Nitrogen export from a boreal stream network following forest harvesting: seasonal nitrate removal and conservative export of organic forms

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Abstract

Boreal streams are under pressure from large scale disturbance by forestry. Recent scenarios predict an increase in forest production in Scandinavia to meet market demands and to mitigate higher anthropogenic CO$_2$ emissions. Increased fertilization and shorter forest rotations are anticipated which will likely enhance the pressure on boreal streams in the near future. Among the major environmental impacts of forest harvesting is the increased mobilization of inorganic nitrogen (N), primarily as nitrate (NO$_3^-$) into surface waters. But whereas NO$_3^-$ inputs to first-order streams have been previously described, their downstream fate and impact is not well understood. We evaluated the downstream fate of N inputs in a boreal landscape that has been altered by forest harvests over a 10 year period to estimate the effects of multiple clear-cuts on aquatic N export in a boreal stream network. Small streams showed substantial leaching of NO$_3^-$ in response to harvests with concentrations increasing by ~15 fold. NO$_3^-$ concentrations at two sampling stations further downstream in the network were strongly seasonal and increased significantly in response to harvesting at the medium size, but not at the larger stream. Nitrate removal efficiency, $E_r$, calculated as the percentage of “forestry derived” NO$_3^-$ that was retained within the landscape using a mass balance model was highest during the snow melt season followed by the growing season, but declined continuously throughout the dormant season. In contrast, export of organic N from the landscape indicated little removal and was essentially conservative. Overall, net removal of NO$_3^-$ between 2008 and 2011 accounted for ~70% of the total NO$_3^-$ mass exported from harvested patches distributed across the landscape. These results highlight the capacity and limitation of N-limited terrestrial and aquatic ecosystems to buffer inorganic N mobilization that arises from multiple clear-cuts within meso-scale boreal watersheds.
1 Introduction

Decades of research have shown that disturbance of forest ecosystems can lead to increased losses of inorganic nitrogen (N) from land (Vitousek et al., 1979; Likens and Bormann, 1995; Aber et al., 2002; Houlton et al., 2003), with potentially negative consequences for water quality in streams and rivers (Martin et al., 2000). Perhaps the clearest demonstrations of how forest disturbance influences terrestrial nutrient mobilization have used experimental harvests in small catchments to document changes in stream chemistry relative to undisturbed controls (Likens et al., 1970; Swank and Vose, 1997). While the magnitude and duration of response to harvest varies among studies (Binkley and Brown, 1993; Kreutzweiser et al., 2008), most have documented increases in stream-water nitrate (NO$_3^-$) concentrations. Such responses reflect the loss of plant nutrient demand (Boring et al., 1981), accelerated rates of soil N mineralization and nitrification (Holmes and Zak, 1999), and increases in hydrologic flux within the catchment (Hornbeck et al., 1997; Andréassian, 2004). By design, the majority of this research has addressed responses to forest disturbance at small spatial scales (e.g., catchments of first-order streams) but has not explored how localized increases in nutrient concentration are translated downstream within fluvial networks.

Whereas studies have addressed the removal of inorganic N at the network scale (Helton et al., 2011; Wollheim et al., 2006; Worrall et al., 2012; Alexander et al., 2009), little has been done to investigate the specific effects of forestry on nitrogen cycling in boreal stream networks. A clearer understanding of how the enrichment of headwater environments through forestry is expressed at larger spatial scales (Futter et al., 2010) is important if policy makers are to consider the broader biogeochemical implications of forest management.

The degree to which surplus NO$_3^-$ derived from forest disturbance is delivered to downstream receiving systems is determined by the balance between hydrologic transport and biological demand within multiple habitats at the terrestrial–aquatic interface (McClain et al., 2003; Seitzinger et al., 2006). For example, when forest harvesting
leaves riparian buffer zones intact, plant nutrient uptake, immobilization by soil heterotrophs, and denitrification in streamside habitats can together greatly reduce the delivery of NO$_3^-$ to streams (Laurén et al., 2005). The efficiency of riparian NO$_3^-$ removal varies among studies (Ranalli and Macalady, 2010; Weller et al., 2011), and is determined, in large part, by topographic and soil properties that influence the rates and efficacy of denitrification through effects on hydrologic transport (Ocampo et al., 2006), soil/sediment redox conditions (Pinay et al., 2000), and depth of groundwater flow-paths relative to biogeochemically active soil layers (Vidon and Hill, 2004; Groffman et al., 2002). Riparian N retention efficiency, and the mechanisms responsible, may also vary in response to changes in plant demand (Sabater et al., 2000), availability of labile carbon (C) to soil and sediment microbes (Starr and Gillham, 1993) and hydrologic forcing during floods that overwhelms biotic potential (Hill, 1993).

