SEASONAL VARIATION IN RATES OF NITRIFICATION ASSOCIATED WITH PATTERNS OF CARBON AND NITROGEN SUPPLY IN A SOUTHERN APPALACHIAN HEADWATER STREAM

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Abstract. Nitrification, the chemoautotrophic process via which ammonium-nitrogen (NH_4-N) is converted to nitrate-nitrogen (NO_3-N), is an important nitrogen (N) transformation in stream ecosystems. Experimental addition of dissolved organic carbon (DOC) has been shown to inhibit rates of nitrification, and rates have been stimulated by NH_4-N addition. Insights regarding the role of particulate organic matter (POM) in this scenario could further enhance our understanding of linkages between ecosystem carbon (C) and N cycles. Hugh White Creek, a headwater stream located in the southern Appalachian mountains of North Carolina, USA, receives large amounts of allochthonous POM inputs each fall. To address the effects of these inputs on nitrification, I conducted a seasonal survey of organic matter standing stocks and nitrification rates along with experimental manipulation of dissolved C and N supplies in stream sediment microcosms to determine: 1) how rates of nitrification compare across seasons, and 2) to what extent nitrification rates are influenced by seasonal changes in standing stocks and relative abundances of both sedimentary and dissolved forms of C and N. Rates of nitrification were most closely and positively related to rates of ammonification, which, in turn were negatively related to C:N of fine benthic organic matter (FBOM). Uniform additions of C and N throughout the year had different effects on rates of nitrification and ammonification due to their changing relative importance as sediment organic matter stocks were depleted and underwent changes in quality. Slow rates of nitrification for much of the year could be attributed to large quantities of C relative to N in stream sediments. To the extent that changes in OM stocks dictate change in C and N availability, seasonal patterns in OM dynamics represent changes in ecosystem structure relevant to rates of nitrification, emphasizing the importance of terrestrial/aquatic linkages for predicting rates of N transformation in aquatic ecosystems.

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Introduction

A firm understanding of the biogeochemical nitrogen (N) cycle is needed to address a plethora of environmental challenges associated with imbalances in ecosystem N, such as global climate change (Houghton 1999), acid rain (Driscoll et al. 2001), drinking water contamination (Canter 1997), and eutrophication of freshwater ecosystems (Hessen and Hender 1997). Bacteria are central to our interpretation of these imbalances because of their strong influence on ecosystem material cycling and energy flow (White 1995, Cole 1999, Cotner and Biddanda 2002).

Nitrifying bacteria are of particular interest because they transform N in the form of ammonium (NH_4-N) to N in the form of nitrate (NO_3-N), a more mobile chemical species (Sprent 1987). The significance of this process in forest ecosystems (Vitousek et al. 1979, Currie 1999) has been well documented, and recent efforts have addressed its relevance in streams (Holmes et al. 1994, Jones et al. 1995, Peterson et al. 2001, Bernhardt et al. 2002).

Studies investigating factors influencing NH_4-N dynamics at the stream-reach scale have found negligible uptake by nitrifying bacteria relative to other processes such as in-stream heterotrophic metabolism (Tank et al. 2000, Webster et al. 2003). However, others addressing stream functioning have described nitrification as a quantitatively important transformation of N (Mulholland et al. 2000, Findlay and Sinsabaugh 2003). Despite these contradictions, few studies have addressed potential variation in rates of nitrification and associated control variables (Bernhardt and Likens 2002, Strauss et al. 2002).

Numerous environmental control variables including temperature, dissolved oxygen (DO), NH_4-N availability, and pH represent physiological constraints known to influence rates of nitrification in controlled environments (Wild et al. 1971, Kuenen and Robertson 1987). Because of this sensitivity, nitrification has been used as a bioindicator in stream systems influenced by mining activities (Niyogi et al. 2003). Of thirteen variables potentially associated with nitrification rates in sediments from 36 streams in northern Wisconsin and the upper peninsula of Michigan, NH_4-N availability and pH were the best predictors of nitrification rates (Strauss et al. 2002). Significant positive

relationships between nitrification and DO availability have also been demonstrated for Kansas prairie streams (Kemp and Dodds 2001).

The tendency of elevated carbon (C) to slow or inhibit rates of nitrification has been observed in agricultural fields (USDA 2000), wastewater treatment facilities (Gilmore et al. 1999), forests (Montagnini et al.1989, Ollinger et al. 2002), and streams (Bernhardt and Likens 2002). Nitrification inhibition by C may be direct via allelopathy (Strauss and Lamberti 2000), whereby chemicals with high C:N are directly toxic to nitrifiers, and indirect via changes in microbial dynamics (Verhagen and Laanbroek 1991, Butturini et al. 2000, Strauss and Lamberti 2000). According to the latter explanation, in situations where C is abundant, heterotrophic microbes out-compete autotrophic nitrifying bacteria for NH_4-N because of more efficient metabolic sequestration. This relationship has been demonstrated via manipulation of dissolved C and N in stream sediment microcosms (Strauss et al. 2002). However, less is known about how other C and N supplies such as particulate matter and interstitial water act to organize rates of nitrification.

In the southern Appalachians, C and N availability in headwater streams is largely influenced by inputs of organic matter (OM), such as leaves and wood (Webster and Meyer 1997, Meyer et al.1998). This terrestrial-aquatic linkage contributes to a complex cyclical pattern of C and N availability (Meyer et al. 1988), and these patterns of seasonal change may influence rates of nitrification.

In this study, I addressed the influence of periodic allochthonous inputs on rates of nitrification in Hugh White Creek, a southern Appalachian headwater stream. I conducted a seasonal survey of organic matter standing stocks and nitrification rates along with experimental manipulation of dissolved C and N supplies in stream sediment microcosms to determine: 1) how rates of nitrification compare across seasons, and 2) to what extent nitrification rates are influenced by seasonal changes in standing stocks and relative abundances of both sedimentary and dissolved forms of C and N.

Site Description

This study took place in the Blue Ridge Physiographic Province at the Coweeta Hydrologic Laboratory (CHL), in western North Carolina, USA. Research described

here was carried out in Hugh White Creek, a headwater stream located in watershed 14. This watershed is characterized by mixed hardwood stands, undisturbed since 1927, and has served as a reference watershed for many comparative ecosystem studies (e.g. Gurtz and Wallace 1984, Swank and Crossley 1988, Golladay et al. 1989, Montagnini et al. 1989, Swank and Vose 1997).

Methods

Seasonal measures of C and N supply

Benthic organic matter was sampled from four evenly-spaced sampling sites within a 100-m study reach in fall (25 Nov. 2002), winter (25 Jan. 2003), spring (25 Apr. 2003), and summer (13 Jul. 2003). Each site included a transect traversing the stream perpendicular to flow. Slow-moving depositional areas (usually at the head of small riffles) were identified near each transect, and a 0.07m^2 circular sampler was inserted at a random location within these areas.

Coarse benthic organic matter (CBOM) in the sampler was collected, dried (50°C) for at least 24 hours, and divided into small wood (<1.5 cm in diameter) and leaves. Wood larger than 1.5 cm diameter was discarded. Dried small wood and leaf samples were weighed and ground, and sub-samples were ashed (550°C for 45 minutes) to determine ash free dry mass (AFDM). Atomic C:N ratios and percent abundance were determined for additional small wood (wood C:N) and leaf (leaf C:N) sub-samples using a VarioMAX CNS Macro Elemental Analyzer (Elementar, New Jersey, USA). Total C and N as leaves (or wood) was calculated by multiplying the percentage of C or N in each sub-sample by the total leaf (or wood) standing stock observed at each transect for each season.

