In search of control points: A study on the interaction of hydrological fluxes and nitrogen in the boreal landscape.

Meredith Blackburn

Faculty of Forest Science
Department of Forest Ecology and Management
Umeå

Doctoral thesis
Swedish University of Agricultural Sciences
Umeå 2018

Cover: Sketches of flowpaths in mires and riparian zones.
   (Meredith Blackburn)

In search of control points: A study on the interaction of hydrological fluxes and nitrogen in the boreal landscape.

Abstract

Nitrogen (N) export from terrestrial ecosystems is strongly influenced by hydrological flux, but losses of reactive N forms through surface waters are generally thought to be under strong biological control. However, losses from terrestrial ecosystems may be fostered by catchment processes that allow N to circumvent biological uptake. The aim of my research was to investigate how boreal landscape attributes interact with hydrological forcing to regulate N delivery to streams. I explored these controls through detailed study of key land-water interfaces, in combination with broader assessments of N concentration and export in the Krycklan Catchment Study (KCS), located in northern Sweden. I found, contrary to the prevailing view, forest riparian zones represented a net source of dissolved organic N (DON) and dissolved inorganic N (DIN) to streams. This pattern is connected to organic-rich riparian soils that promote local N production, potentially decoupling stream N exports from upland forest processes. Mires also acted as important N sources as reduced N in deep peat layers was delivered to streams through preferential flowpaths. At network scales, unique headwater biogeochemical patterns became more synchronous downstream, as mire, forest, and lake signals mixed. Nonetheless, mire and wet riparian areas emerged as important explanatory variables for stream N composition and concentration across the KCS. Finally, the relative importance of hydrological flux as the driver of N export in this system differed according to N form, the temporal scale considered, and catchment structure. DON formed close and consistent relationships with discharge among sites, years, and seasons, while DIN export was more weakly and variably related to flow. Still, surprisingly strong flow-controlled DIN export was observed during snow-free seasons, highlighting the importance of local, riparian N sources. Overall, my results suggest that long term peat accumulation – both in riparian zones and in mires – has created control points that regulate N losses through different mechanisms. The strong influence of these patches may overwhelm the detection of upland forest influences on N export in relatively pristine boreal landscapes.

Keywords: boreal, stream, dissolved organic nitrogen (DON), ammonium, nitrate, riparian zone, mire, forest

Author's address: Meredith Blackburn, SLU, Department of Forest Ecology and Management,
SE-901 83 Umeå, Sweden

To those who stop, see, and not only ask why, but try to find an explanation….

"The aim of science is to seek the simplest explanations of complex facts. We are apt to fall into the error of thinking that the facts are simple because simplicity is the goal of our quest. The guiding motto in the life of every natural philosopher should be, 'Seek simplicity and distrust it."
Alfred North Whitehead, The Concept of Nature: The Tarner Lectures Delivered in Trinity College, 11/1919

Contents

List of publications

I   M. Blackburn*, José L. J. Ledesma, Torgny Näshilm, Hjalmar Laudon, Ryan A. Sponseller (2017). Evaluating hillslope and riparian contributions to dissolved nitrogen (N) export from a boreal forest catchment. *Journal of geophysical research*, vol 122 (2), pp. 324-339.

II   Ryan A. Sponseller*, M. Blackburn, M. B Nilsson, H. Laudon (2017). Headwater Mires Constitute a Major Source of Nitrogen (N) to Surface Waters in the Boreal Landscape. *Ecosystems*, vol (issue),

III Meredith Blackburn*, Hjalmar Laudon, William Lidberg, Martyn Futter, Ryan A. Sponseller. Landscape regulation of nitrogen delivery to boreal streams (manuscript)

IV Meredith Blackburn*, Hjalmar Laudon, Ryan A. Sponseller. Landscape heterogeneity shapes patterns of supply versus transport control of nitrogen export from a boreal landscape. (manuscript)

Papers I-II are reproduced with the permission of the publishers.

* Corresponding author.

The contribution of Meredith Blackburn to the papers included in this thesis was as follows:

I   Blackburn contributed to sample collection and was partly responsible for chemical analysis. Blackburn was also closely involved in planning the investigation, primary responsible for data analysis and writing text.

II   Blackburn contributed to sample collection, assisted with conceptual development of the study, data interpretation and writing the text.

III   Blackburn contributed to sample collection and chemical analysis. Blackburn was primarily responsible for the conceptual development of the study, data analysis and writing the text.

IV   Blackburn assisted with sample collection and chemical analysis. Blackburn was also responsible for the design of study data analysis and writing the text

1   Introduction

A cornerstone of catchment biogeochemistry is that a stream's chemistry reflects the sum of all biogeochemical processes occurring in the catchment it drains (Bormann & Likens 1967). Accordingly, nutrient fluxes measured in streams can be assumed to be the product of solute availability and hydrological transport processes. In this context, plant-soil systems are particularly strong sinks for growth-limiting nutrients such as nitrogen (N) (LeBauer & Treseder 2008). Yet despite this efficient use, broader scale assessments often highlight that even N-limited ecosystems are subject to substantial N losses to surface waters (Perakis 2002). Understanding how, why, and where these losses occur is an important challenge in ecosystem science, with implications for the long-term maintenance of terrestrial nutrient limitation (Menge et al. 2009), patterns of resource delivery to recipient aquatic ecosystems (Lucas et al. 2016), and for predicting how these inputs may change in a warmer, wetter future (Teutschbein et al. 2017)

The apparent contradiction of N leaching from N-limited ecosystems is related to various mechanisms that allow nutrients to circumvent biotic sinks on land. For example, much of the N bound in complex organic molecules (DON; dissolved organic nitrogen) is not readily usable by plants and soil microbes and therefore is exported from terrestrial ecosystems irrespective of biotic demand (Hedin et al. 1995). By comparison, inorganic forms of N (e.g., nitrate (NO_3) and ammonium (NH_4)) are more easily taken up, and thus hydrologic losses are thought to arise through spatial or temporal mismatches in supply and demand that reduce the efficiency of terrestrial retention. Such mismatches may operate over time, for example, when nitrogen mineralization is out of phase with temporal patterns of biological uptake (Augustine & McNaughton 2004). Limiting resources may also be isolated from biotic uptake in space, for example by hydrologic flowpaths that bypass active soil layers (Schiff et al. 2002), or by the vertical relocation of nutrients to deeper soils that are not easily exploited by plants (Walvoord et al. 2003).

While these examples show how catchment-scale processes can shape nutrient cycling and export, riparian zones have also received much attention as hot spots that regulate N delivery to streams (Peterjohn & Correll 1984; McClain et al. 2003; Ocampo et al. 2006). For example, losses of N from riparian soils can arise from several mechanisms, including immobilisation by plant and microbial communities, and coupled nitrification/denitrification under alternating oxic/hypoxic conditions (Vidon et al. 2010). However, in northern landscapes, organic (peat) rich riparian zones are also known to be important sources of dissolved organic carbon (DOC) to surface waters (Dick et al. 2015; Ledesma et al. 2017), and thus likely play the same role for DON. Moreover, organic riparian soils have been shown elsewhere to accumulate inorganic N, with the potential to act as sources of DIN to surface waters (Cirmo & McDonnell 1997; Fölster 2000). However, the circumstances leading to 'net N production' in riparian zones are not well studied, despite their potential important role for understanding nutrient losses from catchments, particularly where upland ecosystems receive low levels of anthropogenic N inputs and thus can be expected to be highly retentive.

In addition to organic-rich riparian zones, extensive peat formations such as mires are widespread across much of boreal and arctic biomes and may also shape patterns of N export from catchments. Peat accumulation in open mires is associated with prolonged hypoxic conditions and a vertical separation between areas of high biological N demand near the surface and deeper strata where nutrient resources may be able to accumulate. While peat storage and turnover is widely studied from a carbon (C) balance perspective (e.g., Nilsson et al. 2008), N bound in organic matter can also accumulate at relatively high rates (Loisel et al. 2010). Once N reaches sufficient depth, it is lost from the biologically active compartment of these systems (Urban et al. 1988) and may persist in reduced forms under near-constant anoxia (Helton et al. 2015). Where such peat forming ecosystems are spatially extensive, exports of N from watersheds may be sustained by deep storage zones, which are often hydrologically connected to streams via preferential or pipe flow (Holden et al. 2012). These linkages are well known to facilitate DOC export from catchments and may influence N delivery in similar ways.

Overall, peat accumulation, whether it be in the form of organic-rich riparian soils or in open mires, has be shown to profoundly facilitate the export of a broad range of chemicals in boreal streams (Lidman et al. 2017; Ledesma et al. 2017) – and thus has a strong potential to also influence stream N dynamics. In this context, these patches in the landscape are candidate 'control points', defined by Bernhardt et al. (2017) as locations that exert disproportionately large influences over elemental cycling and loss by facilitating hydrologic transport and/or

elevated biogeochemical processing rates. In addition, the widespread occurrence of these features in the northern boreal zone, where both forest (Högberg et al. 2017) and mire (e.g., Aerts et al. 1992) plant communities are N limited, also provides an opportunity to explore how long-term landscape development may facilitate nutrient losses by creating mismatches in nutrient supply and demand in space. Ultimately, a better understanding of patterns of hydrological N losses from catchments is important in this region, because the boreal zone is the largest terrestrial biome, and this area is expected to be particularly sensitive to future changes in temperature and precipitation (e.g., Crowther et al. 2016). One expected consequence of these climate changes is a fundamentally altered hydrological regime (Teutschbein et al. 2015), which is likely to have important biogeochemical consequences.

