2	Nitrogen export from a boreal stream network following forest harvesting:							
3	Seasonal nitrate removal and conservative export of organic forms							
4								
5	Running title: Nitrogen export from a boreal stream network							
6								
7	Authors: Schelker, Jakob ^{1,2*} ; Sponseller, Ryan ³ ; Ring, Eva ⁴ ; Högbom, Lars ⁴ ;							
8	Löfgren, Stefan ⁵ and Laudon, Hjalmar ²							
9	Affiliations:							
10	¹⁾ Department of Limnology and Bio-Oceanography, University of Vienna, Vienna Austria.							
11	²⁾ Department of Forest Ecology and Management, Swedish University of Agricultural							
12	Sciences, Umeå, Sweden.							
13	⁴⁾ The Equation Department Department Institute of Sweder (Six of orgin), Unreader Sweder							
14 15	⁵⁾ Department of Aquatic Sciences and Assessment Swedish University of Agricultural							
16	Sciences, Uppsala, Sweden.							
17	* Corresponding Author:							
18	Jakob Schelker, Department of Limnology and Bio-Oceanography,							
19	University of Vienna, Althanstrasse 14, 1090, Vienna, Austria							
20	email: jakob.schelker@univie.ac.at							
21	mobile: (+43) 660 321 5081							
22								
23								
24								
25	Format: Primary research article							
26	Keywords: Nitrate, Organic Nitrogen, Nitrogen Retention, In-Stream Processing,							
27	Denitrification, Boreal Forest, Forest Disturbance, Clear-Cutting, Scaling.							

28 Abstract

Clear-cutting is today the primary driver of large scale forest disturbance in boreal regions of 29 Fennoscandia. Among the major environmental concerns of this practice for surface waters is 30 the increased mobilization of nutrients, such as inorganic nitrogen (DIN) into streams. But 31 32 while DIN loading to first-order streams following forest harvest has been previously 33 described, the downstream fate and impact of these inputs is not well understood. We evaluated the downstream fate of DIN and dissolved organic nitrogen (DON) inputs in a 34 boreal landscape that has been altered by forest harvests over a 10 year period. The small 35 first-order streams indicated substantial leaching of DIN, primarily as nitrate (NO_3^{-}) in 36 response to harvests with NO₃⁻ concentrations increasing by ~15 fold. NO₃⁻ concentrations at 37 two sampling stations further downstream in the network were strongly seasonal and 38 increased significantly in response to harvesting at the mid-sized, but not at the larger stream. 39 DIN removal efficiency, E_r , calculated as the percentage of 'forestry derived' DIN that was 40 41 retained within the stream network based on a mass balance model was highest during the snow melt season followed by the growing season, but declined continuously throughout the 42 dormant season. In contrast, export of DON from the landscape indicated little removal and 43 was essentially conservative. Overall, net removal of DIN between 2008 and 2011 accounted 44 for ~65% of the total DIN mass exported from harvested patches distributed across the 45 46 landscape. These results highlight the capacity of N-limited boreal stream networks to buffer DIN mobilization that arises from multiple clear-cuts within this landscape. Further, these 47 findings shed light on the potential impact of anticipated measures to increase forest yields of 48 49 boreal forests, such as increased fertilization and shorter forest rotations, which may increase the pressure on boreal surface waters in the future. 50

51

52

53 **1. Introduction**

54 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 55 Bormann, 1995; Aber et al., 2002; Houlton et al., 2003), with potentially negative 56 consequences for water quality in streams and rivers (Martin et al., 2000). Perhaps the clearest 57 demonstrations of how forest disturbance influences terrestrial nutrient mobilization have 58 59 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 60 magnitude and duration of response to harvest varies among studies (Binkley and Brown, 61 62 1993; Kreutzweiser et al., 2008), most have documented increases in stream-water nitrate (NO₃) concentrations. Such responses reflect the loss of plant nutrient demand (Boring et al., 63 1981), accelerated rates of soil N mineralization and nitrification (Holmes and Zak, 1999), 64 65 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 66 at small spatial scales (e.g., catchments of first-order streams) and few studies have explored 67 how localized increases in nutrient concentration are translated downstream within fluvial 68 networks (Bernhardt et al., 2003). 69 70 Whereas several recent studies have addressed the removal of inorganic N within river

networks (Helton et al., 2011; Wollheim et al., 2006; Worrall et al., 2012; Alexander et al.,

72 2009), little has been done to investigate these processes in boreal landscapes subject to

73 widespread and active forest management. A clearer understanding of how the enrichment of

⁷⁴ 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

76 of forest management.

The degree to which surplus NO_3^- derived from forest disturbance is delivered to 77 78 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., 79 2003; Seitzinger et al., 2006). For example, when forest harvesting leaves riparian buffer 80 zones intact, plant nutrient uptake, immobilization by soil heterotrophs, and denitrification in 81 streamside habitats can together greatly reduce the delivery of NO_3^- to streams (Laurén et al., 82 2005). The efficiency of riparian NO₃⁻ removal varies among studies (Ranalli and Macalady, 83 2010; Weller et al., 2011), and is determined, in large part, by topographic and soil properties 84 that influence the rates and efficacy of denitrification through effects on hydrologic transport 85 86 (Ocampo et al., 2006), soil/sediment redox conditions (Pinay et al., 2000), and depth of groundwater flow-pathways relative to biogeochemically active soil layers (Vidon and Hill, 87 2004; Groffman et al., 2002). Riparian N retention efficiency, and the mechanisms 88 89 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 90 91 hydrologic forcing during floods that overwhelms biotic potential (Hill, 1993). 92 Where forest harvests extend to channel margins, or when retention of NO₃⁻ in riparian buffer zones is poor, surplus NO_3^- derived from disturbance is delivered directly to streams. 93 94 Rates of nutrient uptake in streams and hyporheic zones can be rapid (Mulholland et al., 2008) and uptake of NO_3^- in headwater environments may reduce watershed exports in response to 95 forest disturbance (Bernhardt et al., 2003; Riscassi and Scanlon, 2009). NO₃⁻ removal in 96 97 streams may be linked to immobilization by autotrophic and heterotrophic microbes, as well as to denitrification in hyporheic sediments (Harvey et al., 2013; Mulholland et al., 2008). The 98 efficiency of this NO₃ removal (i.e., the percentage removed per unit stream length) is 99 determined by the strength of this biological demand relative to nutrient availability 100 (Mulholland et al., 2008), and is further constrained by hydrologic factors that govern 101

residence times in biological active zones (Wollheim et al., 2006). As a result, removal 102 efficiency tends to be lowest during periods of high flow and/or NO₃⁻ flux (Alexander et al., 103 2009; Scanlon et al., 2010). Biological activity and associated nutrient demand in streams is 104 105 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., 106 107 2008). These factors are also modified by disturbance in the surrounding landscape (e.g., 108 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). 109 In this paper we explore the potential for fluvial networks to remove NO_3^- derived from 110 111 forest harvesting in a boreal landscape in northern Sweden, where N limitation of terrestrial 112 (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 113 114 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 115 additional harvests (Figure 1). Enhanced NO₃⁻ loading to headwater streams (first-order) as a 116 result of forest clear-cutting has been reported previously for this site (Löfgren et al., 2009). 117 118 Thus, the study design and history of research in this landscape provide a unique opportunity 119 to explore the downstream implication of forest harvesting. We use a simple modeling 120 approach to ask: i) whether and how NO_3^- exported from recent (<10 yr) clear-cuts influences water chemistry downstream within the same drainage system, and ii) to what degree 121 122 downstream patterns in nutrient concentration arise from simple dilution of upstream inputs versus biological uptake and retention in stream and riparian habitats. 123

