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Hydrologic and biotic control of nitrogen export during snowmelt: A combined conservative and reactive tracer approach

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[1] Dissolved inorganic nitrogen (DIN) and dissolved organic nitrogen (DON) stored in the snowpack are important sources of N in snow-covered ecosystems, yet we have limited knowledge of their fate during the melt period. Our objective was to quantify the role of hydrologic and biogeochemical processes in regulating stream fluxes of DIN (NO_3^- + NH_4^+) and DON in a forest-dominated and a wetland-dominated catchment during the snowmelt period. We combined isotopic hydrograph separation with concurrent measurements of meltwater DIN and DON to calculate "conservative" N export (hydrologic mixing only) and compared it with "reactive" N export (i.e., observed fluxes that include biogeochemical processes). On balance, N was retained in the catchments during snowmelt because of storage of meltwater N in soils, but our N export comparison revealed N generation (mostly as DON) from the mobilization of dissolved organic matter. In contrast, NO_3^-, which was highly enriched in snowpack meltwater, remained below detection in streams, and both catchments were sinks for NO_3^-, suggesting that denitrification and/or uptake may be important at the catchment scale. Over the melt period, the forest catchment was a greater total N source because of the convergence of lateral flow and near-stream riparian N sources in surface soils, which elevated stream DON and to a lesser extent NH_4^+. In contrast, preferential flow in the wetland catchment tended to dilute DIN in saturated peatland soils and in the stream, whereas DON varied little over time. These findings highlight the importance of hydrologic processes that store meltwater N in catchment soils but at the same time deliver DON from riparian sources to the stream. Further, model results suggest that biotic uptake and/or sorption effectively retain much of the meltwater DIN from the snowpack. Collectively, hydrologic storage and biogeochemical processes act to retain N that is likely important for boreal ecosystem production later in the spring and summer seasons.

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1. Introduction

[2] Catchment nitrogen loss or retention during snowmelt is influenced by the nitrogen content of the snowpack, nitrogen sources and sinks in the catchment, and hydrologic flow paths that deliver meltwater and soil nitrogen to the stream. For many years, studies concerning nitrogen cycling in catchments focused on inorganic nitrogen. More recently, it has been recognized that dissolved organic nitrogen (DON) is often the majority of the total nitrogen load in streams [*Hedin et al.*, 1995; *Kortelainen et al.*, 1997; *Campbell et al.*, 2000; *Hood et al.*, 2003], and DON can be an important source of N for stream ecosystems [*Brookshire et al.*, 2005; *Kaushal and Lewis*, 2005].

[3] The degree of hydrologic or biogeochemical influence on nitrogen flux differs between inorganic and organic forms of N. For instance, ionic enrichment of snowpack meltwater may increase stream dissolved inorganic nitrogen (DIN) concentrations, particularly nitrate [*Williams and Melack*, 1991; *Campbell et al.*, 1995; *Williams et al.*, 1995; *Brooks et al.*, 1998]. Stream DIN may remain constant or decline as DIN from the snowpack is attenuated by microbial immobilization and denitrification [*Brooks et al.*, 1996; *Stottlemyer and Toczydlowski*, 1996], or nitrate is diluted by the influx of low-DIN meltwater [*Petrone et al.*, 2006]. In many catchments, DON concentrations increase with flow during snowmelt [*Kaushal and Lewis*, 2003, 2005], and the greatest concentration may precede the hydrograph peak, indicating that organic matter sources are flushed from soils [*Hornberger et al.*, 1994].

[4] Currently, we know little about the role of snowpack chemistry, biotic processes, or hydrologic flow paths in delivering DIN and DON to streams in northern latitudes. However, previous research has shown that DOC dynamics in the spring flood are related to hydrologic flow paths that differ with wetland coverage [*Bishop and Pettersson*, 1996;

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Bishop et al., 2004; *Laudon et al.*, 2004a], suggesting that DON export may also be related to the extent of wetlands. Across a range of ecosystems, wetland coverage is a major factor in determining carbon and nitrogen dynamics, with wetlands serving as a sink for inorganic nitrogen [*Hill*, 1996; *Lepisto et al.*, 2004], a source of organic carbon [*Mulholland and Kuenzler*, 1979], and a source of organic nitrogen [*Pellerin et al.*, 2004]. In northern Scandinavia, wetlands cover more than one quarter of the land area (Swedish National Forest Inventory, http://www-nfi.slu.se). Therefore, in order to predict how climate change or N deposition may affect the nitrogen balance of high-latitude ecosystems and receiving streams, it is necessary to understand how hydrologic and biogeochemical processes in wetland and forest ecosystems influence nitrogen loss and retention during snowmelt.

[5] In boreal watersheds of northern Sweden, the four week period of snowmelt provides nearly 50% of the annual runoff and a majority of the annual flux of carbon and nutrients to streams [*Laudon et al.*, 2004a]. Furthermore, future changes in the duration of snow cover, the depth of the snowpack, and its accumulation of carbon and nutrients are likely sensitive to changes in winter climate and present dynamics are poorly understood. Snowmelt provides an ideal time to examine linkages between terrestrial and aquatic ecosystems because from the onset of snowmelt it is possible to quantify isotopic signatures and volumes of meltwater entering soils and transported to streams. Two-component isotopic hydrograph separation (IHS) has been used widely to separate flow sources (event and preevent flow contributions) in snowmelt-dominated systems [*Hooper and Shoemaker*, 1986; *McNamara et al.*, 1997; *Laudon et al.*, 2002] while other studies have combined the IHS approach with geochemical tracers and hydrometric measurements to identify flow sources as well as hydrologic pathways [*Laudon et al.*, 2004b; *Liu et al.*, 2004]. More recently, isotopic techniques have been used to differentiate between atmospheric and soil sources of NO_3^- [*Ohte et al.*, 2004; *Piatek et al.*, 2005], and various catchment sources of dissolved organic matter [*Hood et al.*, 2003]. To date, however, few studies have quantified how hydrological processes influence sources and sinks of both DIN and DON during the snowmelt period.

[6] Our objectives in this study were to (1) obtain a snowmelt period N input/output budget for two headwater boreal catchments, one forested and one wetland-dominated, (2) develop an IHS-based method to differentiate between N fluxes due to hydrological processes and N transformations due to biogeochemical processes, and (3) use this method coupled with soil and groundwater chemistry measurements to compare the apparent processes controlling N cycling between the two catchments. This approach is unique and informative because it allows us to differentiate the impact of hydrologic processes from biogeochemical processes. We interpret hydrologic processes to be those involving only movement and mixing of water, including storage and release, carrying N with it. Biogeochemical processes in contrast are indicated by changes in concentration or form of N beyond that due to hydrologic mixing, and may include microbial mineralization, microbial or vegetative uptake or release, or mineral soil absorption. In this context, we will refer to "conservative" N export, calculated from N input from the snowpack and mixing of meltwater with stored catchment water, and "reactive" or observed N export throughout the text.

[7] Prior research in the Krycklan catchment in northern Sweden has identified water sources and hydrologic flow paths [*Laudon et al.*, 2002, 2004b] and how these flow paths influence DOC flux during snowmelt in forested and wetland catchments [*Bishop et al.*, 2004; *Laudon et al.*, 2004a]. *Bishop et al.* [2004] reported that a rising groundwater table and lateral flow to the stream mobilize DOC in the riparian zone of the forest catchment. This is in contrast with flow paths in the wetland catchment that show DOC dilution during snowmelt likely from the influx of low-DOC meltwater [*Laudon et al.*, 2004a]. Given these catchment DOC dynamics, we hypothesized that the forest catchment would be an overall greater source of DON compared to the wetland catchment. Lastly, since DIN is readily utilized in N-limited forests of northern Sweden [*Binkley and Högberg*, 1997], we predicted that inorganic N, particularly less mobile NH_4^+ ions, would be retained during snowmelt.