2 Research aims

Overall the aim of this work was to understand how boreal landscape dynamics are reflected in stream N chemistry and how catchment structure and hydrological processes interact to regulate N concentrations and fluxes. These goals were addressed first through the investigation of patterns of N mobilization and hydrologic loss within two key landscape types: forests and mires. The understanding gained from these two dominant landscape elements was then used to inform network scale assessments that addressed pattern and controls of stream N chemistry and export. Specifically I focused on the following questions:

➢ Where is N mobilized along a forest hillslope? To what extent do peat-rich riparian zones regulate the export of N to surface waters? (Paper I)

➢ How do headwater mires influence N cycling in northern boreal landscapes? Does peat formation in mires promote hydrologic losses of N through the separation of zones of supply and demand? (Paper II)

➢ What are the relative roles of catchment-wide versus local features as determinants of N concentration in a boreal stream network? In this context, how does land cover, hydrological connectivity, and catchment size regulate network patterns of stream water N concentration and form? (Paper III)

➢ How does the hydrologic export of N respond to variability in runoff for organic and inorganic forms that differ in biogeochemical reactivity and mobility? How do these 'flow-export' relationships vary seasonally and by landscape structure? (Paper IV)

3   Methods

3.1   General Methods

3.1.1 Site description

The work I present here was conducted within the 68 km^2 Krycklan catchment study (KCS) (64°14'N, 19°46'E) a long term research and monitoring site in Sweden's boreal zone (see Laudon et al. 2013 for a full site description). The KCS consists of 16 long term monitored catchments, eleven of which formed the basis of my work. These nested catchments included in this work, totalling 12.3 km^2 in area, receive around 614 mm of annual precipitation of which 35 to 50 % arrives as snow. In all, this precipitation generates a 30-year average of 311 mm yr^{-1} of runoff. The snow pack that develops in winter remains on average for 167 days per year (Laudon & Ottosson Löfvenius 2016). This melts over a period of 3 to 4 weeks in spring, driving the largest hydrological event of the year, and accounting for around 45 % of annual runoff (Paper IV). Spring in the Krycklan catchment arrives in early May and rapidly transitions into summer. Summers, which are generally cool (July +14.7˚C, 30 year mean), normally extend between June and early September. Autumn is a short and variable season, typified by frequent freeze-thaw events, starting sometime in September and transitioning to winter in late October or early November. Winters, typical of the boreal zone, are long and cold, lasting from November until April (January -9.5˚C, 30 year mean).
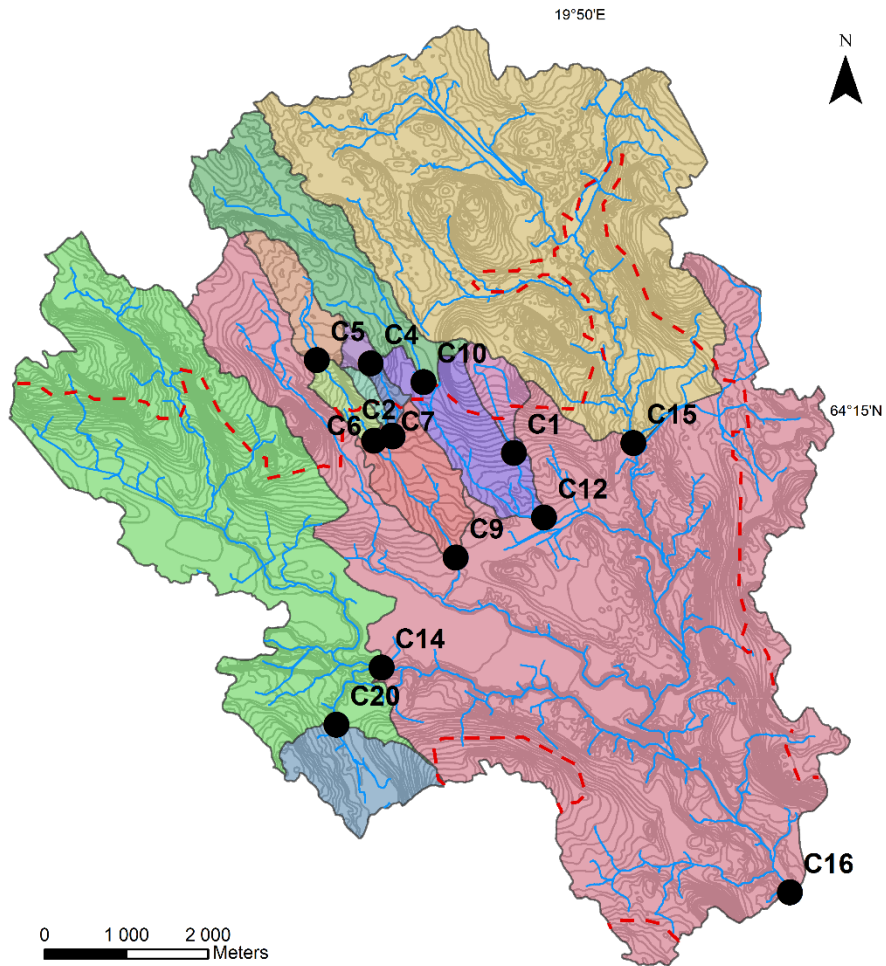
Figure 1. Krycklan catchment study area, surface relief indicated with 10m topographic lines and sub catchments marked in contrasting colours with stream network in blue. Black points represent the sampling site for each sub catchment. A red dashed line indicates the approximate location of a relic coast line.

The glaciated landscape of the KCS is typical of Fennoscandia, having moderate topography with a small amount of exposed bedrock. Surface soils in the study area largely have a sub-glacial or post-glacial origin and are largely underlain by Svecofennian metasediments/metagreywacke. The surface material is divided roughly into two equal areas by a relic, post-glacial coastline at approximately 260 m above the present sea level (Figure 1) (Laudon et al. 2013). Headwater sub-catchments located in the north-western part of the KCS are mostly above the highest coastline and are dominated by glacial till soils that have become podzolized on upslope areas, while peat deposits have developed in depressions and wet areas. The south-eastern portion of the KCS lies mostly below the relic coastline where soils are dominated by post-glacial fluvial and delta sediments. These soils, which are podsolized to a lesser extent than those above the relic coastline, are dominated by thick (up to 50 m) well drained coarse to fine sand deposits.

The KCS comprises a mosaic of forests (88%), mires (11%), lakes (0.7%), and agricultural areas (~1%). Forested areas have highly variable tree cover, which consists of approximately 50% *Pinus sylvestris* L., 17% *Picea abies* L., and 10% broadleaved trees including *Betula sp. Alnus sp. Salix sp.* Forest understory vegetation includes a mixture of bilberry (Vaccinium myrtillus L.) and lingon (*Vaccinium vitis-idaea* L.) and N fixing feather mosses (*Pleurozium sp.* and *Hylocomium sp.*), which transition to hydrophitic mosses (e.g. *Polytrichum commune* Hedw. and *Sphagnum sp.*) in hollows and groundwater discharge zones (Kuglerová et al. 2016). As is the case across much of Fennoscandia the forest has undergone active management which has included logging, and drainage (Hasselquist et al. 2017). Forest drainage was generally carried out in Sweden in the early 20th century. These ditches are now largely unmaintained and have often gradually filled in via sedimentation and paludification. Within the core of the KCS, which includes subcatchments C1, C2, C4, C5, C6, C7, C9, C10, and most of C12 and C13 no commercial forest management has occurred for at least 50 years; outside of this area conventional forest management is ongoing.

3.1.2 Stream monitoring

The research described here made use of samples and data collected from January 2011 to October 2014 (Paper I), 2008 to 2013 (Paper II), and July 2008 to December 2015 (Papers III and IV). These samples, collected by myself and other staff, form part of the stream monitoring program at the KCS (Laudon et al. 2013). Stream water was collected from all sites between 22 and 30 times per year. The timing of sampling was flow weighted so that during the spring flood

period, samples were collected as frequently as every third day, whereas during the summer sampling was approximately every two weeks, and winter base-flow sampling was monthly. Sampling techniques are described in detail in the relevant papers. Briefly, water samples are collected in pre-rinsed polyethylene bottles, filtered at 0.7 µm, and either refrigerated (for total dissolved N) or frozen (for inorganic N) prior analysis. Across the study area, discharge was measured and logged continuously as part of the KCS monitoring program. In key locations, frost-free gauging stations were established during the study to permit year round flow measurements. Winter discharge for locations without frost-free gauging stations were modelled with established flow relationships (Karlsen et al. 2016).

3.1.3 Analytical methods

Methods are described in detail in the relevant papers. In brief, dissolved organic carbon (DOC) and total dissolved nitrogen (TDN) were analysed via the combustion catalytic oxidation method, NH_4-N and NO_3-N were quantified colourimetrically, and NH_4 was analysed using the Berthelot reaction. NO_3 analysis was performed by reduction to NO_2 with a copperized cadmium coil, and quantified colorimetrically. Dissolved organic nitrogen (DON) was calculated as the difference between TDN and dissolved inorganic N.

