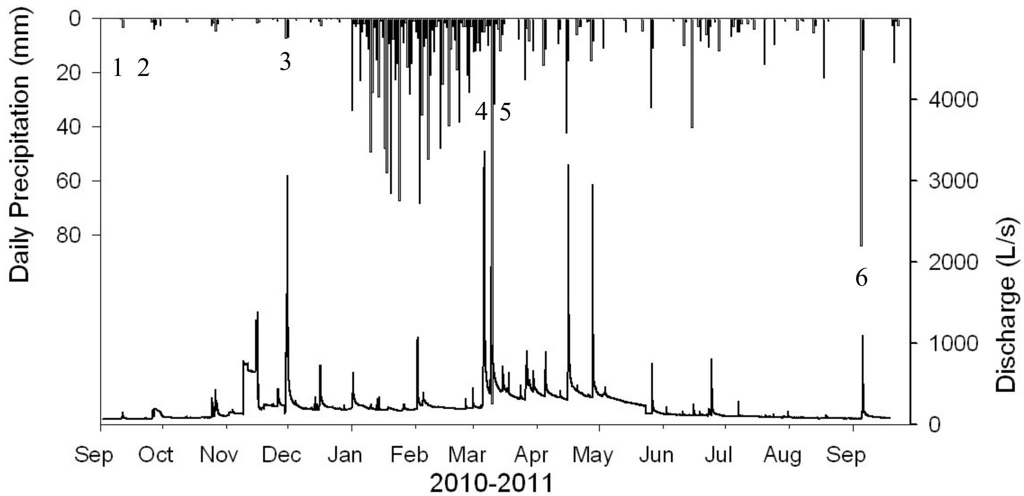



Figure 3. Daily precipitation and Ball Creek discharge at fifteen minute intervals for 2010-2011. The six storms sampled are numbered. Precipitation data from the Coweeta Climate weather station.

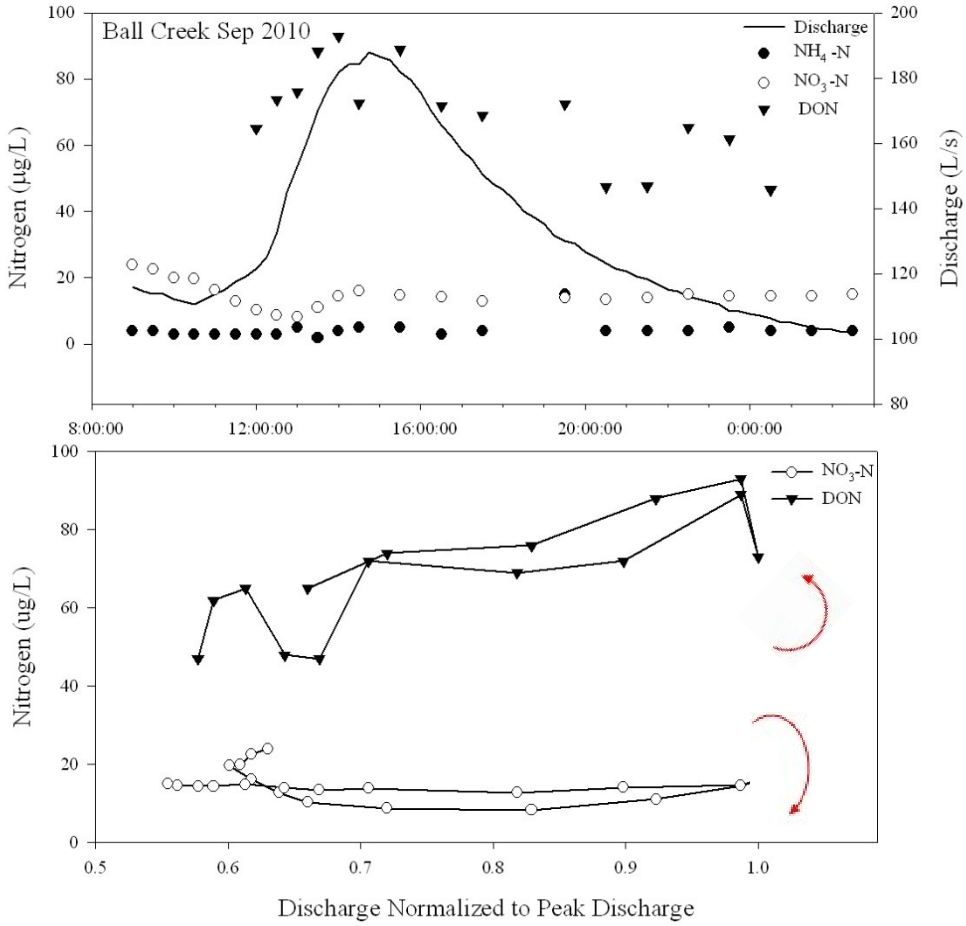



Figure 4. Ammonium ($NH_4^+$), nitrate ($NO_3^-$), and dissolved organic nitrogen (DON) in Ball Creek (most forested) September 2010 storm and the concentration normalized flow graph of DON and $NO_3^-$ for that storm. Arrows indicate the time sequence of samples.

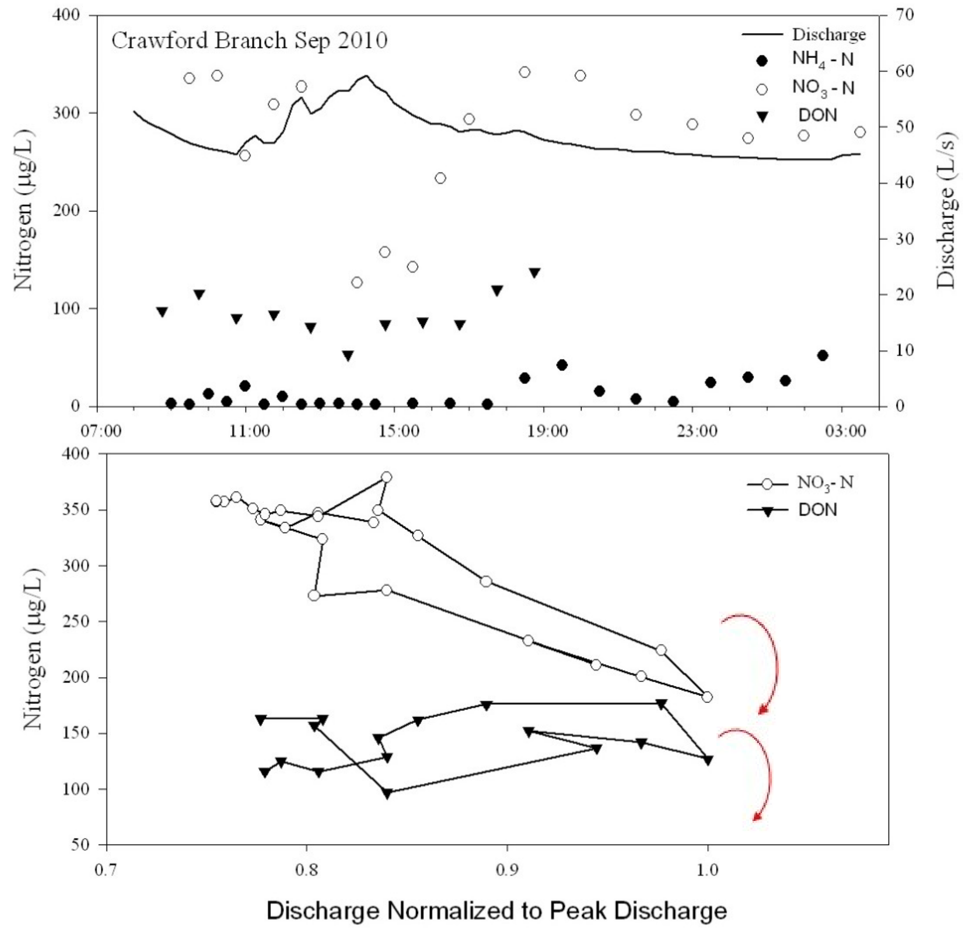



Figure 5. Ammonium ($NH_4^+$), nitrate ($NO_3^-$), and dissolved organic nitrogen (DON) in Crawford Branch (least forested) September 2010 storm and the concentration normalized flow graph of DON and $NO_3^-$ for that storm. Arrows indicate the time sequence of samples.

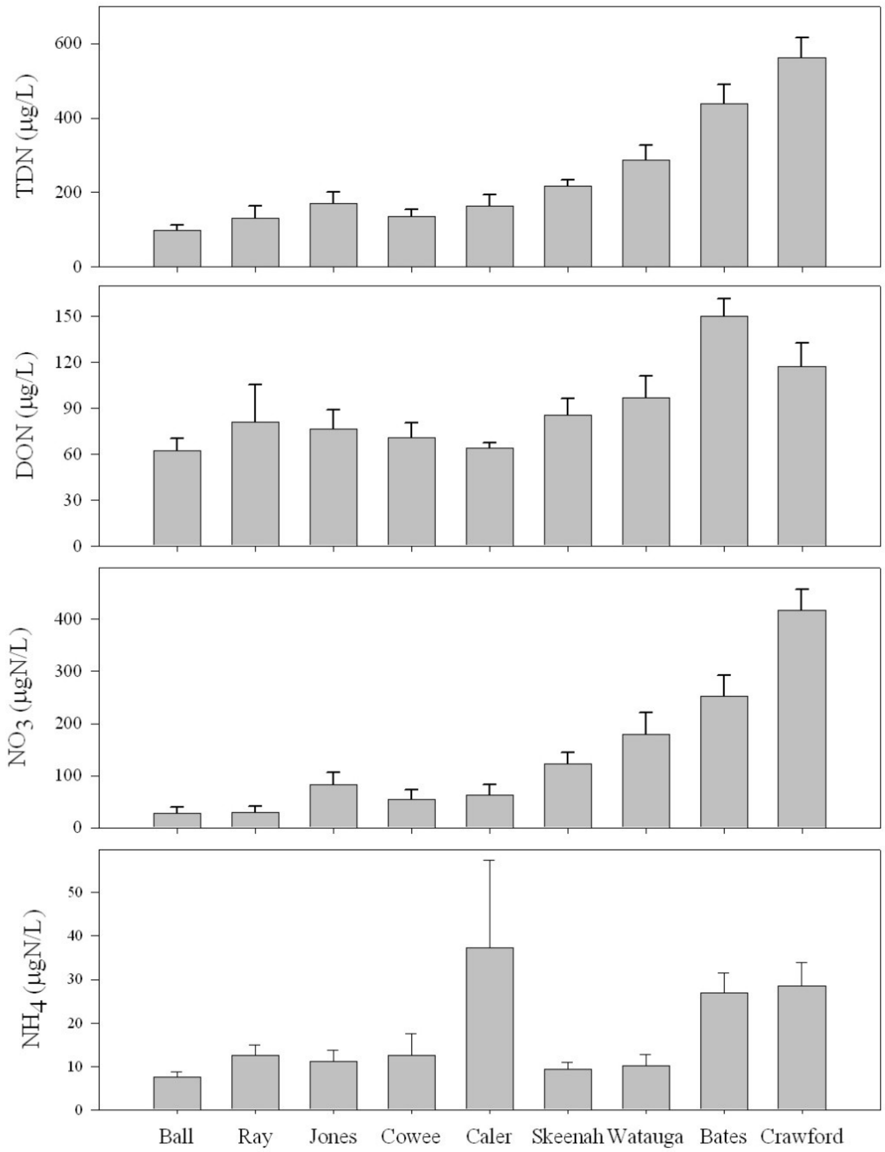



Figure 6. Flow-weighted means of total dissolved nitrogen (TDN), dissolved organic nitrogen (DON), nitrate ($NO_3^-$), and ammonium ($NH_4^+$) for all six storms across sites from most forested (Ball Creek) to least forested (Crawford Branch). Error bars are standard errors.