2. Site Description

[8] This study is part of a multicollaborator project in the 67 km^2 Krycklan catchment approximately 50 km from the Baltic sea coast. The subcatchments used in the current study are located within Vindeln Experimental Forests (64°14′N, 19°46′E). Elevation ranges from 250 to 305 m above sea level, mean annual air temperature is near 1°C, and mean annual precipitation is 600 mm with an average of 325 mm of runoff [*Ottosson Löfvenius et al.*, 2003]. Annual nitrogen deposition is estimated at $\sim$3 kg ha^{-1} yr^{-1} [*Forsum et al.*, 2006]. Vegetation is mainly Norway spruce (Picea abies) in wet areas and Scots pine (Pinus sylvestis) on drier soils. Podzols have developed above glacial till that extends to gneissic bedrock 10–15 m below. Peat deposits up to 1 m deep are found in riparian areas close to the stream. In this study, we focused on two first-order stream catchments differing in wetland coverage. The forest catchment Västrabäcken is 13 ha and 100% forested, whereas the wetland catchment Kallkällsmyren is 19 ha, containing 40% wetland and 60% forest (Figure 1). The wetland is slightly sloping and at its upper end contains an open stand of Scots pine with dwarf shrub understory. The lower portion of the wetland at the stream outlet is treeless and covered with sedge cotton grass.

3. Methods

[9] Stage height was recorded hourly throughout the spring flood (March through May 2004) at two 90° plate weirs using WT-HR height loggers (TruTrack Inc., New Zealand). Manual discharge measurements were taken periodically throughout the spring flood to establish rating curves that were used to convert stage height to discharge. Stream water samples were collected weekly or biweekly during late winter and early summer and approximately every second day during the 5-week period encompassing spring flood (13 dates total). Stream chemistry samples were filtered using 0.45 μm MCE membrane filters within 24 hrs, transferred into 18 ml high-density polyethylene vials, and frozen until analysis.

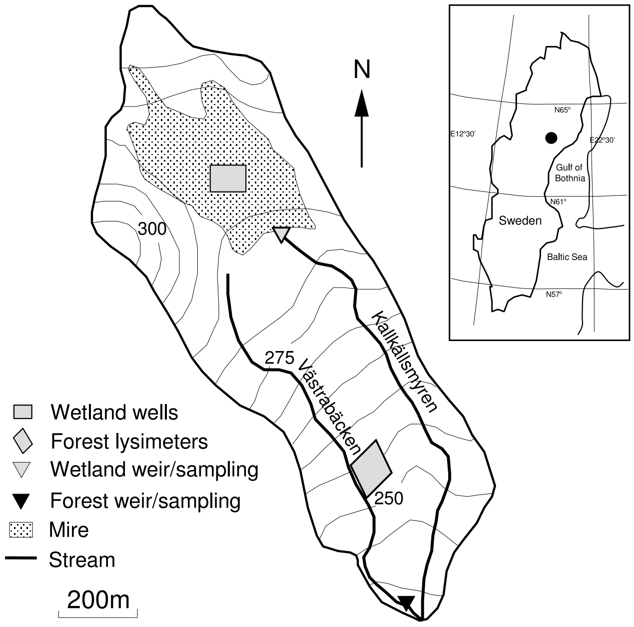

Figure 1. Map of the Västrabäcken (forest) and Kallkällsmyren (wetland) catchments.

[10] Three triplicate sets of snow lysimeters (1.44 m^2) were installed in 1997 and restored in the fall of 2003 at three plots: pine forest, spruce forest and open field. Meltwater was collected in plastic bags on sixteen occasions, every day during peak melt and less frequently during low melt periods. Bags were weighed to obtain the meltwater volume, and transferred to prerinsed HDPE bottles in the field. Lysimeter chemistry samples were filtered and stored in the same way as the stream chemistry samples. Samples for $\delta^{18}O$ were stored in 25ml glass bottles free of headspace and refrigerated before analysis. Replicates within plots were analyzed separately for chemistry, but replicates were pooled for $\delta^{18}O$. On two dates, lysimeters were analyzed separately and differences between replicates were not significant, with an average standard deviation of 0.35‰. $\delta^{18}O$ was analyzed on a Delta plus mass spectrometer using CO_2-water equilibration with reproducibility better than 0.2‰.

[11] Forest soil samples and wetland peat samples were obtained for water extractable NO_3^-, NH_4^+, DON, DOC and total N in October 2004 two weeks prior to soil freezing. In the forest catchment, we used a 5 cm diameter soil coring device and obtained three replicate soil cores in an upland site (20m from the stream) and a riparian site (2m from the stream). In the upland site, we collected cores at three depths: 0–5 cm, 5–15 cm, and 15–40 cm, and in the riparian site, soil samples were collected from 0–10 cm, 10–20 cm, 20–30 cm, and 30–50 cm. In the wetland catchment, we used a peat corer [*Jowsey*, 1966], consisting of a 5 × 5 × 50 cm chamber, to obtain three replicate cores and sampled peat at depths of 200–250 cm, 250–300 cm and 300–350 cm. Cores were taken at the margin of the wetland near the stream outlet.

[12] Nested wetland wells with closed bottom, perforated at the lower 10 cm, were installed 1996 at 75, 100, 125, 150, 175, 200, 225, 250, 300, and 350 cm depth. We obtained samples from each well depth on five dates between 5 April and 30 May 2004. In the forest catchment, we obtained soil solution samples from riparian zone suction lysimeters, installed in 1996, and located 4m from the stream. Lysimeters were located at seven depths: 5, 15, 25, 35, 45, 55, and 65 cm. A 50 psi vacuum was applied to lysimeters a day prior to sampling and the initial volume was discarded prior to collecting samples from the lysimeters.

[13] An autoanalyzer was used to measure NO_3^- by cadmium reduction [*Solorzano*, 1969], and NH_4 by the phenol-hypochlorite method [*Wood et al.*, 1967]. DOC was measured as nonpurgeable organic carbon on a Shimadzu TOC-V_{PCH} analyzer. A persulfate oxidation was used to convert all dissolved nitrogen to NO_3^- and DON was calculated as the difference between total nitrogen and nitrate. Selected DON samples were also run on a Shimadzu TOC-V_{PCH} analyzer equipped with N_2O detector. We found good agreement between the persulfate oxidation and DON combustion techniques ($r^2 = 0.88$, $p < 0.0001$).

3.1. Hydrologic Model

[14] A two-component isotopic hydrograph separation (IHS) was performed using event and preevent water sources that is based on the mass balance of water and hydrologic tracers (equation (1)).

$$Q_s\,C_s = Q_p\,C_p + Q_e\,C_e \tag{1}$$

where Q is discharge and C is the ratio of oxygen 18 ($\delta^{18}O$) in per mil (‰) variation with respect to a standard. The subscripts s, p, and e refer to stream water (sampled runoff water), preevent water (water in the catchment prior to the event), event water (melt or rainwater), respectively. We measured discharge and $\delta^{18}O$ signature in stream water (Q_e and C_e) as well as event water volume and $\delta^{18}O$ signature in snow lysimeters (Q_e and C_e). Finally, we used an average base flow stream $\delta^{18}O$ for the preevent signature (C_p), and we solved for the event water discharge (Q_p) on an hourly time step. We linearly interpolated between dates when $\delta^{18}O$ was measured in stream and lysimeters.

[15] In order to account for the timing and volume of meltwater entering soil and surface soils, we used the runCE model proposed by *Laudon et al.* [2002, 2004b]. This model refines the $\delta^{18}O$ value of the event water component by incorporating a time lag between melting snow collected in snow lysimeters, its storage in soils, and discharge into the stream during the spring flood. At each step a volume weighted, runoff-corrected $\delta^{18}O$ value is calculated for the event water component (equation (2) [*Laudon et al.*, 2002].

$$\delta^{18}O_e(t) = \left(\sum_{i=1}^{t} M(i)\delta^{18}O_m(i) - \sum_{i=1}^{t} E(i)\delta^{18}O_e(i)\right) \bigg/ \left(\sum_{i=1}^{t} M(i) - \sum_{i=1}^{t} E(i)\right) \tag{2}$$

where M(i) is the incrementally collected meltwater (or rainwater) depth, and E(i) is the incrementally calculated event water discharged (equation (1)). $\delta^{18}O_e(i)$ and $\delta^{18}O_m(i)$ are the event and meltwater isotopic compositions, respectively.

