



RESEARCH ARTICLE

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Key Points:

- The riparian zone acted as the primary source of organic and inorganic N to the stream
- A small volume of riparian soil emerged as a hot spot in the landscape for net N mineralization and transport
- Groundwater fluctuations in organic-rich riparian soils may drive catchment N losses in boreal landscapes

Supporting Information:

- Supporting Information S1

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Evaluating hillslope and riparian contributions to dissolved nitrogen (N) export from a boreal forest catchment

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Abstract Catchment science has long held that the chemistry of small streams reflects the landscapes they drain. However, understanding the contribution of different landscape units to stream chemistry remains a challenge which frequently limits our understanding of export dynamics. For limiting nutrients such as nitrogen (N), an implicit assumption is that the most spatially extensive landscape units (e.g., uplands) act as the primary sources to surface waters, while near-stream zones function more often as sinks. These assumptions, based largely on studies in high-gradient systems or in regions with elevated inputs of anthropogenic N, may not apply to low-gradient, nutrient-poor, and peat-rich catchments characteristic of many northern ecosystems. We quantified patterns of N mobilization along a hillslope transect in a northern boreal catchment to assess the extent to which organic matter-rich riparian soils regulate the flux of N to streams. Contrary to the prevailing view of riparian functioning, we found that near-stream, organic soils supported concentrations and fluxes of ammonium (NH₄⁺) and dissolved organic nitrogen that were much higher than the contributing upslope forest soils. These results suggest that stream N chemistry is connected to N mobilization and mineralization within the riparian zone rather than the wider landscape. Results further suggest that water table fluctuation in near-surface riparian soils may promote elevated rates of net N mineralization in these landscapes.

1. Introduction

A central theme in catchment biogeochemistry is that the export of resources limiting to biological activity on land, e.g., dissolved inorganic nitrogen (DIN), is under strong biological control by plants and soil microbes [Hedin *et al.*, 1995; Gerber and Brookshire, 2014]. Implicit in this hypothesis is the idea that hydrological exports of bioavailable nutrients reflect the balance of inputs and removal processes distributed across the contributing terrestrial environment [Bormann and Likens, 1967]. This perspective tends to focus attention on dominant landscape areas (e.g., upland forest soils) as key sources and sinks of dissolved nutrients to streams. Support for the idea that upland forest soils regulate hydrological nutrient losses can be found in the many studies connecting terrestrial dynamics to stream N exports, including responses to clear-cutting [Likens *et al.*, 1970], changes in forest community composition [Lovett *et al.*, 2002], long-term succession [Vitousek and Reiners, 1975], and atmospheric N inputs [Dise and Wright, 1995]. Thus, variation in nutrient export over different spatial and temporal scales can be a broad indicator of forest ecosystem functioning and health [e.g., Dise *et al.*, 2009; Brookshire *et al.*, 2012].

Despite the connection between upland forest soil dynamics and stream nutrient exports, it is also well established that biogeochemically active patches within landscapes can exert disproportionately large influences on the magnitude and timing of terrestrial losses [Morse *et al.*, 2014; Marton *et al.*, 2015]. In this context, riparian zones have received much attention as hot spots for the removal of inorganic N in transport from uplands to stream channels [Peterjohn and Correll, 1984; McClain *et al.*, 2003; Ocampo *et al.*, 2006]. Riparian N removal may be driven by plant uptake at the land-water interface, but also microbial immobilization, and/or denitrification in soils where low redox conditions promote the use of nitrate (NO₃⁻) as a terminal electron acceptor [Ranalli and Macalady, 2010]. However, depending on how rates of N loading from upslope environments compare to internal dissolved organic nitrogen (DON) production, mineralization, and local biological demand, riparian zones may also act as sources of dissolved N to streams [Cirimo and McDonnell, 1997; Fölster, 2000; Lupon *et al.*, 2016]. The circumstances leading to “net N production” in riparian zones are not

well studied but are potentially important for interpreting nutrient losses from catchments, particularly where upland ecosystems receive low levels of anthropogenic N inputs and are thus highly retentive.

The delivery of resources to streams is also regulated by physical and hydrological properties of the land-water interface, which vary as a function of soil structure and regional climate [Lohse *et al.*, 2009]. In northern boreal landscapes, where glacial till deposits are overlain by organic-rich soils, hydrologic conductivity declines exponentially with depth, governing the vertical distribution of flow paths along hillslopes and riparian zones [Rodhe, 1989]. Accordingly, small precipitation or snowmelt events can rapidly elevate the water table and activate more highly conductive and organic-rich strata toward the soil surface [Bishop *et al.*, 2004]. One consequence of this is that an overwhelmingly large fraction of lateral hydrologic transport to streams is forced through a narrow band of near-surface soils with higher conductivity [Bishop *et al.*, 2011]. The juxtaposition of this flow pattern with the vertical distribution of resources stored in soils ultimately regulates solute export in runoff waters. Furthermore, because they are located at the distal end of hillslope flow paths—and often store large amounts of peat—riparian soils in northern ecosystems can serve as the primary source of dissolved organic carbon (DOC) [e.g., Grabs *et al.*, 2012; Dick *et al.*, 2015] and DON [Fölster, 2000; Petrone *et al.*, 2007] to streams. Understanding how these edaphic and hydrologic properties also govern exports of the more biologically reactive solutes such as DIN remains unclear, yet is essential if we aim to use stream chemical signals to detect, interpret, and predict the effects of environmental change on boreal forest nutrient cycles.

Elevated concentrations of DOC in peat-rich, riparian soils should have clear implications for the transport and fate of other biogeochemical elements, particularly N. On one hand, high DOC concentrations in riparian soils may be expected to constrain exports of inorganic N to streams, either by increasing microbial N demand and thus rates of immobilization [Taylor and Townsend, 2010] or by driving redox conditions to the point that NO_3^- is effectively removed as a terminal electron acceptor [Helton *et al.*, 2015]. Yet where saturated soils and low redox conditions persist, constraints on rates of nitrification may also lead to the accumulation of reduced forms of inorganic N (ammonium, NH_4^+) in riparian soils [e.g., Chestnut and McDowell, 2000; Fölster, 2000]. Overall, in DOC-rich waters of boreal riparian soils, we would expect to find strongly reducing conditions below the water table [Lidman *et al.*, 2011], with elevated concentrations of DON and NH_4^+ and comparatively low levels of NO_3^- . However, hydrological dynamics that have been shown in many different systems to drive changes in flushing rate, redox state, and biological resource demand may generate spatial and temporal heterogeneity in these resource pools [e.g., Hedin *et al.*, 1998; MacLean *et al.*, 1999; Hill *et al.*, 2000; O'Donnell and Jones, 2006; Harms and Grimm, 2008] and ultimately constrain the capacity for riparian soils to serve as sources or sinks for N.

In this study we address how N cycling in boreal landscapes is reflected in stream chemical signals by asking the following questions: (1) Where is N mobilized along a forest hillslope? (2) To what extent do peat-rich riparian zones regulate the export of N to surface waters? To answer these questions, we evaluated the controls on hydrological N export in a boreal forest catchment in northern Sweden over a 2 year period. This region is characterized by relatively low-gradient landscapes, where peat-forming processes are widespread and responsible for a mosaic of forest and wetland patches. In addition, atmospheric inputs of reactive N are comparatively low [Gundale *et al.*, 2010], and N limitation of terrestrial vegetation is common [e.g., Högberg *et al.*, 2006]. We characterized vertical and lateral patterns in DIN and DON concentration in soil solution from lysimeter nests organized along a hillslope transect. We then used an established groundwater model to estimate the hydrological fluxes of N from upland, midslope, and riparian zones and compared these hydrological losses with measured export in the receiving stream.