Where forest harvests extend to channel margins, or when retention of NO$_3^-$ in riparian buffer zones is poor, surplus NO$_3^-$ derived from disturbance is delivered directly to streams. Rates of nutrient uptake in streams and hyporheic zones can be rapid (Mulholland et al., 2008) and retention of NO$_3^-$ in headwater environments may reduce watershed exports in response to forest disturbance (Bernhardt et al., 2003; Riscassi and Scanlon, 2009). NO$_3^-$ removal in streams may be linked to uptake by autotrophic organisms, as well as to denitrification in hyporheic sediments (Harvey et al., 2013; Mulholland et al., 2008). The efficiency of this NO$_3^-$ removal (i.e., the percentage removed per unit stream length) is determined by the strength of this biological demand relative to nutrient availability (Mulholland et al., 2008), and is further constrained by hydrologic factors that govern residence times in biological active zones (Wollheim et al., 2006). The result of these relationships is that removal efficiency tends to be lowest during periods of high flow and/or NO$_3^-$ flux (Alexander et al., 2009; Scanlon et al., 2010). Biological activity and associated nutrient demand in streams is strongly influenced by a variety of habitat factors (e.g., incident light, temperature, and organic matter availability) that vary seasonally (Roberts and Mulholland, 2007; Valett et al., 2008). These factors are also modified by disturbance in the surrounding landscape (e.g., through
loss of canopy cover), with the result that in-stream retention of excess NO$_3^-$ may itself change in response to harvesting (Bernhardt et al., 2003; Sabater et al., 2000).

In this paper we explore the potential for fluvial networks to remove NO$_3^-$ derived from forest harvesting in a boreal landscape in northern Sweden, where N limitation of terrestrial (Högberg et al., 2006) and aquatic (Jansson et al., 2001) productivity is common. We compiled 10 years of data on clear-cuts performed in this landscape with 8 years of temporally coinciding stream chemistry data from a third-order stream network. The network includes a replicated paired-catchment harvesting experiment in the headwaters, plus several additional harvests (Fig. 1). Enhanced NO$_3^-$ loading to headwater streams (first-order) as a result of forest clear-cutting has been reported previously for this site (Löfgren et al., 2009). Thus, the study design and history of research in this landscape provide a unique opportunity to explore the downstream implication of forest harvesting. We use a simple modeling approach to ask: (i) whether and how NO$_3^-$ exported from recent (< 10 yr) clear-cuts influences downstream water chemistry, (ii) how the strength of upstream-downstream connections changes seasonally, and (iii) to what degree downstream patterns in nutrient concentration arise from simple dilution of upstream inputs vs. biological uptake and retention in stream and riparian habitats.

2 Methods

2.1 Study site

This study was performed in the “Balsjö paired-catchment experiment” located in the boreal forest of northern Sweden (64°1’37” N 18°55’43” E) (Löfgren et al., 2009). The experiment consists of four first-order streams of which two were clear-cut harvested (clear-cuts = CC-4 and NO-5; controls = RS-3 and NR-7) in 2006 and two third-order downstream sites of different size (BA-1, size = 22.9 km$^2$ and BA-2, size = 8.9 km$^2$, Fig. 1). Clear-cutting at CC-4 was carried out to the stream bank, whereas a small,
~ 10 m wide at each stream side, discontinuous riparian buffer was left intact at NO-5. All clear-cuts in the network were performed as final-fellings for commercial purposes following environmental considerations according to the Swedish Forestry Act, interpreted and applied by the forest owner. Thus leaving small (5–10 m) buffer zones along headwater streams is common practice.