3.2. Nitrogen Flux Model

[16] In this study, we combined the IHS hydrologic model with concurrent measures of nitrogen chemistry from

snow lysimeters in order to calculate "conservative" nitrogen fluxes from the catchment which represent nonreactive mixing of nitrogen in meltwater with soil water and groundwater during the snowmelt period. In addition, we calculate "reactive" nitrogen fluxes which are the product of observed nitrogen concentrations and discharge over the same period. Therefore the difference between "conservative" fluxes and "reactive" fluxes is due to biological and chemical processes that release or attenuate nitrogen between the point of meltwater release to soils and delivery to the stream. Reactive stream nitrogen flux was calculated as the product of discharge and observed stream chemistry on an hourly basis throughout the snowmelt period (equation (3)).

$$N_r(t)\sum_{i=1}^{t}\left(Q_s(i)(NH(i)+NO(i)+DON(i))\right) \tag{3}$$

where N_r is the reactive nitrogen flux, Q_s is total stream discharge, and *NH*, *NO*, and *DON* represent the observed stream concentration of ammonium, nitrate, and dissolved organic nitrogen, respectively. In order to obtain hourly chemical data we linearly interpolated between our 13 chemical sampling dates and then multiplied hourly chemistry (observed or interpolated) by observed hourly discharge values.

[17] Conservative nitrogen flux incorporated the meltwater chemistry of the three replicate snow lysimeters in representative forest types: pine, spruce and open field. The average of the three replicates in each forest type was multiplied by the proportion of the forest type in the Kallkällsmyren (pine 52%, spruce 8%, open field 40%) and Västrabäcken (pine 40%, spruce 60%) catchments. Rainwater chemistry in lysimeters was used as for chemical input after the snowpack melted on 8 May. The chemical signature from snow and rain chemistry was multiplied by the event water fraction of flow during the spring flood to obtain the new water chemical component. Additionally, stream chemistry prior to the onset of snowmelt was used for the preevent chemical signature and multiplied by the preevent fraction of flow to obtain the preevent water chemical component. The conservative nitrogen flux at any point in time is the sum of the event and preevent chemical components (equation (4))

$$\begin{aligned} N_c(t) = \sum_{i=1}^{t} & \left(Q_p(i)\left(NH_p(i)+NO_p(i)+DON_p(i)\right)\right. \\ & \left.+\left(Q_e(i)(NH_e(i)+NO_e(i)+DON_e(i)\right)\right) \end{aligned} \tag{4}$$

where N_c is the conservative nitrogen flux, *Q* is discharge, *NH* is ammonium, *NO* is nitrate, *DON* is dissolved organic nitrogen, and the subscript *p* and *e* represent preevent and event components, respectively. For the reactive and conservative nitrogen fluxes (equations (3) and (4)), discharge and chemistry were linearly interpolated between measured points.

3.3. Uncertainty Analysis

[18] We conducted an uncertainty analysis to quantify the various sources of error in our IHS and N budget calculations. The uncertainty in total N input from snow lysimeters includes the components of the IHS model as well as measured N chemistry. Uncertainty in the IHS was calculated using the method proposed by *Laudon et al.* [2002] that includes analytical uncertainty [e.g., *Genereux*, 1998] and error propagation from the event water calculation. We incorporated the laboratory analytical repeatability of 0.2 ‰ for the δ^{18}O error. Uncertainty in total runoff was estimated as 5% by comparing manual discharge measurements with concurrent data logger measurements and accounting for uncertainty in the catchment area calculations [e.g., *Laudon et al.*, 2004b]. Additionally, we used a 3% error in the lysimeter water volume calculated as the coefficient of variation of replicate lysimeters over the snowmelt period. An average 10% analytical uncertainty in snowpack total N and 11% uncertainty in stream total N was calculated following the Guide to the Expression of Uncertainty Method (GUM) which incorporates repeatability, instrument drift, and uncertainty in the calibration curve [*Kristiansen*, 2001]. Short-term variability in stream N concentration is acknowledged as an additional source of uncertainty [e.g., *Schleppi et al.*, 2006], but we expect that this variation is small (<5%) compared to fluctuations over the entire snowmelt as has been shown previously [*Bishop et al.*, 2000].

[19] A Monte Carlo simulation was performed by summing uncertainties into two components: IHS (δ^{18}O error + lysimeter volume error + discharge error) and N flux (snowpack N error + stream total N error). We randomly varied each daily estimate of IHS and N flux about the mean with the calculated uncertainty and summed the error from each component to obtain a combined error. The final error estimate is the average of 10,000 Monte Carlo simulations performed on 16 dates over the snowmelt period.

4. Results

4.1. Stream Hydrology and Hydrograph Separation

[20] Hydrographs in the forest and wetland catchments followed similar patterns at the beginning of the snowmelt period as small hydrograph peaks were observed in late April for both catchments (Figure 2). These early peaks were followed by a slight recession, and a maximum on 27 April for the wetland catchment which peaked a week earlier than the forest catchment (3 May). Hydrograph recession continued throughout May, declining to near premelt base flow levels at the end of the month. Total runoff during the melt period (April through May) was 75 mm and 98 mm in the forest and wetland catchments, respectively (Table 1). Peak runoff was lower in the forest (4.3 mm day^{-1}) than wetland (5.1 mm day^{-1}) catchment. Rain and meltwater input, measured as an average of the snow lysimeter plots (pine, spruce and open field) and multiplied by the proportion of the coverage in each catchment was 160 and 157 mm for the forest and wetland catchments, respectively (Table 1).

[21] The δ^{18}O of meltwater in the snow lysimeters averaged −18.02‰ at the beginning of snowmelt to −10.38‰ at the end of snowmelt. The δ^{18}O of base flow prior to melt was similar between catchments, averaging −13.07‰ and −12.72‰ for the forest and wetland catchments, respectively, but at peak flow the δ^{18}O was much lower in the wetland catchment (−15.43‰) compared to the forest catchment (−13.74‰). As a result, the total preevent water fraction calculated was much greater for the forest