2. Methods

2.1. Study Area

Research was conducted in a 12 ha headwater catchment, C2 (Figure 1a), that is part of the Krycklan Catchment Study (KCS). The KCS is located in the boreal zone of northern Sweden ($64^{\circ}14'N$, $19^{\circ}46'E$), approximately 60 km from the Baltic Sea coast (see Laudon *et al.* [2013] for a complete site description). Summers are typically short and cool followed by long dark winters (July $+14.7^{\circ}C$, January $-9.5^{\circ}C$, 30 year mean). The KCS receives around 614 mm yr^{-1} of precipitation, of which 35–50% falls as snow, which remains for an average of 167 days per year [Laudon and Ottosson Löfvenius, 2016]. Long-term average runoff is approximately

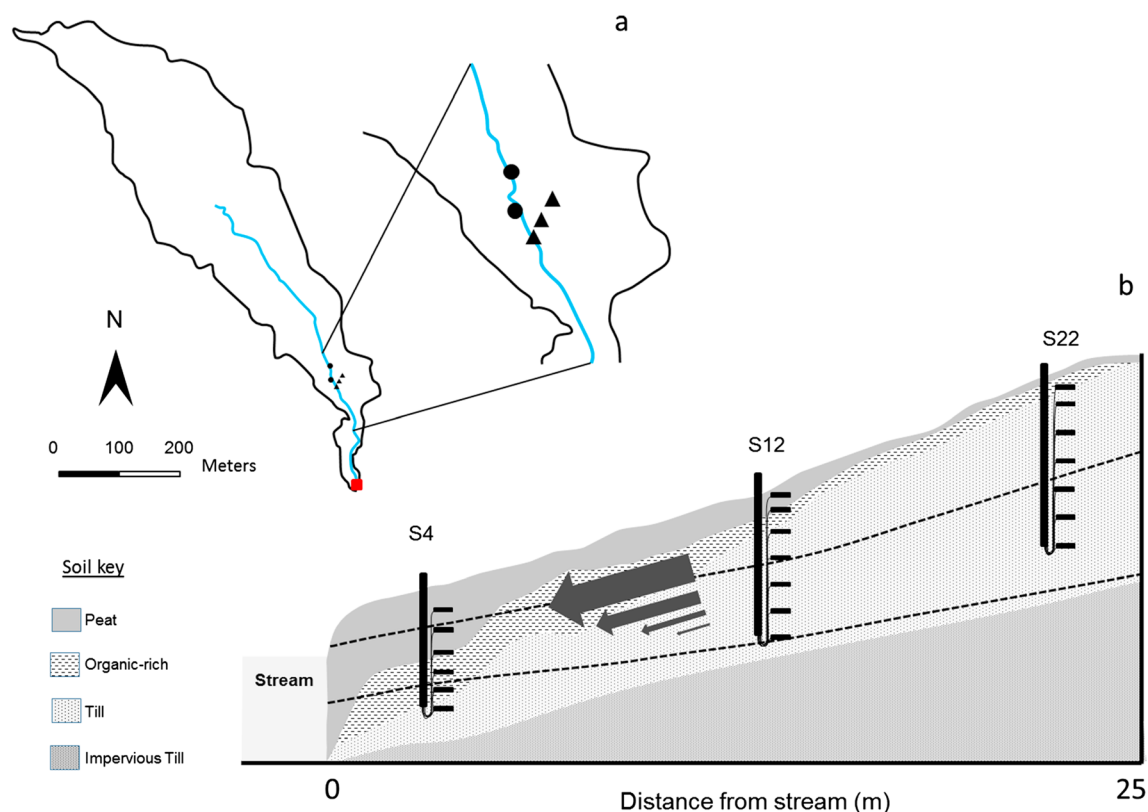


Figure 1. Study site and detail of hillslope installations within the Krycklan Catchment Study Sweden ($64^{\circ}14'N$, $19^{\circ}46'E$). (a) C2 catchment boundaries, stream (blue), stream sampling point, and gauging station (red square). The enlargement shows the lysimeter stations S4, S12, and S22 (black triangles) that run northeast from the stream and the auxiliary riparian lysimeter stations K4 and K6 (black circles). (b) Cross section of the hillslope transect with approximate positions of lysimeters and soil horizons. The relative upper and lower limits of the water table marked with a dashed line, while the approximate porosity of the soil is represented by the width of the black arrows increasing with decreasing depth.

311 mm [Laudon *et al.*, 2013]. During the course of this study, the C2 catchment received 646 and 829 mm of precipitation giving rise to 187 mm and 395 mm of runoff, respectively, during 2011 and 2012. Average annual atmospheric wet N deposition measured at this site from collected precipitation 2002–2006 was $2.17 \text{ kg N ha}^{-1} \text{ yr}^{-1}$, of which approximately 26% was DON (data not shown). These estimates are well within the range of other estimates for northern Sweden [Gundale *et al.*, 2010].

Soils in most of the study area are well-developed podzols formed on glacial till over laying gneissic bedrock. In wetter, near-stream areas, thick surface organic layers have developed to form histosols [Bishop *et al.*, 1994]. C2 is a 100% forested catchment, typical of this part of the boreal zone, dominated by Scots pine (*Pinus sylvestrus*, 64% cover), Norway spruce (*Picea abies*, 36%), and Birch (*Betula sp.*, <0.5%). Understorey vegetation is dominated by ericaceous shrubs, including bilberry (*Vaccinium myrtillus*) and cowberry (*Vaccinium vitis-idaea*) as well as extensive cover by mosses, primarily *Hylocomium splendens* and *Pleurozium schreberi*. The stream which drains the C2 catchment was modified during the 1920s, which probably involved some ditching and channel cleaning, a forestry practice widespread across Fennoscandia at the time [Esseen *et al.*, 1997]

2.2. Soil Monitoring

Soil water along a topographically defined flow path toward the C2 stream was sampled on 18 occasions over a 2 year period using three lysimeter nests (Figures 1b and 2). Overall, the timing of lysimeter sampling was designed to capture the range of seasonal soil water conditions typical of the study region (Figure 2). Lysimeter nests are spaced at 4 (S4), 12 (S12), and 22 (S22) meters from the stream along a well-studied topographical flow path [Laudon *et al.*, 2004]. Previous work at this site has shown direct connection between the lysimeter nests and the stream, including clear links between riparian biogeochemistry and hydrology

