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Nitrogen solutes in an Adirondack forested watershed: Importance of dissolved organic nitrogen

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Abstract. Nitrogen (N) dynamics were evaluated from 1 June 1995 through 31 May 1996 within the Arbutus Lake watershed in the Adirondack Mountains of New York State, U.S.A. At the Arbutus Lake outlet dissolved organic nitrogen (DON), NO_3^- and NH_4^+ contributed 61%, 33%, and 6% respectively, to the total dissolved nitrogen (TDN) flux (259 mol ha^{-1} yr^{-1}). At the lake inlet DON, NO_3^-, and NH_4^+ constituted 36%, 61%, and 3% respectively, of TDN flux (349 mol ha^{-1} yr^{-1}). Differences between the factors that control DON, NO_3^-, and NH_4^+ stream water concentrations were evaluated using two methods for estimating annual N flux at the lake inlet. Using biweekly sampling NO_3^- and NH_4^+ flux was 10 and 4 mol ha^{-1} yr^{-1} respectively, less than flux estimates using biweekly plus storm and snowmelt sampling. DON flux was 18 mol ha^{-1} yr^{-1} greater using only biweekly sampling. These differences are probably not of ecological significance relative to the total flux of N from the watershed (349 mol ha^{-1} yr^{-1}). Dissolved organic N concentrations were positively related to discharge during both the dormant (R^2 = 0.31; $P < 0.01$) and growing season (R^2 = 0.09; $P < 0.01$). There was no significant relationship between NO_3^- concentration and discharge during the dormant season, but a significant negative relationship was found during the growing season (R^2 = 0.29; $P < 0.01$). Biotic controls in the growing season appeared to have had a larger impact on stream water NO_3^- concentrations than on DON concentrations. Arbutus Lake had a major impact on stream water N concentrations of the four landscape positions sampled, suggesting the need to quantify within lake processes to interpret N solute losses and patterns in watershed-lake systems.

1. Introduction

Although DON may be an important component of surface water nitrogen (N) export in some watersheds, controls of DON concentration and flux are poorly understood (Hedin et al. 1995; Phillips 1995; Arheimer et al. 1996; Lovett et al. 1998). Hedin et al. (1995) found that DON constituted 95% of the total dissolved nitrogen (TDN) flux from 31 pristine old growth forests in southern Chile. For 20 watersheds impacted by high rates of atmospheric N deposition in Sweden and Finland, DON averaged 80% of stream water N flux (Arheimer et al. 1996). In the Catskill Mountains of New York State, DON accounted for 17% of the total dissolved N in 39 watersheds (Lovett et al. 1998).

Analysis of stream water NO_3^- concentration has received more attention than DON because NO_3^- can be analyzed more easily and has been identified as an indicator of N saturation (Aber et al. 1989; Stoddard 1994). Nitrate also plays an important role in episodic acidification (Wigington et al. 1990; Schaefer et al. 1990; Wigington et al. 1996a; Wiginton et al. 1996b). Stoddard (1994) described a series of stages that a watershed may experience as the supply of N begins to exceed that needed by the biota. As a watershed begins to have an excess of N, stream water NO_3^- concentrations may increase and the seasonal patterns in stream water NO_3^- concentration may be attenuated (Stoddard 1994). Evaluation of N saturation and determination of whether a watershed is a source or sink of N will be altered by the inclusion of DON in N solute flux estimates. However, traditional views of watershed N cycling that focus on the direct biotic controls associated with dissolved inorganic nitrogen (DIN) loss may not be as applicable to DON loss that is also subject to indirect biotic and abiotic controls (Hedin et al. 1995).

Recent work has attempted to characterize the mobility of DON and controls on stream water DON concentrations (Sollins et al. 1980; Qualls et al. 1991; Hedin et al. 1995; Arheimer et al. 1996; Lovett et al. 1998). DON was ∼95% of TDN in forest floor leachate in soils in Oregon (Sollins & McCorison 1981) and North Carolina (Qualls et al. 1991). The fate of this DON may include long-term storage within mineral soils that constitute the largest N pool in forested watersheds (Sollins et al. 1980; Mitchell et al. 1992a). Release of organic N as DON to stream water may be controlled by erosional losses (Roberts et al. 1984) and eluviation of soluble fulvic acids (Roberts et al. 1984; Hedin et al. 1995). Arheimer et al. (1996) found that DON concentrations were weakly correlated to flow volume, and that other unaccounted factors were also important. Lovett et al. (1998) were also unable to identify specific catchment characteristics that would explain stream water DON concentrations in 39 watersheds within the Catskills.

Because of the high percentage of DON in forest floor leachate and the large pool of organic N sequestered in mineral soil, specific edaphic features may be important in controlling stream water DON concentration. We hypothesized that specific landscape positions within the watershed, as defined by different soils, forest types, and bodies of water, significantly affect stream water DON concentrations and fluxes. We used longitudinal stream sampling to estimate NH_4^+, NO_3^-, and DON flux from several landscape positions within a forested watershed and examined the effect of discharge and season on stream DON and DIN concentrations.