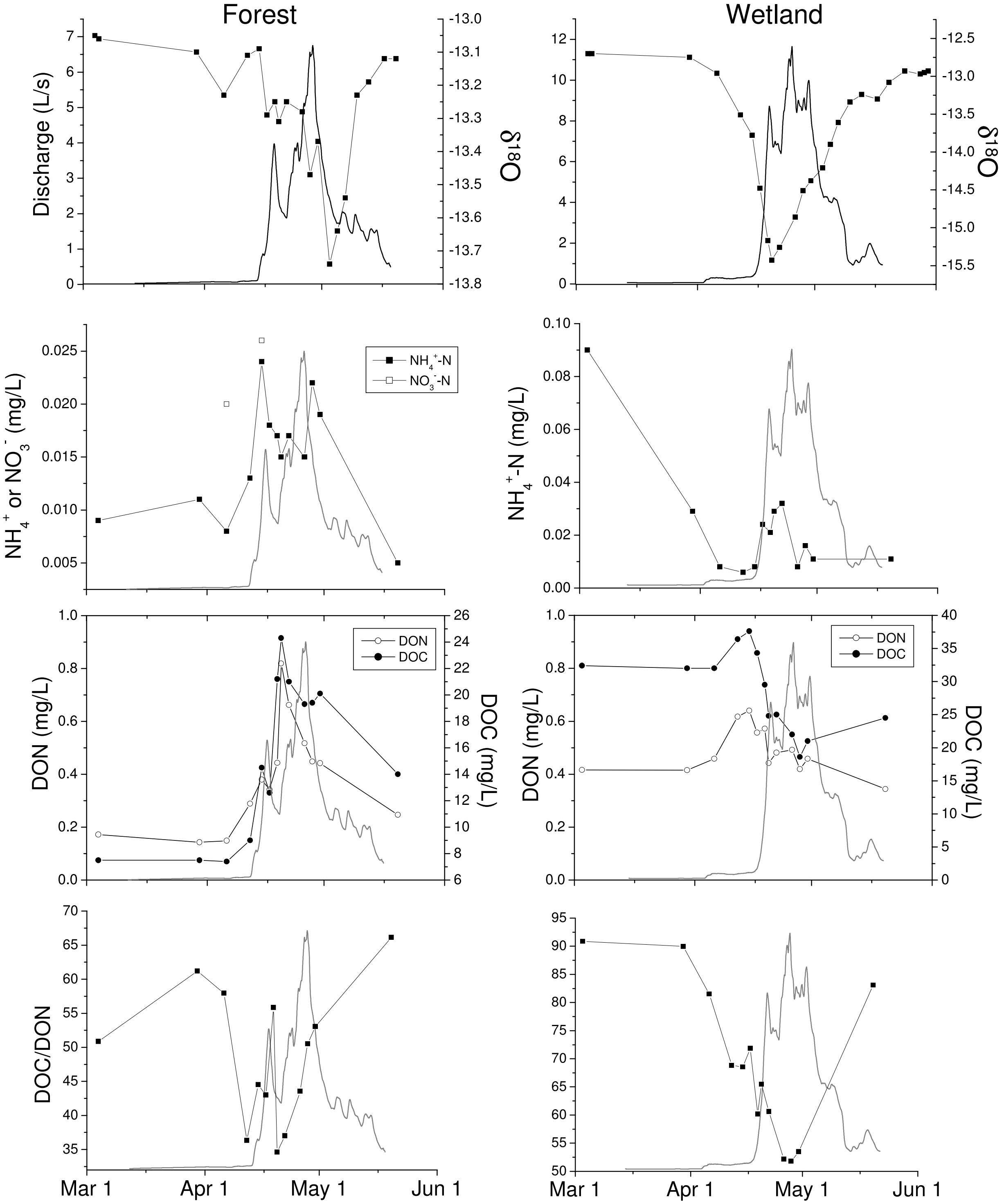

Figure 2. Discharge (gray line) and δ^{18}O, NO_3^-, NH_4^+, DON, and DOC concentration and the DOC:DON ratio during the spring flood, March–May 2004.

catchment (91%) than the wetland catchment (61%; see Table 1).

4.2. Stream Chemistry

[22] Stream chemistry patterns differed between the forest and wetland catchments. In the forest catchment, the greatest DOC and DON concentration coincided with the first peak in flow (Figure 2). In the wetland catchment, the greatest DOC and DON concentration preceded the first hydrograph peak by six days, and occurred during a small (50%) increase in flow. Linear regression explained more of the relationship between DOC and DON in the forest catchment ($p < 0.0001$, n = 14, $R^2 = 0.69$) compared to the wetland catchment ($p < 0.02$, n = 14, $R^2 = 0.34$). DOC ($p < 0.0001$, n = 14, $R^2 = 0.78$) and DON ($p < 0.0001$, n = 14, $R^2 = 0.61$) were positively correlated with discharge in the forest catchment. In contrast, DOC ($p < 0.001$, n = 14,

Table 1. Water Balance and Hydrograph Separation Results for the Forest and Mire Catchments

	Forest, mm	Mire, mm
Total snowmelt[a]	160	157
Total runoff[b]	75	98
Preevent water[c]	68	60
Event water[c]	7	38

[a] Average of triplicate snow lysimeters (meltwater and rain) in each of three vegetation types (pine, spruce, and open field) multiplied by the proportion of coverage in each catchment.

[b] Measured at each catchment weir.

[c] Calculation based on runCE isotopic hydrograph separation model by *Laudon et al.* [2002].

R^2 = 0.57) was negatively correlated with discharge in the wetland catchment while DON was unrelated to flow.

[23] In the forest catchment, DOC:DON declined to a similar level on two occasions that coincided with a rise in DOC and DON concentration. On the other hand, the DOC:DON consistently declined in the wetland catchment throughout snowmelt despite variation in DOC and DON concentration (Figure 2). In both streams, DOC:DON returned to near premelt values on the final sampling date in late May. NH_4^+ was consistently low throughout the study period (<0.05 mg/L) aside from high NH_4^+ prior to snowmelt in the wetland stream. NH_4^+ declined with flow in the wetland stream, but increased slightly with flow in the forest stream (Figure 2). Nitrate was below detection on all but two sampling occasions.

4.3. Snow Lysimeter Chemistry

[24] The nitrogen content of bulk snow was dominated by NO_3^- (60–65%), with lesser amounts of DON (21–24%), and NH_4^+ (11–16%). Meltwater DON, NH_4^+, NO_3^- concentration was enriched compared to bulk snow content at the onset of snowmelt for the pine, spruce and open field snow lysimeters (Figure 3). This enrichment was greatest for the pine site and lowest for the spruce site. Across all sites, nitrogen concentration in meltwater was proportional to that in bulk snow with NO_3^- highest, followed by DON, and NH_4^+. The variability between replicates at each site was proportional to N concentration with the greatest variability in the pine site and lowest in the spruce site (Figure 3).

[25] Using nitrogen chemistry and meltwater volumes from the snow lysimeters, we calculated nitrogen input from snow throughout the snowmelt period. N flux was initially high because of enriched N concentration at the onset of snowmelt, declined for the next few days during a cold period, and then reached a maximum between 18 and 21 April for all sites. N flux was mainly composed of NO_3^- and lesser amounts of DON and NH_4^+.

4.4. Reactive and Conservative Stream N flux

[26] In this study, the difference between the conservative and reactive N flux represents the apparent action of the soils and catchment vegetation as a source or sink for DON, NH_4^+, or NO_3^-. For example, the catchments are hydrologically retentive during snowmelt, and overall N is retained because water and the N carried with it is stored in soils (net output; Table 2). However, the N export is larger than predicted by hydrologic mixing (biogeochemical output; Table 2), thus biogeochemical processes have served to increase N export and change its form (from NO_3^- to DON). The catchments showed consistent patterns between reactive and conservative NO_3^- and DON flux. In both catchments, the reactive DON flux was greater than the conservative DON flux, indicating that the catchments were a biogeochemical source of DON (Table 2 and Figure 4). Conversely, the conservative NO_3^- flux was greater than the reactive NO_3^- flux, indicating that the catchments were a biogeochemical sink for NO_3^-. The reactive vs. conservative NH_4^+ pattern changed from a source to a sink during snowmelt in the forest catchment; reactive NH_4^+ flux was