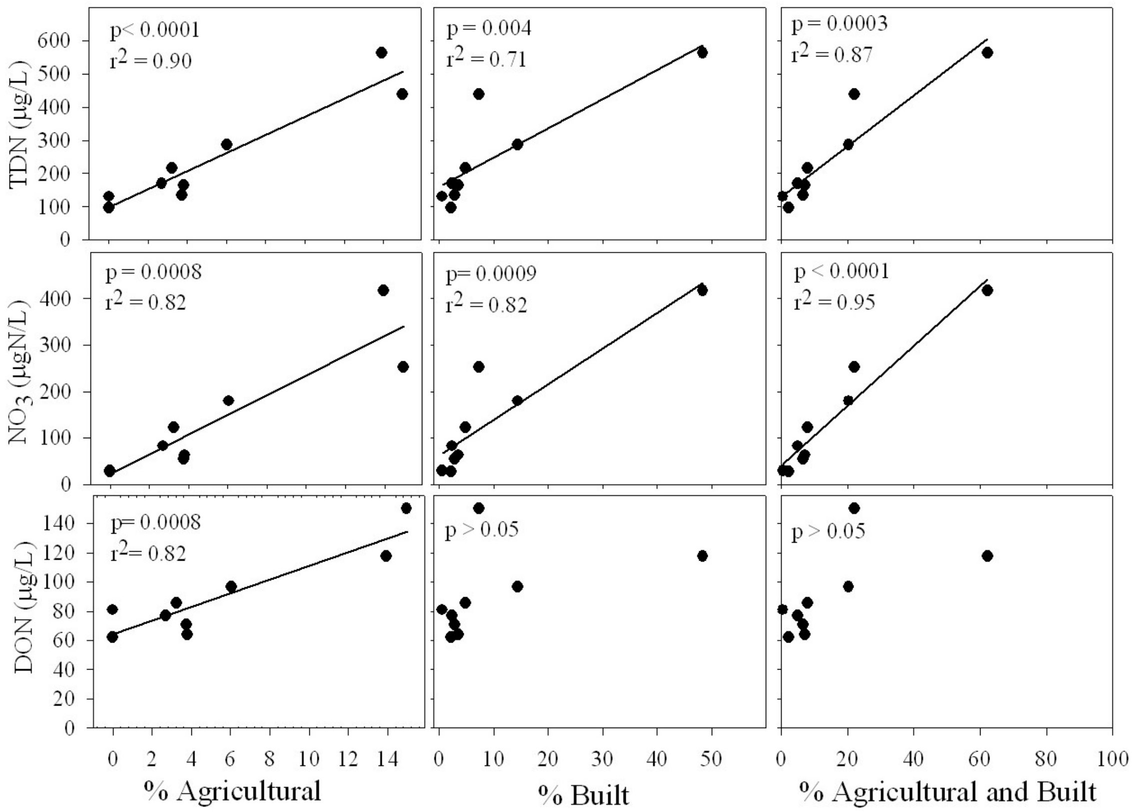



Figure 7. The average of the flow-weighted means of dissolved organic nitrogen (DON), nitrate ($NO_3^-$), and total dissolved nitrogen (TDN) concentrations compared with percent land cover (agricultural, built, and agricultural and built combined) at the watershed scale. Significant linear regressions are reported with p and $r^2$ values.

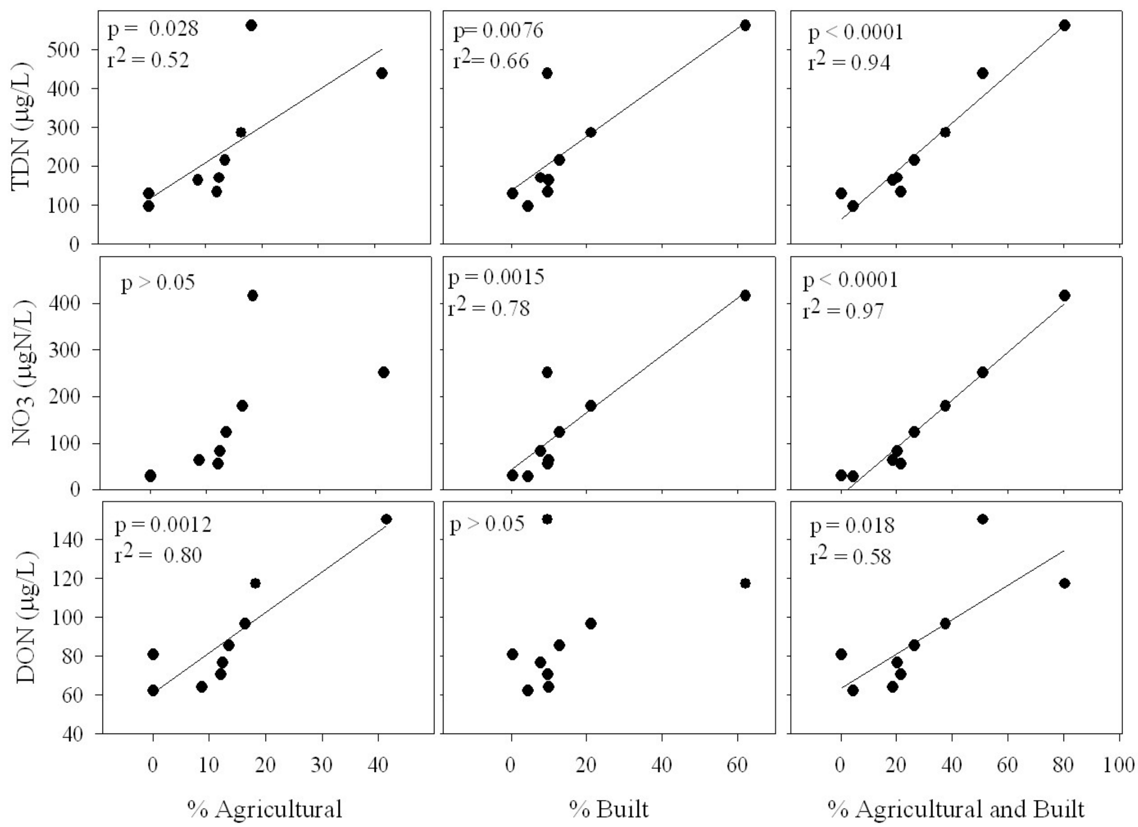



Figure 8. The average of the flow-weighted means of dissolved organic nitrogen (DON), nitrate ($NO_3^-$), and total dissolved nitrogen (TDN) concentrations compared with percent land cover (agricultural, built, and agricultural and built combined) at the 200-m stream corridor scale. Significant linear regressions are reported with p and $r^2$ values.

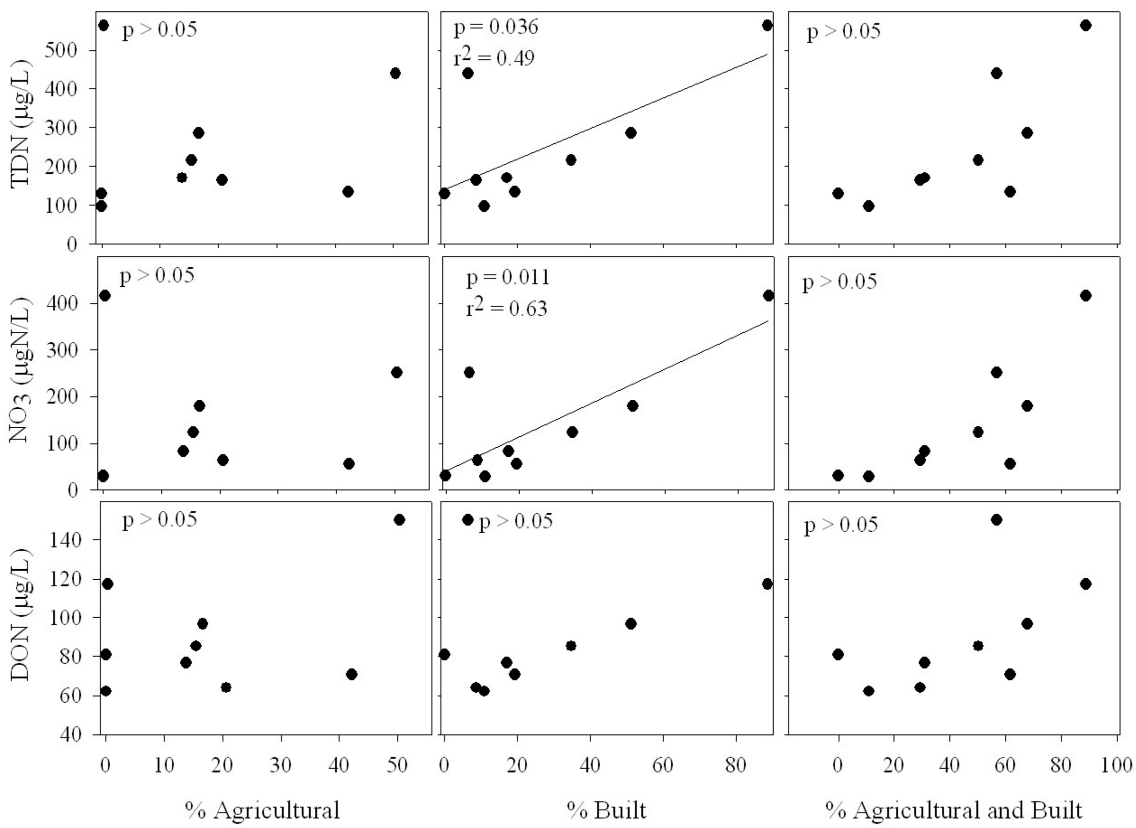



Figure 9. The average of the flow-weighted means of dissolved organic nitrogen (DON), nitrate ($NO_3^-$), and total dissolved nitrogen (TDN) concentrations compared with percent land cover (agricultural, built, and agricultural and built combined) at the 200-m local corridor scale. Significant linear regressions are reported with p and $r^2$ values.