After removal of CBOM, fine benthic organic matter (FBOM, <1mm in diameter) in the sampler was collected by measuring water depth (m), agitating the top 3-5 cm of stream sediment, and collecting a known volume of slurry that was then passed through a 1 mm mesh net. Slurry samples were filtered onto pre-weighed and pre-ashed glass fiber filters (Whatman GFF, 0.7 µm pore size). Filter contents were dried, weighed, and ashed in order to quantify FBOM concentration (gAFDM m^{-3} of known volume of sub-sample).

FBOM concentration was then multiplied by the total water depth within the sampler to determine areal standing stock (gAFDM m^{-2}). The remainder of the sub-sample was dried (50°C) and ground for analysis of atomic C:N ratio; FBOC fine benthic organic carbon (FBOC) and fine benthic organic nitrogen (FBON) were determined in the same manner described above for leaf and wood C and N.

One day following benthic organic matter sampling, a streambed sediment sample was collected from slow-moving depositional areas approximately 5 m upstream from each transect. Single composite samples of multiple sediment cores were collected, transported on ice, and processed in the laboratory within 6-10 hours of sampling. In the lab, each sample was sieved (1 cm mesh) and further homogenized by stirring. Four replicate 50 cm^3 aliquots of the homogenized sediment from each sampling site were placed into experimental microcosms (250 mL Erlenmeyer flasks) for a total of sixteen microcosms. One microcosm from each sampling site was used to assess C and N standing stocks associated with stream sediments. A second microcosm was used to determine initial NH_4-N content ($[NH4\text{-}N]_{initial}$) for calculating ammonification rates. Nitrification assays were conducted in two remaining microcosms to which 100 mL of channel water from Hugh White Creek was added.

Stream sediments in one microcosm from each sample site were amended with 100 mL of deionized water for 1 hour at ambient stream temperature to determine sediment interstitial dissolved organic carbon (IDOC) content (sensu Baker et al. 2000). Thereafter, approximately 50 mL of water sample was removed, centrifuged at 4500 rpm, filtered through a glass fiber filter (Whatman GFF), and analyzed for DOC. Fine benthic organic matter was separated from dried sediment remaining in each microcosm using a sieve (1mm in diameter), weighed, and analyzed for C:N content for comparison with other microcosm observations.

Total NH_4-N content was determined in a second microcosm from each sampling site with KCl extraction to quantify sorbed NH_4-N (Sparks 2003). A mixture of 100 mL of 2N KCl and 100 mL of channel water was added to the microcosm containing 50 cm^3 stream sediment. Microcosms were then shaken at 100 rpm for approximately one hour. Thereafter, approximately 50 mL of water sample was removed, centrifuged at 4500 rpm, filtered through a glass fiber filter (Whatman GFF), and analyzed for NH_4-N. The

portion of NH_4-N sorbed to the sediment (NH_4-N extracted) was calculated as the mass of NH_4-N present in the total analyte minus the mass present in channel water added to this microcosm. I use the term interstitial C:N to describe the ratio of IDOC to adsorbed NH_4-N; interstitial NO_3-N content was negligible.

Seasonal rates of nitrification and experimental manipulations

Benthic nitrification assays (Hall 1984, Strauss 2000) were carried out using two microcosms from each transect; hereafter referred to as reference (Figure 1A) and blocked (Figure 1B) microcosms. Blocked microcosms (Figure 1B) were amended with 2-chloro-6-[trichloromethyl]-pyridine (nitrapyrin), a nitrification inhibitor, dissolved in di-methyl sulfoxide (DMSO). Reference microcosms were amended with DMSO alone. Microcosms were incubated in the lab in the dark at ambient stream temperature on a shaker table agitated at 100 rpm for 12 hours. Following incubation, 100 mL of 2N KCl was added to each flask (final KCl concentration approximately 1N) to terminate incubation and extract sediment NH_4-N. A 50 mL water sample was removed from each flask, centrifuged at 4500 rpm, and filtered through a glass fiber filter (Whatman GFF) for NH_4-N analysis.

Rates of N transformations were determined by comparing changes in NH_4-N extracted from microcosm sediments (Figure 1). N transformations occurring in the reference microcosm include immobilization, ammonification, and nitrification (Figure 1A). These same transformations occur in blocked microcosms, except nitrification, which is eliminated by the addition of nitrapyrin (Figure 1B). Gross rates of nitrification were calculated by subtracting NH_4-N concentrations (µg/L) in reference microcosms ($[NH_4\text{-}N]_{ref}$) from NH_4-N concentrations in blocked microcosms ($[NH_4\text{-}N]_{block}$) and adjusting for sediment volume and incubation time following (1):

$$\text{Gross nitrification } (\mu gN\ cm^{-3}\ hr^{-1}) = \frac{(([NH_4\text{-}N]_{block} - [NH_4\text{-}N]_{ref})\ 0.2)}{(VT)} \quad (1)$$

where V represents the volume of sediment (cm^3) in each microcosm, T the duration of the incubation (hr), and 0.2 (L) is a correction factor to account for total extract volume. Net heterotrophic ammonification was calculated by subtracting initial NH_4-N

concentrations from NH_4-N concentrations in blocked microcosms and adjusting for time and volume using (2):

$$\text{Net heterotrophic ammonification/immobilization } (\mu gN\ cm^{-3}\ hr^{-1}) = \frac{(([NH_4 - N]_{block} - [NH_4 - N]_{initial})\ 0.2)}{(VT)} \quad (2)$$

Negative values from (2) represent net immobilization.

Experimental manipulations

Remaining stream sediment from each transect was used to assess the effects of C and N availability on rates of nitrification in Hugh White Creek during each season. Glucose was chosen as labile C, and N was added in the form of NH_4-N. A randomized complete block design was used to measure the effects of four treatments, which included "+O" (control, no addition), "+C" (glucose addition, final concentration 10 mg/L above background), "+N" (NH_4-N addition, final concentration 300 µg/L above background), and "+CN" (combined NH_4-N and glucose addition). Nitrification rates were determined for each treatment by the same method described above used to assay seasonal rates.

Channel water

Temperature (°C), DO (mg/L), and specific conductance ($\mu S\ cm^{-1}$) were measured using YSI meters (Model 55, YSI Inc., Yellow Springs, Ohio, U.S.A.). One water sample was collected at each of four transects along the 100 m reach. Water was filtered through a glass fiber filter (Whatman GFF) in the field, frozen, and analyzed (See below) within one month of collection for NH_4-N, NO_3-N, and DOC. Channel water C:N ratios were determined from DOC and dissolved inorganic N.

Water Chemistry Analysis

Concentrations of NO_3-N were determined using a cadmium reduction method on a Technicon Autoanalyser II (Saskatoon, SK, Canada), according to the Technicon Industrial Method 100-70W (1973); the regents are similar, but more dilute, than those specified by USEPA(1979). Concentrations of NH_4-N were measured by phenol

hypochlorite analysis on a Technicon autoanalyser (USEPA 1997). Minimum detection limits for both N forms were 1 μg L^{-1}. For samples from nitrification assays, standards were made using a matrix of DMSO, nitrapyrin, KCl, and deionized water in appropriate proportions to address matrix effects on NH_4-N concentrations. Samples were analyzed for DOC using an Oceanography International Model 700 Total Carbon Analyzer by wet persulfate digestion (Menzel and Vaccaro 1964).

Statistical Analysis:

Differences in stream chemistry, OM stocks, mineralization, and nitrification rates among seasons were assessed by one-way ANOVA (season = main effect) followed by Tukey's multiple comparisons test (MCT). Effects of experimental manipulations of dissolved C and N on rates of both nitrification and ammonification within seasons were also assessed by one-way ANOVA followed by Tukey's MCT. A two-way ANOVA was used to assess season/treatment interaction (season and amendment = main factors). When two-way interactions were significant, a linear contrast analysis (Zar 1984) was used to assess treatment effects on N transformations (relative to rates in unamended microcosms) across seasons.