2. Methods

2.1 *Site description*

The Arbutus Lake Watershed is 3.52 km^2 and located within the Huntington Wildlife Forest (43°59′ N, 74°14′ W) in the Hudson River drainage basin of the central Adirondack Mountains of New York State, U.S.A. (Figure 1). Mean annual temperature was 4.4 °C and annual precipitation averaged 1010 mm from 1951 to 1980 (Shepard et al. 1989). Total annual precipitation during the study period, June 1, 1995 to May 31, 1996, was 1298 mm; total runoff was 917 mm at the main inlet to Arbutus Lake (Archer Creek: WS1) and 809 mm at the lake outlet. The watershed has 227 m of relief with an average slope of 11%. Arbutus Lake has a mean residence time of 0.6 years and a maximum depth of 8.4 m (Driscoll & van Dreason 1993). Overstory vegetation is composed mainly of northern hardwoods, and conifers dominate around the lake, within riparian zones, and at high elevations. Dominant tree species include *Fagus grandifolia* Ehrh. (American Beech), *Acer saccharum* Marsh. (sugar maple), *Betula alleghaniensis* Britt. (yellow birch),*Picea rubens* Sarg. (red spruce), and *Abies balsamea* (L.) Miller (balsam fir). *Alnus incana* (L.) Moench. (speckled alder) that fixes N was present along Archer Creek within one forested wetland. Approximately 162 ha were selectively cut in and around the Arbutus watershed in the winter of 1960–1961. The management plan called for a clearcut of all softwood areas removing all softwoods greater than 0.18 m diameter at breast height (DBH) and all hardwoods in softwood areas. In northern hardwood stands 60% of the *Betula alleghaniensis* Britt. (yellow birch) volume, 10% of the *Acer saccharum* Marsh. (sugar maple) volume, and 10% of the *Picea rubens* Sarg. (red spruce) volume over 0.3 m DBH was to be removed. A total of 1.5 million cubic meters were removed.

The mineral soils are dominated by coarse, loamy, mixed, frigid, Typic Haplorthods in the Becket-Mundal association while Greenwood Mucky

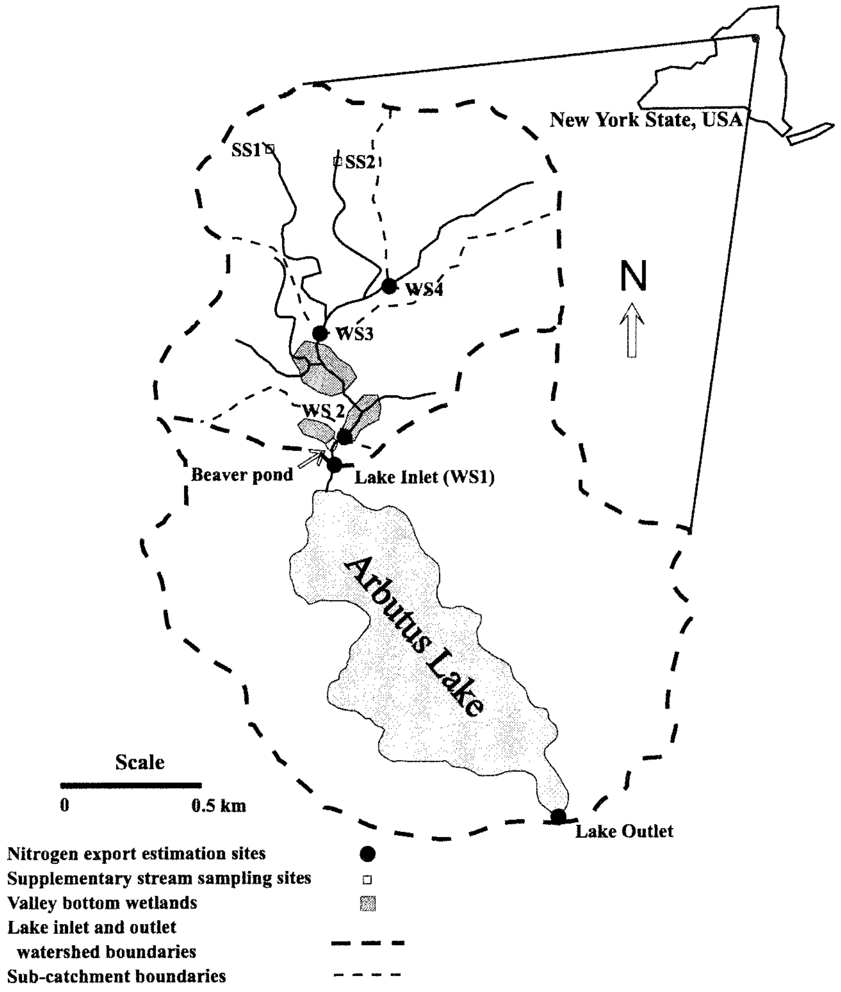

Figure 1. The Arbutus Lake watershed at the Huntington Wildlife Forest in the Adirondack Mountains of New York State.

peats occupy valley bottom wetlands (Somers 1986). The soil depth varies within the watershed, but is typically <1 m and is underlain by a thin bouldery glacial till; bedrock is mainly granitic gneiss with some gabbro-amphibolite. The watershed has no human inhabitants and is 1.6 km from the nearest highway.

