ABSTRACT

Title of Document: ORGANIC NITROGEN AND CARBON TRANSFORMATIONS IN A STREAM NETWORK OF CHESAPEAKE BAY WATERSHED

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Increased export of anthropogenically-derived nitrogen in streams has contributed to increased water quality problems. I investigated in-stream transformations of nitrogen and carbon at the benthic habitat and reach network scale. Both indicated large transformations of dissolved organic nitrogen (DON) and dissolved organic carbon (DOC) along the Gwynns Falls urban stream network. In-stream transformation of DON and DOC declined from headwaters to outflow, with a mean 23% removal of DOC and 57% removal of DON. Transformation rates ranged from in-stream internal loading of 28 g/m^2/day to in-stream removal of 740 g/m^2/day for DOC (mean: uptake 64 g/m^2/day) and in-stream internal loading of 4.8 g/m^2/day to in-stream removal of 74 g/m^2/day for DON (mean: uptake 3.5 g/m^2/day). Urban

stream networks may act as both “transporters” and “transformers” of nitrogen and knowledge regarding in-stream N transformations is critical in predicting the sources and removal of nitrogen en route to adjacent tidal waters.

ORGANIC NITROGEN AND CARBON TRANSFORMATIONS IN A STREAM NETWORK OF CHESAPEAKE BAY WATERSHED

By

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Preface

The content of my Master's research is contained in Chapter One in manuscript format. Additional tables and figures relevant to the research have been included in the appendix.

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INTRODUCTION

Human alteration of the global nitrogen cycle has contributed to increased coastal eutrophication, harmful algal blooms and alterations in aquatic food webs (Seitzinger and Sanders 1997, Vitousek et al. 1997, Kemp et al. 2005). Watershed nitrogen loads have dramatically increased due to atmospheric deposition, land-use change, and wastewater inputs (Galloway et al. 2003). Export of nitrogen contained in organic matter is considered to be an important component of the global nitrogen (N) and carbon (C) cycles in running waters (Perakis and Hedin 2002, Lewis et al. 1999, Hedges et al. 2002, Cole et al. 2006). Although more work has focused on inorganic N, it is becoming increasingly recognized that organic nitrogen can also influence ecosystem dynamics and water quality in forested, agricultural and urban streams (e.g. Seitzinger and Sanders 1997, Kaushal and Lewis 2005, Scott et al. 2007, Petrone et al. 2008, Weigner et al. 2009). Yet, the in-stream transformation of organic N and C in urban and suburban streams is less well-known, compared with measurements of watershed organic N and C exports (e.g. Baker et al. 2001, Groffman et al. 2004, Wollheim et al. 2005, Kaushal et al. 2005). In particular, it is crucial to understand how different watershed land-uses will alter transformations of organic N and C in stream networks in order to identify potential effects on water quality and eutrophication (e.g. Stepanauskas et al. 2005, Stedmon et al. 2006, Petrone et al. 2008, Wiegner et al, 2009). Urbanization may alter the capacity of streams and rivers to transport and transform nitrogen and carbon (e.g. Grimm et al. 2008, Kaushal et al. 2008, Wollheim et al. 2008, Klocker et al. in press).

Quantification and elucidation of factors contributing to in-stream transformations in urban watersheds are critical to developing improved watershed restoration strategies and in predicting delivery of nitrogen from human-dominated landscapes to receiving waters (Roberts and Mulholland 2007, Kaushal et al. 2008). Here, we investigate how urban land-use may alter the fluxes and in-stream transformation of nitrogen and carbon in a stream network in the Chesapeake Bay watershed.

Organic N and C in streams can originate from a variety of diffuse sources including atmospheric deposition, runoff from terrestrial systems, and in-stream sources (e.g. Hedin et al. 1995, Vanderbilt et al. 2003). Atmospheric deposition may be a significant source of organic N to some watersheds and can come from both natural and anthropogenic sources (Peierls and Paerl 1997, Neff et al. 2002). Terrestrial sources of organic N and C from runoff may vary with soil and vegetation type, topography, and soil-stream interactions (Hedin et al. 1998, Kaushal and Lewis 2003, Lajtha et al. 2005). In-stream sources may consist primarily of autotrophic algal growth and exudation, heterotrophic activity by microbial communities, and grazing by meiofauna and macroinvertebrates (Kaplan and Bott 1989, Berman and Bronk 2003). Organic N and C are also abundant in polluted surface waters and may originate from sewage leaks, storm water runoff and oils and hydrocarbons derived from impervious surfaces in the watershed (Pehlivanoglu and Sedlak 2004, Pellerin et al. 2004).

Land-use change has greatly altered the amounts and sources of organic N and C exported from watersheds to aquatic systems (Kaushal and Binford 1999, Boyer et al. 2002, Saenger et al. 2008, Wilson et al. 2009). While changes in the absolute amount of organic N and C may be expected to vary due to land-use change, our understanding of changes in the sources, cycling and bioavailability of organic matter are not well characterized (Pellerin et al. 2004). These include transformation of organic N and C via mineralization to inorganic forms, direct uptake, and mechanisms influencing in-stream generation of organic N and C within stream and river networks (Caraco and Cole 2003).

Transformations may be likely; given bioavailability of dissolved organic nitrogen (DON) may be substantial in a wide array of aquatic ecosystems (e.g. Seitzinger and Sanders 1997, Seitzinger et al. 2002a, Pellerin et al. 2006, Bronk et al. 2007, Petrone et al. 2008). In forests, 2 to 71% of DON may be bioavailable (Stepanauskas and Leonardson 1999, Seitzinger et al. 2002a Kaushal and Lewis 2005). Similarly, research has shown that the percentage of bioavailable DON can vary from 48 to 60% in urban watersheds and 8 to 72% in agricultural watersheds (Seitzinger et al. 2002a, Stepanauskas et al. 2002, Weigner et al. 2006). This suggests that DON contained in runoff from agricultural, suburban, and urban landscapes may contribute to bioavailable nitrogen loading to receiving waters further downstream.

The 3 major objectives of the current study were to: (1) investigate the effects of land-use on patterns in concentrations of organic N and C seasonally and spatially in stream networks, (2) quantify organic N and C transformations and removal in an urban stream network using a mass balance approach, and (3) explore in-stream N and C transformations (leaf litter debris, rocks, and sediments) at a benthic habitat scale using laboratory incubations. Our overall hypothesis was that urban streams are both active “transformers” and “transporters” of organic N and C leading to seasonal changes in the export of bioavailable N and C downstream to Chesapeake Bay.

METHODS

Long-term data on major N chemical fractions has been collected at the Baltimore Ecosystem Study (BES) Long-term Ecological Research (LTER) site for over a decade. In conjunction with this monitoring, we conducted intensive mass balance and laboratory studies of transformations in stream networks of the BES LTER site from March 2008 to February 2009. The major study components were: (1) seasonal synoptic sampling of 60 sites across the stream network to characterize changes in N and C concentrations, forms, and fluxes across forested and urban stream networks, (2) reach-scale mass balance estimates with 26 sampling sites in forested and urban stream networks to examine reach-scale variations in removal and transformation of N and C, and (3) reach-scale habitat mapping and seasonal laboratory bioassays with 3 different benthic substrates to identify locations of N and C transformations in streams.

Study Sites

Stream networks used for this study are sampled routinely as part of the BES LTER site located in Baltimore, Maryland (Table 1, Groffman et al. 2004, Kaushal et al. 2008). The Baltimore metropolitan watersheds drain into the Chesapeake Bay and are a rapidly developing region of the northeastern United States (Jantz et al. 2005). The focal study watershed is the Gwynns Falls with a stream network 36.5 km in length. The Gwynns Falls (76°30', 39°15') is comprised of a 17,150 hectare watershed in the Piedmont physiographic province, which drains into the northwest branch of the Patapsco River, which then flows into the Chesapeake Bay (Figure 1). The headwaters of the Gwynns Falls begin in Baltimore County, which is primarily a rapidly developing suburban and residential area, and then flows along a land-use gradient into a high-density urban area of Baltimore City. Much previous information has been published on long-term nutrient concentrations and hydrologic fluxes at the BES LTER sites (e.g. Groffman et al. 2004, Kaushal et al. 2008, Shields et al. 2008).

The two reference sites were smaller (30 and 400 hectare) streams located in the Gunpowder River watershed, which is also located in the Piedmont physiographic province and drain into Baltimore's drinking water supply. This headwater stream network consisted of a minimally-disturbed first order stream flowing into a low-density residential second order stream. Pond Branch (POBR) is a first order, forested reference stream with 100% forest watershed land cover. Baisman Run (BARN) is downstream of POBR and is a second order stream in a low-density residential area (Table 1, Figure 1).

Seasonal Synoptic Sampling

Sixty synoptic locations were sampled across the Gwynns Falls stream network (suburban and urban), and the POBR-BARN headwater stream network (forested and low-density residential) each season (March, July, October 2008, and January 2009) to investigate seasonal and longitudinal variations in N and C concentration and fluxes during base flow. The length of the stream network in the Gwynns Falls was 36.5 kilometers with 30 tributaries of various sizes. The length of the much smaller POBR-BARN headwater stream network was 1.3 km where 8 locations were sampled. Our synoptic sampling scheme included baseflow discharge measurements and grab sample collection to measure nutrient concentrations. Suburban and urban study reaches of the Gwynns Falls were co-located across 4 main stem sampling sites (GFGL, GFGB, GFVN, GFCP) that are monitored as part of the BES LTER project. Real-time discharge data were available at 9 gauging stations along the Gwynns Falls stream network and smaller POBR-BARN stream network (courtesy of C.A. Welty and USGS). Specific sampling locations of the 52 synoptic sites for the Gwynns Falls were chosen based on tributary junctions and positioning of BES LTER and USGS gauging monitoring stations. Water samples were also collected at each tributary and 100 m downstream (to ensure the sample was well-mixed) of each tributary along the main stem of the Gwynns Falls. Study reaches in the POBR-BARN headwater stream network were co-located at the POBR and BARN USGS gauging stations. Coordinates for seasonal synoptic sites were recorded using a handheld GPS system.

Reach Scale Mass Balance

Routine sampling for mass balance estimates of the Gwynns Falls stream network was conducted during times of base flow from March 2008 to February 2009 at 26 sampling locations, and at a frequency of bi-weekly or monthly depending on season (Burns et al. 1998, Sjodin et al. 1997). Routine sampling at 6 locations was conducted for mass balance in the POBR-BARN headwater stream network. Study reaches in the Gwynns Falls were determined by the location of established BES LTER staff gauges, major tributaries, and information from synoptic sampling. Major tributaries were defined as any tributary contributing 5% or more of the stream flow at that point along the stream channel. Tributary and main stem samples were collected using the same sampling scheme as the seasonal synoptic sampling. Mass balance study reaches in POBR-BARN were determined by the location of established BES LTER staff gauges and information from synoptic sampling.

Mass Balance Calculations

Mass balance calculations were used to determine net transformation rates (either removal or generation) of major nitrogen and carbon fractions per unit area of stream, in reaches from 720m to 5680m in length. Calculations were based on methods by Burns et al. 1998. Transformation rates ($mg/m^2/day$) were calculated for total nitrogen (TN), total dissolved nitrogen (TDN), nitrate, ammonium, and DON, as well as total organic carbon (TOC) and dissolved organic carbon (DOC), using equation (1):

(1) $M_D - (M_U + M_T + M_S + M_M) = \Delta M$,

Where

M_D = mg/day at downstream end of reach
M_U = mg/day at upstream end of reach
M_T = mg/day of major tributaries
M_S = mg/day of seepage
M_M = mg/day of minor tributaries
ΔM = net transformation of constituent (mg/day)

ΔM was then divided by the surface area of each reach to determine the net transformation rate (removal or generation) per unit area. A negative ΔM indicated net removal of the constituent, whereas a positive ΔM indicated net generation of the constituent. Percent removal of each reach was calculated using equation 2 ((inputs – outputs)/inputs) for 11 reaches in the Gwynns Falls and 4 reaches in the POBR-BARN headwater stream network.