124

125 **2. Methods**

126 2.1 Study Site

This study was performed in the 'Balsjö paired-catchment experiment' located in the boreal 127 forest of northern Sweden (N 64° 1'37'' E 18° 55'43'') (Löfgren et al., 2009). The 128 experiment consists of four first-order streams of which two were clear-cut harvested (clear-129 cuts = CC-4 and NO-5; controls = RS-3 and NR-7) in 2006 and two third-order downstream 130 sites of different size (BA-1, size = 22.9 km^2 and BA-2, size = 8.9 km^2 , Figure 1). Clear-131 cutting at CC-4 was carried out to the stream bank, whereas a small, ~10 m wide, 132 discontinuous riparian buffer was left intact on both side of the stream at NO-5. All clear-cuts 133 in the network were performed as final-fellings for commercial purposes following 134 environmental considerations according to the Swedish Forestry Act, interpreted and applied 135 136 by the forest owner. Thus leaving small (5-10 m) buffer zones along headwater streams is considered common practice. However, field observations also showed substantial 137 disturbance of riparian zones by forestry machinery crossing streams and by wind throw 138 139 within narrow stream corridors. Together these impacts likely limit the effect of the environmental considerations for nutrient retention. 140 141 The Balsjö catchment is underlain by highly compacted till layers that have generally low hydraulic conductivities. Runoff generation is thus primarily from shallow saturated soil 142 water entering streams laterally (Bishop et al., 2004; Schelker et al., 2013a) Thus, and in 143 144 contrast to other stream systems, contributions from deep groundwater sources are thought to be minor at the spatial scale of this third order stream network (Schelker et al., 2014). 145 146 147 2.2 Stream water chemistry

148 Concentrations of NO_3^- , ammonium (NH_4^+) and dissolved organic nitrogen (DON), chloride 149 (Cl), and dissolved silica (Si) were determined from unfiltered stream water samples. As 150 fractions of particulate organic matter are generally very low in this landscape (<0.6%; see 151 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, 152 summer, and fall, and at four week intervals during winter low flow. Samples were frozen 153 within 1-2 days after collection and analyzed using colorimetric methods at a SWEDAC 154 accredited laboratory according to method SS-EN ISO 13395:1996 for NO₃⁻ (sulphanil amid 155 method after cadmium reduction), according to Bran & Luebbe Method G-171-96 Rev. 1 156 (Phenate method) for NH₄⁺, and method SS-EN 12260:2004 for total N (combustion to 157 nitrous oxide followed by chemiluminescence detection) (Löfgren et al., 2009). Thus, 158 159 reported concentrations of NO₃⁻ equal the sum of nitrate and nitrite expressed as mass of N (μ g N L⁻¹); DIN concentrations were calculated as the sum of NO₃ and NH₄⁺; concentrations 160 of DON as total N minus DIN. Analysis of Cl and Si are described in previous work (Schelker 161 et al., 2014). Analysis uncertainty for NO_3^- were 5% for the concentrations range of 1-100 µg 162 L^{-1} and 4% for 100-1000 µg L^{-1} ; uncertainties for NH₄⁺ were reported as 14 % for 3–20 µg L^{-1} 163 and 8 % for 20-100 μ g L⁻¹. Uncertainties for total N were 14% for 50-1000 μ g L⁻¹ and 8% for 164 $1-5 \text{ mg L}^{-1}$. 165

166

167 2.3 Mixing model

We used a mixing model to represent the landscape mass-balance for NO_3^- and DON. This 168 model assumes conservative mixing as well as conservative mass transport of water and 169 solutes from two landscape end-members (EMs): clear-cuts and control forests (following 170 Schelker et al. 2014). The chemistry at downstream stations (BA-1 and BA-2) can then be 171 predicted from the simple mixing of the hydro-chemical signal from the upstream EMs. The 172 173 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 174 Schelker et al., (2014) for a full description). These data comprise all clear-cuts from the past 175 10 years (2001-2011, see also Figure 1). Similar to earlier work, we considered harvest prior 176

to this period to have a negligible effect, due to their low spatial extent in the watershed

178 (Schelker et al., 2014), and studies elsewhere in the boreal zone that suggest a ten-year time

179 window within clear-cutting is likely to affect DIN exports (e.g. Palviainen et al., 2010). The

180 remaining area of the catchment was assumed to constitute entirely uncut forest.

181 The concentration at the downstream locations BA-1 and BA-2 ($C_{modelled}$, in $\mu g L^{-1}$) for each

time step was modeled using the area specific mass export (Eq. 1):

$$C_{modelled} = (M_{harvest} A_{harvest} + M_{control} A_{control}) Q_{out}^{-1}$$

with Q_{out} being the specific discharge (mm) at the downstream site, M_i (µg m⁻²) being solute 183 mass export for the site *i* (*i=harvest, control*). M_i was calculated as $M_i = Q_i C_i$, with C_i (µg 184 L^{-1}) being the solute concentration and Q_i (mm) being the discharge. A_i (-) was the fraction of 185 the total area that was harvested or acts as a control for the site *i*, respectively. This mass-186 balance model simulates the contributions of clear-cuts versus control forests to downstream 187 188 sites by considering changes in solute concentrations and water discharge. When measured and modelled concentration are plotted against each other for each sampling date, 189 comparatively higher modeled concentrations (above the 1:1 line) indicate a mass loss of the 190 solute during transport downstream (and vice versa) assuming conservative mass transport 191 192 and mixing.

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 $C_{harvest}$ (µg L⁻¹) in Equation 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. Assuming a linear increase of harvesting effects, this equation extrapolates the difference between observed concentration ($C_{obs,j}$, in µg 200 L^{-1} with *j*=CC-4 or NO-5) and the concentration of the control forest EM, $C_{control}$ (µg L^{-1}), to 201 100% harvest (Eq. 2).

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

The conversion factor, d_j , was defined as $d_j = 1/A_j$, that is, the reciprocal of the fraction of the area harvested (A_j) for the site *j*. Furthermore, $C_{control}$, 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) 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). $Q_{harvest}$ was calculated as the difference between Q_{NR-7} and Q_{NO-5} , a nested downstream catchment with 88% harvest that is assumed to represent a 100% harvest. $Q_{control}$ was set equal to Q_{NR-7} .

214 The definitions of Q have been validated in an earlier application of the mixing model, where it was shown that daily Q at BA-1 was modeled reasonably well and with minimal bias using 215 the above assumptions (relationship of modeled vs. measured Q: $r^2=0.77$; slope=1.01; y-216 intercept=0.0001, see Schelker et al., (2014)). To further evaluate the representativeness and 217 robustness of the mixing model, the two conservative tracers, Cl and Si were also modelled. A 218 219 comparison of the modelled vs. measured concentrations (Figure 2 A to D) revealed modeled concentrations to scatter closely around the 1:1 lines with a slightly better fit for BA-2 than 220 for BA-1 and no indications of systematic deviations. These results suggest the validity of the 221 222 model assumptions for these two conservative tracers.