Relationships between nitrification and potential control variables were assessed with Pearson's product moment correlation and linear regression analyses. Average nitrification and ammonification rates determined in unamended control microcosms were correlated against average measurements in the field. Rates of nitrification and ammonification in unamended microcosms were also regressed against microcosm conditions. All statistical analyses were conducted using SAS (SAS Institute Inc., Cary, North Carolina, U.S.A.). In general, significance level for statisitical assessment was established as a = 0.05 except when describing relationships between whole stream seasonal averages (n=4) when a = 0.10 for descriptive purposes.

Results

Stream characterization

Stream water temperatures varied seasonally ($P < 0.0001$) with minimum temperature in winter (5.1 ºC, Table 1) while mean summer temperatures were 10 ºC

warmer. The stream was well oxygenated throughout the year; inimum DO in the winter was 63% of saturation while DO concentration in other seasons was significantly greater ($P < 0.05$) and nearly 100% saturated. Average specific conductance varied significantly ($P < 0.05$) among seasons but ranged only 1.5 µS (12-13.5 µS, Table 1).

C and N supplies:

The C:N ratio of channel water was nearly identical during spring and summer (74 and 79, respectively, Table 1), was significantly greater during fall when C:N increased to 451, and was of intermediate magnitude during winter (148, Table 1). Average dissolved inorganic N (DIN) concentration was more than two orders of magnitude lower than that of DOC (Table 1). Concentration of DIN was greatest during spring and summer (Table 1), but average values varied by only 11 µg L^{-1} among seasons. Average NO_3-N concentration in summer (8µg/L) was more than double and significantly greater ($P < 0.05$) than that observed in fall and winter. Average fall DOC concentration (1.4 mg/L, Table 1) was significantly greater ($P < 0.05$) than during all other seasons when mean DOC varied from 0.4 to 0.8 mg/L.

Compared to channel water, interstitial C and N concentrations were more similar but did fluctuate seasonally (Table 1). Total NH_4-N extracted from microcosm sediments was relatively constant, ranging from 0.14 to 0.23 µg N/cm^3. In contrast, IDOC concentrations were more variable with maximum concentration occurring in spring (3.45 µg/cm^3, Table 1), nearly three times the summer concentration. Accordingly, interstitial C:N ratios were highest in the spring (29.7, Table 1), nearly seven times those of the summer (4.7, Table 1), with fall and winter ratios intermediate of these.

Mean C:N ratio of total particulate material did not differ significantly ($P > 0.05$) among seasons, however total C:N ratio was substantially lower during summer when values dropped from 48-53, to ca. 32 (Table 2). Total particulate C associated with the streambed averaged 82.7 g/m^2 during fall when standing stocks were greatest, and declined continuously to16.3 g/m^2 by summer when stocks were significantly lower ($P<0.05$). On average, total particulate N for the study reach was maximal in fall (1.83 g/m^2, Table 2) and significantly lower in summer (0.61 g/m^2, $P < 0.05$).

The C:N ratio of leaves declined from 62 in fall to 50 in summer, but values did not differ significantly ($P > 0.05$) among seasons (Table 2). Leaf C was significantly greater ($P < 0.05$) in fall and declined throughout the year. Likewise, leaf N declined steadily during the year such that summer standing stock (0.05 g N/m^2, Table 2) was significantly lower ($P = 0.01$) and only 5% of that occurring during the fall.

In contrast to leaves, C:N ratios of FBOM were virtually unchanged across seasons ($P > 0.05$); mean values of 20-22 varied by less than 10%. Maximum FBOC standing stocks occurred in the winter and were 3 times greater than minimum stocks recorded in the summer. FBON was also maximal during winter (1.09g N/m^2), nearly twice average FBON stock in summer.

The C:N ratio of small wood (94-140, Table 2) was noticeably higher than other forms of particulate organic matter and more variable. Wood C was highest in the winter (28.80 g/m^2, Table 2), sevenfold greater than summer standing stocks, although this difference was not statistically significant ($P = 0.25$). Wood N stocks were at least 6 times greater in the winter and spring than in the fall and summer.

Seasonal variation in rates of nitrification

Rates of nitrification differed among seasons (Figure 2). In fall, rates were highly variable and not significantly different from rates measured during the other seasons. The lowest average nitrification rate occurred in winter (0.19 µg N cm^{-3} day^{-1}, Figure 2), and average rate during spring was 0.09 µg N cm^{-3} day^{-1}. The average rate during summer (0.95 µg N cm^{-3} day^{-1}) was significantly greater ($P < 0.05$) than summer and winter rates, and two to three times higher than rates measured during all other seasons (Figure 2).

Linking nitrification to C and N supplies

Across seasons, rates of nitrification in control or unamended microcosms were variably related to factors associated with microcosm sediments (Figure 3). Rates of nitrification were best predicted by rates of ammonification ($r^2 = 0.45$, $p = 0.004$, Figure 3A) along a nearly 1:1 regression line with a positive slope ($y = 0.87x$). Ammonification rates were loosely related to C:N of FBOM; higher ammonification rates were associated

with lowest C:N (Figure 3B). Using the full data set, this relationship was not statitistically significant ($p = 0.09$, n = 15), but removal of a single outlier improved the fit substantially ($r^2 = 0.48$, $p < 0.01$).

While experimental design dictated low statistical power (i.e., n = 4), average rates of nitrification determined in control microcosms were also related to dissolved (Figure 4A-B) and particulate (Figure 4C-D) C and N supplies measured in the field. Nitrification rates declined with increasing particulate C abundance as illustrated by negative correlations with wood C (Figure 4A, r = -0.98, $p = 0.02$) and FBOM C:N (Figure 4B, r = -0.89, p = 0.10). Rates of nitrification were positively related to extractable NH_4-N (r = +0.90, $p = 0.10$, Figure 4D) and declined with increasing IDOC (r = -0.93, $p = 0.07$, Figure 4C).

The influence of C and N manipulation on nitrification

Across seasons, dissolved C and N manipulation was a significant influence on rates of nitrification (2-way ANOVA, $P = 0.04$), as was season ($P < 0.001$). Additionally, the influence of nutrient amendments on rates of nitrification varied significantly with season (Figure 5, significant treatment x season interaction, 2-way ANOVA, $P = 0.01$).

Within seasons, rates of nitrification in the fall and summer exhibited a broad range of response to C and N amendment. Treatments altered nitrification rates during fall, but average rates of nitrification were not significantly (1-way ANOVA P > 0.05) different reflecting variability within treatment groups (Figure 5A). C and N manipulations had little notable effect during winter and spring when rates were low in all treatment groups (Figure 5A and B). Finally, C and N manipulation produced significant changes in nitrification during summer. Fall trends illustrated that compared to control microcosms, rates of nitrification in +C amended microcosms were 6 times slower, while rates in N amended microcosms were 50% faster, and 25% slower in microcosms receiving combined +CN additions. Similarly, in summer, average rates of nitrification in +C-amended microcosms were 40% lower and significantly different (1-way ANOVA, Tukey $P = 0.02$, Figure 5D) from average rates in +N-amended microcosms (1.62 µg N cm^{-3} day^{-1}), in which the highest nitrification rate recorded during

this study was observed. Rates of nitrification in control and +CN-amended microcosms were intermediate of these (Figure 5D).

Among seasons, comparison of rates of nitrification in nutrient-amended microcosms to control rates revealed the extent of increase in nitrification rates in the +N-amended microcosms was significantly greater (linear contrast analysis, $P < 0.05$) in summer compared to the winter and spring. The +C and +CN treatment effect did not vary across seasons.

The influence of C and N manipulation on ammonification

Dissolved C and N addition showed no significant overall effect on rates of ammonification (2-way ANOVA $P = 0.24$, Figure 5E-H), nor was there a significant treatment x season interaction ($P = 0.13$). However, there were significant differences ($P< 0.0001$) in ammonification rates.