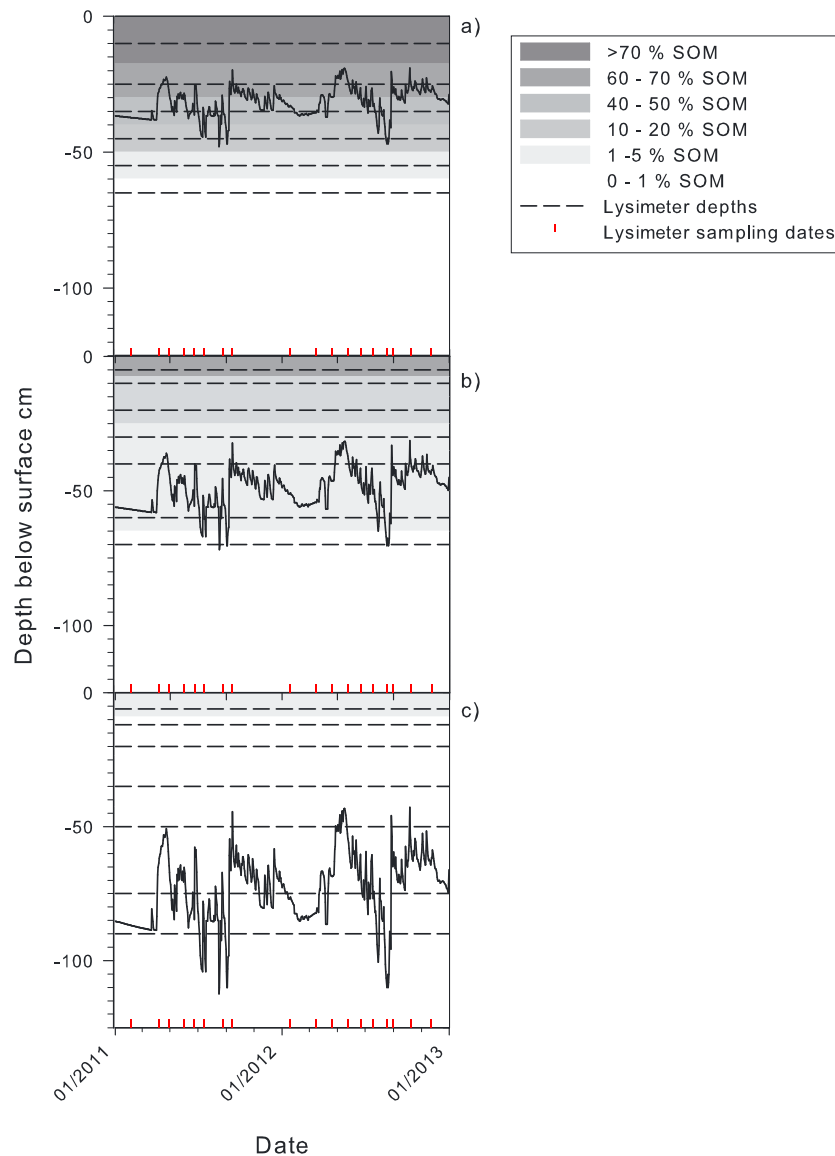


Figure 2. Representation of modeled groundwater table (solid line) over the course of the study at lysimeter nests (a) S4, (b) S12, and (c) S22. Lysimeter cup depths at each nest are marked with dashed horizontal lines and sampling days marked with vertical red dashes on the x axis. SOM content with depth is indicated by greyscale shading. Further detail on the SOM content and number of water samples taken from each lysimeter nest is given in Table 1.

[Peralta-Tapia *et al.*, 2015]. Each location consists of a nest of ceramic suction lysimeters with a pore size of 1 μm placed at depths to best capture fluctuations in groundwater throughout the year (Figure 2) [Laudon *et al.*, 2013]. Accordingly, lysimeters close to the stream (S4) consist of six suction cups covering a shallower, smaller range of depths, while those at the upslope locations (S12 and S22) consist of seven cups each (Figure 1b and Table 1). It was not possible to sample soil water from all lysimeter depths at each nest on all occasions; as a result, the number of samples analyzed for each cup ranged between 4 and 18 (Table 1). Indeed, only two samples were recovered from the shallowest lysimeter cups at S12, and none from S22, as a result values from the most surficial layer at these stations were discarded and the six remaining depths from each nest were evaluated.

The horizontal transition from upland forest (S22) to riparian (S4) lysimeter nests encompasses large variation in the amount and vertical pattern of soil organic matter (SOM) storage estimated from loss on ignition (Table 1 and Figure 2) [see Nyberg *et al.*, 2001]. SOM ranges from 0.4 to 2.5% (mean = 1.0%) at S22, 0.7 to

Table 1. Details of Hillslope Lysimeter Nests in Conjunction With SOM Values (%) for Each Sampling Horizon and the Total Number of Samples Collected From Each Cup

S4			S12			S22		
Depth	SOM (%)	Lysimeter Samples	Depth	SOM (%)	Lysimeter Samples	Depth	SOM (%)	Lysimeter Samples
10	82.8	6	5 ^a	65	2	6 ^a	1.4	0
25	67.8	14	10	18.4	4	12	0.7	15
35	40.4	4	20	11.6	4	20		13
45	12.8	16	30	4.5	18	35	0.7	6
55	2.3	18	40	2.2	18	50	0.7	18
65	1.1	17	60	1.1	18	75	0.5	11
			70	0.7	18	90	0.4	18

^aLysimeter cups that were excluded from the study due to the low numbers collected.

51.4% (mean = 11.5%) at S12, and 1.0 to 86.8% (mean = 31.4%) at S4. At S4, SOM percentage is consistently high (>64%) within the top 35 cm of the profile. This horizontal and vertical distribution of SOM across the hillslope means that, in the near-stream zone, organic matter-rich soils are continually inundated, while in upslope locations, the groundwater interacts primarily with mineral soil (Figure 2).

The groundwater level at each of the lysimeter nests was recorded hourly between June 2013 and October 2014. These measurements were collected using Campbell scientific data logger (CR1000 and AM16/32B) connected to MJK pressure transducers (MJK 1400 with TO3R NTC thermistor) or staff loggers (TruTrack WT-HR 64 K) placed in wells close to the lysimeter nests S4, S12, and S22. Daily values were obtained by averaging hourly values that included a total of 348, 345, and 360 measurements for S4, S12, and S22, respectively [Ledesma *et al.*, 2016]. An empirical model was used to estimate groundwater level and lateral hydrologic flux at each nest for the study period 2011–2012 from measured data in 2013–2014 (see section 2.5.2 below).

Two additional lysimeter nests (K4 and K6), located near the stream (2 m) and within 50 m of the hillslope transect, were sampled on 10 occasions during 2011 and 2010. Both of these nests comprised 5 cups, at 10, 25, 40, 60, and 80 cm depth [Haei *et al.*, 2010]. Although no information was available on groundwater depth, N concentration data from these nests are used here to evaluate the representativeness of the single riparian nest placed along the S transect (S4). Additionally, water was also sampled periodically over the course of the study from groundwater wells integrating the entire soil column and located adjacent to each of the main lysimeter nests (S4, 78.7 cm deep; S12, 55.6 cm deep; S22, 57.0 cm deep). These data were similarly used to provide an additional check on the representativeness of chemical values obtained from lysimeter water.

Prior to each lysimeter sampling, suction cups and tubes were rinsed by attaching a preevacuated 100 mL glass bottle to each line for 24 h to remove stored water. Sampling was then carried out using a 250 mL glass bottle preevacuated to -0.9 bar and connected to each line for 48 h stored in an insulated box to keep the sample cool and dark. During the winter months, lysimeter tubes and the box containing the sample bottles were gently heated during collection to prevent freezing of sample water as it rises to the colder surface. These heating cables were insulated from the surrounding soil in order to prevent unnecessary thawing of the soil. Samples for DOC/total dissolved nitrogen (TDN) analysis were kept cold and dark before analysis within 2 weeks, while all remaining subsamples were immediately frozen and stored until analysis. Sulfate (SO_4^{2-}) was also analyzed and presented here to serve as an additional proxy for groundwater redox conditions. SO_4^{2-} , in addition to NO_3^- , are the first alternative electron acceptors to be used by microbes when oxygen is no longer available [Stumm and Morgan, 1996].

2.3. Stream Water Chemistry

As part of the broader KCS monitoring program, water from the C2 stream was collected approximately 30 times per year at a V notch weir approximately 250 m downstream from S4 (Figure 1a). This sampling regime was flow weighted so that during the spring flood samples were collected as frequently as every 3 days, whereas during the summer sampling was approximately every 2 weeks, and during winter base-flow sampling was monthly. This study made use of samples collected between January 2011 and December 2012, which bracket in time the collection of lysimeter samples. Stream water samples were collected in

acid-washed high density polyethylene bottles and kept cool before subsampling within 3 days of collection. Water was filtered at $0.45\ \mu\text{m}$ and kept cold before analysis within 2 weeks for DOC and TDN. Filtered subsamples were frozen immediately after subsampling and later analyzed for NO_3^- (including nitrite), NH_4^+ , and SO_4^{2-} .