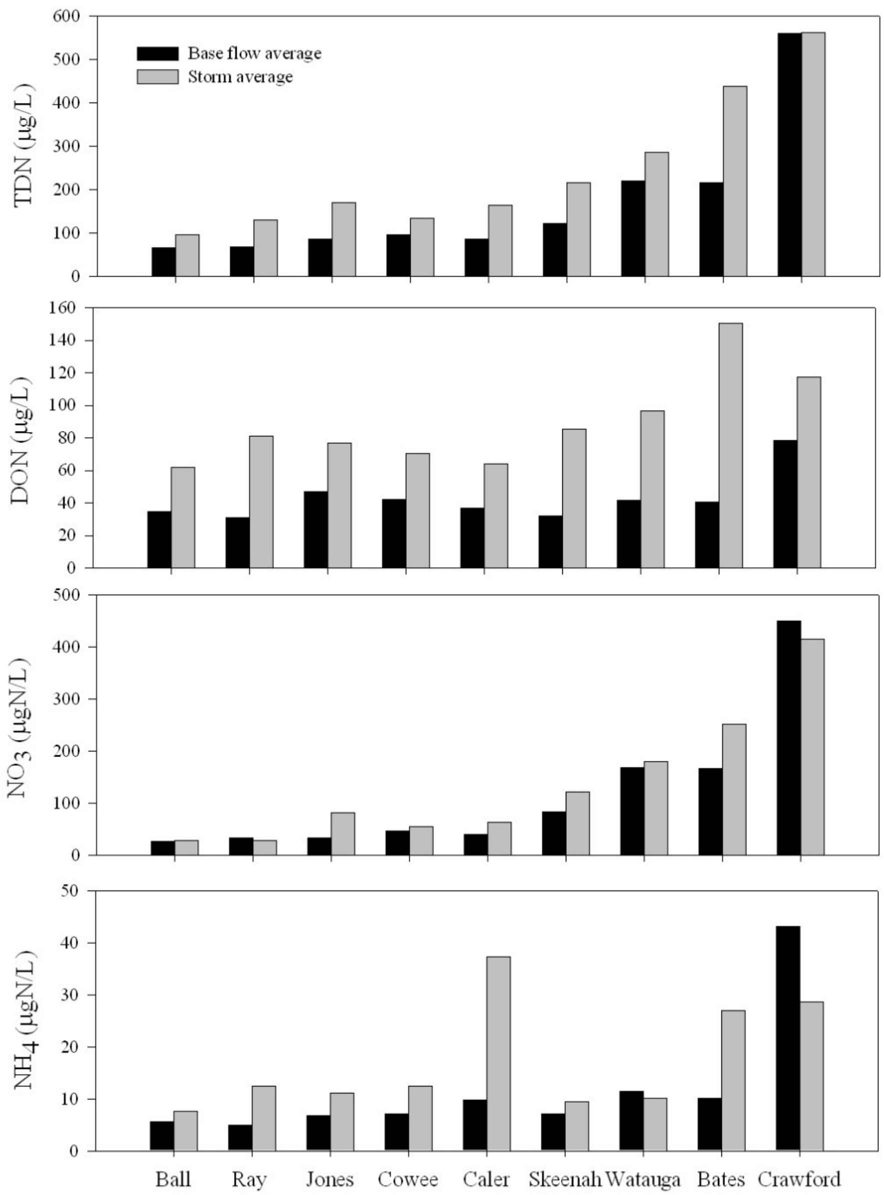



Figure 10. Average total dissolved nitrogen (TDN), ammonium ($NH_4^+$), nitrate ($NO_3^-$), and dissolved organic nitrogen (DON) concentrations for base flow samples (monthly averages, n=12) and average of flow-weighted means of all 6 storm samples compared across sites from most forested (Ball Creek) to least forested (Crawford Branch).

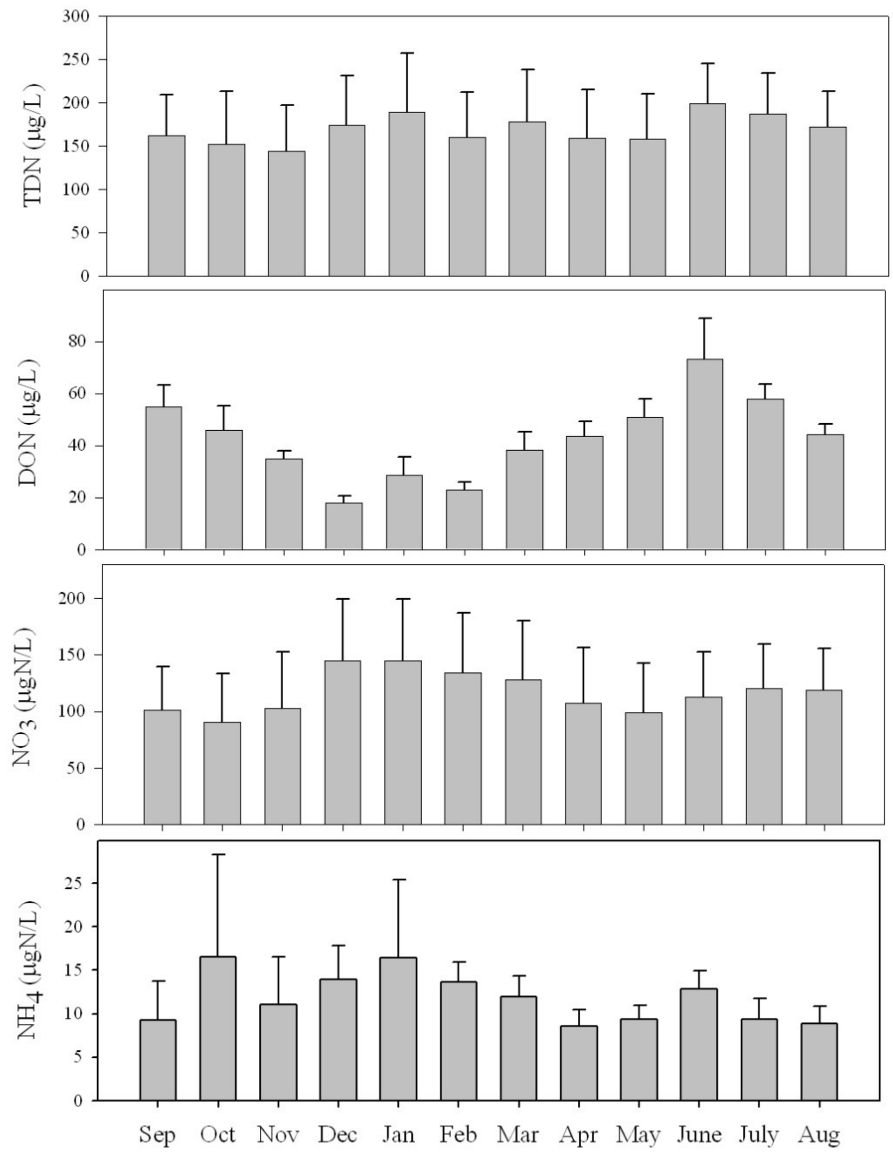



Figure 11. Means across all nine sites of total dissolved nitrogen (TDN), dissolved organic nitrogen (DON), nitrate ($NO_3^-$), and ammonium ($NH_4^+$) for base flow samples for each month from Sep 2010-Aug 2011. Error bars are standard errors.

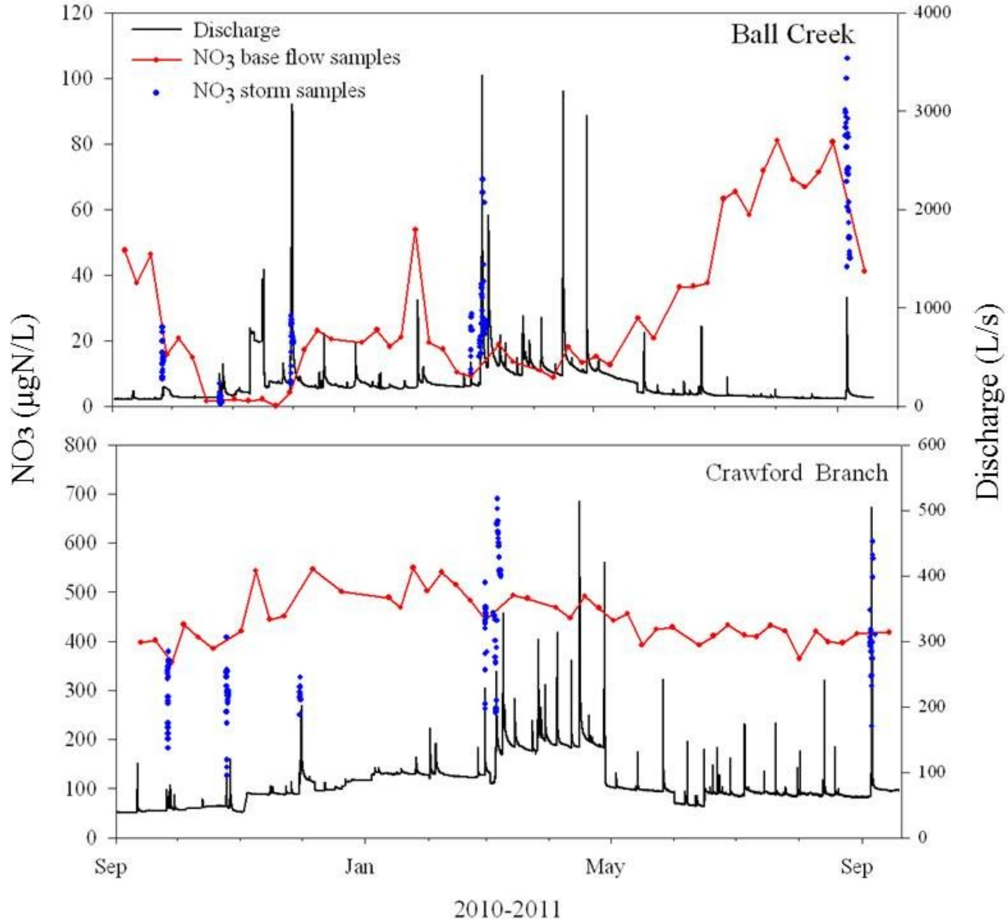



Figure 12. Discharge at fifteen minute intervals and nitrate ($NO_3^-$) concentrations of Ball Creek and Crawford Branch for both storm and base flow samples.