Huntington Wildlife Forest has been the site of several biogeochemical studies (Shepard et al. 1989; Foster et al. 1992; Mitchell et al. 1996a), with specific focus on sulfur cycling (David et al. 1987), nitrate loss (Mitchell et al. 1996b), and acidic deposition (Mollitor & Raynal 1982, 1983; Raynal et al. 1991). It was also a site in the Integrated Forest Study (IFS) (Mitchell et al. 1992a, 1992b). Arbutus Lake is one of the fifty-two lakes included in the Adirondack Long-Term Monitoring Project (Driscoll & van Dreason 1993; Driscoll et al. 1995). Huntington Wildlife Forest is also a National Atmospheric Deposition Program (NADP) and National Trends Network (NTN) site. NADP precipitation water chemistry samples were collected weekly at a clearing 1.3 km from the Arbutus Watershed outlet and analyzed for various solutes including NH_4^+ and NO_3^-. A meteorological station located in this clearing measured hourly precipitation.

2.2 *Sampling design*

Stream flow gages were located at WS1 and the outlet of Arbutus Lake. Stage height was recorded hourly at the lake outlet at a V-notch weir installed by the USGS in October, 1990 (elevation 514 m). We installed an HL-flume in January, 1995 at WS1, 50 m upstream from the lake inlet, stage height was recorded at fifteen-minute intervals. The flume was sealed using potters clay and was water tight. Water chemistry samples were collected at four locations along Archer Creek and at the lake outlet (Figure 1) to measure changes in surface water N chemistry. Sites were chosen to assess how differences in edaphic characteristics and the presence of surface water bodies affected stream water N chemistry. The uppermost sampling location (WS4) drained an area of 0.33 km^2, was upstream from all tributaries, and contained no wetlands. WS3 drained an area of 0.62 km^2 and was immediately upstream from a series of wetlands. Changes in surface water chemistry between WS4 and WS3 occurred within the upland area of the watershed. Two small tributaries (SS1 and SS2: Figure 1) that contributed to stream flow between WS4 and WS3 were sampled throughout the study. Position WS2 was located downstream from the series of wetlands and drained an area of 1.25 km^2 (Figure 1). The water-table was within approximately 0.15 m of the wetland surface year-round. Flow across the surface of the wetlands was uncommon and occurred only during snowmelt and large storms. WS2 was approximately 75 m upstream from WS1 and there was a small uninhabited beaver pond ($\sim$100 m^2) between WS2 and WS1. The HL-flume at WS1 drained an area of 1.35 km^2. The total change in elevation between Arbutus Lake outlet and WS4 was 30 m. Water samples were collected biweekly at all sampling locations from 1 June 1995 through 31 May 1996. Daily samples were collected at WS1 during 1996 snow-melt and several storms were sampled using an automatic sampler.

2.3 *Chemical analyses*

Samples were collected in 500 ml opaque, brown, polyethelene bottles. Sample bottles were washed and then rinsed three times in deionized distilled water. The bottles were then soaked for 24 hours in deionized distilled water. Bottles were not acid washed because this can cause contamination with other ions that samples were analyzed for (i.e., chloride). After collection samples were refrigerated in the field until transported to the laboratory. Samples were not filtered to avoid contamination (i.e., chloride) and loss of NH_4^+ through filters (P. McHale, personal communication). Samples were centrifuged to remove particulate matter and the supernatent was decanted for analyses. Samples were stored at 1 °C until analyzed. The mean holding time for NO_3^- and NH_4^+ was 12 days. The mean holding time for TDN was 149 days. The longest holding for any sample during the study was 313 days for two TDN samples, these longer holding times were caused by the need to rerun some samples. Suppressed ion chromatography was used for NO_3^- analyses and NH_4^+ was analyzed using a Wescan Ammonia Analyzer (Shepard et al. 1989). The limit of quanification for NH_4^+ was 0.5 μmol l^{-1}, 28 samples were below the limit and were assigned values of zero. Total dissolved N was determined by persulfate digestion (Ameel et al. 1993). A 50 μmol l^{-1} NO_3^--N standard, 59 μmol $l^{-1}NH_4^+$-N standard, 20 and 10 μmol l^{-1} TDN standards and a 50 μmol l^{-1}L-cysteine standard were used for the TDN digestion. Recovery of TDN and NH_4^+ standards in the TDN digestion was ± 10% the relative standard deviation of the standard. Dissolved organic N was calculated by subtracting DIN (NO_3^- + NH_4^+) from TDN. If NO_3^- + NH_4^+ equaled or exceeded TDN (<3% of all samples) DON was recorded as zero. The lowest value below zero calculated for a DON value was -62.0 μmol l^{-1}, the average of the below zero values was -10.6 μmol l^{-1}. The overall estimate of analytical uncertainty for the DON analyses was ±5–10%.

2.4 *Flux calculations*

Annual and seasonal wet-only inorganic N input was calculated by multiplying volume-weighted mean monthly NADP precipitation chemistry by total monthly precipitation. Nitrogen flux was calculated at WS1 using biweekly stream samples, samples from six storms and approximately daily samples from the 1996 spring melt (11 March through 31 May 1996). Due to the more labor-intensive procedures involved in NH_4^+ and TDN analyses, fewer samples were analyzed for these solutes (n = 128) than for NO_3^- (n = 251). Nonetheless, sufficient NH_4^+ and TDN samples were selected to account for the rising limb, peak, and falling limb of each storm hydrograph and spring melt. Flux was calculated by multiplying total 15-minute water flux

Table 1. Total volume of water exported during each season (m^3) and mean N solute concentrations (μmol l^{-1}) for Arbutus Lake outlet and WS1. 95% confidence intervals of means are in parentheses.