Discharge for C2 was measured using a 90° V notch weir instrumented with a pressure transducer and data logger within a frost-free building constructed in 2011. Rating curves were established via direct estimates of flow using the salt dilution approach (see *Karlsen et al.* [2016] for a full description of flow measurements). Winter flow measurements for 2011 (January to May) were calculated using a relationship established between an adjacent catchment, C7 (47 ha), and C2 (12 ha) as described by *Ledesma et al.* [2016]. Flow measurements at C7 are derived from a long-established weir located below a confluence, ~ 20 m downstream of C2 (Figure 1a).

2.4. Analytical Methods

DOC and TDN were analyzed via the combustion catalytic oxidation method on a Shimadzu TOC VCPH analyzer (Shimadzu, Duisburg, Germany). NH_4^+ -N and NO_3^- -N were quantified colorimetrically using a SEAL Analytical AutoAnalyzer 3 (SEAL Analytical, Wisconsin, USA). NH_4^+ -N (hereafter NH_4^+) was analyzed using the Berthelot reaction to produce a blue-green-colored complex which was quantified colorimetrically at 660 nm (Method G-171-96 Rev. 12), with a minimum detection limit of $0.3\ \mu\text{g N L}^{-1}$. NO_3^- -N (hereafter NO_3^-) analysis was performed by reduction to NO_2^- with a copperized cadmium coil, followed by sulfanilamide and naphthylethylenediamine dihydrochloride chemistry to produce a reddish-purple azo dye; samples were analyzed colorimetrically (520 to 560 nm) (Method G-384-08 Rev. 2; minimum detection limit: $0.4\ \mu\text{g N L}^{-1}$). DON was calculated as the difference between TDN and dissolved inorganic N (i.e., $\text{NO}_2^- + \text{NO}_3^- + \text{NH}_4^+$). SO_4^{2-} -S (hereafter SO_4^{2-}) was analyzed using an ion chromatograph (Dionex ICS90) equipped with guard column (Dionex IonPacTM AG22) followed by an anion-exchange column (Dionex IonPac TM AS22) and suppressor. The separation was made under alkaline conditions with an eluent flow rate of $0.7\ \text{mL min}^{-1}$.

2.5. Calculations, Modeling, Statistics

2.5.1. Stream Export Calculations

Stream nutrient concentrations were estimated for each day of the study period (January 2011 to December 2012) by linear interpolation between sampling dates. Daily export was then calculated as the product of the interpolated daily concentration and the measured daily discharge from the gauging station at the catchment outlet. Daily export was summed to estimate annual export ($\text{kg N ha}^{-1}\ \text{yr}^{-1}$) for the C2 catchment for 2011 and 2012.

2.5.2. Estimating Soil Solution Lateral Fluxes

Lateral solute fluxes for 2011–2012 were estimated for each soil profile using the methodology described by *Ledesma et al.* [2016] for the same hillslope, which is based on the riparian flow-concentration integration model [*Bishop et al.*, 2004; *Seibert et al.*, 2009]. Lateral flow rates are based on the correlation between the groundwater table and stream-specific discharge, which is characteristic of organic and till soils where hydraulic conductivity decreases exponentially with depth [*Nyberg*, 1995]. Using the logarithmic regression curve of this relationship for soil profiles at each of the three lysimeter nests, it was possible to estimate the daily groundwater table for any given stream discharge. These regression curves were presented by *Ledesma et al.* [2016] and were based on the period June 2013 to October 2014, where both groundwater table and stream discharge data were available. We applied this model to estimate the daily groundwater table at each lysimeter nest for the period of study 2011–2012. Then, through the application of Darcy's law as described by *Seibert et al.* [2009] and *Ledesma et al.* [2013], it was possible to generate estimates of daily lateral flow at every centimeter below the estimated groundwater table (yielding a time series of lateral flow profiles for each lysimeter station).

Solute concentration profiles for each hillslope lysimeter nest were constructed using vertical, linear interpolation of solute concentrations between lysimeter sampling depths and between sampling dates. In each case, where values were missing, linear interpolation was used to gap fill. For the top and bottom of each profile, the upper and lower most values, respectively, were assumed to represent the remainder of the soil profile. Errors arising from this assumption are unlikely to affect the resulting export values. First, toward the

Table 2. Mean, Minimum, and Maximum Concentration of Inorganic and Organic Nitrogen (N) for Lysimeter Nests, Groundwater Wells and the Stream Sampled Between 2011 and 2012^a

Site	Habitat	NH ₄ ⁺ (μg N L ⁻¹)			NO ₃ ⁻ (μg N L ⁻¹)			DON (μg N L ⁻¹)			Samples Per Nest
		Mean	Minimum/Maximum	Mean	Minimum/Maximum	Mean	Minimum/Maximum				
S22	Upland	2.6	0.0 6.6	7.4	0.8 76.9	58.6	0.0 179.6				75
S12	Midslope	4.8	0.0 20.9	6.7	1.3 24.7	184.1	1.9 645.6				82
S4	Riparian	96.3	3.4 208.0	10.1	4.7 27.8	808.7	454.1 2574.9				81
K4	Riparian	159.2	6.7 450.7	9.6	5.6 22.4	705.6	248.6 1756.5				38
K6	Riparian	20.7	2.0 140.7	5.1	1.5 9.8	639.1	318.4 1440.5				26
S22 Well	Upland	6.8	4.2 11.0	8.6	6.1 10.8	92.9	49.7 116.0				5
S12 Well	Midslope	20.5	6.8 34.9	11.7	4.3 18.3	307.3	167.9 508.6				8
S4 Well	Riparian	181.4	94.5 238.0	15.9	8.4 23.1	762.4	610.5 951.3				10
C2	Stream	16.7	2.2 64.0	9.78	4.1 18.85	366.8	188.4 687.8				46

^aLysimeter means are derived from all dates and depths; wells and surface stream means are based on all samples collected during the study.

bottom of the soil profile, lateral flux approaches zero as a result of very low hydrologic conductivity. At the top of the profile, most values are above the groundwater table and therefore do not play a major role in lateral fluxes. Finally, these constructed time series of lateral flow and solute concentration profiles were integrated to estimate lateral NH₄⁺, NO₃⁻, and DON fluxes at S4, S12, and S22. The upper and lower 95% confidence intervals of the groundwater table-discharge relationship were also used to calculate potential upper and lower lateral flows and fluxes as an estimate of uncertainty.

2.5.3. Statistics

The regression curves used in the groundwater models were fitted using MATLAB (R2013b copyright 1994–2016 The MathWorks, Inc.). Relationships between different redox-sensitive solutes measured across the hillslope, as well as connections between soil properties (e.g., SOM percentage) and lysimeter chemistry, were explored using Spearman's rank correlations and graphical representation in Sigma Plot (version 11 copyright 2008 Systat Software, Inc.).

3. Results

3.1. Soil Water Chemistry

Within the three lysimeter nests representing the transition from near stream (S4) to midslope (S12) to upland forest soils (S22), TDN concentrations were highest at S4 and declined rapidly with distance from the stream (Table 2 and Figure 3). Across all sampling nests, DON was the dominant form of TDN, peaking at S4, where concentrations were nearly fourfold greater than S12 and fourteenfold greater than S22 (2574 versus 645 versus 179 μg N L⁻¹, maximum values for S4, S12, and S22, respectively). DIN concentrations at S4 were also strikingly different, reaching values of around 227 μg N L⁻¹, tenfold higher than those observed anywhere else along the transect.