223 2.4 additional calculations

Inorganic nitrogen removal efficiency (E_r , *in* %) was calculated as the difference between modeled and measured DIN concentrations divided by the modeled concentration. Thus, E_r equals the percentage of DIN that was removed between harvested areas and downstream sampling stations during transport, and this value approaches zero when DIN behaves conservatively in the landscape. If differences between measured and modeled [DIN] were <0, E_r was set to zero.

Annual export of DIN and NO_3^- was calculated for each sampling station and year. Solute 230 231 concentrations between the sampling occasions were interpolated linearly. Daily loads were calculated as the product of concentration and stream discharge and are expressed per unit 232 catchment area. In addition, to compare against the observed DIN and NO₃⁻ export, modeled 233 234 estimates of annual export 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 235 were defined as following: dormant season from November to the end of March, snow melt 236 season from April to the end of May and growing season from June to the end of October of 237 each year, respectively. 238

To evaluate whether in-stream processes could be responsible for the modelled removal of N 239 in the landscape, we calculated net areal uptakes rates (U; μ g N m⁻² min⁻¹) for DIN as the 240 difference between modeled and the measured mass fluxes of DIN divided by the total 241 upstream stream surface area. Stream surface areas (Table 1) were estimated by linear 242 243 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 of 244 DIN in streams that would be required to achieve mass conservation (an even mass-balance) 245 246 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 withinadjacent riparian soils.

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

253 **3. Results**

254 3.1 DIN and DON responses to harvest

Forest harvesting increased DIN mobilization into first-order streams. Average concentrations 255 of NO₃⁻ (\pm SD) at the CC-4 catchment increased significantly (p<0.001) by more than 15-fold 256 from 15.6 (±10.9; n=62) µg N L⁻¹ before harvest to 261.0 (±170.4; n=151) µg N L⁻¹ after the 257 treatment (Figure 3B). In the NO-5 catchment, the response to harvests was less pronounced 258 but also significant (11.4 (\pm 8.6; *n*=62) µg N L⁻¹ before harvest and 25.9 (\pm 35.3; *n*=151) µg N 259 L^{-1} after, p<0.001). Average concentrations at the NR-7 control stream were 27.6 (±20.5; 260 n=60) µg N L⁻¹ in the early period of 2004 to 2006, and did not change significantly in the 261 later period from 2007-2012 (23.1 (\pm 22.2; n=151) µg N L⁻¹). At the RS-3 control stream NO₃⁻¹ 262 concentrations were also low, 12.3 (± 9.2 ; n=49) µg N L⁻¹ in the early period, but decreased 263 significantly to 5.8 (\pm 7.5; *n*=151) µg N L⁻¹ during 2007-2012. Similarly, concentrations of 264 NH_4^+ and DON increased in the CC-4 catchment following harvesting (Figure 3, C and D) 265 from 14.7(\pm 6.4; *n*=30) µg N L⁻¹ to 61.8 (\pm 79.9; *n*=151) µg N L⁻¹ and from 324(\pm 108; *n*=30) 266 μ g N L⁻¹ to 484 (±239; *n*=151) μ g N L⁻¹ for NH₄⁺ and DON, respectively. At the reference 267 sites, NH₄⁺ and DON remained at similar levels or decreased in the period after harvesting 268 (Figure 3, C and D). In addition to concentration changes, stream runoff was substantially 269 increased after harvest, which enhanced the relative contribution of clear-cuts versus control 270

forests for downstream mass fluxes. Annual specific runoff of the CC-4 catchment after the harvest (2007-2012) was 518 (\pm 128) mm whereas the northern control site (NR-7) had a lower average specific discharge of 355 (\pm 88) mm.

At the BA-1 downstream site, NO₃⁻ concentrations showed no statistically significant 274 difference between the periods of 2004-2006 (17.2 \pm 14.3 µg N L⁻¹; *n*=37) and 2007-2012 275 $(17.2 \pm 18.9 \text{ µg N L}^{-1}; n=151)$, even though the upstream area that was clear-cut increased 276 from 2.5% in 2004 to 11.2% in 2011 (Figure 2). At the BA-2 site, where harvests ranged from 277 4.6% of the catchment area in 2004 to 17.5% in 2011, average NO₃⁻ concentrations increased 278 modestly (*t*-test, p=0.026) from 15.9 (±9.8; n=30) µg N L⁻¹ during 2004-2006 to 21.3 (±19.1; 279 n=151) µg N L⁻¹ during 2007-2012. Similarly, NH₄⁺ and DON concentrations at the 280 281 downstream sites BA-1 and BA-2 increased slightly from 2006 to 2012 (Figure 3, C and D). Also, the contributions of NH_4^+ to the total inorganic N pool varied at both downstream sites 282 between seasons. On average NH₄⁺ accounted for 23% and 18% during the dormant season, 283 for 45% and 39% during snowmelt and 54% and 46% of the inorganic N pool during the 284 growing season for BA-1 and BA-2, respectively. Furthermore, NO₃⁻ concentrations at these 285 downstream sites, as well as at CC-4 increased continuously throughout the winter period, 286 with the highest values observed just prior to snowmelt. Annual DIN export was generally 287 dominated by NO_3^- (Table 2) and was highest from the CC-4 catchment (1.28 - 1.83 kg N ha⁻¹ 288 y^{-1}), followed by NO-5 (0.10 - 0.17 kg N ha⁻¹ y⁻¹), NR-7 (0.06 - 0.10 kg N ha⁻¹ y⁻¹), and RS-3 289 $(0.03 - 0.07 \text{ kg N ha}^{-1} \text{ y}^{-1}).$ 290

291 3.2 Mixing Model results

When modeled concentrations of DON and DIN at BA-1 and BA-2 were compared to the

293 measured concentrations, distinct patterns emerged. First, modeled and measured DON

concentrations correlated well (relationships: $r^2=0.92$, p<0.001 for BA-2 and $r^2=0.72$,

295 p<0.001 for BA-1; see also Figure 4). In contrast, relationships between modeled and 296 measured DIN concentrations were significant, but explained little of the variability ($r^2=0.23$ 297 for BA-1; $r^2=0.31$ for BA-2) with modelled DIN concentrations usually overestimating the 298 measured values (Figure 4). Similarly, annual modelled DIN exports at the downstream sites 299 were substantially higher than the measured export rates (Table 2).

300 Modelled DIN removal efficiency calculated as the fraction of DIN that was retained in the system showed a strong seasonal signal (Figure 5A). E_r values above 75% were observed just 301 after peak snow melt, with the exception of the snow melt of 2012. E_r then remained high 302 (>75 %) during the summer of 2008, and stayed at intermediate-to-high levels (>50%) during 303 the following summer seasons (Figure 5A). Towards the end of the growing season, E_r 304 305 decreased during all years and was followed by another distinct decline, often with values <40% throughout the winter (Figure 5A). Furthermore, no significant relationships between 306 discharge and E_r were observed (Figure 5B and 5C). DIN removal in the network based on 307 308 this modelling exercise yielded estimates of net retention (U) for BA-2 that were significantly higher during snow melt (9.8 μ g N m⁻² min⁻¹) than the growing (5.4 μ g N m⁻² min⁻¹) and 309 dormant (5.3 μ g N m⁻² min⁻¹) seasons, respectively (Figure 6). Estimates of U for BA-1 were 310 lower, with 2.3, 1.1 and 0.8, μ g N m⁻² min⁻¹ for the snowmelt, growing and dormant season, 311 312 respectively.