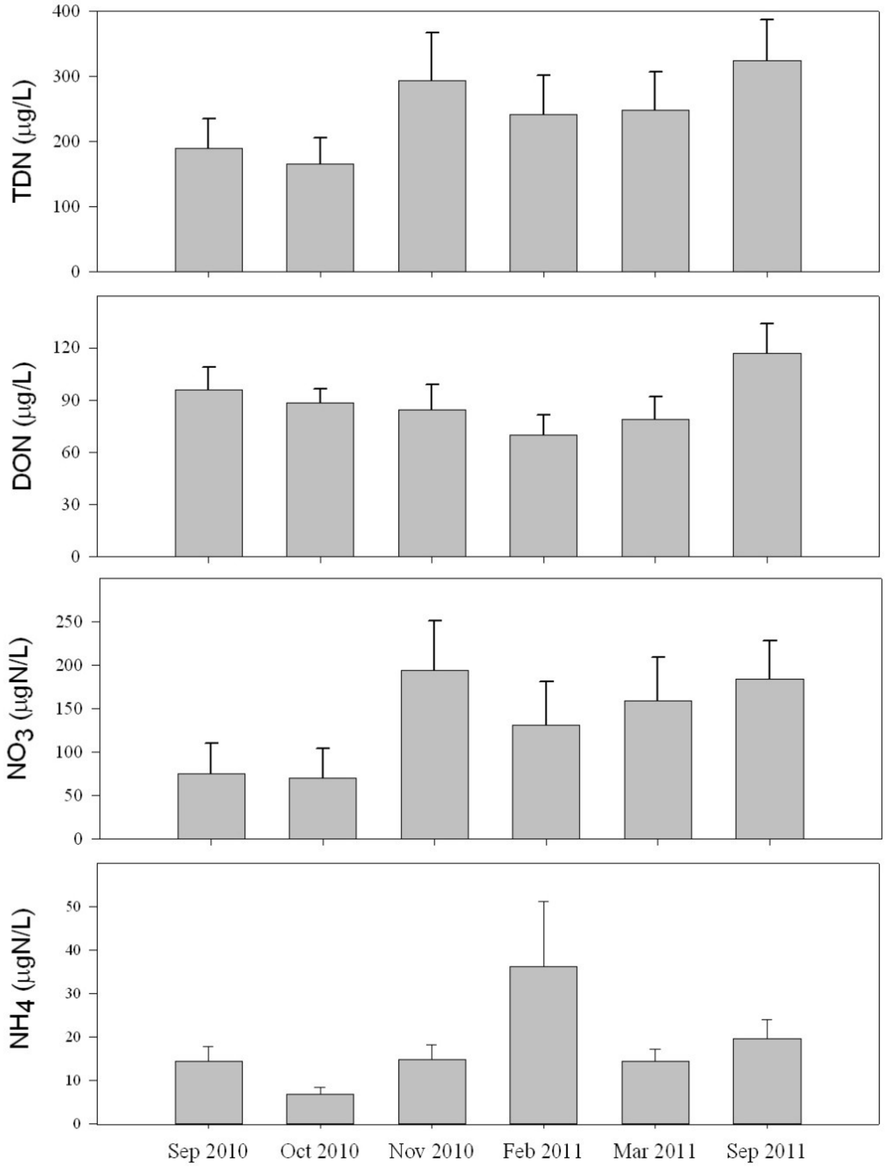



Figure 13. Means across all nine sites of flow-weighted means of total dissolved nitrogen (TDN), dissolved organic nitrogen (DON), nitrate ($NO_3^-$), and ammonium ($NH_4^+$**)** for all nine sites for each storm. Error bars are standard errors.

Table 1. Site characteristics of the nine streams used in this study. Discharge is daily average for Sep. 2010-Aug. 2011. Ag (agricultural), built, forest, barren, scrub, and wetland land cover from 2010 NASA Landsat Thematic Mapper.

| Site | Watershed Size (ha) | Average discharge (L/s) | Percent of Land Cover | | | | | |
|---|---|---|---|---|---|---|---|---|
| | | | Ag | Built | Forest | Barren | Scrub | Wetland |
| Ball Creek | 716 | 162 | 0.0 | 2.2 | 97.4 | 0.3 | 0.1 | 0.0 |
| Ray Branch | 1438 | 305 | 0.0 | 0.6 | 96.9 | 0.4 | 2.1 | 0.0 |
| Jones Creek | 1531 | 302 | 2.7 | 2.3 | 92.1 | 0.7 | 2.2 | 0.0 |
| Cowee Creek | 2913 | 266 | 3.7 | 2.8 | 91.1 | 0.1 | 2.2 | 0.0 |
| Caler Fork | 1867 | 144 | 3.8 | 3.5 | 85.1 | 1.5 | 6.0 | 0.2 |
| Skeenah Creek | 602 | 116 | 3.2 | 4.8 | 84.9 | 0.5 | 6.5 | 0.0 |
| Watauga Creek | 1670 | 185 | 6.0 | 14.4 | 73.2 | 0.9 | 5.5 | 0.0 |
| Bates Creek | 218 | 93 | 15.0 | 7.2 | 70.0 | 0.0 | 7.7 | 0.1 |
| Crawford Branch | 527 | 74 | 13.9 | 48.4 | 29.3 | 0.5 | 7.9 | 0.0 |

Table 2. Base flow average concentrations of total dissolved nitrogen (TDN), ammonium ($NH_4^+$), nitrate ($NO_3^-$), and dissolved organic nitrogen (DON) for September 2010-August 2011.

| Site | TDN (µg/L) | $NH_4^+$ (µgN/L) | $NO_3^-$ (µgN/L) | DON (µg/L) |
|---|---|---|---|---|
| Ball Creek | 70 | 6 | 30 | 36 |
| Ray Branch | 79 | 5 | 44 | 30 |
| Jones Creek | 84 | 7 | 35 | 45 |
| Cowee Creek | 96 | 7 | 47 | 41 |
| Caler Fork | 87 | 9 | 40 | 37 |
| Skeenah Creek | 121 | 7 | 82 | 33 |
| Watauga Creek | 218 | 12 | 167 | 42 |
| Bates Creek | 215 | 10 | 166 | 41 |
| Crawford Branch | 557 | 44 | 447 | 79 |

Table 3. Rating curves used to estimate discharge (Q, L/s) from stage (X, mm) for each of the nine study sties. $r^2$ and number of sample points (n) reported. Ray Branch, Skeenah Creek, and Watauga Creek rating curves used manning equation for high discharge points.

| Watershed | Rating Curve | $r^2$ | n |
|---|---|---|---|
| Ball Creek | $Q= 19.38e^{0.007x}$ | 0.92 | 12 |
| Ray Branch | $Q= e^{(3.76\ln(x)-15.003)}$ | 0.92 | 14 |
| Jones Creek | $Q = 61.54e^{0.006x}$ | 0.55 | 12 |
| Caler Fork | $Q= 40.23e^{(.004x)}$ | 0.30 | 12 |
| Cowee Creek | $Q = 68.046e^{0.006x}$ | 0.71 | 14 |
| Skeenah Creek | $Q= e^{(1.56 \ln(x)-3.53)}$ | 0.73 | 15 |
| Watauga Creek | $Q= e^{(1.78 \ln(x) -3.56)}$ | 0.94 | 15 |
| Bates Creek | $Q = 21.16e^{0.006x}$ | 0.70 | 14 |
| Crawford Branch | $Q = 17.43e^{0.003x}$ | 0.58 | 15 |

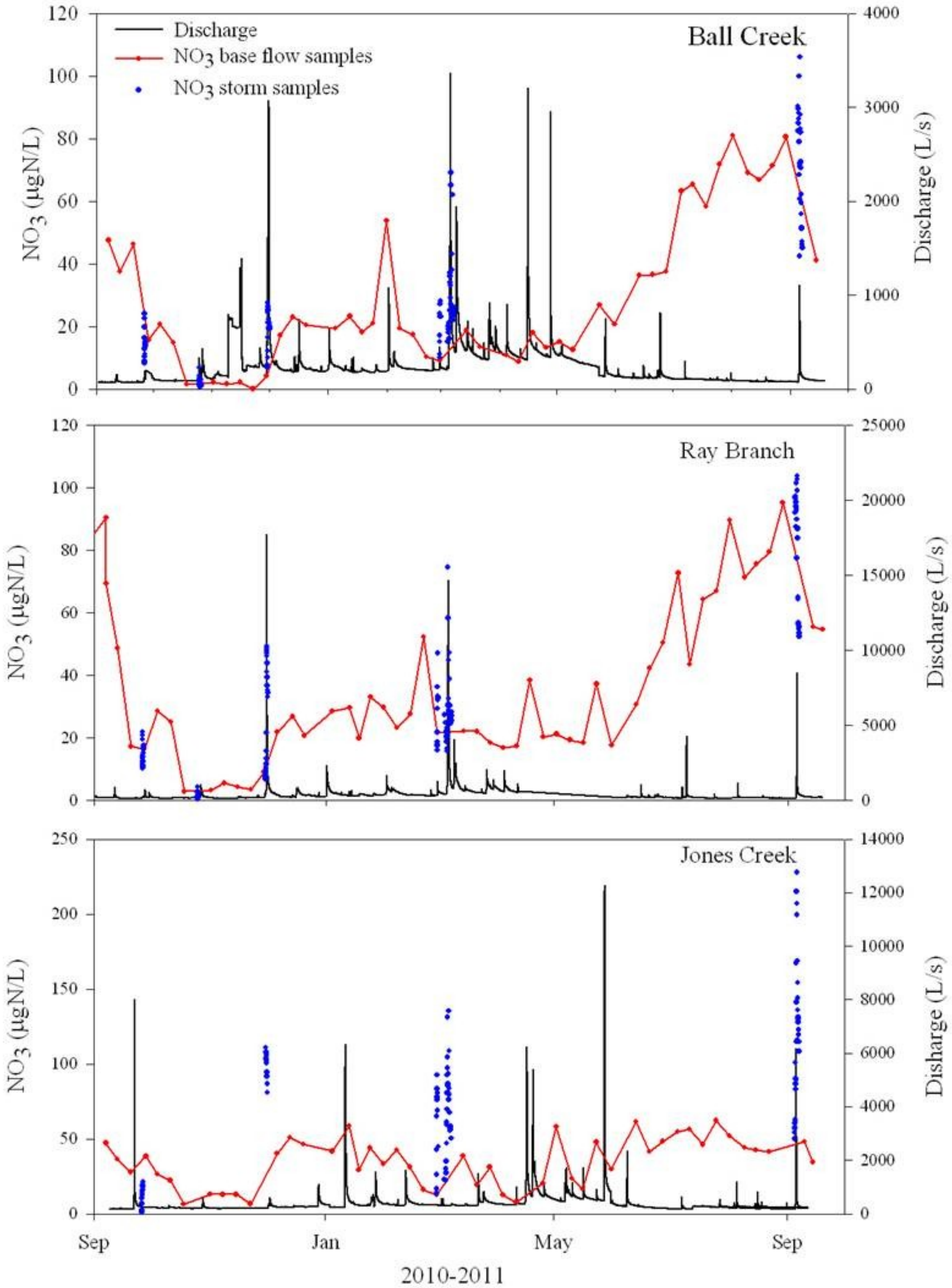
Table 4. Storm characteristics for the six storms sampled from 2010-2011. Approximant total daily precipitation taken from the Coweeta weather station. Antecedent Precipitation ($AP_7$) was for the previous 7 days.