Site	Season Variable	Dormant	Growing
Outlet	Flow	2.5×10^6 m^3	2.6×10^5 m^3
	NH_4^+	2 (1.0)	2 (0.3)
	NO_3^-	11 (5.2)	2 (1.0)
	DON	15 (7.6)	15 (1.7)
WS1	Flow	1.1×10^2 m^3	1.1×10^5 m^3
	NH_4^+	1 (0.5)	1 (0.3)
	NO_3^-	23 (6.6)	11 (2.5)
	DON	10 (3.2)	19 (4.7)

by concentration and dividing by the watershed area. Concentrations were linearly interpolated between sample intervals. Since storm sampling was not possible at all sampling locations, N solute fluxes for each landscape position were calculated using biweekly samples. Daily N concentrations were linearly interpolated between biweekly sample points and multiplied by daily water flux. Discharge at landscape positions WS2, WS3, and WS4 was estimated by prorating the discharge at WS1 by their respective drainage areas.

2.5 *Delineation of seasons and statistical methods*

The dormant season was defined as 1 October–31 May and the growing season as 1 June–30 September. Previous investigations at this site defined the growing season from 1 May–30 September, approximating the time from bud-break to leaf abscission (Shepard 1989; Mitchell 1996b). During the spring of 1996 significant snowfall was recorded on 6 May (Huntington Wildlife Forest unpublished meteorological data). Thus, we have chosen to include May as part of the dormant season. We have chosen to define the water-year the same as that used for Hubbard Brook Experimental Watershed in New Hampshire, 1 June–31 May (Likens & Bormann 1995). Hubbard Brook has a similar climate and hydrological properties to those of the upland watersheds of the Huntington Wildlife Forest, but a much longer record of stream flow (Scott 1987; Likens & Bormann 1995).

Discharge was regressed against N concentrations for different flow conditions (base flow, increasing flow, and decreasing flow) and seasons (dormant and growing seasons). Regression analyses were restricted to the lake outlet and WS1 where actual discharge measurements were recorded. Regressions included transformed (logarithmic) and untransformed discharges and concentrations (P values ≤ 0.05 were considered significant). Annual and seasonal flow-weighted mean concentrations of NH_4^+, NO_3^-, and DON were calculated for all locations. In addition, flow-weighted mean concentrations at baseflow, increasing flow, and decreasing flow and high flow and low flow conditions were calculated for the lake outlet and WS1. The significance of differences between means was tested using Student's two-tailed *t*-test assuming unequal variances at a significance level of $\alpha = 0.05$.

3. Results and discussion

3.1 *Event-based flux estimates*

Previous work has demonstrated that more intensive sampling can improve estimates of NO_3^- flux (Swistock et al. 1997). Event-based N flux estimates were compared to biweekly estimates at WS1 to determine if flux calculations were affected by increased sampling. The TDN flux at WS1 was 345 mol ha^{-1} yr^{-1} using event-based and biweekly sampling and 349 mol ha^{-1} yr^{-1} using only biweekly sampling. Although the two methods gave very similar results for annual TDN flux, the results were less similar for each N chemical species (Figure 2). Nitrate and NH_4^+ fluxes calculated using event based sampling were greater than those calculated using only biweekly samples (10 and 4 mol ha^{-1} yr^{-1} respectively) and DON flux was 18 mol ha^{-1} yr^{-1} less including event samples. Although these results support the findings of Swistock et al. (1997), it is not clear that these small changes in flux (relative to total annual flux) are ecologically significant. Additional years of data could help to address this question.

3.2 *Nitrogen retention and flux*

Neither dry deposition nor wet DON deposition were measured during the period of this study. Previous estimates from 1 May 1986 to 30 April 1988 indicated that 55% of NO_3^- and 12% of NH_4^+ was deposited as dry deposition at this site (Shepard et al. 1989). DON concentrations in precipitation can amount to 25 to 50% of inorganic N deposition (Manny & Owens 1983; Altwicker et al. 1986; Linsey et al. 1987). Using wet-only estimates of inorganic N deposition, 75% of inorganic N inputs were retained at the lake

Table 2. Solute concentration (μmol l^{-1}) versus discharge (mm hr^{-1}) at Arbutus Lake inlet (WS1 in Figure 1) and outlet. Only significant regression results are shown, regression equations are shown in parentheses. Negative relationships are shown in italics.