2.2 Stream water chemistry

Concentrations of NO$_3^-$ and dissolved organic nitrogen (DON) were determined from unfiltered stream water samples. As fractions of particulate organic matter are generally very low in this landscape (< 0.6 %; see Laudon et al., 2011) we consider samples to represent dissolved solute concentrations. Samples were collected between 2004 and 2012 at one to two week intervals during spring, summer, and fall, and at four week intervals during winter low flow. Samples were frozen within 1–2 days after collection and analyzed using colorimetric methods at a SWEDAC accredited laboratory according to method SS-EN ISO 13395:1996 for NO$_3^-$ (sulphanil amid method after cadmium reduction), according to Bran & Luebbe Method G-171–96 Rev. 1 (Phenate method) for ammonium (NH$_4^+$), and method SS-EN 12260:2004 for total N (combustion to nitrous oxide followed by chemiluminescence detection) (Löfgren et al., 2009). Thus, reported concentrations of NO$_3^-$ equal the sum of nitrate and nitrite expressed as mass of N (µg NL$^{-1}$); concentrations for DON were calculated as total N minus inorganic N. Analysis uncertainty for NO$_3^-$ were 5 % for the concentrations range of 1–100 µg L$^{-1}$ and 4 % for 100–1000 µg L$^{-1}$; uncertainties for NH$_4^+$ were reported as 14 % for 3–20 µg L$^{-1}$ and 8 % for 20–100 µg L$^{-1}$. Uncertainties for total N were 14 % for 50–1000 µg L$^{-1}$ and 8 % for 1–5 mg L$^{-1}$.

2.3 Mixing model

We used a mixing model to represent the landscape mass-balance for NO$_3^-$ and DON. This model assumes conservative mixing as well as conservative mass transport of wa-
water and solutes from two landscape end-members (EMs): clear-cuts and control forests. The chemistry at downstream stations (BA-1 and BA-2) can then be predicted from the simple mixing of the hydro-chemical signal from the upstream EMs. The percentage of clear-cut area of each sub-catchment was derived from high-resolution satellite images supplied by the Swedish Forest Agency combined with local ground-truthing (see Schelker et al. (2014) for a full description). This data comprises all clear-cuts from the past 10 years (2002–2012, see also Fig. 1). Similar to earlier work, we considered harvest prior to this period to have a negligible effect, due to their low spatial extent in the watershed (Schelker et al., 2014). Thus, the remaining area was assumed to constitute entirely uncut forest.

The concentration at a downstream location (\(C_{\text{modelled}}\), in mgL\(^{-1}\)) for each time step was modeled using the area specific mass export (Eq. 1):

\[
C_{\text{modelled}} = (M_{\text{harvest}} A_{\text{harvest}} + M_{\text{control}} A_{\text{control}}) Q_{\text{out}}^{-1}
\]

with \(Q_{\text{out}}\) being the specific discharge (mm day\(^{-1}\)) at the downstream site, \(M_i\) (mg m\(^{-2}\) day\(^{-1}\)) being solute mass export for the site \(i\) \((i = \text{harvest, control})\). \(M_i\) was calculated as \(M_i = Q_i C_i\), with \(C_i\) (mg L\(^{-1}\)) being the solute concentration and \(Q_i\) (mm day\(^{-1}\)) being the discharge. \(A_j\) (%) was the percentage of the total area that was harvested or acts as a control for the site \(i\), respectively. This mass-balance model allows simulating the contributions of clear-cuts vs. control forests to downstream sites by considering the changes in solute concentrations and water discharge.

A 100 % harvested catchment did not exist in Balsjö and N leakage into first-order streams following clear-cutting may vary dependent on local factors, such as the presence of riparian forest buffers (Laurén et al., 2005), and was also observed to differ between the two harvested sites in Balsjö (Löfgren et al., 2009). Thus we calculated \(C_{\text{harvest}}\) (mg L\(^{-1}\)) in Eq. (1) for each time step as the average concentration of CC-4 and the NO-5 northern catchment, each scaled to 100 % harvest using a scaling equation. This equation extrapolates the difference between observed concentration \((C_{\text{obs},j},\) in mg L\(^{-1}\) with \(j = \text{CC-4 or NO-5}\) and the concentration of the control forest EM, \(C_{\text{control}}\)
(mgL$^{-1}$), to 100 % harvest (Eq. 2).

$$C_{\text{harvest},j} = C_{\text{control}} + (C_{\text{obs},j} - C_{\text{control}}) d_j$$

(2)

The conversion factor, $d_j$, is defined as the reciprocal of the percentage of the area harvested ($A_j$) for the site $j$. Furthermore, $C_{\text{control}}$, the concentration representing the control forest EM, was calculated as the average concentration of the two forested reference sites RS-3 and NR-7, that differ in terms of stand age and peatland coverage (Schelker et al., 2014; Löfgren et al., 2009).