3.2 Paper specific methods

3.2.1 Evaluating forest and riparian nitrogen flux (Paper I)

This paper focused on questions surrounding N mobilization and loss from soils to streams in a small, forested catchment (C2). I explored these transfers using measurements of N concentration in soil solution and stream water, together with an existing hydrological model to estimate organic and inorganic N flux along a hillslope transect. Stream and soil water chemistry, discharge, and groundwater fluxes were either measured directly or modelled (see paper I for full description). In brief, stream chemistry and discharge were determined as described above for the KCS monitoring program. In addition, soil water was collected 18 times between January 2011 and December 2012 from lysimeter nests located 4, 12, and 22 meters from the stream along a well-studied topographical flow path (Figure 2, Laudon et al. 2004). Previous work at this site has shown direct connection between the lysimeter nests and the stream (Peralta-Tapia et al. 2015). Each lysimeter nest consists of a group of ceramic

suction lysimeters placed at multiple depths to best capture fluctuations in groundwater throughout the year (Laudon et al. 2013). Nearby soil lysimeter nests and groundwater wells were also sampled to provide additional support for soil solution chemistry observed along main hillslope transect.
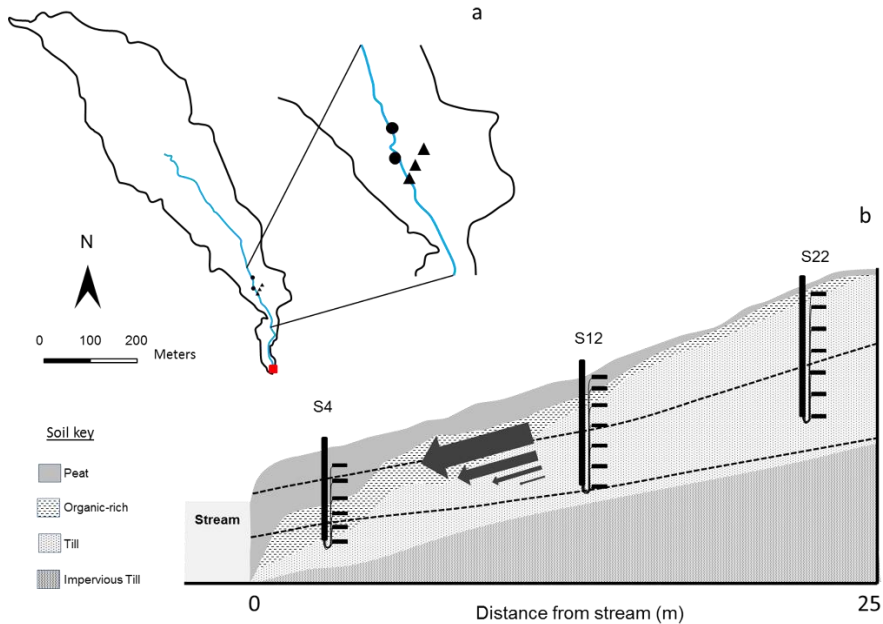
Figure 2. Study site and detail of hillslope installations within the Krycklan Catchment Study Sweden (64°140N, 19°460E). (a) C2 catchment boundaries, stream (blue), stream sampling point, and gauging station (red square). The enlargement shows the lysimeter stations S4, S12, and S22 (black triangles) 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.

Both lysimeter and well water were handled and analysed as described above for stream water; however, I also analysed sulfate (SO_4) to provide an additional proxy for groundwater redox conditions. SO_4 and NO_3 are the first alternative electron acceptors to be used by microbes when oxygen is no longer available (Stumm & Morgan 1996).

Lateral water fluxes in the transect were estimated for one cm deep horizon intervals for each soil profile, which, in conjunction with a matching N concentration profile, was used to calculate N flux through the profile at each lysimeter nest (Ledesma et al. 2016). Lateral flow rates were based on the correlation between the groundwater table and stream specific discharge, which

is characteristic of glacial till soils, where hydraulic conductivity decreases exponentially with depth (Nyberg 1995). As high resolution groundwater measurements were not available for the study period, these relationships were based on a period when both groundwater table and stream discharge data were available (Ledesma et al. 2016).

Solute concentration profiles for each hillslope lysimeter nest were constructed using vertical, linear interpolation of solute concentrations between sampling depths and dates. For the top and bottom of each profile, the upper and lower most values, respectively were assumed to represent the remainder of the profile. Errors arising from this assumption are unlikely to affect the resulting export values. First, toward the bottom of the soil profile, the lateral water flux approaches zero as a result of very low hydrologic conductivity (Nyberg 1995). At the top of the profile, most values are above the groundwater table for nearly the entire year and therefore do not play a major role in the lateral fluxes. As the groundwater table was estimated for the period of the study an error term was associated with this estimate. Thus, we calculated the upper and lower 95% confidence intervals of the groundwater table-discharge relationship and used these to calculate potential upper and lower lateral flows and fluxes as an estimate of uncertainty. Further details on statistical methods, assumptions and software used are given in Paper I.

3.2.2 Mire nitrogen delivery to surface waters (Paper II)

In this work I investigated how headwater mires influence N cycling in boreal landscapes. I addressed this issue using the C4 catchment (Figure 1), which includes a well-studied and heavily instrumented mire ecosystem. This mire is hydrologically connected to the surrounding forest and groundwater system, which in turn feeds a small outlet stream. The lower section of the mire, which is the focus of this study, is instrumented with a single nest of 15 piezometer wells targeting horizons from 0.25 to 4.5 m at 0.25 m intervals.

The broader importance of mires to network-scale N export was assessed in two ways. First, nutrient concentrations and seasonal export patterns were compared between C4 and C2, a directly adjacent forested catchment. Second, the influence of mire cover on average stream N concentrations was assessed using 16 additional monitoring sites within and near the KCS. These additional sites captured a range of catchment size, soil types, and management practices. All surface streams were sampled as part of the KCS monitoring program (see above).

Patterns of concentration and temporal variability of piezometer well chemistry in the mire organized according to the vertical zones, previously

identified by analysis of water isotopes (Peralta-Tapia et al. 2015). These include a surface zone (SZ, 0-0.25 m), a mid-zone (MZ, 0.25 – 2 m), a hydrologically active zone (HAZ, 2-3 m) and a deep zone (DZ, > 3 m) (figure 3). Finally, linear regression was used to investigate the relationships between the long-term (2008-2015) stream N concentrations (NH_4, NO_3 and DON) and percent mire cover across the different study catchments.
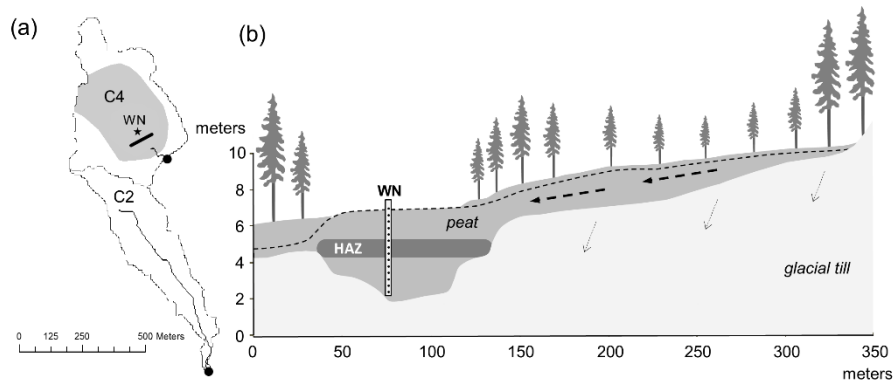
Figure 3. Site map of C4 mire showing (a) the location of catchment C4 and C2 within the Krycklan Catchment Study (KCS) and (b) a cross-sectional representation of the embedded mire within the C4 catchment (modified from Sirin and others 1998). The location of the hydrological active zone (HAZ) in the mire is based on previous research at this site (Peralta-Tapia and others 2015).

Annual export was calculated from daily flow and stream N concentrations gap filled by linear interpolation between sampling dates (see papers II and IV). N export from C4 scaled to the area of the entire sub-catchment likely underestimates the contribution of the embedded mire, through which essentially all water travels before leaving the system. In an effort to 'bracket' potential areal rates of N export from the mire itself, we took two approaches. First, we assumed all N exported from the catchment came from the mire itself, and so rescaled areal losses for the mire alone. Second, we estimated potential N flux from the contributing forest using flux data from C2 (Paper I).

3.2.3 Landscape regulation of nitrogen in boreal streams (Paper III)

In this effort I focused on questions surrounding landscape and seasonal controls on stream nitrogen concentrations. Stream chemistry was collected as described above, and a full description of the methods used can be found in Paper III. In brief I used three key approaches to analyse data spanning a period of 7.5 years and including ten relatively un-managed catchments in the KCS: C1, C2, C4,

C5, C6, C7, C9, C10, C12, and C13 (Figure 1). First I assessed seasonal dynamics of N forms across all sites for each calendar month. Second I analysed the degree of synchronicity in stream N concentrations across the landscape (sensu Kling et al. 2000). Finally, using a multivariate approach, I attempted to explain total stream TDN concentration and the proportion of each N form (DON, NH_4 and NO_3) in the stream water using a number of biotic and abiotic variables (Supplementary material Paper III).

3.2.4 Landscape control on nitrogen flow export response (Paper IV)

In paper IV, I evaluated the response of N export (NH_4 NO_3 and DON) to changes in discharge across KCS over a period of 7.5 years. A detailed description of the methods used in this study can be found in Paper IV and above. To summarise, concentrations of NH_4, NO_3 and DON and daily discharge were determined between July 2008 and December 2015. These data were used to calculate daily (i.e., on each sampling day) and annual export. For annual estimates, concentration data were gap filled using linear interpolation and daily estimates were summed to generate the yearly loss term.
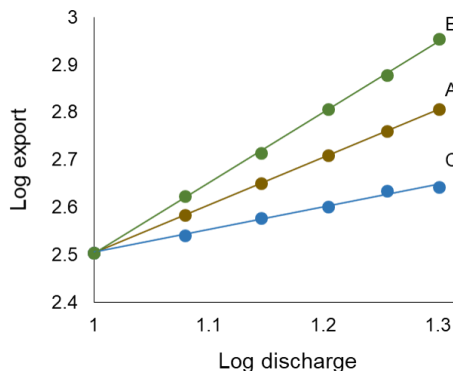
Figure 4. Generation of log discharge-export relationships based on different types chemical responses to hydrological change. Curves are derived from a simulation, of stream responses to a doubling of discharge. Curve A is based on a pure chemostatic response, which generates a line with a slope of 1 (i.e., y=x) and illustrates transport limited dynamics. Curve B is based on a 40% increase in concentration (y=1.5x) and illustrates enrichment during export, which may reflect the activation of solute rich soils as discharge increases. Curve C represents a 30% decrease in concentration (y=0.5x) and illustrates dilution, which may arise through multiple mechanisms. Scatter, or noise, around these lines suggests the emergence of supply limited dynamics, where turnover in soils (e.g., through biotic uptake) more strongly regulates the pool size acted on by hydrologic flow. Note that simulated increases and decreases in concentration are based on a power law response to changing discharge.