313 4. Discussion

Increases in DIN export in response to forest harvesting are well documented (Jerabkova et al., 2011) and illustrate how terrestrial ecosystem disturbance can control N mobilization and delivery to small streams. In this study, increases in streamwater NO_3^- concentrations by up to ~15 fold, together with elevated runoff (Schelker et al., 2013b), resulted in substantial increases in DIN inputs to the fluvial network (Table 2). However, despite obvious effects of

forest harvesting on DIN concentrations in first-order streams, only very subtle responses could be detected for the third-order streams within this same network, suggesting that significant DIN retention occurred between the harvested areas in the landscape and downstream monitoring sites.

323 4.1 Network patterns in DIN concentration

At both downstream sites, and the CC-4 clear-cut catchment, concentrations of NO₃⁻ were 324 higher during the dormant than growing season (Figure 3B). Similar seasonal patterns were 325 observed for NH₄⁺ concentrations (Figure 3C). Overall, such seasonal variation in stream 326 DIN, and specifically stream NO₃⁻ concentration, is common across Sweden (Sponseller et al., 327 2014; Löfgren et al., 2014) and is thought to reflect seasonal changes in terrestrial N demand 328 (e.g. Mitchell et al., 1996). In contrast, NO₃⁻ concentrations at RS-3 did not show such a 329 seasonal pattern, suggesting particularly low inorganic N availability and strong N-limitation 330 persisting throughout the year (Stoddard, 1994). This hypothesis is further supported by the 331 fact that average NO₃⁻ concentrations at this site decreased significantly by 6.5 μ g N L⁻¹ 332 between the period from 2004 to 2006 as compared to 2007 to-2012, indicating that local 333 factors, such as the presence of actively growing forest stands with dense riparian vegetation, 334 335 resulted in particularly high terrestrial N demand and thus low stream concentrations at this 336 site.

Temporal variation in NO_3^- concentrations at the CC-4 clear-cut stream during the dormant season (Figure 2) was closely correlated with temporal changes in NO_3^- concentration at downstream sites (Supplementary Figure S1), indicating temporal coherence in concentration change (*sensu* Kling et al., 2000) across the stream network during this period. In contrast, temporal changes in upstream and downstream NO_3^- concentrations were not correlated during the growing season (Supplementary Figure S1). 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 NO₃⁻ 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.

348 4.2 Comparison of modeled and measured streamwater N

We found a close correspondence between modelled and measured DON concentrations, 349 similar to relationships previously observed for dissolved organic carbon (Schelker et al., 350 2014), as well as the two conservative tracers, dissolved silica and chloride (Figure 2). This 351 close relationship between observed and predicted concentrations is indicative of an 352 approximately conservative downstream transport of DON in the network. These patterns 353 provide additional support for the applicability of our mixing model in this landscape, and 354 they are consistent with the idea that bulk DON is composed primarily of organic compounds 355 of low bioavailability that are exported from landscapes without strong biotic controls (Hedin 356 et al., 1995). For this reason, DON also often represents the major loss vector for N in 357 catchments that are not subject to large anthropogenic inputs of DIN (Perakis, 2002; 358 Kortelainen et al., 1997). Importantly, DON exports at CC-4 also increased following 359 360 harvesting (Figure 3D), a response which has been reported elsewhere in Scandinavia (Smolander et al., 2001). While this response was more subtle than that observed for DIN, the 361 conservative behavior of DON in the stream network suggests that it likely represents an 362 363 important and largely unappreciated source of terrestrially derived N to downstream receiving systems (Rosén et al., 1996). 364

In contrast to DON, we observed generally poor relationships between measured and

modelled DIN concentrations at BA-1 and BA-2 (Figure 4, data for BA-2 not shown). This

367 mismatch most likely results from seasonal NO_3^- removal, a pattern illustrated by the

temporal variation of E_r for both sites (Figure 5). Low dormant season values of E_r suggest an

ostensibly weak NO₃⁻ demand in cold, snow-covered streams and thus low strength of the 369 370 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 upstream-371 downstream synchrony in nutrient concentrations observed during this period (S1) and the 372 few wintertime occasions where E_r was near-zero. These occasions suggest that either (i) all 373 374 NO_3 was transported downstream (e.g. that NO_3 transport was conservative) or (ii) that the 375 downstream reaches of the stream network acted as source areas of NO₃⁻. The latter has been previously hypothesized to cause discrepancies of reach scale N mass-balances (von Schiller 376 et al., 2011). 377

Interestingly, E_r did not show a direct dependence on stream discharge at any of the 378 379 downstream sites (Figure 5), suggesting that N-demand rather than flow and/or transient storage (Ensign and Doyle, 2006) were controlling DIN removal in the fluvial network. In 380 addition, high removal efficiencies during spring and summer had substantial effects on 381 382 overall annual net DIN uptake as estimated by the difference of modeled and measured annual DIN exports. These estimates $(\pm SD)$ showed that $67(\pm 3)\%$ and $65(\pm 8)\%$ of the DIN inputs to 383 the BA-1 and BA-2 catchments were removed before reaching these monitoring stations 384 385 (Table 2). These estimates are of course sensitive to how the clear-cut EM was represented in the mixing model. For example, if we assume that all clear cut areas would follow the less 386 pronounced concentration response of NO-5 then the average annual DIN removal would sum 387 388 to 22% for BA-1 and only 9% for BA-2, with the latter even acting as a source of DIN (+2%) during one year (2009). However, we consider this extreme scenario unrealistic for at least 389 390 two reasons. First, several harvests in the drainage area of the stream network, but outside the experimental harvest of NO-5 and CC-4, showed substantial disturbance of riparian soils, for 391 example from multiple stream crossings of forestry machines and from wind throw of trees in 392 393 the riparian zone. These disturbances will likely result in a concentration response closer to

that of CC-4, than that of NO-5. Second, the CC-4 clear cut is located within the BA-2 394 395 drainage area and represents an important fraction of the harvested area within this catchment (Tabe1). Thus the CC-4 harvest would itself not be correctly represented in this modeling 396 scenario. Indeed, this omission gives rise to the hypothetical gain of DIN within BA-2 in 397 2009, which suggests a missing source of DIN in the catchment under this scenario. 398 Regardless, further research characterizing the spatial and temporal variation in DIN runoff 399 400 responses following harvests would lend more confidence to estimates of N removal based on this mass balance approach. 401

Our estimates of net DIN removal within this stream network suggest that, during most 402 periods, reasonable levels of in-stream activity (i.e., net uptake) could account for the 403 discrepancy between measured and modeled fluxes at downstream stations. Assuming that all 404 DIN retention was occurring within the stream channels, median values and interquartile 405 ranges (25th to 75th percentile) of U for the BA-2 catchment were 5.4 (2.2; 10.4) µg N m⁻² 406 min⁻¹ for the entire year. Even lower rates of instream uptake would be sufficient to account 407 for the differences between modeled and observed DIN at BA-1. While these values fall well 408 within the range of net uptake estimates made elsewhere for small streams (Bernhardt et al., 409 410 2003; Roberts and Mulholland, 2007; von Schiller et al., 2011), further efforts to directly quantify rates of DIN removal in boreal streams are warranted. 411

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 (Figure 6). 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 areal uptake do not account for losses that occur to the outside of the stream, as for example in riparian habitats, embedded wetlands, lakes and/or into deep groundwater aquifers. In particular,

embedded wetlands and small lakes upstream of BA-1 and BA-2 (Table 1) are common
features of boreal landscapes and may play a particularly important role in N removal at the
scale of stream networks. Overall, these seasonal removal estimates are surprising, and more
work is required to understand the hydrological and biogeochemical mechanisms
underpinning these patterns.