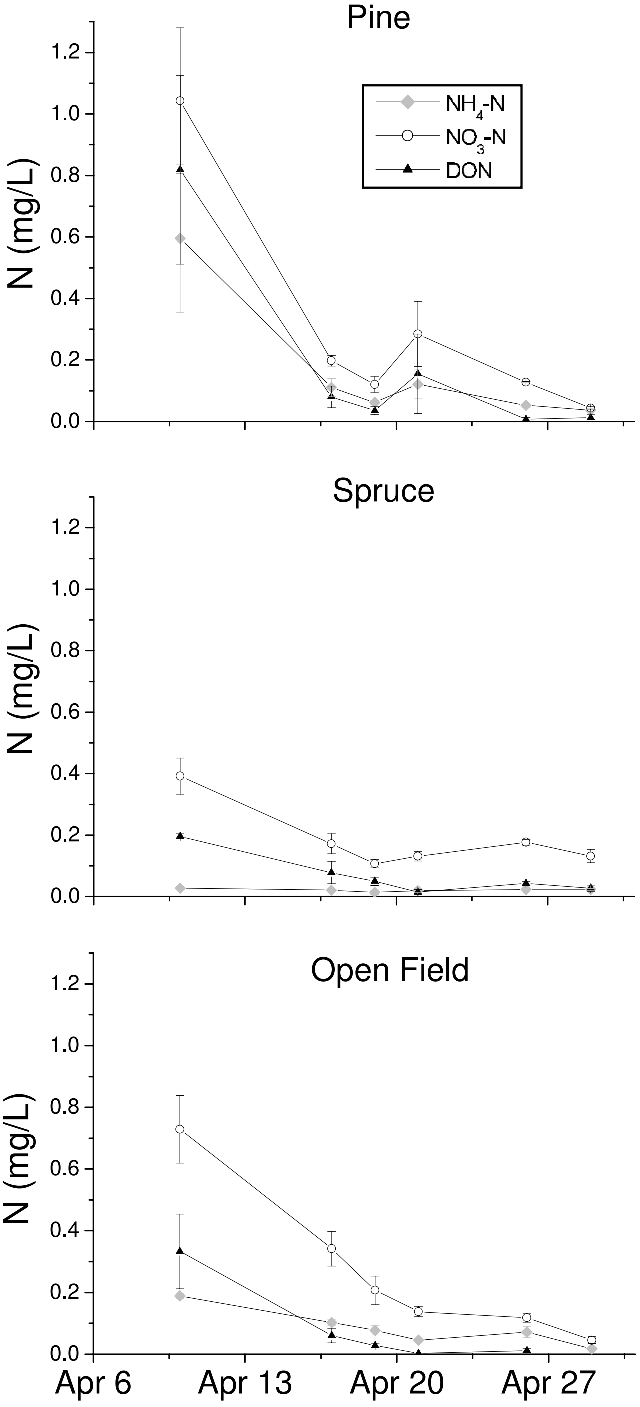

Figure 3. Chemistry of meltwater in snow lysimeters in the pine, spruce, and open field sites (mean and SE of three replicate plots), 10–27 April.

Table 2. Conservative and Reactive Nitrogen Fluxes Over the Snowmelt Period (10 April to 31 May) for the Forest and Wetland Catchments[a]

	Snow and Rain Input		Reactive Output[b]		Conservative Output[c]		Net Output[d]		Biogeochemical Output[d]	
	Forest	Wetland	Forest	Wetland	Forest	Wetland	Forest	Wetland	Forest	Wetland
$NH_4^+ - N$	0.132	0.171	0.011	0.014	0.010	0.032	0.121	0.157	−0.0001	0.018
$NO_3^- - N$	0.276	0.332	0.001	0.001	0.008	0.043	0.276	0.331	0.007	0.042
DON	0.127	0.154	0.310	0.424	0.103	0.284	−0.183	−0.270	−0.207	−0.140
Total N	0.535	0.658	0.322	0.438	0.121	0.358	0.214	0.219	−0.200	−0.080

[a] Units are kg ha^{-1}season^{-1}. Conservative fluxes are calculated from meltwater chemistry input and mixing using EMMA hydrograph separation whereas reactive fluxes (observed) include biogeochemical processes.

[b] Observed output from stream chemistry.

[c] Calculated output from IHS model and snowmelt N input.

[d] Net source (negative) or sink (positive). Net output is input minus reactive, and biogeochemical output is conservative minus reactive.

higher than the conservative flux on the rising limb of the hydrograph, but less than the conservative flux on the descending limb of the hydrograph. Overall, the differences between conservative and reactive NH_4^+ fluxes in the forest catchment were within the error of the uncertainty analysis. The wetland catchment was a biogeochemical sink for NH_4^+ during snowmelt since the reactive NH_4^+ flux was lower than the conservative NH_4^+ flux (Figure 4).

4.5. Wetland Hydrology and Chemistry

[27] We identified two flow paths in the saturated zone of the wetland from the depletion of $\delta^{18}O$ in the wetland wells toward the mean snowpack $\delta^{18}O$ signature of −17.0 ‰ during the snowmelt period (Figure 5). As snowmelt progressed, the $\delta^{18}O$ signature shifted from −11.4 (5 April and 19 April) to between −13.2 to −13.4 ‰ (27 April through 30 May) in the shallow well (75 cm), indicating that the snowpack meltwater mixed with the preevent wetland water. Similarly, the $\delta^{18}O$ signature shifted in the deeper water zone (175 to 250 cm), and was most pronounced at the 225 cm depth. At this depth, $\delta^{18}O$ began near −12‰ and became progressively depleted starting on 27 April (−13.48‰), reaching a minimum on 8 May (−14.35‰), and then increased on 30 May (−13.89‰).

[28] The pattern of NH_4^+, DON, and DOC concentration in the wetland profile changed in response to water flow in the surface and deep water flow zones (Figure 5). NH_4^+ was depleted in the surface (75 cm) and deep zone (200 and 225 cm) wells to less than 0.05 mg/L while NH_4^+ remained higher at most other depths during the snowmelt period (0.1 to 0.4 mg/L). DOC concentration was progressively depleted in the surface (75 cm) and one deep well (225 cm). DOC was greater than 30 mg/L on the first two sampling dates (19 and 27 April), but declined to less than 20 mg/L on 8 May, and increased again on 30 May. The DON pattern was more variable, but the lowest concentrations were observed at the 225 cm depth. Overall, the DOC:DON ratio was variable, ranging from 34 to 94, but average DOC:DON at each depth was between 55 and 65. NO_3^- was below detection on all dates in the wetland wells.

4.6. Forest Hydrology and Chemistry

[29] In the forest site, the groundwater (GW) table depth varied between 53 and 55 cm in the first week of April and rose on 7 April, coinciding with the onset of snowmelt. The maximum GW level observed (30 cm) was on 20 April and gradually dropped through the end of May (Figure 6). NH_4^+ was variable with depth in the riparian zone lysimeters, ranging from 0.01 to 0.07 mg/L (Figure 6). At 65 cm, NH_4^+ was consistently low while the highest concentrations were observed at 55 cm. From 35 to 45 cm depth, NH_4^+ concentration was intermediate and tended to increase throughout the snowmelt period. In contrast to the variable NH_4^+ patterns, DON and DOC concentrations were consistent across sampling dates and concentrations increased from deep to shallow lysimeter depths. Low DON concentration (0.3 to 0.4 mg/L) was found at the lowest lysimeter depths (45 to 65 cm), but increased to over 0.5 mg/L at 35 cm and 1.0 mg/L at the 25 cm. Similarly, DOC increased from 20 mg/L at the lowest depths, to between 25–40 mg/L at 35 cm, and over 60 mg/L at 25 cm (Figure 6). As with the wetland wells, the lysimeter DOC:DON ratio was variable, ranging from 49 to 98, but when averaged across dates DOC:DON at each depth was between 55 and 65.

4.7. Water Extractable Soil Chemistry

[30] In the forest catchment, extractable NO_3^-, NH_4^+, DON, %C and %N consistently declined with depth in the upland and riparian soil profiles (Table 3). Despite the decline in N and C with depth, there was no observed pattern in the C:N ratio with depth, which ranged from 43.9 to 55.0 in the upland site and from 28.8 to 30.9 in the riparian site. In the saturated wetland peat soils, extractable NO_3^-, NH_4^+ and DON was depleted at the intermediate depth (250–300 cm), %C, and %N was greatest at the shallow depth (200–250 cm), and C/N tended to decline with depth (Table 3).