A comparison of rates of ammonification in nutrient-amended microcosms revealed no significant difference in rates of ammonification in +N –amended microcosms (ANOVA, $P > 0.05$). Rates of ammonification in +C –amended microcosms were higher in summer ($P < 0.05$) compared to spring when the treatment effect resulted in net uptake (i.e., immobilization). Similarly, the +CN treatment effect was greater in the summer and winter relative to the fall and spring ($P < 0.05$).

Discussion

C and N supply associated with organic matter inputs

My results reveal a seasonally variable template of C and N supply at Hugh White Creek that is most likely connected to watershed characteristics, i.e. the adjacent forest which contributes seasonal organic matter inputs. These findings support an established body of research concerning the fate of allochthonous organic matter after it enters the stream (Webster et al. 1999), especially with respect to C supply. Decomposition of leaves and small wood may be reflected in increasing FBOM standing stocks (Ward et al. 1994). Elevated channel DOC concentrations in the fall are also attributed to leaf litter leachate (Meyer et al. 1998), resulting in concentrations that greatly surpass those of

other seasons. Maximal concentrations of IDOC were observed during the cooler seasons; this pattern in IDOC was reported for a different Coweeta stream (Crocker and Meyer 1987, Table 1) and linked to trends in C uptake by trees during the growing season. Seasonal patterns of particulate N standing stocks may be linked to those for C described above (Ward et al. 1994), but stocks of extractable N are less understood.

The seasonal nature of dissolved and particulate C and N observed in this one-year study are confirmed by long-term data sets for Hugh White Creek. Our estimates of annual average leaf standing stock (49.2 g AFDM/m^2) were ca. 50% of a more extensive assessment of the annual mean for HWC (Webster et al. 2001). However the pattern of relative seasonal abundance observed in our study is similar to that reported by Webster et al. (2000). Our measures of wood and FBOM standing stocks are also within ranges reported by others for Hugh White Creek (Golladay et al. 1989).

Seasonal patterns in DOC reported here are consistent with long-term averages for HWC (Coweeta LTER, Data Set Summary 3005), with the exception of lower (i.e., 0.7 mg/L below long term values) winter estimates. Our measures of dissolved NH_4-N concentrations are within 0.7 ug/L of long-term monthly averages, but measures of NO_3-N are 3-5 ug/L lower than long-term averages. It should be noted that water samples collected for our study were taken a considerable distance from the location of long-term monitoring, and represent a single day's sampling per season.

Extractable NH_4-N may be an important N source for stream processes (Triska et al. 1994). During fall, quantities of extracted NH_4-N from Hugh White Creek sediments were double those of non-extracted sediments, a difference similar in magnitude to that observed for Juday Creek sediment slurries (Strauss and Lamberti 2000) where channel water N concentrations are an order of magnitude greater. A potential source of adsorbed NH_4-N in Hugh White Creek may be the large quantities of mica observed in the streambed, a clay mineral with great potential to sorb NH_4-N (Holloway et al. 1998, Sparks 2003). Average exchangeable NH_4-N/cm^3 sediment, adjusted using a 2:1 sediment weight/volume ratio, is equivalent to 0.10 µg N g $sediment^{-1}$ at Hugh White Creek. This estimate is comparable yet lower than values reported for streams with similar channel water NH_4-N concentration such as Little Lost Man Creek (0.4-1.7 µg N

g sediment^{-1}, Triska et al. 1994) and Bear Brook (1-9 µg N g sediment^{-1}, Richey 1985). Together, channel and interstitial measures suggest that N is in short supply at HWC.

Seasonal and spatial variation in rates of nitrification

My estimates of nitrification rates in Hugh White Creek sediments contribute to a growing number of estimates for stream ecosystems (Table 3). It is evident that the estimates are highly variable across time and space (Table 3). Explanation of this variation must address comparison of whole-stream (solute injection) to stream sediment microcosm scales of assessment, which yield different rates of nitrification for the same stream assessed under similar conditions (Dodds et al. 2000). Likewise, interaction between temporal and spatial variation complicates cross-site comparison. Further understanding of potential control variables associated with rates of nitrification may yield valuable information that can assist in future cross-site comparison of N cycling in streams.

Factors influencing rates of nitrification

Entire books have been written on the many chemicals shown to influence nitrification (Richardson 1985). Traditional measures of ecosystem structure most commonly associated with microbial processes, such as temperature and DO availability, varied significantly across seasons in Hugh White Creek and were positively related to rates of nitrification. Though these relationships were not statistically significant in our study, the small sample size dictated low statistical power. My focus here, however, will is on the influences that C and N availability may have on rates of nitrification in Hugh White Creek.

Linking nitrification to C and N supplies

Relationships between rates of nitrification and control variables in experimental microcosms are consistent with the hypothesis that increased C availability may stimulate heterotrophic metabolism and reduce the ability of nitrifiers to compete for NH_4-N (Verhagen and Laanbroek 1991, Strauss and Lamberti 2000). The positive relationship

between nitrification and ammonification suggests that nitrification is primarily dictated by net heterotrophic demand for NH_4-N. Nitrification is often correlated with ammonification in studies of N transformation in forest soils (Holmes and Zak 1999, Ollinger et al. 2002). Ammonification, in turn, has been linked to foliage litter quality (Scott and Binkley 1997). In our study, the correlation between ammonification and FBOM quality (i.e. low C:N ratio) suggests a similar relationship between NH_4-N production and sediment detrital quality. Algae represent a similar detrital N source for nitrifiers in autotrophic streams (Holmes et al. 1994). Other aspects of microbial processing linked to detrital quality include denitrification (Bonin et al. 2000) and uptake (Tank and Webster 1998), and these relationships may vary seasonally (Bonin et al. 2000) and spatially (Findlay et al. 2002).

Relationships between rates of nitrification and field measures of C and N confirm relationships observed in experimental microcosms described above and may be interesting for generating new hypotheses about which forms of dissolved and particulate C and N may influence rates of nitrification at the stream reach scale. Field measures of C and N that best predicted average nitrification rates were not only FBOM C:N, but also wood C and measures of interstitial C and N.

Leaves and wood were not directly included in microcosms in which I measured rates of nitrification. So it is interesting to note that nitrification rates were negatively correlated with field measures of wood standing stocks. Even though leaves were absent from the microcosms, their ability to influence microbial community structure prior to microcosm construction may have been reflected in NH_4-N uptake. Other studies indicate that leaves and wood constitute a large demand for N (Tank and Webster 1998, Sanzone et al. 2001); as a result, our measures of heterotrophic NH_4-N demand may have been underestimated, especially in the fall when leaf standing stocks were highest. Furthermore, estimates of rates of nitrification for this season determined in microcosms may be higher than estimates at the whole-stream scale if microcosms release nitrifiers from competition with heterotrophic microbes via removal of leaves and/or wood.

Interstitial porewater may represent a more constant source of C and N with lower turnover, i.e., a longer residence time, and this resource may be more relevant at the scale of microbial processes. A substantial amount of NH_4-N present on HWC sediment

exchange sites may represent a largely unconsidered source of N for nitrifiers (but see Triska et al. 1994, Strauss 2002). In contrast, IDOC may inhibit rates of nitrification in a variety of ways. Strauss and Lamberti (2001) suggest that increased C may have an allelopathic effect on nitrifiers. This explanation of our results is also plausible since IDOC was closely related to rates of nitrification and this C source is presumably less transient and, thus, more refractory and of lower quality as a substrate.

Comparison of channel water influence to other forms of C and N

Findings comparing nitrification rates to both field and microcosm variables suggest that both dissolved and particulate C and N can be sources of microbial activity (Sobzak et al. 1998). Sediment nutrients are recognized as important organizers of microbial activity (Crenshaw et al. 2002), and our measures of standing stocks of C and N associated with the streambed sediments were more closely related to rates of nitrification than concentrations of these nutrients in channel water. These findings may indicate that channel water C:N is less effective at organizing microbial dynamics associated with rates of nitrification in Hugh White Creek than other variables such as interstitial porewater or FBOM. This latter perspective may useful in understanding the effects of dissolved C and N addition on rates of nitrification observed in our study.