Important mechanisms that control DIN removal from stream water during the growing 424 season are biological uptake by riparian vegetation (Sabater et al., 2000) and immobilization 425 426 by in-stream autotrophs and heterotrophs. These in-stream sinks may also change in response to forest harvesting, for example, if elevated light conditions foster increased 427 photoautotrophic production (Bernhardt and Likens, 2004). Indication that such increased in-428 429 stream DIN demand during the growing season may also be present in the Balsjö stream network is given by ~30 fold greater summertime accumulation of algal biomass (chlorophyll 430 a) onto ceramic tiles in the CC-4 stream as compared to RS-3 (R. Sponseller, unpublished 431 432 data). Similarly, a recent survey of boreal streams (including CC-4 and RS-3) showed that heterotrophic biofilm respiration can be strongly N-limited and reported the highest rates of 433 biofilm respiration at the clear cut stream of CC-4 (Burrows et al., 2015). However, 434 435 immobilization by autotrophs and heterotrophs does not necessarily result in permanent 436 removal of N from the stream, as a large portion of this nutrient pool may be rapidly recycled as biofilm materials decay (Tank et al., 2000). Nevertheless, these observations highlight the 437 438 importance of N as limiting factor in northern, boreal streams and support the idea that these systems may respond strongly to elevated N loading following harvests. 439

440 An additional process that may account for the permanent removal of NO_3^- observed in this

study and thus for the seasonal differences in U is denitrification (Mulholland et al., 2008).

442 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, 444 445 experimental studies have demonstrated that denitrification is often found to be co-dependent on terrestrial NO₃⁻ inputs and bioavailable dissolved organic matter (DOM) as an electron 446 447 donor (Baker et al., 1999). More specifically, hot moments of denitrification, that is, periods of disproportionally high and short-lived NO₃⁻ demand, can be generated by experimental 448 additions of labile DOM (Zarnetske et al., 2011). Such enhanced demand in response to labile 449 450 DOM inputs has further been shown to regulate uptake rates in streams (Bernhardt and Likens, 2002) and hyporheic sediments (Sobczak et al., 2003). 451

Transferring this well-established process knowledge from the reach-scale to the network 452 scale suggests that NO_3^- removal at the landscape scale may be dependent on a sufficient 453 supply of labile DOM to all stream reaches within the network that are located downstream of 454 harvests. Bulk DOM contributions in Balsjö have been observed to increase as a response to 455 harvesting (Schelker et al., 2012) and other studies in boreal headwater streams have shown 456 457 that terrestrially-derived, low molecular weight DOM (e.g., free amino acids, carboxylic acids and carbohydrates), can achieve high concentrations during the spring snow melt (Berggren et 458 al., 2009). These terrestrial inputs have further been suggested to support the microbial C 459 demand of downstream aquatic ecosystems during a timeframe of days to weeks following the 460 spring freshet (Berggren et al., 2009) – a period when E_r was also highest in our study. Thus 461 we hypothesize that limitation of heterotrophic processes, such as denitrification and 462 463 immobilization, occurs via restricted supply of bioavailable DOM from terrestrial sources during the dormant season as a plausible mechanism that inhibits DIN removal at the network 464 465 scale. In turn, the restricted supply of DIN relative to bioavailable C during the other times of the year would then limit heterotrophic activities and foster efficient N removal in the 466 network – a coupling that has been suggested previously for boreal streams (Berggren et al., 467 468 2007).

In summary our work agrees with earlier studies in that terrestrial ecosystem disturbance 469 470 enhances DIN mobilization into first-order streams (Likens et al., 1970) and that such increased NO₃⁻ concentrations can potentially be transferred downstream during some 471 portions of the years (Alexander et al., 2007). The hypothesis that stream and riparian 472 processing of NO₃⁻ may dampen the effect at downstream sites (Bernhardt et al., 2003) was 473 supported during the snow melt, as well as during the growing season when rates of biological 474 475 activity and supply of bioavailable C are likely to be high. During the dormant season, however, results suggest that limited DIN uptake rates constrain the potential for DIN 476 removal within the fluvial network. Considering the measures to increase forest production of 477 478 either increased fertilization or shorter forest rotations (Egnell et al., 2011), we argue that both are likely to increase downstream export of DIN, provided that instream removal rates remain 479 the same as under current conditions. More specifically, shorter forest rotations would 480 481 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 DIN leakage 482 into surface waters particularly during the dormant season (Binkley et al., 1999) when the 483 biological demand for DIN is low within boreal stream networks. 484

485 5. Acknowledgements

Funding for this work was provided by the Swedish Environmental Protection Agency, EU
Life (Forest for Water), CMF, Future Forests and the Formas (ForWater). We thank Peder
Blomkvist, Viktor Sjöblom and Ida Taberman for help in the field and the laboratory.

489

490 6. References

Aber, J. D., Ollinger, S. V., Driscoll, C. T., Likens, G. E., Holmes, R. T., Freuder, R. J., and
Goodale, C. L.: Inorganic nitrogen losses from a forested ecosystem in responseto
physical, chemical, biotic, and climatic perturbations, Ecosystems, 5, 0648-0658,
10.1007/s10021-002-0203-8, 2002.

- Alexander, R., Boyer, E. W., Smith, R. A., Schwarz, G. E., and Moore, R. B.: The role of
 headwater streams in downstream water quality1, JAWRA Journal of the American
 Water Resources Association, 43, 41-59, 10.1111/j.1752-1688.2007.00005.x, 2007.
- Alexander, R., Böhlke, J., Boyer, E., David, M., Harvey, J., Mulholland, P., Seitzinger, S.,
- Tobias, C., Tonitto, C., and Wollheim, W.: Dynamic modeling of nitrogen losses in
 river networks unravels the coupled effects of hydrological and biogeochemical
 processes, Biogeochemistry, 93, 91-116, 10.1007/s10533-008-9274-8, 2009.
- Andréassian, V.: Waters and forests: From historical controversy to scientific debate, J.
 Hydrol., 291, 1-27, 2004.
- Baker, M. A., Dahm, C. N., and Valett, H. M.: Acetate retention and metabolism in the
 hyporheic zone of a mountain stream, Limnology and Oceanography, 44, 1530-1539,
 1999.
- Berggren, M., Laudon, H., and Jansson, M.: Landscape regulation of bacterial growth
 efficiency in boreal freshwaters, Global Biogeochem. Cycles, 21, GB4002,
 doi:4010.1029/2006GB002844, 2007.
- Berggren, M., Laudon, H., Haei, M., Strom, L., and Jansson, M.: Efficient aquatic bacterial
 metabolism of dissolved low-molecular-weight compounds from terrestrial sources,
 ISME J, 4, 408-416, 2009.
- Bernhardt, E. S., and Likens, G. E.: Dissolved organic carbon enrichment alters nitrogen
 dynamics in a forest stream, Ecology, 83, 1689-1700, 2002.
- Bernhardt, E. S., Likens, G. E., Buso, D. C., and Driscoll, C. T.: In-stream uptake dampens
 effects of major forest disturbance on watershed nitrogen export, Proceedings of the
 National Academy of Sciences, 100, 10304-10308, 10.1073/pnas.1233676100, 2003.
- 519 Bernhardt, E. S., and Likens, G. E.: Controls on periphyton biomass in heterotrophic streams,
- 520 Freshwater. Biol., 49, 14-27, 10.1046/j.1365-2426.2003.01161.x, 2004.