| Storm | Date | Duration (hr:min) | Total precipitation (mm) | $AP_7$ (mm) | Comment |
|---|---|---|---|---|---|
| 1 | 26-27 Sep 2010 | 17:30 | 5.46 | 0.043 | |
| 2 | 25-26 Oct 2010 | 26:15 | 4.14 | 0.01 | Jones Creek not sampled due to equipment failure |
| 3 | 30 Nov – 1 Dec 2010 | 35:00 | 14.25 | 0.32 | |
| 4 | 28 Feb – 1 Mar 2011 | 25:00 | 38.35 | 41.86 | Watauga Creek not sampled due to equipment failure |
| 5 | 5 -8 Mar 2011 | 93:00 | 114.05 | 32.93 | |
| 6 | 4-7 Sep 2011 | 58:00 | 173.74 | 0 | |

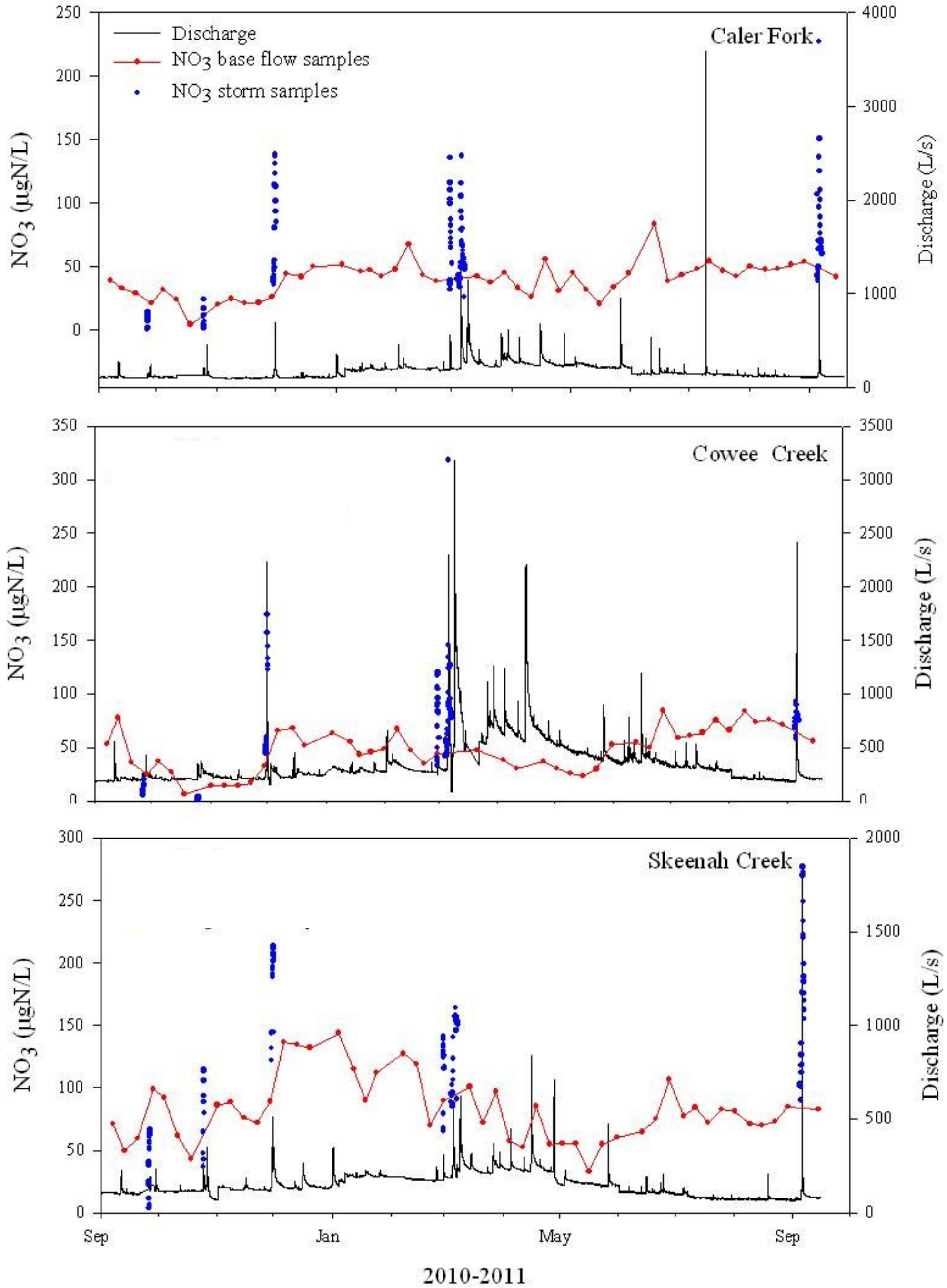
Table 5. General properties of the concentration/discharge relationship for the six storms. Positive slope indicates increase nitrogen with increase discharge. Negative slope indicates decrease nitrogen with increase discharge. "CW" indicates clockwise, while "CCW" indicates a counter clockwise hysteresis. "Var" indicates inconsistency/variable. Sites are arranged from most to least forested.

| Watershed | TDN | | $NO_3$ | | DON | |
|---|---|---|---|---|---|---|
| | Slope | Hysteresis | Slope | Hysteresis | Slope | Hysteresis |
| Ball | + | CW | + | CCW | + | CW |
| Ray | + | Var | + | CCW | + | CW |
| Jones | + | CW | + | CCW | + | CW |
| Cowee | + | CW | + | CW | + | CW |
| Caler | + | CW | + | CCW | + | CW |
| Skeenah | + | Var | + | CCW | + | CW |
| Wautaga | + | CCW | + | CCW | + | CW |
| Bates | + | CCW | + | CCW | + | CCW |
| Crawford | - | CCW | - | CCW | + | CCW |