Stream discharge ($Q$ in mm day$^{-1}$) for each EM was determined using approaches described previously (Schelker et al., 2014). In short, $Q$ was derived from waterlevel timeseries that were recorded hourly by two Trutrack WTH staff loggers at the sites NR-7, NO-5, CC-4 and BA-1 from which discharge was calculated using well established rating curves at V-notch weirs (Schelker et al., 2012). $Q_{\text{harvest}}$ was calculated as the difference between $Q_{\text{NR-7}}$ and $Q_{\text{NO-5}}$, a nested downstream catchment with 88 % harvest that is assumed to represent a 100 % harvest. $Q_{\text{control}}$ was set equal to $Q_{\text{NR-7}}$. These definitions of $Q$ have been validated in an earlier application of this mixing model, were it was shown that daily $Q$ at BA-1 was modeled reasonably well using these assumptions (relationship of modeled vs. measured $Q$ : $r^2 = 0.77$; slope = 1.01; y intercept = 0.0001, see Schelker et al., 2014).

Nitrate removal efficiency ($E_r$ in %) was calculated as the difference between measured and modeled NO$_3^-$ concentrations divided by the modeled concentration. Thus, $E_r$ equals the percentage of NO$_3^-$ that was removed between harvested areas and downstream sampling stations during transport, and this value approaches zero when NO$_3^-$ behaves conservatively in the landscape. If differences between measured and modeled [NO$_3^-$] were < 0, $E_r$ was set to zero.

To evaluate whether in-stream processes could be responsible for the calculated removal of N in the landscape, we calculated net uptakes rates ($U$; µgN m$^{-2}$ min$^{-1}$) for NO$_3^-$ as the difference between modeled and the measured mass fluxes of NO$_3^-$ divided by the total upstream stream surface area. Stream surface areas were estimated
by linear interpolation from known transects within the network combined with a manual analysis of high resolution air photographs. These coarse estimates of $U$ thus represent the net removal in streams that would be required to achieve mass conservation (an even mass-balance) in the landscape mixing model. Thus, these estimates also represent maximum potential rates as they assume that all uptake would occur within the stream boundaries and not within adjacent riparian soils.

Statistical analysis of differences in measured concentrations before and after treatment in the same stream, as well as between sampling sites were performed as two sample student $t$ tests, accounting for unequal variance. If data was not normally distributed, a Mann–Whitney Rank Sum test was used instead for pairwise comparisons.

Annual export of NO$_3^-$ was calculated for each sampling station and year. NO$_3^-$ concentrations between the sampling occasions were interpolated linearly. Daily loads were calculated as concentration times stream discharge and are expressed per unit catchment area. In addition, to compare against the observed NO$_3^-$ export, modeled estimates of annual loss were calculated for BA-1 and BA-2 assuming conservative transport of N from upstream sources. To further infer seasonal effects on N exports, seasons were defined as following: dormant season from November to the end of March, snow melt season from April to the end of May and growing season from June to the end of October of each year, respectively.

### 3 Results

Forest harvesting increased NO$_3^-$ mobilization into first-order streams. Average concentrations of NO$_3^-$ (±SD) at the CC-4 catchment increased significantly ($p < 0.001$) by more than 15-fold from 15.6 (±10.9; $n = 62$) $\mu$g NL$^{-1}$ before harvest to 261.0 (±170.4; $n = 151$) $\mu$g N L$^{-1}$ after the treatment (Fig. 2). In the buffer catchment NO-5, the response to harvests was less pronounced but also significant (11.4 (±8.6; $n = 62$) $\mu$g NL$^{-1}$ before harvest and 25.9 (±35.3; $n = 151$) $\mu$g NL$^{-1}$ after, $p < 0.001$). Average concentrations at the NR-7 control stream were 27.6 (±20.5; $n = 60$) $\mu$g NL$^{-1}$
before harvest and did not change significantly after the treatment (23.1 (±22.2; 
\(n = 151\)) µg NL\(^{-1}\)). At the RS-3 control stream NO\(_3^-\) concentrations were also low, 12.3 (±9.2; \(n = 49\)) µg NL\(^{-1}\) before harvest, but decreased significantly to 5.8 (±7.5; 
\(n = 151\)) µg NL\(^{-1}\) after the treatment. In addition, stream runoff was substantially 
increased after harvest, which enhanced the relative contribution of clear-cuts vs. control 
forests for downstream mass fluxes. Annual specific runoff of the CC-4 catchment after 
the harvest (2007–2012) was 518 (±128) mm whereas the northern control site (NR-7) 
had a lower average specific discharge of 355 (±88) mm.