- Binkley, D., and Brown, T. C.: Forest practices as nonpoint sources of pollution in north
 america, JAWRA Journal of the American Water Resources Association, 29, 729-740,
 10.1111/j.1752-1688.1993.tb03233.x, 1993.
- Binkley, D., Burnham, H., and Lee Allen, H.: Water quality impacts of forest fertilization
 with nitrogen and phosphorus, For. Ecol. Manage., 121, 191-213, 10.1016/S03781127(98)00549-0, 1999.
- Bishop, K., Seibert, J., Köhler, S., and Laudon, H.: Resolving the double paradox of rapidly
 mobilized old water with highly variable responses in runoff chemistry, Hydrol.
 Process., 18, 185-189, 2004.
- Boring, L. R., Monk, C. D., and Swank, W. T.: Early regeneration of a clear-cut southern
 appalachian forest, Ecology, 1244-1253, 1981.
- Burrows, R. M., Hotchkiss, E. R., Jonsson, M., Laudon, H., McKie, B. G., and Sponseller, R.
 A.: Nitrogen limitation of heterotrophic biofilms in boreal streams, Freshwater. Biol.,
 in press, 10.1111/fwb.12549, 2015.
- Egnell, G., Laudon, H., and Rosvall, O.: Perspectives on the potential contribution of swedish
 forests to renewable energy targets in europe, Forests, 2, 578-589, 2011.
- Ensign, S. H., and Doyle, M. W.: Nutrient spiraling in streams and river networks, Journal of
 Geophysical Research: Biogeosciences, 111, G04009, 10.1029/2005jg000114, 2006.
- 539 Futter, M. N., Ring, E., Högbom, L., Entenmann, S., and Bishop, K. H.: Consequences of
- nitrate leaching following stem-only harvesting of swedish forests are dependent on
 spatial scale, Environ. Pollut., 158, 3552-3559, 2010.
- Groffman, P. M., Boulware, N. J., Zipperer, W. C., Pouyat, R. V., Band, L. E., and Colosimo,
 M. F.: Soil nitrogen cycle processes in urban riparian zones, Environ. Sci. Technol.,
 36, 4547-4552, 2002.
- Hall, R. O., Baker, M. A., Arp, C. D., and Kocha, B. J.: Hydrologic control of nitrogen
 removal, storage, and export in a mountain stream, Limnology and Oceanography, 54,
 2128-2142, 2009.
- Harvey, J. W., Böhlke, J. K., Voytek, M. A., Scott, D., and Tobias, C. R.: Hyporheic zone
 denitrification: Controls on effective reaction depth and contribution to whole-stream
 mass balance, Water Resour. Res., 49, 6298-6316, 10.1002/wrcr.20492, 2013.
- Hedin, L. O., Armesto, J. J., and Johnson, A. H.: Patterns of nutrient loss from unpolluted,
 old-growth temperate forests: Evaluation of biogeochemical theory, Ecology, 76, 493509, 10.2307/1941208, 1995.

554	Helton, A. M., Poole, G. C., Meyer, J. L., Wollheim, W. M., Peterson, B. J., Mulholland, P.
555	J., Bernhardt, E. S., Stanford, J. A., Arango, C., Ashkenas, L. R., Cooper, L. W.,
556	Dodds, W. K., Gregory, S. V., Hall Jr, R. O., Hamilton, S. K., Johnson, S. L.,
557	McDowell, W. H., Potter, J. D., Tank, J. L., Thomas, S. M., Valett, H. M., Webster, J.
558	R., and Zeglin, L.: Thinking outside the channel: Modeling nitrogen cycling in
559	networked river ecosystems, Frontiers in Ecology and the Environment, 9, 229-238,
560	2011.
561	Hill, A. R.: Nitrogen dynamics of storm runoff in the riparian zone of a forested watershed,
562	Biogeochemistry, 20, 19-44, 1993.
563	Högberg, P., Fan, H. B., Quist, M., Binkley, D., and Tamm, C. O.: Tree growth and soil
564	acidification in response to 30 years of experimental nitrogen loading on boreal forest,
565	Glob. Change Biol., 12, 489-499, DOI 10.1111/j.1365-2486.2005.01102.x, 2006.
566	Holmes, W. E., and Zak, D. R.: Soil microbial control of nitrogen loss following clear-cut
567	harvest in northern hardwood ecosystems, Ecol. Appl., 9, 202-215, 10.1890/1051-
568	0761(1999)009[0202:smconl]2.0.co;2, 1999.
569	Hornbeck, J. W., Martin, C. W., and Eagar, C.: Summary of water yield experiments at
570	hubbard brook experimental forest, new hampshire, Can. J. For. Res., 27, 2043-2052,
571	1997.
572	Houlton, B. Z., Driscoll, C. T., Fahey, T. J., Likens, G. E., Groffman, P. M., Bernhardt, E. S.,
573	and Buso, D. C.: Nitrogen dynamics in ice storm-damaged forest ecosystems:
574	Implications for nitrogen limitation theory, Ecosystems, 6, 431-443, 10.1007/s10021-
575	002-0198-1, 2003.
576	Jansson, M., Bergström, A. K., Drakare, S., and Blomqvist, P.: Nutrient limitation of
577	bacterioplankton and phytoplankton in humic lakes in northern sweden, Freshwater.
578	Biol., 46, 653-666, 2001.
579	Jerabkova, L., Prescott, C. E., Titus, B. D., Hope, G. D., and Walters, M. B.: A meta-analysis
580	of the effects of clearcut and variable-retention harvesting on soil nitrogen fluxes in
581	boreal and temperate forests, Can. J. For. Res., 41, 1852-1870, 10.1139/x11-087,
582	2011.
583	Kling, G. W., Kipphut, G. W., Miller, M. M., and O'Brien, W. J.: Integration of lakes and
584	streams in a landscape perspective: The importance of material processing on spatial
585	patterns and temporal coherence, Freshwater. Biol., 43, 477-497, 2000.

- Kortelainen, P., Saukkonen, S., and Mattsson, T.: Leaching of nitrogen from forested
 catchments in finland, Global Biogeochem. Cycles, 11, 627-638, 10.1029/97gb01961,
 1997.
- 589 Kreutzweiser, D. P., Hazlett, P. W., and Gunn, J. M.: Logging impacts on the
 590 biogeochemistry of boreal forest soils and nutrient export to aquatic systems: A
 591 review, Environ. Rev., 16, 157-179, 10.1139/A08-006, 2008.
- Laudon, H., Berggren, M., Agren, A., Buffam, I., Bishop, K., Grabs, T., Jansson, M., and
 Kohler, S.: Patterns and dynamics of dissolved organic carbon (doc) in boreal streams:
 The role of processes, connectivity, and scaling, Ecosystems, 14, 880-893, DOI
 10.1007/s10021-011-9452-8, 2011.