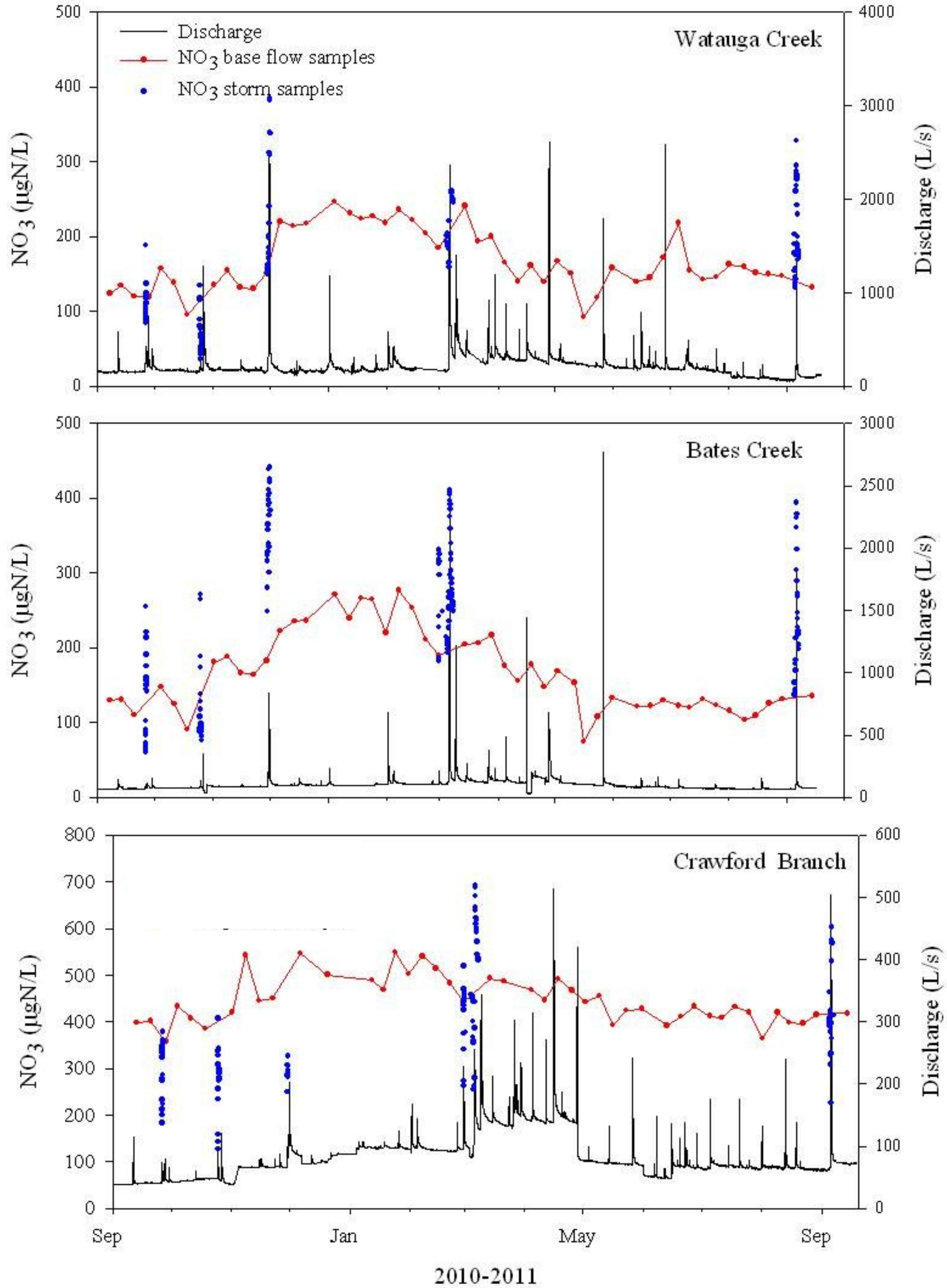
**Appendices**



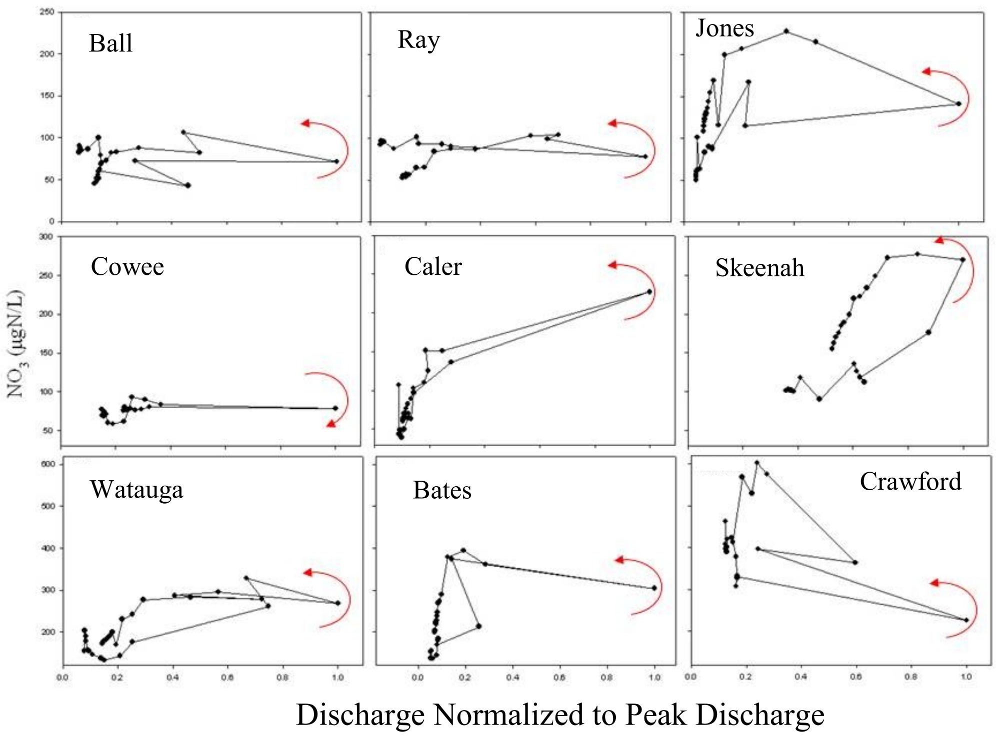

Appendix 1. Sites annual flow and nitrate ($NO_3^-$) for storm and base samples for Ball Creek, Ray Branch, and Jones Creek



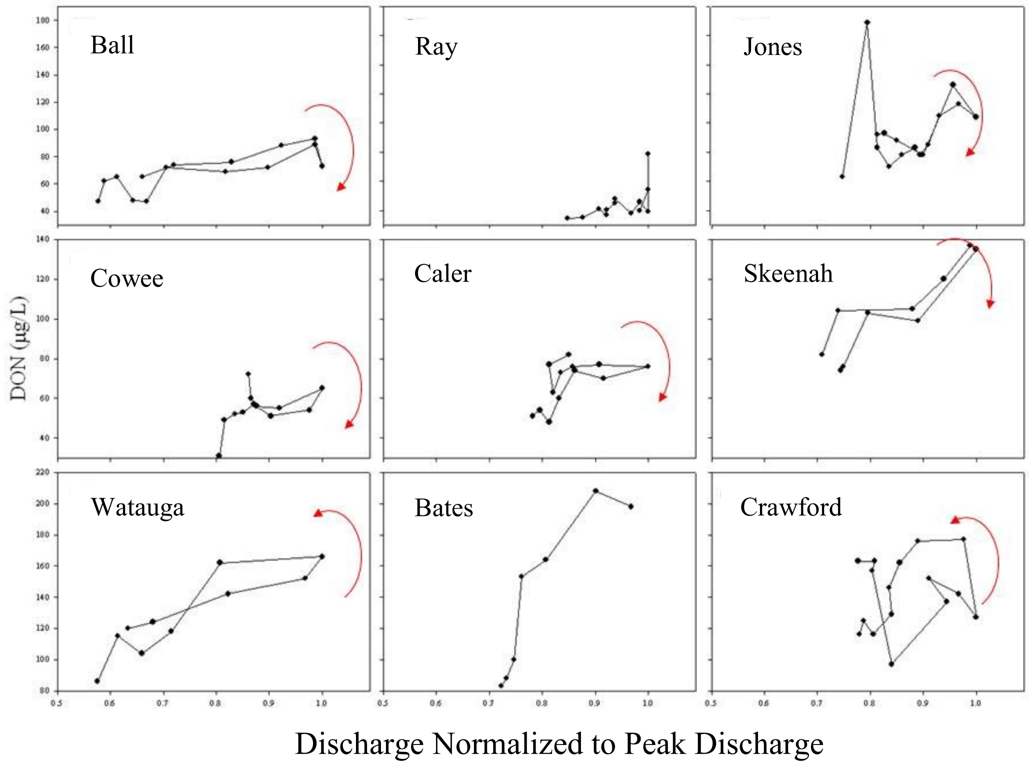

Appendix 2. Sites annual flow and nitrate ($NO_3^-$) for storm and base samples for Caler Main, Cowee Creek, and Skeenah Creek.



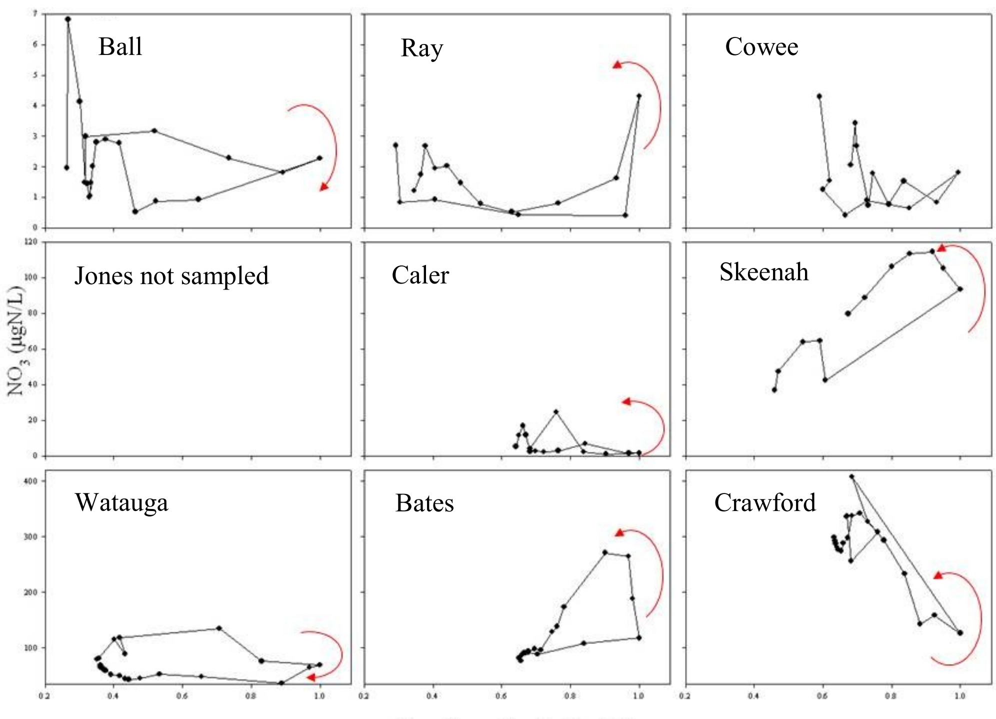

Appendix 3. Sites annual flow and nitrate ($NO_3^-$) for storm and base samples for Bates Creek, Watauga Creek, and Crawford Branc




Appendix 4. Nitrate ($NO_3^-$) concentration versus normalize discharge for the Sept 2010 storm. Arrows indicate the time sequence of samples.

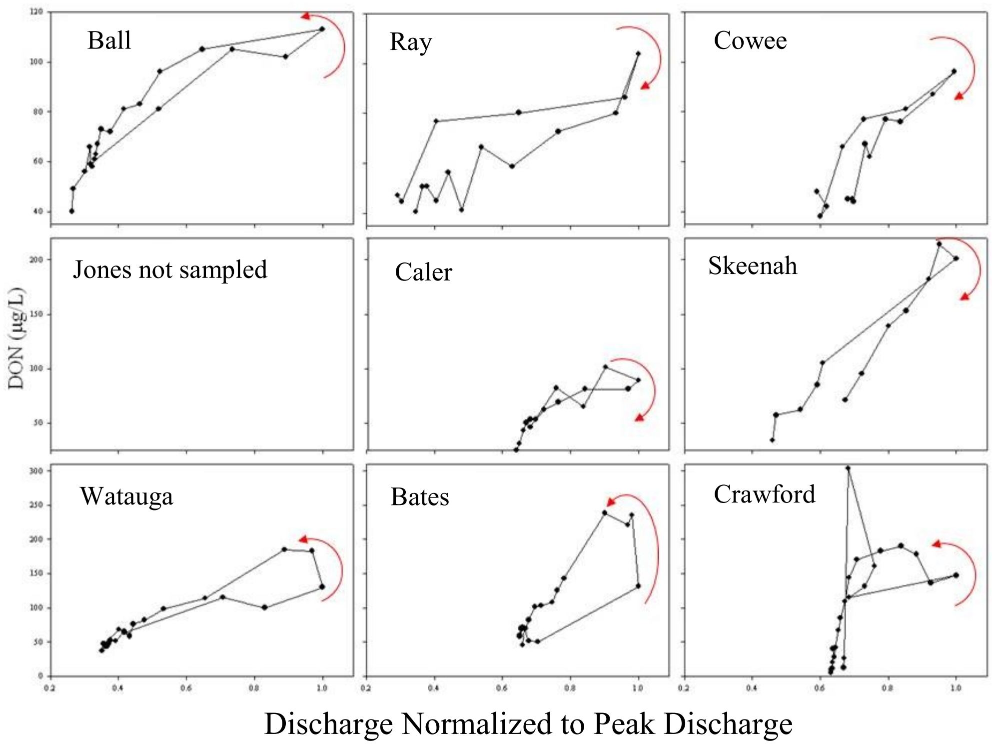



Appendix 5. Dissolved organic nitrogen (DON) concentration versus normalize discharge for the Sept 2010 storm.  Arrows indicate the time sequence of samples