Variance in DIN concentrations across lysimeter nests was driven largely by NH₄⁺, while NO₃⁻ concentrations were very low across all nests and depths. In the near-stream zone (S4), NH₄⁺ concentrations were low (<6 μg N L⁻¹) near the soil surface but increased rapidly with depth, reaching maximum values between 150 and 200 μg N L⁻¹ at 35 cm (Figure 3a). This peak in NH₄⁺ concentration coincided with the mean water table depth (Figure 3a). In contrast, DON concentrations at S4 were highest in the most surficial layers (10 to 25 cm), falling off as NH₄⁺ peaked. NO₃⁻ at S4 showed no vertical change in concentration and only contributed a small portion of the DIN pool. This pattern of high NH₄⁺ and DON values in conjunction with low NO₃⁻ found at S4 was consistent with two other nearby riparian lysimeter nests and riparian well chemistry (K4 and K6 and S4 well; Figure 1a and Table 2).

Moving upslope, the mean groundwater table dropped relative to the soil surface, and vertical trends for N also changed. At S12, mean NH₄⁺ concentrations increased with depth, exceeding those of NO₃⁻ at around 70 cm depth, which coincided with the lowest water table depth observed (Figure 3b). This vertical transition from NO₃⁻ to NH₄⁺ dominance was not found at S22, where the deepest sampling point was above the

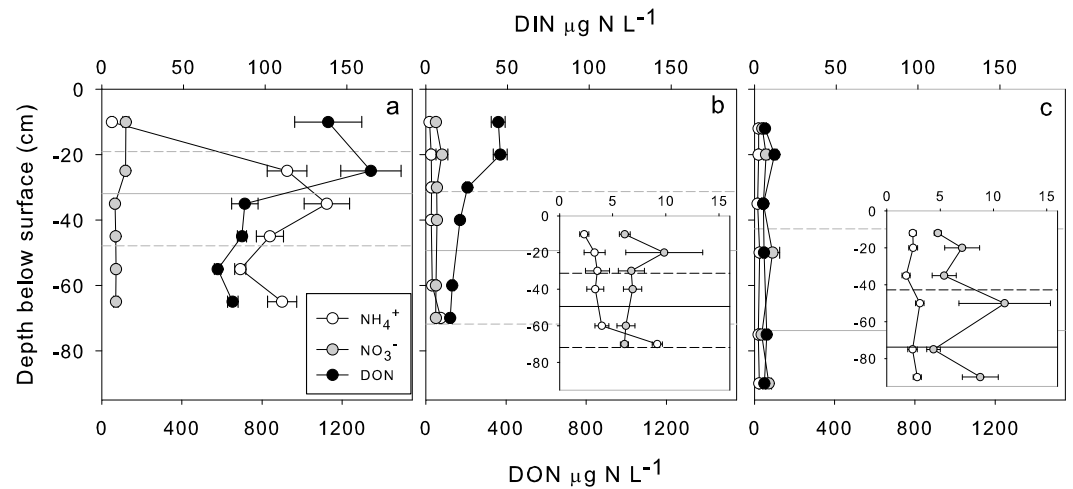


Figure 3. Concentration-depth profiles across the hillslope transect. Values represent mean concentrations \pm SE between January 2011 and December 2012 ($n = 4\text{--}18$ depending on depth/site) for (a) riparian (S4), (b) midslope (S12), and (c) upland (S22) lysimeter nests. Solid and dashed horizontal reference lines represent the modeled mean, minimum, and maximum groundwater depth, respectively, for each lysimeter station for the period of study. Insets in panels b and c show detail of NH_4^+ and NO_3^- patterns with depth for S12 and S22.

minimum observed water table depth (Figure 3c). These overall patterns were also borne out by values obtained from groundwater wells at S12 and S22 (Table 2).

The average DOC:DON ratios were similar for S4, S12, and S22 over the course of the study (53.9, 57.5, and 60.4, respectively). At S4, the variance in DOC:DON for the nest as a whole over the course of the study was relatively low ($\text{CV} = 12.8\%$), but the mean ratio changed with depth. In particular, at 25 cm, the DOC:DON ratio (45:1) was significantly lower than elsewhere in the profile ($p < 0.001$) (Figure S1 in the supporting information). This shift occurred at approximately the same position as the mean water table depth (Figure 3a) and was the result of a relative increase in DON concentration at this depth, rather than shifts in the DOC concentration.

The spatial variation in N chemistry across lysimeter nests corresponded to gradients in SOM or local redox conditions, depending on the solutes considered. For example, average DON concentration increased strongly among nests and depths with SOM percentage (Spearman's $r = 0.80$, $p < 0.001$; Figure 4a). It is notable, however, that the three deepest lysimeter samples from S4 had considerably higher DON concentrations than sampling locations elsewhere on this hillslope having similar SOM percentage (Table 1). In contrast to DON, there was no clear relationship between SOM percentage and NH_4^+ (Figure 4b). Instead, at S4, we found a strong negative correlation between NH_4^+ and the apparent redox state as represented by groundwater SO_4^{2-} concentrations (Figure 5a; Spearman's $r = -0.84$, $p < 0.001$). NH_4^+ was also positively correlated with DON at this same location ($r = 0.67$, $p < 0.001$; Figure 4b).

3.2. Stream Nitrogen Concentrations and Fluxes

Overall, DON concentrations in C2 stream water were approximately an order of magnitude greater than those of DIN (Table 2). Mean DON concentrations were $367 \mu\text{g N L}^{-1}$ (± 14.9 SE) with a range of $188 \mu\text{g N L}^{-1}$ to $688 \mu\text{g N L}^{-1}$, while mean DIN concentrations were $25.8 \mu\text{g N L}^{-1}$ (± 2.3 SE), with a range of $9.1 \mu\text{g N L}^{-1}$ to $73.5 \mu\text{g N L}^{-1}$. The DIN pool was composed of NO_3^- and NH_4^+ in similar proportions ($\text{NH}_4^+/\text{NO}_3^-$ ratio 1.87 mean, 0.29 min, 8.36 maximum). Changes in discharge between sampling dates were associated with variation NH_4^+ , NO_3^- , and DON and DOC concentrations; however, discharge alone was a poor predictor of concentration with significant correlations only found between discharge and NO_3^- (Spearman's rank 0.39, $p < 0.01$) and DOC (Spearman's rank 0.42, $p < 0.01$) (Figure S2 in the supporting information). Overall, annual flow in the C2 catchment appeared to have little impact on DIN export which remained almost constant between 2011 and 2012 ($0.07 \text{ kg N ha}^{-1} \text{ yr}^{-1}$ versus $0.06 \text{ kg N ha}^{-1} \text{ yr}^{-1}$) despite the water export more than doubling (187 mm and 395 mm for 2011 and 2012, respectively). In contrast,