At the BA-1 downstream site, NO\(_3^-\) concentrations remained statistically similar 
between the periods of 2004–2006 (17.2 ± 14.3 µg NL\(^{-1}\); \(n = 37\)) and 2007–2012 
(17.2 ± 18.9 µg NL\(^{-1}\); \(n = 151\)), even though the upstream area that was clear-cut in-
creased from 2.5 % in 2004 to 11.2 % in 2011 (Fig. 2). At the BA-2 site, where harvests 
ranged from 4.6 % of the catchment area in 2004 to 17.5 % in 2011, average NO\(_3^-\) 
concentrations increased significantly (\(t\) test, \(p = 0.026\)) from 15.9 (±9.8; \(n = 30\)) µg N 
L\(^{-1}\) during 2004–2006 to 21.3 (±19.1; \(n = 151\)) µg NL\(^{-1}\) during 2007–2012. Furthe-
more, NO\(_3^-\) concentrations increased continuously throughout the winter period, with 
the highest values observed just prior to snowmelt at the BA-1 and BA-2 sites.

When modeled concentrations of DON and NO\(_3^-\) at BA-1 and BA-2 were compared 
to the measured concentrations, distinct patterns emerged. First, modeled and mea-
sured DON concentrations correlated well (relationships: \(r^2 = 0.92, p < 0.001\) for BA-2 
and \(r^2 = 0.72, p < 0.001\) for BA-1; see also Fig. 3). In contrast, relationships between 
modeled and measured NO\(_3^-\) concentrations were significant, but explained little of the 
variability (\(r^2 = 0.25\) for BA-1; \(r^2 = 0.31\) for BA-2) with modelled concentrations nearly 
exclusively overestimating the measured concentrations (Fig. 3).

Modelled NO\(_3^-\) removal efficiency calculated as the fraction of NO\(_3^-\) that was retained 
showed a strong seasonal signal (Fig. 4). \(E_r\) values above 75 % were observed just af-
fter peak snow melt, with the exception of the snow melt of 2012. \(E_r\) then remained high 
(> 75%) during the summer of 2008, and stayed at intermediate-to-high levels (> 50 %) 
during the following summer seasons (Fig. 4). Towards the end of the growing season,
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4 Discussion

The observed changes in NO$_3^-$ export in response to harvesting in first-order streams suggest that terrestrial ecosystem disturbance controls N mobilization into small streams. The concurrent increase in NO$_3^-$ concentrations by up to ~15 fold with significant increases in stream runoff, the latter primarily caused by low evapotranspiration in clear cuts during summer (Schelker et al., 2013), are thus governing substantial increases in NO$_3^-$ inputs to the fluvial network (Table 1). However, despite obvious effects of forest harvesting on NO$_3^-$ concentrations in first-order streams, only very subtle responses could be detected for the third-order streams within this same network, suggesting that significant NO$_3^-$ retention occurred between the harvested areas in the landscape and downstream monitoring sites.

At both downstream sites, and the CC-4 clear-cut catchment, concentrations of NO$_3^-$ were higher during the dormant season as compared to the growing season (Fig. 2). Similarly, these seasonal variations were also largely paralleled by NH$_4^+$ concentrations (data not shown). However, contributions of NH$_4^+$ to the total inorganic N pool varied at both downstream sites between seasons. On average NH$_4^+$ accounted for 23 and 18% during winter low flow, for 45 and 39% during snowmelt and 54 and 46% of the inorganic N pool for BA-1 and BA-2, respectively. Overall such seasonal variation in stream inorganic N, and specifically stream NO$_3^-$ concentrations, is common across Sweden (Sponseller et al., 2014; Löfgren et al., 2014) and is thought to reflect seasonal changes in terrestrial N demand (Mitchell et al., 1996). In contrast, NO$_3^-$ concentrations
at RS-3 did not show such a seasonal pattern, suggesting particularly low inorganic N availability and strong N-limitation persisting throughout the year (Stoddard, 1994). This hypothesis is further supported by the fact that average NO$_3^-$ concentrations at this site decreased significantly by $-6.5 \mu g \text{NL}^{-1}$ between the pre-treatment and the treatment period, indicating that local factors, such as the presence of actively growing forest stands with dense riparian vegetation, resulted in a high inorganic N demand and thus low stream concentrations at this site.