4.8. Uncertainty Analysis

[31] Uncertainty in the IHS calculation was slightly greater in the forest catchment (6 to 13%) compared to the wetland catchment (5 to 11%). The combined uncertainty from the Monte Carlo simulation of the IHS model and the N flux model averaged 15% and 14% for the forest and wetland catchments. For both catchments, error increased throughout snowmelt and reached a maximum at the end of May. The range of error was slightly greater in

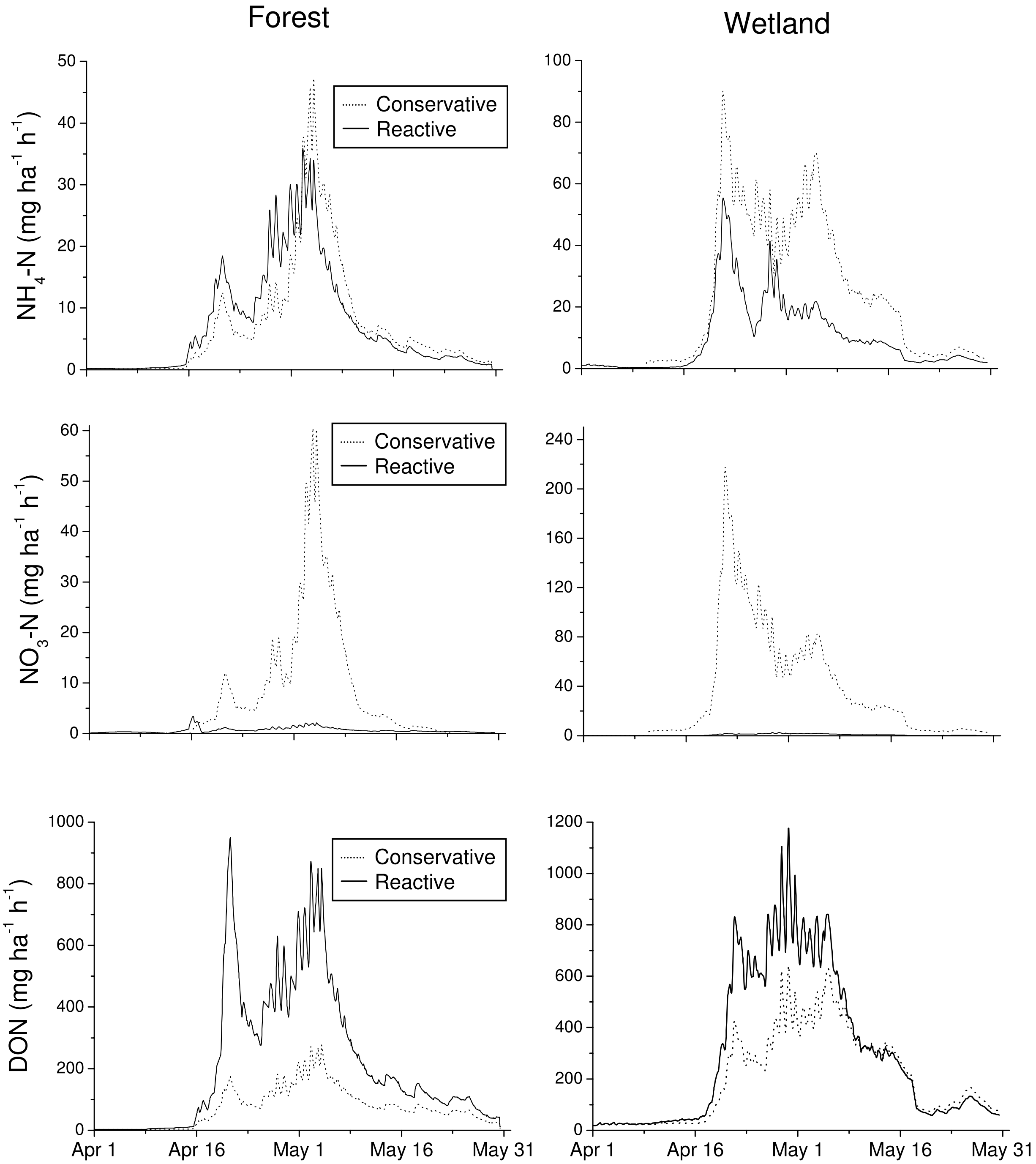

Figure 4. Reactive (solid line) and conservative (dotted line) fluxes of NH_4^+, NO_3^-, and DON from the forest and wetland catchments.

the forest catchment (13 to 17%) compared to the wetland catchment (12 to 16%).

5. Discussion

5.1. Nitrogen Export

[32] N loss during the snowmelt period can be a significant fraction of the annual N loss in snowmelt-dominated systems [*Petrone et al.*, 2006]. Estimates of annual N deposition in the Krycklan catchment average 2.7 kg ha^{-1} yr^{-1} (www.internat.environ.se). Our estimates of snowmelt N input (0.535 to 658 kg ha^{-1} $season^{-1}$) and observed N loss in streamflow (0.322 and 0.438 kg ha^{-1} $season^{-1}$) were 20–24% and 12–16% of the annual average; respectively. These mass balance results demonstrate the importance of catchment storage during snowmelt. On the basis of the net difference between measured input and output as above, both catchments were sinks for N (0.214 to 0.219 kg ha^{-1} $season^{-1}$). However, we found that much of this sink was due to water and N storage in catchment soils, while catchments were still a source of N ("biogeochemical" output = 3 to 7% of the annual N deposition) because of DON mobilization. Overall, this recharge of meltwater and N to catchment soils is likely an important source of water

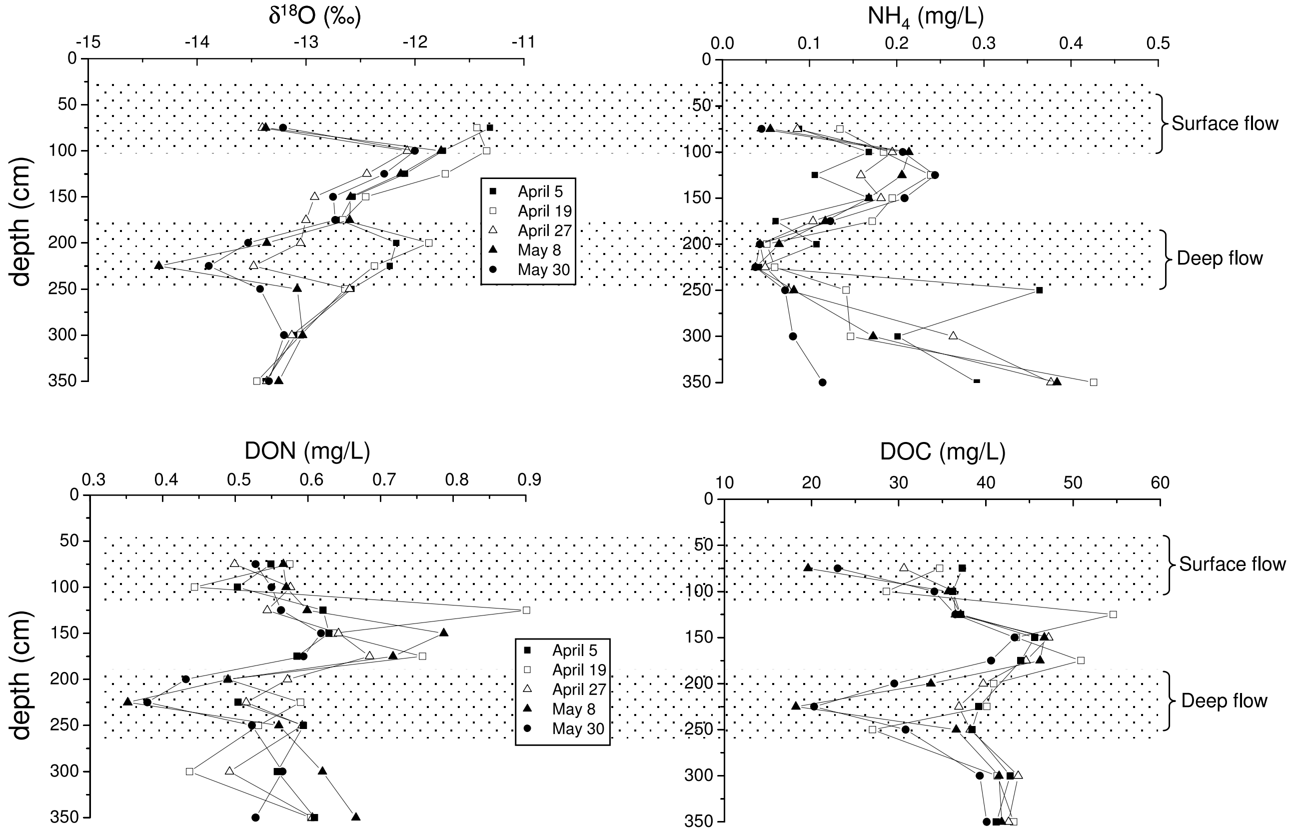

Figure 5. Wetland profiles of δ^{18}O, NH_4^+, DON, and DOC in the wetland wells between 5 April and 30 May. Surface and deep flow zones are delineated by the progressively lighter δ^{18}O throughout snowmelt.

and nutrients for ecosystem production during the later spring and summer months.