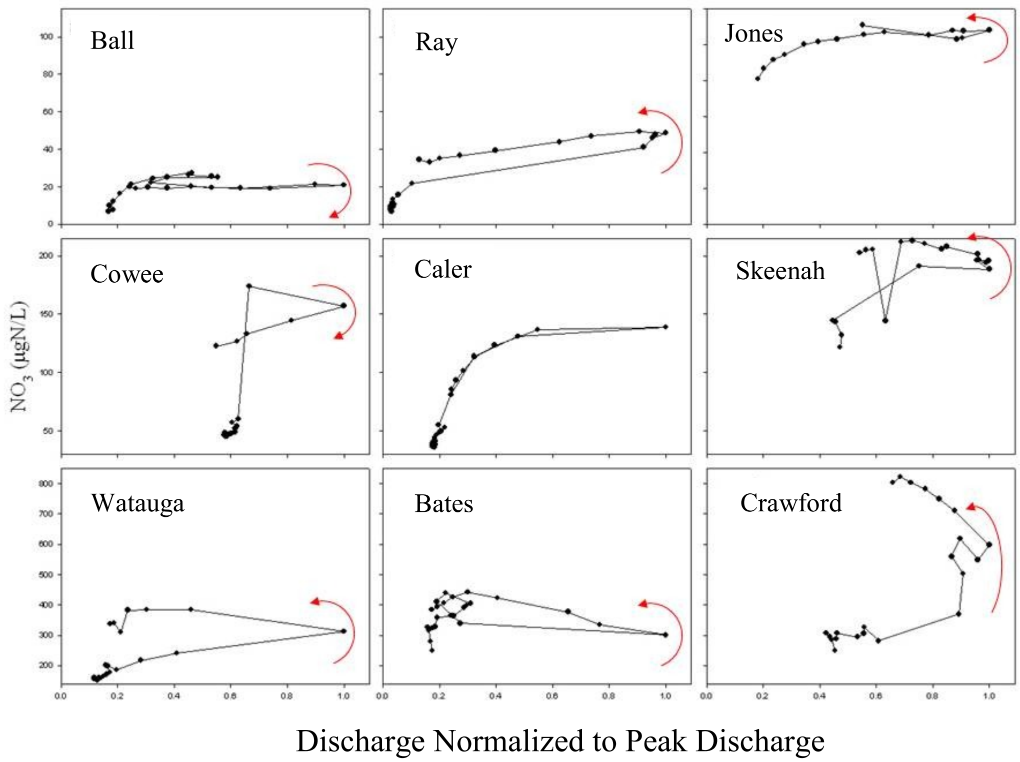



Discharge Normalized to Peak Discharge

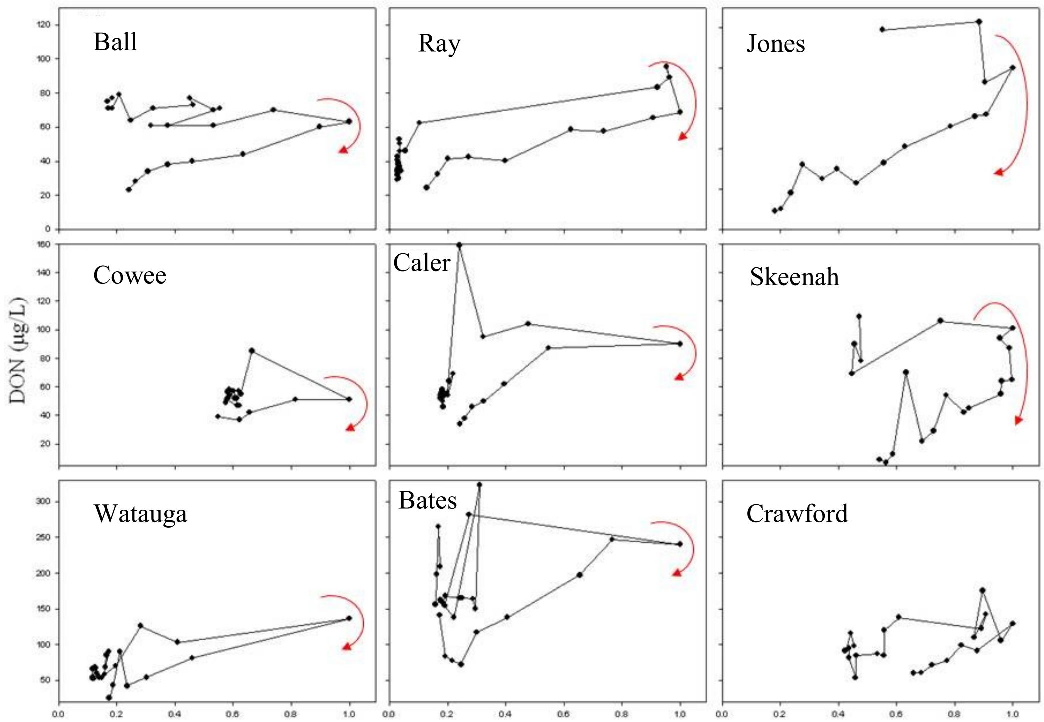
Appendix 6. Nitrate ($NO_3^-$) concentration versus normalize discharge for the Oct 2010 storm. Arrows indicate the time sequence of samples.



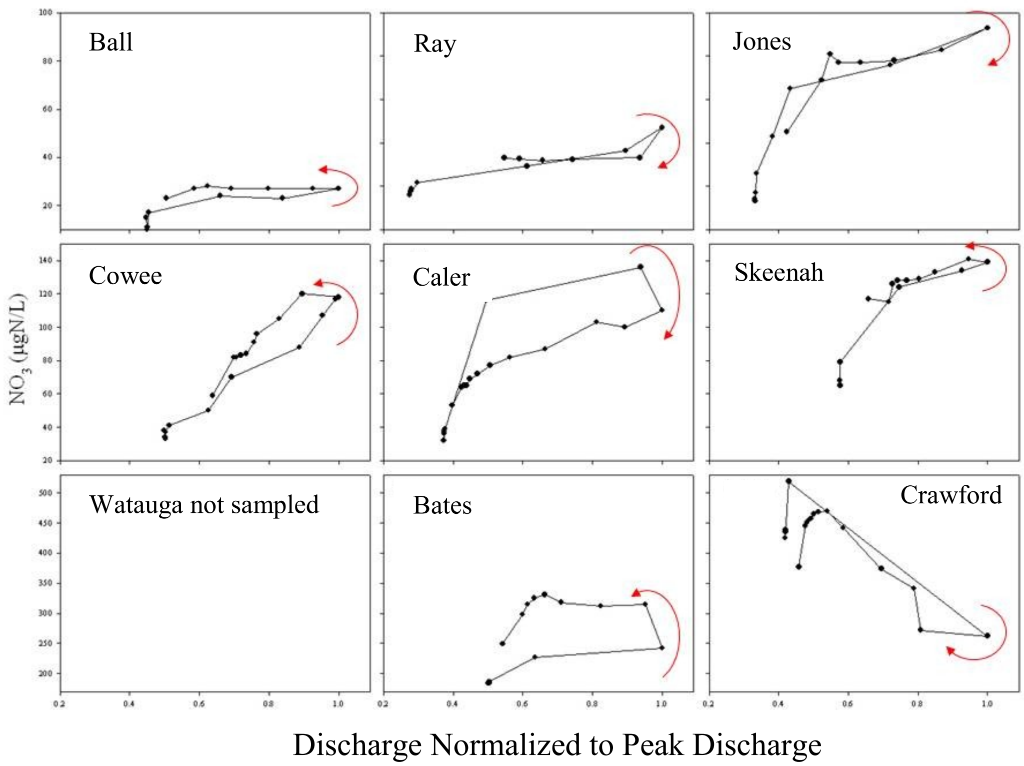

Appendix 7. Dissolved organic nitrogen (DON) concentration versus normalize discharge for the Oct. 2010 storm. Arrows indicate the time sequence of samples



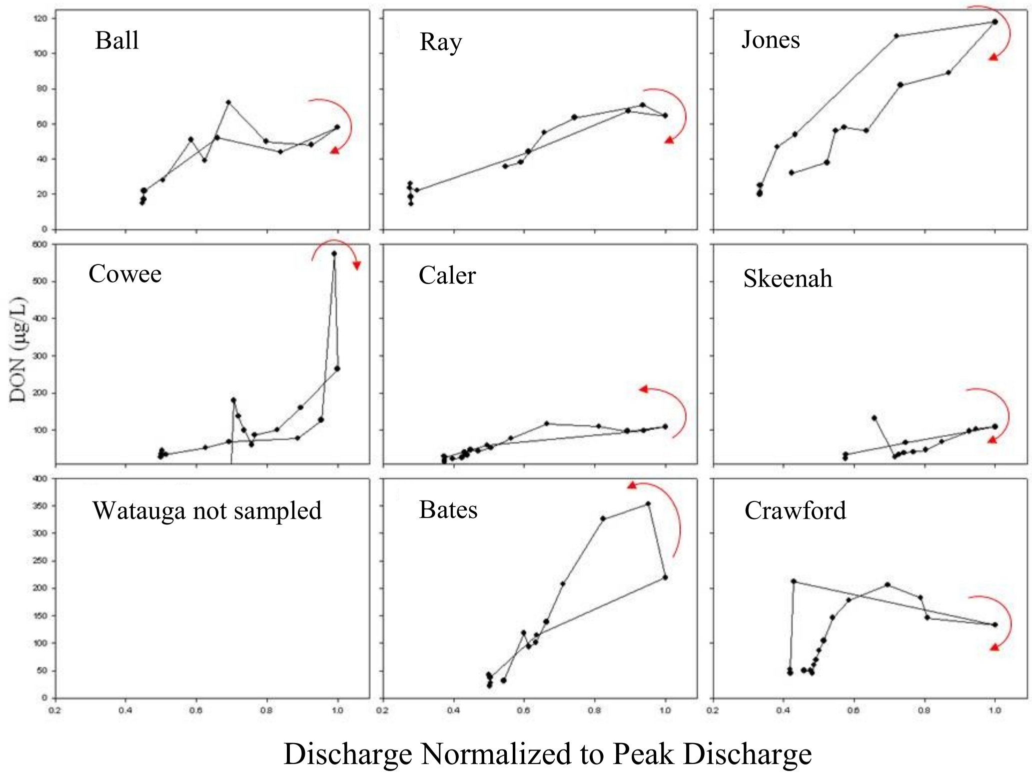

Appendix 8. Nitrate ($NO_3^-$) concentration versus normalize discharge for the Nov 2010 storm. Arrows indicate the time sequence of samples.