Seasonal variations in NO$_3^-$ concentrations at the CC-4 clear-cut during the dormant season (Fig. 2) were related closely with temporal changes in NO$_3^-$ concentration at the downstream sites (Fig. SS1), indicating a temporal coherence in concentration change (sensu Kling et al., 2000) within the network. Overall, these observations suggest (i) a common seasonal control where NO$_3^-$ retention in most catchments declines throughout the dormant season, (ii) that enhanced upstream inputs of NO$_3^-$ in headwaters are translated downstream during the dormant season, and (iii) that temporal nutrient dynamics at upstream and downstream reaches become uncoupled during the spring and the summer growing season.

Poor relationships between measured and modelled NO$_3^-$ concentrations at BA-1 and BA-2 (Fig. 3, data for BA-2 not shown) are likely to result from seasonal NO$_3^-$ removal, a pattern supported by the temporal variation of $E_r$ for both sites (Fig. 4). In contrast, the relationships of modelled and measured DON concentrations are similar to those previously observed for dissolved organic carbon, as well as the two conservative tracers, dissolved silica and chloride (Schelker et al., 2014). These relationships are thus indicative for an approximately conservative downstream transport of DON in the network. Furthermore, these patterns provide additional support for the applicability of our mixing model in this landscape, as they are consistent with the idea that bulk DON is composed primarily of organic compounds of low bioavailability that is exported from landscapes without strong biotic controls (Hedin et al., 1995). For this reason, DON also often represents the major loss vector for N in catchments that are not subject to large anthropogenic inputs of inorganic N (Perakis, 2002; Kortelainen...
et al., 1997). Given that clear cutting led to increased DOC export from these same catchments (Schelker et al., 2014), and that DOC and DON are assumed to belong to the same organic matter pool and are thus often highly correlated in boreal catchments (Sponseller et al., 2014), losses of DON in response to harvesting may represent an important and largely unappreciated source of terrestrially derived N to downstream receiving systems (Rosén et al., 1996).

Low dormant season values of $E_r$ suggest an ostensibly weak NO$_3^-$ demand in cold, snow-covered streams and thus low strength of the biological sink within the fluvial network. During this period a large fraction of NO$_3^-$ entering the stream network was also exported downstream, which is exemplified by the few wintertime occasions where $E_r$ was near-zero. These occasions suggest that either (i) all NO$_3^-$ was transported downstream (e.g. that NO$_3^-$ transport was conservative) or (ii) that the downstream reaches of the stream network acted as source areas of NO$_3^-$. The latter has been previously hypothesized to cause discrepancies of reach scale N mass-balances (von Schiller et al., 2011).

Interestingly, $E_r$ did not show a direct dependence on stream discharge at any of the downstream sites (Fig. 4), suggesting that N-demand rather than flow (Hill, 1993) and/or transient storage (Ensign and Doyle, 2006) were controlling NO$_3^-$ removal in the fluvial network. In addition, high removal efficiencies during spring and summer had substantial effects on overall annual net NO$_3^-$ removal as estimated by the difference of modeled and measured annual NO$_3^-$ exports. These estimates (±SD) showed that 71(±4) % and 67(±10) % of the NO$_3^-$ inputs to the BA-1 and BA-2 catchments were removed before reaching the outlets (Table 1).

Furthermore, our estimates of net NO$_3^-$ removal suggest that during most periods, reasonable levels of in-stream activity could account for the discrepancy between measured and modeled fluxes at downstream stations. Assuming that all NO$_3^-$ retention was occurring within the stream channels, median values and interquartile ranges (10th to 90th percentile) for the BA-2 catchment were $-5.8$ ($-21.9; -1.3$) µg N m$^{-2}$ min$^{-1}$ for the entire year. These values fall well within the range of net uptake estimates made else-
where for small streams (Bernhardt et al., 2003; Roberts and Mulholland, 2007; von Schiller et al., 2011).

As with $E_r$, estimates of $U$ were significantly higher during snow melt as compared to the growing season and, interestingly, there was no significant difference in median values between growing and dormant seasons (Fig. 5). While other recent studies indicate the potential for high rates of nutrient uptake during the snowmelt period (Hall et al., 2009), these seasonal comparisons should be made with some caution as our estimates of net removal do not account for losses that occur to the outside of the stream, as for example losses to the hyporheic zone, riparian habitats or into deep groundwater.