(2) $((M_U + M_T + M_S + M_M) - M_D) / (M_U + M_T + M_S + M_M)$

M_S was estimated using a flow measurement attained from a water budget of each stream and water chemistry data from 64 samples from groundwater wells distributed throughout the Gwynns Falls and 38 samples throughout the combined POBR-BARN stream network. The discharge of M_S was estimated by subtraction using a water budget including all other components of the mass balance (equation 3):

(3) $F_D - (F_U + F_T + F_M) = F_S$

Where

F_D = L/day at downstream end of reach
F_U = L/day at upstream end of reach
F_T = L/day of major tributaries
F_M = L/day of minor tributaries
F_S = L/day of seepage

Since groundwater data was not collected in conjunction with each mass balance sampling, groundwater concentration was estimated using the mean concentration over the entire year and across the entire stream network. Groundwater contributions were characterized for 11 subreaches of the entire stream network using equation 3 for each sampling date. For each sampling date, the flux of M_S was then estimated for all of the subreaches and treated as distributed flow for the mass balance calculations, weighted for each stream subreach based on the length of the subreach.

M_M was determined using discharge and water chemistry data from extensive synoptic seasonal sampling in which minor tributaries (<5% of the stream flow) were sampled in addition to the routine sampling scheme that included major stream tributaries (> 5%). Both internal storage and atmospheric exchange were assumed to be in steady state for each stream reach.

Substrate Incubation Experiments

In laboratory incubations, nitrogen (TDN, nitrate, ammonium), DOC and dissolved oxygen (DO) concentrations were measured in incubation jars containing unfiltered stream water and different substrate types: sediment (cylindrical core 7.6 cm deep, 5.1 cm diameter), rock (various sizes), debris (primarily leaf litter) and unfiltered stream water only (control). These substrates were collected from streams draining 4 different land-use categories: urban, suburban, residential and forest.

Incubation jars were kept in an environmental control chamber at 20° Celsius, with a diurnal light cycle of 12 hours light and 12 hours dark. Light was represented by full spectrum light bulbs to mimic natural light. The experiments were conducted each season in conjunction with the seasonal synoptic sampling in August, October, January and April of 2008-2009.

Water samples (60 mL) were collected at 0, 6, 12, 24, and 72 hour increments using a syringe (for minimal disturbance). DO was measured using a WTW Oxi 1970i DO meter. This also gently stirred the sample with the stir rod attached to the DO probe so the water was not completely stagnant.

Analytical Methods

All samples were filtered through 0.45 micron glass fiber filters within 24 hours of collection and then frozen until analysis. Nitrate and ammonium were analyzed using an enzyme catalyzed reduction method on an Aquakem (Nutrient Analytical Services, Chesapeake Biological Laboratory). Analyses showed that almost all nitrate/nitrite on sampling dates was comprised of nitrate, and we will refer to this fraction as nitrate throughout. TDN and DOC concentrations were measured using a Shimadzu Total Organic Carbon Analyzer (TOC-V CPH/CPN). DON was calculated by subtraction: TDN – (nitrate + ammonium). Particulate C and particulate N were analyzed by combustion of glass-fiber filters after filtration of a known volume of water using a Costech Elemental Analyzer.

Statistical Analyses

Differences in concentrations of major C and N fractions across varying land-uses were tested using Dunnett's Post-Hoc test for ANOVA in SAS (SAS Institute Inc., Cary, NC, USA). Differences in stream concentration for the incubation experiment were also tested using a Dunnett's ANOVA test. Relationships between DOC and nitrate were tested using Spearman's correlation with $\alpha = 0.05$. The data were separated by season because a significant difference in the correlation coefficients of the different seasons was observed. All subsequent analyses were separated by season; the data set from each month was included for each season. Relationships between transformation rates, removal values, C:N ratios, and geomorphic controls were all tested using correlation (rather than linear regression) because a clear cause and effect relationship was not known. Spearman's correlation was used because assumptions of normality were not met.

RESULTS

Temporal and longitudinal patterns in stream water chemistry

In 2008-2009, temporal patterns of TN, TDN, DON, TOC, and DOC concentrations in the Gwynns Falls varied with each constituent (Appendix B). DON was the most variable, with no consistent seasonal or land-use patterns. TOC and DOC had two distinctive peaks in concentration in summer and early winter. TN and

TDN were less variable at each site, but the highest concentrations were observed in late summer and winter. DOC displayed the greatest range in concentration, ranging from 0.55 to 6.43 mg/L across all sites. POBR (forested reference site) had lower and less variable TN (0.06 to 0.86 mg/L) and TDN concentrations (0.06 to 0.38 mg/L) than sites with anthropogenic inputs (GFCP, GFVN, GFGB, GFGL, BARN) (TN: 0.42 to 4.72 mg/L, TDN: 0.33 to 2.59 mg/L, $p<0.05$). This trend was not observed for DON, TOC, or DOC, where the concentrations at the forested site fell within the range of concentrations of sites with anthropogenic disturbance.

During 2008-2009, organic nitrogen (particulate and dissolved) varied greatly in the Gwynns Falls, comprising 0 to 70% of TN concentration, with a mean value of 16.5% across sampling dates. Of the total organic nitrogen, approximately 58.6% was DON and 41.4% was particulate organic nitrogen (PON), with the highest mean proportion of PON in the fall (60.1%) across sampling dates and the highest mean proportion of DON in the summer (75.8%) across sampling dates. Concentrations of total organic N in BARN ranged from 0 to 86.0% of the TN concentration, with a mean value of 7.8% across sampling dates. Of the total organic nitrogen in BARN, approximately 60.2% was DON and 39.8% was PON. In POBR, organic nitrogen ranged from 44.5 to 98.6% of the TN concentration, with a mean value of 72.8% across sampling dates. Of the total organic nitrogen in POBR, approximately 47.9% was DON and 52.1% was PON.

The C:N ratios of concentration (mol/L) in the Gwynns Falls ranges from 0.15:1 to 8.08:1 (mean ± S.E. 2.19:1 ± 0.12). The C:N ratios increased moving downstream, with a mean of 1.81:1 at the headwaters and a mean of 2.95:1 at the outflow. The summer and fall had the highest C:N ratios at the outflow, which was 3.77:1. The C:N ratios were higher in the forested reference stream ($p=0.05$), Pond Branch, which ranged from 5.90 to 29.28 (mean ± S.E. 12.33:1 ± 1.06).

Estimates of groundwater concentrations surprisingly showed that DON was the dominant form of nitrogen input into the Gwynns Falls via ground water (90.6% of TDN). For BARN also, DON comprised 86.1% of groundwater inputs, while in POBR, DON was also elevated at 83.6%. Groundwater measurements were taken less frequently than the surface water sampling and therefore, the mean of groundwater concentration over the entire year was used in this mass balance of the Gwynns Falls and the POBR-BARN stream network. This means the same mean concentration was used for each mass balance throughout the year, in each of the 4 stream reaches of POBR-BARN and in each of the 11 reaches of the Gwynns Falls. Because the mean yearly groundwater concentration was used, this could be contributing to some uncertainty in the mass balance calculations.

There was a strong inverse relationship longitudinally from the headwaters to the outflow of the Gwynns Falls between DOC and nitrate concentrations during each season (Figure 2). Consistent spatial patterns were observed: high nitrate in the headwaters, but then decreased downstream, and low DOC concentrations in the headwaters while increasing farther downstream. No inverse relationship was observed between nitrate and DOC in the reference forested (POBR) and low-residential (BARN) stream reaches, however.

Reach-scale mass balance

The mass balance of the Gwynns Falls stream network displayed a substantial amount of C and N transformations (Figure 3). The rates were highly variable but DON had transformation rates of removal throughout the Gwynns Falls, except in winter where DON was generated by in-stream internal loading. There was net removal of DON along most of the suburban and urban reaches, except for the small reach near the outflow of the stream network, which generated N in the fall and winter (Figure 4, Appendix C). In the winter, nitrogen displayed transformation rates higher than other seasons by approximately one order of magnitude and was more variable longitudinally. Both the concentration and flow of the Gwynns Falls was higher in the winter, leading to these increased transformation rates. Across all seasons, transformation rates of nitrate and DON showed an inverse pattern longitudinally along the stream network, particularly at the headwaters of the stream (Figure 6). Ammonium was present in the stream but the transformation rates were at least 2 orders of magnitude lower than the other nitrogen fractions and are lower than the margin of error and are not included in this analysis.

There was an overall pattern of decreasing N removal in reaches from headwaters to the outflow of the Gwynns Falls (Appendix C). For example, removal of nitrogen ranged from 0 to 52% of TN and 0 to 100% of DON, with higher values at the headwaters and lower values farther downstream (in some months, a net generation was observed at the outflow of the Gwynns Falls) (Figure 4). Total organic nitrogen removal at the reach scale was high but quite variable, ranging from 0 to 100% (average of 15%). DON removal at the reach scale ranged from 70 to 100% in the headwaters and 0 to 82% farther downstream. Surprisingly, nitrate showed a very different pattern, with little or no net removal throughout the Gwynns Falls stream network, and a high level of in-stream internal loading at the headwaters (Figure 7).

TOC was also transformed throughout the Gwynns Falls, with net removal in the upper reaches, but the transformation rates of TOC and DOC were more variable than nitrogen and a high rate of generation was observed at the outflow of the Gwynns Falls each season (Figure 3, Appendix C). Both TOC and DOC had high removal in the headwaters (TOC: 58 to 71%, DOC: 60 to 80%) and lower removal toward the outflow of the stream network (-20 to 41%) (Figure 4, Appendix C). TOC and DOC also displayed very high and variable transformation rates in the winter, similar to DON.

The net transformation rate for the reference low-density residential BARN reach was similar to the Gwynns Falls. However, the forest POBR reach generally had smaller transformation rates for TN and DON (Figure 5, Appendix D). The inverse pattern of nitrate and DON was not observed in POBR or BARN. While the Gwynns Falls displayed the highest transformation rates in the winter, the highest transformation rates in BARN and POBR were observed in the fall for DON and DOC. Percent removal of BARN was variable, ranging from -28.3 to 81.9% for DON, with an average of 27%. DOC removal also ranged from -28.3 to 81.9%, with an average of 9.3% (Appendix D). The removal of TN, TDN, TOC and DOC was higher in summer and fall and lower in spring and winter in BARN. DON exhibited no consistent longitudinal pattern across seasons. Unlike the Gwynns Falls, BARN exhibited higher removal of nitrate and a lower removal of DON. Percent removal of

TN in POBR ranged from 29.1 to 79.9%, and removal of DON ranged from 59.7 to 68.8%. While DON was retained throughout the reach (33 to 69%), a net export of nitrate was observed in POBR during the summer and winter.

Regardless of the form of nitrogen, transformation rates at the reach scale were strongly linked to carbon removal and transformation in the Gwynns Falls. There were strong, positive, linear correlations between TOC and TN during all seasons (spring: R=0.55, summer: R=0.52, fall: 0.83, winter: R=0.63) Also, between DOC transformation and TDN transformation rates, all seasons except winter were shown to have significant relationships (spring: R=0.96, summer: R=0.49, fall: R=0.57) and between transformation rates of DOC and TN (spring: R=0.95, summer: R=0.49, fall: R=0.76). Similarly, a significant correlation was found between DON and DOC transformation rates (spring: R=0.75, fall: R=0.42, winter: R=0.58) and total organic N and DOC transformation rates (spring: R=0.85, fall: R=0.72, winter: R=0.63). Nitrate followed the same correlation with DOC with regard to transformation rates (spring: R=0.76, summer: R=0.51, winter: R=0.64).