	R^2 of regression model ($P < 0.05$)			
	NO_3^-		DON	
Flow/season	Inlet	Outlet	Inlet	Outlet
Base flow	0.05 (y = 81x + 13)	0.56 (y = 285x − 1.5)	–	–
Increasing flow	–	–	0.44 (y = 7x + 13)	0.1 (y = 33x + 11)
Decreasing flow	0.12 (y = 19x + 17)	–	0.08 (y = 5x + 14)	–
Growing season	*0.29 (y = −13x + 9)*	–	0.09 (y = 10x + 13)	–
Dormant season	–	–	0.31 (y = 7x + 12)	0.05 (y = 19x + 11)

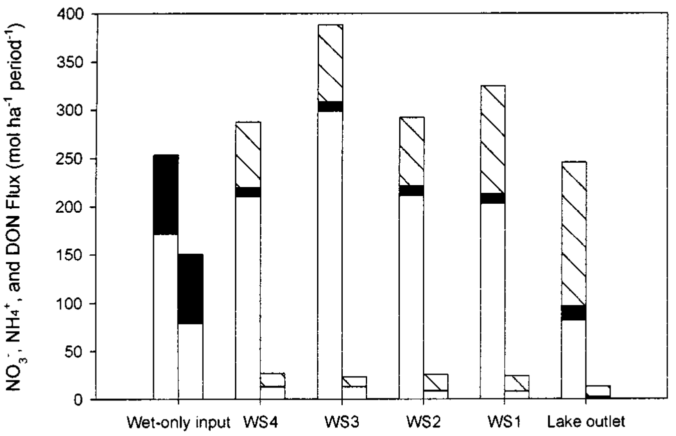

Figure 2. Annual and seasonal wet-only N solute input from the National Atmospheric and Deposition Program site at the Huntington Wildlife Forest and N solute fluxes from the Arbutus Lake outlet and sampling locations WS1-WS4 (in mol ha^{-1} period^{-1}). Dormant season fluxes are shown to the left of each location, growing season fluxes are to the right. Clear bars are NO_3^-, solid bars are NH_4^+, diagonally hatched bars are DON.

outlet and 45% were retained at WS1 (Figure 2). Including DON as part of N drainage estimates reduced N retention to 36% at the lake outlet and 13% at WS1. These results support the suggestion by Hedin et al. (1995) that determination of whether a watershed is “leaking” N may depend upon whether DON is included in N fluxes.

The proportion of DON in TDN flux varied both spatially and seasonally. At the lake outlet DON, NO_3^-, and NH_4^+ accounted for 61%, 33%, and 6% respectively of annual TDN flux (259 mol ha^{-1} yr^{-1}) (Figure 2). Dissolved organic N was 36%, NO_3^- 61%, and NH_4^+ 3% of annual TDN flux (349 mol ha^{-1} yr^{-1}) at WS1 (Figure 2). The greatest changes in annual DIN flux between sites occurred within Arbutus Lake (Figure 2). During the dormant season DON was the major component of TDN flux at the lake outlet (61%) while NO_3^- accounted for most TDN upstream from the lake (63 to 77%) (Figure 2). During the growing season DON was the major component of TDN flux at the lake outlet (79%), WS1 (64%), and WS2 (64%).

On an annual basis the watershed changed from a NO_3^- dominated system to a DON dominated system through Arbutus Lake. This was mainly due a decrease in NO_3^- concentration, although DON did increase through the lake. The decrease in NO_3^- concentration occurred during both the dormant and growing seasons. One possible reason for the decrease is dilution from low NO_3^- groundwater and tributaries to the lake. No estimate of groundwater influx to the lake was made and none of the smaller tributaries to the lake were sampled. The NO_3^- concentration of groundwater within WS1, as represented by groundwater spring SS2, was significantly higher (two tailed *t*-test, $\alpha = 0.05$) than stream water at WS1 (mean annual concentrations of 67 μmol l^{-1} with a 95% confidence interval (C.I.) of 5.1, and 25 μmol l^{-1}, C.I. = 2.1 respectively). Mean annual NO_3^- concentration was also higher, though not significantly, at groundwater spring SS1 (26 μmol l^{-1}, C.I. = 2.6). Means were not volume weighted because no flow measurements were available for SS1 and SS2. There are only four small tributaries to Arbutus Lake in addition to Archer Creek, and though they were not gauged, they only drained a combined area of 27 ha. It is unlikely that they contributed a significant amount of runoff to the lake. Consequently, dilution is probably not responsible for the decrease in NO_3^- through Arbutus Lake. Other possible causes of decreased NO_3^- flux through Arbutus Lake include denitrification within the water column during the dormant season and from lake sediments year-round, along with algal and bacterial uptake and assimilation (Ahlgren 1994).

An increase in DON concentration occurred within Arbutus Lake during the dormant season. There are two likely sources for this increase, (1) conversion of inorganic to organic nitrogen through algal and bacterial uptake and assimilation (Ahlgren et al. 1994), and (2) flushing of DON from lake sediments during lake turnover. Arbutus Lake is dimictic, it turns over in the spring and fall (Owens 1995), that could allow DON to be flushed from lake sediments; however, we have no direct evidence that this was the cause of increased DON flux. Therefore, further study is required to test this hypothesis.