[33] In this study, we have not measured rates of N transformation, but rather we use model results together with measurements of soil and groundwater chemistry to infer the role of N sources/sinks and hydrologic flow paths that deliver N to streams. We found that catchment vegetation and soils effectively retain all NO_3^- that enters from the snowpack, but release DON in excess of snowpack inputs. Overall, the forest catchment was a greater total N source (0.200 kg ha^{-1}) compared to the wetland catchment (0.080 kg ha^{-1}) over the snowmelt period despite a greater amount of event water reaching the stream in the wetland catchment (24%) than the forest catchment (4%). In a previous study in the forest catchment using IHS and hydrometric data, *Laudon et al.* [2004b] determined that preevent water was mobilized by event water which generated lateral flow to the stream in the upper 90 cm of soils. Here we demonstrate that this mechanism for streamflow generation is also important for N flux in the forest catchment as stream N flux is largely regulated by the mobilization of stored DON, and to a lesser extent, NH_4^+, in catchment soils by preevent groundwater and soil water during snowmelt.

[34] Organic matter sources are often mobilized and flushed from soils during high-flow periods in the spring, yielding high concentration and flux of DOC [*Hornberger et al.*, 1994; *Boyer et al.*, 1997], and DON [*Campbell et al.*, 2000; *Williams et al.*, 2001; *Hood et al.*, 2003]. Our findings are consistent with previous estimates of organic solute losses in this region showing that a smaller proportion of the annual DOC flux occurs during snowmelt in wetland-dominated catchments compared to forested catchments [*Laudon et al.*, 2004a]. The lesser role of DON export in wetland catchments is related to hydrologic flow paths that have a small effect on DON, whereas DON concentration in the forested catchment was positively related to flow and remained elevated above base flow levels during snowmelt.

[35] While DON loss from catchments is often related to bulk soil properties and hydrology [*Aitkenhead-Peterson et al.*, 2005], strong microbial demand for DIN often contributes to DIN retention in soils [*Neff et al.*, 2001]. Our findings support this pattern with respect to NO_3^- as its concentration was mainly below detection in stream water despite ionic enrichment of meltwater in early snowmelt. Furthermore, our model results indicate a sink of NO_3^- in both catchments that is not explained by hydrologic mixing since reactive NO_3^- fluxes were less than conservative NO_3^- fluxes. However, while the wetland catchment was still a consistent sink for NH_4^+, the forest catchment was a source for NH_4^+ on the rising limb of the hydrograph, and overall, at a steady state with respect to NH_4^+.

[36] The contrast between NO_3^- and NH_4^+ dynamics in the forest catchment is surprising for a few reasons. First, NO_3^- concentration in meltwater and flux into soils was greater than NH_4^+so we would expect a greater potential for NO_3^- loss during melt. Second, NO_3^- is considered to be a more mobile than NH_4^+ since it is less prone to retention by sorption and cation exchange. Lastly, NH_4^+ is readily nitrified in soils and energetically favorable as a nitrogen source for plant and microbes. For these reasons, the strong

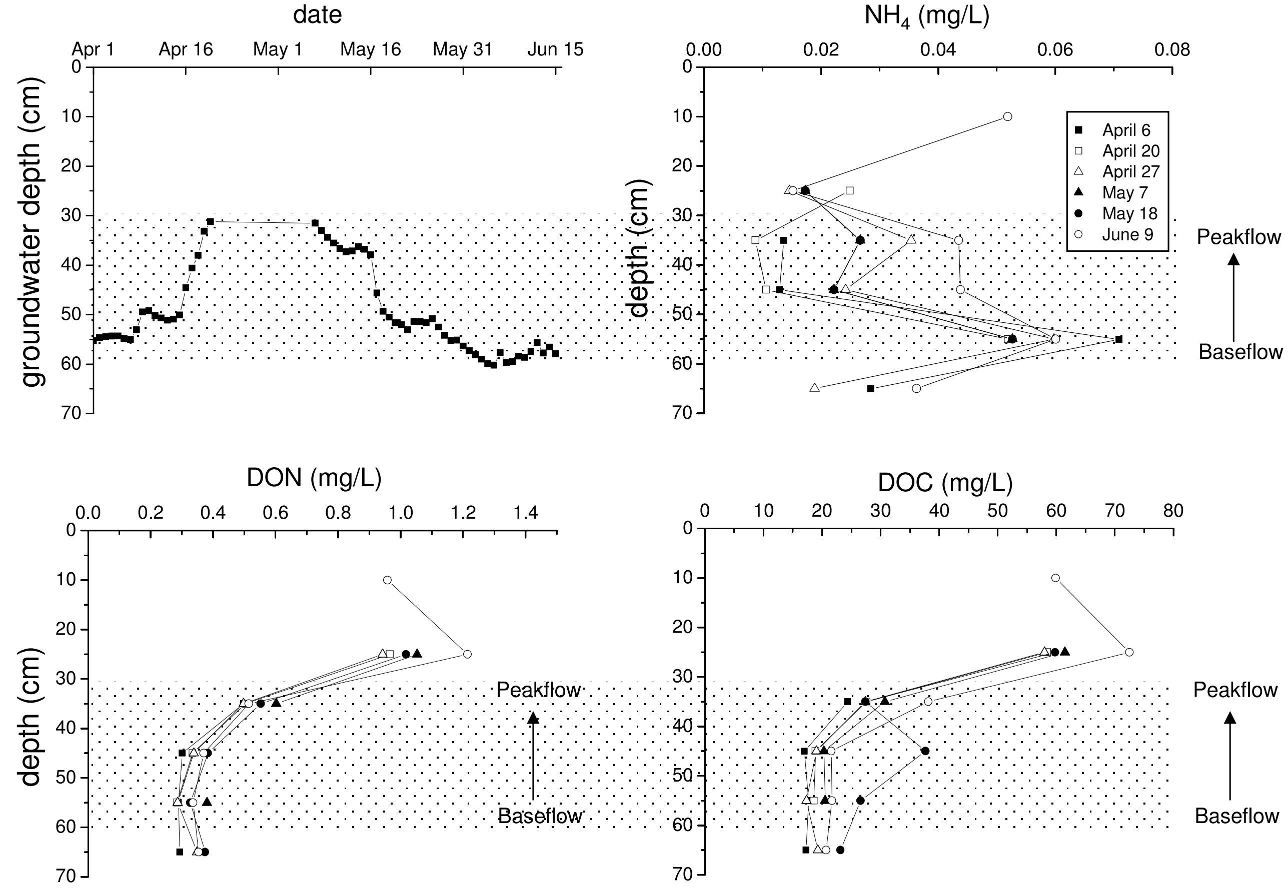

Figure 6. Groundwater depth and concentration profiles of NH_4^+, DON, and DOC in the riparian zone of the forest catchment between 6 April and 9 June.

retention of NO_3^- suggests that either NH_4^+ is generated in catchment soils, or denitrification and nitrate uptake may be important in soils over winter and during the spring flood. For instance, Forsum et al. in press recently found that a bryophyte (*Hylocomium splendens*) assimilated ^{15}N labeled glycine, NH_4^+, and NO_3^- applied in situ. Bryophytes can also assimilate much of the meltwater NO_3^- generated during the snowmelt period [*Woolgrove and Woodin*, 1996].