Much of this paper was based on an analysis of the statistical relationship between discharge and N export (hereafter: QER), following Basu et al. (2011). Importantly, the slope and strength-of-fit, as determined by the coefficient of determination (r^2), are diagnostic of the type of flow response (e.g., transport versus source limitation) and the overall importance of hydrology as the key driver of N loss (figure 4). I analysed QERs at two different temporal scales. First, on an interannual basis, QERs were characterised from annual export estimates across four different headwater catchment that drain unique landscape elements (here: forest, mires, and lakes). Second, I assessed QERs on a seasonal basis across all study streams by organizing each sampling date into one of four seasons based climate criteria (see Paper IV). The QER slope and associated coefficient of determination (r^2) were thus used as key diagnostics of both interannual and seasonal export across the KCS sites. Using these metrics I assessed changing controls on the export of each N form in relation to season and landscape structure. In this case, structural variables included the percentage cover of peat soils in the catchment, the percentage pine cover in wet areas, the percentage birch cover in wet areas, and two separate metrics which estimate wet areas around streams (DtW and TWI 1).

4 Key Results and Discussion

When we think of the sources of N to surface waters in any given landscape we turn, instinctively, to the areas which appear to be the most dominant. This is an approach which has frequently been represented in the literature (eg., Likens et al. 1970; Dise & Wright 1995; Lovett et al. 2002). However, there is ample evidence to show that specific locations within a landscape can be disproportionately important as sinks or sources of terrestrially derived solutes (eg., Morse et al. 2014; Marton et al. 2015). While the boreal forest is generally seen as being N limited (Högberg et al. 2017) surface waters carry small but important losses of both highly available NH_4 and NO_3 and larger quantities of DON, which may also be bioavailable (Stepanauskas & Leonardson 1999). It remains largely unclear where these losses originate and what processes allow N starved terrestrial ecosystems to lose bioavailable N. Below I go into some depth to describe and discuss some of the key findings that have come out of this work.

4.1 Evaluating forest and riparian nitrogen flux (Paper I)

The key result in the first paper is that boreal riparian zones have the potential to act as important sources of DON and DIN to surface streams, contrary to the prevailing view of these interfaces as sinks of terrestrial N (e.g., Vidon et al. 2010). N losses changed consistently over the transition from upslope forest to the near stream zone (Figure 2). DON was positively correlated with soil organic matter content (SOM), and generally increased from upslope mineral soils to organic-rich, near stream soils. By contrast, NH_4 concentrations only peaked in the near stream zone, while NO_3 concentrations remained very low at most sampling locations and dates (Figure 5). Furthermore, while NH_4 and NO_3 concentrations only varied slightly throughout the soil profiles at the mid- and upslope lysimeter nests, NH_4 at the near-stream nest increased sharply with

depth. At this riparian location, NH_4 concentrations peaked at 35 cm depth, at just over 200 µg N l^{-1}, a concentration that was ten-fold higher than anywhere else in the soil transect. Water from a nearby riparian well and from additional riparian lysimeters along this stream confirmed the high concentrations of riparian NH_4 observed at the study transect.
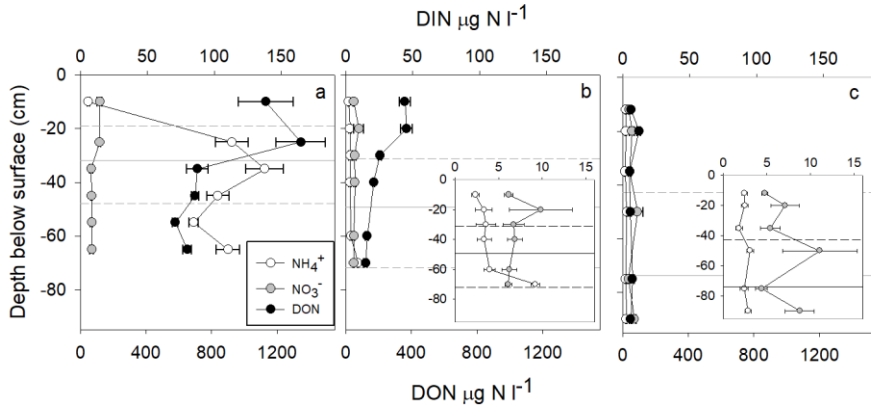
Figure 5. Concentration-depth profiles across the hillslope transect. Values represent mean concentrations +/- SE between January 2011 and December 2012 (n=4 to 18 depending on depth/site) for (a) riparian (S4), (b) midslope (S12), and (c) upland (S22) lysimeter nests. Solid and dashed horizontal reference lines represent the modelled 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.

The peak in riparian NH_4 concentration at intermediate soil depths coincided with a region of the soil profile termed the 'dominant source layer' (Ledesma et al. 2017). This layer arises from the overlap between the long-term water table position and the exponential decline in hydraulic conductivity in riparian soils (Bishop et al. 2004). Put simply, this represents a volume soil where inundation is relatively frequent yet conductivity is still relatively high. This combination has the effect of forcing around 90% of the annual hydrological flux through the soil horizons between 20 and 40 cm below the surface in the observed transect. Thus, as a result more than 90% of all DIN exported from the riparian zone was mobilized from this region. The question remains what mechanisms and drivers permit these NH_4 concentrations to persist in this location.

The available data did not permit the identification with certainty of the mechanisms that underlie the observed patterns of N concentration. However, evidence points toward the importance of a fluctuating groundwater table and associated periods of hypoxia as drivers of net N mineralization and NH_4 accumulation. We found a close negative correlations between NH_4 and SO_4

concentrations, and also a decline in NO_3 concentrations when NH_4 concentrations peaked. Both NO_3 and SO_4 are important alternative electron acceptors when oxygen supply becomes limiting for respiration (Hedin et al. 1998), and these overall patterns are consistent with the redox sensitivity of these different molecules (e.g., Helton et al. 2015). Together, the results provide strong evidence that NH_4 is only accumulating under conditions of hypoxia. Hypoxic conditions are well known to have profound influences on the functioning of both microbial and plant communities (e.g., McLatchey & Reddy 1998). Furthermore, it has been suggested that redox fluctuation can speed rates of mineralisation (Hall et al. 2015), but also retard or inhibit the growth of plant roots and their fungal symbionts (Glenz et al. 2006), thus increasing net N mineralization. However, it seems that during the growing season, when groundwater levels fall, fine roots can proliferate at these same depths (Blume-Werry et al. 2016). In this key 20 to 40 cm horizon, root densities are low in the spring and increase over the summer, so it seems probably that some root death occurs during the autumn or winter possibly as a result of the onset of hypoxia in inundated soils as groundwater rises. These senescent roots may form an important input of fresh, more labile, litter to a zone that is otherwise dominated by older peat deposits, thereby fuelling biogeochemical processes.

Dramatic as the accumulation of mobile N in the riparian zone may be, fluxes of DIN in the near stream zone were considerably higher than those in the stream (0.21 verses 0.07 kg N ha^{-1} yr^{-1} respectively). However, it is clear from other work at this site that this riparian zone is hydrologically connected to the stream (Peralta-Tapia et al. 2015). This discrepancy between stream and riparian N fluxes may be accounted for by a number of factors including: 1) variation in riparian conditions and inputs along the length of the stream (Grabs et al. 2012), 2) closely coupled nitrification/denitrification in the final meters of flow path (Hedin et al. 1998), 3) immobilization/uptake of N by microbial or plant communities (Vidon et al. 2010), and/or 4) net nutrient uptake in the stream (Bernhardt et al. 2003). In this context, a more fine scale assessment of the land-water interface is warranted to address several of these mechanism and resolve the fate of N. Regardless, results from this paper provide strong evidence for the near stream zone functioning as a control point capable of decoupling stream N fluxes from the wider catchment at this site.

4.2 Mire nitrogen delivery to surface waters (Paper II)

I found that headwater minerogenic mires are capable of shaping stream N dynamics through effects on both hydrology and redox condition that promote NH_4 accumulation and transport. Most notably, hydrological routing through

the mire was characterized by preferential flowpath (hydrologically active zone; HAZ), located 2-3 m below the surface. In addition, while the vegetation of northern mire ecosystems are known to be N limited (Aerts et al. 1992; Wiedermann et al. 2007), the depth of peat formation at this site has separated surface layers of the mire (the acrotelm) from deeper strata, allowing NH_4 concentrations to rise up to 2 mg N l^{-1} in the catotelm (Figure 6). This considerable build-up of NH_4 within the mire was poorly connected to the flow paths that carry the bulk of the annual hydrological flux through this system. Indeed, the upper (0.25-2 m) and lower (3-4.5 m) portions of the mire showed little or no seasonal pattern in chemistry, but appeared to act as a diffusion limited source of solutes to the HAZ. During periods of low flow in the winter, the HAZ was effectively disconnected from the outlet stream and accumulated concentrations of NH_4 greater than 500 µg N l^{-1} – equal to or greater than that of DON. During the spring snowmelt, however, the HAZ is flushed and NH_4 concentrations fell to around 15 µg N l^{-1}, levels comparable with those found in forest soils in Paper I. While concentrations in this zone recovered somewhat during the snow free period they only reached their maximum again the following winter.

The patterns of dilution during periods of high flow in the HAZ were mirrored in the outlet stream. However, despite this dilution response, over the course of a year the mire stream exported considerably more NH_4 and DON per unit area than the adjacent forest catchment (C2, 0.026 and 0.737 C4, 0.124 and 1.519 kg N ha^{-1} yr^{-1} respectively). The influence of the mire stream on DIN export in the wider catchment was particularly great during lower flow rates, indeed the ratio of mire (C4) to forest (C2) export peaked during the summer (C4:C2≈4) and winter (C4:C2≈3.5).