The influence of DOC and NH_4-N manipulation

Rates of nitrification in microcosms amended with dissolved C and N were not significantly different from ambient rates during any given season. Nevertheless, trends of C inhibition and N stimulation of nitrification observed by Strauss (2000) were evident during fall and summer in Hugh White Creek, whereby summer effects were more pronounced. In the winter and the spring, C and N addition did not influence rates of nitrification in any evident manner. Instead rates were low and varied little among treatments. I suspect that other factors are controlling nitrification during these seasons, the most likely of these being temperature (Sheibley et al. 2003). However, temperature recorded during the spring was higher than in the fall. I contend that during spring, ambient rates of nitrification are at seasonal lows as a result of low quality FBOM and high C:N of interstitial porewater (Tables 2 and 3).

Further support for this contention is provided by observations of net immobilization in the fall and spring in response to +C addition, indicating the possibility of nitrification inhibition by heterotrophic NH_4-N consumption during these seasons. In winter, inhibition of nitrification by C may be less efficient as is indicated by net ammonification in these microcosms. Net immobilization did not occur in summer when +N addition was more effective compared to spring and winter, indicating reduced C constraint.

A conceptual model of these results (Figure 6) depicts how the influence of particulate and interstitial forms of C and N on nitrification rates may vary seasonally in forested headwater streams. As organic matter stocks of C and N are depleted and undergo annual changes in quality, rates of nitrification are influenced by not only channel N and C, but other measures of C and N availability such as FBOM and IDOC. The vertical line represents a point at which C:N ratios reach the critical value above which increased particulate and interstitial C availability constrains rates of nitrification and below which this constraint is minimized and dissolved C and (especially) N additions are more likely to stimulate nitrification.

Conclusion

C and N supplies dictate rates of nitrification in streams, but this control is situated within the context of watershed characteristics such as seasonal leaf litter inputs. Due to seasonal changes in the relative availability of C and N in different organic matter compartments, the relative influence of C and N supply on microbial processes is difficult to assess. Our study of Hugh White Creek, a southern Appalachian headwater stream, has shown that slow rates of nitrification for much of the year may be attributed to large quantities of particulate and interstitial C in streambed sediments. Uniform additions of dissolved C and N throughout the year have different effects on rates of nitrification and ammonification due to their changing relative importance as organic matter stocks are depleted and undergo changes in quality. To the extent that fluctuations in OM stocks dictate change in C and N availability, seasonal patterns in OM dynamics represent changes in ecosystem structure relevant to rates of nitrification, emphasizing the

importance of terrestrial/aquatic linkages for predicting rates of N transformation in aquatic ecosystems.

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TABLE 1. Seasonal water characteristics in Hugh White Creek, NC. Data are means ± SE; n = 4. Significant differences among seasons for each compartment (ANOVA , Tukey's MCT $P < 0.05$) are denoted by different superscripts. N.A. = not available.

	Fall	Winter	Spring	Summer
Temperature (°C)	9.3 ± 0.1^{a}	5.1 ± 0.1^{b}	12.7 ± 0.03^{c}	15.2 ± 0.1^{d}
Dissolved Oxygen (mg/L)	10.21 ± 0.05^{a}	7.37 ± 0.02^{c}	9.92 ± 0.03^{b}	9.64 ± 0.05^{ab}
Specific conductance (µS)	13.50 ± 0.00^{a}	N.A.	12.10 ± 0.00^{b}	12.03 ± 0.11^{b}
DOC (mg/L)	1.4 ± 0.05^{a}	0.4 ± 0.00^{b}	0.8 ± 0.09^{b}	0.7 ± 0.2^{b}
IDOC (µg /cm^3)	2.26 ± 0.11	2.83 ± 0.69	3.45 ± 0.92	1.23 ± 0.23
NO_3-N (µg/L)	2 ± 1^{cb}	1 ± 1^{c}	6 ± 1^{ab}	8 ± 1^{a}
NH_4-N (µg/L)	1 ± 1	2 ± 1	4 ± 1	3 ± 3
NH_4-N extract (µg/cm^3)	0.19 ± 0.05	0.19 ± 0.08	0.14 ± 0.02	0.23 ± 0.32
C:N Channel	451.1 ± 260.0^{a}	148.3 ± 26.0^{b}	73.9 ± 29.8^{b}	78.6 ± 15.0^{b}
C:N Interstitial	13.5 ± 3.8	17.37 ± 7.9	29.7 ± 7.8	4.7 ± 1.2

TABLE 2. Seasonal particulate C and N standing stocks (mean ± SE, g/m^2) and C:N ratios in Hugh White Creek, NC. Significant differences among seasons for each compartment (ANOVA, followed by Tukey's MCT $P < 0.05$) are denoted by different superscripts.

	Fall	Winter	Spring	Summer
Carbon				
FBOC	11.84 ± 2.54	20.73 ± 8.86	10.94 ± 6.20	7.20 ± 2.62
C leaves	54.83 ± 8.84^{a}	28.83 ± 1.90^{b}	10.42 ± 0.47^{b}	1.95 ± 0.58^{b}
C wood	15.89 ± 5.63	28.80 ± 12.67	18.94 ± 6.10	3.97 ± 1.46
Total Particulate C	82.75 ± 8.27^{a}	70.34 ± 18.95^{a}	50.62 ± 4.29^{ab}	16.26 ± 1.70^{b}
Nitrogen				
FBON	0.62 ± 0.14	1.09 ± 0.11	0.56 ± 0.31	0.40 ± 0.13
N leaves	1.03 ± 0.25^{a}	0.58 ± 0.17^{ab}	0.23 ± 0.01^{b}	0.05 ± 0.015^{b}
N wood	0.02 ± 0.16	0.24 ± 0.10	0.23 ± 0.07	0.04 ± 0.014
Total Particulate N	1.83 ± 0.37^{a}	1.71 ± 0.18^{a}	1.17 ± 0.29^{ab}	0.61 ± 0.12^{b}
C:N Ratio				
C:N FBOM	22.31 ± 6.40	22.17 ± 2.79	22.74 ± 13.54	20.84 ± 7.48
C:N Leaves	61.91 ± 17.35	57.84 ± 25.76	52.26 ± 11.65	50.15 ± 18.11
C:N Wood	96.67 ± 34.90	139.29 ± 78.65	94.41 ± 34.27	111.82 ± 44.89
C:N Particulate	52.84 ± 9.55	47.85 ± 10.07	50.54 ± 15.03	31.19 ± 6.13

TABLE 3. Rates of nitrification in this study compared to rates measured by others using the same method as reported in this study or a via a solute injection experiment (indicated by a **). N. A. = not available

Nitrification (mg N m^{-2} d^{-1})	Stream	Characteristics	Time of sampling	Reference
47.5	Hugh White Creek, NC	Appalachian headwater stream	August	*this study*
45	Juday Creek, IN	coolwater third order stream that flows through an area of mixed land use	Summer	Strauss and Lamberti 2000
14	Hugh White Creek, NC	Appalachian headwater stream	April	*this study*
77	Kings Creek, KS	upland prairie stream	April-May	Dodds et al. 2000
7**	Kings Creek, KS	upland prairie stream	April	Webster et al. 2003, Peterson et al. 2001
64.5	Sycamore Creek, AZ	intermittant desert stream	N.A.	Grimm et al. 1991
3**	Sycamore Creek, AZ	intermittant desert stream	May	Webster et al. 2003, Peterson et al. 2001
6**	Walker Branch, TN	Appalachian first order stream	April	Webster et al. 2003, Peterson et al. 2001
9.5	Hugh White Creek, NC	Appalachian headwater stream	January	*this study*
25.5	Hugh White Creek, NC	Appalachian headwater stream	November	*this study*
9**	Ball Creek, NC	Appalachian second order stream	November	Webster et al. 2003