Laurén, A., Finér, L., Koivusalo, H., Kokkonen, T., Karvonen, T., Kellomäki, S.,

- Mannerkoski, H., and Ahtiainen, M.: Water and nitrogen processes along a typical
 water flowpath and streamwater exports from a forested catchment and changes after
 clear-cutting: A modelling study, Hydrology & Earth System Sciences, 9, 2005.
- Likens, G. E., Bormann, F. H., Johnson, N. M., Fisher, D. W., and Pierce, R. S.: Effects of
 forest cutting and herbicide treatment on nutrient budgets in the hubbard brook
 watershed-ecosystem, Ecol Monogr, 40, 23-47, 10.2307/1942440, 1970.
- Likens, G. E., and Bormann, F. H.: Biogeochemistry of a forested ecosystem, Springer-Verlag
 New York, Inc., 1995.
- Löfgren, S., Ring, E., von Brömssen, C., Sørensen, R., and Högbom, L.: Short-term effects of
 clear-cutting on the water chemistry of two boreal streams in northern sweden: A
 paired catchment study, Ambio, 38, 347-356, 10.1579/0044-7447-38.7.347, 2009.
- Löfgren, S., Fröberg, M., Yu, J., Nisell, J., and Ranneby, B.: Water chemistry in 179
 randomly selected swedish headwater streams related to forest production, clear-
- felling and climate, Environ. Monit. Assess., 1-22, 10.1007/s10661-014-4054-5, 2014.

611 Martin, C. W., Hornbeck, J. W., Likens, G. E., and Buso, D. C.: Impacts of intensive

- harvesting on hydrology and nutrient dynamics of northern hardwood forests, Can. J.
 Fish. Aquat. Sci., 57, 19-29, 10.1139/f00-106, 2000.
- McClain, M. E., Boyer, E. W., Dent, C. L., Gergel, S. E., Grimm, N. B., Groffman, P. M.,
- Hart, S. C., Harvey, J. W., Johnston, C. A., Mayorga, E., McDowell, W. H., and
- 616 Pinay, G.: Biogeochemical hot spots and hot moments at the interface of terrestrial and
- aquatic ecosystems, Ecosystems, 6, 301-312, 2003.

- Mitchell, M. J., Driscoll, C. T., Kahl, J. S., Murdoch, P. S., and Pardo, L. H.: Climatic control
 of nitrate loss from forested watersheds in the northeast united states, Environ. Sci.
 Technol., 30, 2609-2612, 10.1021/es9600237, 1996.
- Mulholland, P. J., Helton, A. M., Poole, G. C., Hall, R. O., Hamilton, S. K., Peterson, B. J.,
- Tank, J. L., Ashkenas, L. R., Cooper, L. W., Dahm, C. N., Dodds, W. K., Findlay, S.
- E. G., Gregory, S. V., Grimm, N. B., Johnson, S. L., McDowell, W. H., Meyer, J. L.,
- Valett, H. M., Webster, J. R., Arango, C. P., Beaulieu, J. J., Bernot, M. J., Burgin, A.
- 525 J., Crenshaw, C. L., Johnson, L. T., Niederlehner, B. R., O/'Brien, J. M., Potter, J. D.,
- 626 Sheibley, R. W., Sobota, D. J., and Thomas, S. M.: Stream denitrification across
- biomes and its response to anthropogenic nitrate loading, Nature, 452, 202-205,
- 628 10.1038/nature06686, 2008.
- Ocampo, C. J., Oldham, C. E., and Sivapalan, M.: Nitrate attenuation in agricultural
 catchments: Shifting balances between transport and reaction, Water Resour. Res., 42,
 2006.
- 632 Palviainen, M., Finér, L., Laiho, R., Shorohova, E., Kapitsa, E., and Vanha-Majamaa, I.:
- 633 Carbon and nitrogen release from decomposing scots pine, norway spruce and silver
 634 birch stumps, For. Ecol. Manage., 259, 390-398,
- 635 <u>http://dx.doi.org/10.1016/j.foreco.2009.10.034</u>, 2010.
- Perakis, S. S.: Nutrient limitation, hydrology and watershed nitrogen loss, Hydrol. Process.,
 16, 3507-3511, 10.1002/hyp.5078, 2002.
- Pinay, G., Black, V., Planty-Tabacchi, A., Gumiero, B., and Decamps, H.: Geomorphic
 control of denitrification in large river floodplain soils, Biogeochemistry, 50, 163-182,
 2000.
- Ranalli, A. J., and Macalady, D. L.: The importance of the riparian zone and in-stream
 processes in nitrate attenuation in undisturbed and agricultural watersheds–a review of
 the scientific literature, J. Hydrol., 389, 406-415, 2010.
- Riscassi, A. L., and Scanlon, T. M.: Nitrate variability in hydrological flow paths for three
 mid-appalachian forested watersheds following a large-scale defoliation, Journal of
- 646 Geophysical Research: Biogeosciences, 114, G02009, 10.1029/2008jg000860, 2009.
- 647 Roberts, B. J., and Mulholland, P. J.: In stream biotic control on nutrient biogeochemistry in
- a forested stream, west fork of walker branch, Journal of Geophysical Research:
- 649 Biogeosciences (2005-2012), 112, 2007.

- Rosén, K., Aronson, J.-A., and Eriksson, H. M.: Effects of clear-cutting on streamwater
 quality in forest catchments in central sweden, For. Ecol. Manage., 83, 237-244,
 10.1016/0378-1127(96)03718-8, 1996.
- Sabater, F., Butturini, A., MartÍ, E., Muñoz, I., Romaní, A., Wray, J., and Sabater, S.: Effects
 of riparian vegetation removal on nutrient retention in a mediterranean stream, J N Am
 Benthol Soc, 609-620, 2000.
- Scanlon, T. M., Ingram, S. M., and Riscassi, A. L.: Terrestrial and in stream influences on
 the spatial variability of nitrate in a forested headwater catchment, Journal of
 Geophysical Research: Biogeosciences (2005–2012), 115, 2010.
- Schelker, J., Eklöf, K., Bishop, K., and Laudon, H.: Effects of forestry operations on
 dissolved organic carbon concentrations and export in boreal first-order streams, J.

661 Geophys. Res., 117, G01011, 10.1029/2011jg001827, 2012.

- Schelker, J., Grabs, T., Bishop, K., and Laudon, H.: Drivers of increased organic carbon
 concentrations in stream water following forest disturbance: Separating effects of
 changes in flow pathways and soil warming, Journal of Geophysical Research:
 Biogeosciences, 118, 2013JG002309, 10.1002/2013jg002309, 2013a.
- Schelker, J., Kuglerová, L., Eklöf, K., Bishop, K., and Laudon, H.: Hydrological effects of
 clear-cutting in a boreal forest snowpack dynamics, snowmelt and streamflow

668 responses, J. Hydrol., 484, 105-114, 10.1016/j.jhydrol.2013.01.015, 2013b.

- Schelker, J., Öhman, K., Löfgren, S., and Laudon, H.: Scaling of increased dissolved organic
 carbon inputs by forest clear-cutting what arrives downstream?, J. Hydrol., 508, 299306, 10.1016/j.jhydrol.2013.09.056, 2014.
- Seitzinger, S., Harrison, J. A., Böhlke, J. K., Bouwman, A. F., Lowrance, R., Peterson, B.,
 Tobias, C., and Drecht, G. V.: Denitrification across landscapes and waterscapes: A
 synthesis, Ecol. Appl., 16, 2064-2090, 10.1890/1051-
- 675 0761(2006)016[2064:dalawa]2.0.co;2, 2006.
- Smolander, A., Kitunen, V., and Mälkönen, E.: Dissolved soil organic nitrogen and carbon in
 a norway spruce stand and an adjacent clear-cut, Biol. Fertil. Soils, 33, 190-196, 2001.
- 678 Sobczak, W. V., Findlay, S., and Dye, S.: Relationships between doc bioavailability and
- nitrate removal in an upland stream: An experimental approach, Biogeochemistry, 62,
 309-327, 2003.
- Sponseller, R. A., Temnerud, J., Bishop, K., and Laudon, H.: Patterns and drivers of riverine
 nitrogen (n) across alpine, subarctic, and boreal sweden, Biogeochemistry, 120, 105120, 10.1007/s10533-014-9984-z, 2014.