Interestingly while NH_4 was highly dynamic in the HAZ, DON was less so. One reason for this difference probably lies with the chemistry of the water passing through the HAZ during high flow events. This event water transiting the HAZ is likely derived from forest soils further upslope. Groundwater from the adjacent C2 catchment had a DON concentration of around 300 µg N l^{-1} (Paper I) not dissimilar to the concentrations found in the HAZ during the spring melt. In this way, DON export ratios between C4 and C2 during the spring melt and summer periods were around one. However, the winter period was different: the C4:C2 export ratio rose to two, which likely reflects a shift in the forest stream water origin from surficial to deeper sources (e.g., Peralta-Tapia et al. 2015).

Finally, the importance of mires as sources of DIN, and to some extent DON, to surface waters, remains clear when assessed at a landscape scale. I found strong significant correlations between the percentage mire cover and the long-

term average concentrations of NH_4 ($r^2=0.83$, $p<0.001$), DIN ($r^2=0.86$, $p=<0.001$) and DON ($r^2=0.38$, $p<0.01$). While these losses are important in this otherwise N limited landscape, overall the rates of N export are modest from all of these catchments, and within the range of other boreal catchments.
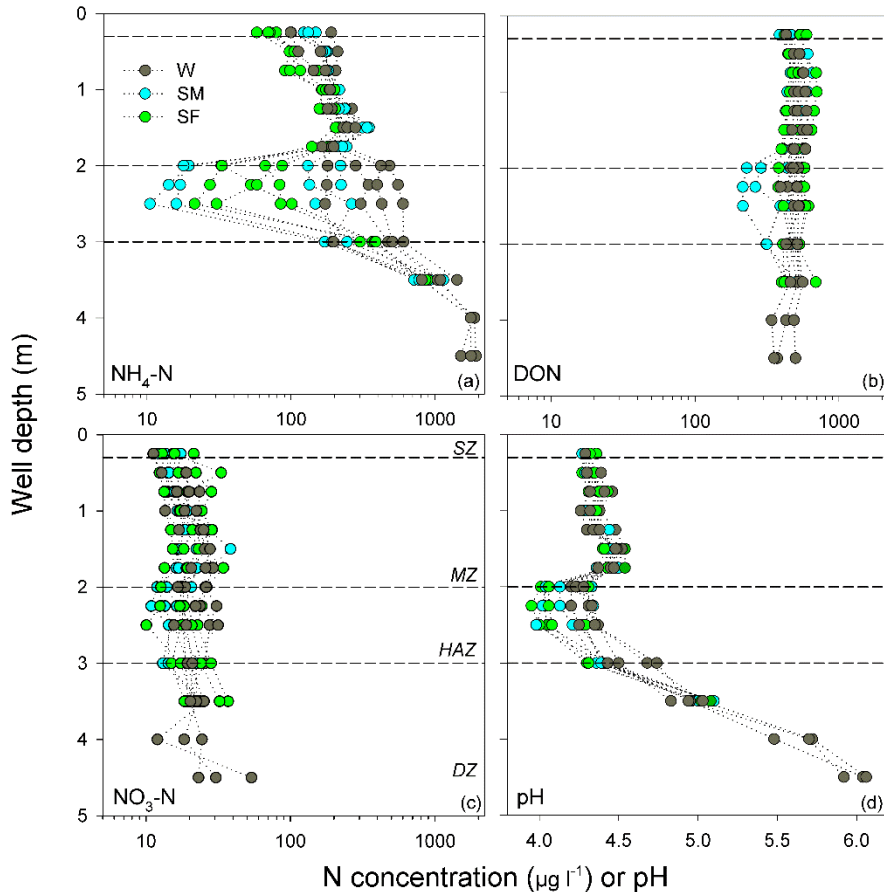
Figure 6. Vertical distribution of dissolved NH_4 (panel a), DON (panel b), NO_3, (panel c) and pH (panel d) evaluated at approximately monthly intervals for a year (2012-13). Symbol colour denoting season, winter (W) gray, spring melt (SM) blue, snow free (SF) green. Abbreviations for vertical mire zones, surface zone (SZ), mid zone (MZ), hydrologically active zone (HAZ), and deep zone (DZ). Note identical log x-axis for NH_4, DON, and NO_3.

Overall this headwater mire was an important actor in shaping the supply of N to headwaters streams. The patterns of N concentration and export from this mire appear to be driven by the interaction of waters from the bulk peat with that of hydrologically active zones. The low porosity of the bulk peat and the resulting slow water flux through this material, are in contrast to the rapid water

movement through the HAZ fundamental in regulating export patterns over the course of the year. In this way, the interaction of the HAZ with over and underlying peats form conditions consistent with a transport limited control point (Bernhardt et al. 2017). Furthermore, minerogenic mires with similar patterns of hydrological flowpaths are likely common across Fennoscandia and so provide a potentially important control points within the wider landscape.

4.3 Landscape regulation stream nitrogen (Paper III)

In papers I and II, I found evidence to suggest that landscape structure, specifically peat accumulation in mires and riparian zones could have profound influences on N concentration and form in boreal headwater streams. In Paper III, I evaluated the relative importance of these elements of the landscape to broader spatial and temporal patterns of stream N concentration across the KCS network.

Across all sites in the stream network, I found that the concentration of organic and inorganic N had opposing seasonal trends overall, with the DON peaking during summer and DIN in late winter. However, there was considerable variability in concentration among sites in the network, and this also differed according of N form. DON had the lowest variance in monthly mean concentration across sites (CV 20% to 40%) while NH_4 and NO_3 were more dynamic (CV 57% to 88% and 42% to 74%, respectively). Synchrony analysis revealed headwater catchments dominated by a single landscape characteristic (i.e. forests, lake, or mire) had the most unique temporal patterns of DIN chemistry, while synchrony increased among the larger catchments (i.e., sites further downstream) in the KCS. In contrast, DON showed much stronger synchrony across sites in the landscape.

These findings follow what might be expected for N limited landscapes, where concentrations of more reactive DIN forms in streams are closely linked to seasonal biological demand on land (Sponseller et al. 2014), but also are likely therefore show more variability (Thompson et al. 2011) and localized 'uniqueness' (Schiff et al. 2002) than less reactive solutes. Similarly, patterns of DON concentration across the KCS stream network were also consistent with an N-limited, boreal system where organic losses are frequently an order of magnitude greater than inorganic counterparts (e.g., Kortelainen et al. 2006). The patterns of higher DON concentrations during the summer have been observed elsewhere (Sponseller et al. 2014) and are consistent with the activation of surficial soil horizons during the snow free period as well as the influence of temperature resource production in riparian soils (e.g., Winterdahl et al. 2011).

Overall, across the network we found that once catchment size reached about 50 ha, incorporating both mires and forests landscape elements, all streams showed fairly synchronous seasonal patterns. This pattern highlights the potential for the channel network to incorporate diverse upstream inputs (Schelker et al. 2016) and in doing so create new, emergent patterns downstream. However this also draws into question the relevance of the unique controls described here (Papers I and II) and elsewhere at a network scale. It is indeed possible that increasing synchrony reflects the decline in the relative cover of mires lower down in the network, and thus a reduction in their influence on chemical patterns. However, in addition to simple mixing, there is also potential for instream N processing (e.g. nitrification, denitrification and uptake) in headwater streams (Peterson 2001; Mulholland et al. 2008). Together, the processes of mixing, instream transformation, and removal potentially lead to a convergence in temporal patterns of N chemistry downstream. In fact, the relatively stronger synchrony observed between forested headwaters (C1 and C2) and downstream sampling stations for DON compared to DIN is consistent with the idea that additional instream processes may influence these more reactive forms (Scanlon et al. 2010).

Interestingly, while the synchrony analysis suggested headwater differences become less important downstream, statistical models aimed at predicting N concentration and composition across all sampling dates and sites showed that local- rather than catchment-scale variables were typically the strongest predictors. In particular, near stream zones and peat soils emerged as important factors in combination with hydrological variables. In this way, while the influence of headwaters becomes difficult to discern downstream, an appreciable amount of variation in stream N concentration and composition can be linked to these more localized landscape features that characterize the land-water interface. These correlations provide addition evidence that riparian and mire areas behave as key control points that regulate hydrological connections to streams and act as sources of N to the drainage network.

4.4 Landscape control on nitrogen flow export response (Paper IV)

The differing influence of discharge on stream N concentration and form across the landscape was clear from the work I completed in papers I-III. In an N limited ecosystem, such as those of the northern boreal landscape (Högberg et al. 2017), it is likely that catchment losses of bioreactive N forms (e.g., NO_3 and NH_4) would be under tight biological control. This 'supply control' is predicted to result in a weak or nonexistent flow-export relationship (QER) (Basu et al.

2011). However, the key results from Papers I and II also suggest that peat accumulation can disconnect zones of nutrient limitation from areas of accumulation. A disconnect of this sort could permit hydrologically, rather than biologically controlled exports of DIN, regardless of upland nutrient status. In contrast to DIN, we would predict DON export to be more dependent on discharge as it is generally considered to be a less available N form and one that we have previously found to have more uniform patterns across the network (Paper III).

Assessments at an interanual scale demonstrated that, despite close proximity, mean annual N export differed between headwater catchments by 2, 5, and 8 times for DON, NH$_4$, and NO$_3$, respectively. This variation highlights how differences in catchment hydrology and structure can shape large variations in organic and inorganic N release, retention, and loss among subcatchments. These differences were not only driven by N concentrations but also by variation in area normalized discharge (i.e., specific discharge) among sites and years. In general, patterns of discharge were correlated with variation in total N export and the seasonal timing of export. In particular, sites with greater mire cover had higher specific discharge (Karlsen et al. 2016) and were characterized by relatively greater N export during baseflow compared to snowmelt periods.