Important mechanisms that control $\text{NO}_3^-$ removal from stream water during the growing season are biological uptake by riparian vegetation (Sabater et al., 2000) and immobilization by in-stream primary producers. These in-stream sinks may also change in response to forest harvesting, for example, if elevated light conditions foster increased autotrophic production (Bernhardt and Likens, 2004). Indication that such increased in-stream $\text{NO}_3^-$ demand during the growing season may also be present in the Bal-sjö stream network is given by ∼30 fold greater summertime accumulation of algal biomass (chlorophyll $a$) onto ceramic tiles in the CC-4 stream as compared to RS-3 (R. Sponseller, unpublished data). However, uptake by autotrophs is not necessarily a permanent removal of N from the stream ecosystem, because substantial amounts of N may be recycled when algal material decays (Tank et al., 2000). Similarly, a recent study found heterotroph microbial respiration in boreal streams to be strongly N-limited, with the highest observed heterotroph respiration rate (∼70 $\mu$g $\text{O}_2$ cm$^{-2}$ h$^{-1}$) in the CC-4 clear cut stream of this study (Burrows et al., 2015). This indicates the widespread N-limitation of biofilms in boreal streams and their immediate response to higher terrestrial N loadings following harvests.

An additional process that may account for the permanent removal of $\text{NO}_3^-$ observed in this study and thus for the seasonal differences in $U$ is denitrification (Mulholland et al., 2008). Environments that have been observed to favor the direct conversion of
NO$_3^-$ to gaseous N by denitrification are (i) stream biofilms (Teissier et al., 2007), (ii) stream hyporheic zones (Harvey et al., 2013) and (iii) riparian sediments (Starr and Gillham, 1993). Furthermore, experimental studies have demonstrated that the process of denitrification is often found to be co-dependent on terrestrial NO$_3^-$ inputs and bioavailable dissolved organic matter (DOM) as an electron donor (Baker et al., 1999). More specifically, *hot moments* of denitrification, that is, a disproportionally high and evanescent assimilatory NO$_3^-$ demand, can be generated by experimental additions of labile DOM (Zarnetske et al., 2011). Such enhanced demand has further been shown to regulate uptake rates in stream reaches (Bernhardt and Likens, 2002) and hyporheic sediments (Sobczak et al., 2003). Additional reach scale NO$_3^-$ retention could also be linked to dissimilatory NO$_3^-$ demand caused by the reduction of NO$_3^-$ to NH$_4^+$. Such demands could also be causing the seasonally varying proportions of NH$_4^+$ of the total inorganic N pool. However, this processing does not represent a permanent removal of inorganic N from streams (Mulholland et al., 2008) as NH$_4^+$ may be re-oxidized to NO$_3^-$ in downstream environments that favor nitrification.

Transferring this well-established process knowledge from the reach-scale to the network scale suggests that NO$_3^-$ removal at the landscape scale may be dependent on a sufficient supply of labile DOM to all stream reaches within the network that are located downstream of harvests. Research in boreal headwater streams has shown that terrestrially-derived low molecular weight DOM, commonly consisting of free amino acids, carboxylic acids and carbohydrates, can achieve high concentrations during the spring snow melt (Berggren et al., 2009). These terrestrial inputs have further been suggested to be able to support the microbial C demand of downstream aquatic ecosystems during a timeframe of days to weeks following the spring freshet (Berggren et al., 2009) – times when $E_r$ was also highest in our study. Thus we suggest a limitation of heterotrophic processes, such as denitrification and immobilization, by the restricted supply of bioavailable DOM from terrestrial sources during the dormant season as a plausible mechanism that inhibits net NO$_3^-$ removal at the network scale. In turn, the limited supply of inorganic N relative to bioavailable C during the other times
of the year would then limit heterotroph turnover of DOM – a coupling that has been suggested previously for boreal streams (Berggren et al., 2007).

In summary our work agrees with earlier studies in that terrestrial ecosystem disturbance enhances $\text{NO}_3^-$ mobilization into first-order streams (Likens et al., 1970) and that such increased $\text{NO}_3^-$ concentrations can potentially be transferred downstream (Alexander et al., 2007). The hypothesis that stream and riparian processing of $\text{NO}_3^-$ may dampen the effect at downstream sites (Bernhardt et al., 2003) was supported during the snow melt, as well as during the growing season when rates of biological activity and supply of bioavailable C are likely to be high. During the dormant season, however, results suggest that limited net $\text{NO}_3^-$ uptake rates constrain the potential for $\text{NO}_3^-$ removal within the fluvial network. Considering the two mentioned measures to increase forest production (Egnell et al., 2011), we argue that both are likely to increase downstream export of $\text{NO}_3^-$, if the stream network’s removal rates remain the same as under current conditions. More specifically, shorter forest rotations would increase the frequency of disturbance due to harvesting and thus the periods where elevated leaching may occur. Similarly, increased fertilization may enhance the risk of $\text{NO}_3^-$ leakage into surface waters particularly during the dormant season (Binkley et al., 1999) when the biological demand for inorganic N is low within boreal stream networks.