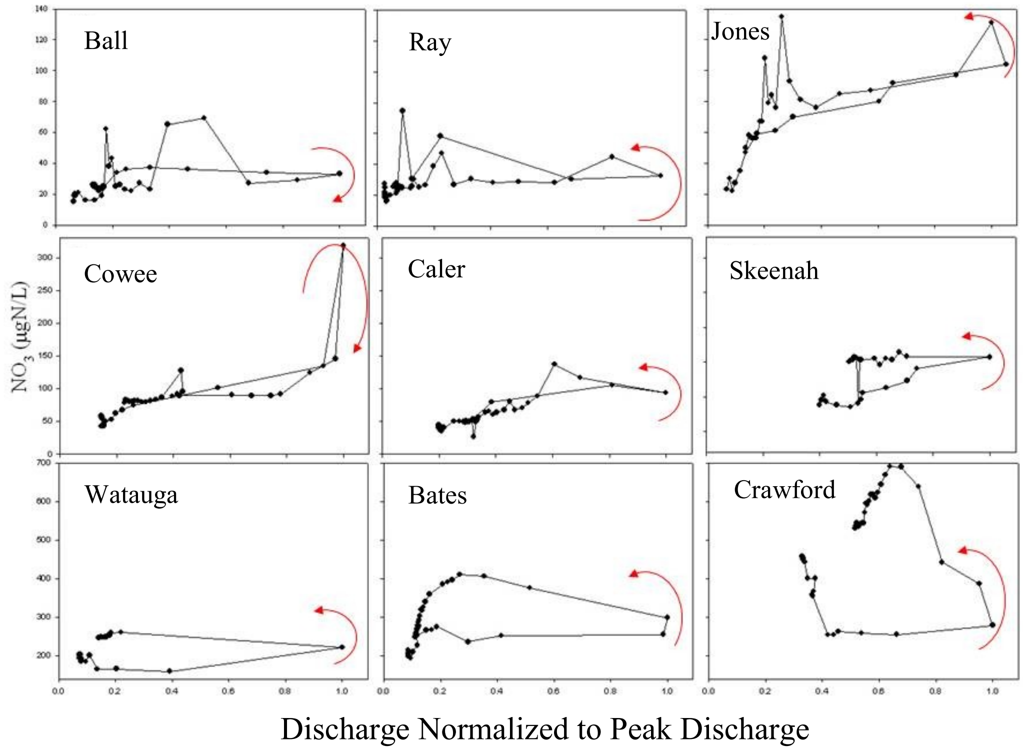

Appendix 9**.** Dissolved organic nitrogen (DON) concentration versus normalize discharge for the Nov. 2010 storm. Arrows indicate the time sequence of samples.



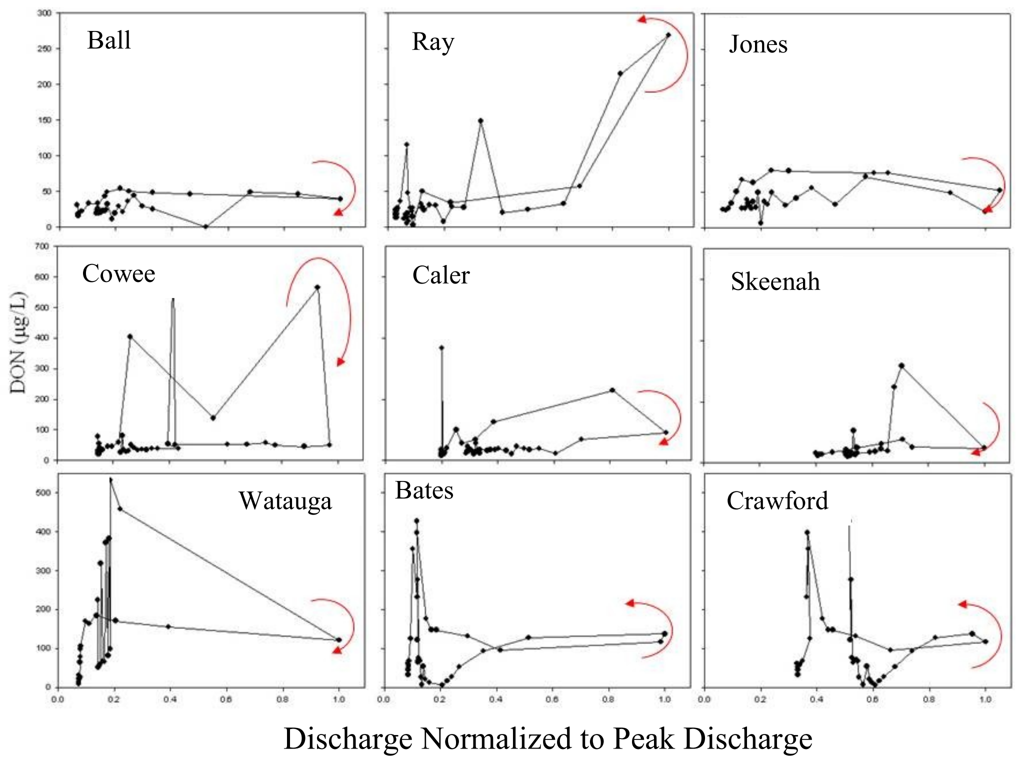

Appendix 10. Nitrate ($NO_3^-$) concentration versus normalize discharge for the Feb. 2011 storm. Arrows indicate the time sequence of samples.



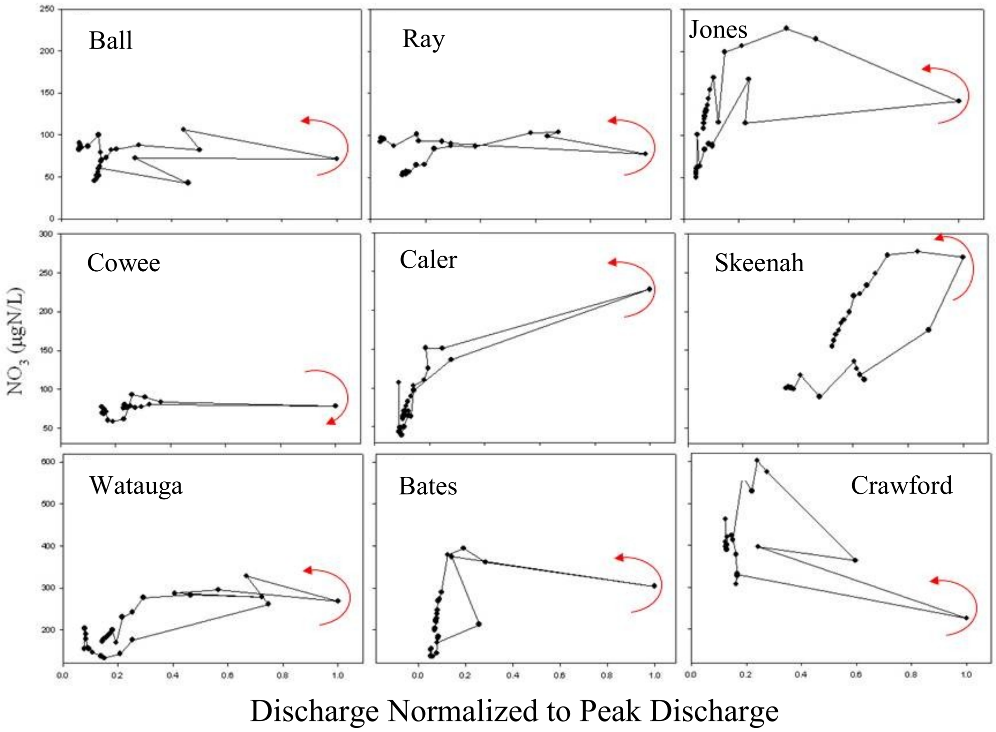

Appendix 11. Dissolved organic nitrogen (DON) concentration versus normalize discharge for the Feb. 2011 storm. Arrows indicate the time sequence of samples.



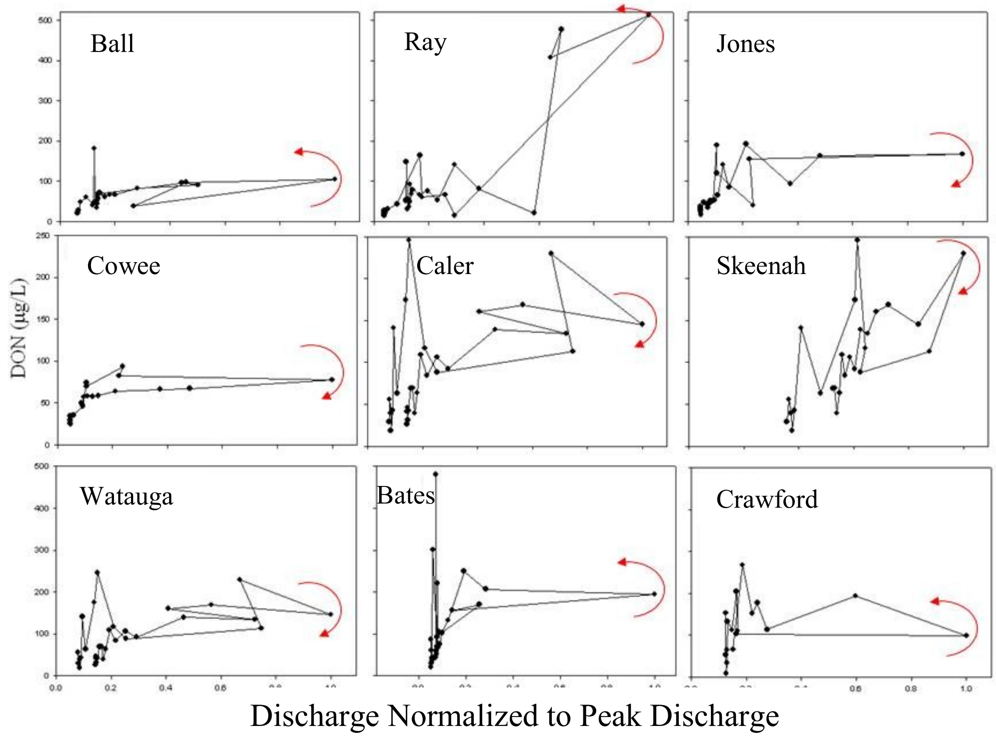

Appendix 12. Nitrate ($NO_3^-$) concentration versus normalize discharge for the Mar 2011 storm. Arrows indicate the time sequence of samples.




Appendix 13. Dissolved organic nitrogen (DON) concentration versus normalize discharge for the Mar 2011 storm. Arrows indicate the time sequence of samples.




Appendix 14. Nitrate ($NO_3^-$) concentration versus normalize discharge for the Sept 2011 storm. Arrows indicate the time sequence of samples.




Appendix 15. Dissolved organic nitrogen (DON) concentration versus normalize discharge for the Sept 2011 storm. Arrows indicate the time sequence of samples.