Analysis of QER's at an annual level between headwater sites supported the idea that labile N export is largely regulated by strong biological control. Assessments of NH$_4$ and NO$_3$ QERs between catchments gave weak relationships (NO$_3$ r^2=0.25, NH$_4$ r^2=0.39) while within catchment relationships were either weak (NO$_3$ r^2 0.02 to 0.47) or absent (NH$_4$ r^2=0). Together this is consistent with supply limitation (Basu et al. 2011) where the mobilization of solutes for export is related to biological processes rather than hydrologic flux. In contrast, DON export among headwater sites and years was strongly (r^2=0.86) related to annual discharge with a slope that was consistent with chemostatic responses previously observed for geogenic solutes (Godsey et al. 2009) and DOC (Creed et al. 2015). Within catchment QERs for DON were more variable (slope: 0.51 to 1 and r^2: 0.36 to 0.8) suggesting a more nuanced and variable response to variable annual discharge across sites dominated by either forests (Paper 1), mires (Paper 2), or headwater lakes.

Analyzing seasonal QER responses across the whole network provided a more nuanced assessment than at the annual time scale. In particular, the distribution of sites and seasons organized by slope and r^2 (Figure 7) shows a broad range of hydrological response types and marked variation in the overall importance of discharge. Across the whole stream network, I found that DON responses were more frequently transport limited (with slopes >1) than was suggested at the interannual scale. This conservative response for DON export

is consistent with existing findings for DOC export from forested catchments in the KCS (Laudon et al. 2011) and elsewhere (Musolff et al. 2015; Moatar et al. 2017). Moreover transport limitation of DON (i.e., slopes >1) is consistent with our measurements of increasing DON concentration in surficial soils (Figure 5) coupled with a rapid rise in water table with increasing flow as predicted by the transmissivity feedback model (Bishop et al. 2004).
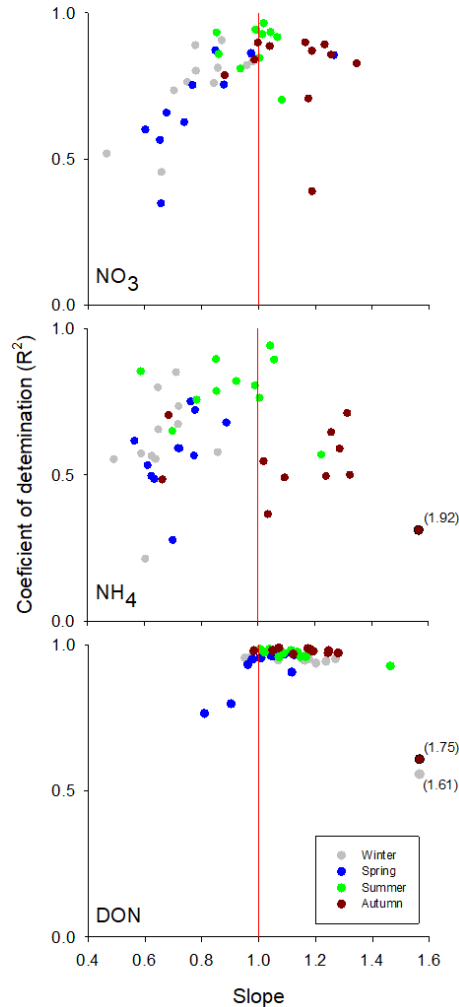

Figure 7. Slope and r^2 values for discharge export relationships (QER) for all study catchments separated by season between July 2008 and December 2015, n for each site (individual graph point) winter=53, spring=65, summer=60, autumn=20.

In contrast to DON, QER slopes and r^2 values were far more variable for NH_4 and NO_3. Winter and Spring QERs for these forms typically exhibited source limitation as demonstrated by slopes <1 combined with relatively poor statistical relationships between export and discharge (Figure 7). This pattern likely reflects a mixture of factors including: peak flow driven dilution (e.g. (Petrone, Hinzman, et al. 2007); spatial and temporal variability in how soil solute pools interact with flowpaths during melt events (e.g., Herndon et al. 2015) as well as variation in soil flushing characteristics (Petrone, Buffam, et al. 2007). In addition, other factors not addressed here may further weaken QERs for NH_4 such as, sorption to mineral soils (e.g., Kothawala & Moore 2009) and the potential for NH_4 to become rapidly nitrified in oxic soils and waters.

Summer and autumn patterns for NH_4 and NO_3 were markedly different from those seen at other times. All catchments (for NO_3) and many (for NH_4) had QER slopes close to or greater than 1 (slope=>0.8, Figure 7) during these seasons, implying chemostatic or transport limitation of labile N export during periods when we could expect the most intense biological activity. This result is consistent with the findings of Paper I, that peat formation in riparian zones can separate areas of N limitation from zones of DIN accumulation that have the potential to supply N to surface waters. The accumulation of inorganic forms of N in riparian soils has been reported elsewhere (Cirmo & McDonnell 1997; Chestnut & McDowell 2000; Fölster 2000) emphasizing the potential for its importance as a sources of DIN to surface waters (see also, Paper I).

Correlations between QER slopes and landscape characteristics for each season across all catchments provided further evidence of the important role of catchment structure. In particular, during the spring for all N forms, and for NO_3 in the autumn, QER slope was negatively correlated with the percentage of peat cover (spearman's r= -0.62 to -0.98 p<0.04). A response probably driven by the way in which mire streams undergo dilution during high flows (Laudon et al. 2004). This dilution is a function of mire hydrology, where peat is drained by preferential flowpaths (Holden et al. 2012), and appear to have limited interaction with the surrounding bulk peat and are thus readily flushed. In addition to landscape structure, there was also evidence for a different set of drivers regulating hydrological responses at the largest catchment scale in the study. The largest catchment had the lowest annual DON export, the statistically weakest hydrological responses for all N forms (i.e., lowest r^2), and yet during the autumn and winter the highest QER slopes were observed. All of these attributes are consistent with the non-linear, downstream change of stream chemistry that has recently been documented in the KCS (Laudon & Sponseller 2017). This shift, from the smallest to the largest streams, is driven primarily by the addition of a deep groundwater source with increasing drainage size (Peralta-

Tapia et al. 2015). Having different temporal dynamics from that of surface waters, deep groundwater can become a dominant source when surface water contributions decline downstream (Tiwari et al. 2017). Thus a shift from deeper groundwater low in NH_4 and DON to richer headwater sources during high flows can exaggerate the QER slope and cause large variation reducing the statistical strength of the relationship.

5 Conclusion

In my work, I have found that the export of N from typical Fennoscandian headwater catchments is strongly influenced by the interaction of groundwater with peat deposits. Indeed, I believe that this interaction in riparian zones and mires represents two key ecological control points (sensu Bernhardt et al. 2017) in this boreal forest catchment. In forested catchments of the KCS, the interactions of peat accumulation and groundwater fluctuation within the riparian zone operate as the primary mechanism to regulate N supply to streams. Importantly, these interactions, and their potential to facilitate the production and transport of N to surface waters, appear to decouple catchment exports from N cycling processes distributed across the broader landscape (e.g., upland forest uptake). In mires, the role of peat accumulation is different but nonetheless important: here the key interaction seems to lie between preferential flowpaths within deep peat layers (i.e., in the catotelm) and the surrounding bulk peat. Here, bioreactive forms of N are mobilized far below the rooting zone and can be conveyed to streams outside of any strong biotic influence. These interactions create distinct flow-concentration and export responses across time and space in a relatively predictable manner.

These findings, while highly relevant to low gradient boreal Fennoscandia, might not be directly applicable to other boreal areas or biomes. However, several of the processes we highlight may be more universal, including the capacity to accumulate bioreactive N in deep peat layers. My results also emphasize the importance of understanding how the long-term development of landscapes can lead to both edaphic and hydrologic patterns that foster nutrient losses, regardless of changes in terrestrial demand. In the northern boreal zone, this development is largely associated with the widespread, post-glacial accumulation of peat in open mires and in low lying areas along streams. Similar peat deposits occur from the equator to polar-regions and, when hydrologically connected, have been shown to influence stream water chemistry in proportion to their prominence in the landscape (Creed et al. 2003). My results suggest that

this organic matter accumulation over time has served to separate surface vegetation from useable N forms at depth while at the same time facilitating hydrological processes in riparian zones and mires that route these resources to streams.

6   Future perspectives

6.1 Riparian zones

My work also generated several questions about the controls over N delivery to boreal streams that remain unanswered. For example, while the peak in concentration of NH_4 at approximately the mean water table position in riparian zones seems clear, we know little about its short-term temporal dynamics, or its origin. Previous studies along the same hillslope transect I used in Paper I suggest that the DOC in the stream water is of relatively recent origin, when compared to the likely age of the riparian peats (Ledesma et al. 2015). This suggests that an appreciable fraction of the dissolved organic matter (DOM) that is produced in the riparian zone consists of recently fixed carbon, and this may form the proximal source of NH_4, and/or facilitate the mineralization of the N from peat (e.g., through 'priming'; Finzi et al. 2015). However, it is currently difficult to know whether this N has been translocated from surface horizons, either passively or actively, or is the product of decomposing the older riparian peat. Alternatively, this N could be the result of the breakdown of roots or their fungal symbionts that have senesced as a result of a seasonally fluctuating water table. Indeed, one interesting avenue of future research would be to address the interplay of root exploration of this redox-dynamic zone and water table fluctuations. Indeed, it is also perhaps worth considering what might happen to the functioning of this key ecological control point under the predicted long-term changes in hydrology that are expected as a result of global changes in climate (Teutschbein et al. 2015).