The C:N ratios of transformation rates (mol/m^2/day) in the Gwynns Falls ranges from 0.06:1 to 1369.4:1 (mean ± S.E. 9.60:1 ± 9.20). The C:N ratios increased moving downstream, with a mean of 2.91:1 at the headwaters and a mean of 10.06:1 at the outflow. The C:N ratios of the forested reference stream, Pond Branch, also varied greatly, ranging from 0.18:1 to 75.33:1 (mean ± S.E. 7.15 ± 6.88).

Substrate Incubation Experiments

The substrate consistently exhibiting the most activity was the leaf litter debris incubations, which showed the most change in terms of both total N loss and conversion between the different N fractions (nitrate, ammonium, and DON) in the Gwynns Falls (Figure 8, Appendix E). Nitrate concentration decreased over time in many of the incubation jars and DOC concentration increased in nearly all of the incubation jars. The C:N ratios of dissolved species in water overlying the leaf litter debris showed an increasing pattern, starting out with a sharp increase and then leveling off after 24 hours, ranging from 0.71:1 to 162.5 (mean 30.5:1). Other substrates (rock and sediment) showed no significant patterns.

DISCUSSION

Gwynns Falls urban stream network: a transporter and *transformer of nitrogen*

We found evidence linking land-use to elevated concentrations of nitrogen. This finding confirms many previous studies linking urbanization and human activity to nitrogen loading (Boyer et al. 2002, Groffman et al. 2004, Stanley and Maxted 2008, Kaushal et al. 2008). While nitrate was the dominant form of N in the Gwynns Falls, total organic nitrogen made up a sizable portion of the total N fraction (across all sampling dates; total organic N comprised 27.9% of the N in the outflow of the stream network (GFCP), which is 10% higher than total organic N in the headwaters (GFGL)). This is consistent with previous work quantifying DON concentrations and loads in urban streams (Pellerin et al. 2006, Scott et al. 2007, Kaushal et al. 2008).

Relatively high removal of nitrogen and carbon at the reach scale was observed in the Gwynns Falls and POBR-BARN headwater stream networks, regardless of size and land-use. In the headwaters of the Gwynns Falls, a substantial proportion of the total amount of DON and DOC entering the stream (92.2 to 100% of DON and 60.4 to 80.4% of DOC) was removed from the surface waters. While previous literature in natural systems shows lower transformation rates, the transformation rates of N in this study are consistent with uptake rates found in other studies examining urban streams (Bernot and Dodds 2005, Grimm et al. 2005, Roberts and Mulholland 2007, Mulholland et al. 2008). For example, Grimm et al. 2005 found that in urban streams in the southwest United States, uptake rates of N ranged from 32.8 – 106,358.4 $mg/m^2/day$. Transformation rates of C were also similar to previous studies, such as McDowell and Likens 1988, that found the mean flux of DOC to be 54,795 mg/ha/day in a stream in Hubbard Brook Valley in New Hampshire (McDowell and Likens, 1988, Weigner et al. 2005, Kaplan et al. 2008,). While the smaller portion of the streams showed very high removal of N and C, the larger stream reaches still retained a sizeable fraction of total N and C inputs. Although transformation rates varied greatly, mass balance calculations indicate there is both transformation and transport of N and C over the entire stream network of the Gwynns Falls (Figure 3). Additionally, comparing the export of DON at the headwaters of the Gwynns Falls and at the outflow of the Gwynns Falls indicates that at the headwaters, 7.4% of total N export (mg/day) was DON. However, at the outflow of the Gwynns Falls, 16.0% of the total N export (mg/day) was DON, indicating an increasing importance of DON going from the headwaters downstream toward the outflow.

Some previous work using mass balance approaches has estimated substantial uptake and transformation in both small streams and larger rivers (Boynton et al. 1995, Sjodin et al. 1997, Burns et al. 1998). It is important to consider both small streams and larger rivers, as they both have the potential to remove substantial amounts of N and C (e.g. Boynton et al. 1995, Seitzinger et al. 2002b, Wollheim et al. 2008).

DON-DIN conversions in the Gwynns Falls

Watershed restoration efforts have largely focused on denitrification as a primary pathway for N removal in freshwater streams. Recent studies have proposed that other N removal pathways, however, could be contributing a considerable amount of N removal in freshwater streams (Bronk and Ward 2005, Arango et al. 2008). Active transformations of nitrogen between DIN and DON observed in the Gwynns Falls suggests that multiple pathways of N processing could be present. Our findings, however, indicate that rather than remove N from the surface waters of the stream, DON-DIN conversions could be a source of internal loading of DIN in the Gwynns Falls (Figure 6). Strong inverse patterns between not only nitrate and DON concentrations, but also between nitrate and DON transformation rates and percent change suggest the importance of mineralization of DON to DIN (nitrate), especially in the headwaters of the Gwynns Falls. At the headwaters, DON removal rates are 1420 mg/m^2/day, while DIN (nitrate) generation rates are on average -909 mg/m^2/day. Additionally, at least 92% of DON was removed each season from the reach at the headwaters, while nitrate was increased by almost 300%. Therefore, our mass balance results suggest that in-stream transformation of DON to DIN may contribute to DIN loading downstream of urban stream networks. Similar results regarding the importance of organic N mineralization have been found in other urban and agricultural streams and rivers (Pribyl et al. 2005).

Results from mass balances imply organic N may have been “subsidizing” production of nitrate in the headwaters of the stream, and that uptake capacity for DON decreased further downstream leading to an increased proportion of DON export downstream. Previous work has shown an exponential decrease in the biotic demand for DON with increasing nitrate concentrations in streams, and that mineralization of DON in streams can be important depending on the C:N stoichiometry of streams (Kaushal and Lewis 2003, Kaushal and Lewis 2005).

Further evidence of potential DIN-DON transformations can be found in the leaf litter debris incubations. By examining the concentrations of DON and nitrate over time, it was observed that, while nitrate concentrations decreased, DON concentrations increased in many of the leaf litter debris incubation jars (Figure 8). Because the jars are carbon rich and also have low dissolved oxygen concentrations, it is possible that nitrate could have decreased due to denitrification. However, high C:N ratios and decrease of nitrate concentrations combined with the increase in DON concentrations indicated that DIN transformations into DON is a may have been a likely N processing pathway in these incubation jars (Kaushal and Lewis 2005).

Active DON-DIN transformations throughout the stream network indicate that organic nitrogen may play an important role in N cycling in urban streams and can lead to enhanced DIN loading further downstream with important effects on downstream water quality downstream. This is consistent with recent studies that have found DON to be biologically available (e.g. Seitzinger and Sanders 1997, Wolfe et al, 1999, Kaushal and Lewis 2005, Weigner et al. 2006). While the mass balance study conducted in this research quantifies in-stream processing of nitrogen, more research investigating N processing mechanisms in urban watersheds at the stream network scale is recommended in order to understand the transformations contributing to N removal. Denitrification and organic N transformations may be related to competing pathways for N uptake and transformation in stream networks (Pellerin et al. 2004), but the relative importance of each and how they change is poorly known along stream networks.

Influence of carbon availability on N cycling

Carbon availability may control the dynamics of nitrogen in N saturated ecosystems (Arango et al. 2007). Though previous studies have observed the relationship between DOC and nitrate concentrations in sediments (hyporheic and riparian) (Findlay et al. 1993, Hedin et al. 1998, Baker et al. 1999, Lonberg and Sondergaard 2009) and stream reaches (Bernhardt et al. 2002, Kaushal and Lewis 2003, Goodale et al. 2005), less research has explored DOC and N linkages at the larger stream network scale. We observed significant inverse relationships between DOC and nitrate concentrations each season, suggesting that N and C transformations are tightly coupled along urban stream networks, which may have management implications. Longitudinally along the Gwynns Falls, DOC concentration increased from headwaters to the outflow of the stream, while the nitrate concentrations decreased. This relationship was found to be significant throughout each season. This could mean that, toward the outflow of the stream, carbon quality is limiting and therefore less N is being removed. These ideas are supported by high N removal rates values at the headwaters of the stream and lower rates toward the outflow of the stream network. Additionally, the relationship between DOC and TDN transformation rates showed a positive, linear relationship, further indicating that nitrogen and carbon transformations and cycling are strongly linked.

Results from patterns of nitrogen and carbon concentrations in the incubation experiments with leaf litter debris were also consistent with strong coupling of nitrogen and carbon dynamics in the Gwynns Falls. The incubation experiment indicates that the amount and quality of organic carbon has the potential to influence nitrogen cycling, which is consistent with our observations of strong inverse relationships between DOC and nitrate longitudinally. Bernhardt and Likens (2002) illustrate that high quality DOC can significantly reduce nitrate loading downstream in a forested reach. The presence of highly bioavailable DOC may stimulate immobilization and heterotrophic generation of DON in streams when nitrate is available (Kaushal and Lewis 2005). While the current study provides evidence that DOC is influencing N dynamics, further research into the mechanistic coupling of the two elements (e.g. denitrification vs. DON generation) is needed to draw significant conclusions for urban stream networks (Pellerin et al. 2006).

In-stream processing: an important component to the nitrogen budget

The Gwynns Falls stream network exhibited active transformations between inorganic and organic forms of nitrogen at the reach scale, suggesting that in-stream processes may be an important component of the nitrogen cycle during baseflow conditions. Previous studies quantifying N removal in the Gwynns Falls (Groffman et al. 2004, Kaushal et al. 2008) have examined N removal at a watershed scale. Groffman et al. 2004 and Kaushal et al. 2008 reported an interannual (1999-2004) average of 64% (35 to 83%) of TN inputs was retained in the suburban watershed (GFGL). The current study shows the removal of TN entering the stream to be on average 31% (0 to 52%) during base flow. By converting both of these studies to similar units (kg N/year), it may be possible to roughly estimate the relative contribution of in-stream processing, in relation to the N processing of the entire watershed. By doing so, it is found that in-stream processing can comprise 7.3 to 40 % of total watershed N removal (average 17.3%). Combining these two mass balances does not make a closed budget; however, it does suggest the relative importance of in-stream N processing in the suburban watershed. This estimate of relative contribution of in-stream processing to watershed processing varies so much based on interannual climate variability (Kaushal et al 2008). Between 1999-2004 hydrologic conditions varied greatly from drought years to wet years in the Gwynns Falls (Kaushal et al. 2008). This indicates that in-stream processing can be proportionally more important depending on the hydrologic conditions of the stream, but may always play a role in the watershed processing of N. Relatively little is known regarding the complex underlying mechanisms on a stream network scale, explaining in-stream N transformations and the relative importance of removal in streams vs. uplands. Our results display a strong need to examine in-stream processing as a possible pathway of N removal in urban stream ecosystems (Grimm et al. 2005, Wollheim et al. 2005).

Groundwater: an important component to watershed cycling

Groundwater can be a significant source of organic N and can influence the composition of nitrogen in streams and is often overlooked in nitrogen budgets (Valiela, et al. 1990, Wollheim et al. 2005, Kroeger et al. 2006). In particular, the contribution of groundwater with elevated DON levels may be substantial (Table 2, Kroeger et al. 2006, Cole et al. 2006, van Kessel et al. 2009). Previous research has illustrated that groundwater export of DON increases with anthropogenic activity, indicating that even in suburban watersheds, ground water can be an important source of DON (Kroeger et al. 2006). At times of low flow, anthropogenic inputs can make a proportionately larger impact on groundwater N concentrations (Kemp and Dodds 2001), so it may be imperative to sample ground water in conjunction with the sampling of surface waters to accurately complete the mass balance. Previous work has suggested the interannual hydroclimatic flushing of N in ground water in suburban and urban watersheds may be important in influencing N exports (Kaushal et al. 2008).