The greatest seasonal change in NO_3^- flux occurred within the upland area of the watershed between WS4 and WS3 (Figure 2). During the dormant season, there was an increase of 88 mol ha^{-1} between the two sites. During the growing season there was no increase between these sites. Two groundwater springs (SS1 and SS2) contributed NO_3^- between WS4 and WS3. The mean annual NO_3^- concentration was significantly greater (two tailed *t*-test, $\alpha = 0.05$) at SS1 (26 μmol l^{-1}, C.I. = 2.6 μmol l^{-1}) and SS2 (67 μmol l^{-1}; C.I. = 5.1μmol l^{-1}) than at WS4 (20 μmol l^{-1}; C.I. = 4.5 μmol l^{-1}). Again, the means were not flow-weighted. Evidence of groundwater sources of NO_3^- to stream flow has also been reported for the Turkey Lakes Watershed in south-eastern Canada (Creed et al. 1996) and in the Catskill Mountains of New York State, U.S.A. (Burns et al. 1998). Mineralization and nitrification of organic nitrogen within the stream could also have contributed to the increase. The lack of an increase in NO_3^- concentration during the growing season is likely due to in-stream biotic uptake and denitrification (Burns 1998; Triska et al. 1993; Duff & Triska 1990).

DON flux did not increase as the stream passed through the wetlands (from WS3 to WS2: Figure 2) as might be expected due to erosional losses of peat and eluviation of fulvic acids (Roberts et al. 1984). Because flow across the surface of the wetlands was uncommon and stream channels through the wetlands are incised to an average depth of 0.5 m erosional loss of peat is unlikely except during large storms. Hydraulic conductivity was measured at depths of 0.5, 1.5, and 2.5 m in five piezometer nests within the wetlands and averaged 2×10^{-4} m s^{-1} (C.I. = 1.9×10^{-4} m s^{-1}). Therefore, it is unlikely that large volumes of groundwater were contributed to stream flow through the wetlands.

There were large seasonal differences in N flux for all N solutes (Figure 2). Both the concentration of each solute and the amount of flow affect these differences. At both sites the reduction in NH_4^+ and DON flux during the growing season was a result of the lower flow volume (Table 1). For NO_3^- a combination of both lower flows and lower concentrations caused the decrease in flux (Table 1).

3.3 *Relationships between N solute concentrations and discharge*

Flow based regressions

Regressions without logarithmic transformations had the lowest residuals so only those results are reported (Table 2). No significant relationships were detected between NH_4^+ and any flow conditions at WS1 or the lake outlet. Positive relationships were found between NO_3^- concentration using all flow data, base flow data, and decreasing flow data at WS1 (Figure 3(A)). For DON concentrations, positive relationships were found using all flow data, increasing flow data, and decreasing flow data (Figure 3(B)). A positive relationship was detected between NO_3^- concentrations and base flow at the lake outlet (Figure 3(C)). There were significant relationships between DON concentration using all flow data and during periods of increasing flow at the lake outlet (Figure 3(D)).

Using all flow data from WS1, discharge accounted for 26% of the variability in DON concentration while during increasing flow discharge accounted for 44% of DON variability. The positive slope for DON discharge-concentration relationships during increasing flow conditions suggests that stream water DON concentration exhibited a flushing response similar to that described for dissolved organic carbon (DOC) by Hornberger et al. (1994). Arheimer et al. (1996) also reported significant correlations between DON concentration and flow in 71% of the catchments they investigated.

At the lake outlet, NO_3^- concentrations versus discharge at baseflow had the only significant relationship with $R^2 > 0.1$ (Figure 3(C)). Runoff during baseflow at the outlet ranged from 0.0005 to 0.08 mm hr^{-1}. Consequently,

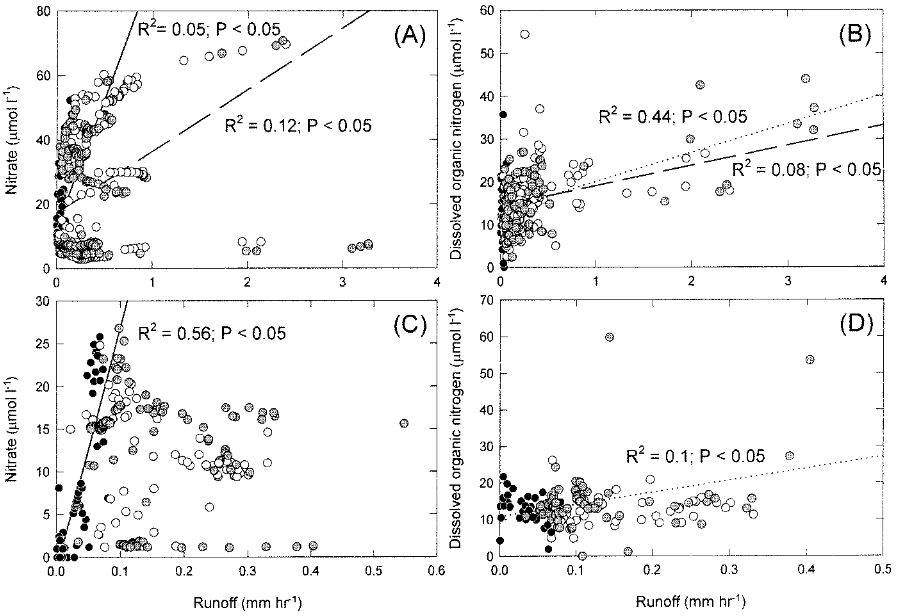

Figure 3. Solute concentration versus discharge rates at Arbutus Lake inlet (WS1) (A) NO_3^- and (B) DON and Arbutus Lake outlet (C) NO_3^- and (D) DON. Only significant regression lines are shown ($P \leq 0.05$). Significant baseflow regressions are indicated by a solid line, increasing flow with a dashed line, decreasing flow with a dotted line. Solid circles are for baseflow, shaded circles are for increasing flow, and open circles are for decreasing flow.