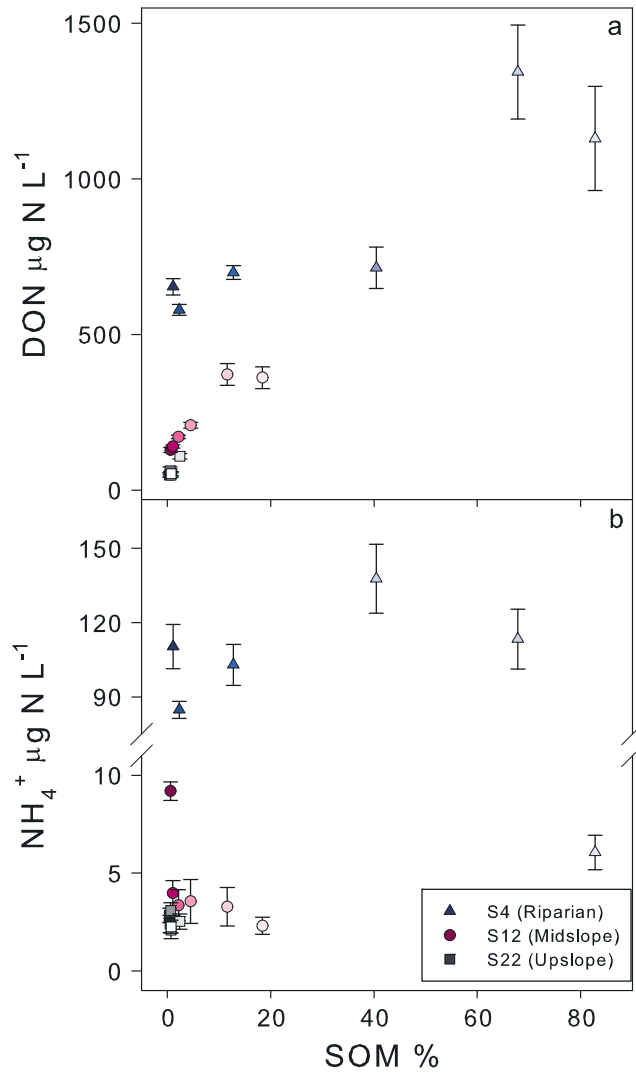


Figure 4. The relationship between soil organic matter content (SOM), NH_4^+ (a), and DON (b) concentrations ($\mu\text{g N L}^{-1}$, mean \pm SE) at upslope (S22, squares dark grey to white), midslope (S12 circles dark to light pink), and near-stream (S4, triangles dark to light blue) lysimeter nests, during 2011 and 2012. Symbols are shaded to indicate depth, with dark to light indicating deep to surficial lysimeter cups. The correlation between SOM and DON was highly significant (Spearman's $r = 0.80$, $p < 0.001$), while no significant relationship existed between SOM and NH_4^+ .

annual DON flux tracked the annual discharge trends and nearly doubled from 2011 to 2012 ($0.81 \text{ kg N ha}^{-1} \text{ yr}^{-1}$ versus $1.39 \text{ kg N ha}^{-1} \text{ yr}^{-1}$; Table 3).

3.3. Modeled Hillslope Versus Stream N Export

Estimates of hillslope N export showed that fluxes in the near-stream zone (S4) were fivefold (2011) and eightfold (2012) greater than upslope areas (S12 and S22) (Table 3). Within the S4 site, we found that 60% and 66% of total DIN export occurred between 21 and 30 cm depth during 2011 and 2012, respectively, while losses above and below this layer were modest (Figure 6 and Table S1 in the supporting information). The most surficial horizons (0–20 cm) contributed 1% and 5% of DIN export during 2011 and 2012, respectively. Similarly, losses below 40 cm totaled less than 4% and 2% of DIN export during 2011 and 2012, respectively. DON fluxes in this profile were similar with the dominant source layer also occurring between 21 and 30 cm depth (60% and 67% of annual flux for 2011 and 2012, respectively; Table S1 in the supporting information). These estimates of flux are based on an assumption of how groundwater level changes with discharge. We explored how uncertainty in this assumption of groundwater depth influences estimates of solute export by using the hydrologic flux from the best fit, upper and lower 95% confidence intervals from the

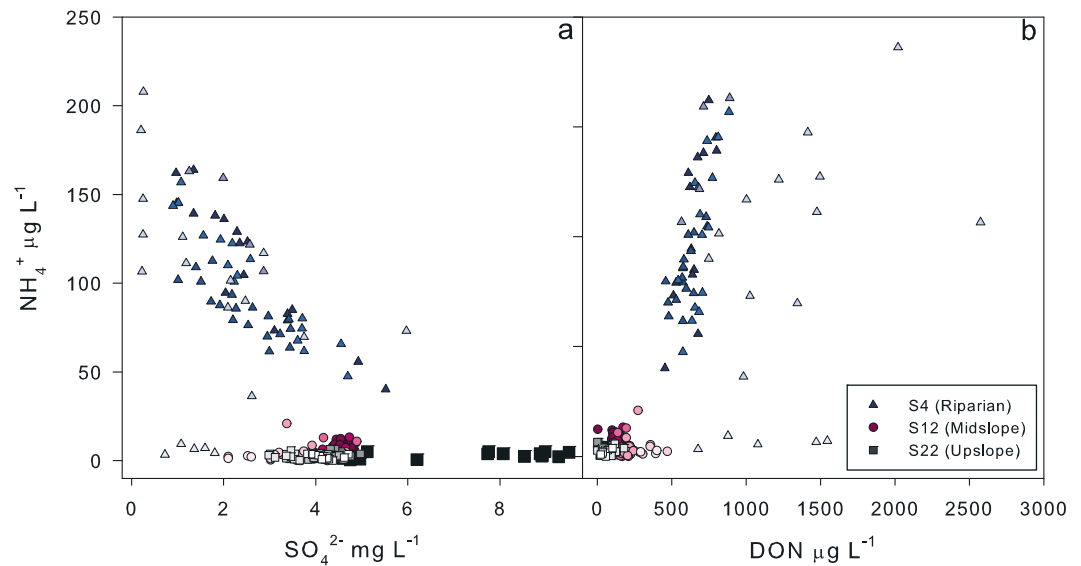


Figure 5. The relationship between NH_4^+ ($\mu\text{g N L}^{-1}$) with SO_4^{2-} (mg S L^{-1}) and DON ($\mu\text{g N L}^{-1}$), for all measured depths at the upslope (S22, squares dark grey to white), mid slope (S12 circles dark to light pink), and near-stream (S4, triangles dark to light blue) lysimeter nests, during 2011 and 2012. Symbols are shaded to indicate depth, with dark to light indicating deep to surficial lysimeter cups. (a) NH_4^+ at S4 (triangles, blue spectrum) was negatively correlated with SO_4^{2-} (Spearman's $r = -0.84$, $p < 0.001$). (b) NH_4^+ at S4 was positively correlated with DON (Spearman's $r = 0.67$, $p < 0.001$).

groundwater model (Figure 6 and Table 2). Such changes in the estimated water table level had varying effects depending on the solute (i.e., DIN versus DON) and year, but did not alter the relative difference in modeled N flux among lysimeter nests (Table 3).

The changes in precipitation and resulting flow between 2011 and 2012 also had variable effects on modeled exports across the hillslope. Our estimates indicate that, in the midslope and upslope nests (S12 and S22), hydrological N losses showed little change between 2011 and 2012 despite greater water export. However, at S4, the model estimated that slightly more than double the amount of N was exported during 2012 than 2011. Finally, compared to measured stream exports, the modeled hydrologic losses at S4 were twofold to threefold higher for DON during both 2011 and 2012. Despite this difference, a consistent relationship through time was found between modeled S4 and measured C2 DON daily exports (Figure S3 in the supporting information). Compared to DON, the difference between fluxes estimated for the S4 lysimeter nest and the adjacent stream was larger for DIN, being threefold and eightfold greater during 2011 and 2012, respectively.