The input of groundwater flows to the Gwynns Falls at base flow ranged from 27 to 67%, consistently contributing a substantial portion of the water budget. Groundwater concentrations were taken at 16 representative sites, three times per year, rather than along the length of the stream with each monthly sampling scheme. Therefore, this could be a significant source of organic N that may perhaps be underestimated in this mass balance. More detailed sampling of ground water and source characterization in urban watersheds may be necessary to accurately represent its contribution to N loading in urban streams. There is a large discrepancy in the concentration of DON in groundwater (2.51 mg/L) and in the stream surface water (0.19 mg/L). Therefore, more detailed sampling could provide an estimate of the relative contribution of groundwater DON to the DON in the surface waters of the stream. Severely elevated N levels detected in ground water could indicate leaks in the sewer system infrastructure and/or long-term contamination from other nonpoint sources (Groffman et al. 2004, Bernhardt et al. 2008, Kaushal et al. 2008).

CONCLUSIONS

Elevated N inputs from urban landscapes caused considerable N fluxes to be exported downstream. As urbanization and human populations continue to increase, increased N and C exports will continue to increase water quality problems, making urban watersheds a priority in future nutrient cycling studies and watershed restoration activities. In particular, the contributions of groundwater dynamics and in-stream processing are lesser known components of urban watershed N budgets, and may be important factors in N cycling in urban stream networks.

This study provides evidence of in-stream transformations within urban stream networks, but mechanisms at a stream network scale behind these transformations remain unknown. These stream networks may exhibit tightly coupled N and C biogeochemical cycles where carbon concentrations and transformation rates are strongly linked to N cycling. Rapid mineralization of organic N and substantial in-stream generation of nitrate may have been important in the urban stream network. The role of ground water as an organic N source and stoichiometric controls should be further investigated in urban watersheds for predicting generation and consumption of reactive nitrogen. Further research elucidating the biogeochemical role of urban stream networks as both “transformers” *and* “transporters” of organic nitrogen will help us further understand and properly manage and reduce nitrogen en route to sensitive coastal waters.

TABLES AND FIGURES

Table 1. Study site descriptions for the Gwynns Falls and POBR-BARN stream networks. There are 4 main sampling points along the Gwynns Falls stream network representing different dominant land-uses. POBR-BARN lie in the Gunpowder watershed and represent a stream network draining forest and low-residential land use.

Site **Gwynns Falls**	**Dominant land-use**	**Population Density (people/ha)**	**Reach Drainage Area (ha)**	**River km**
Glyndon (GFGL)	Suburban (headwaters)	9.4	81	0
Gwynnbrook (GFGB)	Suburban	16.4	985	4.5
Villa Nova (GFVN).	Suburban / urban boundary	12.2	7,282	20.85
Carroll Park (GFCP)	Urban	19.7	7,930	36.45
Site	**Land-use**		**Catchment Size**	**Reach length (km)**
Baisman Run	Residential	1	381	0.90
Pond Branch	Forest	0	32.3	0.25

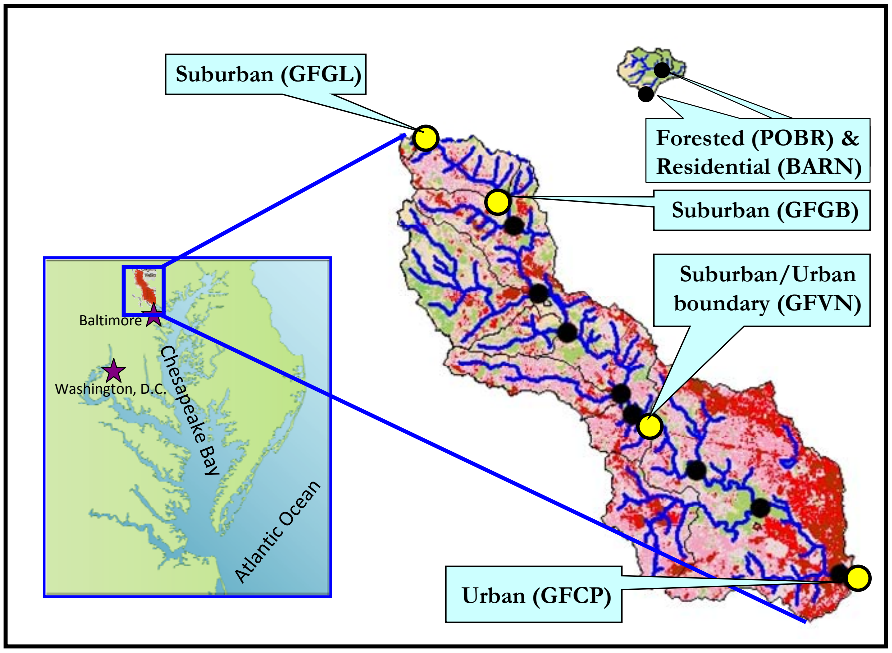
(Groffman et al. 2004, Kaushal et al. 2008)

Table 2. Concentrations of DON and DIN in groundwater from ecosystems of different land uses. Unless otherwise noted, DIN is nitrate + ammonium.

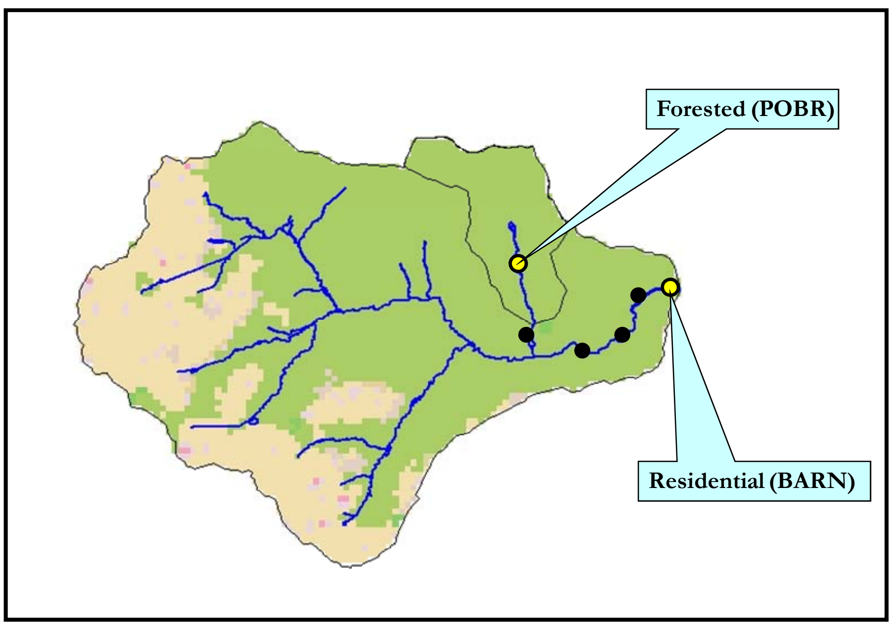
Land-use	**Ecosystem**	**Location**	**DON (mg/L)**	**DIN (mg/L)**	**% DON**	**Reference**
Forested	Pond Branch	Baltimore, MD	1.27	0.25	83.6	Current study
Suburban/urban	Gwynns Falls	Baltimore, MD	2.51	0.26	90.6	Current study
Residential	Baisman Run	Baltimore, MD	0.10	0.02	86.1	Current study
Residential (32%), Natural vegetation (62%)	Green Pond watershed	Cape Cod, MA	140*	74*	66	Kroeger et al. 2006
Residential (24%), Natural vegetation (75%)	Childs River watershed	Cape Cod, MA	22*	90*	19	Kroeger et al. 2006
Residential (15%), Natural vegetation (75%)	Quashnet River watershed	Cape Cod, MA	29*	20*	59	Kroeger et al. 2006

* μmol/L

Figure 1. Land cover map of the Gwynns Falls and POBR-BARN watersheds, indicating the study sites in each stream. Pink and red indicate suburban and urban land uses and green is forested land-use. All circles mark a sampling point; circles with yellow centers mark a USGS routine sampling point. (A) Gwynns Falls, (B) POBR-BARN.



(A)



(B)

Figure 2. The Gwynns Falls shows a significant, inverse relationship between DOC and nitrate concentrations (mg/L). Sampling points are located longitudinally from the headwaters to the outflow of the Gwynns Falls. R values are Spearman correlation coefficients.

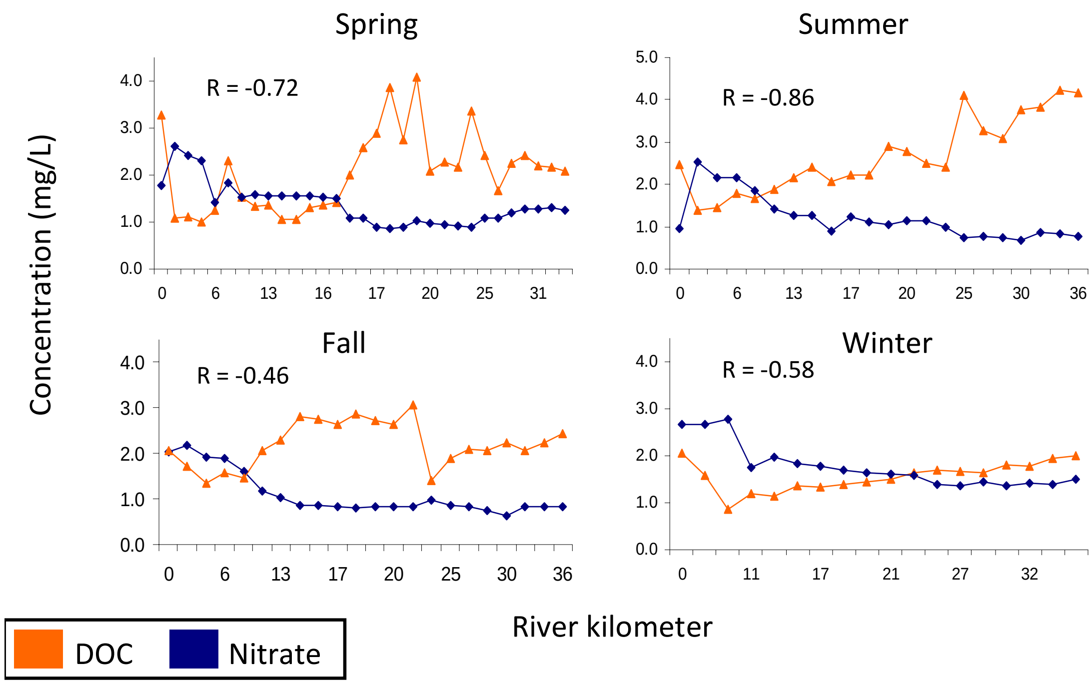


Figure 3. Transformation rates of DON and DOC in the Gwynns Falls (mg/m^2/day). The grey bars are percent error of each point, which is the mean for each season.