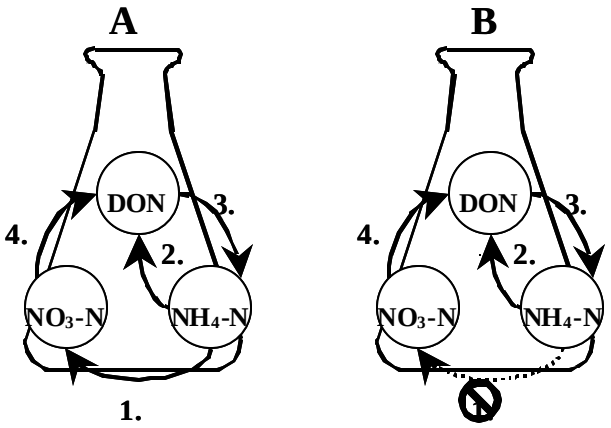

Figure 1. Nitrogen transformations in reference microcosms (A), and in microcosms in which nitrification has been blocked (B). 1: Nitrification, 2: NH_4-N Immobilization, 3: NH_4-N Ammonification, 4: NO_3-N Assimilation. Comparison of reference and blocked microcosms provide measures of gross nitrification rates (Hall 1984, Strauss and Lamberti 2000).

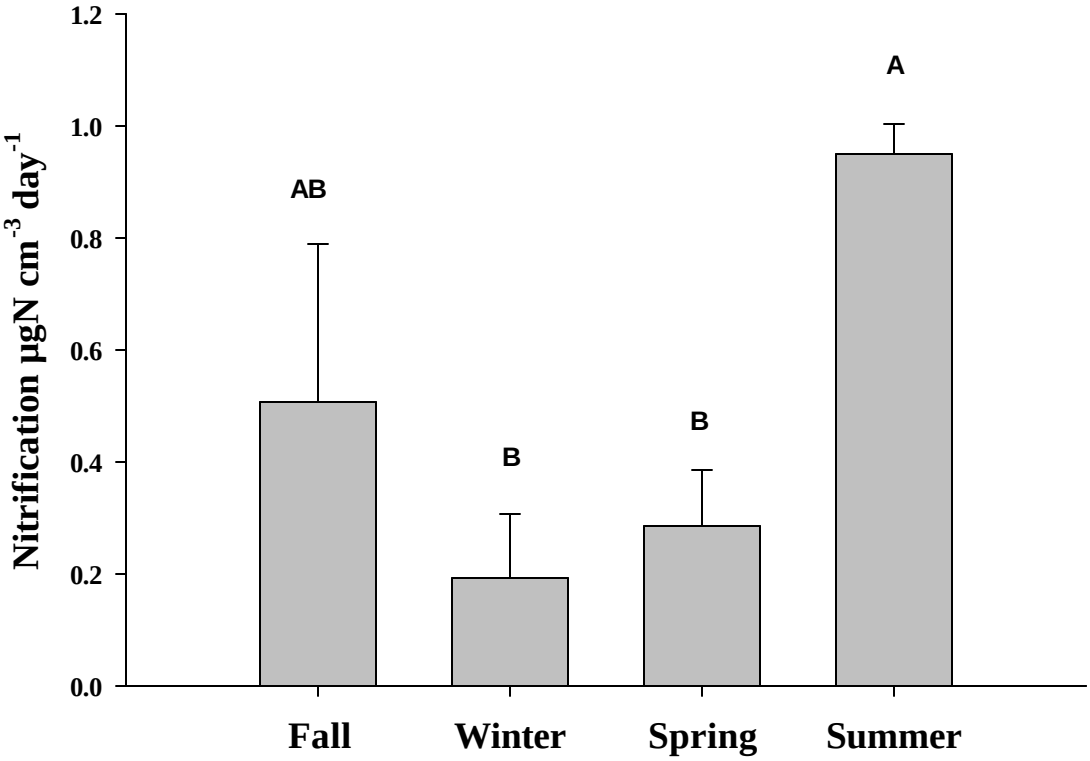

Figure 2. Seasonal variation in nitrification rates (mean ± 1SE) in Hugh White Creek Significant differences in seasonal rates (ANOVA, Tukey's MCT $P < 0.05$) are denoted by different superscripts.

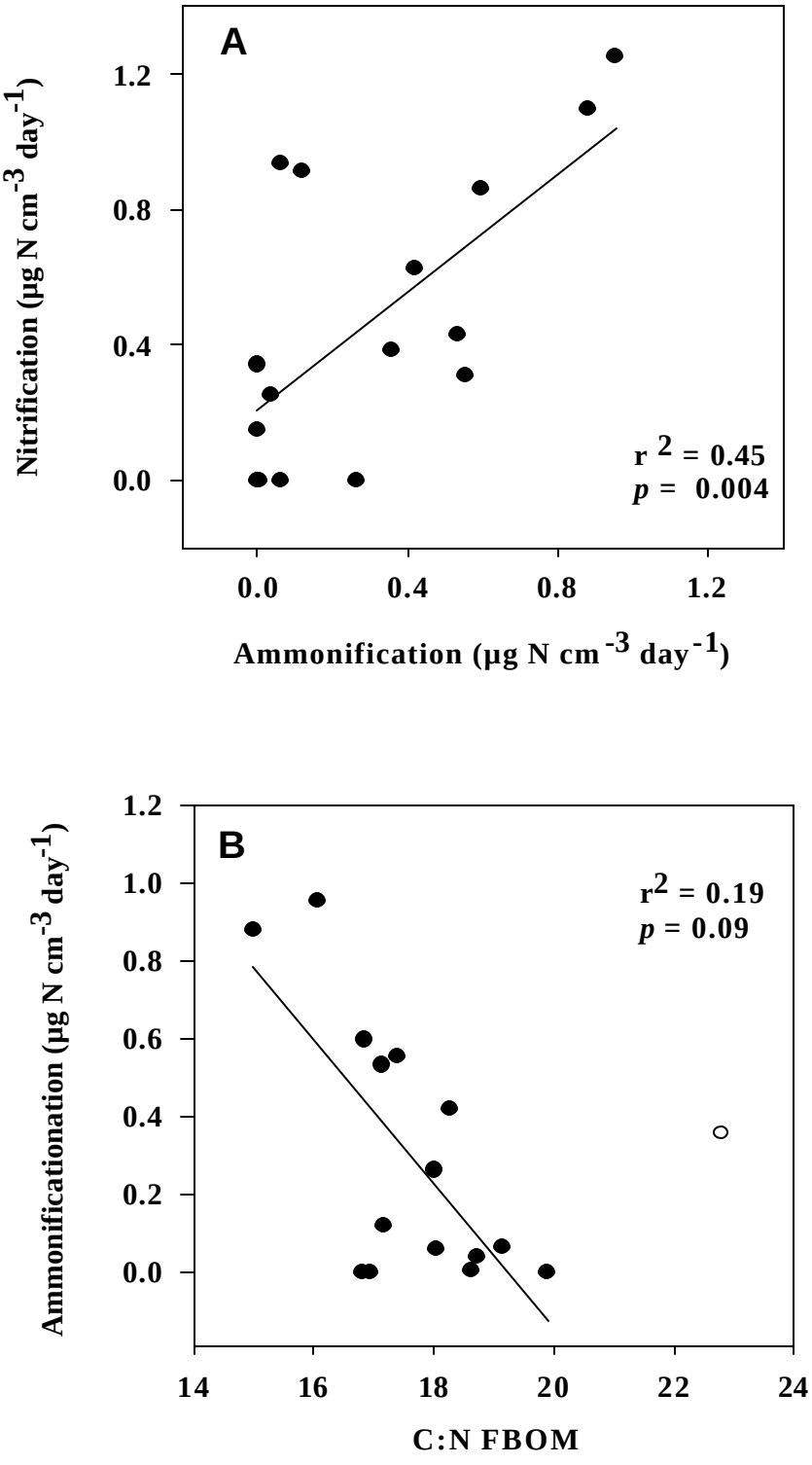

Figure 3. Linear relationships between rates of ammonification and nitrification (A) and C:N FBOM (B) in control, i.e., unamended microcosms. An outlier is indicated by the open circle.