5.2. Stream Chemistry

[37] The predominance of DON as a vector for N loss (>95% of total N) is consistent with other reported studies of stream chemistry in central and northern Scandinavia with low rates of N deposition [*Kortelainen et al.*, 1997; *Fölster*, 2000; *Mattsson et al.*, 2005]. Stream DON and DOC concentrations are often related during snowmelt [*Goodale et al.*, 2000], but in some cases the relationship between DON and DOC may be weak [*Hood et al.*, 2003] or insignificant [*Stepanauskas et al.*, 2000; *Williams et al.*, 2001] because of changes in catchment organic matter sources on the rising and falling limb of the hydrograph [*Kaushal and Lewis*, 2003]. In this study, a stronger relationship between DOC and DON in the forest catchment (R^2 = 0.69, p < 0.0001) than the wetland catchment (R^2 =

Table 3. Water Extractable N (NH_4^+, NO_3^-, and DON) and Bulk C and N Contents for Forest Catchment Soils (Riparian and Upland) and Wetland Peat

Site	Depth, cm	$NH_4 - N$,[a] μg/g	SE	$NO_3 - N$,[b] μg/g	SE	DON,[b] μg/g	SE	%C	%N	C/N
Forest-Upland	0–5	2.0	0.1	1.1	0.2	29.9	1.8	45.0	1.0	46.1
	5–15	0.3	0.04	0.2	0.02	0.5	0.3	1.0	0.02	55.0
	15–40	0.2	0.01	0.1	0.01	—	—	0.8	0.02	43.9
Forest-Riparian	0–10	3.8	2.3	0.9	0.3	12.8	6.4	34.0	1.1	30.3
	10–20	1.7	0.3	0.4	0.1	9.8	3.6	17.7	0.6	28.8
	20–30	1.0	0.2	0.5	0.1	5.5	1.8	6.5	0.2	30.9
	30–50	0.6	0.04	0.4	0.03	2.1	0.3	3.1	0.1	30.6
Wetland	200–250	10.2	1.9	5.2	0.3	17.4	1.2	47.9	1.7	27.6
	250–300	5.8	0.6	2.2	0.2	13.0	3.5	29.8	1.2	25.2
	300–350	19.8	0.8	3.4	0.3	19.7	3.1	23.3	1.3	18.6

[a] Units are μg/g of dry soil.

[b] The standard error of three sample replicates.

0.34, $p < 0.02$) suggests that DOM sources were more similar throughout snowmelt in the forest catchment. Furthermore, flow elevated the levels of DOC and DON in the forest catchment while DOC was diluted in the wetland catchment and DON was unrelated to flow. These contrasting patterns of DOC, DON and flow indicate that hydrologic flow paths and the mechanism of organic matter delivery to the stream were different during snowmelt for each catchment.

[38] We found a strong decline in the DOC and DON content with depth in the forest catchment that is consistent with other studies [*McDowell and Wood*, 1984; *Boyer et al.*, 1997] and is likely due to abiotic sorption in mineral soils [*Qualls and Haines*, 1992; *Yano et al.*, 2005]. Previous research in this forest catchment has determined that transmissivity feedback (i.e., greater lateral hydraulic conductivity and water movement) in the upper soil layers generates streamflow during snowmelt as the groundwater table rises [*Nyberg et al.*, 2001]. More recently, *Laudon et al.* [2004b] reported that this flow is a mixture of preevent and event water and is limited to the upper 90 cm of soil. Hydrological flow pathways through these organic-rich upper soil layers mobilizes DOC during high flow [*Bishop and Pettersson*, 1996; *Bishop et al.*, 2004].

[39] Our findings support the convergence of flow and organic matter sources in upper soil layers in the riparian zone since DOC and DON were correlated and increased with flow in the forest catchment. The riparian zone may also be a source of ammonium in the forest catchment since NH_4^+ increased with flow and soils were a source for NH_4^+ on the rising limb of the hydrograph. Although NH_4^+ concentrations were variable in the upper soil lysimeters, water extractable NH_4^+ was elevated in riparian surface soils (Table 3) and could serve as a NH_4^+ source to stream water during infiltration. Mineralization of organic matter may also occur under the snowpack and during the melt period, contributing to NH_4^+ flux in the spring [*Brooks et al.*, 1996]. The decline we observed in stream DOC:DON during snowmelt in the forest catchment (Figure 2) cannot be explained by the variable DOC:DON in riparian lysimeters, but may be indicative of the lower bulk C:N ratio of riparian soils (28.8 to 30.6) as soil C:N has been shown to be a good predictor of DOC:DON in surface waters [*Aitkenhead-Peterson et al.*, 2005]. Furthermore, recent studies suggest that DOC mobility may be lower compared to DON in forest soils because of greater concentration of DOC in the hydrophobic portion of DOM [*Kaushal and Lewis*, 2003; *Lajtha et al.*, 2005]. Similar partitioning of DOC and DON within the organic matter pool in our catchment and preferential sorption of DOC in surface soils might also explain the decline in DOC:DON that we observed during snowmelt.

[40] In the wetland catchment, NH_4^+ and DOC declined at peak flow, indicating a dilution of high base flow concentrations from the influx of meltwater. This pattern is supported by our well data that show a decline in NH_4^+ and DOC concentrations at the surface and deep flow zones as snowmelt progressed. However, at the beginning of snowmelt, we also observed an increase in DOC and DON with only a slight increase in discharge that cannot be explained by our groundwater data. *McGlynn and McDonnell* [2003] recently observed that DOC dynamics are influenced by a mixture of discrete organic matter sources within catchments that may change during a storm. Similarly, near-stream organic matter sources that have not been measured may also be important in the wetland catchment at the onset of snowmelt. However, at the peak of snowmelt, overland flow in the surface zone and preferential flow at 175 to 250 cm depth dominate the stream N chemistry. As with the forest catchment, groundwater data do not explain the sharp decline in stream DOC:DON with flow, but greater sorption of DOC over DON would support the pattern we observed.

5.3. Ecosystem Implications

[41] Quantifying catchment N loss during the spring flood is important for understanding N cycling processes in catchment soils as well as seasonal changes in the N status of receiving rivers and streams. *Stepanauskas et al.* [2000] found that DON bioavailability increased at peak flow in northern Swedish streams and was correlated with the concentration of combined amino acids. In Krycklan streams, we have also observed an increase in concentrations of free and combined amino acids in some streams during snowmelt (Näsholm, unpublished data, 2003), suggesting a release of labile DON. Changes in DOM quality with flow may be generated from the flushing of partially decomposed leaf litter or overwinter microbial decomposition that may be further enhanced by freeze-thaw cycles leading to physical soil disruption and fine root mortality [*Fitzhugh et al.*, 2001; *Groffman et al.*, 2001]. Recently, it has been found that DON is readily assimilated by microbes in streams and may be an important source of N when inorganic N concentrations are low [*Kaushal and Lewis*, 2005; *Brookshire et al.*, 2005]. Future catchment studies may be able to combine the IHS and bulk DON approach we have used in this study with characterization of organic matter to identify how biotic processes in soils may contribute to stream DIN and DON utilization. This information is critical in order to predict how catchment and in-stream processes may regulate the downstream transport of N in high-latitude landscapes in a changing climate.

6. Conclusion

[42] In this study, we have demonstrated that isotopic hydrograph separation can be used in conjunction with elemental flux to distinguish hydrologic mixing from catchment biogeochemical processes that attenuate or release nitrogen such as sorption, leaching, immobilization or uptake. Using this approach, we found that both forest and wetland catchments were biogeochemical sources of DON and sinks for NO_3^- throughout the snowmelt period, in spite of being hydrologic sinks. Our results support our hypothesis regarding catchment N loss; the forest catchment was a greater source of nitrogen and DON was mobilized by a rising water table due to the convergence of flow and organic matter sources in upper soil horizons. Inorganic N patterns followed our prediction for the most part except that the riparian zone was a source of NH_4^+ in early snowmelt. Strong NO_3^- retention in both catchments suggests that nitrate is readily denitrified or utilized during the snowmelt period. Our findings underscore the importance of hydrologic flow paths in delivering organic N to the stream and the role of biogeochemical processes in retaining much

of snowpack N in catchment soils. Future changes in the timing and delivery of snowpack water and N may influence the mobility of catchment N sources. Furthermore, modification of freeze-thaw cycles due to reduced extent of snow cover or rising ambient temperatures at high latitudes may also affect microbial processing of N during the winter and snowmelt period.

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