though the relationship accounts for 56% of the variability in NO_3^- concentration, it did not have a large impact on the overall NO_3^- flux. The lack of a significant regression between flow and NO_3^- concentration at WS1 is due to a dichotomous response of NO_3^- to flow (Figure 3(A)). During two early winter melt events there was a strong positive relationship between NO_3^- concentration and runoff ($R^2 = 0.76$; $P < 0.01$; y = 14.8x + 39.4). In contrast, during two autumn storms, though the range in runoff was similar to the winter melts, there was very little change in NO_3^- concentration. These results emphasize the difficulty of predicting stream water N concentrations; flow accounts for only a small percentage of the variability of any of the N species concentrations. Stream water N concentration is affected by mineralization and nitrification, denitrification, and uptake, as well as flow pathways and flow volume. Mineralization, nitrification, and uptake can vary significantly with landscape position and season at this site (Ohrui & Mitchell 1998; Bischoff et al. 1998) and denitirification rates have been shown to be dependent upon soil moisture conditions, available NO_3^- and available carbon (Paul & Clark 1989). All of these factors can contribute to the variability of stream water N

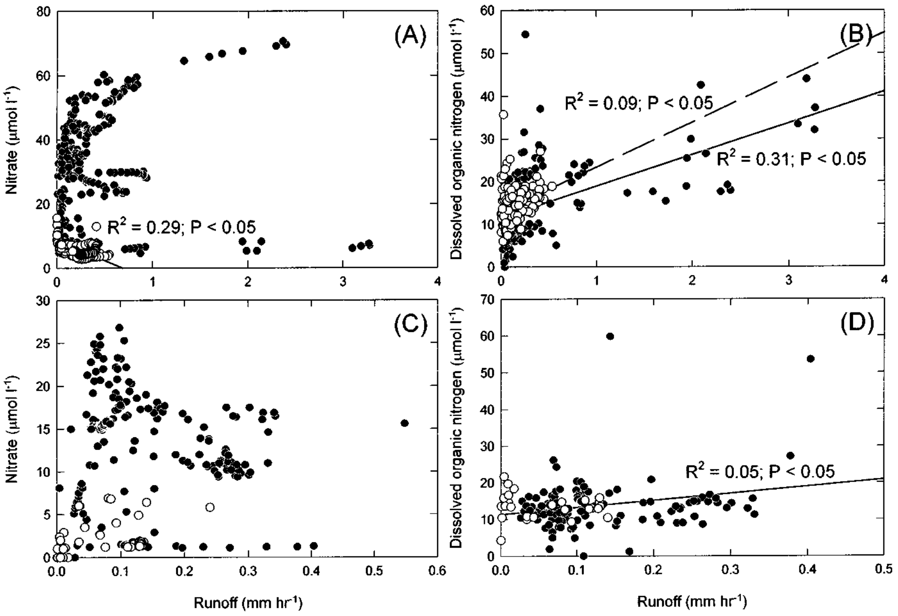

Figure 4. Solute concentrations during the dormant (solid circles) and growing (open circles) seasons versus discharge rates at Arbutus Lake inlet (WS1) for (A) NO_3^- and (B) DON and at Arbutus Lake outlet (C) NO_3^- and (D) DON. Only significant regression lines are shown ($P \leq 0.05$). Significant growing season regressions are shown as a solid line, dormant season as a dashed line.

concentration and help to explain the low amount of variability accounted for by flow alone.

Seasonal regressions

To attempt to incorporate some of the biotic factors that influence stream water N concentrations, additional regressions were completed based on a seasonal separation (Table 2). No relationships between discharge and NH_4^+ concentration were detected at WS1 for either season. A negative relationship between discharge and NO_3^- concentration was evident for the growing season (Figure 4(A)). Positive relationships were detected at WS1 between discharge and DON concentration during both the dormant and growing seasons (Figure 4(B)). However, R^2 was greater for the dormant season. At Arbutus Lake outlet there were no significant relationships between discharge and NH_4^+ or NO_3^- concentrations during either the dormant or growing season (Figure 4(C)). A positive relationship between discharge and DON concentration was found for the dormant season at the lake outlet (Figure 4(D)).

Regression analyses for the dormant and growing seasons suggest that DON concentrations were less affected by season than NO_3^- concentrations (Figure 4). The relationship between discharge and DON concentration was positive throughout the year at WS1. There was no relationship between NO_3^- and discharge during the dormant season at WS1, and the relationship was negative during the growing season (Figure 4). Mean dormant season flow-weighted NO_3^- concentration was 22 μmol l^{-1} higher than that during the growing season at WS1. For DON the difference was 2 μmol l^{-1}. These results show that the shift in the dominant form of TDN flux at WS1 from NO_3^- to DON during the growing season was a result of a decrease in NO_3^- concentration rather than an increase in DON concentration. The decrease in NO_3^- during the growing season can be attributed to the greater biotic demand for N during this period. Other studies have also documented a marked decrease in stream NO_3^- concentrations during the growing season (Mitchell et al. 1996b; Arheimer et al. 1996; Stoddard 1994; Murdoch & Stoddard 1993). On an annual basis, biotic activity as expressed by season seems to be the most important factor in affecting NO_3^- concentration (Murdoch & Stoddard 1993; Stoddard 1994; Arheimer et al. 1996; Mitchell et al. 1996b), the influence of biotic activity on DON concentration was less evident.