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References


Nitrogen export from a boreal stream network following forest harvesting

J. Schelker et al.


**Table 1.** Measured and modelled annual NO$_3$ loads per unit catchment area from all six Balsjö catchments during 2008–2011.

<table>
<thead>
<tr>
<th>Site</th>
<th>BA-1 (mg N m$^{-2}$ yr$^{-1}$)</th>
<th>BA-2 (mg N m$^{-2}$ yr$^{-1}$)</th>
<th>RS-3 (mg N m$^{-2}$ yr$^{-1}$)</th>
<th>CC-4 (mg N m$^{-2}$ yr$^{-1}$)</th>
<th>NO-5 (mg N m$^{-2}$ yr$^{-1}$)</th>
<th>NR-7 (mg N m$^{-2}$ yr$^{-1}$)</th>
<th>BA-1 (mg N m$^{-2}$ yr$^{-1}$)</th>
<th>BA-2 (mg N m$^{-2}$ yr$^{-1}$)</th>
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<tr>
<td>Unit/Year</td>
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<td>4.3</td>
<td>1.2</td>
<td>106.3</td>
<td>3.5</td>
<td>15.3</td>
<td>20.6</td>
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<tr>
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<td>2009</td>
<td>4.4</td>
<td>3.8</td>
<td>135.2</td>
<td>5.3</td>
<td>16.5</td>
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<tr>
<td></td>
<td>2010</td>
<td>4.4</td>
<td>1.6</td>
<td>121.4</td>
<td>5.3</td>
<td>14.3</td>
<td>18.8</td>
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<tr>
<td></td>
<td>2011</td>
<td>5.1</td>
<td>1.4</td>
<td>98.1</td>
<td>6.1</td>
<td>15.7</td>
<td>22.3</td>
<td></td>
</tr>
</tbody>
</table>

*Assuming conservative mixing and solute transport.*
Figure 1. The “Balsjö Paired Catchment Experiment” including the catchments RS-3, CC-4, NO-5 and NR-7, as well as the two downstream sites BA-2 and BA-1 that integrate the larger 22.9 km² Balsjö Stream Network. Areas harvested during 2001–2011 are shown as orange. Solid blue lines represent the stream network; solid blue areas show ponds with open water. Solid black lines indicate the catchment boundaries, black pyramids the location of water sampling.
Figure 2. First Panel: trimonthly nitrate (NO$_3^-$) concentrations and standard deviations (whiskers) of two first-order streams, the clear-cut catchment (CC-4) and the reference south (RS-3), as well as for two third-order downstream sites BA-2 (size = 8.7 km$^2$) and BA-1 (size = 22.9 km$^2$). Second panel: discharge at the BA-1 outlet. Third panel: satellite derived percentage of catchment area that has been clear-cut harvested since 2001 within BA-2 and BA-1.
Figure 3. Results of the mass-balance modeling approach for DON (left) and NO$_3^-$ (right) for the downstream site BA-1. Higher modeled than measured concentrations (above the 1 : 1 line) indicate a mass loss of the solute during transport downstream (and vice versa) assuming conservative mass transport and mixing.
Figure 4. Panel (a): Stream discharge ($Q$) and sample drawing at the BA-1 site. Panel (b): Seasonal variation in $\text{NO}_3^-$ removal efficiency ($E_r$), that is, the difference between measured and modeled $\text{NO}_3^-$ concentration divided by the modeled concentration for the two downstream sites BA-1 and BA-2; lines represent moving averages with $n = 5$. Panel (c): $E_r$ vs. $Q$ for the BA-1 (left) and the BA-2 (right) catchment outlets, respectively indicating little dependency of $E_r$ on $Q$ at both sites.
Figure 5. Boxplot of the seasonal differences in net NO$_3^-$ uptake rates ($U$) per unit stream area during 2008–2011 in the BA-2 catchment. Solid lines represent median values, boxes the 25th to 75th percentile range, whiskers the 90th to 10th percentiles and dots the 95th and the 5th percentiles. Pairs of letters indicate highly significant differences between seasons ($p < 0.001$; Mann–Whitney Rank Sum Test). Values for BA-1 site are generally lower, but show similar seasonal differences.