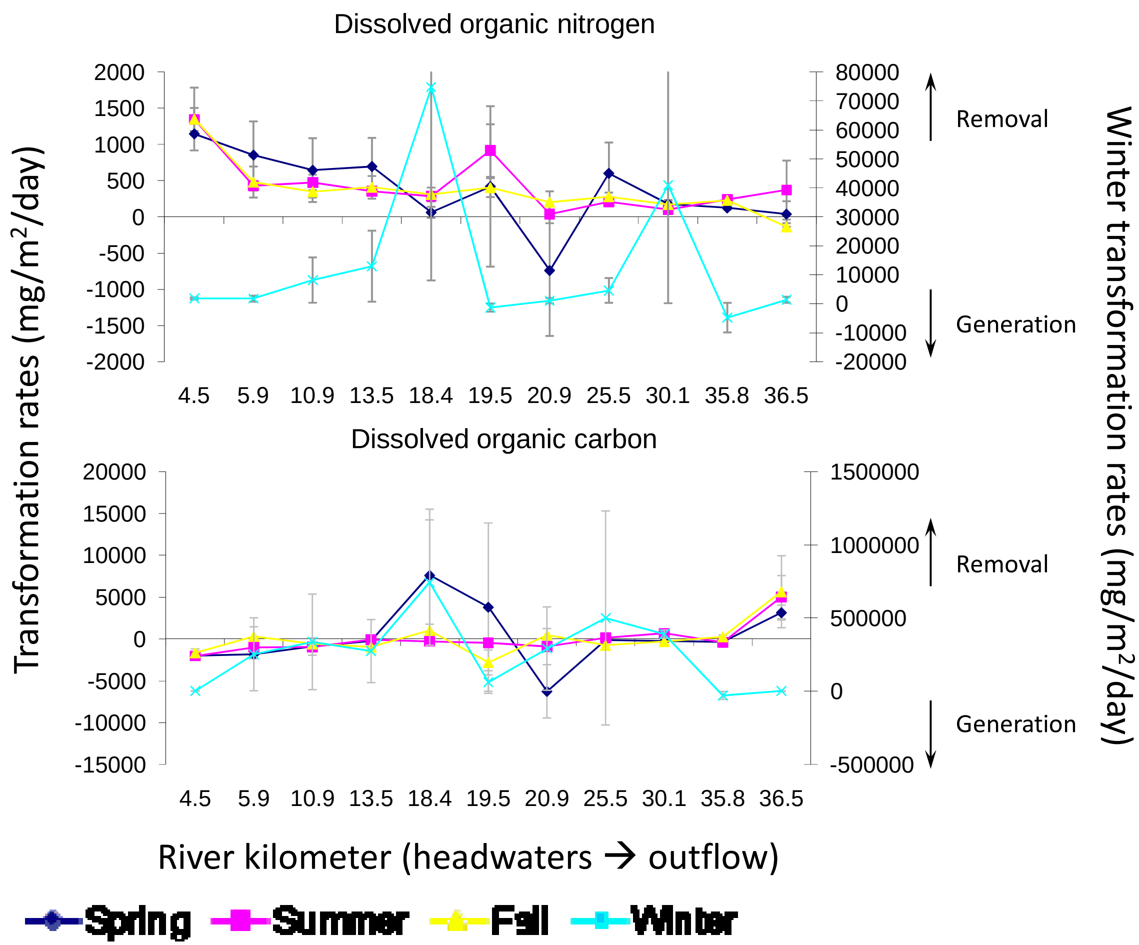


Figure 4. Percent transformation of inputs into each stream reach of the Gwynns Falls stream network. The grey bars are percent error of each point, which is the mean for each season.

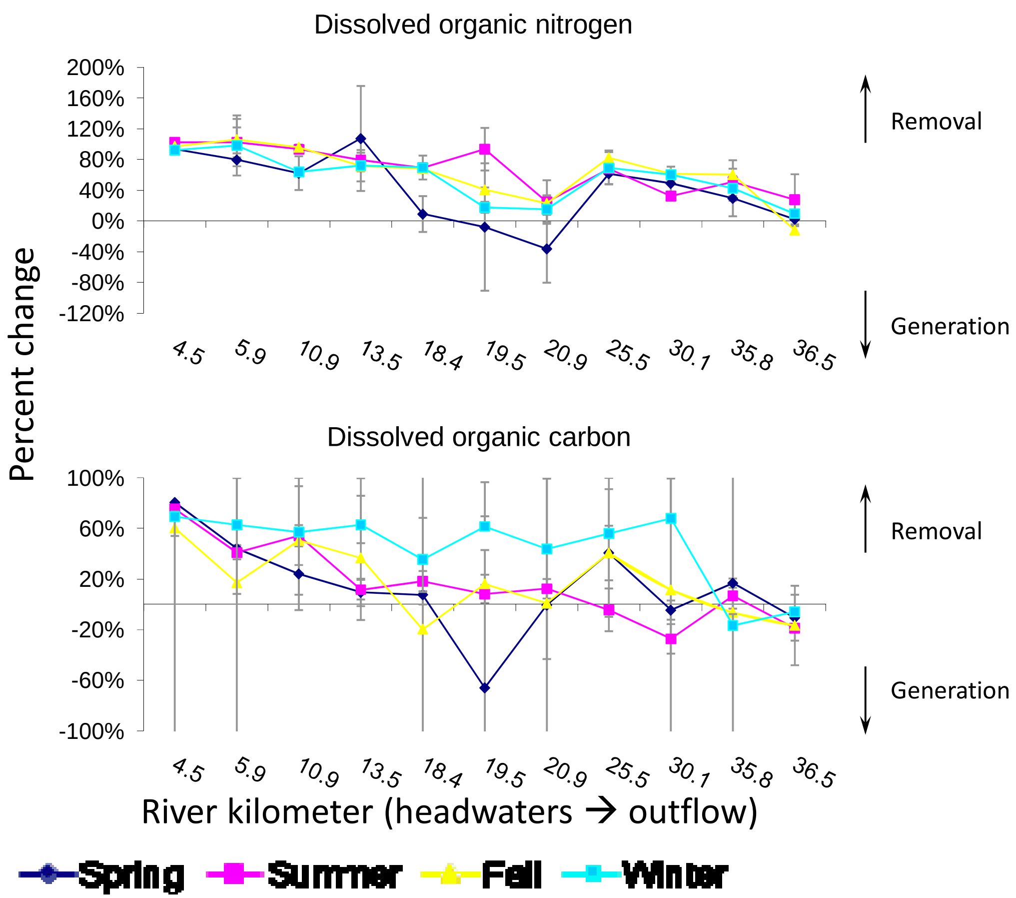


Figure 5. Transformation rates (mg/m²/day) in the POBR-BARN headwater stream network. The grey bars are percent error of each point, which is the mean for each season.

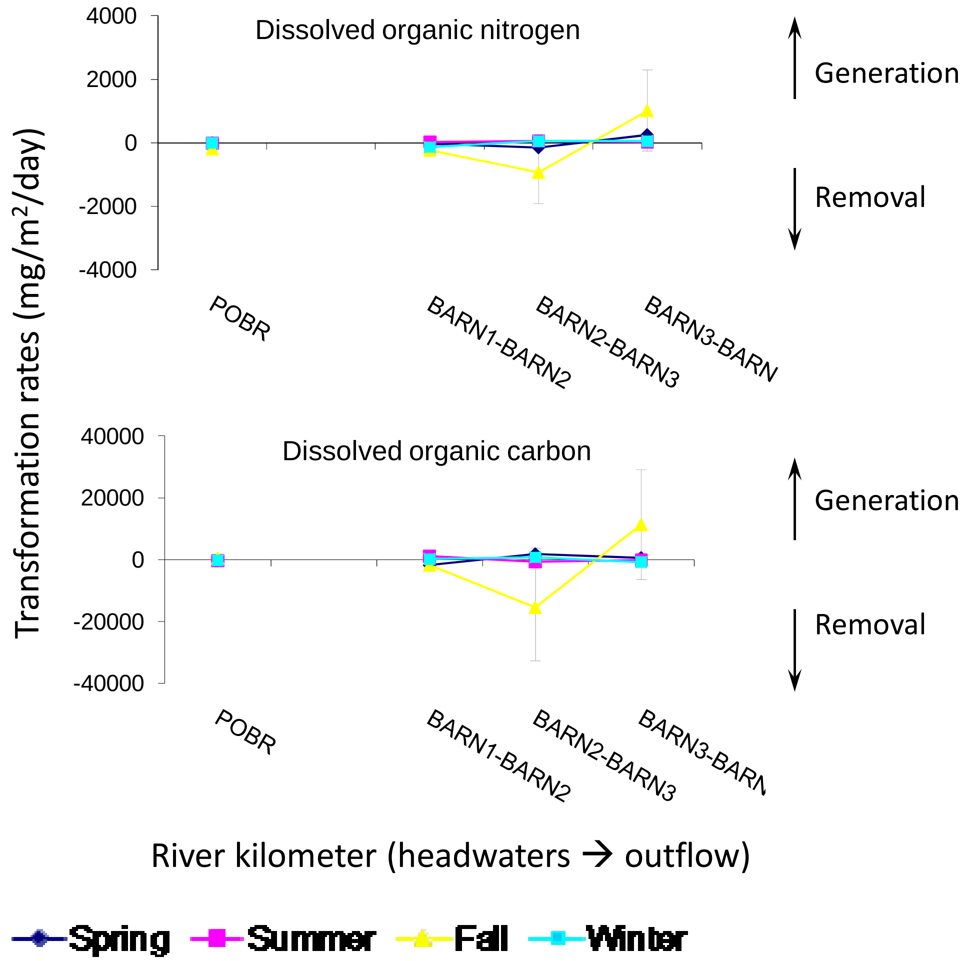


Figure 6. (A) Transformation rates (mg/m^2/day) of nitrate and DON along the Gwynns Falls watershed. Nitrate is in purple and DON is blue. (B) Percent transformation of nitrate (dashed lines) and DON (solid lines).

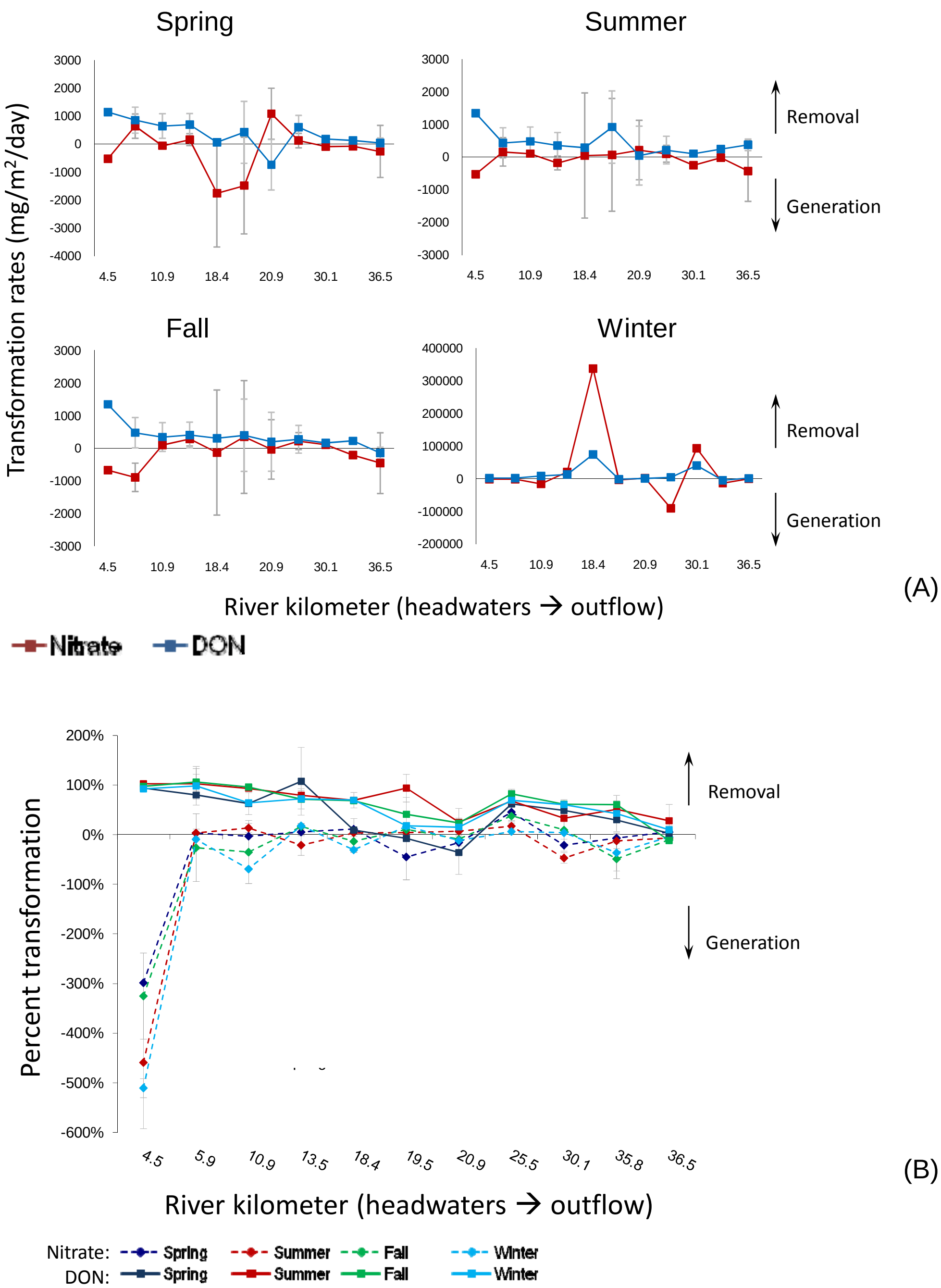


Figure 7. Relationship between N and C transformation rates for each season. R values are Spearman's correlation coefficients.