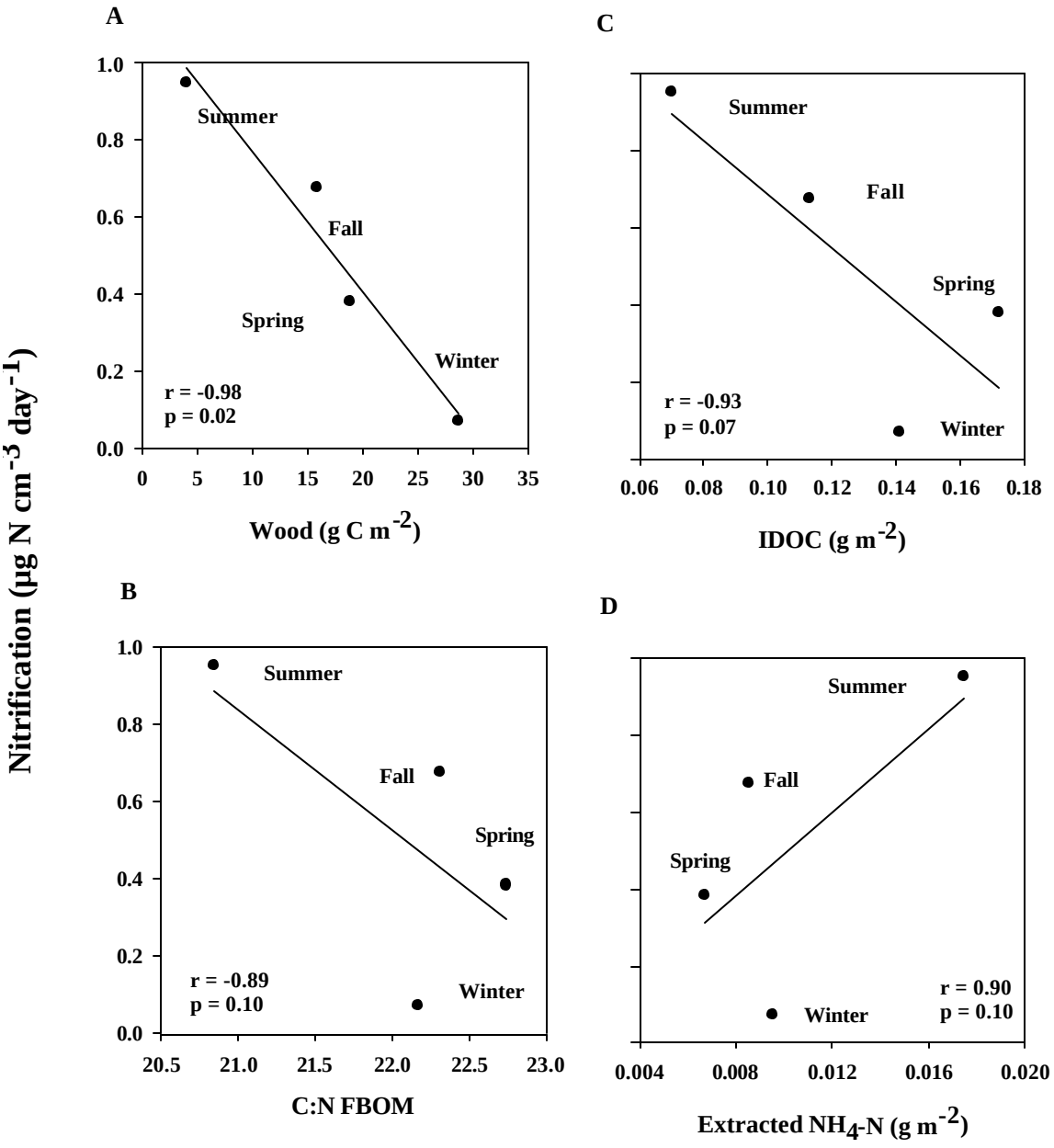

Figure 4. Correlations between average seasonal rates of nitrification and average field conditions. (A) Wood standing stock (B) C:N FBOM (C) Interstitial DOC (D) Extracted NH_4-N

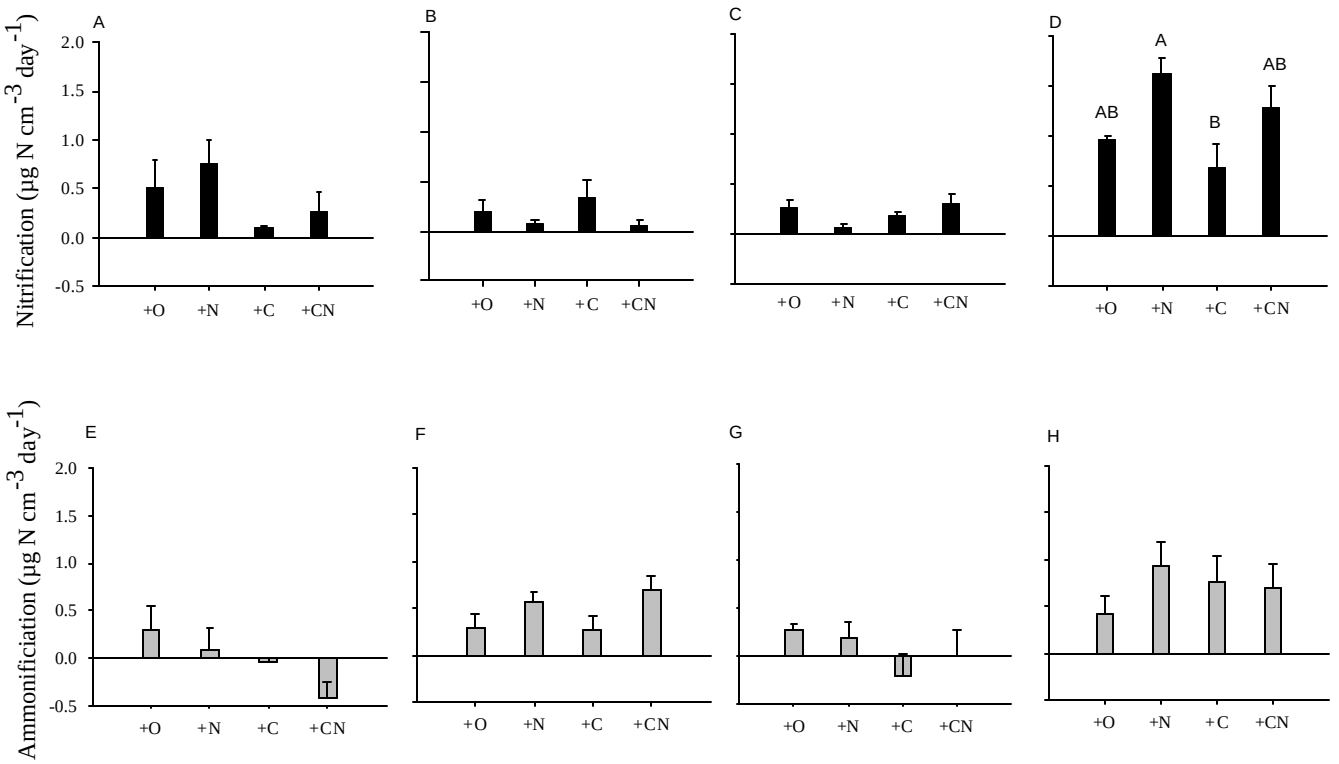

Figure 5. Effect of nutrient amendments on rates of nitrification (black bars) and ammonification (gray bars) in Hugh White Creek in Fall (A,E), Winter (B, F), Spring (C,G), and Summer (D, H). Data are means + SE (n = 4). Significant differences within seasons for each treatment (ANOVA, Tukey's MCT $P < 0.05$) are denoted by different superscripts.