4. Discussion

4.1. Overview

It is well accepted that terrestrial sources dominate nutrient supply to headwater streams, but the processes that regulate how soil nutrient pools on land influence patterns of surface water chemistry remain less clear [Morse *et al.*, 2014]. In general, landscape elements that are most spatially extensive are commonly assumed to determine the overall nutrient supply, while smaller, biogeochemically active zones are thought to be more important for removal or retention, e.g., via denitrification in riparian soils [McClain *et al.*, 2003]. In contrast to this view, we found that the upland forest soils in this boreal landscape were highly retentive of N when compared to the riparian zone, where concentrations and fluxes of all N species to the stream were markedly higher (Table 3). Indeed, DIN fluxes estimated for S22 and S12 were insufficient to support the flux estimated at S4, suggesting that N moving through this riparian zone is derived from locally mineralized and mobilized sources, as has been found for DOC in these [Ledesma *et al.*, 2015] and other northern streams [Dick *et al.*, 2015]. In this way, stream nutrient signatures provide little information about the ecosystem dynamics of the surrounding forest soils, which historically has been a key motivation of the “small watershed approach” [Bormann and Likens, 1967]. This disconnection between uplands and streams is potentially

Table 3. Export Calculated for Each Sampling Station in $\text{kg N ha}^{-1} \text{yr}^{-1}$ ^a

Site	DIN 2011			DON 2011			DIN 2012			DON 2012		
	Best Fit	Upper/Lower		Best Fit	Upper/Lower		Best Fit	Upper/Lower		Best Fit	Upper/Lower	
S22	0.03	0.03	0.02	0.15	0.15	0.15	0.03	0.03	0.04	0.16	0.18	0.15
S12	0.02	0.03	0.02	0.35	0.46	0.30	0.04	0.03	0.04	0.50	1.00	0.41
S4	0.21	0.19	0.19	1.75	1.89	1.48	0.53	0.39	0.54	4.18	4.10	3.75
C2 (stream)	0.07	n/a	n/a	0.81	n/a	n/a	0.06	n/a	n/a	1.39	n/a	n/a

^aBest fit, upper and lower columns represent the export calculated with the respective fit lines from the ground water regression model. Upper and lower estimates are based on the 95% confidence intervals

characteristic of many low-gradient catchments but is likely exacerbated in regions where peat accrual along channel margins is widespread. By contrast, for higher-gradient catchments with more rapid drainage, upland ecosystem processes are likely better integrated by streams as short transit times may limit the potential for chemical transformation [Doyle and Bernhardt, 2011].

4.2. N Flux Along the Hillslope

As observed elsewhere in Fennoscandia [e.g., Kortelainen et al., 1997], we found that the upland forest soils in this study were highly efficient at retaining N. Total modeled N flux at S22 was around 15 times less than estimates of atmospheric wet N deposition at this site ($0.18 \text{ kg N ha}^{-1} \text{yr}^{-1}$ versus $2.7 \text{ kg N ha}^{-1} \text{yr}^{-1}$). Furthermore, N export was largely in the form of DON (84%), with very little DIN lost from the upland soil lysimeter nest ($0.03 \text{ kg N ha}^{-1} \text{yr}^{-1}$). These modest fluxes are in line with expectations for boreal forests in this region given that total “new” N inputs to this system are unlikely to exceed $6 \text{ kg N ha}^{-1} \text{yr}^{-1}$ ($2.7 \text{ kg N ha}^{-1} \text{yr}^{-1}$ deposition + $<3 \text{ kg N ha}^{-1} \text{yr}^{-1}$ via N fixation [Lindo et al., 2013]), while plant N demand is likely between 15 and $50 \text{ kg N ha}^{-1} \text{yr}^{-1}$ [Sponseller et al., 2016], much of which must be met through internal cycling [Cleveland et al., 2013]. More generally, the balance between forms of N exported from this location is consistent with the prediction that N losses from N-limited ecosystems be dominated by organic forms that are less readily available to biota [Hedin et al., 1995].

The transition from upland forest soils to riparian soils captured a gradient of increasing N concentration in soil solution (Figure 3) and greater lateral fluxes (Table 3). This pattern was driven largely by increased

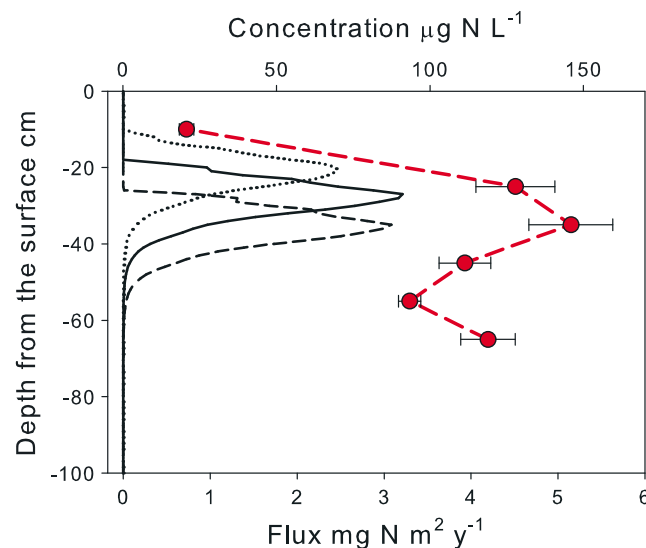


Figure 6. Modeled annual DIN flux (lower x axis) and average DIN concentration (upper x axis) plotted against soil depth in the riparian zone (S4). Black dotted, solid, and dashed lines represent values calculated using the upper best fit and lower 95% confidence intervals for the groundwater model (GWM), respectively. Red dashed line with circles represents mean DIN concentration (\pm SE) during 2011 and 2012.

DON export, which was closely correlated with parallel increases in SOM content with downslope position. SOM accrual along small drainage systems is typical of the region [Grabs et al., 2012] and potentially results from historical peat accumulation in shallow depressions which frequently form zero- and first-order streams. However, DIN concentrations and fluxes along the same transect were not directly related to SOM, and only increased in the near-stream zone (S4), at depths at and below the mean groundwater depth (Figure 3). This disconnection between DIN flux and SOM storage across the hillslope is likely driven by high soil C:N ratios which favor net immobilization over net mineralization within the microbial pool [Gundersen et al., 2006] as well as by the capacity of root uptake to outpace rates of hydrologic N flux

[Gerber and Brookshire, 2014]. Moreover, it is also possible that depolymerized organic N is taken up at sufficiently high rates in surface soils to preclude significant mineralization in the first place [Wild *et al.*, 2015].

The N pool in the riparian zone (S4) was distinguished from that of the upslope lysimeter nests by a dramatic increase in NH_4^+ and small decline in NO_3^- concentrations between 10 and 35 cm depth, despite having a similar SOM content as upslope locations. This change corresponded in vertical space to the mean and upper limit of the groundwater table, whereas at upslope lysimeter nests (S12 and S22), the top 30 cm of soil profile remained above the water table throughout the year (Figure 2). The nonlinear accumulation of reduced inorganic N suggests an abrupt transition from oxic to anoxic conditions where organic matter-rich soils are subject to prolonged groundwater inundation in near-stream environments. Consistent with this apparent redox gradient, NH_4^+ concentrations across depths in the riparian zone were negatively correlated with SO_4^{2-} (Figure 5a), which is consumed as an electron acceptor in the absence of sufficient oxygen and NO_3^- [Hedin *et al.*, 1998]. It is well known that redox conditions influence the balance of inorganic N species in groundwater [Helton *et al.*, 2015], and other studies have reported the accumulation of reduced N in riparian groundwater, particularly where hydrologic conductivity is low [e.g., Chestnut and McDowell, 2000]. In this study, however, the highest concentrations of NH_4^+ were observed in near-surface and hydrologically active layers of the riparian zone (25–35 cm; Figure 3a). The bulk of annual hydrologic flux also occurs through this narrow soil layer (94% and 90% in 2011 and 2012, respectively), and as a result 93% to 95% (2011 and 2012, respectively) of all DIN exported from the riparian zone was mobilized between 20 and 40 cm depth (Figure 6 and Table S1 in the supporting information). Although NH_4^+ concentrations were also relatively high in deeper soil horizons at S4 (Figure 3), low hydrological flux rates mean that these layers export comparatively little DIN toward the stream (2% to 4% from 41 to 90 cm).