6.2 Mires

While it seems clear that mires can act as a key source of reactive N to surface waters, especially during periods of low flow, the origin of the NH_4 leaving the mire remains unclear. While it is probable that the bulk peat is the ultimate source, it is also possible that there are important interactions between N cycling processes in the bulk peat and solutes that are imported from the surrounding catchment or underlying sediments. In addition to this, there is also much more to learn about how mire hydrology regulates N losses, including a better understanding of preferential flowpaths that connect deep peat layers to outlet streams. While correlations between mire cover and N concentrations across the KCS (e.g., Paper II) suggest that these ecosystems are effectively 'plumbed' into the stream network, the origin, structure, and configuration of preferential flowpaths remain poorly described. In addition, results from the seasonal assessment of well chemistry (Paper II), as well as interannual patterns of export (Paper IV), suggest that diffusion of NH_4 from hydrologically inactive to active peat layers sets the constraint on hydrological losses. According this hypothesis, these flowpaths operate as transport control points (Bernhardt et al., 2017) and the mechanisms regulating their interactions with the surrounding peat merit further study. Overall, while mire ecosystems are typically effective N sinks in northern landscapes (Lamers et al. 2000), the observed losses of nutrients from below the rooting zone likely have important ecological consequences for downstream ecosystems that are often N limited (e.g., Bergström et al. 2008; Burrows et al. 2015).

6.3 Network scale patterns

In this study, I have been able to link landscape characteristics to patterns in stream water N chemistry and export and so identify potential control points for the regulation of stream N dynamics. My work highlights the potential for large differences in N chemistry among headwater streams, generated by the distinct land-water connections described above. At the same time, results also suggest a fairly rapid convergence in the chemical signals among streams – with only small increases in drainage size. In this context, resolving the relative roles of hydrological mixing, N transformation (e.g., nitrification), and N uptake requires further research. At even larger scales, results from Paper IV also suggested the emergence of additional processes regulating N responses to hydrological change in the KCS outlet. At this scale, patterns of N chemistry and export reflect periodic interactions between the deep groundwater inputs that sustain baseflow and waters derived from near-surface flowpaths upstream. The biogeochemical implications of this mixing are not well understood, but it likely a common

phenomenon for many larger rivers in the region (Tiwari et al. 2017). Finally, while it seems likely that many, if not all, of the proposed processes are relevant in this low gradient system, it would be valuable to expand the scope of the study to investigate if these remain important for N losses at larger scales, or in higher gradient systems where the interactions between peat and groundwater likely are very different.

References

Aerts, R., Wallen, B. & Malmer, N., 1992. Growth-Limiting Nutrients in Sphagnum-Dominated Bogs Subject to Low and High Atmospheric Nitrogen Supply. Journal of Ecology , Vol . 80 , No . 1 (Mar ., 1992), pp . 131-140

Augustine, D.J. & McNaughton, S.J., 2004. Temporal asynchrony in soil nutrient dynamics and plant production in a semiarid ecosystem. *Ecosystems*, 7(8), pp.829–840.

Basu, N.B., Thompson, S.E. & Rao, P.S.C., 2011. Hydrologic and biogeochemical functioning of intensively managed catchments: A synthesis of top-down analyses. *Water Resources Research*, 47(10), pp.1–12.

Bergström, A., Jonsson, A. & Jansson, M., 2008. Phytoplankton responses to nitrogen and phosphorus enrichment in unproductive Swedish lakes along a gradient of atmospheric nitrogen deposition. *Aquatic Biology*, 4, pp.55–64.

Bernhardt, E.S. et al., 2017. Control Points in Ecosystems: Moving Beyond the Hot Spot Hot Moment Concept. *Ecosystems*, 20(4), pp.665–682.

Bernhardt, E.S. et al., 2003. In-stream uptake dampens effects of major forest disturbance on watershed nitrogen export. *Proceedings of the National Academy of Sciences*, 100(18), pp.10304–10308.

Bishop, K. et al., 2004. Resolving the Double Paradox of rapidly mobilized old water with highly variable responses in runoff chemistry. *Hydrological Processes*, 18(1), pp.185–189.

Blume-Werry, G. et al., 2016. Short-term climate change manipulation effects do not scale up to long-term legacies: effects of an absent snow cover on boreal forest plants F. Gilliam, ed. *Journal of Ecology*, 104(6), pp.1638–1648.

Bormann, F.H. & Likens, G.E., 1967. Nutrient Cycling; Small watersheds can provide invaluable information about terrestrial ecosystems. *Science*, 155(37), p.424 to 429.

Burrows, R.M. et al., 2015. Seasonal resource limitation of heterotrophic biofilms in boreal streams. *Limnology and Oceanography*, 62(1), pp.164–176.

Chestnut, T.J. & McDowell, W.H., 2000. C and N dynamics in the riparian and hyporheic zones of a tropical stream, Luquillo Mountains, Puerto Rico. *Journal of the North American Benthological Society*, 19(2), pp.199–214.

Cirmo, C.P. & McDonnell, J.J., 1997. Linking the hydrologic and biogeochemical

controls of nitrogen transport in near-stream zones of temperate-forested catchments: a review. *Journal of Hydrology*, 199(1–2), pp.88–120.

Creed, I.F. et al., 2003. Cryptic wetlands: integrating hidden wetlands in regression models of the export of dissolved organic carbon from forested landscapes. *Hydrological Processes*, 17(18), pp.3629–3648.

Creed, I.F. et al., 2015. The river as a chemostat: fresh perspectives on dissolved organic matter flowing down the river continuum R. Smith, ed. *Canadian Journal of Fisheries and Aquatic Sciences*, 72(8), pp.1272–1285.

Crowther, T.W. et al., 2016. Quantifying global soil carbon losses in response to warming. *Nature*, 540(7631), pp.104–108.

Dick, J.J. et al., 2015. Modelling landscape controls on dissolved organic carbon sources and fluxes to streams. *Biogeochemistry*, 122(2–3), pp.361–374.

Dise, N.B. & Wright, R.F., 1995. Nitrogen leaching from European forests in relation to nitrogen deposition. *Forest Ecology and Management*, 71(1–2), pp.153–161.

Finzi, A.C. et al., 2015. Rhizosphere processes are quantitatively important components of terrestrial carbon and nutrient cycles. *Global Change Biology*, 21(5), pp.2082–2094.

Fölster, J., 2000. The near-stream zone is a source of nitrogen in a swedish forested catchment. *Journal of Environment Quality*, 29(3), p.883.

Glenz, C. et al., 2006. Flooding tolerance of Central European tree and shrub species. *Forest Ecology and Management*, 235(1–3), pp.1–13.

Godsey, S.E., Kirchner, J.W. & Clow, D.W., 2009. Concentration-discharge relationships reflect chemostatic characteristics of US catchments. *Hydrological Processes*, 23(13), pp.1844–1864.

Grabs, T. et al., 2012. Riparian zone hydrology and soil water total organic carbon (TOC): implications for spatial variability and upscaling of lateral riparian TOC exports. *Biogeosciences*, 9(10), pp.3901–3916.

Hall, S.J. et al., 2015. Lignin decomposition is sustained under fluctuating redox conditions in humid tropical forest soils. *Global Change Biology*, 21(7), pp.2818–2828.

Hasselquist, E.M. et al., 2017. Identifying and assessing the potential hydrological function of past artificial forest drainage. *Ambio*, pp.1–11.

Hedin, L.O. et al., 1998. Thermodynamic constraints on nitrogen transformations and other biogeochemical processes at soil-stream interfaces. *Ecology*, 79(2), pp.684–703.

Hedin, L.O., Armesto, J.J. & Johnson, A.H., 1995. Patterns of Nutrient Loss from Unpolluted, Old-Growth Temperate Forests: Evaluation of Biogeochemical Theory. *Ecology*, 76(2), pp.493–509.

Helton, A.M., Ardón, M. & Bernhardt, E.S., 2015. Thermodynamic constraints on the utility of ecological stoichiometry for explaining global biogeochemical patterns. *Ecology Letters*, 18(10), pp.1049–1056.

Herndon, E.M. et al., 2015. Landscape heterogeneity drives contrasting concentration–discharge relationships in shale headwater catchments. *Hydrology and Earth System Sciences*, 19(8), pp.3333–3347.

Högberg, P. et al., 2017. Tamm Review: On the nature of the nitrogen limitation to plant growth in Fennoscandian boreal forests. *Forest Ecology and Management*, 403, pp.161–185.

Holden, J. et al., 2012. Natural pipes in blanket peatlands: major point sources for the release of carbon to the aquatic system. *Global Change Biology*, 18(12), pp.3568–3580.

Karlsen, R.H. et al., 2016. The assumption of uniform specific discharge: unsafe at any time? *Hydrological Processes*, 30(21), pp.3978–3988.

Kling, G.W. et al., 2000. Integration of lakes and streams in a landscape perspective: the importance of material processing on spatial patterns and temporal coherence. *Freshwater Biology*, 43(3), pp.477–497.

Kortelainen, P. et al., 2006. Sediment respiration and lake trophic state are important predictors of large CO_2 evasion from small boreal lakes. *Global Change Biology*, 12(8), pp.1554–1567.

Kothawala, D.N. & Moore, T.R., 2009. Adsorption of dissolved nitrogen by forest mineral soils. *Canadian Journal of Forest Research*, 39(12), pp.2381–2390.

Kuglerová, L. et al., 2016. Relationships Between Plant Assemblages and Water Flow Across a Boreal Forest Landscape: A Comparison of Liverworts, Mosses, and Vascular Plants. *Ecosystems*, 19(1), pp.170–184.

Lamers, L.P.M., Bobbink, R. & Roelofs, J.G.M., 2000. Natural nitrogen filter fails in polluted raised bogs. *Global Change Biology*, 6(5), pp.583–586.

Laudon, H. et al., 2004. Hydrological flow paths during snowmelt: Congruence between hydrometric measurements and oxygen 18 in meltwater, soil water, and runoff. *Water Resources Research*, 40(3).