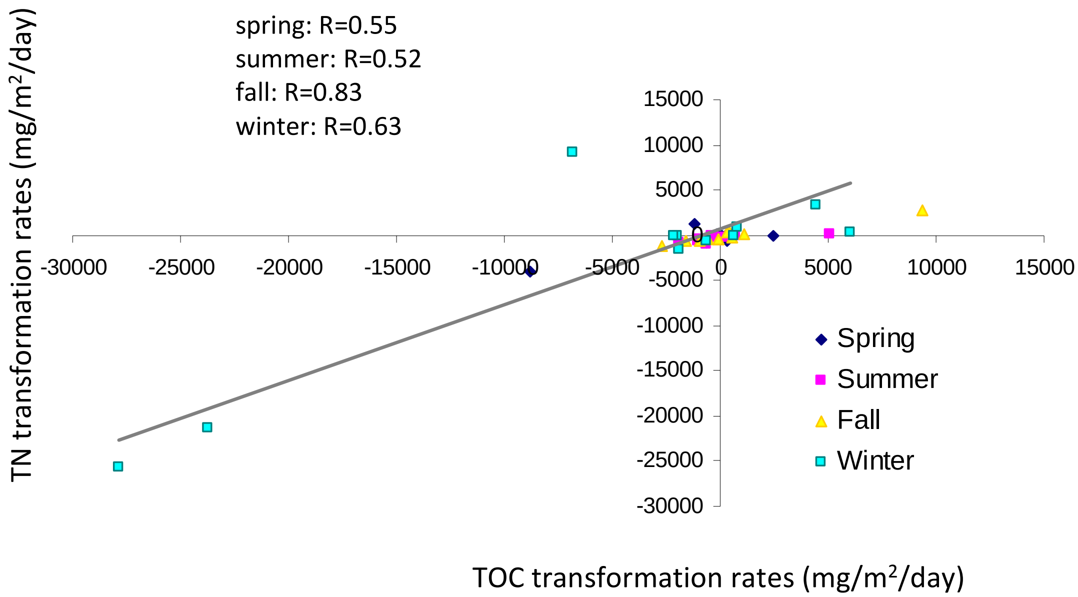
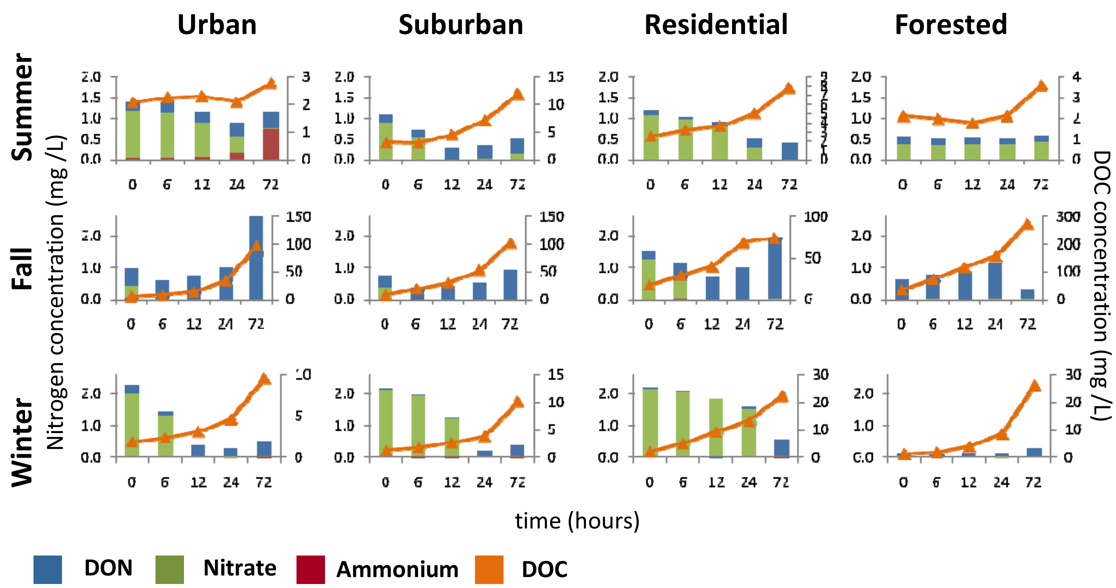


Figure 8. Nitrogen fractions for a leaf litter debris incubation experiment. Bars represent total dissolved nitrogen, divided into colors by constituent. Nitrate is green, ammonium is red and DON is blue. The orange bars represent DOC concentration.



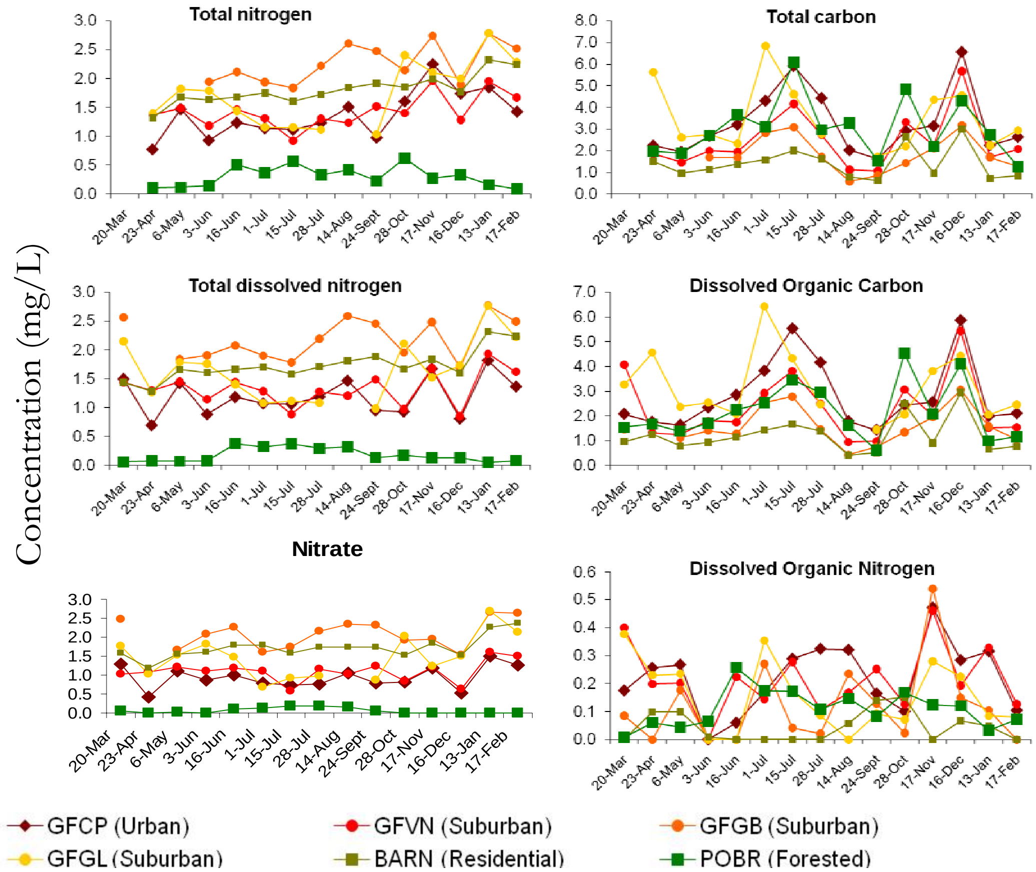
Appendices

Appendix A. Uncertainty Analysis

Uncertainty in mass balance estimates were investigated using coefficient of variation measurements of the mean of transformation rates for each reach each season. There was a large range in the coefficient of variation in the transformation rates overall, from 1.9 % to 4000%, with an average of 146%. This large range in CV values is due in part to small sample sizes in each season. The larger CV values occur when the mean of the transformation rate is close to zero. When large transformation (removal or generation) rates were observed (>1000 mg/m^2/day), the CV was much less variable (26% - 263%) with a smaller average (93%). Most of our research is focused on areas of the stream in which active transformations are present, which is where the CV values indicate that our mass balance calculations are less variable. Uncertainty due to imprecise discharge measurements is estimated to be 12 %, but it is assumed that the CV calculated using the mean of each season accounts for this. In some basic calculation manipulation, the range of discharge measurements that could be considered by this 10% error margin did not change the overall pattern or value of the transformation rates, the calculation only varied slightly. Even considering an uncertainty scenario in which our discharge measurements could range up to 10%, neither the pattern nor the value of the mass balance was substantially different. Therefore, our calculations provide a reliable estimate of transformation rates considering uncertainty. A larger contributor to uncertainty may have been groundwater concentrations and fluxes. It is possible that groundwater loads were overestimated. Pipe outflows could have been missed and sewer leaks were not taken into consideration, but most of the stream reach was observed during field work and we are confident that our measurements are good estimates of stream concentration and flux. We discuss this further in the discussion section.

Appendix B. Yearly trends in nitrogen, carbon and phosphorus concentrations

Temporal variations over 12 months during 2008-2009 for 6 sampling sites representing land-uses ranging from urban (GFCP) to completely forested (POBR).



Appendix C. Gwynns Falls transformation rates and percent change

Watershed scale mass balance for the Gwynns Falls, net transformation in mg/m^2/day. Suburban reach is from GFGL - GFVN, urban reach is from GFVN - GFCP. A negative number indicates net removal of nutrients and a positive number indicates net generation.