4.3. Groundwater Controls on Net Mineralization in Riparian Soils

Maintaining relatively high NH_4^+ concentrations in soil layers through which most of the annual hydrologic flux passes requires considerably higher rates of net N mineralization and/or lower rates of plant uptake when compared to overlying and underlying strata. We hypothesize that this overall vertical pattern reflects shifts in the balance between gross N mineralization and biological demand that result from the fluctuating patterns of groundwater inundation throughout the year. Accordingly, for surficial soils that are rarely inundated, plant roots and mycorrhizae compete with free-living microbes for N in an environment fueled by belowground inputs of photosynthates from root exudation and senescence [Högberg *et al.*, 2001; Näsholm *et al.*, 2013]. Here strong biological demand and rapid rates of nutrient recycling likely serve to maintain low concentrations of inorganic N in soil solution. At the other extreme, deeper riparian soils (below 50 cm) are perpetually inundated and characterized by slow rates of hydrologic turnover, sustained anoxic conditions, and potentially poor organic matter quality [Bergman *et al.*, 2000]. Together, such circumstances can lead to low rates of microbial activity and nutrient turnover [e.g., McLatchey and Reddy, 1998] in an environment where oxygen stress largely excludes plant roots [Glenz *et al.*, 2006]. Thus, at these depths, both nutrient supply and demand are likely to be low, and NH_4^+ may accumulate simply because rates of lateral hydrologic flushing are slow and redox conditions prevent nitrification [Chestnut and McDowell, 2000].

In contrast to the zones above and below, the soils between 20 and 40 cm depth were characterized by peaks in NH_4^+ accumulation and transport toward the stream. This soil zone experiences periods of prolonged inundation and potentially extended anoxic conditions throughout the year, driven by snowmelt and rainfall events. Studies from other regions have similarly shown that periodic inundation of riparian soils has important consequences for N cycling processes [McClain *et al.*, 1994; Harms and Grimm, 2008]. While the mechanisms underlying net production of NH_4^+ in this study cannot be resolved with our current data, we did observe significantly lower C:N ratios at this depth (Figure S1 in the supporting information), consistent with a localized change in biogeochemical processing. Moreover, a recent study of DOC processing with soil depth at this same site also reported peaks in bacterial production, carbon consumption, and growth efficiency at 25 cm [Panneer Selvam *et al.*, 2016]. These results suggest the potential for comparatively high rates of nutrient turnover in soils where, at least for some portion of the year, biological nutrient demand (including root uptake) is likely constrained by low redox conditions, thus leading to a hot spot of net NH_4^+ production.

Ultimately, multiple factors within this zone may interact to foster sustained net NH_4^+ production in these soil layers. For example, soil frost, which has been reported as extending down to 29 cm at this site [Panneer

Selvam *et al.*, 2016], may stimulate DOC production [Haei *et al.*, 2010] and soil N turnover [Brooks *et al.*, 2011] for strata that are subsequently inundated/anoxic throughout the spring, leading to NH_4^+ production in excess of demand. In addition, fluctuations in redox state alone may drive elevated rates of SOM degradation [Hall *et al.*, 2015] and lead to a greater net release of NH_4^+ [Aller, 1994] when compared to environments that are permanently oxic or anoxic. Finally, N mineralization rates may be stimulated in this zone by periodic inputs of more labile organic matter. Recent research at S4 has shown that fine roots seasonally proliferate and die within these soil layers (20–40 cm [Blume-Werry *et al.*, 2016]), representing a potential source of fresh organic matter. Similarly, DOM leaching from surface and near-surface environments [Kaiser and Kalbitz, 2012] may also be available for microbial use in these strata. Together, such inputs of more readily useable carbon could facilitate the turnover of bulk SOM and promote net N mineralization (via “priming” [Finzi *et al.*, 2015]). Overall, given the clear significance of near-surface riparian soils to boreal stream chemistry [Grabs *et al.*, 2012], a more detailed assessment of the potential mechanisms underlying these patterns is warranted.

4.4. Disparity in Stream Versus Riparian Fluxes

The predicted N fluxes from S4 and the adjacent stream (C2) might be expected to match if there was no significant net processing of N between the riparian lysimeter nest and the downstream gauging station and if all inputs to the stream matched those observed at the study transect. However, we found that riparian fluxes of DON, while closely correlated with C2 fluxes over time, were consistently 2–3 times greater (Figure S3a in the supporting information). For DIN, there was little temporal synchrony between riparian and stream fluxes, and the magnitude of export from the riparian zone relative to the stream was even greater (as much as threefold to eightfold greater; Figure S3b in the supporting information). Similar discrepancies between near-stream and stream fluxes have been previously reported in other regions [McClain *et al.*, 1994; Chestnut and McDowell, 2000]. In this system, there are likely to be multiple, nonmutually exclusive explanations for these discrepancies, which relate to (1) landscape heterogeneity in soil conditions that governs variation in resource supply to streams, (2) biotic and abiotic retention of N at the land-water interface (along the hydrological flow path between S4 and the stream), and (3) the net retention of N within the stream channel itself.

It is unlikely that the N flux estimates from S4 perfectly represent all water moving toward the stream channel along its entire length. Overall, the concentrations measured from lysimeters at S4 were quite similar to those observed from the adjacent well (Table 2). However, comparison of S4 lysimeter data with other riparian nests along this stream (K4 and K6; Table 2) does point to a potentially wider range of local riparian flux rates. More broadly, Grabs *et al.* [2012] showed that there can be large variation in total organic carbon (TOC) concentrations in soil water from different riparian zones across the KCS (e.g., those dominated by organic versus mineral soils). This heterogeneity was sufficient to explain much of the variation in stream TOC concentrations. It is reasonable to suppose that similar differences in contributing water will affect both DON and DIN delivery to the stream. In this sense, the observed discrepancy between riparian and catchment N fluxes could simply reflect that estimates from S4 tend to be greater than the average inputs distributed along the length of this stream.

In addition to catchment-scale heterogeneity in inputs, retention and removal of N in the riparian zone and stream potentially contribute to this discrepancy. Indeed, 4 m of soil separates the S4 lysimeter and the channel and this distance could provide ample opportunity for N retention or removal en route to the stream. First, sorption to particles can play an important role in immobilizing solutes, particularly positively charged molecules like DON and NH_4^+ . However, this mechanism is normally associated with soils having high mineral content [Kothawala and Moore, 2009], which we lack in this riparian zone. In addition, biogeochemical transformations of N are well known to arise from steep redox gradients that develop across small spatial scales in riparian zones [Hedin *et al.*, 1998]. Here the co-occurrence of oxic and anoxic conditions in close spatial or temporal proximity may foster elevated rates of biotic uptake, support the coupling of nitrification and denitrification [McClain *et al.*, 2003], and thereby reduce N delivery across the land-water interface. Lastly, net removal of N within the stream itself can also reduce downstream export [e.g., Bernhardt *et al.*, 2003]. However, nutrient uptake and release in many small streams are in balance [Brookshire *et al.*, 2009], and strong net removal of DIN and DON seems unlikely in this well-shaded, woodland stream, where light and thermal constraints on aquatic productivity are likely to result in a relatively weak N sink.

5. Conclusions

Our results highlight the challenge of using small stream N exports alone to understand the dynamics of the surrounding forest soils, as is often done in small watershed studies. Other recent studies have similarly reported riparian soils to be sources of N to streams in temperate [e.g. *Duncan et al.*, 2015] and Mediterranean [*Lupon et al.*, 2016] catchments. While the underlying mechanisms in these studies differ from those highlighted here, together such observations suggest that this landscape pattern may be more common than is currently appreciated. In this study, both DIN and DON in the stream appear derived primarily from peat-rich riparian soils. DON production from this pool of SOM is not surprising and agrees with work on DOC and DON export in other studies from the boreal zone [*Fölster*, 2000; *Petrone et al.*, 2007; *Grabs et al.*, 2012]. Further, our results suggest a hot spot for NH_4^+ mineralization within near-surface riparian soils that potentially reflects the interaction between groundwater fluctuation, shifting redox conditions, and SOM. The resulting stream exports of N from this landscape thus may have little to do with N dynamics of the upland forest soils but instead be more dependent on internal biogeochemical processes and hydrologic routing through the riparian zone.

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