Additional flow-based regression analyses were completed for each season at WS1 only. There were too few samples for each flow condition to complete the analyses at the lake outlet. For NO_3^-, at baseflow conditions during the growing season there was a negative relationship between concentration and flow ($R^2 = 0.46$; $P < 0.01$; $y = -58.8x + 12.0$). This relationship supports the evidence presented in section 3.2 of groundwater as a source of stream water NO_3^-. At baseflow as discharge decreased, and presumably the contribution of groundwater increased, NO_3^- concentration also increased. In contrast, there was a positive relationship between flow and NO_3^- concentration at baseflow conditions during the dormant season ($R^2 = 0.38$; $P < 0.01$; $y = 225x + 14.3$). During the dormant season NO_3^- is likely contributed from soil water as well as groundwater because the demand from the biota has decreased. Therefore, an increase in stream flow due to an increase in the soil water contribution would result in an increase in stream water NO_3^- concentration. In the Catskill Mountains of New York State, a similar system has been described in which summer stream flow is sustained by high NO_3^- concentration groundwater while during spring melt NO_3^- is contributed from both groundwater and soil water (Burns et al. 1998). The only other significant relationship that resulted from these analyses was a positive relationship between increasing flow conditions and DON concentration during the dormant season ($R^2 = 0.51$; $P < 0.01$; $y = 7.36x + 11.9$). These results indicate that the flushing response of DON described earlier is confined to the dormant season. This is probably true because there is a wider range of flows during the dormant season (0.00475–3.28 mm hr^{-1} during the dormant season compared to 0.00134–1.07 mm hr^{-1} during the growing season at WS1) than during the growing season. Consequently, there is likely more flux of DON due to erosion and flushing of soil humic substances.

4. Conclusions

This study supports the conclusions of Arheimer et al. (1996) and Swistock et al. (1997) that failure to sample throughout the range of flow conditions that occur at a site can result in less accurate N flux estimates. Nevertheless, our results were not as convincing as those reported for the earlier studies, perhaps due to the length of sample collection (1 year). It is clear, however, that confining sampling to limited flow conditions (i.e. baseflow) can result in less accurate estimates of N flux.

There were significant differences in N flux between sampling sites, most notably within Arbutus Lake. The watershed changed from a NO_3^- dominated system at WS1 to a DON dominated system at the lake outlet. Extensive N cycling within lakes has been documented in several studies (McCarty et al. 1982; Seitzinger 1988; Ahlgren et al. 1994). Consequently, interpretations of N cycling and N saturation based on lake outlet chemistry may not provide a clear indication of the status of N saturation of upland areas of watersheds. The amount of impact that a lake may have on surface water chemistry is dependent on factors such as its depth, residence time, geologic setting, and rates of biogeochemical cycling (Driscoll & van Dreason 1993; Ahlgren et al. 1994; Driscoll et al. 1995). Interpretations of N cycling based on surface water chemistry need to consider the roles of lakes, particularly in the Adirondack Mountains where lakes are common landscape features.

Another significant spatial difference in N flux was an increase in NO_3^- flux between WS4 and WS3. Higher NO_3^- concentrations from two groundwater springs that contribute to flow between WS4 and WS3 suggests that groundwater is the source of this additional NO_3^-. This conclusion is supported by results from regression analyses. There was a significant negative relationship between NO_3^- concentration and flow during baseflow at WS1 that implies that as flow decreases, and presumably the contribution of groundwater to stream flow increases, NO_3^- concentration also increases. Burns et al. (1998) presented evidence for a groundwater source of NO_3^- in three Catskill Mountain watersheds in New York State, U.S.A. They used hydrologic budgets to identify times of watershed recharge and residence time modeling to identify flow paths that allowed NO_3^- rich snow melt to recharge deep groundwater and supply NO_3^- to the stream during baseflow. In the Turkey Lakes watershed in Ontario, Canada Creed et al. (1996) used an N flushing index to identify an NO_3^- draining mechanism, where NO_3^- in snow melt is transferred to deeper groundwater and released slowly throughout the year. Burns et al. (1998) concluded that due to the proposed flowpaths, high baseflow concentrations of NO_3^- during the growing season does not provide sufficient evidence that those watersheds have reached N saturation.

Dissolved organic N was positively related to flow during increasing flow, suggesting that DON exhibits a flushing response similar to that reported for DOC by Hornberger et al. (1994). Hedin et al. (1995) found variations in DON to be positively correlated with DOC in 31 watersheds in southern Chile. They attributed the similarity in response to a link between DON losses and leaching of soil humic substances. Our results support the idea that there is less of a biological control on DON loss than is apparent for inorganic N loss. DON was positively related to flow during both the dormant and growing seasons and there was no significant difference in volume weighted DON concentration between seasons. Our regression results were similar to those of Arheimer et al. (1996), in that they explained only a small amount of the variability in DON concentration. Notwithstanding, there were large differences in DON flux between sampling sites, future research focused on controls of leaching losses of soil humic substances might help to explain more of the variability in watershed DON loss.

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