- Starr, R. C., and Gillham, R. W.: Denitrification and organic carbon availability in two
 aquifers, Ground Water, 31, 934-947, 10.1111/j.1745-6584.1993.tb00867.x, 1993.
- 686 Stoddard, J. L.: Long-term changes in watershed retention of nitrogen, in: Environmental
- chemistry of lakes and reservoirs, edited by: Baker, L. A., Advances in chemistry,
 237, American Chemical Society, Washington D.C. , 223-284, 1994.
- Swank, W. T., and Vose, J. M.: Long-term nitrogen dynamics of coweeta forested watersheds
 in the southeastern united states of america, Global Biogeochem. Cycles, 11, 657-671,
 10.1029/97gb01752, 1997.
- Tank, J. L., Meyer, J. L., Sanzone, D. M., Mulholland, P. J., Webster, J. R., Peterson, B. J.,
 Wollheim, W. M., and Leonard, N. E.: Analysis of nitrogen cycling in a forest stream
 during autumn using a 15n-tracer addition, Limnology and Oceanography, 45, 10131029, 2000.
- Teissier, S., Torre, M., Delmas, F., and Garabétian, F.: Detailing biogeochemical n budgets in
 riverine epilithic biofilms, J N Am Benthol Soc, 26, 178-190, 10.1899/08873593(2007)26[178:dbnbir]2.0.co;2, 2007.
- Valett, H., Thomas, S., Mulholland, P., Webster, J., Dahm, C., Fellows, C. S., Crenshaw, C.,
 and Peterson, C.: Endogenous and exogenous control of ecosystem function: N
 cycling in headwater streams, Ecology, 89, 3515-3527, 2008.
- Vidon, P. G. F., and Hill, A. R.: Landscape controls on nitrate removal in stream riparian
 zones, Water Resour. Res., 40, W03201, 10.1029/2003wr002473, 2004.
- Vitousek, P. M., Gosz, J. R., Grier, C. C., Melillo, J. M., Reiners, W. A., and Todd, R. L.:
 Nitrate losses from disturbed ecosystems, Science, 204, 469-474,
 10.1126/science.204.4392.469, 1979.
- von Schiller, D., Bernal, S., and Martí, E.: Technical note: A comparison of two empirical
 approaches to estimate in-stream net nutrient uptake, Biogeosciences, 8, 875-882,
 10.5194/bg-8-875-2011, 2011.
- Weller, D. E., Baker, M. E., and Jordan, T. E.: Effects of riparian buffers on nitrate
 concentrations in watershed discharges: New models and management implications,
 Ecol. Appl., 21, 1679-1695, 2011.
- Wollheim, W. M., Vörösmarty, C. J., Peterson, B. J., Seitzinger, S. P., and Hopkinson, C. S.:
 Relationship between river size and nutrient removal, Geophysical Research Letters,
 33, 2006.
- Worrall, F., Burt, T. P., Howden, N. J. K., and Whelan, M. J.: The fluvial flux of nitrate from
 the uk terrestrial biosphere an estimate of national-scale in-stream nitrate loss using

- an export coefficient model, J. Hydrol., 414–415, 31-39,
- 719 10.1016/j.jhydrol.2011.09.020, 2012.
- 720 Zarnetske, J. P., Haggerty, R., Wondzell, S. M., and Baker, M. A.: Labile dissolved organic
- carbon supply limits hyporheic denitrification, Journal of Geophysical Research:
- 722 Biogeosciences, 116, G04036, 10.1029/2011jg001730, 2011.
- 723
- 724
- 725

726 **7. Tables**

Table 1: Catchment characteristics of the six nested Balsjö catchments. Site Name	Short Name	Catchment Area	Prop Clea Cut* 2011	ortion r- 7, 2004;	Wetland Area	Total Stream Length	Lake Area*	Stream Surface Area	Total Water Area
Unit		[ha]	[[%]	[ha]	[m]	[m ²]	[m ²]	[m ²]
Balån River 1 Outlet	BA-1	2291	2%	11%	337	37521	87829	185738	2735
Balån River 2	BA-2	868	5%	18%	88	15754	6590	19249	2583
Southern Reference	RS-3	156	0%	3%	4	2195	0	2195	2195
Southern Clear Cut	CC-4	41	0%	56%	3	1650	0	660	660
Northern Catchment	NO-5	40	0%	33%	5	1386	0	554	554
Northern Reference	NR-7	24	0%	16%	4	835	0	334	334

* estimated from satellite data

- 728
- 729
- 730

Table 2: Measured and modelled annual DIN loads per unit catchment area from all six Balsjö

catchments during 2008-2011. The percentage of NO_3^- of the total load is given in brackets.

Measured						Modelled*		
Site	BA-1	BA-2	RS-3	CC-4	NO-5	NR-7	BA-1	BA-2
Unit / Year	mg N m ⁻² yr ⁻¹							
				134.8	10.2			27.1
2008	6.1 (60%)	6.4 (66%)	3.1 (39%)	(79%)	(42%)	6.1 (58%)	20.6 (74%)	(76%)
		13.1		182.9	17.2			31.0
2009	8.0 (56%)	(72%)	7.0 (54%)	(74%)	(54%)	9.3 (57%)	24.5 (67%)	(68%)
				149.1	12.2			24.4
2010	6.5 (68%)	8.9 (70%)	3.5 (46%)	(81%)	(68%)	7.9 (67%)	18.9 (75%)	(77%)
		11.2		128.3	14.7			30.6
2011	8.2 (63%)	(63%)	3.9 (37%)	(76%)	(69%)	9.6 (63%)	22.1 (71%)	(73%)

*assuming conservative mixing and solute transport.

733

734 8. Figure Captions

735

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

738 22.9 km² Balsjö Stream Network. Areas harvested during 2001-2011 are shown as orange.

739 Solid blue lines represent the stream network; solid blue areas show ponds with open water.

740 Solid black lines indicate the catchment boundaries, black pyramids the location of water

741 sampling.

742

Figure 2: Comparison of modelled and measured Cl and Si concentrations for BA-1 (panel Aand C), and BA-2 (B and D).

745

Figure 3, 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 andBA-1.

Figure 4: Results of the mass-balance modeling approach for DON (left) and DIN (right) forthe downstream site BA-1.

Figure 5, Panel (A): Stream discharge (Q) and sample drawing at the BA-1 site. Panel (B):

Seasonal variation in NO₃⁻ removal efficiency (E_r), 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.

Figure 6: Boxplot of the seasonal differences in net NO₃⁻ uptake rates (U) per unit stream area

during 2008-2011 in the BA-2 catchment. Solid lines represent median values, boxes the 25th

to 75^{th} percentile range, whiskers the 90^{th} to 10^{th} percentiles and dots the 95^{th} and the 5^{th}

percentiles. Pairs of letters indicate highly significant differences between seasons (p<0.001;

- 762 Mann-Whitney Rank Sum Test). Values for BA-1 site are generally lower, but show similar
- 763 seasonal differences.





