		Reaches										
		Suburban								Urban		
Nutrient	**Season**	**GL1-GB1**	**GB1-VN1**	**VN1-VN2**	**VN2-VN3**	**VN3-VN4**	**VN4-VN5**	**VN5-VN6**	**VN6-CP1**	**CP1-CP2**	**CP2-CP3**	**CP3-CP4**
TOC	**Spring**			-94.2	-280.5	578.8	8840.7	1201.7	655.8	-269.8	125.8	-2467.3
	Summer	1913.5	1034.0	883.6	31.8	201.2	596.5	1022.4	-363.2	-712.1	430.7	-5096.0
	Fall	1591.3	-396.8	559.3	951.3	-1118.0	2715.0	-554.7	100.4	116.2	-336.4	-9370.8
	Winter	1976.8	2121.7	6824.0	27891.2	-4421.0	1936.3	-5992.2	608.1	23738.3	-800.5	-635.3
DOC	**Spring**	1972.3	1828.8	908.5	218.7	-7619.5	-3812.7	6251.3	113.6	257.4	350.9	-3159.8
	Summer	2018.3	976.9	936.0	64.5	269.3	434.7	906.1	-159.2	-668.4	398.6	-5002.3
	Fall	1641.0	-329.1	583.4	946.9	-1035.1	2799.4	-484.8	752.1	300.1	-274.4	-5648.6
	Winter	2622.9	253020.7	337409.4	274865.4	742347.5	63080.6	291959.7	500979.1	390064.2	-27785.3	1999.3
TN	**Spring**	0.0	0.0	121.0	659.0	199.3	4091.9	-1231.7	795.1	6.8	-161.0	43.6
	Summer	885.2	586.7	596.3	161.5	278.4	997.6	379.1	281.6	-2.5	8.9	-144.5
	Fall	636.8	-520.0	439.6	710.8	-42.9	1102.5	262.6	363.2	491.5	-237.7	-2779.8
	Winter	74.8	61.4	-9087.9	25736.3	-3349.9	1595.9	-266.7	648.4	21286.9	-919.1	42.3
TDN	**Spring**	644.4	1038.1	594.8	866.4	201.3	-980.2	-2365.8	1766.8	43.5	31.0	178.3
	Summer	899.2	589.1	599.2	181.3	273.9	994.1	233.8	275.3	-126.7	190.4	-154.0
	Fall	733.3	-396.1	462.8	715.0	192.1	753.1	186.7	509.8	304.4	32.5	-578.5
	Winter	5359.2	393.1	-7305.6	33724.8	-4787.5	1929.9	-447.3	659.5	17782.9	-615.7	31.9
Nitrate	**Spring**	-530.8	639.6	-59.3	158.3	-1764.5	-1486.0	1083.5	123.0	-90.5	-83.2	-265.0
	Summer	-534.5	153.7	101.1	-185.3	42.4	63.3	210.2	96.3	-254.8	-22.8	-431.3
	Fall	-665.7	-888.6	100.6	287.8	-128.6	349.1	-31.9	223.3	114.6	-203.9	-453.7
	Winter	-1906.5	-1462.5	-15779.2	20177.6	337860.4	-4032.3	1431.0	-90394.7	93718.6	-13215.6	-272.2
DON	**Spring**	1146.2	853.8	644.6	696.0	61.3	419.2	-739.6	601.1	179.1	123.6	38.7
	Summer	1343.6	428.2	475.6	352.3	286.3	915.1	39.9	208.8	100.8	242.7	369.9
	Fall	1349.9	480.3	347.7	407.6	309.3	402.8	202.5	277.9	170.1	228.0	-140.3
	Winter	1852.6	1787.9	8189.1	12960.5	74794.7	-1313.2	1066.4	4593.0	40850.8	-4774.1	1360.2

Percent removal of nutrients along the Gwynns Falls. The suburban reach is GFGL – GFVN and the urban reach is GFVN - GFCP. Negative numbers indicates more constituent was exported than imported, indicating in-stream generation of that constituent.

-	-	Reaches										-
-		Suburban							Urban			
	Season	**GL1-GB1**	**GB1-VN1**	**VN1-VN2**	**VN2-VN3**	**VN3-VN4**	**VN4-VN5**	**VN5-VN6**	**VN6-CP1**	**CP1-CP2**	**CP2-CP3**	**CP3-CP4**
TOC	**Spring**			-3.0%	-4.3%	14.1%	52.9%	14.3%	31.5%	-14.9%	5.0%	-14.6%
	Summer	71.1%	37.7%	47.5%	9.3%	13.5%	8.7%	12.9%	-14.4%	-24.9%	4.8%	-16.5%
	Fall	58.4%	13.9%	46.1%	34.8%	-22.2%	15.5%	-0.6%	25.9%	-4.3%	-3.8%	-20.3%
	Winter	65.9%	34.4%	26.7%	29.6%	5.9%	22.8%	-27.3%	22.5%	14.1%	-9.4%	-4.6%
DOC	**Spring**	80.4%	44.3%	24.0%	9.5%	7.6%	-65.8%	-0.6%	40.6%	-4.6%	16.8%	-10.6%
	Summer	75.5%	40.8%	54.2%	11.6%	18.4%	8.2%	12.3%	-4.3%	-27.3%	6.6%	-19.0%
	Fall	60.4%	17.1%	50.5%	36.7%	-19.7%	16.2%	0.8%	40.6%	11.4%	-6.4%	-16.7%
	Winter	69.2%	62.9%	57.1%	62.7%	35.5%	61.6%	43.9%	55.9%	67.9%	-16.6%	-5.9%
TN	**Spring**			5.5%	16.8%	9.7%	46.6%	-29.8%	52.2%	0.7%	-11.1%	3.5%
	Summer	51.8%	22.1%	44.4%	10.2%	19.6%	20.9%	12.7%	30.5%	3.9%	-10.8%	-2.0%
	Fall	31.2%	-3.8%	22.5%	27.2%	-0.8%	17.2%	3.6%	41.4%	28.2%	-13.2%	-23.7%
	Winter	6.3%	11.7%	-20.4%	25.1%	-0.4%	17.1%	-4.1%	24.2%	16.8%	-14.1%	-2.2%
TDN	**Spring**	44.8%	16.1%	16.6%	26.5%	11.6%	-30.8%	-24.3%	49.1%	1.3%	3.1%	3.9%
	Summer	54.9%	22.6%	45.3%	11.6%	19.9%	21.2%	7.1%	31.6%	-11.8%	7.0%	-2.2%
	Fall	37.5%	-1.8%	25.9%	30.9%	16.3%	16.1%	0.6%	52.8%	30.2%	-0.3%	-9.8%
	Winter	35.7%	13.6%	-18.9%	29.8%	-2.8%	19.6%	-7.6%	24.5%	15.1%	-5.2%	-2.3%
Nitrate	**Spring**	-298.6%	2.9%	-3.2%	5.1%	11.0%	-45.0%	-16.1%	45.3%	-21.4%	-7.0%	5.2%
	Summer	-459.4%	3.1%	13.3%	-21.2%	3.5%	4.3%	6.7%	17.1%	-47.2%	-12.7%	-6.9%
	Fall	-325.2%	-26.1%	-35.1%	16.3%	-13.4%	10.2%	-9.1%	37.7%	9.4%	-48.9%	-10.3%
	Winter	-510.8%	-9.5%	-69.4%	17.9%	-30.8%	16.9%	-11.9%	6.2%	3.7%	-36.6%	-4.9%
DON	**Spring**	93.8%	79.7%	62.3%	107.4%	9.2%	-7.8%	-36.1%	61.7%	49.0%	29.6%	2.5%
	Summer	102.4%	102.3%	93.2%	79.6%	69.1%	93.5%	24.7%	67.9%	32.7%	50.9%	27.7%
	Fall	97.3%	106.0%	95.9%	71.4%	68.3%	40.7%	23.2%	82.3%	61.4%	60.4%	-11.7%
	Winter	92.2%	98.3%	64.1%	72.0%	69.5%	17.8%	15.1%	68.9%	60.4%	42.6%	9.7%

Appendix D. POBR-BARN transformation rates and percent change

Watershed scale mass balance for POBR-BARN (transformation rates in mg/m^2/day). A negative number indicates net removal of nutrients and a positive number indicates net generation.

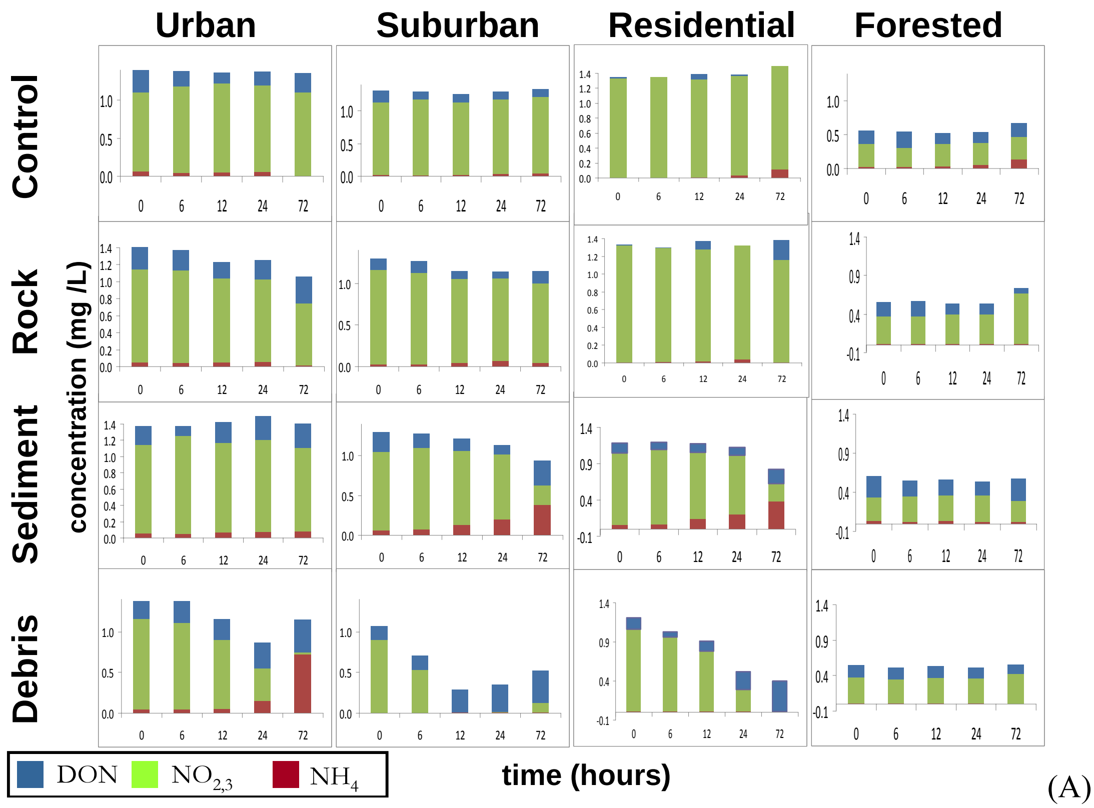
		Reaches			
Nutrient	**Season**	POBR	BARN1-BARN2	BARN2-BARN3	BARN3-BARN
TOC	**Spring**	477.4	-2672.2	2023.8	723.3
	Summer	404.7	1155.3	-1080.5	-560.8
	Fall	-750.2	-1773.3	-16376.3	11394.0
	Winter	372.9	125.4	738.7	-1196.3
DOC	**Spring**	341.6	-1835.4	1843.0	574.1
	Summer	270.1	1118.3	-743.8	-85.2
	Fall	-523.9	-1746.9	-15482.5	11333.1
	Winter	224.9	150.2	748.3	-823.4
TN	**Spring**	7.4	-1787.0	580.8	907.7
	Summer	204.0	1069.1	-1842.9	-72.1
	Fall	217.5	-1043.1	-11282.0	7977.3
	Winter	340.6	-1127.5	-33.3	-3108.1
TDN	**Spring**	12.4	-1724.3	560.1	889.1
	Summer	25.4	1044.6	-1786.3	-34.2
	Fall	220.8	-870.7	-10161.5	7469.6
	Winter	-0.1	-1051.3	-32.8	-3058.6
Nitrate	**Spring**	3.0	-1683.5	709.1	643.8
	Summer	9.3	962.4	-1905.3	-110.1
	Fall	19.3	-629.7	-9179.7	6422.5
	Winter	-2.0	-884.0	-44.1	-3601.6
DON	**Spring**	9.3	-34.4	-152.6	242.9
	Summer	17.0	29.0	52.8	23.2
	Fall	192.6	-235.8	-936.4	1015.5
	Winter	9.7	-135.3	49.4	50.4