Laudon, H. et al., 2011. Patterns and Dynamics of Dissolved Organic Carbon (DOC) in Boreal Streams: The Role of Processes, Connectivity, and Scaling. *Ecosystems*, 14(6), pp.880–893.

Laudon, H. et al., 2013. The Krycklan Catchment Study-A flagship infrastructure for hydrology, biogeochemistry, and climate research in the boreal landscape. *Water Resources Research*, 49(10), pp.7154–7158.

Laudon, H. & Ottosson Löfvenius, M., 2016. Adding snow to the picture - providing complementary winter precipitation data to the Krycklan Catchment Study database. *Hydrological Processes*, 30(13), pp.2413–2416.

LeBauer, D.S. & Treseder, K.K., 2008. Nitrogen Limitation of Net Primary Productivity in Terrestrial Ecosystems is Globally Distributed. *Ecology*, 89(2), pp.371–379.

Ledesma, J.L.J. et al., 2016. Boreal forest riparian zones regulate stream sulfate and dissolved organic carbon. *Science of The Total Environment*, 560–561, pp.110–122.

Ledesma, J.L.J. et al., 2015. Potential for long-term transfer of dissolved organic carbon from riparian zones to streams in boreal catchments. *Global Change Biology*, 21(8), pp.2963–2979.

Ledesma, J.L.J. et al., 2017. Towards an Improved Conceptualization of Riparian Zones in Boreal Forest Headwaters. *Ecosystems*, pp.1–19.

Lidman, F. et al., 2017. From soil water to surface water - how the riparian zone

controls the transport of major and trace elements from a boreal forest to a stream. *Biogeosciences Discussions*, (December), pp.1–29.

Likens, G.E. et al., 1970. Effects of forest cutting and herbicide treatment on nutrient budgets in the hubbard brook watershed-ecosystem. *Ecological Monographs*, 40(1), pp.23–47.

Loisel, J., Garneau, M. & Helie, J.-F., 2010. Sphagnum 13C values as indicators of palaeohydrological changes in a peat bog. *The Holocene*, 20(2), pp.285–291.

Lovett, G.M., Weathers, K.C. & Arthur, M.A., 2002. Control of Nitrogen Loss from Forested Watersheds by Soil Carbon:Nitrogen Ratio andTree Species Composition. *Ecosystems*, 5(7), pp.712–718.

Lucas, R.W. et al., 2016. Long-term declines in stream and river inorganic nitrogen (N) export correspond to forest change. *Ecological Applications*, 26(2), pp.545–556.

Marton, J.M. et al., 2015. Geographically isolated wetlands are important biogeochemical reactors on the Landscape. *BioScience*, 65(4), pp.408–418.

McClain, M.E. et al., 2003. Biogeochemical Hot Spots and Hot Moments at the Interface of Terrestrial and Aquatic Ecosystems. *Ecosystems*, 6(4), pp.301–312.

McLatchey, G.P. & Reddy, K.R., 1998. Regulation of Organic Matter Decomposition and Nutrient Release in a Wetland Soil. *Journal of Environment Quality*, 27(5), p.1268.

Menge, D.N.L., Pacala, S.W. & Hedin, L.O., 2009. Emergence and maintenance of nutrient limitation over multiple timescales in terrestrial ecosystems. *The American naturalist*, 173(2), pp.164–75.

Moatar, F. et al., 2017. Elemental properties, hydrology, and biology interact to shape concentration-discharge curves for carbon, nutrients, sediment, and major ions. *Water Resources Research*, 53(2), pp.1270–1287.

Morse, J.L. et al., 2014. Searching for biogeochemical hot spots in three dimensions: Soil C and N cycling in hydropedologic settings in a northern hardwood forest. *Journal of Geophysical Research: Biogeosciences*, 119(8), pp.1596–1607.

Mulholland, P.J. et al., 2008. Stream denitrification across biomes and its response to anthropogenic nitrate loading. *Nature*, 452(7184), pp.202–5.

Musolff, A. et al., 2015. Catchment controls on solute export. *Advances in Water Resources*, 86, pp.133–146.

Nilsson, M. et al., 2008. Contemporary carbon accumulation in a boreal oligotrophic minerogenic mire - a significant sink after accounting for all C-fluxes. *Global Change Biology*, 14(10), pp.2317–2332.

Nyberg, L., 1995. Water flow path interactions with soil hydraulic properties in till soil at Gårdsjön, Sweden. *Journal of Hydrology*, 170(1–4), pp.255–275.

Ocampo, C.J., Oldham, C.E. & Sivapalan, M., 2006. Nitrate attenuation in agricultural catchments: Shifting balances between transport and reaction. *Water Resources Research*, 42(1).

Perakis, S.S., 2002. Nutrient limitation, hydrology and watershed nitrogen loss.

Hydrological Processes, 16(17), pp.3507–3511.

Peralta-Tapia, A. et al., 2015. Scale-dependent groundwater contributions influence patterns of winter baseflow stream chemistry in boreal catchments. *Journal of Geophysical Research: Biogeosciences*, 120(5), pp.847–858.

Peterjohn, W.T. & Correll, D.L., 1984. Nutrient dynamics in an agricultural watershed: observations on the role of a riparian forest. *Ecology*, 65(5), pp.1466–1475.

Peterson, B.J., 2001. Control of Nitrogen Export from Watersheds by Headwater Streams. *Science*, 292(5514), pp.86–90.

Petrone, K., Hinzman, L.D., et al., 2007. The influence of fire and permafrost on sub-arctic stream chemistry during storms. *Hydrological Processes*, 21(4), pp.423–434.

Petrone, K., Buffam, I. & Laudon, H., 2007. Hydrologic and biotic control of nitrogen export during snowmelt: A combined conservative and reactive tracer approach. *Water Resources Research*, 43(6).

Scanlon, T.M., Ingram, S.M. & Riscassi, A.L., 2010. Terrestrial and in-stream influences on the spatial variability of nitrate in a forested headwater catchment. *Journal of Geophysical Research: Biogeosciences*, 115(*G02022*).

Schelker, J. et al., 2016. Nitrogen export from a boreal stream network following forest harvesting: seasonal nitrate removal and conservative export of organic forms. *Biogeosciences*, 13(1), pp.1–12.

Schiff, S.L. et al., 2002. Two adjacent forested catchments: Dramatically different NO 3 − export. *Water Resources Research*, 38(12), pp.28-1-28–13.

Sponseller, R.A. et al., 2014. Patterns and drivers of riverine nitrogen (N) across alpine, subarctic, and boreal Sweden. *Biogeochemistry*, 120(1–3), pp.105–120.

Stepanauskas, R. & Leonardson, L., 1999. Bioavailability of wetland-derived DON to freshwater and marine bacterioplankton. *Limnology and Oceanography*, 44(6), pp.1477–1485.

Stumm, W. & Morgan, J.J., 1996. *Aquatic Chemistry Chmical Equlibria and Rates in Natrul Waters* 3rd ed., Wiley.

Teutschbein, C. et al., 2017. Future Riverine Inorganic Nitrogen Load to the Baltic Sea From Sweden: An Ensemble Approach to Assessing Climate Change Effects. *Global Biogeochemical Cycles*, 31(11), pp. 1674–1701.

Teutschbein, C. et al., 2015. Hydrological response to changing climate conditions: Spatial streamflow variability in the boreal region. *Water Resources Research*, 51(12), pp.9425–9446.

Thompson, S.E. et al., 2011. Relative dominance of hydrologic versus biogeochemical factors on solute export across impact gradients. *Water Resources Research*, 47(10).

Tiwari, T. et al., 2017. Inferring scale-dependent processes influencing stream water biogeochemistry from headwater to sea. *Limnology and Oceanography*, 62(S1), pp.S58–S70.

Urban, N.R., Eisenreich, S.J. & Bayley, S.E., 1988. The relative importance of denitrification and nitrate assimilation in midcontinental bogs. *Limnology*

and Oceanography, 33(5), pp.1611–1617.

Vidon, P. et al., 2010. Hot spots and hot moments in riparian zones: Potential for improved water quality management. *Journal of the American Water Resources Association*, 46(2), pp.278–298.

Walvoord, M.A. et al., 2003. A Reservoir of Nitrate Beneath Desert Soils. *Science*, 302(5647), pp.1021–1024.

Wiedermann, M.M. et al., 2007. Global Change Shifts Vegetation and Plant–Parasite Interactions in a Boreal Mire. *Ecology*, 88(2), pp.454–464.

Winterdahl, M. et al., 2011. Riparian Zone Influence on Stream Water Dissolved Organic Carbon Concentrations at the Swedish Integrated Monitoring Sites. *AMBIO*, 40(8), pp.920–930.

Acknowledgements

It is said it takes a village to raise a child, I've just been lucky enough to have a very big village, and without them I would never have got here. From the enthusiasm of Trevor Piearce for earth worms to the passion for the ecology of Alastair Fitter; Angela Hodge's arbuscular mycorrhizae to learning boreal soil N and C fluxes and mycorrhizae of a different sort in the Höberg lab, you all taught me something valuable. However it was the welcome and enthusiasm of the CCrew, but in particular that of Peder Blomkvist, Hjalmar Laudon, Ryan Sponseller, and Torgny Näsholm, first as your lab technician and then as a student. You gave me a home, a safe space to be myself, to try, fail, and try again in science and in life, each time learning valuable lessons I did not expect. There have been many others who have been there, come rain, come shine, making this journey a lot more fun, exciting and interesting than it might have been. However some of you deserve special thanks, in no particular order: Lisbet Bach, Anna (I had a screw loose, then I lost it) Larsson, William Lidberg, Åsa Boily, Rosie Goodman, Noelia Saavedra Berlanga, Ida Taberman, Linda Gruffman and Danial Lussetti, you listened, helped and laughed when I most needed it. Thank you all!