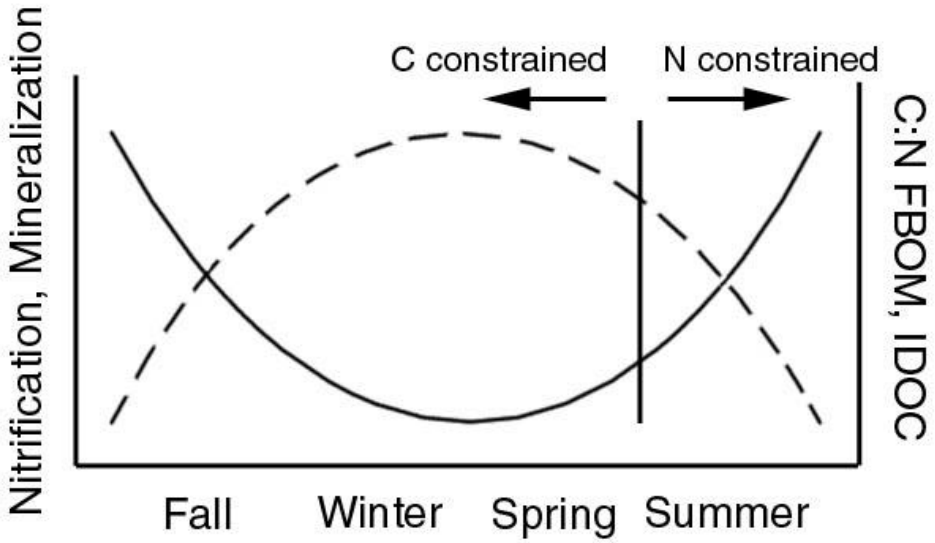

Figure 6. Conceptual model of how the influence of particulate and interstitial C and N on nitrification rates may vary seasonally in forested headwater streams. As organic matter stocks of C and N are depleted and undergo annual changes in quality, rates of nitrification and mineralization (solid curve) are influenced by not only channel N and C, but other measures of C and N availability such as C:N FBOM and IDOC, indicated by the dotted curve. The vertical line represents a point at which C:N ratios reach the critical value above which increased particulate and interstitial C availability constrains rates of nitrification and below which this constraint is minimized and dissolved C and (especially) N additions are more likely to stimulate nitrification.

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CURRENT POSITION: doctoral candidate enrolled in the stream ecology program, Virginia Polytechnic and State University, Blacksburg, VA since Fall/2000

ACADEMIC PREPARATION:

American University Washington, DC	M.S. Environmental Science	2000
Institute for Limnological Studies 1999Mondsee, Austria	Fulbright Scholar	1998-
University of Salzburg Salzburg, Austria	Guest student	1998-1999
Rocky Mountain Biological Laboratory, Gothic, Colorado	Research Assistant/Student	1998
American University	B.A. Environmental Studies	1998

PROFESSIONAL SOCIETY/RESEARCH AFFILIATIONS:

Member, North American Benthological Society, since 2000
Virginia Tech Biology Graduate Student Association (BGSA), since 2000

INTERNSHIPS/RELEVANT WORK EXPERIENCE:

Research Assistant, Virginia Tech Stream Ecology Program, part-time, Spring 2004.

Staff Assistant, American Institute for Pollution Prevention (Washington, DC) 1997-1998.

Intern, World Wildlife Fund (Vienna, Austria) 1996.

Engineering and Scientific Intern, PA Department of Environmental Protection (Harrisburg, PA)1995.

TEACHING CERTIFICATION:

Certificate of training to administer the Virginia Department of Environmental Quality's Project Wet and Wild programs by the Virginia Tech Museum and the Virginia Department of Game and Inland Fisheries: April 17, 2003.

TEACHING EXPERIENCE:

Teaching Assistant, Plant Anatomy Lab, Virginia Polytechnic and State University, Spring 2004. Assisted in lab preparation and provided feedback on written assignments.

Teaching Assistant, Freshwater Ecology Lab, Virginia Polytechnic and State University, Fall 2003. Guided one section of senior level students in project design demonstrated appropriate research tools

Teaching Assistant, Field and Lab Ecology, Virginia Polytechnic and State University, Spring 2002. Assisted course instructor in preparation of weekly course outings and activities; ordered supplies; transported students in a university vehicle

Teaching Assistant, General Biology Lab, Virginia Polytechnic and State University, 2000-2003. Instructed three sections of 25 students in hands-on activities accompanying the general biology lecture

Teaching Assistant, English as a foreign language, Wirtschaftkuendliches Bundesrealgymnasium, Salzburg, 1998-1999. Organized lessons and led several classes at different experience levels twenty hours a week

Educational Aide, Smithsonian National Museum of American History's Hands On Science Center, 1995-1995. Instructed museum visitors; assisted in exhibit preparation

COMMUNITY SERVICE:

Member, Board of Directors, Friends of the Brown Farm, since 2001
Community Service Chair, BGSA, since 2001
Member, Sierra Club since 1995

ABSTRACTS, POSTERS, AND PRESENTATIONS:

Presentation:
O. Starry and H. M. Valett. Nitrification rates associated with C and N availability in a

southern Appalchian headwater stream. 2003. North American Benthological Society Meeting. Athens, GA. Bulletin of the North American Benthological Society Vol 20:1.

Posters:

O. Starry and H. M. Valett. Nitrification rates in headwater stream substrates with varying litter inputs and low stream water ammonium concentrations. 2002. North American Benthological Society Meeting. Pittsburgh, PA. Bulletin of the North American Benthological Society Vol 19:1.

M. Schreiber, H. Valett, J. Lare, M. Fuller, L. Chiehowsky, S. Thomas, and O. Starry Arsenic cycling in the hyporheic zone of a headwater stream. 2001. Society of Environmental Toxicology and Chemistry Meeting.

PUBLICATIONS:

B. Mindl, C. Griebler, N. Wirth and O. Starry, 1999. Biodegradability of DOC and metabolic response of heterotropic bacteria in groundwater. Verh. Internat. Verein. Limnol.: 27:1-7.

Starry, Olyssa, Josef Waenzenboeck , and Dan Danielopol, 1998. Tendency of the amphipod Gammarus roeseli GERVAIS to colonize coarse sediment habitats under fish predation pressure. Internat. Rev. Hydrobiol.:371- 380.

GRANTS/AWARDS:

Graduate Research Development Project, Graduate Student Assembly, Fall 2003, Virginia Polytechnic Institute and State University, $250 awarded for project entitled, "An approach to estimating nitrification rates in streams and identifying associated control variables."

Award in Support of Graduate Research and Professional Development in Mathematical, Natural and Physical Sciences. 2002-2003, Virginia Tech College of Arts and Sciences Cultural Diversity Committee, $2000 for project entitled, "An approach to estimating nitrification rates in streams and identifying associated control variables."

Graduate Research Development Project, Graduate Student Assembly, Fall 2001, Virginia Polytechnic Institute and State University, $500 awarded for project entitled, "An approach to estimating nitrification rates in streams and identifying associated control variables."

Departmental matching funds for all of the above, except for the $2000 award for which the match was $500

Travel fund award. Jan.-June 2003, Virginia Tech Graduate Student Association, $200 for travel to 2003 North American Benthological Society meeting.