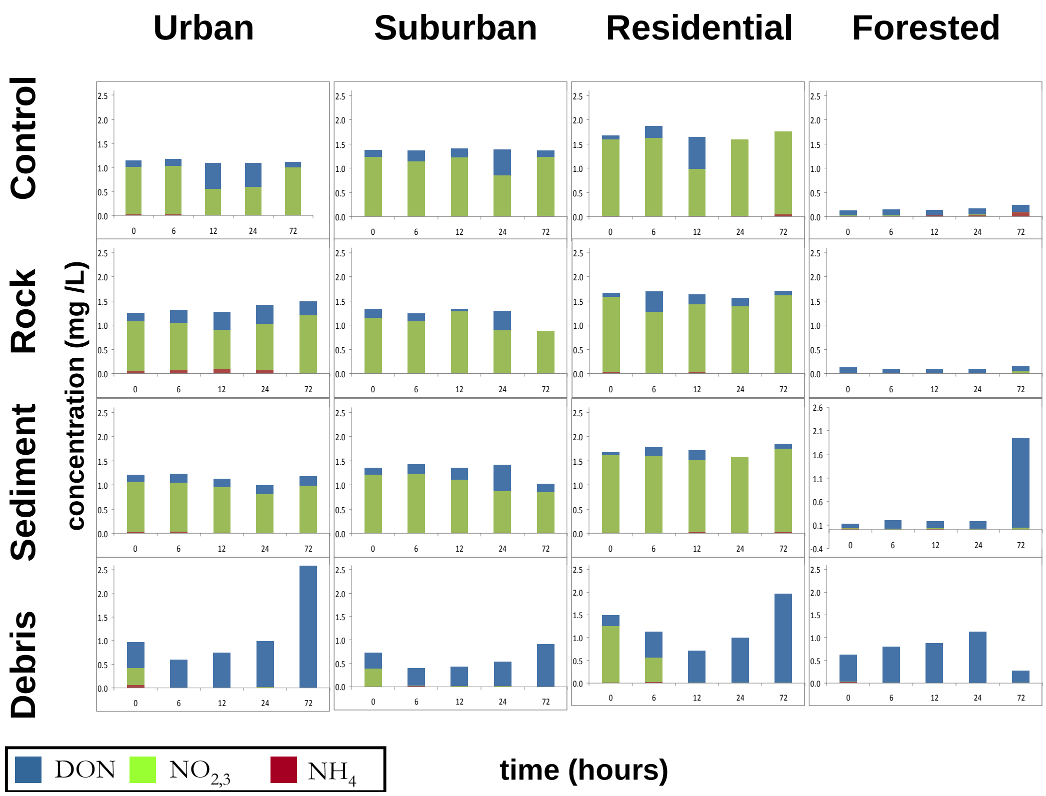
Percent removal of nutrients longitudinally along the POBR-BARN stream network. Negative numbers indicates more constituent was exported than imported, indicating in-stream generation of that constituent.

		Reaches			
Nutrient	**Season**	POBR	BARN1-BARN2	BARN2-BARN3	BARN3-BARN
TOC	**Spring**	70.2%	-53.9%	16.6%	14.3%
	Summer	40.5%	24.0%	-39.5%	-32.9%
	Fall	-52.5%	-17.1%	-81.6%	14.1%
	Winter	39.1%	4.7%	19.5%	-47.3%
DOC	**Spring**	69.2%	-42.7%	21.1%	15.4%
	Summer	51.3%	28.3%	-32.7%	-19.2%
	Fall	-39.6%	-17.3%	-81.9%	22.5%
	Winter	35.0%	6.8%	19.8%	-31.4%
TN	**Spring**	29.1%	-39.7%	7.1%	17.6%
	Summer	79.9%	16.3%	-64.2%	-23.9%
	Fall	36.0%	-17.7%	-80.7%	5.4%
	Winter	76.5%	-30.4%	2.7%	-119.3%
TDN	**Spring**	48.7%	-39.1%	7.1%	17.6%
	Summer	49.9%	16.0%	-63.3%	-22.7%
	Fall	66.7%	-16.4%	-81.9%	17.4%
	Winter	-11.6%	-29.9%	2.6%	-118.4%
Nitrate	**Spring**	43.9%	-41.4%	10.2%	14.3%
	Summer	-39.5%	14.0%	-64.2%	-28.1%
	Fall	75.7%	-13.1%	-85.1%	11.6%
	Winter	-98.4%	-29.3%	2.2%	-148.8%
DON	**Spring**	59.7%	-9.6%	-37.5%	49.8%
	Summer	62.2%	65.9%	61.6%	65.9%
	Fall	68.8%	-59.8%	-61.7%	63.8%
	Winter	23.8%	0.0%	3.9%	0.1%

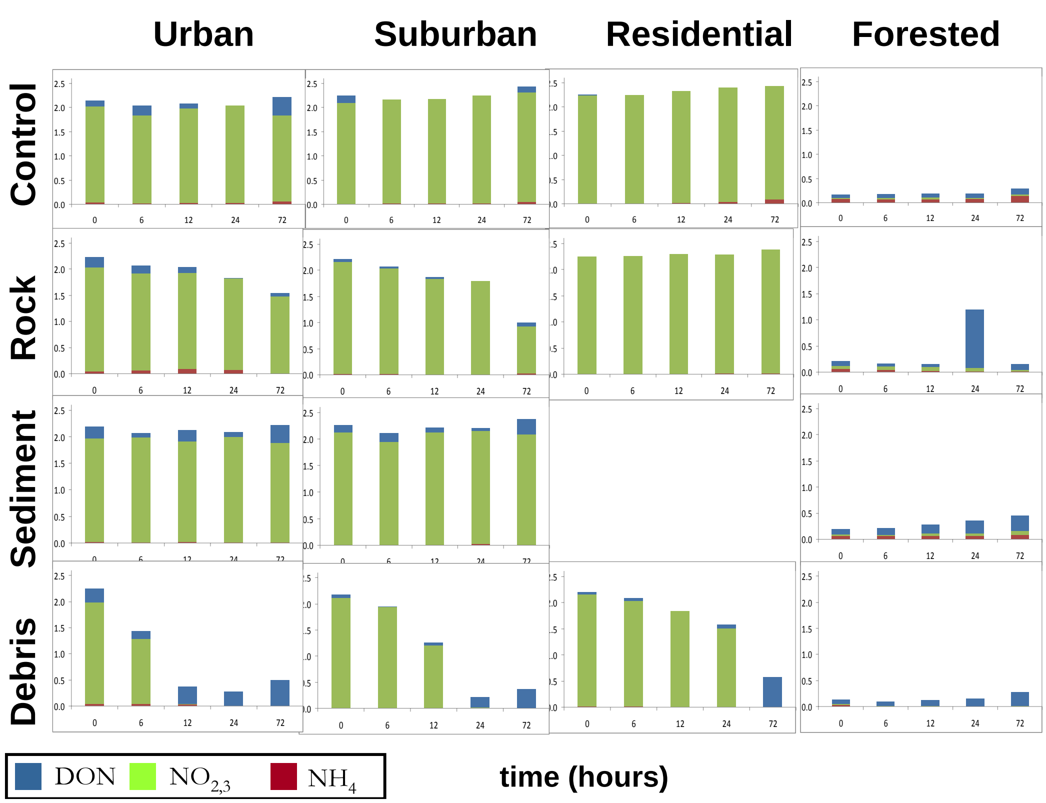
Appendix E. Nitrogen fractions from incubation experiment

Nitrogen fractions for the incubation experiment. Bars represent total dissolved nitrogen, divided into colors by constituent. Nitrate is green, ammonium is red and DON is blue. Panel A)Summer, B) Fall C) Winter




Urban
Suburban
Residential
Forested
Control
Rock
Sediment
Debris
concentration (mg /L)
DON
$NO_{2,3}$
NH_4
time (hours)

(B)


Urban
Suburban
Residential
Forested
Control
Rock
Sediment
Debris
DON
$NO_{2,3}$
NH_4
time (hours)

(C)

Appendix F. Comparison between geomorphic controls and transformation rates in the Gwynns Falls

Statistical correlations were tested to observe relationships between transformation rates or percent removal of TN, TON, TDN, DON, TOC and DOC with geomorphic features, such as width, depth and depth:width ratios and are summarized in Table 2. The transformation rates of TON and DON were almost always correlated with these geomorphic figures. Correlation between transformation rates and removal of all constituents and geomorphic features were observed most frequently during the summer.

Findings in this study are consistent with previous research (Alexander et al. 2000, Peterson et al. 2001), which suggests that there can be substantial nitrogen removal in headwater streams. In this study, inverse linear relationships illustrated a significant correlation between stream width and depth and percent removal of TDN, DON and DOC. The inverse relationship with removal of these N and C fractions illustrates that there is an association between N and C removal and stream width and depth; N and C removal increases with both decreasing stream width and depth.

Moreover, the percent removal of TDN, DON and DOC decreases longitudinally from the headwaters to the outflow of the Gwynns Falls stream network. This could be for several reasons but stream channel size may likely influence nutrient uptake and removal, particularly during spring and summer months (when biotic activity is highest). This idea supports previous suggestions placing emphasis on restoring headwater areas (e.g. Bukaveckas 2007, Kaushal et al. 2008, Craig et al. 2008). Previous work has shown that stream depth influences autotrophic activity by affecting light availability (Roberts and Howarth, 2006, Hill et al. 2001, Mulholland, 1992). Our results suggest that as depth decreases, nitrogen and carbon removal increases. While significant relationships varied in strength across seasons, percent removal of TDN, DON and DOC all had significant inverse linear relationships with average depth of reach during summer months. Because this was observed during the growing season, we speculate that autotrophic activity may be contributing to the removal of nitrogen and carbon. Decreasing depth of surface water indicated a higher percent removal of N and C, which could be due to the decrease in light attenuation. The same inverse linear relationships were observed when comparing average depth to TDN, DON and DOC transformation rates. Relationships between channel geomorphology and N removal may potentially be useful in evaluating stream restoration designs and consideration of N and C uptake and depth of the stream, however, more work is needed to clarify these relationships.

Appendix H Table 1. Summary of R values for correlation relationships between geomorphic controls (average depth of reach, average width of reach and depth:width ratio) and nutrient removal (percent removal and transformation rates). Significance was measured using α=0.05. An n.s. notation indicates the relationship was not significant.

Linear Regression relationships		Percent Removal (%)						Transformation ($mg/m^2/day$)					
		TN	TON	TDN	DON	TOC	DOC	TN	TON	TDN	DON	TOC	DOC
Average depth	Spring	n.s.	n.s.	n.s.	R=-0.35	n.s.	n.s.	n.s.	n.s.	n.s.	n.s.	n.s.	n.s.
	Summer	R=-0.29	R=-0.47	R=-0.32	R=-0.47	R=-0.59	R=-0.60	n.s.	R=0.34	n.s.	R=0.37	R=0.32	R=0.34
	Fall	n.s.	R=-0.50	n.s.	R=-0.55	n.s.	n.s.	n.s.	n.s.	n.s.	n.s.	n.s.	n.s.
	Winter	n.s.	n.s.	n.s.	n.s.	n.s.	n.s.	n.s.	n.s.	n.s.	R=-0.40	n.s.	n.s.
Average width	Spring	n.s.	n.s.	n.s.	n.s.	n.s.	n.s.	n.s.	n.s.	n.s.	n.s.	n.s.	n.s.
	Summer	R=-0.44	R=-0.60	R=-0.53	R=-0.57	R=-0.75	R=-0.75	R=0.42	R=0.47	R=0.44	R=0.48	R=0.57	R=0.58
	Fall	n.s.	R=-0.41	n.s.	R=-0.55	R=-0.41	R=-0.40	n.s.	R=0.54	n.s.	R=0.64	R=0.45	R=0.44
	Winter	n.s.	n.s.	n.s.	R=-0.38	R=-0.43	n.s.	n.s.	R=0.64	n.s.	R=0.81	R=0.45	n.s.
Width: depth ratio	Spring	n.s.	n.s.	n.s.	n.s.	R=0.47	R=0.47	n.s.	R=-0.42	n.s.	R=-0.37	R=-0.52	R=-0.51
	Summer	n.s.	R=0.33	R=0.23	R=0.30	n.s.	n.s.	R=-0.36	n.s.	R=-0.38	n.s.	n.s.	n.s.
	Fall	n.s.	n.s.	n.s.	n.s.	R=0.37	R=0.36	R=-0.42	R=-0.53	R=-0.41	R=-0.57	R=-0.49	R=-0.48
	Winter	n.s.	n.s.	n.s.	n.s.	n.s.	n.s.	n.s.	R=-0.74	n.s.	R=-0.72	R=-0.47	n.s.

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